TRANSITION METALS IN ORGANIC SYNTHESIS
ANNUAL SURVEY COVERING THE YEAR 1980 *

Louis S. Hegedus
Department of Chemistry, Colorado State University, Fort Collins, CO 80523 U.S.A.

CONTENTS

---

* Previous review see J. Organometal. Chem., 207(1981)185-341.

I. General Comments

This annual survey covers the literature for 1980 dealing with the use of transition metal intermediates for organic synthetic transformations. It is not a comprehensive review but is limited to reports of discrete systems that lead to at least moderate yields of organic compounds, or that allow unique organic transformations, even if low yields are obtained. Catalytic reactions that lead cleanly to a major product and do not involve extreme conditions are also included. This is not a critical review, but rather a listing of the papers published in the title area.

The papers in this survey are grouped primarily by reaction type rather than by organometallic reagent, since the reader is likely to be more interested in the organic transformation affected than the metal causing it. Specifically excluded are papers dealing with transition metal catalysed hydrosilation, since these are covered by another survey in this series. Also excluded are structural and mechanistic studies of organometallic systems unless they present data useful for synthetic application. Finally, reports from the patent literature have not been surveyed since patents are rarely sufficiently detailed to allow reproduction of the reported results.

The number of papers published in this area continues to increase precipitously, and this review now cites over one thousand papers. This increase is partly due to an increase in activity in this area. However, other major factors in this increase are: the trend to publish smaller and smaller fragments of research as individual papers (a number of papers cited in this review report a single experiment); the habit of publishing a number of short papers, reporting essentially the same chemistry, in several different journals at the same time; and the mindless generation of data, reporting cases 47 through 56 of somebody elses chemistry. The responsibility for these problems lie equally among the scientists who write these papers and the referees and editors who accept them for publication.

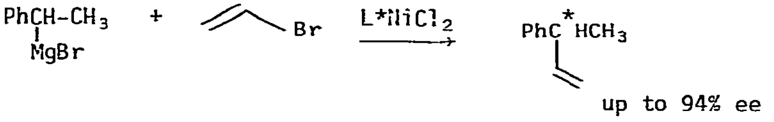
II. Carbon-Carbon Bond Forming Reactions

A. Alkylations

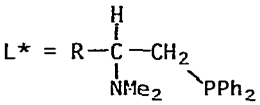
1. Alkylation of Organic Halides and Tosylates

Group VIII catalyzed cross coupling reactions of Grignard reagents with organic halides is becoming increasingly useful in organic synthesis. Nickel and palladium catalyzed cross coupling reactions of organometallics with organic halides has recently been reviewed [1]. The full experimental details for the synthesis of chiral ferrocenyl phosphines ligands for use in the above reaction, as well as others have been published [2]. The cross coupling reaction of butylmagnesium bromide with o-dichlorobenzene catalyzed by nickel-phosphine complexes produced 1,2-dibutylbenzene in 79-83% yield [3].

β-Bromostyrene reacted with t-butylmagnesium chloride in the presence of nickel (II) complexes of ferrocenyldiphosphines to give β-t-butylstyrene in 67% yield [4]. Nickel (II) complexes of a new chiral ligand synthesized from chiral α-amino acids were excellent catalysts for the asymmetric Grignard cross-coupling reaction (equation 1) [5]. These same ligands were attached to an insoluble polymer support, and nickel(II) complexes were used in the reaction in equation 1. Although the chemical yields were acceptable, the optical yields were rather low (34-50% ee) [6].



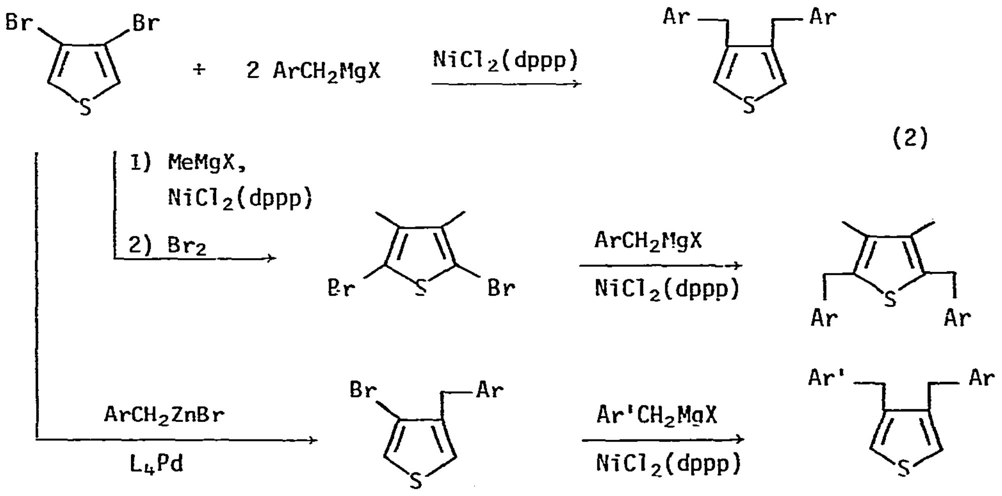
(1)



$L^* = R-C(H)(NMe_2)-CH_2PPh_2$

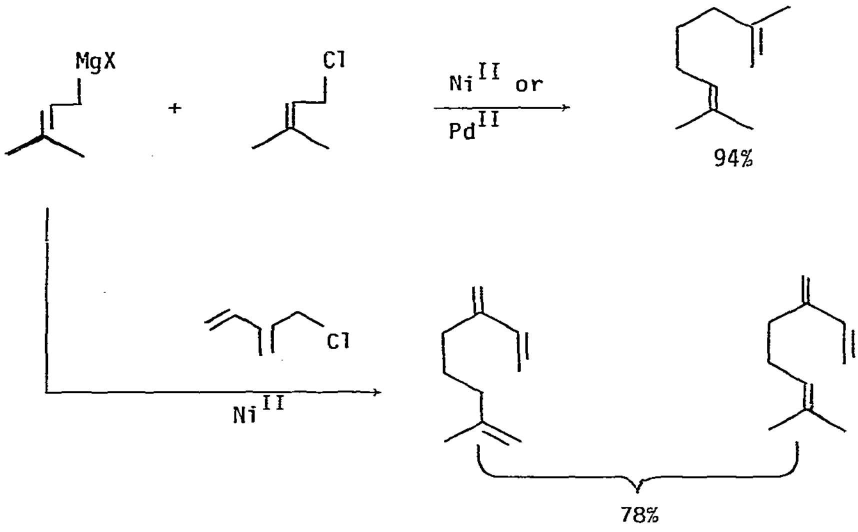
R = Me, Ph, i-Pr

Ligands were synthesized using the nickel (II) and/or palladium (0) catalyzed cross coupling of benzylmagnesium halides with dibromothiophenes (equation 2) [7]. Aromatic dihalides including dibromothiophenes and dihalopyridines were mono alkylated or arylated by Grignard or organozinc reagents in the presence of palladium (0) catalysts [8]. Isoprenylmagnesium halides

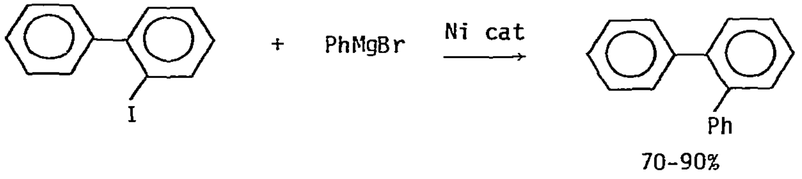


(2)

cross coupled with isoprenyl chloride in the presence of nickel (II) or palladium (0) catalysts (equation 3) [9]. Phenylmagnesium bromide arylated 2-iodobiphenyl in the presence of seventeen different nickel complexes as catalysts (equation 4) [10].



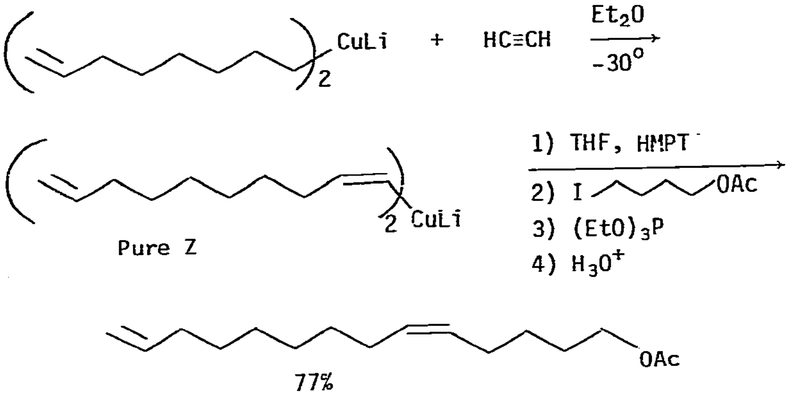
(3)



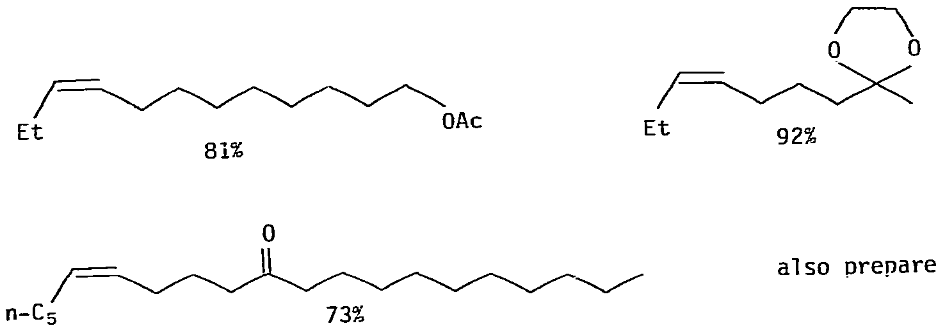
(4)

Ni cat = Ni"O_4", Ni"S_4", Ni"O_2N_2", Ni"O_3N_3", Ni"N_6", Ni$(C_5)_2$
ligands = salen, Cp, acac, tfa, dpn etc.

Organocuprate chemistry was used to synthesize a number of insect pheromones (equation 5) [11]. Isoprene bromohydrin reacted with organolithium reagents in the presence of copper (I) iodide to produce rearranged 2-alkyl-4-penten-2-ols, in contrast to the reactions in the absence of copper (I) iodide, which gave 2-methyl-4-alkyl-2-buten-1-ols [12]. Menaquinones and cymopol were synthesized by the reaction of the organocuprate of quinone diketals with allylic halides (equation 6) [13]. Bromobenzofuran reacted with trifluoromethyl

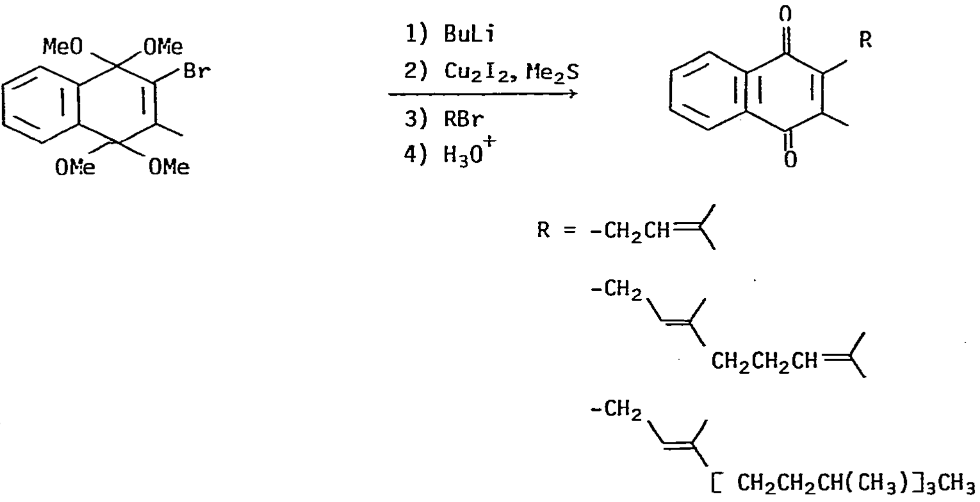


(5)

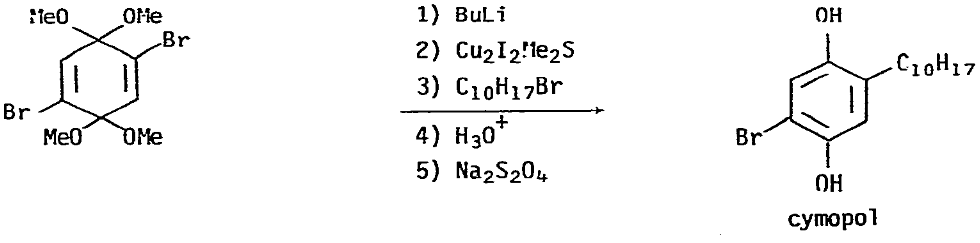


also prepared.

(6)

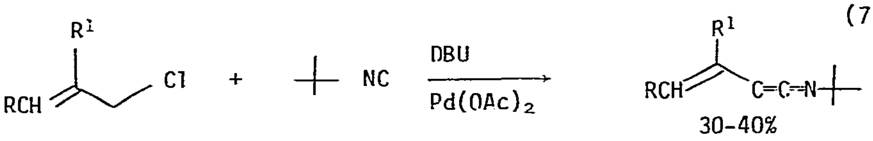


and

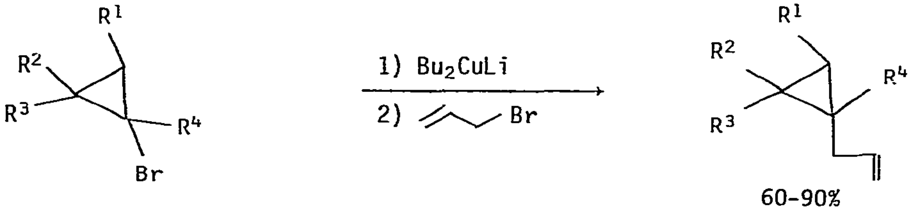


iodide and copper powder to give a complex mixture of products arising from reactions of perfluoroalkyl radicals [14]. In contrast, $CuCF_3$ cleanly trifluoromethylated iodobenzene, p-nitro, and 2,4-dinitroiodobenzene, 2-iodopyridine, and p-nitrobenzyl bromide [15]. The relative reactivities of methyl iodide and methyl tosylate with a variety of transition metal nucleophiles were measured [16]. The complexes were thought to react by a common S_N2 mechanism, and the rate constants spanned a range of 10^{11}, while the ratio of rate constants of the iodide vs tosylate ranged from 10^{-3} to 10^9

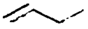
Allyl chlorides reacted with isonitriles in the presence of DBU and palladium acetate as a catalyst to produce N-t-butylvinylketenimines (equation 7) [17]. Cyclopropyl bromides reacted with lithium dibutylcuprate followed by an alkyl iodide to give alkylated products (equation 8) [18]. Bromobenzene



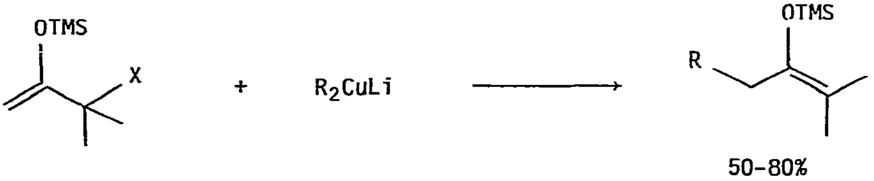
(7)



(8)

R^1 = H ⎫ $-(CH_2)_4-$ R^2 = Ph, H, nC_6, $PhCH_2OCH_2$
R^3 = H, Ph, Me, ⎭ R^4 = H, Me, 

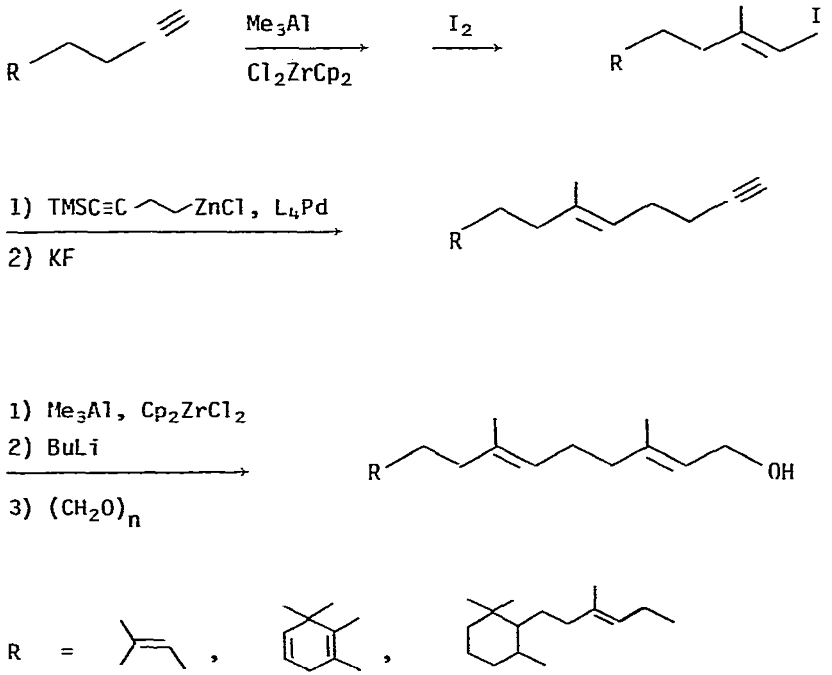
behaved in a similar manner. Allylic halides of silylenol ethers underwent alkylation by organocuprates with allylic transposition (equation 9) [19]. Benzene and toluene reacted with allylic chlorides in the presence of tungsten hexachloride to alkylate the allylic position and add hydrogen chloride to the olefin [20].



(9)

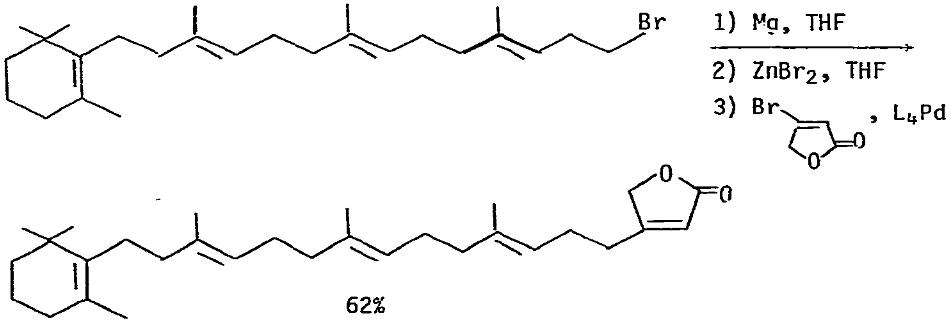
R = Bu, Me, Ph

Palladium (0) complexes catalyzed the cross coupling reaction of homoallylic and homopropargylic organozinc reagents to produce 1,5-dienes and 1,5-enynes (equation 10) [21]. This same chemistry was used to synthesize mokupalide (equation 11) [22].

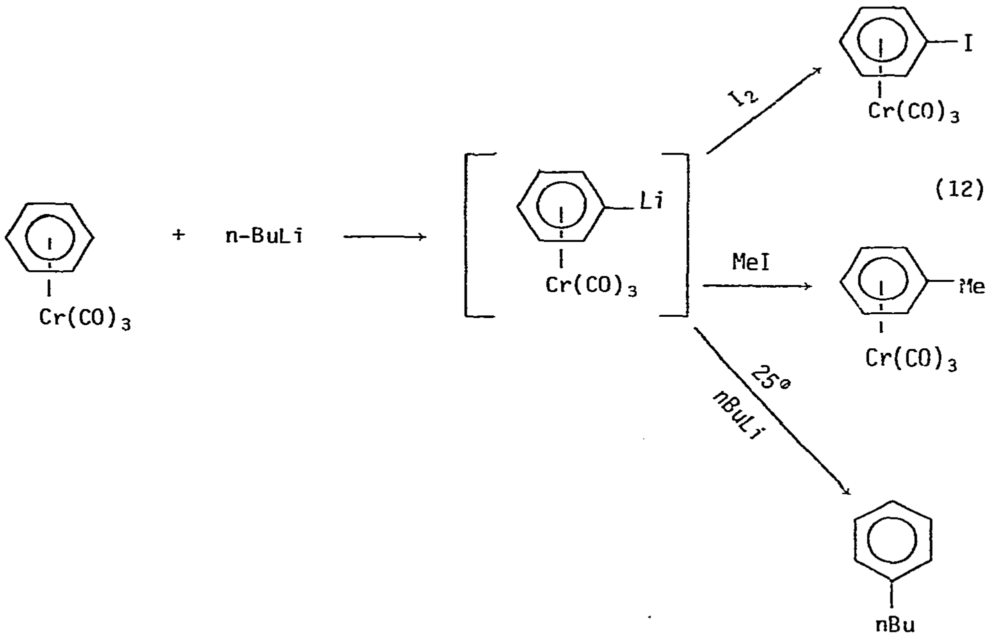


(10)

(11)



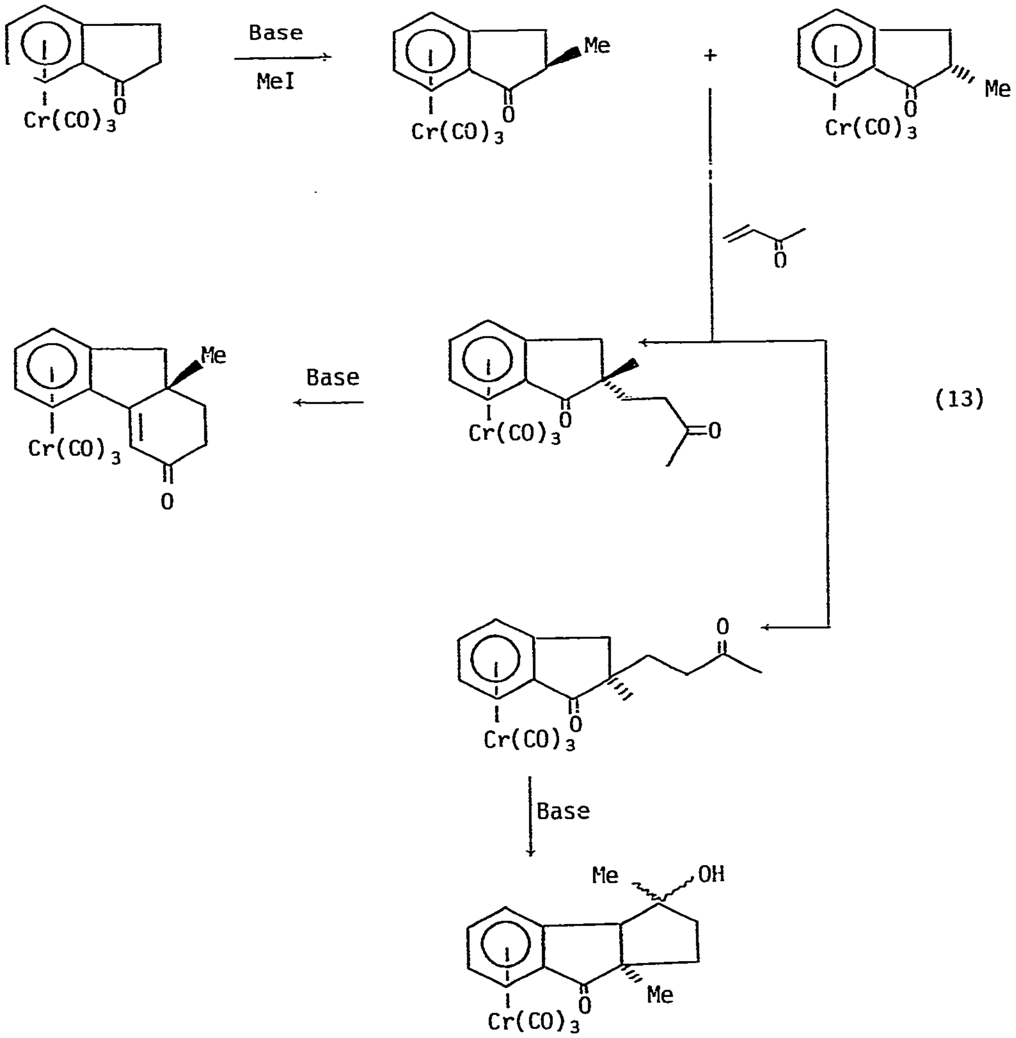
Arenechromium tricarbonyl complexes were arene-ring lithiated by butyllithium, and this resulting complex reacted with a variety of electrophiles (equation 12) [23]. Reactions of substituted arenechromium tricarbonyl complexes were studied in a similar manner. With monoalkyl arenes lithiation occurred in the meta position, with fluorobenzene, in the ortho position, and with anisole in both ortho positions, giving 2,6-disubstitution [24]. Chromium tricarbonyl complexes of indanone and tetralone underwent deprotonation alkylation reactions α to the carbonyl group followed by cyclization (equation 13) [25].



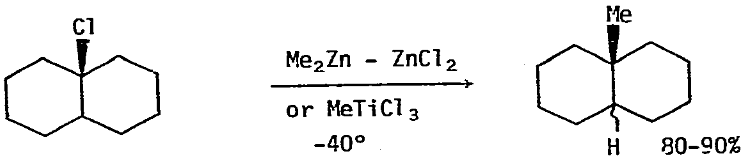
(12)

Tertiary chlorides, including chlorodecalins, underwent clean alkylation when treated with organozinc or titanium complexes (equation 14) [26a, 26b]. Aryl halides reacted with trimethylsilyl acetylene in the presence of a mixed copper iodide-palladium (II) catalyst to give ethynylarenes (equation 15) [27]. Terminal alkynes reacted with alkynylbromides in the presence of copper(I) chloride to produce diynes (equation 16) [28]. Alkynylbromides were cleanly alkylated by organocuprate complexes to give internal alkynes [29].

Iodoallenyl ethers reacted with organocuprates to produce 1-alkynyl ethers in good yield (equation 16a) [30]. Homoallylic cobalt (III) complexes reacted with dihalocarbene precursors and irradiation to produce cyclopropanes (equation 17) [31]. Homoallylic iron complexes reacted with both electro-

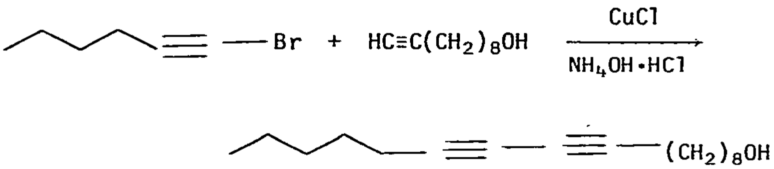


(13)



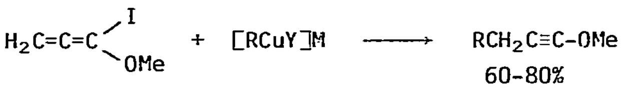
(14)

$$\mathrm{ArX} \quad + \quad \mathrm{HC{\equiv}C\text{-}TMS} \quad \xrightarrow{L_2PdCl_2/CuI} \quad \mathrm{ArC{\equiv}CTMS} \qquad (15)$$



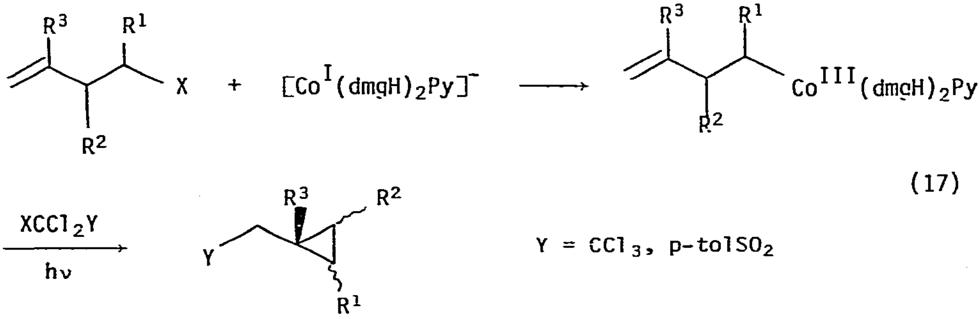
(16)

philes and free radicals at the δ carbon to give cyclopropyl carbonyl compounds (equation 18) [32]. Imidoyl chlorides were coupled to diazadienes by anionic nickel carbonyl complexes (equation 19) [33].



$$\mathrm{H_2C{=}C{=}C}\begin{matrix}\mathrm{I}\\ \mathrm{OMe}\end{matrix} + [\mathrm{RCuY}]\mathrm{M} \longrightarrow \underset{60\text{-}80\%}{\mathrm{RCH_2C{\equiv}C\text{-}OMe}} \qquad (16a)$$

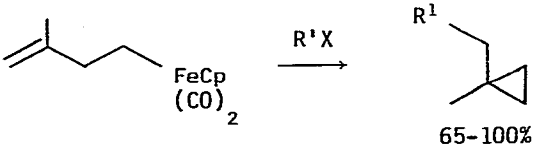
R = alkyl, vinyl, aryl, RC≡C-



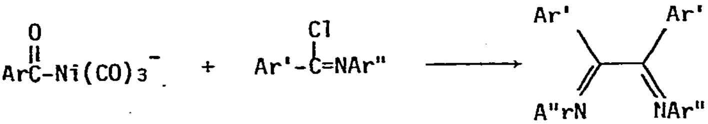
(17)

Y = CCl3, p-tolSO2

(18)



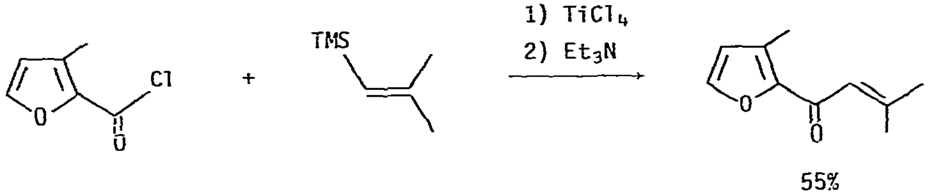
R1 = H, CCl3, CBr3, ArSO2



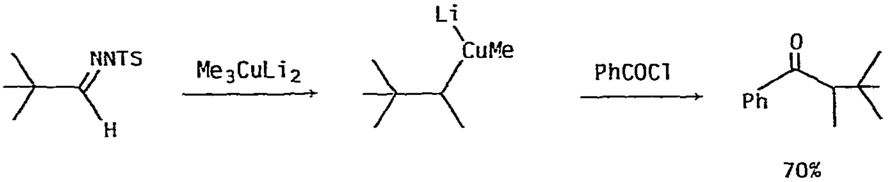
(19)

2. Alkylation of Acid Halides

Furanoyl chlorides reacted with vinylsilanes in the presence of titanium tetrachloride to produce conjugated ketones (equation 20) [34]. Copper (I) bromide catalyzed the alkylation of benzylic acid chlorides to ketones using Grignard reagents [35]. The complexes $BrMgPh_2Cu$ and $IMgMe_2Cu$ were synthesized and characterized, and their reactions with acid chlorides to give ketones were studied [36]. Hindered alkylcuprates were prepared from aldehyde tosylhydrazones, and studied in their reactions with acid chlorides (equation 21) [37]. These cuprates added in a 1,4 fashion to conjugated aldehydes.



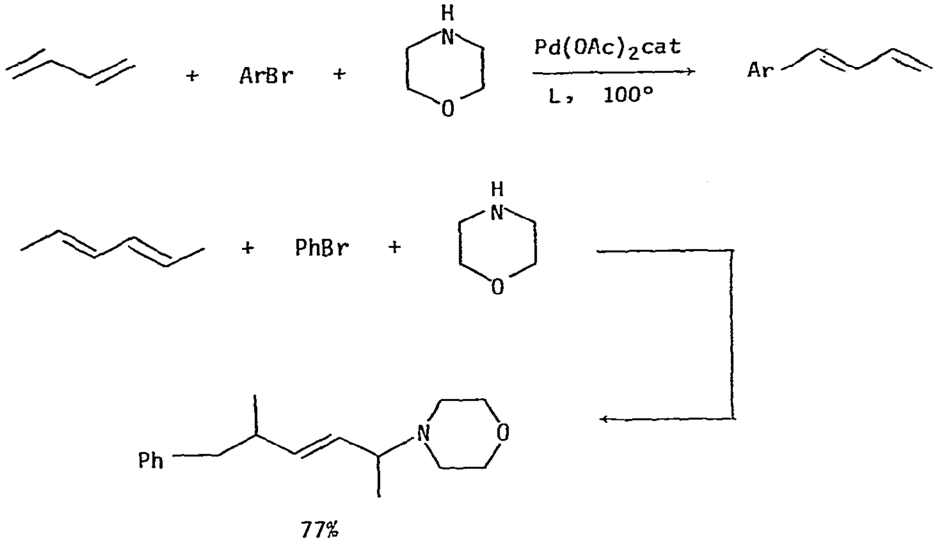
(20)



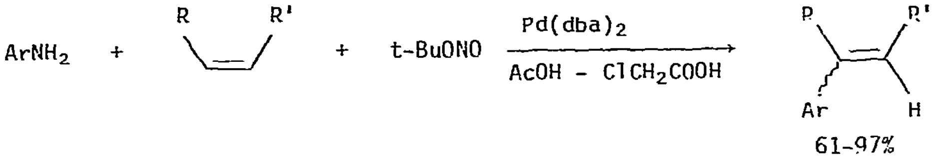
(21)

3. Alkylation of Olefins

Aryl halides arylated dienes in the presence of palladium (II) acetate catalysts to produce phenylbutadienes. The reaction was thought to occur by oxidative addition of the aryl halide to palladium (0), insertion of the diene into aryl-palladium bond to give a phenyl-π-allylpalladium complex, and abstraction of a proton by added secondary amine to regenerate the diene. In some instances amine addition to the π-allylpalladium complex occurred (equation 22) [38]. Olefins were arylated by treatment with diaryltellurium halides and a palladium (II) catalyst. The olefins included styrene, acrylate esters, acrylonitrile, acrylaldehyde, allyl alcohol, allyl bromide, and allyl acetate. Arylation always occurred at the less substituted olefin position, typical of a cis insertion process [39]. Olefins were arylated by aryl amines in the presence of t-butylnitrile and a palladium (0) or palladium (II) catalyst (equation 23) [40, 41]. Mercurated purine bases added to styrene at the β-position in the presence of palladium catalysts and an oxidizing agent (equation 24) [42].



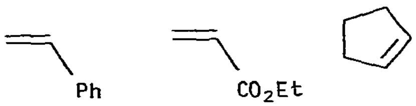
(22)

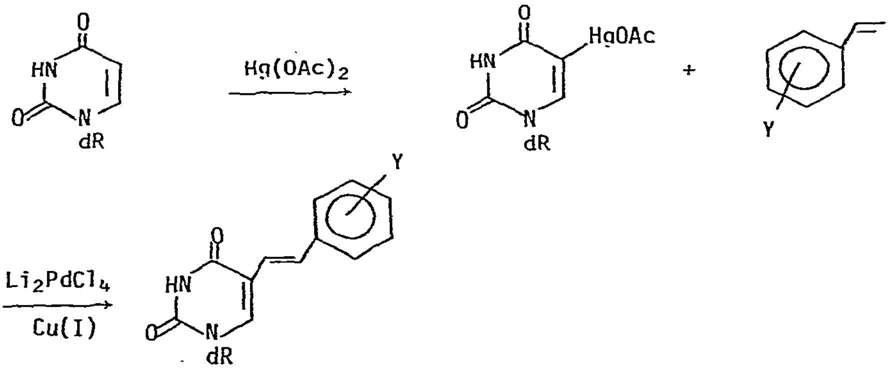


(23)

Ar = Ph, p-tol, p-ClPh, p-BrPh, pNO$_2$Ph, o-NO$_2$Ph, 3-Pyr

Olefin =





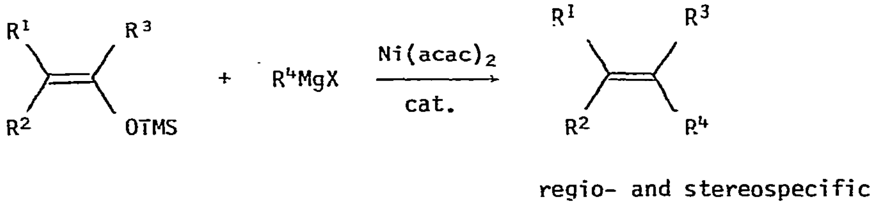
(24)

dR = deoxyribose, deoxyribose phosphate

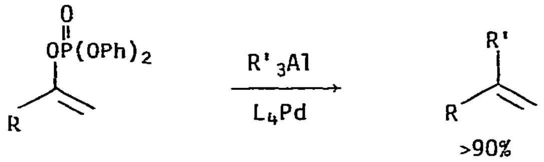
Y = NO$_2$, NH$_2$, N$_3$

Both styrene and dienes react with n-propylmagnesium bromide in the presence of Cp_2TiCl_2 to produce the corresponding benzyl- or allyl magnesium halides from formal addition of "HMgZ" to the olefin [43]. Ethyl cyanoacetate was alkylated by olefins in the presence of copper oxide by a free radical process [44].

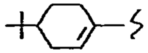
A number of procedures for the alkylation of enol ethers to produce olefins have been developed. Trimethylsilylenol ethers reacted with Grignard reagents in the presence of nickel (II) catalysts to produce olefins (equation 25) [45]. Enol phosphates were alkylated by trialkylaluminum reagents using a palladium (0) catalysts (equation 26) [46], enol triflates were alkylated by dialkylcuprates (equation 27) [47], and aryl, vinyl, and allyl selenides were alkylated by Grignard reagents and nickel (II) catalysts (equation 28) [48].



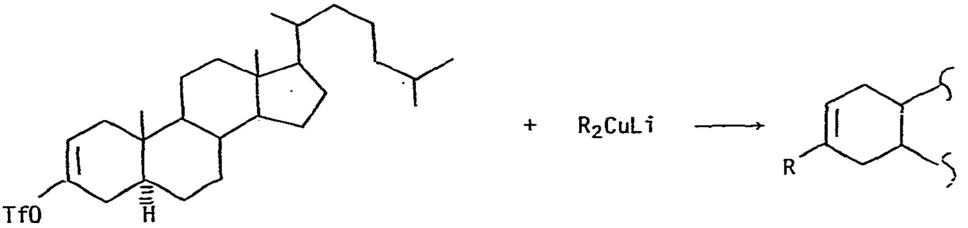
(25)



(26)

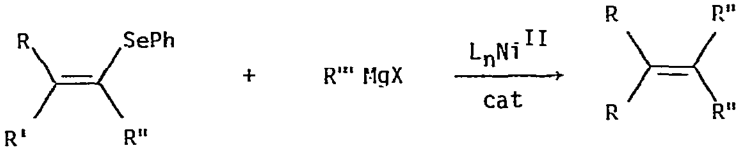
R = n-C_{10}, Ph, 

R' = Me, Et, PhC≡C, n-C_5C≡C-, nC_5C=C



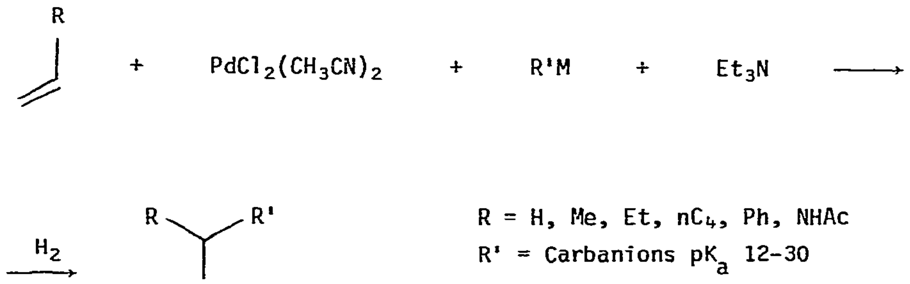
(27)

R = Me, *n*-Bu, Ph, 



(28)

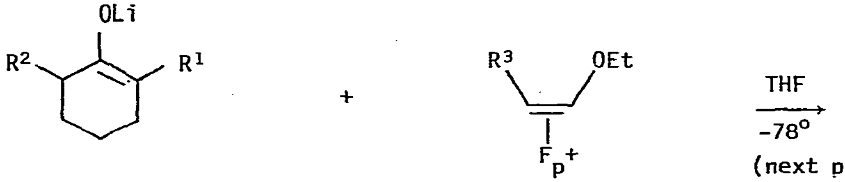
The full details of the alkylation of olefins with carbanions in the presence of palladium (II) salts have been published (equation 29) [49]. This work was the topic of a dissertation [50]. The alkylation of palladium-olefin complexes by ester enolates has again been reported [51]. Enol-ether iron complexes served as vinyl cation equivalents in the vinylation of enolates (equation 30) [52].



(29)

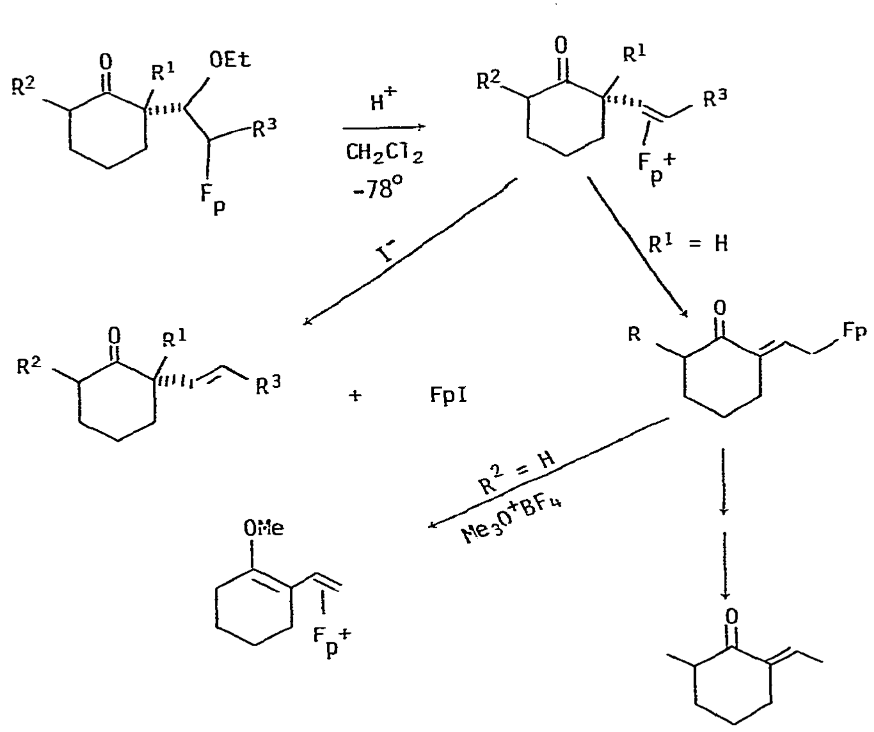
R = H, Me, Et, nC_4, Ph, NHAc
R' = Carbanions pK_a 12-30

(30)



(next page)

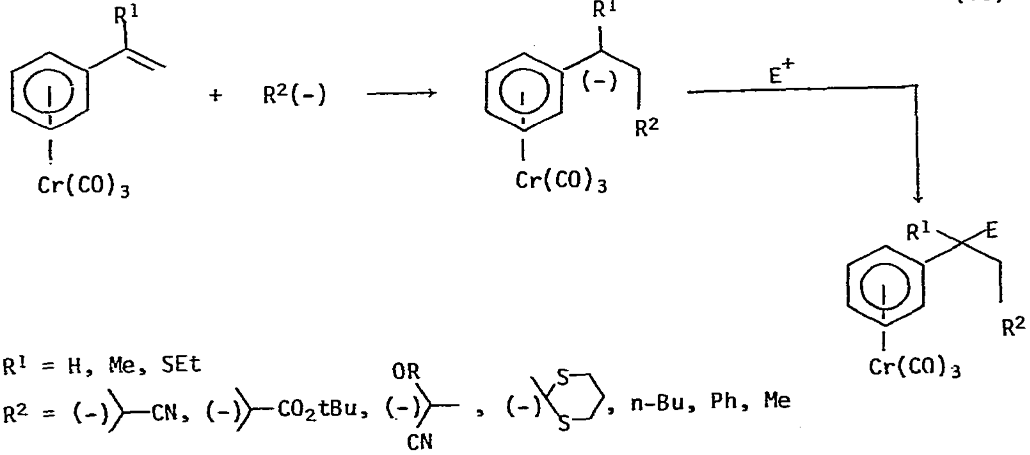
(30)



F_p = CpFe(CO)$_2$

Stryene chromium tricarbonyl complexes underwent β-alkylation by carbanions, and the resulting chromium-stabilized benzyl anion reacted further with electrophiles (equation 31) [53].

(31)

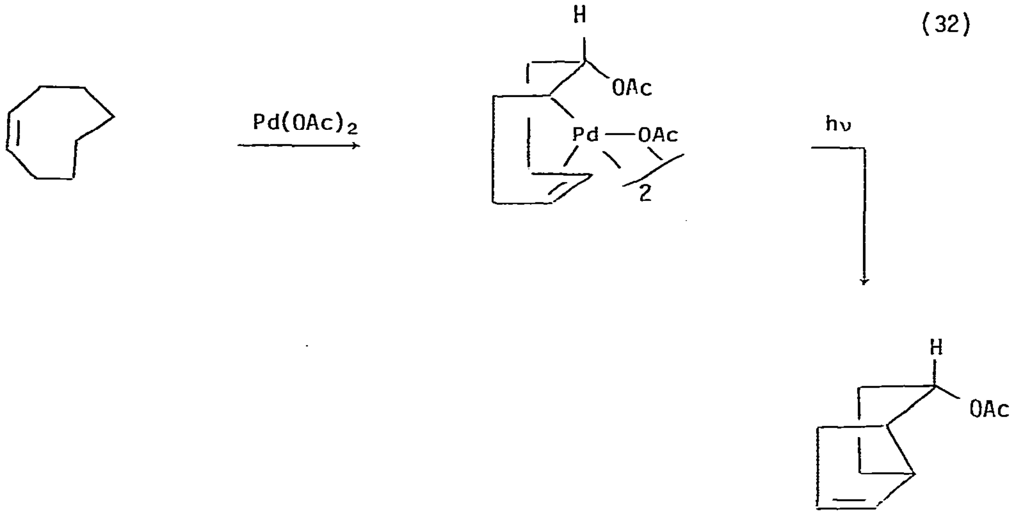


R^1 = H, Me, SEt

R^2 = (-)⟩—CN, (-)⟩—CO$_2$tBu, (-)(OR)(CN)⟩— , (-)(1,3-dithiane), n-Bu, Ph, Me

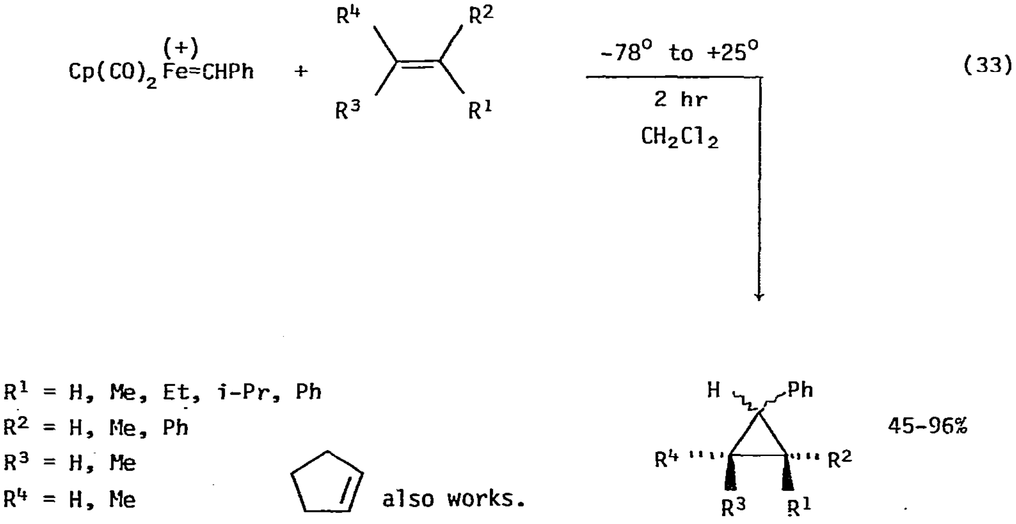
E = H^+, MeI, AcCl, PhSSPh

Photolysis of acetoxypalladation produci of cis, trans-1,5-cyclooctadiene produced a bridged bicyclic product (equation 32) [54].



(32)

A number of new cyclopropanation procedures have been developed. Perhaps the most generally useful relies upon a cationic iron-carbene complex (equation 33) [55]. Olefins reacted with dibromomalonates in the presence of copper powder in DMSO to produce cyclopropanes (equation 34) [56]. Car-2-ene was synthesized via a copper-carbenoid intermediate [57].

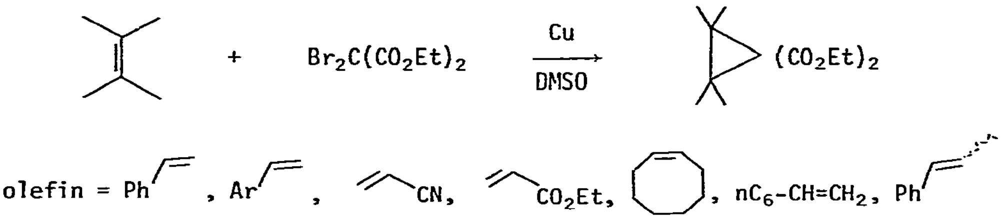


(33)

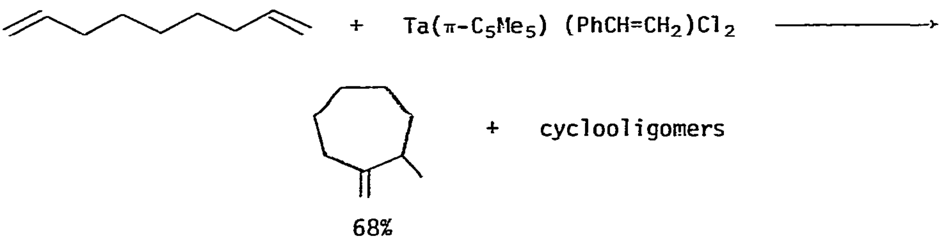
R^1 = H, Me, Et, i-Pr, Ph
R^2 = H, Me, Ph
R^3 = H, Me
R^4 = H, Me

also works.

(34)

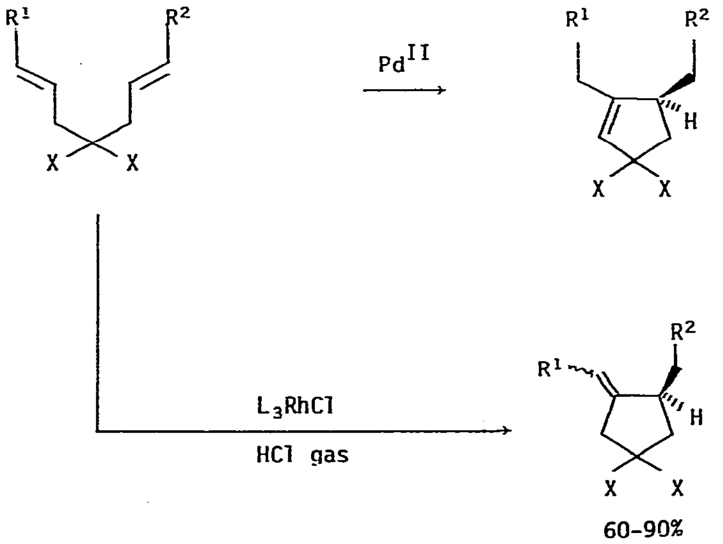


The complex Cp_2TiCH_2 reacted with ethylene to produce propene via a metallacycle intermediate [58]. The substrate 1,8-nonadiene cyclized to 2-methylvinylcycloheptene when treated with a tantalum styrene complex (equation 35) [59]. Palladium (II) and rhodium (I) complexes also cyclized dienes (equation 36) [60]. Norbornene reacted with β-bromostyrene in the presence of rhodium (I) catalysts to give β-norbornylstyrene, whereas palladium (0) catalysts produced cyclopropylcarbynyl compounds (equation 37) [61].



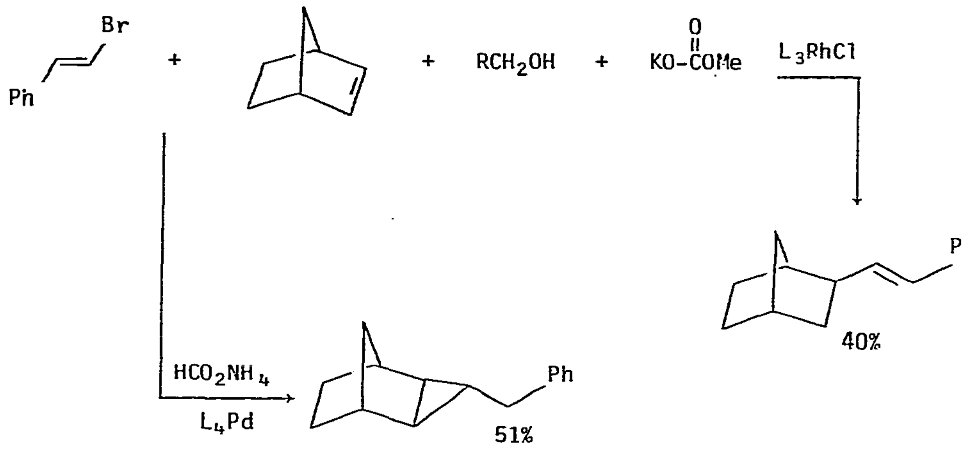
(35)

(36)

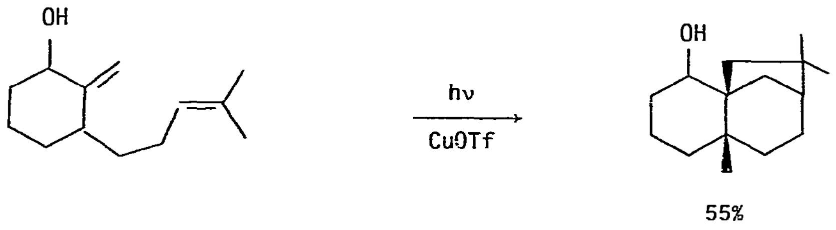


X = COMe, CO_2Et, COPh

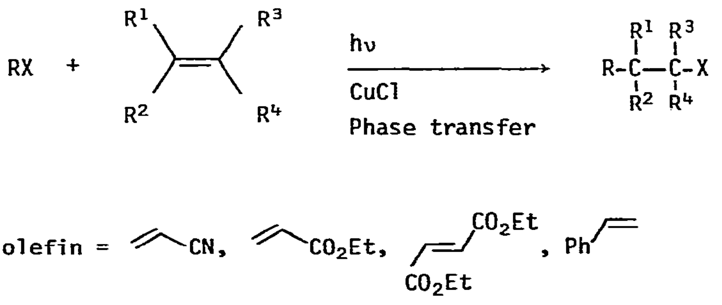
(37)



Photolysis of olefin-containing allylic alcohols in the presence of copper (I) triflate led to cyclization (equation 38) [62]. Organic halides added to olefins when photolyzed in the presence of copper (I) chloride under phase transfer conditions (equation 39) [63].



(38)

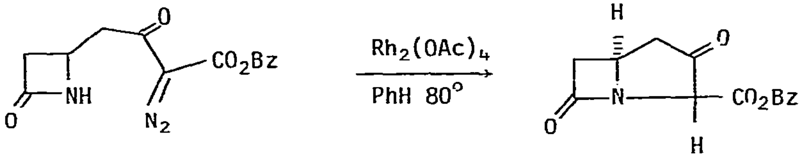


(39)

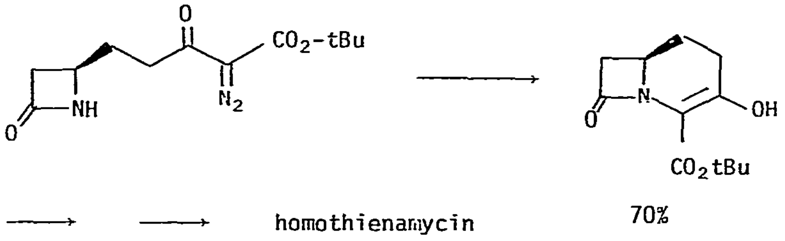
R = $CHCl_2$, CH_2Cl, Ph

4. Decomposition of Diazoalkanes

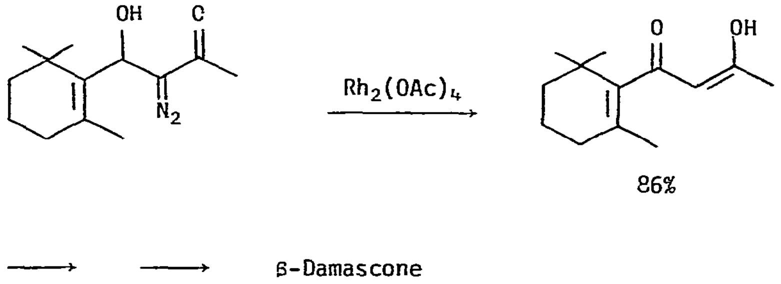
Metal-salt-catalyzed decomposition of diazoalkanes has been reviewed [64]. Carbapenam [65] and carbacepham β-lactams [66] have been synthesized using rhodium (II) acetate catalyzed decomposition of diazoalkanes as the key step (equations 40, 41). Cyclopropanation of olefins by rhodium catalyzed decomposition of ethyl diazoacetate yielded primarily cis products [67]. In contrast, rhodium (II) acetate-catalyzed decomposition of the diazoketone in equation 42 did not result in insertion [68].



(40)

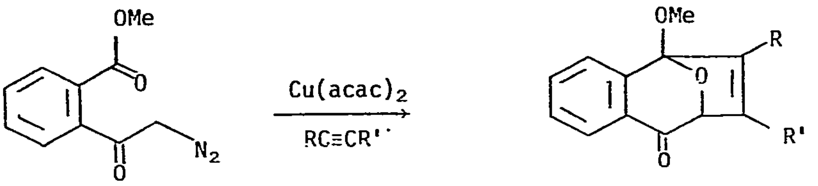


(41)



(42)

The copper (II) acetylacetonate-catalyzed decomposition of ethyl diazoacetate in the presence of a number of olefins was studied [69]. Cyclohexene, 4-t-butylcyclohexene, styrene, and indene all gave cyclopropenes, while 1-methyl cyclohexene and 1,2-dimethylcyclohexene gave complex mixtures of products. Unusual polycyclic materials were produced by carrying out this type of process (equation 43) [70].

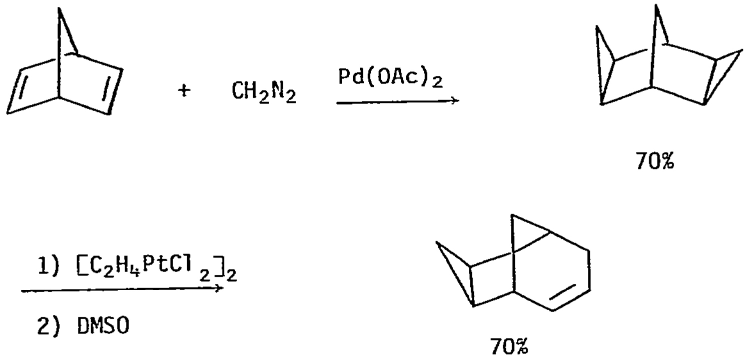


(43)

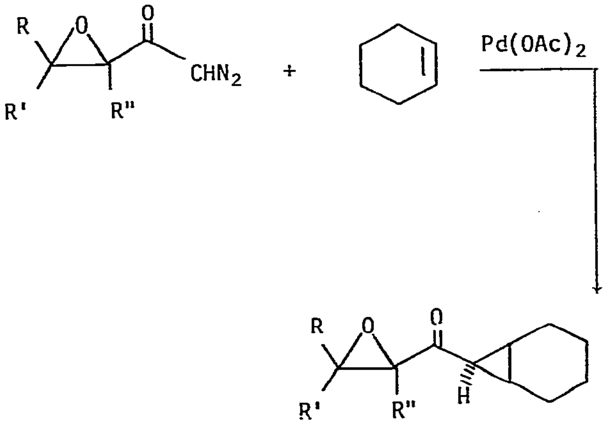
60-70%

R, R' = PhCO, CO_2Me

Palladium (II) complexes catalyzed the decomposition shown in equation 43a [71] and equation 44 [72].



(43a)



(44)

R = Ph

R' = Ph, Me, H

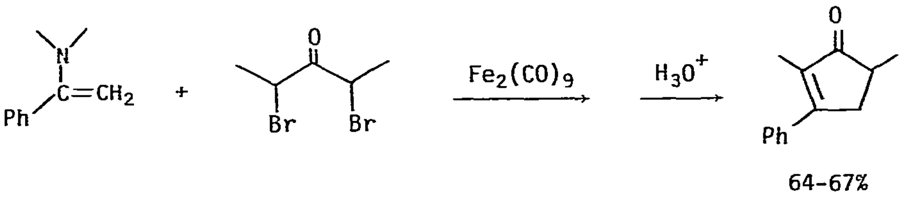
R" = H, Me, Ph

also works.

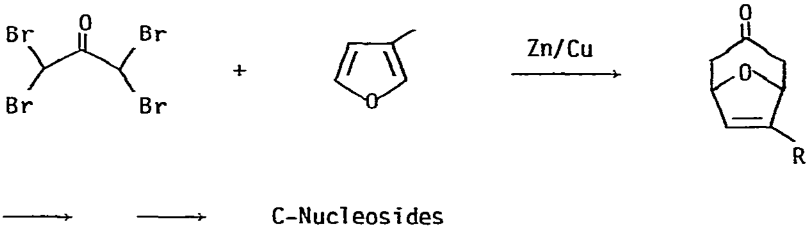
The use of palladium, rhodium and copper complexes to catalyze the cyclopropanation of olefins by diazo compounds is the subject of a review [73]. In a careful study of diazo compounds and their metal-catalyzed reactions with olefins, it was found that rhodium (II) catalysts promoted a carbenoid mechanism involving electrophilic attack on the uncomplexed olefin, whereas palladium (II) catalysts coordinate the olefin, and olefins which coordinate more strongly give better selectivity [74]. Molybdenum hexacarbonyl catalyzed the cyclopropanation of acrylonitrile, methacrylonitrile, and ethyl acrylate by ethyl diazoacetate or α-diazoacetophenone. Chromium hexacarbonyl also catalyzed this process, but tungsten hexacarbonyl did not [75].

5. Cycloaddition Reactions

α,α'-Dibromoketones reacted with enamines to form cyclopentenones after hydrolysis (equation 45) [76]. This same type of cycloaddition was used to synthesis 2'-methylated c-nucleosides (equation 46) [77]. Palladium (0) complexes catalyzed the unusual cycloaddition in equation 47 [78].



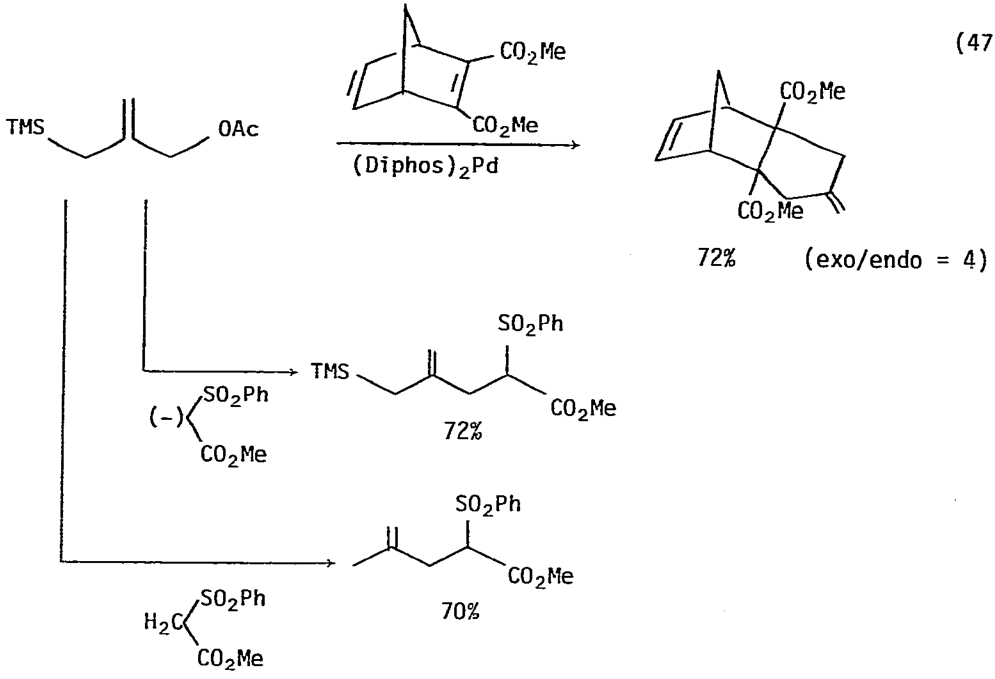
(45)



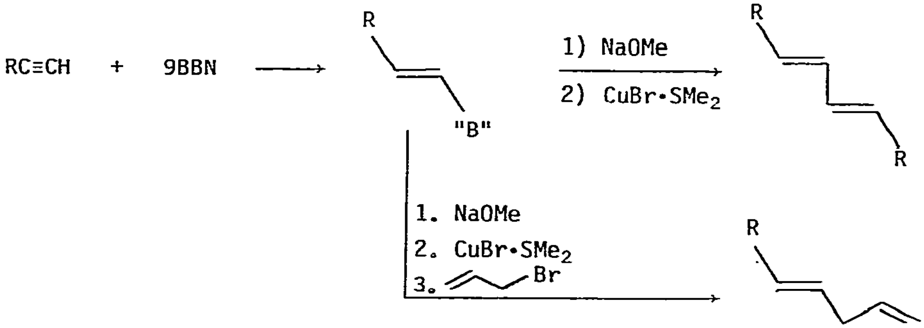
(46)

6. Alkylation of Alkynes

A number of procedures for the alkylation of vinylboranes have been developed. Since these vinylboranes are prepared from alkynes, these methods provide procedures for the alkylation of alkynes. Hydroboration of acetylenes with dialkylboranes, followed by treatment with sodium methoxide and copper(I) bromide dimethylsulfide produced symmetrical E,E-dienes (equation 48) [79]. These same copper intermediates reacted with allylic bromides (equation 49) [80][81][82]. Dialkylvinyl boranes reacted with palladium (II) acetate and triethylamine to produce trans olefins with an alkyl group from the borane;

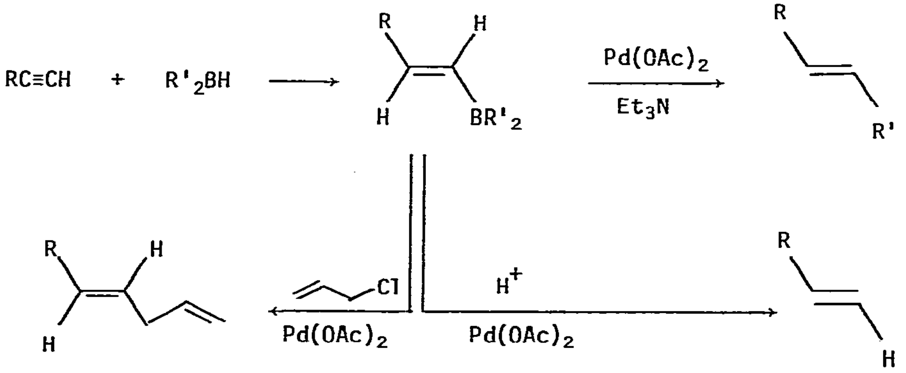

TMS
OAc
CO$_2$Me
CO$_2$Me
(Diphos)$_2$Pd
CO$_2$Me
CO$_2$Me
72%
(exo/endo = 4)
SO$_2$Ph
TMS
CO$_2$Me
(-)
SO$_2$Ph
CO$_2$Me
72%
SO$_2$Ph
CO$_2$Me
70%
H$_2$C
SO$_2$Ph
CO$_2$Me

(47)


RC≡CH
+
9BBN
R
"B"
1) NaOMe
2) CuBr•SMe$_2$
R
R
1. NaOMe
2. CuBr•SMe$_2$
3.
Br
R

(48)

(49)

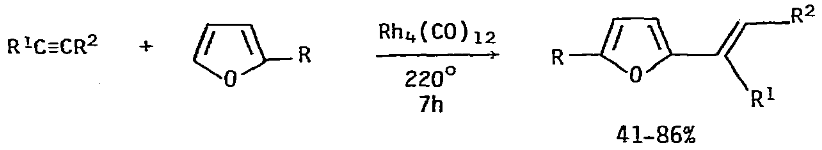

RC≡CH
+
R'$_2$BH
R
H
H
BR'$_2$
Pd(OAc)$_2$
Et$_3$N
R
R'
R
H
H
Cl
Pd(OAc)$_2$
H$^+$
Pd(OAc)$_2$
R
H

(50)

treatment with acid and palladium (II) acetate led to protonolysis, whereas reaction with allyl chloride produced 1,4-dienes (equation 50) [83]. Benzyl bromides reacted in a similar fashion [84], using palladium (0) catalysts.

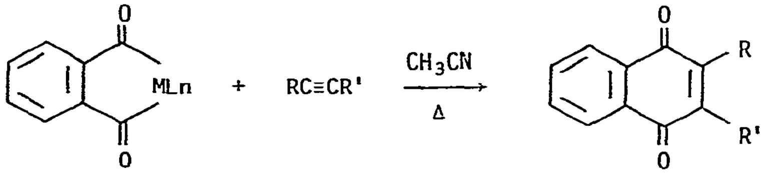
Iron (III) chloride catalyzed the reaction of aliphatic terminal alkynes with trialkyl aluminum complexes to produce 2,2-dialkyl terminal olefins [85]. Under some conditions oligomerization was observed. Phenyl acetylene and allylacetate reacted in the presence of nickel (0) or palladium (0) complexes to result in alkylation of the alkyne [86].

Furans were alkylated by internal alkynes in the presence of $Rh_4(CO)_{12}$ as a catalyst (equation 51) [87]. Thiophene and N-methylpyrrole react in a similar manner. Alkynes insert into diacylrhodium, cobalt or iron complexes to produce quinones (equation 52) [88]. Chlorodisilanes similarly add to acetylene itself to produce (Z)-1,2-bis(chlorosilyl)ethenes (equation 53) [89].



(51)

R^1 = Ph, p-tolyl, Me   R = Me, CO_2Me, Ac, CHO
R^2 = Ph, p-tolyl

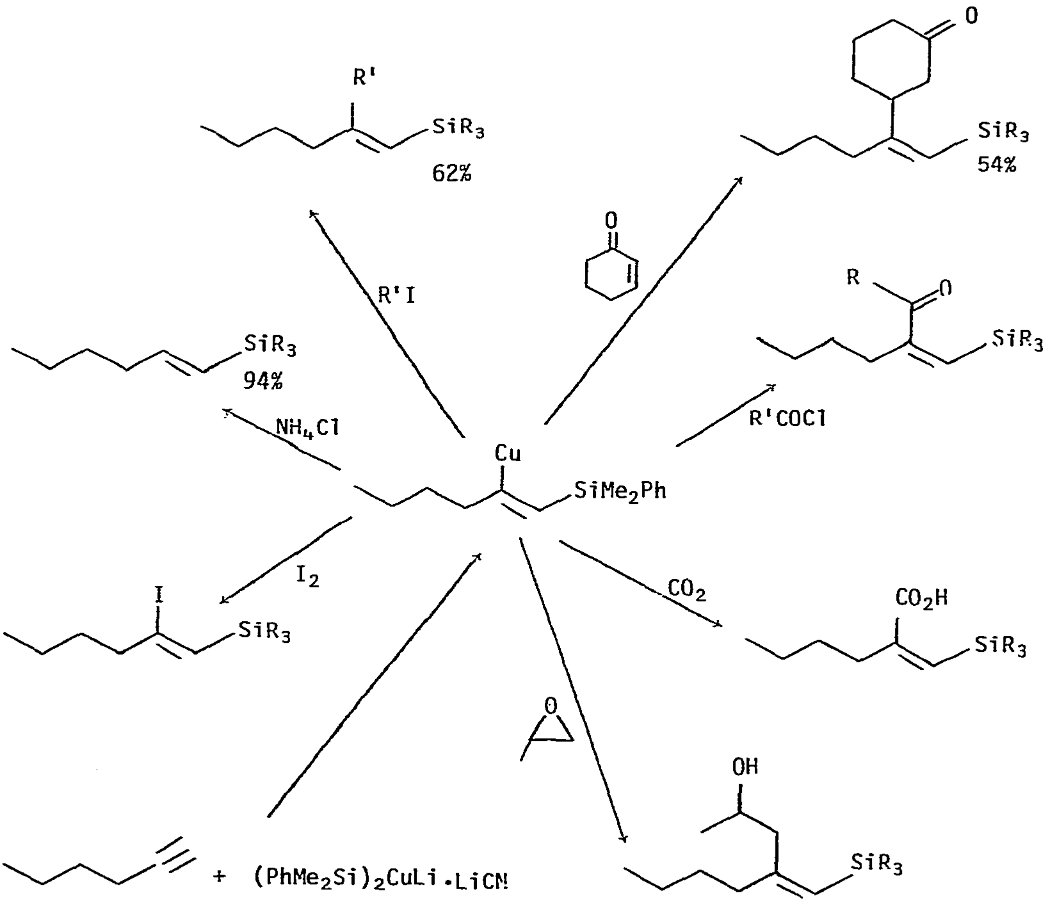


(52)

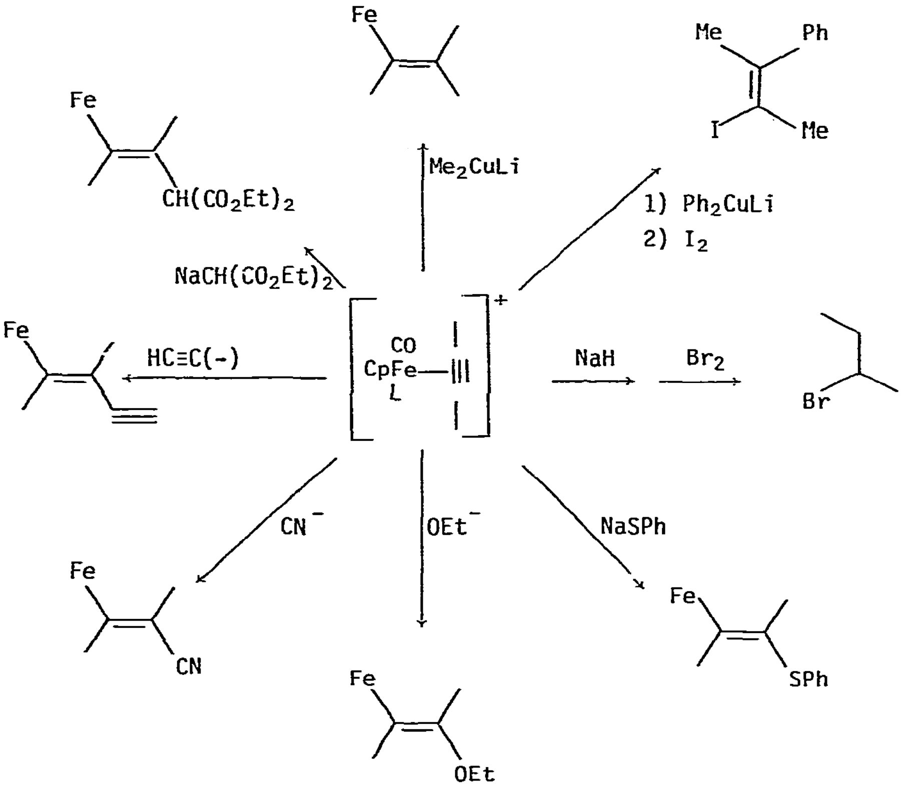
R = Me, Et, Ph, n-Bu, EtO
R' = Me, Et, Ph, H, allyl, TMS, COMe, CO_2Et, $(CH_2)_2OH$
M = Rh, Co, Fe

$$\mathrm{Cl_mMe_{3-m}SiSiMe_{3-n}Cl_n} + \mathrm{HC{\equiv}CH} \xrightarrow{L_4Pd} \mathrm{Cl_mMe_{3-m}SiCH{=}CHSiMe_{3-n}Cl_n} \qquad (53)$$

Two new procedures, one involving copper (Scheme I) [90], and the other involving iron (Scheme II) [91], offer extensive opportunities for the indirect alkylation of alkynes.



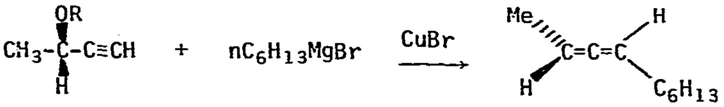
SCHEME I



SCHEME II

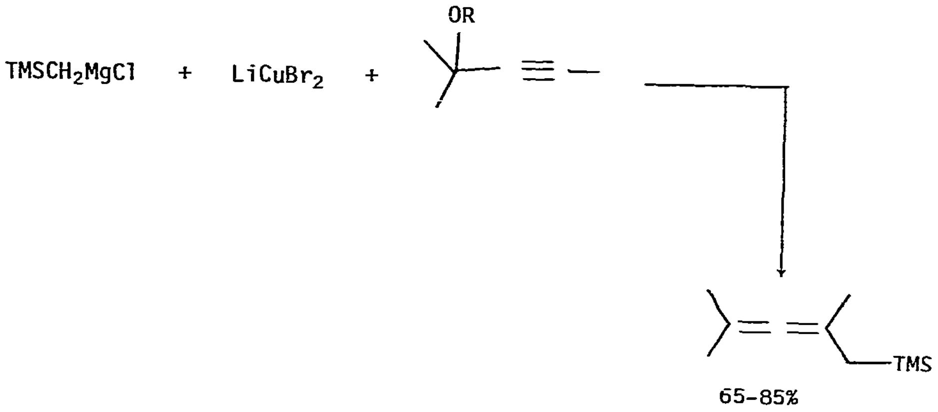
7. Alkylation of Allyl and Propargyl Alcohols and Acetates

n-Hexylmagnesium bromide with a copper catalyst reacted with optically active propargyl systems to produce optically active allenes with up to 79% ee (equation 54) [92]. Trimethylsilylmethylmagnesium bromide alkylated propargyl esters in the presence of copper (I) bromide exclusively by an S_N2' process, producing allenes (equation 55) [93]. Conjugated enyne propargyl mesylates reacted with organosilver complexes to produce 1,2,3-trienes (equation 56) [94].

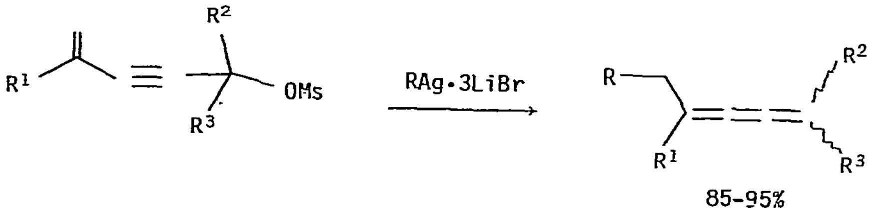


(54)

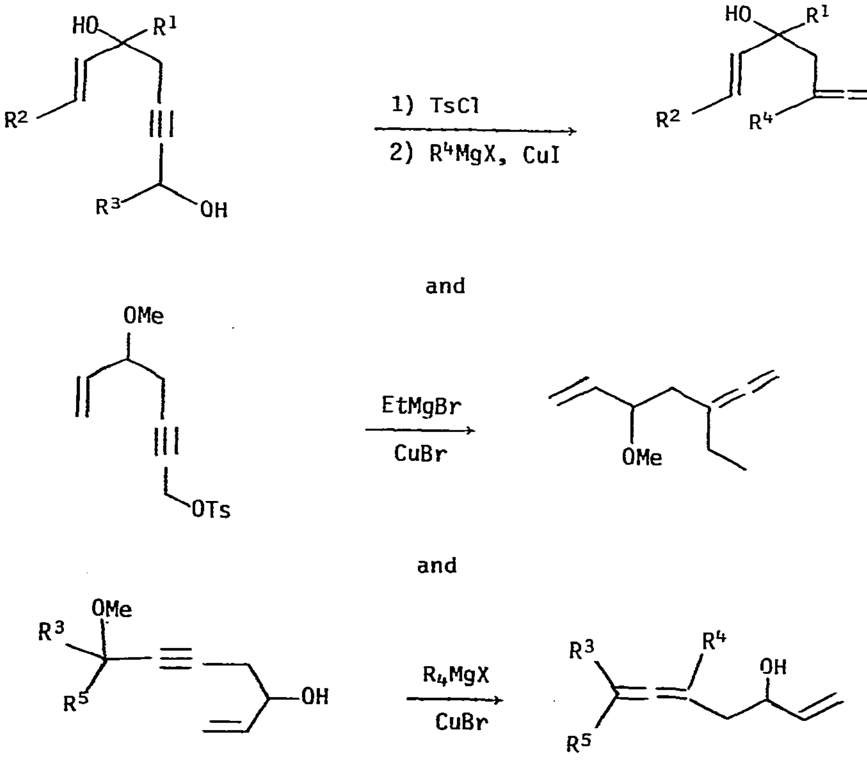
R = Me, Ac, $MeSO_2$, NEt_2
ee = 16, 79, 66, 16%



(55)



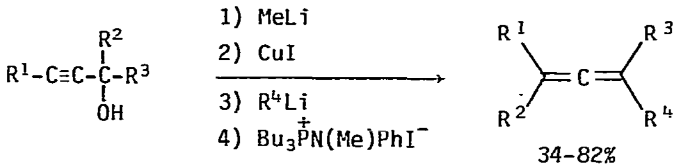
(56)



(57)

References p. 414

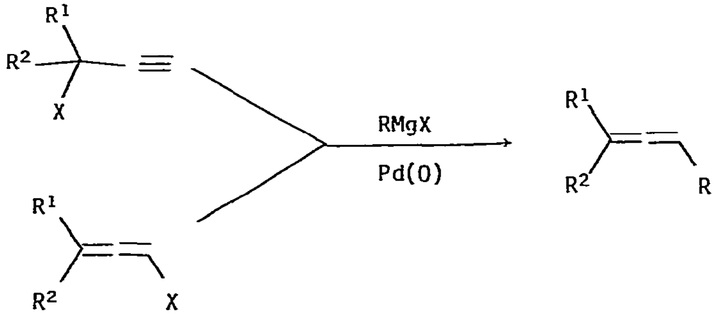
Grignard reagents added to propargyl esters (tosylates) or ethers in preference to allyl esters or ethers in the presence of copper (I) bromide (equation 57). Propargyl alcohols were converted regioselectively to allenes using the copper chemistry shown in equation 58 [96].



(58)

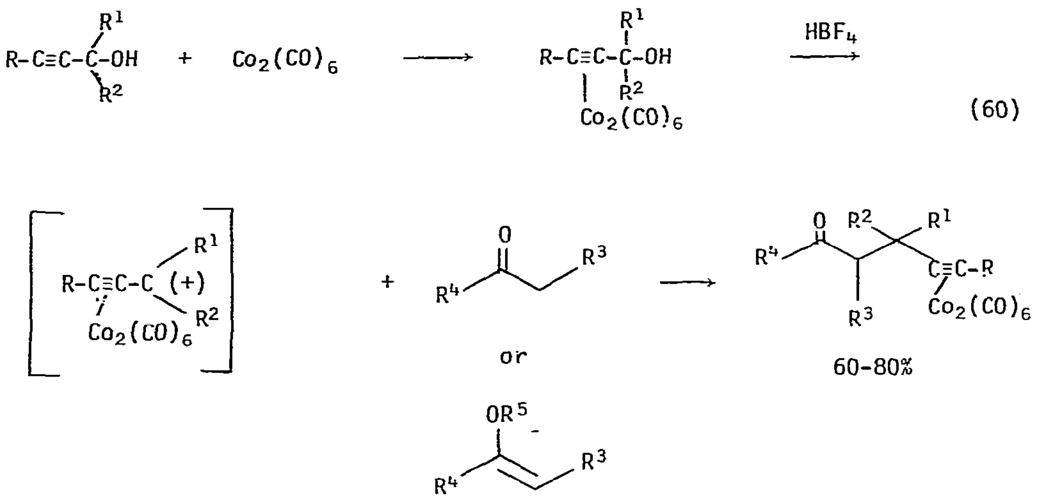
R^1 = Ph, $PhSCH_2$, TMS, nBu
R^2 = H, Ph, Et, n-Bu
R^3 = H, Me

Allylic alcohols reacted with Grignard reagents in the presence of chiral nickel (II) catalysts to result in alkenes by S_N2 and S_N2' displacement of the oxygen with up to 16% optical yield [97]. Secondary Grignard reagents reacted with allylic alcohols in the presence of palladium(II) complexes of ferrocenylphosphines, again with both S_N2 and S_N2' displacements [98]. Propargyl and allenyl halides react with Grignard reagents in the presence of palladium(0) catalysts to produce the same allene (equation 59) [99].

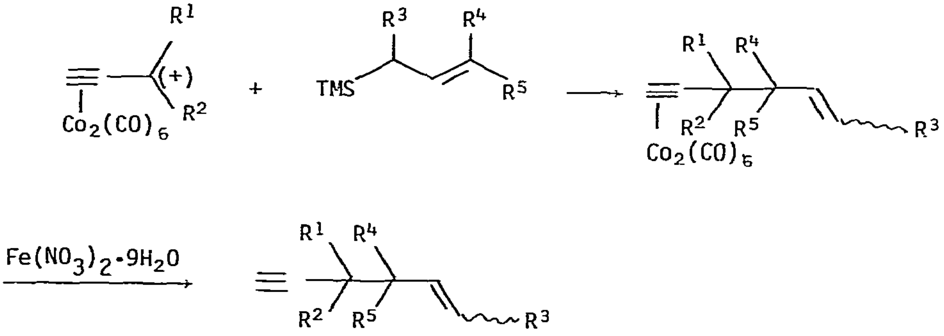


(59)

Propargyl alcohols were complexed to dicobalt octacarbonyl, then treated with tetrafluoroboric acid to produce cobalt-stabilized propargyl cations. These reacted with enol ethers or acetates (equation 60) [100][101] and with allylsilanes (equation 61) [102].

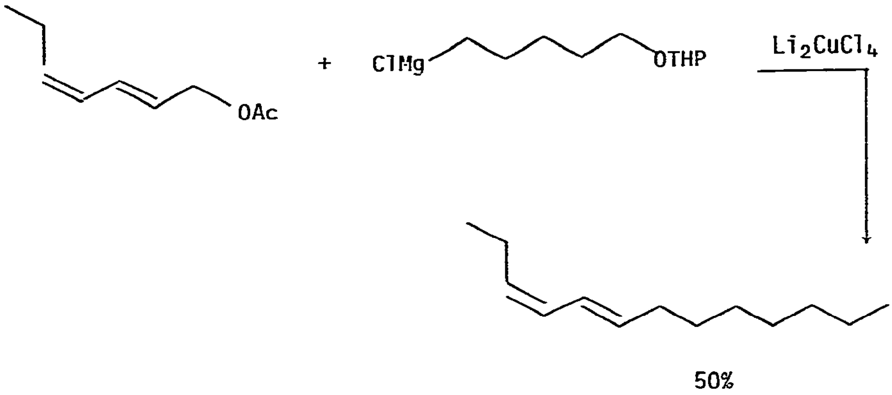


(60)



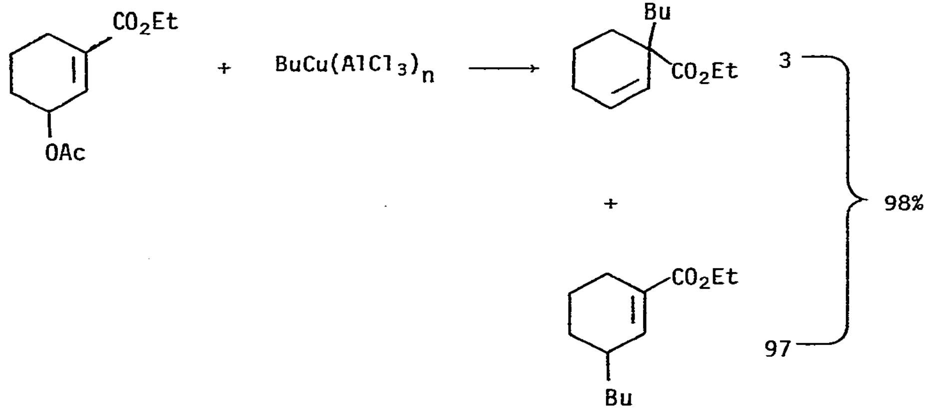
(61)

The nature of the organocopper reagent used in the alkylation of propargyl systems was the major determinant of whether allenes or alkynes were produced, with MeCu•LiBr•MgBrI producing allenes while R_2CuLi and R_3CuLi_2 favored propargyl systems [103]. The reactions of allylic alcohols or halides with $RCu \cdot BF_3$ resulted in clean S_N2' displacement of the leaving group. Similarly, propargyl halides reacted exclusively at the δ position, to produce allenes, regardless of the specific leaving group, or the substitution pattern of the substrate [104]. Long chain dienes and enynes were synthesized by the reaction of allyl acetates with Grignards in the presence of copper salts (equation 62) [105]. α-Acetoxy-α,β-unsaturated esters underwent almost exclusive α-alkylation when treated with $BuCu(AlCl_3)_n$, whereas BuCu failed to react at all, and Bu_2CuLi reduced the acetate (equation 63) [106a]. Allylic sulfoxides and sulfones underwent S_N2' displaced when treated with lithium dialkylcuprates [106b].



(62)

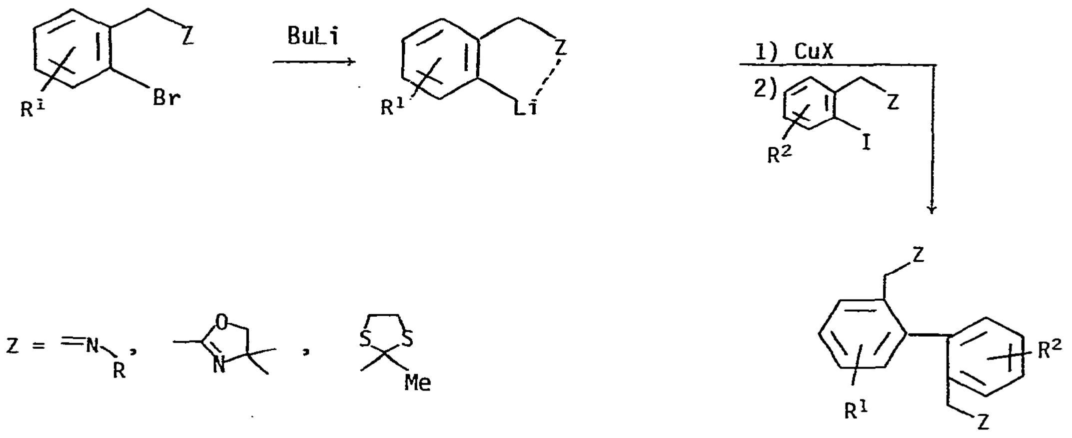
(63)



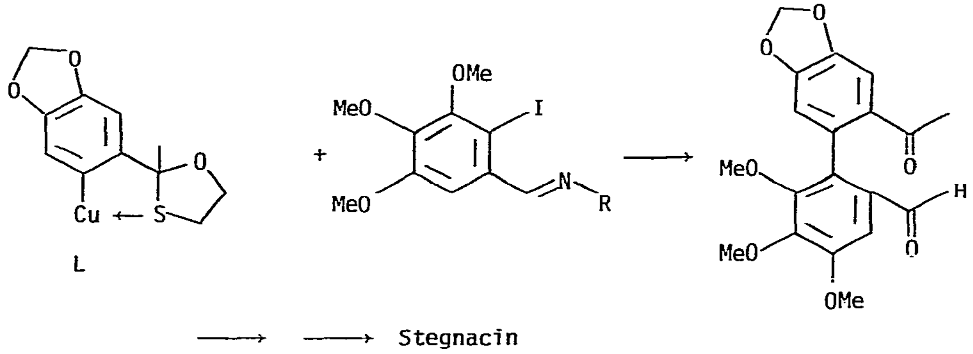
8. Coupling Reactions

Reduction of cobalt, nickel and iron (II) halides with lithium metal produced highly reactive metal powders which coupled aryl bromides to biaryls [107]. The reactions also produced Ar_2M complexes which underwent other useful reactions. "Syntheses using the Ullmann and modified Ullmann reactions" was the topic of a dissertation [108]. Copper powder in DMF was used to couple polychloroaromatic compounds, as well as to reduce them. Pentachloropyridines were reduced to tetrachloropyridines, but did not couple [109]. An efficient procedure for the cross coupling of aryl halides involved ligand-directed metallation followed by exchange with copper halide, and reaction with aryl iodides (equation 64) [110]. This chemistry was used to synthesize stegnacin (equation 65). Chiral esters of 1-bromo-2-naphthoic acid coupled when

(64)

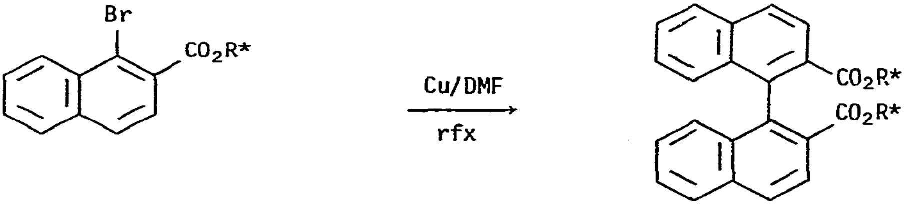


(65)



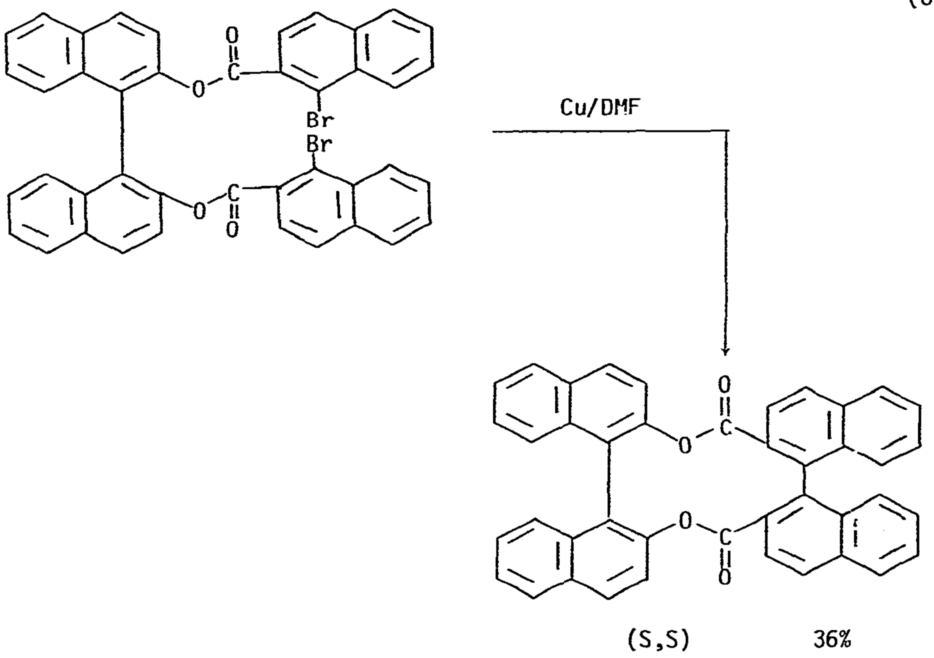
treated with copper powder in DMF to give binaphthyls having up to 13% ee (equation 66) [111]. This chemistry was used to synthesize the unusual chiral compound in equation 67 [112]. A review entitled "Modern Methods of Aryl-Aryl Bond Formation" has appeared [113].

(66)



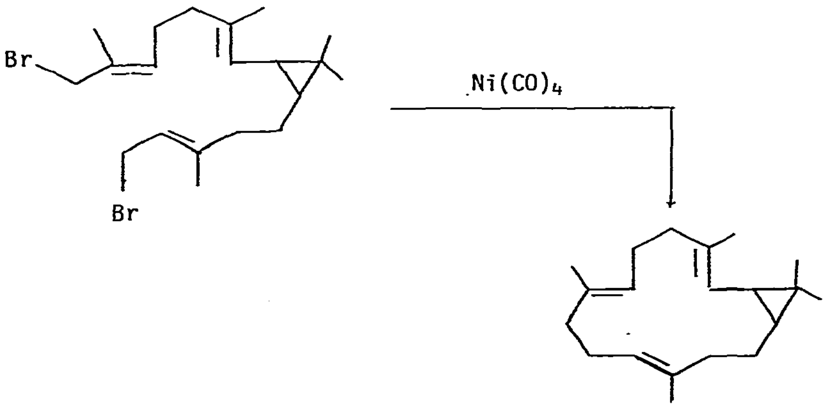
R* = l-menthol
cholesterol
+ 1-phenylethanol

(67)

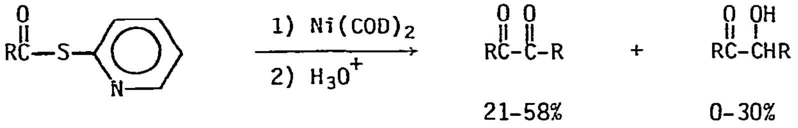


The macrocyclic diterpene casbene was synthesized using the nickel carbonyl coupling of a <u>bis</u> allylic halide (equation 67a) [114]. Aryl halides were electrochemically coupled to biaryls in the presence of nickel (II) chloride-phosphine complex [115]. Organic halides were coupled electrochemically using nickel (II) salen complexes as catalysts. Methyl acrylate was alkylated at the β-position by the electrochemical reduction of organic halides in the presence of this same catalyst [116].

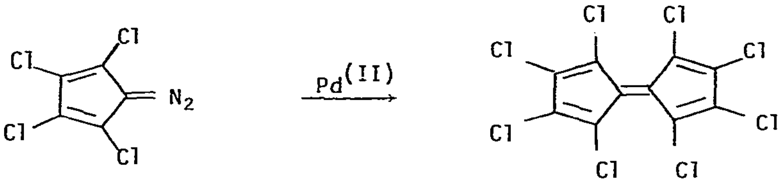
(67a)



Aliphatic S-(2-pyridyl)thiolates were coupled to α-diketones and α-hydroxyketones by bis-(cyclooctadiene) nickel (equation 68) [117]. Aryl S-(2-pyridyl)thiolates coupled to diaryl ketones under the same conditions [118]. Iodoarenes were converted to biaryls by palladium amalgam [119]. Tetrahalo-diazocyclopentadiene coupled to produce the corresponding fulvene when treated with palladium (II) complexes (equation 69) [120]. The dimerization of 1,4-dichlorotetrasilanes to 1,8-dichlorooctasilanes was effected by L_4RuH_2 [121].

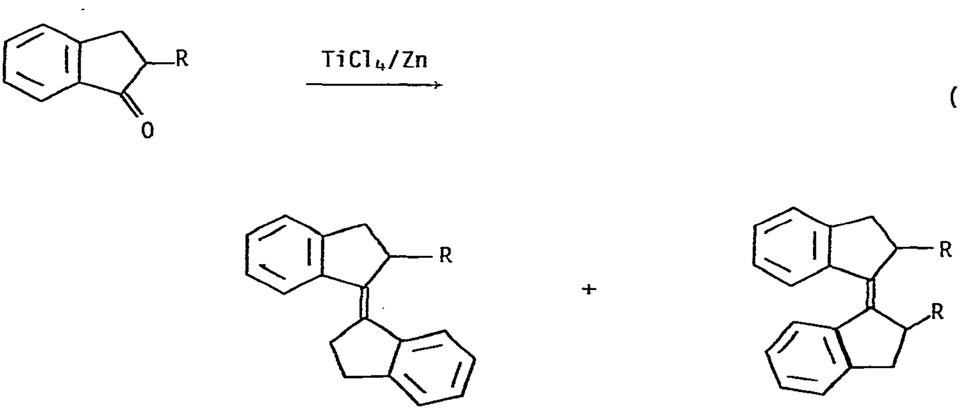


(68)



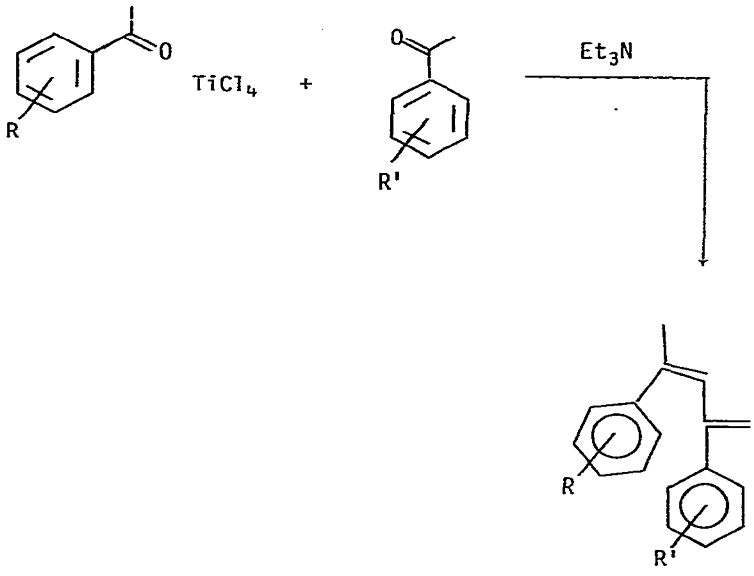
(69)

Titanium tetrachloride/zinc coupled indanone to the dimer, but poly-methylated indanone underwent reduction of the ketone to the hydrocarbon (equation 70) [122]. Aryl aldehydes dimerized to form diarylglycols when treated with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ [123]. Aryl ketones underwent aldol-type condensation when treated with titanium tetrachloride (equation 71) [124]. Titanium trichloride/lithium aluminum hydride coupled (S)(+)-1,1-diphenyl-1,3-butanediol to optically pure (R)(-)-1-methyl-2,2-diphenylcyclopropane [125].



(70)

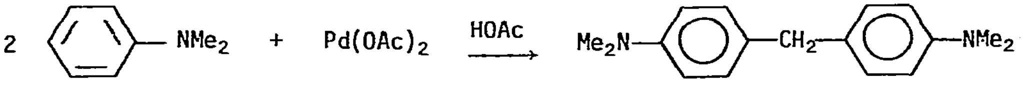
(71)



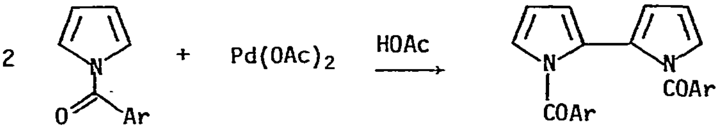
50-80%

Palladium (II) acetate coupled N,N-dimethylaniline to 4,4'-*bis*-dimethylamino diarylmethanes (equation 72) [126]. N-Acetylpyrroles coupled to dimers at the 2 position when treated with this same catalyst (equation 73) [127]. Ketone enolates dimerized to 1,4 diketones when treated with either $FeCl_3$ in dry DMF [128] or copper (II) trifluoroacetate (equation 74) [129].

(72)

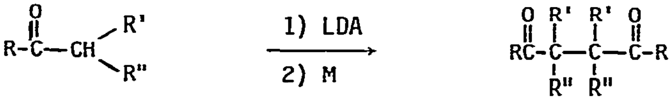


76%



(73)

38-43%

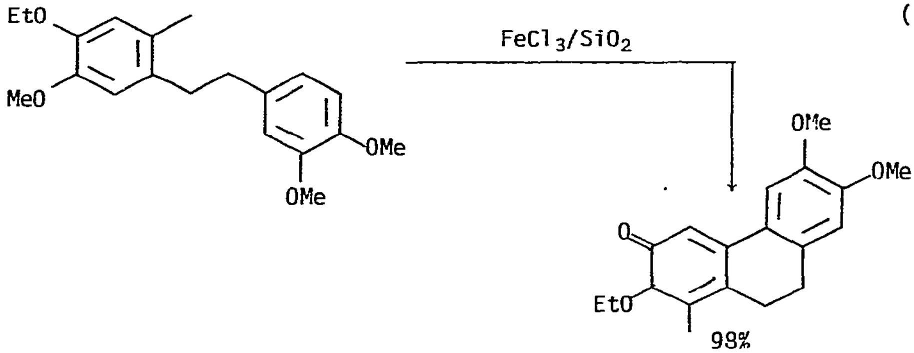


$$R\text{-}\overset{O}{\overset{\|}{C}}\text{—}CH\begin{matrix}R'\\R''\end{matrix}\xrightarrow[\text{2) M}]{\text{1) LDA}}R\overset{O}{\overset{\|}{C}}\text{-}\underset{R''}{\overset{R'}{C}}\text{—}\underset{R''}{\overset{R'}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{-}R$$

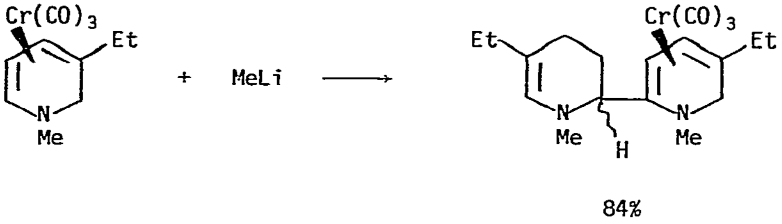
(74)

Iron (III) chloride on silica gel oxidatively coupled electron rich aromatic compounds. This procedure worked well intramolecularly (equation 75) [130]. Thermal decomposition of Wilkinson's catalyst, $RhCl(PPh_3)_3$ above 140° produced biphenyl [131]. Dihydropyridine chromium tricarbonyl complexes reacted with methyllithium to produce mixtures of bipyridines (equation 76) [132]. Olefins dimerized in a tail to tail fashion when treated with a tantalum complex catalyst (equation 77) [133].

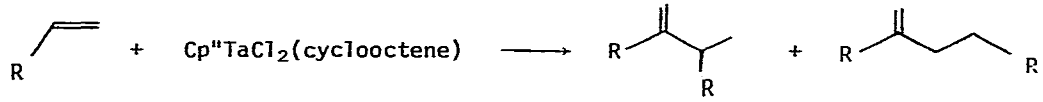
(75)



(76)



(77)



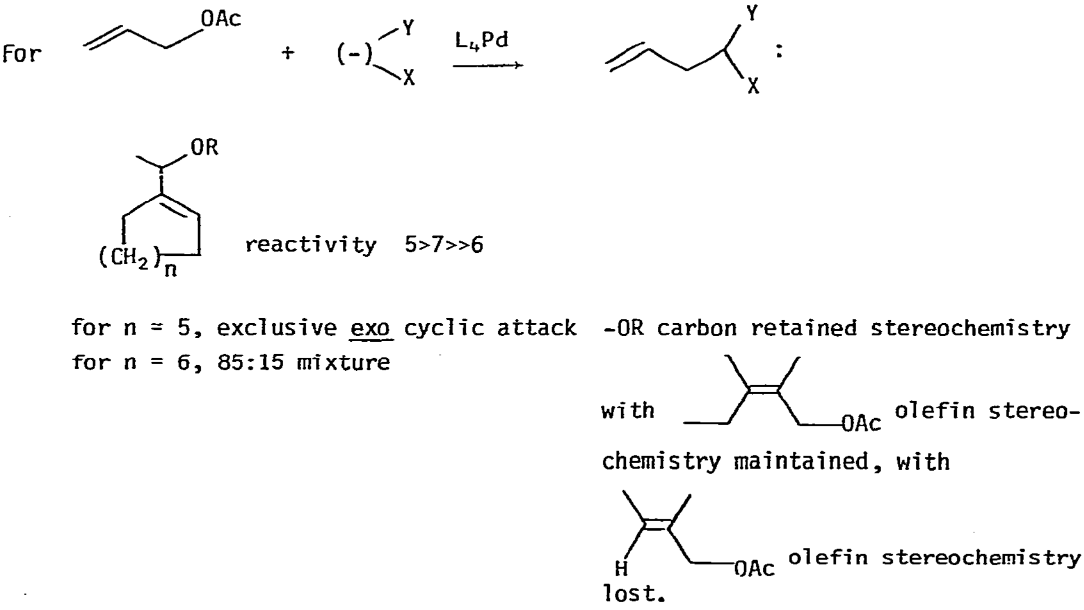
R = H, Me, nPr, $(CH_2)_5$, CH_2CHMe_2, CH_2CMe_3

The mechanism of 1,1-reductive elimination from dialkylpalladium (II) complexes was studied [134]. A review entitled "Use of Isotope Crossover Experiments in Investigating Carbon-Carbon Bond Forming Reactions of Binuclear

Dialkyl-Cobalt Complexes" has appeared [135]. The formation of carbon-carbon and carbon-nitrogen bonds mediated by organometallic cobalt complexes is the topic of a dissertation [136].

9. π-Allylpalladium Alkylations

Allylic alkylations involving π-allylpalladium intermediates continued to be extensively studied and exploited. Palladium-catalyzed allylic alkylation was the topic of a dissertation [137]. A new procedure for the preparation of a new π-allylmetal complexes using highly reactive metal powders and allylic halides has been developed [138]. Olefins formed π-allylpalladium halide complexes quickly and in high yield when treated with palladium (II) trifluoroacetate. Cyclohexene, however, disproportionated under these conditions [139]. A review on new rules of selectivity: allylic alkylations catalyzed by palladium has appeared [140]. The full experimental details (20 pages) of the stereo- and regioselectivity in the palladium (0) catalyzed reactions of stabilized carbanions with allylic acetates have been published [141]. The findings are summarized in Scheme III. Allyl sulfones reacted with stabilized carbanions in the presence of palladium (0) catalysts. With unsymmetrical allyl sulfones the regiochemistry of the reaction depended on the nature of the carbanion (equation 78) [142].



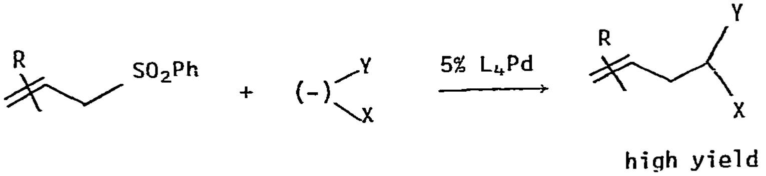
for n = 5, exclusive exo cyclic attack

for n = 6, 85:15 mixture

-OR carbon retained stereochemistry

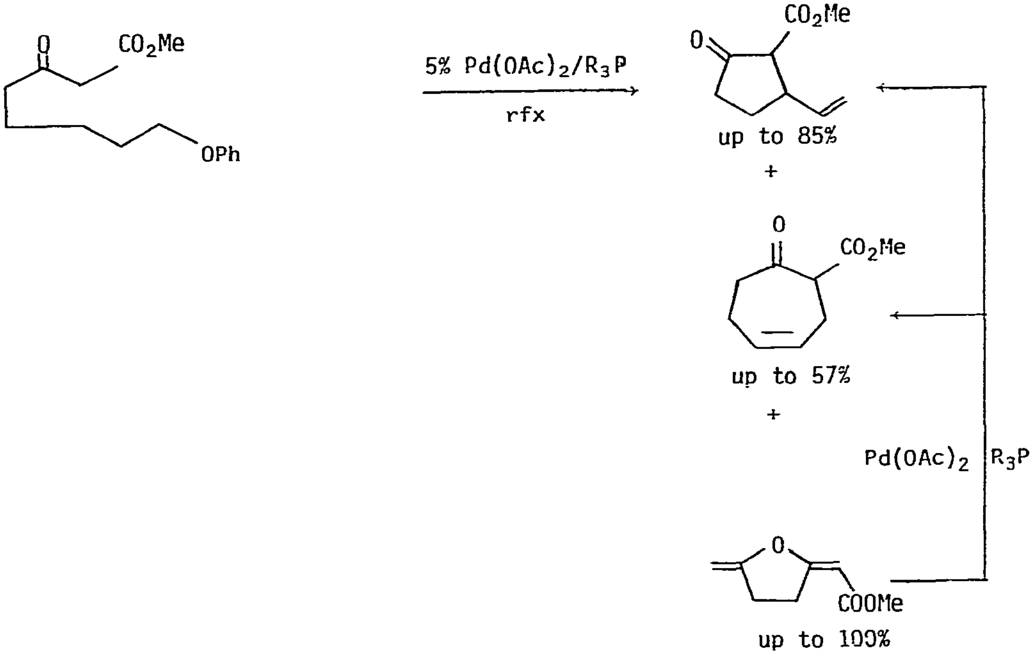
SCHEME III

(78)

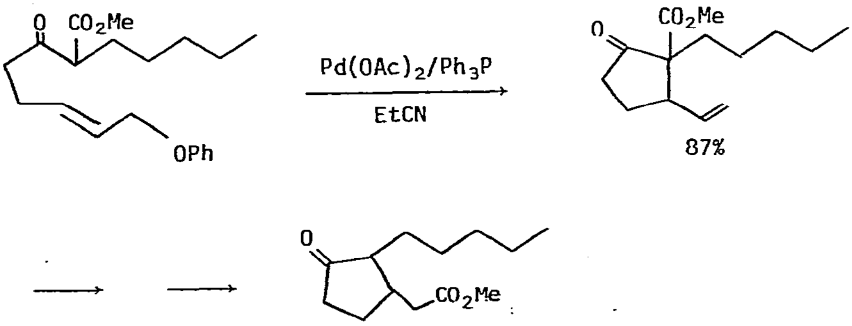


$X = CO_2Et$; $Y = CO_2Et$, $PhSO_2$

(79)

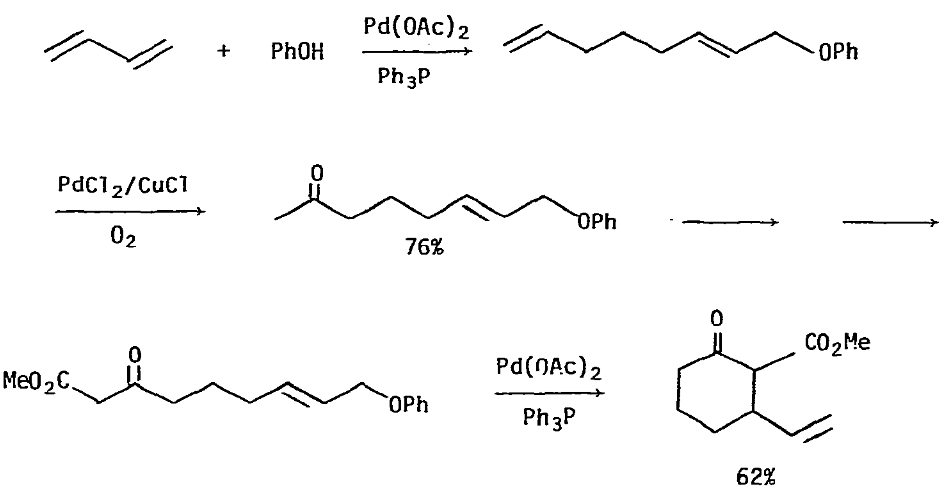


(80)

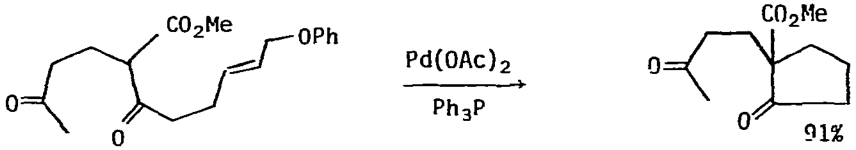


Intramolecular versions of this alkylation reaction have been used to synthesize a number of interesting carbocycles. The formation of five and six membered rings from allyl phenyl ethers by the chemistry was controlled by the solvent and the base (equation 79). This chemistry was used to synthesize natural compounds (equation 80, 81) [143], as well as the C,D rings of steroids bearing functionalized 18-methyl groups (equation 82, 83) [144]. The synthesis of macrolides from intramolecular alkylation of allyl acetates relied on palladium (0) catalysts. Under these conditions, the larger of the two possible rings was always the major product. Recifeiolide was synthesized in this manner (equation 84) [145], as were 4, 5, 6, 10, 12, 14, and 16 membered ring com-

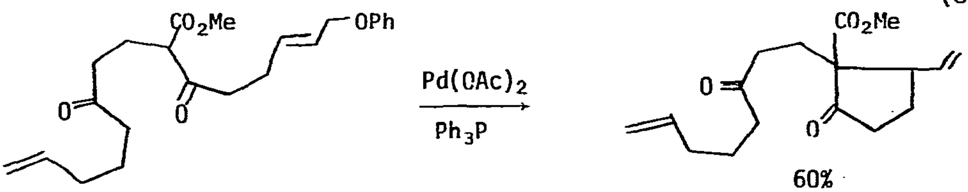
(81)



(82)

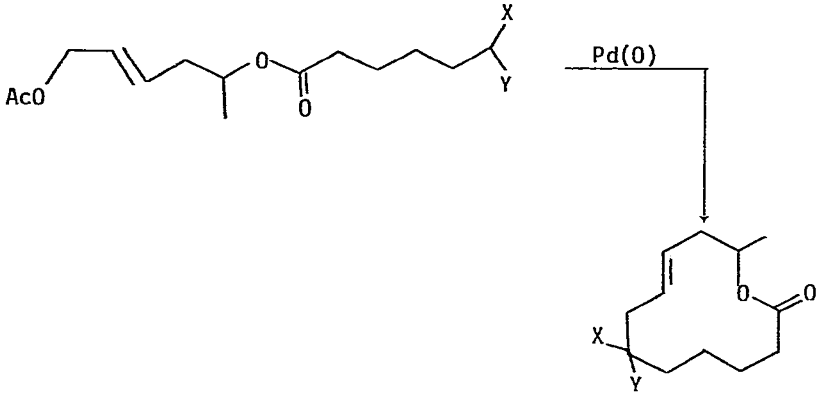


(83)



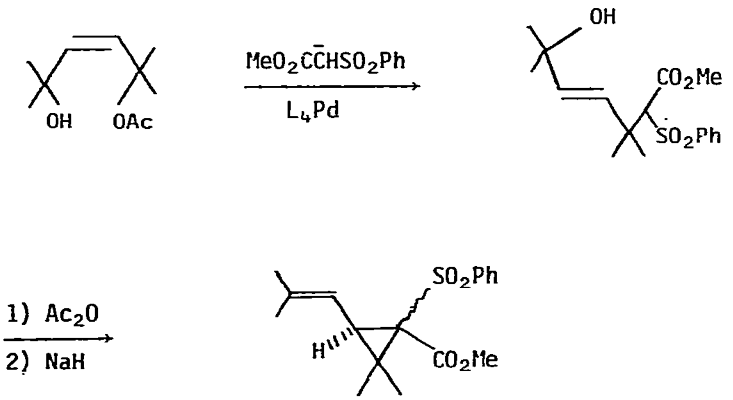
pounds. The regioselectivity of the reaction of dimethyl malonate anion and cyclopentadiene anion with allylic acetates in the presence of palladium (0) catalysts was studied with several differently substituted substrates. In all cases examined under this specific set of conditions, attack at the less substituted position predominated [146].

(84)



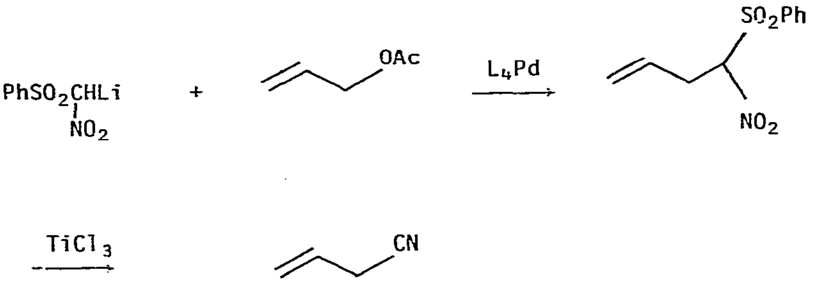
Allylic bromides cross coupled to trialkyl allyltin compounds in the presence of palladium (0) catalysts. The reaction resulted in the production of 1,5-hexadienes in which the allyl group from tin had undergone allylic transposition, but the allylic bromide had not [147][148]. Tributyl tin enolates of ketones alkylated allylic acetates in the presence of palladium (0) catalysts [149].

Trans-chrysanthemic acid was synthesized from an intermediate produced by the alkylation of an allylic acetate with a stabilized carbanion in the presence of palladium (0) catalysts (equation 85) [150].



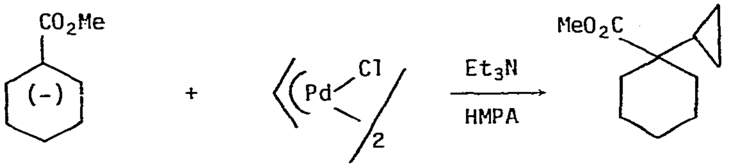
(85)

Allylic nitriles were produced using the palladium (0) catalyzed alkylation of allyl acetate by nitro stabilized carbanions (equation 86) [151].



(86)

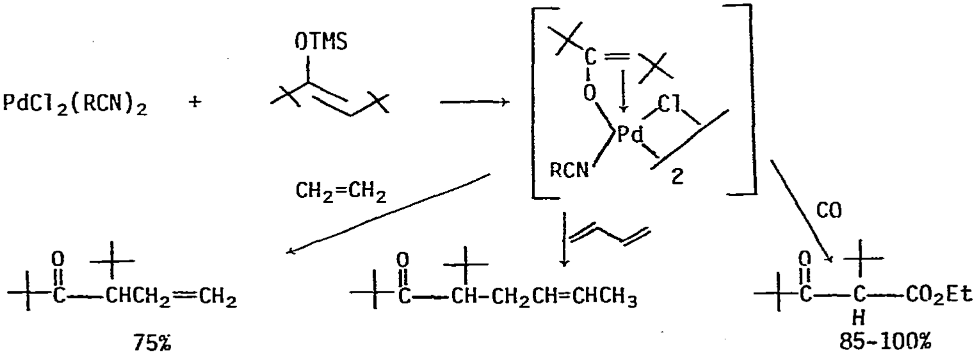
Branched ester enolates reacted with π-allylpalladium halide complexes in the presence of triethylamine and HMPA to produce cyclopropanes resulting from alkylation of the central carbon of the π-allyl group (equation 87) [152].



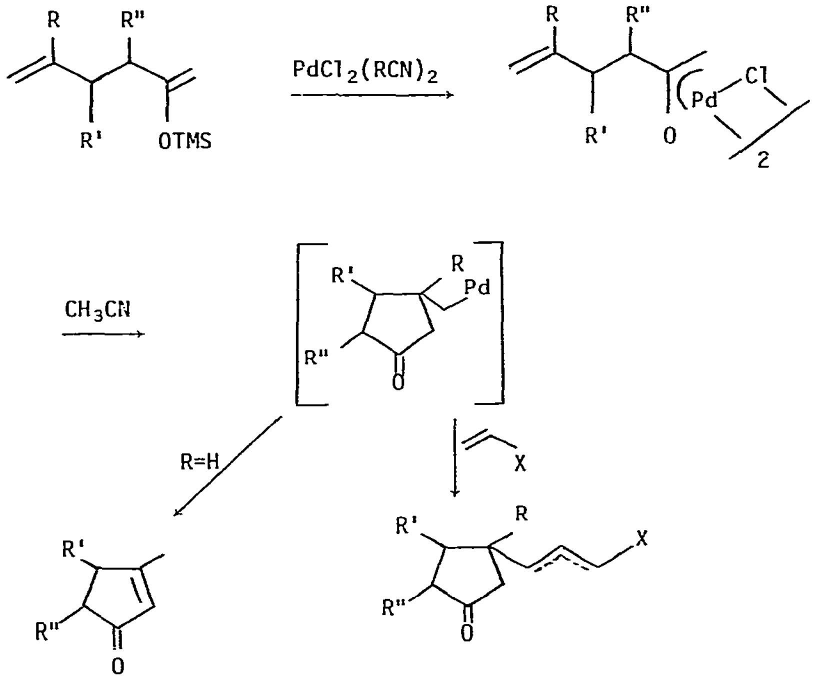
(87)

Irradition of π-allylpalladium chlorides in acetonitrile led to coupling of the allyl groups to give 1,5-dienes [153]. Trimethylsilyl enol ethers reacted with palladium (II) chloride to produce oxallylpalladium II halide complexes. These inserted dienes to give unsaturated ketones, olefins to give unsaturated ketones, and carbon monoxide to give ketoesters (equation 88) [154].

(88)



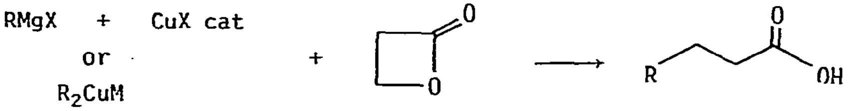
When the starting enol ethers contained remote olefins, cyclization occurred (equation 89) [155]. Steroidal π-allylpalladium chloride complexes reacted with vinyl zirconates to result in vinyl transfer from zirconium to the less substituted terminus of the π-allyl system [156]. Cationic π-allyl complexes of molybdenum reacted with nucleophiles to produce propene complexes incorporating the nucleophile in the propene portion [157].



(89)

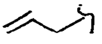
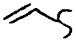
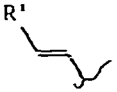
10. Alkylation of Carbonyl Compounds

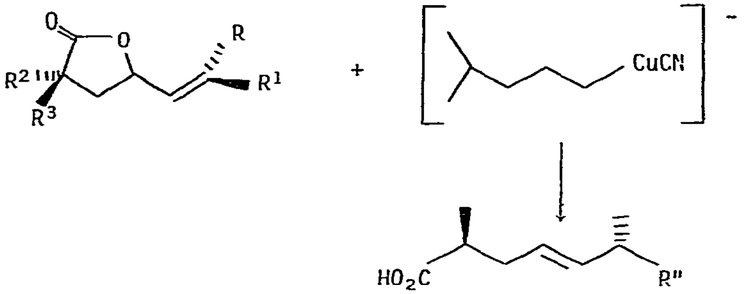
A number of essentially identical papers reporting the reaction of Grignard reagents with β-lactones in the presence of copper catalysts have appeared (equation 90) [158-161]. Overall, virtually all types of alkyl groups could be used. However, the yields were somewhat dependent on the metal and on whether stoichiometric or catalytic amounts of copper was used. Chirality transfer from a remote lactone position in the alkylation of allyl lactones by a mixed organocuprate was developed (equation 91). This process went by an S_N2' mechanism, and the stereochemistry depended on the conformation of the substrate [162]. α-Pyrones underwent a ring opening-alkylation when treated with Grignard reagents, methyl iodide, and copper (I) chloride (equation 92) [163]. Esters reacted with Grignard reagents in the presence of small amounts of Cp_2TiCl_2 to undergo reductive alkylation to the secondary alcohol, whereas the use of larger amounts of this titanum catalyst produced the primary alcohol (equation 93) [164].



(90)

(M = MgX, Li)

R = Me, n-Bu, i-Pr, t-Bu, , , Ph, t-amyl, 

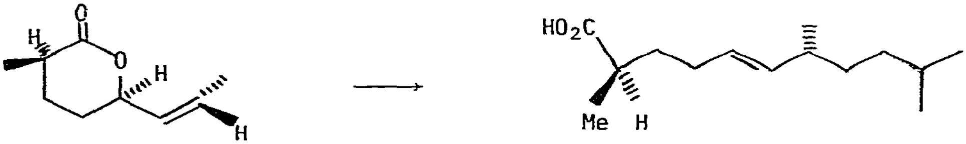


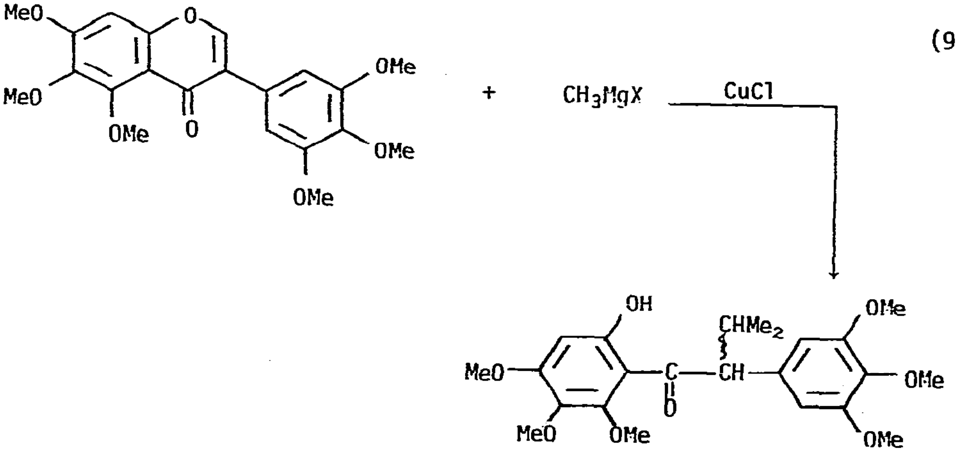
(91)

$R = R^2 = Me$
$R^1 = R^3 = H$ (Z isomer)

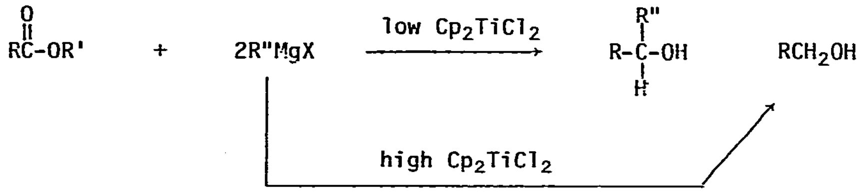
Single isomer R" = i-C_6H_{13}

but





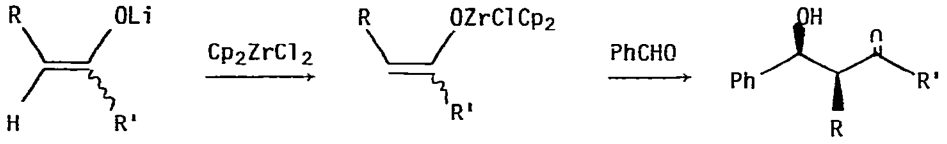
(92)



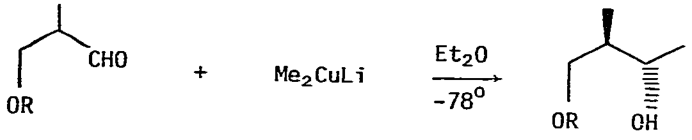
(93)

Transition metals have been used to control the erythro-threo ratios resulting from aldol condensations. Treatment of zirconium enolates of esters, amides, thio esters [165] or ketones [166] with an aldehyde led to very high proportions of erythro products, in comparison to the same reactions with the corresponding lithium enolates (equation 94). Treatment of β-alkoxyaldehydes with lithium dimethylcuprate produced β-alkoxyalcohols with very high threo/erythro ratios (equation 95). α-Alkoxy groups gave low stereoselectivity [167].

(94)



R' = Me, Et, OR, SR, NR_2 R = Ph, Me   R, R' = $-(CH_2)_5-$, $-CH_2)_4-$

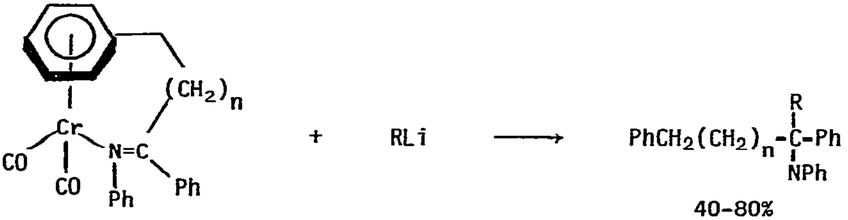


(95)

>20:1 threo:erythro   90%

Treatment of the chiral chelating imino arylchromium tricarbonyl complex in equation 96 with organolithium reagents produced the chiral amine having 94% optical purity [168]. Threonine was synthesized from the dipeptide gly-gly by alkylation with acetaldehyde of a chiral copper-cymantrene complex of the dipeptide. The optical yield was 95-100% [169].

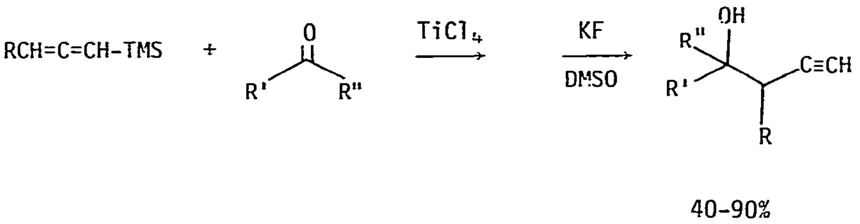
(96)



40-80%

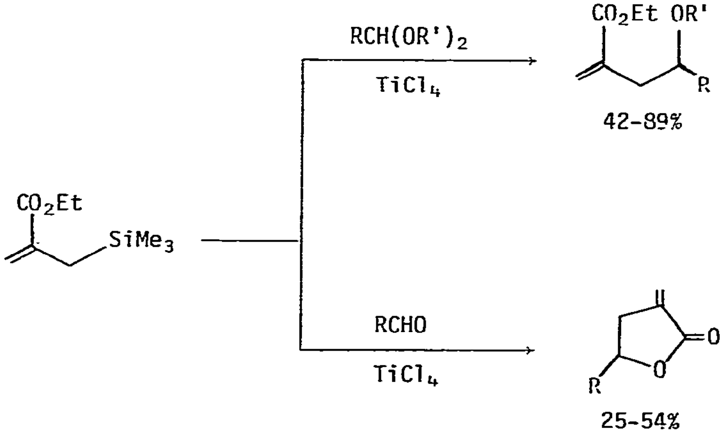
R = Me, Bu   94% opt. purity

Treatment of allenyl silanes with ketones and titanium tetrachloride produced propargyl alcohols (equation 97) [170]. 2-Alkoxycarbonyl allyl silanes reacted with acetals to produce δ-alkoxyesters, and with aldehydes to produce α-methylene-γ-butyrolactones (equation 98) [171]. Camphoronic acid was synthesized by the titanium tetrachloride promoted Knoevenagel condensation of ethyl cyanoacetate with ethyl 2,2-dimethylacetoacetate [172].



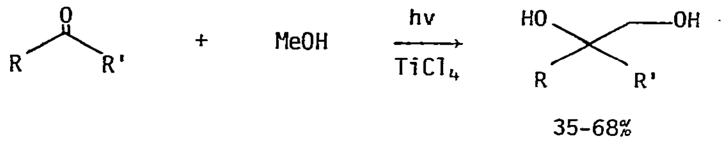
(97)

(98)

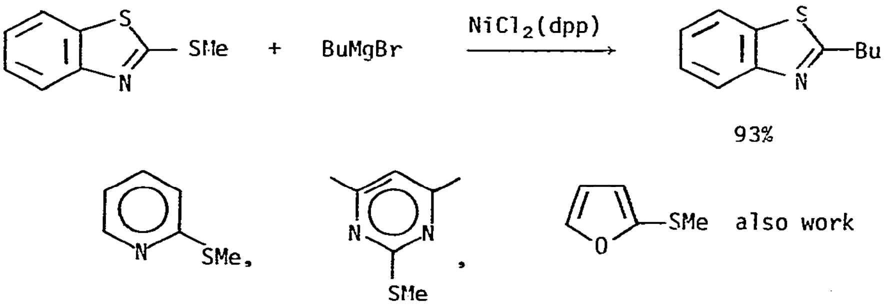


The aldol condensation of aldehydes with ketones was catalyzed by 2,2'-bipyridine complexes of cobalt (II), nickel (II), copper (II), and zinc (II), producing high yields of crossed aldol condensation products with little self-condensation [173]. The kinetics of the aluminum, iron, and chromium sesquioxide catalyzed self aldol condensation of butyraldehyde has been examined [174]. Nickel and copper acetylacetonates catalyzed the reaction of phenyl isocyanate with N,N-diethylamide acetoacetate [175]. Photolysis of ketones in methanol in the presence of titanum tetrachloride produced 1,2-diols as the main products (equation 99) [176]. Nickel (II) phosphine complexes catalyzed the alkylation of the heterocycles shown in equation 100 by Grignard reagents [177].

(99)



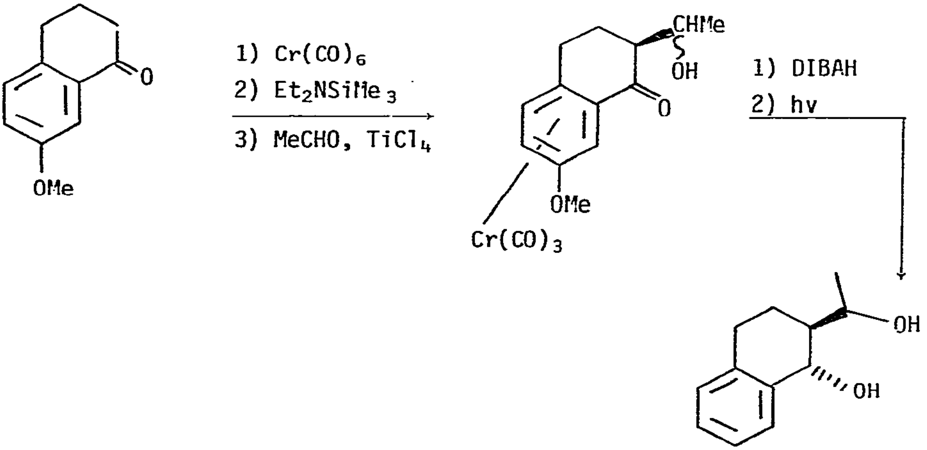
R' = Me, Et, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$
R = Et, n-Pr

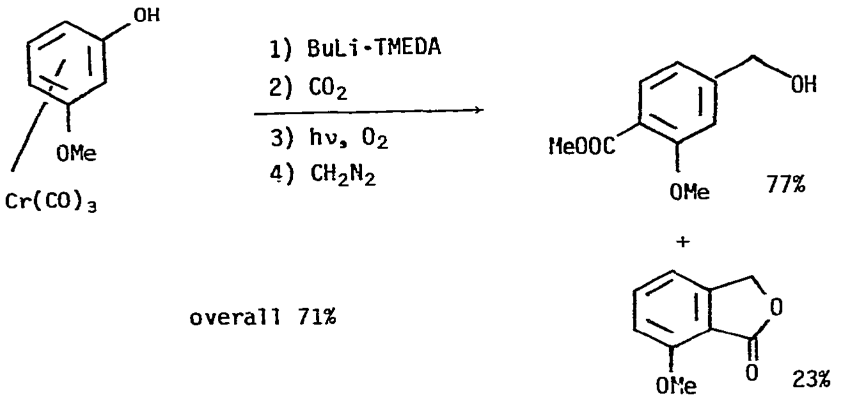


(100)

Chromium tricarbonyl complexes of tetralones were α-alkylated by treatment with titanium tetrachloride and acetaldehyde and the resulting aldol condensation product was reduced with diisobutylaluminumhydride. Since both alkylation and reduction occurred from the face opposite the metal pure _trans_ compound was obtained. The same sequence of reactions on the uncomplexed tetralone gave mostly _cis_ product (equation 101) [178]. The chromium tricarbonyl complex of _m_-methoxybenzyl alcohol underwent lithiation primarily _para_ to the benzyl alcohol group, whereas _m_-methoxyphenol lithiated between the two substituents (equation 102, 103) [179].

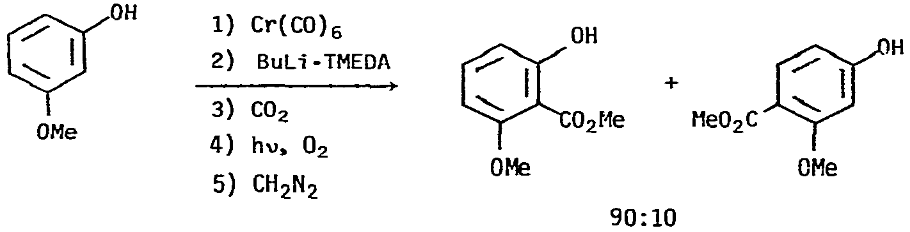
(101)



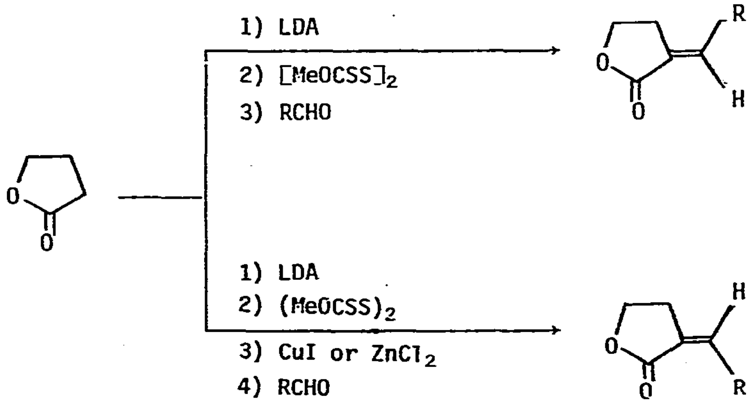


(102)

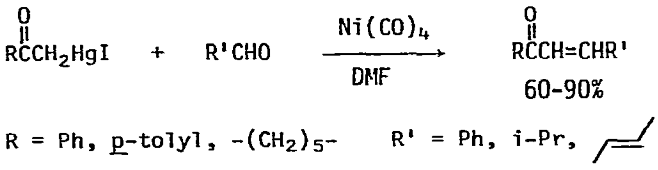
(103)



A reagent for the selective alkylation of carbonyl compounds, $(i\text{-PrO})_3TiCH_3$, has been developed. The compound methylated aldehydes at -70° to -20°, whereas ketones required +25° to +80°. Esters, nitriles, and epoxides were unreactive and nitro groups were tolerated at low temperatures. Conjugated ketones underwent 1,2-alkylation [180a, 180b]. In the α-alkylation of butyrolactone by LDA and aldehydes, addition of copper (I) iodide changed the stereochemistry of the α-methylene group introduced (equation 104)[181]. Treatment of ketones or aldehydes with α-mercurated ketones and nickel carbonyl resulted in an aldol condensation (equation 105) [182].



(104)



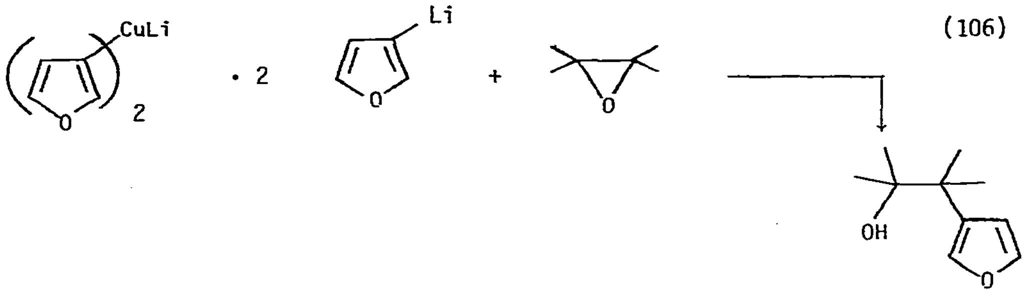
$$\mathrm{RC(=O)CH_2HgI} + \mathrm{R'CHO} \xrightarrow[\text{DMF}]{\mathrm{Ni(CO)_4}} \underset{60\text{-}90\%}{\mathrm{RC(=O)CH{=}CHR'}} \qquad (105)$$

R = Ph, p-tolyl, $-(CH_2)_5-$ R' = Ph, i-Pr,

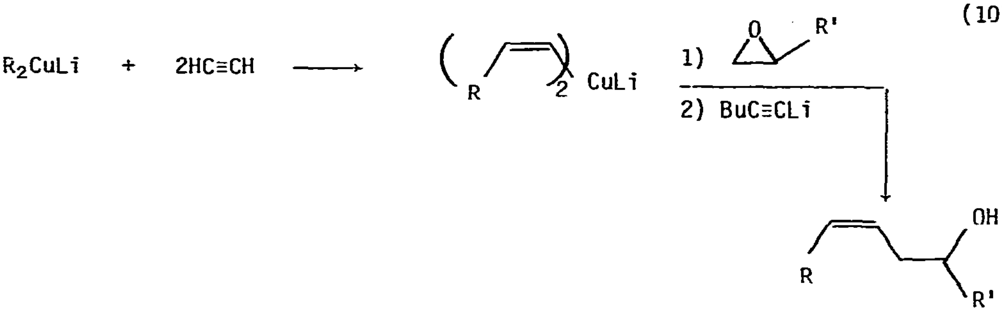
11. Alkylation of Epoxides

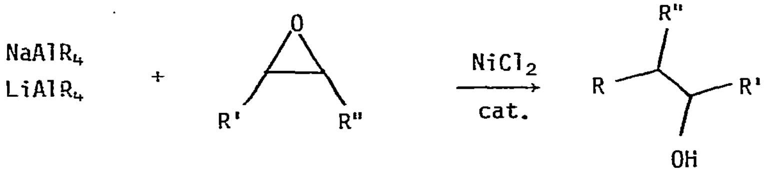
The complex $R_2CuLi{\cdot}2RLi$ was found to be more reactive towards epoxides than R_2CuLi itself (equation 106) [183]. Divinyl cuprates were prepared by the addition of dialkylcuprates to acetylene. In reactions of these complexes with epoxides, both vinyl groups were available for transfer when the lithium salt of 1-hexyne was added to the reaction mixture (equation 107). This same process permitted the transfer of both vinyl groups in carboxylation with CO_2, formylation with formaldehyde, and in conjugate additions to enones, ynones, and cyclopropyl esters [184]. Nickel chloride was observed to greatly enhance the rate of reaction of epoxides with $NaAlEt_4$ and $LiAlBu_4$ (equation 108) [185]. Tri-

(106)



(107)

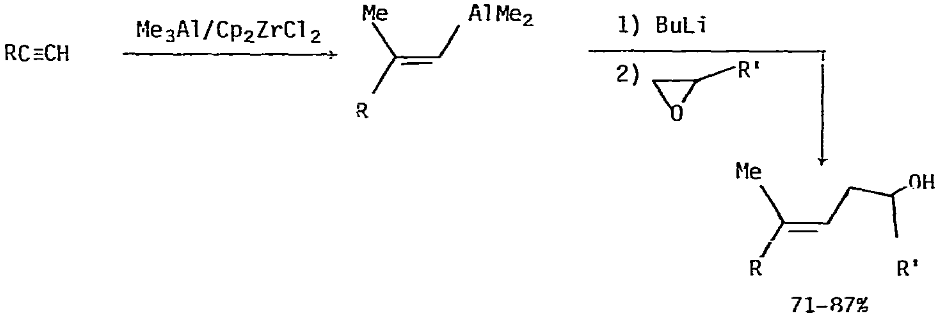




(108)

methylaluminum was added to terminal alkynes in the presence of Cp_2ZrCl_2 to produce a vinylalane. This was converted to the "ate" complex and reacted with epoxides to produce unsaturated alcohols (equation 109) [186].

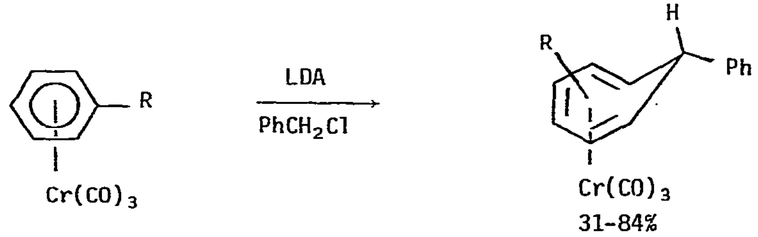
(109)



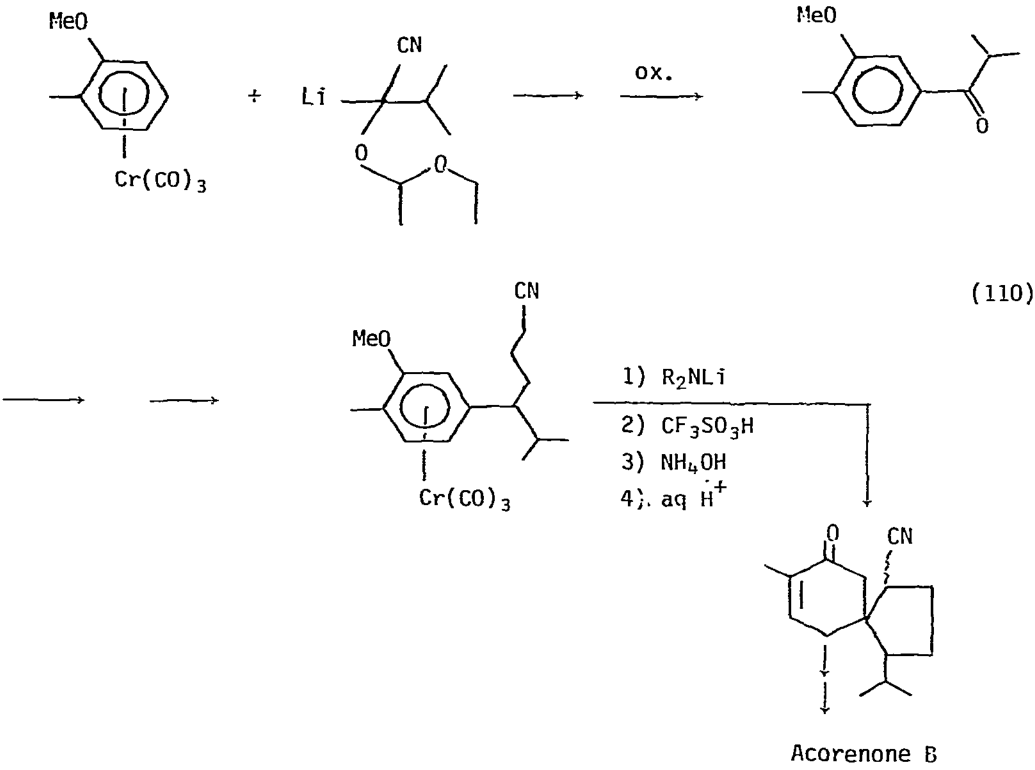
12. Nucleophilic Aromatic Substitution

Acorenone B was synthesized using the alkylation of arenechromium tricarbonyl complexes with carbanions in two key steps, including the formation of the spiro ring system (equation 110) [187]. Alkylation of lithiated arenechromium tricarbonyl complexes with benzyl chloride produced cycloheptatriene complexes (equation 111) [188]. Heating 1-aroylpyrroles with palladium (II) acetate resulted in cyclization (equation 112). Some dimerization was also noted [189].

(111)

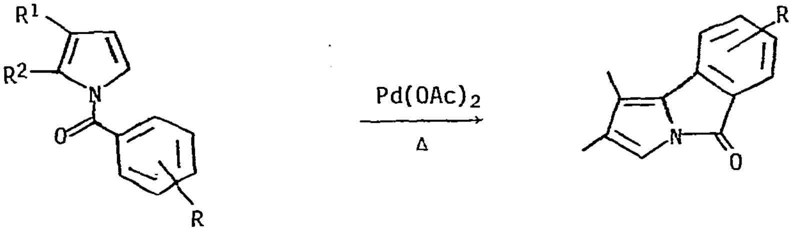


R = H, Et, Ph, Bz, CH_2OH, CH_3O



(110)

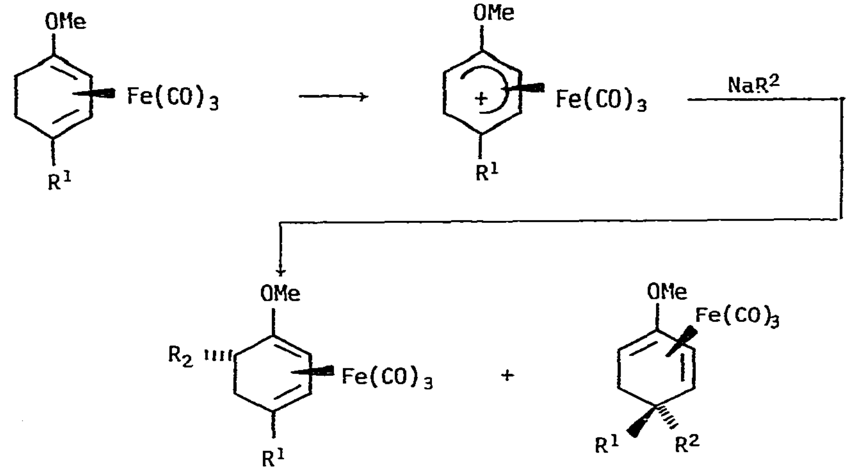
(112)



13. Alkylation of Dienyl Complexes

The use of cationic iron dienyl complexes in organic synthesis has undergone extensive development this year, and a great deal of new work has been published. The topic has recently been reviewed [190a]. Dienyliron complexes, when treated with a variety of stabilized carbanions, underwent alkylation to produce mixtures of regioisomers of the diene iron complexes (equation 113) [190b]. Nitromethane (equation 114) and cyanide (equation 115) also alkylated dienyliron complexes [191]. By using cyclic stabilized

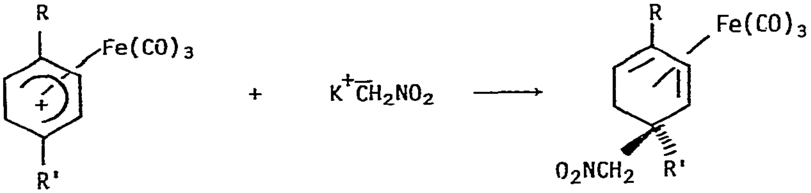
(113)



R^1 = CH_2CO_2Me, CH_2CO_2H, CH_2CH_2OH, CH_2CH_2OAc, etc.

R^2 = $CH(CN)_2$, $CH(CO_2R)_2$, $CH(COMe)(CO_2R)$

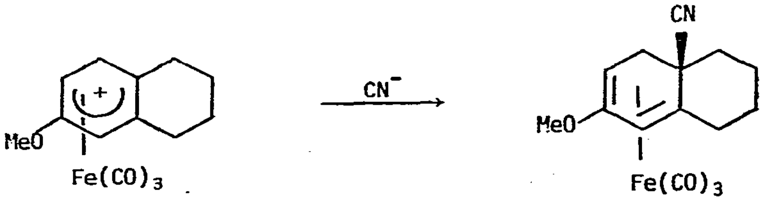
(114)



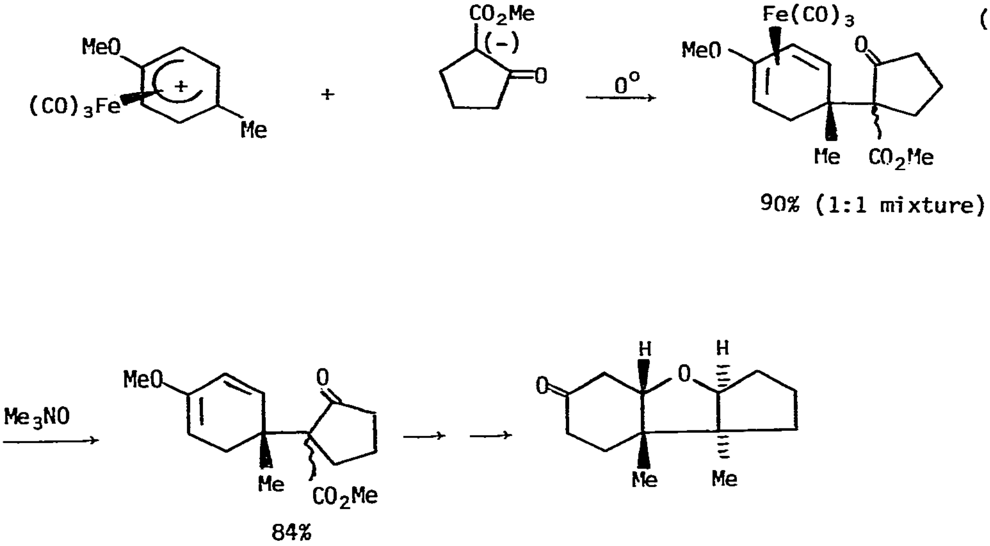
R = R' = H 55% R = OMe, R' = H 85%

R = OMe, R' = H 71%, R = R' = OMe <10%

(115)

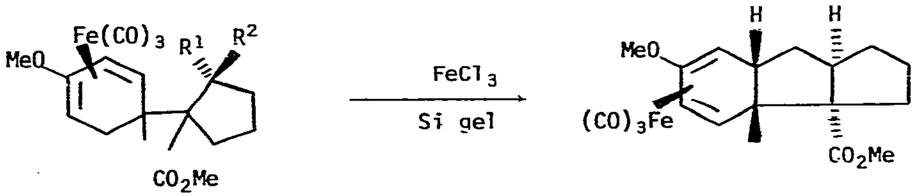


carbanions, polycyclic compounds were prepared (equation 116) [192], (equation 117) [193], (equation 118) [194], (equation 119) [195]. Spirocyclic systems (equation 120) [196], (equation 121) [197], the quaternary carbon corresponding to C-20 in aspidosperma alkaloids (equation 122) [198], and other cyclic compounds (equation 123, 124) [199], were also prepared in this manner.

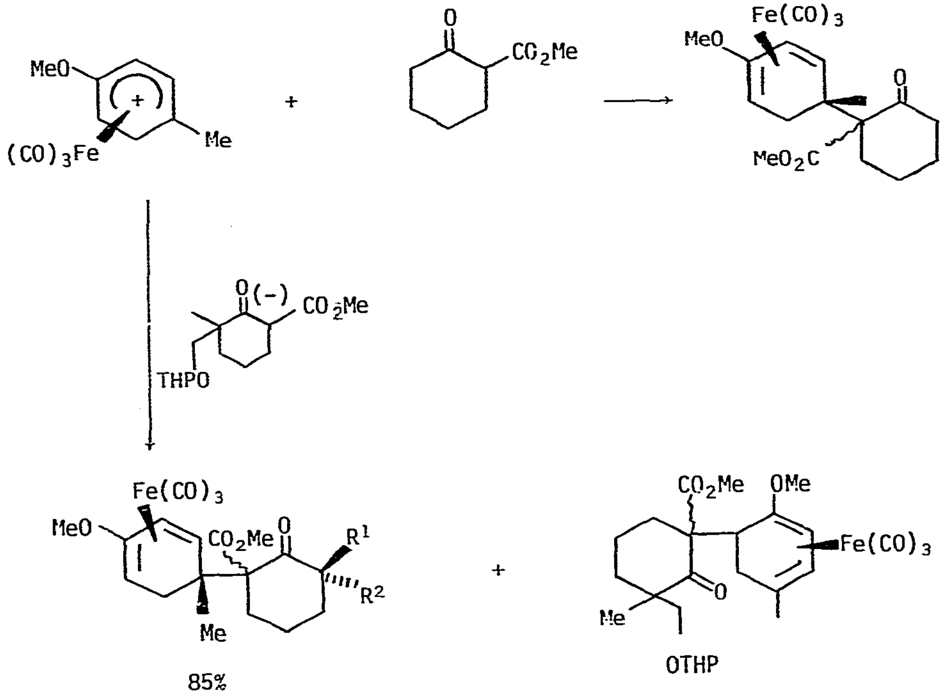


(116)

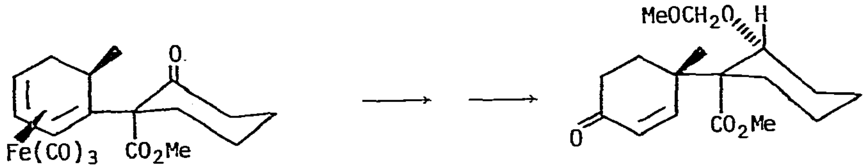
(117)



(118)

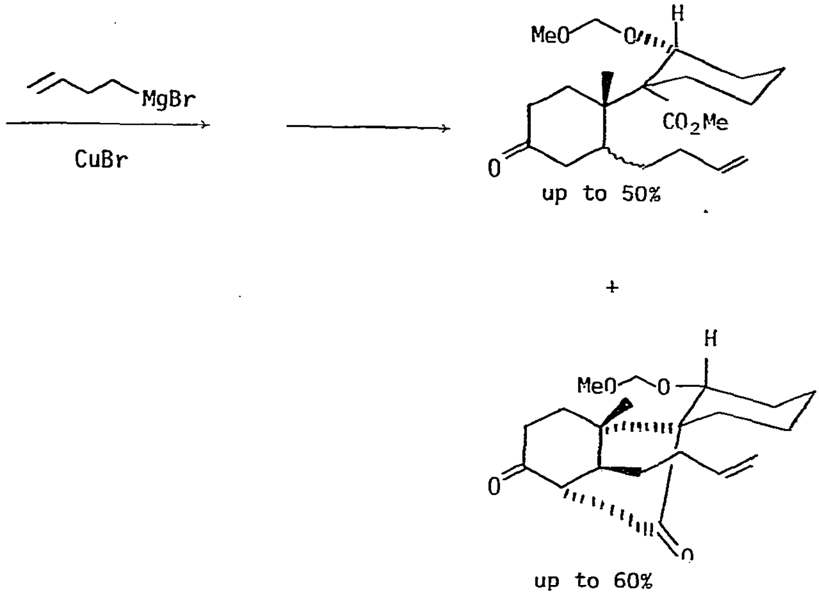


(119)



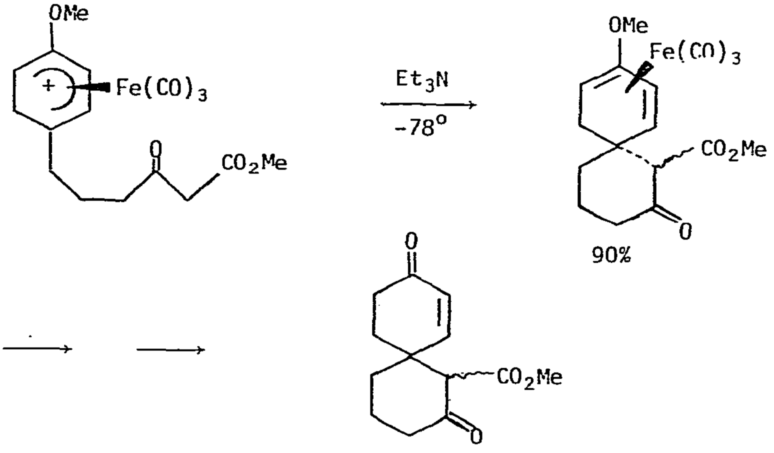
(next page)

(119)



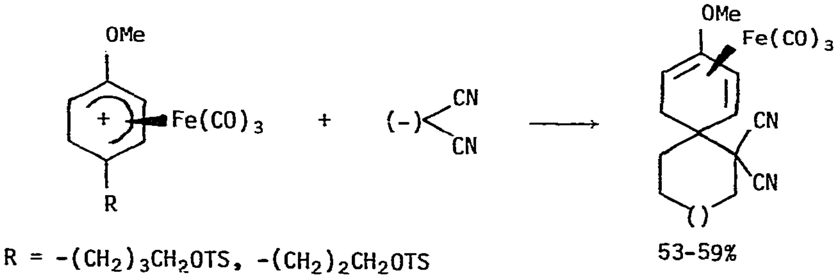
MgBr
CuBr
MeO
O
H
CO$_2$Me
O
up to 50%
+
H
MeO
O
O
O
up to 60%

(120)



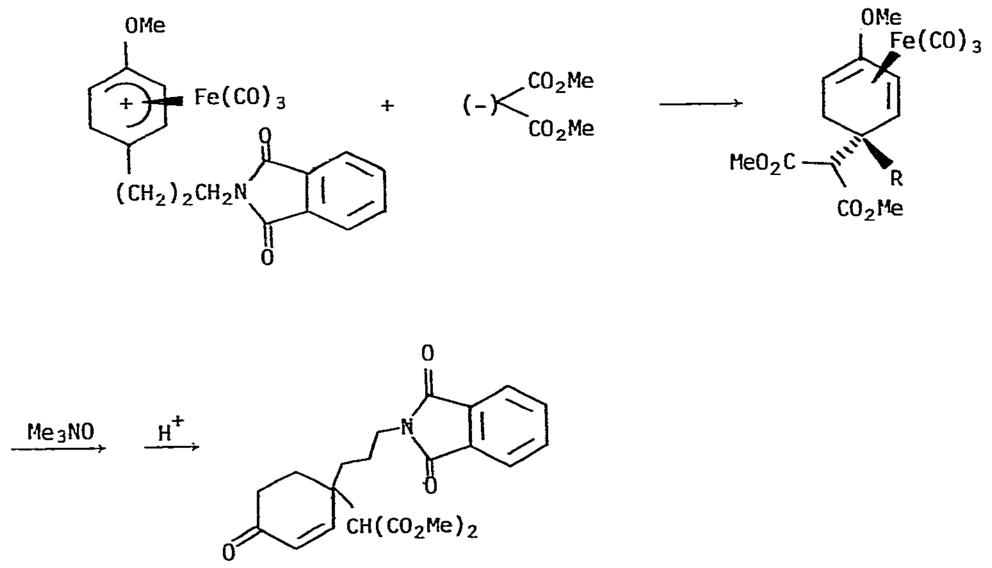
OMe
+
Fe(CO)$_3$
O
CO$_2$Me
Et$_3$N
-78°
OMe
Fe(CO)$_3$
CO$_2$Me
O
90%
O
CO$_2$Me
O

(121)

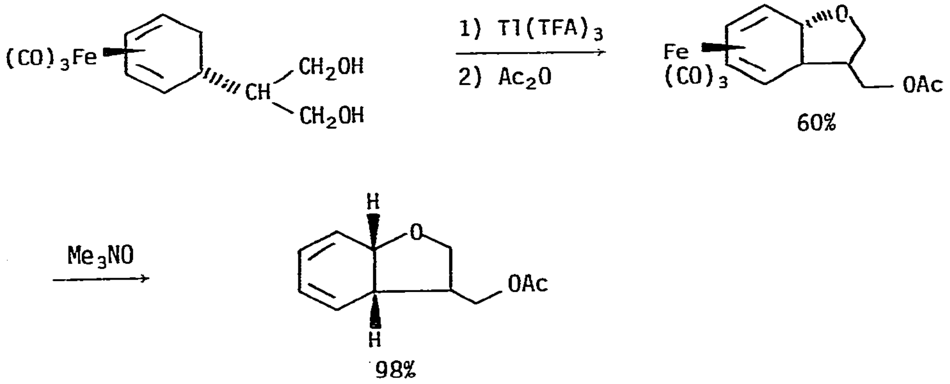


OMe
+
Fe(CO)$_3$
R
+
(-)
CN
CN
OMe
Fe(CO)$_3$
CN
CN
( )
53-59%
R = -(CH$_2$)$_3$CH$_2$OTS, -(CH$_2$)$_2$CH$_2$OTS

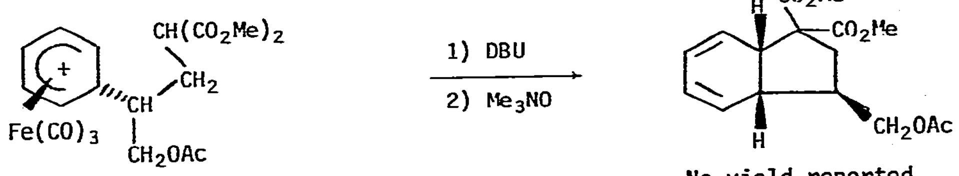
(122)



(123)



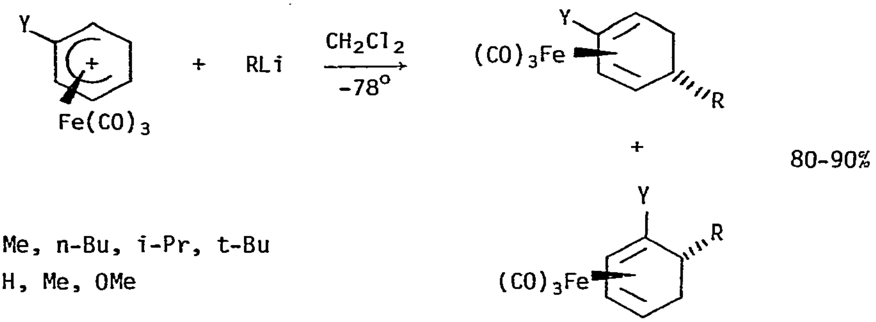
(124)



No yield reported

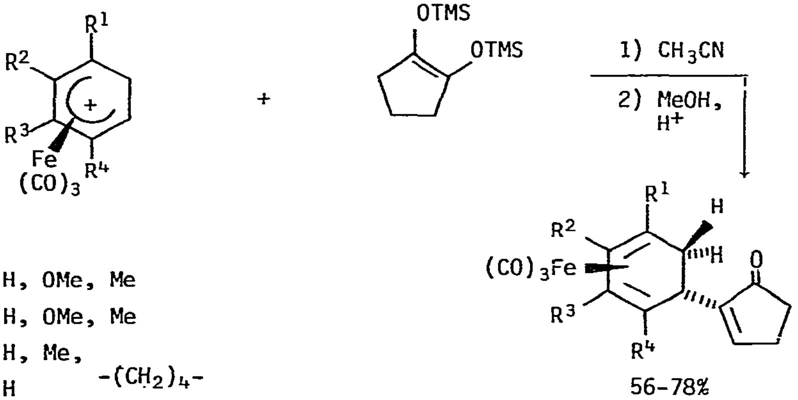
Nonstabilized carbanions also alkylated these dienyliron complexes (equation 125) [200], as do silylenolethers (equation 126) [201], (equation 127) [202], (equation 128) [203], and allyltrimethylsilanes (equation 129) [204].

(125)



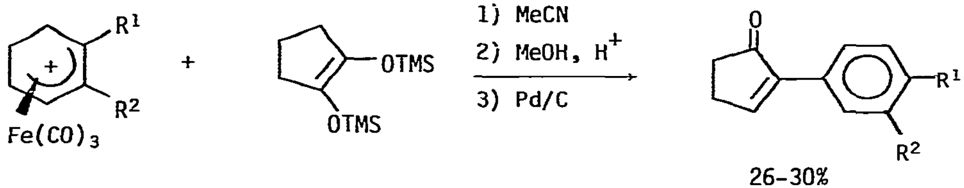
R = Me, n-Bu, i-Pr, t-Bu
Y = H, Me, OMe

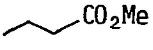
(126)



R^1 = H, OMe, Me
R^2 = H, OMe, Me
R^3 = H, Me,
R^4 = H $-(CH_2)_4-$

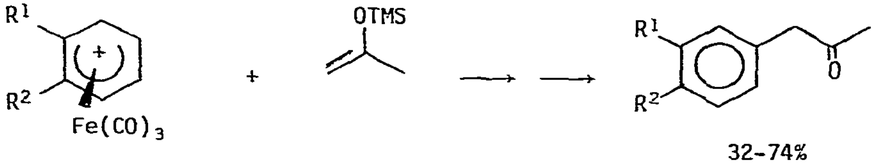
(127)



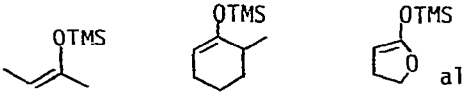
R^1 = H, Me, OMe,


R^2 = H, Me

(128)

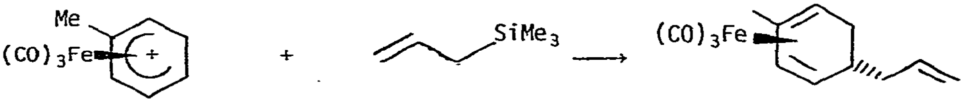


R^1 = CO_2Me
R^2 = Me



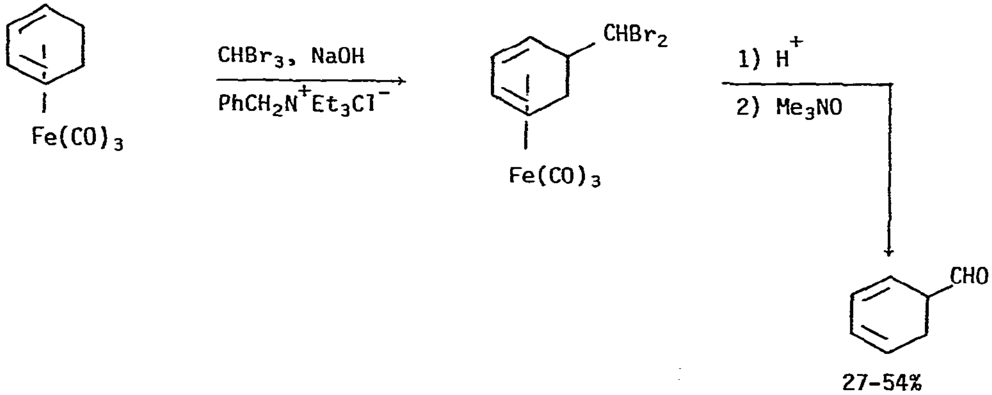
also work, as does the tetraline complex.

(129)



Optically active 1,3-diene complexes of iron were prepared by the direct transfer of the $Fe(CO)_3$ group from (+)-pulegone and (-) steroid complexes to prochiral dienes [205]. Alternatively the dieneiron complex of 1-carboxycyclohexa-1,3-diene was resolved via its α-phenethylamine salts [206]. Stereospecific and regiospecific formations and reactivities of some substituted tricarbonyl cyclohexadieneiron complexes has been reviewed [207]. Dibromocarbene inserted into a C-H bond in the iron tricarbonyl complex of 1,3-hexadiene under phase transfer conditions (equation 130) [208].

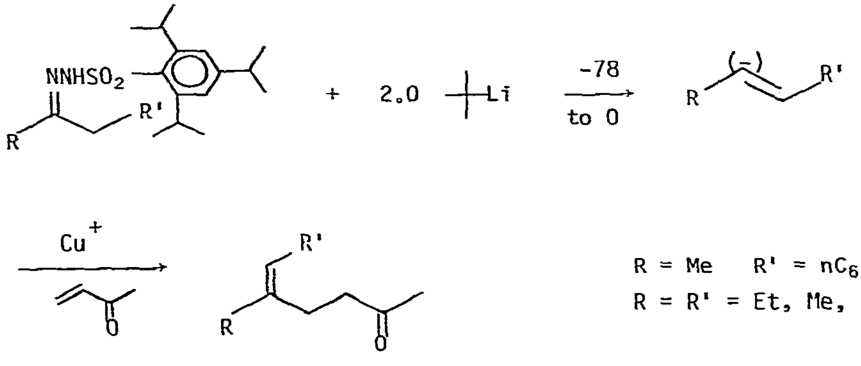
(130)



B. Conjugate Addition

Organocuprates continued to be extensively used for a wide variety of conjugate (1,4 or 1,6) additions to unsaturated systems, and procedures continued to be refined. Tosyl hydrazones were used as a source of the R group for R_2CuLi, used for conjugate additions of vinyl groups to conjugated enones (equation 131) [209]. New conditions for the conjugate addition reaction, which require only one equivalent of organolithium reagent, have been developed. They relied on the use of phosphine ligands, and the resulting enolate did not react cleanly with aldehydes (equation 132) [210]. A new mixed cuprate reagent which is capable of transferring both of its R groups in conjugate addition reactions, has been developed (equation 133) [211].

(131)

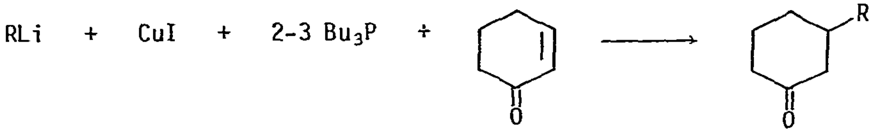


40-80%

$R = Me \quad R' = nC_6$

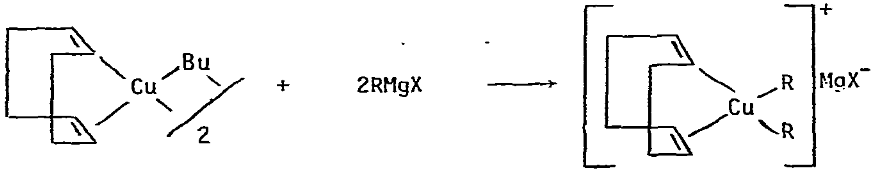
$R = R' = Et, Me, -(CH_2)_5-$

(132)



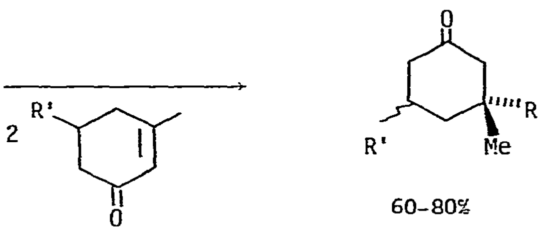
73-94%

(133)

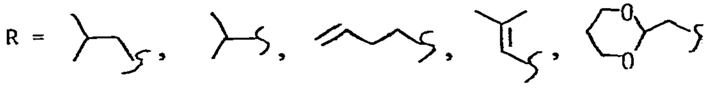


(next page)

(133)

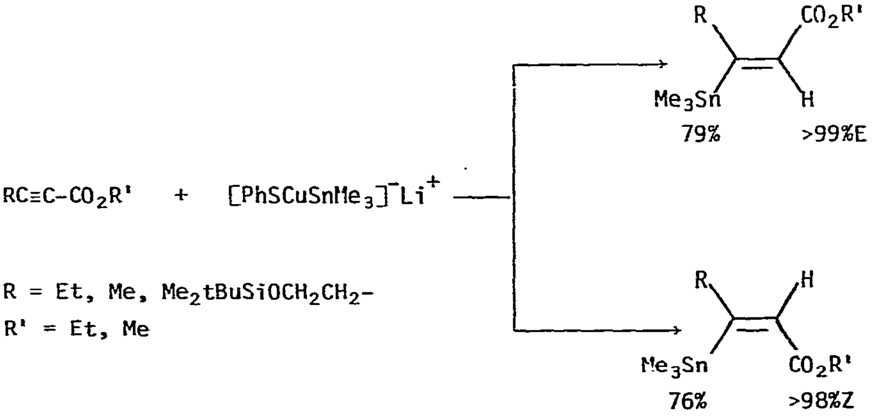


R' = H, Me



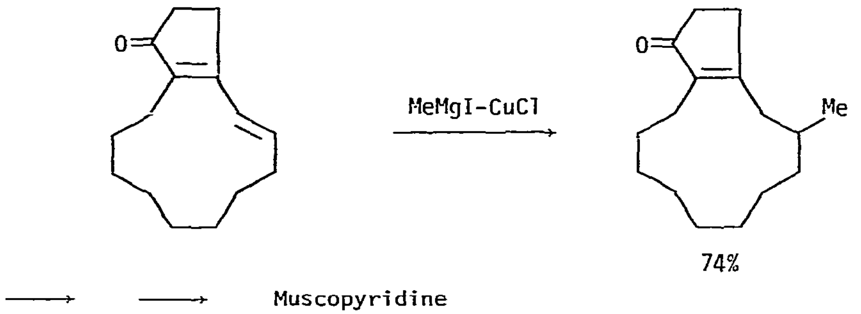
In the reaction of mixed magnesium diorganocuprates, formed by the reaction of Grignard reagents with RCu, with 4-phenyl-3-buten-2-one the R group of the Grignard reagent selectively transferred in this 1,4-addition process [212]. Conjugated aldehydes underwent almost exclusive 1,4-addition of lithium dialkylcuprates when the reaction was run in nonpolar solvents at low temperature. An exception to this was tetrasubstituted aldehydes, which underwent 1,2-addition instead [213]. The conjugate addition of $[R_2Cu]^-MgX^+$ to α,β-unsaturated ketones was studied. The best yields were obtained with a three to four fold excess of the R_2CuMgX, the reaction was slower than was the corresponding copper-catalyzed Grignard reaction, and electron donating groups on the α carbon slowed the reaction [214]. Trimethyltin groups were introduced β to the ester group of acetylenic esters using a mixed copper-tin reagent. The stereochemistry of addition was controlled by the reaction conditions (equation 134) [215]. Muscopyridine was synthesized using a 1,6-alkylation process (equation 135) [216].

(134)



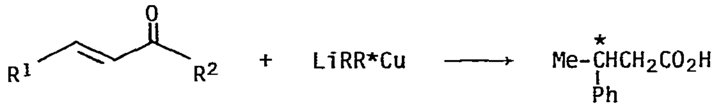
R = Et, Me, $Me_2tBuSiOCH_2CH_2-$
R' = Et, Me

(135)



Cyclohexenone was treated with lithium dimethylcuprate followed by acetyl chloride, producing 2-acetyl-3-methylcyclohexanone in 87%yield, with exclusive C-alkylation [217]. The enolate resulting from the conjugate addition of R_2CuLi to 2-phenylselenocyclopentenone was studied extensively for its uses in synthesis [218]. The stereochemistry and mechanism of the reaction of Me_2CuLi with β-cyclopropyl-α,β-unsaturated ketones was the topic of a dissertation chapter [219]. A number of approaches to induce asymmetry in conjugate addition reactions of organocuprates have been attempted. Addition of a dialkylcuprate containing a nontransferable chiral group to conjugated esters having OR' groups from chiral alcohols resulted in up to 49% enantiomeric excess (equation 136) [220]. Lower optical yields were obtained when mixed cuprates containing a chiral alkoxide group were used (equation 137) [221]. Quite high optical yields were obtained when copper complexes containing chiral aminoalcohols ligands were used (equation 138) [222].

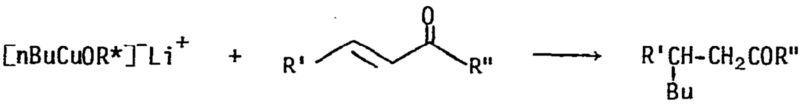
(136)



$R = Me, Ph$
$R^1 = Ph, Me$
$R^2 = \text{chiral OR}$
$R^* = 2(1\text{-dimethylaminoethyl})\text{phenyl}$

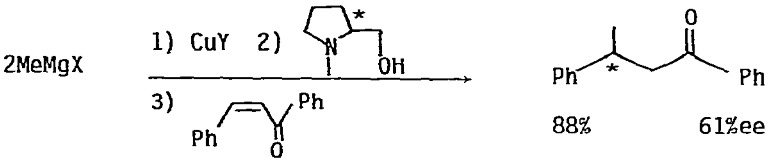
40-70%
up to 49%ee

(137)



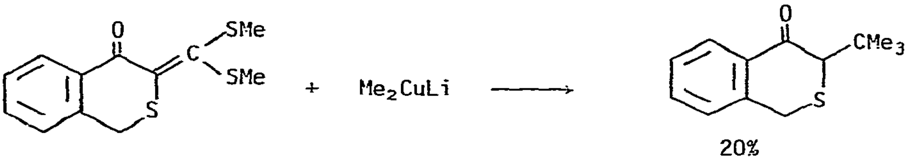
up to 15% ee

(138)

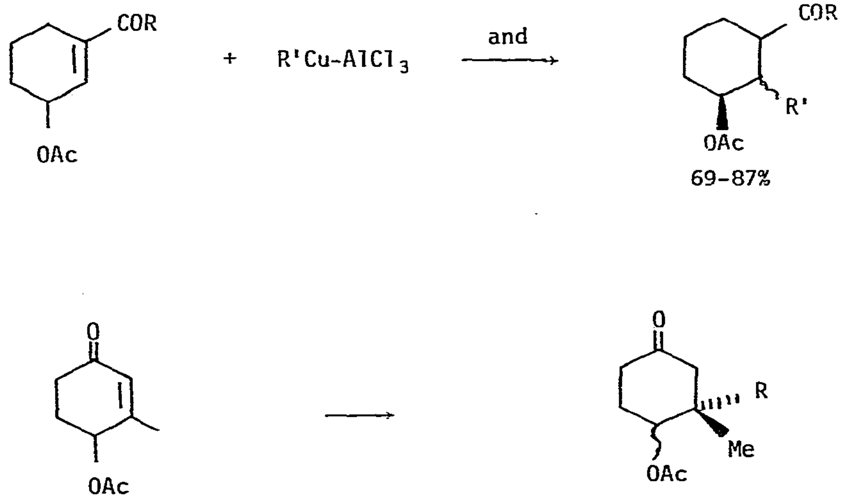


Alkylthio-α,β-unsaturated ketones reacted with lithium dimethylcuprate to give a low yield of product resulting from both conjugate addition and substitution (equation 139) [223]. Mixed copper-aluminum compounds were used to affect conjugate addition (alkylation) to γ-acetoxy or γ-siloxy-α,β-unsaturated ketones without displacement of this allylic acetate (equation 140) [224a] [224b]. Alkylation of β-iodovinylketones to give β-alkylvinylketones was carried out using the organocuprate from EtLi and $PrC\equiv CCu\cdot 2HMPA$ [225]. Dialkylcuprates were also effective for *bis* β,β' conjugate addition reactions (equation 141) [226].

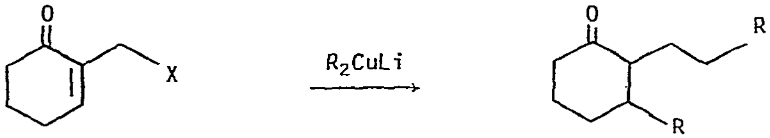
(139)



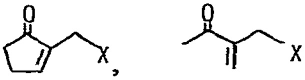
(140)



(141)



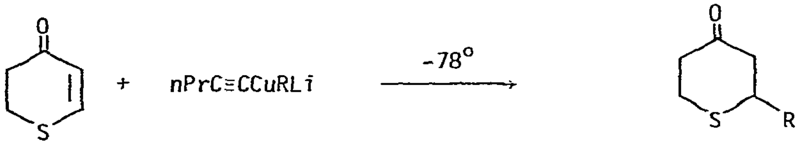
X = OAc, SPh, Cl, OTMS



also work.

Conjugate addition reactions of organocuprates have been used to synthesize a variety of complex molecules, including δ-thioketones (equation 142) [227]. Furopelargone A and b (equation 143) [228], cephalosporins (equation 144) [229], and chiral alcohols (equation 145) [230]. As usual, a large number of prostaglandin type compounds have also been made by this procedure. Some rely on the chemistry of bicyclic esters (equation 146) [231], cyclopropylketones (equation 147) [232], epoxides (equation 148) [233], and tricyclic esters (equation 149) [234]. Thromboxane A (equation 150) [235] and Brefeldin A (equation 151) [236]

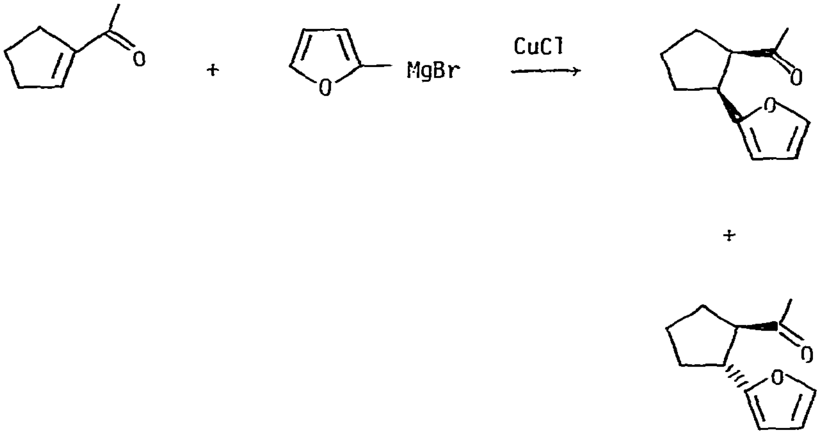
(142)



28-70%

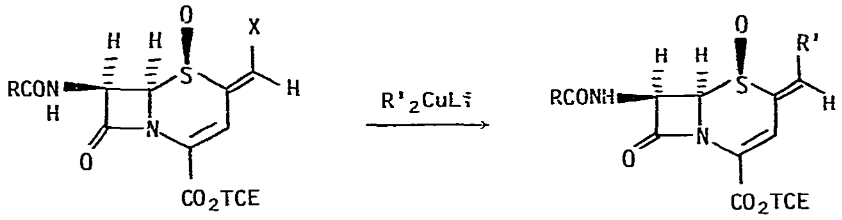
R = Me, nBu, t-Bu, Ph

(143)



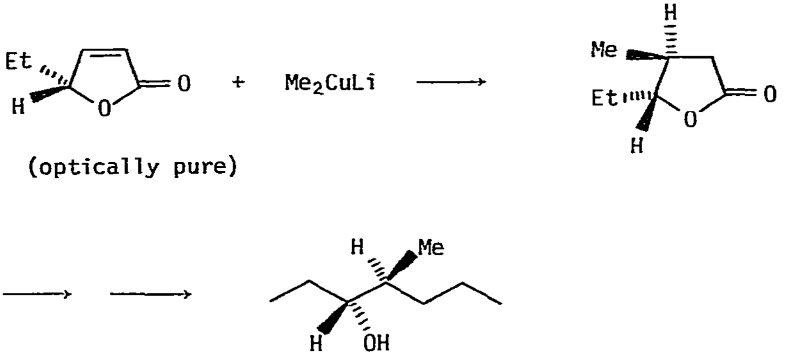
1:1 25%

(144)



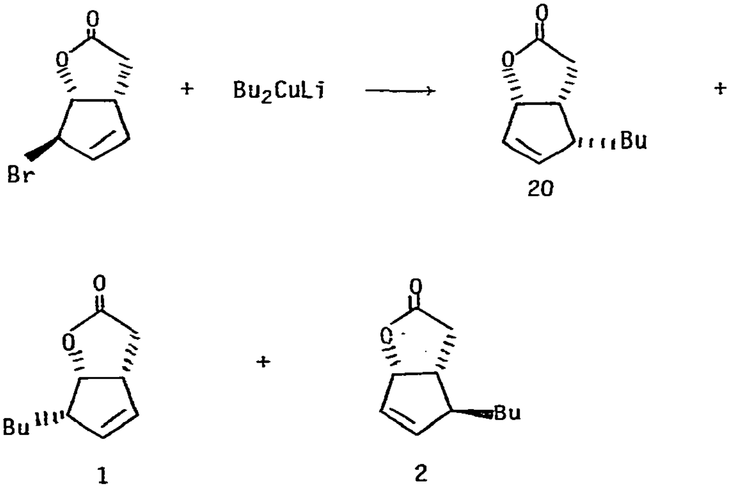
48-80% R' = Me, Bu

(145)

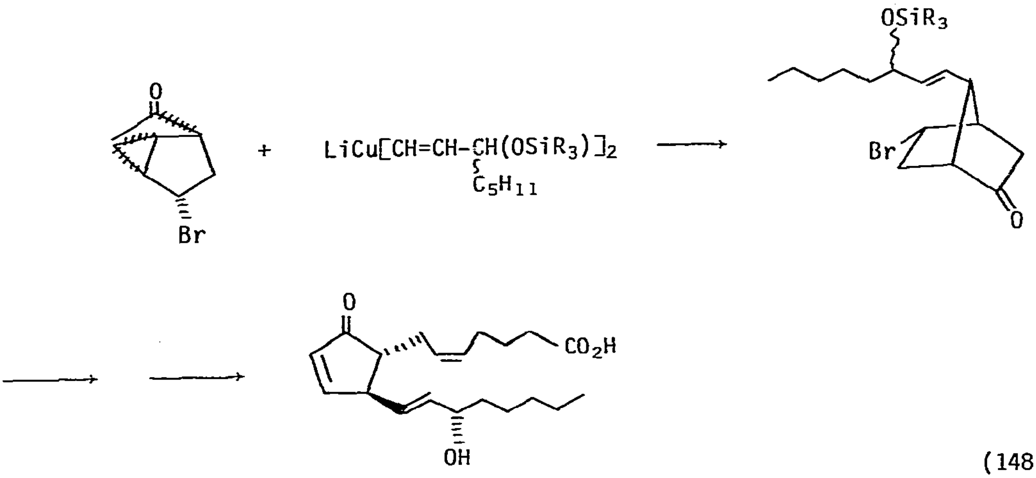


(optically pure)

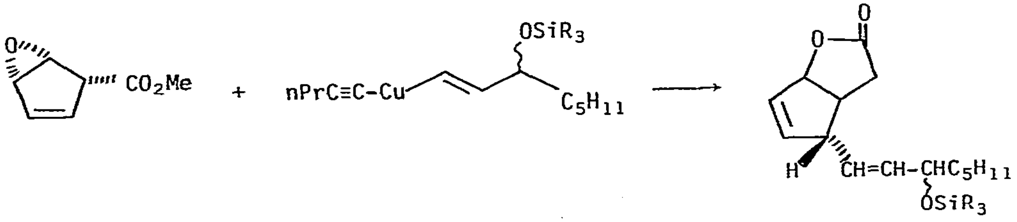
(146)



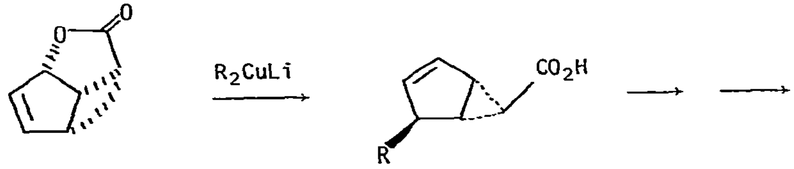
(147)



(148)



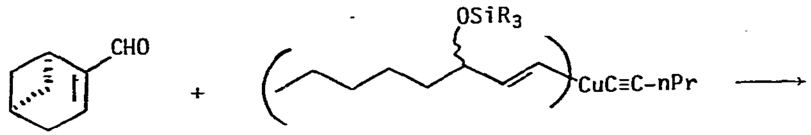
(149)



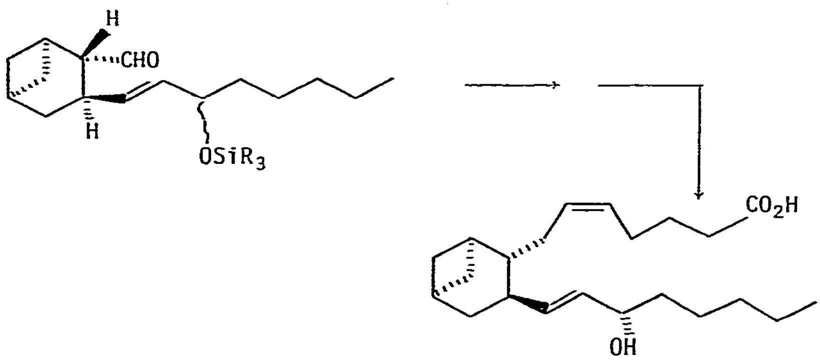
9-deoxa-9,10-dihydroprostaglandin D_2

$R = CH{=}CH{-}\underset{OSiR_3}{C}HC_5H_{11}$

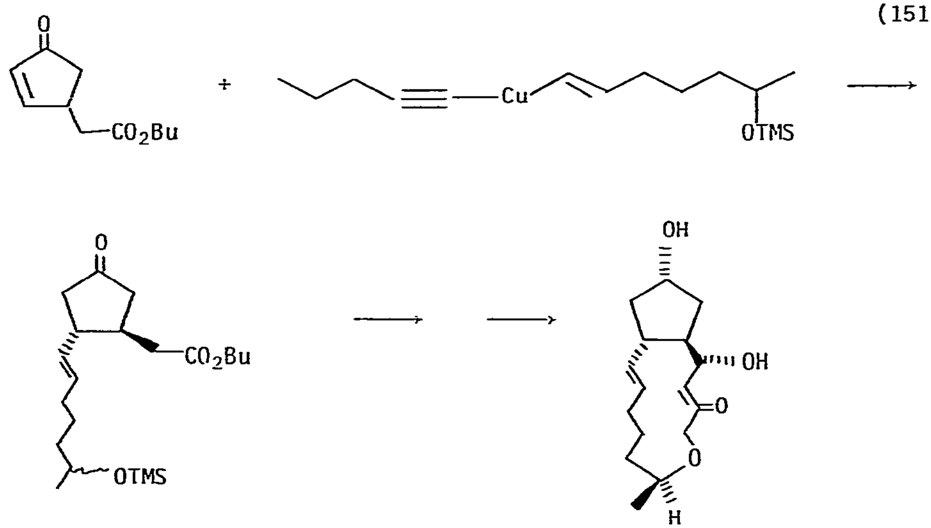
(150)



(next page)

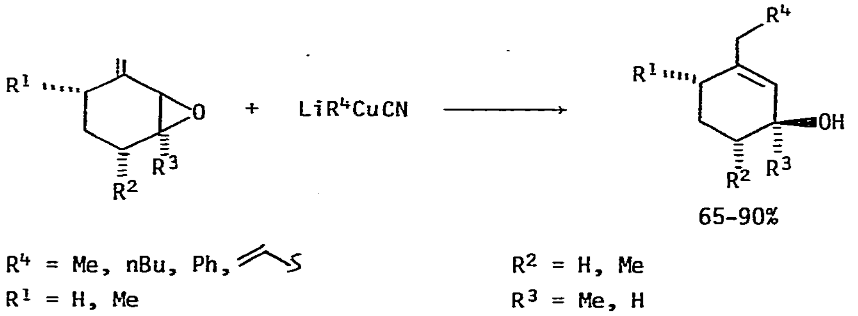


(151)



have also been synthesized using organocuprate conjugate additions. Conjugate epoxides also reacted with mixed cuprates (equation 152) [237].

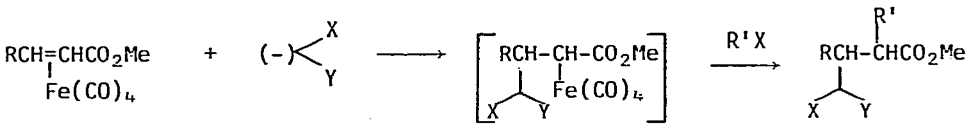
(152)



R^4 = Me, nBu, Ph,
R^1 = H, Me
R^2 = H, Me
R^3 = Me, H

Iron (0) complexes of conjugated enones reacted with stabilized carbanions at the β-position, and the resulting iron enolate reacted further with electrophiles to result in disubstitution (equation 153) [238]. A similar reaction with α-chloro-α,β-unsaturated esters resulted in dialkylation (equation 154) [239].

(153)



R = H, Me

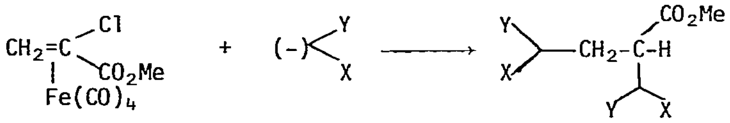
R' = Me, Et, n-Pr

X = CO_2Et

Y = CO_2Et, COMe, CN

40-60%

(154)

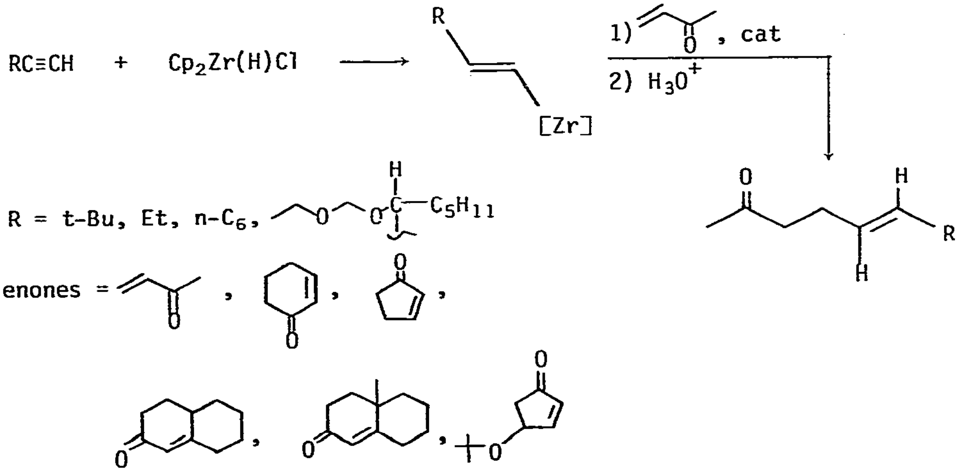


X = CO_2Me, CO_2Et

Y = CO_2Me, CO_2Et, COMe, CN

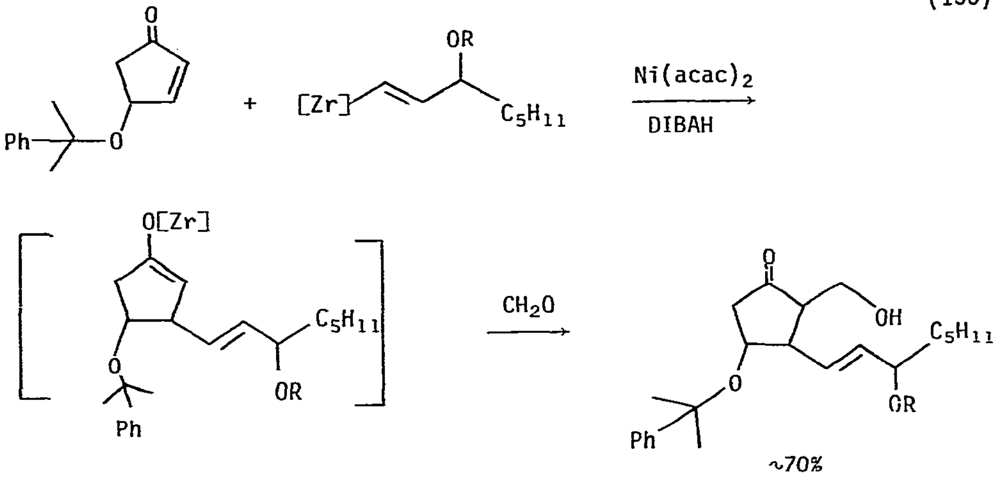
Nickel salts have been used to catalyze conjugate addition reactions of a number of different metal-carbanion species. Nickel-catalyzed additions of alkenylzirconium species was the topic of a dissertation [240]. In a general study of the conjugate addition of vinylzirconium complexes to conjugated enones, a 1:1 mixture of nickel (II) acetylacetonate-diisobutylaluminum hydride proved the most efficient catalyst (equation 155). Prostaglandin precursors

(155)

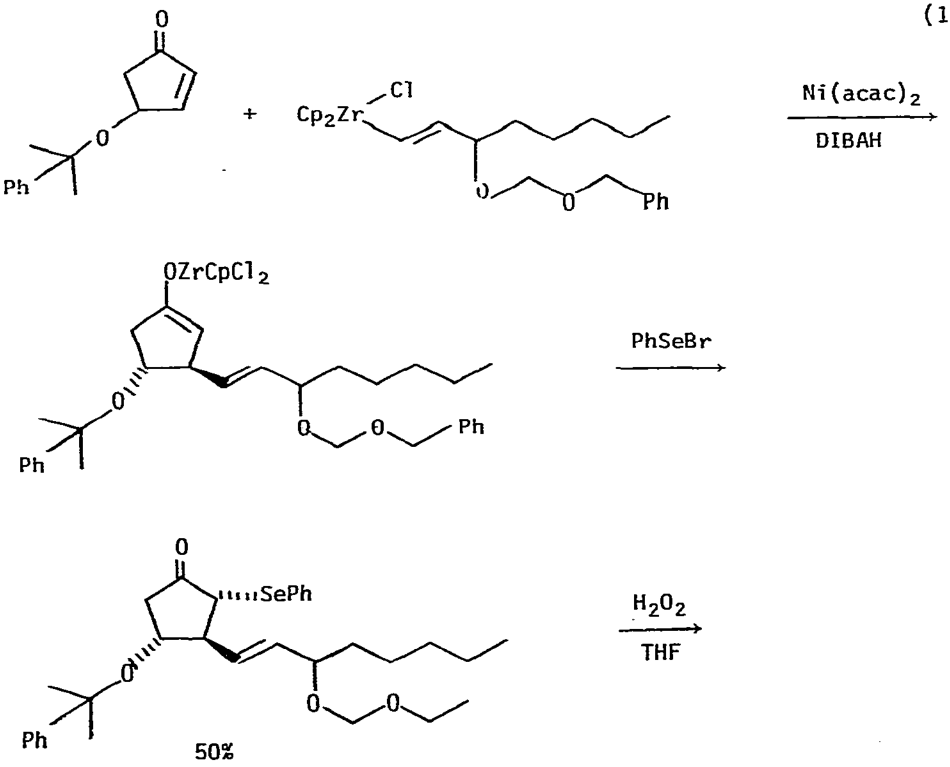


were synthesized using this reaction (equation 156) [241] (equation 157) [242]. Acetylenic alanes similarly added to conjugated enones in a 1,4-manner in the presence of this catalyst (equation 158) [243].

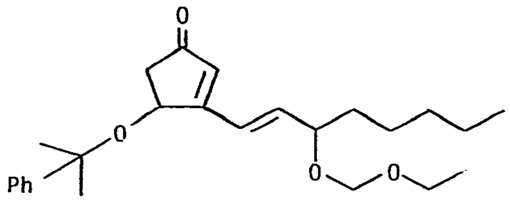
(156)



(157)

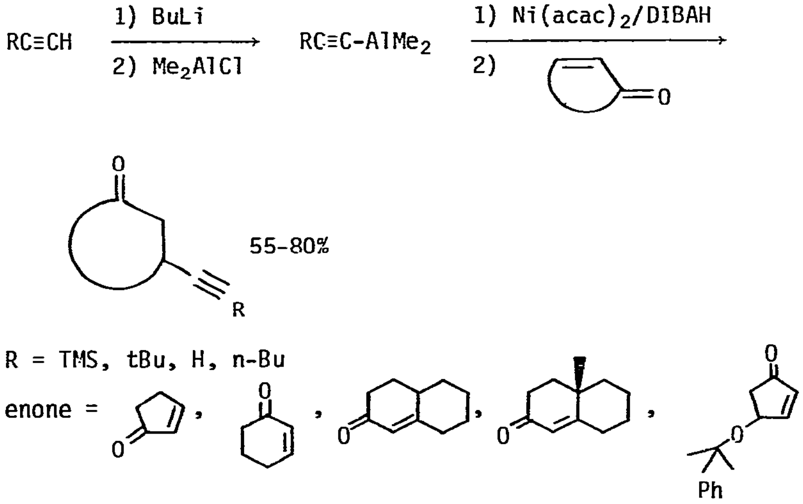


(next page)



70%

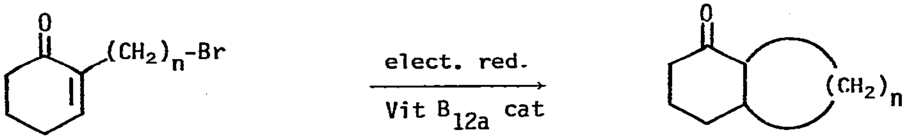
(158)



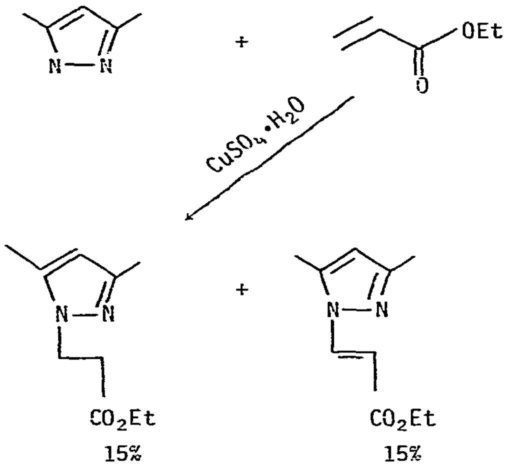
R = TMS, tBu, H, n-Bu

As little as 1% of nickel (II) acetylacetonate catalyzed the Michael addition of stabilized enolates (β-dicarbonyl anions) to conjugated enones in high yield under mild conditions, without the necessity of strong base [244]. The mechanism of the β-benzoylation of methyl acrylate by benzoyl chloride and nickel (0) catalysts was studied [245]. Benzene added in a 1,4 fashion to α,β-unsaturated ketones in a two phase system in the presence of tetrabutylammonium palladium trichloride as a catalyst [246]. Bicyclic systems were synthesized by electrochemical methods involving conjugated enones (equation 159) [247]. Mixtures of iron carbonyl and iodine promoted the Michael addition of malonic ester to acrylonitrile [248]. Copper salts promoted the Michael addition of 3,5-dimethylpyrazole to ethyl acrylate. (equation 160) [249].

(159)

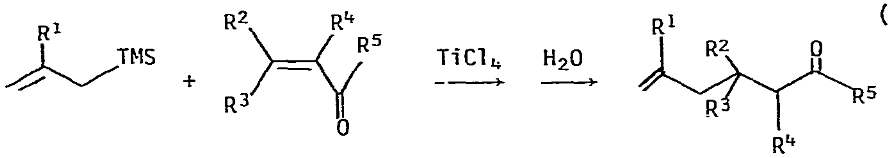


95% n = 4 <2% n = 3 76% n = 5

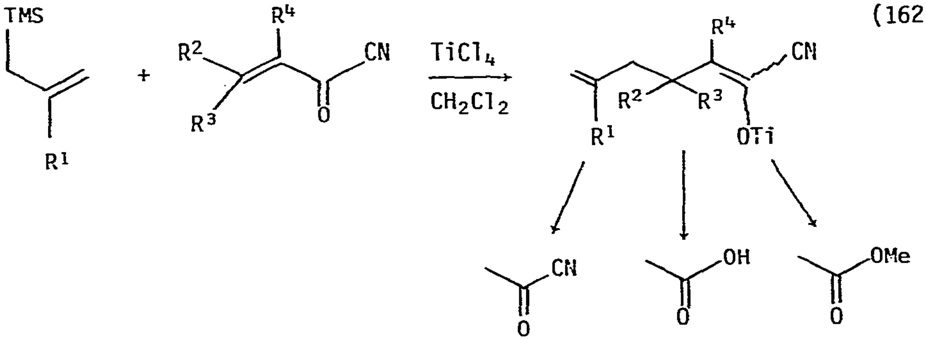


(160)

Titanium tetrachloride promoted the conjugate addition of allylsilanes (equation 161) [250] (equation 162) [251] and alkynylborates (equation 163) [252] to conjugated enones.

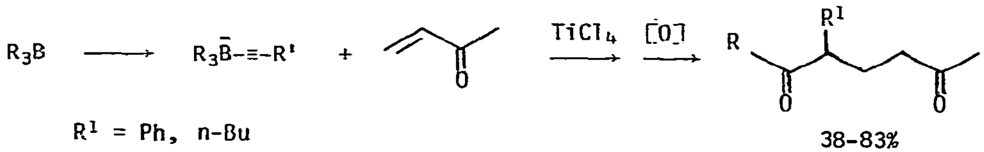


(161)



(162)

(163)

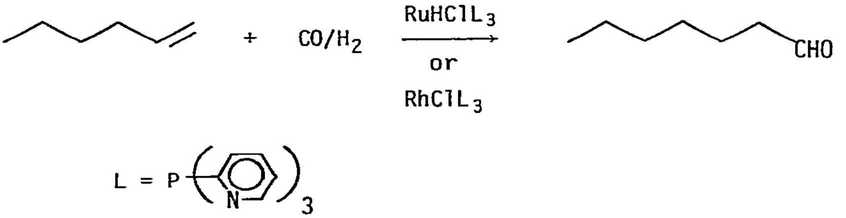


R^1 = Ph, n-Bu
R = n-Pr, n-Bu, i-Bu, n-Hex

C. Carbonylation

1. Hydroformylation

The hydroformylation of alkanes and alkadienes has been reviewed [253], as has the mechanism and stereochemistry of the process [254]. An enormous review (1970 ref) concerning hydroformylation, oxo syntheses, and Roelen reactions has appeared [255]. Propene hydroformylation using $RhH(CO)(PPh_3)_3$ as a catalyst was examined, and it was found that the catalyst underwent extensive degradation during the course of the reaction [256]. Theoretical studies of the reactivities of cobalt carbonyls and hydrocarbonyls in relation to the hydroformylation process have been carried out [257]. These calculations were in good agreement with what was already known about these complexes. High pressure infrared spectroscopy was used to study rhodium-catalyzed hydroformylation reactions. Several intermediates including $EtRh(CO)_4$ and $HRh(CO)_3(C_2H_4)$ were detected by this method [258]. The homogeneous ruthenium catalyzed hydroformylation of 1-pentene using water gas was compared to rhodium-catalyzed hydroformylation and hydroxymethylation of the same substrate [259]. The mechanism of hydroformylation of ethylene using rhodium catalysts was examined. The rate of the reaction was first order in ethylene with an activation energy of 33.18 kJ/mole [260]. 1-Hexene was hydroformylated under low pressure of H_2/CO to give terminal aldehyde in the presence of rhodium and ruthenium catalysts containing pyridinyl phosphines as ligands (equation 164) [261]. Cyclohexene underwent homogeneous hydroformylation using diaquobis (acetylacetonato) cobalt(II) [262].

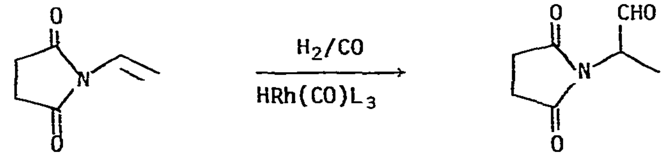


(164)

Cluster complexes also catalyzed hydroformylation reactions. In the hydroformylation of 1-hexene using $MeCCo_3(CO)_9$ as a catalyst it was shown that the cluster fragmented to produce $Co_2(CO)_8$, which was responsible for the observed catalysis [263]. The anionic cluster $[HRu_3(CO)_{11}]^-$ catalyzed the hydroformylation of propene to n-butyraldehyde with a high specificity for formation of linear aldehyde [264]. The mixed clusters $Ru_2Fe(CO)_{12}$ and $RuFe_2(CO)_{12}$ hydroformylated propene in methanol to give methyl butyrate [265].

Rhodium(I) phosphine complexes were attached to poly(methylsiloxanes) and were used as catalysts for the hydroformylation of 1-hexene [266]. Extensive catalyst degradation was noted. Propene was hydroformylated by $HRh(CO)(PPh_3)_3$ supported on alumina or silica gel [267]. The proportion of linear aldehyde could be increased by having excess phosphine present in the silica supported catalysts [268]. Ruthenium complexes were supported on zeolites and were used to catalyze ethylene hydroformylation [269]. The rhodium catalyzed hydroformylation of allyl alcohol using both homogeneous and polymer bound $RhH(CO)(PPh_3)_3$ was studied [270]. The activity, selectivity, and spectroscopic properties of homogeneous and polymer supported rhodium-phosphine catalysts in hydroformylation were compared [271].

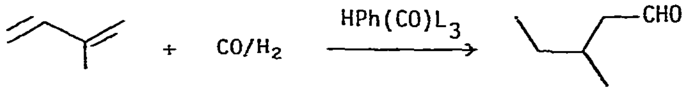
N-vinylsuccinimides and N-vinylphthalimides were hydroformylated using rhodium(I) DIOP or DIPHOL chiral catalysts to give up to 41% enantiomeric excess (equation 165) [272]. Isoprene was hydroformylated in 25% chemical yield and 32% optical yield using rhodium(I) DIOP catalysts. Butadiene, 2,3-dimethylbutadiene, and 2-methylbutene failed to react in appreciable yield (equation 166) [273]. Formaldehyde was hydroformylated to hydroxyacetaldehyde in 43% yield using $RhCl(CO)L_2$ as a catalyst. Methanol was also formed [274]. The effect of phosphine ligands on the $Co_2(CO)_8$ catalyzed hydroformylation of methyl acrylate was examined (equation 167) [275]. Diphos proved to be the most effective catalyst. The hydroformylation of this same substrate using homogeneous and polymer attached $RhH(CO)(PPh_3)_2$ as a catalyst was carried out and the results were compared [276].



(165)

L = DIOP

up to 41% ee



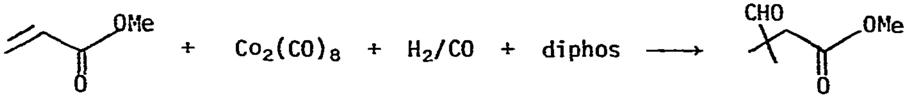
(166)

L = (-)DIOP

25% yield

32% opt. yield

(167)

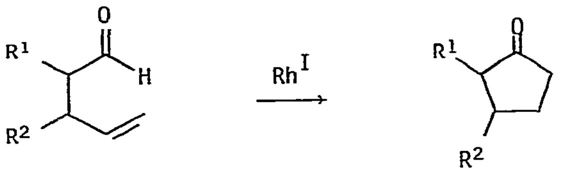


85%

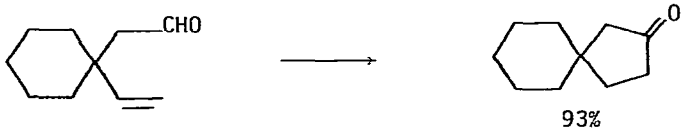
19.5 β/α

2. Carbonylation of Alkenes and Alkynes

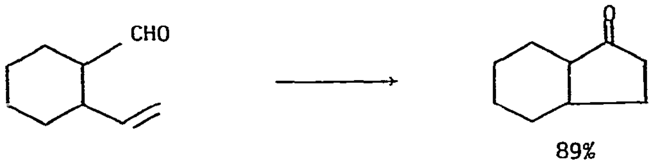
Transition metal catalyzed hydroacylation of olefins has accounted for a number of interesting procedures. 4-Pentenal cyclized to 2-methylcyclopentanone in the presence of $RhCl(PPh_3)_3$ as a catalyst [277a]. This process was the subject of an extensive mechanistic investigation [277b]. A catalyst derived from bis(ethylene)Rh(acac) promoted the addition of 4-pentenal to ethylene to give primarily 6-hepten-3-one [278]. This process was used to synthesize a number of cyclopentanones (equations 168-171) [279]. The catalyst used in this case was generated from $[(cyclooctene)_2RhCl]_2$ and a tertiary phosphine. The hydroacylation tolerated COOH, COOR, C≡N, C=O, halide, and alcohol groups, but amines suppressed the reaction. The amount of catalyst required was 10%. The presence of methyl groups at the 2 or 5 positions cut the yield in half, while disubstitution at those positions completely suppressed the desired reaction and led to nothing identifiable. In contrast, substitution at the 3 or 4 positions had no effect. A model complex for the hydroacylation of olefins has been made [280]



(168)

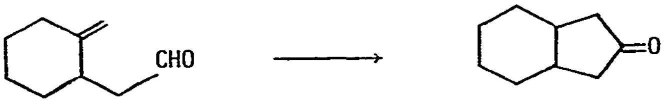


(169)



cis 27
trans 73

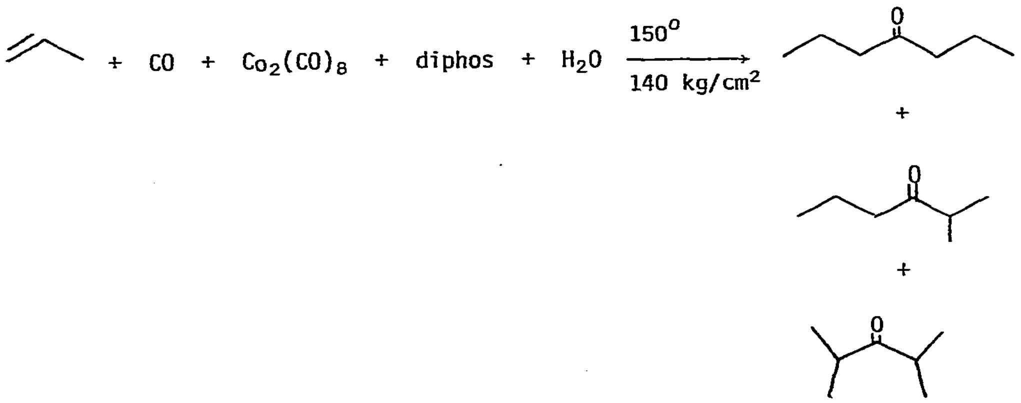
(170)



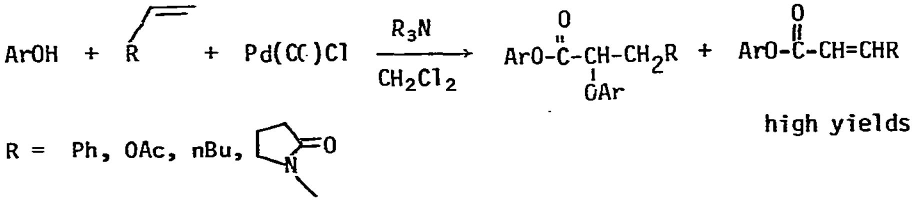
(171)

Propene and carbon monoxide reacted in the presence of $Co_2(CO)_8$ and diphos and water to give up to 81% of a mixture of ketones resulting from dimerization-acylation of propene (equation 172) [281]. Olefins underwent alkoxy carbonylation when treated with phenols and carbon monoxide in the presence of a palladium catalyst (equation 173) [282]. Olefins were carboacylated by reaction of their palladium(II) complexes with carbanions, followed by carbon monoxide and methanol (equations 174 and 175) [283]. Olefinic tosylates underwent cyclization with concommitant carbonylation when treated with disodium tetracarbonylferrate (equations 176-178) [284]. Allyl amines cyclized to butyrolactams when carbonylated over a rhodium(I) catalyst (equation 179). In contrast, allyl alcohol, allyl chloride, and vinyl chloride were all converted to esters (equations 180-182) [285]. α,β-Unsaturated acids and amides cyclized to anhydrides or imides when treated with <u>bis</u>-(cyclooctadiene)nickel, a tertiary phosphine, and carbon monoxide (equation 183) [286].

(172)



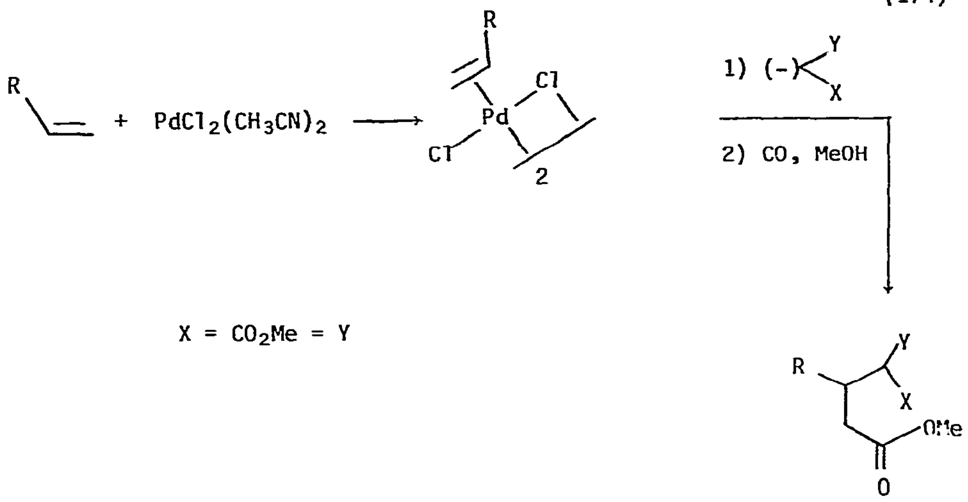
(173)



R = Ph, OAc, nBu,

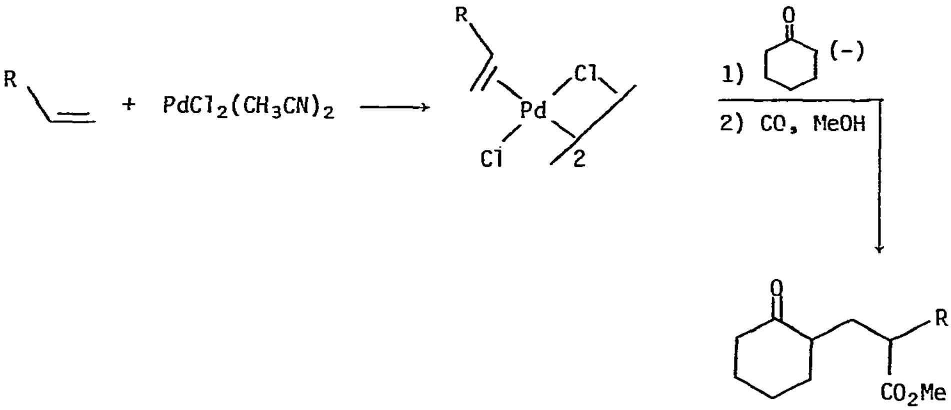
high yields

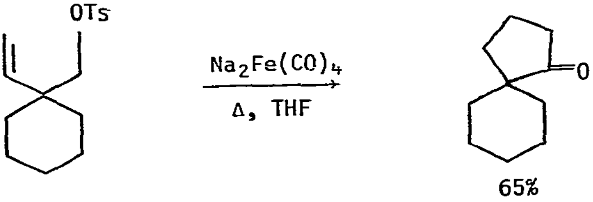
(174)



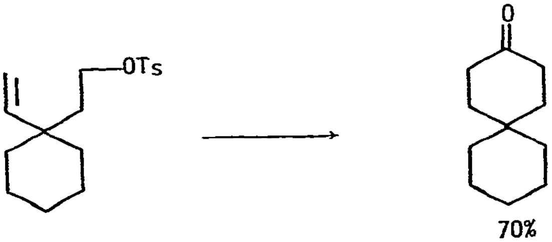
$X = CO_2Me = Y$

(175)



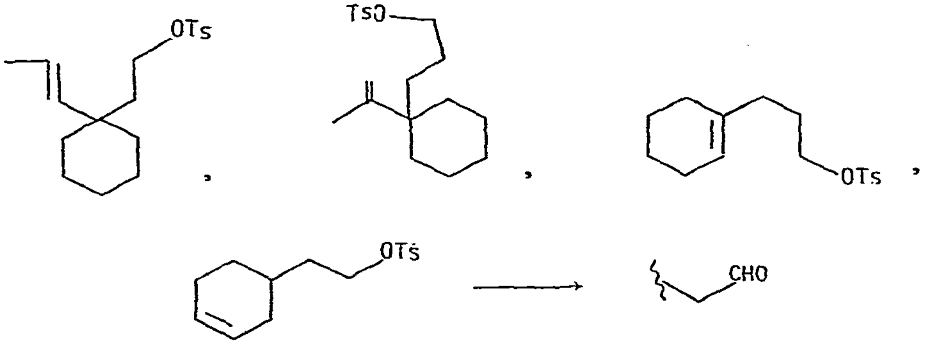


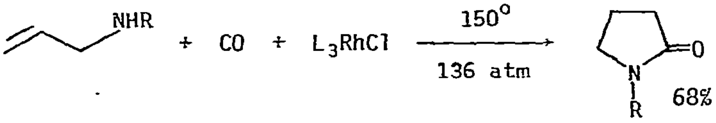
(176)



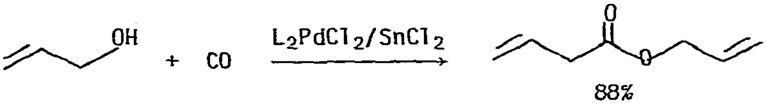
(177)

(178)

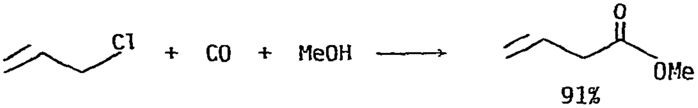




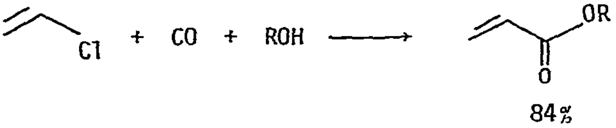
(179)



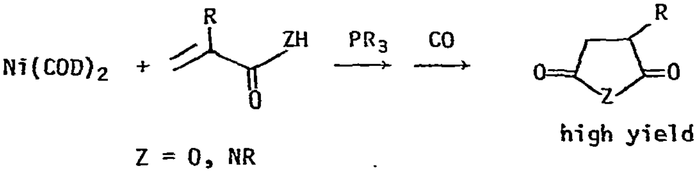
(180)



(181)

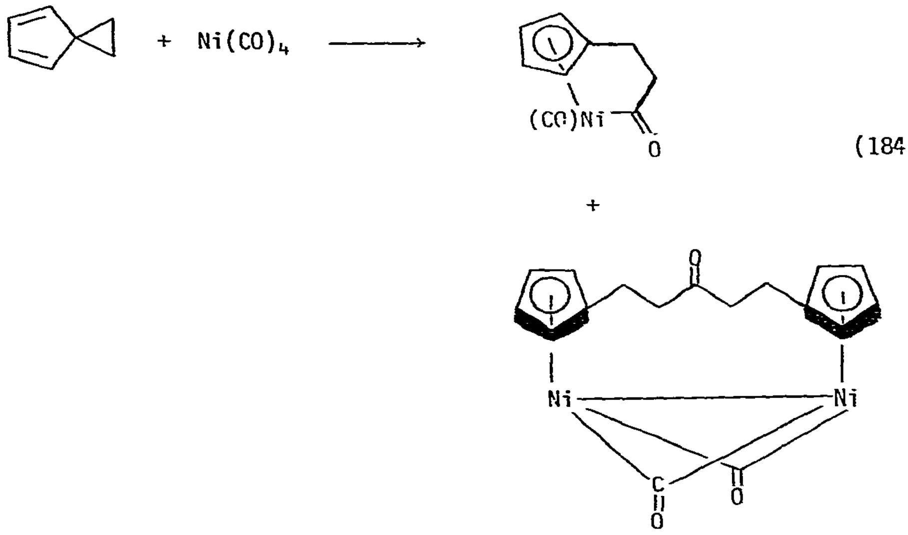


(182)

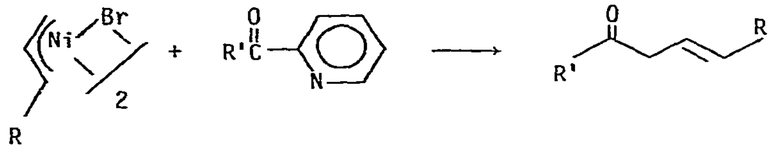


(183)

3,8-Nonadienoate esters were prepared by the palladium(II)-amine complex catalyzed carbonylation of butadiene. The yields were quite high [287]. The catalysis of diene carbonylation has been reviewed [288]. Acetylene carboxylates were produced from the carbonylation of terminal acetylenes with CO at room temperature and atmospheric pressure using palladium(II) chloride as a catalyst [289]. Tertiary propargyl alcohols were carbonylated to mixtures of esters using either palladium black or $Co_2(CO)_8$ as a catalyst [240]. Nickel carbonyl ring opened and acylated the spiro compound in equation 184 [291]. π-Allylnickel halide complexes reacted with 2-acylpyridines to produce β,δ-unsaturated ketones (equation 185) [292].



(184)

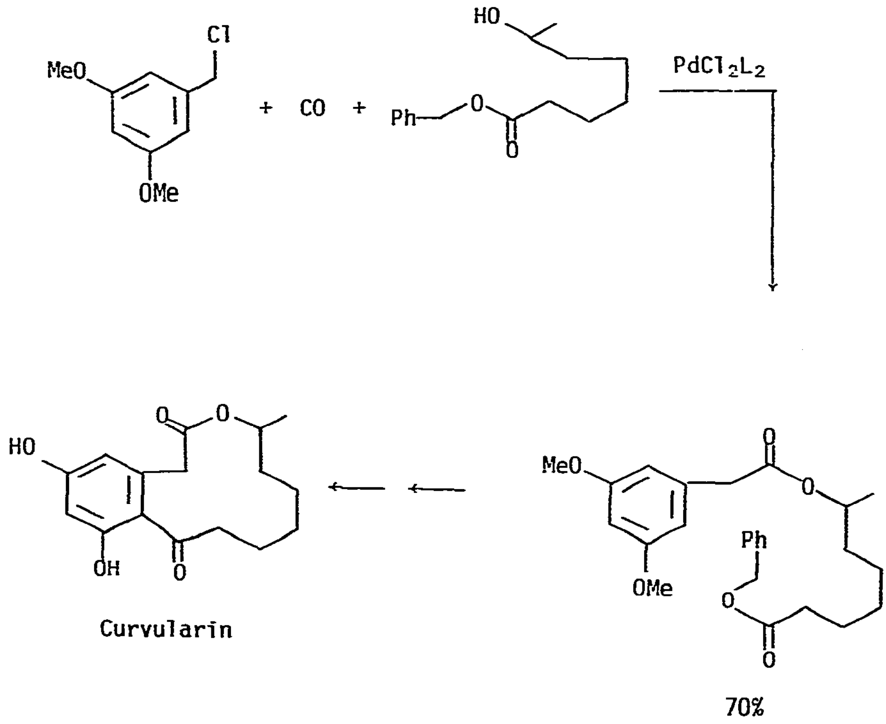


(185)

3. Carbonylation of Halides

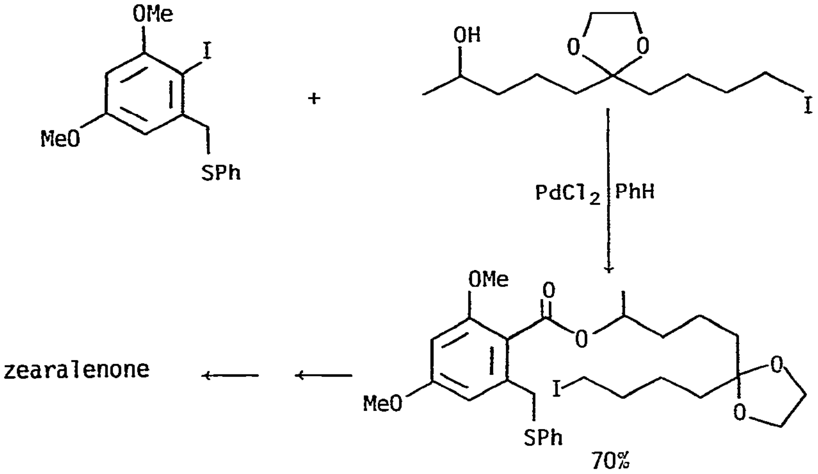
The carboxylation of benzyl halides by $Co(CO)_4^-$ in a biphasic system was shown to involve residence of $R_4\overset{+}{N}Co(CO)_4^-$ in the organic phase and the product carboxylate $PhCH_2COO^-$ in the aqueous phase [293]. Methanolic solutions of $Co(CO)_4^-$ in the presence of an acid converted organic halides to hydrocarbons or aldehydes. Aliphatic and benzyl halides were primarily carbonylated to aldehydes [294]. Phase transfer catalysis was used in the carboxylation of allyl chlorides to mixtures of β,δ- and α,β-unsaturated carboxylic acids, using nickel carbonyl as the carbonylating agent [295]. Treatment of aryl bromides with carbon monoxide over a palladium phthalocyanine-active carbon catalyst produced the corresponding esters. The mechanism was shown to proceed by a free radical process [296]. Methyl 6-bromohexanoate was converted to methyl 7-oxoheptanoate by treatment with $Na_2Fe(CO)_4$ [297].

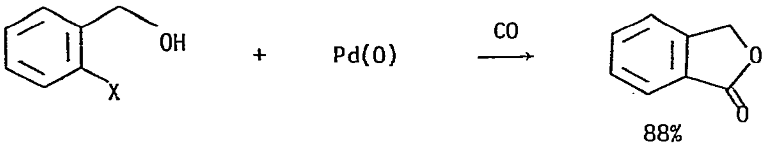
Both curvularin and zearalenone were synthesized by processes involving palladium catalyzed carbonylation of a benzyl halide (equation 186) [298], (equation 187) [299]. Haloalcohols were converted to lactones by a palladium(0) catalyzed carbonylation process (equations 188-191) [300]. Isoindoles (equation 192), isoquinolinones (equation 193), and quinolinones (equation 194) were prepared in a similar manner [301]. The process was even useful to synthesize β-lactams (equation 195) [302]. Treatment of diiodobenzene with nickel carbonyl and acetylenes produced indanones (equation 196) [303].



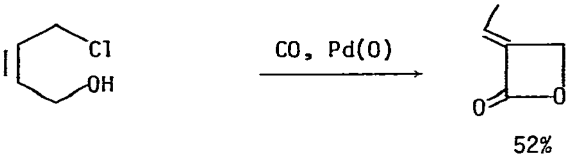
(186)

(187)

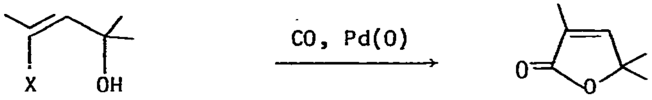




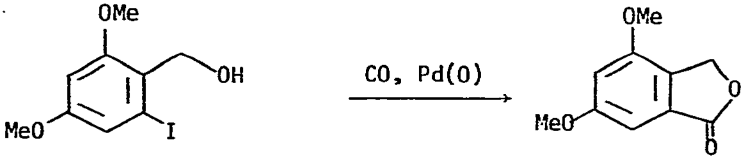
(188)



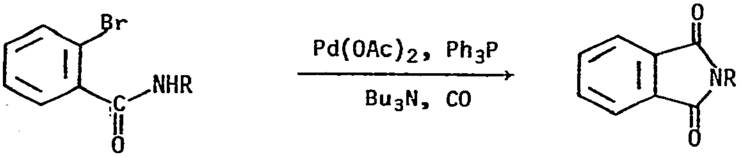
(189)



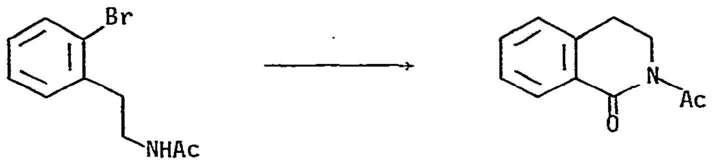
(190)



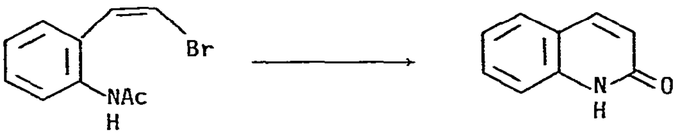
(191)



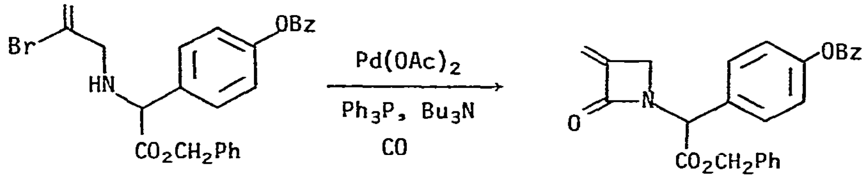
(192)



(193)

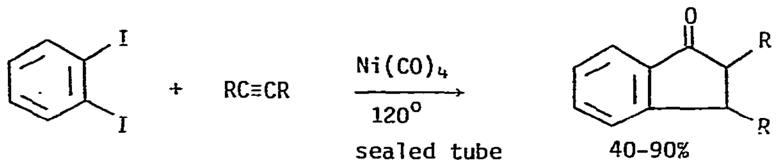


(194)



36-63%

(195)



(196)

R's = Et, Me, Ph, H

4. Carbonylation of Nitrogen Compounds

A great deal of effort continued to be expended on the carbonylation of nitroaromatics to aryl isocyanates, because of their commercial Importance. Up to 80% yields of phenyl isocyanate were obtained from the carbonylation of nitrobenzene at 50 atm CO pressure and 205°, using $[Rh(CO)_2Cl]_2$ and pyridinium hydrochloride as a catalyst system [304][305]. Another catalyst system that worked well was $RhH(CO)(PPh_3)_3$ modified by the addition on molybdenum pentachloride. This system catalyzed the reaction at 25° and 80 atmospheres of CO, considerably milder than usual [306][307]. In the reaction using $[RhCl(CO)_2]_2MoCl_5$ as the catalyst, the reaction was first order with respect to nitroaromatic, and the rate limiting step was deoxygenation [308]. In a somewhat different process, nitroaromatics were carbonylated in benzene, using $Rh_4(CO)_{12}$ as the catalyst. Amides in which benzene had been incorporated were the products (equation 197) [309].

$$ArNO_2 + PhH + CO \xrightarrow[220^\circ]{Rh_4(CO)_{12}} \underset{32\text{-}54\%}{ArNHCOPh} \qquad (197)$$

Ar = p- H, Me_2N, MeO, Cl, CH_3, CN, CH_3CO, CH_3O_2C, m-Me, o-Me

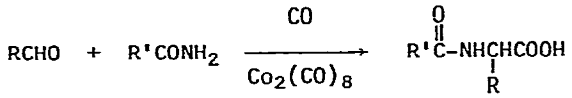
Palladium catalysts were also popular for the conversion of nitroaromatics to isocyanates. Para-nitrotoluene was converted to p-tolylisocyanate at 230 atmospheres and 220° with a $PdCl_2(pyridine)_2/(Pyridine\ H)_2Fe_2Cl_8(pyridine)_2$ catalyst [310]. Other catalyst systems studied included $(Bu_4N)_2Pd_2Cl_6/VCl_3\cdot 3THF$ [311], $(Bu_4N)_2PdCl_6$/ isoquinolinium hydrochloride $FeCl_3$ at 180 atmospheres and 250° [312], and palladium chloride/metal oxide [313][314] at 125 atmospheres and 200°. The optimum temperature for isocyanate formation using palladium chloride-pyridine catalysts was lowered from 200° to 160° by activating the catalyst with methyl iodide [315]. The use of mixed heterogeneous-homogeneous catalyst systems for this conversion was also examined [316].

Amines such as piperidine and butylamine were oxidatively carbonylated to ureas by carbon monoxide and mixed palladium-copper catalysts [317]. The kinetics of this process were studied [318]. Benzyl trialkylammonium complexes were carbonylated to phenyl acetic acid by cobalt carbonyl and methyl iodide under basic conditions (equation 198) [319].

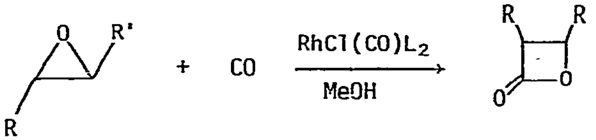
$$PhCH_2\overset{+}{N}Et_3Cl^- + CO \xrightarrow[\substack{MeI,\ PhH \\ 1atm.\ 25^\circ}]{Co_2(CO)_8} \underset{95\%}{PhCH_2CO_2H} \qquad (198)$$

5. Carbonylation of Oxygen Compounds

The use of heterogenized homogeneous rhodium catalysts for the carbonylation of methanol has been reviewed [320]. Methanol was both carbonylated and homologated in its reaction with carbon monoxide and hydrogen using $Ru(CO)_4I_2$, $Ru_3(CO)_{12}$, or $Ru(acac)_3$ as catalyst and methyl iodide or sodium iodide as promoters [321]. N-acyl-α-aminoacids were prepared by the cobalt catalyzed carbonylation of aldehydes in the presence of amides (equation 199) [322]. Styrene oxide was converted to a propriolactone by carbonylation using $RhCl(CO)L_2$ as a catalyst. A number of other epoxides failed to undergo this reaction (equation 200) [323].



$$RCHO + R'CONH_2 \xrightarrow[Co_2(CO)_8]{CO} R'\overset{\overset{O}{\|}}{C}\text{-}NH\underset{\underset{R}{|}}{C}HCOOH \qquad (199)$$



(200)

R = Ph, R' = H 67%

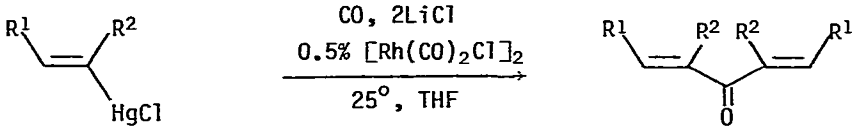
R = Me, Ph -$(CH_2)_4$- 0-5%
R' = H, Ph

6. Miscellaneous Carbonylations, Decarbonylations, and Carboxylations

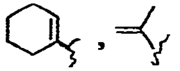
Carbon monoxide insertion into transition metal carbon sigma bonds has been reviewed [324]. The effects of strong Lewis acids on the methyl migration (carbonyl insertion) in η^5-$C_5H_5Mo(CO)_3Me$ have been probed [325].

Vinylmercurials underwent a carbonylation-dimerization when treated with carbon monoxide in the presence of $[Rh(CO)_2Cl]_2$ as a catalyst (equation 201). Arylmercuric chlorides behaved similarly (equation 202) [326]. The alkylmercuric chloride resulting from mercury(II) ring opening of trimethylsiloxylcyclopropanes underwent a palladium(II) catalyzed carbonylation (equation 203) [327]. Aryl thallium complexes were converted to benzoic acids by treatment with carbon monoxide and a palladium(II) catalyst (equation 204). This was used to make several heterocyclic systems (equations 205 and 206) [328]. Chromium carbyne complexes reacted with thiophenoxide to produce thioesters (equation 207) [329].

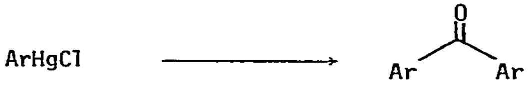
(201)



50-90%

R^1 = t-Bu, nBu, Ph,  , H, Cl

R^2 = H, Me

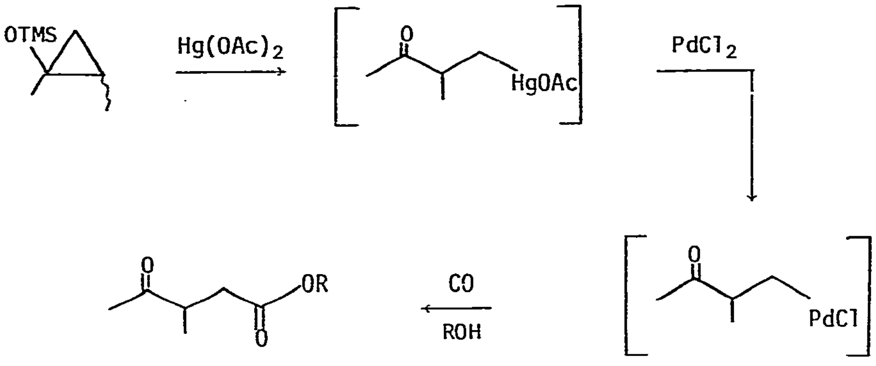


(202)

40-90%

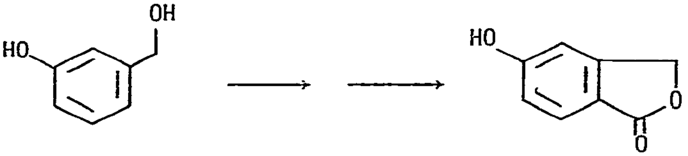
Ar = 2-Naphthyl, 2-thienyl, m-NO_2Ph

(203)



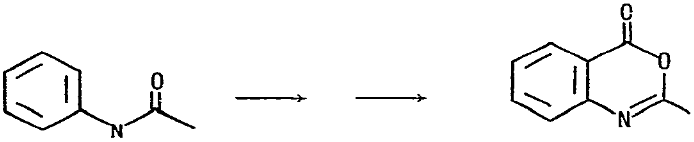
46-52%

$$\mathrm{ArH} \xrightarrow{\mathrm{Tl(OTFA)_3}} \mathrm{ArTl(TFA)_2} \xrightarrow[\substack{\mathrm{LiCl/MgO} \\ \mathrm{MeOH}}]{\mathrm{CO,\ 10\%\ PdCl_2}} \mathrm{ArCO_2H} \quad (204)$$



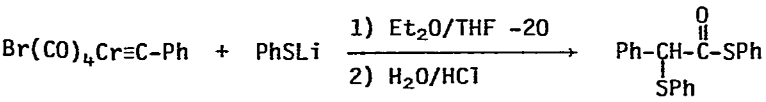
89%

(205)



40%

(206)

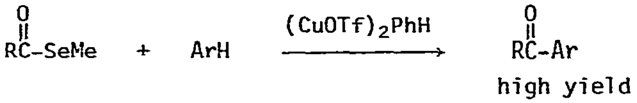


$$\mathrm{Br(CO)_4Cr{\equiv}C\text{-}Ph} + \mathrm{PhSLi} \xrightarrow[\text{2) } \mathrm{H_2O/HCl}]{\text{1) } \mathrm{Et_2O/THF}\ -20} \mathrm{Ph\text{-}\underset{\substack{| \\ SPh}}{C}H\text{-}\overset{\substack{O \\ \|}}{C}\text{-}SPh} \quad (207)$$

Cyclopropane was carbonylated to mixtures of cyclobutanone, dipropyl ketone, and 2- or 3-methylcyclohexanone by carbon monoxide in the presence of $[Rh(CO)_2Cl]_2$ as a catalyst [330]. Arenes were carbonylated to carboxylic acids by carbon monoxide and palladium acetate as a catalyst (equation 208) [331]. Arenes were acylated by seleno esters in the presence of copper triflate (equation 209). These seleno esters reacted with isonitriles to produce oxazoles (equation 210) [332]. Copper(I) chloride and $CuCl(PPh_3)$ promoted the Gattermann-Koch synthesis of aromatic aldehydes [333].

$$ArH + CO + \underset{cat}{Pd(OAc)_2} \xrightarrow[100^{\circ}]{15\ atm} \underset{12\text{-}48\%}{ArCOOH} \qquad (208)$$

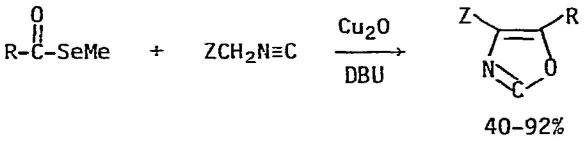
ArH = PhH, PhOMe, $PhCH_3$, p-ClPhH, furan, thiophene



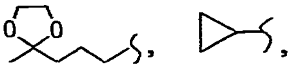
$$R\overset{O}{\overset{\|}{C}}\text{-}SeMe + ArH \xrightarrow{(CuOTf)_2PhH} \underset{\text{high yield}}{R\overset{O}{\overset{\|}{C}}\text{-}Ar} \qquad (209)$$

R = n-hexyl, 

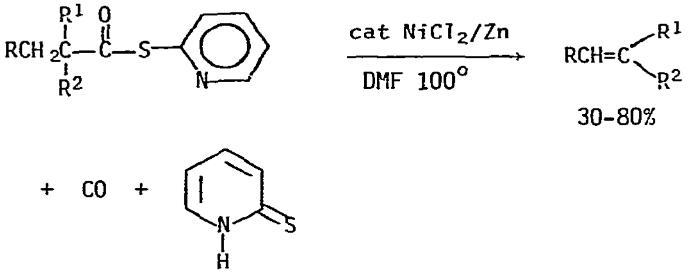
Ar = anisole, furan, thiophene, pyrrole, N-methyl indole



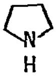
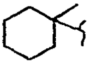
(210)

R = Ph, , n-C_6, n-C_7
Z = CO_2Et, Ts

Catalytic decarbonylation reactions using cationic rhodium(I) complexes of chelating diphosphine ligands was the subject of a dissertation [334]. A catalyst formed by the reaction of ruthenium tetraphenylporphyrin with a large excess of tri-n-butylphosphine was an efficient catalyst for the decarbonylation of aromatic aldehydes to the hydrocarbon. Aliphatic aldehydes gave some side products, but still gave acceptable yields. Cinnamaldehyde failed to decarbonylate cleanly [335]. Palladium supported on alumina and on carbon decarbonylated furfural to furan [336]. Cationic rhodium(I) complexes containing chelating diphosphine ligands were more active for aldehyde decarbonylations than was $RhCl(PPh_3)_3$ [337]. The role of decarbonylation of primary alcohols, used as solvents in catalytic hydrogenations, in catalyst poisoning was examined [338]. Nickel chloride/zinc catalyzed the decarbonylation of S-(2-pyridyl) thiolates to olefins (equation 211) [339].



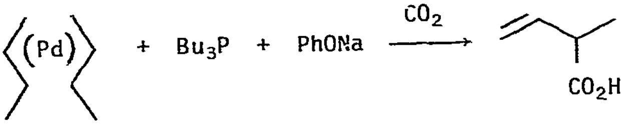
(211)

R = nC_9, Ph, Me, n-Bu, , , $PhCH_2$, 

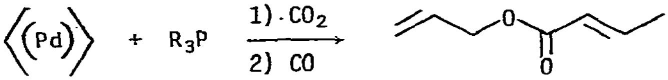
R^1 = H, Ph, PhO, Et

R^2 = H, Me

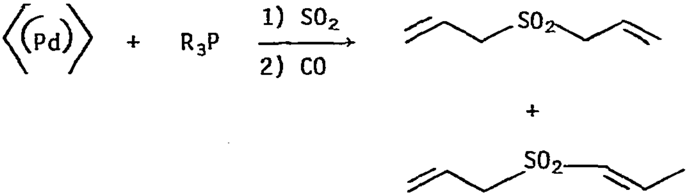
Carbon dioxide reacted with *bis* π-allyl palladium complexes to produce unsaturated carboxylic acids (equation 212) [340]or esters (equation 213) [341]. Sulfur dioxide also inserted (equation 214) [341]. Enolates (equation 215) and epoxides (equation 216) were carboxylated by carbon dioxide and a copper catalyst that "fixed" CO_2 [342].



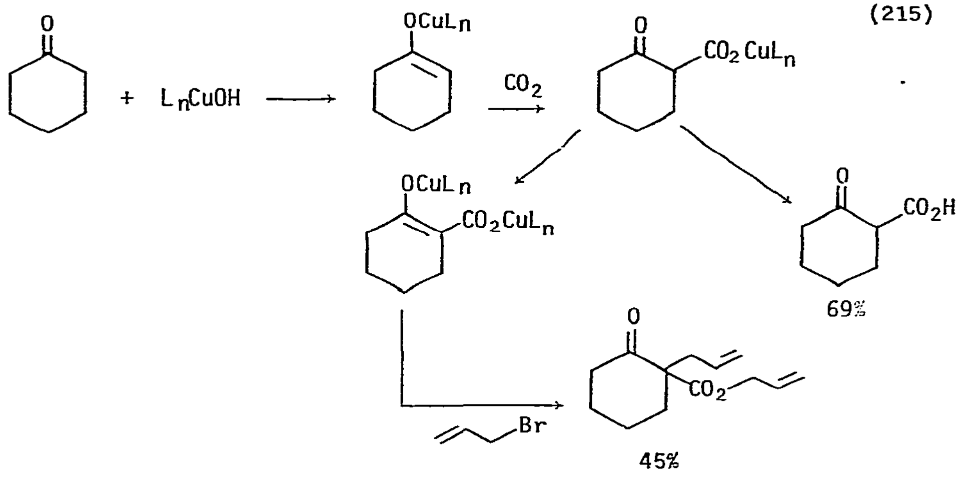
(212)



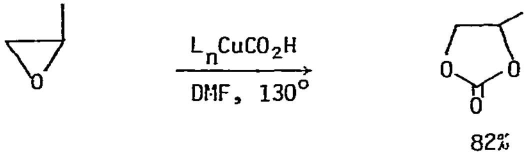
(213)



(214)



(215)



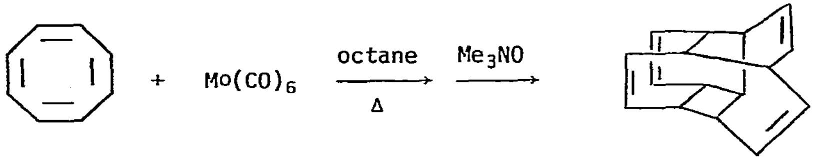
(216)

D. Oligomerizations

Catalysts prepared from nickel(0) butadiene complexes and diethylaluminum chloride/triphenylphosphine were very active for the oligomerization of ethylene [343]. Butenes were produced from ethylene at 100° and 10-15 atmospheres pressure in the presence of palladium on aluminosilicate catalysts [344]. An especially productive Ziegler catalyst for ethylene polymerization was produced by treating Cp_2ZrMe_2 with the solid phase $[Al(CH_3)_2O-]_n$ [345]. The catalytic activity of the system π-allylnickel bromide (tricyclohexyl)phosphine and ethylaluminum dichloride for the dimerization of propene was found to be one thousand times greater than originally thought [346]. The catalyst produced from the treatment of an 87:12 mixture of alumina and silica gel with $(CpNi)_3(CO)_2$ at 150° was an effective oligomerization catalyst for the conversion of ethylene to a mixture of C_4 to C_{20} olefins. Butenes (34%) and hexenes (36%) predominated [347]. The kinetics of the dimerization of ethylene by palladium(II) chloride in chloroform was studied [348]. The dimerization and codimerization of ethylene and propene was catalyzed by π-allylnickel bromide complexes in the presence of titanum tetrachloride, aluminum bromide, and phosphines [349]. Immobilization of the rhodium-tin complex $[Rh(SnCl_3)_2Cl_4]^{3-}$ on an ion exchange resin produced a highly active, stable, and selective catalyst for the dimerization of ethylene to 2-butenes in acid media [350]. Nickel silicate was active for the dimerization of ethylene and the rearrangement of butene [351]. The role of tantalacyclopentanes in catalytic olefin dimerization has been reviewed [352]. In n-octane, the active catalyst for propene dimerization was based on $[NiCH(COMe)_2]$-$(Me_2CHCH_2)_2AlCl$ [353]. Palladium(II) adsorbed on a carboxyl cation exchange resin oxidatively dimerized styrene 10^3xfaster than palladium acetate itself [354]. Addition of benzoquinone to palladium chloride-benzonitrile catalysts improved the system for the dimerization of acrylic acid derivatives [355]. Ethylene oligomerized to α-olefins in the presence of homogeneous solutions of a nickel-phosphorous ylide complex, $LNiPh_3P{=}CHBz$ [356]. Norbornene was polymerized by $RuCl_3{\cdot}3H_2O$ and by $RuCl_2(PPh_3)_2$. The kinetics of this process were studied [357].

Stereoregular and sequence regular polymerization of butadiene has been reviewed [358]. A review comparing transition metal and non transition metal oligomerizations of isoprene for the synthesis of terpenes has been published [359]. The zirconium-based catalyst $Zr(OBu)_4/Ph_3P/Et_2AlCl$ was effective for the linear dimerization and codimerization of butadiene, 2,3-dimethylbutadiene, myrcene, and α-farnesene [360]. Butadiene cyclodimerized to vinylcyclohexene in the presence of $Fe(NO)_2$ generated by the reaction of $[Fe(NO)_2Cl]_2$ with nickel(0) complexes [361]. The same catalyst also cyclodimerized isoprene and piperylenes. Copper(I) containing Y-zeolites were effective catalysts for the cyclodimerization of butadiene to 4-vinylcyclohexene [362]. The structure of this catalyst system was examined by an X-ray structural analysis [363]. A kinetic study of the cyclooligomerization of butadiene in the presence of $Ni(acac)_2/Et_2AlOEt/R_3P$ catalysts has been carried out [364]. The chelated lithium complex $FeCl(BH_4)[MeN(CH_2CH_2NMe_2)_2]$ was an active catalyst for butadiene dimerization [365]. Cyclooctatetraene dimerized when heated in octane in the presence of molybdenum hexacarbonyl (equation 217) [366].

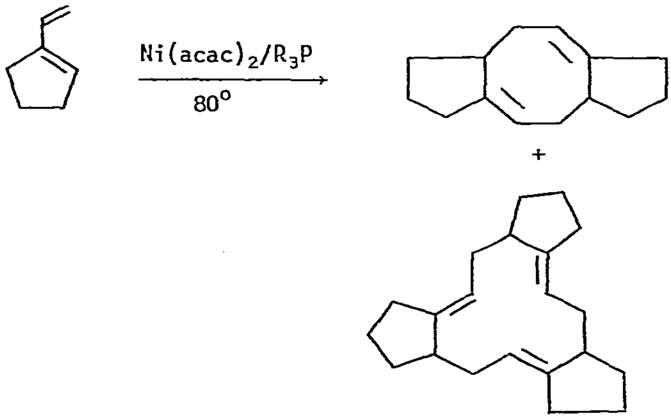
(217)



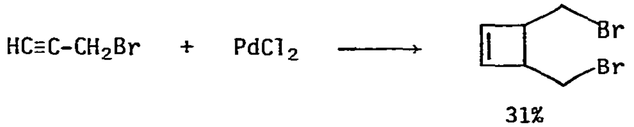
An extensive study of nickel(0) catalyzed cyclooligomerization of butadiene has been carried out. The nickel catalyzed cooligomerization of butadiene with N-isopropyl-2-methyleneaziridine or 2-aza-1,3-dienes could be controlled by variation of the properties and concentrations of the nickel ligands [367]. Ligand concentration control maps of the nickel/butadiene/diphenylphenoxyphosphane has been published [368]. The method of inverse titrations for control of metal-catalyzed processes have also been published [369], as has a study of the role of steric [370] and electronic factors in nickel catalyzed cyclooligomerizations of butadiene [371].

Nickel acetylacetonate/phosphine catalysts converted 1-vinyl-1-cyclopentene to cyclodimers and trimers (equation 218) [372]. The kinetics of the cyclotrimerization of butadiene to 1,5,9-cyclododecatriene over $TiCl_4$-Et_2AlCl were studied [373]. The effect of butadiene concentration in this process was also studied [374].

(218)



Iron pentacarbonyl and nickel tetracarbonyl polymerized perchlorocyclopentadiene to $(C_5Cl_4CO)_{17}$ and $C_{10}Cl_{10}$ [375]. Palladium(II) chloride dimerized propargyl bromide (equation 219) [376].

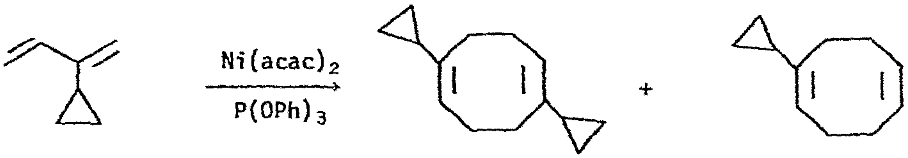


(219)

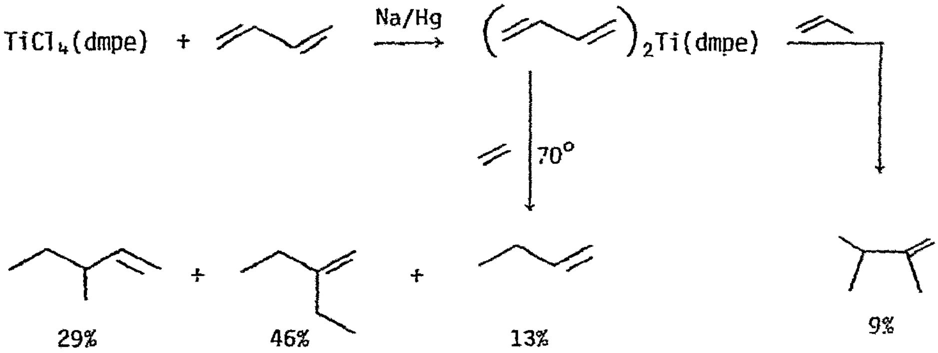
31%

Cyclohexa-1,3-diene and ethylene codimerized in the presence of a catalyst produced from *bis*(cyclooctadiene)nickel, diethylaluminum chloride, and a chiral aminophosphine to produce 3-vinylcyclohexene in 87% yield with a 73% optical yield [377]. Butadiene codimerized with 2-cyclopropylbutadiene in the presence of $Ni(acac)_2/P(OPh)_3$ catalyst (equation 220) [378]. The diene complex $(butadiene)_2Ti$ dmpe dimerized propene, and codimerized butadiene with ethene (equation 221). Butadiene itself polymerized, and other olefins as well as cyclopropene, were inert [379]. The complex $[Rh(diphos)(CO)_2][BPh_4]$ polymerized allene to 1,2,1,2,-polyallene, and oligomerized propyne [380]. α-Olefins dimerized and codimerized over a

(220)

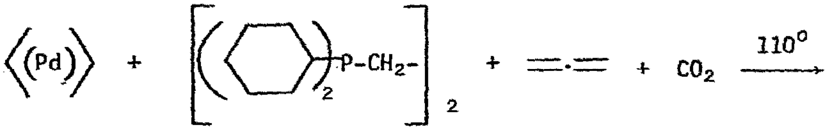


(221)



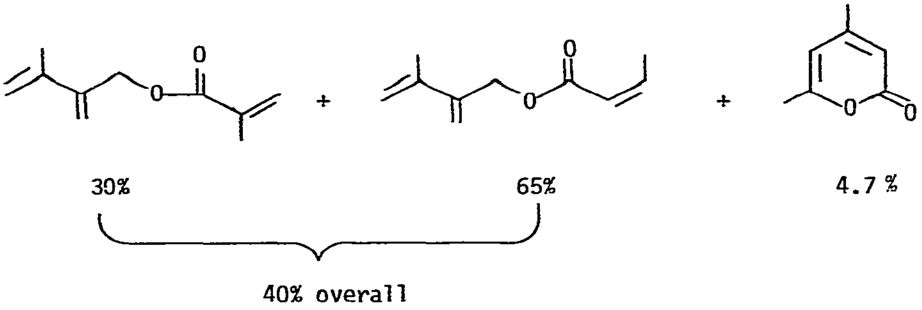
catalyst containing 1:12 $Zr(OBu)_4$-Et_2AlCl [381]. Conjugated cyclodienes (cyclopentadiene, cyclohexadiene, cycloheptadiene) underwent addition reactions with ethylene to give 3-vinylcyclenes in the presence of nickel or palladium catalysts L_2MX_2 and Et_nAlCl_m [382]. Palladium(II) complexes catalyzed the cooligomerization of acetylenes and allylic halides to produce pentadienes and heptatrienes [383]. Allene and carbon dioxide combined in the presence of bis π-(allyl)palladium and a diphosphine to produce a mixture of carboxylated oligomers (equation 222) [384]. A slightly different complex catalyzed a similar reaction between butadiene and carbon dioxide (equation 223) [385].

(222)

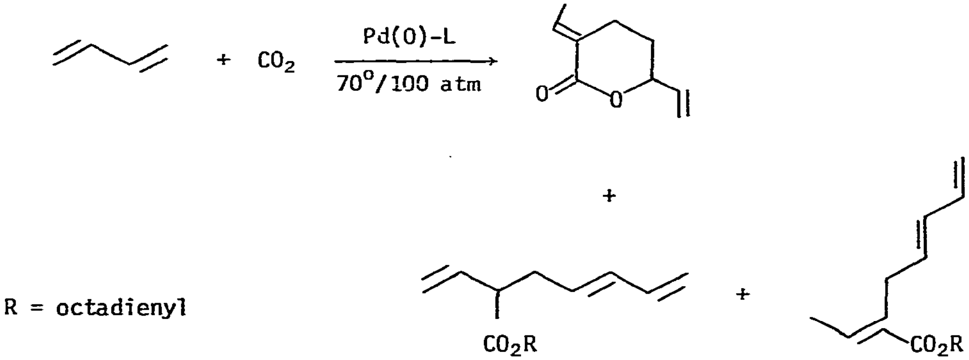


(next page)

(222)

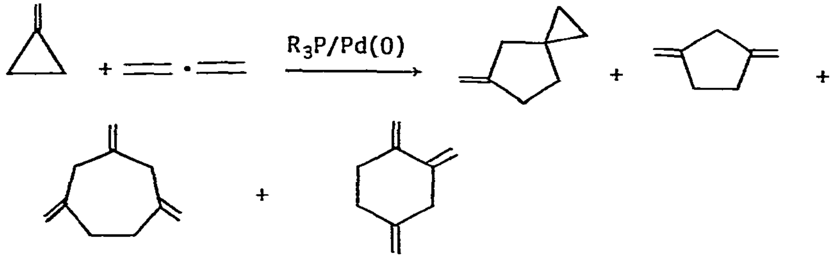


(223)

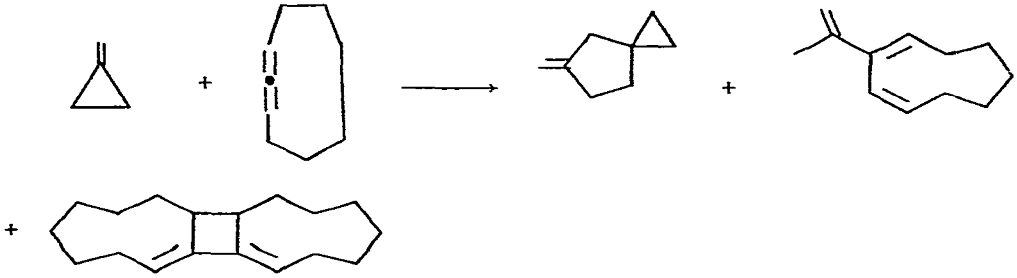


Methylene cyclopropane cyclooligomerized with allene (euqation 224) and 1,2-cyclononadiene (equation 225) in the presence of palladium(0) phosphine complexes [386]. The same system codimerized methylenecyclopropane with ethylene, norbornene, dicyclopentadiene, or norbornadiene to produce methylenecyclopentane derivatives [387]. Dimethylcyclopropene cyclodimerized or cyclotrimerized in the presence of palladium(0) catalysts (equation 226) [388]. Cyclopropane alkylated benzene in the presence of a number of group VIII metal salts (equation 227) [389]. Prostanoid cyclopentenones were produced by the reaction of cobalt-alkyne complexes with olefins (equation 228 and 229) [390].

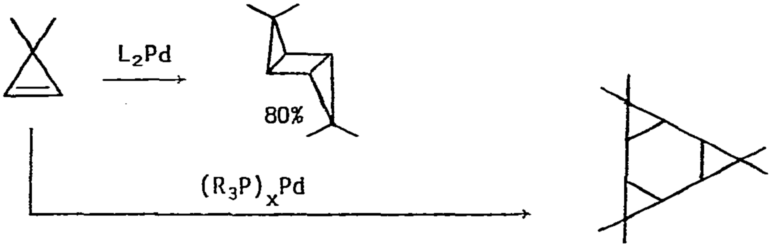
(224)



(225)

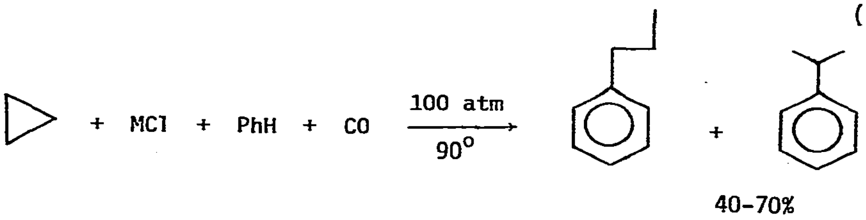


(226)



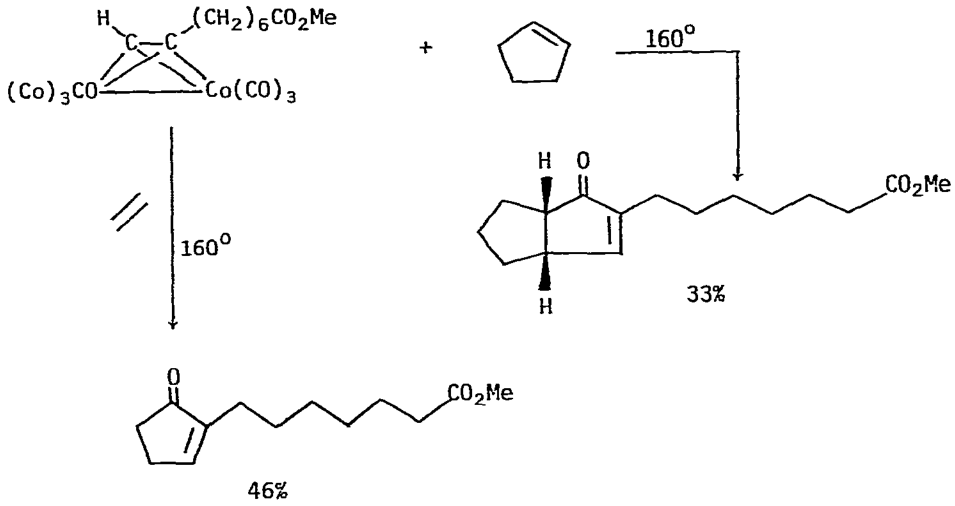
L = DBA, COD, NB

(227)

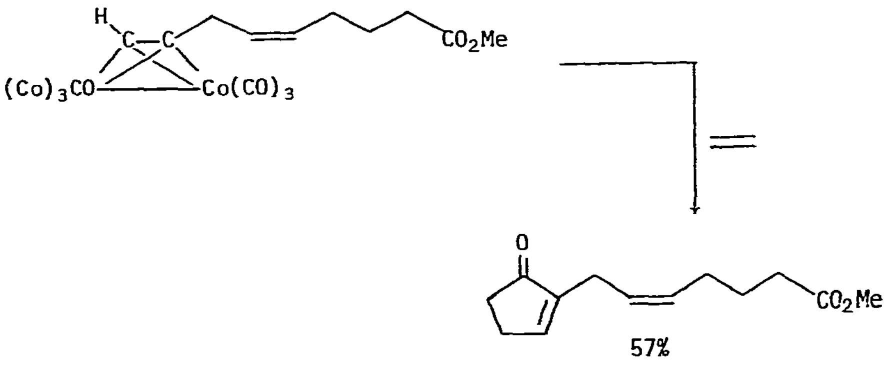


MCl = $RuCl_3$, $OsCl_3$, $RhCl_3$, $IrCl_3$, $PdCl_2$, $PtCl_2$

(228)

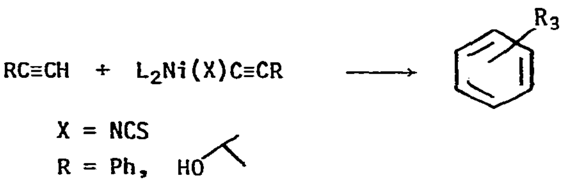


(229)

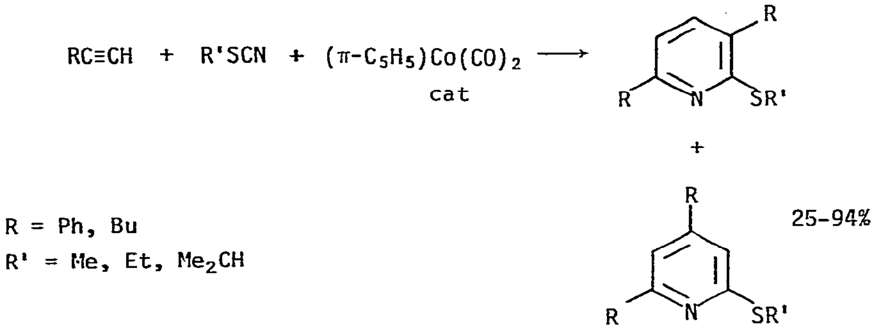


Phenylacetylene cyclotrimerized to mixtures of 1,2,4- and 1,3,5-triphenylbenzene in the presence of $NbCl_5$ or $TaCl_5$. The corresponding fluoride salts led to linear oligomerization of this alkyne as well [391]. Silica-supported V_2O_5 catalyzed the trimerization of acetylene to benzene [392]. Nickel acetylides catalyzed the cyclotrimerization of alkynes to benzene (equation 230) [393]. Chromium Y-zeolites cyclized acetylene to benzene [394].

(230)



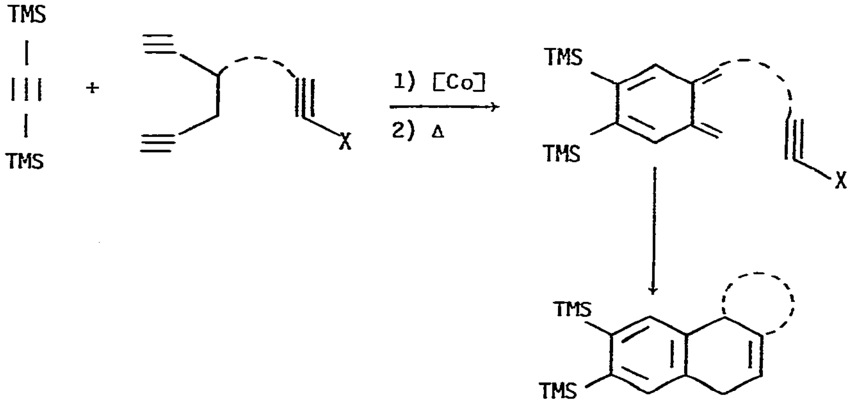
The cobalt-catalyzed cyclotrimerization of alkynes has recently been used extensively for the synthesis of natural products. Much of this work is covered in a review entitled "Thermal, Photochemical, and Transition-metal Mediated Routes to Steroids by Intramolecular Diels-Alder Reactions of o-Xylylenes" [395]. Cobalt-catalyzed co-oligomerization of diacetylenes with nitriles -a new route to annelated pyridines - was the topic of a dissertation [396]. Alkylthiopyridines were synthesized by the cobalt catalyzed cyclotrimerization of thiocyanates and alkynes (equation 231) [397]. The full experimental details of the synthesis of tricyclic species from acyclic polyacetylenes via cobalt catalyzed cyclotrimerization reactions (equation 232) have been published [398]. "The Cobalt Way to Estrone" is the title of a review [399] which describes the synthesis of estrone via cobalt-catalyzed co-cyclotrimerization of acetylenes. The full experimental details of this estrone synthesis have also been published (equation 233) [400].



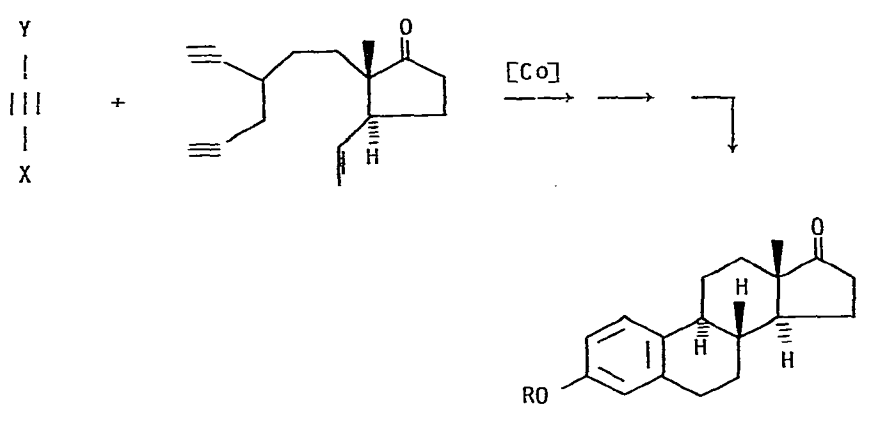
R = Ph, Bu
R' = Me, Et, Me$_2$CH

(231)

(232)

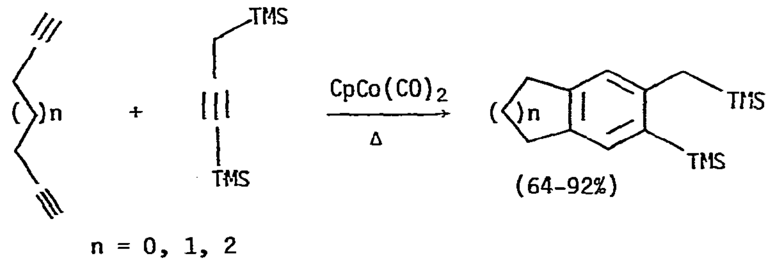


(233)

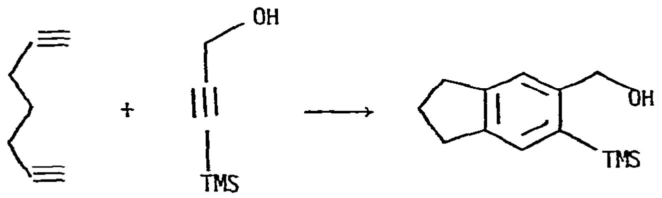


The cocyclotrimerization of *bis*-1,3-trimethylsilylpropyne with diynes has been used to make bicyclic systems (equation 234) [401]. The protected propargyl alcohol underwent a similar reaction (equation 235). Complex chiral polycycles were synthesized by the cobalt mediated cyclization of linear achiral diynes (equation 236) [402]. Complexed cyclopentadienones were synthesized by the cobalt assisted cyclization-carbonylation of trimethylsilyl acetylenes (equations 237 and 238) [403]. The THP ether of propargyl alcohol also cocyclotrimerized with diynes in the presence of cobalt catalysts (equations 239 and 240) [404]. Chromium carbene complexes reacted with 1,4-enynes to produce naphthoquinones (equation 241) [405].

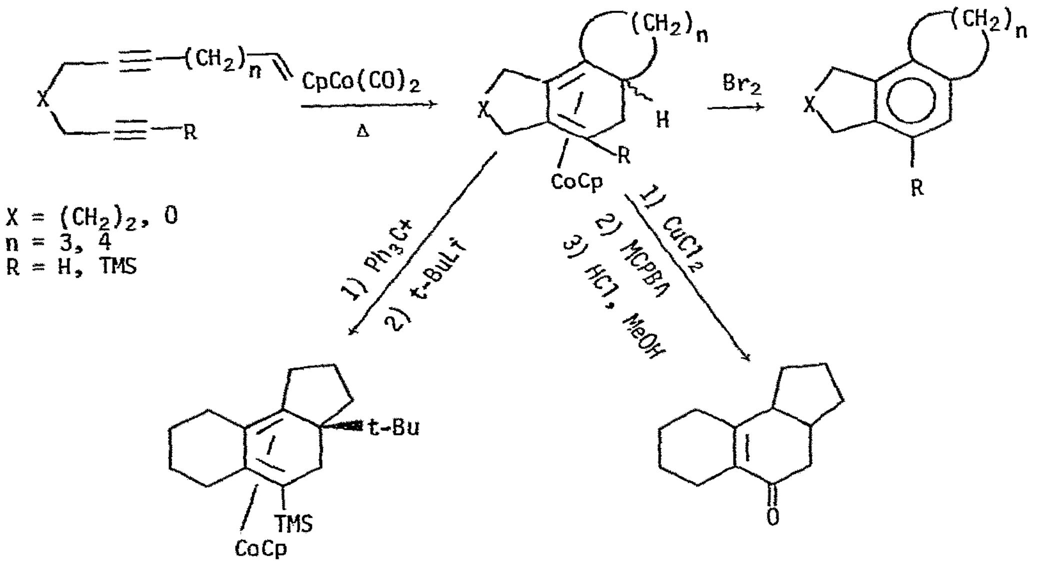
(234)



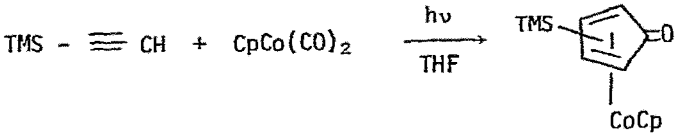
(235)



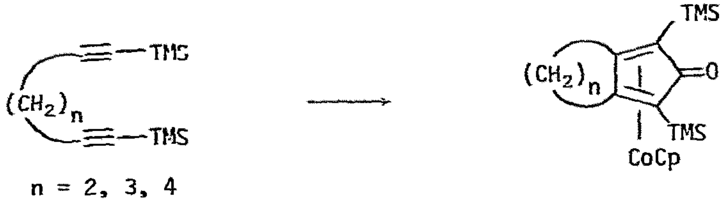
(236)



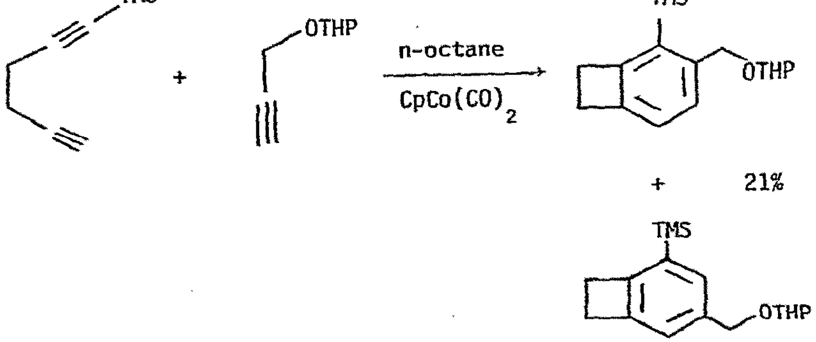
(237)



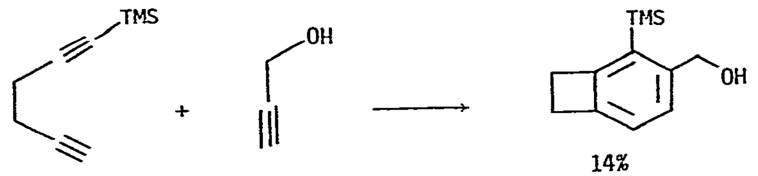
(238)



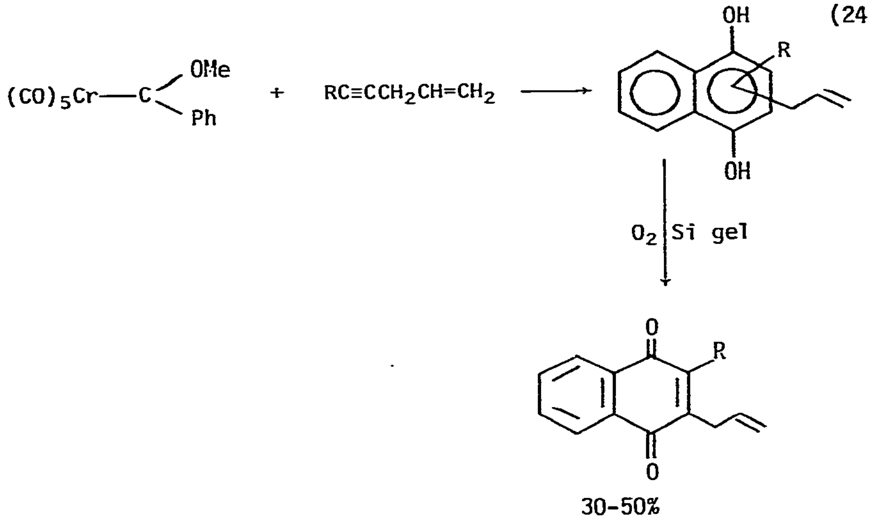
(239)



(240)



(241)

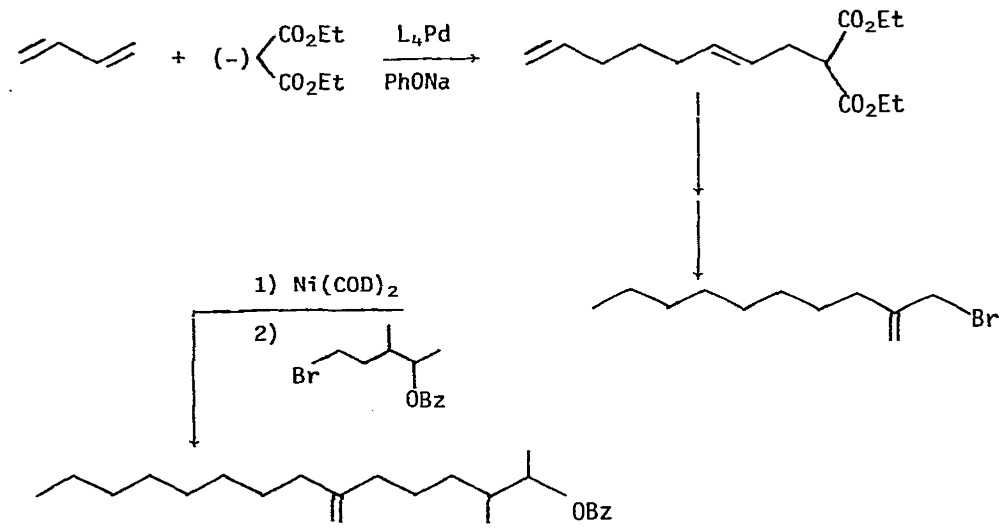


The effects of polar aprotic solvents on the transition metal catalyzed trimerization of phenyl isocyanate were studied, and were shown to greatly enhance the rate of the reaction [406]. Iron pentacarbonyl initiated the telomerization and cotelomerization of vinylidene chloride and propylene with 1,1,1-trichloroethane [407]. Iron complexes in mixed oxidation states catalyzed the radical addition-telomerization of carbon tetrachloride with butadiene [408]. A similar reaction between ethylene and carbon tetrachloride was initiated by $Mn_2(CO)_{10}$ [409].

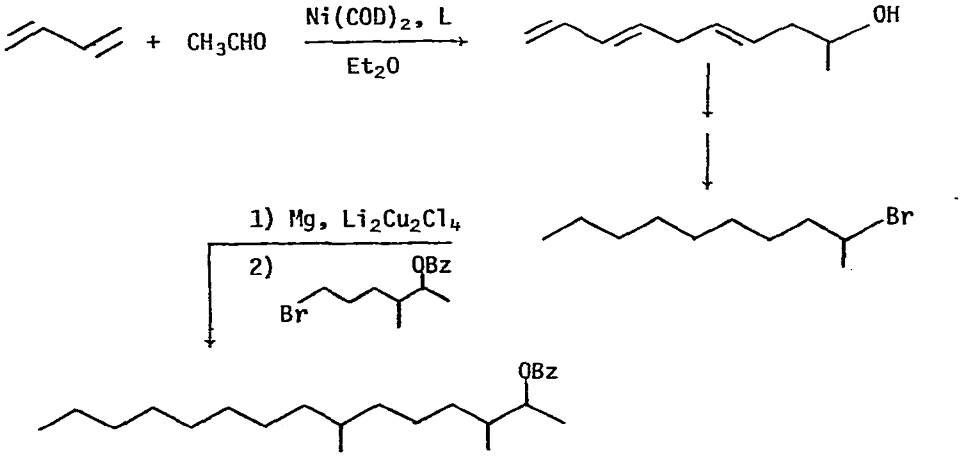
The palladium catalyzed telomerization of butadiene has resulted in the production of a number of interesting substrates suitable for further transformation into natural products. The product from butadiene and diethyl malonate was used to synthesize the pine saw fly pheromone (equation 242), whereas the nickel catalyzed product from butadiene and acetaldehyde was used to prepare the reduced analog (equation 243) [410]. Sulfur stabilized carbanions such as $PhSO_2CH_2CO_2Et$ oligomerized with butadiene in the presence of $Pd(acac)_2/Ph_3P/Et_3Al$ to give $PhSO_2CH(CO_2Et)CH_2CH{=}CH(CH_2)_3CH{=}CH_2$ [411]. Butadiene reacted with N-alkyloxazolidines in the presence of the same catalyst system to give a bis octadienyl oxazolidine (equation 244)

[412]. α-Acetamidoketones (equation 245) and α-acetamidomalonic esters (equation 246) telomerized with butadiene in the presence of palladium(II) chloride to give octadienyl products [413]. α-Hydroxyketones behaved in a similar fashion, but some o-alkylation was observed under certain conditions (equation 247) [414]. Treatment of pyrrole with butadiene in the presence of a Pd(acac)$_2$/PPh$_3$/Et$_3$Al catalyst produced *bis*-2,5-octadienylpyrroles (equation 248) [415].

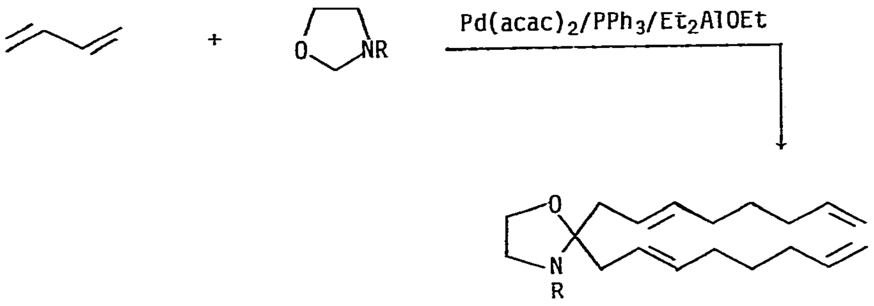
(242)



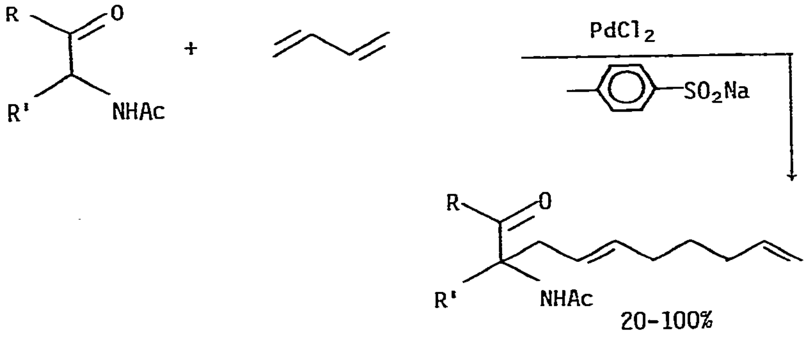
(243)



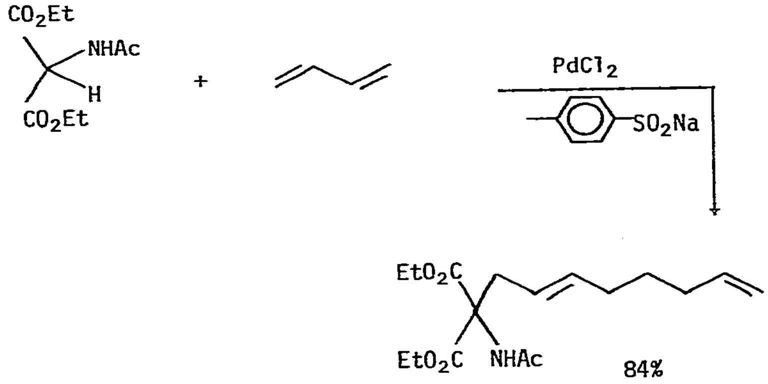
(244)


+
O
NR
Pd(acac)$_2$/PPh$_3$/Et$_2$AlOEt
O
N
R

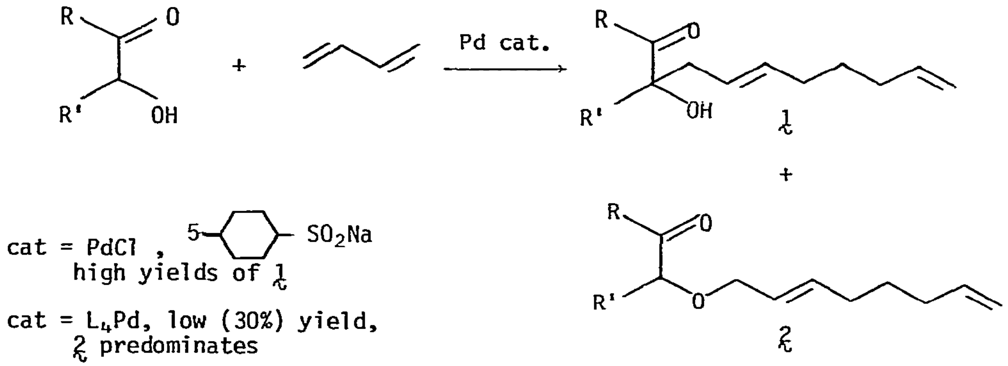
(245)


R
O
R'
NHAc
+
PdCl$_2$
SO$_2$Na
R
O
R'
NHAc
20-100%

(246)


CO$_2$Et
NHAc
H
CO$_2$Et
+
PdCl$_2$
SO$_2$Na
EtO$_2$C
EtO$_2$C
NHAc
84%

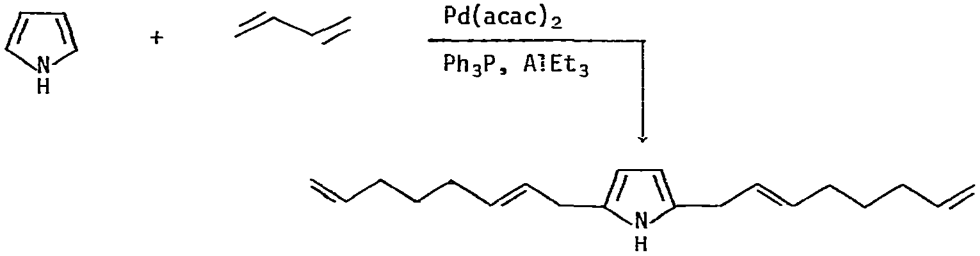
(247)



cat = PdCl , 5-⬡-SO_2Na
high yields of 1

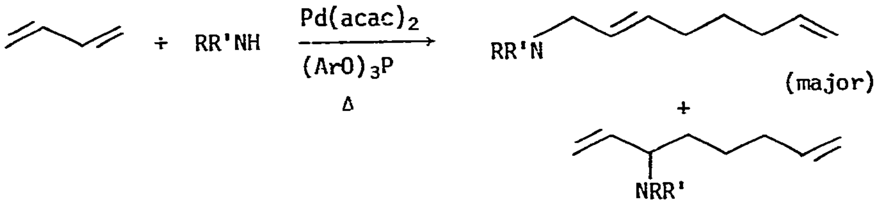
cat = L_4Pd, low (30%) yield,
2 predominates

(248)

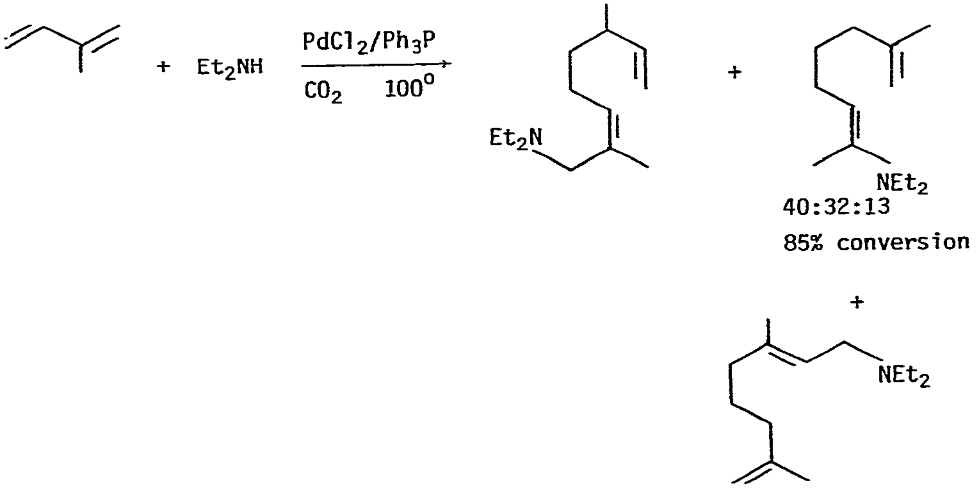


Amines also telomerized butadiene in the presence of palladium catalysts. In the palladium acetate-phosphine system for telomerizing secondary amines and butadiene, $(ArO)_3P$ ligands greatly increased both the rate of the reaction and the selectivity for linear product (equation 249) [416]. Three different adducts were obtained in the telomerization of isoprene with diethyl amine using a palladium catalyst (equation 250) [417]. Use of ammonium bicarbonate as the amine component led to the production of a mixture of *mono*-, *bis*-, and *tris*-octadienyl amines [418]. Telomerization of 3,3-dimethyldiaziridine over a palladium catalyst led to mixtures of linear and branched octadienyldiaziridines (equation 251) [419]. Butadiene and morpholine telomerized in the presence of chiral nickel catalysts to N-octadienyl morpholine plus 4-ethylcyclohexene which was optically active [420]. The effect of the basicity of the amine on the telomerization of butadiene and amines over palladium catalysts was studied [421]. Palladium complexes were also used to telomerize butadiene with pyrazolines (equation 252) [422]. Butadiene telomerized with hydroxymethylamines in the presence of palladium complexes to produce unsaturated tertiary amines (equation 253) [423]. Nickel catalyzed reactions of olefins with imines, hydrazones, diazabutadienes and azabutadienes has been reviewed [424].

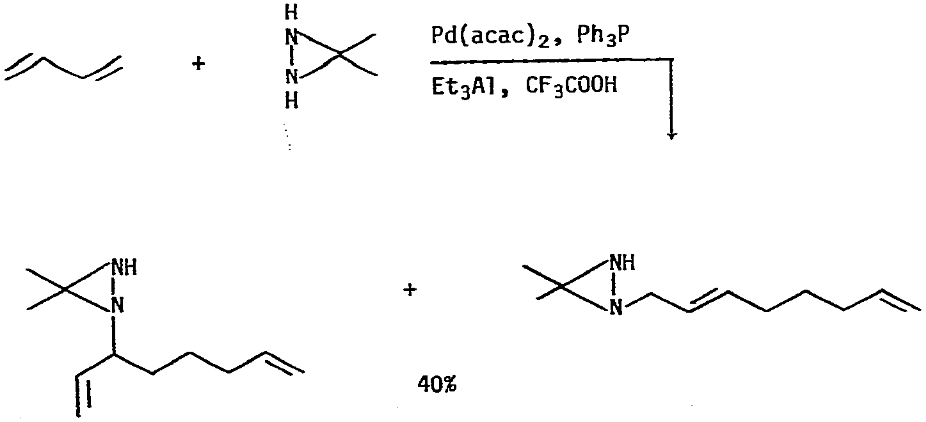
(249)


+ RR'NH
Pd(acac)$_2$
(ArO)$_3$P
Δ
RR'N
(major)
+
NRR'

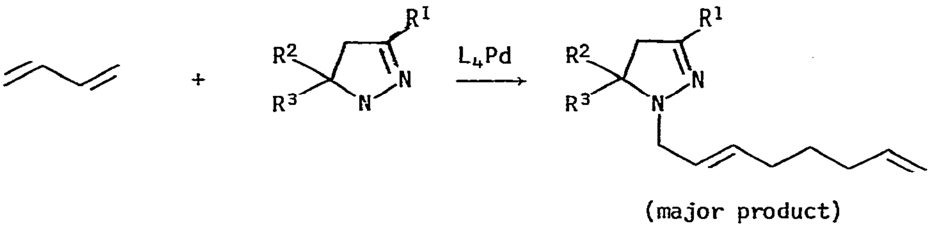
(250)


+ Et$_2$NH
PdCl$_2$/Ph$_3$P
CO$_2$ 100°
Et$_2$N
+
NEt$_2$
40:32:13
85% conversion
+
NEt$_2$

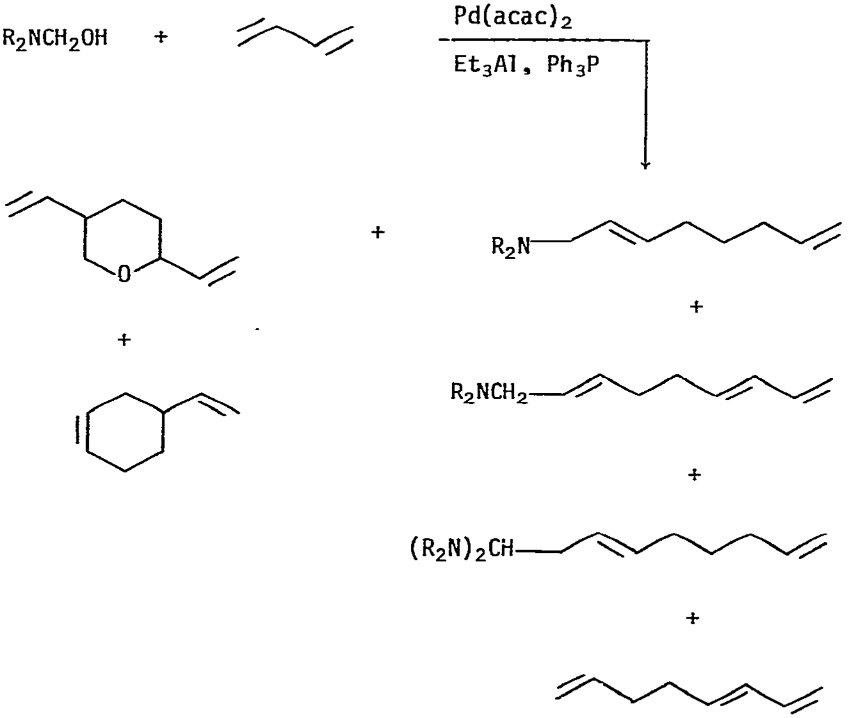
(251)


+
H
N
N
H
Pd(acac)$_2$, Ph$_3$P
Et$_3$Al, CF$_3$COOH
NH
N
+
40%
NH
N

(252)

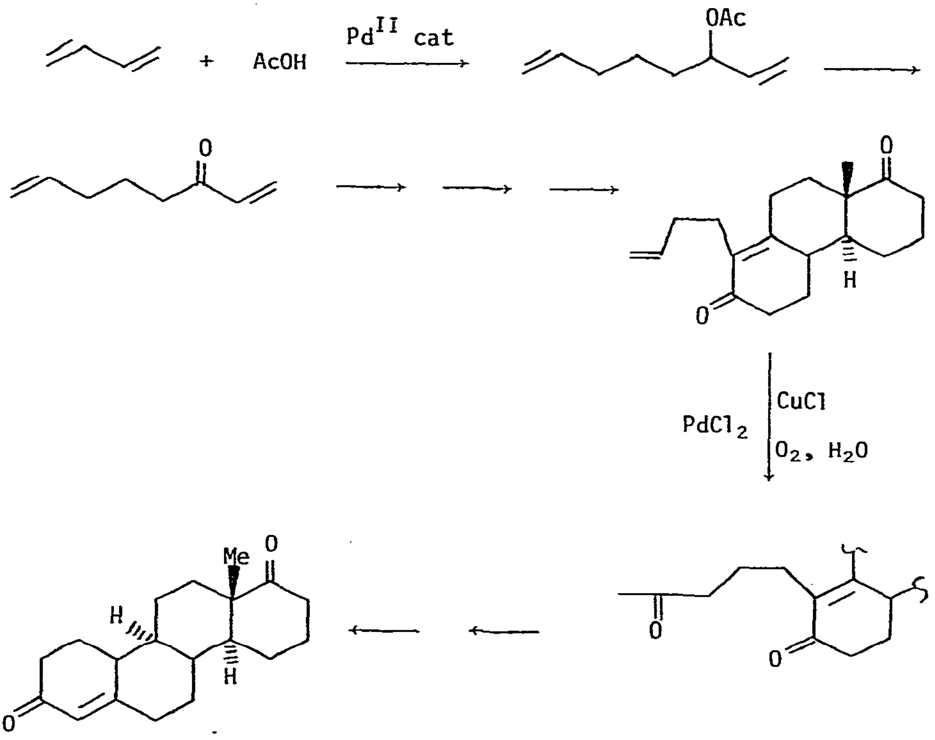


(253)

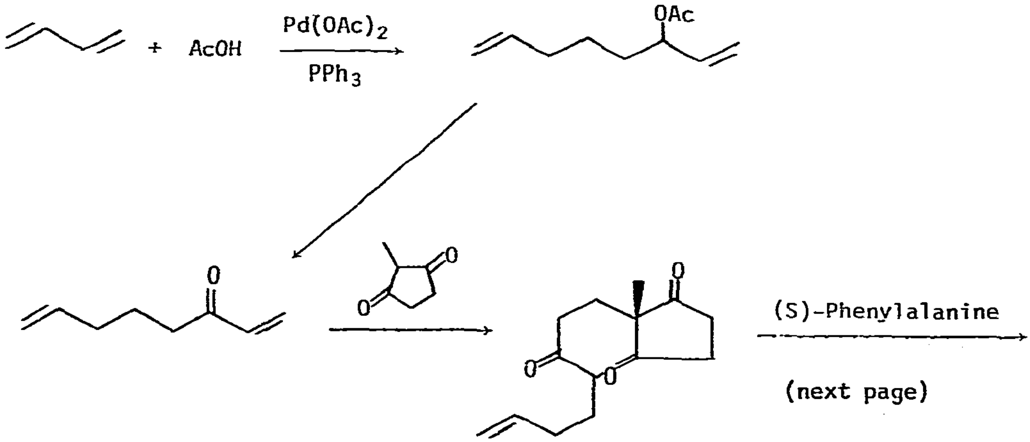


New synthetic methods for natural products using butadiene telomers obtained by palladium-catalyzed telomerization has been reviewed (93 references) [425]. The use of butadiene telomers to synthesize homoestrenedione (equation 254) [426] and (+)-19-nortestosterone (equation 255) [427, 428] has recently been developed. Mono- and bis-octadienyl ethers were prepared in high yield by the palladium catalyzed telomerization of butadiene with ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3- and 1,4-butylene glycol, and glycerol [429].

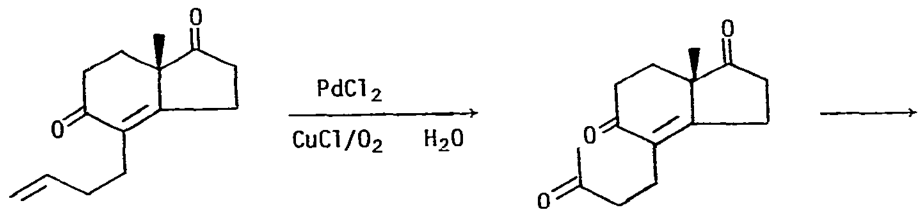
(254)


+ AcOH
Pd^{II} cat
OAc
O
Me
H
$PdCl_2$
CuCl
O_2, H_2O

(255)


+ AcOH
$Pd(OAc)_2$
PPh_3
OAc
O
(S)-Phenylalanine
(next page)

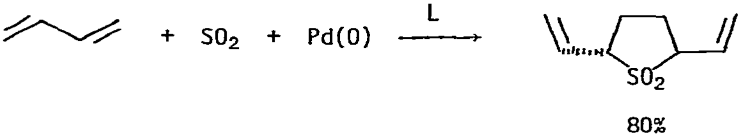
(255)



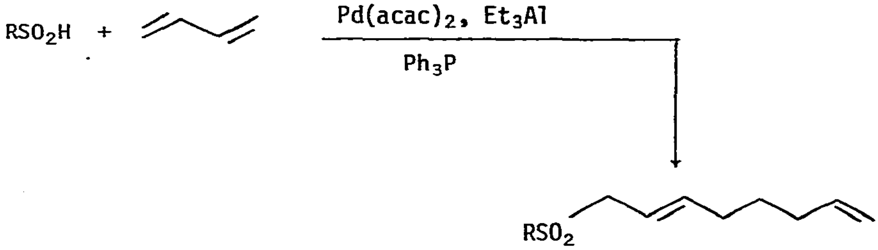
→ (+)-19-Nortestosterone

Palladium(0) complexes catalyzed the telomerization of butadiene with sulfur dioxide to produce a dienyl cyclic sulfone (equation 256) [430]. Sulfinic acids similarly telomerized with butadiene to give linear sulfones (equation 257) [431]. Isoprene, dimethylacetylene dicarboxylate, and a cyclododecatriene nickel catalyst reacted to produce complex large ring compounds (equation 258) [432].

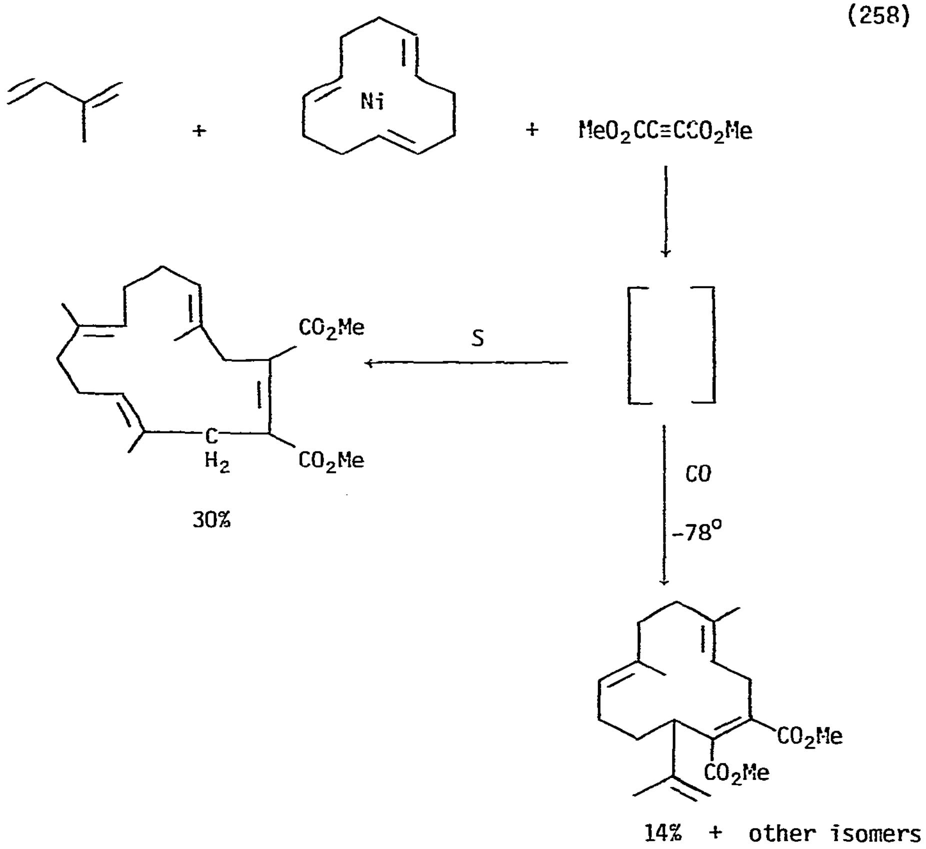
(256)



(257)



(258)

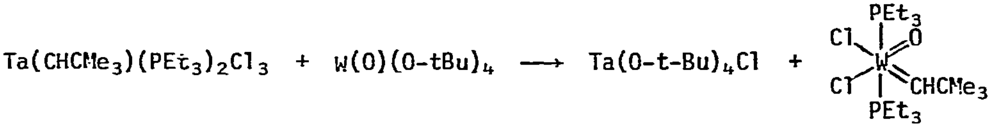


E. Rearrangements

1. Metathesis

Intense activity in the field of the olefin metathesis reaction continued. A number of general reviews of the field appeared [433-436]. New catalyst systems continue to be developed. 1-Octene was metathesized by a catalyst prepared from $WOCl_4$-$EtAlCl_2$ [437]. An active metathesis catalyst was produced by the reaction of a tantalum-carbene complex and a tungsten alkoxide complex (equation 259). In the presence of aluminum chloride, olefin metathesis ensued [438].

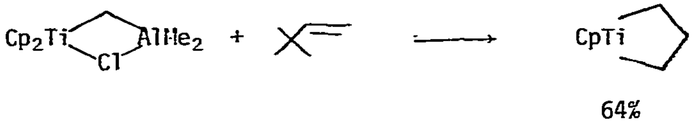
(259)



$$Ta(CHCMe_3)(PEt_3)_2Cl_3 + W(O)(O\text{-}tBu)_4 \longrightarrow Ta(O\text{-}t\text{-}Bu)_4Cl + WCl_2(O)(CHCMe_3)(PEt_3)_2$$

Alumina-supported rhenium-tin complexes of the type $Ph_xSn[Re(CO)_5]_{4-x}$ were catalysts for propene metathesis. Those with the highest amount of aryl groups (x = 3) were the most active catalysts [439]. The effect of catalyst pretreatment on the olefin metathesis catalyzed by alumina-supported rhenium oxide was the topic of a dissertation [440]. The stereoselectivity of the metathesis reaction of 2-butene on a β- titanium oxide supported molybdenum oxide catalyst was examined [441]. Tungsten oxides supported on MgO, Al_2O_3, SiO_2, TiO_2, and ZrO_2 catalyzed the metathesis of propene [442]. Chromium(II) supported on silica gel catalyzed the metathesis of olefins at temperatures in excess of 150^{o} [443]. A mixed metal system consisting of $CpW(CO)_3$-SnR_x or -$GeR_x$was chemically bound to high surface silica in hopes of developing an olefin metathesis catalyst. However, only rearrangements took place with this catalyst [444].

The mechanism of the olefin metathesis reaction was hotly pursued again this year. It was the subject of a review [445], and the topic of a dissertation [446]. *Ab initio* calculations were applied to the mechanism of the olefin metathesis reaction catalyzed by chromium and molybdenum metal-oxo bonds. It was claimed that spectator oxo bonds played a role in activating metal carbene bonds for metallacycle formation [447]. Mechanistic studies of the metathesis of olefins over $Mo(CO)_6/Al_2O_3$ confirmed the role of metallacyclobutanes in the process [448]. A study of the active centers involved in the rhenium VII oxide/MgO catalyst for olefin metathesis indicated that the system was inactive below temperatures at which metallic rhenium forms [449]. Photo induced metathesis of olefins with tungsten hexacarbonyl in carbon tetrachloride produced $RCH{=}CCl_2$, indicating the probable presence of metalladichlorocarbene complexes [450]. The role of carbene complexes of transition metals in the chain reactions of cycloolefin polymerization with ring opening and olefin disproportionation was the subject of a review [451]. The role of metal-carbene-alkene complexes in olefin metathesis was probed by studying the decomposition of a number of these complexes and examining the products obtained [452]. In studies examining the metathesis catalyst forming step,alkyltungsten complexes were thermally decomposed. The results agreed with the intermediacy of a tungsten hydride as the key step in metathesis catalyst formation [453]. When WCl_6 was the catalyst precursor, some hydride source was necessary. When tungsten(0) complexes were used, oxygen was required. Complex tungsten(II) hydrides were active, but those of tungsten VIwere not [454]. Alkylidenetungsten complexes formed from WCl_6 and $CH_2(MgI)_2$ were efficient catalysts for olefin metathesis [455]. The stereoselectivity of the olefin metathesis reaction depended on the coordination sphere of the precursor catalyst as well as the various repulsive interactions in the transition state metallacyclobutene [456]. The factors affecting the stereochemistry of the metathesis of olefins by Group VI transition metal catalysts were examined [457]. A titanium carbene complex converted to a metallacyclobutane when treated with an olefin, mimicing a proposed step in the olefin metathesis reaction (equation 260) [458]. The reaction of nickel metallacyclopentanes, -hexanes, and -butanes were studied, particularly their thermal decomposition reactions. α-Elimination was an important process with the nickelacyclohexane [459].



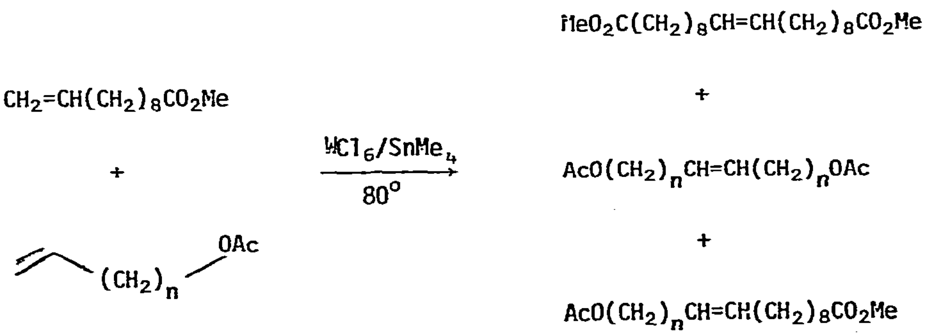
(260)

The metathesis reaction is finally beginning to be used to synthesize unusual organic compounds. Triacontanol was synthesized by the metathesis of hexadecene (equation 261) [460]. Long chain unsaturated esters were prepared by metathesis of medium chain terminal olefins. The catalyst system is one of the few that tolerates functional groups (equations 262 and 263) [461]. Macrolides including civetone were synthesized by a metathesis process (equations 264 and 265) [462]. The use of olefin metathesis in petrochemistry has been reviewed [463].

(261)

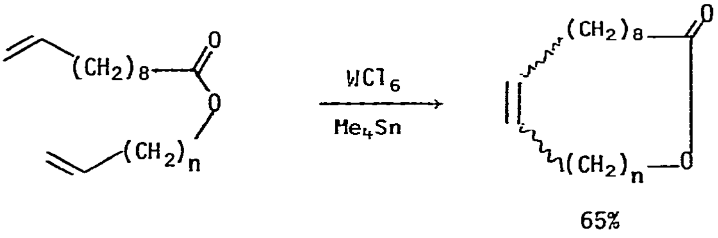
$$CH_3(CH_2)_{13}CH{=}CH_2 \xrightarrow[SnBu_4]{WCl_6} \underset{40\text{-}60\%}{CH_3(CH_2)_{13}CH{=}CH(CH_2)_{13}CH_3} \xrightarrow[160^\circ \quad 2)\ H_2O_2,\ NaOH]{1)\ BH_3,\ \text{diglyme}} \underset{47\%}{CH_3(CH_2)_{28}CH_2OH}$$

(262)

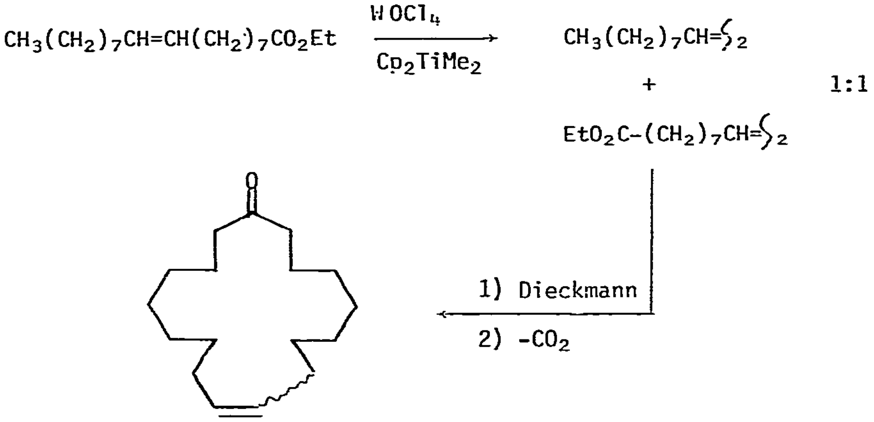


n = 3, 4

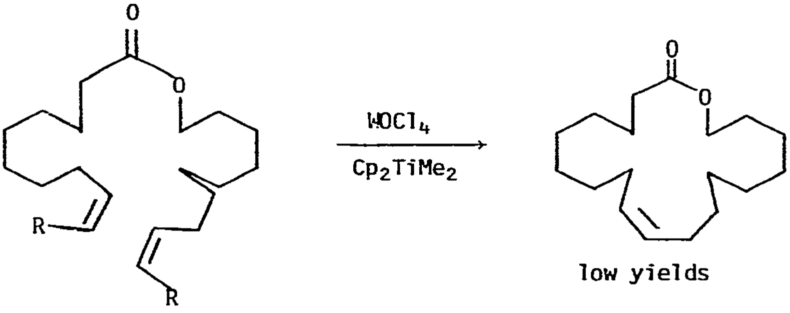
(263)



(264)



(265)

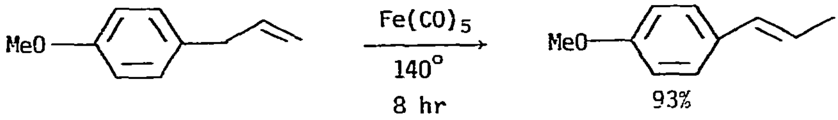


The tungsten carbene complex $(CO)_5W = CXPh$ where X was Ph or OMe was a catalyst for the polymerization of alkynes. The reaction was slow, but the yields of polymer were higher than those from other methods. The reaction was thought to go by a "metathesis" like mechanism involving metallacyclobutene intermediates [464]. This same complex polymerized cycloalkenes in the presence of phenyl acetylene as a promoter [465, 466].

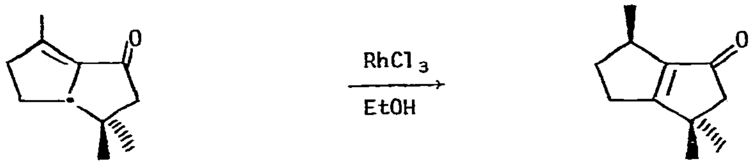
2. Olefin Isomerization

The catalyst produced from $EtAlCl_2$ and $Ni(PPh_3)_4$ was an effective promoter of olefin isomerization reactions particularly for C_5 or C_6 olefins, which rearranged in up to 90% yield [467]. Treatment of $[CODRhCl]_2$ with i-propylmagnesium bromide in the presence of 4-vinylcyclohexene gave neutral diamagnetic complexes of the type (η-cycloenyl) (1,5-cyclooctadiene) rhodium(I), which catalyzed olefin rearrangements [468]. 1-Butene was isomerized by $Rh_2Cl_2(PPh_3)_4$ [469]. Iron carbonyls were anchored to phosphinated polystyrene resins then irradiated to produce catalysts active for the isomerization of 1-pentene [470][471]. Nickel(I) phosphine complexes of the type $NiX(PPh_3)_3$ catalyzed a selective cis isomerization of 1-pentene [472].

Iron carbonyl catalyzed the rearrangement of allylbenzenes to styrenes at 140° (equation 266) [473]. Rhodium trichloride was used to rearrange a double bond into carbonyl conjugation in a bicyclic system (equation 267) [474]. Ruthenium hydride complexes converted allyl ethers into vinyl ethers (equation 268) [475]. Iron carbonyl isomerized (+)-citronellol to (+)-dihydrocitronellol in 16% optical yield [476].

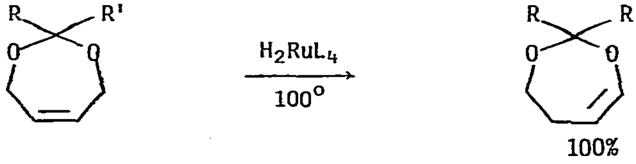


(266)



(267)

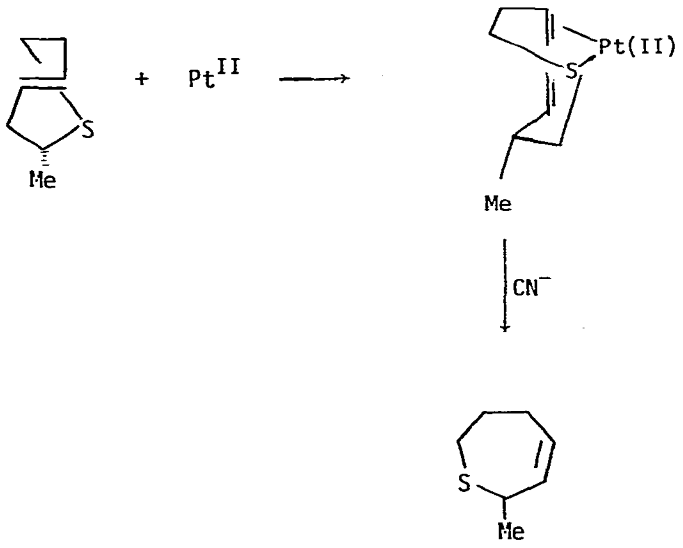
(268)



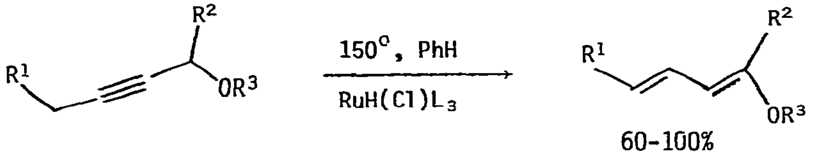
R = H, Me, Et, nPr, i-Pr, nBu, nC_5, nC_6, Ph, CH_3COCH_2 } $-(CH_2)_4-$, $-(CH_2)_5-$
R' = H, Et, Me

Coordination of a trans cycloheptene system to platinum(II) followed by decomplexation with cyanide resulted in the rearrangement to cis of the double bond (equation 269) [477]. Propargyl ethers isomerized to dienyl ethers when treated with RuH(Cl)L_3 (equation 270) [478]. Allene was in equilibrium with methyl acetylene at 165° over iron catalyst [479]. The double bond isomerization in equation 271 was catalyzed by Cp_2TiCl_2 and $LiAlH_4$ [480].

(269)

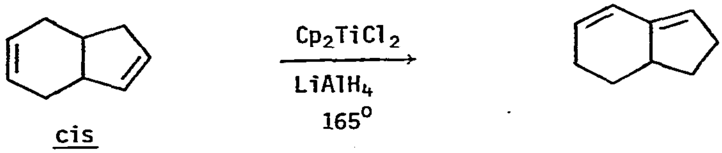


(270)



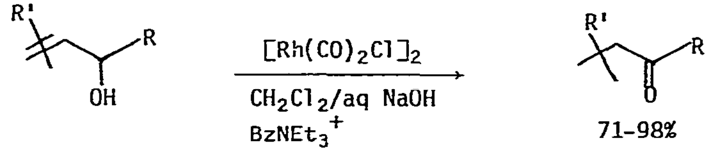
R^1 = OTMS, OMe, n-Pr, n-Pentyl, Me
R^2 = H, Me, Et
R^3 = TMS, Me

(271)



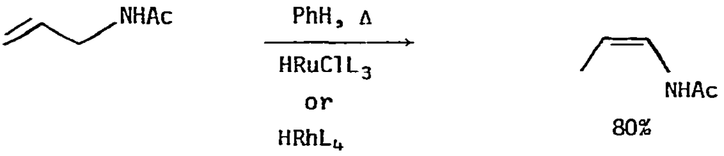
3. Rearrangements of Allylic and Propargylic Oxygen and Nitrogen Compounds

Allylic alcohols rearranged to carbonyl compounds when treated with a $[Rh(CO)_2Cl]_2$ catalyst under phase-transfer conditions (equation 272) [481]. N-allylamides rearranged to enamides in the presence of ruthenium or rhodium hydride catalysts (equation 273) [482]. Propargyl esters isomerized to allenyl esters when heated with copper(II) chloride (equation 274) [483].



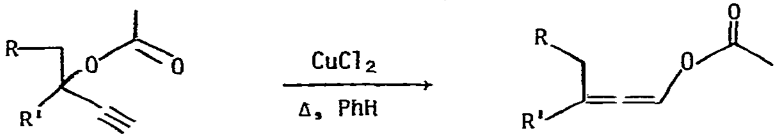
(272)

R' = H, Me, Ph



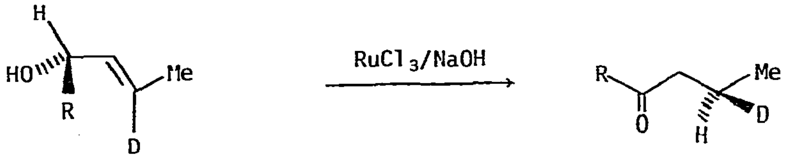
(273)

(274)

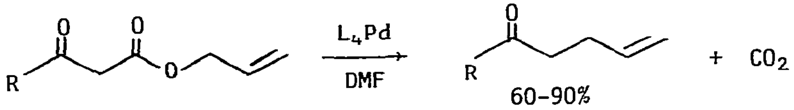


Chiral β-deuterated ketones were prepared by the ruthenium(III) chloride catalyzed isomerization of chiral β-deuterated allylic alcohols (equation 275). Chirality transfer resulted in an inversion of configuration with up to 22% optical purity being obtained [484]. β-Ketoallyl esters underwent an isomerization with a concommitant decarboxylation. This provided an easy route to α-allylketones from Claisen type condensation products (equation 276) [485]. Substituted allylic esters of acetoacetic acid underwent a similar isomerization with decarboxylation (equation 277) [486].

(275)

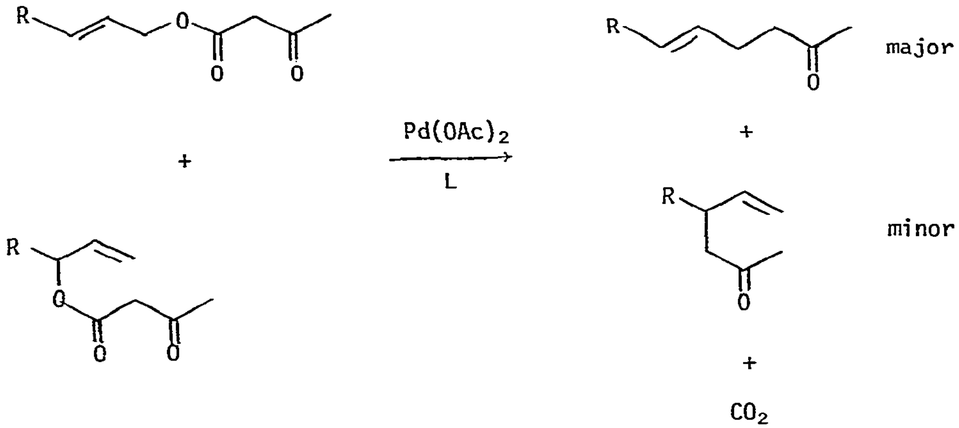


17-22% optical purity, inversion



(276)

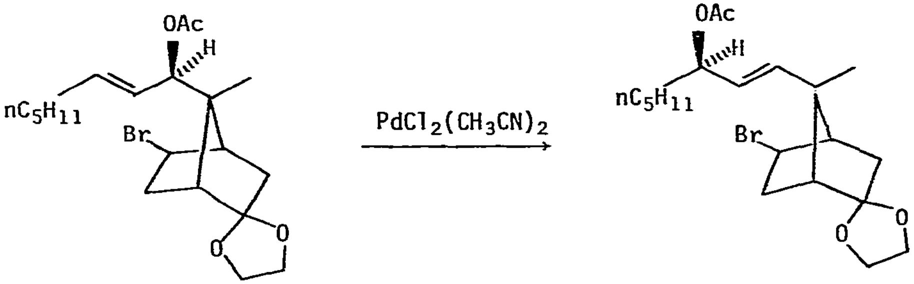
(277)

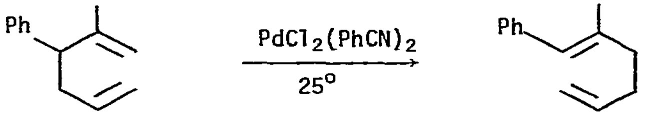


4. Claisen Type Rearrangements

Palladium chloride catalyzed a [3.3]-sigmatropic rearrangement of allylic acetates with complete transfer of chirality. This was used to control stereochemistry in the synthesis of prostaglandins (equation 278) [487]. Palladium chloride also catalyzed the low temperature Cope rearrangement of acyclic 1,5-dienes. With 2-methyl-3-phenyl-1,5-hexadiene, the $T^{\frac{1}{2}}$ for the rearrangement in the absence of catalyst was 13 hr at 170°, whereas the reaction went to completion in 24 hr at 25° in the presence of catalyst (equation 279). A substituent at C-2 or C-5 was required for this rearrangement [488]. Palladium(II) salts also catalyzed the Claisen rearrangement of S-allylthioimidates to N-allylthioamides (equation 280). Phosphines inhibited the process, palladium(0), nickel(II), copper(I), and mercury(II) salts failed to catalyze the process, and the regiospecifity of the catalyzed process ruled out the intermediacy of π-allyl complexes (equations 281 and 282) [489]. Palladium(0) complexes catalyzed a 1,3-O-to-C alkyl shift, and this process has been used to prepare useful organic compounds (equation 283-285) [490]. A similar rearrangement of β-methylene lactones to butenolides was catalyzed by palladium(0) complexes in the presence of CO_2 (equation 286) [491].

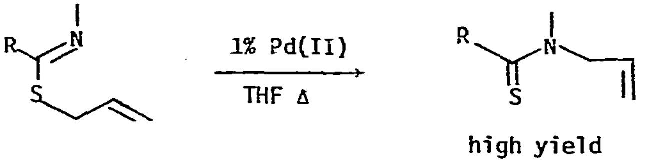
(278)



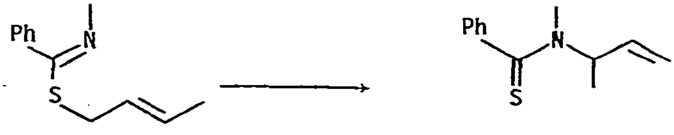


(279)

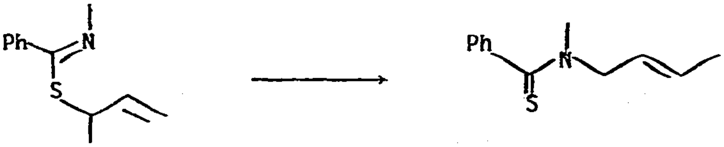
2-Me, 5-Me 1,2-diMe, 2,6-diMe, 2,3,6-triMe rearrange unsub., 1-Me, 6-Me, 3,6-diMe, 2,5-diMe fail



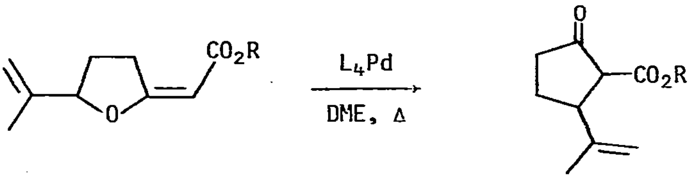
(280)



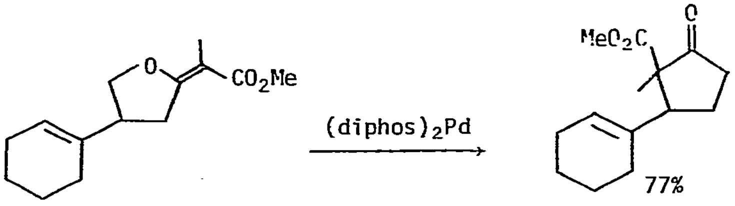
(281)



(282)

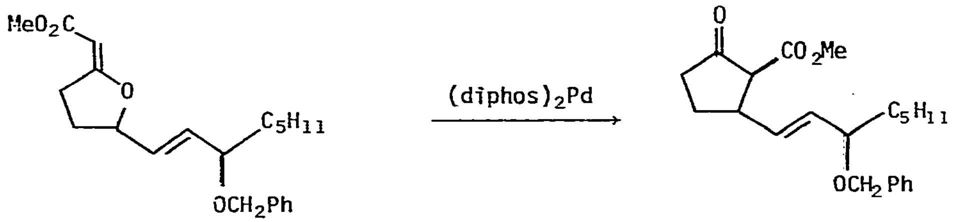


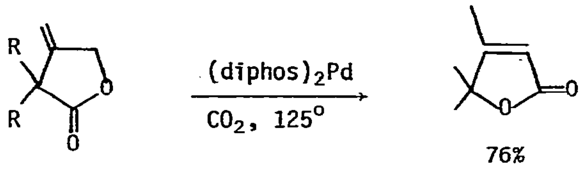
(283)



(284)

(285)





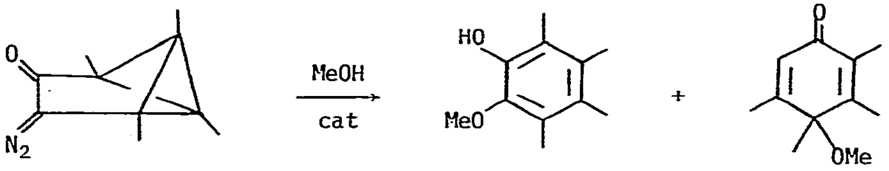
(286)

$R = Me, -(CH_2)_5-$

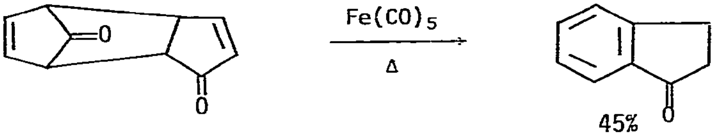
5. Skeletal Rearrangements

Skeletal isomerization of hydrocarbons on metals has been reviewed [492]. The bridged polycyclic systems in equations 287 [493] and 288 [494] rearranged to aromatic systems under transition metal catalysis. Diazopenams rearranged, via carbene intermediates, to monocyclic heterocycles (equation 289) [495]. Barbaralyl systems were synthesized by rearrangements of dienyliron complexes (equations 290 and 291) [496]. Spirocyclopentadienes were ring-opened by boiling in benzene solutions of $Fe_2(CO)_9$ (equation 292) [497] or $Mo(CO)_6$ (equation 293) [498].

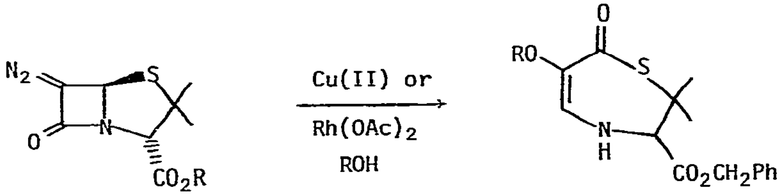
(287)



$Cu(acac)_2$	45%	0
$Ru_2(OAc)_4$	30%	13%

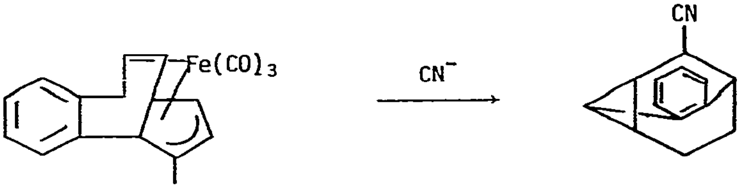


(288)

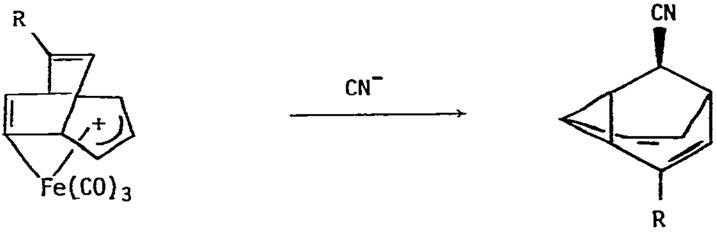


6-55%

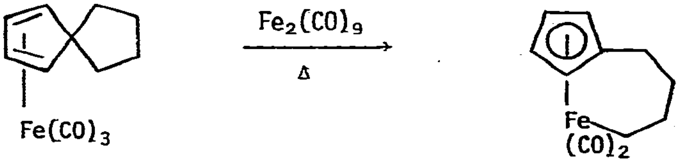
(289)



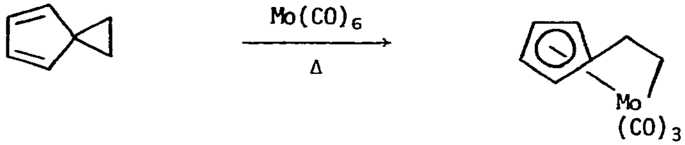
(290)



(291)



(292)

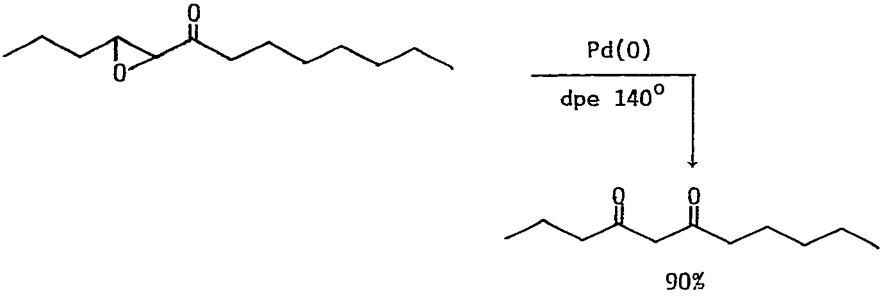


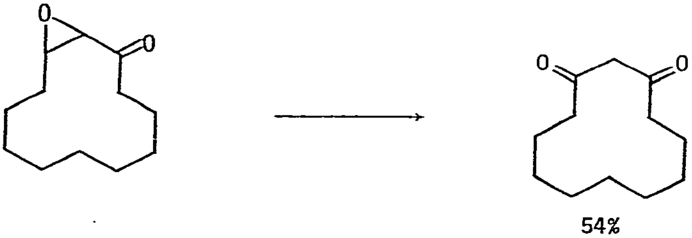
(293)

6. Miscellaneous Rearrangements

α,β-Epoxyketones rearranged to β-diketones in the presence of palladium(0) catalysts (equations 294 and 295) [499]. Aldohexoses and aldopentoses epimerized when heated with $Mo(CO)_2(acac)_2$ in DMF at 50° [500]. Aminoacid ligands in Λ-β_2-$[Co(tetraamine)(aminoacid)]^{2+}$ underwent base catalyzed epimerization at pH 10-12 to give equilibrium mixtures of diastereomeric D- and L-aminoacid complexes [501]. Camphene rearranged to isobornyl methyl ether in 85% yield when heated at reflux in methanol in the presence of copper(II) chloride [502].

(294)





(295)

III. Oxidation

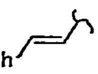
A. Oxidation of Alcohols

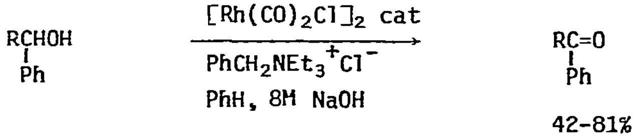
Methanol was oxidized to acetaldehyde using vanadium pentoxide as a catalyst and stannic oxide as a promoter [503]. 1-Butanol was oxidized to butyric acid using platinum on carbon as a catalyst [504]. The kinetics of the ruthenium(III) catalyzed oxidation of aromatic aldehydes by sodium metaperiodate were studied [505][506] as were the kinetics of the palladium chloride oxidation of isopropanol[507, 508], and the osmium(VIII) oxide catalyzed oxidation of primary alcohols by chloramine T [509].

Alcohols were electrochemically oxidized using $(trpy)(bpy)Ru(OH_2)^{2+}$/$(trpy)(bpy)RuO^{2+}$ as a catalyst [510]. Secondary alcohols oxidized to ketones, primary alcohols to aldehydes, then acids, aryl methyl groups to carboxylic acids, and cyclohexene to benzoquinone under these conditions [510]. Primary benzylic and allylic alcohols oxidized to aldehydes with copper(I) chloride as a catalyst (equation 296). Aliphatic alcohols were oxidized to the one carbon shorter homolog aldehyde [511]. Secondary benzyl alcohols oxidized to the ketone using $[Rh(CO)_2Cl]_2$ under phase transfer conditions (equation 297) [512]. Diols were selectively oxidized to lactones by benzoyl peroxide in the presence of nickel bromide (equation 298) [513]. The same system oxidized secondary alcohols to ketones [514].

$$RCH_2OH \xrightarrow{CuCl/O_2/phen} \underset{80\%}{RCHO} \quad \text{but} \quad RCH_2CH_2OH \longrightarrow RCHO \qquad (296)$$

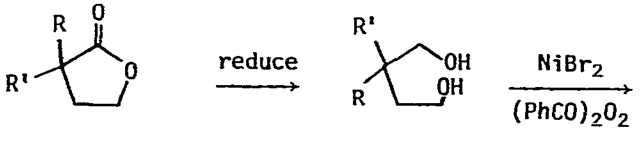
R = Ph, Ph





$$\underset{\displaystyle Ph}{RCHOH} \xrightarrow[\substack{PhCH_2NEt_3^+Cl^- \\ PhH,\ 8M\ NaOH}]{[Rh(CO)_2Cl]_2\ cat} \underset{\displaystyle Ph}{RC{=}O} \qquad (297)$$

42-81%



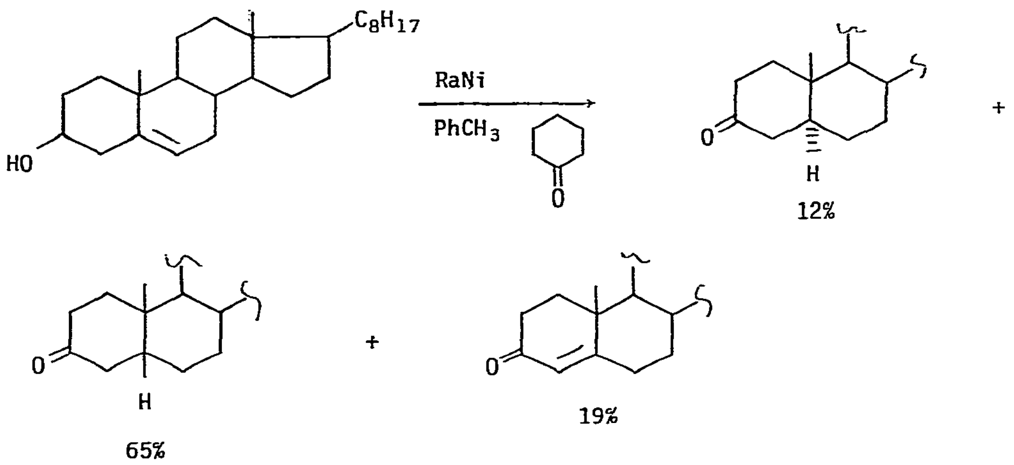
(298)

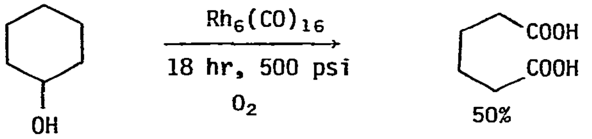
R = Ph, Et, Me
R' = Ph, Me

high yield

Homoallylic steroidal alcohols were converted to the corresponding saturated ketones by activated Raney nickel catalysts (equation 299) [515]. Substituted phenols were oxidized to quinones and diphenoquinones by CrO_2Cl_2 or $VOCl_3$ [516]. Cyclohexanol was converted to adipic acid by oxidation over $Rh_6(CO)_{16}$ or $Re_2(CO)_{10}$ (equation 300) [517]. Studies of this process showed that smaller fragments of the Rh_6 cluster were responsible for this oxidation [518].

(299)





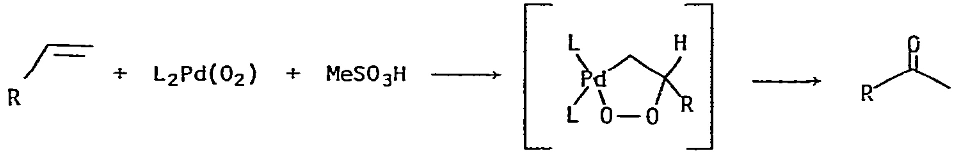
(300)

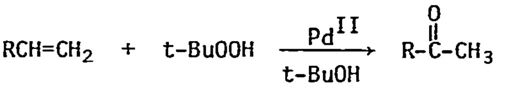
B. Oxidation of Alkenes and Alkynes

The details of the oxidation of ethylene to acetic acid using mixed palladium(II) vanadiumpentoxide catalyst have been examined [519], and the kinetics of the process have been studied [520]. Catalysis of this same process by supported palladium complexes [521], and aqueous solutions of palladium(II) and iron(III) has also been studied [522]. Two reviews on the Wacker oxidation of ethylene to acetaldehyde using palladium(II) as a catalyst have appeared [523, 524]. The rate of the oxidation of higher 1-alkenes by aqueous palladium chloride solutions was increased by the addition of basic solvents such as methanol, glyme and N-methyl-2-pyrrolidone [525].

The organic chemistry of transition metal dioxygen complexes has been reviewed [526]. Terminal olefins were oxidized to methyl ketones by palladium oxygen complexes (equation 301) [527]. This same transformation was affected by t-butylhydroperoxide in the presence of palladium(II) catalysts (equation 302) [528]. Allyl acetate was oxidized to α-acetoxyacetone, but cyclohexene and methyl acrylate were inert. This reaction proceeded through a palladium(II) hydroperoxide complex which was characterized by X-ray crystallography.. When internal olefins were exposed to this complex, π-allylpalladium complexes formed (equation 303) [530]. Rhodium(III) complexes of oxygen also catalyzed the oxidation of terminal olefins to methyl ketones. It was shown that the keto oxygen arose from molecular oxygen [531].

(301)

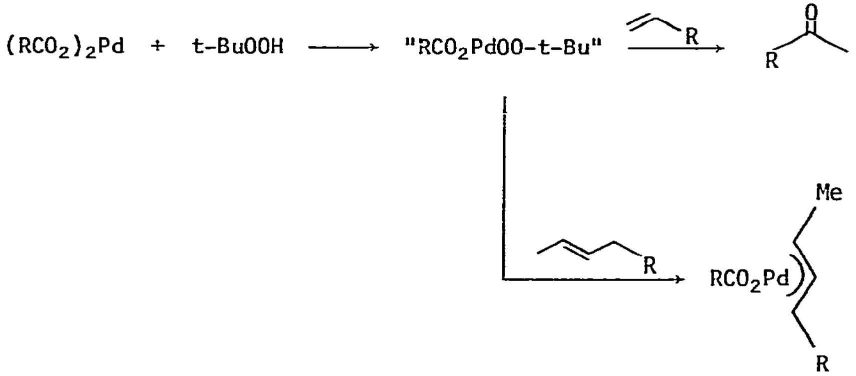




$$\mathrm{RCH{=}CH_2} + \text{t-BuOOH} \xrightarrow[\text{t-BuOH}]{\mathrm{Pd^{II}}} \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}CH_3} \qquad (302)$$

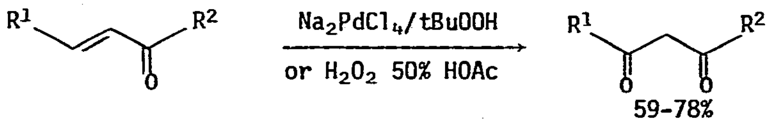
400 cat turns/hr

(303)



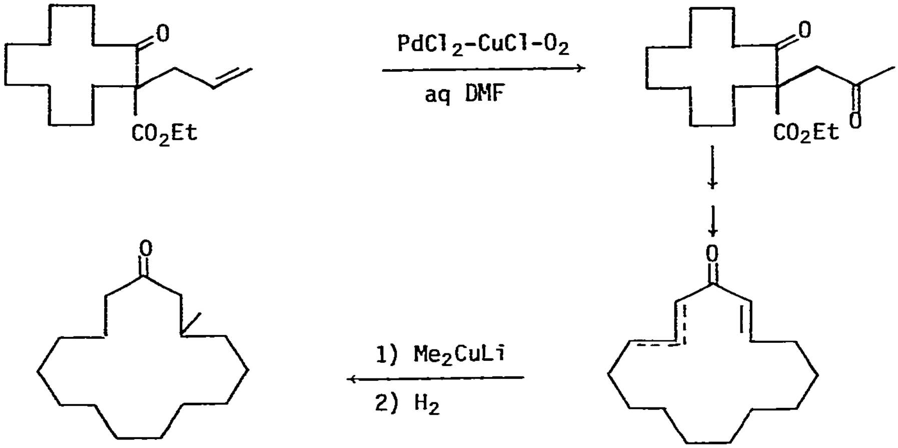
α,β-Unsaturated ketones were converted to 1,3-diketones by treatment with t-butylhydroperoxide or hydrogen peroxide and sodium tetrachloro palladate (equation 304) [532]. Terminal olefins were oxidized to methyl ketones by $PdCl_2$-CuCl-O_2 in aqueous DMF. This process was used in the synthesis of muscone (equation 305) [533]. Cyclopentenones were available from α,δ-unsaturated aldehydes via this oxidation (equation 306) [534]. Terminal olefins were also oxidized to methyl ketones by cobalt nitro compounds, oxygen, and a palladium(II) catalyst (equation 307) [535].

(304)

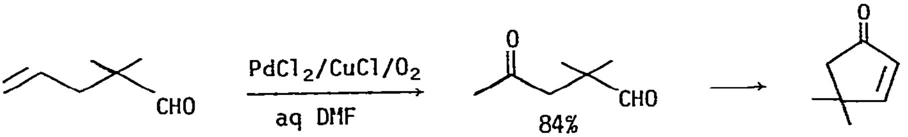


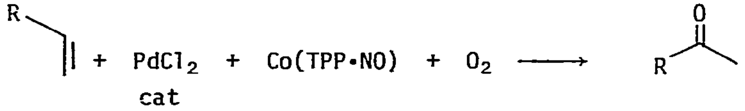
R^1 = Me, n-Pr, i-Pr, i-Bu, n-Hex, Ph
R^2 = OMe, Me

(305)



(306)

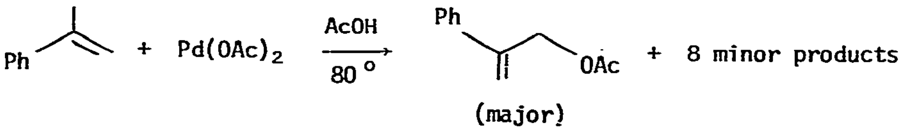




(307)

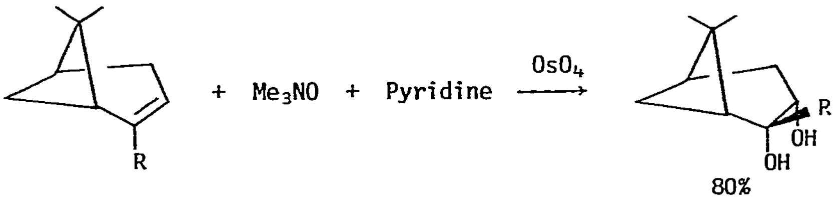
α-Methylstyrene was oxidized to the allylic acetate by palladium(II) acetate in acetic acid (equation 308). Small amounts of styrene dimers (1,3-dienes) were also formed [536]. Palladium on alumina was also used to acetoxylate olefins [537].

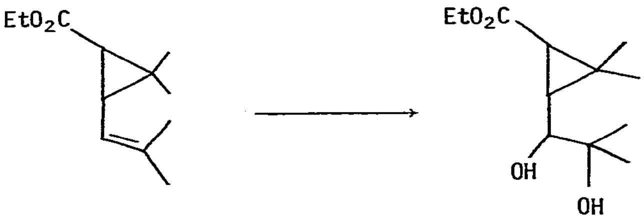
(308)



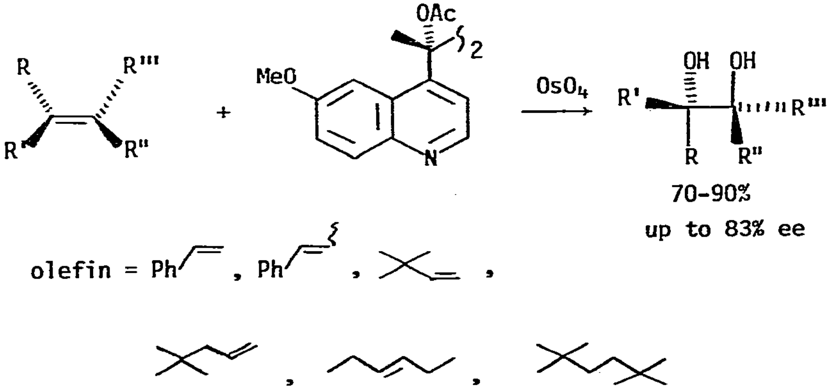
Osmium catalyzed cis hydroxylation of unsaturated substrates has been reviewed [538]. Hindered olefins were oxidized to diols by amine oxides using osmium tetroxide as a catalyst (equations 309 and 310) [539]. Cyclohexene was oxidized to the cis diol with the same system [540]. Asymmetric induction in the cis hydroxylation of prochiral olefins by osmium tetroxide was accomplished by the use of chiral tertiary amines as ligands (equation 311) [541]. The cis hydroxylation of endo-dicyclopentadiene by permanganate proceeded through a relatively stable organomanganese complex [542]. The oxamination of olefins by $tBuNOsO_3$ was improved by alteration of a number of reaction conditions, particularly by the use of quinuclidine in DME as solvent [543]. Even better results were obtained using N-chloro-N-metallocarbamates (equation 312) [544]. Copper(I) or copper(II) chloride catalyzed the cyanoselenation of olefins (equation 313) [545].

(309)

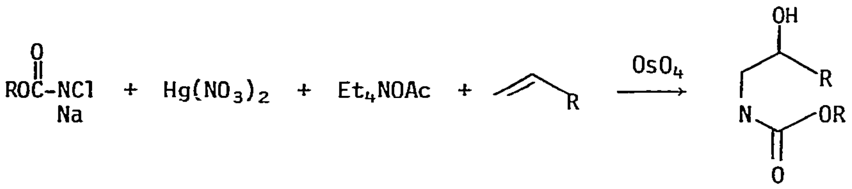


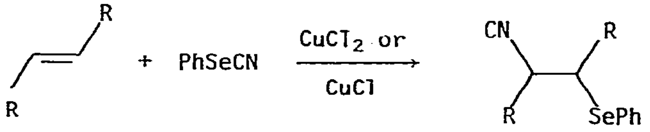


(310)

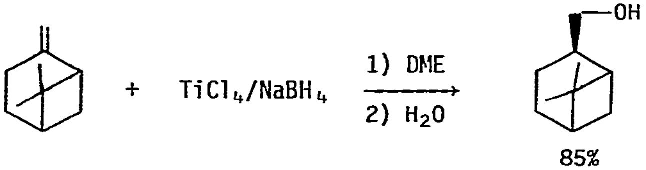


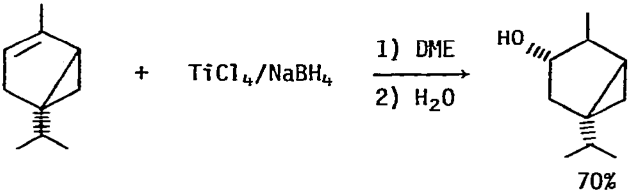
(311)

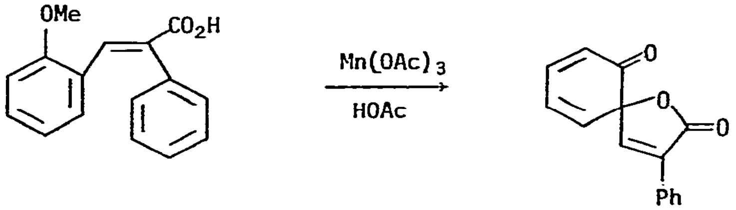

(312)


(313)

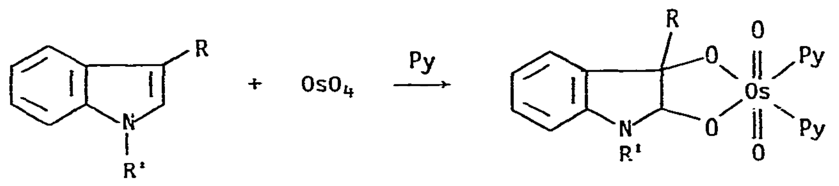
Olefins were converted to the less substituted alcohols by hydrozirconation-oxidation (bicyclic olefins) [546], or by hydroboration followed by oxidation of the borane by $MoO_5\cdot Py\cdot HMPA$ [547]. This oxidation went with retention [547] Bicyclic olefins reacted with titaniumtetrachloride/sodium borohydride to produce alcohols (equations 314 and 315) [548]. Manganese(III) acetate oxidized α-phenylcinnamic acids to oxaspiro compounds (equation 316) [549].


(314)

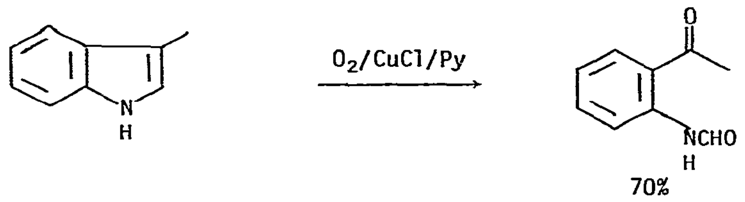

(315)


(316)

Oxidation of indoles with osmium tetroxide led to stable oximate esters (equation 317) [550]. 3-Methylindole was oxidatively cleaved by oxygen in the presence of copper(I) chloride-pyridine complexes (equation 318) [551].



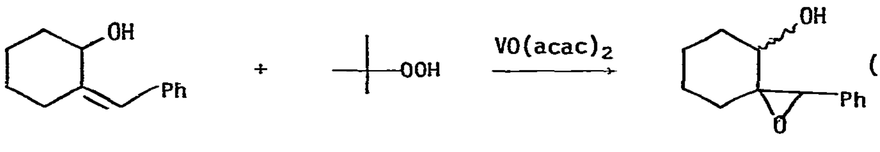
(317)



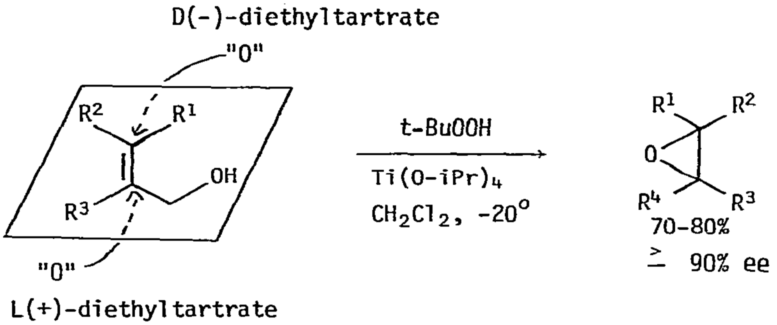
(318)

C. Epoxidations

Three reviews dealing with metal-catalyzed epoxidations have been published. They deal with the role of vanadium catalysts in the oxidation and ammoxidation of organic compounds [552], metal catalyzed highly selective oxygenation of olefins and acetylenes with t-butylhydroperoxide [553], and new ways in the catalytic epoxidation of olefins by hydrogen peroxide [554]. The mechanism of the epoxidation of cyclohexene with t-butylhydroperoxide catalyzed by molybdenum V oxalate has been studied [555], as has the same reaction of 4-vinylcyclohexene [556]. The allylic alcohol in equation 319 underwent nonstereoselective epoxidation by t-butylhydroperoxide in the presence of vanadyl acetylacetonate [557]. The mechanism of this oxidizing system has been studied [558]. Hydroperoxides epoxidized 1-nonene in the presence of $Mo(O_2)(OCH_2CH_2OH)_2$ as a catalyst [559]. Prochiral olefins were epoxidized with very high yield and enantiomeric excess by t-butylhydroperoxide and titanium isopropoxide in the presence of diethyl tartrate. The stereochemistry of epoxidation depended on which enantiomers of the tartrate was used (equation 320) [560]. A preformed molybdenum peroxo complex epoxidized allylic alcohols with stereoselectivity that differed from molybdenum catalyzed epoxidations (equation 321) [561]. The complex also oxidized alcohols to aldehydes or ketones. A manganese-porphyrin complex promoted the epoxidation of stryene by sodium hypochlorite (equation 322) [562]. The oxidation of cyclohexene by oxygen in the presence of vanadium catalysts gave a multitude of products. The best results are found in equation 323 [563]. In the oxidation of cholesteryl acetate, hydrogen peroxide in the presence of $Fe(acac)_3$ led to epimeric 5,6-epoxides [564].

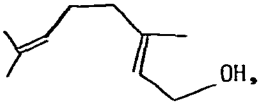


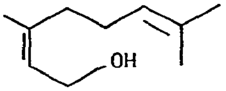
(319)



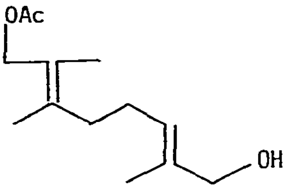
(320)

studied

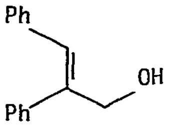




,

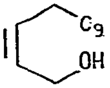


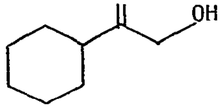
,

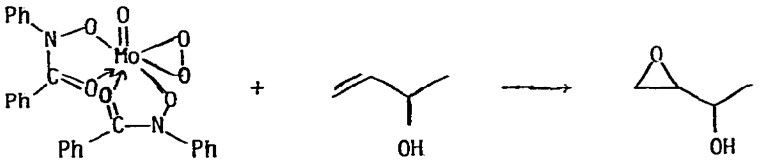


,

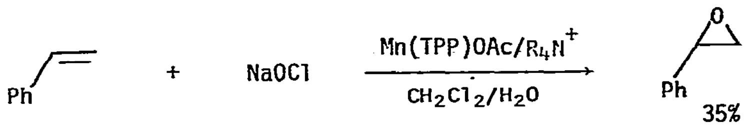
,



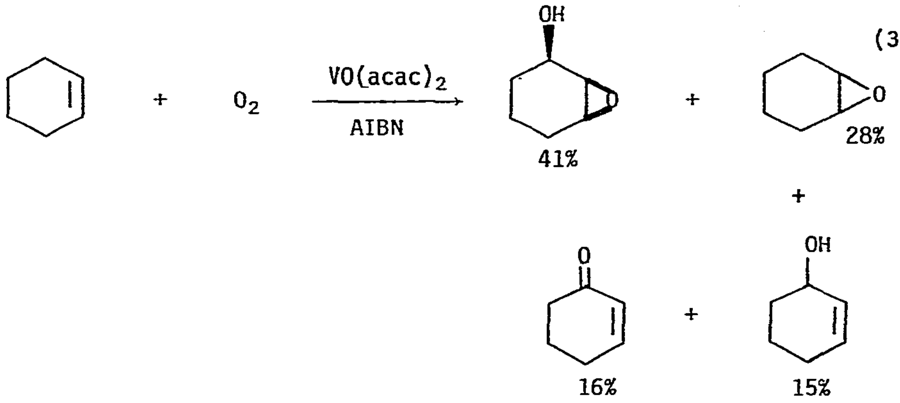




(321)



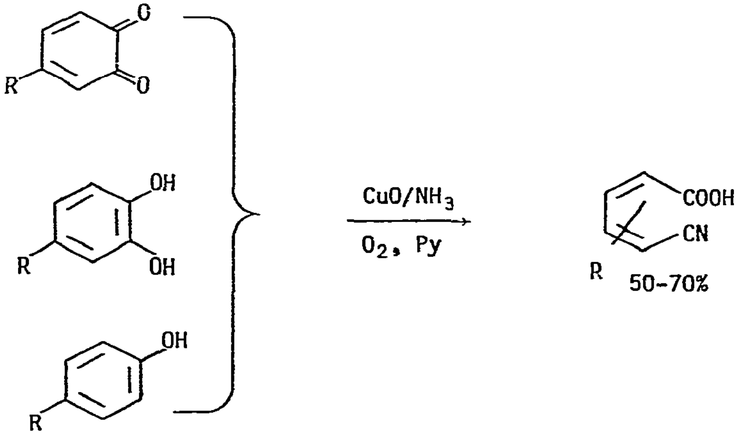
(322)



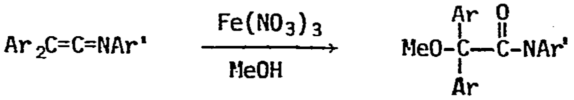
(323)

D. Oxidation of Ketones and Aldehydes

Ketones were oxidized to α-diketones and carboxylic acids by oxygen in the presence of a cobalt(II) phenanthroline complex [565]. Cyclic ketones were oxidized to lactones by hydrogen peroxide in the presence of molybdenum peroxo species such as $H^+[Mo(O)(O_2)_2(picolinato)]$ [566]. Manganese(III) acetate oxidized methyl ketones to carboxylic acids by a radical mechanism [567]. Catechols, phenols, and o-quinones were oxidized to mononitriles of muconic acid by an oxygen/copper(I) chloride/ammonia mixture claimed to produce "CuO/NH_3" (equation 324) [568]. Aryl ketenimines were oxidized to amides by iron(III) nitrate in methanol (equation 325) [569].



(324)

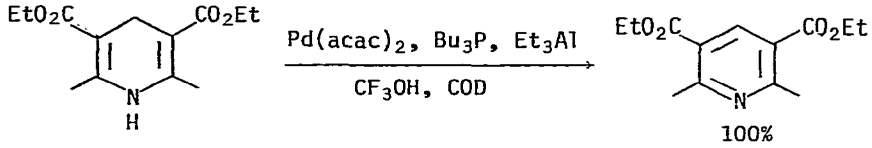


$$Ar_2C{=}C{=}NAr' \xrightarrow[MeOH]{Fe(NO_3)_3} MeO{-}\underset{Ar}{\overset{Ar}{C}}{-}\overset{O}{\overset{\|}{C}}{-}NAr'$$

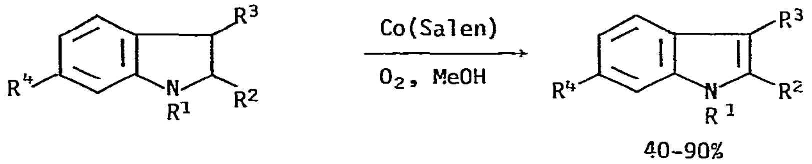
(325)

E. Dehydrogenations

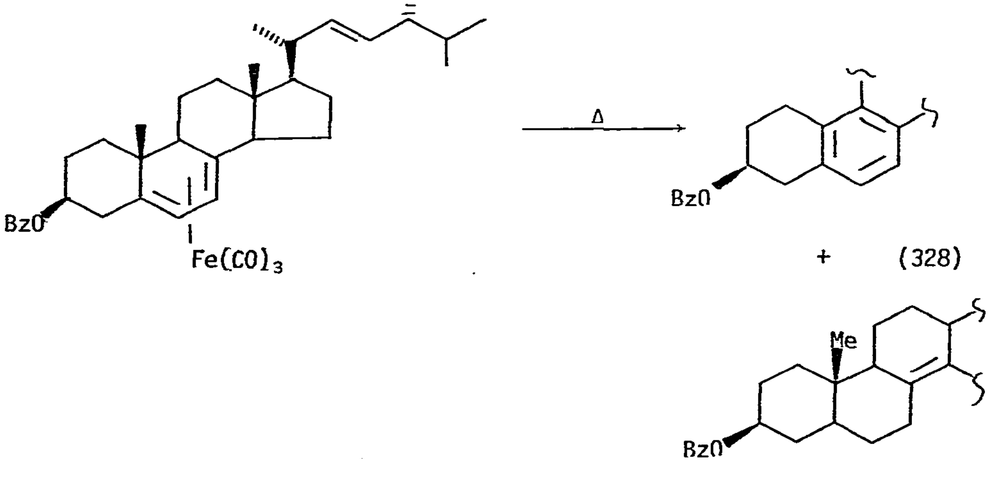
Catalytic dehydrogenation by platinum metals has been reviewed [570]. Treatment of dihydropyridines with Pd(acac)$_2$, Bu$_3$P, AlEt$_3$, CF$_3$COOH, and 1,5-cyclooctadiene gave pyridines in quantitative yield (equation 326) [571]. Dihydroindoles were oxidized to indoles by treatment with oxygen and a cobalt salen complex (equation 327) [572]. Pyrolysis of an iron tricarbonyl diene complex of ergosteryl benzoate led to aromatization (equation 328) [573]. Treatment of 1,3-bis[2-(diphenylphosphino)phenyl]propane with rhodium(I) complexes resulted in dehydrogenation of the ligand to give the coordinated olefinrhodium complex (equation 329) [574]. Olefins were produced from alkyliron complexes by treatment with triphenyl methyl cation (equation 330) [575]. Cyclohexadiene disproportionated to benzene and cyclohexene when treated with iron(II) or copper(II) chloride and titanium(IV) isopropoxide [576].



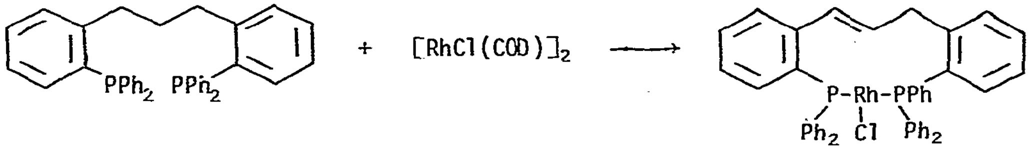
(326)



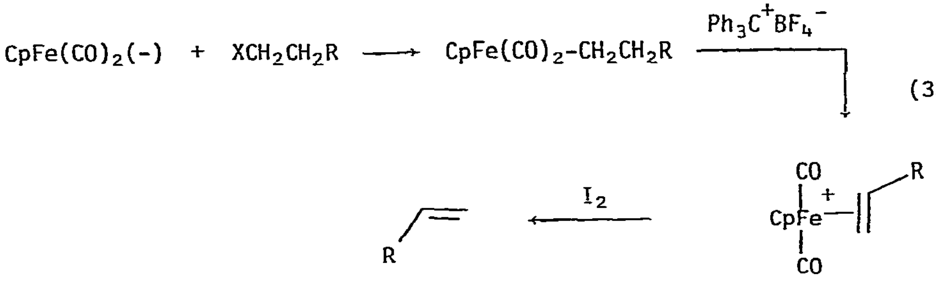
(327)



(328)



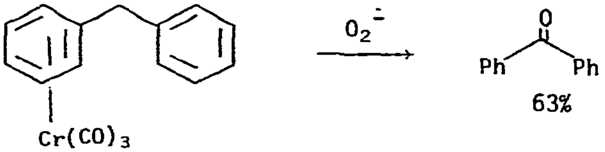
(329)



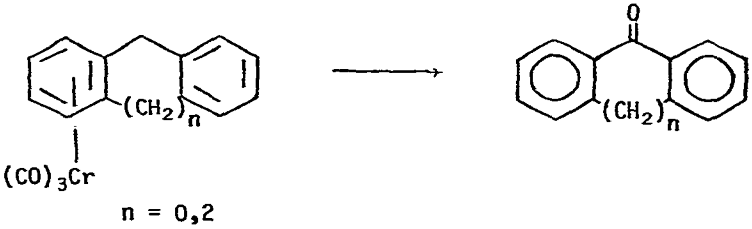
(330)

F. Oxidation of Hydrocarbons

Palladium catalyzed oxidation of hydrocarbons was the subject of a book [577]. Chromium complexed diaryl methanes were oxidized to diaryl ketones (equations 331 and 332) [578]. Alkyllithiums and alkylmagnesium halides reacted with ethylene and nickel(II) chloride to produce olefins by a regioselective β-hydride abstraction [579]. Palladium clusters catalyzed the oxidation of toluene to acetoxytoluene by oxygen [580]. Chromic acid oxidized alkanes in the presence of iridium IV chloride [581].



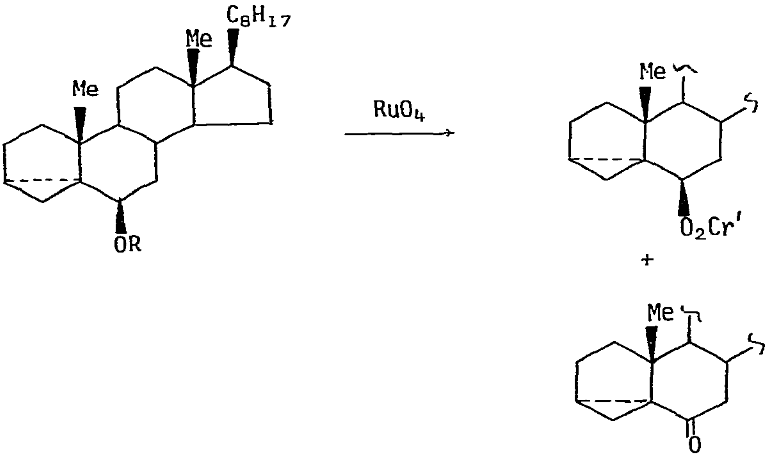
(331)



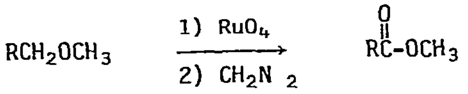
(332)

G. Miscellaneous Oxidations

Oxidation over copper, silver, and gold catalysts has been reviewed [582], as has the application of nickel peroxide oxidation in organic synthesis [583], and nickel peroxide as an oxidizing agent in organic chemistry [584]. Organic sulfides oxidatively coupled to disulfides when treated with nickel peroxide [585], or with hydrogen peroxide and vanadium V salts [586]. Carbon dioxide oxidized phosphines to phosphine oxides in the presence of $(Ph_3P)_3RhCl$ or $[(cyclooctene)_2RhCl]_2$ [587]. The ruthenium tetroxide oxidation of steroidal ethers gave esters and ketones (equation 333) [588]. The same compound also oxidized simple ethers (equation 334-337) [589]. Cobalt salen complexes catalyzed the oxidative rearrangement of a p-hydroxybenzaldehyde imine (equation 338) [590].

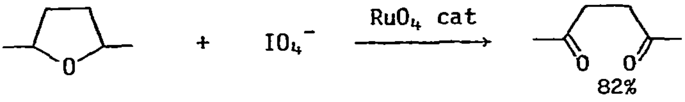


(333)

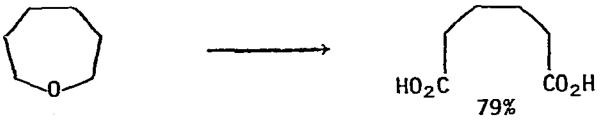


$$RCH_2OCH_3 \xrightarrow[\text{2) } CH_2N_2]{\text{1) } RuO_4} R\overset{O}{\overset{\|}{C}}\text{-}OCH_3$$

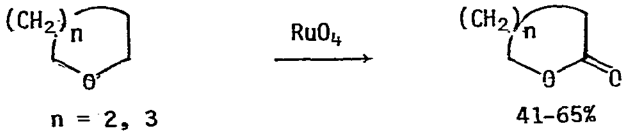
(334)



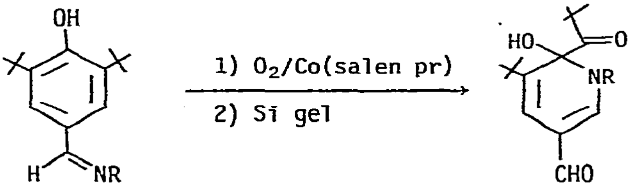
(335)



(336)



(337)



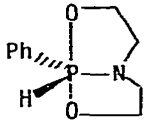
(338)

IV. Reductions

Reductions, mostly of olefins, continued to be studied with a passion not commensurate with the interest of the transformation, and accounted for over three hundred papers this year. Asymmetric hydrogenation was the most active single area, with the development of a multitude of new catalysts and ligands to reduce α-acetamidoacrylic and cinnamic acids with optical yields often approaching those reported in previous years.

A. Olefins

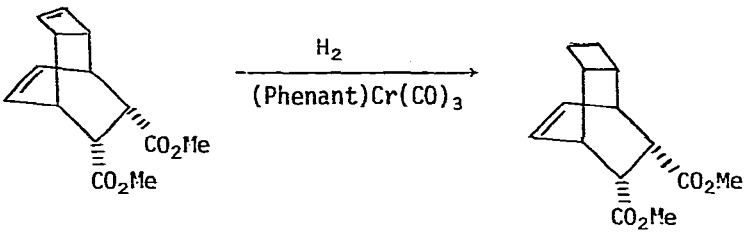
Iridium hydride complexes formed by the reduction of precursor catalysts such as $[Ir(COD)Lpy]PF_6$ in nonpolar solvents such as dichloromethane were exceptionally active for the catalytic hydrogenation of olefins, including highly substituted ones [591]. Rhodium(I) complexes of bidentate phosphorous nitrogen ligand 1 were active catalysts for the reduction of olefins [592]. Dinuclear rhodium(I) and iridium complexes of the type $[M_2Cl(CO)_n(Ph_2PCH_2PPh_2)_2]^+$ were active catalysts for the reduction of alkynes and alkenes. Alkynes reduced to cis alkenes initially, then reduced further to the alkane [593]. Dinuclear thiolato bridged rhodium(I) complexes of the type $[Rh_2(\mu\text{-}SR)_2(CO)_2L_2]$ and $[Rh_2(\mu\text{-}SR)_2(P(OR)_3)_4]$ were very active catalysts for the hydrogenation of 1-hexene and cyclohexene at 20° and one atmosphere pressure [594]. Mixed ligand platinum complexes of the type $PtLL'Cl_2$ where L was Ph_3P, and L' was SMe_2 or p-toluidine was an effective catalyst for the reduction of styrene to ethyl benzene, in the presence of tin(II) chloride dihydrate [595]. The complex catalyst composed of mixtures of nickel(II) acetate, sodium hydride, and t-amyloxide selectively catalyzed the reduction of olefins to alkanes in the presence of carbonyl groups. Alkynes reduced cleanly to cis alkenes [596]. The nickel cluster $Ni_4H_3(C_5H_5)_4$, with bridging hydride ligands, acted as a catalyst for the reduction of



1

non hindered terminal double bonds. The bridging hydrides were not transferred during the reduction [597]. Rhodium(I) complexes having phosphine ligands containing varying length alkylsilane groups were prepared and their catalytic activity in the reduction of olefins was compared to that of silica bound catalysts of similar constitution. The activity of these was about three times higher than the silica supported catalysts because of the increased basicity of the ligand [598]. The complex [closo-1,3-μ-(η^2-3,4-CH_2=$CHCH_2CH_2$)-3-H-3-Ph_3P-3,1,2-$RhC_2B_9H_{10}$] was an exceedingly active catalyst for the hydrogenation of olefins [599]. Hydridocobalt tetracarbonyl reduced 9-methylidenefluorene in a stoichiometric process [600].

The catalytic role of arenechromium tricarbonyl complexes in the hydrogenation of olefins was the subject of a review [601]. Replacing carbonyl groups with phosphines in arenechromium tricarbonyl complexes reduced the activity of these as olefin hydrogenation catalysts [602]. The stereospecific reduction of a tricyclic diene was catalyzed by phenanthrene chromium tricarbonyl (equation 339) [603]. Specifically deuterated prostaglandins were prepared by the catalytic reduction of unsaturated precursors using $RhCl(PPh_3)_3$ as a catalyst [604].

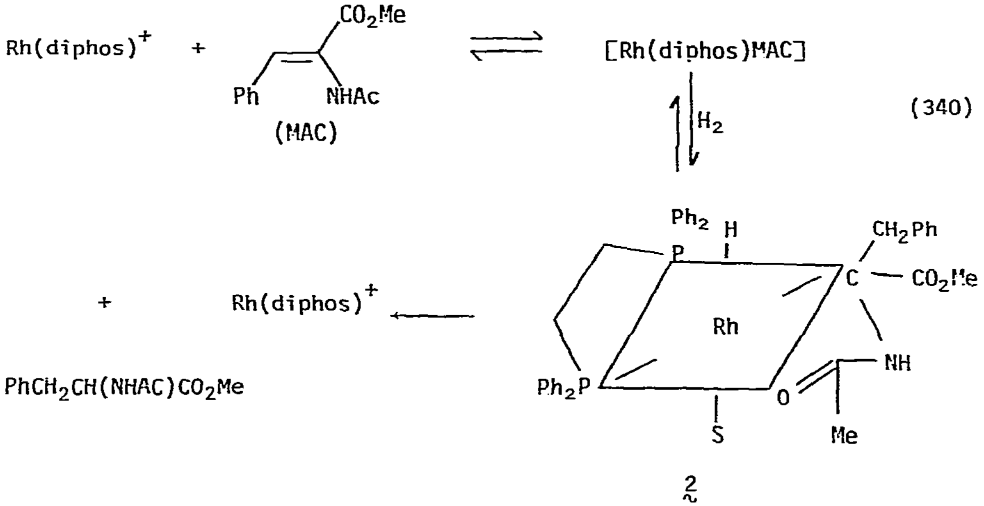


(339)

Reductions using the water gas shift reaction to provide hydrogen have been developed, and reviewed briefly (4 references) [605]. The complexes $M(CO)_6$ where M = Cr, Mo, W and $M_3(CO)_{12}$ where M = Ru, Os catalyzed the water gas shift reaction in the presence of excess sulfide, whereas $Fe(CO)_5$ did not [606]. Ethylene and propene were reduced under water gas shift conditions using a catalyst system consisting of K_2PtCl_4, $SnCl_4{\cdot}5H_2O$ in HCl/AcOH/H_2O [607]. Irradiation of Cp_2TiR_2 produced an efficient catalyst for the hydrogenation of linear and cyclic olefins. When R was phenyl, the catalyst selectively reduced dienes to monoenes [608].

A mechanistic comparison of noble metal catalysts in olefin hydrogenation has been made [609]. In the reduction of α-acetamidoacrylic acid derivatives by rhodium(I) diphos cationic complexes an intermediate (2) has been isolated and characterized by ^1H, ^{31}P, and ^{13}C nmr. This, combined with kinetic studies, suggests the mechanism shown in equation 340 [610]. Ab initio

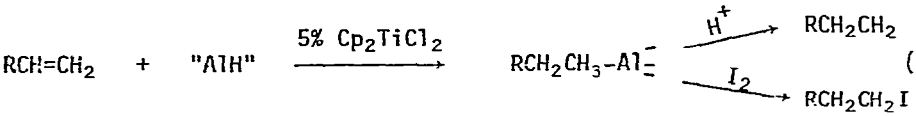
LCAO-MO-SCF calculations for the complexes $RhClL_2$, H_2RhClL_3, H_2RhClL_2, $H_2RhClL_2(C_2H_4)$, and $HRhClL_2(C_2H_5)$ have been carried out [611]. From these calculations it was claimed that the transfer of the first hydrogen to the coordinated olefin was a complex process involving rearrangements of the non-reacting ligands. In the reaction of $(Ph_3P)_2Pt(C_2H_4)$ and $(Ph_3P)_4Pt$ with H_2SO_4 and F_3CSO_2H it was concluded that the ethylene complex was a sufficiently strong reducing agent to convert ethylene to ethane, and the phosphine complex was a sufficient reducing agent to generate hydrogen [612]. The complex $K^+[Co(C_2H_4)L_3]^-$ was studied as a model compound for homogeneous catalysis [613].



(340)

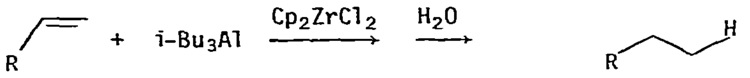
Pretreatment of palladium-alumina hydrogenation catalysts with hydrogen prior to their exposure to olefins reduces the activity of the catalysts [614]. Palladium(II) acetylacetonate modified by Et_3Al and R_3P was an effective catalyst for the reduction of alkenes [615]. The effect of composition of $Co\text{-}Mo/Al_2O_3$ catalysts on the kinetics of cyclohexene hydrogenation has been probed [616]. In the competitive hydrogenation of methylenecyclohexane and 2-methylmethylene cyclohexane over platinum group metal catalysts, the unsubstituted olefin was the most reactive toward all catalysts studied [617].

Olefins were reduced by a wide variety of aluminum hydrides by hydroalumination in the presence of Cp_2TiCl_2 followed by hydrolysis of the alane (equation 341) [618]. Alkynes were converted to alkenes by the process. The complex Cp_2ZrCl_2 catalyzed a similar process, and tolerated the presence of OH, Br, and SPh groups (equation 342) [619]. Allyl alcohols and ethers were similarly reduced by lithium aluminum hydride in the presence of zirconium(IV) chloride (equation 343) [620]. Hafnium complexes catalyzed similar processes [621].

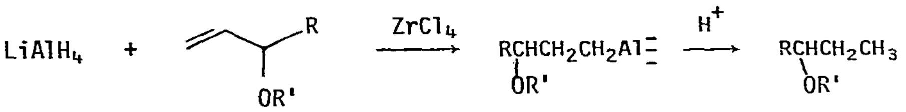


$$RCH{=}CH_2 + \text{"AlH"} \xrightarrow{5\%\ Cp_2TiCl_2} RCH_2CH_3\text{-}Al\overset{-}{\underset{-}{}} \begin{cases} \xrightarrow{H^+} RCH_2CH_2 \\ \xrightarrow{I_2} RCH_2CH_2I \end{cases} \qquad (341)$$

"AlH" = $LiAlH_4$, $NaAlH_4$, $LiAlMe_3H$, $NaAlMe_3H$, $LiAlH_2(NR_2)_2$, $NaAlH_2(NR_2)_2$
vitride



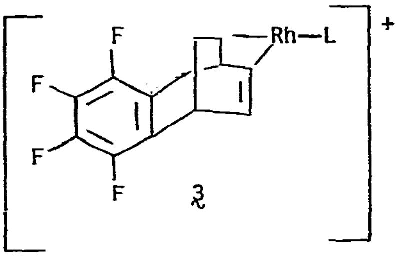
(342)



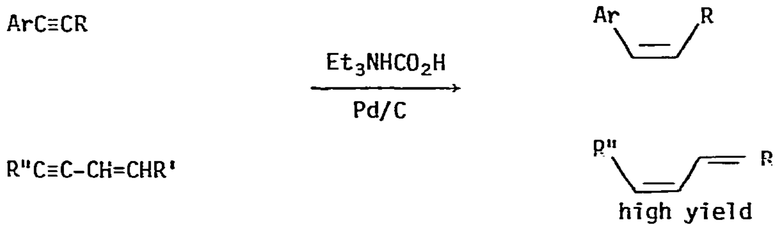
(343)

B. Alkynes

Palladium(II) chloride in DMF catalyzed the reduction of alkynes to alkenes [622]. Dienes were reduced to monoolefins. Nickel(II) stearate/ Et_3Al catalyzed similar transformations [623]. The cluster $H_4Ru_4(CO)_{11}L$ catalyzed the reduction of 2-pentyne to cis-2-pentene [624]. Molecular A-frame rhodium complexes generated from hydrogen and $[Rh_2(CO)_2dpm_2]$ reduced acetylene efficiently [625]. Diphenylacetylene was reduced to cis-stilbene by sodium borohydride and $[Fe_4S_4(SR)_4]^{2-}$ [626]. The rhodium(I) diene complex 3 was an effective catalyst for the reduction of 1-hexyne [627]. Alkynes and enynes were reduced to cis olefins by triethylammonium formate in the presence of palladium on carbon (equation 344) [628]. The material produced from the reaction of nickel(II) acetate, sodium hydride, and sodium alkoxides in THF were heterogeneous, storable, nonpyrophoric compounds which catalyzed the reduction of alkynes to cis alkenes quickly, under mild conditions [629].

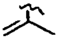


3



(344)

Ar = Ph, p-CHOPh, p-NO_2Ph

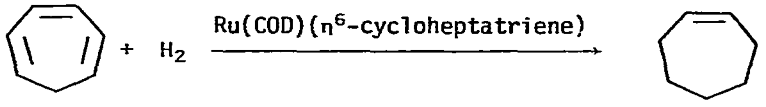
R = nC_4, Ph, 

R" = Ph, cyclohex, nBu

R' = CO_2Me

C. Dienes

The catalyst system comprised of Bu_3P, Et_3Al, and $Co(acac)_2$ effectively reduced isoprene to methyl butenes [630]. Cyclohexadiene reduced butadiene in the presence of cobalt(II) sulfide. This was a catalytic transfer hydrogenation [631]. The complex catalyst system produced from $Ni(acac)_2$, $Et_3Al_2Cl_3$, and Ph_3P reduced 2,3-dimethyl-1,3-butadiene to monoenes rapidly at 40° under one atmosphere pressure [632]. Cyanoaminocobaltates catalyzed the conversion of cis-1,3-pentadiene to the trans isomer, then reduced it to a mixture of 1 and 2-pentenes [633]. Cyclododecatriene was reduced using $(Ph_3P)_2NiI_2$ as a catalyst [634]. Cycloheptatriene was reduced to cycloheptene by a ruthenium(0) catalyst (equation 345) [635].

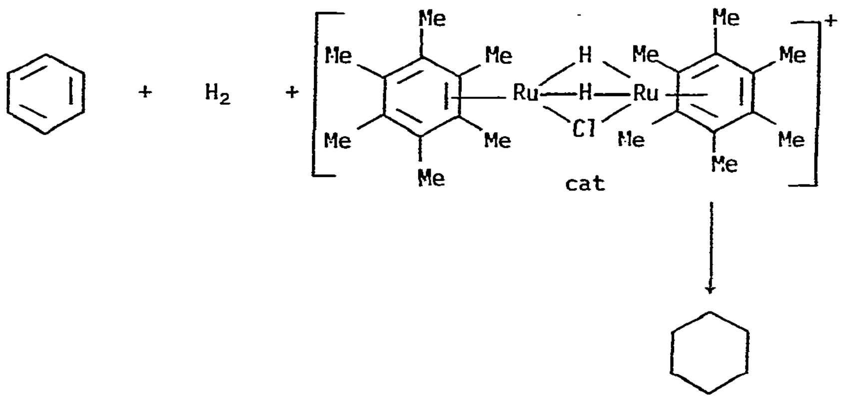


100%

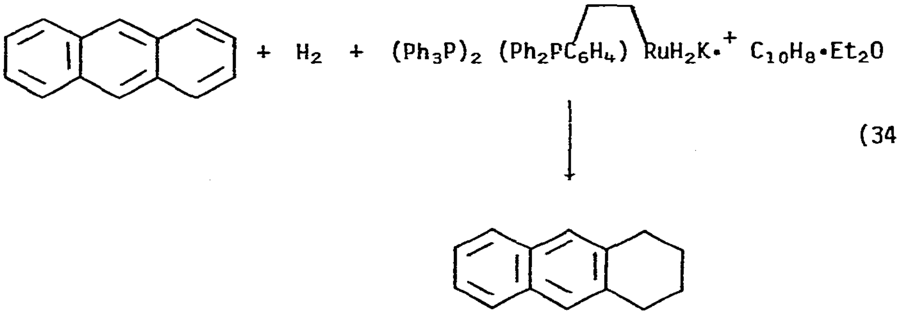
(345)

D. Aromatics

The reduction of benzene to cyclohexane was efficiently catalyzed by hydridoruthenium arene complexes (equation 346) [636]. Substituted benzenes were also reduced, but nitro groups were reduced to amino groups, and chlorides and phenyl ethers were hydrogenolyzed. Polynuclear aromatics were selectively reduced by anionic ruthenium hydride catalysts (equation 347) [637].



(346)



(347)

E. Asymmetric Catalytic Reduction

A number of reviews in this area appeared this year. They are:

Asymmetric hydrogen transfer in preparative organic chemistry. (16 references) [638]

Asymmetric hydrogen transfer in organic synthesis (part 2). (37 references) [639]

Asymmetric hydrogenation of α-acylaminoacrylic acid derivatives with chiral phosphine-rhodium complex catalyst. (31 references) [640]

Homogeneous asymmetric catalysis by transition metal complexes. (121 references) [641]

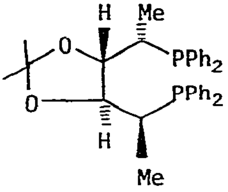
Asymmetric homogeneous hydrogenation of prochiral olefins and control of the metal configuration in labile optically active organotransition metal complexes. (22 references) [642]

Rational approaches to asymmetric hydrogenation. (61 references) [643]

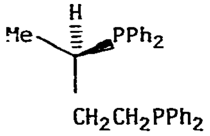
Newer methods in selective and asymmetric reductions using homogeneous transition metal catalysts. (43 references) [644]

Asymmetric hydrogenation of alkenes using chiral rhodium catalysts. [645]

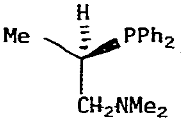
Sugars and carbohydrates have been used as starting materials for chiral ligands to use in asymmetric hydrogenation reactions. Compounds **4**-**6** were prepared from D-mannitol, behaved as bidentate ligands, and induced asymmetry in the reduction of α-acetamidocinnamic acids [646]. Cationic rhodium(I) complexes of ligands **7** and **8** catalyzed the reduction of α-acetamidocinnamic acid. Ligand **7** led to up to 96% ee of the **S** enantiomer, and complex **8** resulted in up to 39% ee of the **R** isomer [647]. Rhodium(I) complexes of ligands **9**-**12** were used to catalytically reduce α-acetamido- and α-methylcinnamic acids and esters, atropic acid, and methyl atropate in fair optical yield [648]. Ligands **13**, from mannitol and **14** from xylose were synthesized [649]. These, and other chiral phosphine derivatives of glucose, menthol, tartaric acid, and α-phenethyl amine were used as chiral ligands for the rhodium(I) catalyzed reduction of σ-acetamidocinnamic acids. The optical yields ranged from 1.4% to 36% [650]. The π-allylpalladium chloride complex of **15** was used to asymmetrically reduce the same substrate, as well as itaconic and citraconic acids and their esters [651].



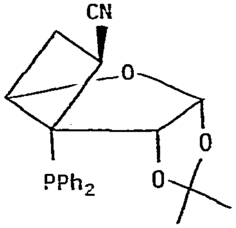
4



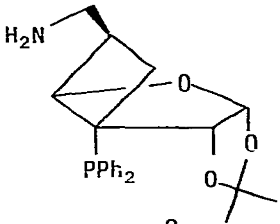
5



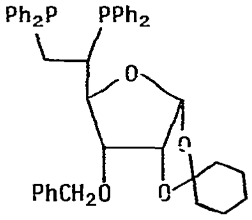
6



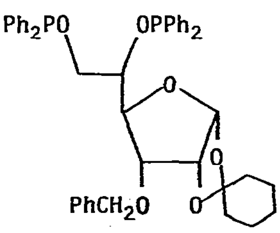
7



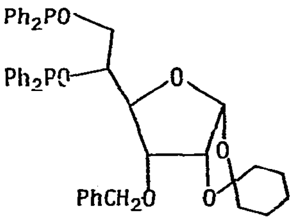
8



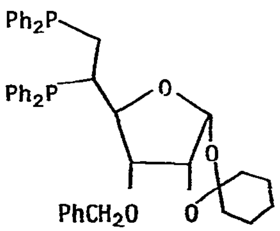
9



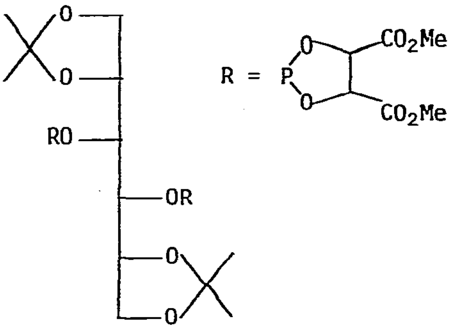
10



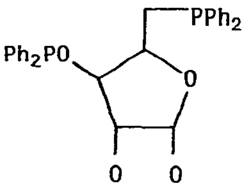
11



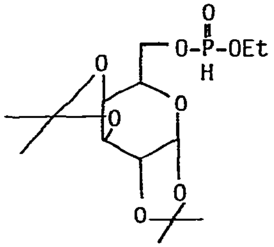
12



13



14

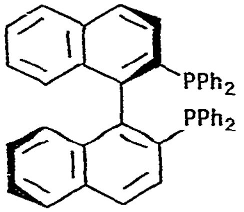


15

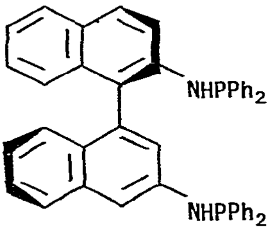
17

Chiral phosphine ligands were attached to polymer molecules, particularly polystyrene, and the rhodium(I) complexes of these were studied as hydrogenation catalysts [652]. By using a hydroxymethyl acrylate polymer, insoluble catalyst systems that swelled in ethanol were obtained. These chiral, polymer bound catalysts gave the same yields and optical yields as did their homogeneous analogs, in the reduction of α-acetamido acrylic acids [653]. The unit 17 was attached to a polystyrene polymer, and its rhodium(I) complexes were used to reduce α-methyl cinnamic acids and citraconic acids. The behavior of soluble and insoluble polymer supports was assessed, and it was concluded that insoluble, noncrosslinked polymers were required for practical asymmetric synthesis [654].

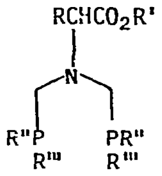
Two very similar axially disymmetric ligands, 18 [655]and 19 [656], have been synthesized, and used as ligands for cationic rhodium(I) in the reduction of α-acetamido acrylic acids and esters. Optical yields were from 79% to 100%. Rhodium(I) complexes of the aminodiphosphine ligand 20 reduced the same substrates in up to 29% ee [657], while those of ligand 21 were used to reduce an array of substrates (equation 348). In this latter case, addition of triethyl amine increased the optical yield [658].



18

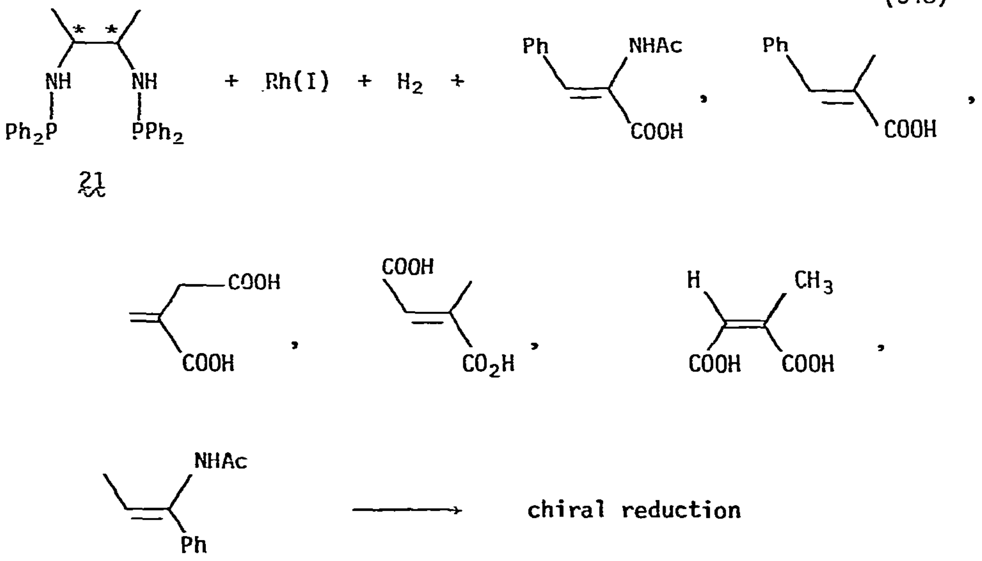


19



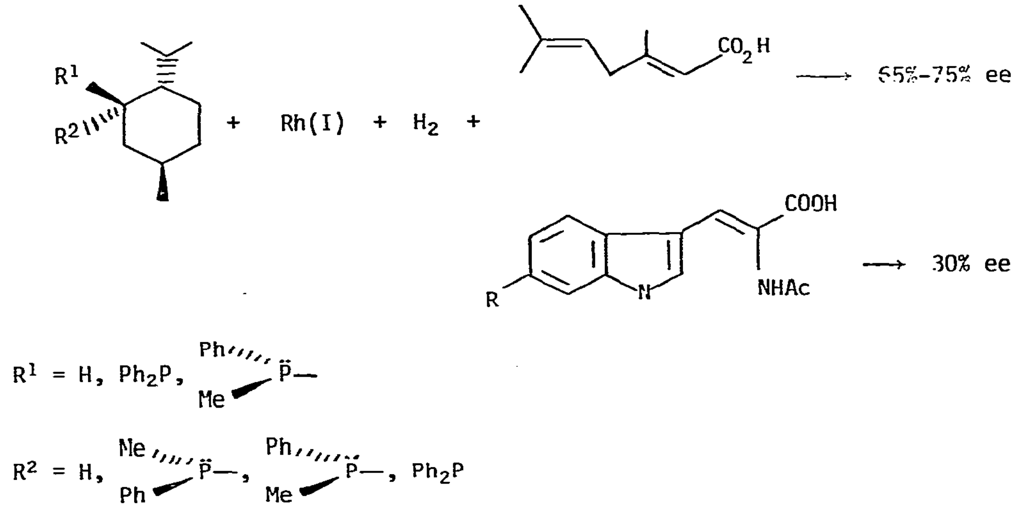
20

(348)

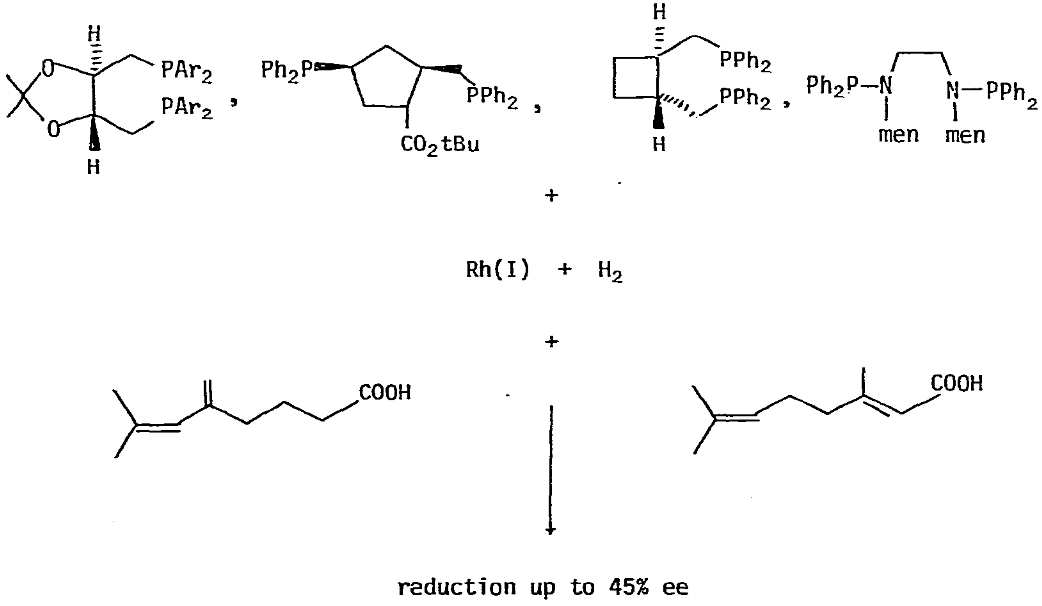


Impure chiral diphosphine ligands such as DIOP were heated to reflux in ethanol with copper(I) chloride, producing crystalline, easily purified copper complexes, the treatment of which with $[RhCl(olefin)_2]_2$ led to complete transfer of the ligand from copper to rhodium [659]. Chiral menthyl or neomenthyl diphosphines were synthesized and used for ligands in the rhodium(I) catalyzed reduction of olefins (equation 349) [660]. Terpenic acrylic acids were reduced in modest optical yield by rhodium(I) complexes of a number of chiral diphosphines (equation 350) [661].

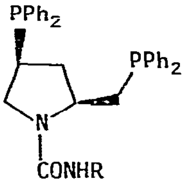
(349)



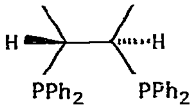
(350)



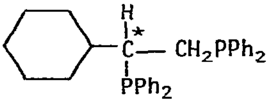
Methoxylation of DIOP reversed the stereochemistry of the rhodium(I) catalyzed reductions of enamides [662]. Rhodium(I) complexes of ligand **22** reduced α-acetamidocinnamic acids in 90-97% optical yield [663], while those of **23**, synthesized from tartaric acid, led to 83-98% optical yield [664] and those of **24** led to 87-94% optical yield [665]. This last ligand, as is the case with most chiral catalysts, was considerably less effective with simple conjugated acids lacking the chelating α-acetamido group.



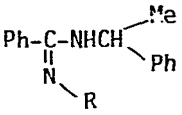
22



23



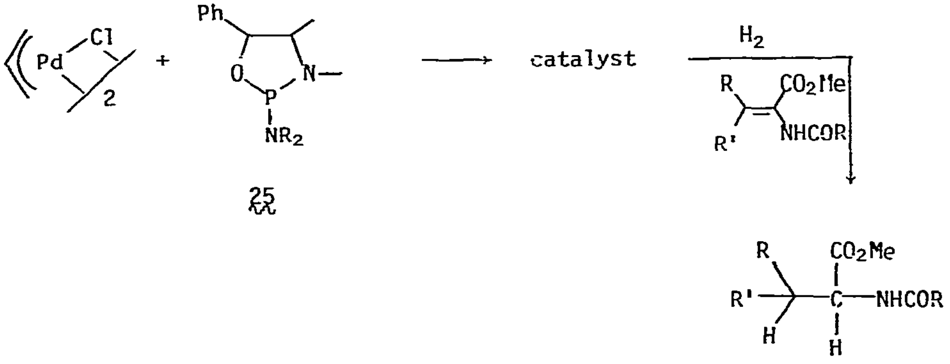
24



26

Palladium(II) complexes of ligand **25** reduced enamides in from 4% to 16% optical yields (equation 351) [666]. Rhodium(I) complexes of chiral amidines **26** were even worse, giving between 0% and 2% optical yields in the same reduction [667]. Rhodium(I) complexes of chiral Schiff bases such as benzylidene-S-alanine reduced these same substrates in 88-93% optical yield [668].

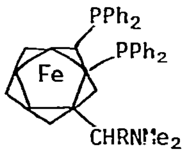
(351)



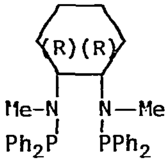
25

4-16% opt. yield

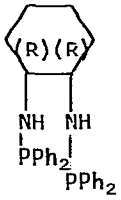
The chiral ferrocene, BPPFA (**27**) and its analogs were complexed to rhodium(I) and used to reduce α-acetamidoacrylic and cinnamic acid esters in up to 86% optical yield. These catalysts were poor (3-34% optical yield) for itaconic and atropic acids and α-ethyl styrene [669]. Rhodium(I) complexes of chiral aminophosphines **28**-**31** reduced α-acetamidoacrylic esters in up to 94% ee. The catalytic reduction of both itaconic acid and α-acetamidoacrylic acids by chiral pyrrolidinodiphosphine complexes of rhodium(I) showed a marked dependency of optical yield on hydrogen pressure [671].



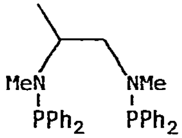
27



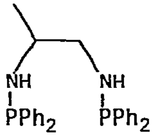
28



29



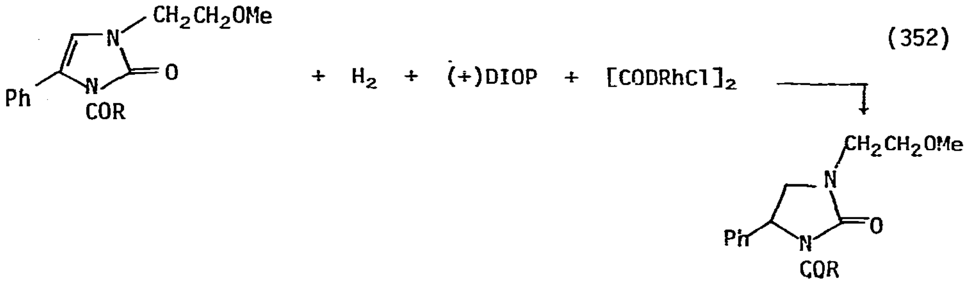
30



31

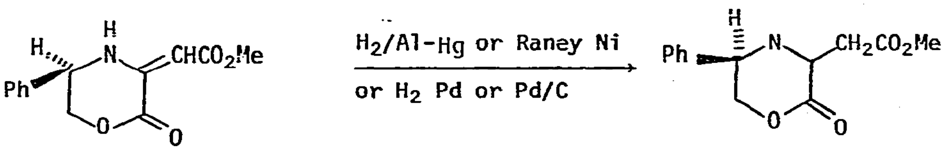
Prochiral carboxylic acids were reduced undercatalytic transfer hydrogenation conditions using $H_4Ru_4(CO)_8[(-)DIOP]_2$ as a catalyst and secondary alcohols as a hydrogen source [672]. DIOP complexes of Ru_2Cl_4 were used to reduce simple acrylic and cinnamic acids in 3-27% optical yields [673]. Rhodium(I) DIOP complexes catalyzed the reduction of imidazolinones in high yield and up to 33% ee (equation 352) [674]. Hydrogenation of optically active oxazines over palladium produced aspartic acid in 12-16% optical yield (equation 353) [675]. 1,1,1-Trifluoro-2-(acetyloxy)-2-propene was reduced in high optical yield by rhodium(I) complexes of a chiral diphosphine (equation 354) [676].

(352)

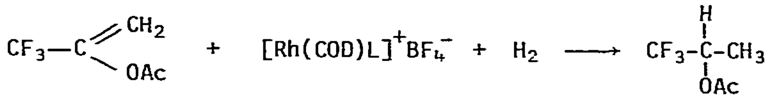


90% yield, ≤33% ee

(353)



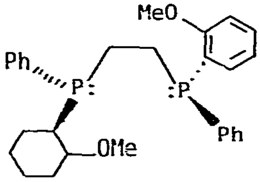
40-70%
12-17% optical yield



$$CF_3{-}C(=CH_2)OAc + [Rh(COD)L]^+BF_4^- + H_2 \longrightarrow CF_3{-}CH(OAc){-}CH_3 \qquad (354)$$

high optical yield

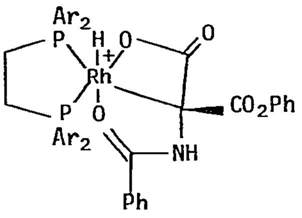
L =



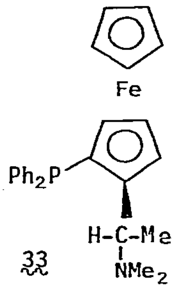
The mechanism of asymmetric hydrogenation continued to be studied. Asymmetric hydrogenations with rhodium chiral phosphine catalysts has been reviewed [677]. The crystal and molecular structure of the methyl (Z)-α-acetamidocinnamic ester adduct of 1,2-bis(diphenylphosphino)ethane rhodium(I) has been elucidated, and it was shown that both the olefin and the acetamido oxygen of the substrate was coordinated to the rhodium [678]. This oxygen coordination was an important factor in determining the stereochemistry of the hydrogenation. A number of attempts to correlate optical yields with structural features of ligand or complex were made, and much speculation was advanced, but little definitive information came to light. Using rhodium(I) complexes of trans 1,2-bis-(diphenylphosphinomethyl) cycloalkanes as catalysts, it was found that optical yields did not correlate to the PCH_2CCCH_2P torsional angle, but appeared related to the flexibility of heptagonal chelate ring [679]. A ^{31}P nmr study of the intermediates of rhodium(I) catalyzed reductions of α-acetamidocinnamic acids was launched [680], and the existence of the hydrogenated enamide 32 was demonstrated [681]. A similar nmr study showed that only the Z-ester of α-acetamidocinnamic ester coordinated to rhodium(I) well (equation 355) [682]. However, in the key paper in this area, Halpern showed that the major catalyst substrate complex reacted very slowly. Thus the preferred mode of substrate binding was not responsible for enantioselectivity. Rather it was the relative rates of reduction of the diastereoisomeric substrate-catalyst pairs which is responsible, and in the case studied, this was the minor diastereoisomer [683]. This observation makes a great deal of published speculation specious.

From X-ray studies of the (norbornadiene) rhodium(I) PPFA complex (33) it was claimed that diastereotopic discrimination was a result of steric interaction of the substrate olefin with the PPFA ligand [684]. The induced chirality in the reduction of α-acetamidocinnamic acids catalyzed by rhodium(I) complexes of ligands 34 and 35 was claimed to be due to the chiral helical conformation of the phenyl groups on phosphorus [685]. In mechanistic studies of the reduction of olefins using $HRuCl(DIOP)_2$ as a catalyst, loss of one DIOP ligand was required during reaction [686, 687].

Dipeptides were synthesized asymmetrically by reducing α-acylamino-cinnamoyl (S) aminoacid esters with chiral rhodium(I) complexes (equation 356). These workers claimed that chirality of the C-terminal aminoacid had no effect on the asymmetric induction [688]. However, other doing essentially the same chemistry claimed to observe an influence on the asymmetry of the reduction [689]. The procedure did provide an efficient procedure for the synthesis of optically active dipeptides (equations 357 and 358) [690, 691]. Catalytic reduction of α,β-dehydroamino acid residues over Pd/C gave 99.1% chiral induction (equation 359) [692].

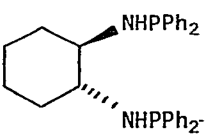


32

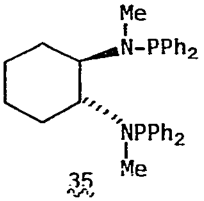


33

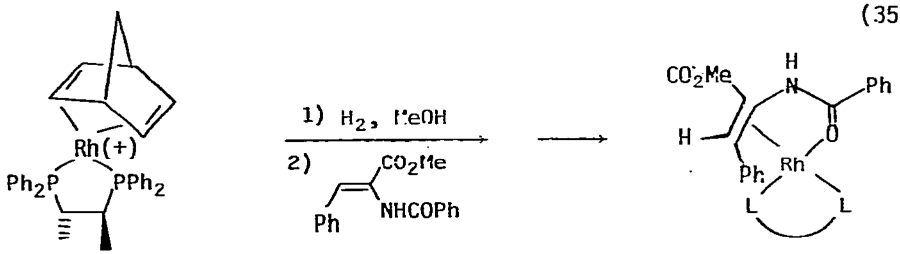
PPFA



34

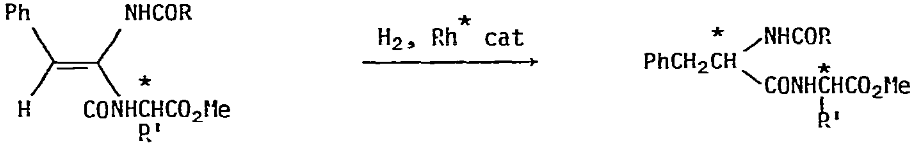


35

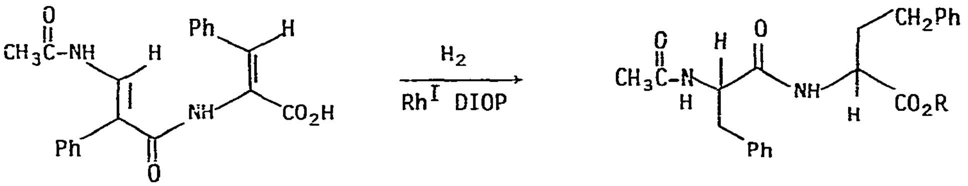


(355)

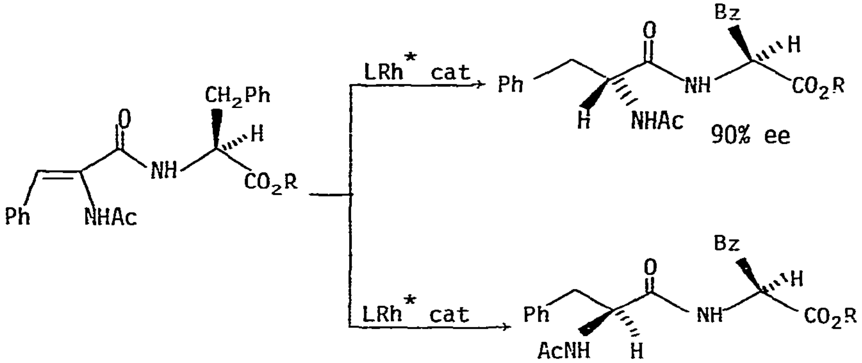
(356)



(357)



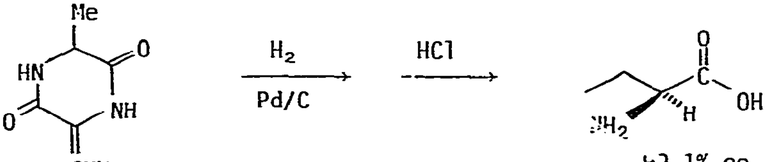
2-diastereo isomers - one in 79% ee



(358)

L = (+) or (-) DIOP, BPPM, diPAMP

>90% ee



93.1% ee

(359)

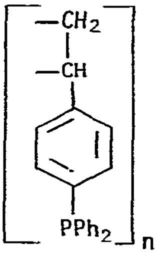
A number of chiral reductions of ketones have been carried out. Rhodium (I) DIOP complexes reduced aryl ketones to alcohols in benzene solvent and with added Et_3N in 40-90% chemical yield and 5-84% optical yield [693]. α-Ketoesters and lactones were reduced to chiral α-hydroxy compounds using both DIOP and BPPM as ligands. The effect of conditions on optical yield was studied [694]. Catalytic transfer hydrogenations of ketones using isopropanol or indoline as the hydrogen source and $H_4Ru_4(CO)_8$ (-)DIOP as a catalyst produced compounds in only 9.8% maximum optical yield [695].

The absorption mode of 2-hydroxy acids on Raney nickel was studied in relation to modifying Raney nickel for asymmetric reductions [696]. Using a Raney-nickel-tartrate-sodium bromide modified catalyst for the reduction of 4-hydroxy-2-butanone produced (S)-1,3-butane diol in 100% yield and 69% optical purity [697]. A similar catalyst reduced β-diketones to 1,3-diols in high optical purity [698]. A study of the factors affecting asymmetric hydrogenations over modified Raney Nickel catalysts has been published [699]. Modified Raney Cobalt catalysts gave only low optical yields in the reduction of β-diketones or β-ketoesters [700]. The asymmetric reduction of benzil to benzoin by a cobalt dimethylglyoxime system was carried out [701]. Methyl pyruvate was reduced to (R)(+)-methyl lactate in 86.8%optical yield over Pt-Al_2O_3 containing a small amount of quinine [702].

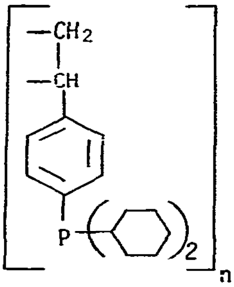
The kinetics of the hydrosilation of phenyl t-butylketone by $[Rh(COD)\text{-}DIOP]^+$ were studied [703]. Optically active alcohols were prepared by hydrosilation of ketones in the presence of rhodium(I) DIOP catalysts. Up to 34% ee was observed [704].

F. Solid Supported Reduction Catalysts

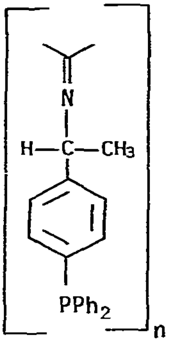
Styrene polymers (**36**, **37**, **38**) of three different monomers were synthesized so as to have a phosphorus ligand on <u>every</u> repeating unit. Rhodium(I) complexes were made of these polymers and ^{31}P nmr spectra were taken, giving some unusual results. When the starting rhodium complex was $[(COD)RhCl]_2$ a single phosphine rhodium complex having the constitution [CODRh(Cl)-P] was formed. In contrast the bis olefin rhodium(I) complex formed a myriad of different species, including $[\sim PRh(C_2H_4)Cl]_2$, $[\sim P_2RhCl]_2$, $\sim P_2RhCl_2Rh(C_2H_4)_2$, $\sim PRhCl(C_2H_4)_2$, $\sim P_2RhCl(C_2H_4)$, and P_3RhCl [705]. Rhodium (I) complexed to polystyrene bound anthranilic acid was effective for the reduction of alkenes, aromatics, benzonitrile, and nitrobenzene. Polymer bound palladium catalysts carried out the same chemistry [706], as did polymer-bound nickel catalysts [707]. The cluster $Ir_4(CO)_{12}$ was attached to polystyrene-bound Ph_2P groups or DIOP groups to give catalysts that reduced ethene at 40^{o} and one atmosphere of hydrogen [708]. Polymer-bound $[H_4Ru_4(CO)_{12-x}(PPh_3)_x]$ was also studied as an olefin hydrogenation catalyst [709]. Infrared studies of polymer membranes functioning as catalysts in olefin hydrogenations and containing $[Ir_4(CO)_{12-x}(PPh_3)_x]$ (where X = 1, 2, 3) as a catalyst showed that the major species present was that which was originally attached to the polymer. At over 120^{o} iridium crystallites formed [710]. Similar studies were carried out using polymer bound $[H_4Ru_4(CO)_{12-x}(PPh_3)_x]$ [711]. The effect of degree of crosslinking on the activity of polystyrene-bound rhodium(I) phosphine complexes was studied.



36



37



38

Polymers containing between 25 and 40% crosslinking gave good results [712]. Polymer-bound rhodium(I) catalysts prepared as in equation 360 [713a] were modestly active in the reduction of styrene and 1-hexene, but not cyclohexene [713b]. The kinetics of heptene reduction using soluble poly(siloxy)alkyldiphenylphosphine-rhodium(I) complex catalysts were examined [714].

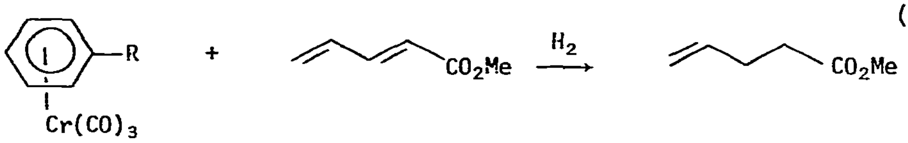
$$Cl_3Si(CH_2)_nPPh_2 + Rh(I) \longrightarrow \text{complex} \xrightarrow{H_2O} \{[O_{3/2}Si(CH_2)_2PPh_2]_3RhCl\cdot(O_{3/2}SiCH_3)_{200}\}_x \qquad (360)$$

Hollow poly(ethylenimine) beads containing palladium(II) acetate reduced by sodium borohydride catalyzed the hydrogenolysis of the carbobenzoxy-group in peptides, using formic acid as solvent [715]. Polymer-protected colloidal nickel boride was an effective hydrogenation catalyst. Soluble nylon was the best polymer studied [716]. Polymer bound $RhCl(PPh_3)_3$ showed kinetic selectivity in the competitive hydrogenation of 1-hexene and cyclohexene [717]. Silica-supported zirconium hydrides catalyzed the rapid isomerization of olefins to their thermodynamic mixtures [718]. Tris(allyl) rhodium (III) was adsorbed onto silica gel, then reduced with hydrogen to produce a silica bound catalysts purported to be $[-SiO\text{-}Rh^{-}H_2]$, which was an effective reduction catalyst for olefins, including tetrasubstituted ones, but a poor isomerization catalyst [719]. Catalyst consisting of rhodium crystallites on silica were prepared by reduction of mononuclear rhodium(I) complexes coordinated to silica bound phosphine or amine groups [720]. A number of phosphine substituted rhodium clusters were studied as reduction catalysts for cyclohexene. The supported clusters had higher thermal stability than those same clusters adsorbed on silica gel [721]. Modification of silica-supported rhodium catalysts by tin, lead, molybdenum, or tungsten ions changed the catalytic properties of the system [722]. The rhodium cluster $Rh_6(CO)_{16}$, when attached to silica supported ethylene diamine and used as a hydrogenation catalyst, fragments into mononuclear $Rh(CO)_2$ units, which are the active catalysts [723]. The same supported ethylene diamine ligand was treated with $(Cl_2RhPy_4)Cl$ to generate a catalyst for the $NaBH_4$ reduction of olefins and dienes [724]. Binuclear palladium complexes attached to phosphine containing silica catalyzed the reduction of cyclopentadiene to cyclopentene and cyclopentane [725]. The silica-bound osmium cluster $[H_2Os_3(CO)_9PPh_2C_2H_4SIL]$ formed $[H_3Os_3(CO)_8(CMe)PPh_2C_2H_4SIL]$ when exposed to hydrogen and ethylene [726]. The influence of particle size on catalytic properties of alumina supported rhodium catalysts was studied [727]. Fischer-Tropsch type catalysts were prepared by impregnating SiO_2 or Al_2O_3 with potassium Group VIII metal carbonyl complexes, then thermally decomposing them [728].

G. Conjugate Reduction of α,β-Unsaturated Carbonyl Compounds

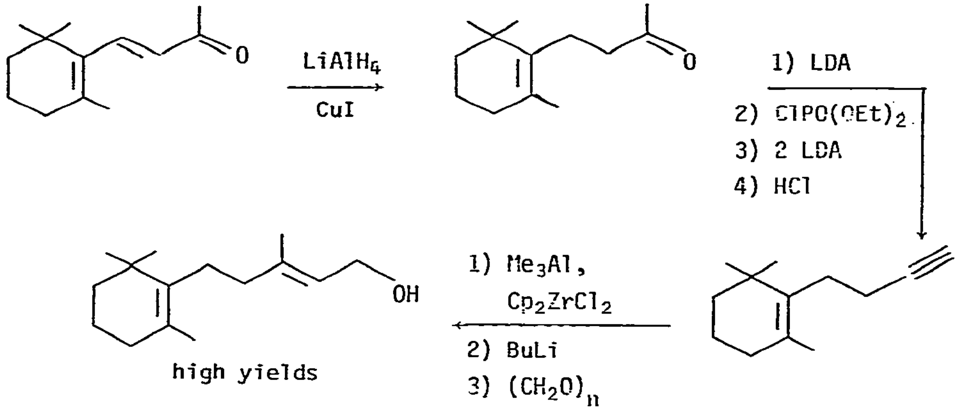
Arene chromium tricarbonyl complexes catalyzed the reduction of methyl sorbate. The activity of the catalyst was highly dependent upon the substitution on the aromatic ring (equation 361) [729]. A general procedure for the conversion of methyl ketones to terminal acetylene groups has been developed (equation 362) [730]. Conjugated ketones, aldehydes, and esters underwent clean 1,4 reduction when treated with lithium aluminum hydride and copper(I) iodide in HMPA at -78°C [731]. Copper(I) bromide/Vitride reduced the polycyclic unsaturated nitrile in equation 363 in a 1,4 fashion [732]. Methanol solutions of $Co(CO)_4^-$ were effective stoichiometric reducing agents for the 1,4-reduction of α,β-unsaturated ketones and esters [733]. Conjugated enones underwent 1,4-reduction when treated with $K_3[Co(CN)_5H]$ under phase transfer conditions. β-Substitution on the enone prevented this process [734]. Steroids having 3-oxo-4-ene and 3-oxo-1,4-diene functional groups were reduced using palladium black/amines as a catalyst to give 5-β-ketosteroids. With p-methoxypyridine very high stereoselectivity for 5-β-ketosteroid production was observed (equation 364) [735]. Iridium and ruthenium complexes were used for the bulk hydrogenation of α,β-unsaturated ketones to ketones [736].

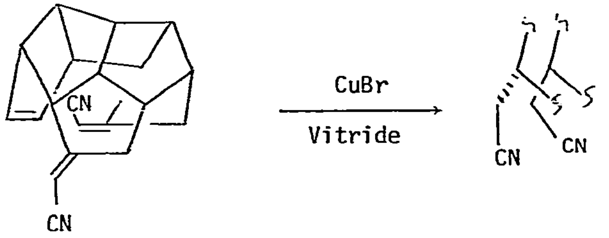
(361)



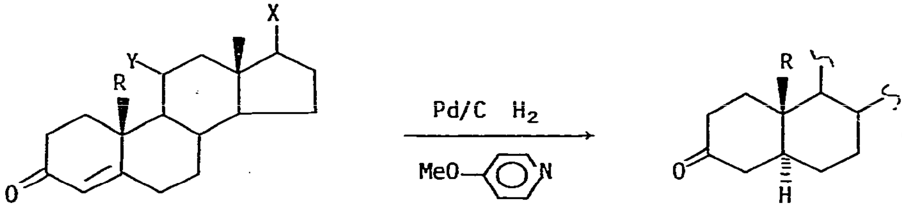
R = OMe	100% at 120°, 0% at 100°
R = 1, 2, 3-TriOMe	100% at 80°
R = CO_2Me	0% at 120°

(362)





(363)



(364)

R = H, Me
Y = H, =O
X = β-C_8, =O, β-OH, βAc, αOH

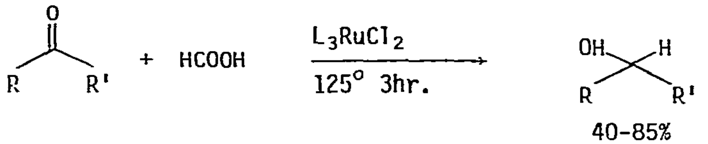
H. Carbonyl Compounds

The complex $Cl_2Ru(CO)_2(P(cyclohexyl)_3)_2$ was the most efficient catalyst for the bulk reduction of α,β-unsaturated aldehydes to allylic alcohols [737]. Aldehydes disproportionated to the corresponding acids and alcohols in the presence of a number of catalysts (equation 365) [738].

$$2\ RCHO + H_2O \overset{cat}{\rightleftharpoons} RCH_2OH + RCOOH \qquad (365)$$

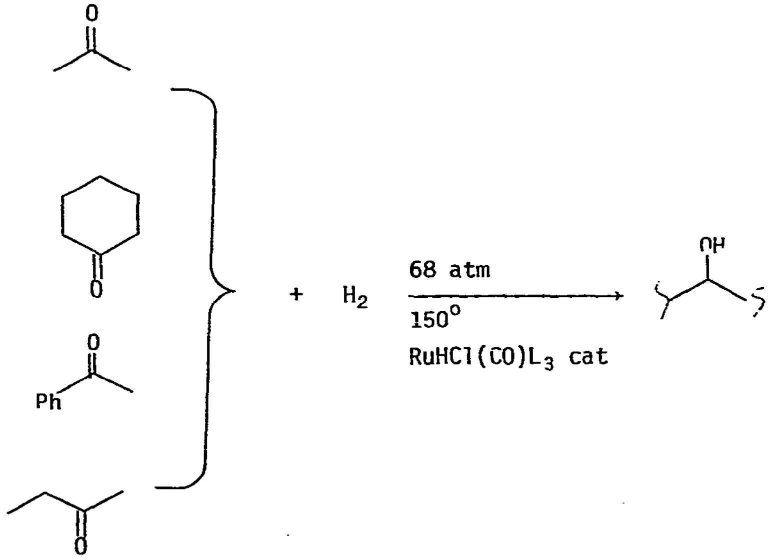
cat = $[Rh_2(C_5Me_5)_2(OH)_3]Cl$, Ru_2(p-Cymene)$_2Cl_4$, $[Ru_2(C_6Me_6)(OH)_3]Cl$, $M_2(C_5Me_5)_2Cl_4$
M = Ir, Rh

Complexes of the type $RuCl_2L_2$, $HRuClL_3$, $HRu(OAc)L_3$, and $HRuCl(CO)L_3$ for which L was the water soluble *m*-sulfophenyl-diphenylphosphine, catalyzed the reduction of pyruvic acid to the α-hydroxy acid [739]. Formic acid in the presence of L_3RuCl reduced ethyl pyruvate, as well as a number of other ketones (excepting β-ketoesters) to alcohols in reasonable yield (equation 366) [740]. The ruthenium complex $RuHCl(CO)L_3$ was also effective in the catalytic hydrogenation of ketones to alcohols (equation 367) [741]. Ketones reacted with isopropylmagnesium chloride in the presence of Cp_2TiCl_2 catalyst to produce alcohols. Aryl and vinyl ketones were not reduced under these conditions [742]. Urushibara nickel catalyzed the reduction of 3-oxochalestanes to axial 3-alcohols, while axial 3β alcohols were produced with Urushibara cobalt [743]. 5α and 5β-cholestan-3-ones were 30 and 17 times more reactive than was 4-*t*-butylcyclohexanone toward palladium catalyzed hydrogenation in t-butanol [744]. Colloidal nickel boride, activated by sodium hydroxide, was an effective catalyst for the reduction of ketones and aldehydes [745].



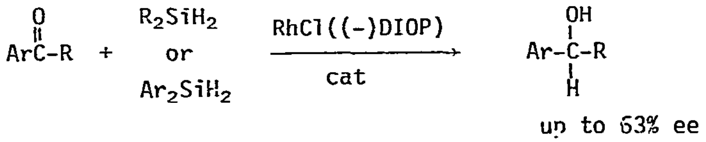
(366)

R = Ph, Et, nPr, nBu
R' = Ph, Me, Et



(367)

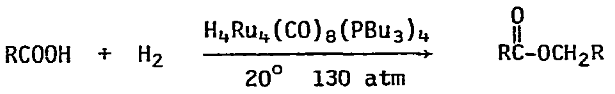
Aryl ketones were reduced by asymmetric catalyzed hydrosilation to produce benzyl alcohols in up to 63% ee (equation 368) [746]. Raney nickel modified by R,R tartaric acid catalyzed the reduction of 3-oxotetradecanoic acid to the 3-hydroxy acid in 85% ee [747]. Ketones were sequentially condensed (aldol) and simultaneously hydrogenated by using immobilized acid catalysts and Pd/C under hydrogen [748].



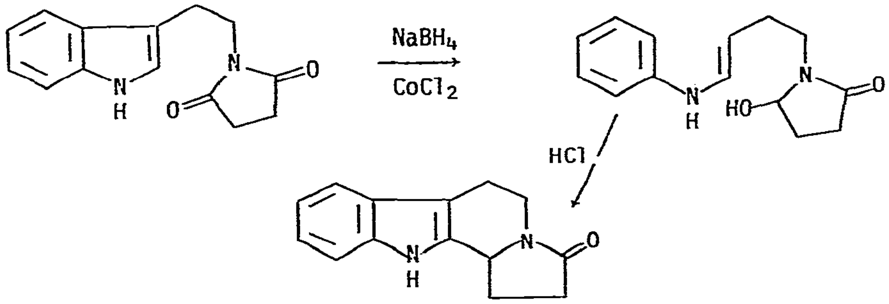
$$\mathrm{Ar\overset{O}{\overset{\|}{C}}\text{-}R} + \begin{matrix}\mathrm{R_2SiH_2}\\ \text{or}\\ \mathrm{Ar_2SiH_2}\end{matrix} \xrightarrow[\text{cat}]{\mathrm{RhCl((-)DIOP)}} \mathrm{Ar\text{-}\underset{H}{\overset{OH}{C}}\text{-}R} \qquad (368)$$

up to 63% ee

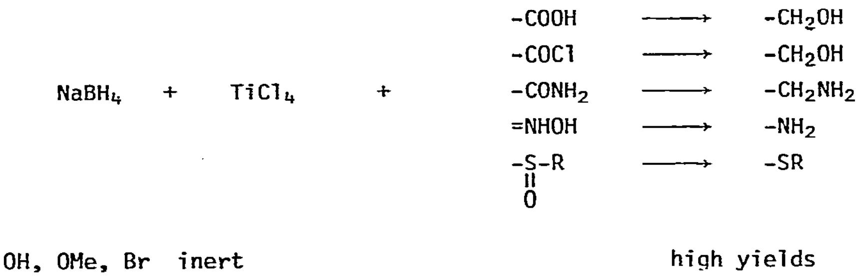
Carboxylic acids were reduced and condensed to esters by a ruthenium catalyst (equation 369) [749]. Esters of trifluoroacetic acid were reduced to alcohols over an anionic phosphide ruthenium catalyst [750]. Sodium borohydride/cobalt(II) chloride reduced one carbonyl group of a succinamide (equation 370) [751]. Treatment of vanadium(III) chloride with lithium hydride gave a complex that reduced aldehydes, ketones, and esters to alcohols in high yield. Terminal olefins also reduced but alkynes and internal olefins did not [752]. Another generally useful reducing agent was produced in the reaction of titanium tetrachloride with sodium borohydride (equation 371) [753]. Cobalt and rhodium DMG complexes were efficient catalysts for the reductive amination of carbonyl compounds [754, 755].



$$\mathrm{RCOOH} + \mathrm{H_2} \xrightarrow[20^\circ \quad 130\ \text{atm}]{\mathrm{H_4Ru_4(CO)_8(PBu_3)_4}} \mathrm{R\overset{O}{\overset{\|}{C}}\text{-}OCH_2R} \qquad (369)$$



(370)



$$\mathrm{NaBH_4} + \mathrm{TiCl_4} + \begin{array}{lcl} \mathrm{-COOH} & \longrightarrow & \mathrm{-CH_2OH} \\ \mathrm{-COCl} & \longrightarrow & \mathrm{-CH_2OH} \\ \mathrm{-CONH_2} & \longrightarrow & \mathrm{-CH_2NH_2} \\ \mathrm{=NHOH} & \longrightarrow & \mathrm{-NH_2} \\ \mathrm{-\underset{\underset{O}{\|}}{S}-R} & \longrightarrow & \mathrm{-SR} \end{array} \qquad (371)$$

OH, OMe, Br inert high yields

I. Carbon Monoxide

The following is a list of titles of papers concerning the reduction of carbon monoxide, the Fischer-Tropsch synthesis, and the reductive homologation of carbon monoxide.

On the mechanism of the Fischer-Tropsch synthesis. (26 references) [756]

Fischer-Tropsch synthesis over a ruthenium catalyst: infrared and kinetic studies. [757]

Mechanisms of carbon monoxide reduction with zirconium hydrides. (34 references) [758]

Catalytic synthesis of light hydrocarbons from carbon monoxide/hydrogen over metal catalysts. [759]

Chemicals from coal: the cobalt octacarbonyl catalyzed homologation of methanol to ethanol. (82 references) [760]

Fischer-Tropsch synthesis over a ruthenium catalyst: infrared and kinetic studies. [761]

Formation and evolution of the active site for methanol carbonylation on oxide catalysts containing rhodium(III) chloride. [762]

Activity of supported cobalt carbonyl catalysts for the synthesis of aliphatic hydrocarbons from carbon monoxide and hydrogen. [763]

Selectivity of Fischer-Tropsch synthesis on supported nickel catalysts. [764]

Activity and mechanism of carbon monoxide methanation on activated carbon-supported nickel. [765]

Selective formation of propene from carbon monoxide and hydrogen or ethylene with $Fe_3(CO)_{12}$ supported on inorganic oxides. Mechanistic implication in Fischer-Tropsch synthesis. [766]

Catalytic synthesis of low molecular weight olefins from carbon monoxide and hydrogen with pentacarbonyliron, dodecacarbonyltriiron, and hydridoundecacarbonyltriiron anion supported on inorganic oxides. [767]

Rhodium-carbonyl cluster chemistry under high pressure of carbon monoxide and hydrogen. [768]

Synthesis of aliphatic hydrocarbons from carbon monoxide and molecular hydrogen over rhodium-complex catalysts. [769]

High pressure homogeneous hydrogenation of carbon monoxide in polar and nonpolar solvents. [770]

Hydrogenation of carbon monoxide and related molecules. [771]

Synthesis of hydrocarbons from carbon monoxide and hydrogen in the liquid phase over cobalt catalysts. [772]

Organometallic chemistry. XIV. Methanol homologation catalyzed by homogeneous cobalt derivatives. [773]

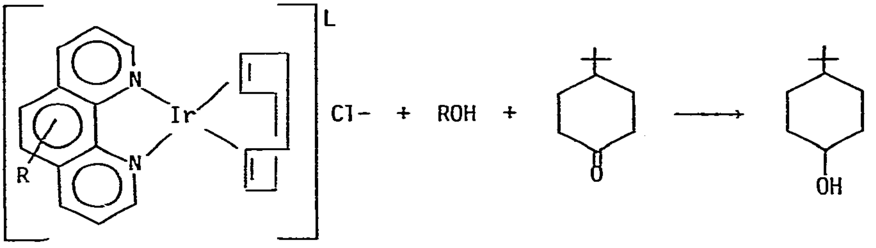
Hydrogenation of carbon monoxide to methanol and ethylene glycol by homogeneous ruthenium catalysts. [774]

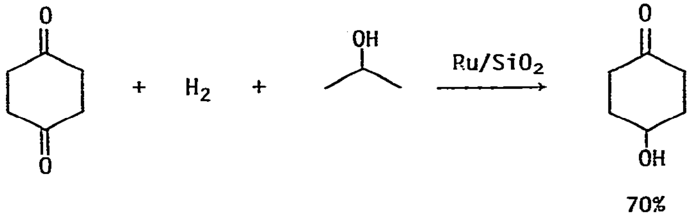
Formation of methane and ethane by reduction of carbon monoxide coordinated through both carbon and oxygen on $Mg[CpFe(CO)_2]_2 \cdot 4THF$. [775]

J. Catalytic Transfer Hydrogenation

Catalytic transfer hydrogenation and transfer hydrogenolysis has been reviewed (97 references) [776]. Iridium(I) complexes of bipyridine ligands catalyzed the reduction of 4-t-butylcyclohexanone to the alcohol in high yield. 3,4,8,7-Tetramethyl-1,10-phenanthroline was the best ligand (equation 372) [777]. Cationic rhodium(I) cyclooctadiene-phosphine complexes were also effective for the same transformation [778]. Cyclohexane-1,4-dione was reduced by isopropanol in the presence of ruthenium metal on silica gel (equation 373) [779]. Iridium(I) complexes of bipyridine type ligands catalyzed the reduction of conjugated ketones to saturated alcohols (equation 374) [780]. D-Glucose was reduced by a number of hydrogen-donor solvents in the presence of $Cl_2Ru(PPh_3)_3$ to sorbitol [781]. The complex $RuHCl(CO)[P(C_6H_{11})_3]_3$ in the presence of KOH was an efficient catalyst for transfer hydrogenation of acetophenone [782]. Allyl acetates were reduced to olefins by $NaBH_4$ or $NaBH_3CN$ in the presence of palladium(0) catalysts [783].

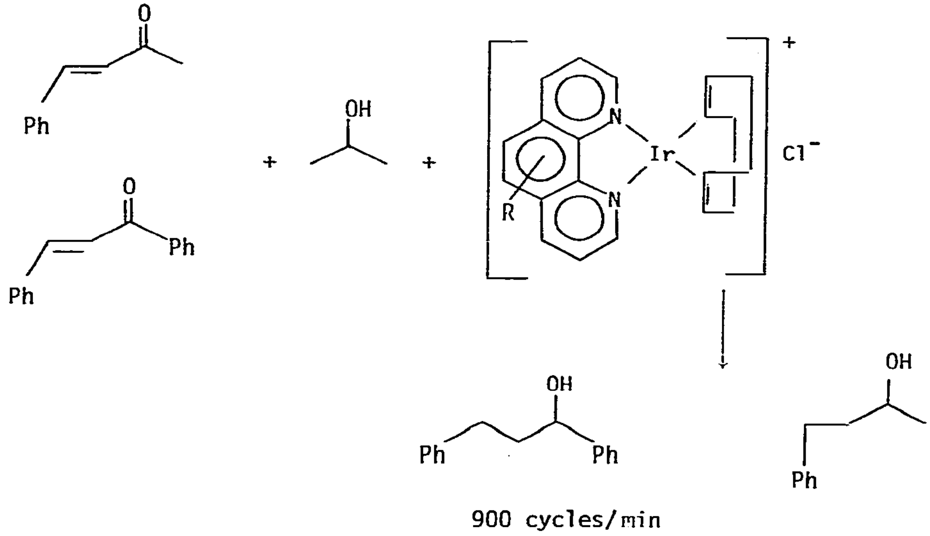
(372)





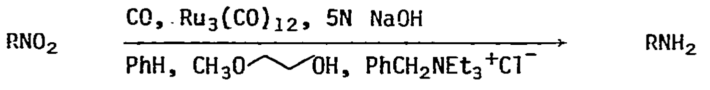
(373)

(374)

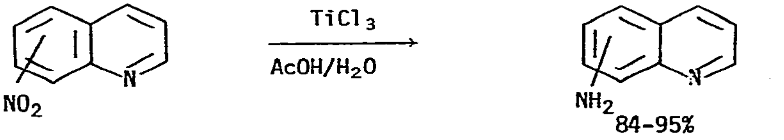


K. Nitrogen Compounds

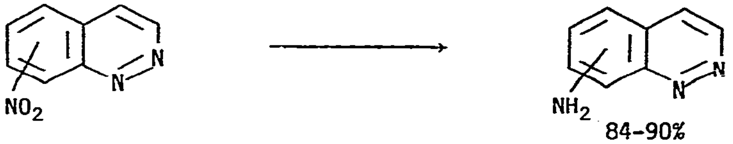
The ruthenium cluster $Ru_3(CO)_{12}$ reduced nitro compounds to amines under phase transfer conditions (equation 375) [784]. Titanium trichloride in aqueous acetic acid was a very effective reducing agent for nitroaromatics containing a variety of other reducible groups (equations 376-379) [785]. Dinitroaromatics were selectively reduced to aminonitro compounds by triethylammonium formate over palladium on carbon (equation 380) [786]. Palladium and platinum complexes of 1,2-dihydroxyanthraquinone catalyzed the reduction of nitrobenzene to aniline [787]. Similarly the bis isocyanide complex of palladium(II) catalyzed this same reduction [788], as did palladium and platinum complexes of azo dyes in the presence of sodium borohydride [789]. The stereochemistry of palladium and platinum catalyzed reductions of nitro sugar epoxides was extensively studied. Both the regio- and stereospecificity of the ring opening and the fate of the nitro group were examined [790].



(375)



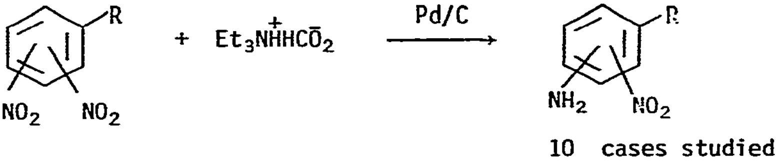
(376)



(377)

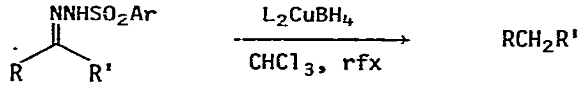
(378)

(379)

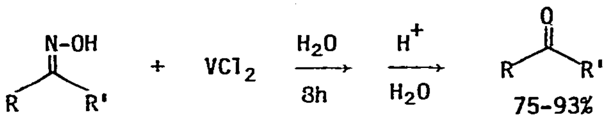


(380)

Copper borohydride complexes reduced tosyl hydrazones of ketones in high yield, and those of aldehydes in fair yield, to hydrocarbons (equation 381) [791]. Aromatic ketones and conjugated ketones gave very low yields. Aqueous vanadium(II) chloride reduced cyclic, acyclic, bicyclic, and aromatic oximes to ketones in 75-93% yield (equation 382) [792]. The reagent produced by the reaction of molybdenum pentachloride with zinc produced a molybdenum(III) species which reduced azides and hydrazines to amines in the presence of halogen [793]. Rhodium(I) and ruthenium(II) complexes catalyzed the reduction of azobenzene to aniline by isopropanol [794].

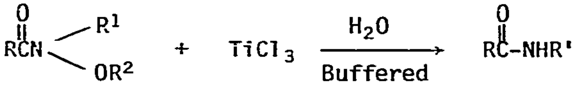


(381)



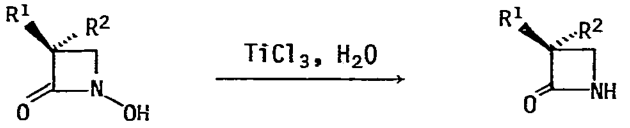
(382)

Titanium trichloride reduced hydroxamic acids, including N-hydroxy-2-azetidinones, to amides in good yield (equations 383 and 384) [795]. Titanium tetrachloride reduced N-nitrosamines to amines in the presence of sodium borohydride in 75-95% yield. Nickel chloride-sodium borohydride was also effective [796]. The same titanium system reduced pyridine and quinoline N-oxides to the free amines [797].



$$RC(=O)N(R^1)OR^2 + TiCl_3 \xrightarrow[\text{Buffered}]{H_2O} RC(=O)\text{-}NHR' \qquad (383)$$

R = Ph,	R^1 = H	R^2 = H	85%
$PhCH_2$	Me	H	64%
Ph	H	$PhCH_2$	91%
Ph	H	COPh	91%
$PhCH_2$	Me	CH_2Ph	N.R.



67-79%

(384)

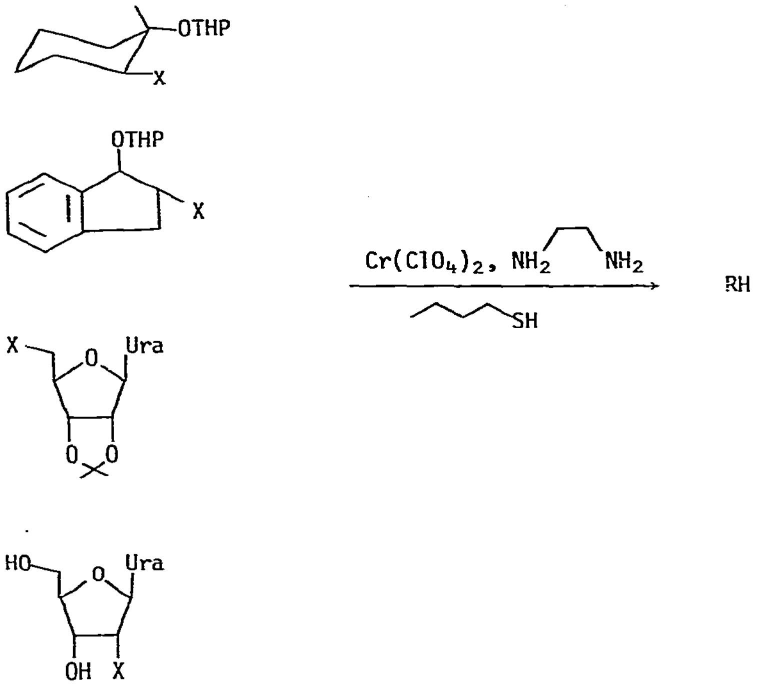
L. Halides, Allyl Ethers

The hydrogenolysis of organic halides has been reviewed (450 references) [798]. Cobalt tetracarbonyl anion reduced organic halides to hydrocarbons under carbon monoxide. Carbonylation of the halide to the aldehyde was a competing reaction (equation 385) [799]. A variety of secondary halides were reduced to the hydrocarbon with little competing elimination by chromium(II) salts (equation 386) [800].

$$Co(CO)_4^- + RX \xrightarrow[CO]{MeOH} RH + RCHO \qquad (385)$$

R = Ar, ArCO, RO_2CCH_2X	RH major product
R = Me, Et, nBu, Bz	40-60% RCHO

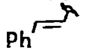
11α-chlorotetracycline ⟶ RH 94%



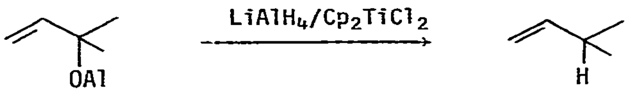
(386)

The full paper describing the reduction of acid chlorides to aldehydes using $(Ph_3P)_2CuBH_4$ has appeared [801]. A number of variations on this procedure have been developed. The reagent $[(Ph_3P)_2Cu(BH_3)CN]_2$ reduced acid chlorides to aldehydes under neutral conditions, and aldehydes and ketones to alcohols in acid media [802][803]. Sodium borohydride reduced acid chlorides to aldehydes, but left alkyl, aryl, and benzyl halides unaffected in the presence of copper(I), copper(II), cadmium(II), and zinc(II) salts [804]. Trialkyltin hydrides reduced acid chlorides to aldehydes in the presence of a palladium(0) catalyst in 75-97% yield (equation 387) [805].

$$\mathrm{RCOCl} + \mathrm{R'_3SnH} \xrightarrow{L_4Pd} \underset{75\text{-}97\%}{\mathrm{RCHO}} \qquad (387)$$

R = Ph, 1-Naphth, 2-Naphth, , nC_{10}

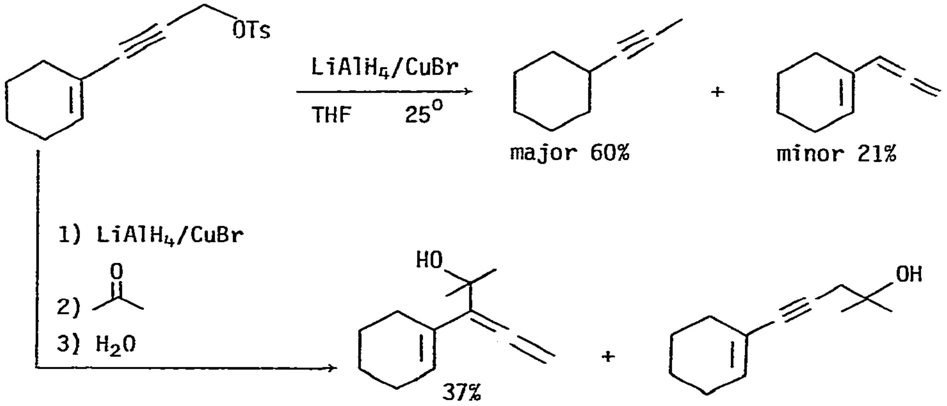
Allyl acetates were reduced to olefins by sodium borohydride or sodium cyanoborohydride in the presence of phosphine palladium(0) complexes. A mixture of regioisomers was obtained, and the relative amounts of S_N2 and S_N2' displacement depended on steric and electronic factors [806]. Allyl and benzyl alkoxides were reduced to olefins by lithium aluminum hydride in the presence of Cp_2TiCl_2 (equation 388) [807]. Lithium aluminum hydride in the presence of copper(I) bromide reduced propargyl tosylates to alkynes and allenes. The intermediate underwent reaction with ketones to give alcohols (equation 389) [808]. Propargyl halides of ketals of propargyl aldehydes were reduced to cumulated trienes by chromous ion (equation 390) [809].

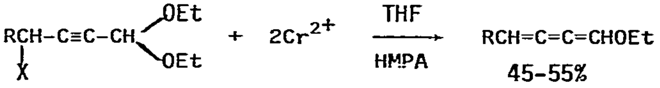


14 cases studied
good yields

(388)

(389)





$$\underset{\displaystyle X}{\mathrm{RCH}}\text{-}C{\equiv}C\text{-}CH(OEt)_2 + 2Cr^{2+} \xrightarrow[\text{HMPA}]{\text{THF}} \underset{45\text{-}55\%}{RCH{=}C{=}C{=}CHOEt} \qquad (390)$$

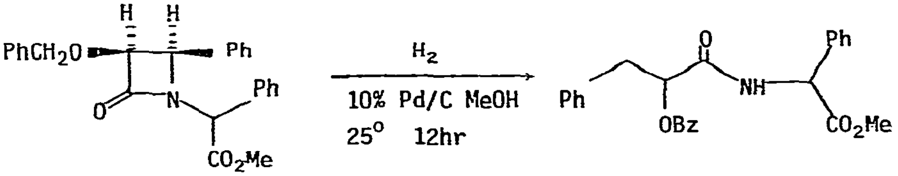
R = Et, nC$_8$, Ph

M. Reduction by Hydrosilylation

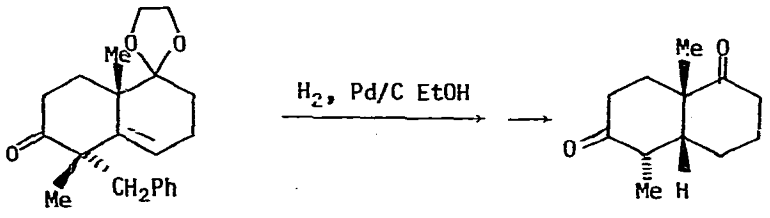
The relative addition rates of dichloro- and trichlorosilane to 2-pentene and 1-octene have been measured in the presence of H_2PtCl_6, and Cl_3SiH was found to add much more rapidly than Cl_2SiH_2 [810]. The factors controlling the regioselectivity of hydrosilylation of alkynes [811], and the relative reactivities of alkynes to hydrosilylation catalyzed by platinum hydride dimers has been studied [812]. The same platinum complexes, $[Pt(\mu\text{-}H)(SiR_3)(PR_3')]_2$ catalyzed the 1,4 hydrosilylation of α,β-unsaturated aldehydes [813]. Triphenylphosphine (5 eq) greatly enhanced the hydrosilylation of olefins catalyzed by π-complexes of nickel [814]. The consequences of steric effects in the hydrosilylation of styrene, α- methylstyrene, and β-methylstyrene catalyzed by rhodium(I) or platinum(IV) complexes was studied [815], as were the effects of solvents [816]. In the latter study it was found that polar solvents suppressed the formation of the α-adduct [816]. The influence of the structure of the hydrosilane on the rhodium(I) catalyzed hydrosilylation of phenylacetylene was investigated [817]. In careful studies it was found that the hydrosilylation of alkenes or alkynes in the presence of L_3RhCl did not proceed when everything was absolutely pure and air free, but that oxygen or hydroperoxide promoted the reaction [818]. The effects of n- and π-donor ligands on the $Co_2(CO)_8$ catalyzed hydrosilylation of olefins was studied [819]. The activity of metal carbonyl clusters for the hydrosilylation of olefins decreased in the following order: $Rh_4(CO)_{12} >> [Co(CO)_4]_2Sn > Co_2(CO)_8 > Co_4(CO)_{12} > [Co(CO)_4]_4Sn \sim [Co(CO)_4]_2SnCl_2 > Rh_6(CO)_{16} \sim Co_6(CO)_{16}$ [820]. Olefins were hydrosilylated by $(RO)_3SiH$ in the presence of $RuCl_2(PPh_3)_3$ [821].

N. Hydrogenolysis

Dipeptides were synthesized by hydrogenolysis of β-lactams (equation 391) [822]. An octalone was debenzylated upon catalytic hydrogenation (equation 392) [823]. Benzyl ester bound peptide resins were cleaved by palladium(II) acetate catalyzed reduction [824]. The selectivity of palladium and platinum catalysts in the hydrogenolysis of 4-hydroxy- and 4-methoxycyclohexanones was probed [825]. Treatment of L_4RuH_2, L_4RhH, L_3RuCl_2, and L_3RhCl where L = Ph_3P with hydrogen donors produced benzene by almost complete hydrogenolysis of phosphorous carbon bonds [826].



(391)



(392)

O. Miscellaneous Reviews

The following reviews dealing with reduction have appeared:

Homogeneous catalytic hydrogenation: a retrospective account. (81 references) [827]

Homogeneous hydrogenations catalyzed by metal complexes. I. (40 references) [828]

Homogeneous hydrogenation catalyzed with metal complexes. II. (30 references) [829]

Homogeneous catalytic hydrogenation of unsaturated compounds with chromium carbonyl catalysts. (24 references) [830]

Catalyses by platinum-group metals. IX. V. Selective hydrogenation. (48 references) [831]

Catalytic hydroalumination in olefins. (35 references) [832]

Choosing and using noble metal hydrogenation catalysts. (12 references) [833]

Catalyses by platinum-groups metals. X. 5. Selective hydrogenation. (127 references) [834]

Catalyses by platinum-group metals. XI. 5. Selective hydrogenation. (58 references) [835]

Catalyses by platinum-group metals. XII. 5. Selective hydrogenation. (56 references) [836]

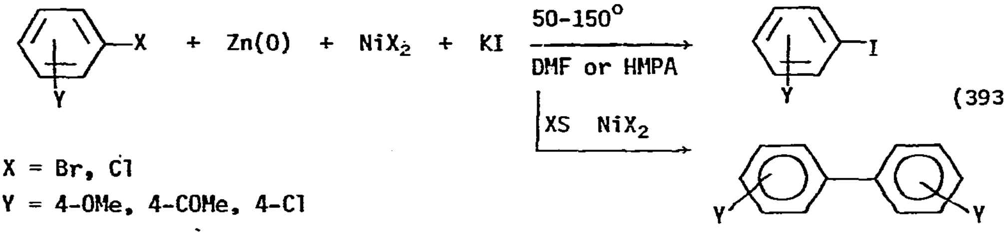
Catalyses by platinum-group metals. XIII. 5. Selective hydrogenation. (48 references) [837]

Catalyses by platinum-group metals. XIV. 5. Selective hydrogenation. (60 references) [838]

V. Functional Group Preparations

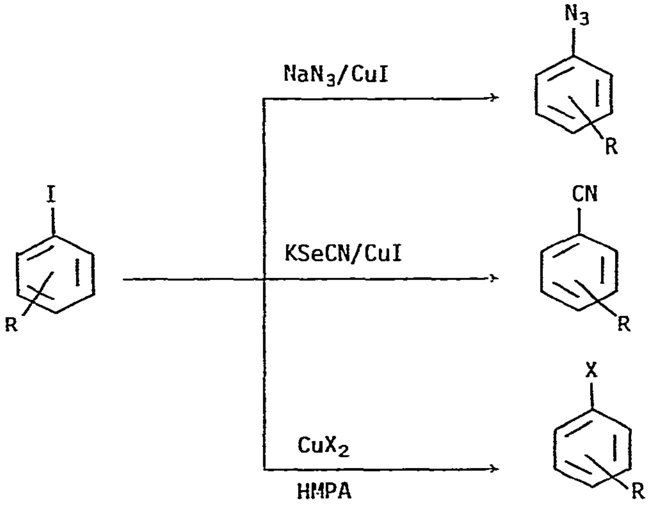
A. Halides

Aryl halides were converted to iodides by their reaction with zinc metal, nickel halide, and potassium iodide (equation 393) [839]. In turn, aryl iodides were converted to other halides by copper(II) halides in HMPA. This same process was used to make aryl azides and nitriles (equation 394) [840]. Aryl halides resulted from the reaction of anilines with nitroso or nitrito compounds in the presence of copper(II) halides (equation 395) [841]. Tribromoaromatics were the products of the reaction of anilines with bromine and t-butylnitrite in the presence of copper(II) bromide (equation 396) [842]. Nickel(0) and nickel(I) complexes catalyzed the halide exchange reaction of aryl and vinyl bromides (equations 397-400) [843].



(393)

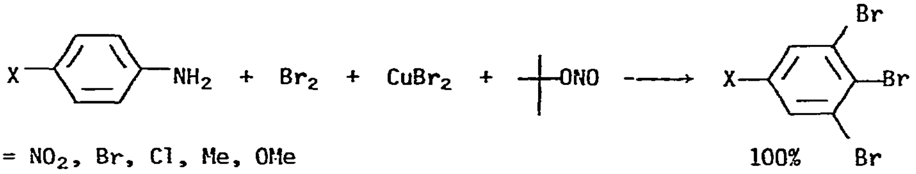
X = Br, Cl
Y = 4-OMe, 4-COMe, 4-Cl
3-CO$_2$Me, 2-Me, 2-OMe



(394)

$$ArNH_2 + \begin{matrix} t\text{-}BuS\text{-}NO \\ or \\ t\text{-}BuSNO_2 \end{matrix} \xrightarrow[CH_3CN \quad 0\text{-}25^{\circ}]{CuX_2} \begin{matrix} ArX + N_2 \\ \text{good yields} \end{matrix} \qquad (395)$$

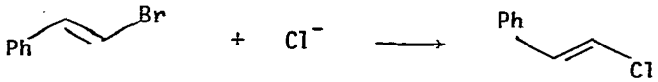
(396)



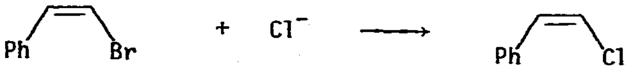
X = NO_2, Br, Cl, Me, OMe

$$ArI + Bu_4NBr \overset{Ni(0)}{\rightleftharpoons} ArBr \qquad (397)$$

$$ArBr + Bu_4NCl \rightleftharpoons ArCl \qquad (398)$$



(399)

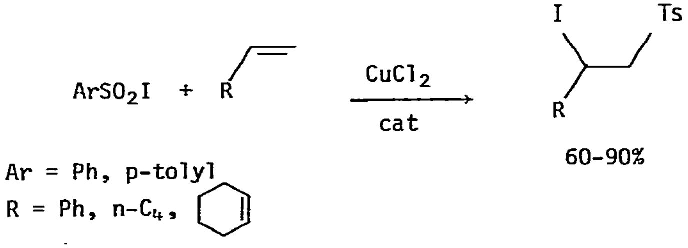


(400)

Copper(II) or iron(III) chloride converted trimethylsilyl enol ethers to α-chloroketones in 58-70% yield [844]. Olefins were converted to chiral halides via a metal-catalyzed hydrosilylation followed by an oxidative cleavage (equation 401) [845]. Copper(II) chloride catalyzed the addition of tosyl iodide to olefins (equation 402) [846]. Iron carbonyls catalyzed the addition of carbon tetrachloride to olefins (equation 403) [847]. Tungsten carbonyl in carbon tetrachloride converted olefins to gem-dichloro-olefins (equation 404) [848].

$$RCH{=}CHR' \xrightarrow[\text{Pd-PPFA*}]{HSiCl_3} R\overset{*}{C}HCH_2R' \,(\underset{|}{}SiCl_3) \xrightarrow[\text{2) NBS}]{\text{1) KF}} R\overset{*}{C}HCH_2R' \,(Br) \qquad (401)$$

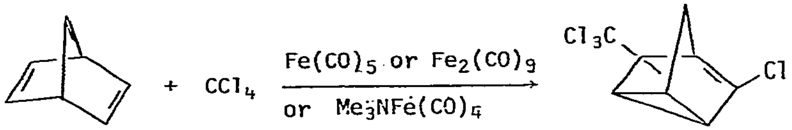
up to 50% ee



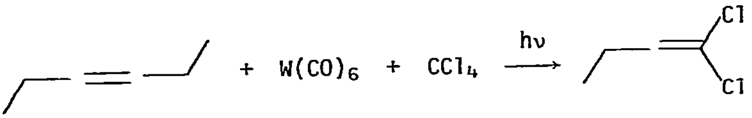
Ar = Ph, p-tolyl

R = Ph, n-C_4,

(402)



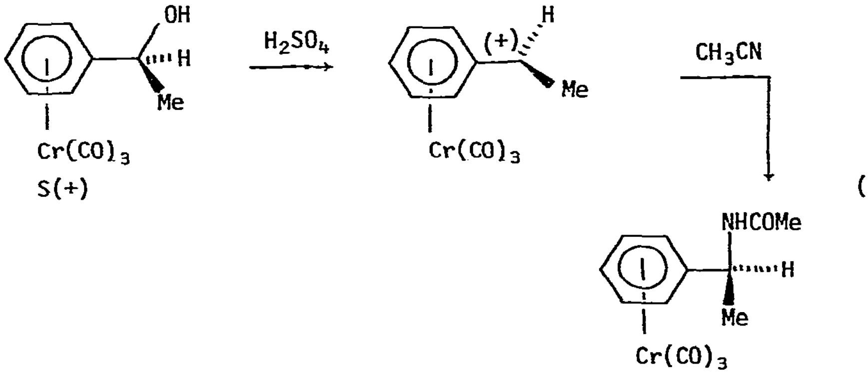
(403)



(404)

B. Amides, Nitriles

Acrylonitrile was hydrolyzed to acrylamide at 50-70° in the presence of [PdCl(OH)$_2$(bipy)(H$_2$O)] [849]. Complexes of the type Pt(OH)RL$_2$ and Pt(NHCOMe)RL$_2$ catalyzed the hydrolysis of nitriles to amides, but were less efficient than $(R_3P)_nPt$ [850]. Rhodium(III) chloride accelerated the conversion of esters to amides by reaction with amines [851]. Benzyl amides were prepared in high optical yield by the reaction of chromium stabilized benzyl cations with acetonitrile (equation 405) [852]. The complex [DIOP]Pd catalyzed the addition of HCN to norbornene to give 2-exo-cyanonorbornane in 30% optical yield [853].

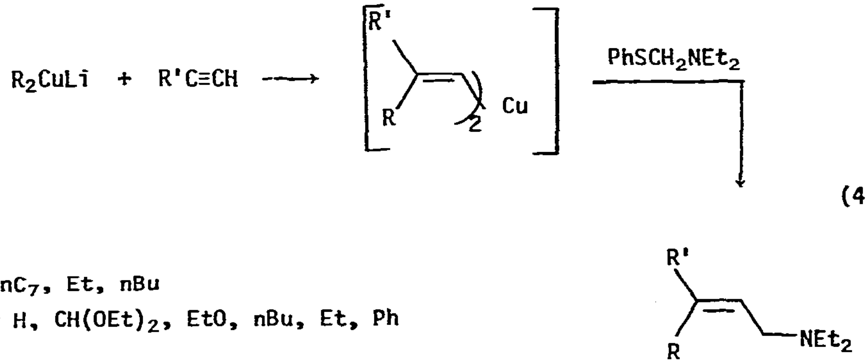


92% optical purity

(405)

C. Amines, Alcohols

Allyl amines were prepared from vinylcuprates by reaction with $PhSCH_2NEt_2$ (equation 406) [854]. Olefins were aminomethylated by amines and carbon monoxide in the presence of $Rh_6(CO)_{16}$ or $Fe_3(CO)_{12}$ catalysts (equation 407) [855]. Copper(II) bromide catalyzed the amination of 2-chloro-benzimidazole (equation 408) [856]. 1-Aminoanthraquinones, available from the stoichiometric reaction of primary amines with anthraquinones in the presence of rhodium(I) complexes [857], were aminated in the 4 position by reaction with primary amines in the presence of Cobalt(II) chloride and oxygen (equation 409) [858, 859]. The reaction of amines with chromium-stabilized benzyl cations produced benzyl amines in fair to good yield (equation 410) [860].

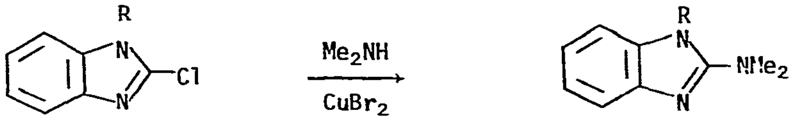


60-90%

(406)

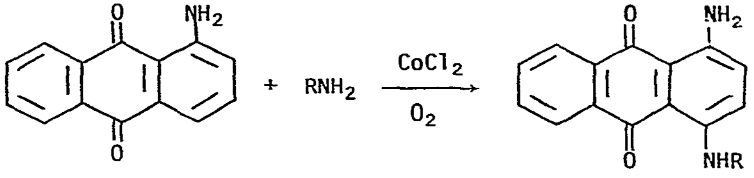
R = nC_7, Et, nBu
R' = H, $CH(OEt)_2$, EtO, nBu, Et, Ph

$$R'_2NH + RCH{=}CH_2 + CO + H_2 \xrightarrow{Rh_6(CO)_{16}} R(CH_2)_3NR'_2 + CO_2 \qquad (407)$$



(408)

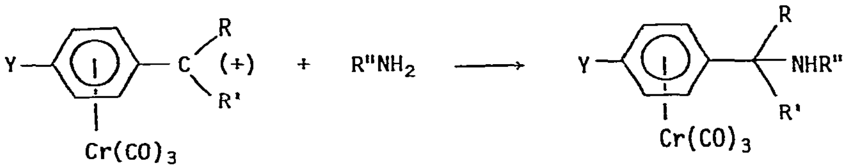
R = Me, Ph, H



(409)

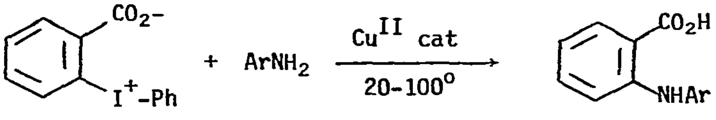
R =	Me,	nBu,	secBu	n-C_8,	cyclohexyl,	$PhCH_2$
	39%	79%	38%	34%	52%	6%

(410)



30-90%

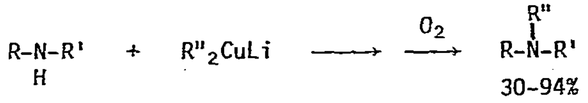
Nickel(II) or cobalt(II) acetate-bipyridine complexes catalyzed the Michael addition of aniline to α,β-unsaturated ketones, esters, and nitriles [861]. Amines reacted with diphenyliodonium-2-carboxylates to produce o-aminobenzoic acids (equation 411) [862]. Aniline was produced in the reaction of o-nitrochlorobenzene with ammonia in the presence of copper compounds [863].



60-90%

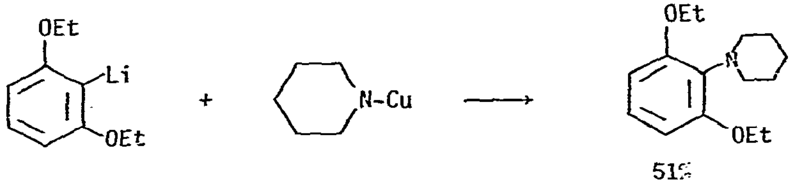
(411)

Secondary amines were alkylated by treatment with dialkylcuprates followed by an oxidative isolation procedure (equation 412). Alternatively, aryllithium reagents were aminated by copper amine complexes (equation 413) [864]. Rhodium, iridium, ruthenium, and osmium carbonyl clusters scrambled alkyl groups on tertiary amines (equation 414) [865]. Tertiary amines were dealkylated by treatment with PhSeNa in the presence of reduced ruthenium (equations 415-418) [866]. Palladium and nickel promoted amination of olefinic double bonds was the subject of a review (78 references) [867]. The full experimental details of the palladium assisted oxyamination of olefins have been published (equation 419) [868]. Alkenes were diaminated by reaction with NO and $CpCo(CO)_2$, followed by reductive cleavage (equation 420) [869]. Sodium borohydride converted alkenes to alcohols in the presence of titanium tetrachloride, in a process whose product resembled that formed by hydroboration-oxidation [870]. Bis-(cyclooctadiene)nickel decarboxylated aryl carboxylates to produce olefins and phenols (equation 421) [871].



$$\underset{H}{R\text{-}N\text{-}R'} + R''_2CuLi \longrightarrow \xrightarrow{O_2} \overset{R''}{R\text{-}N\text{-}R'} \quad 30\text{-}94\% \qquad (412)$$

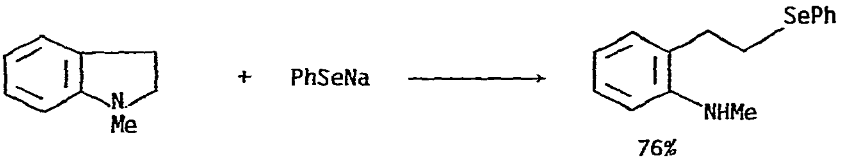
R = n-C_6, cyclo C_6, Bz, n-C_{10}, Ph
R' = nC_4, cyclo C_6, Bz, H, Me, Ph
R'' = nBu, Me, Ph, t-Bu



(413)

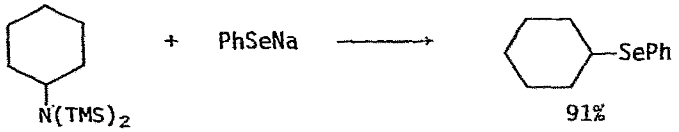
$$Et_3N + nPr_3N \underset{}{\overset{cat.}{\rightleftharpoons}} Et_2NPr + Pr_2NEt \qquad \text{cat} = Rh_6(CO)_{16}, Ir_4(CO)_{12}, Ru_3(CO)_{12}, Os_3(CO)_{12} \qquad (414)$$

$$R^1R^2R^3N + PhSeNa \xrightarrow[2)\ H_2O]{1)\ RuCl_3/K,\ 80\text{-}150^\circ} R^1SePh + R^2R^3NH \qquad (415)$$

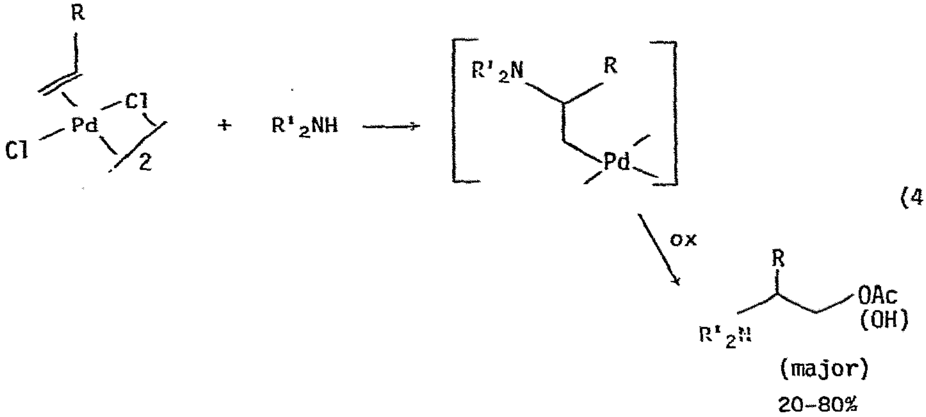


(416)

(417)

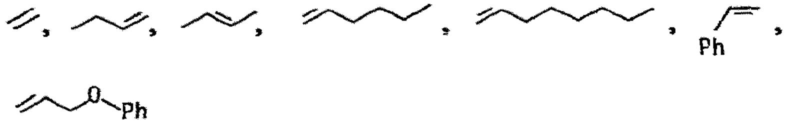


(418)



(419)

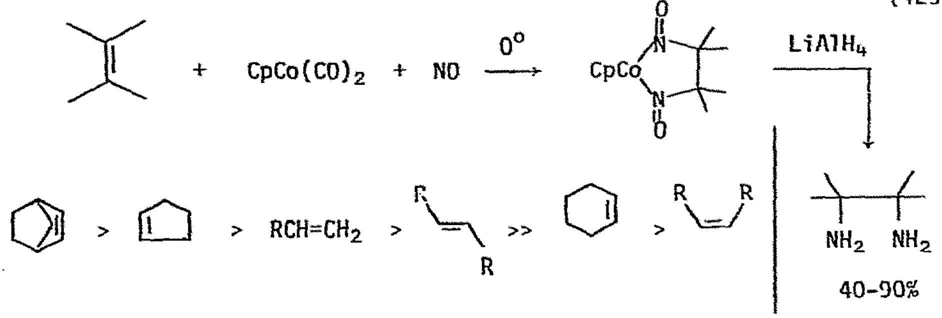
olefin =



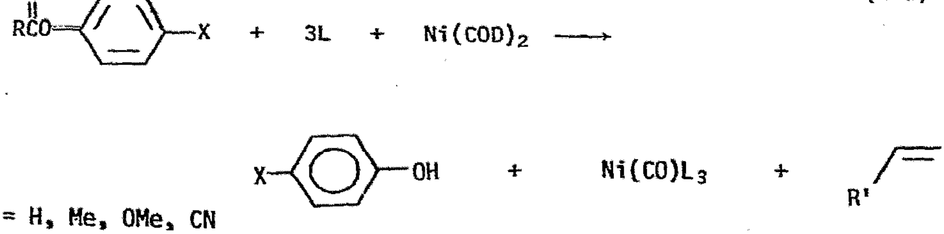
R'$_2$NH = Et_2NH, $PhCH_2NHMe$, Me_2NH

OX = NBS, $Pb(OAc)_4$, Br_2

(420)



(421)



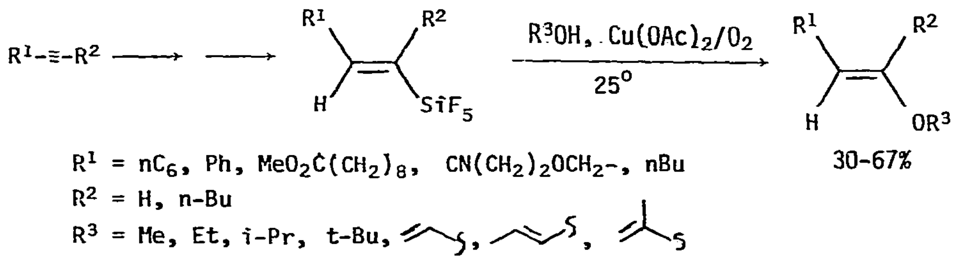
X = H, Me, OMe, CN

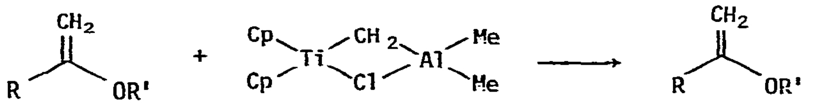
R = Et, nPr

D. Ethers, Esters, Acids

Vinyl ethers were prepared from alkynes by hydrosilylation followed by copper(II) acetate oxidation in alcohol solvent (equation 422) [872]. A titanium carbene complex converted esters to vinyl ethers in excellent yield (equations 423-427) [873]. The alcohol portion of vinyl ethers exchanged with other alcohols in the presence of silica-bound palladium-phosphine complexes [874]. Allyl ethers, used as hydroxyl protecting groups in carbohydrate chemistry, rearranged to vinyl ethers, for subsequent removal by hydrolysis, when treated with L_3RhCl. In contrast, prenyl ethers did not rearrange under these conditions. Hence the allyl group could be removed in the presence of the prenyl group [875]. Cyclohexadiene was converted to trans-3-acetoxy-6-methoxycyclohex-1-ene in a palladium(II) assisted dialkoxylation (equation 428) [876]. The complex $Pd_4(CO)_4$-$(OAc)_4$ converted olefins into allyl ethers when treated with methanol and oxygen in the presence of bipyridine [877]. Copper(II) bromide in methanol converted a 9-anthracenyl-methyl group to a methyl ether group (equation 429) [878]. A number of catalysts converted diphenylcarbinol to mixtures of products among which was dibenzyl ether (equation 430) [879]. Ferric chloride catalyzed the glycosylation of alcohols by 2-acylamido-2-deoxy-β-D-glucopyranose-1-acetates [880], and catalyzed the coupling of protected sugar acceptors to the same substrate [881].

(422)

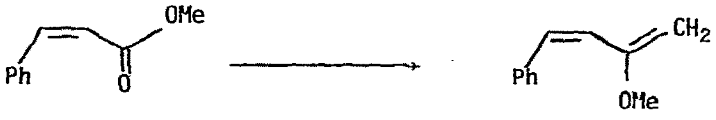




(423)

(424)

96%



79% (90% Z)

(425)

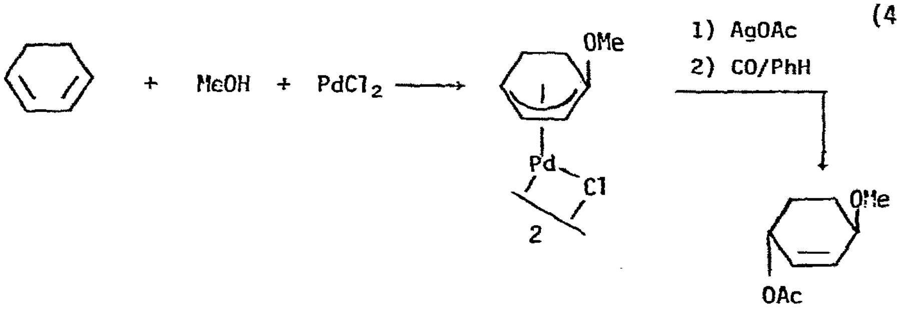
85%

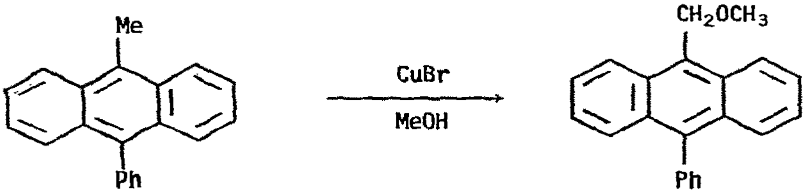
(426)

81%

(427)

(428)





(429)

(430)

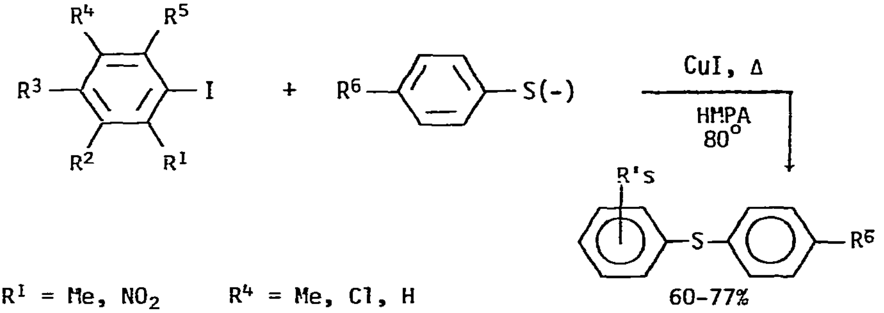
$$Ph_2CHOH + cat. \xrightarrow{200^\circ} (Ph_2CH_2)_2O + (Ph_2CH)_2 + Ph_2CO + Ph_2CH_2 + Ph_2CHOH$$

cat = L_4Pt, $PtCl_2L_2$, $PdCl_2L_2$, L_3RhBr, L_3RhCl, $[Rh(CO)_2Cl]_2$

Palladium(0) complexes coupled aryl halides with thiols to produce thioethers (equation 431) [882]. Copper(I) iodide promoted a similar coupling of aryl iodides to thiophenoxides (equation 432) [883]. Arenesulfonyl chlorides reacted with allyl and crotylcobaloximes to produce allyl and cyclopropylcarbinyl sulfides (equation 433) [884]. Copper(I) triflate converted thioacetals to vinyl sulfides in 76-94% yield [885]. Acid chlorides were converted to thioesters by reaction with RSCu (equation 434) [886].

$$\mathrm{ArX} + \mathrm{RSH} \xrightarrow[\mathrm{DMSO},\ 100^\circ]{L_4\mathrm{Pd}} \underset{6\text{-}100\%}{\mathrm{ArSR}} \qquad (431)$$

Ar = Ph, p-tolyl, p-OMe, p-Cl
R = Ph, t-Bu, Et

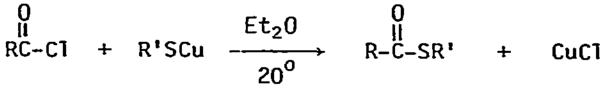


(432)

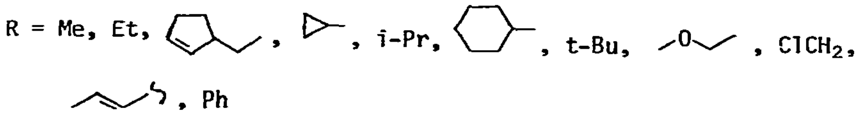
R^1 = Me, NO_2
R^2 = Me, H
R^3 = Me, H

R^4 = Me, Cl, H
R^5 = Me, H
R^6 = H, Cl

(433)



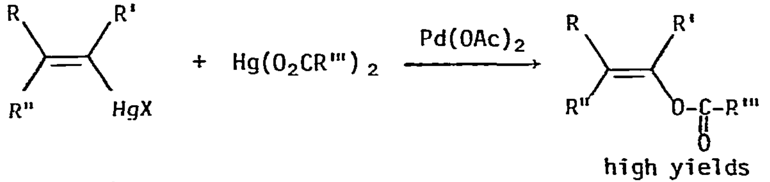
$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}Cl} + \mathrm{R'SCu} \xrightarrow[20^\circ]{\mathrm{Et_2O}} \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}SR'} + \mathrm{CuCl} \qquad (434)$$



R = Me, Et, , , i-Pr, , t-Bu, , $ClCH_2$, , Ph

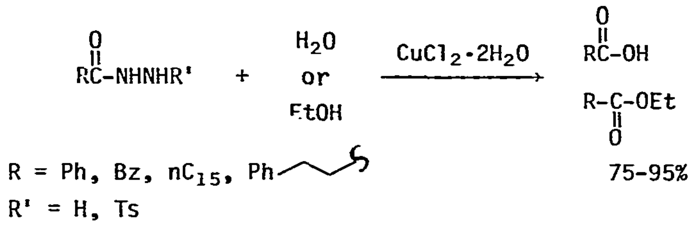
R' = Ph, p-tolyl, p-ClPh, t-Bu

Palladium(II) acetate catalyzed the reaction of vinylmercuric halides with mercury(II) carboxylates to produce vinyl ethers (equation 435) [887]. Aryl amines were converted to aryl carboxylic acids by diazotization followed by reaction with carbon monoxide in the presence of palladium catalysts [888]. Copper(II) chloride assisted the solvolysis of acid hydrazines to acids or esters (equation 436) [889]. Acetic anhydride fully acetylated carbohydrates in the presence of iron(III) chloride [890]. Aryl diazonium salts reacted with carboxylic acid salts in the presence of palladium(II) acetate to produce mixed acid anhydrides in 40-80% yield [891]. Sodium chloropalladate converted γ-benzyl glutamate to pyroglutamic acid [892].



(435)

R = t-Bu, Ph, OAc, nBu
R' = H, Me, Ph, tolyl, Et
R" = H, Et, OAc



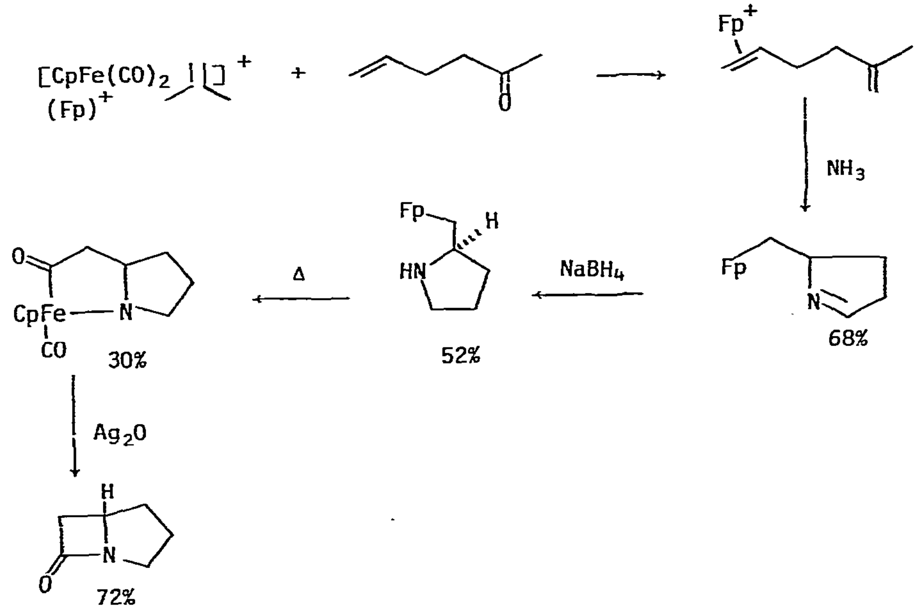
(436)

R = Ph, Bz, nC_{15}, Ph
R' = H, Ts

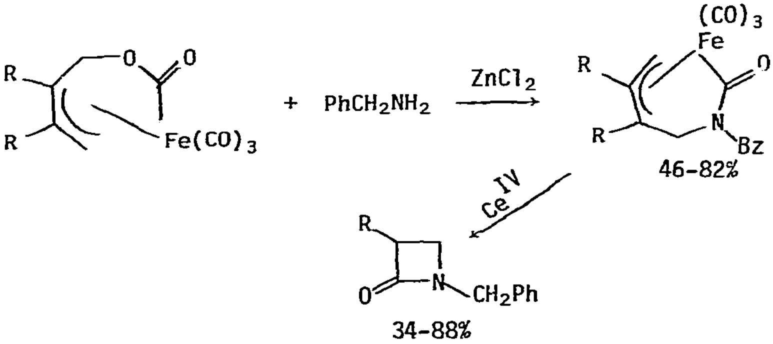
E. Heterocycles

The synthesis of heterocycles via organometallic complexes has been reviewed in two separate articles [893] (72 references) [894] (86 references). β-Lactams were synthesized from γ,δ-unsaturated ketones using $CpFe(CO)_2^+$ chemistr (equation 437) [895]. Simple β-lactams were produced by the oxidative cleavage of a π-allyliron carbamoyl complex (equation 438) [896]. Trimethylsilylenol ethers condensed with imines to produce β-lactams (equation 439) [897] [898]. Penicillanic acid rearranged to a fused β-lactam system when treated with copper(II) acetylacetonate (equation 440) [899].

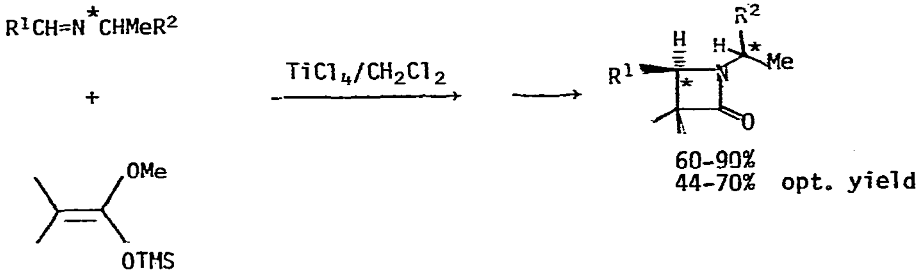
(437)



(438)

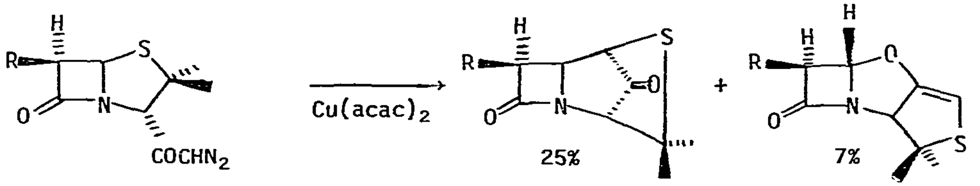


(439)



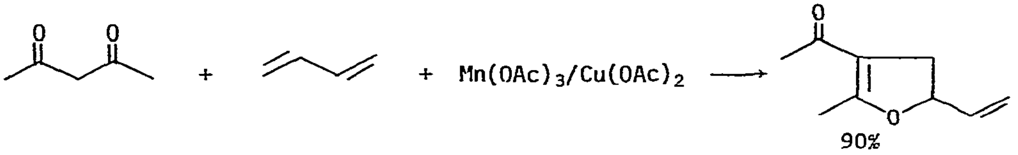
R^1 = Et, n-Pr, i-Pr, i-Bu, nBu
R^2 = Ph, 1-Np

(440)

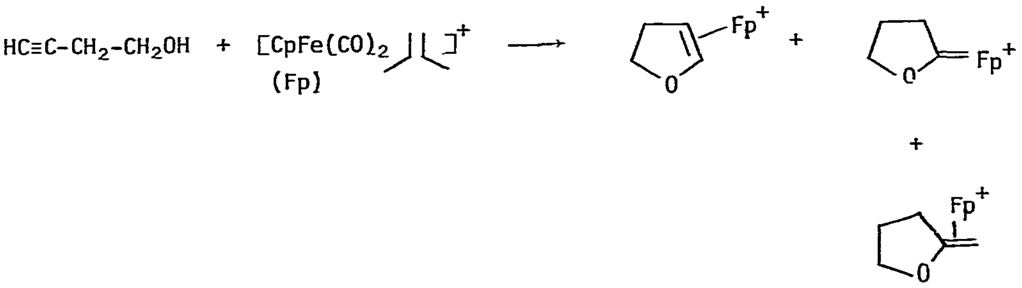


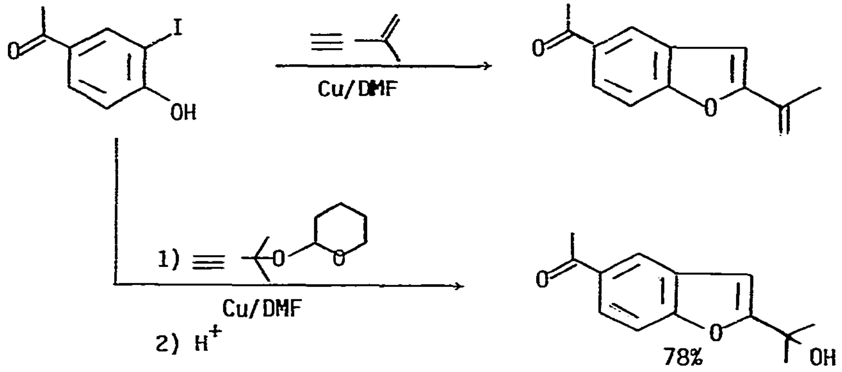
Acetylacetone reacted with butadiene in the presence of manganese(III) acetate/copper(II) acetate to produce dihydrofurans (equation 441) [900]. γ,δ-Acetylenic alcohols reacted with [CpFe(CO)$_2$(olefin)]$^+$ complexes to produce dihydrofuran complexes (equation 442) [901]. Terminal alkynes and o-iodophenols combined to produce benzofurans in the presence of copper powder (equation 443) [902]. Tolan reacted with σ-alkyliron complexes under irradiation to give furans or thiophenes (equations 444 and 445) [903]. Benzopyrans were produced from arene chromium tricarbonyl complexes (equation 446). Arene rhodium complexes catalyzed this transformation (equation 447) [904].

(441)

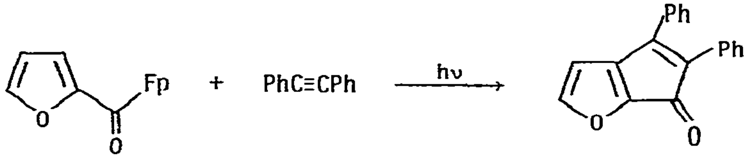


(442)



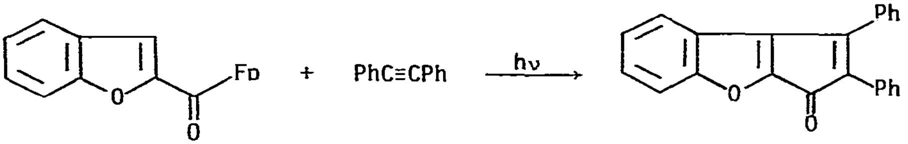


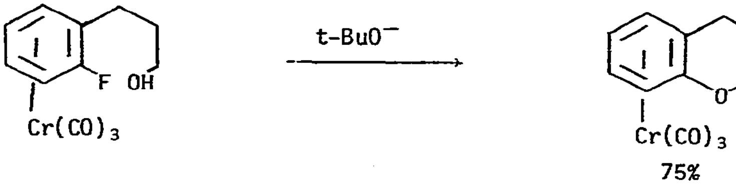
(443)



(444)

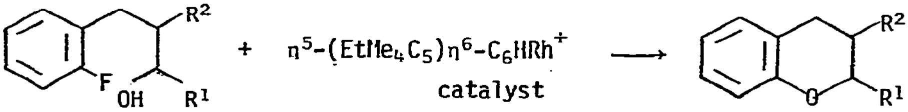
(445)



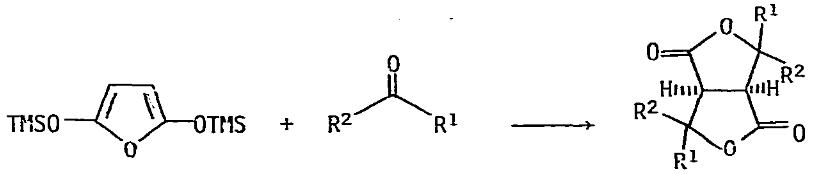


(446)

(447)



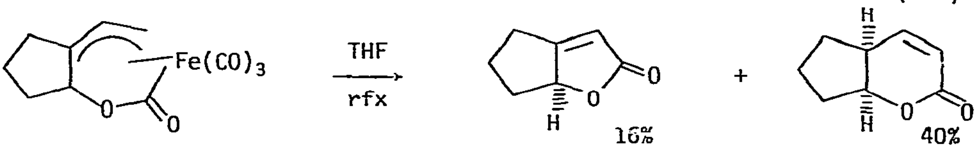
Titanium(IV) chloride converted 2,5-bis(trimethylsiloxyl)furan into fused bis lactones (equation 448) [905]. Lactones were produced by the thermal decomposition of π-allyliron carbonato complexes (equation 449) [906]. Isocoumarins were produced in the reaction of *o*-iodobenzoic acids with copper acetylides (equation 450) [907]. Aldehydes condensed with phenols to form cyclic acetals in the presence of potassium and titanium(IV) chloride (equation 451) [908]. Cyclic carbonates were produced in the reaction of epoxides with carbon dioxide in the presence of copper or nickel [909] or cobalt, iron, or molybdenum catalysts (equation 452) [910].



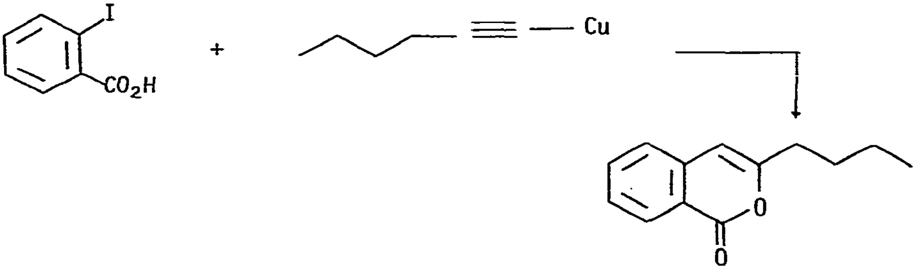
(448)

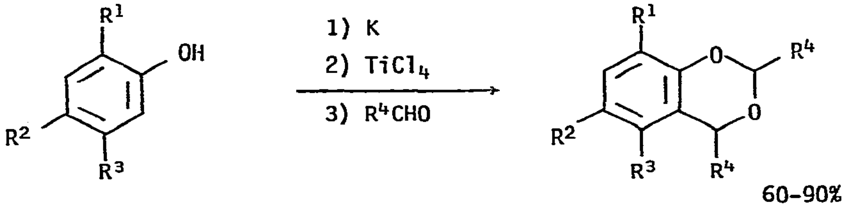
R's = Me, H, Ar, i-Bu

(449)

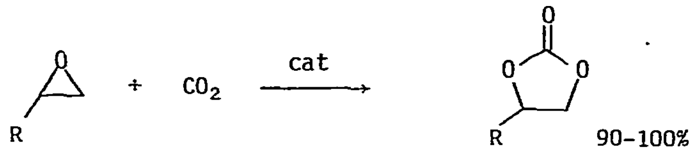


(450)





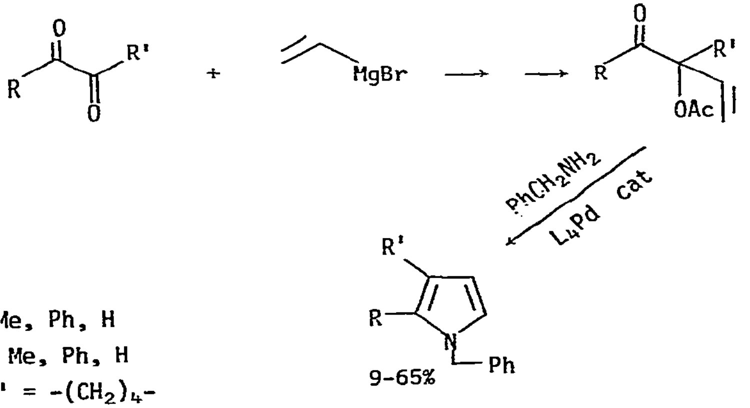
(451)



(452)

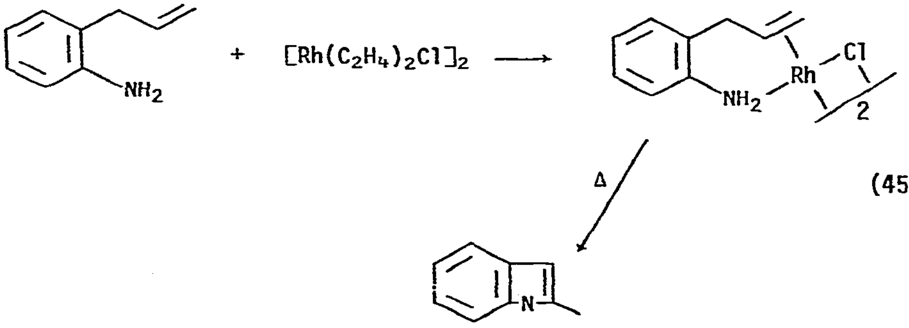
cat = $CuCl_2$, $NiCl_2$, $CoCl_2$, $FeCl_3$, $MoCl_5$
+ Ph_3P

β-Dicarbonyl systems reacted with vinylmagnesium bromide to yield, after acylation, α-ketoallylacetates. Reaction of these with benzyl amine and palladium(0) catalysts produced pyrroles (equation 453) [911]. 4-Amino pentenes very slowly cyclized to pyrrolidines and piperidines when exposed to $PtCl_4^{=}$ in acidic media [912]. The reaction of 2-allylaniline with rhodium(I) complexes produced stable aminoolefin complexes which when heated produced 2-methylindole (equation 454) [913]. In contrast, the same set of reactions with N-allylaniline produced a complex which reacted with diphenylacetylene to produce pyrroles (equation 455) [913].



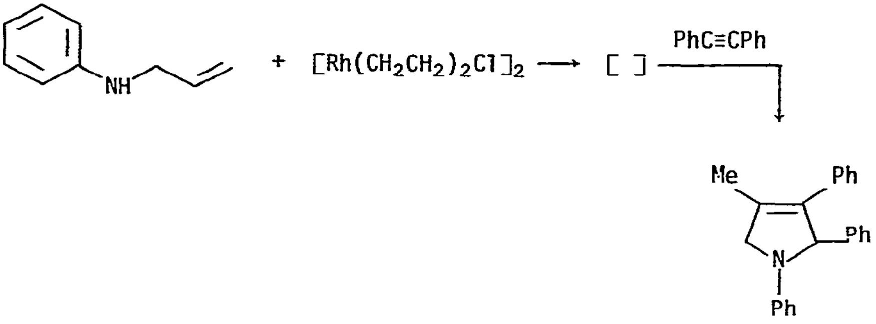
(453)

R = Me, Ph, H
R' = Me, Ph, H
R, R' = $-(CH_2)_4-$



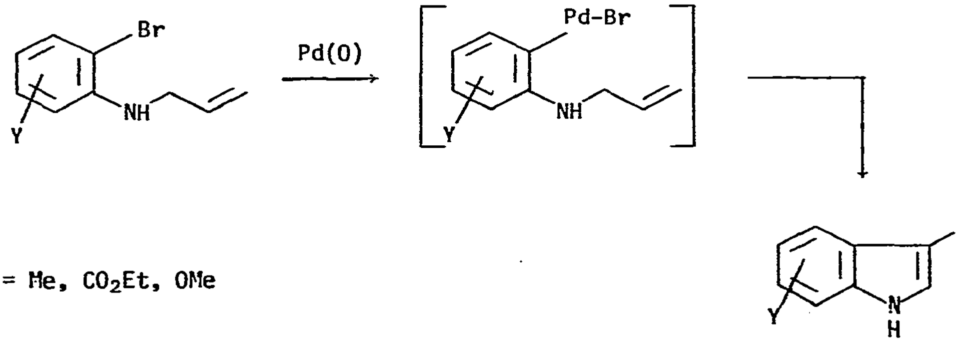
(454)

(455)



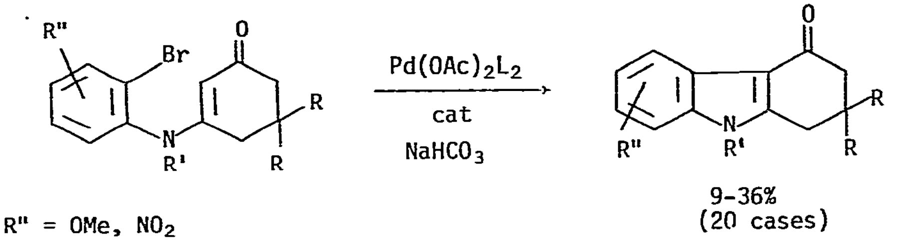
Palladium(0) catalyzed the cyclization of 2-halo-N-allylanilines to indoles by an oxidative addition-insertion process (equation 456) [914]. Carbazoles were produced in a similar fashion, by insertion of enaminones (equation 457) [915]. Unsaturated N-acyl-2-haloanilines cyclized to oxindoles when treated with electrochemically generated nickel(0) complexes (equation 458) [916]. N-Arylanilines cyclized to indoles when treated with palladium(II) acetate and trifluoroacetic acid (equation 459) [917]. Indoles and oxindoles were produced by the cyclization of *o*-bromophenylacetamides by copper(I) iodide and sodium hydride (equation 460) [918]. Aryl hydrazines reacted with ketones in the presence of a rhodium catalyst at 180° to produce indoles in a process reminiscent of the Fischer indole synthesis (equation 461) [919]. Palladium(II) chloride catalyzed the cyclization of 2-allylanilines to α-alkyl palladium complexes which inserted CO (equation 462) and conjugated enones (equation 463) to give functionalized indolines. When the conjugated enone was in the form of an acrylamide tricyclic material was formed in excellent yield (equation 464) [920]. Palladium(II) acetylacetonate in glacial acetic acid catalyzed the 1 and 3 alkylation of indoles (equation 465) [921].

(456)

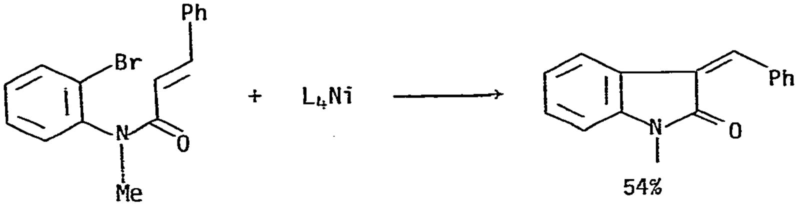


Y = Me, CO_2Et, OMe

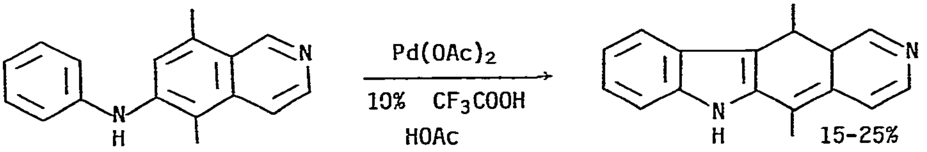
good yield
(8 cases)



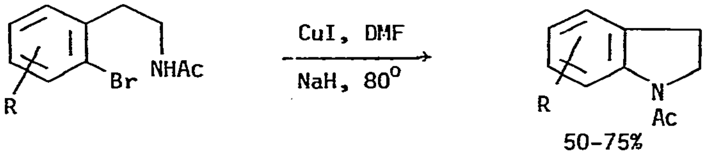
(457)



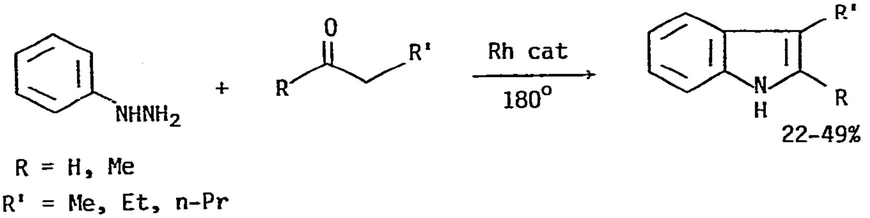
(458)



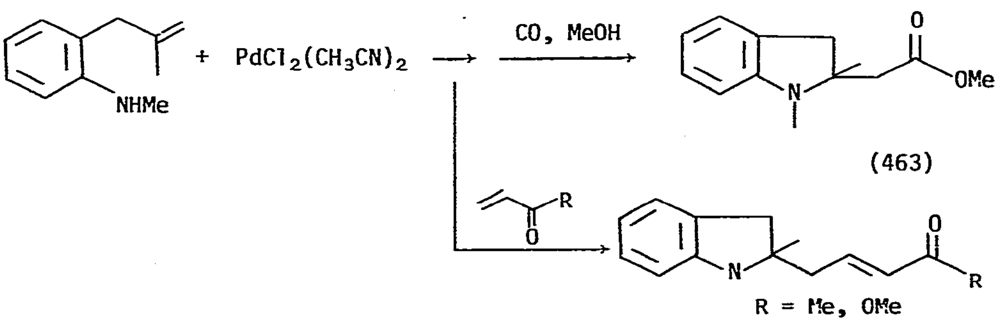
(459)



(460)

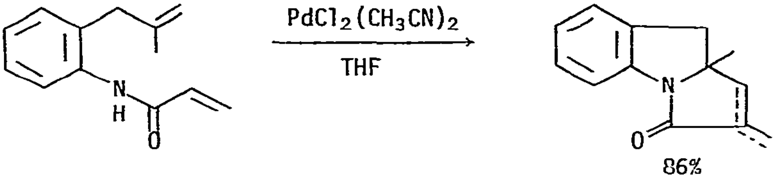


(461)



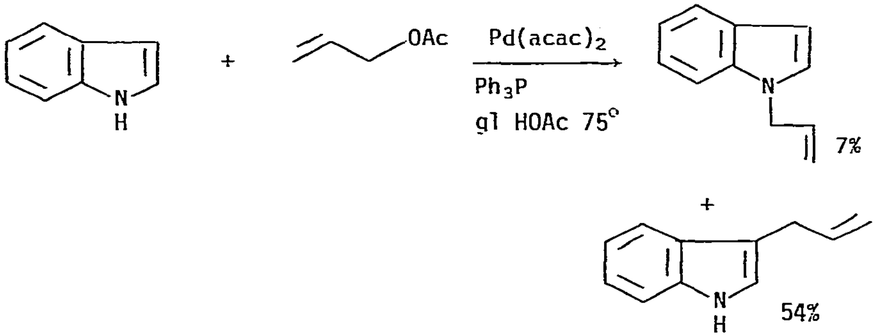
(462)

(463)



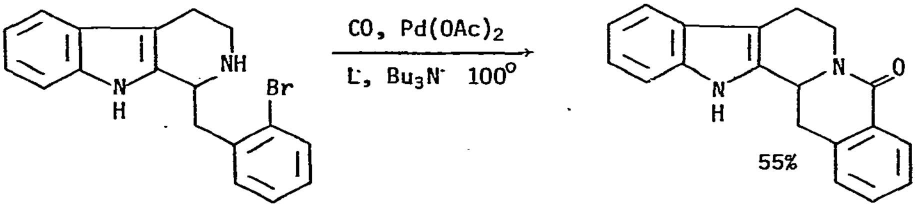
(464)

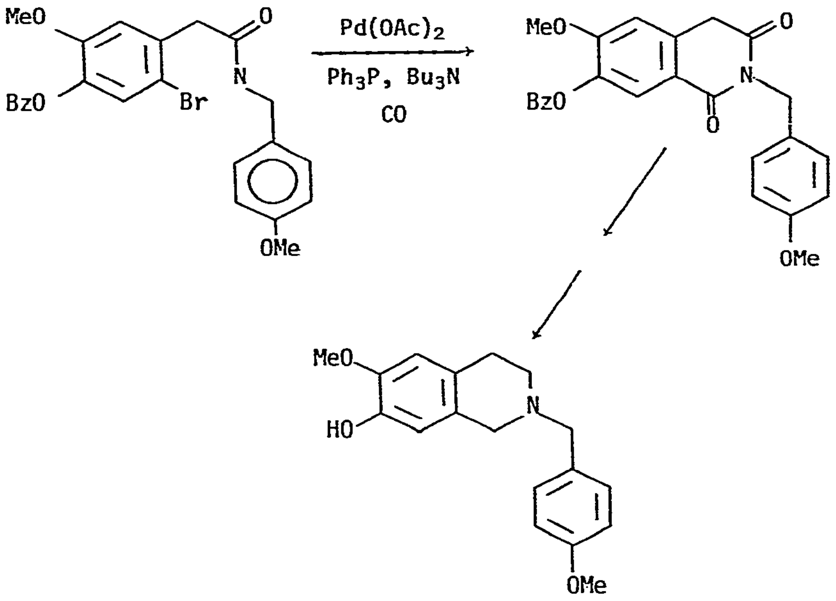
(465)



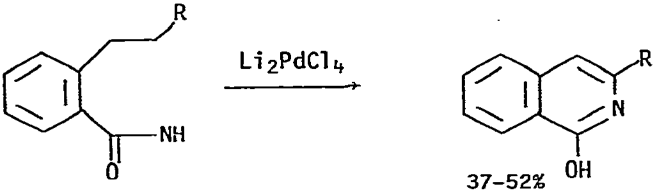
The yohimbane skeleton was synthesized using a palladium(0) catalyzed cyclization-carbonylation process (equation 466) [922]. Identical chemistry was used in a synthesis of sendevarine, for which no yields were reported (equation 467) [923]. Using a reaction reported several years ago, 1-hydroxyisoquinolines were synthesized from o-amidostilbene by palladium catalysis (equation 468) [924]. Nitrobenzene and butyraldehyde reacted with carbon monoxide in the presence of a rhodium-palladium catalyst to produce quinolines (equation 469) [925]. Aniline and ethylene reacted to form quinaldine and N-ethylaniline when heated to 150-200° for several days in the presence of rhodium(III) chloride [926]. Propargyl alcohol, piperidine and 2-bromopyridine combined to form 3-(dialkylamino)indolizines when treated with palladium(II) and copper(I) salts (equation 470) [927]. Novel chromium carbonyl complexes of dihydropyridines and their application to the synthesis of dehydrosecodine was the topic of a dissertation [928].

(466)





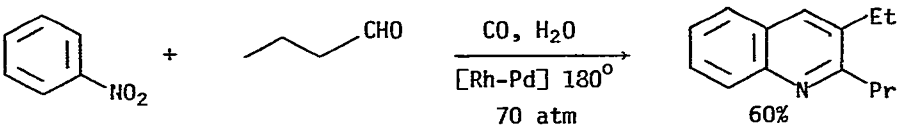
(467)



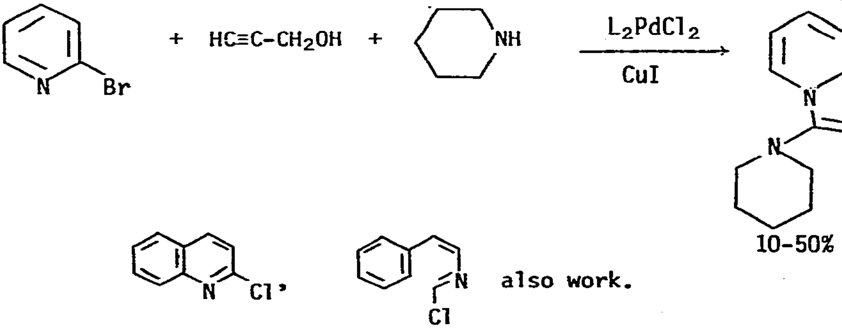
(468)

R = p-tolyl, PhCO, CN

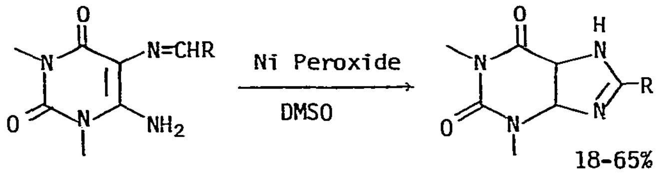
(469)



(470)

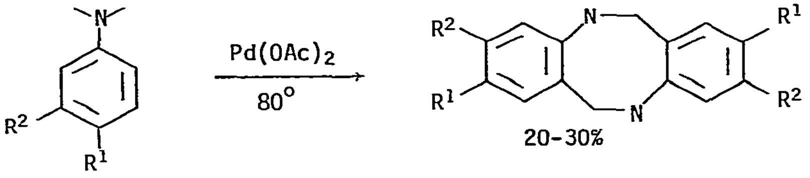


8-Substituted theophyllines were synthesized from pyrimidine imines by a nickel peroxide assisted cyclization (equation 471) [929]. N,N-Dimethylanilines dimerized when treated with palladium(II) acetate at 80° (equation 472) [930]. Copper(I) and copper(II) chloride annulated ethylene diamine onto 1,4-dihydroxyanthraquinone (equation 473) [931].



(471)

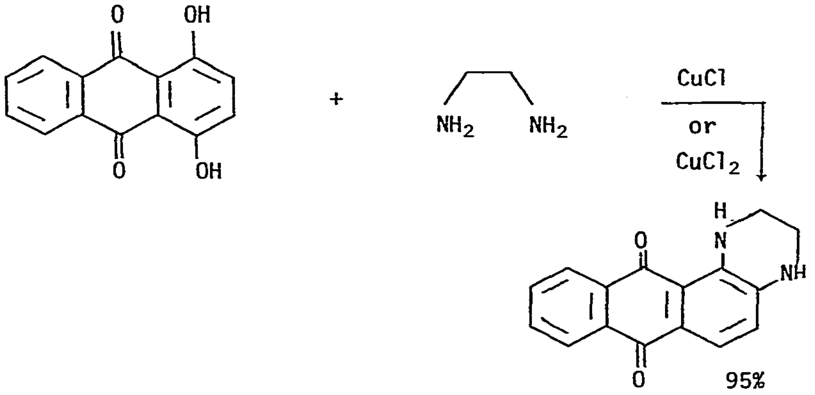
R = Ph, p-OMePh, p-ClPh, p-NO_2Ph, 2-Py



(472)

R^1 = OMe, Me R^2 = H, Me

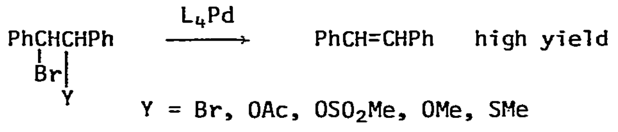
(473)



F. Alkenes, Dienes

Stilbenes were produced by palladium(0) catalyzed eliminations of vicinal leaving groups (equation 474) [932]. The same catalyst produced dienes from β-carboxyallylacetates (equation 475). The chemistry was used to synthesize codlemone (equation 476) [933]. Similar elimination reactions involving π-allylpalladium intermediates were used to prepare steroidal dienes (equation 477) [934] and pellitorine (equation 478) [935]. The chemistry in equation 479 produced terminal methylene compounds [936].

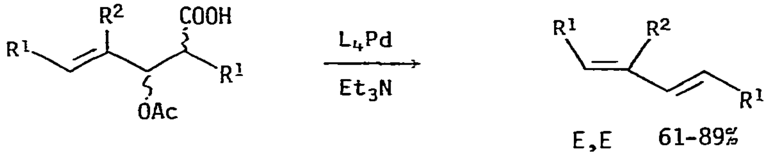
Copper bromide catalyzed the decomposition of aryldiazomethanes to produce mixtures of <u>cis</u> and <u>trans</u> stilbenes [937]. Iron carbonyl complexed to two adjacent double bonds of symmetrical 1,3,5-trienes, and acted as a protecting group for that diene unit, while permitting reactions at the uncomplexed site [938].



$$\underset{\substack{|\\ Br}}{PhC}H\underset{\substack{|\\ Y}}{C}HPh \xrightarrow{L_4Pd} PhCH{=}CHPh \quad \text{high yield}$$

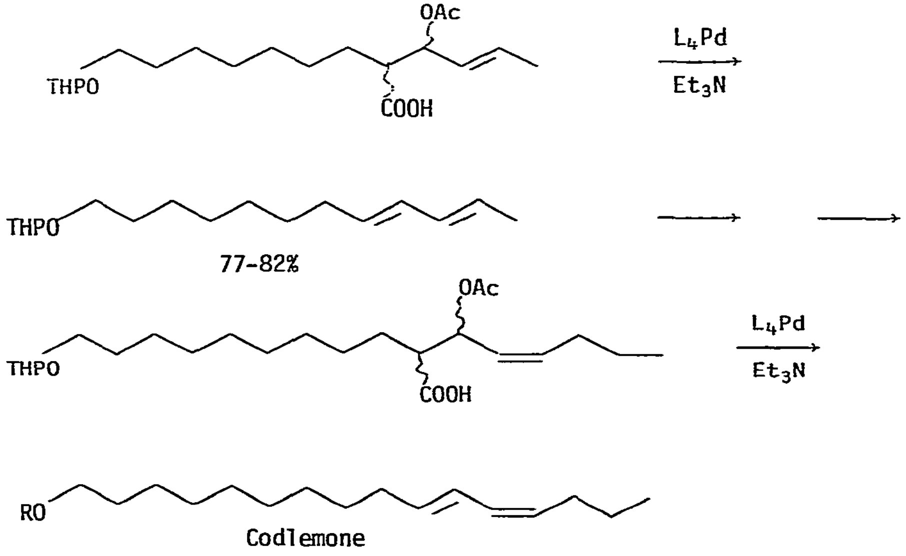
Y = Br, OAc, OSO_2Me, OMe, SMe

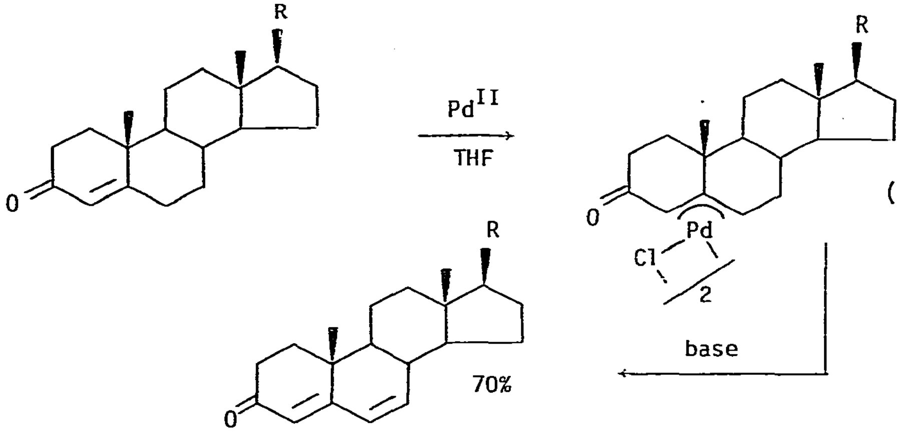
(474)



(475)

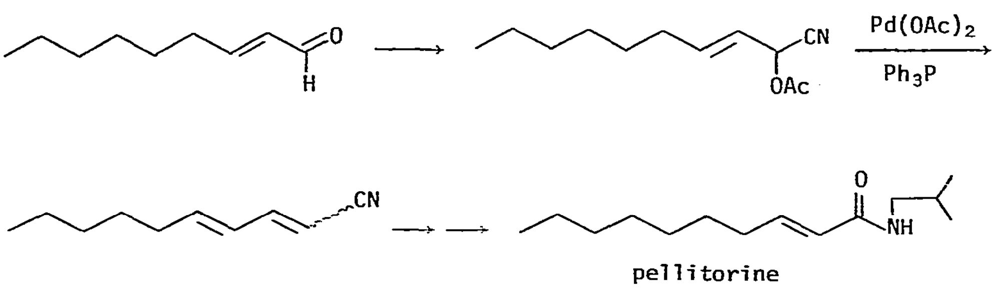
(476)

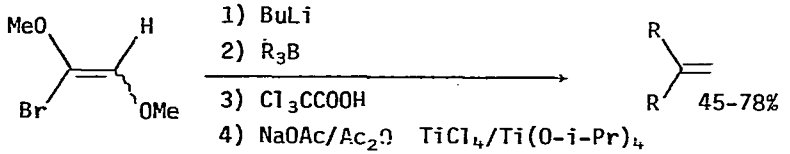




(477)

(478)



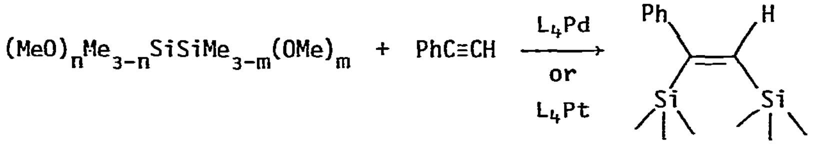


(479)

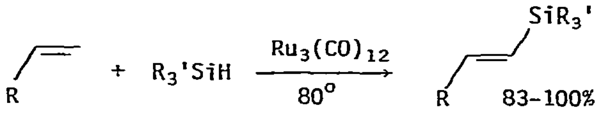
R = i-Bu, sec Bu, nC_5, cyclo C_5, nC_6, cyclo C_6

G. Organosilanes

Hexamethyldisilane reacted with benzoyl chlorides in the presence of π-allylpalladium chloride catalyst to produce substituted benzoyltrimethyl silanes [939]. Aryl, benzyl, and allyl chlorides reacted with $Cl_2MeSiSiMeCl_2$ in the presence of nickelocene as catalyst to produce the corresponding trichlorosilanes, $ArSiCl_3$, $ArCH_2SiCl_3$, and allyl $SiCl_3$ [940]. These same chlorinated disilanes added 1,4 to substituted butadienes to produce 1,4-disilyl-2-butenes in the presence of a palladium(0) catalyst [941]. Alkynes underwent disilylation when reacted with methoxy disilanes (equation 480) [942]. Trialkylvinyl silanes were prepared from olefins by reaction with trialkylsilanes in the presence of a ruthenium catalyst (equation 481) [943].



(480)

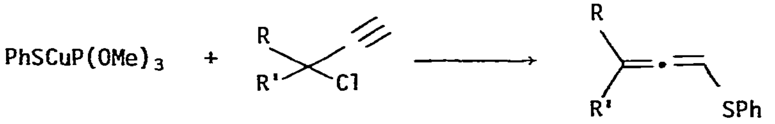


(481)

R = Ph, p-tolyl, p-ClPh, p-OMePh, 2-napht., $PhOCH_2$
R' = Et, Me

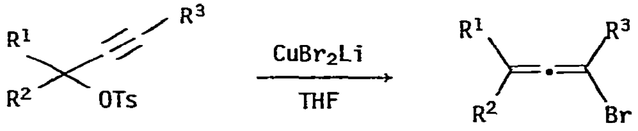
H. Miscellaneous

Thiophenoxide complexes of copper converted propargyl chlorides to allenylsulfides (equation 482) [944]. Allenyl bromides were produced from propargyl tosylates using LiBr/CuBr (equation 483) [945].



good yields

(482)



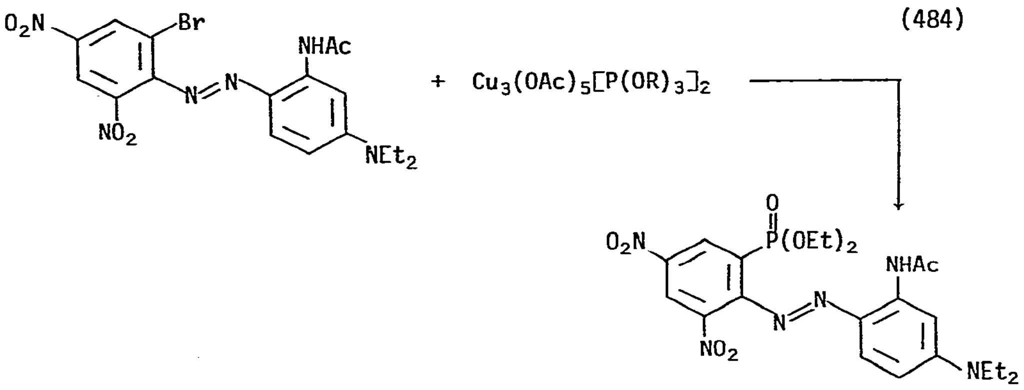
60-80%

(483)

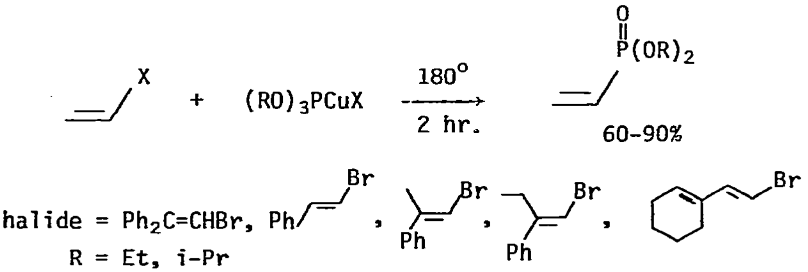
R^1 = n-Pr, Me, Ph, n-C_5, cyclo C_6
R^2 = H, Me
R^3 = H, Ph

Aryl halides were converted to aryl phosphonates by copper complexes of trialkylphosphites (equation 484) [946]. Vinyl halides underwent a similar reaction (equation 485) [947], and the same vinyl phosphonates were available from the palladium(0) catalyzed reaction of vinyl bromides with $(RO)_2P(H)O$

(equation 486) [948]. The mechanism of the nickel catalyzed Arbuzov reaction was studied [949].

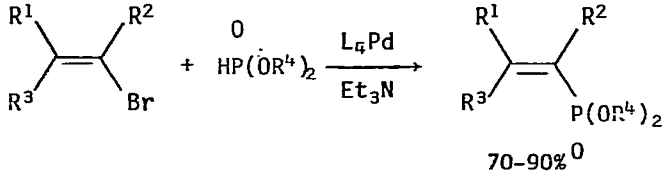


(484)



(485)

halide = $Ph_2C{=}CHBr$,
R = Et, i-Pr

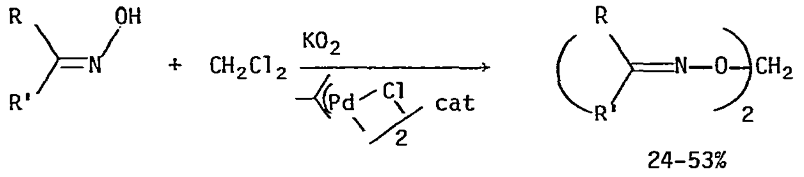


(486)

R^1 = Ph, H, Me
R^2 = H, Ph
R^3 = H, Ph
R^4 = Et, i-Pr, n-Bu

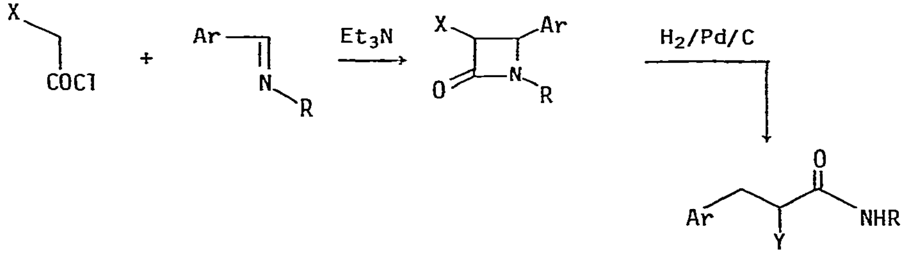
Potassium superoxide coupled ketoximes in the presence of π-allylpalladium catalysts (equation 487) [950]. Aryl β-lactams hydrogenolyzed over Pd on carbon to amides in high yield (equation 488) [951]. Aryl alcohols which could form stable carbanions (e.g., Ph_3COH) were deoxygenated to the hydrocarbon with potassium and iron carbonyl in toluene and HCl [952].

Thiols were desulfurized to the hydrocarbon by reaction with silica-adsorbed molybdenum hexacarbonyl [953].



(487)

(488)



$X = N_3$, $Y = NH_2$

$X = PhCH_2O$ $Y = OH$

high yield
(17 cases studied)

VI. Reviews

The following reviews have appeared:

New reagents. Part 13. In search of new organometallic reagents for organic synthesis. (65 references) [954]

Applications of novel organometallic reagents in organic synthesis. (Dissertation) [955]

Transition Metal Mediated Organic Synthesis. (24 references) [956]

Transition Metals in Organic Synthesis. (no references) [957]

Organic syntheses using transition metal catalysts. (20 references) [958]

Metal complex catalysis in chemistry and the chemical industry. (47 references) [959]

The transition metal-carbon bond and its importance for development in chemistry. (106 references) [960]

Organometallic complexes in fine chemistry. (54 references) [961]

Specialist Periodical Reports: Organometallic Chemistry, Vol. 8 [A Review of the Literature Published in 1978]. [962]

Patterns in organometallic chemistry with application in organic synthesis. (33 references) [963]

New aspects of organic syntheses catalyzed by Group VIII metal complexes. (32 references) [964]

Studies in organometallic chemistry. (Dissertation) [965]

General and synthetic methods. Organometallics in synthesis. (193 references) [966]

Activation of organic and inorganic molecules by organo transition metal complexes. (31 references) [967]

Using some compounds of transition metals in organic synthesis. (165 references) [968]

Uses of transition metals in organic synthesis: Fascinating novel synthetic routes in the synthesis of complex molecules. (20 references) [969]

New applications of metal carbonyls as reagents and catalysts in synthesis. (20 references) [970]

Synthesis chemistry using metal carbonyls. (24 references) [971]

Use of metal carbonyls in organic synthesis. Part 2. (35 references) [972]

Organic reactions of selected π-complexes. Annual survey covering the year 1978. (302 references) [973]

Novel synthetic reactions by means of palladium, nickel, and rhodium complex catalysts. (10 references) [974]

Organomercury, -rhodium, and -palladium compounds in organic synthesis. (Dissertation) [975]

Palladium catalyzed reactions of vinylic halides with amines and olefins. (no references) [976]

Application of palladium catalysts to natural product syntheses. (31 references) [977]

Nucleophilic attack on palladium coordinated olefins: Applications in organic synthesis. (Dissertation) [978]

Organic syntheses using palladium and ruthenium compounds. (199 references) [979]

Applications of palladium-catalyzed or promoted reactions to natural product syntheses. (101 references) [980]

Triarylphosphine-palladium complexes. [981]

Trimethylphosphane complexes of Ni, Co, Fe- model compounds for homogeneous catalysis. (108 references) [982]

Synthesis with electron-rich nickel triad complexes. (182 references) [983]

Iron. The preparation and reactions of tetracarbonylferrates. (20 references) [984]

Development of new organic synthesis. Reaction of iron carbonyl with polybromoketone. (3 references) [985]

Synthesis and reactivity of iron carbene complexes. (Dissertation) [986]

Platinacyclobutane chemistry. (82 references) [987]

Metallacycles as novel organic reagents. (116 references) [988]

Reaction modes of unsaturated three-membered carbocycles at transition metal catalysts. (19 references) [989]

Early transition metal organometallic reactivity. Catalytic acetylene hydrogenation and dimerization, carbene migratory insertion reactions. (Dissertation) [990]

Organozirconium compounds in organic synthesis: Cleavage reactions of carbon-zirconium bonds. (30 references) [991]

Applications of organozirconium complexes in organic synthesis. (17 references) [992]

Molybdenum and tungsten compounds utilized in organic synthesis. (69 references) [993]

Tricarbonyl(diene)iron complexes: Synthetically useful properties. [994]

Application of (arene)tricarbonylchromium complexes in organic synthesis. (17 references) [995]

Improved new synthetic methods. II. (11 references) [996]

Metal complex catalysis in the synthesis chemistry of organic sulfur compounds. (no references) [997]

Lithium, copper, mercury, selenium, and thallium compounds for organic syntheses. (60 references) [998]

Synthesis of acetylene derivatives using organometallic complexes. (109 references) [999]

Part I: Aspects of organocopper chemistry. Part II: Studies directed toward the synthesis of a sesquiterpene guaianolide α-methylene-γ-butyrolactones. (Dissertation) [1000]

Reactions of copper and silver organoacetylides. (270 references) [1001]

Synthetic methods using α-heterosubstituted organometallics. (536 references) [1002]

Hydrometalation and carbometalation reactions applicable to organic synthesis. (Dissertation) [1003]

Organic syntheses via hydroalumination of olefins catalyzed by titanium or zirconium compounds. (47 references) [1004]

Further perspectives in organometallic chemistry. [1005]

The insertion of diene hydrocarbons in a transition metal ligand bond. (242 references) [1006]

Phase-transfer catalysis in transition metal chemistry. (34 references) [1007]

Carbon-hydrogen and carbon-oxygen bond activation by transition metal complexes. Oxidative addition and reductive elimination. (120 references) [1008]

Reactivity patterns of transition metal hydrides and alkyls. (Dissertation) [1009]

Metal-catalyzed dehydrocyclization of alkyl-aromatics. (60 references) [1010]

Asymmetric synthesis with complex catalysts. (no references) [1011]

Recent advances in asymmetric synthesis. (235 references) [1012]

Chiral ligands in asymmetric catalysis by transition metal complexes. (64 references) [1013]

Asymmetric homogeneous catalysis. (22 references) [1014]

Diastereotopy in transition metal complexes. (63 references) [1015]

Stereochemistry of the oxidative addition of benzyl halides to tetrakis(triphenylphosphine)nickel(0) and the palladium(0) catalyzed synthesis of lactones. (Dissertation) [1016]

Dynamic and stereochemical studies by phosphorus-31 NMR spectroscopy on polyphosphine complexes of heavy metals. (33 references) [1017]

The structure and ^{31}P NMR spectra of Rh enamide complexes containing 1R,2R-Trans-1,2-Bis(diphenylphosphinomethyl) cyclobutane. [1018]

Polymer supports in organic synthesis. (2 references) [1019]

Polymer-attached homogeneous catalysis. [1020]

Supported metal catalysts for the transformation of hydrocarbons (New approaches to the preparation and study), Pt. 1. [1021]

Supported metal catalysts for the transformation of hydrocarbons (New approaches to the preparation and study), Pt 2. [1022]

Selectivity effects using polymer-bound catalysts in organic synthesis. [1023]

Catalysis of polymer-bound palladium complexes. [1024]

Synthesis and catalytic properties of palladium complexes fixed on silica gel. (35 references) [1025]

Homogeneous catalysis by transition metal complexes. (231 references) [1026]

Basic concepts of homogeneous catalysis with metal complexes. (31 references) [1027]

Organometallic chemistry in homogeneous catalysis. (15 references) [1028]

Contributions to homogeneous catalysis 1955-1980. (81 references) [1029]

Some aspects of selecting metal-complex catalytic systems. (77 references) [1030]

Electrochemical contributions to the synthesis and characterization of active species in homogeneous catalysis. [1031]

Nucleophilic and organometallic displacement reactions of allylic compounds: Stereo and regiochemistry. (149 references) [1032]

Nucleophilic addition to transition metal complexes. (69 references) [1033]

Clusters in catalysis. (50 references) [1034]

Radical pathways in reactions of transition metal organometallic compounds. (61 references) [1035]

The role of electron transfer and charge transfer in organometallic chemistry. (36 references) [1036]

Free radicals in organometallic chemistry and in organic reactions catalyzed by metal complexes. (47 references) [1037]

Formation, stability, and reactivity of the transition metal-carbon σ-bond. (40 references) [1038]

Molecular orbital approach to σ-π rearrangements of organotransition metal complexes in catalysis. (62 references) [1039]

Reaction mechanisms in heterogeneous catalysis. (75 references) [1040]

Reactivity and bonding in early transition metal complexes. (32 references) [1041]

Mechanistic study of organonickel chemistry. (Dissertation) [1042]

Phosphorus-31 NMR studies of catalytic systems containing rhodium complexes of chelating diphosphines. (42 references) [1043]

Carbon-hydrogen bond activation by d^8 metal complexes; studies of electronic and steric influences. (17 references) [1044]

Photoactivation of organometallic catalysts. (41 references) [1045]

REFERENCES

1. M. Kumada, *Pure Appl. Chem.*, **52**, 669 (1980).
2. T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, and M. Kumada, *Bull. Chem. Soc. Jap.*, **53**, 1138 (1980).
3. M. Kumada, K. Tamao, and K. Sumitani, *Org. Syn.*, **58**, 127 (1978).
4. T. Hayashi, M. Konishi, K-i Yokota, M. Kumada, *Chem. Lett.*, 767 (1980).
5. T. Hayashi, M. Fukushima, M. Konishi, M. Kumada, *Tetrahedron Lett.*, **21**, 79 (1980).
6. T. Hayashi, N. Nagashima, M. Kumada, *Tetrahedron Lett.*, **21**, 4623 (1980).
7. A. Minato, K. Tamao, K. Suzuki, M. Kumada, *Tetrahedron Lett.*, **21**, 4017 (1980).
8. A. Minato, K. Tamao, T. Hayashi, K. Suzuki, and M. Kumada, *Tetrahedron Lett.*, **21**, 845 (1980).
9. Y. Kajihara, K. Ishikawa, H. Yasuda, A. Nakamura, *Bull. Chem. Soc. Jap.*, **53**, 3035 (1980).
10. E. Ibuki, S. Ozasa, Y. Fujioka, M. Okada, and K. Terada, *Bull. Chem. Soc. Jap.*, **53**, 821 (1980).
11. G. Cahiez, A. Alexakis, and J. F. Normant, *Tetrahedron Lett.*, **21**, 1433 (1980).
12. S. Araki and Y. Butsugan, *Chem. Lett.*, 185 (1980).
13. B. L. Chenard, M. J. Manning, P. W. Reynolds, and J. S. Swenton, *J. Org. Chem.*, **45**, 378 (1980).
14. Y. Kobayashi and I. Kumadaki, *J. Chem. Soc. Perkin Trans. I*, 661 (1980).
15. N. V. Kondratenko, E. P. Vechirko, and L. M. Yagupolski, *Synthesis*, 932 (1980).
16. R. G. Pearson and P. E. Figdore, *J. Amer. Chem. Soc.*, **102**, 1541 (1980).
17. Y. Ito, T. Hirao, N. Ohta, and T. Saegusa, *Synth. Comm.*, **110**, 233 (1980).
18. T. Hiyama, H. Yamamoto, K. Nishio, K. Kitatani, and H. Rozaki, *Bull. Chem. Soc. Jap.*, **52** 3632 (1979).
19. H. Sakurai, A. Shirahata, Y. Araki, A. Hosomi, *Tetrahedron Lett.*, **21**, 2325 (1980).
20. I. Mochida, K. Takeshita, M. Ohgai, and T. Seiyama, *Ind. Eng. Chem. Prod. Develop.*, **19**, 392 (1980).
21. E-i Negishi, L. F. Valenti, and M. Kobayashi, *J. Amer. Chem. Soc.*, **102**, 3298 (1980).
22. M. Kobayashi and E-i Negishi, *J. Org. Chem.*, **45**, 5223 (1980).
23. R. J. Card and W. S. Trahanovsky, *J. Org. Chem.*, **45**, 2555 (1980).
24. R. J. Card and W. S. Trahanovsky, *J. Org. Chem.*, **45**, 2560 (1980).
25. A. Meyer and O. Hofer, *J. Amer. Chem. Soc.*, **102**, 4410 (1980).

26a M. T. Reetz, B. Wenderoth, R. Peter, R. Steinbach, and J. Westermann, *J. Chem. Soc. Chem. Commun.*, 1202 (1980).

26b M. T. Reetz, J. Westermann, and R. Steinbach, *Angew. Chem. Int. Ed.*, **19**, 900 (1980).

27. S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis*, 627 (1980).

28. P. I. Svirskaya, C. C. Leznoff, and W. L. Roelofs, *Synth. Comm.*, **10**, 391 (1980).

29. A. Commercon, J. F. Normant, and J. Villieras, *Tetrahedron*, **36**, 1215 (1980).

30. J. M. Oostveen, H. Westmijze, and P. Vermeer, *J. Org. Chem.*, **45**, 1158 (1980).

31. M. R. Ashcroft, A. Bury, C. J. Coolssey, A. G. Davies, B. DassGupta, M. D. Johnson, and H. Morris, *J. Organomet. Chem.*, **195**, 89 (1980).

32. A. Bury, M. D. Johnson, and M. J. Stewart, *J. Chem. Soc. Chem. Commun.*, 622 (1980).

33. H. Alper, M. Tanaka, and K. Hachem, *J. Organomet. Chem.*, **190**, 95 (1980).

34. J. P. Pillot, B. Bennetau, J. Dunogues, and R. Calas, *Tetrahedron Lett.*, **21**, 4717 (1980).

35. L. Colombo, C. Gennari, M. Santandrea, E. Narisano, and C. Scolastico, *J. Chem. Soc, Perkin Trans.I*, 136 (1980).

36. M. T. Rahman, A. K. M. M. Hoque, I. Siddique, D. A. N. Chowdhury, S. K. Naltar, and S. L. Salia, *J. Organomet Chem.*, **188**, 293 (1980).

37. S. H. Bertz, *Tetrahedron Lett.*, **21**, 3151 (1980).

38. F. G. Stakem and R. F. Heck, *J. Org. Chem.*, **45**, 3584 (1980).

39. S. Uemura, M. Wakasugi, M. Okano, *J. Organomet. Chem.*, **194**, 277 (1980).

40. K. Kikukawa, K. Maemura, K. Nagira, F. Wada, and T. Matsuda, *Chem. Lett.*, 551 (1980).

41. F. Akiyama, H. Miyazaki, K. Kaneda, S. Teranishi, Y. Fujiwara, M. Abe, and H. Taniguchi, *J. Org. Chem.*, **45**, 2359 (1980).

42. C. F. Bigge, P. Kalarites, J. R. Peck and M. P. Mertes, *J. Amer. Chem. Soc.*, **102**, 2033 (1980).

43. F. Sato, H. Ishikawa, and M. Sato, *Tetrahedron Lett.*, **21**, 365 (1980).

44. M. Hajek and J. Malek, *Collect. Czech. Chem. Commun.*, **44**, 3695 (1979).

45. T. Hayashi, Y. Katsuro, and M. Kumada, *Tetrahedron Lett.*, **21**, 3915 (1980).

46. K. Takai, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **21**, 2531 (1980).

47. J. E. McMurry and W. J. Scott., *Tetrahedron Lett.*, **21**, 4313 (1980).

48. H. Okamura, M. Miura, K. Kosugi, and H. Takei, *Tetrahedron Lett.*, **21**, 87 (1980).

49. L. S. Hegedus, R. E. Williams, M. A. McGuire, and T. Hayashi, *J. Amer. Chem. Soc.*, **102**, 4973 (1980).

50. R. E. Williams, *Diss. Abstr. Int. B*, **41**, 1377 (1980).

51. G. P. Chiusoli, M. Costa, G. Terenghi, and A. Mari, *Transition Met. Chem.*, **5**, 379 (1980).

52. T. C. T. Chang, M. Rosenblum, and S. B. Samuels, *J. Amer. Chem. Soc.*, **102**, 5930 (1980).

53. M. F. Semmelhack, W. Seufert, and L. Keller, *J. Amer. Chem. Soc.*, **102**, 6584 (1980).

54. M. Akbarzadeh and C. B. Anderson, *J. Organomet. Chem.*, **197**, C5 (1980).

55. M. Brookhart, M. B. Humphrey, H. J. Kratzer, and G. O. Nelson, *J. Amer. Chem. Soc.*, **102**, 7802 (1980).

56. N. Kawabata and M. Tanimoto, *Tetrahedron*, **36**, 3517 (1980).

57. R. B. Weisenfeld, *Diss. Abstr. Int. B*, **41**, 207 (1980).

58. G. W. Parshall, T. Herskovitz, F. N. Tebbe, A. D. English, and J. V. Zeile, *Fundam. Res. Homogeneous Catal.*, **3**, 95 (1979).

59. G. Smith, S. J. McLain, and R. R. Schrock, *J. Organomet. Chem.*, **202**, 269 (1980).

60. R. Grigg, T. R. B. Mitchell, and A. Ramasubbu, *J. Chem. Soc., Chem. Comm.*, 27 (1980).

61. M. Catellani, G. P. Chiusoli, W. Giroldini, and G. Salerno, *J. Organomet. Chem.*, **199**, C21 (1980).

62. J. E. McMurry and W. Choy, *Tetrahedron Lett.*, **21**, 2477 (1980).

63. M. Mitani, M. Nakayama, and K. Koyama, *Tetrahedron Lett.*, **21**, 4457 (1980).

64. D. S. Wulfman and B. Poling, *React. Intermed.*, **1**, 321 (1980).

65. R. W. Ratcliffe, T. N. Salzmann, and B. G. Christensen, *Tetrahedron Lett.*, **21**, 31 (1980).

66. T. N. Salzmann, R. W. Ratcliffe, and B. G. Christensen, *Tetrahedron Lett.*, **21**, 1193 (1980).

67. H. J. Callot and C. Piechocki, *Tetrahedron Lett.*, **21**, 3489 (1980).

68. R. Pellicirari, E. Sisani and R. Fringuelli, *Tetrahedron Lett.*, **21**, 4039 (1980).

69. M. E. Alonso, P. Jano S., and M. I. Hernandez, *J. Org. Chem.*, **45**, 5299 (1980).

70. T. Ibata and K. Jitsuhiro, *Bull. Chem. Soc. Japan*, **52**, 3582 (1979).

71. T. H. Johnson and S. S. Cheng, *Synth. Comm.*, **10**, 381 (1980).

72. F. L. M. Smeets, L. Thijs, and B. Zwaneburg, *Tetrahedron*, **36**, 3269 (1980).

73. N. Petiniot, A. F. Noels, J. A. Anciaux, A. J. Hubert, and P. Teyssie, *Fundam. Res. Homogeneous Catal.*, **3**, 421 (1979).

74. A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot, and P. Teyssie, *J. Org. Chem.*, **45**, 695 (1980).

75. M. P. Doyle and J. G. Davidson, *J. Org. Chem.*, **45**, 1538 (1980).

76. R. Noyori, K. Yokoyama, and Y. Hayakawa, *Org. Synth.*, **58**, 56 (1978).

77. T. Sato, H. Kobayashi, and R. Noyori, *Tetrahedron Lett.*, **21**, 1971 (1980).

78. B. M. Trost and D. M. T. Chan, *J. Amer. Chem. Soc.*, **102**, 6360 (1980).

79. J. B. Campbell and H. C. Brown, *J. Org. Chem.*, **45**, 549 (1980).
80. H. C. Brown and J. B. Campbell, *J. Org. Chem.*, **45**, 550 (1980).
81. H. Yatagai, *J. Org. Chem.*, **45**, 1640 (1980).
82. N. Miyaura, T. Yano, and A. Suzuki, *Bull. Chem. Soc. Japan*, **53**, 1471 (1980).
83. H. Yatagai, *Bull. Chem. Soc. Japan*, **53**, 1670 (1980).
84. N. Miyaura, T. Yano, and A. Suzuki, *Tetrahedron Lett.*, **21**, 2865 (1980).
85. A. M. Caporusso, G. Giacomelli, and L. Lardicci, *J. Chem. Soc., Perkin Trans. I*, 3139 (1979).
86. U. Bersellini, M. Catellani, G. P. Chiusoli, W. Giroldini, and G. Salerno, *Fundam. Res. Homogeneous Catal.*, **3**, 893 (1979).
87. P. Hong, Bo-Re Cho, and H. Yamazaki, *Chem. Lett.*, 507 (1980).
88. L. Liebeskind, S. L. Baysdon, and M. S. South, *J. Amer. Chem. Soc.*, **102**, 7397 (1980).
89. H. Matsumoto, I. Matsubara, T. Kato, K. Shono, H. Watanabe, and Y. Nagai, *J. Organomet. Chem.*, **199**, 43 (1980).
90. I. Fleming and F. Roessler, *J. Chem. Soc., Chem. Commmun.*, 276 (1980).
91. D. L. Reger, P. J. McElligott, *J. Amer. Chem. Soc.*, **102**, 5923 (1980).
92. L-I Olsson and Alf. Claesson, *Acta Chem. Scand. B*, **33**, 679 (1979).
93. M. Montury, B. Psaume, and J. Gore, *Tetrahedron Lett.*, **21**, 163 (1980).
94. H. Kleijn,H. Westmijze, J. Meijer, and P. Vermeer, *J. Organomet. Chem.*, **192**, 275 (1980).
95. A. Doutheau, G. Balime, M. Malacria, and J. Gore, *Tetrahedron*, **36**, 1953 (1980).
96. Y. Tanigawa and S-i Murahashi, *J. Org. Chem.*, **45**, 4536 (1980).
97. G. Consiglio, F. Morandini, and O. Piccolo, *Helv. Chim. Acta*, **63**, 987 (1979).
98. T. Hayashi, M. Konishi, and M. Kumada, *J. Organomet. Chem.*, **186** C1 (1980).
99. T. Jeffrey-Luong and G. Linstrumelle, *Tetrahedron Lett.*, **21**, 5019 (1980).
100. S. Padmanabhan and K. M. Nicholas, *Synth. Comm.*, **10**, 503 (1980).
101. K. M. Nicholas, M. Mulvaney, and M. Bayer, *J. Amer. Chem. Soc.*, **102**, 2508 (1980).
102. J. E. O'Boyle and K. M. Nicholas, *Tetrahedron Lett.*, **21**, 1595 (1980).
103. T. L. Macdonald, D. R. Reagan, and R. S. Brinkmeyer, *J. Org. Chem.*, **45**, 4740 (1980).
104. Y. Yamamoto, S. Yamamoto, H. Yatagai, and K. Maruyama, *J. Amer. Chem. Soc.*, **102**, 2318 (1980).
105. G. Cassani, P. Massardo, and P. Piccardi, *Tetrahedron Lett.*, **21**, 3497 (1980).
106a T. Ibuka and H. Minakata, *Synth. Comm.*, **10**, 119 (1980).
106b Y. Masaki, K. Sakuma, and K. Kaji, *J. Chem. Soc., Chem. Commun.*, 434 (1980).

107. A. V. Kavaliunas and R. D. Rieke, *J. Amer. Chem. Soc.*, **102**, 5944 (1980).
108. E. A. W. Becker, *Diss. Abstr. Int. B*, **41**, 955 (1980).
109. A. G. Mack, H. Suschitzky, and B. J. Wakefield, *J. Chem. Soc., Perkin Trans. 1*, 1682 (1980).
110. F. E. Ziegler, I. Chluvner, K. W. Fowler, S. J. Kanfer, S. J. Kno, and N. D. Sinka, *J. Amer. Chem. Soc.*, **102**, 790 (1980).
111. S. Miyano, M. Tobita, S. Suzuki, Y. Nishikawa, and H. Hashimoto, *Chem. Lett.*, 1027 (1980).
112. S. Miyano, M. Tobita, M. Nawa, S. Sato, and H. Hashimoto, *J. Chem. Soc., Chem. Commun.*, 1233 (1980).
113. M. Sainsbury, *Tetrahedron*, **36**, 3327 (1980).
114. L. Crombie, G. Kneen, G. Pattenden, and D. Whybrow, *J. Chem. Soc., Perkin Trans, 1*, 1711 (1980).
115. M. Troupel, Y. Rollin, S. Sibille, J-F. Fauvarque, and J. Perichon, *J. Chem. Res.*, 26 (1980).
116. C. Gosden and D. Pletcher, *J. Organomet. Chem.*, **186**, 401 (1980).
117. M. Onaka, Y. Matsuoka, and T. Mukaiyama, *Chem. Lett.*, 905 (1980).
118. T. Goto, M. Onaka, and T. Mukaiyama, *Chem. Lett.*, 51 (1980).
119. R. Nakajima, Y. Shintani, and T. Hara, *Bull. Chem. Soc. Japan*, **53**, 1767 (1980).
120. E. W. Abel and G. M. Pring, *Inorg. Chim. Acta*, **44**, L161 (1980).
121. J. Towarnicky and E. P. Schram, *Inorg. Chim. Acta*, **44**, 305 (1980).
122. D. Lenoir and P. Lemmen, *Chem. Ber.*, **113**, 3112 (1980).
123. K. Ito, S. Nakanishi, and Y. Otsuji, *Chem. Lett.*, 1141 (1980).
124. L. J. Mazza and A. Guarna, *Synthesis*, 40 (1980).
125. H. M. Walborsky and M. P. Murari, *J. Amer. Chem. Soc.*, **102**, 426 (1980).
126. T. Sakakibara, Y. Pogomori, and Y. Tsuzuki, *Bull. Chem. Soc., Japan*, **52**, 3592 (1980).
127. T. Itahara, *J. Chem. Soc., Chem. Commun.*, 49 (1980).
128. R. H. Frazier Jr. and R. L. Harlow, *J. Org. Chem.*, **45**, 5408 (1980).
129. Y. Kobayashi, T. Taguchi, T. Morikawa, E. Tokuno, and S. Sekiguchi, *Chem. Pharm. Bull.*, **28**, 262 (1980).
130. T. C. Jempty, L. L. Miller, and Y. Mazur, *J. Org. Chem.*, **45**, 749 (1980).
131. M. Lewin, Z. Aizenshtat, and J. Blum, *J. Organomet. Chem.*, **184**, 255 (1980).
132. J. P. Kutney, T. C. W. Mak, D. Mostowicz, J. Trotter, and B. R. Worth, *Heterocycles*, **12**, 1517 (1979).
133. S. J. McLain, J. Sancho, and R. R. Schrock, *J. Amer. Chem. Soc.*, **102**, 5610 (1980).
134. A. Gillie and J. K. Stille, *J. Amer. Chem. Soc.*, **102**, 4933 (1980).
135. R. G. Bergman, *Acc. Chem. Res.*, **13**, 113 (1980).
136. M. A. White, *Diss. Abstr. Int. B*, **40**, 3179 (1980).

137. T. R. Verhoeven, *Diss. Abstr. Int. B*, **40**, 2199 (1979).

138. R. D. Rieke, A. V. Kavaliunas, L. D. Rhyne, and D. J. J. Fraser, *J. Amer. Chem. Soc.*, **101**, 246 (1979).

139. B. M. Trost and P. J. Metzner, *J. Amer. Chem. Soc.*, **102**, 3572 (1980).

140. B. M. Trost, *Acc. Chem. Res.*, **13**, 385 (1980).

141. B. M. Trost and T. R. Verhoeven, *J. Amer. Chem. Soc.*, **102**,4730 (1980).

142. B. M. Trost, N. R. Schmuff, and M. J. Miller, *J. Amer. Chem. Soc.*, **102**, 5979 (1980).

143. J. Tsuji, Y. Kobayashi, H. Katoaka, and T. Takahashi, *Tetrahedron Lett.*, **21**, 1475 (1980).

144. J. Tsuji, Y. Kobayashi, H. Kataoka, and T. Takahashi, *Tetrhedron Lett.*, **21**, 3393 (1980).

145. B. M. Trost and T. R. Verhoeven, *J. Amer. Chem. Soc.*, **102**, 4743 (1980).

146. J. C. Fiaud and J. L. Mallevon, *Tetrahedron Lett.*, **21**, 4437 (1980).

147. J. Godschalx and J. K. Stille, *Tetrahedron Lett.*, **21**, 2599 (1980).

148. B. M. Trost and E. Keinan, *Tetrahedron Lett.*, **21**, 2595 (1980).

149. B. M. Trost and E. Keinan, *Tetrahedron Lett.*, **21**, 2591 (1980).

150. J. P. Genet, F. Piau, and J. Ficini, *Tetrahedron Lett.*, **21**, 3183 (1980).

151. P. A. Wade, S. D. Morrow, S. A. Hardinger, M. S. Saft, and H. R. Hinney, *J. Chem. Soc., Chem. Commun.*, 287 (1980).

152. L. S. Hegedus, W. H. Darlington, and C. E. Russell, *J. Org. Chem.*, **45**, 5193 (1980).

153. J. Muzart and J-P Pete, *J. Chem. Soc., Chem. Commun.*, 257 (1980).

154. Y. Ito, M. Nakatsuka, N. Kise, and T. Saegusa, *Tetrahedron Lett.*, **21**, 2873 (1980).

155. Y. Ito, H. Aoyama, and T. Saegusa, *J. Amer. Chem. Soc.*, **102**, 4519 (1980).

156. J. S. Temple and J. Schwartz, *J. Amer. Chem. Soc.*, **102**, 7381 (1980).

157. J. A. McCleverty and A. J. Murray, *Transition Met. Chem.*, **4**, 273 (1979).

158. J. F. Normant, A. Alexakis, and G. Cahiez, *Tetrahedron Lett.*, **21**, 935 (1980).

159. T. Fujisawa, T. Sato, T. Kawara, M. Kawashima, H. Simizu, and Y. Ito, *Tetrahedron Lett.*, **21**, 2181 (1980).

160. T. Sato, T. Kawara, M. Kawashima, and T. Fujisawa, *Chem. Lett.*, 571 (1980).

161. T. Fujisawa, T. Sato, T. Kawara, and K. Naruse, *Chem. Lett.*, 1123 (1980).

162. B. M. Trost and T. P. Klun, *J. Org. Chem.*, **45**, 4256 (1980).

163. C. K. Sehgal, P. L. Kachroo, and K. L. Dhar, *Indian J. Chem., Sect. B*, **17B**, 182 (1979).

164. F. Sato, T. Jinbo, and M. Sato, *Tetrahedron Lett.*, **21**, 2175 (1980).

165. D. A. Evans and L. R. McGee, *Tetrahedron Lett.*, **21**, 3975 (1980).

166. Y. Yamamoto and K. Maruyama, *Tetrahedron Lett.*, **21**, 4607 (1980).

167. W. Clark Still and J. A. Schneider, *Tetrahedron Lett.*, **21**, 1035 (1980).

168. A. Solladie-Cavallo, J. Suffert, and J-L. Haesslein, *Angew. Chem. Internat. Edit.*, **19**, 1005 (1980).

169. Yu. N. Belokon, I. E. Zel'Tzer, N. M. Loim, V. A. Tsyryapkin, G. G. Aleksandrov, D. N. Kursanov, Z. N. Parnes, Yu. T. Struchkov, and V. M. Belikov, *Tetrahedron*, **36**, 1089 (1980).

170. R. L. Danheiser and D. J. Carini, *J. Org. Chem.*, **45**, 3925 (1980).

171. A. Hosomi, H. Hashimoto, and H. Sakurai, *Tetrahedron Lett.*, **21**, 951 (1980).

172. J. Lange, J. M. Kanabus-Kaminska, and A. Kral, *Synth. Commun.*, **10**, 473 (1980).

173. K. Irie and K. Watanabe, *Bull. Chem. Soc., Japan*, **53**, 1366 (1980).

174. L. Nondek and J. Malek, *Collect. Czech. Chem. Commun.*, **44**, 2384 (1979).

175. J. H. Nelson, P. N. Howells, G. L. Landen, G. C. DeLullo, and R. A. Henry, *Fundam. Res. Homogeneous Catal.*, **3**, 921 (1979).

176. T. Sato, H. Kaneko, and S. Yamaguchi, *J. Org. Chem.*, **45**, 3778 (1980).

177. H. Takei, M. Miura, H. Sugimura, and H. Okamura, *Chem. Lett.*, 1447 (1979).

178. M. Uemura, N. Nishiwaka, S. Tokuyama, and Y. Hayashi, *Bull. Chem. Soc., Japan*, **53**, 293 (1980).

179. M. Uemura, N. Nishiwaka, and Y. Hayashi, *Tetrahedron Lett.*, 2069 (1980).

180a. B. Weidmann and D. Seebach, *Helv. Chim. Acta*, **63**, 2451 (1980).

180b. M. T. Reetz, R. S. Steinbach, J. Westermann, and R. Peter, *Angew. Chem. Internat. Edit.*, **19**, 1011 (1980).

181. K. Tanaka, N. Tamura, and A. Kaji, *Chem. Lett.*, 595 (1980).

182. I. Rhee, I. Ryu, H. Omura, S. Murai, and N. Sonada, *Chem. Lett.*, 1435 (1979).

183. Y. Kojima and N. Kato, *Tetrahedron Lett.*, **21**, 4365 (1980).

184. A. Alexakis, G. Cahiez, and J. F. Normant, *Tetrahedron*, **36**, 1961 (1980).

185. G. Boireau, D. Abenhaim, and E. Henry-Basch, *Tetrahedron*, **36**, 3061 (1980).

186. M. Kobayashi, L. F. Valente, and E-i Negishi, *Synthesis*, 1034 (1980).

187. M. F. Semmelhack and A. Yamashita, *J. Amer. Chem. Soc.*, **102**, 5926 (1980).

188. G. Simonneaux, G. Jaouen, and R. Dabard, *Tetrahedron*, **36**, 893 (1980).

189. T. Itahara, *Fukusokan Kagaku Toronkai Koen Yoshishu*, 86 (1979).

190a A. J. Pearson, *Accts. Chem. Res.*, **13**, 463 (1980).

190b. A. J. Pearson and M. Chandler, *J. Chem. Soc., Perkin I*, 2238 (1980).

191. A. J. Pearson and M. Chandler, *J. Organomet. Chem.*, **202**, 175 (1980).

192. A. J. Pearson and P. R. Raithby, *J. Chem. Soc., Perkin I*, 395 (1980).

193. C. W. Ong and A. J. Pearson, *Tetrahedron Lett.*, **21**, 2349 (1980).

194. A. J. Pearson, E. Mincione, M. Chandler, and P. R. Raithby, *J. Chem. Soc., Perkin I*, 2774 (1980).

195. A. J. Pearson, *Tetrahedron Lett.*, **21**, 3929 (1980).

196. A. J. Pearson, *J. Chem. Soc., Perkin I*, 400 (1980).

197. A. J. Pearson, P. Ham, and D. C. Rees, *Tetrahedron Lett.*, **21**, 4637 (1980).

198. A. J. Pearson and D. C. Rees, *Tetrahedron Lett.*, **21**, 3937 (1980).

199. A. J. Pearson and M. Chandler, *Tetrahedron Lett.*, **21**, 3933 (1980).

200. B. M. Ratnayake Bandara, A. J. Birch, and T-C Khov, *Tetrahedron Lett.*, **21**, 3625 (1980).

201. A. J. Birch, A. S. Narula, P. Dahler, G. R. Stephenson, and L. F. Kelly, *Tetrahedron Lett.*, **21**, 979 (1980).

202. A. J. Birch, P. Dahler, A. S. Narula, and G. R. Stephenson, *Tetrahedron Lett.*, **21**, 3817 (1980).

203. L. F. Kelly, A. S. Narula, and A. J. Birch, *Tetrahedron Lett.*, **21**, 2455 (1980).

204. L. F. Kelly, A. S. Narula, and A. J. Brich, *Tetrahedron Lett.*, **21**, 871 (1980).

205. A. J. Birch, W. D. Raverty, and G. R. Stephenson, *Tetrahedron Lett.*, **21**, 197 (1980).

206. A. J. Birch, and B. M. Ratnayake Bandara, *Tetrahedron Lett.*, **21**, 2981 (1980).

207. A. J. Birch, *Ann. N. Y. Acad. Sci.*, **333**, 107 (1980).

208. H. Alper and S. Amaratunga, *Tetrahedron Lett.*, **21**, 1589 (1980).

209. A. S. Kende and L. N. Jungheim, *Tetrahedron Lett.*, **21**, 3849 (1980).

210. M. Suzuki, T. Suzuki, T. Kawagishi, and R. Noyori, *Tetrahedron Lett.*, **21**, 1247 (1980).

211. F. Leyendecker and F. Jesser, *Tetrahedron Lett.*, **21**, 1311 (1980).

212. R. Sjoholm and P. Backlund, *Finn. Chem. Lett.*, 28 (1980).

213. C. Chuit, J. P. Foulon, and J. F. Normant, *Tetrahedron*, **36**, 2305 (1980).

214. M. T. Rahman, S. L. Saha, and A. T. Hansson, *J. Organomet. Chem.*, **199**, 9 (1980).

215. E. Piers and H. E. Morton, *J. Org. Chem.*, **45**, 4263 (1980).

216. H. Saimoto, T. Hiyama, and H. Nozaki, *Tetrahedron Lett.*, **21**, 3897 (1980).

217. S. Bernasconi, P. Garibaldi, G. Jommi, and M. Siste, *Tetrahedron Lett.*, **21**, 2337 (1980).

218. G. Zima, C. Barnum, and D. Liotta, *J. Org. Chem.*, **45**, 2736 (1980).

219. M. C. Cesa, *Diss. Abstr. Int. B*, **40**, 5668 (1980).

220. B. Gustafsson, A-T. Hansson, and C. Ullenius, *Acta Chem. Scand. B*, **34**, 113 (1980).

221. B. Gustafsson, G. Hallnemo, and C. Ullenius, *Acta Chem. Scand. B*, **34**, 443 (1980).

222. T. Imamoto and T. Mukaiyama, *Chem. Lett.*, 45 (1980).

223. O. H. Johansen and K. Undheim, *Acta.Chem. Scand., Ser. B*, **B33**, 460 (1979).

224a T. Ibuka, H. Minakata, Y. Mitsui, K. Kinoshita, and Y. Kawami, *J. Chem. Soc., Chem. Comm.*, 1193 (1980).

224b T. Ibuka, H. Minakata, Y. Mitsui, K. Kinoshita, Y. Kauami, and N. Kimura, *Tetrahedron Lett.*, **21**, 4073 (1980).

225. M. Lopp, A. Pals, and U. Lille, *Eesti NSV Tead. Akad. Toim. Keem.*, **29**, 191 (1980).

226. A. B. Smith III, B. A. Wexler, and J. S. Slade, *Tetrahedron Lett.*, **21**, 3237 (1980).

227. R. J. Batten, J. D. Coyle, and R. J. K. Taylor, *Synthesis*, 910 (1980).

228. A. Takeda, K. Shinhama, and S. Tsuboi, *J. Org. Chem.*, **45**, 3125 (1980).

229. D. O. Spry, *Tetrahedron Lett.*, **21**, 1293 (1980).

230. J. P. Vigneron, R. Meric, and M. Dhaenens, *Tetrahedron Lett.*, 2057 (1980).

231. C. B. Chapelo, M. A. W. Finch, S. M. Roberts, G. T. Woolley, R. F. Newton, and D. W. Selby, *J. Chem. Soc., Perkin I*, 1847 (1980).

232. S. Mubarik Ali, M. A. W. Finch, and S. M. Roberts, *J. Chem. Soc., Chem. Comm.*, 74 (1980).

233. C. B. Chapelo, M. A. W. Finch. T. V. Lee, S. M. Roberts, and R. F. Newton, *J. Chem. Soc., Perkin I*, 2084 (1980).

234. S. Mubarik Ali, C. B. Chapelo, M. A. W. Finch, S. M. Roberts, G. T. Woolley, R. J. Cave, and R. F. Newton, *J. Chem. Soc., Perkin I*, 2093 (1980).

235. K. C. Nicolaou, R. L. Magolda, and D. A. Claremou, *J. Amer. Chem. Soc.*, **102**, 1404 (1980).

236. A. E. Greene, C. LeDrian, and P. Crabbe, *J. Amer. Chem. Soc.*, **102**, 7584 (1980).

237. J. P. Marino and H. Ake, *Synthesis*, 872 (1980).

238. B. W. Roberts, M. Ross, and J. Wong, *J. Chem. Soc., Chem. Comm.*, 428 (1980).

239. M. A. Baar and B. W. Roberts, *J. Chem. Soc., Chem. Comm.*, 1129 (1979).

240. M. J. Loots, *Diss. Abstr. Int. B*, **40**, 3159 (1980).

241. J. Schwartz, M. J. Loots, and H. Kosugi, *J. Amer. Chem. Soc.*, **102**, 1333 (1980).

242. J. Schwartz and Y. Hasyasi, *Tetrahedron Lett.*, **21**, 1497 (1980).

243. J. Schwartz, D. B. Carr, R. T. Hansen, and F. M. Dayrit, *J. Org. Chem.*, **45**, 3053 (1980).

244. J. H. Nelson, P. N. Howells, G. C. DeLullo, G. L. Landen, and R. A. Henry, *J. Org. Chem.*, **45**, 1246 (1980).

245. A. Biavati, G. P. Chiusoli, M. Costa, and G. Terenghi, *Transition Met. Chem.*, **4**, 398 (1979).

246. S. Cacchi, F. La Torre, and D. Misiti, *Tetrahedron Lett.*, 4591 (1979).

247. R. Scheffold, M. Dike, S.Dike, T. Herold, and L. Walder. *J. Amer. Chem. Soc.*, **102**, 3642 (1980).

248. R. K. Freidlina, L. V. Vinogradova, and F. K. Velichko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1210 (1980).

249. P. Brun, A. Tenaglia, and B. Waegell, *J. Organomet. Chem.*, **194**, C39 (1980).

250. A. Hosomi, H. Kobayashi, and H. Sakurai, *Tetrahedron Lett.*, **21**, 955 (1980).

251. A. Jellal and M. Santelli, *Tetrahedron Lett.*, **21**, 4487 (1980).

252. S. Hara, K. Kishimura, and A. Suzuki, *Chem. Lett.*, 221 (1980).

253. C. Botteghi, S. Gladiali, V. Bellagamba, R. Ercoli, and A. Gamba, *Chim. Ind., Milan*, **62**, 604 (1980).

254. C. Botteghi, S. Gladiali, V. Bellagamba, R. Ercoli, and A. Gamba, *Chim. Ind., Milan*, **62**, 757 (1980).

255. B. Cornils, *React. Struct. Concepts Org. Chem.*, **11**, 1 (1980).

256. G. Gregorio, G. Montrasi, M. Tampieri, P. Cavalieri d'Oro, G. Pagani, and A. Andreetta, *Chim. Ind., Milan*, **62**, 389 (1980).

257. V. Bellagamba, R. Ercoli, A. Gamba, and B. Giuseppe, *J. Organomet. Chem.*, **190**, 381 (1980).

258. R. B. King, A. D. King, Jr., M. Z. Iqbal, and K. Tanaka, *Ann. Acad. Sci., New York*, **333**, 74 (1980).

259. R. M. Laine, *Ann. Acad. Sci., New York*, **333**, 124 (1980).

260. M. Polievka, L. Uhlar, and V. Macho, *Petrochemia*, **20**, 33 (1980).

261. K. Kurtev, D. Ribola, R. A. Jones, D. J. Cole-Hamilton, and G. Wilkinson, *J. Chem. Soc., Dalton*, 55 (1980).

262. T. K. Banerjee and C. R. Saha, *Indian J. Chem., Sect. A*, **19A**, 898 (1980).

263. K. Murata and A. Matsuda, *Nippon Kagaku Kaishi*, 1077 (1980).

264. G. Süss-Fink, *J. Organomet. Chem.*, **193**, C20 (1980).

265. E. Z. Gil'denberg, L. L. Krasnova, S. D. Pirozhkov, and A. L. Lapidus, *Kinet. Katal.*, **21**, 810 (1980).

266. C. H. Van Dyke, M. O. Farrell, and L. J. Boucher, *Fundam. Res. Homogeneous Catal.*, **3**, 659 (1979).

267. J. Hjortkjaer, M. S. Scurrell, and P. Simonsen, *J. Mol. Catal.*, **10**, 127 (1980).

268. J. Hjortkjaer, M. S. Scurrell, and P. Simonsen, *J. Mol. Catal.*, **6**, 405 (1979).

269. P. F. Jackson, B. F. G. Johnson, J. Lewis, R. Ganzerla, and M. Lenarda, *J. Organomet. Chem.*, **190**, C1 (1980).

270. C. U. Pittman, Jr. and W. D. Honnick, *J. Org. Chem.*, **45**, 2132 (1980).

271. A. R. Sanger, *Prep. - Can. Symp. Catal.*, 5th, 281 (1977).

272. Y. Becker, A. Eisenstadt, and J. K. Stille, *J. Org. Chem.*, **45**, 2145 (1980).

273. C. Battegli, M. Branca, and A. Saba, *J. Organomet. Chem.*, **184**, C17 (1980).

274. A. Spencer, *J. Organomet. Chem.*, **194**, 113 (1980).

275. K. Murata and A. Matsuda, *Bull. Chem. Soc., Japan*, **53**, 214 (1980).

276. C. U. Pittman, Jr., W. D. Honnick, and J. J. Yang, *J. Org. Chem.*, **45**, 684 (1980).

277a R. E. Campbell, Jr. and R. G. Miller, *J. Organomet. Chem.*, **186**, C27 (1980).

277b R. E. Campbell, Jr., C. F. Lochow, K. P. Vora, and R. G. Miller, *J. Amer. Chem. Soc.*, **102**, 5824 (1980).

278. K. P. Vora, C. F. Lochow, and R. G. Miller, *J. Organomet. Chem.*, **192**, 257 (1980).
279. R. C. Larock, K. Oertle, and G. F. Potter, *J. Amer. Chem. Soc.*, **102**, 190 (1980).
280. T. B. Rauchfuss, *Fundam. Res. Homogeneous Catal.*, **3**, 1021 (1979).
281. K. Murata and A. Matsuda, *Chem. Lett.*, 11 (1980).
282. J. E. Hallgren and R. O. Matthews, *J. Organomet. Chem.*, **192**, C12 (1980).
283. L. S. Hegedus and W. H. Darlington, *J. Amer. Chem. Soc.*, **102**, 4980 (1980).
284. J. E. McMurry and A. Andrus, *Tetrahedron Lett.*, **21**, 4687 (1980).
285. J. F. Knifton, *J. Organomet. Chem.*, **188**, 223 (1980).
286. T. Yamamoto, K. Igarashi, S. Komiya, and A. Yamamoto, *J. Amer. Chem. Soc.*, **102**, 7448 (1980).
287. J. F. Knifton, *J. Catal.*, **60**, 27 (1979).
288. J. F. Knifton, *Ann. Acad. Sci., New York*, **333**, 264 (1980).
289. J. Tsuji, M. Takahashi, and T. Takahashi, *Tetrahedron Lett.*, **21**, 849 (1980).
290. B. P. Gusev, E. A. El'perina, V. F. Kucherov, S. D. Pirozhkov, A. L. Lapidus, *Izv. Akad. NaukSSSR, Ser. Khim*, 603 (1980).
291. P. Eilbracht, U. Mayser, and G. Tiedtke, *Chem. Ber.*, **113**, 1420 (1980).
292. M. Gnaka, T. Goto, and T. Mukaiyama, *Chem. Lett.*, 1483 (1979).
293. H. des Abbayes and A. Buloup, *Tetrahedron Lett.*, **21**, 4343 (1980).
294. F. Ungvary and L. Marko, *J. Organomet. Chem.*, **193**, 379 (1980).
295. M. Foa and L. Cassar, *Gazz. Chim. Ital.*, **109**, 619 (1979).
296. Y. Ohkatsu, K. Nakazawa, and T. Osa, *Sekiyu Gakkaishi*, **22**, 388 (1979).
297. R. G. Finke and T. N. Sorrell, *Org. Synth.*, **59**, 102 (1980).
298. T. Takahashi, H. Ikeda, and J. Tsuji, *Tetrahedron Lett.*, **21**, 3885 (1980).
299. J. Tsuji, T. Takahashi, and T. Nagashima, *Chem. Lett.*, 369 (1980).
300. A. Cowell and J. K. Stille, *J. Amer. Chem. Soc.*, **102**, 4193 (1980).
301. M. Mori, K. Chiba, N. Ohta, and Y. Ban, *Heterocycles*, **13**, 329 (1979).
302. K. Chiba, M. Mori, and Y. Ban, *J. Chem. Soc., Chem. Commun.*, 770 (1980).
303. L. S. Liebeskind and M. S. South, *J. Org. Chem.*, **45**, 5426 (1980).
304. S. S. Novikov, V. I. Manov-Yuvenskii, A. V. Smetanin, and B. K. Nefedov, *Doklady Chem.*, **251**, 135 (1980).
305. V. I. Manov-Yuvenskii, A. V. Smetanin, and B. K. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2556 (1980).
306. L. V. Gorbunova, I. L. Knyazeva, E. A. Davydova, and G. A. Abakumov, *Bull. Akad. Nauk. SSSR, Ser. Khim. Sci.*, **29**, 761 (1980).
307. L. V. Gorbunova, I. L. Knyazeva, and E. A. Davydova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1054 (1980).

308. K. Unverferth, R. Hoentsch, and K. Schwetlick, J. Prakt. Chem., 321, 928 (1979).
309. T. Mise, P. Hong, and H. Yamazaki, Chem. Lett., 439 (1980).
310. H. Tietz, K. Unverferth, and K. Schwetlick, Z. Chem., 20, 256 (1980).
311. H. Tietz, K. Unverferth, and K. Schwetlick, Z. Chem., 20, 295 (1980).
312. H. Tietz, K. Unverferth, and K. Schwetlick, Z. Chem., 20, 411 (1980).
313. V. I. Manov-Yuvenskii, B. A. Redoshkin, B. K. Nefedov, and G. P. Belyaeva, Kinet. Katal., 21, 1333 (1980).
314. V. I. Manov-Yuvenskii, B. A. Redoshkin, B. K. Nefedov, and G. P. Belyaeva, Bull. Akad. Nauk SSSR, 29, 106 (1980).
315. V. I. Manov-Yuvenskii and B. K. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 2139 (1979).
316. V. I. Manov-Yuvenskii, Issled. Obl. Khim. Vysokomol. Soedin. Neftekhim. 15 (1977).
317. V. A. Golodov, Y. L. Sheludyakov, and D. V. Sokol'skii, Fundam. Res. Homogeneous Catal., 3, 239 (1979).
318. Y. L. Sheludyakov, V. A. Golodov, and D. V. Sokol'skii, Dokl. Akad. Nauk SSSR, 249, 658 (1979).
319. S. Gambarolta and H. Alper, J. Organomet. Chem., 194, C19 (1980).
320. M. S. Scurrell, Chim. Ind., Milan, 61, 652 (1979).
321. G. Braca, G. Sbrana, G. Valentini, G. Andrich, and G. Gregorio, Fundam. Res. Homogeneous Catal., 3, 221 (1979).
322. J. J. Parnaud, G. Campari, and P. Pino, J. Mol. Catal., 6, 341 (1979).
323. Y. Kamiya, K. Kawato, and H. Ohta, Chem. Lett., 1549 (1980).
324. E. J. Kuhlmann and J. J. Alexander, Coord. Chem. Rev., 33, 195 (1980).
325. S. B. Butts, E. M. Holt, S. H. Strauss, N. W. Alcock, R. E. Stimson, and D. F. Shriver, J. Amer. Chem. Soc., 101, 5864 (1979).
326. R. C. Larock and S. S. Hershberger, J. Org. Chem., 45, 3840 (1980).
327. I. Ryu, K. Matsumoto, M. Ando, S. Murai, and N. Sonada, Tetrahedron Lett., 21, 4283 (1980).
328. R. C. Larock and C. A. Fellows, J. Org. Chem., 45, 363 (1980).
329. E. O. Fischer and W. Roll, Angew Chem. Int. Ed. Engl., 19, 205 (1980).
330. M. Hidai, M. Orisaku, and Y. Uchida, Chem. Lett., 753 (1980).
331. Y. Fujiwara, T. Kawauchi, and H. Taniguchi, J. Chem. Soc., Chem. Commun., 220 (1980).
332. A. Kozikowski and A. Ames, J. Amer. Chem. Soc., 102, 860 (1980).
333. L. Toniolo and M. Graziani, J. Organomet. Chem., 194, 221 (1980).
334. D. H. Doughty, Diss. Abstr. Int. B, 40, 5257 (1980).
335. G. Domazetis, B. Tarpey, D. Dolphin, and B. R. James, J. Chem. Soc., Chem. Commun., 939 (1980).
336. H. Single, M. Prasad, and R. D. Srivastava, Chem. Technol. Biotechnol., 30, 293 (1980).

337. D. H. Doughty, M. F. McGuiggan, H. Wang, and L. H. Pignolet, *Fundam. Res. Homogeneous Catal.*, **3**, 909 (1979).

338. L. Kollar, S. Toros, B. Heil, and L. Marko, *J. Organomet. Chem.*, **192**, 253 (1980).

339. T. Goto, M. Onaka, and T. Mukaiyama, *Chem. Lett.*, 709 (1980).

340. T. Ito, Y. Kindaichi, and Y. Takami, *Chem. Ind.*, **2**, 83 (1980).

341. T. Hung, P. W. Jolly, and G. Wilke, *J. Organomet. Chem.*, **190**, C5 (1980).

342. T. Tsuda, Y. Chujo, and T. Sagusa, *J. Amer. Chem. Soc.*, **102**, 431 (1980).

343. F. Kurbanova, *Mater. Nauchn. Konf, Aspir. Akad. Nauk. Az. SSR,* **1**, 89 (1980).

344. A. L. Lapidus, M. I. Magan'ya, V. V. Mal'tsev, and Kh. M. Minachev, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, **7**, 1580 (1980).

345. H. Sinn, W. Kaminsky, H-J Vollmer, and R. Woldt, *Angew Chem. IE*, **19**, 390 (1980).

346. B. Bogdanovic', B. Splielhoff, and G. Wilke, *Angew Chem. IE*, **19**, 622 (1980).

347. D. L. Beach and T. P. Kobylinski, *J. Chem. Soc., Chem. Comm.*, 933 (1980).

348. R. F. Camacho, D. S. Delgado, and A. R. Alvaro, *Ing. Quim.*, **12**, 83 (1980).

349. N. A. Borisova, E. A. Mushina, G. P. Karpacheva, and B. A. Krentsel, *Nauchn. Osn. Pererab. Nefti Gaza Neftekhim., Tezisy Dokl., Vses. Konf.*, 156 (1977).

350. P. G. Antonov, N. V. Borunova, V. I. Anufriev, and V. M. Ignatov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **22**, 952 (1979).

351. J. R. Sohn and A. Ozaki, *J. Catal.*, **61**, 29 (1980).

352. R. Schrock, S. McLain, and J. Sancho, *Pure Appl. Chem.*, **52**, 729 (1980).

353. T. N. Nikonova, V. S. Tkach, F. K. Shmidt, and I. I. Moiseev, *Neftekhimiya* **20**, 534 (1980).

354. A. K. Yatsimirskii, A. S. Erokhin, and I. V. Berezin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 42 (1980).

355. H. Pracejus, H. J. Krause, and G. Oehme, *Z. Chem.*, **20**, 24 (1980).

356. W. Keim and F. H. Kowaldt, *Compend. Dtsch. Ges. Mineraloelwiss. Kohlechem.*, **78-79**, 453 (1978).

357. C. Tanielian, A. Kiennemann, and T. Osparpucu, *Can. J. Chem.*, **58**, 2813 (1980).

358. J. Furukawa, *Accts. Chem. Res.*, **13**, 1 (1980).

359. A. J. Chalk and S. A. Magennis, *Ann. N. Y. Acad. Sci.*, **333**, 286 (1980).

360. U. M. Dzhemilev, A. G. Ibragimov, O. S. Vostrikova, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2071 (1979).

361. E. Leroy, D. Huchette, A. Mortreux, and F. Petit, *Nouv. J. Chim.*, **4**, 173 (1980).

362. I. E. Maxwell, R. S. Downing, and S. A. J. Van Langen, *J. Catal.*, **61**, 485 (1980).

363. I. E. Maxwell, J. J. De Boer, and R. S. Downing, *J. Catal.*, **61**, 493 (1980).

364. U. M. Dzhemilev, A. G. Kukovinets, G. A. Tolstikov, S. I. Spivak, Z. Sh. Akhmadishin, A. S. Shmelev, and F. S. D'yachkovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1509 (1980).

365. W. R. Moser and A. W. Langer, Jr., *Catal. Org. Synth.*, 219 (1980).

366. A. H. Connop, F. G. Kennedy, S. A. R. Knox, R. M. Mills, G. H. Riding, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 518 (1980).

367. A. Busch, P. Heimbach, R. V. Meyer, and H. Schenkluhn, *J. Chem. Res. Synop.*, 228 (1979).

368. A. Sisak, H. Schenkluhn, and P. Heimbach, *Acta Chim. Acad. Sci. Hung.*, **103**, 377 (1980).

369. P. Heimbach, J. Kluth, and H. Schenkluhn, *Jerusalem Symp. Quantum Chem. Biochem.*, **12**, 227 (1979).

370. P. Heimbach, J. Kluth, H. Schenkluhn, and B. Weimann, *Angew Chem.*, **92**, 567 (1980).

371. P. Heimbach, J. Kluth, H. Schenkluhn, and B. Weimann, *Angew Chem.*, **92**, 569 (1980).

372. U. M. Dzhemilev and L. Yu. Gubaidullin, *Issled. Obl. Khim. Vysokomol. Soedin. Neftekhim.*, 12 (1977).

373. A. M. Proskurnin, Yu. A. Malakhovskaya, N. M. Shel'pova, and T. L. Nyrkova, *Khim. Prom-st, (Moscow)*, 278 (1980).

374. N. M. Shel'pova, Yu. A. Malakhovskaya, and A. M. Proskurnin, *Khim. Prom-st., (Moscow)*, 207 (1980).

375. M. K. Chaudhuri, *Indian J. Chem., Sect. A*, **19A**, 125 (1980).

376. S. Paraskewas, N. Janovicz, and D. Konstandinidis, *Chem. Ing. Tech.*, **52**, 157 (1980).

377. G. Buono, G. Peiffer, A. Mortreux, and F. Petit, *J. Chem. Soc., Chem. Commun.*, 937 (1980).

378. U. M. Dzhemilev, R. I. Khusnutdinov, V. A. Dokichev, G. A. Tolstikov, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2634 (1979).

379. S. Datta, M. B. Fischer, and S. S. Wreford, *J. Organomet. Chem.*, **188**, 353 (1980).

380. P. Albano and M. Aresta, *J. Organomet. Chem.*, **190**, 243 (1980).

381. O. S. Vostrikova, A. G. Ibragimov, G. A. Tolstikov, L. M. Zelenova, and U. M. Dzhemilev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2320 (1980).

382. G. Peiffer, X. Cochet, and F. Petit, *Bull. Soc. Chim. Fr.*, 415 (1979).

383. K. Kaneda, T. Uchiyama, M. Terasawa, T. Imanaka, and S. Teranishi, *Rev. Port. Quim.*, **19**, 341 (1977).

384. A. Dohring and P. W. Jolly, *Tetrahedron Lett.*, **21**, 3021 (1980).

385. A. Musco, *J. Chem. Soc., Perkin I*, 693 (1980).

386. P. Binger and U. Schuchardt, *Chem. Ber.*, **113**, 1063 (1980).

387. P. Binger and U. Schuchardt, *Chem. Ber.*, **113**, 3334 (1980).

388. P. Binger, J. McMeeking and U. Schuchardt, Chem. Ber., 113, 2372 (1980).

389. T. H. Johnson and T. F. Baldwin, J. Org. Chem., 45, 140 (1980).

390. R. F. Newton, P. L. Pauson, and R. G. Taylor, J. Chem. Res., 277 (1980).

391. T. Masuda, T. Mouri, and T. Higashimura, Bull. Chem. Soc., Japan, 53, 1152 (1980).

392. R. E. Mardaleishvili, Zh. Ya. Smorodinskaya, and A. Kh. Keroglu, Vestn. Mosk. Univ., Ser. 2: Khim., 21, 475 (1980).

393. P. Bicev, A. Furlani, and M. V. Russo, Gazz. Chim. Ital., 110, 25 (1980).

394. J. Leglise, T. Chevreau, and D. Cornet, C. R. Seances Acad. Sci., Ser. C, 291, 41 (1980).

395. R. L. Funk and K. P. C. Vollhardt, Chem. Soc. Rev., 9, 41 (1980).

396. A. Naiman, Diss. Abstr. Int. B, 41, 202 (1980).

397. H. Boennemann and G. S. Natarajan, Erdoel Kohle, Erdgas, Petrochem., 33, 328 (1980).

398. R. L. Funk and K. P. C. Vollhardt, J. Amer. Chem. Soc., 102, 5245 (1980).

399. K. P. C. Vollhardt, Ann. N. Y. Acad. Sci., 333, 241 (1980).

400. R. L. Funk and K. P. C. Vollhardt, J. Amer. Chem. Soc., 102, 5253 (1980).

401. E. R. F. Gesing, J. A. Sinclair, and K. P. C. Vollhardt, J. Chem. Soc., Chem. Commun., 286 (1980).

402. E. D. Sternberg and K. P. C. Vollhardt, J. Amer. Chem. Soc., 102, 4839 (1980).

403. E. R. F. Gesing, J. P. Tane, and K. P. C. Vollhardt, Angew Chem. Internat. Ed., 19, 1023 (1980).

404. R. L. Hillard, III and K. P. C. Vollhardt, Tetrahedron, 36, 2435 (1980).

405. K. H. Dotz and I. Pruskil, Chem. Ber., 113, 2876 (1980).

406. S. Dabi and A. Zilkha, Eur. Polym. J., 16, 95 (1980).

407. N. A. Grigor'ev, N. A. Kuz'mina, E. Ts. Chukovskaya, A. L. Tumanskaya, and R. Kh. Freidlina, Izv. Akad. Nuak SSSR, Ser. Khim., 1333 (1980).

408. I. P. Lavrent'ev, L. G. Korableva, A. I. Kuzaev, Yu. M. Shul'ga, and M. L. Khidekel, Izv. Akad. Nauk SSSR, Ser. Khim., 1995 (1980).

409. A. B. Terent'ev, M. A. Moskalenko, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1406 (1980).

410. R. Baker and P. M. Winton, Tetrahedron Lett., 21, 1175 (1980).

411. R. V. Kunakova and F. V. Sharipova, Issled. Obl. Khim. Vysokomol. Soedin. Neftekhim., 11 (1977).

412. R. V. Kunakova, G. A. Tolstikov, Z. N. Baibulatova, S. S. Zlotskii, D. L. Rakhmankulov, V. V. Zorin, and U. M. Dzhemilev, Zh. Org. Khim., 16, 1775 (1980).

413. Y. Tamaru, R. Suzuki, M. Kagotani, and Z. Yoshida, Tetrahedron Lett., 21, 3791 (1980).

414. Y. Tamaru, R. Suzuki, M. Kagotani, and Z. Yoshida, Tetrahedron Lett., 21, 3787 (1980).

415. U. M. Dzhemilev, F. A. Selimov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2652 (1979).

416. J. Berger and F. Meier, *J. Prakt. Chem.*, **322**, 69 (1980).

417. M. Hidai, H. Mizuta, K. Hirai, and Y. Uchida, *Bull. Chem. Soc., Japan*, **53**, 2091 (1980).

418. R. N. Fakhretdinov and U. M. Dzhemilev, *Issled. Obl. Khim. Vysokomol. Soedin. Neftekhim.*, 18 (1977).

419. U. M. Dzhemilev, R. I. Khusnutdinov, Z. S. Muslimov, G. A. Tolstikov, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 220 (1980).

420. U. M. Dzhemilev, R. N. Fakhretdinov, A. G. Telin, and G. A. Tolstikov, *Bull. Akad. Nauk SSSR, Ser. Khim.*, **29**, 944 (1980).

421. U. M. Dzhemilev, R. N. Fakhreldinov, A. G. Telin, M. Yu. Dolomatov, E. G. Galkin, and G. A. Tolstikov, *Bull. Akad. Nauk SSSR, Ser. Khim.*, **29**, 148 (1980).

422. U. M. Dzhemilev, F. A. Selimov, G. A. Tolstikov, E. A. Galkin, and V. I. Khvostinko, *Bull. Acad. Nauk SSSR, Ser. Khim.*, **29**, 473 (1980).

423. U. M. Dzhemilev, F. A. Selimov, and G. A. Tolstikov, *Bull. Akad. Nauk SSSR, Ser. Khim.*, **29**, 263 (1980).

424. D. Reinehr, *Pure and Appl. Chem.*, **52**, 2417 (1980).

425. J. Tsuji, T. Takahashi, I. Shimuzu, and H. Nagashima, *Yuki Gosei Kagaku Kyokaish*, **38**, 219 (1980).

426. J. Tsuji, Y. Kobayashi, and T. Takahashi, *Tetrahedron Lett.*, **21**, 483 (1980).

427. J. Tsuji, I. Shimizu, H. Suzuki, and Y. Naito, *Tennen Yuki Kagobutsu Toronkai Koen Yoshishu, 22nd*, 40 (1979).

428. I. Simizu, Y. Naito, and J. Tsuji, *Tetrahedron Lett.*, **21**, 487 (1980).

429. U. Dzhemilev, R. V. Kunakova, N. Z. Barbulatova, G. A. Tolstikov, and A. A. Panasenko, *J. Org. Chem., USSR*, **16**, 999 (1980).

430. U. M. Dzhemilev, R. V. Kunakova, Yu. T. Struchov, P. A. Tolstikov, F. V. Sharipova, L. G. Kumina, and S. R. Rafikov, *Dokl. Chem.*, **250**, 1 (1980).

431. U. M. Dzhemilev, R. V. Kunakova, R. L. Gaisin, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2702 (1979).

432. R. Baker and M. G. Kelly, *J. Chem. Soc., Chem. Commun.*, 307 (1980).

433. J. M. Basset and M. Leconte, *Chem. Tech. Rev.*, **10**, 762 (1980). A review with 50 references.

434. R. L. Banks, *Catal. Org. Synth.*, 233 (1980). A review with 29 references.

435. J. Otton, *Inf. Chim.*, **201**, 161 (1980). A review with 54 references.

436. M. L. H. Green, *Ann. N. Y. Acad. Sci.*, **333**, 229 (1980). A review with 15 references.

437. J. A. K. Du Plessis and P. J. Heenop, *S. Afr. J. Chem.*, **33**, 51 (1980).

438. J. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, and W. J. Young, *J. Amer. Chem. Soc.*, **102**, 4515 (1980).

439. O. L. Kosinskii, A. A. Kadushin, O. V. Krylov, F. K. Shmidt, N. E. Kolobova, and Yu. V. Maksimov, *Geterog. Katal.*, 4th, 403 (1979).

440. J-C. Hsu, *Diss. Abstr. Int. B*, **40**, 1810 (1979).

441. K. Tanaka, K. Tanaka, and K. Miyahara, *J. Chem. Soc., Chem. Commun.*, 666 (1980).

442. T. Yamaguchi, Y. Tanaka, and K. Tanabe, *J. Catal.*, **65**, 442 (1980).

443. H. L. Krauss and E. Hums, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **34B**, 1628 (1979).

444. J. P. Van Linthoudt, L. Delmulle, and G. P. Van Der Kelen, *J. Organomet. Chem.*, **202**, 39 (1980).

445. R. H. Grubbs, *Prepr. Div. Pet. Chem., Am. Chem. Soc.*, **24**, 388 (1979), A review with 21 references.

446. R. L. Tucker, *Diss. Abstr. Int. B*, **40**, 5665 (1980).

447. A. K. Rappe and W. A. Goddard III, *J. Amer. Chem. Soc.*, **102**, 5114 (1980).

448. M. F. Farona and R. L. Tucker, *J. Mol. Catal.*, **8**, 85 (1980).

449. R. Edreva-Kardzheva and A. Andreev, *Geterog. Katal.*, 4th, 313 (1979).

450. F. Garnier, P. Krausz, and H. Rudler, *J. Organomet. Chem.*, **186**, 77 (1980).

451. K. L. Makovetskii, B. A. Dolgoplosk, Yu. V. Korshak, I. A. Oreshkin, and E. I. Tinyakova, *Zh. Vses. Khim. O-va.*, **24**, 513 (1979).

452. C. P. Casey, D. M. Scheck, and A. J. Shusterman, *Fundam. Res. Homogeneous Catal.*, **3**, 141 (1979).

453. J. Levisalles, H. Rudler, and D. Villemin, *J. Organomet. Chem.*, **192**, 375 (1980).

454. J. Levisalles, H. Rudler, and D. Villemin, *J. Organomet. Chem.*, **192**, 195 (1980).

455. J. Levisalles, H. Rudler, and D. Villemin, *J. Organomet. Chem.*, **193**, 235 (1980).

456. M. Leconte and J. M. Bassett, *Ann. N. Y. Acad. Sci.*, **333**, 165 (1980).

457. J. M. Basset and M. Leconte, *Fundam. Res. Homogeneous Catal.*, **3**, 285 (1979).

458. T. R. Howard, J. B. Lee, and R. H. Grubbs, *J. Amer. Chem. Soc.*, **102**, 6876 (1980).

459. R. H. Grubbs and A. Miyashita, *Fundam. Res. Homogeneous Catal.*, **3**, 151 (1979).

460. K. Maruyama, K. Terada, and Y. Yamamoto, *J. Org. Chem.*, **45**, 737 (1980).

461. D. Villemin, *Tetrahedron Lett.*, **21**, 1715 (1980).

462. J. Tsuji and S. Hashiguchi, *Tetrahedron Lett.*, **21**, 2955 (1980).

463. S. Warwel, *Compend. - Dtsch. Ges. Mineraloelwiss. Kohlechem.*, **78-79**, 437 (1978). A review with 31 references.

464. T. J. Katz and S. J. Lee, *J. Amer. Chem. Soc.*, **102**, 422 (1980).

465. T. J. Katz, S. J. Lee, M. Nair, and E. B. Savage, *J. Amer. Chem. Soc.*, **102**, 7940 (1980).

466. T. J. Katz, S. J. Lee, M. Nair, and E. B. Savage, *J. Amer. Chem. Soc.*, **102**, 7942 (1980).

467. J. A. K. Du Plessis and P. J. Heenop, *S. Afr. J. Chem.*, **32**, 115 (1979).

468. H. O. Stuehler, Z. Naturforsch., *B: Anorg. Chem., Org. Chem.*, **35B**, 340 (1980).

469. F. D'Amico, J. Von Jouanne, and H. Kelm, *J. Mol. Catal.*, **6**, 327 (1979).

470. C. U. Pittman, Jr., W. D. Honnick, M. S. Wrighton, R. D. Sanner, and R. G. Austin, *Fundam. Res. Homogeneous Catal.*, **3**, 603 (1979).

471. R. D. Sanner, R. G. Austin, M. S. Wrighton, W. D. Honnick, and C. U. Pittman Jr., *Adv. Chem. Ser.*, **184**, 13 (1980).

472. H. Kanai, K. Kushi, K. Sakanoue, and N. Kishimoto, *Bull. Chem. Soc., Japan*, **53**, 2711 (1980).

473. R. J. De Pasquale, *Synth. Comm.*, **10**, 225 (1980).

474. L. A. Paquette, W. E. Fristad, D. S. Dime, and T. R. Bailey, *J. Org. Chem.*, **45**, 3017 (1980).

475. H. Suzuki, H. Yashima, T. Hirose, M. Takahashi, Y. Moro-oka, and T. Ikawa, *Tetrahedron Lett.*, **21**, 4927 (1980).

476. E. Weissberger, A. Stockis, D. D. Carr, and J. Giebfried, *Bull. Soc., Chim. Belg.*, **89**, 281 (1980).

477. L. Busetto, *J. Organomet. Chem.*, **186**, 411 (1980).

478. K. Hirai, H. Suzuki, Y. Moro-oka, and T. Ikawa, *Tetrahedron Lett.*, **21**, 3413 (1980).

479. C. P. Khulbe and R. S. Mann, *Prepr. - Can. Symp. Catal.*, 5th, 384 (1977).

480. F. Turecek, H. Antropiusova, K. Mach, V. Hanus, and P. Sedmera, *Tetrahedron Lett.*, **21**, 637 (1980).

481. H. Alper and K. Hachem, *J. Org. Chem.*, **45**, 2269 (1980).

482. J. K. Stille and Y. Becker, *J. Org. Chem.*, **45**, 2139 (1980).

483. R. C. Cookson, M. C. Cramp, and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 197 (1980).

484. W. Smadja, G. Ville, and C. Geargoulis, *J. Chem. Soc., Chem. Commun.*, 594 (1980).

485. T. Tsuda, Y. Chujo, Se-i. Nishi, K. Tawara, and T. Saegusa, *J. Amer. Chem. Soc.*, **102**, 6381 (1980).

486. I. Shimizu, T. Yamada, and J. Tsuji, *Tetrahedron Lett.*, **21**, 3199 (1980).

487. P. A. Grieco, T. Takigawa, S.L. Bongers, and H. Tanaka, *J. Amer. Chem. Soc.*, **102**, 7587 (1980).

488. L. E. Overman and F. M. Knoll, *J. Amer. Chem. Soc.*, **102**, 865 (1980).

489. Y. Tamura, M. Kagotani, and Z-i. Yoshida, *J. Org. Chem.*, **45**, 5221 (1980).

490. B. M. Trost, T. A. Runge, and L. N. Jungheim, *J. Amer. Chem. Soc.*, **102**, 2840 (1980).

491. Y. Inoue, T. Hibi, Y. Kawashima, and H. Hashimoto, *Chem. Lett.*, 1521 (1980).

492. F. Garin and F. G. Gault, *NATO Adv. Study Inst. Ser., Ser. E*, **39**, 351 (1980). A review with 49 references.

493. J. Elzinga, H. Hogeveen, and E. P. Schudte, *J. Org. Chem.*, **45**, 4337 (1980).

494. T-Y. Luh, C. H. Lai, and S. W. Tam, *J. Chem. Soc., Perkin Trans. I*, 444 (1980).

495. S. A. Matlin and L. Chan, *J. Chem. Soc., Chem. Commun.*, 798 (1980).

496. S. Abramson and A. Eisenstadt, *Tetrahedron*, **36**, 105 (1980).

497. P. Eilbracht and P. Dahler, *Chem. Ber.*, **113**, 542 (1980).

498. P. Eilbracht, P. Dahler, U. Mayser, and E. Henkes, *Chem. Ber.*, **113**, 1033 (1980).

499. M. Suzuki, A. Watanabe, and R. Noyori, *J. Amer. Chem. Soc.*, **102**, 2095 (1980).

500. Y. Abe, T. Takizawa, and T. Kunieda, *Chem. Pharm. Bull.*, **28**, 1324 (1980).

501. M. Yamaguchi, S. Yamamatsu, T. Furusawa, S. Yano, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **19**, 2010 (1980).

502. R. K. Thappa, S. C. Taneja, K. L. Dhar, and C. K. Atal, *Indian Perfum.*, **23**, 172 (1979).

503. N. V. Kudrina, L. N. Kurina, *Khim. Kinet. Katal.*, 186 (1979).

504. V. V. Mahajani, *Indian Chem. Eng.*, **21**, 45 (1979).

505. P. S. Radhakrishnamurti and P. C. Misra, *Indian J. Chem. Sect. A*, **19A** 427 (1980).

506. M. P. Rao, B. Sethuram, and T. N. Rao, *Curr. Sci*, **48**, 990 (1979).

507. I. V. Kozhevnikov, V. E. Taraban'ko, and K. I. Matveev, *Kinet. Katal.*, **21**, 947 (1980).

508. I. V. Kozhevnikov, V. E. Taraban'ko, and K. I. Matveev, *Kinet. Katal.*, **21**, 940 (1980).

509. K. V. Uma and S. M. Mayanna, *J. Catal.*, **61**, 165 (1980).

510. B. A. Moyer, M. S. Thompson, and T. J. Meyer, *J. Amer. Chem. Soc.*, **102**, 2310 (1980).

511. C. Jallabert and H. Riviere, *Tetrahedron*, **36**, 1191 (1980).

512. H. Alper, K. Hachem, and S. Gambarota, *Can. J. Chem.*, **58**, 1599 (1980).

513. M. P. Doyle, R. L. Dow, V. Bagheri, and W. J. Patrie, *Tetrahedron Lett.*, **21**, 2795 (1980).

514. M. P. Doyle and R. L. Dow, *Synth. Comm.*, **10**, 881 (1980).

515. J. Forsek, *Tetrahedron Lett.*, **21**, 1071 (1980).

516. J. F. Harrod and A. Pathak, *Can. J. Chem.*, **58**, 686 (1980).

517. D. M. Roundhill, M. K. Dickson, N. S. Dixit, and B. P. Sudha-Dixit, *J. Amer. Chem. Soc.*, **102**, 5538 (1980).

518. M. K. Dickson, B. P. Sudha, and D. M. Roundhill, *J. Organomet. Chem.*, **190**, C43 (1980).

519. J. L. Seoane, P. Boutry, and R. Montarnal, *J. Catal.*, **63**, 182 (1980).

J. L. Seoane, P. Boutry, and R. Montarnal, *J. Catal.*, **63**, 191 (1980).

A. Omar, G. Djega-Mariadassou, and F. Bozon-Verduraz, *J. Catal.*, **60**, 295 (1979).

C. S. Li, A. N. Astanina, P. A. Sharbatyan, and A. P. Rudenko, *Khim. Kinet. Katal.*, 133 (1979).

N. Tamura, *Shokubai*, **21**, 168 (1979).

N. Tamura, *Shokubai*, **21**, 379 (1979).

A. Kaszonyi, J. Vojtko, and M. Hrusovsky, *Petrochemia*, **19**, 109 (1979).

A. Nishinaga, *Kagaku no Ryoiki*, **34**, 689 (1980).

F. Igersheim and H. Mimoun, *Nouv. J. Chim.*, **4**, 711 (1980).

M. Roussel and H. Mimoun, *J. Org. Chem.*, **45**, 5387 (1980).

H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, and R. Weiss, *J. Amer. Chem. Soc.*, **102**, 1047 (1980).

F. Igersheim and H. Mimoun, *Nouv. J. Chim.*, **4**, 161 (1980).

J. Tsuji, H. Nagashima, and K. Hori, *Chem. Lett.*, 257 (1980).

J. Tsuji, T. Yamada, and I. Shimizu, *J. Org. Chem.*, **45**, 5209 (1980).

P. D. Magnus, M. S. Nobbs, *Synth. Commun.*, **10**, 273 (1980).

B. S. Tovrog, F. Mares, and S. E. Diamond, *J. Amer. Chem. Soc.*, **102**, 6616 (1980).

R. O. C. Norman, C. B. Thomas, and G. Watson, *J. Chem. Soc., Perkin II*, 1099 (1980).

S. F. Politanskii, A. M. Shkitov, E. S. Shpiro, G. V. Antoshin, K. M. Minachev, I. I. Moiseev, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1947 (1980).

M. Schroeder, *Chem. Rev.*, **80**, 187 (1980).

R. Ray and D. S. Matteson, *Tetrahedron Lett.*, **21**, 449 (1980).

V. VanRheenen, D. Y. Cha, and W. M. Hartley, *Org. Synth.*, **58**, 43 (1978).

S. G. Hentges and K. B. Sharpless, *J. Amer. Chem. Soc.*, **102**, 4263 (1980).

T. Ogino, *Tetrahedron Lett.*, **21**, 177 (1980).

S. G. Hentges and K. B. Sharpless, *J. Org. Chem.*, **45**, 2257 (1980).

E. Herranz and K. B. Sharpless, *J. Org. Chem.*, **45**, 2710 (1980).

A. Toshimitsu, T. Aoai, S. Uemura, and M. Okano, *J. Org. Chem.*, **45**, 1953 (1980).

M. S. Miftakhov, N. N. Sidorov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2748 (1979).

M. M. Midland and S. B. Preston, *J. Org. Chem.*, **45**, 4514 (1980).

S. Kano, Y. Tanaka, and S. Hibino, J. Chem. Soc., Chem. Comm., 414 (1980).

K. Oishi and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **53**, 179 (1980).

J. S. Deetz and E. J. Behrman, *J. Org. Chem.*, **45**, 135 (1980).

J. Tsuji and H. Takayanagi, *Chem. Lett.*, 65 (1980).

S. K. Ray, R. N. Bhattacharyya, and P. N. Mukherjee, *Proc. Symp. Sci. Catal. Its Appl. Ind.*, 156 (1979).

553. K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, **12**, 63 (1979).

554. M. Pralus, J. C. Lecoq, and J. P. Schirmann, *Fundam. Res. Homogeneous Catal.*, **3**, 327 (1979).

555. G. A. Konishevskaya, A. P. Filippov, Y. Sobchak, Y. Y. Zyulkovskii, K. B. Yatsimirskii, and V. M. Belousov, *Kinet. Katal.*, **21**, 933 (1980).

556. S. D. Mekhtiev, F. Z. Abdullaev, N. I. Garibov, B. R. Serebryakov, and S. Y. Ragimova, *Dokl. Akad. Nauk Az. SSR*, **36**, 55 (1980).

557. Y. S. Sanghvi and A. S. Rao, *Indian J. Chem., Sect B*, **19B**, 608 (1980).

558. F. Di Furia, G. Modena, R. Curci, and J. O. Edwards, *Gazz. Chim. Ital.*, **109**, 571 (1979).

559. L. D. Tyutchenkova and Z. K. Maizus, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2196 (1979).

560. T. Katsuki and K. B. Sharpless, *J. Amer. Chem. Soc.*, **102**, 5974 (1980).

561. H. Tamioka, K. Takai, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **21**, 4843 (1980).

562. E. Guilmot and B. Meunier,*Tetrahedron Lett.*, **21**, 4449 (1980).

563. K. Kaneda, K. Jitsukawa, T. Itoh, and S. Teranishi, *J. Org. Chem.*, **45**, 3004 (1980).

564. M. Kimura and T. Muto, *Chem. Pharm. Bull.*, **28**, 1836 (1980).

565. V. P. Tret'yakov, G. P. Zimtseva, E. S. Rudakov, A. V. Bogdanov, and D. M. Palade, *Kinet. Katal.*, **21**, 283 (1980).

566. S. E. Jacobson, R. Tang, and F. Mares, *J. Chem. Soc., Chem. Commun.*, 888 (1978).

567. R. M. Dessau and E. I. Heiba, *Colloq. Int. C. N. R. S.*, 271 (1978).

568. T. R. Pemmin and M. M. Rogic, *J. Org. Chem.*, **45**, 2737 (1980).

569. S. I. Perumal and M. W. Barker, *Indian J. Chem., Sect. B*, **19B**, 508 (1980).

570. T. Yamanaka, *Kagaku Kogyo*, **30**, 947 (1979).

571. U. M. Dzhemilev and A. Z. Yakupova, *Issled. Obl. Khim. Vysokomol. Soedin. Neftekhim.*, 5 (1977).

572. A. Inada, Y. Nakamura, and Y. Morita, *Chem. Lett.*, 1287 (1980).

573. M. Fernandez Mateos and S. G. Davies, *An. Quim.*, **75**, 385 (1979).

574. M. A. Bennett and H. Neumann, *Aust. J. Chem.*, **33**, 1251 (1980).

575. D. E. Laycock, J. Hartgerink, and M. C. Baird, *J. Org. Chem.*, **45**, 291 (1980).

576. C. B. Hanson, *Tetrahedron Lett.*, **21**, 1581 (1980).

577, P. M. Henry, "Catalysis by Metal Complexes," Vol. 2, (1980).

578. S. Top, G. Jaouen, and M. McGlinchey, *J. Chem. Soc., Chem. Commun.*, 642 (1980).

579. M. T. Reetz and W. Stephan, *Liebigs Ann. Chem.*, 171 (1980).

580. M. K. Starchevskii, M. N. Vargaftik, and I. I. Moiseev, *Kinet. Katal.*, **20**, 1163 (1979).

581. L. N. Arzamaskova, A. V. Romanenko, and Y. I. Ermakov, *React. Kinet. Catal. Lett.*, **13**, 391 (1980).

582. R. W. Clayton and S. V. Norval, *Catalysis (London)*, **3**, 70 (1980).

583. K. Nakagawa, *Tokushima Bunri Daigaku Kenkyu Kiyo*, **20**, 65 (1980).

584. E. Ross, *Kontakte*, 19 (1979).

585. K. Nakagawa, S. Shiba, M. Horikawa, K. Sato, H. Nakamura, N. Harada, and F. Harada, *Synth. Commun.*, **10**, 305 (1980).

586. F. Di Furia and G. Modena, *Fundam. Res. Homogeneous Catal.*, **3**, 433 (1979).

587. K. M. Nicholas, *J. Organomet. Chem.*, **188**, C10 (1980).

588. W. J. Rodewald and J. W. Morzycki, *Pol. J. Chem.*, **53**, 1373 (1979).

589. A. B. Smith,III and R. M. Scarborough, Jr, *Synth. Commun.*, **10**, 205 (1980).

590. A. Nishinaga, T. Shimizu, and T. Matsuure, *Tetrahedron Lett.*, **21**, 4097 (1980).

591. R. H. Crabtree, D. F. Chodosh, J. M. Quirk, H. Felkin, T. Khan-Fillebeen, and G. E. Morris, *Fundam. Res. Homogeneous Catal.*, **3**, 475 (1979).

592. D. Bondoux, D. Houalla, C. Pradat, J. G. Riess, I. Tkatchenko, and R. Wolf, *Fundam. Res. Homogeneous Catal.*, **3**, 969 (1979).

593. A. R. Sanger, *Prepr. Can. Symp. Catal.*, **6**, 37 (1979).

594. P. Kalck, R. Poilblanc, R. P. Martin, A. Rovera, and A. Gaset, *J. Organomet. Chem.*, **195** C9 (1980).

595. H. C. Clark, C. Billard, and C. S. Wong, *J. Organomet. Chem.*, **190**, C105 (1980).

596. P. Gallois, J. J. Brunet, and P. Caubere, *J. Org. Chem.*, **45**, 1946 (1980).

597. J. Mueller, B. Passon, and S. Schmitt, *J. Organomet. Chem.*, **195**, C21 (1980).

598. M. Jakoubkova and M. Capka, *Collect. Czech, Chem. Commun.*, **45**, 2219 (1980).

599. M. S. Delaney, C. B. Knobler, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 849 (1980).

600. T. E. Nalesnik and M. Orchin, *J. Organomet. Chem.*, **199**, 265 (1980).

601. M. Cais, *Chim. Ind. (Milan)*, **61**, 395 (1979).

602. R. Dabard, G. Jaouen, G. Simonneaux, M, Cais, D. H. Kohn, A. Lapid, and D. Tatarsky, *J. Organomet. Chem.*, **184**, 91 (1980).

603. M. Cais and D. Fraenkel, *Ann. N. Y. Acad. Sci.*, **333**, 23 (1980).

604. A. H. Andrist and J. E. Graas, *Prostaglandins*, **18**, 631 (1979).

605. R. Pettit, K. Cann, T. Cole, C. H. Mauldin, and W. Slegeir, *Ann. N. Y. Acad. Sci.*, **333**, 101 (1980).

606. A. D. King, R. B. King, and D. B. Yang, *Chem. Commun.*, 529 (1980).

607. C-H. Cheng, L. Kuritzkes, and R. Eisenberg, *J. Organomet. Chem.*, **190**, C21 (1980).

608. E. Samuel, *J. Organomet. Chem.*, **198**, C65 (1980).

609. R. L. Augustine, J. F. Van Peppen, and F. Yaghmaie, *Prepr. Can. Symp. Catal.*, **6**, 256 (1979).

610. A. S. C. Chan and J. Halpern, *J. Amer. Chem. Soc.*, **102**, 838 (1980).

611. A. Dedieu, *Inorg. Chem.*, **19**, 375 (1980).

612. P. Foley and G. M. Whitesides, *Inorg. Chem.*, **19**, 1402 (1980).

613. H. F. Klein, R. Hammer, J. Wenninger, and J. Gross, *Jerusalem Symp. Quantum Chem. Biochem.*, **12**, 285 (1979).

614. S. Sato, *J. Res. Inst. Catal. Hokkaido Univ.*, **27**, 89 (1979).

615. Y. S. Levkovskii, N. M. Ryutina, and F. K. Shmidt, *Kinet. Katal.*, **21**, 797 (1980).

616. V. Vyskocil and M. Kraus, *Collect. Czech. Chem. Commun.*, **44**, 3676 (1979).

617. K. Taya, S. Morimoto, C. Abe, K. Nomura, O. Nomura, and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **53**, 1034 (1980).

618. E. C. Ashby and S. A. Noding, *J. Org. Chem.*, **45**, 1035 (1980).

619. E. Negishi and T. Yoshida, *Tetrahedron Lett.*, **21**, 1501 (1980).

620. F. Sato, Y. Tomuro, H. Ishikawa, and M. Sato, *Chem. Lett.*, 99 (1980).

621. U. M. Dzhemilev, O. S. Vostrikova, A. G. Ibragimov, and G. A. Tolstikov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 2134 (1980).

622. A. Sisak, I. Jablonkai, and F. Ungvary, *Acta Chim. Acad. Sci. Hung.*, **103**, 33 (1980).

623. M. B. Izteleuova, N. F. Noskova, D. V. Sokol'skii, N. A. Gafarova, and N. K. Nadirov, *Zh. Org. Khim.*, **16**, 1131 (1980).

624. L. Michelin, G. A. Vaglio, and M. Valle, *Inorg. Chim. Acta*, **36**, 213 (1979).

625. C. P. Kubiak and R. Eisenberg, *J. Amer. Chem. Soc.*, **102**, 3637 (1980).

626. T. Itoh, T. Nagano, and M. Hirobe, *Tetrahedron Lett.*, **21**, 1343 (1980).

627. R. Uson, L. A. Oro, R. Sariego, M. Valderrama, and C. Rebullida, *J. Organomet. Chem.*, **197**, 87 (1980).

628. J. R. Weir, B. A. Patel, and R. F. Heck, *J. Org. Chem.*, **45**, 4926 (1980).

629. J. J. Brunet, P. Gallois, and P. Caubere, *J. Org. Chem.*, **45**, 1937 (1980).

630. F. K. Shmidt, Y. S. Levkovskii, N. M. Ryutina, and V. G. Lipovich, *React. Kinet. Catal. Lett.*, **12**, 475 (1979).

631. K. Tanaka, K. Tanaka, and K. Miyahara, *J. Catal.*, **59**, 423 (1979).

632. Y. Sakakibara, S. Yagi, M. Sakai, and N. Uchino, *Nippon Kagaku Kaishi*, 240 (1980).

633. L. K. Freidlin, L. I. Gvintev, and L. N. Suvorova, *J. Org. Chem. USSR*, **15**, 1636 (1979).

634. T. E. Zhesko, Y. N. Kukushkin, A. G. Nikitina, V. P. Kotel'nikov, and N. S. Barinov, *Zh. Obshch. Khim.*, **49**, 2254 (1979).

635. M. Airoldi, G. Deganello, G. Dia, and G. Gennaro, *J. Organomet. Chem.*, **187**, 391 (1980).

636. M. Bennett, *CHEMTECH*, **10**, 444 (1980).

637. R. A. Grey, G. P. Pez, and A. Wallo, *J. Amer. Chem. Soc.*, **102**, 5948 (1980).

638. L. Horner, *Kontakte*, **3** 3 (1979)

639. L. Horner, *Kontakte*, 37 (1980).

640. M. Kumada and T. Hayashi, *Kagaku (Kyoto)*, **34**, 574 (1979).

641. P. Pino and G. Consiglio, *Fundam. Res. Homogeneous Catal.*, **3**, 519 (1979).

642. H. Brunner, *Jerusalem Symp. Quantum Chem. Biochem.*, **12**, 255 (1979).

643. J. M. Brown, P. A. Chaloner, B. A. Murrer, and D. Parker, *ACS Symp. Ser.*, **119**, 169 (1980).

644. I. Ojima, *Strem. Chem.*, **8**, 1 (1980).

645. R. A. DeVries, *Diss. Abstr. Int. B*, **41**, 959 (1980).

646. H. B. Kagan, J. C. Fiaud, C. Hoornaert, D. Meyer, and J. C. Poulin, *Bull. Soc. Chim. Belg.*, **88**, 923 (1979).

647. Y. Nakamura, S. Saito, and Y. Morita, *Chem. Lett.*, 7 (1980).

648. T. H. Johnson and G. Rangarajan, *J. Org. Chem.*, **45**, 62 (1980).

649. H. Brunner and W. Pieronczyk, *J. Chem. Res.*, 74 (1980).

650. H. Brunner and W. Pieronczyk, *J. Chem. Res.*, 76 (1980).

651. E. E. Nifant'ev, T. S. Kukhareva, L. S. Gorshkova, V. A. Pvalov, and E. I. Klabunovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1915 (1979).

652. J. K. Stille, *Colloq. Int. C. N. R. S.*, **281**, 185 (1978).

653. J. K. Stille, S. J. Fritschel, N. Takaishi, T. Masuda, H. Imai, and C. A. Bertelo, *Ann. N. Y. Acad. Sci.*, **333**, 35 (1980).

654. K. Ohkubo, K. Fujimori, and K. Yoshinaga, *Inorg. Nucl. Chem. Lett.*, **15**, 231 (1979).

655. A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, and R. Noyori, *J. Amer. Chem. Soc.*, **102**, 7932 (1980).

656. S. Miyano, M. Naiva, and H. Hashimoto, *Chem. Lett.*, 729 (1980).

657. K. Kellnev, A. Tzschach, Z.Nagy-Magos, and L. Marko, *J. Organomet. Chem.*, **193**, 307 (1980).

658. K-i Onuma, T. Ito, and A. Nakamura, *Bull. Chem. Soc. Jpn.*, **53**, 2012 (1980).

659. J. M. Townsend, J. F. Blount, R. C. Sun, S. Zawoiski, and D. Valentine, Jr., *J. Org. Chem.*, **45**, 2995 (1980).

660. D. Valentine, Jr, K. K. Johnson, W. Priester, R. C. Sun., K. Toth, and G. Saucy, *J. Org. Chem.*, **45**, 3698 (1980).

661. D. Valentine, Jr, R. C. Sun, and K. Toth, *J. Org. Chem.*, **45**, 3703 (1980).

662. J. M. Brown and B. Murrer, *Tetrahedron Lett.*, **21**, 581 (1980).

663. I. Ojima and N. Yoda, *Tetrahedron Lett.*, **21**, 1051 (1980).

664. J. Koettnerand G. Greber, *Chem. Ber.*, **113**, 2323 (1980).

665. D. P. Riley and R. E. Shumate, *J. Org. Chem.*, **45**, 5187 (1980).

666. V. A. Pavlov, E. N. Rasadkina, E. I. Karpeiskaya, G. V. Chel'tsova, L. N. Kaigorodova, and E. I. Klabunovskii, *Bull. Akad. Nauk. SSSR, Ser. Khim. Sci.*, **29**, 7921 (1980).

667. H. Brunner and G. Argufoglio, *Monat. für Chem.*, **111**, 275 (1980).

668. L. M. Koroleva, V. K. Latov, M. B. Saporovskaya, and V. M. Belikov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 2390 (1979).

669. K. Yamamoto, J. Wakatsuki, and R. Sugimoto, *Bull. Chem. Soc. Jpn.*, **53**, 1132 (1980).

670. K. Kashiwabara, K. Hanaki, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **53**, 2275 (1980).

671. I. Ojima, T. Kogure, and N. Yoda, *J. Org. Chem.*, **45**, 4728 (1980).

672. M. Bianchi, U. Matteoli, G. Menchi, P. Frediani, F. Piacenti, and C. Botteghi, *J. Organomet. Chem.*, **195**, 337 (1980).

673. K. Ohkubo, I. Terada, and K. Yoshinaga, *Inorg. Nucl. Chem. Lett.*, **15**, 421 (1979).

674. S. Raghu, A. Zweig, and W. A. Henderson, Jr., *Fundam. Res. Homogeneous Catal.*, **3**, 565 (1979).

675. M. Tamura and K. Harada, *Bull. Chem. Soc. Jpn.*, **53**, 561 (1980).

676. K. E. Koenig, G. L. Bachman, and B. D. Vineyard, *J. Org. Chem.*, **45**, 2362 (1980).

677. K. E. Koenig, M. J. Sabacky, G. L. Bachman, W. C. Christopfel, H. D. Barnstorff, R. B. Friedman, W. S. Knowles, B. R. Stults, B. D. Vineyard, and D. J. Weinkauff, *Ann. N. Y. Acad. Sci.*, **333**, 16 (1980).

678. A. S. C. Chan, J. J. Pluth, and J. Halpern, *Inorg. Chim. Acta*, **37**, L477 (1979).

679. R. Glaser, S. Geresh, M. Twaik, *Isr. J. Chem.*, **20**, 102 (1980).

680. J. M. Brown and D. Parker, *J. Chem. Soc., Chem. Commun.*, 342 (1980).

681. J. M. Brown and P. A. Chaloner, *J. Chem. Soc., Chem. Commun.*, 344 (1980).

682. J. M. Brown and P. A. Chaloner, *J. Amer. Chem. Soc.*, **102**, 3040 (1980).

683. A. S. C. Chan, J. J. Pluth, J. Halpern, *J. Amer. Chem. Soc.*, **102**, 5952 (1980).

684. W. R. Cullen, F. W. B. Einstein, C-H. Huang, A. C. Willis, and E. Shanyeh, *J. Amer. Chem. Soc.*, **102**, 988 (1980).

685. K-i Onuma, T. Ito, and A. Nakamura, *Bull. Chem. Soc. Jpn.*, **53**, 2016 (1980).

686. B. R. James and D. K. W. Wang, *Prepr. Can. Symp. Catal.*, **6**, 29 (1979).

687. B. R. James and D. K. W. Wang, *Can. J. Chem.*, **58**, 245 (1980).

688. I. Ojima and T. Suzuki, *Tetrahedron Lett.*, **21**, 1239 (1980).

689. K-i Onuma, T. Ito, and A. Nakamura, *Chem. Lett.*, 481 (1980).

690. J. C. Poulin, D. Meyer, and H. B. Kagan, *C. R. Acad. Sci. Paris*, **291**, 69 (1980).

691. D. Meyer, J. C. Poulin, H. B. Kagan, H. Levine-Pinto, J. L. Morgat, and P. Fromageot, *J. Org. Chem.*, **45**, 4680 (1980).

692. T. Kanmera, H. Aoyagi, S. Lee, and N. Izumiya, *Pept. Chem.*, 59 (1979).

693. S. Toros, B. Heil, L. Kollar, and L. Marko, *J. Organomet. Chem.*, **197**, 85 (1980).

694. I. Ojima and T. Kogure, *J. Organomet. Chem.*, **195**, 239 (1980).

695. M. Bianchi, U. Matteoli, G. Menchi, P. Frediani, S. Pratesi, and F. Piacenti, *J. Organomet. Chem.*, **198**, 73 (1980).

696. T. Harada, *Bull. Chem. Soc. Jpn.*, **53**, 1019 (1980).

697. S. Murakami, T. Harada, and A. Tai, *Bull. Chem. Soc. Jpn.*, **53**, 1356 (1980).

698. K. Ito, T. Harada, and A. Tai, *Bull. Chem. Soc. Jpn.*, **53**, 3367 (1980).

699. G. V. Smith and M. Musoiu, *J. Catal.*, **60**, 184 (1979).

700. E. I. Klabunovskii, V. I. Neupokoev, Y. I. Petrov, A. B. Fasmau, and G. K. Areshidze, *Bull. Akad. Nauk. SSSR*, **29**, 106 (1980).

701. S. Tyrlik, M. M. Kucharska, and I. Wolochowicz, *J. Mol. Catal.*, **6**, 393 (1979).

702. Y. Orito, S. Imai, and S. Niwa, *Noppon Kagaku Kaishi*, 670 (1980).

703. I. Kolb and J. Hetflejs, *Coll. Czech. Chem. Commun.*, **45**, 2224 (1980).

704. J. F. Peyronel, J. C. Fiaud, and H. B. Kagan, *J. Chem. Res., Synop.*, 320 (1980).

705. A. J. Naaktgeboren, R. J. M. Nolte, and W. Drenth, *J. Amer. Chem. Soc.*, **102**, 3350 (1980).

706. N. L. Holy, *Fundam. Res. Homogeneous Catal.*, **3**, 691 (1979).

707. N. L. Holy and R. Shalvoy, *J. Org. Chem.*, **45**, 1418 (1980).

708. J. Lieto, J. J. Rafalko, J. V. Minkiewicz, P. W. Rafalko, and B. C. Gates, *Fundam. Res. Homogeneous Catal.*, **3**, 637 (1979).

709. Z. Otero-Schipper, J. Lieto, J. J. Rafalko, and B. C. Gates, *Stud. Surf. Sci. Catal.*, **4**, 535 (1980).

710. J. Lieto, J. J. Rafalko, and B. C. Gates, *J. Catal.*, **62**, 149 (1980).

711. Z. Otero-Schipper, J. Lieto, and B. C. Gates, *J. Catal.*, **63**, 175 (1980).

712. C. Graillat, H. Jacobelli, M. Bartholin, and A. Guyot, *Rev. Port. Quim.*, **19**, 279 (1977).

713a Z. C. Brzezinska and W. R. Cullen, *Can. J. Chem.*, **58**, 744 (1980).

713b Z. C. Brzezinska, W. R. Cullen, and G. Strukul, *Can. J. Chem.*, **58** 750 (1980).

714. V. Kavan and M. Capka, *Coll. Czec. Chem. Commun.*, **45**, 2085 (1980).

715. D. R. Coleman and G. P. Royer, *J. Org. Chem.*, **45**, 2268 (1980).

716. Y. Nakao and S. Fujishige, *Bull. Chem. Soc. Jpn.*, **53**, 1267 (1980).

717. G. Innorta, A. Modelli, F. Scagnolari, and A. Foffani, *J. Organomet. Chem.*, **185**, 403 (1980).

718. J. Schwartz and M. D. Ward, *J. Mol. Catal.*, **8**, 465 (1980).

719. M. D. Ward, T. V. Harris, and J. Schwartz, *J. Chem. Soc., Chem. Commun.*, 357 (1980).

720. E. W. Thornton, H. Knoezinger, B. Tesche, J. J. Rafalko, and B. C. Gates, *J. Catal.*, **62**, 117 (1980).

721. A. K. Smith, W. Abboud, J. M. Basset, W. Reimann, G. L. Rempel, J. L. Bilhou, V. Bilhou-Bougnol, W. F. Graydon, and J. Dunogues, *Fundam. Res. Homogeneous Catal.*, **3**, 621 (1979).

722. Y. I. Ermakov, B. N. Kuznetsov, and E. M. Chelganov, *React. Kinet. Catal. Lett.*, **14**, 37 (1980).

723. H. Knoezinger, E. W. Thornton, and M. Wolf, *Fundam. Res. Homogeneous Catal.*, **3**, 461 (1979).

724. S. Z. Bernadyuk, G. V. Kudryavtsev, and G. V. Lisichkin, *Koord. Khim.*, **5**, 1834 (1979).

725. V. A. Semikolenov, D. K. Mikhailova, Y. V. Sobchak, V. A. Likholobov, and Y. I. Ermakov, *Kinet. Katal.*, **21**, 526 (1980).

726. S. C. Brown and J. Evans, *J. Organomet. Chem.*, **194**, C53 (1980).

727. S. Fuentes and F. Figueras, *J. Catal.*, **61**, 443 (1980).

728. G. B. McVicker and M. A. Vannice, *J. Catal.*, **63**, 25 (1980).

729. P. LeMaux, J. Y. Saillard, D. Grandjean, and G. Jaouen, *J. Org. Chem.*, **45**, 4525 (1980).

730. E-i Negishi, A. O. King, W. L. Klima, W. Patterson, and A. Silveria, *J. Org. Chem.*, **45**, 2526 (1980).

731. T. Tsuda, T. Fujii, K. Kawasaki, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 1013 (1980).

732. M. E. Osborn, J. F. Pegues, and L. A. Paquette, *J. Org. Chem.*, **45**, 167 (1980).

733. F. Ungvary, A. Sisak, and L. Marko, *J. Organomet. Chem.*, **188**, 373 (1980).

734. D. L. Reger, M. M. Habib, and D. J. Fauth, *J. Org. Chem.*, **45**, 3860 (1980).

735. N. Tsuji, J. Suzuki, M. Shiota, I. Takahashi, and S. Nishimura, *J. Org. Chem.*, **45**, 2729 (1980).

736. W. Strohmeier, M. Michel, and L. Weigelt, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **35B**, 648 (1980).

737. W. Strohmeier and K. Holke, *J. Organomet. Chem.*, **193**, C63 (1980).

738. J. Cook, J. E. Hamlin, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 144 (1980).

739. Z. Toth, F. Joo, and M. T. Beck, *Inorg. Chim. Acta*, **42**, 153 (1980).

740. Y. Watanabe, T. Ota, and Y. Tsuji, *Chem. Lett.*, 1585 (1980).

741. R. A. Sanchez-Relgado and O. L. DeOchoa, *J. Organomet. Chem.*, **202**, 427 (1980).

742. F. Sato, T. Jinbo, and M. Sato, *Tetrahedron Lett.*, **21**, 2171 (1980).

743. M. Ishige and M. Shiota, *Can. J. Chem.*, **58**, 1061 (1980).

744. S. Nishimura, M. Murai, and M. Shiota, *Chem. Lett.*, 1239 (1980).

745. Y. Nakao and S. Fujishige, *Chem. Lett.*, 673 (1980).

746. J. F. Peyronel, J. C. Fiaud, H. B. Kagan, *J. Chem. Res.*, 320 (1980).

747. A. Tai, M. Nakahata, T. Harada, Y. Izumi, S. Kusumoto, M. Inage, and T. Shiba, Chem. Lett., 1125 (1980).

748. C. U. Pittman, Jr. and Y. F. Liang, J. Org. Chem., **45**, 5048 (1980).

749. M. Bianchi, G. Menchi, F. Francalanci, F. Piacenti, U. Matteoli, P. Frediani, and C. Botteghi, J. Organomet. Chem., **188**, 109 (1980).

750. R. A. Grey, G. P. Pez, A. Wallo, and J. Corsi, J. Chem. Soc., Chem. Commun., 782 (1980).

751. A-u Rahman, M. Ghazala, N. Sultana, and M. Bashir, Tetrahedron Lett., 1773 (1980).

752. E. C. Ashby and S. A. Noding, J. Org. Chem., **45**, 1041 (1980).

753. S. Kano, Y. Tanaka, E. Sugino, and S. Hibino, Synthesis, 695 (1980).

754. M. V. Klyuev, Fiz. Khim. Protsessy Gazov. Kondens. Fazakh, 39 (1979).

755. M. V. Klyuev and M. L. Khidekel, Transition Met. Chem. (Weinheim Ger.), **5**, 134 (1980).

756. P. Biloen, Recl. Trav. Chim. Pays-Bas, **99**, 33 (1980).

757. J. G. Ekerdt, Diss. Abstr. Int. B, **40**, 3278 (1980).

758. P. T. Wolczanski and J. E. Bercaw, Acc. Chem. Res., **13**, 121 (1980).

759. C-H Yang, Diss. Abstr. Int. B, **40**, 2775 (1979).

760. D. W. Slocum, Catal. Org. Synth., 245 (1980).

761. J. G. Ekerdt, Energy Res. Abstr, 4, (1979).

762. A. Krzywicki and M. Marczewski, J. Mol. Catal., **6**, 431 (1979).

763. A. L. Lapidus, A. Y. Krylova, and L. T. Kondrat'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 1432 (1980).

764. H. Schruebbers, P. J. Plath, and G. Schulz-Ekloff, React. Kinet. Catal. Lett., **13**, 255 (1980).

765. T. Wigmans and J. A. Moulijn, J. Chem. Soc., Chem. Commun., 170 (1980).

766. F. Hugues, B. Besson, and J. M. Basset, J. Chem. Soc., Chem. Commun., 719 (1980).

767. D. Commereuc, Y. Chauvin, F. Hugues, J. M. Basset, and D. Olivier, J. Chem. Soc., Chem. Commun., 154 (1980).

768. J. L. Vidal and W. E. Walker, Inorg. Chem., **19**, 896 (1980).

769. A. L. Lapidus and M. M. Savel'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 335 (1980).

770. W. Keim, M. Berger, and J. Schlupp, J. Catal., **61**, 359 (1980).

771. H. M. Feder and J. W. Rathke, Ann. N. Y. Acad. Sci., **333**, 45 (1980).

772. M. Blanchard, D. Vanhove, and A. Derovault, J. Chem. Res., Synop., 404 (1979).

773. H. Dumas, J. Levisalles, and H. Rudler, J. Organomet. Chem., **187**, 405 (1980).

774. B. D. Dombek, J. Amer. Chem. Soc., **102**, 6855 (1980).

775. A. Wong, M. Harris, and J. D. Atwood, J. Amer. Chem. Soc., **102**, 4529 (1980).

776. H. Haertner, *Kontakte*, 3 (1980).

777. G. Mestroni, G. Zassinovich, A. Camus, and F. Maritnelli, *J. Organomet. Chem.*, **198**, 87 (1980).

778. R. Spogliarich, G. Zassinovich, G. Mestroni, and M. Graziani, *J. Organomet. Chem.*, **198**, 81 (1980).

779. M. Bonnet, P. Geneste, and M. Rodriguez, *J. Org. Chem.*, **45**, 91 (1980).

780. A. Camus, G. Mestroni, and G. Zassinovich, *J. Organomet. Chem.*, **184**, C10 (1980).

781. S. Rajagopal, S. Vancheesan, J. Rajaram, and J. C. Kuriacose, *Proc. Natl. Symp. Catal.*, 380 (1980).

782. B. Graser and H. Steigerwald, *J. Organomet. Chem.*, **193**, C67 (1980).

783. R. O. Hutchins and R. P. Fulton, *Ventron Alembic*, **17**, 2 (1980).

784. H. Alper and S. Amaratunga, *Tetrahedron Lett.*, **21**, 2603 (1980).

785. M. Somei, K. Kato, and S. Inoue, *Chem. Pharm. Bull.*, **28**, 2515 (1980).

786. M. O. Terpko and R. F. Heck, *J. Org. Chem.*, **45**, 4992 (1980).

787. A. V. Bulatov and M. L. Khidekel, *Transition Met. Chem. (Weinheim, Ger.)*, **5**, 123 (1980).

788. T. K. Mondal, T. K. Banerjee, and D. Sen, *Indian J. Chem., Sec. A*, **19A**, 846 (1980).

789. A. D. Shebaldova, L. A. Safronova, and M. L. Khidekel, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 464 (1980).

790. H. H. Baer, C. B. Madumelu, Z. S. Hanna, and P. G. Potvin, *Carbohydr. Res.*, **76**, 141 (1979).

791. G. W. J. Fleet, P. J. C. Harding, and M. J. Whitcombe, *Tetrahedron Lett.*, **21**, 4031 (1980).

792. G. A. Olah, M. Arvanaghi, and G. K. S. Prakash, *Synthesis*, 220 (1980).

793. S. Polanc, B. Stanovnik, and M. Tisler, *Synthesis*, 830 (1980).

794. V. Z. Sharf, B. M. Savchenko, V. N. Krutii, and L. K. Freidlin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 456 (1980).

795. P. G. Mattingly and M. J. Miller, *J. Org. Chem.*, **45**, 410 (1980).

796. S. Kano, Y. Tanaka, E. Sugino, S. Shibuya, and S. Hibino, *Synthesis*, 741 (1980).

797. S. Kano, Y. Tanaka, and S. Hibino, *Heterocycles*, **14**, 39 (1980).

798. A. R. Pinder, *Synthesis*, 425 (1980).

799. F. Ungvary and L. Marko, *J. Organomet. Chem.*, **193**, 379 (1980).

800. J. Wellmann and E. Steckhan, *Angew. Chem. Int. Ed. Engl.*, **19**, 46 (1980).

801. T. N. Sorrell and P. S. Pearlman, *J. Org. Chem.*, **45**, 3449 (1980).

802. R. O. Hutchins and M. Markowitz, *Tetrahedron Lett.*, **21**, 813 (1980).

803. R. O. Hutchins and M. Markowitz, *Ventron Alembic*, **18**, 2 (1980).

804. I. D. Entwistle, P. Boehm, R. A. W. Johnstone, and R. P. Telford, *J. Chem. Soc., Perkin Trans. 1*, 27 (1980).

805. F. Guike, P. Four, and H. Riviere, *J. Chem. Soc., Chem. Commun.*, 432 (1980).

806. R. O. Hutchins, K. Learn, and R. P. Fulton, *Tetrahedron Lett.*, **21**, 27 (1980).

807. F. Sato, Y. Tomuro, H. Ishikawa, T. Oikawa, and M. Sato, *Chem. Lett.*, 103 (1980).

808. F. Delbecq, R. Baudouy, and J. Gore, *J. Chem. Res.*, 88 (1980).

809. A. Gorgnes and A. LeCoq, *Tetrahedron Lett.*, **21**, 5007 (1980).

810. R. A. Benkeser and W. C. Muench, *J. Organomet. Chem.*, **184**, C3 (1980).

811. C. A. Tsipis, *J. Organomet. Chem.*, **187**, 427 (1980).

812. C. A. Tsipis, *J. Organomet. Chem.*, **188**, 53 (1980).

813. A. P. Barlow, N. M. Boag, F. G. A. Stone, *J. Organomet. Chem.*, **191**, 39 (1980).

814. N. A. Moldavskaya, T. P. Khvatova, N. K. Skvortsov, and V. O. Reikhsfel'd, *Zh. Obshch. Khim.*, **50**, 851 (1980).

815. G. Kuncova and V. Chvalovsky, *Coll. Czec. Chem. Commun.*, **45**, 2085 (1980).

816. G. Kuncova and V. Chvalovsky, *Coll. Czec. Chem. Commun.*, **45**, 2240 (1980).

817. V. B. Pukhnarevich, L. I. Kopylova, M. Capka, J. Hetflejs, E. N. Satsuk, M. V. Sigalov, V. Chvalovsky, and M. G. Voronkov, *Zh. Obshch. Khim.*, **50**, 1554 (1980).

818. H. M. Dickers, R. N. Haszeldine, L. S. Malkin, A. P. Mather, and R. V. Parish, *J. Chem. Soc., Dalton*, 308 (1980).

819. G. K. Magomedov, O. V. Shkol'nik, B. A. Izmailov, and S. A. Sigachev, *Koord. Khim.*, **6**, 761 (1980).

820. G. K. Magomedov, G. V. Druzhkova, V. G. Syrkin, and O. V. Shkol'nik, *Koord. Khim.*, **6**, 767 (1980).

821. B. Marciniec and J. Gulinski, *J. Mol. Catal.*, **10**, 123 (1980).

822. I. Ojima, S. Suga, and R. Abe, *Tetrahedron Lett.*, **21**, 3907 (1980).

823. A. S. Sarma and P. Chattopadhyay, *Tetrahedron Lett.*, **21**, 1079 (1980).

824. O. J. Goodmonson, M. G. Scaros, J. M. Schlatter, and R. H. Mazur, *Catal. Org. Synth.*, 35 (1978).

825. S. Teratani and T. Chihara, *Chem. Lett.*, 807 (1980).

826. T. Nishiguchi, K. Tanaka, and K. Fukuzumi, *J. Organomet. Chem.*, **193**, 37 (1980).

827. J. Halpern, *J. Organomet. Chem.*, **200**, 133 (1980).

828. K. Mita and K. Hotta, *Kagaku to Kogyo (Osaka)*, **54**, 248 (1980).

829. K. Mita and K. Hotta, *Kagaku to Kogyo (Osaka)*, **54**, 284 (1980).

830. E. N. Frankel, *Catal. Org. Synth.*, 185 (1980).

831. T. Yamanaka, *Kagaku Kogyo*, **31**, 116 (1980).

832. F. Sato, *Shokubai*, **21**, 363 (1979).

833. P. N. Rylander, *Aldrichimica Acta*, **12**, 53 (1979).
834. T. Yamanaka, *Kagaku Kogyo*, **31**, 208 (1980).
835. T. Yamanaka, *Kagaku Kogyo*, **31**, 308 (1980).
836. T. Yamanaka, *Kagaku Kogyo*, **31**, 516 (1980).
837. T. Yamanaka, *Kagaku Kogyo*, **31**, 860 (1980).
838. T. Yamanaka, *Kagaku Kogyo*, **31**, 963 (1980).
839. K. Takagi, N. Hayama, and S. Inokawa, *Bull. Chem. Soc. Jpn.*, **53**, 3691 (1980).
840. H. Suzuki, M. Miyoshi, and M. Shinoda, *Bull. Chem. Soc. Jpn.*, **53**, 1765 (1980).
841. S. Oae, K. Shinhama, and Y. H. Kim, *Bull. Chem. Soc. Jpn.*, **53**, 1065 (1980).
842. M. P. Doyle, M. A. Van Lente, R. Mowat, and W. F. Fobare, *J. Org. Chem.*, **45**, 2570 (1980).
843. T. T. Tsou and J. K. Kochi, *J. Org. Chem.*, **45**, 1930 (1980).
844. Y. Ito, M. Nakatsuka, and T. Saegusa, *J. Org. Chem.*, **45**, 2022 (1980).
845. T. Hayashi, K. Tamao, Y. Katsuro, I. Nakae, and M. Kumada, *Tetrahedron Lett.*, **21**, 1871 (1980).
846. L. K. Liu, Y. Chi, and K-y Jeu, *J. Org. Chem.*, **45**, 406 (1980).
847. J. Elzinga and H. Hogeveen, *J. Org. Chem.*, **45**, 3957 (1980).
848. F. Garnier and P. Krausy, *J. Organomet. Chem.*, **186**, 77 (1980).
849. G. Villain, P. Kalck, and A. Gaset, *Tetrahedron Lett.*, **21**, 102 (1980).
850. D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.*, **199**, 119 (1980).
851. Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 835 (1980).
852. S. Top, G. Jaouen, and M. J. McGlinchey, *J. Chem. Soc., Chem. Commun.*, 1110 (1980).
853. P. S. Elmes and W. R. Jackson, *Ann. N. Y. Acad. Sci.*, **333**, 225 (1980).
854. C. Germon, A. Lexakis, and J. F. Normant, *Tetrahedron Lett.*, **21**, 3763 (1980).
855. R. M. Laine, *J. Org. Chem.*, **45**, 3370 (1980).
856. C. P. Whittle, *Aust. J. Chem.*, **33**, 1545 (1980).
857. K. Mita, T. Yamagishi, and M. Hida, *J. Chem. Soc., Chem. Commun.*, 1036 (1980).
858. K. Yoshida, M. Matsuoka, Y. Yamashita, S. Nagamori, and T. Kitao, *Bull. Chem. Soc. Jpn.*, 3725 (1980).
859. K. Yoshida, M. Matsuoka, Y. Yamashita, and T. Kitao, *Bull. Chem. Soc. Jpn.*, **53**, 2552 (1980).
860. S. Top and G. Jaouen, *J. Organomet. Chem.*, **197**, 199 (1980).
861. K. Irie, K-i Miyazu, and K-i Watanabe, *Chem. Lett.*, 353 (1980).
862. R. A. Scherrer and H. R. Beatty, *J. Org. Chem.*, **45**, 2127 (1980).
863. S. A. Kondratov and S. M. Shein, *Zh. Org. Khim.*, **15**, 2387 (1979).

H. Yamamoto and K. Maruoka, *J. Org. Chem.*, **45**, 2739 (1980).

Y. Shvo and R. M. Laine, *J. Chem. Soc., Chem. Commun.*, 753 (1980).

S-i Murahashi and T. Yano, *J. Amer. Chem. Soc.*, **102**, 2456 (1980).

K. Siirala-Hansen, *Chem. Commun., Univ. Stockholm*, 54 (1979).

J. E. Baeckvall and E. E. Bjoerkman, *J. Org. Chem.*, **45**, 2893 (1980).

P. N. Becker, M. A. White, and R. G. Bergman, *J. Amer. Chem. Soc.*, **102**, 5676 (1980).

S. Kano, *Ventron Alembic*, **19**, 2 (1980).

T. Yamamoto, J. Ishizu, T. Kohara, S. Komiya, and A. Yamamoto, *J. Amer. Chem. Soc.*, **102**, 3758 (1980).

K. Tamao, T. Kakui, and M. Kumada, *Tetrahedron Lett.*, **21**, 4105 (1980).

S. H. Pine, R. Zahler, D. A. Evans, and R. H. Grubbs, *J. Amer. Chem. Soc.*, **102**, 3270 (1980).

S. I. Chistyakov, V. A. Semikolenov, V. A. Likholobov, and Y. I. Yermakov, *React. Kinet. Catal. Lett.*, **12**, 177 (1979).

R. Gigg, *J. Chem. Soc. Perkin Trans. 1*, 738 (1980).

J. E. Baeckvall, R. E. Nordberg, E. E. Bjoerkman, and C. Moberg, *J. Chem. Soc., Chem. Commun.*, 943 (1980).

T. A. Stromnova and M. N. Vargaftik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 478 (1980).

J. M. Mancilla, D. C. Nonhebel, and I. Scullion, *J. Chem. Res., Synop.*, 100 (1980).

I. Pri-Bar, O. Buchman, H. Schumann, H. J. Kroth, and J. Blum., *J. Org. Chem.*,**45**, 4418 (1980).

M. Kiso and L. Anderson, *Carbohydr. Res.*, **72**, C12 (1979).

M. Kiso and L. Anderson, *Carbohydr. Res.*, **72**, C15 (1979).

T. Migita, T. Shimizu, Y. Asami, J. Shiobara, Y. Kato, and M. Kosugi, *Bull. Chem. Soc. Jpn.*, **53**, 1385 (1980).

H. Suzuki, H. Abe, and A. Osuka, *Chem. Lett.*, 1363 (1980).

M. R. Ashcroft, B. D. Gupta, and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 1*, 2021 (1980).

T. Cohen, R. J. Ruffner, D. W. Shull, E. R. Fogel, and J. R. Falck, *Org. Synth.*, **59**, 202 (1980).

H-U Reissig and B. Scherer, *Tetrahedron Lett.*, **21**, 4259 (1980).

R. C. Larock, K. Oertle, and K. M. Beatty, *J. Amer. Chem. Soc.*, **102**, 1966 (1980).

K. Nagira, K. Kikukawa, F. Wada, and T. Matsuda, *J. Org. Chem.*, **45**, 2365 (1980).

O. Attanasi and F. Serra-Zanetti, *Synthesis*, 314 (1980).

F. Dasgupta, P. P. Singh, and H. C. Srivastava, *Carbohydr. Res.*, **80**, 346 (1980).

891. K. Kikukawa, K. Kono, K. Nagira, F. Wada, and T. Matsuda, *Tetrahedron Lett.*, **21**, 2877 (1980).

892. A. Odani and O. Yamauchi, *Chem. Lett.*, 93 (1980).

893. G. A. Tolstikov and U. M. Dzhemilev, *Khim. Geterotsikl. Soedin.*, 147 (1980).

894. M. Mori and Y. Ban, *Kagaku no Ryoiki, Zokan*, 97 (1979).

895. S. R. Berryhill and M. Rosenblum, *J. Org. Chem.*, **45**, 1984 (1980).

896. G. D. Annis, E. H. Hebblethwaite, and S. V. Levy, *J. Chem. Soc., Chem. Commun.*, 297 (1980).

897. I. Ojiama and S-i Inaba, *Tetrahedron Lett.*, 2077 (1980).

898. I. Ojiama and S-i Inaba, *Tetrahedron Lett.*, 2081 (1980).

899. R. J. Ponsford, *Tetrahedron Lett.*, **21**, 2451 (1980).

900. M. G. Vinogradov, N. L. Radyukina, M. S. Pogosyan, S. P. Verenchikov, A. Y. Shteinshneider, and G. I. Nikishin, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1949 (1980).

901. D. F. Marten, *J. Chem. Soc., Chem. Commun.*, 341 (1980).

902. G. E. Schneiders and R. Stevenson, *Synth. Commun.*, **10**, 699 (1980).

903. N. E. Kolobova and L. V. Goncharenko, *Khim. Geterotsikl. Soedin.*, 1461 (1979).

904. R. P. Houghton, M. Voyle, and R. Price, *J. Chem. Soc., Chem. Commun.*, 884 (1980).

905. P. Brownbridge and T-H Chan, *Tetrahedron Lett.*, **21**, 3427 (1980).

906. G. D. Annis, S. V. Ley, C. R. Self, and R. Sivaramakrishnan, *J. Chem. Soc., Chem. Commun.*, 299 (1980).

907. G. Batu and R. Stevenson, *J. Org. Chem.*, **45**, 1532 (1980).

908. F. Bigi, G. Casikaghi, G. Casnati, and G. Sartori, *Synthesis*, 724 (1980).

909. J. E. Backvall, O. Karlsson, and S. O. L. Junggren, *Tetrahedron Lett.*, **21**, 4985 (1980).

910. M. Ratzenhofer and H. Kisch, *Angew. Chem.*, **92**, 303 (1980).

911. B. M. Trost and E. Keinan, *J. Org. Chem.*, **45**, 2741 (1980).

912. J. Ambuehl, P. S. Pregosin, L. M. Venanzi, G. Ughetto, and L. Zambonelli, *J. Organomet. Chem.*, **160**, 329 (1978).

913. M. Aresta and M. De Fazio, *J. Organomet. Chem.*, **186**, 109 (1980).

914. R. Odle, B. Blevins, M. Ratcliff, and L. S. Hegedus, *J. Org. Chem.*, **45**, 2709 (1980).

915. H. Iida, Y. Yuasa, and C. Kibayashi, *J. Org. Chem.*, **45**, 2938 (1980).

916. M. Mori, Y. Hashimoto, and Y. Ban, *Tetrahedron Lett.*, **21**, 631 (1980).

917. R. B. Miller and T. Moock, *Tetrahedron Lett.*, **21**, 3319 (1980).

918. T. Kametani, T. Ohsawa, and M. Ihara, *Heterocycles*, **14**, 277 (1980).

919. Y. Watanabe, M. Yamamoto, S. C. Shim, S. Miyanaga, and T. Mitsudo, *Chem. Lett.*, 603 (1980).

920. L. S. Hegedus, G. F. Allen, and D. J. Olsen, *J. Amer. Chem. Soc.*, **102**, 3583 (1980).

W. E. Billups, R. S. Erkes, and L. E. Reed, *Synth. Commun.*, **10**, 147 (1980).

G. Pandey and K. P. Tiwari, *Synth. Commun.*, **10**, 523 (1980).

M. Masood and K. P. Tiwari, *Synth. Commun.*, **10**, 541 (1980).

A. Kasahara, T. Izumi, and O. Saito, *Chem. Ind. (London)*, 666 (1980).

Y. Watanabe, N. Suzuki, S. C. Shim, M. Yamamoto, T. Mitsuda, and M. Takegami, *Chem. Lett.*, 429 (1980).

S. E. Diamond, F. Mares, and A. Szalkiewicz, *Fundam. Res. Homogeneous Catal.*, **3**, 345 (1979).

A. Ohsawa, Y. Abe, and H. Igeta, *Bull. Chem. Soc. Jpn.*, **53**, 3273 (1980).

V. E. Ridaura-Sanz, *Diss. Abstr. Int. B*, **40**, 5279 (1980).

S. Mineo, H. Ogura, and K. Nakagawa, *Chem. Pharm. Bull.*, **28**, 2835 (1980).

T. Sakakibara and H. Matsuyama, *Chem. Lett.*, 1331 (1980).

M. Matsuoka, Y. Makino, T. Takei, and T. Kitao, *Chem. Lett.*, 743 (1980).

T. Sugita, Y. Shirawa, M. Hasegawa, and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, **52**, 3629 (1979).

B. M. Trost and J. M. Fortunak, *J. Amer. Chem. Soc.*, **102**, 2841 (1980).

R. K. Haynes, W. R. Jackson, and A. Stragalinov, *Aust. J. Chem.*, **33**, 1537 (1980).

T. Mandai, J. Gotoh, J. Otera, and M. Kawada, *Chem. Lett.*, 313 (1980).

T. Yogo and A. Suzuki, *Chem. Lett.*, 591 (1980).

T. Oshima and T. Nagai, *Tetrahedron Lett.*, **21**, 1251 (1980).

J. Martelli, R. Gree, and R. Carrie, *Tetrahedron Lett.*, **21**, 1953 (1980).

K. Yamamoto, S. Suzuki, and J. Tsuji, *Tetrahedron Lett.*, **21**, 1653 (1980).

M. Lefort, C. Simmonet, M. Birot, G. Deleris, J. Dungues, and R. Calas, *Tetrahedron Lett.*, **21**, 1857 (1980).

H. Matsumoto, K. Shono, A. Wada, I. Matsubara, H. Watanabe, and Y. Nagai, *J. Organomet. Chem.*, **199**, 185 (1980).

H. Watanabe, M. Kolayashi, K. Higuchi, and Y. Nagai, *J. Organomet. Chem.*, **186**, 51 (1980).

Y. Seki, K. Takeshita, K. Kawamoto, S. Murai, and N. Sonada, *Angew. Chem. Int. Ed.*, **19**, 928 (1980).

A. J. Bridges, *Tetrahedron Lett.*, **21**, 4401 (1980).

M. Montury and J. Gore, *Synth. Commun.*, **10**, 873 (1980).

J. A. Conner, A. C. Jones and R. Price, *J. Chem. Soc., Chem. Commun.*, 137 (1980).

G. Axelrad, S. Laosookathit, and R. Engel, *Synth. Commun.*, **10**, 933 (1980).

T. Hirao, T. Masunaga, Y. Ohshiro, and T. Agawa, *Tetrahedron Lett.*, **21**, 3595 (1980).

T. M. Balthazor, *J. Org. Chem.*, **45**, 5425 (1980).

950. T. Hosokawa, T. Ohta, Y. Okamoto, and S. Murahashi, *Tetrahedron Lett.*, **21**, 1259 (1980).
951. I. Ojima, S. Suga, and R. Abe, *Chem. Lett.*, 853 (1980).
952. H. Alper and M. Salisova, *Tetrahedron Lett.*, **21**, 801 (1980).
953. H. Alper and C. Blais, *J. Chem. Soc., Chem. Commun.*, 169 (1980).
954. T. Kauffmann, *Top. Curr. Chem.*, **92**, 109 (1980).
955. S. Brandt, *Diss. Abstr. Int. B*, **41**, 1766 (1980).
956. D. W. Slocum and O. R. Hughes, *Ann. N. Y. Acad. Sci.*, **33**, 1 (1980).
957. J. Schwartz, *Bull. Soc. Chim. Fr. II*, 330 (1980).
958. J. Tsuji, *Kagaku (Kyoto)*, **35**, 325 (1980).
959. M. E. Vol'pin and I. I. Moiseev, *Zh. Vses. Khim. O-va.*, **25**, 515 (1980).
960. R. Taube, *Wiss. Z. Tech. Hochsch*, **22**, 262 (1980).
961. R. P. A. Sneeden, *Actual. Chim.*, 11 (1980).
962. E. W. Abel and F. G. A. Stone, eds., "Specialist Periodical Reports: Organometallic Chemistry," Vol. 8, (1980).
963. J. Schwartz and J. A. Labinger, *J. Chem. Educ.*, **57**, 170 (1980).
964. G. P. Chiusoli, *Pure Appl. Chem.*, 52, 635 (1980).
965. T. J. McNeese, *Diss. Abstr. Int. B*, **40**, 5260 (1980).
966. D. J. Thompson and M. G. Hutchings, *Gen. Synth. Methods*, **3**, 183 (1980).
967. M. A. Bennett, *Chem. Aust.*, **46**, 275 (1979).
968. S. Toma, *Chem. Listy*, **73**, 1049 (1979).
969. K. P. C. Vollhardt, *Chem. Ztg.*, **103**, 309 (1979).
970. H. Alper, *Pure Appl. Chem.*, **52**, 607 (1980).
971. A. Matsuda, *Saishin no C_1 Kagaku to Sono Gijutsu ni kansuru Koshukai Tekisuto*, 63 (1979).
972. H. A. Kurmeier, *Kontakte*, **3** (1978).
973. B. W. Rockett and G. Marr, *J.Organomet. Chem.*, **189**, 251 (1980).
974. R. Oda, *Kagaku Kogyo*, **31**, 745 (1980).
975. S. S. Hershberger, *Diss. Abstr. Int. B*, **40**, 5672 (1980).
976. R. F. Heck and B. Patel, *Catal. Org. Synth.*, 195 (1980).
977. J. Tsuji, *Ann. N. Y. Acad. Sci.*, **333**, 250 (1980).
978. G. F. Allen, *Diss. Abstr. Int. B*, **40**, 1713 (1979).
979. S. Murahashi and T. Hosokawa, *Yuki Gosei Kagaku Kyokaishi*, **37**, 1086 (1979).
980. J. Tsuji, *Top. Curr. Chem.*, **91**, 29 (1980).
981. R. F. Heck, *Platinum Met. Rev.*, **24**, 58 (1980).
982. H. F. Klein, *Angew. Chem. IE*, **19**, 362 (1980).
983. E. Uhlig and D. Walther, *Coord. Chem. Rev.*, **33**, 3 (1980).
984. Y. Watanabe, *Yuki Gosei Kagaku Kyokaishi*, **37**, 1053 (1979).
985. R. Noyori and Y. Hayakawa, *Gendai Kagaku*, **108**, 14 (1980).
986. F. B. McCormick, *Diss. Abstr. Int. B*, **41**, 950 (1980).
987. R. J. Puddephatt, *Coord. Chem. Rev.*, **33**, 149 (1980).

988. A. Nakamura and H. Yasuda, *Yuki Gosei Kagaku Kyokaishi*, **38**, 975 (1980).

989. P. Binger, M. Cetinkaya, M. J. Doyle, A. Germer, and U. Schuchardt, *Fundam. Res. Homogeneous Catal.*, **3**, 271 (1979).

990. R. S. Threlkel, *Diss. Abstr. Int. B*, **41**, 952 (1980).

991. J. Schwartz, *Pure Appl. Chem.*, **52**, 733 (1980).

992. M. Yoshifuji, *Yuki Gosei Kagaku Kyokaishi*, **37**, 1037 (1979).

993. A. Nakamura, *Yuki Gosei Kagaku Kyokaishi*, **37**, 1041 (1979).

994. A. J. Pearson, *Acc. Chem. Res.*, **13**, 463 (1980).

995. M. Yoshifuji, *Yuki Gosei Kagaku Kyokaishi*, **37**, 1034 (1979).

996. R. Oda, *Kagaku (Kyoto)*, **34**, 605 (1979).

997. G. A. Tolostikov, U. M. Dzhomilev, R. V. Kunakova, F. I. Sharipova, F. Y. Kanzafarov, R. L. Gaisin, and Y. A. Sangalov, *Katal. Sint. Org. Soedin. Sery*, 15 (1979).

998. S. Pennanen, *Kem. Kemi.*, **7**, 62 (1980).

999. K. Sonogashira and S. Takahashi, *Yuki Gosei Kagaku Kyokaishi*, **38**, 648 (1980).

1000. K. A. Babiak, *Diss. Abstr. Int. B*, **41**, 193 (1980).

1001. A. M. Sladkov and I. R. Gol'ding, *Russ. Chem. Rev.*, 868 (1980).

1002. A. Krief, *Tetrahedron*, **36**, 2531 (1980).

1003. D. E. Van Horn, *Diss. Abstr. Int. B*, **40**, 1728 (1979).

1004. F. Sato, *Yuki Gosei Kagaku Kyokaishi*, **38**, 234 (1980).

1005. *J. Organomet. Chem.*, **200**, 1 (1980).

1006. M. I. Lobach and V. A. Kormer, *Russ. Chem. Rev.*, **48**, 758 (1979).

1007. L. Cassar, *Ann. N. Y. Acad. Sci.*, **333**, 208 (1980).

1008. S. Komiya, A. Yamamoto, and T. Yamamoto, *Yuki Gosei Kagaku Kyokaishi*, **38**, 633 (1980).

1009. W. D. Jones, II, *Diss. Abstr. Int. B*, **40**, 1708 (1979).

1010. S. M. Csicsery, *Adv. Catal.*, **28**, 293 (1979).

1011. S. Ohtsuka, *Gendai Kagaku*, **105**, 48 (1979).

1012. J. W. Ap-Simon and R. P. Seguin, *Tetrahedron*, **35**, 2797 (1979).

1013. H. B. Kagan, *Ann. N. Y. Acad. Sci.*, **333**, 1 (1980).

1014. D. J. Thompson, *Enzymic Non-Enzymic Catal.*, 203 (1980).

1015. G. B. Shul'pin, *Usp. Khim.*, **49**, 1214 (1980).

1016. A. B. Cowell, *Diss. Abstr. Int. B*, **40**, 5670 (1980).

1017. D. W. Meek, T. J. Mazanec, and K. D. Tau, *Ann. N. Y. Acad. Sci.*, **333**, 141 (1980).

1018. J. M. Brown, P. A. Chaloner, R. Claser, and S. Geresh, *Tetrahedron*, **36**, 815 (1980).

1019. C. U. Pittman, Jr., *Polym. News*, **6**, 223 (1980).

1020. R. H. Grubbs and S. C. H. Su, *Enzymic Non-Enzymic Catal.*, 223 (1980).

1021. Y. I. Ermakov, ed., "Supported Metal Catalysts for the Transformation of Hydrocarbons," Pt. 1, (1978).

1022. Y. I. Ermakov, ed., "Supported Metal Catalysts for the Transformation of Hydrocarbons, Pt 2, (1978).

1023. C. U. Pittman, Jr. and G. Wilemon, *Ann. N. Y. Acad. Sci.*, **333**, 67 (1980).

1024. K. Kaneda, M. Terasawa, T. Imanaka, and S. Ternakishi, *Fundam. Res. Homogeneous Catal.*, **3**, 671 (1979).

1025. Y. I. Ermakov and V. A. Likholobov, *Kinet. Katal.*, **21**, 1208 (1980).

1026. C. White, *Organomet. Chem.*, **8**, 400 (1980).

1027. G. Wilke, *Fundam. Res. Homogeneous Catal.*, **3**, 1 (1979).

1028. G. W. Parshall, *Science*, **208**, 1221 (1980).

1029. G. Wilke, *J. Organomet. Chem.*, **200**, 349 (1980).

1030. V. A. Likholobov and Y. I. Ermakov, *Kinet. Katal.*, **21**, 904 (1980).

1031. N. El Murr and J. Tirouflet, *Fundam. Res. Homogeneous Catal.*, **3**, 1007 (1979).

1032. R. M. Magid, *Tetrahedron*, **36**, 1901 (1980).

1033. P. L. Pauson, *J. Organomet. Chem.*, **200**, 207 (1980).

1034. M. Hronec and J. Ilavsky, *Petrochemia*, **19**, 115 (1979).

1035. T. L. Brown, *Ann. N. Y. Acad. Sci.*, **333**, 80 (1980).

1036. J. K. Kochi, *Pure Appl. Chem.*, **52**, 571 (1980).

1037. J. K. Kochi, *Colloq. Int. C. N. R. S.*, 247 (1978).

1038. R. Taube, H. Drevs, D. Steinborn, N. G. Pham, and G. Honymus, *Theory-Struct. Prop. Complex Compd., Invit. Pap. Int. Summer Sch. Coord. Chem.*, 289 (1979).

1039. K. Tatsumi and M. Tsutsui, *Fundam. Res. Homogeneous Catal.*, **3**, 55 (1979).

1040. F. G. Gault, *Gazz. Chim. Ital.*, **109**, 255 (1979).

1041. J. H. Teuben, H. J. Meijer, *Recl. Trav. Chim. Pays-Bas*, **99**, 1 (1980).

1042. T-T Tsou, *Diss. Abstr. Int. B*, **41**, 207 (1980).

1043. D. A. Slack, I. Greveling, and M. C. Baird, *Fundam. Res. Homogeneous Catal.*, **3**, 983 (1979).

1044. K. Vrieze, S. Hietkamp, and D. J. Stufkens, *Fundam. Res. Homogeneous Catal.*, **3**, 317 (1979).

1045. M. S. Wrighton, J. L. Graff, C. L. Reichel, and R. D. Sanner, *Ann. N. Y. Acad. Sci.*, **333**, 188 (1980).