TRANSITION METALS IN ORGANIC SYNTHESIS
ANNUAL SURVEY COVERING THE YEAR 1979

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

CONTENTS

I. General Comments

This annual survey covers the literature for 1979 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.

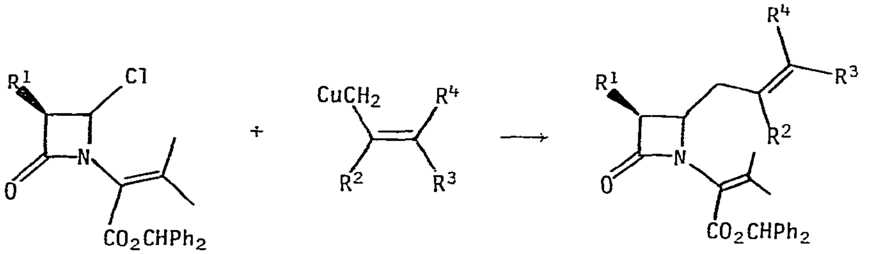
The papers in this survey are grouped primarily by reaction type rather than by organometallic reagent, since the reader is likely to be more interested in the organic transformation affected than the metal causing it. Specifically excluded are papers dealing with transition metal catalyzed hydrosilation, 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.

II. Carbon-Carbon Bond Forming Reactions

A. Alkylations

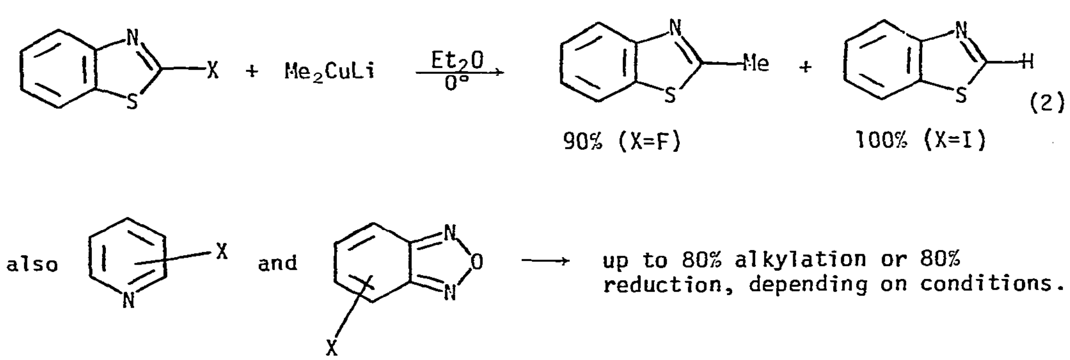
1. Alkylation of Organic Halides and Tosylates

Organocuprates and copper-catalyzed Grignard reactions continue to be used extensively for the alkylation of organic halides and tosylates. Chlorinated β-lactams react with allylcuprates to introduce the allylic side chain. This process has been used to synthesize carbapenam esters (eq. 1) [1].

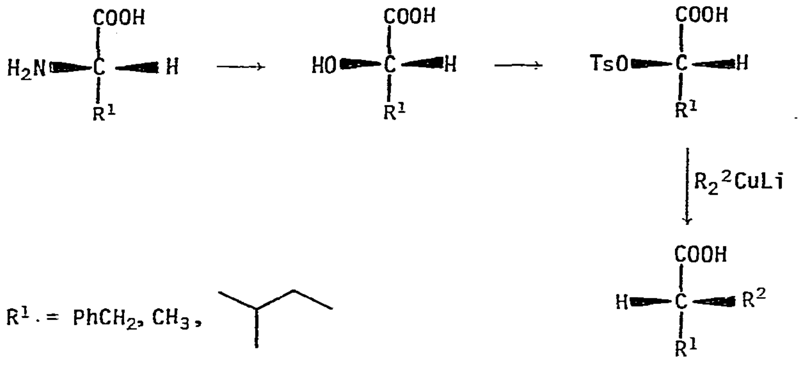


(1)

Heterocyclic halides react with lithium dimethylcuprate to either alkylate or reduce depending on the halide and the reaction conditions (eq. 2) [2]. Optically active α-alkyl or α-aryl acids were synthesized from L-α-amino acids by reaction of the corresponding α-tosylates with organocuprates. The reactions went with clean inversion of configuration, but yields varied from 30% to 70% and side products were evident (eq. 3) [3]. Cyclopentadienyl(tributylphosphine)-copper(I) reacted with α-bromoacids to produce α-cyclopentadienyl carboxylic acids. Nickelocene in the presence of triphenylphosphine reacted in a similar fashion [4]. Allylic and propargylic halides reacted with the cuprate produced



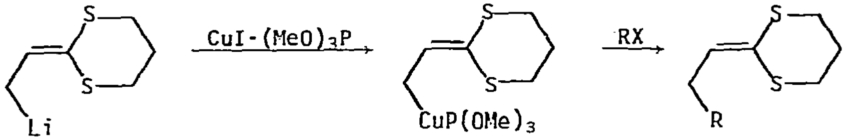
(2)


(3)

$R^1 = PhCH_2, CH_3,$

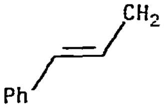
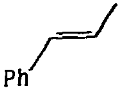
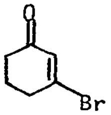
R^2 = Me, Ph, n-Bu

from an allyl dithiane exclusively at the γ position of the anion. The ratios of S_N2' to S_N2 products always exceeded 0.67 (eq. 4) [5].

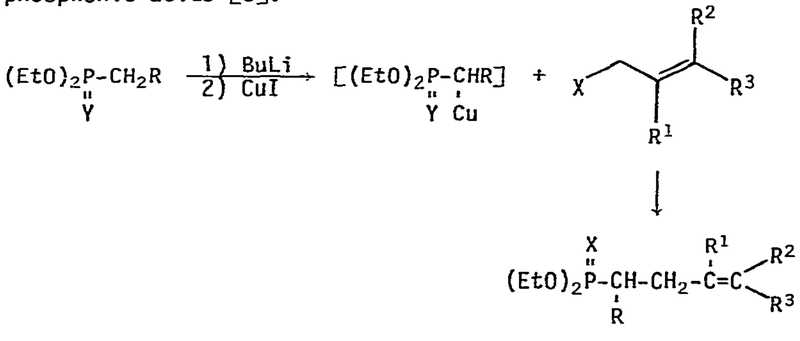

(4)

Treatment of trifluoromethyl iodide with copper powder in HMPA at 120°, followed by reaction with organic halides resulted in replacement of halogen by a trifluoromethyl group (eq. 5) [6].

$$CF_3I + \text{Cu powder} \xrightarrow[120°]{HMPA} \xrightarrow{RX} RCF_3 \qquad (5)$$

$R = PhCH_2,$  , $n\text{-}C_{10}$, PhCOBr,  , 

α-Cuprophosphonates reacted with allylic halides to produce homoallylicphosphonates (eq. 6) [7]. This process was used in the synthesis of aminoalkenephosphonic acids [8].

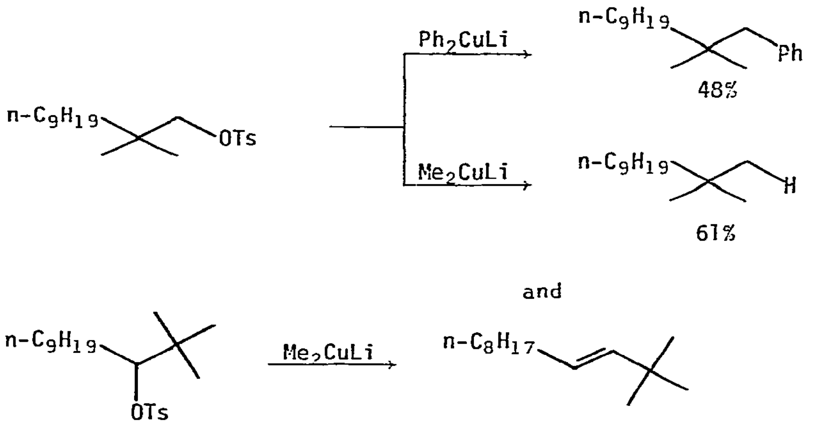

60-90%

(6)

Y = O, S
X = Cl, Br
R = H, Me, Et

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

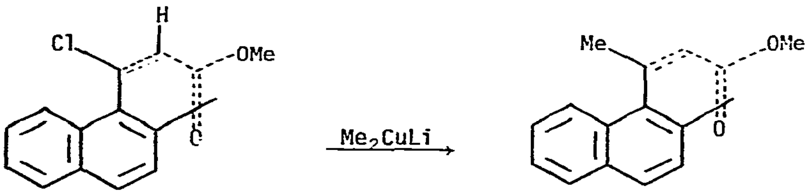
The reactions of homogeneous and polymer-supported lithium diorganocuprates were compared. Copper iodide was bound to polymer supports through a polymer-bound triaryl phosphine, treated with two equivalents of RLi (R = Me, Bu, Me_3C, EtCHMe, Ph), and the resulting reagent treated with alkyl halides, tosylates and conjugated enones. The yields were comparable or superior to those obtained using the corresponding homogeneous reagent [9]. Organic tosylates were reacted with lithium diphenylcuprate and lithium dimethylcuprate. Depending on the nature of the tosylate and the cuprate, displacement, reduction or elimination was observed (eq. 7) [10].



(7)

Benzylic and allylic amines were displaced (alkylated) by lithium dimethyl- or diphenylcuprate by conversion to the corresponding N,N-bis-trifluoromethanesulfonimides first. The reaction proceeded by an S_N2 mechanism [11].

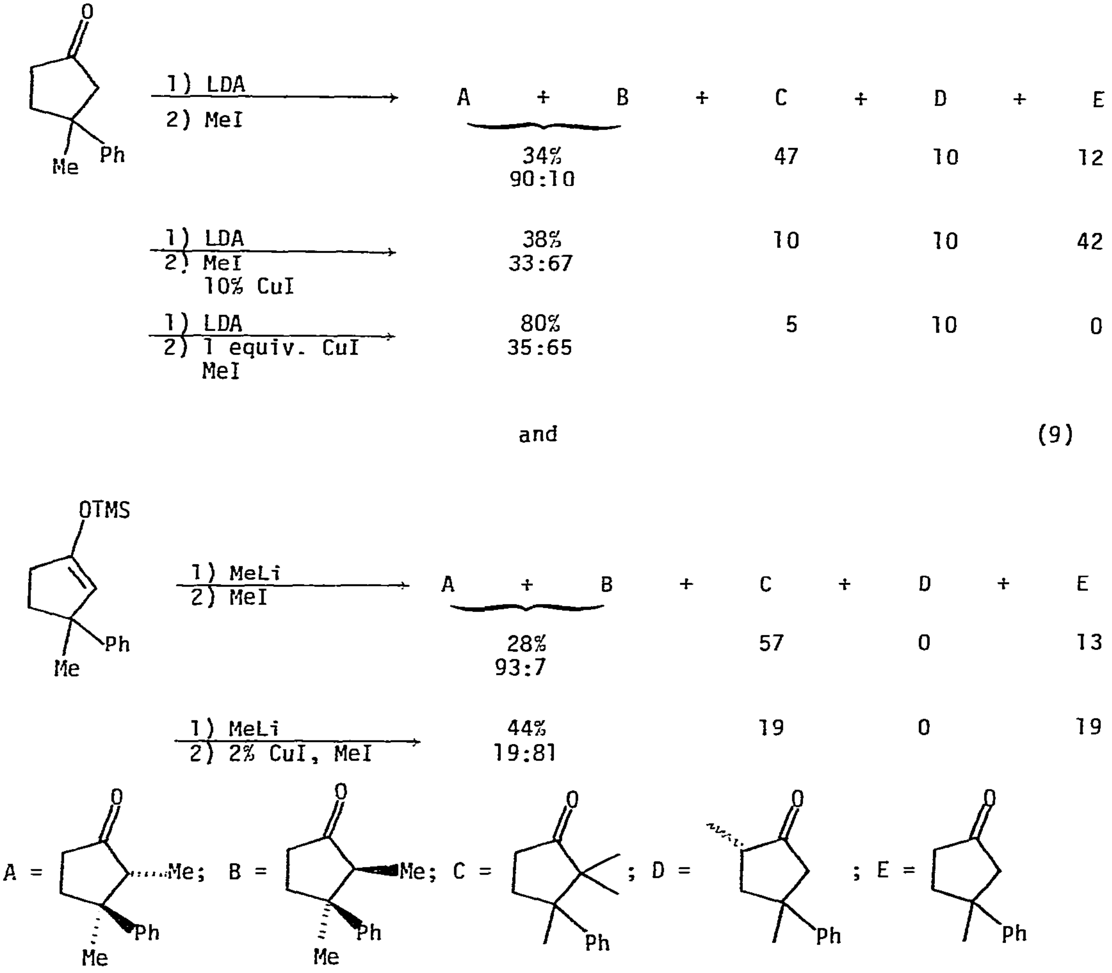
In a study to determine if the alkylation of β-chloro conjugated enones proceeded by electron transfer, addition-elimination, or a concerted oxidative addition process, one atrope isomer of a 2-methylnaphthalene derivative was alkylated by lithium dimethylcuprate (eq. 8). No isomerization was observed,



(8)

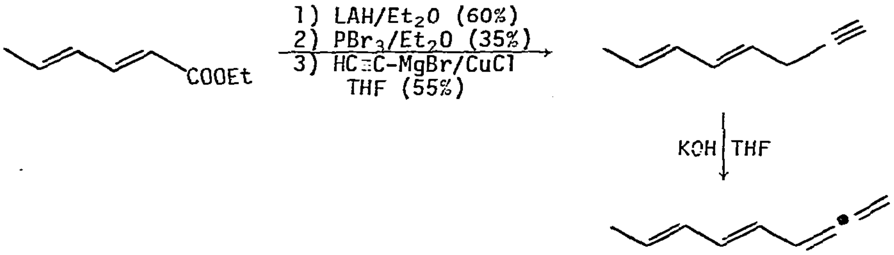
hence the reaction was claimed to proceed by a concerted oxidative addition process [12]. Copper catalyzed Grignard reactions attacked the carbonyl group to give tertiary alcohols. Lithium dimethylcuprate reacted with 4-halophenylethylenes and with 6-halo(phenylsulfonyl)ethylenes to produce mainly cross-coupled products. Reductive dehalogenation was also observed in some cases. The reactions of vinyl halides were claimed to proceed by a concerted substitution mechanism, while the sulfonyl compounds were thought to react by an addition-elimination mechanism [13]. The effects of added copper(I) iodide

(2-10%) on the reactions of lithium enolates with methyl iodide were studied and are summarized in eq. 9. It is seen that even small amounts of copper severely limited polyalkylation and had drastic effects on the stereochemistry of the reaction [14]. Hence, although the conjugate addition of organocuprates to conjugated enones results in the formation of lithium enolates, (House) the presence of small amounts of copper drastically alters the reactivity of these lithium enolates.



(9)

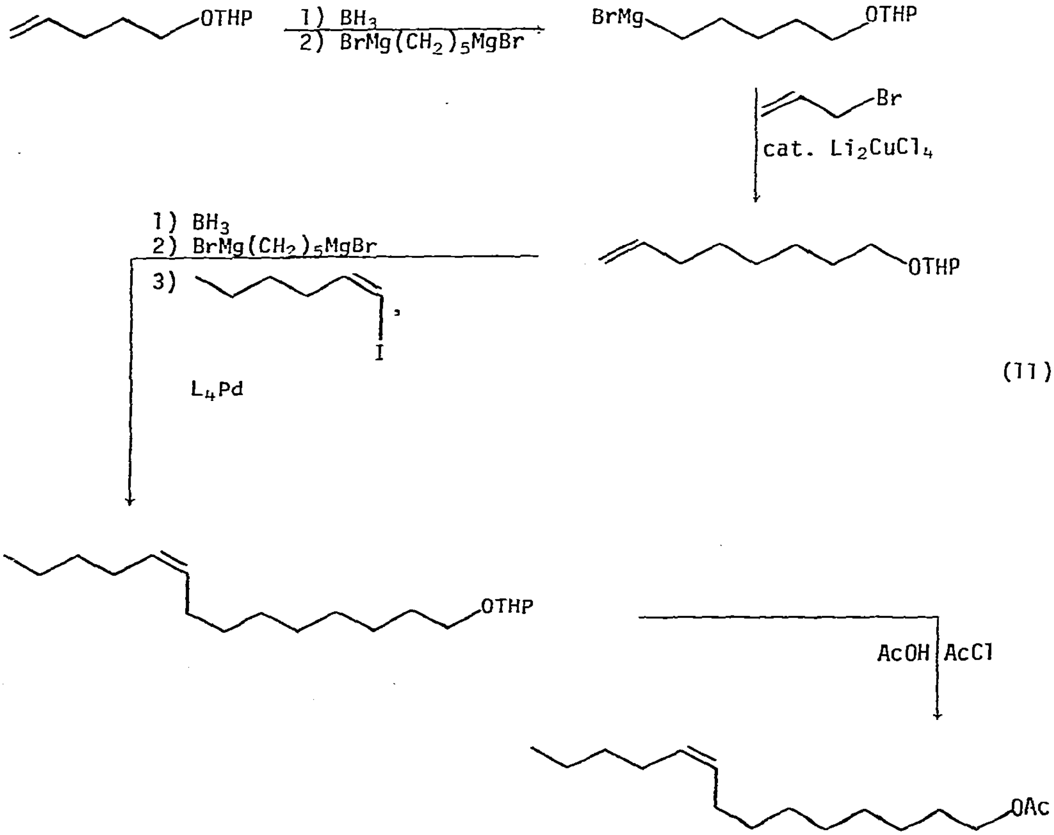
Copper-catalyzed Grignard reactions find continued use in organic synthesis. Aliphatic Grignard reagents reacted with ω-bromoesters in the presence of Li_2CuCl_4 to give 37-79% coupling product. In contrast, ω-bromoaldehydes reacted primarily at the carbonyl carbon to give alcohols [15]. α,β,γ,δ-Unsaturated esters were alkynylated by a sequence involving reduction of the ester, conversion of the alcohol to the bromide, and reaction with alkynyl Grignards using a copper(I) chloride catalyst (eq. 10) [16].



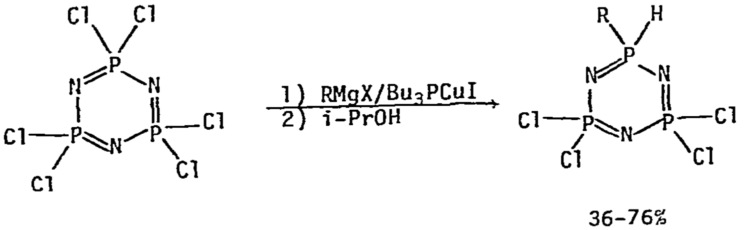
(10)

The synthesis of the sex pheromone of the Southern army worm moth was synthesized using a copper-catalyzed Grignard reaction as the key coupling step (eq. 11) [17]. Chlorophosphine-nitrogen heterocycles were alkylated by reaction with Grignard reagents in the presence of Bu_3PCuI (eq. 12) [18]. Allylic bromohydrins reacted with Grignard reagents in the presence of a copper(I) iodide catalyst to alkylate with an unusual rearrangement (eq. 13) [19]. Copper(I) methyl trialkylborate complexes reacted with α-chloroenamines to result ultimately in α-alkylated ketones (eq. 14) [20]. The use of these copper-borate complexes in organic synthesis has been reviewed [21].

Other transition metal complexes also catalyze the reaction of organic halides with Grignard reagents. Most notable are complexes of nickel(II) and palladium(II).

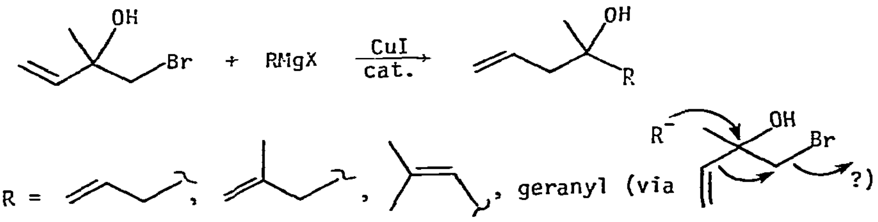


(11)

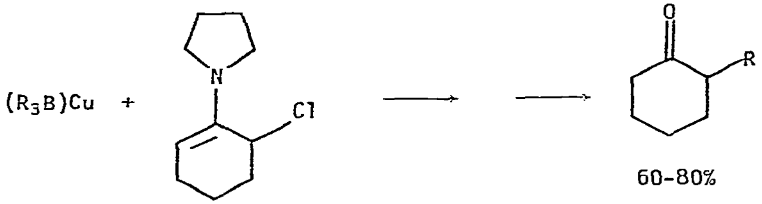


(12)

R = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, t-Bu



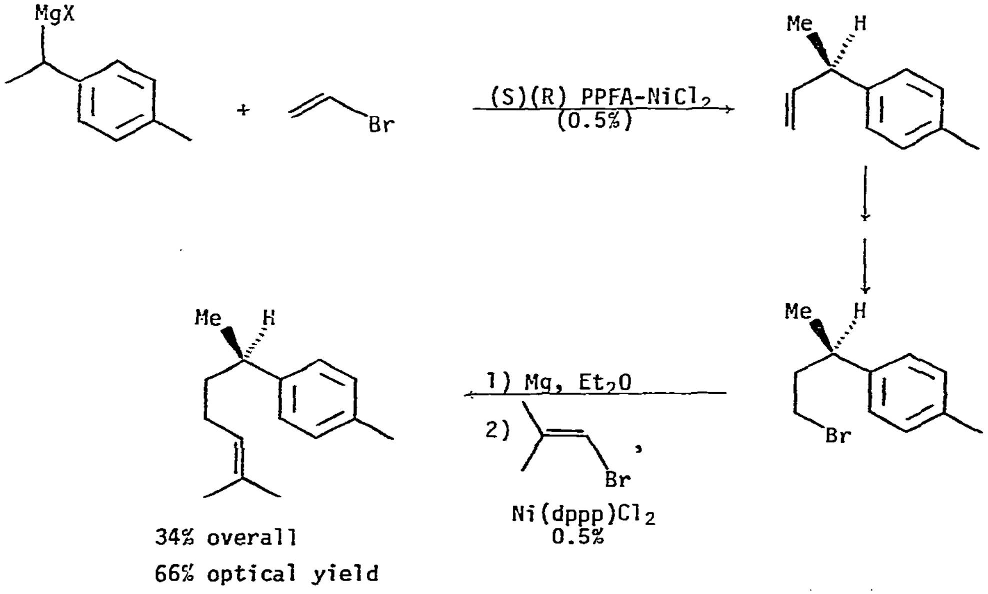
(13)



(14)

R = n-Pr, n-Bu, i-Bu, n-hexyl

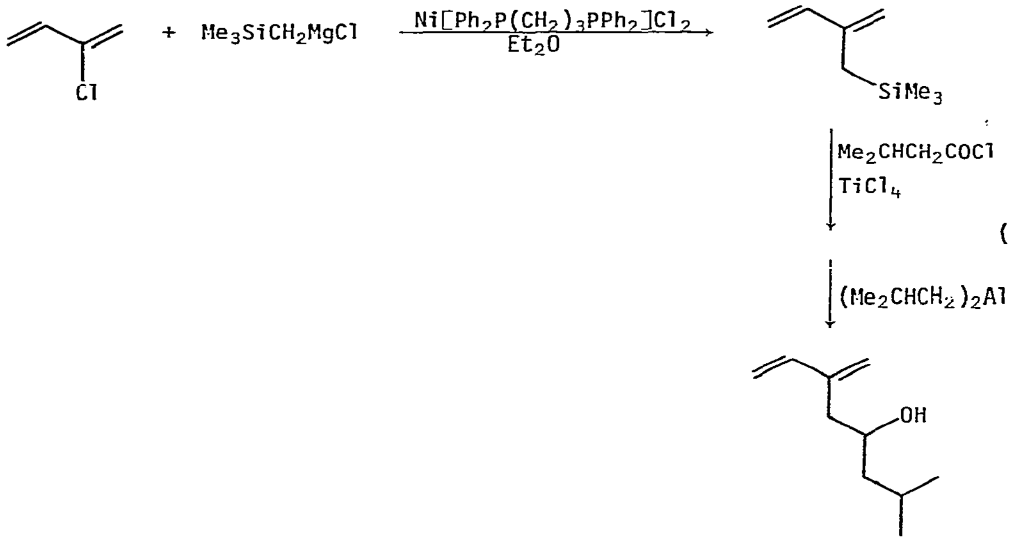
α-Curcumene was synthesized in high optical purity using a chiral nickel catalyst to promote the reaction of a Grignard reagent with vinyl halides (eq. 15) [22].



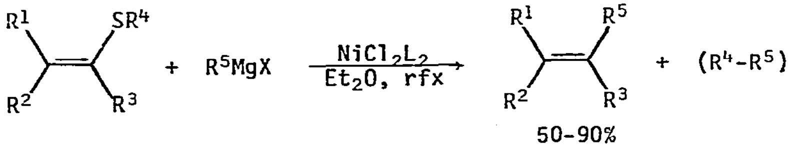
(15)

A similar reaction between sec-butylmagnesium bromide and halobenzenes using an (+)(R) prophos complex of nickel(II) chloride as a catalyst gave 2-phenylbutane in 70-85% and up to 44% optical yield [23]. The pheromone of Ips paraconfusus, ipsenol and ipsdienol were synthesized using the nickel(II) catalyzed coupling of trimethylsilylmethylmagnesium chloride with 2-chloro-1,3-butadiene, followed by reaction with electrophiles in the presence of the Lewis acid $TiCl_4$ (eq. 16) [24]. Vinyl sulfides were alkylated by reaction with Grignard reagents in the presence of L_2NiX_2 (eq. 17) [25]. The mechanism of the reaction of aromatic halides with nickel(0) complexes was examined in detail [26]. This reaction has some bearing on the mechanism of the nickel-catalyzed Grignard reactions discussed above.

Palladium(II) complexes with 1,1'-bis(diphenylphosphine)ferrocene as a ligand were effective catalysts for the reaction of secondary alkyl Grignard reagents with vinyl halides [27]. Similarly, phosphine-palladium(0) complexes catalyzed



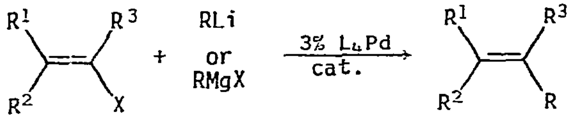
(16)



(17)

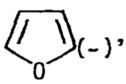
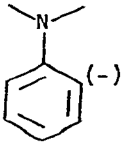
R^5 = Ph, n-Bu

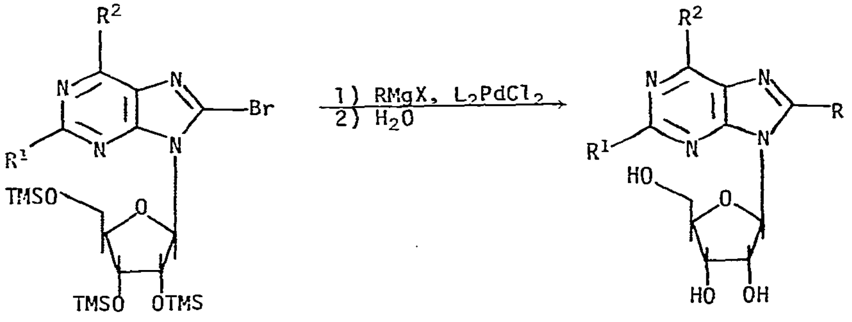
reactions of organolithium and Grignard reagents and thiophenoxide with vinyl halides. The stereochemistry of the double bond was maintained in these reactions (eq. 18) [28]. This sort of chemistry was used to alkylate bromo nucleosides with Grignard reagents (eq. 19) [29].



80-90%
99-100% isomeric purity

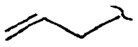
(18)

R = Me⁻, Bu⁻, p-tol⁻, PhS⁻, EtS⁻, , 

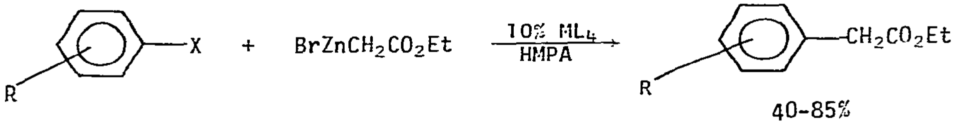


15-35%

(19)

R = Me, , Ph, p-anisyl, p-F-Ph

Nickel(0) and palladium(0) complexes also catalyzed the reactions of aryl halides with Reformatsky (organozinc) reagents (eq. 20) [30].

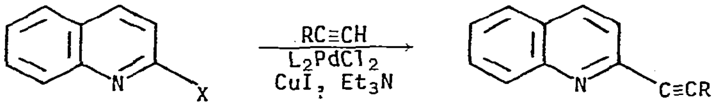


40-85%

(20)

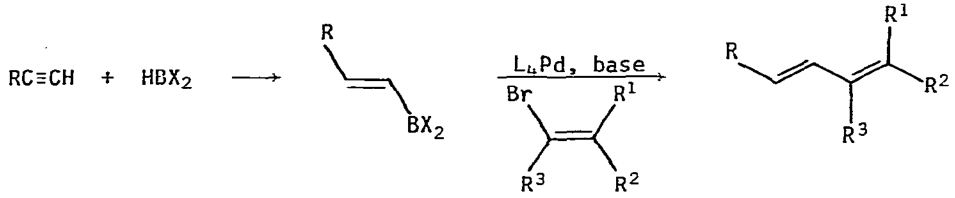
M = Pd, Ni; R = H, COOH, CN, MeO, MeCO, NO_2

Mixtures of palladium(II) complexes and copper(I) iodide catalyzed the reactions of bromoquinolines and bromoisoquinolines with alkynes (eq. 21) [31].



(21)

Vinyl boranes (from hydroboration of alkynes) reacted with vinyl halides in the presence of palladium(0) complexes as catalysts. Dienes were produced in this fashion (eq. 22) [32]. Aryl halides reacted in a similar fashion [33].



(22)

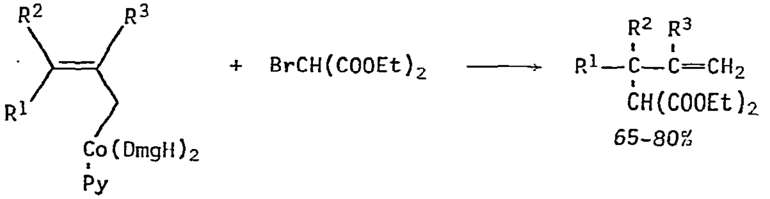
Organic halides reacted with tetraorganotin reagents in the presence of palladium catalysts to produce coupled products (eq. 23) [34]. The mechanism of this process was studied extensively [35].

$$RX \quad + \quad R'_4Sn \xrightarrow[HMPA]{PhCH_2Pd(L_2)Cl} RR' \quad + \quad R'_3SnX \qquad (23)$$

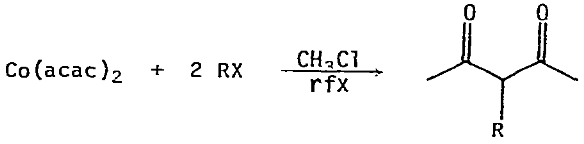
$R = PhCH_2$, Ph, Ar

R' = Me, Ph, n-Bu

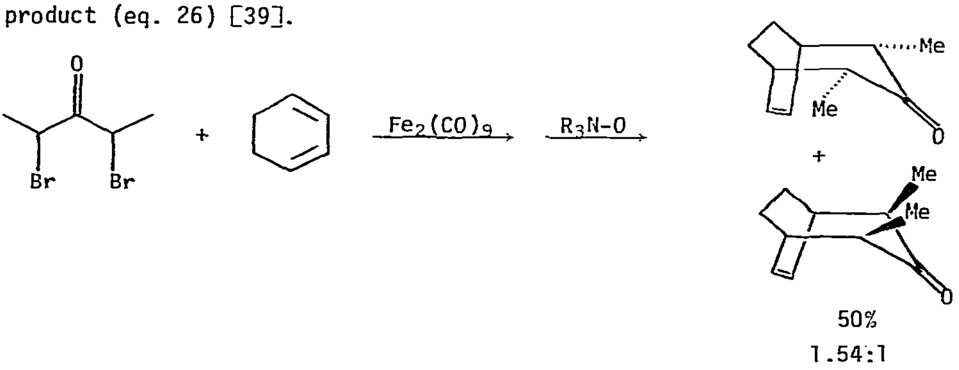
Allylcobaloxime complexes reacted with bromomalonic ester with resulting coupling at the most substituted allyl position (eq. 24) [36]. Cobalt(II) acetylacetonate reacted with benzylic and allylic halides to produce alkylated acetylacetones (eq. 25) [37]. Manganese(III) acetylacetonate reacted with triphenylaluminum in the presence of phosphines to produce a diphenylmanganese complex. This reacted with allyl bromide to give allyl benzene, and with carbon dioxide to give benzoic acid [38]. Bridged bicyclic ketones were made by the reaction of 1,3-cyclohexadiene with α,α'-dibromoketones and $Fe_2(CO)_9$. Oxidation of the resulting iron complexes with tertiary amine oxides freed the organic product (eq. 26) [39].



(24)

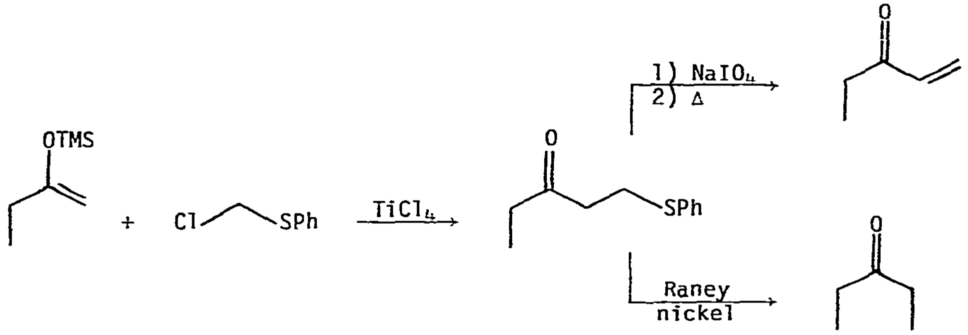


(25)



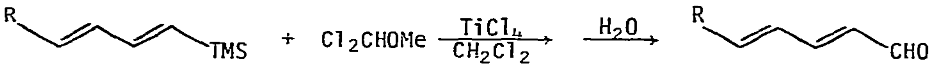
(26)

Ketones were regiospecifically α-methylated and α-methylenated by the titanium(IV) chloride assisted reaction of silylenol ethers with chloromethylphenyl sulfide (eq. 27) [40]. The silylated enolates of aldehydes, esters and lactones reacted in a similar fashion [41]. Dienylsilanes were converted to



(27)

α,β,γ,δ-unsaturated aldehydes by treatment with dichloromethyl methyl ether and titanium tetrachloride (eq. 28) [42].

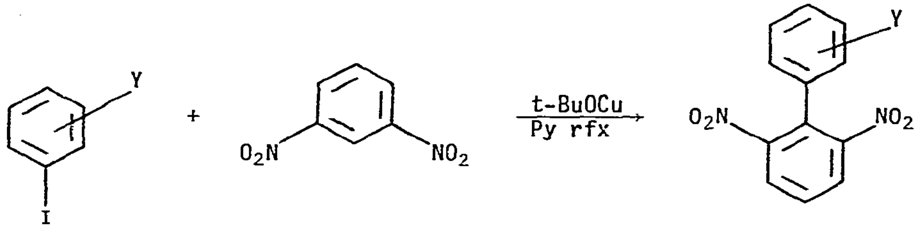


(28)

50-72%

R = Ph, n-Pr, n-pentyl

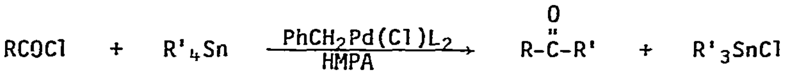
Aryl iodides coupled with m-dinitrobenzene when treated with copper(I) t-butoxide in pyridine to give unsymmetrical biaryls (eq. 29) [43].



(29)

2. Alkylation of Acid Halides

A very efficient conversion of acid chlorides to ketones has recently been developed. It involves the reaction of tetraorganotin reagents with acid chlorides using a palladium(II) catalyst. Thirty cases were cited, including aryl, aliphatic, sterically hindered, conjugated and heterocyclic acid halides. The reaction tolerated the presence of CN, NO_2, Cl, OMe, COOR, and CHO groups (eq. 30) [44]. Fluorinated aromatic copper reagents reacted with perfluoroalkyl

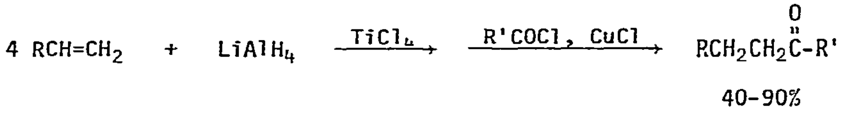


$$RCOCl \quad + \quad R'_4Sn \xrightarrow[HMPA]{PhCH_2Pd(Cl)L_2} R\text{-}\overset{O}{\overset{\parallel}{C}}\text{-}R' \quad + \quad R'_3SnCl \qquad (30)$$

high yields

R' = Me, Ph, Bz, n-Bu, CH_2=CH

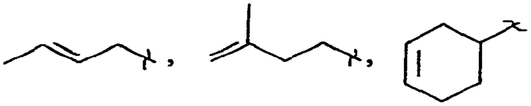
acid halides to produce fluoroketones [45]. Terminal olefins were "hydro-acylated" by sequential titanium tetrachloride assisted hydroalumination of followed by reaction with acid halides in the presence of copper(I) chloride (eq. 31) [46].



$$4\ RCH{=}CH_2 \quad + \quad LiAlH_4 \xrightarrow{TiCl_4} \xrightarrow{R'COCl,\ CuCl} RCH_2CH_2\overset{O}{\overset{\|}{C}}\text{-}R' \qquad (31)$$

40-90%

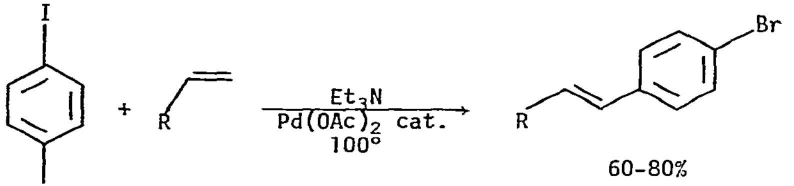
R = H, n-Bu,



R' = Ph, Me, Et, i-Pr, n-Bu, $MeOCH_2CH_2$

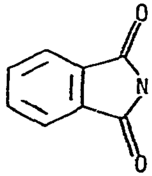
3. Alkylation of Olefins

Palladium-catalyzed reactions of organic halides with olefins have recently been reviewed [47]. These "Heck" arylations and alkylations rely upon the oxidative addition of aryl, benzyl, heteroaromatic and vinyl halides to the palladium(0) catalyst followed by insertion of the olefin into the α-alkyl-palladium complex thus formed. The stereochemistry of the process is consistent with a syn addition-syn elimination mechanism. Heck arylation of styrene, methyl acrylate, acrylic acid, and N-vinylphthalimide using bromoiodo aromatics as the halide component alkylated exclusively at the site of the iodide to give brominated aromatic compounds (eq. 32) [48]. Enol ethers and acetates also functioned as the olefinic component in these "Heck" arylations. The regio-selectivity of the process was dependent on the enol ether component (eq. 33) [49]. With bromothiophene as the halide and allyl alcohols as the olefin, thiophenes containing keto side chains were prepared (eq. 34) [50]. This chemistry was used in the synthesis of the Queen bee substance.

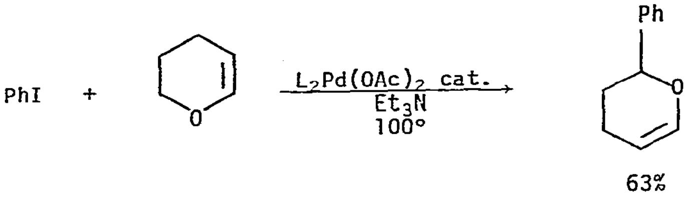


(32)

R = COOMe, Ph, COOH,

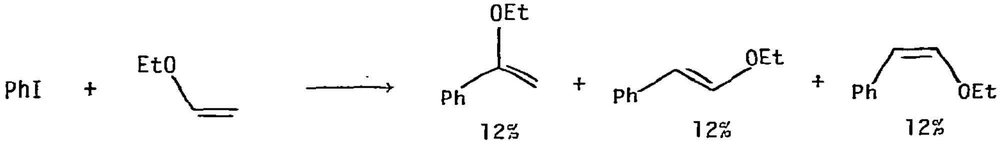


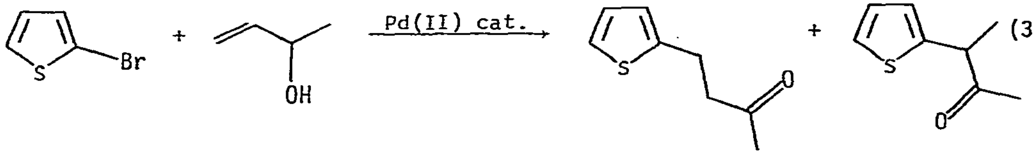
Organopalladium(II) complexes made by transmetallation reactions with organomercury, tin, copper or magnesium compounds also alkylate (insert) olefins. Mercurated nucleosides reacted with substituted styrenes in the presence of a



(33)

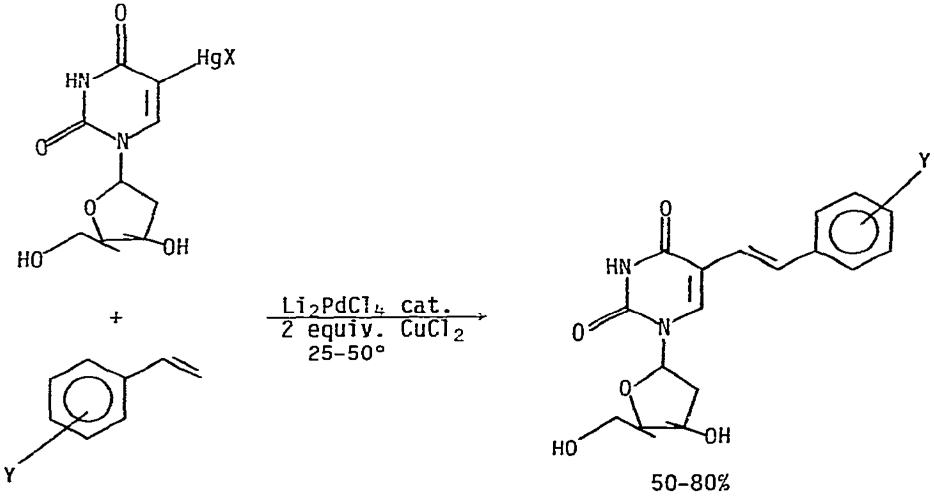
but





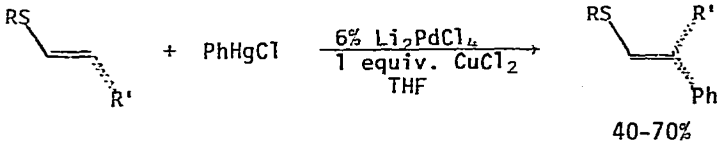
(34)

mixed palladium(II)-copper(II) catalyst (eq. 35) [51]. Vinylsulfides reacted with phenylmercuric chloride in the presence of Li_2PdCl_4 to produce β-phenylated vinylsulfides (eq. 36). Intramolecular versions of this reaction failed with



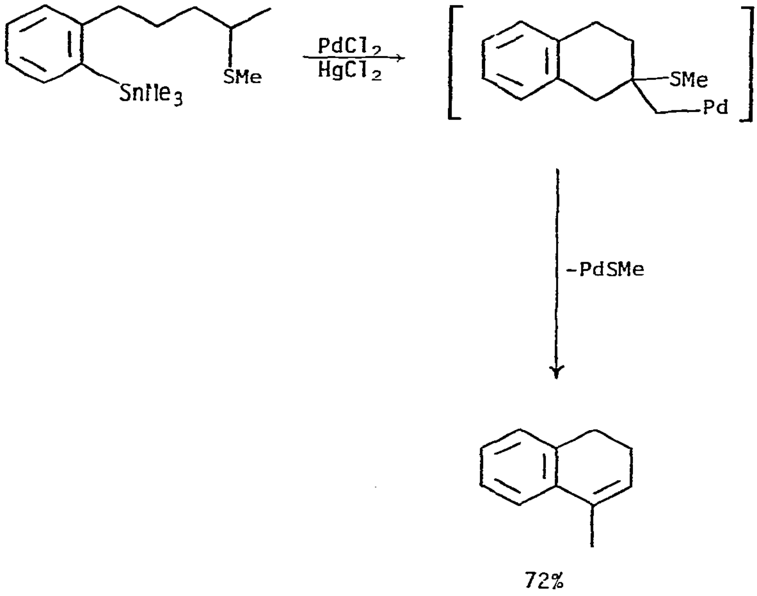
(35)

Y = m-NO_2, H, p-NO_2

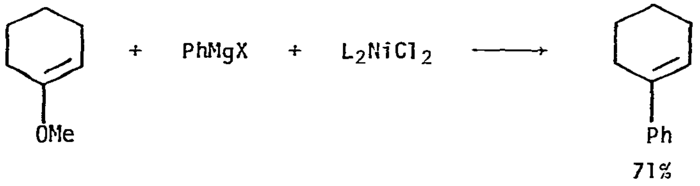


(36)

vinylmercuric halides but the corresponding aryltrimethyltin complexes reacted well, and alkylated α to the sulfur, which was then lost in the elimination step (eq. 37) [52]. Styrene and butyl acrylate reacted with lithium diphenylcuprate in the presence of palladium(II) salts to produce stilbenes and β-phenylacrylates, respectively [53]. Enol ethers reacted with Grignard reagents in the presence of nickel(II) catalysts to replace the ether group with a group provided by the Grignard reagent (eq. 38) [54].



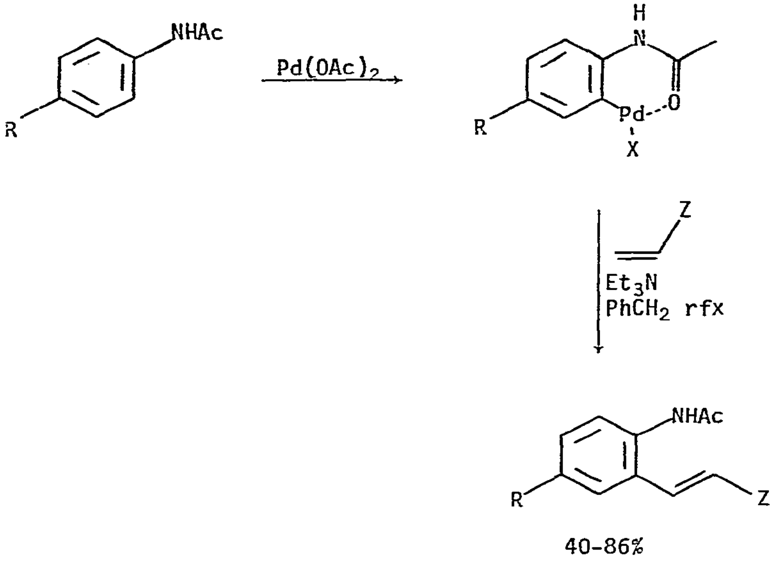
(37)



(38)

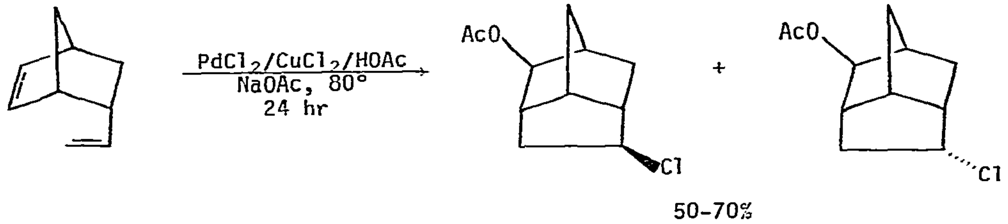
Acetanilides were ortho alkylated by an ortho palladation olefin insertion sequence (eq. 39) [55]. Bridged polycyclic compounds were synthesized using a palladium-assisted acetoxylation of an olefin followed by olefin insertion into the thus-formed σ-alkylpalladium(II) complex (eq. 40) [56,57]. Electrophilic olefins were converted to vinyl cyclopentanes by the reaction presented in eq. 41 [58].

Under relatively severe conditions, palladium(II) salts will undergo

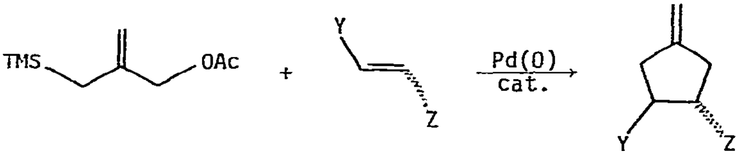


(39)

Z = Ar, CN, CHO, COOMe, COMe, OCOMe



(40)

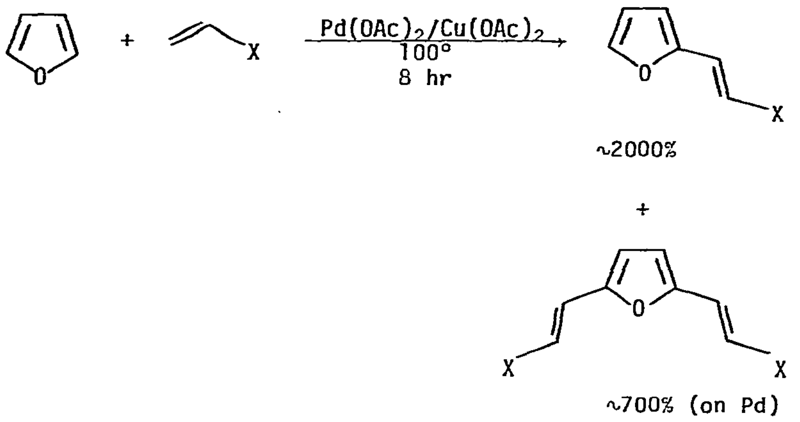


(41)

Y = H, Me, n-C_5, COOMe, Ph

Z = COOMe, CN, $COCH_3$, COPh

electrophilic substitutions with aromatic hydrocarbons, permitting direct alkylation of aromatic hydrocarbons with olefins. Furan reacted with methyl acrylate or acrylonitrile in the presence of a palladium(II) acetate catalyst to produce the 2-substituted furan (eq. 42) [59]. The kinetics of the arylation of styrene by $(Ph_3P)_2Pd(OAc)_2$ to give stilbenes was studied [60]. Triphenylphosphine was the

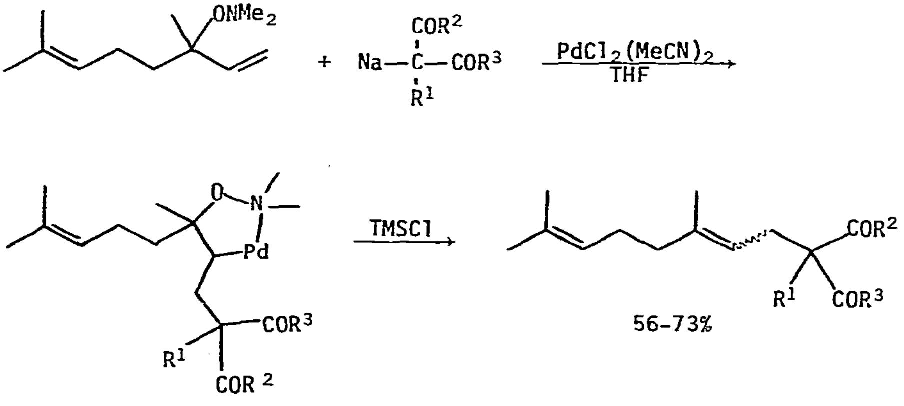


(42)

X = COOMe, CN

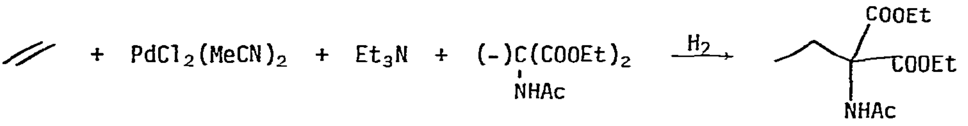
source of the aryl group in this reaction. The kinetics of the arylation of styrene by benzene or naphthalene in the presence of palladium(II) acetate were also studied [61]. Ethylene was arylated by benzene, thiophene, and furan using palladium(II) catalysts in the presence of phosphorus-molybdenum-vanadium heteropolyacids [62]. Benzene reacted with ethylene and carbon monoxide in the presence of $Rh_4(CO)_{12}$ at 220° and 55 kg/cm pressure to produce styrene and 3-pentanone [63]. The reaction of methylcobalt complexes with ethylene to give propene was shown to go by an insertion of the olefin into the cobalt-methyl bond rather than by a β-elimination-carbene-metallacycle process [64].

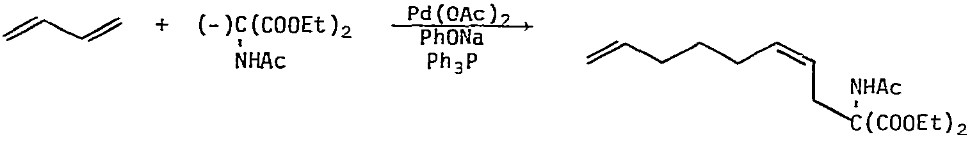
Olefins coordinated to palladium(II) complexes can be directly alkylated by carbanions. Using the complex $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)(CH_2{=}CH_2)]^+$, it was demonstrated that β-diketocarbanions reacted with the coordinated ethylene exclusively trans to the metal [65]. Allylethers of oximes reacted with stabilized carbanions to alkylate the allyl olefin. The resulting α-alkylpalladium complex was decomposed by TMSCl to produce alkylated product (eq. 43) [66]. α-Amino

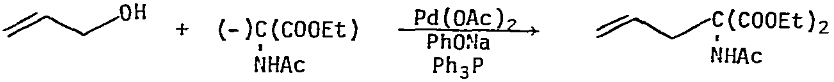


(43)

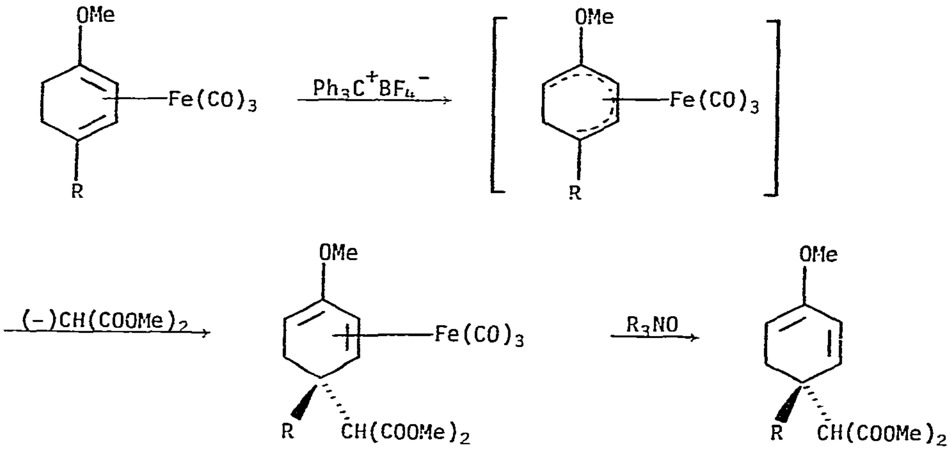
R^1 = H, Me, Bu; R^2 = MeO, Me, Et; R^3 = MeO, EtO acids were synthesized by alkylation of palladium(II) coordinate olefins with diethylacetamidomalonates (eqs. 44-46) [67].


(44)

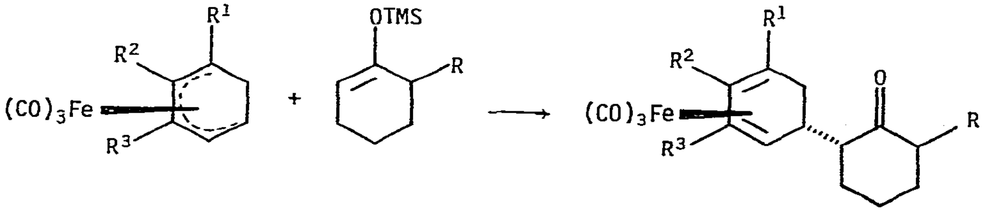

(45)


(46)

Cyclohexadienyl complexes of iron were treated with stabilized carbanions (eq. 47) [68] and trimethylsilylenol ethers (eq. 48) [69], resulting in alkylation.


(47)

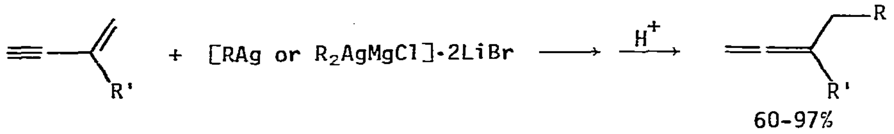
38% overall


(48)

R^1 = H, COOMe; R^2 = H, OMe; R^3 = H, Me

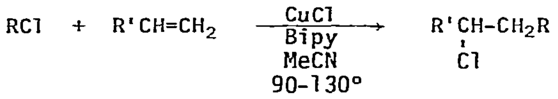
70-84%

Enynes reacted with alkylsilver or dialkylargentates by an apparent S_N2' mechanism to produce alkylated allenes (eq. 49) [70]. α-Chloro esters [71], benzyl halides [72], and α-chloronitriles [73] added to olefins when treated with copper(I) chloride and 2,2'-bipyridine in acetonitrile or DMF (eq. 50). With 1,3-dienes both 1,2 and 1,4 addition were observed.



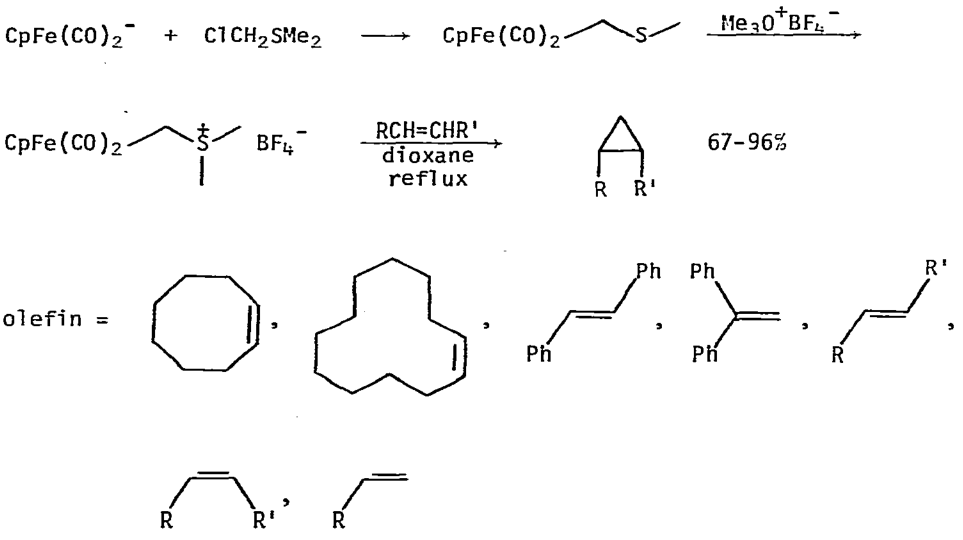
(49)

R' = H, Me; R = Bu, i-Pr, t-Bu

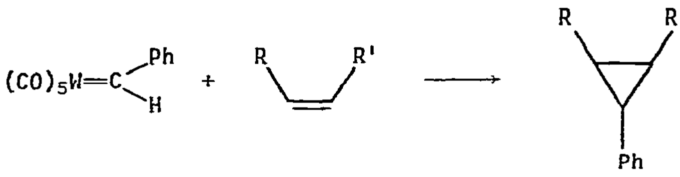

$$RCl + R'CH{=}CH_2 \xrightarrow[\substack{MeCN \\ 90\text{-}130^\circ}]{CuCl \ Bipy} R'\underset{\substack{| \\ Cl}}{CH}\text{-}CH_2R \qquad (50)$$

R = $-CH_2COOMe$, $ArCH_2$,$-CH_2CN$; R' = Me, Ph, n-hexyl, n-octyl

A number of new cyclopropanating agents have been developed recently. Treatment of $CpFe(CO)_2^-$ with chloromethylmethyl sulfide followed by alkylation of the sulfur produced a very stable and storable salt. Treatment of olefins with this salt in refluxing dioxane resulted in the formation of cyclopropanes in high yield (eq. 51) [74]. The reaction was thought to involve a cationic iron-carbene complex. The stereochemistry of the olefin was maintained. The phenylcarbene complex of tungsten carbonyl reacted with a variety of olefins to produce phenylcyclopropanes in fair to excellent yields (eq. 52) [75].



(51)

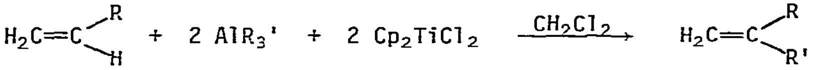


40-80%

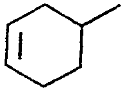
(52)

Electrophilic olefins such as acrylonitrile, methyl acrylate, and methyl vinyl ketone were converted to cyclopropanes in 50-75% yield by treatment with dibromomethane and nickel(0) phosphine complex catalysts. Addition of sodium iodide and zinc increased the yields [76]. Olefins were converted to cyclopropanes by treatment with diiodomethane and copper powder, in a process similar to the Simmons-Smith reaction [77].

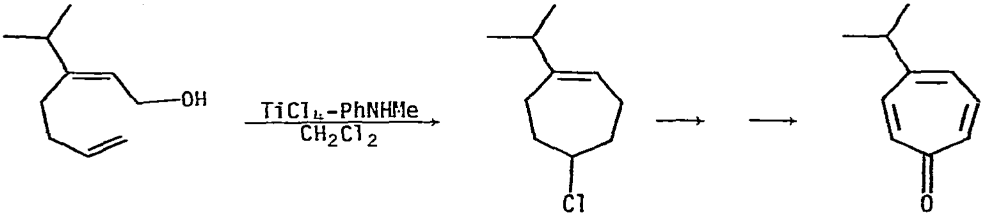
Terminal olefins were alkylated by trialkylaluminum reagents in the presence of Cp_2TiCl_2 (eq. 53) [73]. Allylic alcohols containing remote unsaturation reacted with titanium(IV) halides and N-methylaniline to produce cyclic products. This procedure was used to synthesize nezukone (eq. 54) [79]. Olefins were arylated by zirconium-bound benzyne to produce zirconacyclopentanes (eq. 55) [80].



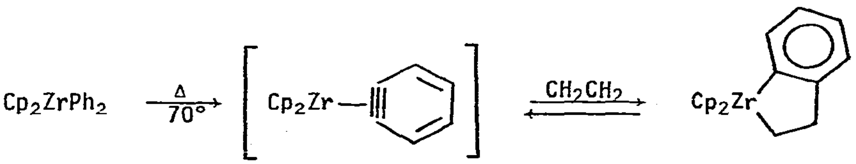
$$H_2C{=}C(R)(H) + 2\ AlR_3' + 2\ Cp_2TiCl_2 \xrightarrow{CH_2Cl_2} H_2C{=}C(R)(R') \qquad (53)$$

R = n-C_8,  , $MeCO_2(CH_2)_4$, $TMSO(CH_2)_4$, $NC\text{-}(CH_2)_4$, $Br(CH_2)_4$-

R' = Me, Et, n-Bu, i-Bu



(54)



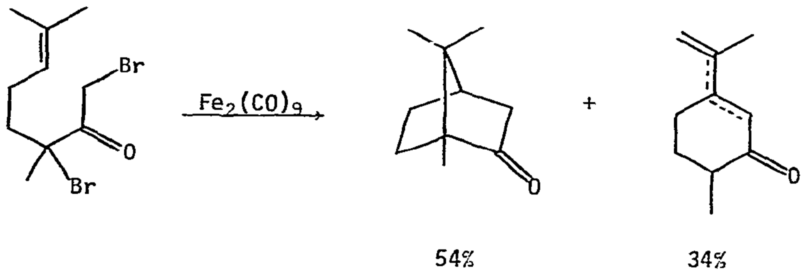
(55)

4. Decomposition of Diazoalkane

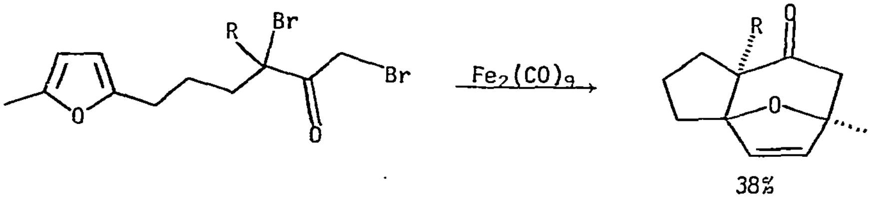
The reaction of ethyl diazoacetate with N-methylpyrrole gave mixtures of α- and β-N-methylpyrroloacetic esters. The effects of N-substitution, and the metal catalyst on the ratio of these two products (which ranged from 16:1 α/β to 3:2) were studied [81]. Chrysanthemumic acid and esters were prepared by the reaction of unsymmetrical olefins with ethyl diazoacetate in the presence of asymmetric organocopper complexes [82].

5. Cycloaddition Reactions

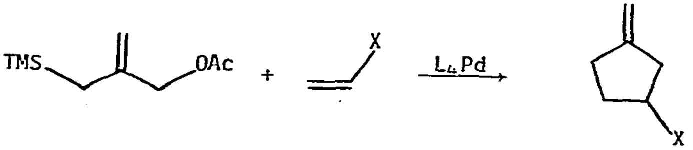
An intramolecular version of the iron(0) catalyzed formal 3+2 cycloaddition of α,α'-dibromoketones to olefins was used to synthesize a number of terpenes (eq. 56). A similar intramolecular version of the corresponding 4+3 cycloaddition to furan was also developed (eq. 57) [83]. Palladium(0) complexes reacted with 2-acetoxymethyl-3-allyltrimethylsilane to provide an equivalent of trimethylenemethane for cycloaddition to electron deficient olefins, producing methylenecyclopentanes (eq. 58) [84]. Cationic iron complexes of enol ethers underwent a cycloaddition reaction with TCNE to produce substituted cyclopentanes (eq. 59) [85]. Iron(0) complexes catalyzed the cycloaddition of ynamines and butadiene to give aminocyclohexadi-1,4-enes (eq. 60) [86]. Norbornene, nortricyclane, and furan underwent 2+2 cycloadditions with dimethylacetylene



(56)

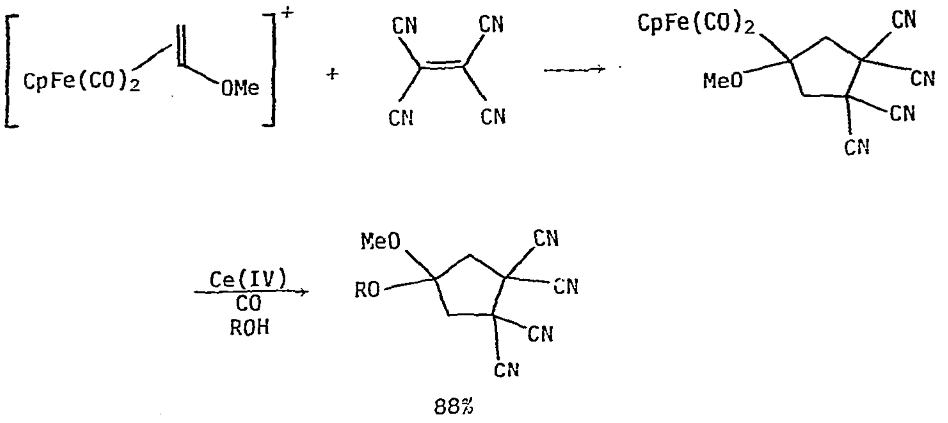


(57)

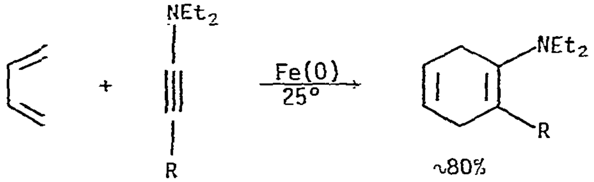


(58)

$X = COOR, CN, COR, SO_2R$



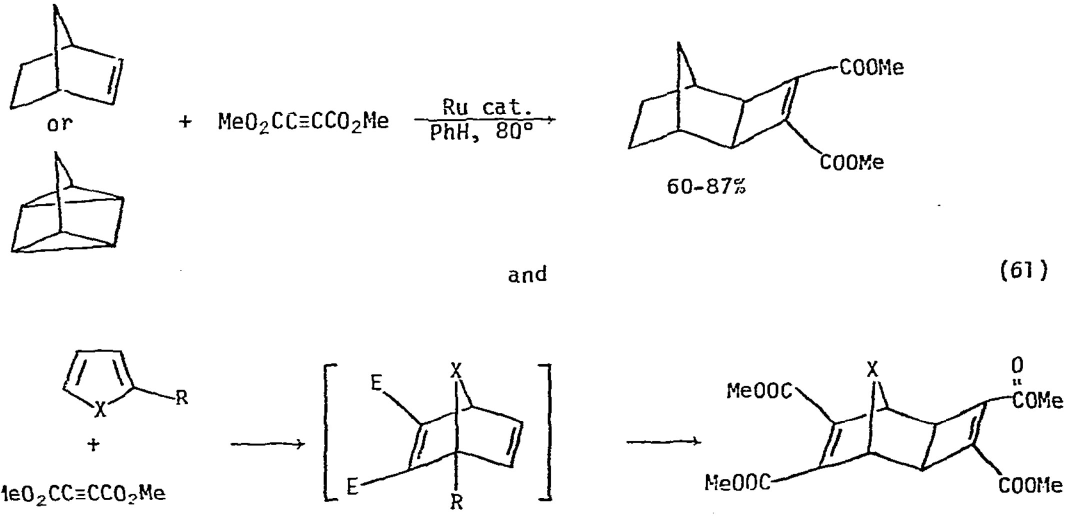
(59)



(60)

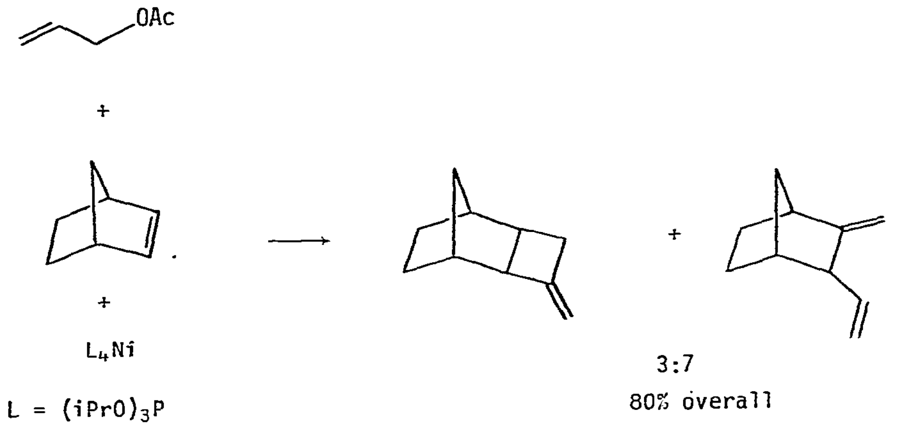
R = Me, i-Pr, C_5H_{11}, Ph

dicarboxylate to form cyclobutenes (eq. 61) [87]. Nickel(0) complexes catalyzed the reaction of allylacetate with norbornene to produce both vinylcyclobutanes and dienes (eq. 62) [88].



(61)

X = CH_2, O; R = H, Me; Ru cat. = L_4RuH_2, $RuH_2(CO)L_3$

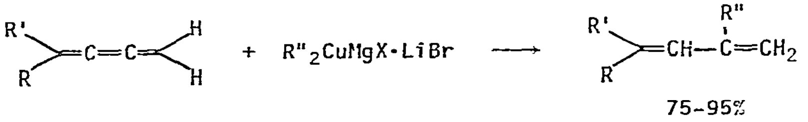


(62)

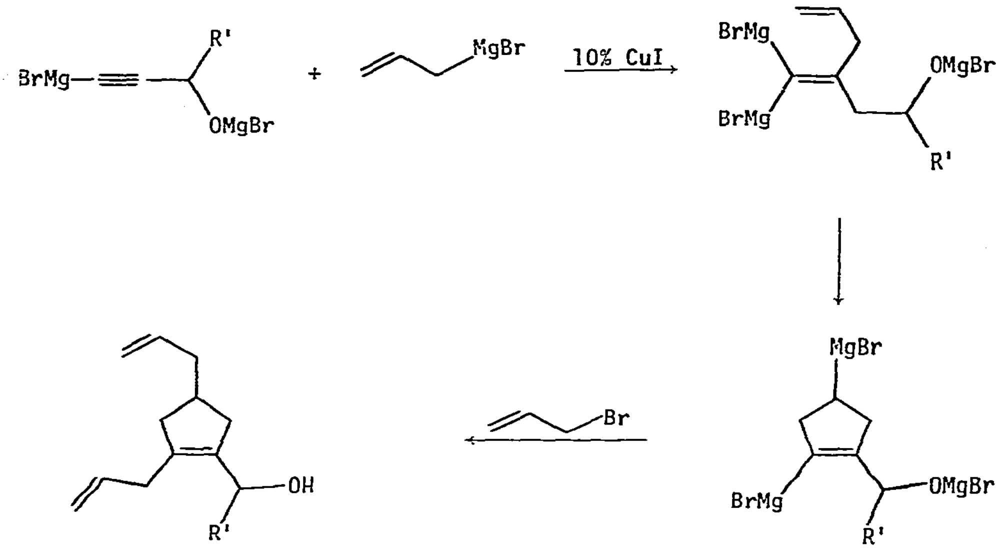
6. Alkylation of Alkynes

Among the best methods for forming vinyl copper species for further use in organic synthesis is the addition of organocopper derivatives to acetylenes. With acetylene itself, the best reagents were lithium dialkylcuprates, which reacted to form Z-dialkenylcuprates which were iodinated stereospecifically to afford Z-1-iodoalkenes. ω-Functionalized dialkylcuprates also added cleanly to acetylene [89]. Under appropriate conditions the thus formed vinylcuprates reacted with a number of organic halides to produce Z-internal olefins in good yield. Twenty cases were studied [90]. The use of stoichiometric versus catalytic amounts of copper in the addition of organolithium and magnesium compounds to acetylenes has been reviewed [91].

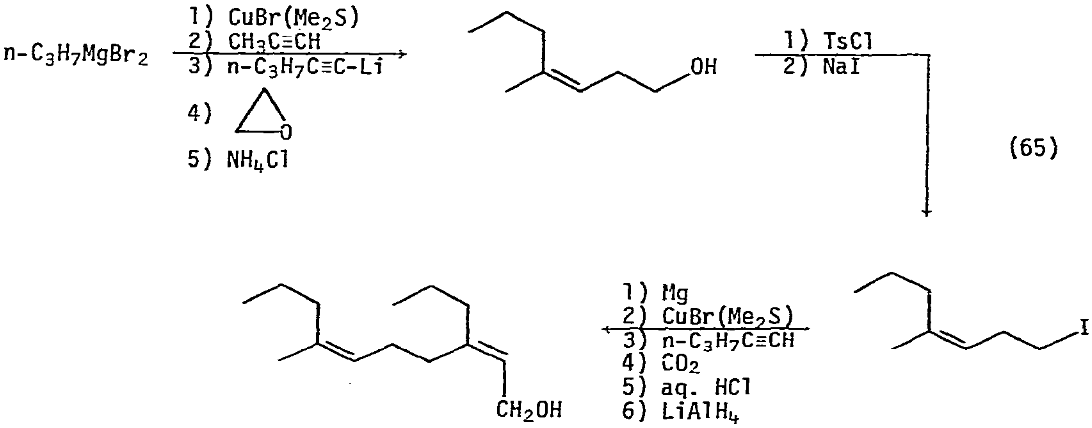
Cumulenes reacted with lithium dialkylcuprates to produce dienes in good yield (eq. 63) [92]. Allylmagnesium bromide reacted with acetylenic Grignard reagents in the presence of copper(I) iodide. Further reaction ensued (eq. 64) [93]. A sequence involving copper-catalyzed addition of Grignard reagents to alkynes was used as a key step in the synthesis of the codling moth substance (eq. 65) [94]. The reagent $CH_3Cu(Me_2S)MgBr$ was formed to add cleanly to terminal alkynes to produce 2,2-disubstituted alkenyl copper intermediates. The reactions of these complexes with a variety of electrophiles, including allyl and acid halides, conjugated enones, and epoxides were studied in detail (eq. 66) [95]. Metallated vinyl silanes were prepared by the reaction of methylmagnesium bromide with trimethylsilylacetylenes, trimethyl aluminum and nickel(II) acetylacetonate (eq. 67) [96].



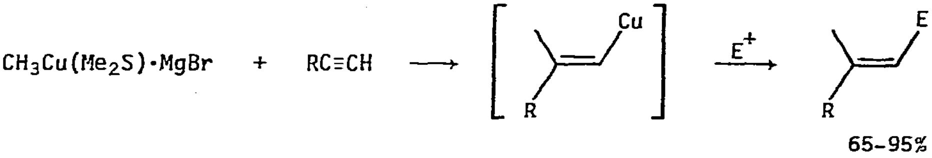
(63)


BrMg
R'
OMgBr
+
MgBr
10% CuI
BrMg
BrMg
OMgBr
R'
MgBr
BrMg
OMgBr
R'
Br
OH
R'

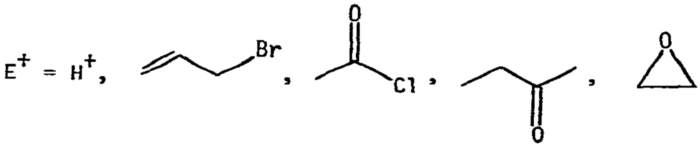
(64)

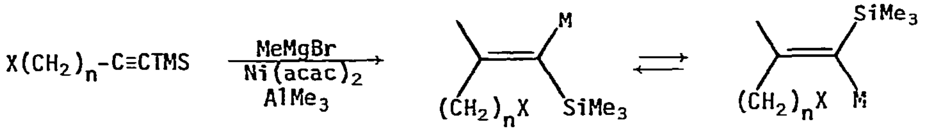

n-C3H7MgBr2
1) CuBr(Me2S)
2) CH3C≡CH
3) n-C3H7C≡C-Li
4)
O
5) NH4Cl
OH
1) TsCl
2) NaI
I
1) Mg
2) CuBr(Me2S)
3) n-C3H7C≡CH
4) CO2
5) aq. HCl
6) LiAlH4
CH2OH

(65)


CH3Cu(Me2S)·MgBr
+
RC≡CH
Cu
R
E+
E
R
65-95%

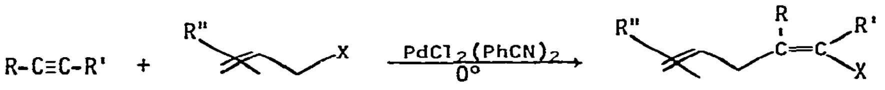
(66)


E+ = H+,
Br
O
Cl
O



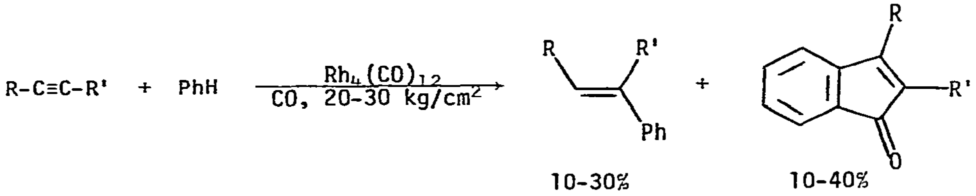
(67)

Internal acetylenes reacted with allylic halides in the presence of palladium(II) chloride to give chloro-1,4-dienes (eq. 68). The reaction was



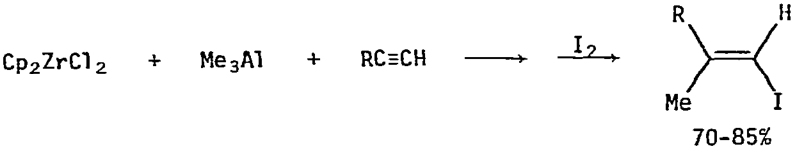
(68)

thought to proceed by chloropalladation of the alkyne, insertion of the allyl halide, and β-elimination of palladium chloride [97]. Internal alkynes reacted with benzene in the presence of $Rh_4(CO)_{12}$ to give styrenes and indenones (eq. 69) [98]. Terminal alkynes were stereoselectively converted to (E)-2-methyl-



(69)

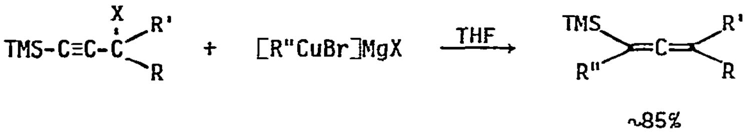
1-alkenyl iodides by reaction with Cp_2ZrCl_2 and trimethylaluminum, followed by iodine (eq. 70) [99]. The corresponding titanium complexes effected similar chemistry [100].



(70)

7. Alkylation of Allyl and Propargyl Alcohols and Acetates

Propargyl tosylates and mesylates react with organocuprates to produce allenes by an S_N2' type reaction. A number of trimethylsilylpropargylic systems reacted with [RCuBr]MgX to produce trimethylsilylallenes (eq. 71) [101].



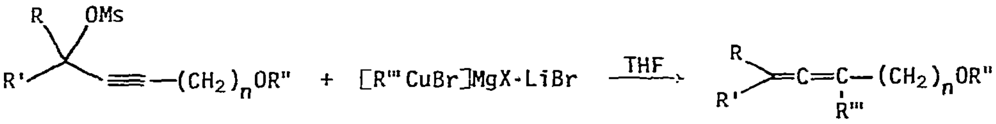
(71)

R = H, t-Bu, Me

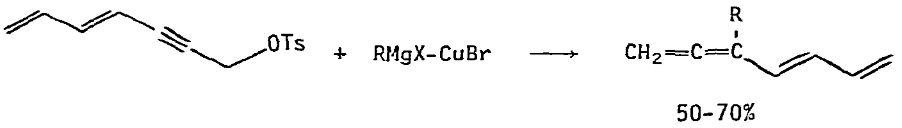
R' = H, Me, $(CH_2)_4$, $-(CH_2)_5-$

R" = Et, n-Bu, i-Pr, c-C_6H_{11}, Ph, sec-Bu, Me

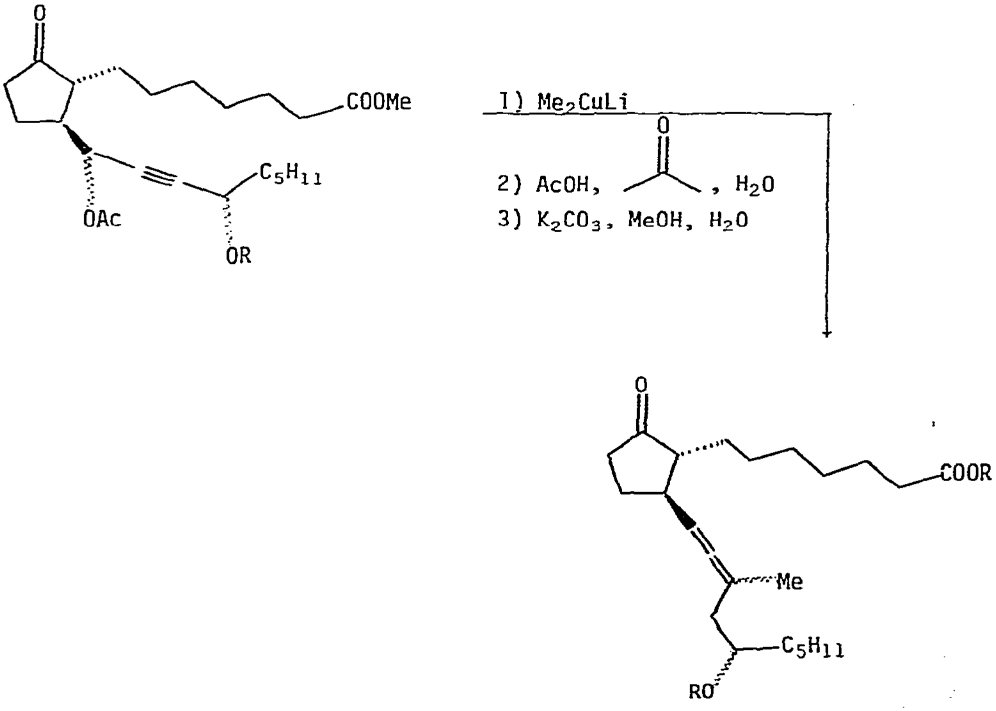
Propargyl mesylates having remote ether functionality reacted in a similar fashion (eq. 72) [102], as did polyunsaturated propargyl tosylates (eq. 73) [103]. Allenic prostanoids were synthesized using this methodology (eqs. 74, 75) [104]. Chromium(II) reduced a propargyl bromide to the allene. The intermediate allenic chromium complex could be trapped with ketones (eq. 76) [105].



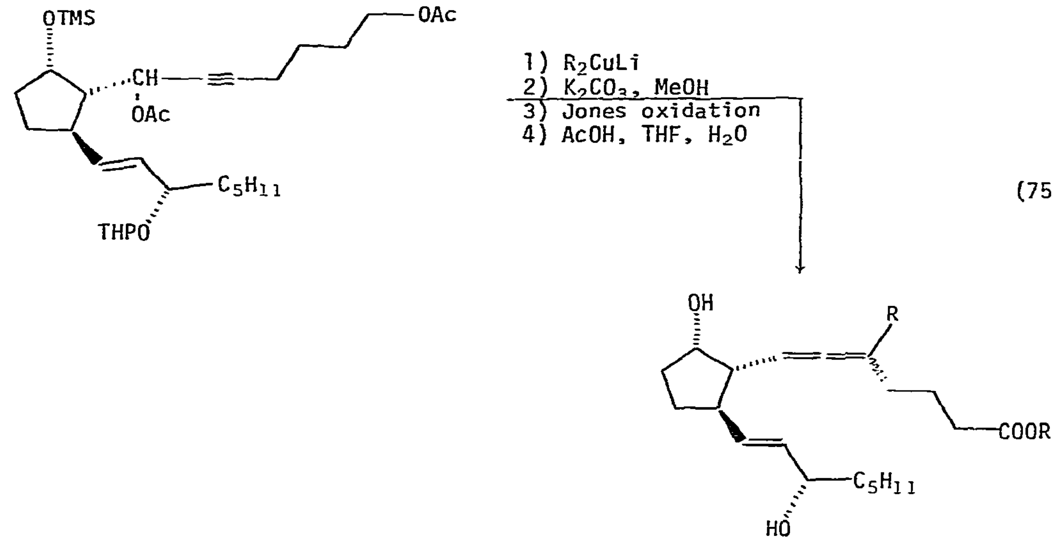
(72)



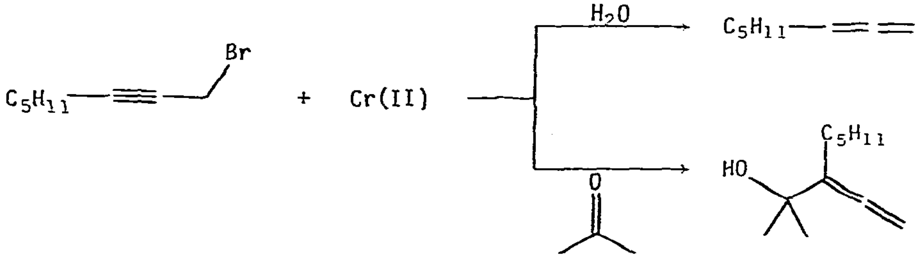
(73)



(74)

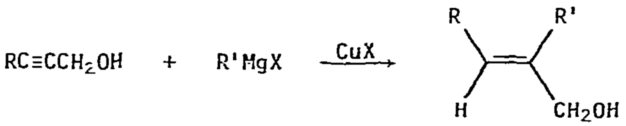


(75)



(76)

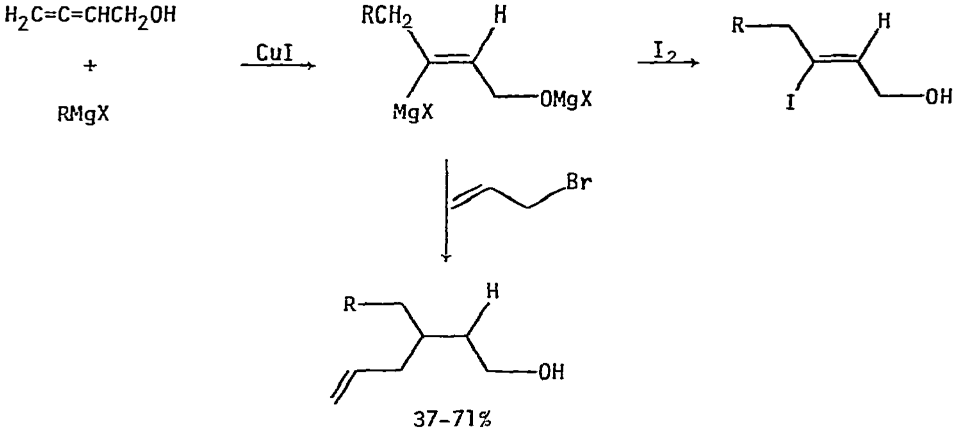
Primary α-acetylenic alcohols reacted with Grignard reagents regio- and stereospecifically in the presence of copper(I) halides as catalyst to produce disubstituted allyl alcohols (eq. 77) [106]. The vinylcopper intermediates,



(77)

when treated with iodine, produced vinyl halides [107]. Allenic alcohols added Grignard reagents to the terminal carbon to produce vinyl complexes which reacted further with electrophiles (eq-78) [107]. Copper(I) catalyzed Grignard reactions were used to synthesize 1,4-diynes (eq. 79)[108].

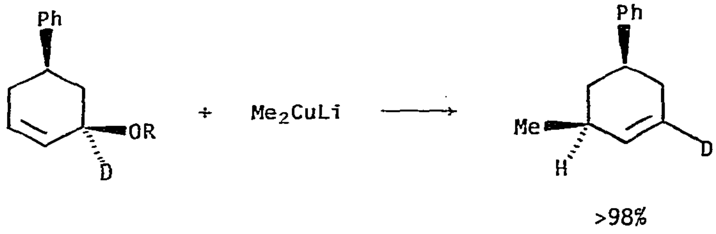
Allylic sulfones reacted with Grignard reagents and copper(I) acetylacetonate catalysts primarily by an S_N2 process when primary sulfones were used, but by an S_N2' process when secondary sulfones were used. The regioselectivity also depended on the other substituents and on the solvent [109]. With a phenyl substituted cyclohexenyl allylic ester system, reactions with lithium dialkylcuprates went exclusively by an S_N2' process when the carbamate was used, but reacted virtually 1:1 S_N2-S_N2' with all other esters (eq. 80) [110].



(78)

$$HC\equiv CCH_2OTs \quad + \quad BrMgC\equiv CR \xrightarrow[THF]{CuBr} HC\equiv C\text{-}CH_2C\equiv CR$$

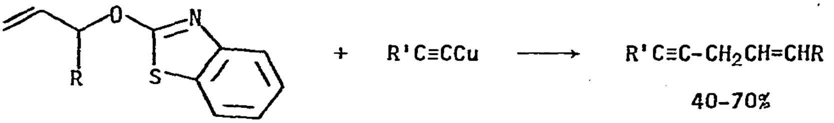
60-80% (79)



(80)

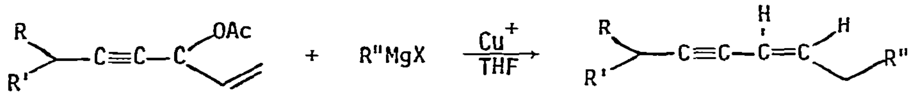
R = CONHPh

Allylic alcohols reacted with copper acetylides with clean allylic transposition when converted to a heterocyclic derivative (eq. 81) [111]. Allylic-propargylic acetates reacted with Grignard reagents in the presence of a copper(I) catalyst by an S_N2' process at the olefinic site to give exclusively Z enynes

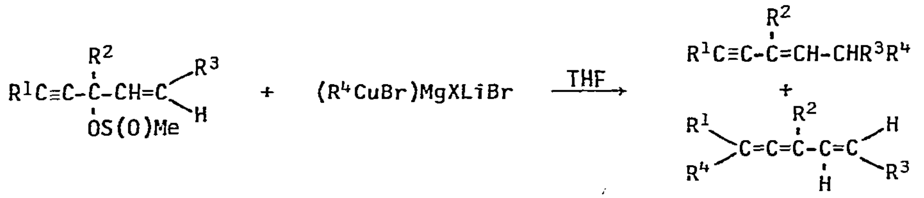


(81)

(eq. 82) [112]. Allylic-propargylic sulfones reacted with [RCuBr]MgX·LiBr reagents to form enynes or allenes depending on the substituents (eq. 83) [113]. In the reaction of allyl acetates with Grignard reagents and copper(I)

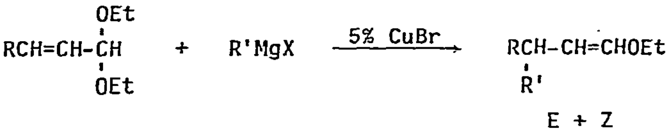


(82)



(83)

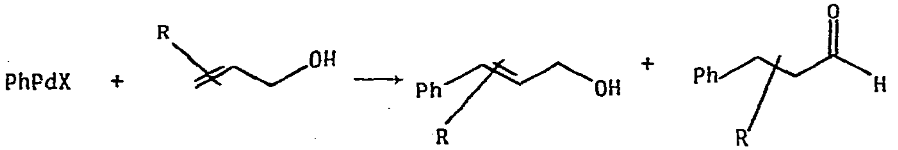
bromide catalysts the reaction was claimed to occur by an antarafacial attack, and the leaving group was required to be quasiorthogonal to the plane of the double bond [114]. Allyl ethers reacted with Grignard reagents in the presence of copper(I) catalysts to give substitution with both S_N2 and S_N2' regiochemistry. The amount of S_N2' depended on the substrate structure [115]. Allylic acetals reacted with Grignard reagents and copper catalysts to give mixtures of E and Z enol ethers, by clean S_N2' chemistry (eq. 84) [116]. Allylic sulfides reacted



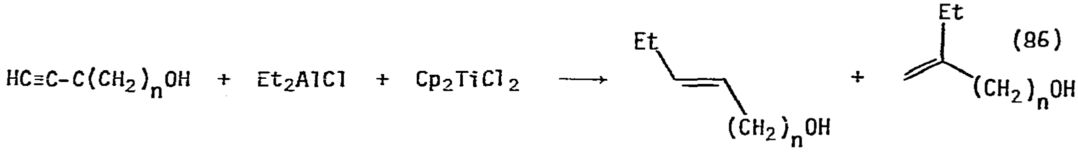
$$\mathrm{RCH{=}CH\text{-}\underset{OEt}{\overset{OEt}{CH}}} + \mathrm{R'MgX} \xrightarrow{5\%\ \mathrm{CuBr}} \underset{\mathrm{E\ +\ Z}}{\mathrm{R\underset{R'}{C}H\text{-}CH{=}CHOEt}} \qquad (84)$$

with Grignard reagents in the presence of phosphine nickel(II) halide catalysts to give substitution products from both S_N2 and S_N2' displacement [117]. The reaction of allylic esters with sodiodiethylmalonate was catalyzed by a number of complexes including $Fe(CO)_3NO^-$, η^3-crotyl $Fe(CO)_2NO$, η^3-crotyl $Co(CO)_2L$ and $Co(CO)_4^-$ to give mixtures of S_N2 and S_N2' displacement products. The intermediacy of η^3-allyl complexes was claimed [118].

Allylic alcohols reacted with arylpalladium(II) complexes to give both alcohol and carbonyl compounds. The ratio depended on the nature of the allylic alcohol (eq. 85)[119]. Alkynols were alkylated by treatment with diethylaluminum chloride using Cp_2TiCl_2 as a catalyst (eq. 86) [120].



(85)

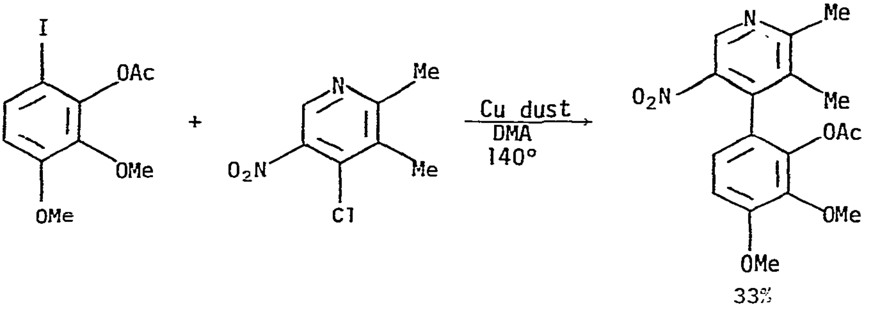


(86)

n = 2-4

8. Coupling Reactions

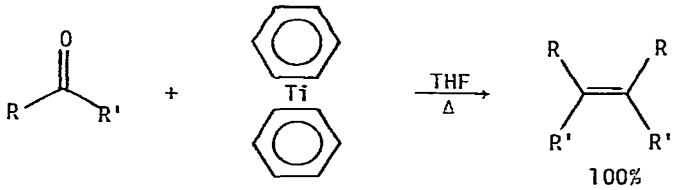
The C-D ring portion of streptonigrin was synthesized by an unsymmetrical Ullmann coupling of an iodobenzene and a chloropyridine using copper dust (eq. 87) [121]. Symmetrical biaryls were synthesized by coupling iodoarenes with a nickel(0) species generated in situ by reduction of nickel(II) chloride with zinc [122]. Extremely reactive copper and uranium powders for Ullmann coupling were produced by reduction of the corresponding metal chloride or iodide with potassium metal in the presence of naphthalene. In this fashion pentafluoroiodobenzene was coupled to perfluorobiphenyl in 83% yield [123]. The nickel catalyzed coupling of aryl halides to biaryls was studied in great detail and was claimed to be a radical chain process involving both nickel(II) and nickel(III) intermediates (eq. 88) [124].



(87)

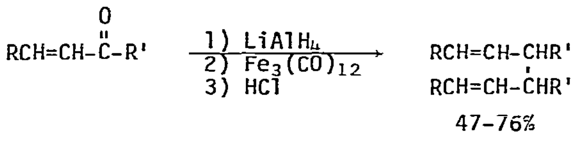
$$
\begin{array}{llll}
\mathrm{Ni(I)X} + \mathrm{ArX} & \longrightarrow & \mathrm{ArNi(III)X_2} & \\
\mathrm{ArNi(III)X_2} + \mathrm{Ar'Ni(II)X} & \longrightarrow & \mathrm{Ni(II)X_2} + \underset{\mathrm{Ar'}}{\mathrm{ArNi(III)X}} & (88) \\
\underset{\mathrm{Ar'}}{\mathrm{ArNi(III)X}} & \longrightarrow & \mathrm{Ar\text{-}Ar'} + \mathrm{Ni(I)X}, \text{ etc.} &
\end{array}
$$

Aromatic ketones when treated with titanium(IV) chloride in acetonitrile condensed to give Ritter type condensation products [125]. Ketones were reductively coupled to vic diols by n-butyllithium using $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ to mediate the electron transfer [126]. Ketones were reductively dimerized to alkenes by treatment with bis benzenetitanium (eq. 89) α-Diketones were



(89)

converted to alkynes, benzyl alcohol was reduced to toluene, allyl alcohol to propene, and propylene oxide was deoxygenated to propene by this reagent [127]. Conjugated ketones were coupled at the carbonyl carbon to produce 1,5-dienes upon treatment with lithium aluminum hydride, $Fe_3(CO)_{12}$ and HCl consecutively (eq. 90) [128].



$$RCH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}R' \xrightarrow[\text{3) HCl}]{\text{1) LiAlH}_4\ \ \text{2) Fe}_3\text{(CO)}_{12}} \begin{array}{c} RCH{=}CH{-}CHR' \\ | \\ RCH{=}CH{-}CHR' \end{array}$$

(90)

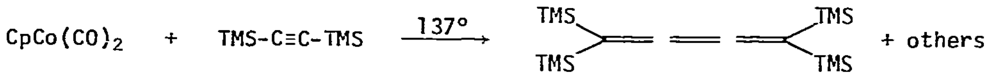
47-76%

all possible isomers

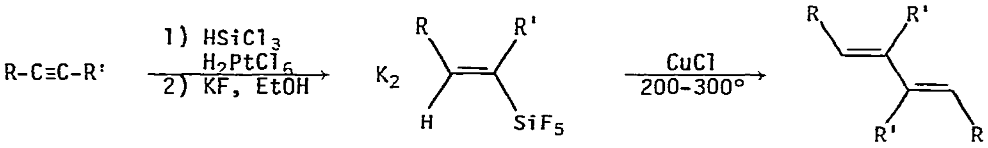
R = Ph, p-tolyl, p-anisyl, p-ClPh, 2-thiophene

R' = Ph, p-tolyl, styryl

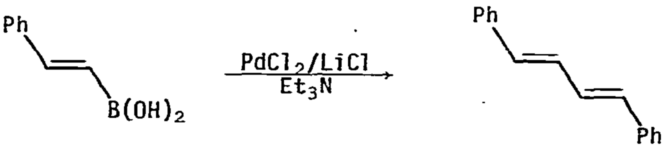
Bis-trimethylsilylacetylene was coupled to a cumulene by reaction with $CpCo(CO)_2$ (eq. 91) [129]. Acetylenes were coupled to 1,3-dienes by conversion to pentafluorosilicate, followed by treatment with solid copper(I) chloride at 200-300° (eq. 92) [130]. Vinyl boranes were converted to 1,3-dienes by treatment with palladium chloride in triethylamine (eq. 93) [131].



(91)



(92)



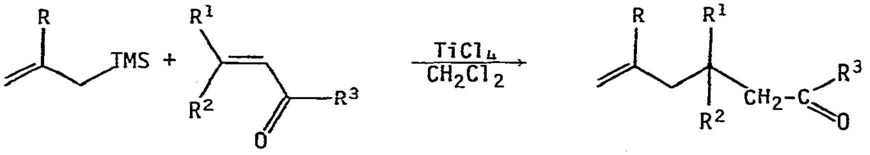
(93)

94%

Methylacrylate was dimerized by self-coupling at the β-position by treatment with palladium(II) phosphine complexes and silver tetrafluoroborate (eq. 94)[132].

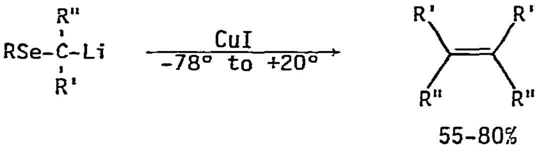
$$2\ CH_2{=}CHCOOMe \xrightarrow[3\ AgBF_4]{L_2PdCl_2} MeO_2CCH_2CH{=}CHCH_2COOMe \qquad (94)$$

Allyltrimethylsilanes coupled to conjugated ketones in a Michael sense upon treatment with titanium tetrachloride (eq. 95) [133]. α-Lithioselenides coupled



(95)

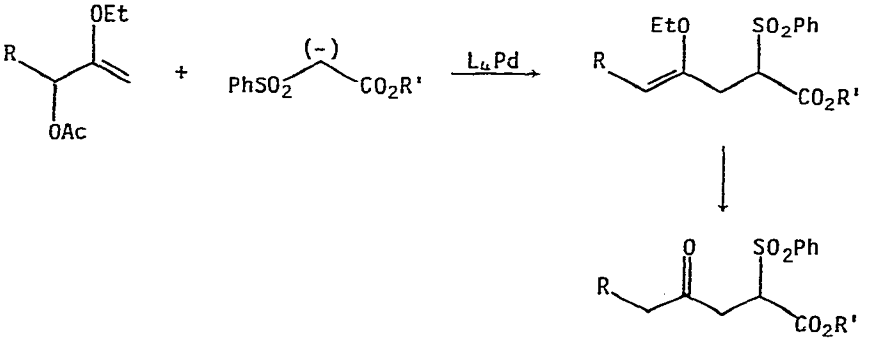
to give olefins upon treatment with copper(I) iodide (eq. 96). Cross coupling of two different selenides led to all possible products [134]. Addition and coupling reactions of organometallic compounds in the presence of transition metal catalysts has been reviewed [135].



(96)

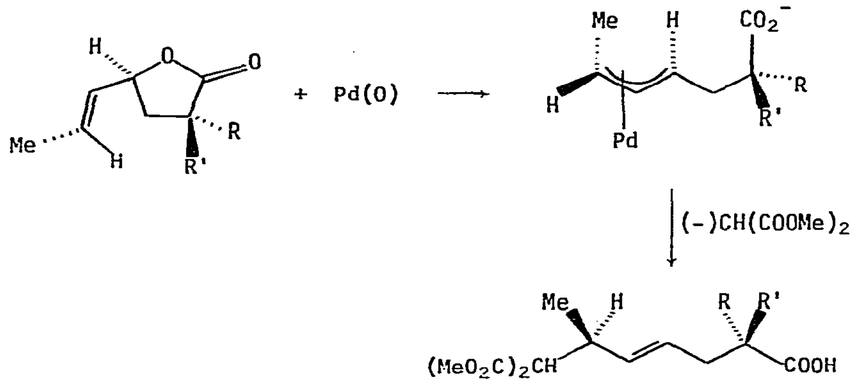
9. π-Allylpalladium Alkylations

Alkylation of π-allylpalladium halide complexes by stabilized carbanions continues to grow in importance in organic synthesis. Enol ether-acetates were used as substrates in the palladium(0) catalyzed alkylation of allylic acetates by stabilized carbanions to give highly functionalized products (eq. 97) [136].



(97)

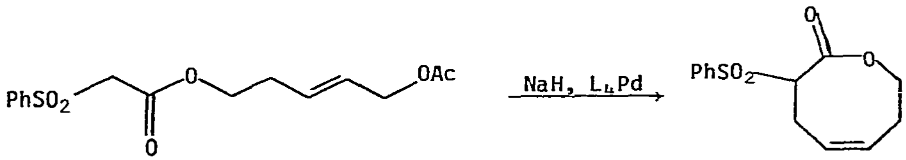
Allylic lactones having defined stereochemistry α to the carbonyl group were used to control the stereochemistry of the palladium(0) catalyzed allylic alkylations of these lactones (eq. 98) [137]. In the intramolecular allylic alkylation of allyl acetates by palladium(0) catalysts to form macrocyclic lactones, formation of the larger of the two possible rings was always observed. Thus eight-membered rings predominated over six, nine over seven, and ten over eight (eqs. 99-101) [138]. 2-Acetoxy-3-allyltrimethylsilane reacted with



90% yield

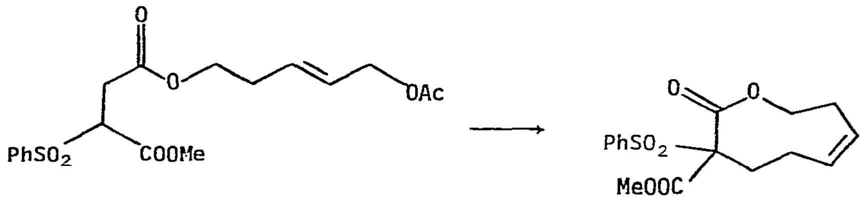
>98% regiospecific

(98)

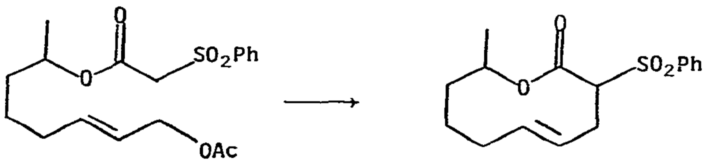


94%

(99)

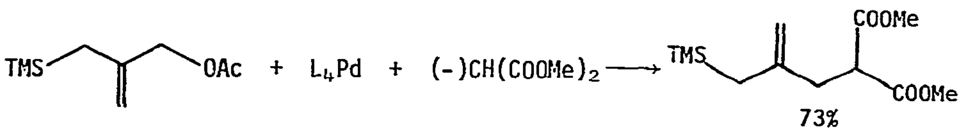


(100)



(101)

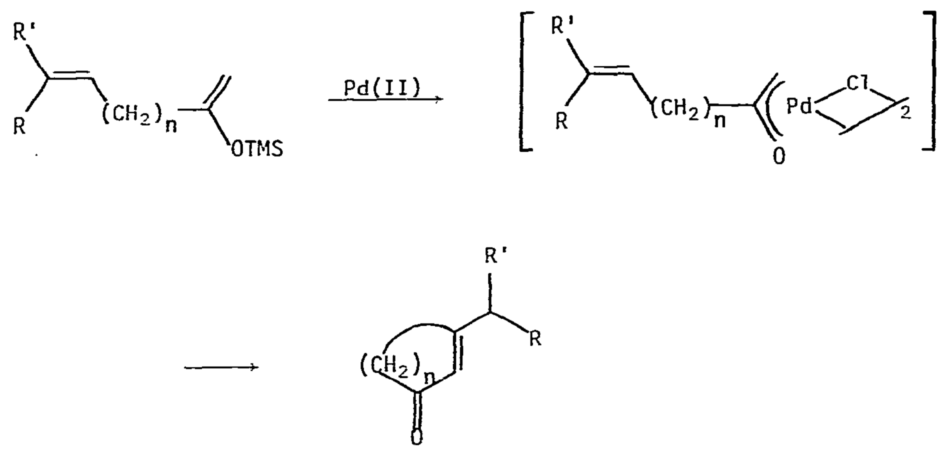
carbanions in the presence of palladium(0) catalysts to alkylate in high yield (eq. 102) [139].



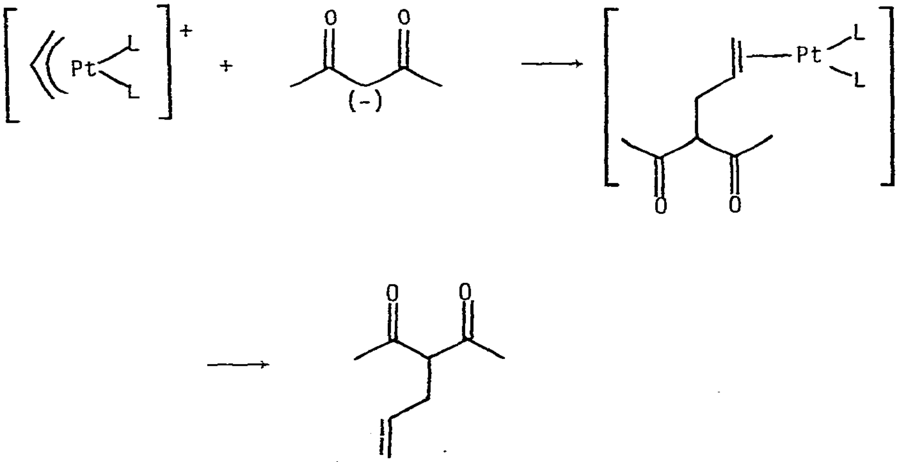
73%

(102)

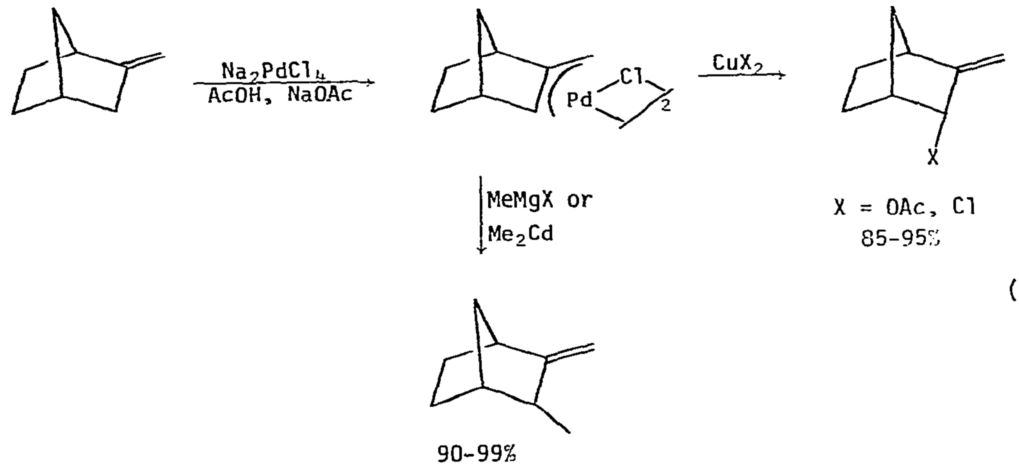
Trimethylsilylenol ethers with remote "olefinic groups" were cyclized to cyclopentenones or cyclohexenones by treatment with palladium(II) salts. The reaction was claimed to proceed via an oxallylpalladium complex which then inserted the remote olefin (eq. 103)[140]. Cationic phosphine-π-allylplatinum complexes reacted with acetylacetone anion to produce allyl acetylacetone in high yield. Platinum(0) complexes catalyzed the same reaction of allyl acetates with acetylacetone anions. An alkylated olefin-platinum complex was detected as an intermediate in these reactions (eq. 104) [141]. A bridged bicyclic π-allylpalladium chloride complex was halogenated by copper(II) halides and alkylated by methylmagnesium iodide or dimethylcadmium (eq. 105) [142]. Methylenecyclopropane reacted with cyclohexenones in the presence of palladium(0) catalysts to produce 2-allylcyclohexenones (eq. 106) [143].



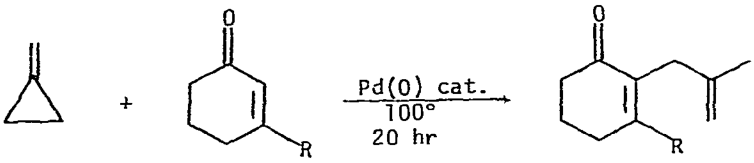
(103)



(104)



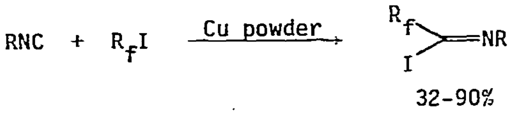
(105)



(106)

10. Alkylation of Ketones and Aldehydes.

Aldehydes reacted with lithium dialkylcuprates in the presence of chiral 1,4-bis(dimethylamino)-2,3-dimethoxybutane to give tertiary alcohols in up to 15% optical yield [144]. Aldol condensations were catalyzed using cobalt(III) salts complexed to vinylpyridine-styrene-divinylbenzene copolymers. It was claimed that this system suppressed self condensation. However, only aromatic aldehydes and ketones worked [145]. Copper(I) salts of enamines reacted with 2-allyloxybenzimidazoles to produce allylated ketones in good yield. Primary allylethers reacted at the α-carbon with retention of configuration while secondary ethers reacted primarily at the γ-carbon [146]. Isonitriles reacted with perfluoroalkyliodides in the presence of copper powder to give perfluoroiodoimines (eq. 107) [147].

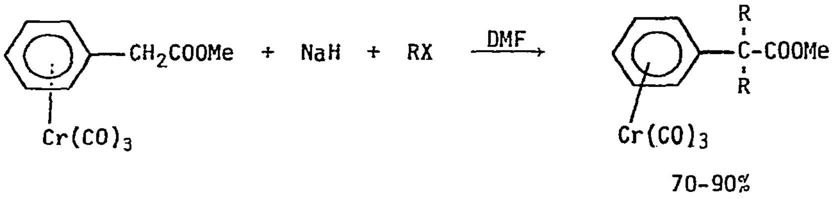


$$RNC + R_fI \xrightarrow{\text{Cu powder}} R_f(I)C{=}NR \quad (107)$$

32-90%

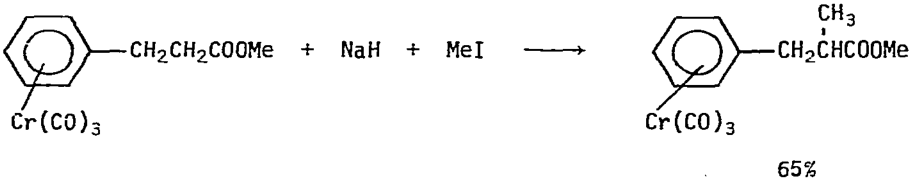
R = nBu, t-Bu, cyclohexyl, Bz

The η^6-chromium carbonyl complex of methyl phenylacetate underwent clean dialkylation at the α position when treated with sodium hydride and alkyl halides (eq. 108). Replacement of one carbonyl group by triphenylphosphite resulted in monoalkylation. Methyl 3-phenylpropanoate complexed to chromium tricarbonyl

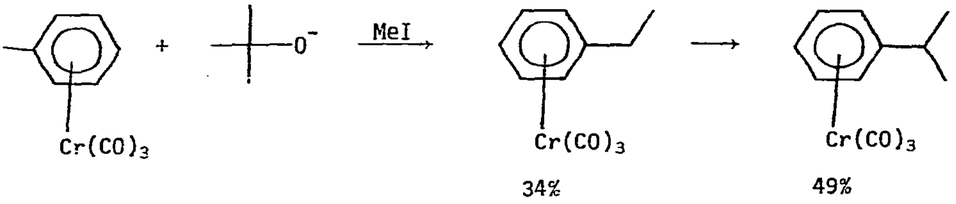


(108)

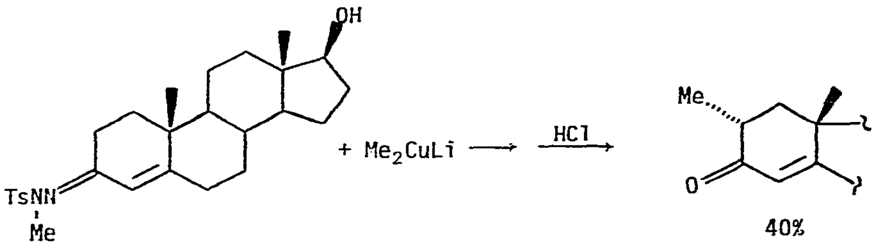
alkylated α to the ester (eq. 109), and complexed toluene was converted to ethyl benzene or isopropyl benzene (eq. 110) [148]. The methyltosylhydrazone of androstenone reacted with lithium dimethylcuprate to give methylandrostenone (eq. 111) [149].



(109)



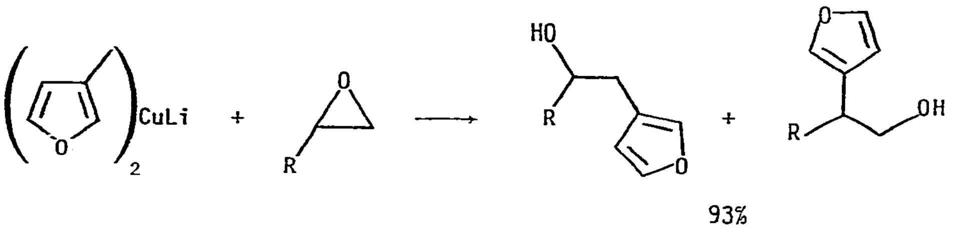
(110)



(111)

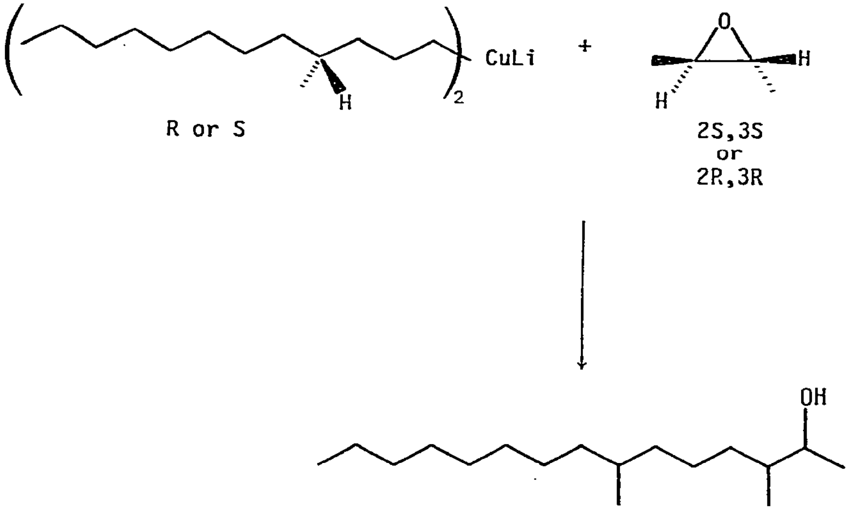
11. Alkylation of Epoxides

Lithium bis(2-furanoyl)cuprate reacted with epoxides to give alkylation products in excellent yield (eq. 112) [150]. Grignard reagents reacted with cyclohexene oxide in the presence of copper(I) catalyst to give primarily trans ring opening of the epoxide. Four-membered cyclic ethers also reacted to give

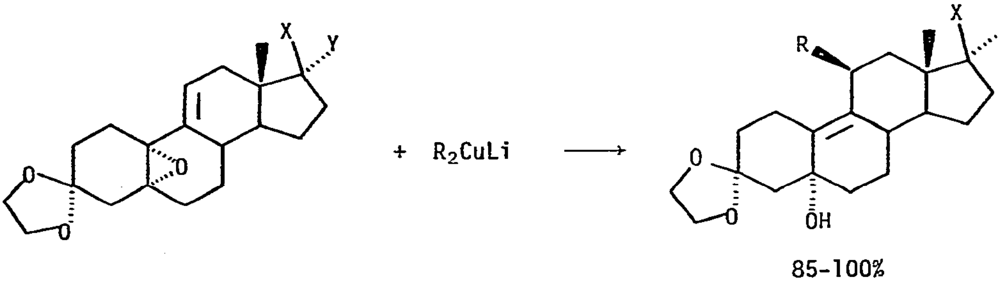


(112)

primary alcohols. When allylic Grignard reagents were used, no allylic transposition was observed [151]. All four stereoisomers of the sex pheremone of the pine saw fly were synthesized using chiral aliphatic lithium dialkylcuprates and chiral epoxides (eq. 113) [152]. α,β-Unsaturated steroidal epoxides reacted with lithium dialkylcuprates with allylic transposition to produce 11-β-substituted-19-norsteroids (eq. 114) [153].

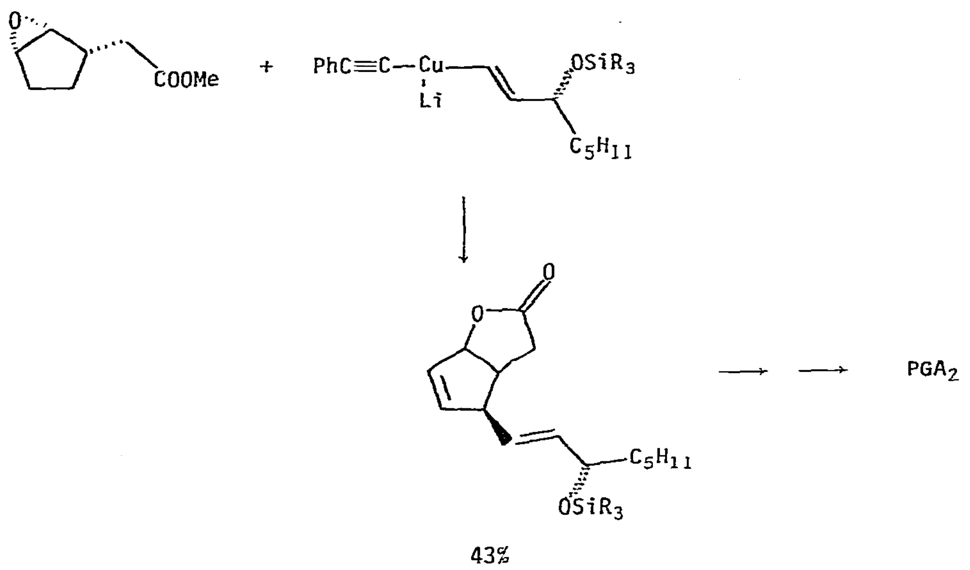


(113)

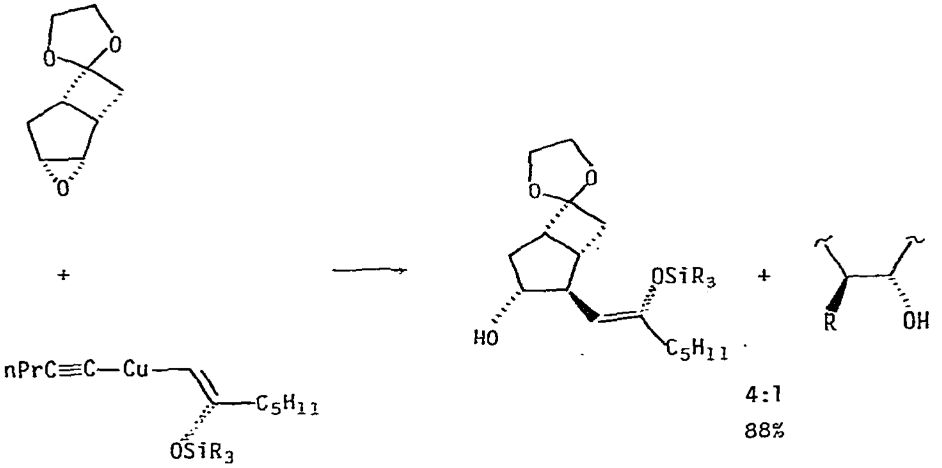


(114)

The ring opening of epoxides by vinylcuprates was used in two synthetic approaches to prostaglandins (eq. 115) [154], (eq. 116) [155].



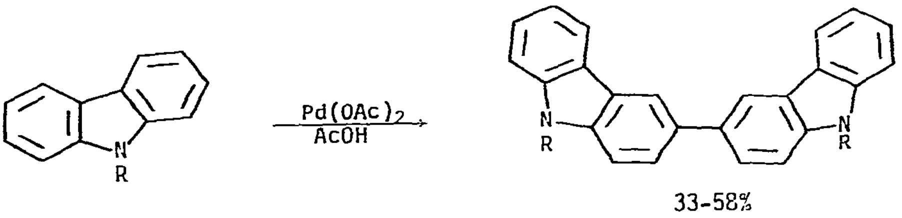
(115)



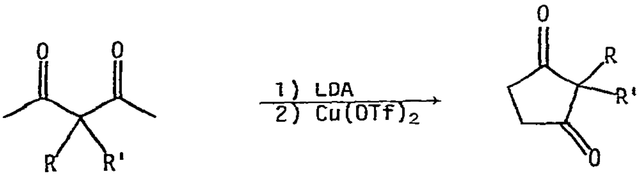
(116)

12. Oxidative Coupling.

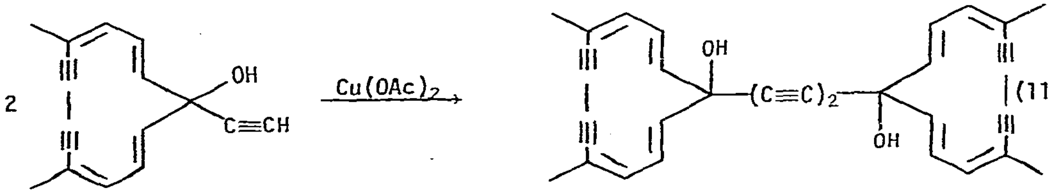
Oxidative coupling of aromatic systems under the influence of transition metal compounds has recently been reviewed [156]. Soluble polymer bound complexes of copper(II) chloride catalyzed the oxidative coupling of 2,6-dimethylphenol and the coupling of 2,6-diphenylphenol [157]. The products of the oxidation of copper(I) chloride by oxygen in polar aprotic media were useful catalysts for the oxidative coupling of phenols [158]. Carbazole was oxidatively dimerized by treatment with palladium(II) acetate in acetic acid (eq. 117) [159]. Copper(II) trifluoromethane sulfonate was used to oxidatively couple 3,3-disubstituted-2,4-pentanediones intramolecularly to form 1,3-cyclopentadienones (eq. 118) [160]. Macrocyclic acetylenic alcohols were oxidatively coupled by reaction with anhydrous copper(II) acetate (eq. 119) [161].



(117)



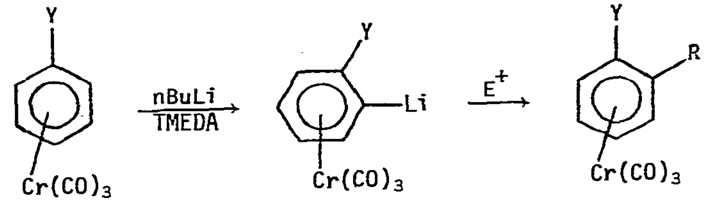
(118)



(119)

13. Nucleophilic Aromatic Substitution

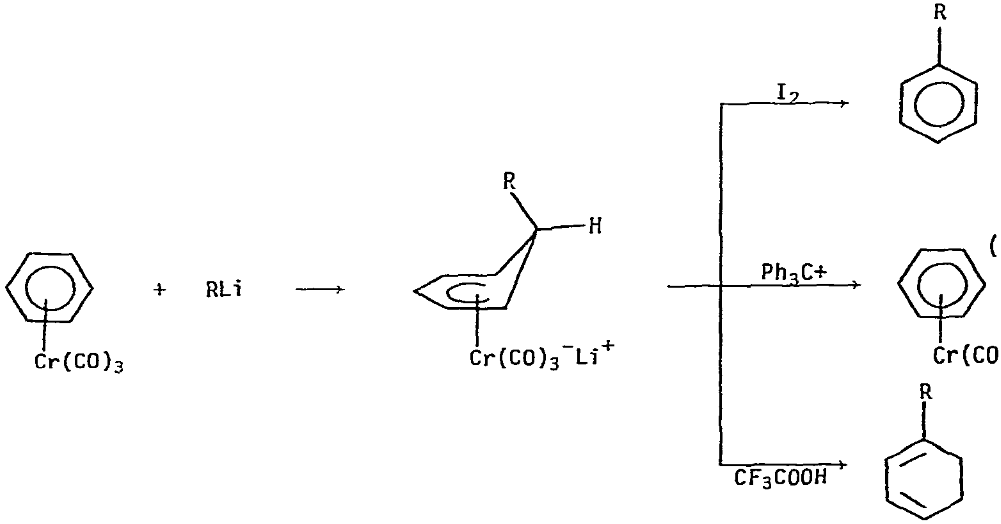
Substituent effects in the addition of nitrile and ester stabilized carbanions to arene chromium tricarbonyl complexes were studied. Methoxy groups were strongly *meta* directing, while methyl and chloro groups also led to some *ortho* substitution. Trimethylsilyl and trifluoromethyl groups were *para* directing [162]. The arene ring in arenechromium tricarbonyl complexes was lithiated by treatment with n-butyllithium-TMEDA, and then reacted with a number of electrophiles (eq. 120) [163]. The full experimental details of the reaction of arenechromium tricarbonyl complexes with carbanions have been published. The initial product of alkylation was a η^5-cyclohexadienyltricarbonylchromium(0) complex, which was characterized by X-ray diffraction analysis. Oxidizing agents free the alkylated arene ligand, electrophiles regenerate the arene complex; and trifluoroacetic acid produces substituted cyclohexadienes (eq. 121) [164]. Nucleophilic addition of nitrile-stabilized carbanions to anisole chromium tricarbonyl complexes followed by acid cleavage produced



(120)

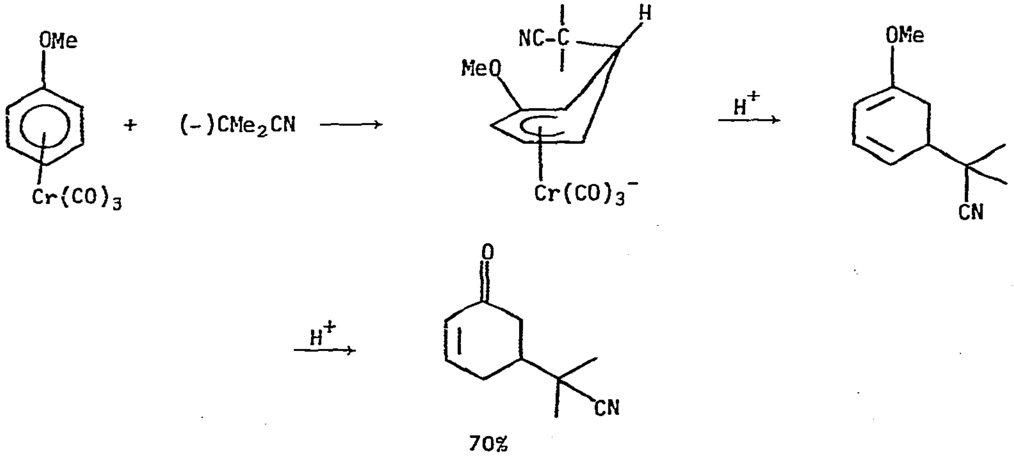
$Y = H, OMe, F, Cl$

$E^+ = CO_2, CH_3COCH_3, PhCHO, I_2, TMSCl$



(121)

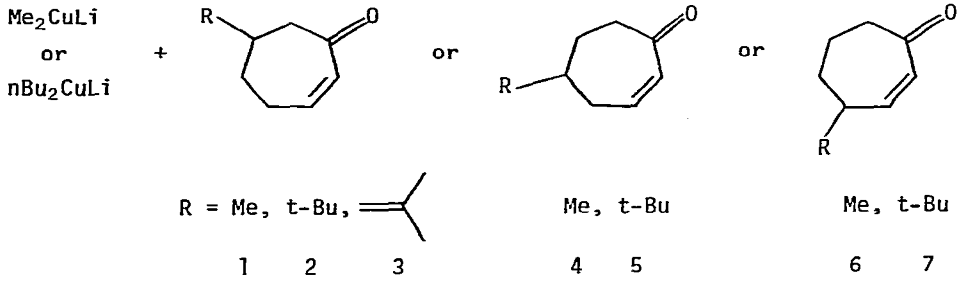
3-substituted cyclohexenones (eq. 122) [165]. Finally, arene exchange reactions of arene chromium tricarbonyl complexes with free arenes established the following order of stability: $C_6Me_6 > C_6H_2Me_4 > C_6H_3Me_3 > PhNMe_2 >> C_6H_4Me_2 > PhMe \sim C_6H_6 > PhCOMe \sim PhOMe > BzOMe > PhCl \sim PhF > C_{10}H_8$ [166].



(122)

B. Conjugate Addition

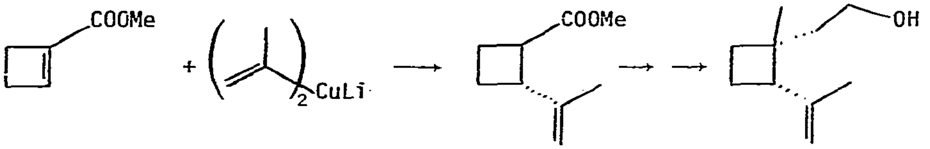
Organocopper complexes continued to be the reagents of choice for a wide variety of conjugate (1,4 or 1,6) additions to unsaturated systems. The stereochemistry of conjugate addition of lithium dimethyl and dibutylcuprate to 4-, 5-, and 6-substituted cycloheptenones was studied. The stereoselectivity depended upon both the structure of the enone and the cuprate (eq. 123) [167].



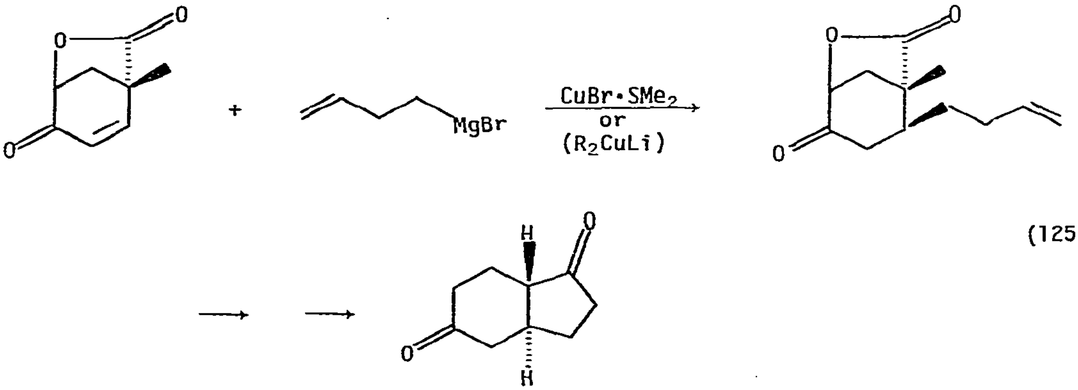
(123)

With 2, 4 and 7	20:80 cis to trans
With 1 and 5	82:18 cis to trans
With 6	2:98 cis to trans

Procedures for the 1,4 addition of lithium dimethyl-, diethyl-, dibutyl- and diphenylcuprate to citral have been published [168]. The conjugate addition of organocuprates to cyclobutenyl esters has been used in the synthesis of (±)-grandisol (eq. 124) [169]. The stereochemistry of conjugate addition of homoallylic cuprates to conjugated cyclohexenones was controlled by imposing a rigid bicyclic structure (via a fused lactone) upon the enone (eq. 125) [170].

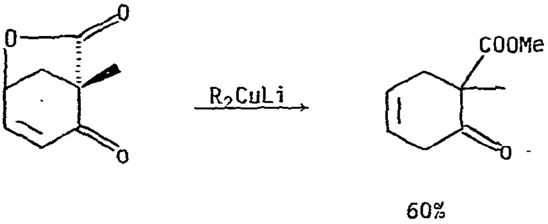


(124)

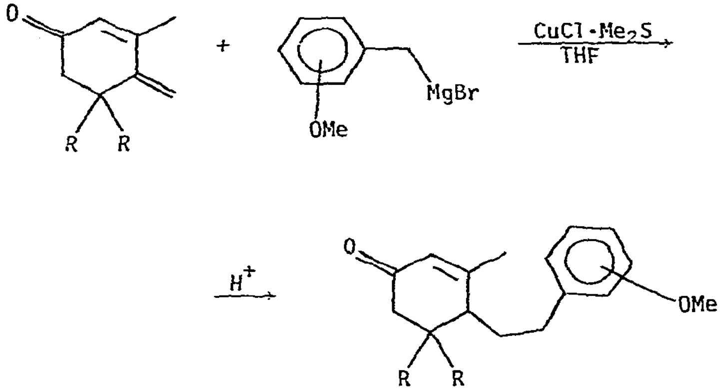


(125)

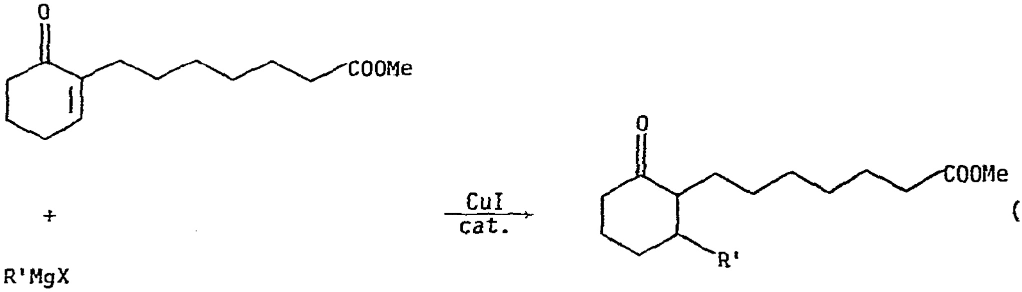
The structure of the fused lactone had a profound effect on the conjugate addition reaction (eq. 126) [171]. The copper-catalyzed reaction of a benzylmagnesium halide with an α,β,γ,δ-unsaturated enone resulted in exclusive 1,6-addition (eq. 127) [172]. Copper catalyzed Grignard reactions were used in the synthesis of a number of 11a homoprostaglandins (eq. 128) [173].



(126)



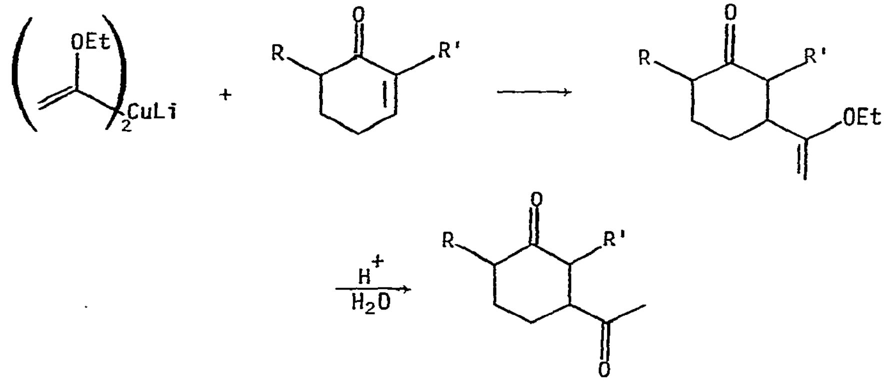
(127)



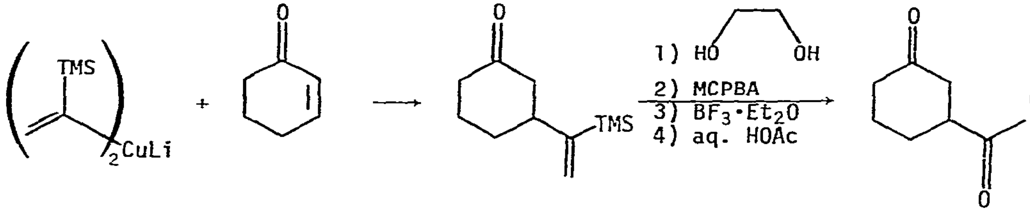
(128)

R' = prostaglandin side chain

Functionalized organocuprates also react with conjugated enones. Methods for the conjugate addition of enolate and acyl anion equivalents to conjugated enones have recently been developed. These involve the use of cuprates made from lithio salts of enol ethers or vinyl silanes (eqs. 129, 130) [174]. The

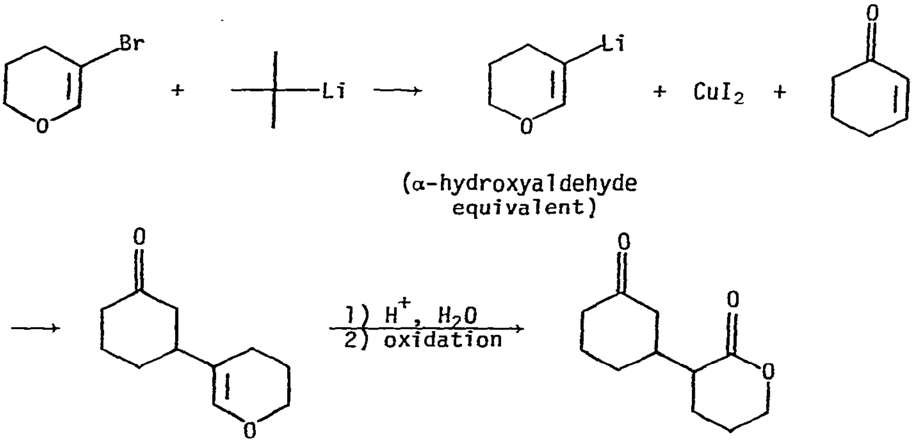


(129)

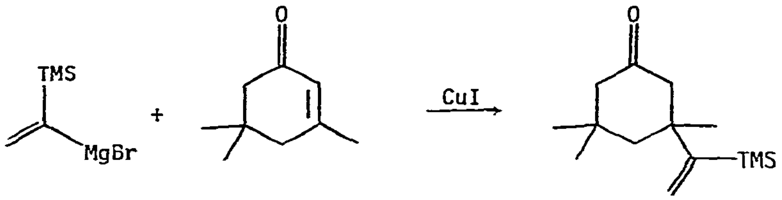


(130)

3-lithio salt of 2,3-dihydropyran reacted in a conjugate fashion with α,β-unsaturated ketones in the presence of copper(II) iodide. Hydrolysis followed by oxidation resulted in the formation of lactones (eq. 131) [175]. 3-(Dimethylamino)-1-propyne was used as the non-transferrable group in mixed cuprates for conjugate addition reactions [176]. Grignard reagents of vinyl silanes added 1,4 to conjugated ketones in the presence of copper(I) iodide (eq. 132). These same reagents were alkylated by treatment with organic halides and copper(I) iodide [177].

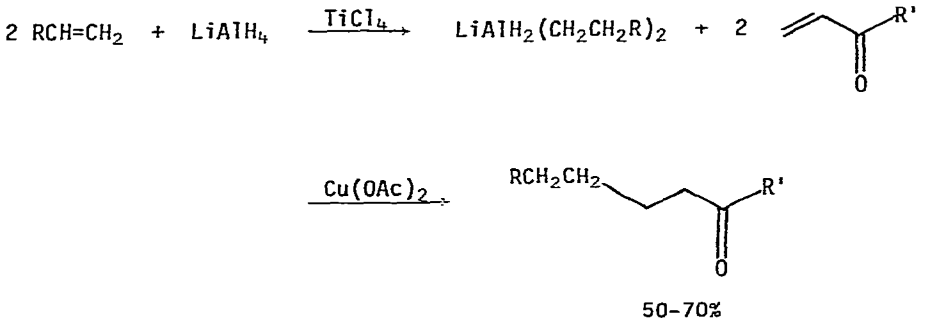


(131)



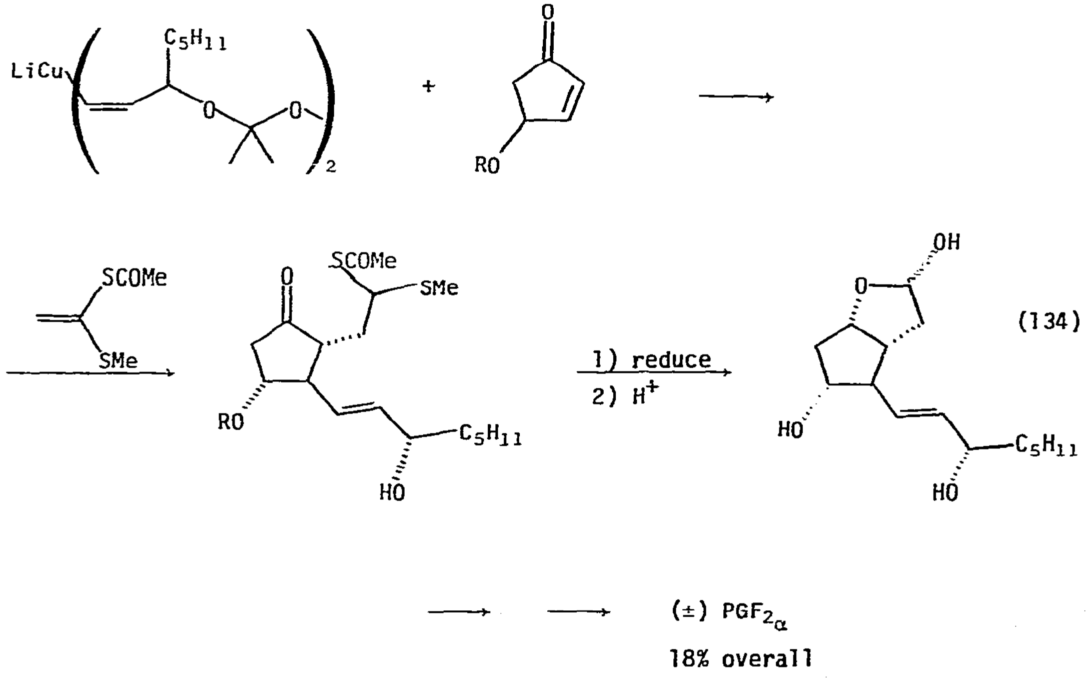
(132)

Organoaluminates, prepared from olefins and lithium aluminum hydride in the presence of titanium tetrachloride, added 1,4 to acrolein and methyl vinyl ketone in the presence of stoichiometric amounts of copper(II) acetate (eq. 133) [178].



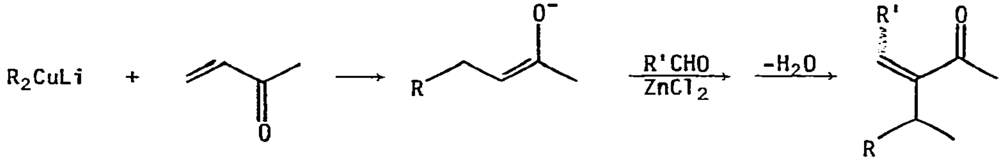
(133)

The conjugate addition of organocuprates to conjugated enones followed by trapping of the resulting enolate has been used to synthesize a number of prostaglandins (eq. 134) [179]. The enolate resulting from conjugate addition of



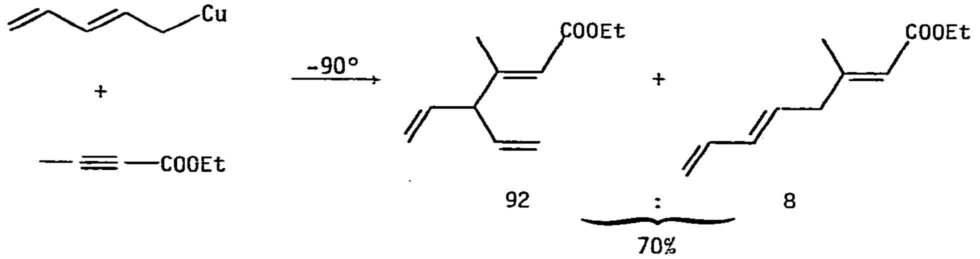
(134)

organocuprates to α,β-unsaturated ketones reacted with aldehydes via an aldol condensation in the presence of zinc(II) chloride (eq. 135) [180].

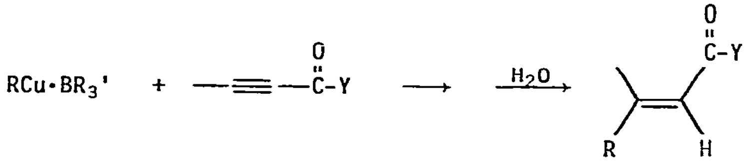


(135)

α-Acetylenic esters reacted with allylic copper (not cuprate) complexes at -90°C to give mixtures of triene esters (eq. 136) [181], by an overall <u>cis</u> addition. These same substrates reacted with $RCu{\cdot}BR_3'$ complexes with very high regio- and stereoselectivity at low temperatures (eq. 137) [182].



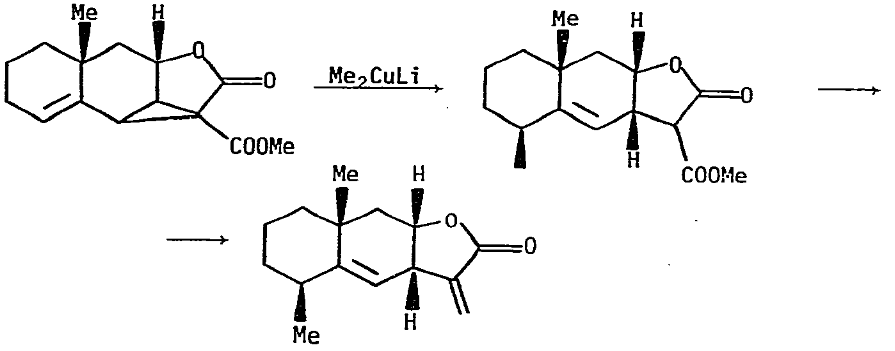
(136)



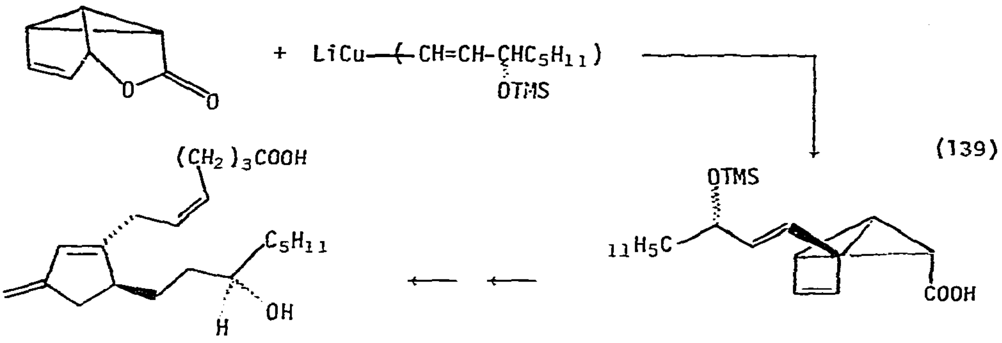
(137)

R = Me, Bu
Y = OR, OH

α-Cyclopropyl ketones and esters also react with organcuprates in a 1,4 sense. This reaction was used in the synthesis of d,l-7,8-epialantolactone (eq. 138) [183]; and a prostaglandin (eq. 139) [184]. A stereospecifically



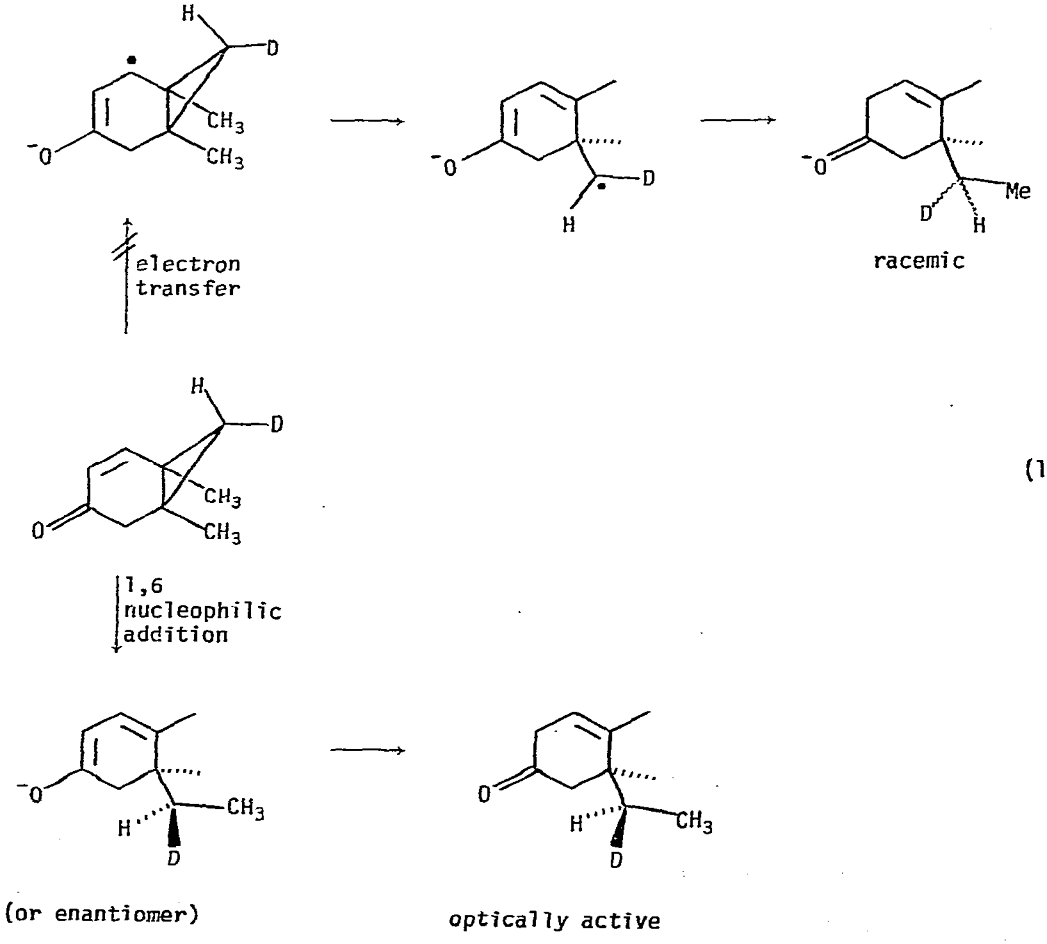
(138)



(139)

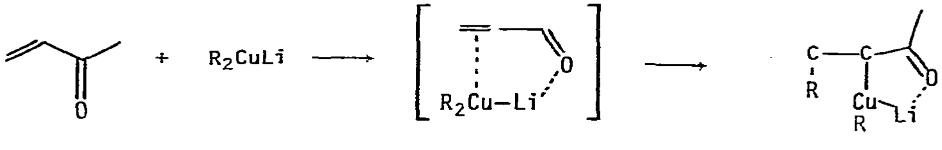
9-deoxa-9,10-dehydroprostaglandin-D_2

deuterated β,γ-cyclopropylcyclohex-2-enone reacted with lithium dimethylcuprate without loss of stereochemistry at the chiral cyclopropyl carbon. This result was used to argue against the intermediacy of radicals via electron transfer in conjugate additions of organocuprates to conjugated enones (eq. 140) [185].

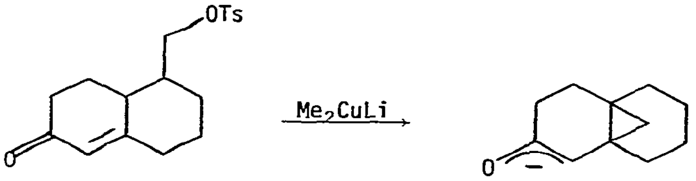


(140)

In another study of this mechanism, it was claimed that formation of a transient copper substrate complex followed by 1,2-addition to the double bond was the main reaction path (eq. 141) [186]. On the other hand evidence for an electron transfer process has also been claimed (eq. 142) [187]. Thus the controversy over the mechanism of conjugate addition of organocuprates to conjugated enones continues.

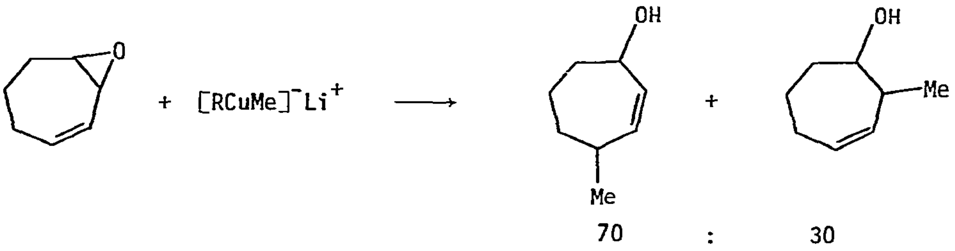


(141)

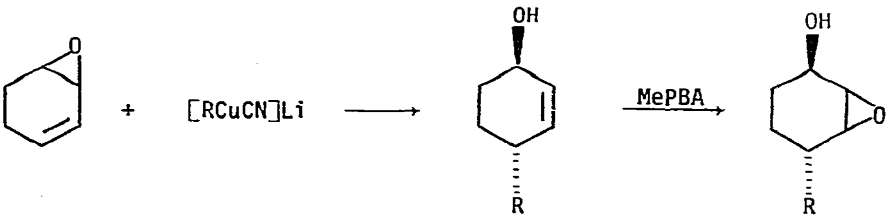


(142)

1,3-Cycloheptadiene monoepoxide reacted with lithium dialkylcuprates to give mixtures of S_N2 and S_N2' epoxide ring opened products (eq. 143) [188], but 1,3-cyclohexadiene monoepoxide reacted both regio- and stereospecifically (eq. 144) [189].



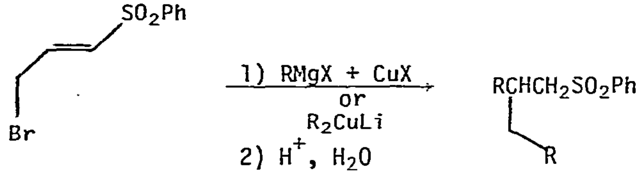
(143)



(144)

R = Me, Ph

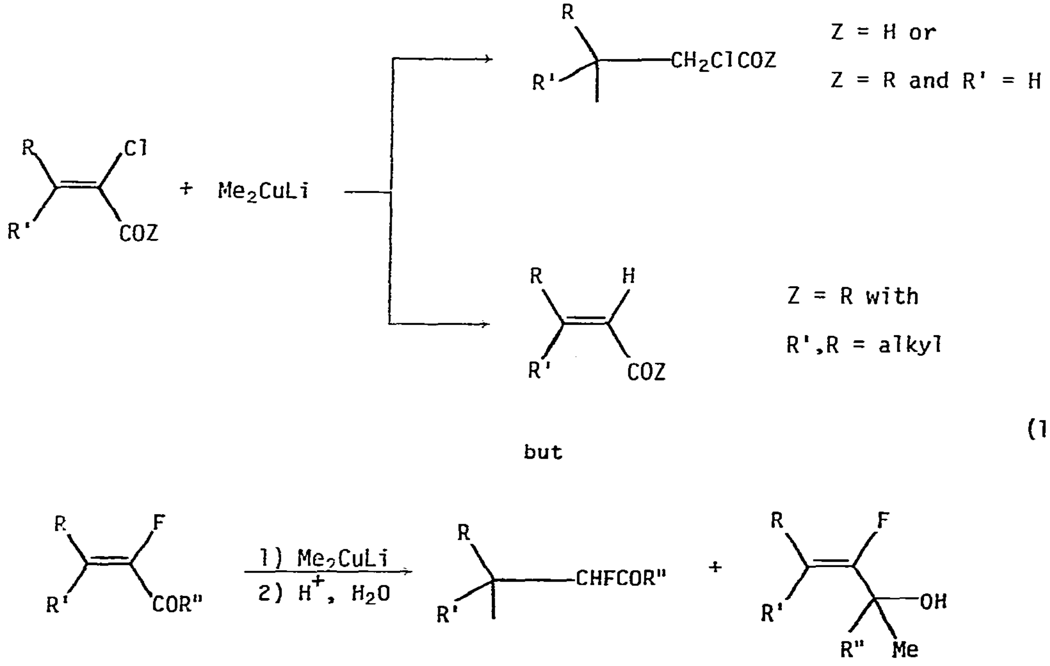
α-Bromovinylsulfones underwent a double alkylation when treated with lithium dialkylcuprates or Grignard reagents with copper catalysts (eq. 145) [190].



(145)

R = Me, Et

α-Chloro conjugated enones reacted with lithium dimethylcuprate to give 1,4-addition or reduction products, depending on the substituents on the double bond. In contrast, α-fluoro conjugated enones underwent competitive 1,4 and 1,2 addition, with the ratio of products depending on the steric hindrance at the β-position (eq. 146) [191].



Z = H or

Z = R and R' = H

Z = R with

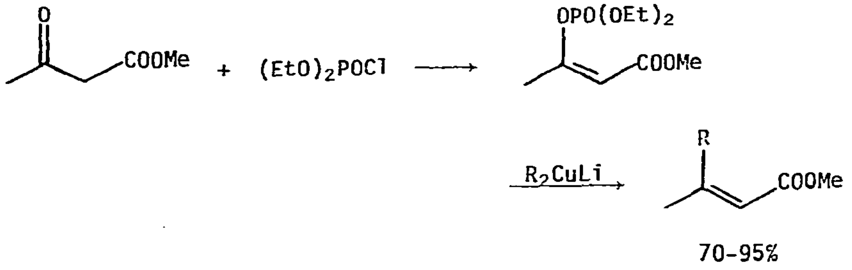
R',R = alkyl

(146)

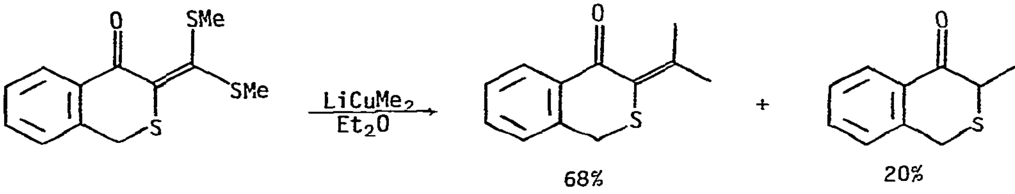
but

β-Ketoesters were converted to α,β-unsaturated esters in good yield by conversion to the enol phosphate followed by reaction with primary lithium dialkylcuprates (eq. 147) [192]. The dithioacetal of β-aldehydoketones reacted with lithium dimethylcuprate to produce β,β-dimethyl conjugated enones (eq. 148) [193].

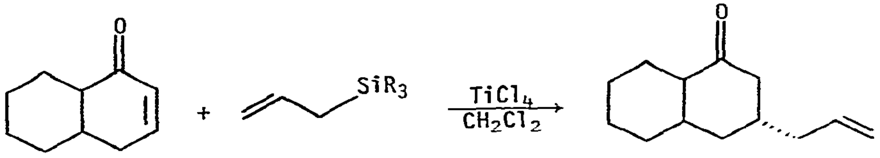
Allylsilanes added 1,4 to conjugated enones in the presence of titanium tetrachloride (eq. 149) [194]. o-Palladated aromatics inserted conjugated



(147)

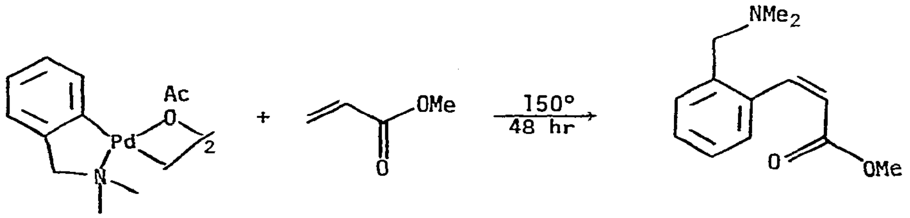


(148)

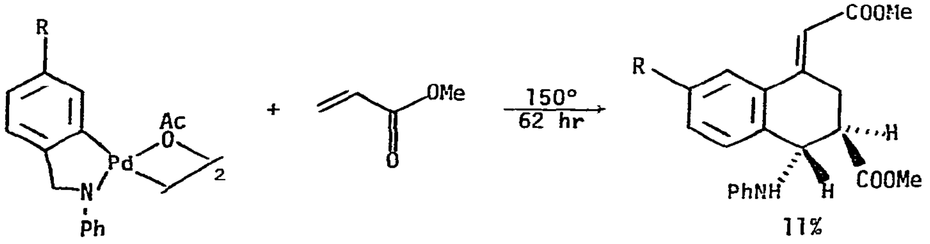


(149)

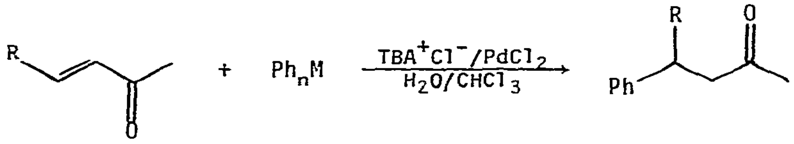
esters upon heating to 150° for prolonged periods (eqs. 150 and 151) [195]. Phenyl mercuric chloride and tetraphenyltin alkylated α,β-unsaturated ketones at the β-position when treated with palladium(II) chloride under phase transfer conditions (eq. 152) [196]. 1,4-Naphthoquinone was arylated in the presence of palladium(II) chloride [197].



(150)



(151)

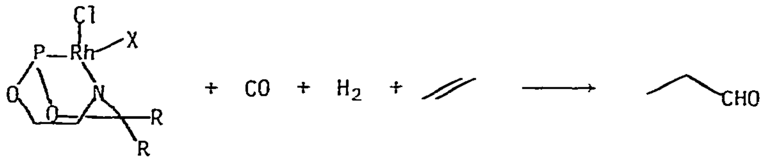


(152)

C. Carbonylation

1. Hydroformylation

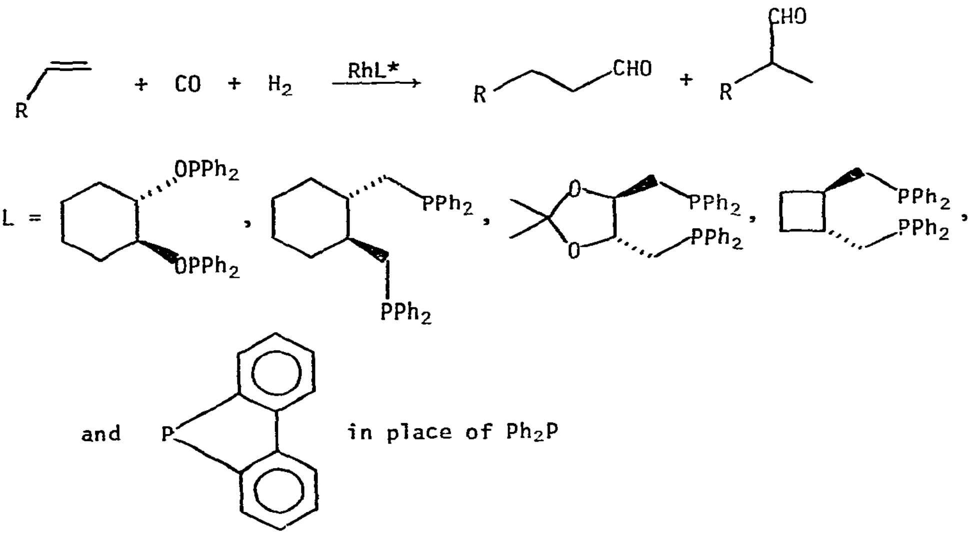
Hydroformylation has been reviewed [198]. The relation between effects of carbon monoxide pressure and phosphine concentration on rhodium catalyzed hydroformylation of 1-hexene was examined. A narrow range of carbon monoxide pressures and phosphine concentrations that favored linear aldehyde formation was found [199]. The kinetics of hydroformylation of cyclododecene in the presence of hydrocarbonyltris(triphenylphosphine)rhodium(I) showed the reaction to be first order in hydrogen partial pressure regardless of phosphine concentration, and zero order in carbon monoxide partial pressure with excess phosphine, but without excess phosphine the rate increased with increasing carbon monoxide partial pressure [200,201]. Side reactions in the hydroformylation of 1-propene with rhodium carbonyl complex catalysts and triphenylphosphine were studied [202]. Homogeneous hydroformylation of 1-hexene using $[Rh(cod)_2]^+PF_6^-$, $[Rh(cod)(PPh_3)py]^+PF_6^-$, and $[Rh(cod)(PPh_3)_2]^+PF_6^-$ as catalysts was studied [203]. In the hydroformylation of 1-hexene using $RhHCO(PPh_3)_3$ as catalyst, the yield of linear aldehyde was increased by increasing the amount of added triphenylphosphine, by carrying out the reaction at 90°, and by lowering the partial pressure of carbon monoxide [204]. The hydroformylation of higher olefins in the presence of cobalt carbonyl catalysts showed the same effects as those for lower olefins [205]. The use of dibenzophospholes as ligands in rhodium and cobalt-catalyzed hydroformylations caused a considerable rate enhancement over that observed with diphenylphosphines as ligands [206]. Alkyl-rhodium tetracarbonyl complexes were detected by infrared in the hydroformylation of ethane using a variety of rhodium(I) complexes as catalyst precursors [207]. Treatment of olefins with hydrogen and carbon monoxide in benzil in the presence of rhodium catalysts produced α-benzoylbenzyl carboxylates [208]. Rhodium(I) complexes of a cyclic mixed phosphorus-nitrogen ligand catalyzed the hydroformylation of olefins (eq. 153) [209]. Dicobalt octacarbonyl hydroformylated propene in high



(153)

yield when treated with carbon monoxide and water at 135°. The requisite hydrogen came from a cobalt catalyzed water gas shift reaction [210]. By using $PtCl_2$-$SnCl_2$-$Ph_2P(CH_2)_4PPh_2$ as a catalyst very high reaction rates and 99:1 linear to branch aldehyde were obtained in the hydroformylation of 1-pentene. Both the rate and the linear/branched ratio depended on the length of the chelating diphosphine chain [211].

Attempts to induce asymmetry in hydroformylation reactions by using chiral catalysts have met with only modest success. Vinylacetate was converted to (S)-α-acetoxypropionaldehyde in 10-24% optical yield by hydroformylation in the presence of a rhodium(I) catalyst produced by reaction of $[(CO)_2RhCl]_2$ with two equivalents of (-)-DIOP [212]. A number of chiral phosphines were used as ligands for rhodium catalyzed hydroformylation of styrene, 1-butene, cis-2-butene and α-methylstyrene (eq. 154). Up to 40% optical purity was obtained [213].



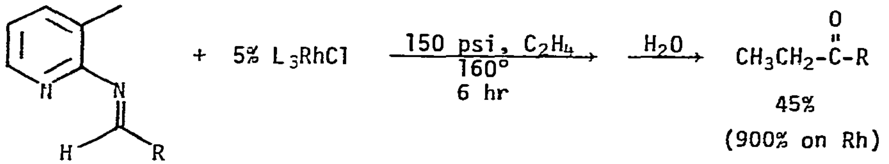
(154)

Use of a chiral β-ketoenolate as a ligand for rhodium(I) catalyzed hydroformylation led to no optical induction and no change in linear to branched products. This was taken as evidence for cleavage of the ligand from rhodium prior to hydroformylation [214]. 3-Methyl-1-pentene was deuterioformylated using rhodium catalysts and the diastereomeric composition of both isomers was examined. These experiments showed that the (S)-enantiomer reacted preferentially at the si-si face while the (R)-enantiomer reacted on the re-re face [215]. Hydroformylation of cis-2-butene and norbornene in the presence of ruthenium complexes of (-)-DIOP gave low optical yields of (R) product [216].

Solid-supported complexes have also been used in hydroformylation reactions. The copolymer of styrene, divinylbenzene, and 2-(p-styryl)-4,5-bis[(tosyloxy)-methyl]-1,3-dioxolane was prepared, and the tosyl groups were displaced by $NaPPh_2$ or Na-dibenzophosphole to give a polymer bound optically active DIOP type ligand. Rhodium(I) was introduced by exchange, and the complex was characterized by ^{31}P nmr, T_1, and electron induced X-ray emission, which showed an even distribution of rhodium throughout the polymer particle. Use of this material as a hydroformylation catalyst gave low (3-30%) enantiomeric excesses. The corresponding homogeneous catalyst gave a branched to normal ratio of 2, while polymer bound Ph_2P catalyst gave 6, and polymer-bound phosphole gave 20. The catalyst was recovered in active form by merely filtering [217]. Polymer supported $(C_5H_5)Co(CO)_2$ and $(C_5H_5)Rh(CO)_2$ catalyzed the hydroformylation of 1-pentene to hexanal at 130°[218]. The normal 9:1 selectivity for normal to branched aldehyde formation in hydroformylation of olefins by $(Ph_3P)_2PtCl_2$-$SnCl_2$ catalysts was increased to 150:1 by anchoring the catalyst to a polymer support. This catalyst has a short lifetime however [219]. Rhodium, cobalt, and rhodium-cobalt bimetallic clusters were dispersed on zinc oxide and pyrolyzed to produce crystallites. The resulting materials were used as hydroformylation catalysts [220]. Other oxides, such as MgO, TiO_2, and La_2O_3 also gave active catalysts, but basic oxides such as alumina, silica and V_2O_5 led to inactive systems [221]. Phosphinoalkylorganosilicon compounds were used as ligands in the rhodium(I) catalyzed hydroformylation of 1-hexene. The catalytic activity was similar to that of simple phosphine ligand-rhodium(I) complexes [222].

The clusters $Co_4(CO)_{12}$ and $Co_2(CO)_8$ were used as catalysts to hydroformylate 1-octene. Both appeared to react via $HCo(CO)_4$ [223]. The cobalt cluster $[(CO)_3Co]_3COR$ was an active hydroformylation catalyst [224].

The aldehyde C-H bond was activated to undergo an oxidative addition by formation of a 2-aminopyridylaldimine. This was used in a rhodium promoted hydroacylation of olefins (eq. 155) [225].

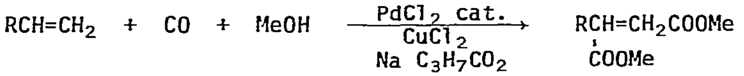


(155)

R = Ph, p-OMePh, p-ClPh

2. Carbonylation of Alkenes and Alkynes.

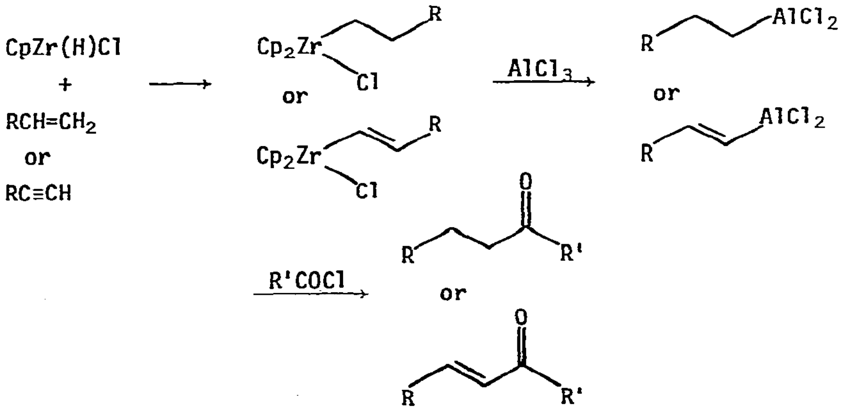
Propene was hydrocarboxylated by treatment with a number of alcohols and carbon monoxide in the presence of $PdCl_2(PPh_3)_2$ as catalyst, at 90-130° and 40 to 120 atmospheres pressures [226]. At low carbon monoxide pressure the reaction resulted almost exclusively in production of the linear ester [227]. The active catalyst in this system was claimed to be a palladium(II) acyl complex, trans-$Pd(COR)Cl(PPh_3)_2$, whose structure was determined by X-ray crystallography [228]. The mechanism of the conversion of ethylene to propanoic acid by carbon monoxide in water using a rhodium iodide as catalyst and iodine as a promoter, was shown to proceed by: (1) formation of HI; (2) addition to the rhodium catalyst to form HRh(CO)I; (3) coordination of ethylene to produce $HRh(C_2H_4)I$ followed by insertion to give EtRh(III)I; (4) reaction with CO to give EtCORhI followed by reductive elimination producing EtCOI; (5) hydrolysis to form propionic acid and HI [229]. Olefins were converted to mixtures of linear and branched acids by treatment with carbon monoxide and acetic acid. HI or HBr was used as a promoter, and the catalysts were palladium on carbon or palladium on zeolite [230]. Palladium on silica also was an effective catalyst [231]. The full details of the bis carboxylation of olefins by carbon monoxide in methanol, and palladium(II) catalysts with copper(II) chloride as reoxidant, have been published [232]. Monoenes, conjugated and nonconjugated dienes, and conjugated enones reacted in good yield (eq. 156). This work was



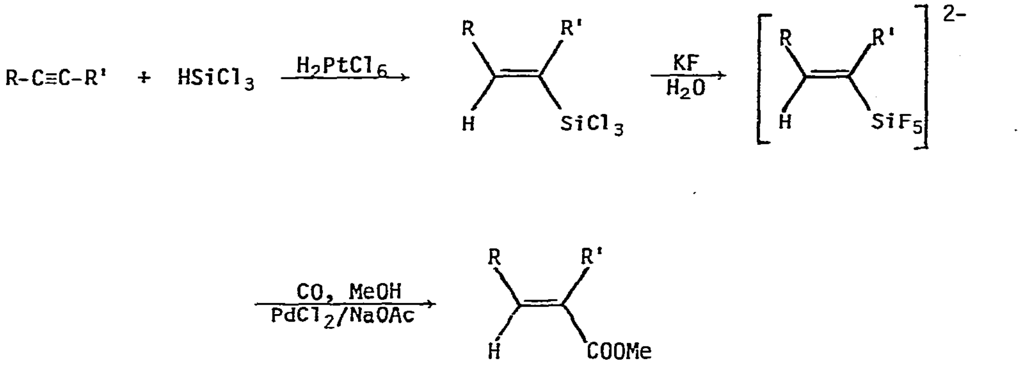
$$\mathrm{RCH{=}CH_2 \;+\; CO \;+\; MeOH \;\xrightarrow[\substack{CuCl_2\\ Na\ C_3H_7CO_2}]{PdCl_2\ cat.}\; RC\underset{\substack{|\\ COOMe}}{H}{=}CH_2COOMe} \qquad (156)$$

also the subject of a dissertation [233]. Styrene was converted to methyl cinnamate by treatment with carbon monoxide and methanol, using palladium(II) chloride as a catalyst and copper(I) chloride, sodium acetate, and magnesium chloride as coreactants. At least 100 turns on catalyst was achieved [234]. Alkenes, alkynes and dienes were acylated by treatment with $Cp_2Zr(H)Cl$, followed by aluminum trichloride, followed by an acid halide (eq. 157). This was also a facile preparation of $RAlCl_2$ species in which R was derived from an alkene or alkyne with the stereo- and regiochemistry of hydrozirconation [235].

Acetylene was carbonylated by carbon monoxide using $PdBr_2$-$(PhO)_3P$-HBr-BuOH as a catalyst system [236]. The effects of other ligands such as Cl^-, Br^-, I^-, and SCN^- on this system were also examined [237]. Alkynes were converted to α,β-unsaturated esters by platinum(IV)-catalyzed hydrosilation, followed by conversion to the pentafluorosilicate, followed by palladium(II) catalyzed carbonylation by carbon monoxide and methanol (eq. 158) [238]. The development of palladium catalysts for the cyclocarbonylation of acetylenic alcohols to α-methylene lactones was the subject of a dissertation [239].



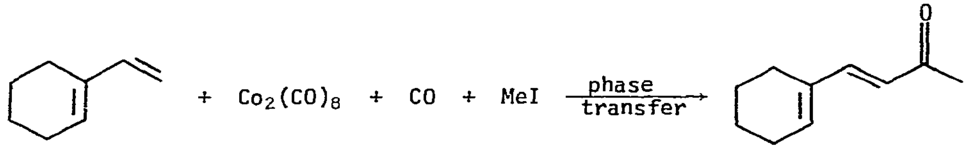
(157)



(158)

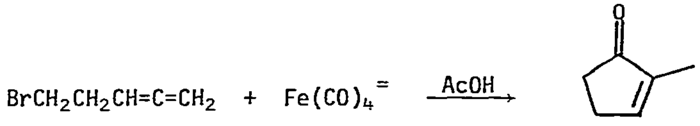
R = n-hexyl, t-Bu, Ph, $MeOCH_2$-, $MeO_2C(CH_2)_8$
R' = H, n-Bu

Conjugated dienes were converted to α,β,γ,δ-unsaturated ketones by treatment with dicobalt octacarbonyl and methyl iodide under phase transfer conditions (eq. 159) [240]. ω-Bromoolefins and allenes were converted to cyclic ketones by reaction with sodium tetracarbonylferrate (eqs. 160,161) [241].



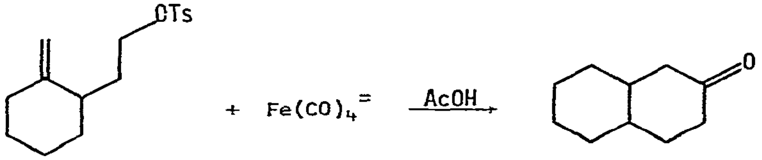
63%

(159)



30-40%

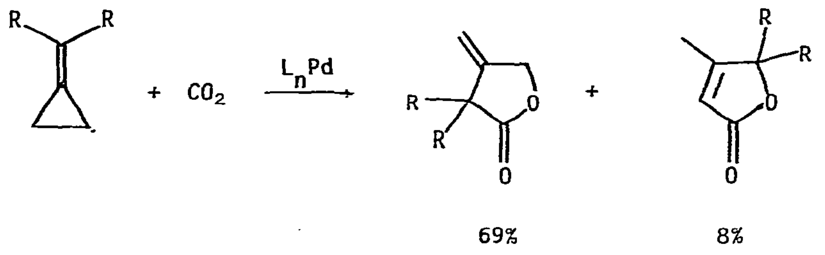
(160)



65%

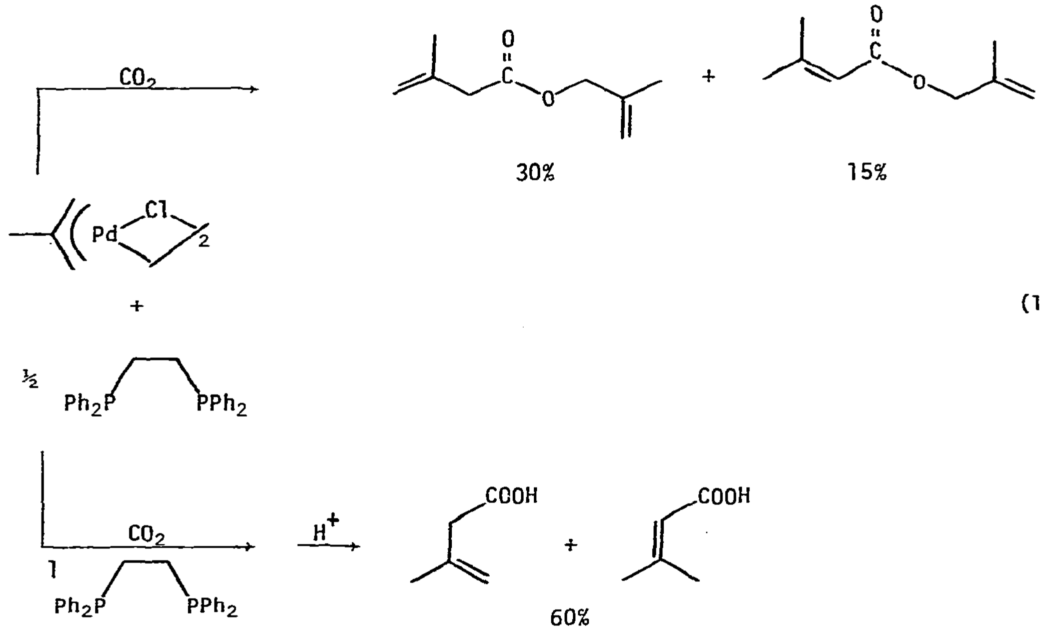
(161)

Methylenecyclopropanes were converted to butenolides and β-methylene lactones by reaction with carbon dioxide in the presence of palladium(0) catalysts (eq. 162) [242]. π-Allylpalladium chloride complexes reacted with carbon dioxide in the presence of diphos to give allyl esters or unsaturated acids (eq. 163) [243].



(162)

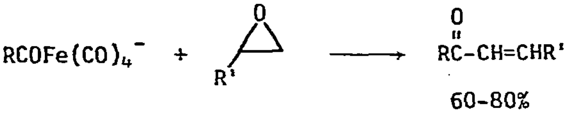
R = Me, $-(CH_2)_5-$



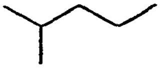
(163)

3. Carbonylation of Halides.

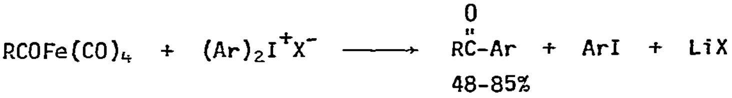
Aryl halides were converted to neopentyl esters by treatment with NaH/neopentyl ONa/Co$(OAc)_2$/CO in THF followed by hydrolysis. The reaction proceeded under one atmosphere of carbon monoxide and was catalytic with respect to cobalt [244]. Organic halides were converted to symmetrical ketones by reaction with iron pentacarbonyl and sodium hydroxide under phase transfer conditions. Unsymmetrical ketones were produced in low to moderate yield by initial reaction of an organic bromide to produce an alkyl-tetracarbonyl ferrate, followed by reaction with an organic iodide [245]. Acid anhydrides were converted to ketones by the reagent produced in the reaction of Grignard reagents or organolithium reagents with manganese(II) chloride and lithium chloride. With allylic Grignards, complete allylic transposition was observed [246]. Acyl tetracarbonylferrates reacted with epoxides to produce α,β-unsaturated ketones (eq. 164) [247]. Acyltetracarbonyl ferrates reacted with aryl iodonium salts to give aryl ketones (eq. 165) [248]. Aryl tellurium trichlorides reacted with nickel carbonyl in DMF to produce aryl carboxylic acids after hydrolysis [249].



(164)

R = n-Bu, 

R' = Ph, Me



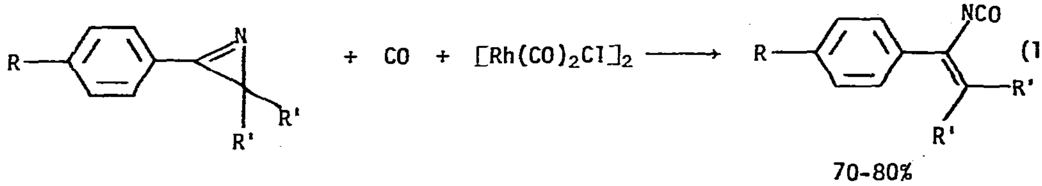
$$RCOFe(CO)_4 + (Ar)_2I^+X^- \longrightarrow \underset{48\text{-}85\%}{R\overset{O}{\overset{\|}{C}}\text{-}Ar} + ArI + LiX \qquad (165)$$

R = Me, n-Bu, Ph
Ar = Ph, p-tolyl, p-anisyl-, p-chloro, p-bromo

4. Carbonylation of Nitrogen Compounds

Intensive activity continued in the study of the conversion of aryl nitro compounds to isocyanates. Aryl isocyanates were produced in 38-90% yield from the corresponding nitro compound by treatment with carbon monoxide at 100 atm pressure and 200°C. Palladium(II) chloride was the catalyst, and pyridine the promoter. Oxides of V, Mo, Nb, W and Ta were also required [250,251]. The effects of pyridine base additives on yield were studied [252]. An increase of two to six fold was noted in the presence of these bases. Mixed oxides of molybdenum and lanthanides such as La, Ce, Pr and Nd in the form of $mLn_2O_3{\cdot}nMoO_3$ increased both the activity and selectivity of these reactions [253]. Using $Rh_2Cl_2(CO)_4/MoCl_5$ as a catalyst at one atmosphere of CO and 100° nitroarenes were converted to aryl isocyanides in 26% yield with 50% selectivity [254]. The iron compound $Fe_2O_3{\cdot}V_2O_5$ was found to increase the catalytic activity of $PdCl_2(Py)_2$ for this conversion [255].

Phenylazirines were converted to styryl isocyanates by reaction with $[Rh(CO)_2Cl]_2$ (eq. 166) [256]. Aryl amides were produced from 1,3-diaryltriazenes by reaction with carbon monoxide in the presence of $PdCl_2(PPh_3)_2$ as catalyst (eq. 167) [257]. Secondary amines were formylated to N-formylamines by treatment with DMF in the presence of $Ni(acac)_2$-phosphine-Et_3Al catalysts [258].



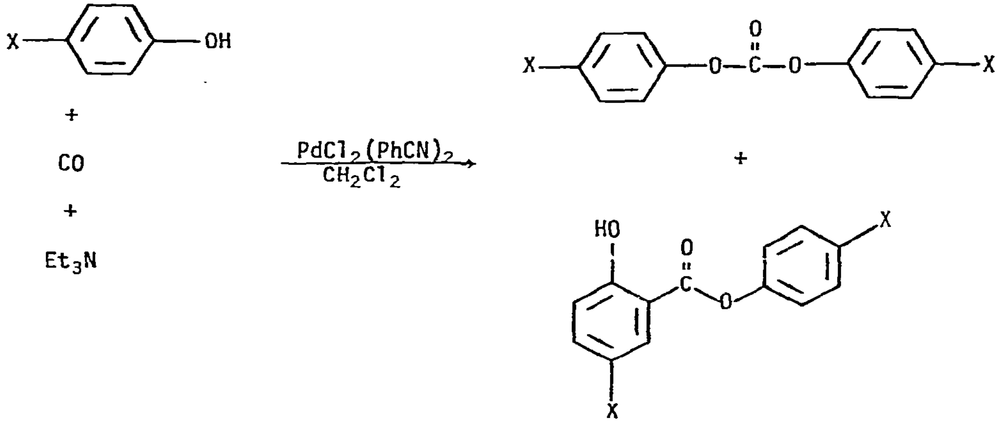
(166)

R = H, Me, OMe, Br
R' = H, Me

$$\mathrm{ArNHN{=}NAr} + \mathrm{CO} \xrightarrow{\mathrm{PdCl_2(PPh_3)_2}} \mathrm{ArNHCOAr} \qquad (167)$$

5. Carbonylation of Oxygen Compounds

The topic of mechanistic pathways in the catalytic carbonylation of methanol by rhodium and iridium complexes has been reviewed [259]. The effects of added sodium iodide on the cobalt, rhodium and iridium-catalyzed carbonylation of methanol to acetic acid have been studied. No effect on the rhodium catalyzed reaction was noted, but the iridium catalyzed reaction was retarded [260]. The kinetics of methanol carbonylation over rhodium-y-zeolite catalyst were studied. A mechanism similar to that found with homogeneous rhodium catalysts was proposed [261]. Methanol was carbonylated with carbon monoxide to give dimethyloxalate and dimethyl carbonate using palladium(II) acetate as a catalyst and tertiary amines and phosphines as additives [262]. Phenols reacted with carbon monoxide and triethylamine in the presence of $PdCl_2(PhCN)_2$ to produce diphenyl carbonates and salicylates. Use of Pd(CO)Cl complexes as catalysts led exclusively to carbonate esters (eq. 166) [263].

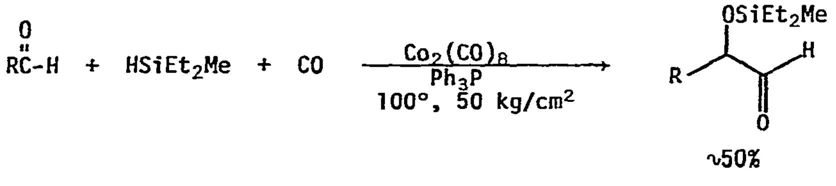


(167)

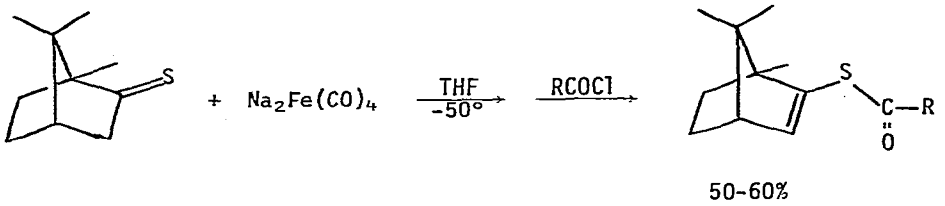
X = H, Me, Cl, MeO

6. Miscellaneous Carbonylations.

Formaldehyde was carbonylated to α-hydroxyacetaldehyde by reaction with hydridocobalt tetracarbonyl and carbon monoxide at 0° and 1 atmosphere pressure [264]. Aldehydes were converted to higher α-siloxyaldehydes by treatment with trialkylsilanes and carbon monoxide in the presence of dicobalt octacarbonyl and phosphines (eq. 168) [265]. Thioketones were converted to thioesters by reaction with sodium tetracarbonyl ferrate and acid halides (eq. 169) [266].

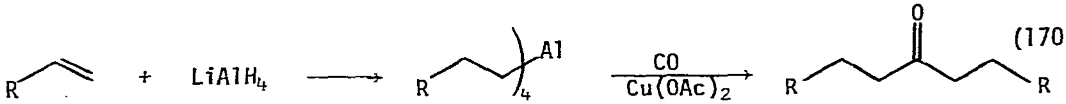


(168)



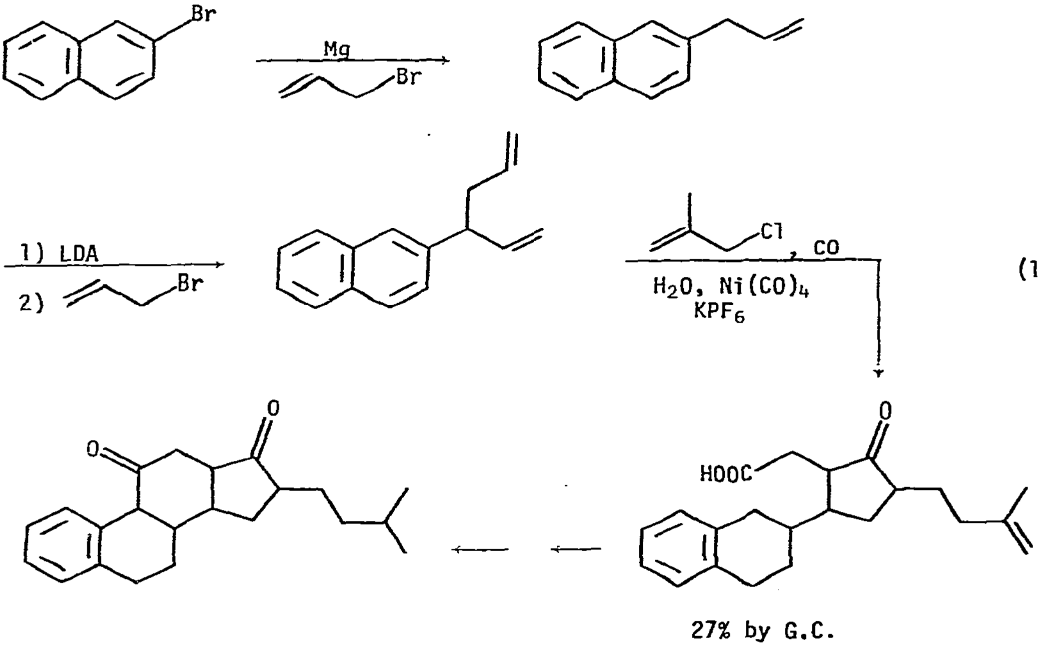
(169)

Olefins were converted to symmetrical ketones by hydroalumination followed by treatment with carbon monoxide and copper(II) acetate (eq. 170) [267].

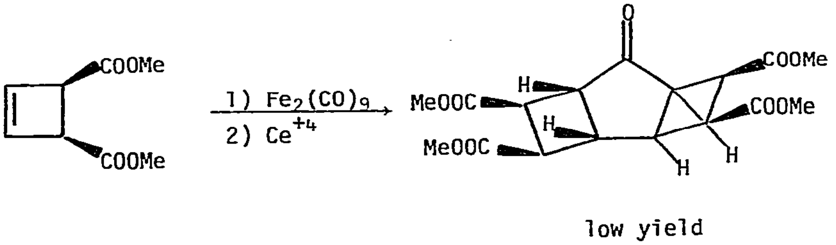


(170)

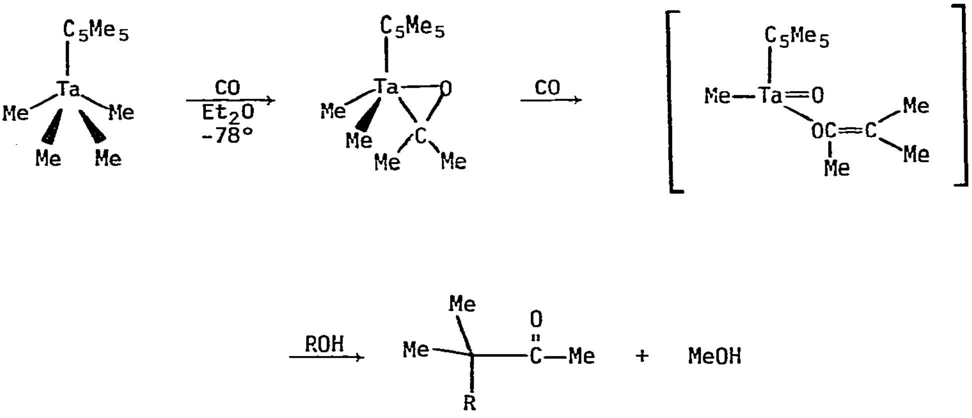
Thermal decomposition of dicyclopentadiene dimers in the presence of $Cr(CO)_6$, $Mo(CO)_6$ or $W(CO)_6$ produced indanone [268]. Terminal acetylenes reacted with iron pentacarbonyl upon irradiation to give mixtures of substituted quinones [269]. The steroid ring system was built up by the series of coupling and carbonylation reactions shown in eq. 171 [270]. Internal alkynes were cyclodimerized to substituted cyclopentadienones by carbon monoxide and palladium(II) chloride. Only six to eight turns of the catalyst were observed [271]. Diesters of cyclobutene were converted to tricyclic ketones by reaction with $Fe_2(CO)_9$ (eq. 172) [272]. Carbon monoxide was methylated and reductively coupled by $CpTaMe_4$ (eq. 173) [273].



(171)



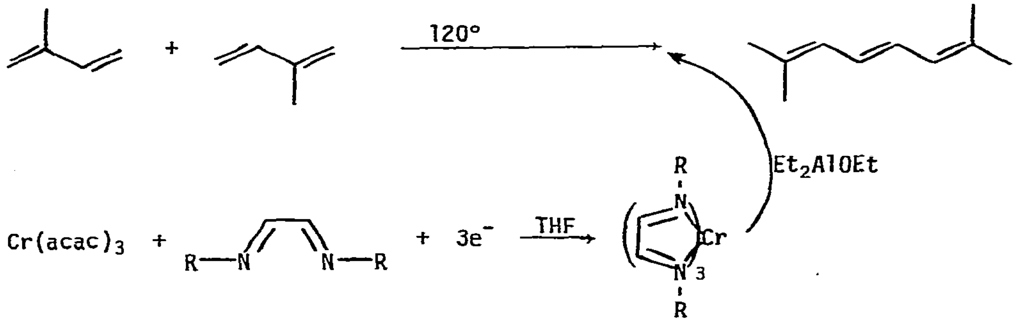
(172)



(173)

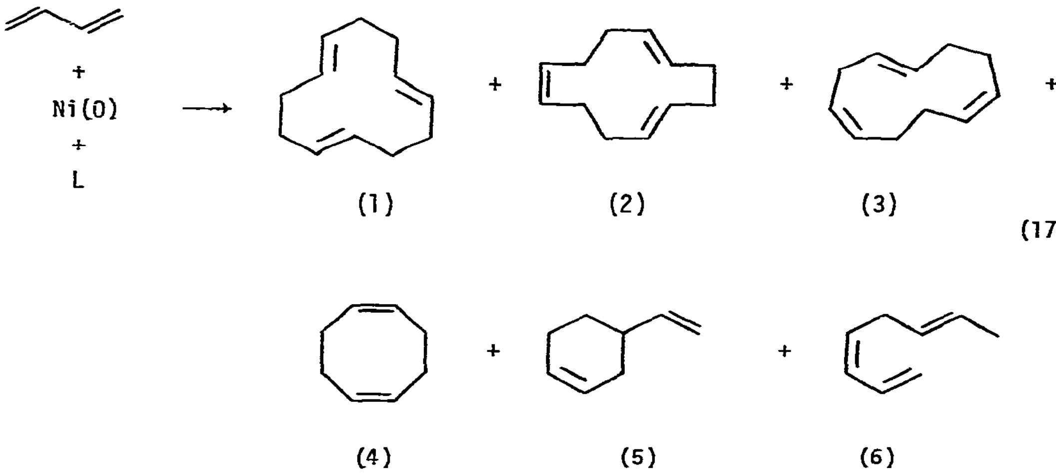
D. Oligomerization

A catalyst prepared from nickel(II) acetylacetonate, triethylaluminum and tributylphosphine reacted with butadiene at 100° in the presence of aziridine to produce 80% linear dimers, with 2,4,6-octatriene predominating. Isoprene dimerized with exclusive head-to-tail regiospecificity in 90% yield [274]. The catalyst resulting from reaction of $(COD)_2Ni$ with triphenylphosphine dimerized butadiene to mixtures of linear octadienes. Morpholine was required for activity and formaldehyde acted as the hydrogen source [275]. A similar $(COD)_2Ni$-triphenylphosphine catalyst dimerized 1-cyclopropylbuta-1,3-diene to 4-cyclopropyl-1,5,7,9-undecatetraene in 50% yield [276]. Butadiene was selectively dimerized to 4-vinylcyclohexene when treated with "$Fe(NO)_2$" generated electrochemically [277]. The same reagent catalyzed (300 turns) the conversion of norbornadiene to the exo-trans-exo-dimer [278]. Linear, regular isoprene oligomers were produced using $Ni(acac)_2/Et_3Al$/borate catalysts. Up to 57% farnesane was produced in this manner. Some cyclooligomers were also obtained [279]. In the nickel catalyzed oligomerization of isoprene, addition of cyclic amines enhanced formation of cyclic dimers such as dimethylcyclooctadiene and dipentene [280]. Isoprene was catalytically dimerized to 2,7-dimethyl-2-trans-4,6-octatriene by a homogeneous chromium catalyst (eq. 174) [281].



(174)

Selectivity control in nickel-catalyzed olefin oligomerization has been reviewed [282]. The reaction of butadiene with nickel(0) catalysts and phosphine to produce oligomers (eq. 175) was studied by varying the concentration of ligand and nickel, and plotting the log {[L]/[Ni]}. This treatment of the data showed



(175)

log [L]/[Ni] = -3 75% 1
15% 3

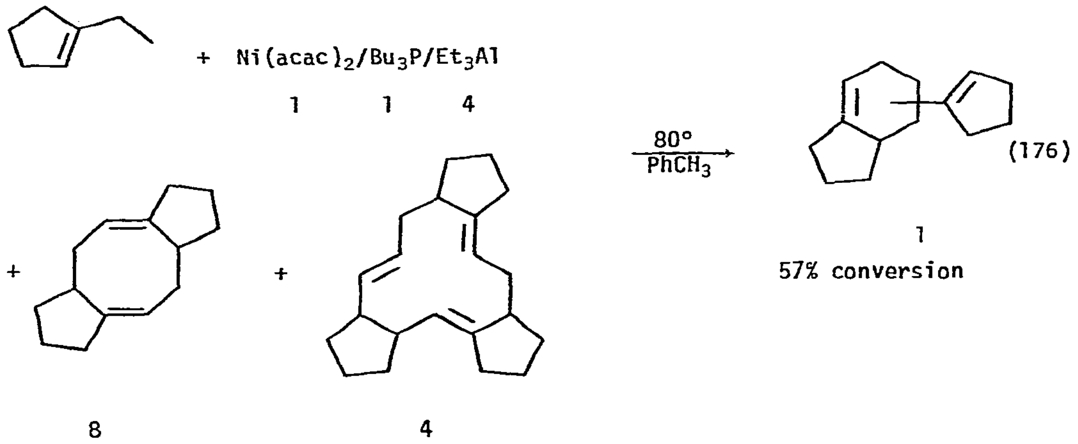
log [L]/[Ni] = 0 70% 4
20% 5

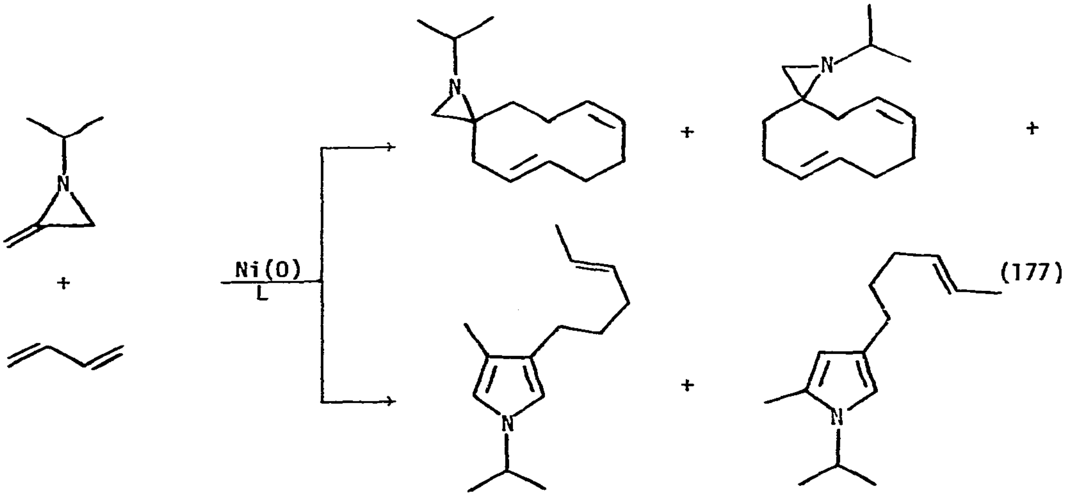
log [L]/[Ni] = 2 70% 5, etc.

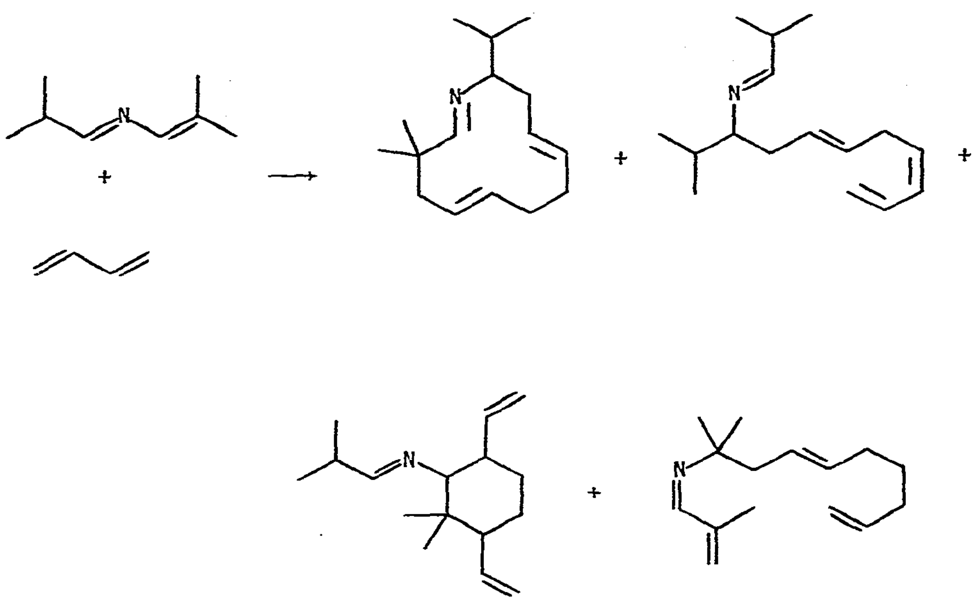
the response of product distribution to changes in the ratio and allowed optimization of the reaction for the desired product [283,284]. Butadiene was cyclodimerized to 1,5-cyclooctadiene with a 95% selectivity by using nickel(0)-tris-(2-ethoxyphenyl)phosphite as a catalyst [285]. 1-Vinylcyclopentene was cyclooligomerized by a Ni(acac)$_2$/Bu$_3$P/Et$_3$Al catalyst system (eq. 176) [286].

Butadiene and ethylene were codimerized by homogeneous rhodium catalysts

[287]. Codimerization of butadiene and ethylene in the presence of a catalyst system consisting of CpTi(OTMS)$_3$-MeMgI produced vinyl cyclobutanes [288]. 3-Vinylcycloalkenes were produced by codimerization of 1,3-dienes and ethylene using nickel(0) catalysts anchored to highly porous styrene-2%-divinylbenzene copolymers onto which pendent aminophosphine groups had been grafted [289]. Vinyl silane cooligomerized with butadiene using nickel(0) catalysts to produce 1-trimethylsilyl-1,4,9-decatriene [290]. Butadiene and a vinyl aziridine cyclo-oligomerized in the presence of Ni(0) catalysts. The ratio of products depended upon the [L]/[Ni] ratio (eqs. 177,178) [291].

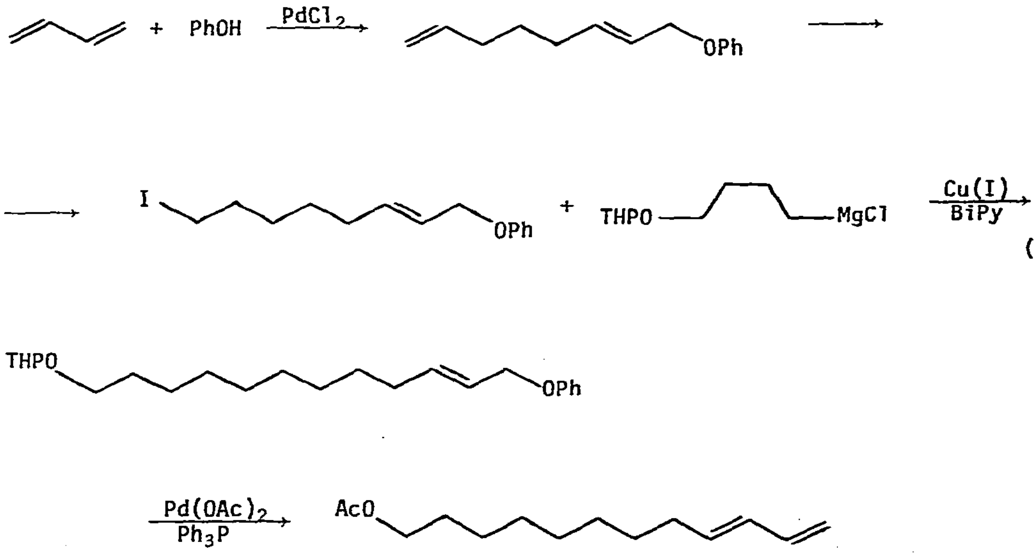




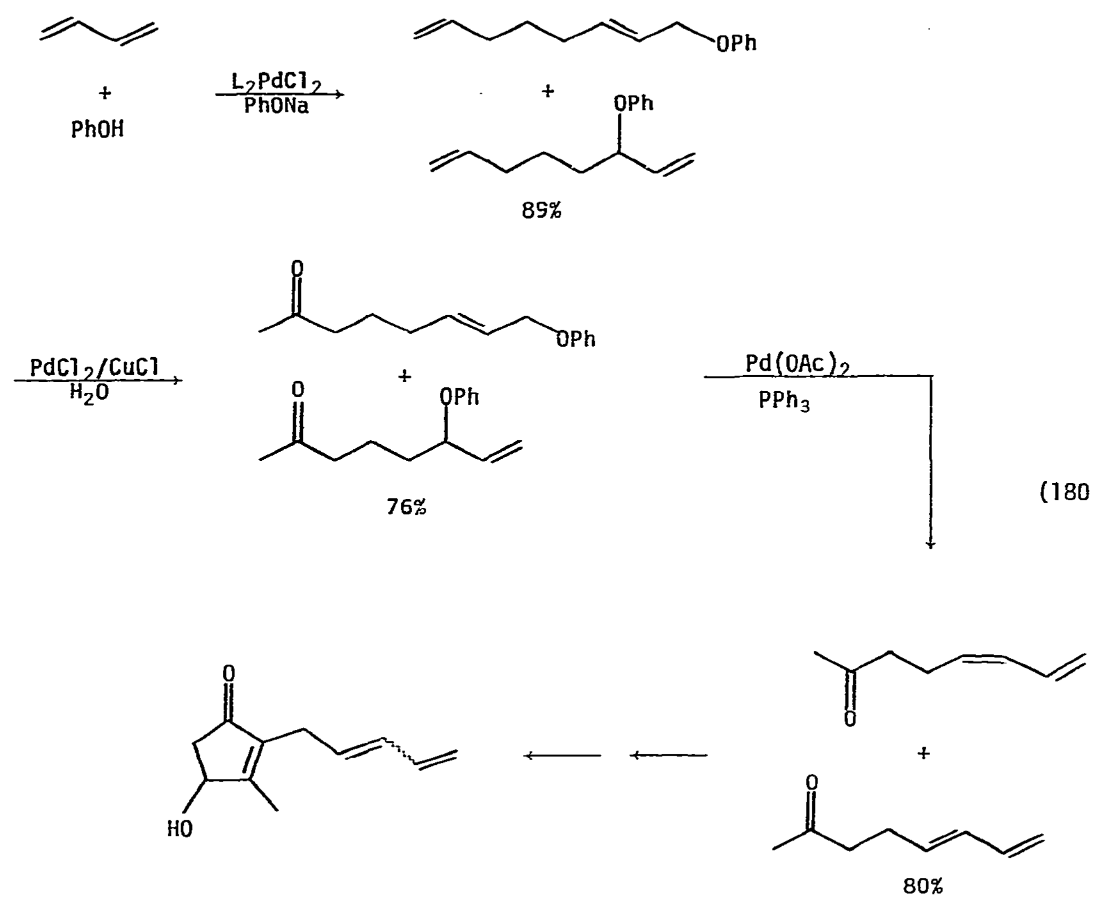


(178)

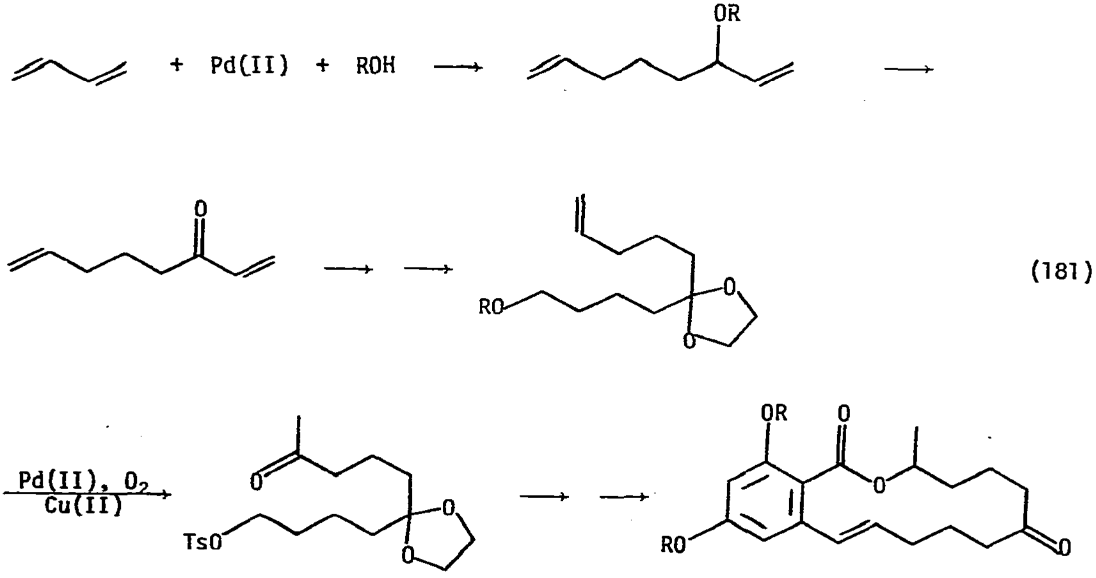
Palladium-catalyzed nucleophilic attack-oligomerization has been used in the synthesis of a number of natural products including the sex pheremone of the red bollworm moth (eq. 179) [292]. E,Z-Pyrethrolone (eq. 180) [293], (±)-Zearalenone (eq. 181) [294], dihydrojasmone (eq. 182) [295], and steroids (eq. 183) [296] were synthesized in a similar fashion.



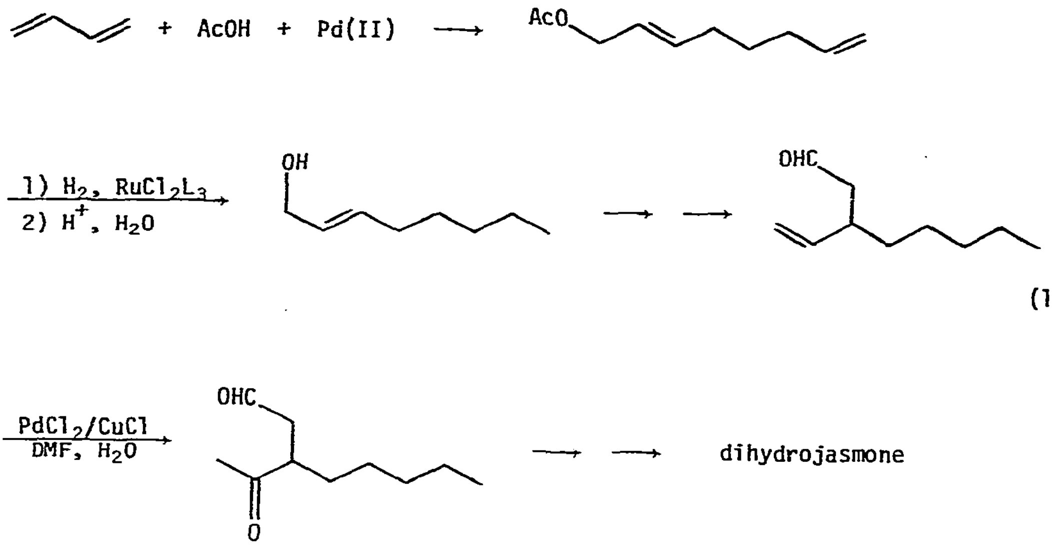
(179)


+
PhOH
L2PdCl2
PhONa
OPh
+
OPh
89%
PdCl2/CuCl
H2O
O
OPh
+
O
OPh
76%
Pd(OAc)2
PPh3
O
+
O
80%
O
HO

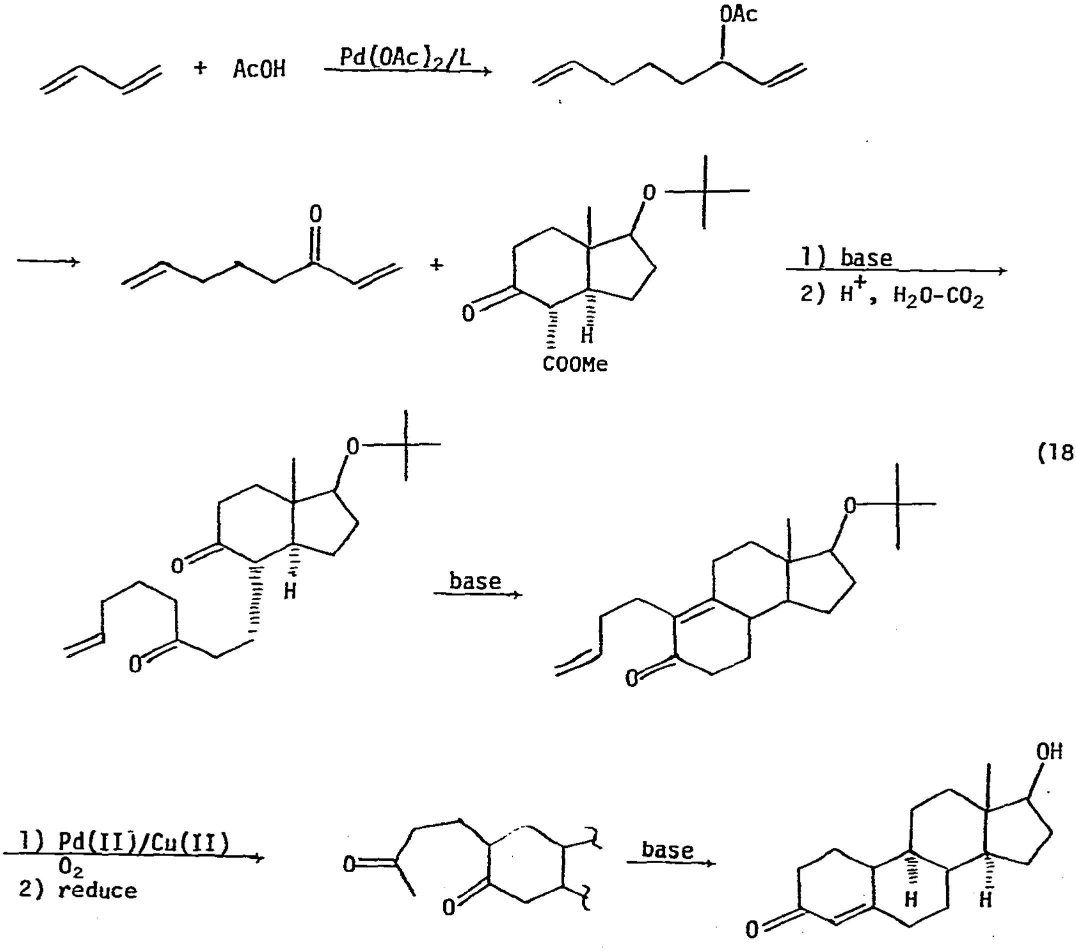
(180)


+ Pd(II) + ROH
OR
O
RO
O
O
Pd(II), O2
Cu(II)
O
TsO
O
O
OR
O
O
RO
O

(181)

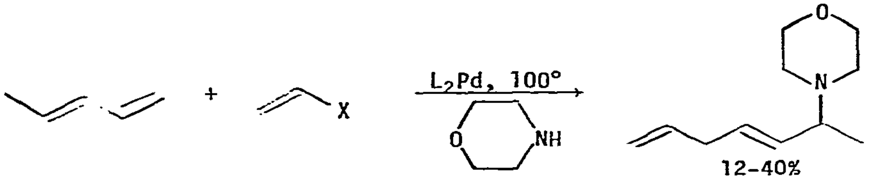

AcOH
Pd(II)
AcO
1) H_2, $RuCl_2L_3$
2) H^+, H_2O
OH
OHC
$PdCl_2/CuCl$
DMF, H_2O
OHC
O
dihydrojasmone

(182)


AcOH
$Pd(OAc)_2/L$
OAc
O
O
O
H
COOMe
1) base
2) H^+, H_2O-CO_2
O
O
O
H
base
O
O
1) Pd(II)/Cu(II)
O_2
2) reduce
O
O
base
OH
O
H
H

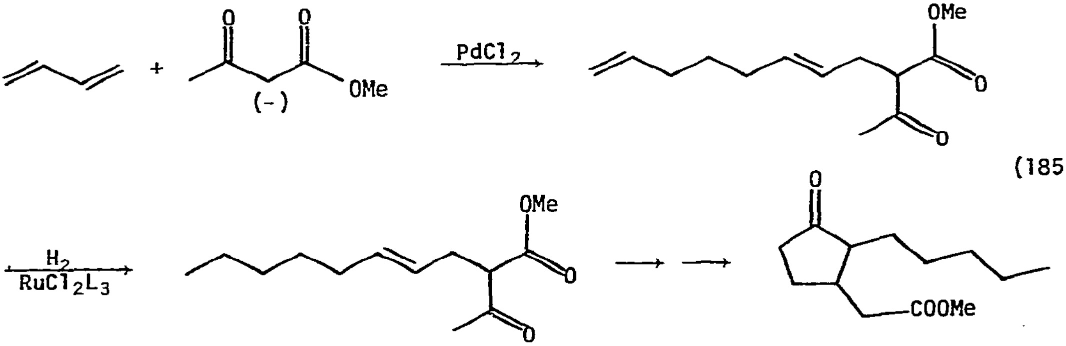
(183)

1,3-Dienes, vinyl halides and secondary amines condensed in the presence of palladium(0) catalysts to produce tertiary 2,5-dienyl amines (eq. 184) [197].

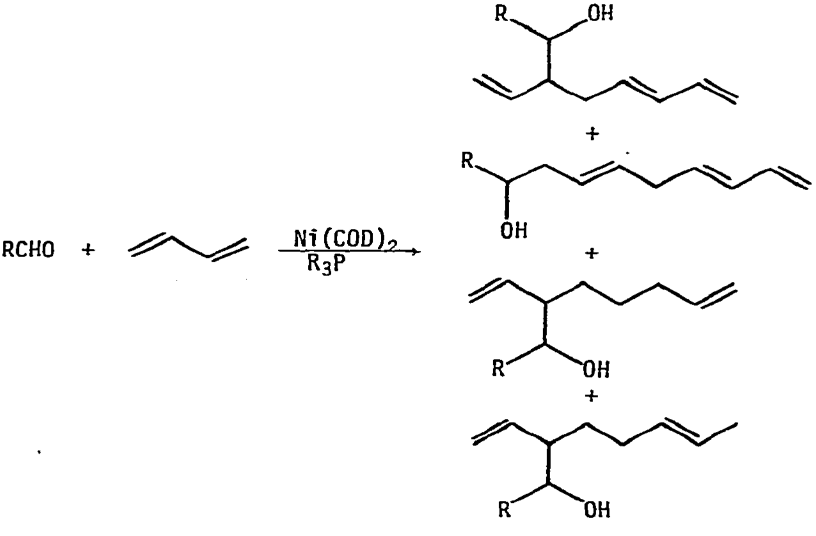


(184)

Methyl dihydrojasmonates was prepared in a synthesis involving palladium(II) assisted alkylation-dimerization of butadiene (eq. 185) [298]. In a similar fashion phenylmagnesium bromide reacted with butadiene in the presence of a $Ni(acac)_2/P(OPh)_3/Et_3Al$ catalyst to give 1-phenyl-2,7-octadiene, as well as other oligomers of butadiene not containing phenyl groups [299]. Butadiene dimerized and reacted with aldehydes when treated with $Ni(COD)_2$ and tertiary phosphines (eq. 186) [300]. Methyl furfuraldimine reacted with butadiene in the presence of nickel(0) catalysts to give a number of cooligomerization products (eq. 187) [301]. Dimethylfulvene dimerized when codeposited with nickel vapor (eq. 188) [302].

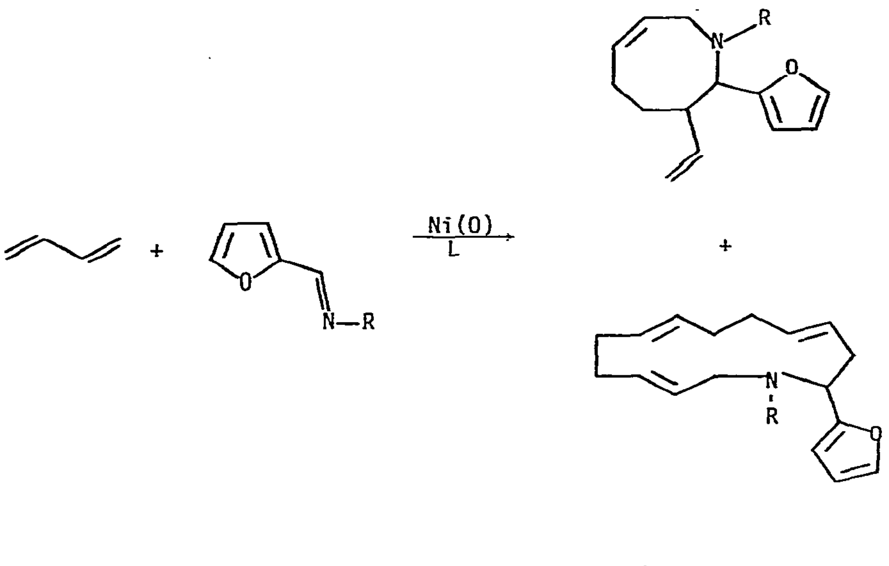


(185)

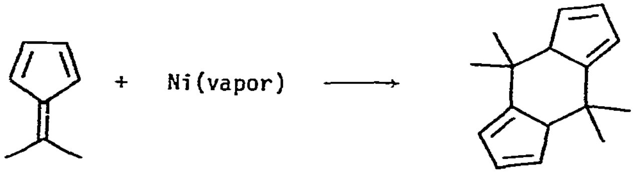


(186)

Ratio depends on L and R

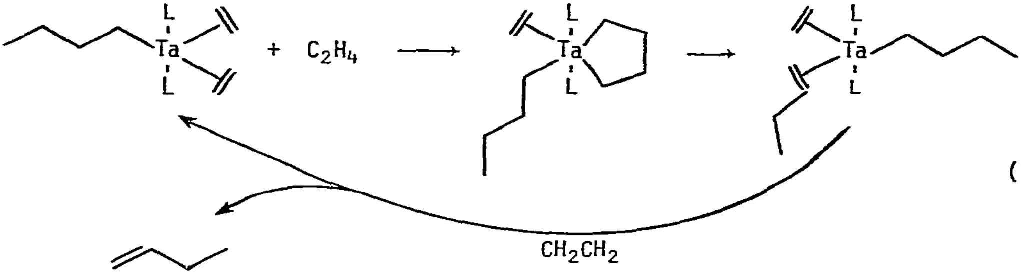


(187)



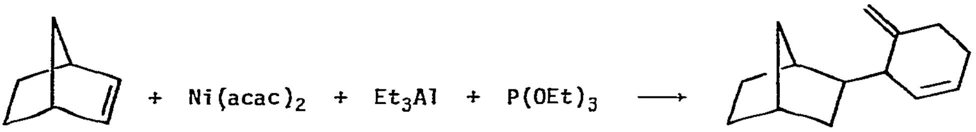
(188)

The mechanism of dimerization of ethylene to 1-butene by tantalum complexes was shown to proceed via a metallacyclopentane intermediate (eq. 189) [303].



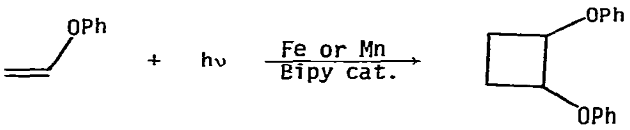
(189)

The selectivity in ethylene dimerization over supported nickel oxide catalysts (SiO_2 or Al_2O_3) was examined [304]. The dimerization of norbornadiene to Binor-S by a $(C_7H_8)_2Co_2(CO)_4$-$BF_3 \cdot OEt_2$ catalyst system was claimed to proceed via a mononuclear cobalt catalyst, and not by a π-complex-multicenter process [305]. The complex produced by the reaction of $Ni(acac)_2$ with Et_3Al and $P(OEt)_3$ catalyzed the homodimerization of bicyclo[2.2.1]hept-2-ene (eq. 190) [306]. η^4-Cyclooctenyl complexes of nickel containing fluorinated acetylacetonate ligands oligomerized α-olefins in the absence of cocatalysts. The results were rationalized by semi-empirical calculations [307]. Photolysis of $(neopentyl)_4Cr$



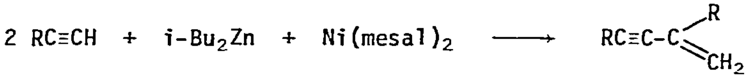
(190)

and (mesityl)$_3$Cr(THF) produced catalysts active for the polymerization of ethylene, styrene, acrylates, and vinyl acetate [308]. Electron rich olefins such as enol ethers, indene and sytrene cyclodimerized when irradiated in the presence of iron and manganese complexes of 2,2'-bipyridine or 1,10-phenanthroline (eq. 191) [309].



(191)

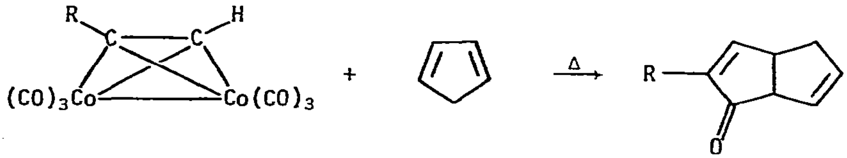
Trialkylaluminum reagents react with terminal alkynes in the presence of nickel [310], manganese [311], and iron salts [312] to give mixtures of linear dimers, alkylated monomers and dimers, linear oligomers and aromatic compounds from cyclotrimerization of the alkyne. The product distribution depends on the conditions and catalyst used, but mixtures were always obtained. Terminal acetylenes were dimerized to enynes by reaction with i-Bu$_2$Zn and a nickel(II) catalyst (eq. 192) [313].



$$2\ RC{\equiv}CH + i\text{-}Bu_2Zn + Ni(mesal)_2 \longrightarrow RC{\equiv}C\text{-}C(R){=}CH_2 \qquad (192)$$

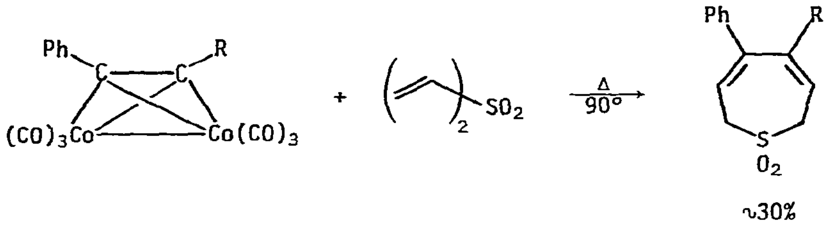
R = linear and branched hydrocarbons

Dicobalt hexacarbonyl complexes of terminal acetylenes reacted with fulvenes, indene, cyclopentadiene and acenaphthylene to give polycyclic, acylated products (eq. 193, for example) [314]. The same complexes produced thiepin dioxides when

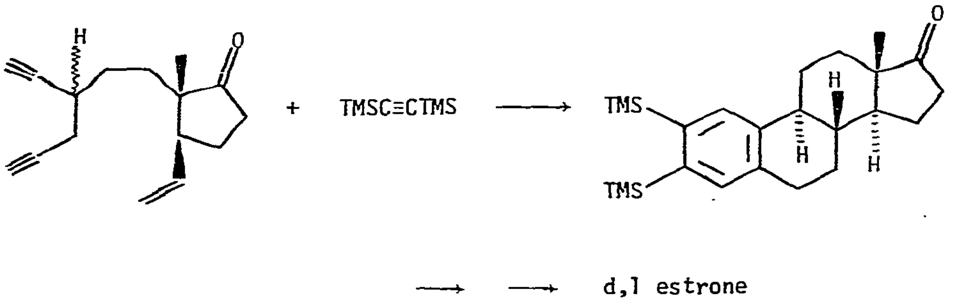


(193)

heated with divinylsulfone (eq. 194) [315]. Racemic estrone was synthesized by a cobalt catalyzed cocyclotrimerization of bis-trimethylsilylacetylene and a functionalized diyne (eq. 195) [316]. This general process was the subject of a dissertation [317].

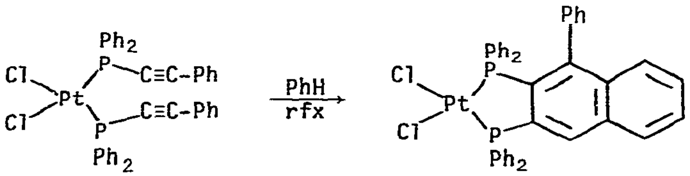


(194)



(195)

The acetylene groups of the ligand $Ph_2PC{\equiv}CPh$ coupled when the bis phosphine complex of platinum(II) chloride was refluxed in benzene (eq. 196) [318].



(196)

Acetylene was polymerized in acetone solution at one atmosphere and 25° by these salts: $(Me_4N)[Ni_5(CO)_{12}]$, $(Me_4N)_2[Ni_6(CO)_{12}]$, $(Me_4N)[Ni_{12}(CO)_{21}H_2]$, and $(Et_4N)[Ni_{12}CO_{21}H]$ [319]. The bis benzonitrile complex of palladium(II) chloride was an active catalyst for the codimerization of acetylenes with allylic halides to produce 1,4-diene codimers [320]. Rhodium catalysts reacted with carbon monoxide, hydrogen and methanol to produce ethanol with up to 50% selectivity [321].

E. Rearrangements.

1. Metathesis.

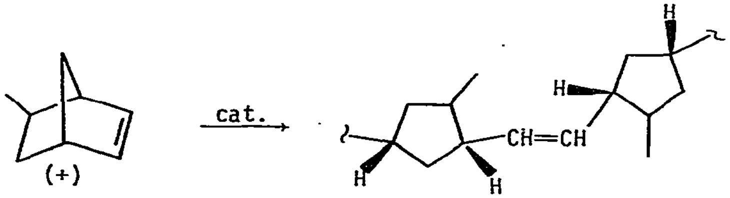
The olefin metathesis reaction has been the subject of a review [322]. The stereoselectivity of the metathesis of cis and trans $RCH{=}CH{-}CH_3$ type alkenes using a catalyst consisting of $Mo(NO)_2X_2L_2$ or the corresponding tungsten complex and ethylaluminum dichloride was studied. The stereoselectivity decreased as the bulk of R increased, was independent of the nature of X, and decreased on going from molybdenum to tungsten. The stereoselectivity was related to steric interactions both upon olefin coordination and in the metallacyclobutane

[323]. The titanium complex $Cp_2TiCH_2AlClMe_2$ was shown to be a metathesis catalyst for terminal vinyl groups by reacting labelled isobutene with methylene cyclohexane and showing redistribution of the label between the two alkenes [324]. The metathesis of α-olefins on tungsten halide-organogermanium and organotin complex catalysts has been studied [325]. In the metathesis of 1-octene with tungsten hexachloride-ethylaluminum dichloride catalysts, addition of $[(PhO)_3P]_4Ni$ suppressed polymerization reactions and alkylation of the solvent, and rather directed the reaction towards production of internal olefins [326]. Cyclopentene was metathesized in fair yield by the catalyst $W_2(CH_2SiMe_3)_6$. However, other olefins were inert to this catalyst [327]. The catalyst resulting from irradiation of tungsten hexacarbonyl in carbon tetrachloride metathesized cis and trans olefins of the type $RCH{=}CH{-}CH_3$ to produce 2-butene with very high trans but low cis stereoselectivity. A severely sterically strained dinuclear tungsten intermediate was claimed [328]. The catalyst resulting from treatment of MoO_x on β-TiO_2 with N_2O and hydrogen at 200° was found to catalyze olefin metathesis without hydrogen scrambling or isomerization through cationic intermediates [329].

A metathesis catalyst consisting of Re_2O_7 and Al_2O_3 with a tetramethyltin promoter metathesized functionalized olefins at 25° (eq. 197). Allylic ethers, esters and ketones were tolerated [330]. Molybdenum trioxide/alumina catalysts both isomerized and metathesized 2-butenes [331]. The bridged bicyclic compound (+)-exo-5-methylbicyclo[2.2.1]hept-2-ene was metathesized to polymeric material (eq. 198). The all cis polymer was totally syndiotactic, the 11:89 cis/trans was syndiotactic at the cis junctions and atactic at the trans junctions [332].

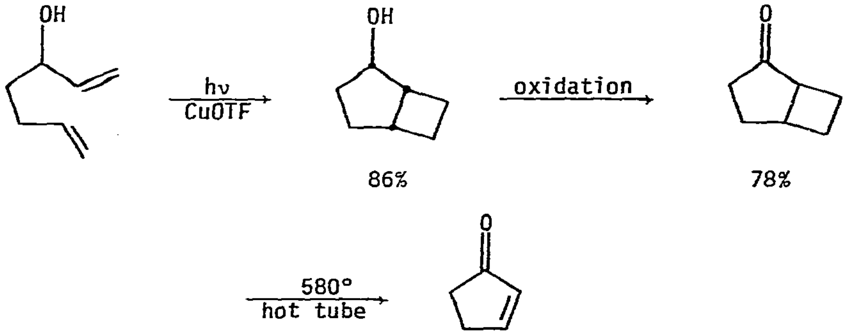
$$CH_2{=}CHCH_2R \rightleftharpoons CH_2CH_2 + RCH_2CH{=}CHCH_2R \tag{197}$$

R = OAc	17% conversion	96% selective
R = OEt	46%	98%
R = CH_2COMe	35%	97%

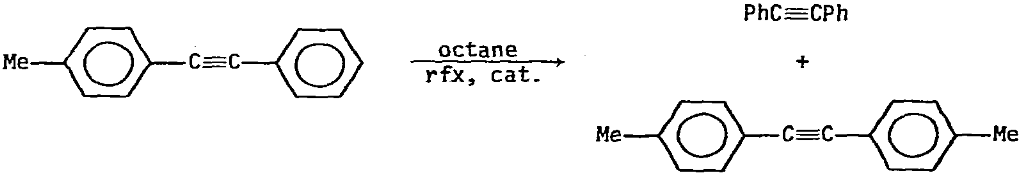


(198)

Manganese methylene complexes were formed in the gas phase by reaction of MnO^+ with ethylene and were studied by ICR [333]. It was concluded that strong metal-carbene bonds were required for effective olefin metathesis catalysts. The mechanism of olefin metathesis and cyclopropanation was discussed in detail and the Chauvin mechanism was found to be consistent with most experimental observations [334]. The metathesis of cis,cis-2,8-decadiene was used to study the mechanism of olefin metathesis [335]. A non-pairwise exchange-metal carbene mechanism best fits the experimental observations. Transition metal carbene complexes were generated by the reaction of CD_3Li with tungsten hexachloride and molybdenum pentachloride followed by decomposition. These complexes were active catalysts for olefin metathesis and cycloolefin ring-opening polymerization [336]. Photolysis of 3-hydroxyhepta-1,6-dienes in the presence of copper(I) triflate led to olefin metathesis to produce bicyclo[3.2.0]heptan-3-ol. These were converted to cyclopentenones by thermolysis (eq. 199) [337]. Cyclobutadiene metal complexes were considered as potential intermediates in alkyne metathesis [338]. Diarylacetylenes were metathesized by a number of different molybdenum carbonyl complexes (eq. 200) [339]. Electrochemical reduction of tungsten hexachloride at aluminum electrodes generated an efficient metathesis catalyst. The active species was thought to have been generated in the first reduction step [340].



(199)

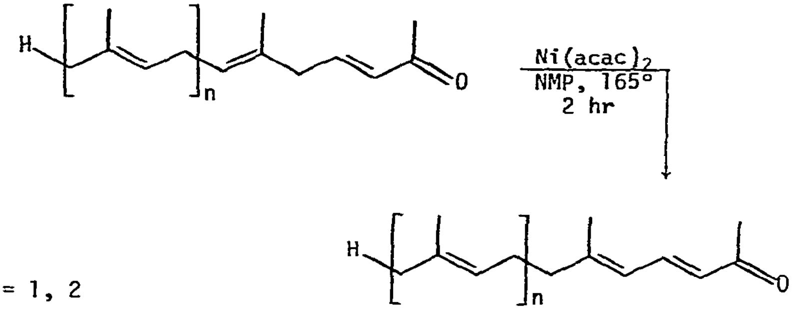


(200)

cat. = $Mo(CO)_3(PhOH)_3$, $Mo(CO)_3(NH_3)_3$, $Mo(CO)_3(MeCN)_3$, trans-$Mo(CO)_4L_2$, cis-$Mo(CO)_2(Ph_2PCH_2PPh_2)_2$

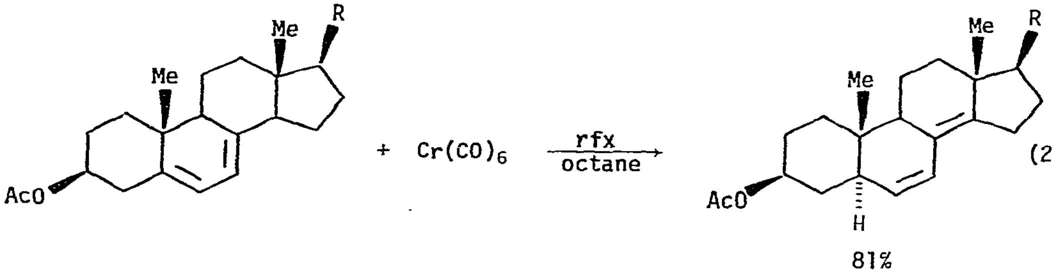
2. Olefin Isomerization.

cis- and trans-2-Butenes were slowly isomerized to an equilibrium mixture of the three possible n-butenes by $RhCl(PPh_3)_3$ in dichloromethane [341]. The kinetics of this isomerization as well as that of 1-butene [342] were studied, and the reaction simulated on an analog computer [343]. Iron pentacarbonyl catalyzed the isomerization of 3-cyclohexene-1-carbonitrile to 1-cyclohexene-1-carbonitrile under carbon monoxide pressure at 180-250° [344]. Allyl benzene was isomerized to β-methylstyrene by $(Ph_3P)_4Ru(\pi\text{-}CH_3CN)(CH_3CN)$. The rearrangement was believed to go via a π-allylruthenium species [345]. Olefins were isomerized by carbonylpalladium(I) complexes [346]. Nickel acetylacetonate catalyzed the rearrangement of 2,5-dienones to 2,4-dienones (eq. 201) [347]. A steroidal diene was isomerized by heating with chromium hexacarbonyl in octane (eq. 202) [348].



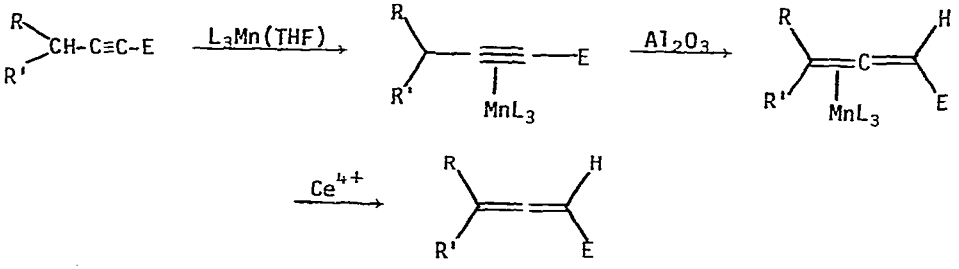
(201)

n = 1, 2



(202)

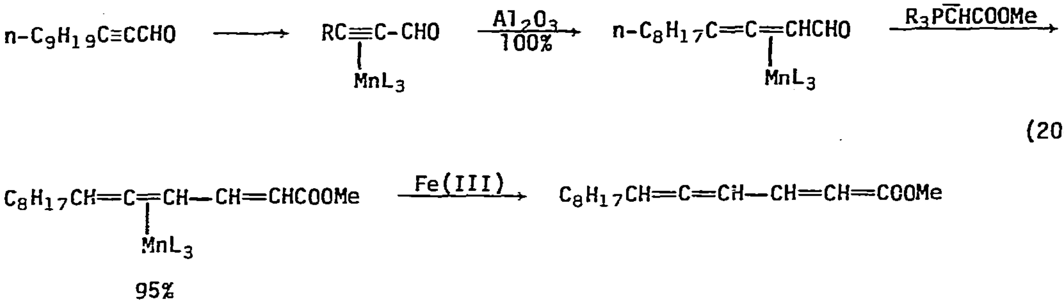
Electron deficient alkynes were isomerized to allenes by formation of manganese complexes, treatment with alumina, and removal of manganese by cerium(IV) oxidation (eq. 203). This was of some use in organic synthesis (eq. 204) [349]. Chiral allenes were racemized by reaction with $(nBu)_2CuLi$, EtMgBr-CuBr, and MeMgI-CuI. An electron transfer mechanism was claimed [350].



(203)

R = H, n-Bu
R' = H } $(CH_2)_5$

E = COOEt, COOMe, $COCH_3$, CHO $L_3M = CpMn(CO)_2$



$$n\text{-}C_9H_{19}C{\equiv}CCHO \longrightarrow \underset{MnL_3}{RC{\equiv}C\text{-}CHO} \xrightarrow[100\%]{Al_2O_3} n\text{-}C_8H_{17}C{=}\underset{MnL_3}{C}{=}CHCHO \xrightarrow{R_3P\bar{C}HCOOMe}$$

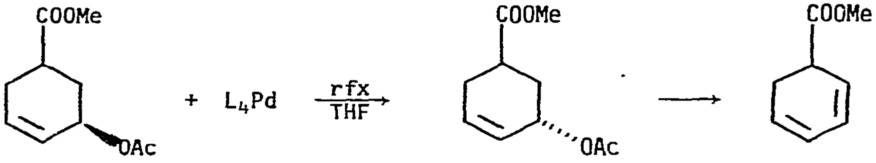
(204)

$$C_8H_{17}CH{=}\underset{MnL_3}{C}{=}CH{-}CH{=}CHCOOMe \xrightarrow{Fe(III)} C_8H_{17}CH{=}C{=}CH{-}CH{=}CH{=}COOMe$$

95%

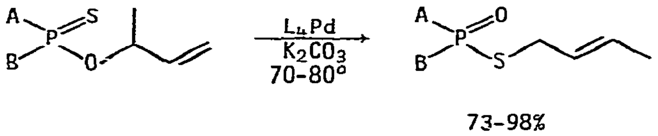
3. Rearrangements of Allyl Acetates, Allyl Ethers, Allyl Alcohols and Allyl Amines.

Cyclohexenylacetates were rapidly isomerized by reaction with L_4Pd complexes. The mixture of isomers slowly lost acetate to give cyclohexadienes (eq. 205)



(205)

[351]. In allylthiophosphate esters, the allyl group rearranged from oxygen to sulfur in the presence of L_4Pd catalysts (eq. 206). Allylic transposition was

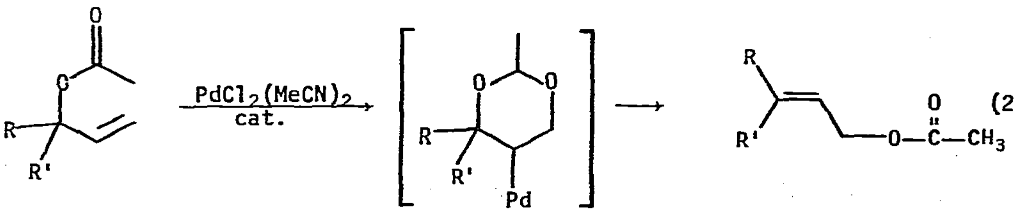


(206)

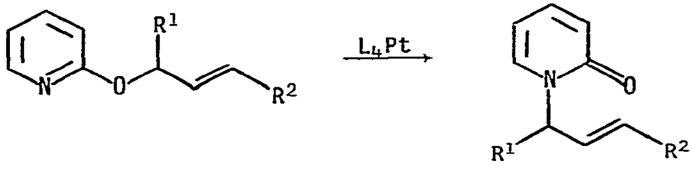
A = MeO, EtO, Ph

B = MeO, EtO, Et_2N, Et_2S

observed, and π-allylpalladium complexes were claimed as intermediates [352]. Palladium(II) complexes catalyzed the rearrangement of allyl acetates in high yield (eq. 207) [353]. Allyl ethers of 2-hydroxypyridine rearranged to N-allylpyridones upon reaction with platinum(0) complexes (eq. 208) [354].



(207)

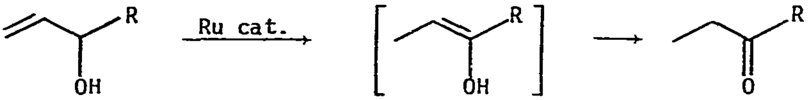


100%

(208)

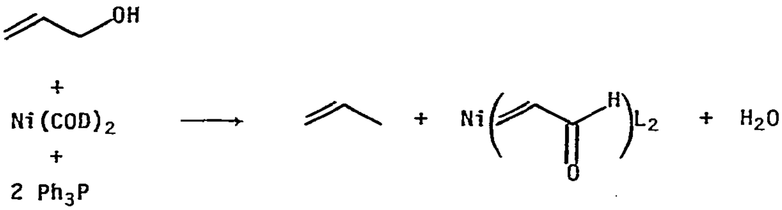
$R^1 = R^2 = H$
$R^1 = H$; $R^2 = Me$
$R^1 = Me$; $R^2 = H$

Allylic esters of 3-butenoic acids rearranged to heptadienoic acids in reactions catalyzed $Rh(PPh_3)_3Cl$ under mild conditions [355]. "Rhodium(I) catalysis of vinylcyclopropane epimerization-stereochemical course and mechanism" as well as "Claisen rearrangements of allyloxyketone enol ethers" were topics of a dissertation [356]. Allyl alcohols were isomerized to ketones by water soluble ruthenium catalysts in a two phase system (eq. 209) [357]. Allyl alcohols

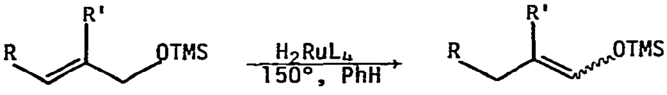


(209)

disproportionated to alkenes and conjugated aldehydes upon treatment with $(COD)_2Ni$ and triphenylphosphine or bipyridine (eq. 210) [358]. Allyl trimethylsilyl ethers were isomerized to silylenol ethers by H_2RuL_4 (eq. 211) [359].



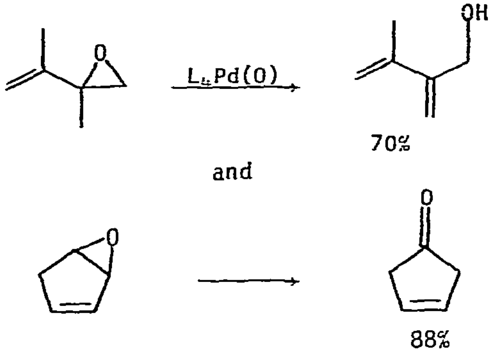
(210)



60-100%

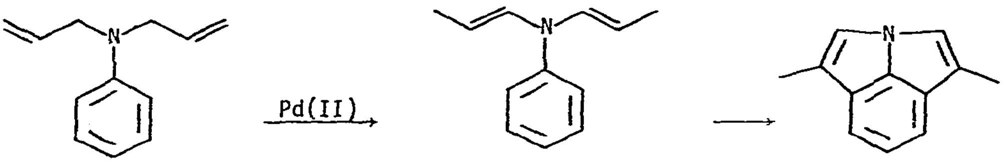
(211)

Diene epoxides rearranged to allylic alcohols when treated with palladium(0) catalysts (eq. 212) [360]. N-Allylaniline underwent C-N bond cleavage to give aniline and methyl acetylene when treated with platinum(II) or palladium(II)



(212)

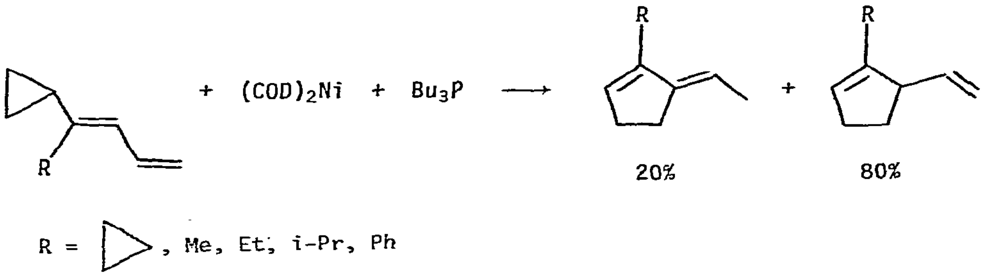
salts at room temperature in polar solvents [361]. The platinum(II) complex of N,N-diallylaniline isomerized then cyclized to 1,2,4,5-tetrahydro-2,4-dimethylpyrrolo[3,2,1-h,i]indole (eq. 213) [362].



(213)

4. Skeletal Rearrangements

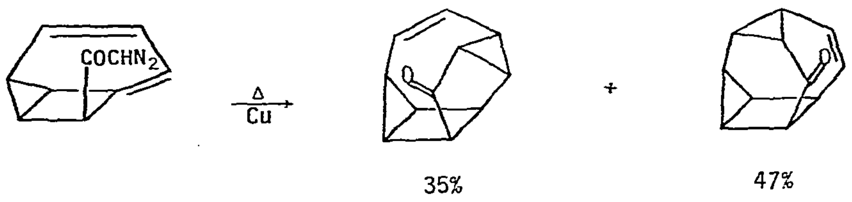
Nickel(0) catalyzed reactions of strained ring systems have been reviewed [363]. The skeletal rearrangements of 3-methylpentane and methyl cyclopentane in the presence of Pt/C, Pt-black, Pt/SiO_2 and Pt/Al_2O_3 were studied and compared [364]. Nickel(0) complexes catalyzed the vinylcyclopropane to cyclopentene rearrangement (eq. 214) [365]. Copper salts catalyzed the decomposition



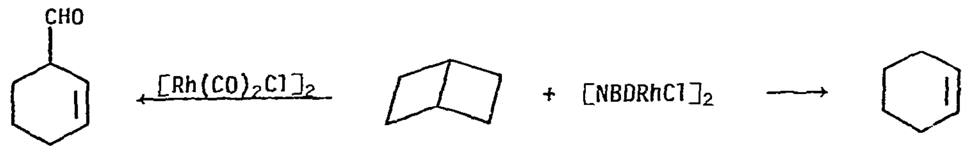
(214)

of homooctayalenyldiazomethyl ketone (eq. 215) [366]. Strained molecules containing fused cyclobutane rings isomerized when treated with rhodium(I) complexes (eqs. 216,217) [367]. Valence isomerization of quadricyclane was catalyzed by rhodium(I) complexes (eq. 218) [368]. The reaction was thought to proceed through a rhodiacyclobutane.

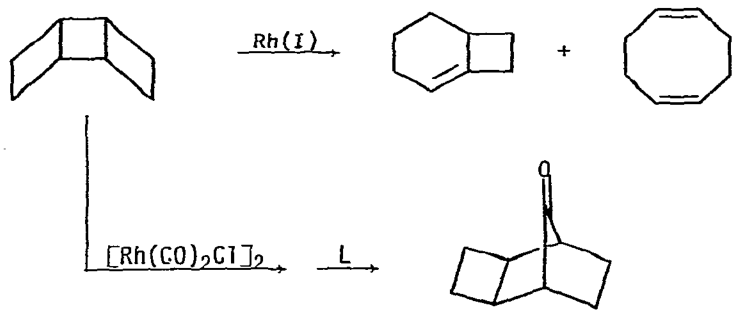
Catalysis of the quadricyclane to norbornadiene rearrangement was actively investigated, since this reaction holds promise for storage of photochemical



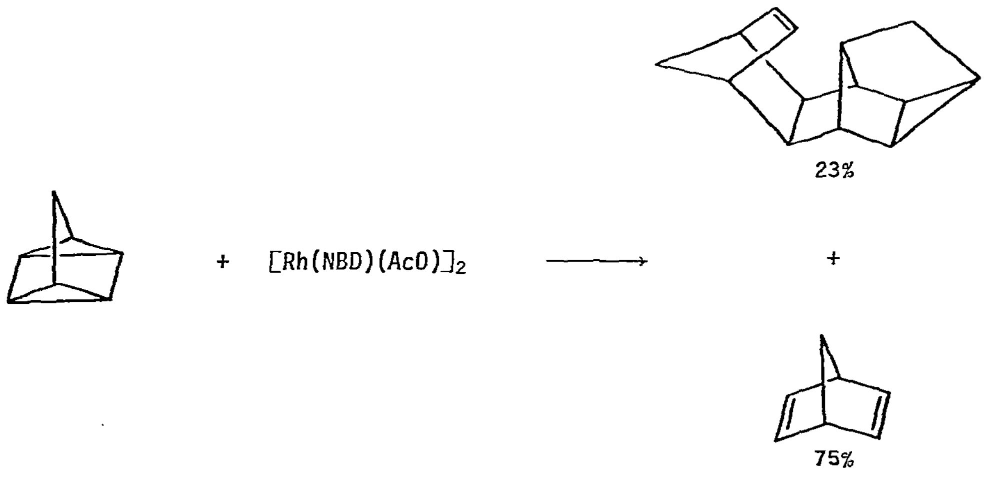
(215)



(216)

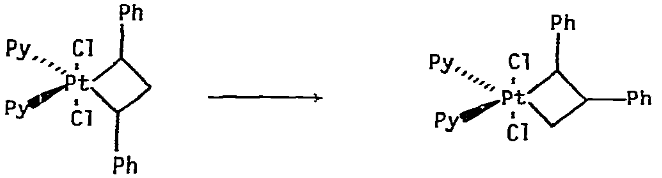


(217)

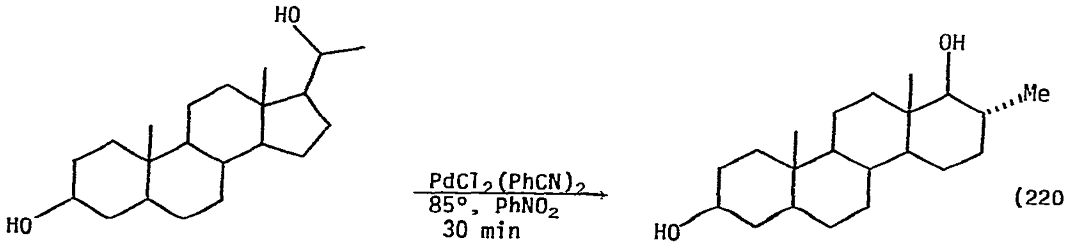


(218)

solar energy. This rearrangement was catalyzed by cobalt tetraarylporphyrin supported on a polystyrene backbone. The catalyst slowly lost activity, presumably because of partial oxidation [369]. Derivatives of triphenylcyclopropyl nickel also catalyzed the reaction [370]. The photochemical conversion of norbornadiene to quadricyclane was sensitized by $Cu(Ph_3P)_2BH_4$ with 0.76 sensitizer yield and by $Cu(PPh_2Me)_3BH_4$ with a 0.54 sensitizer yield [371]. Substituted platinacyclobutanes rearranged readily with retention of stereochemistry (eq. 219). The process was thought to proceed by a concerted mechanism [372]. Palladium(II) complexes promoted the conversion of 5α-pregnane-3β,20β-diol to uraneliol (eq. 220) [373].

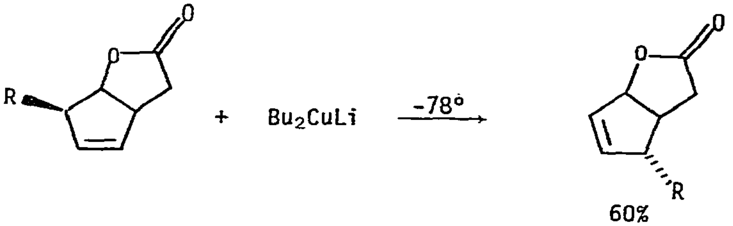


(219)



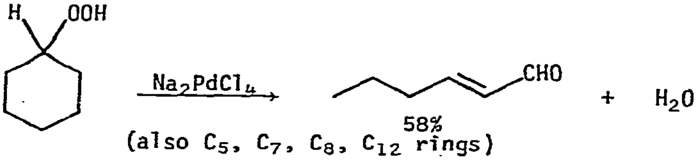
(220)

Bicyclic unsaturated esters rearranged by a process involving inversion by copper displacement, followed by a <u>syn</u> migration of R (eq. 221) [374]. Cyclic



(221)

hydroperoxides were decomposed by palladium(II) complexes to α,β-unsaturated aldehydes (eq. 222) [375]. The yields dropped as ring size increased. The use of optically active metal complexes to epimerize α-amino acids has been reported [376a].

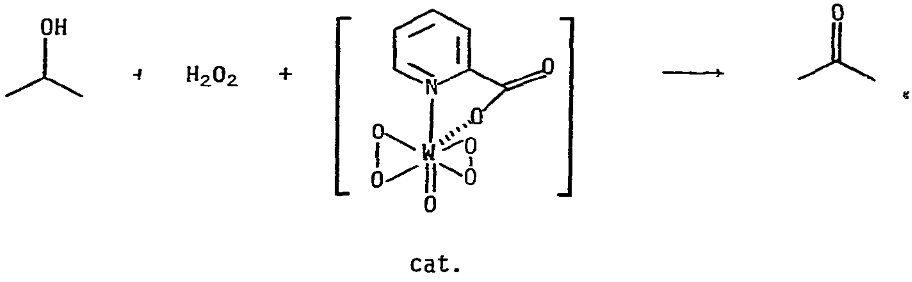


(222)

III.Oxidation

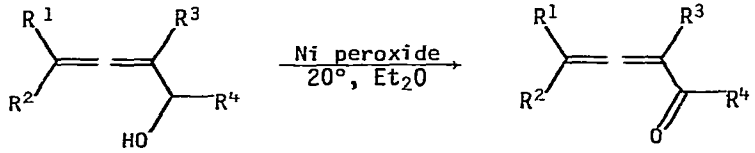
A. Oxidation of Alcohols

A wide range of secondary alcohols were oxidized to ketones by hydrogen peroxide in the presence of a tungsten catalyst (eq. 223). The rate limiting



(223)

step was thought to be a two electron transfer [376b]. Allenic alcohols were oxidized to allenic ketones by nickel peroxides (eq. 224) [377]. Secondary



(224)

60-90%

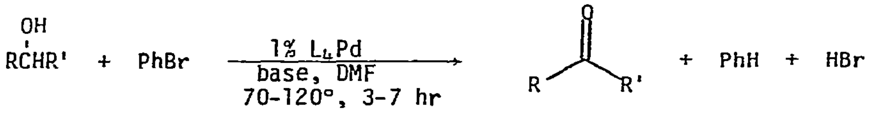
R^1 = H, Me, Et, Ph
R^2 = R^3 = R^4 = H, Me

alcohols were oxidized to ketones in high yield by benzoyl peroxide in the presence of nickel(II) bromide as catalyst. Primary alcohols were oxidized to aldehydes or acids. To prevent overoxidation an excess of nickel(II) bromide over alcohol (2.5) was required [378]. Persulfate catalyzed the oxidation of benzyl alcohol and benzaldehyde to benzoic acid, cyclopentanol to cyclopentanone, benzyl amine to benzonitrile, and aliphatic amines to acids in the presence of K_2RuO_4 as catalyst. Cyclohexene, t-butanol and dimethylacetylene dicarboxylate were inert [379].

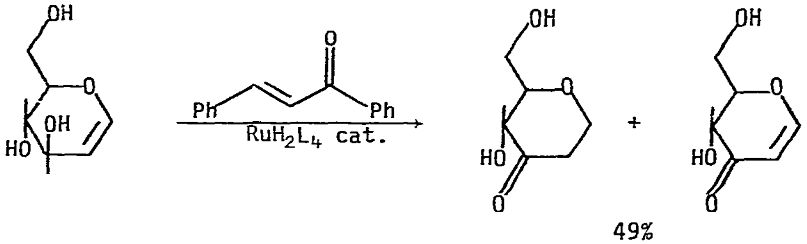
The enantioselective dehydrogenation of racemic 1-phenylethanol by chiral rhodium(I) phosphine complexes was examined in detail [380], as was the same process catalyzed by chiral ruthenium(II) phosphine complexes [381]. Cyclohexanol, isopropanol, diphenylcarbinol and α-phenethyl alcohol were oxidized to ketones using RhCl(COD)L and IrCl(COD)L as catalysts. Cyclohexene and cyclopentene were used as hydrogen acceptors [382].

Pyridinium dichromate in DMF or CH_2Cl_2 oxidized aliphatic, aromatic heterocyclic and terpenoid alcohols to ketones. Nonconjugated aldehydes and primary alcohols were oxidized to the corresponding acids [383]. Competing carbon-carbon bond cleavages observed in the CrO_3 oxidations of secondary alcohols were suppressed by carrying the oxidations out in acetone or in the presence of oxalic acid. Chromium(IV) species were implicated in the carbon-carbon bond cleavage reaction [384]. Alcohols, aldehydes, and triphenylphosphine were oxidized by $CrOCl_4^-$ [385].

The kinetics of the oxidation of aliphatic alcohols and diols by alkaline hexacyanoferrate(III) in the presence of ruthenium(III) chloride as catalyst were examined [386]. Primary alcohols coordinated to ruthenium(II) amine complexes were oxidized by oxygen or hydrogen peroxide to the corresponding acids [387]. Aqueous DMSO oxidized primary alcohols to aldehydes and secondary alcohols to ketones when irradiated in the presence of copper(I) or silver(I) salts. The yields were high [388]. Secondary alcohols were oxidized to ketones by bromobenzene using palladium(0) complexes as catalyst (eq. 225) [389]. Unsaturated sugars were allylically oxidized by chalcone using RuH_2L_4 as a hydrogen transfer catalyst (eq. 226) [391].

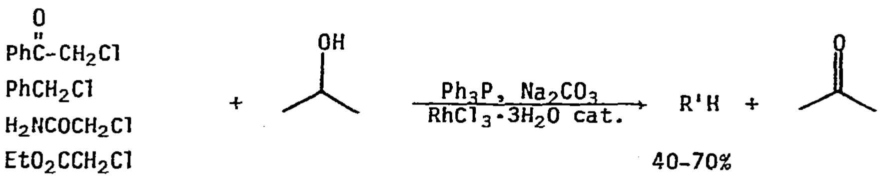


(225)



(226)

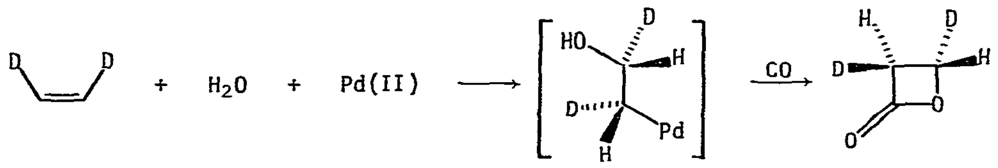
The kinetics of the oxidation of isopropanol and acetone by ceric sulfate in the presence of iridium(III) catalysts were studied [392]. Ethanol, methanol and isopropanol were oxidized by benzyl chloride, α-haloketones, and α-haloacid derivatives in the presence of rhodium(III) catalysts (eq. 227) [393].



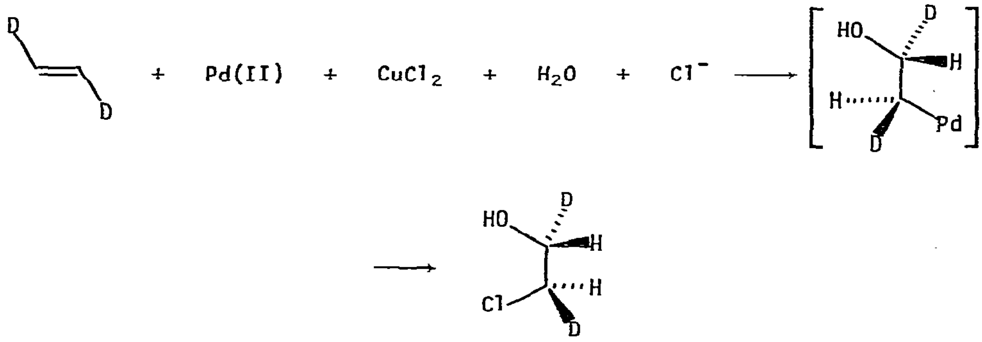
(227)

B.Oxidation of Alkenes and Alkynes.

The stereochemistry of the hydroxypalladation of ethene, the first step in the Wacker oxidation of ethene, was shown to be trans (eq. 228) [394], (eq. 229) [395]. The kinetics and mechanism of the gas phase catalytic oxidation of ethylene to acetaldehyde on a palladium(II)-V_2O_5/Al_2O_3 catalyst were studied [396]. Ethylene was oxidized to β-chloroethylethers by



(228)

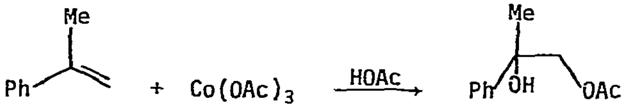


(229)

palladium(II) chloride-copper(II) chloride solutions (eq. 230) [397].

$$CH_2CH_2 + EtOH + PdCl_2 \xrightarrow{CuCl_2} EtOCH_2CH_2Cl \qquad (230)$$

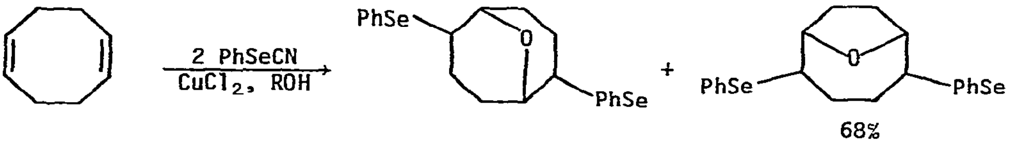
α-Methylstyrene was oxidized to the hydroxyacetate by cobalt(III) acetate in acetic acid (eq. 231). β-Methylstyrene was oxidized primarily to cinnamyl



(231)

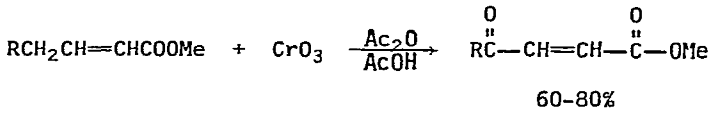
acetate by this reagent [398]. The oxidation of olefins in homogeneous and heterogeneous phases by oxygen and metal oxo species has been reviewed [399].

Cycloocta-1,5-diene was oxidized to mixtures of bicyclic ethers by phenyl selenium cyanide and copper(II) chloride in the presence of alcohols (eq. 232) [400]. Conjugated esters were oxidized to γ-keto-α,β-unsaturated esters by chromium trioxide in acetic anhydride (eq. 233) [401].



(232)

95:5 to 0:100 depending on ROH



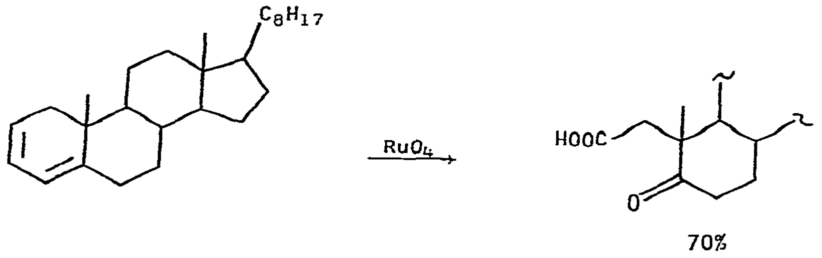
$$RCH_2CH{=}CHCOOMe + CrO_3 \xrightarrow[AcOH]{Ac_2O} R\overset{O}{\overset{\|}{C}}-CH{=}CH-\overset{O}{\overset{\|}{C}}-OMe \qquad (233)$$

60-80%

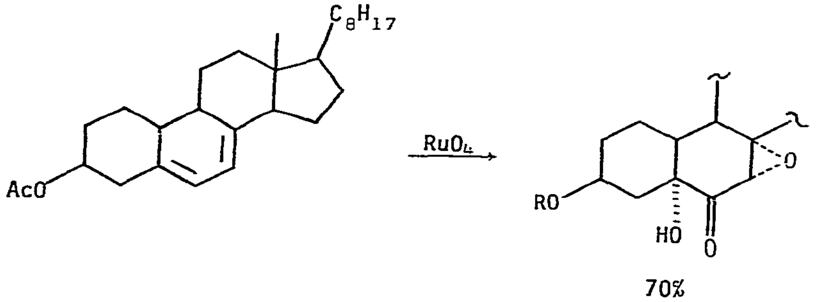
R = n-C_6, Et, n-C_3, n-C_4, n-C_5

Fluorinated or partially fluorinated olefins were oxidatively cleaved to carboxylic acids by ruthenium tetroxide (eq. 234) [402] and periodic acid, peracetic acid or sodium hypochlorite. Steroidal dienes were oxidatively cleaved by ruthenium tetroxide (eqs. 235,236) [403]. Secoestratetraenes were oxidatively cleaved by Jones oxidation (eq. 237) [404].

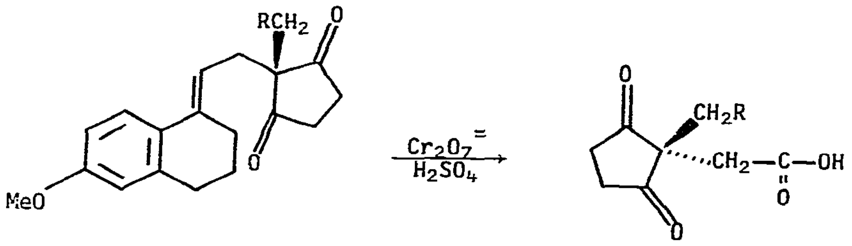
$$CF_3(CF_2)_5CH{=}CH(CF_2)_5CF_3 + NaIO_4 \xrightarrow{RuO_4} CF_3(CF_2)_5COOH \qquad (234)$$



(235)



(236)

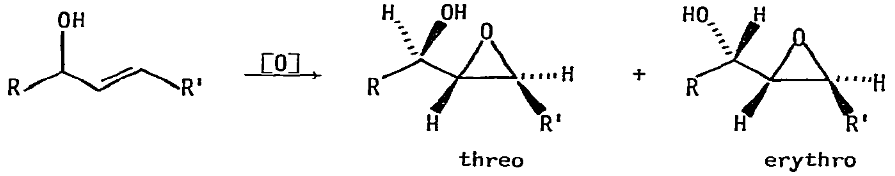


(237)

Cyclohexene and cycloheptene were oxidized to allylic phosphates by t-butylperoxyphosphates in the presence of copper salts [405]. Alkynes were oxidized at the triple bond by CrO_3, but both direct and α-oxidation products were obtained from CrO_2Cl_2, $CrO_2(OAc)_2$ and $CrO_2(OtBu)_2$ [406].

C. Epoxidations

The $VO(acac)_2$ catalyzed epoxidations of cyclic allylic alcohols by t-butylhydroperoxide gave cis epoxides preferentially from medium ring alcohols (5-9 membered). In contrast MCPBA gave exclusively trans epoxides with 8- and 9-membered alcohols [407]. The vanadium catalyzed epoxidation of trans-5-t-butyl-2-cyclohexen-1-ol was 34 times faster than the cis isomer, when alkyl hydroperoxides were used as the oxidizing agents. With the cis isomer, competing oxidation to the α,β-unsaturated ketone was observed [408]. The stereochemistry of the vanadium(V) and molybdenum(VI) catalyzed epoxidation of allylic alcohols by t-butylhydroperoxide has been corrected (eq.238) [409,410].

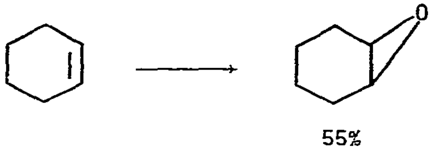


(238)

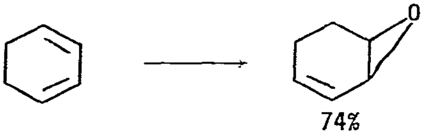
R = n-Pr, Me, Et, t-Bu	$VO(acac)_2$/t-BuOOH	60:40 erythro-threo
R' = Et, Md, n-Pr	$Mo(CO)_6$/t-BuOOH	40:60 erythro-threo
	MCPBA	30:70 erythro-threo

The rate constants and activation energies of the epoxidation of olefins by hydroperoxide in the presence of homogeneous molybdenum catalysts were measured [411]. The epoxidation of dimers from Diels-Alder reactions of cyclopentadiene and butadiene using hydrogen peroxide and molybdenum(VI) and tungsten(VI) catalyst was studied [412]. Rate and equilibrium constants for the epoxidation of cyclohexene by organic hydroperoxides in the presence of $Mo(O)_2DMF$ were measured [413]. This process was inhibited by alkali and and alkali earth metals such as Li, Na, K and Mg stearates [414]. Propylene was epoxidized by t-butyl hydroperoxide in the presence of a polymer supported bis(acetylacetonate)molybdenum(VI) oxide catalyst [415]. Other molybdenum(VI) catalysts active in the process were the naphthenate, the acetylacetonate and the molybdenum(V) 1,2-propyleneglycolates [416]. The mechanism of propylene epoxidation by hydroperoxides catalyzed by molybdenum(VI) naphthenate was studied [417] as was the catalytic degradation of α-phenethylhydroperoxide by molybdenum(VI) naphthenate [418].

Allyl chloride was epoxidized by organic hydroperoxides using $Mo(O)(OH)_3$ supported on silica gel [419]. Olefins were epoxidized by the reaction of iodosylbenzene in the presence of chloro-α,β,γ,δ-tetraphenylporphinatoiron(III) as a catalyst (eqs. 239,240) [420]. Cyclohexene was oxidized to 1,2-epoxy-3-cyclohexanol by oxygen in the presence of mixed rhodium(II) carboxylate-vanadium or molybdenum epoxidation catalysts [421].

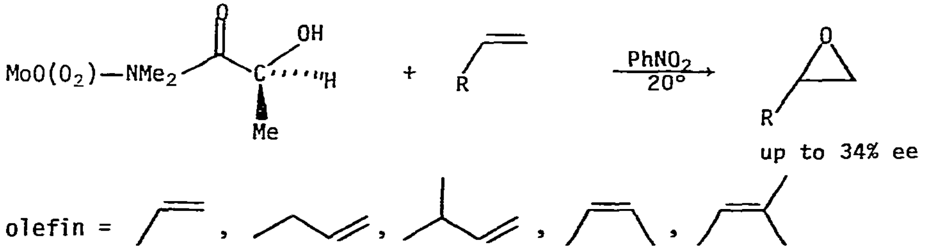


(239)



(240)

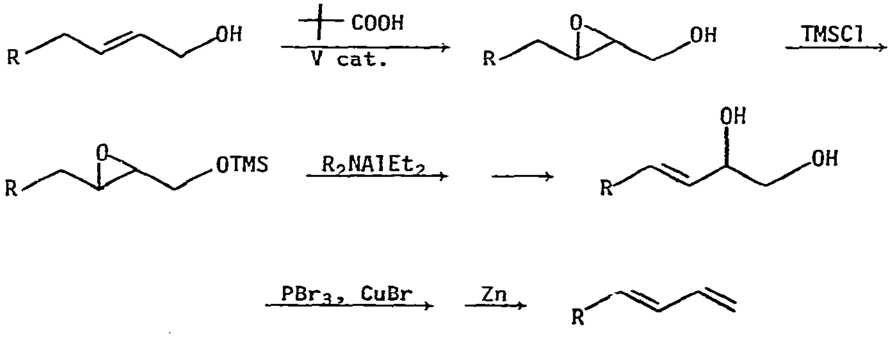
Phosphine and arsine complexes of rhodium(I) of the type $(Ph_3M)RhCl$ catalyzed the oxygenation of 1-octene by oxygen in a process involving direct oxygen transfer from a rhodium-O_2 complex [422]. Complexes of the type $MoO(O_2)_2L$ in which L is (S)-N,N-dimethylacetamide epoxidized olefins in up to 78% yield and with up to 34% enantiomeric excess (eq. 241) [423]. Olefins were



(241)

epoxidized in high chemical yield but low optical yield using t-butylhydroperoxide and an $Mo(O)_2acac$ catalyst in the presence of optically active diols. In this fashion squalene was converted to 3(S)-2,3-oxidosqualene in 31% yield and 14% optical yield. The optically active diol was tartrate [424].

Allylic alcohols were converted to 1,3-dienes in a process involving vanadium catalyzed epoxidation as a first step (eq. 242) [425]. The kinetics of the molybdate catalyzed epoxidation of allyl chloride by hydrogen peroxide have been studied [426]. Sodium molybdate also catalyzed the epoxidation of α,β-unsaturated acids by hydrogen peroxide [427].



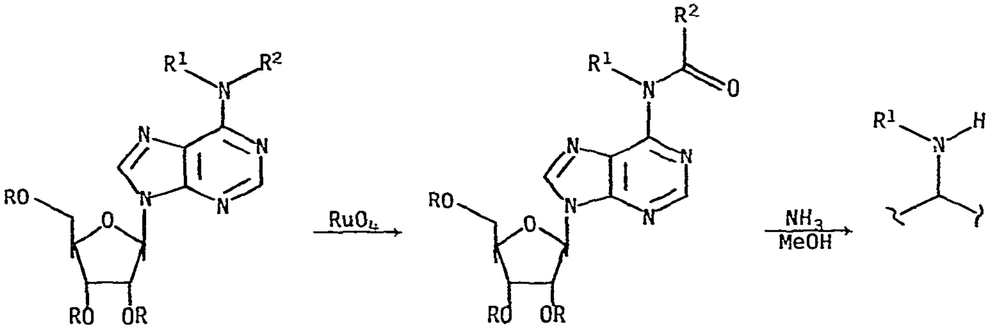
(242)

D. Oxidation of Ketones and Aldehydes.

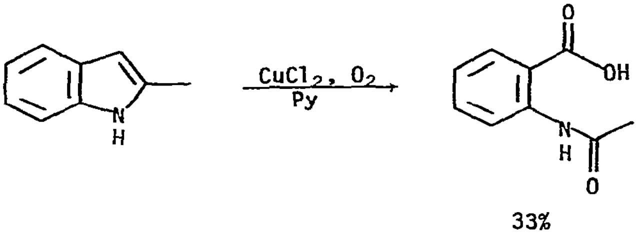
Aromatic aldehydes, furfural, and octanal were aminoxidized by reaction with ammonia and nickel peroxide in the presence of anhydrous sodium sulfate, producing the corresponding nitrile in 58-77% yield [428]. The kinetics of the ruthenium(III) catalyzed oxidation of ketones with potassium bromate in acid medium [429], the oxidation of linear aldehydes by $K_3Cu(OH)_2(H_4TeO_6)_2$ [430]. and the osmium(VIII) oxide catalyzed oxidation of benzaldehydes by alkaline hexacyanoferrate [431] have all been studied.

E. Other Oxidations.

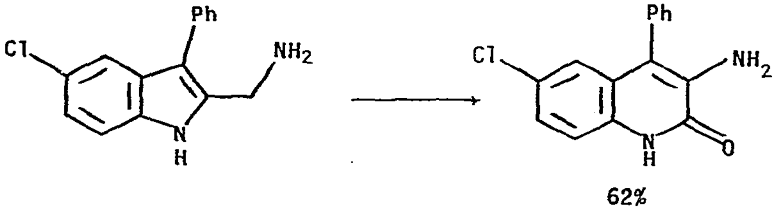
The structure and catalytic activities of cobalt complexes of the type $Co(OMe)_2OAc$ and molybdenum complexes of the type $H_2[Mo_2O_4L_2(H_2O)_2]$ in the homogeneous oxidation of hydrocarbons has been studied [432]. Saturated hydrocarbons were oxidized under both homogeneous and heterogeneous conditions by Cr(VI), Mn(III) and HNO_3 oxidants in the presence of ruthenium(IV) complexes [433]. Ruthenium tetroxide was useful for the monodealkylation of N^6,N^6-dialkyladenosines by an oxidation to the corresponding amide (eq. 243) [434]. Indoles were oxidatively cleaved to amido ketones by copper(II) chloride, oxygen and pyridine (eqs. 244, 245) [435]. α-Methylene ketones and esters were oxidatively cleaved at the α-bond to give carboxylates by $Ru(NH_3)_5NO^{+3}$



(243)

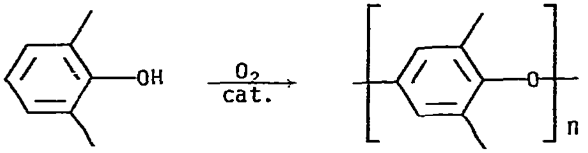


(244)

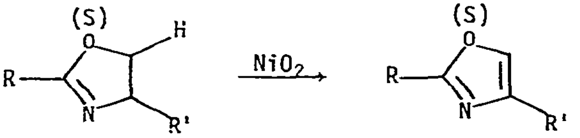


(245)

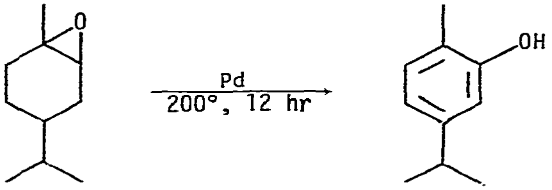
[436]. Aryl halides and nitrobenzene were oxidized to biphenyl and terphenyl by palladium(II) trifluoroacetate [437]. Phenols were oxidatively coupled to polyethers by reaction with oxygen in the presence of copper(II) complexes of octameric oligo[1-(N-phenylcarbamoyl)aziridine] (eq. 246) [438]. Oxazolines were converted to oxazoles, thiazolines to thiazoles, and other heterocycles were similarly dehydrogenated by nickel peroxide (eq. 247) [439]. Carvomenthene epoxide was converted to carvacrol by reaction with palladium at 200° (eq. 248). Platinum, ruthenium, and rhodium were less effective [440]. Benzoylformic acid was oxidatively decarboxylated by aqueous acidic solutions of iron salts [441]. The mechanism of the oxidation of ArSMe compounds by hydrogen peroxide in the presence of $VO(acac)_2$ as a catalyst was studied [442]. The oxidation of carbon monoxide over supported palladium catalysts was the topic of a dissertation [443]. Homogeneous catalytic oxidation was the subject of a review with 126 references [444].



(246)



(247)

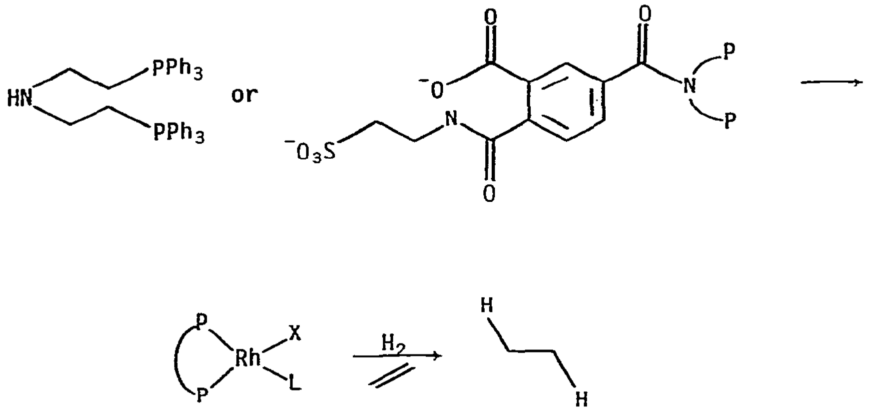


(248)

IV. Reductions

A. Olefins.

Hydrogenation of alkenes and alkynes catalyzed by metals and metal complexes has been reviewed (140 references) [445]. Water soluble diphosphine ligands were prepared, and rhodium(I) hydrogenation catalysts incorporating these ligands were used to reduce olefins and α-acetamidocinnamic esters in aqueous solution. These catalysts were as effective as normal catalysts were in organic solvents (eq. 249) [446]. Complexes of the type $[Rh(diphos)]^+$, and their alkene and



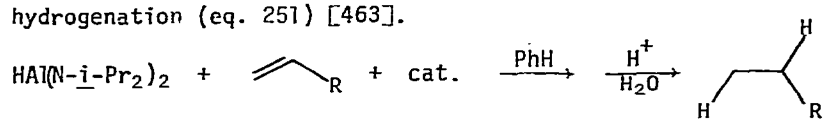
(249)

arene adducts were characterized, and the role of such complexes in homogeneous catalytic hydrogenation was studied [447]. Cationic rhodium(I) complexes containing norbornadiene and amines as ligands were prepared and examined as hydrogenation catalysts [448]. Reaction of isopropenyl cyclobutane with hydrogen in the presence of Pd/C, Pt/C or Rh/C catalysts resulted in reduction to isopropylcyclobutane, hydrogenolysis to 2-methylhexane and 2,3-dimethylpentane, double bond migration, and ring expansion to cyclopentanes [449]. Olefins were catalytically reduced when treated with hydrogen and mixed ligand rhodium(I) complexes of the type Rh(Cl)LL'L". The catalysts were prepared by reduction of $[RhCl(O_2)(PPh_3)_2]_2$ in ethanol in the presence of phosphines such as $P(C_6H_4X)_3$ [450]. The rate of hydrogenation of cyclohexene in benzene using $RhCl(PPh_3)_3$ as a catalyst was studied. The rate limiting step appeared to be formation of $RhH_2Cl(PPh_3)_2(C_6H_{10})$ [451]. The complex trans-$PtH(NO_3)(PEt_3)_2$ was a hydrogenation catalyst at 60° and 600 psi hydrogen pressure. The order of reactivity was 1-hexene > trans-2-hexene > trans-3-hexene. Dienes and electron deficient olefins reacted very slowly [452]. Dihydridoiridium diolefin complexes such as $[IrH_2(COD)L_2]PF_6$ were observed directly by pmr spectroscopy and appeared to be important intermediates in the catalytic hydrogenation of cyclooctadiene by these catalysts [453]. The stereochemistry of the reduction of bicycloolefins by $RhCl(PPh_3)_3$ catalysts was studied. Platinum(II) oxide catalysts gave the same results [454].

The stereoselectivity in the catalytic reduction of conformationally rigid cycloolefins such as 2-substituted-2-methylene-1,3-dioxanes using a wide range of heterogeneous catalysts was studied [455]. The trimeric ruthenium complex $[Ru_3O(OAc)_6(H_2O)_3]OAc$ reacted with hydrogen in DMF to produce a catalyst which reduced alkenes and alkynes. It was claimed that only one of the ruthenium atoms was active for both hydrogen activation and olefin coordination. The other two ruthenium acted merely as ligands for the one ruthenium that worked [456]. 1-Decene was hydrogenated in the presence of dimethylamine-borane and the catalysts $RuCl_2(PMe_3)(C_6H_6)$, $RuCl_2(PMe_3)_4$ and $RuCl_2(CO)_2(PMe_3)_4$[457].

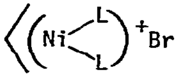
The complex $RuH_2(PPh_3)_4$ was used as a model to study the mechanism of olefin hydrogenation, isomerization, and hydrogen-deuterium exchange [458]. Mono- and disubstituted olefins were selectively reduced by sodium borohydride and cobalt(II) salts. The order of reactivity was mono > di > trisubstituted olefins. Alkynes were reduced to alkanes [459].

1-Hexene was reduced by $NaBH_4$, LiH, CaH_2 and $NaAlH_4$-reduced palladium [460]. The use of $AlH_3 \cdot Me_3N$, $AlHCl_2 \cdot Et_2O$, AlH_2NMe_2, $HAl(NMe_2)_2$, and $(AlHNHR)_n$ plus Cp_2TiCl_2, $Ti(oPr\text{-}i)_4$, $VO(O\text{-}Bu\text{-}\underline{n})_3$, $V(NEt_2)_4$, $Fe(acac)_2$ and $Co(acac)_3$ as catalysts for the reduction of olefins by hydrogen has been reported [461]. The results of a detailed study of the reduction of olefins by $HAl(N\text{-}Pr_2\text{-}i)_2$ in the presence of transition metal complexes are summarized in eq. 250 [462]. Sodium borohydride reduced $Rh(III)(DMG)_2X$ to produce a catalyst for olefin hydrogenation (eq. 251) [463].

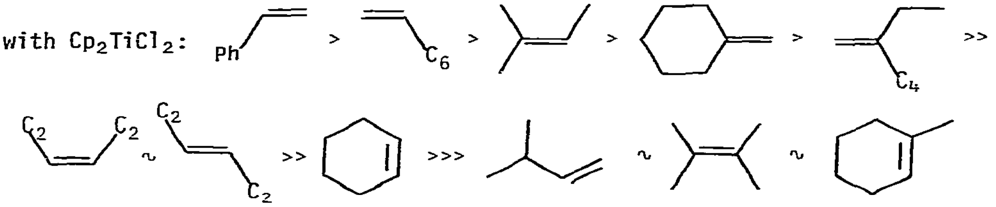


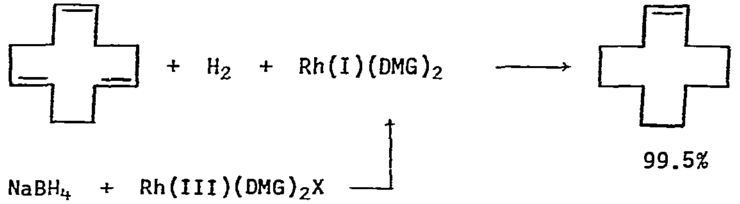
(250)

cat. = $TiCl_3$, $TiCl_4$, $CoCl_2$, $NiCl_2$, Cp_2TiCl_2, CpNiLCl, $(Et_3P)_2NiBr$,



with Cp_2TiCl_2:



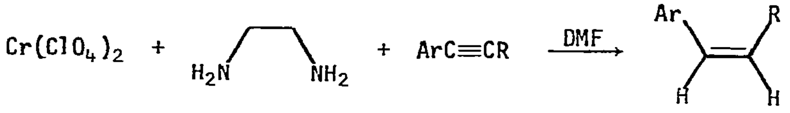


(251)

The 5-Z and 5-E isomers of Vitamin D_3 underwent regiospecific reduction of the $\Delta^{10(19)}$ double bond by treatment with Cp_2ZrHCl followed by protonation [464]. Olefins were both hydrogenated and isomerized over highly active nickel oxide catalysts [465]. The hydrogenation of ethylene over lanthanium transition metal perovskites was the topic of a dissertation [466].

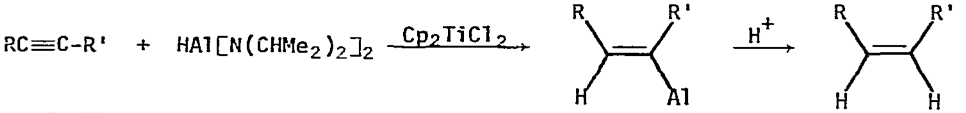
B. Alkynes

The use of metal clusters to catalyze the hydrogenation of triple bonds with organometallic compounds has been reviewed (36 references) [467]. The cluster $(CpFeCO)_4$ catalyzed the reduction of alkynes to alkenes at 130° and 100-1000 psi. Terminal alkynes were reduced over internal alkynes and electrophilic olefins such as methyl vinyl ketone were also reduced. The cluster appeared to remain intact [468]. Palladium(II) chloride in DMF was an effective homogeneous catalyst for hydrogenation of alkynes and conjugated dienes [469]. Palladium(II) complexes anchored to polymer supports were effective hydrogenation catalysts for the reduction of alkynes to alkenes. Conjugated acetylenes were reduced to conjugated olefins. Oxygen-containing solvents gave the most activity [470]. Acetylenes complexed to cationic iron species to give $CpFe(CO)_2(alkyne)^+$ complexes which were reduced to σ-vinyl species by hydride reagents [471]. Chromium(II) amine complexes reduced alkynes to cis-alkenes in good yield (eq. 252). Dialkyl



(252)

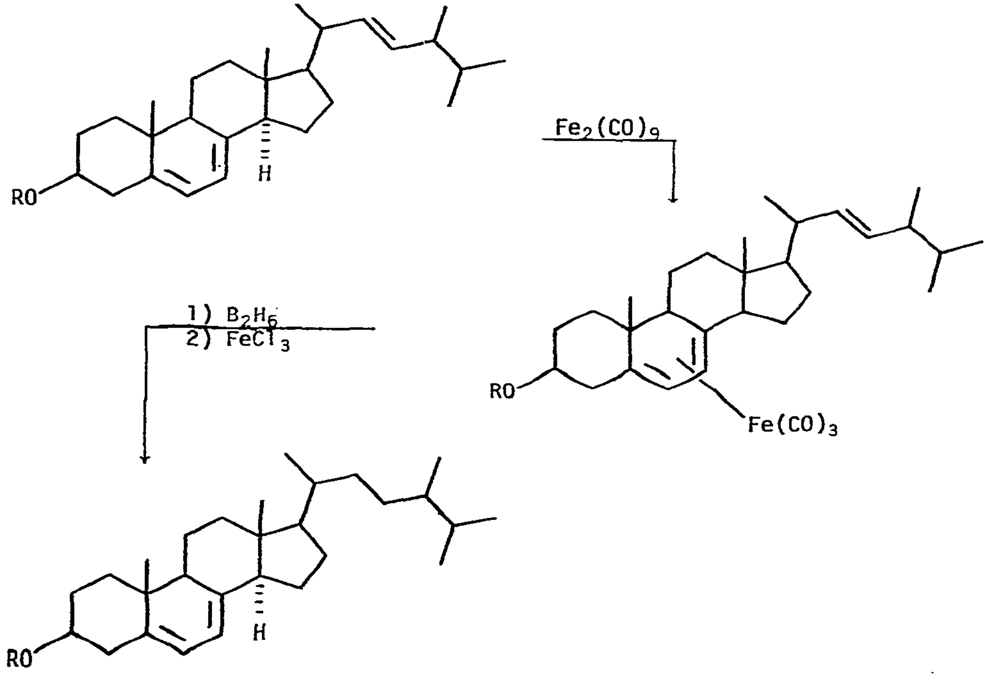
acetylenes did not react, but terminal and 1-phenyl-2-alkylacetylenes did [472]. Alkynes were stereospecifically reduced to cis alkenes by a Cp_2TiCl_2 catalyzed hydroalumination reaction followed by an aqueous quench (eq. 253) [473].



(253)

C. Dienes.

The dienes 1,5-cyclooctadiene and 1,4- and 1,7-octadienes were cleanly reduced to monoenes using π-allylpalladium halides as catalysts in dimethyl acetamide under hydrogen. The reaction selectively gave monoenes because the mechanism involved π-allylpalladium species not accessible from monoenes [474]. The 22(23) double bond of a steroidal diene was hydroborated in the presence of a 5,6-diene by complexation of the diene to $Fe(CO)_3$ (eq. 254) [475].

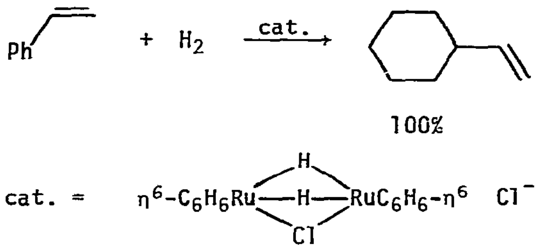


(254)

Both 1,3-pentadiene and cyclopentadiene were homogeneously hydrogenated in the presence of palladium(II) chloride-sodium borohydride stabilized by polyvinylpyrrolidone [476]. 2,4-Dimethyl-2,3-pentadiene was reduced to 2,4-dimethyl-1- and -2-pentene by triisobutylaluminum in the presence of nickel(II) acetylacetonate [477]. The product distribution from the reduction of dienes by hydridopentacyanocobaltate(II)-catalyzed hydrogenation was altered by addition of neutral surfactants capable of forming micelles [478]. Conjugated dienes were reduced to monoenes by $CoX(PPh_3)_3$ complexes activated by $BF_3 \cdot OEt_2$ [479]. Catalysts for the selective hydrogenation of dienes and acetylenes to hydrocarbons were produced by the reaction of $NiCl_2$, $PdCl_2$ or $RhCl_3$ with chelating nitrogen-containing ligands such as tyrosine, o-phenanthroline, or poly(ethylenimine) [480]. Chelating diphosphine complexes of nickel(II) halides catalyzed the reduction of 1,5,9-cyclododecatriene [481]. Homogeneous catalytic hydrogenation of conjugated dienes under micellar and phase transfer reaction conditions was the subject of a dissertation [482].

D. Aromatics

Catalytic hydrogenation of aromatic hydrocarbons has recently been reviewed (38 references) [483], as has pentamethylcyclopentadienylrhodium and iridium complexes as catalysts for olefin and arene hydrogenation (21 references)[484]. Arenes coordinated to molybdenum, ruthenium and titanium in a η^6 fashion were reluctant to undergo hydrogenation. It was suggested that for catalysis in arene hydrogenation η^4-arene bonding was important [485]. Benzene was reduced to cyclohexane under hydrogen using chelated amine complexes of nickel or cobalt [486]. The effect of pressure on the catalytic hydrogenation of aromatic hydrocarbons on rhodium catalysts was examined [487]. A hydridoruthenium-η^6-arene dimer complex was a very stable and very active catalyst for the reduction of arenes at 50° and 50 atmospheres hydrogen pressure (eq. 255) [488].



$$\eta^6\text{-}C_6H_6Ru\overset{H}{\underset{Cl}{-H-}}RuC_6H_6\text{-}\eta^6 \quad Cl^- \qquad (255)$$

PhOMe, PhOH, PhCOOMe, $PhCOCH_3$, PhCOPh, $PhNMe_2$ -- high yields

$PhNO_2 \longrightarrow PhNH_2$ 38%

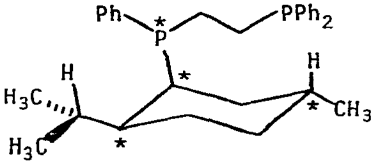
PhBr, PhCl, PhF, PhOPh -- not reduced

E. Asymmetric Catalytic Reduction

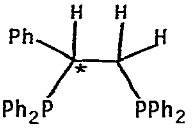
The following reviews or dissertations concerning asymmetric catalytic reduction have appeared: Catalytic Asymmetric Synthesis with Transition Metal Complexes (30 references) [489]; Asymmetric Homogeneous Catalysts for the Synthesis of

Amino Acids (92 references) [490]; Asymmetric Homogeneous Hydrogenation with Chiral Phosphine-Rhodium(I) Catalysts (dissertation) [491]; Asymmetrical Synthesis of Amino Acids using Rhodium Complexes (87 references) [492]; Asymmetric Synthesis, The Use of Chiral Rhodium-Diphosphine Complexes as Homogeneous Asymmetric Hydrogenation Catalysts (dissertation) [493].

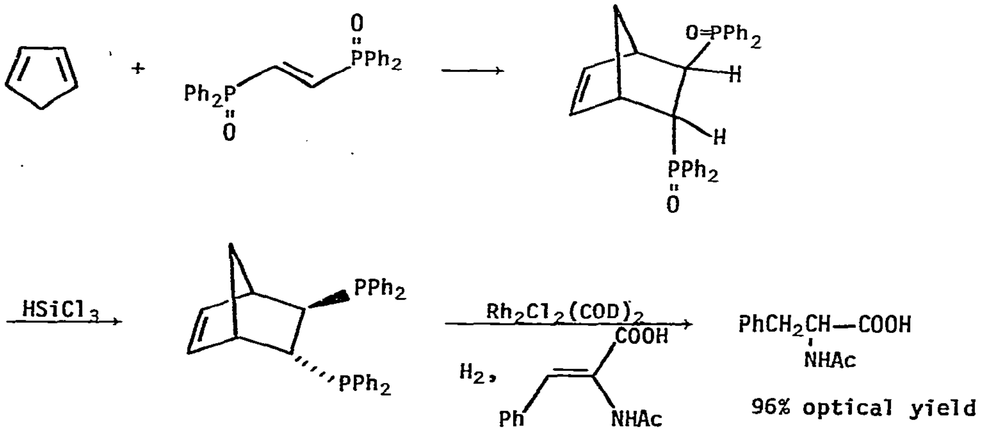
The synthesis of new chiral ligands for use in asymmetric reduction continued unabated. A phosphine ligand containing a chiral neomenthyl group, and chiral at phosphorus as well (1) was used with a rhodium(I) hydrogenation catalyst for the reduction of α-acylamidocinnamic acids. Diastereoisomers differing in configuration only at phosphorus gave different amounts of optical induction. One diastereoisomer gave 31-85% ee, while the other gave 42-56% ee [494]. The use of diphosphine made from mandelic acid (2) as a ligand on rhodium(I) complexes produced catalysts which reduced α-acetamidocinnamic esters and acids in 78-88% optical yields [495]. Other unsaturated acids gave low optical yields. Rhodium(I) carboxylate complexes of +-mandelic acid were used as catalysts for the reduction of unsaturated carboxylic acids. The best optical yield obtained was 13% [496]. A bridged bicyclic diphosphine ligand was synthesized and used as a ligand for rhodium(I) complexes. The resulting catalysts reduced α-acetamidocinnamic acids in high optical yield (eq. 256) [497]. Similarly rhodium(I) complexes containing the terpenoid bridged bicyclic diphosphine ligand were catalysts for reduction of these same substrates in 94-95% ee (eq. 257) [498]. The catalytic activity of chiral phosphines 3 and the corresponding



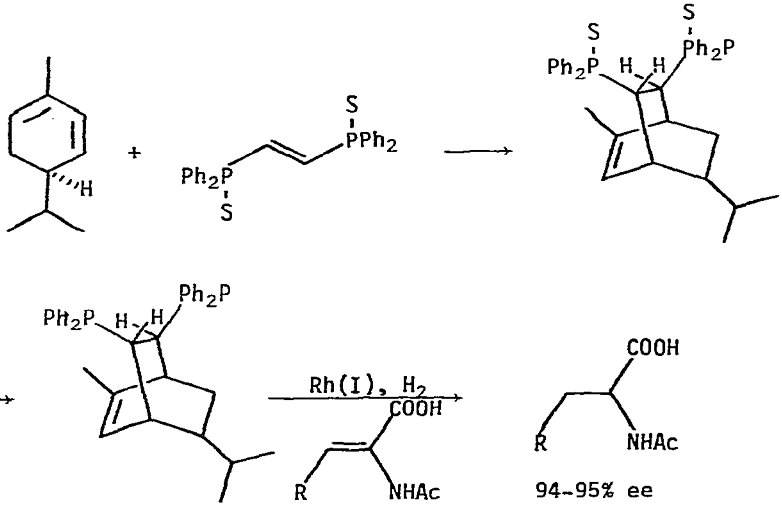
1



2

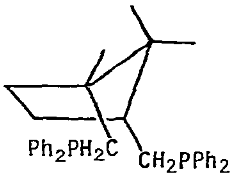


(256)

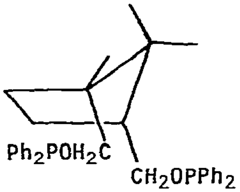


(257)

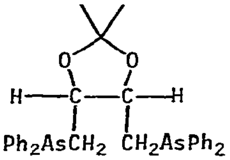
phosphinites 4 in the rhodium(I) catalyzed reduction of prochiral olefins was compared. The phosphines gave the highest optical yields with acids while the phosphinites were best for esters. Both gave only low optical yields [499]. The arsine analog of DIOP (5) was prepared, and catalytic hydrogenations using rhodium(I) complexes of the ligand were studied. In the reduction of α-acetamidocinnamic acids, the optical yields were lower than obtained with DIOP, and the products were of opposite chirality. The arsine catalysts were comparable to DIOP for the hydrosilation of ketones, giving up to 42% optical yield [500].



3



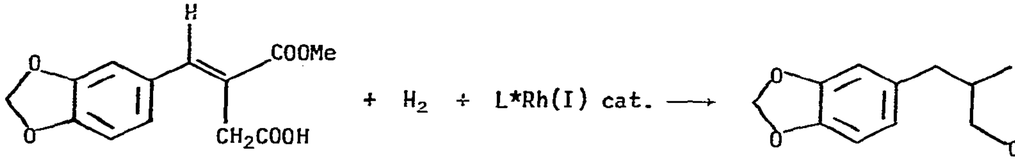
4



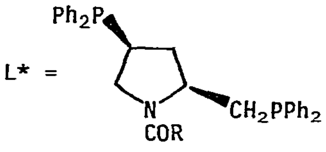
5

The chiral pyrrolidinephosphine complex 6 was used as a ligand for rhodium(I) hydrogenation catalysts. The resulting complexes were used in the asymmetric synthesis of α-acetamidophenylacetic acids, salsolidine pentolactone, β-amino and 1,2-dicarboxylic acids in nearly quantitative yields [501]. The same catalyst was used to produce chiral lignans (eq. 258) [502].

Chiral rhodium(I) complexes of ferrocenylphosphine 7 were used to catalyze the reduction of α-acetamidocinnamic and acrylic acids, ketones, and imines, giving high optical yields in some cases [503]. The chiral 1,2-diaminocyclohexane 8 was used as a ligand for rhodium(I) complexes used to catalyze the reduction of α-acetamidocinnamic acids. It was found that methylation

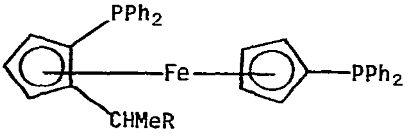


(258)

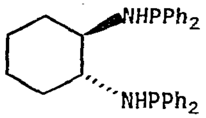


5

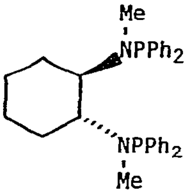
of the nitrogen to give 9 changed the chirality of the reduction products from (R) with 8 to (S) with 9 [504,505].



7

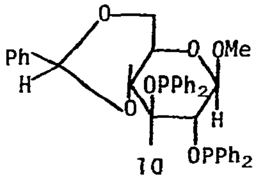


8

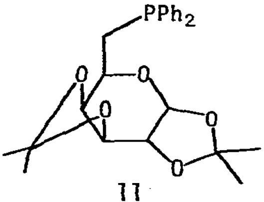


9

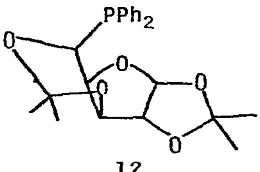
Sugar-derived phosphines and phosphinites have also been used as ligands in rhodium(I) catalyzed reductions of α-acetamido unsaturated carboxylic acids. With ligand 10, the β form was more active than the α, the (S) enantiomer was obtained in up to 91% ee from acids and 88% ee from esters, the neutral rhodium(I) complexes were less active than the cationic complexes, and if the substrate lacked the α-acetamido group, no reduction occurred [506]. Ligands 11-15 [507] and 16-18 [508] produced active chiral rhodium(I) reduction catalysts.



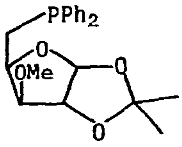
10



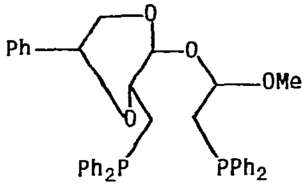
11



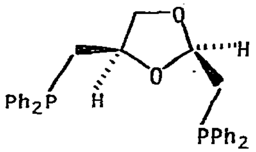
12



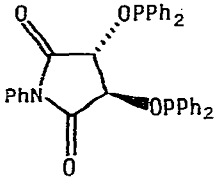
13



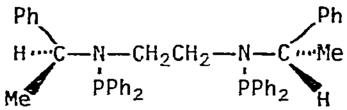
14



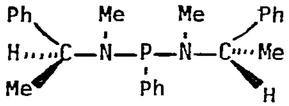
15



16

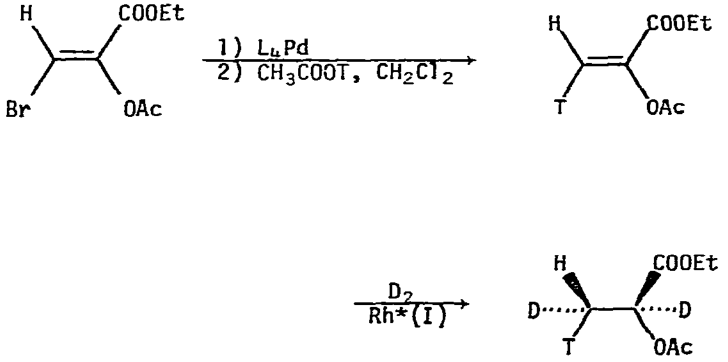


17



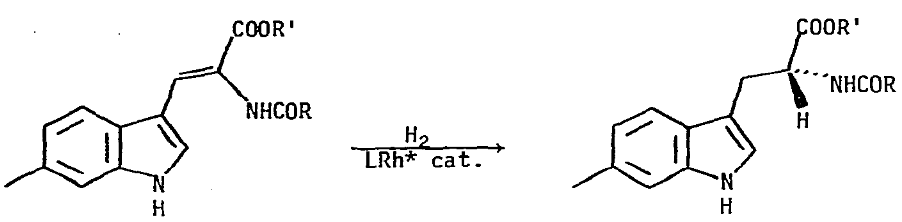
18

REDAL reduced prochiral olefins to saturated compounds in 7-15% ee in the presence of Cp_2TiCl_2 complexes containing (-)-menthylcyclopentadienyl or (+)-neomenthylcyclopentadienyl groups [509]. All twelve possible permutations of label and chirality of chiral methyl-chiral lactic acid were accessible by R-prophos Rh^+ or S,S chiraphos Rh^+ catalyzed reductions of the tritiated olefin (eq. 259) [510]. Chiral tryptophans were produced by asymmetric reduction of the corresponding unsaturated acid (eq. 260) [511].



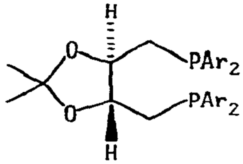
(259)

81% optical purity

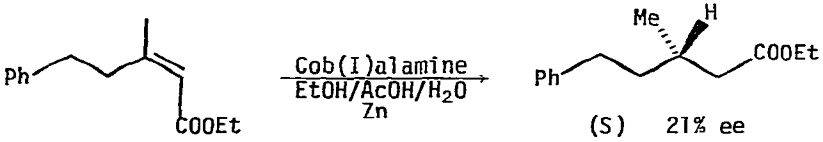


(260)

60%
82% ee

L =


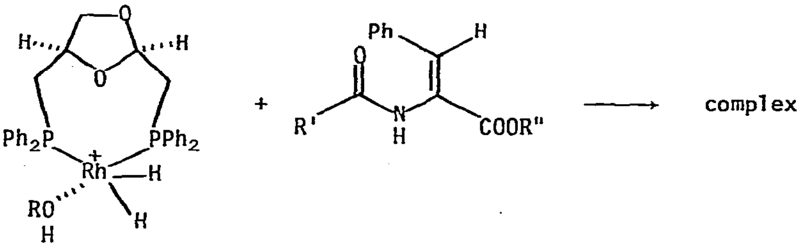
Chiral Cob(I)alamine catalyzed the reduction of 3-methyl-5-phenylpent-2-enoic esters by zinc in ethanol/acetic acid/water solutions in high chemical yield and up to 21% ee. The Z isomer reduced to the (S) saturated product while the E isomer gave the (R) saturated product. The free acid, the ethyl ester and disubstituted amides reacted as well (eq. 261) [512,513].



(261)

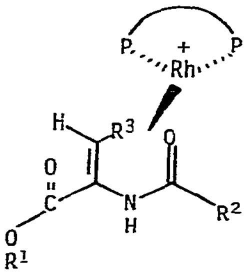
(S) 21% ee
85% yield

A significant number of studies have addressed the mechanism of optical induction by chiral catalysts. The selectivity, isotope effect, and chiral recognition in olefin-rhodium(I) π-complexation has been probed [514]. Using ^{31}P nmr the reaction of the chiral rhodium complex in equation 262 with α-acetamidocinnamic esters was followed. The addition of triethylamine was shown

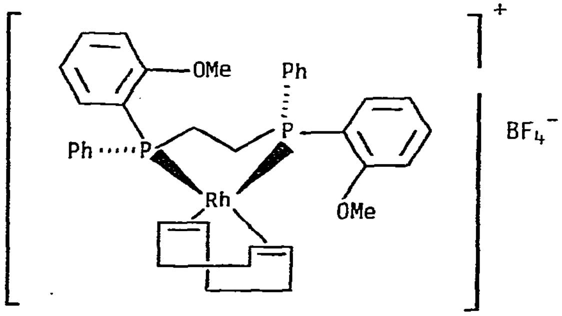


(262)

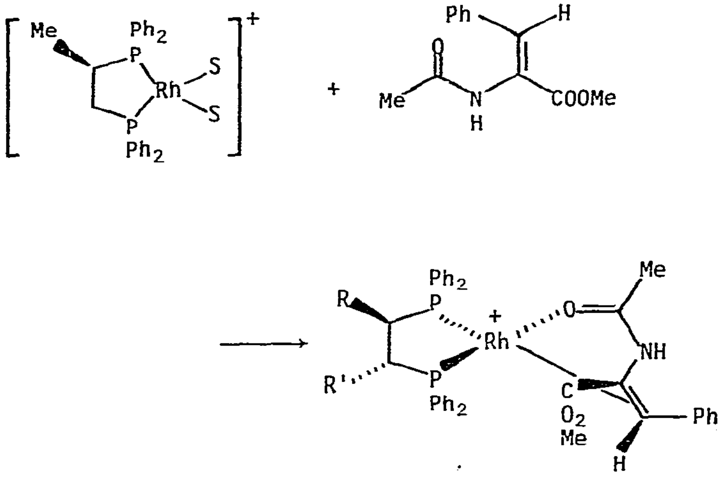
to greatly increase the rate of substrate complex formation [515]. By ^{13}C nmr the mode of bonding of enamide ester substrates to rhodium(I) complexes was claimed to be as in 19 [516]. By ^{31}P nmr the reaction in equation 263 was shown to give two complex isomers, which were regioisomers, not stereoisomers [517]. Asymmetric homogeneous hydrogenation of Z-α-N-methylacetamidocinnamic acids and esters by chiral rhodium(I) complexes of DIOP and its carbocyclic analog has been studied [518].



19



20

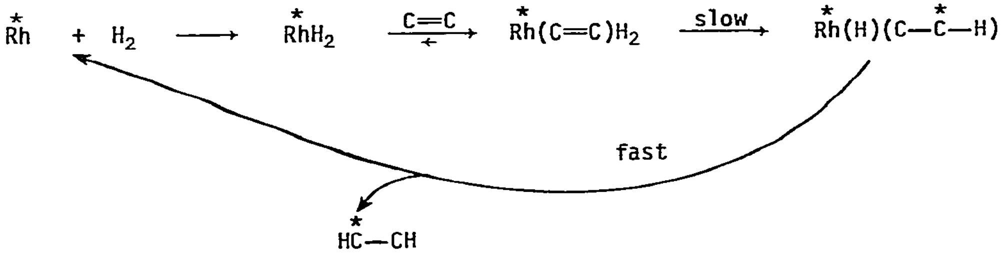


(263)

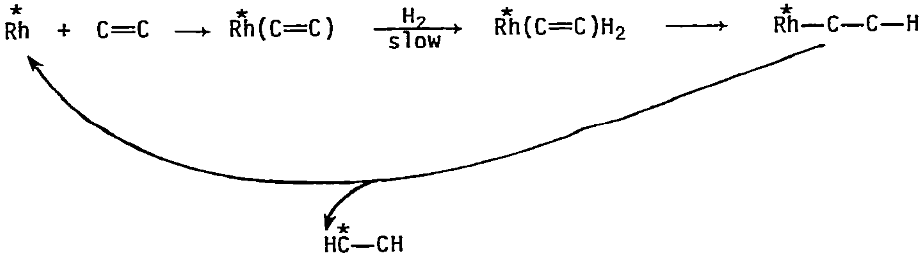
(a) R = Me; R' = H
(b) R = H; R' = Me

The reduction of α-acetamidocinnamic acid by hydrogen in the presence of neutral and cationic rhodium(I) complexes of BPPM, (-)DIOP and DIPAMP was studied as a function of hydrogen pressure and added triethylamine. At one atmosphere the (R) product formed in 60-90% ee, but at one hundred atmospheres pressure the (S) isomer was formed in 8-15% ee. In the presence of triethylamine, the (R) isomer always predominated. The high and low pressure mechanisms proposed are shown in equations 264 and 265 [519].

Using ^{31}P and ^{1}H nmr studies of the complexes $[\overset{\frown}{L^{*}\quad L}]Rh(S—S')^{+}ClO_4^{-}$ where



(264)

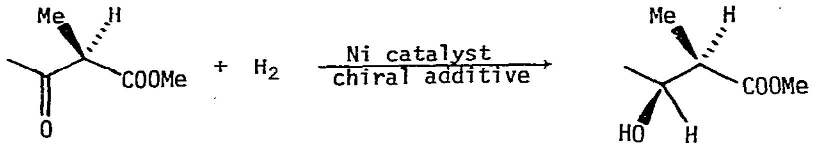


(265)

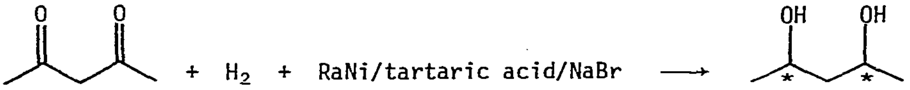
L* L was BPPM and PPPM, and S—S' was itaconic acid and α-acetamidocinnamic acid, claims of regioselective and stereoselective complexation of these bidentate substrates leading to asymmetric induction were made [520]. The conformations of pyrrolidine phosphine complexed (structure 6) to rhodium(I) were examined by ^{31}P nmr studies [521]. Complex 20 was used as a catalyst for the reduction of itaconic acid. A bidentate coordination of substrate was thought necessary for good asymmetric induction. Itaconic acid was a poor substrate for this catalyst because hydrogen bonding (dimerization) prevented this. The pyrrolidine phosphine ligand (6) was thought to work well with itaconic acid by breaking up the hydrogen bonding [522]. Olefins were reduced using mixed hydride complexes of rhodium(I), triphenylphosphine, and d-α-methylbenzyl amine. Formation of these mixed complexes was monitored by CD, ^{31}P nmr, and electronic spectra [523]. The dependence of enantioselectivity on the structure of chiral ligands in aminophosphine rhodium(I) catalysts for asymmetric hydrogenation was studied [524].

Rhodium(I) complexes of dimenthylphenylphosphine anchored to a polystyrene support catalyzed the reduction of α-acetamidocinnamic acids in 60% optical yields [525]. The DIOP ligand was attached to graphite, and rhodium(I) catalysts of this supported ligand were used to reduce α-acetamidocinnamic acids and to hydrosilate ketones. Low optical yields were obtained [526].

Raney nickel catalysts modified by the addition of chiral compounds such as tartaric and glutaric acid, and valine were used to reduce β-ketoesters. Up to 56% optical yields were obtained (eq. 266) [527]. Similar catalysts were used to reduce acetylacetone to the diol (eq. 267) [528] and methyl aceto-



(266)



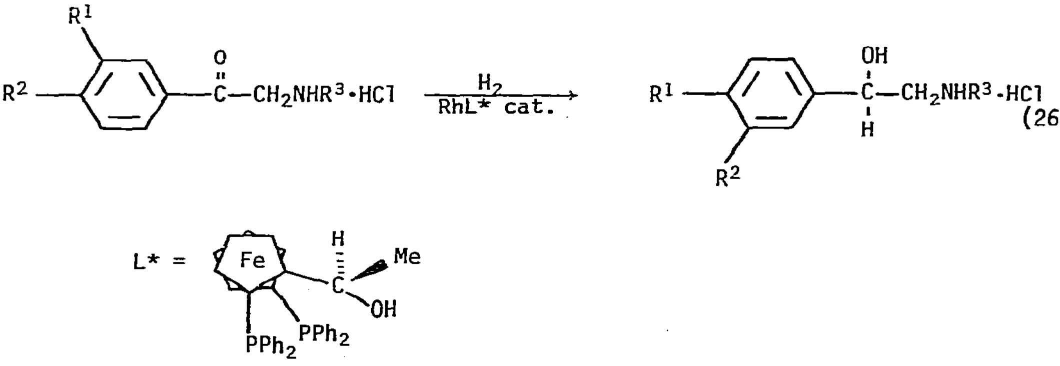
2R,4R
65% isolated yield
100% optical purity

(267)

acetate to methyl hydroxybutyrate [529]. Similar substrates were reduced using Raney copper modified with chiral amino acids [530].

Methyl pyruvate was reduced to the (+) α-hydroxyester in 78% optical yield using platinum on carbon as a catalyst in the presence of cinchondine [531]. Methyl benzoyl formate was reduced by the same catalyst in 92% yield and 82% optical yield [532]. Dehydroalanine residues in cyclodipeptides were asymmetrically reduced over Pd/C catalysts with 85-98% chiral induction [533]. Azlactones were asymmetrically reduced over a palladium catalyst in the presence of (S)-α-phenethylamine [534].

Prochiral benzophenones were reduced to the alcohols in up to 26% ee using chiral DIOP rhodium(I) complexes to catalyze hydrosilation of the ketone [535]. Both rhodium(I) and ruthenium(II) complexes of DIOP and (+)-$Ph_2PCH_2CHMePPh_2$ catalyzed the asymmetric reduction of aryl ketones to alcohols [536]. Chiral rhodium(I) complexes catalyzed the reduction of α-amino-1-arylketones in up to 95% enantioselectivity (eq. 268) [537].



(268)

R^1, R^2 = OMe, H

F. Solid Supported Reduction Catalysts.

Polymer supported transition-metal organometallic compounds as hydrogenation catalysts has been reviewed (15 references) [538]. Infrared and kinetic studies of polymer-bound rhodium cluster catalysts for hydrogenation [539], and preparation and characterization of polymer-bound tetrairidium cluster catalysts for olefin hydrogenation [540] were both topics of dissertations.

Anthanilic acid was anchored to Amberlite XAD-4 polystyrene beads, treated with rhodium(III) chloride, followed by reduction with sodium borohydride. ESCA showed the species to be a rhodium(I) complex. This complex catalyzed the reduction of olefins, aromatics, carbonyls, nitriles, and nitro groups, was insensitive to poisons, and had a long lifetime [541]. Rhodium(I) compounds were complexed to phosphinated silica to produce an air insensitive reusable catalyst for the reduction of olefins [542]. Cyclopentadiene groups were synthetically attached to a 20% divinylbenzene-polystyrene macroporous polymer, which was then reacted to produce polymer-bound $CpRh(CO)_2$ and $CpCo(CO)_2$ complexes. The rhodium complex catalyzed olefin, ketone, and aldehyde reduction, olefin isomerization and disproportionation of cyclohexadiene, turning black in all instances. Both the cobalt and rhodium species catalyzed hydroformylation reactions [543]. Phosphine ligands were attached to a polymer backbone through long (C_{10}) hydrocarbon chains. Rhodium(I) complexes of these supported ligands catalyzed the reduction of 1-octene, and were equal to or superior to the homogeneous system. The idea was to make the catalyst sites more accessible to reactants by removing it from close proximity to the polymer [544]. Swelled-mica-type silicates were intercalated with $Rh_2(OAc)_3^+$ and triphenylphosphine to produce intercalated L_nRh^+ type catalysts. In methanol 1-hexene was reduced without rearrangement. These intercalated catalysts discriminated between large and small alkynes, compared to homogeneous catalysts, producing <u>cis</u> alkenes [545]. Rhodium(I) complexes of $(EtO)_3Si(CH_2)_3$-PPh_2 were prepared, and the catalytic activities compared with those of silica anchored catalysts. The supported catalysts were more active and more stable [546].

Amino-containing silica gels were treated with Na_2PdCl_4, and the resulting complexes were used as reduction catalysts for allylbenzene, cyclopentadiene, propargyl alcohols and Schiff bases [547]. Polystyrene-attached bipyridine was treated with palladium acetate, and the resulting supported complex catalyzed the reduction of alkynes preferentially to alkenes. Alkenes were reduced more slowly, but also isomerized. Ketone, nitro, halo and benzyl alcohol groups were inert [548,549]. Aqueous solutions of K_2PdCl_4 were exchanged onto basic, OH group-containing ion exchange resins, then reduced. The activity of the resulting catalyst for the reduction of allyl alcohol to propanol depended on the amount of surface OH remaining. Addition of HCl decreased the catalytic selectivity to that of Pd/C, while addition of NaOH increased it [550]. Enynes were selectively reduced to monoenes over polymer supported complexes of palladium phosphine/stannous chloride [551]. A highly active olefin hydrogenation catalyst was prepared by adsorbing palladium(II) chloride and poly-γ-aminopropylsiloxane on fumed silica gel [552]. Palladium catalysts on sulfide and metallic forms of alumina were studied by exoelectronic emission spectroscopy [553]. Silica supported palladium, rhodium, and iridium catalysts were shown to reduce acetylene directly to ethane by carrying out the hydrogenation in the presence of ^{14}C labelled ethene and showing no ^{14}C in the ethane produced [554].

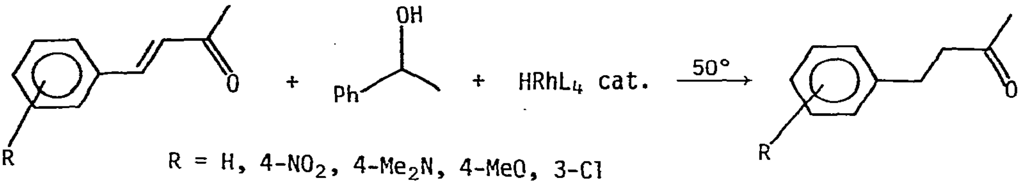
Platinum on nylon catalyzed the reduction of benzene only slowly, but reduced cyclohexene rapidly. It was claimed that with this catalyst benzene coordinated in a dihapto fashion [555].

Iron pentacarbonyl was coordinated to triphenylphosphine groups attached to a 1% crosslinked polystyrene resin, and the resulting solid supported complex was activated (stripped of CO) by photolysis or by heating. The material catalyzed the isomerization of 1-pentene, and the hydrosilation of 1-pentene to n-pentane, triethyl-n-pentylsilane, cis- and trans terminal vinyl silanes and the corresponding allylic silane. The activity of this supported catalyst was comparable to that of the related homogeneous catalyst [556]. The iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ were physisorbed on γ-alumina under air-free conditions to give highly dispersed supported catalysts of potential use for olefin hydrogenation and hydroformylation [557]. Cyclopentadiene groups were attached to 1% crosslinked microporous polystyrene and 3% crosslinked macroporous polystyrene, either as phenyl cyclopentadiene or benzyl cyclopentadiene groups, and $Co(CO)_2$ groups were attached to give polymer supported "$CpCo(CO)_2$" complexes. Irradiation or vacuum pyrolysis removed all of the CO's (the process was reversible) to give supported "CpCo" catalysts which reacted with a 3:1 mixture of carbon monoxide and hydrogen at 200° to give a mixture of straight chain hydrocarbons in a Fischer-Tropsch type process. This same catalyst was relatively inactive in cyclotrimerization of alkynes and hydroformylation reactions. Since $CpCo(CO)_2$ was not active in Fischer-Tropsch chemistry under the same conditions, polymer support led to novel activity [558]. Site separation of polymer bound ligands was probed by preparing a number of chloromethylated resins by copolymerization, incorporating imidazole, then complexing $Co(DPGB)_2 \cdot 2MeOH$ through coordination of a polymer-bound imidazole at the axial position. ESR studies showed both 1:1 and 1:2 cobalt-to-imidazole adducts, depending on the polymer [559].

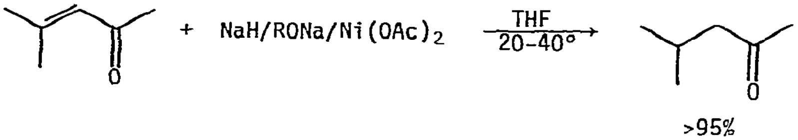
Silica gel was treated with $CpTiCl_3$, then butyllithium to produce a solid supported catalyst for olefin hydrogenation [560]. Both silica gel supported $TiCl_4$ and polystyrene-bound Cp_2TiCl_2 were catalysts for the hydroalumination of olefins [561]. Finally, bimetallic clusters were supported on silica gel and polystyrene, and then studied as ethylene hydrogenation catalysts. The systems studied were: $Fe_2Pt(CO)_8(PPh_2\text{-}\textcircled{P})_2$; $RuPt_2(CO)_5(PPh_2\text{-}\textcircled{P})_3$; $HAuOs_3(CO)_{10}\text{-}L\text{-}\textcircled{Si}$; $H_4Ru_4(CO)_{12-x}L\text{-}\textcircled{Si}$; $H_2Os_3(CO)_9\text{-}L\text{-}\textcircled{Si}$ [562].

G. Conjugate Reduction of α,β-Unsaturated Carbonyls.

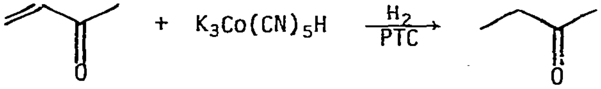
The rhodium(I) complex $Rh(H)(PPh_3)_4$ catalyzed the transfer hydrogenation of conjugated enones to saturated ketones, using α-phenethyl alcohol as the hydrogen source (eq. 269) [563]. The mixed reducing agent prepared from NaH, RONa and $Ni(OAc)_2$ selectively reduced conjugated enones in a 1,4 fashion. Magnesium bromide increased the activity of this system. In contrast the system NaH, RONa, $ZnCl_2$ reduced conjugated enones in a 1,2 fashion to give allyl alcohols (eq. 270) [564]. Under phase-transfer conditions $K_3Co(CN)_5H$ reduced a number of conjugated systems (eqs. 271-272). The catalyst was long-lived and gave many turnovers because of the phase transfer conditions used [565].



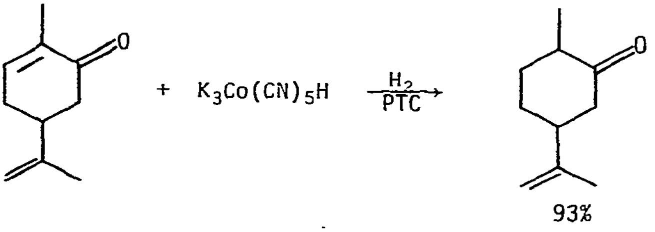
(269)



(270)

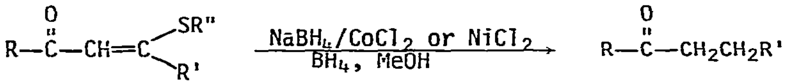


(271)



(272)

Cinnamaldehyde was reduced to a mixture of β-phenylpropionaldehyde and its dimethylacetal by hydrogenation over palladium catalysts in methanol [566]. Methyl linoleate was reduced to the saturated ester by dicobalt octacarbonyl and hydrogen [567]. Dimethylmaleate was isomerized and reduced to dimethylsuccinate using $H_4Ru_4(CO)_8[P(OEt)_3]_4$ as a catalyst [568]. Methylene succinic acid was reduced using a number of chelating diphosphine complexes of rhodium(I) of the type $HRh(Ph_2P\text{-}(CH_2)_nPPh_2)$ as catalysts. Catalytic activity increased as n increased from 1 to 4 [569]. Finally, β-thio-α,β-unsaturated ketones were reduced to saturated ketones by sodium borohydride and cobalt(II) or nickel(II) chloride (eq. 273) [570].



$$R-\overset{O}{\overset{\|}{C}}-CH{=}C\begin{matrix}SR''\\R'\end{matrix} \xrightarrow[BH_4,\ MeOH]{NaBH_4/CoCl_2\text{ or }NiCl_2} R-\overset{O}{\overset{\|}{C}}-CH_2CH_2R' \qquad (273)$$

R = Ph, Me

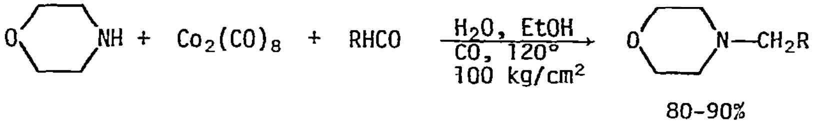
R' = Me, H, Ph

R" = Et, n-Pr, Ph

H. Ketones and Aldehydes.

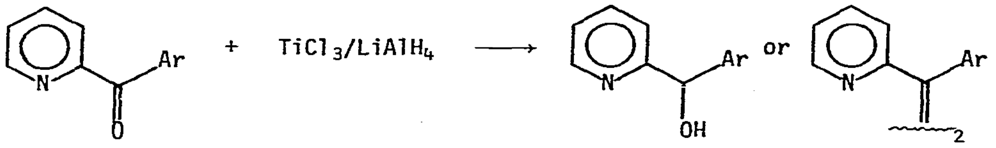
The effect of phosphine structure in the catalysts $RhCl(PR_3)_2(CO)$ on the catalytic activity in the reduction of acetone to isopropanol was studied [571]. Ketones were selectively hydrogenated in the presence of olefins by the rhodium(I) catalyst $[Rh(2,2'\text{-bipyridine})_2]^+$ [572]. Aliphatic, aromatic, and cyclic ketones were reduced to the corresponding alcohols at 160°/15 bar in the absence of solvent using $RuCl_2(PPh_3)_3$, $RuH_2(CO)(PPh_3)_3$ and $Ru(CF_3CO_2)_2(CO)(PPh_3)_2$ as homogeneous catalysts [573]. Similar ruthenium catalysts reduced aldehydes to alcohols [574].

Aldehydes were reductively aminated in aqueous ethanol using dicobalt octacarbonyl as catalyst, and carbon monoxide-water in place of hydrogen (water gas shift conditions) (eq. 274) [575]. 2-Aryl 2-pyridyl ketones were reduced or reductively coupled by titanium(III) chloride and lithium aluminum hydride, depending on conditions (eq. 275) [576]. Acetophenone was reduced to the alcohol using catalysts produced from $Rh(Cl)(PPh_3)_3$ and triethylamine, or $[Rh(NBD)Cl]_2$, triethylamine, and phosphines. The triethylamine was required for activity. With chiral phosphines, up to 35% ee was obtained [577]. A procedure for the reduction of ketones in the presence of aldehydes, and the reduction of conjugated aldehydes in the presence of saturate aldehydes is described in equations 276 and 277 [578]. Both saturated and conjugated ketones were reduced to alcohols by transition metal complexes of heterocyclic amine borane complexes (eq. 278) [579].

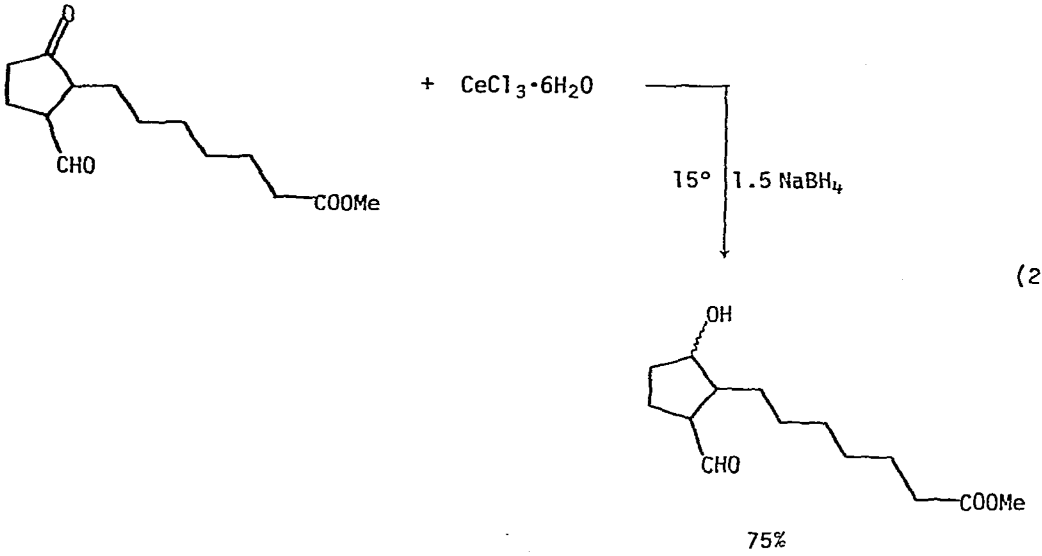


(274)

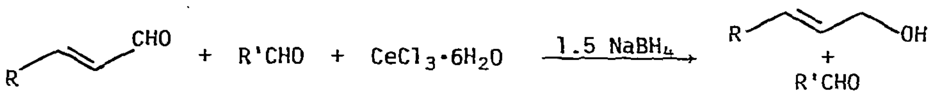
R = H, CH_3, Ph, p-tolyl, p-anisyl, p-chloro



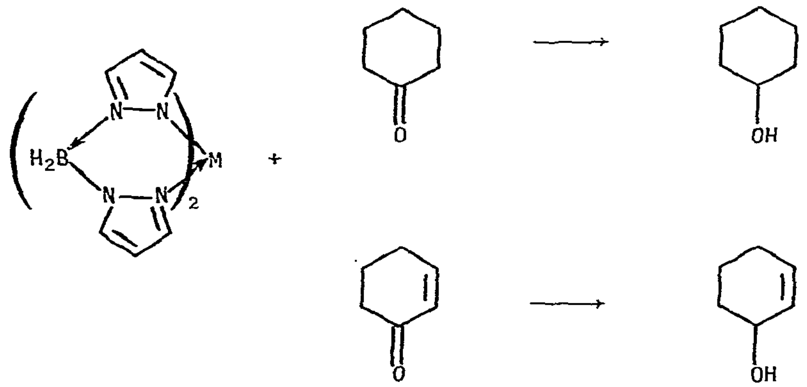
(275)



(276)



(277)

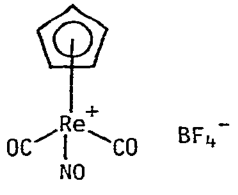


(278)

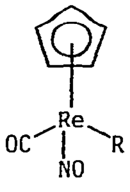
M = Co, Ni, Cu, Zn, Cd

I. Carbon Monoxide.

Mechanistic features of catalytic carbon monoxide hydrogenation reactions have been reviewed (93 references) [580], as has the heterogeneously catalyzed hydrogenation of carbon monoxide (140 references) [581]. Investigation of the reduction of carbon monoxide by heterogeneous and homogeneous catalysts [582], and models for the metal-catalyzed reduction of carbon monoxide by hydrogen [583] were dissertation titles. Soluble ruthenium catalysts converted a 40:60 mixture of carbon monoxide and hydrogen to a 4:1 mixture of methanol and methyl formate at 268° and 1300 atmospheres pressure [584]. Reaction rate measurements and infrared spectra of adsorbed species were studied in the synthesis of hydrocarbons from CO and H_2 using silica supported ruthenium catalysts [585]. Reductions of rhenium complexes 21 and 22 were studied as model reactions of the Fischer-Tropsch reaction [586]. The cluster $Ru_3(CO)_{12}$ was a catalyst precursor for the Fischer-Tropsch reaction [587]. Coordinated carbon monoxide was reduced to "zirconoxy" carbenes by permethylzirconocene dihydride (eq. 279) [588].

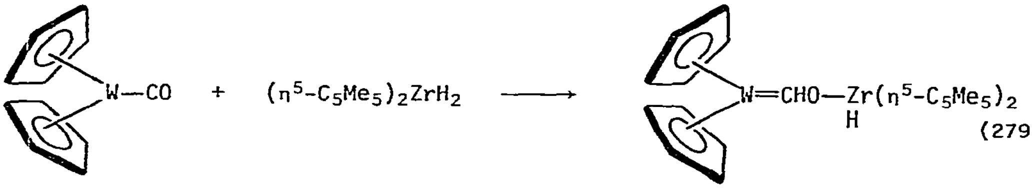


21



22

R = CHO, CH_2OH, CH_3



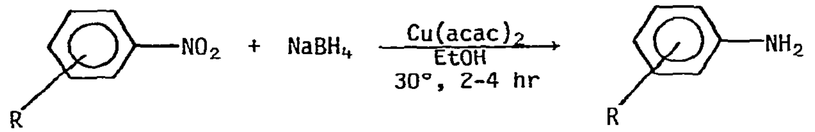
(279)

J. Catalytic Transfer Hydrogenation

Isopropanol reduced cyclohexanone, 4-t-butyl cyclohexanone,and acetophenone to the corresponding alcohols in the presence of an $[Rh(diene)L_2]^+$ catalyst and KOH [589]. The complex $[Rh(4,7\text{-dimethylphenanthroline})_2Cl_2]Cl$ behaved in a similar fashion [590]. Isopropanol reduced 4-alkylpiperidinones in the presence of triphenylphosphine complexes of rhodium(I) and ruthenium(II) [591]. Iridium(I) complexes of 2,2'-bipyridine and 9,10-phenanthroline were active catalysts for transfer hydrogenation of ketones by isopropanol [592]. D-Glucose was reduced by tetrahydrofurfuryl alcohol or 2-methoxyethanol in the presence of $RuCl_2(PPh_3)_3$[593]. Formic acid was the hydrogen source in the Pd black-catalyzed hydrogenolysis of benzyl and benzyloxy groups from peptides [594,595]. Olefins were used as hydrogen donors in the 10% Pd/C-$FeCl_3$ catalyzed reductions of aldehydes and ketones. Limonene was the best donor. This system reduced aryl chlorides and cyclopropyl ketones as well [596]. Raney nickel catalyzed the reduction of olefins, ketones and certain aromatic hydrocarbons by isopropanol [597]. Optically active esters of α- and β-methylcinnamic acids were reduced over Raney nickel, palladium or platinum, giving up to 68% optical yields [598].

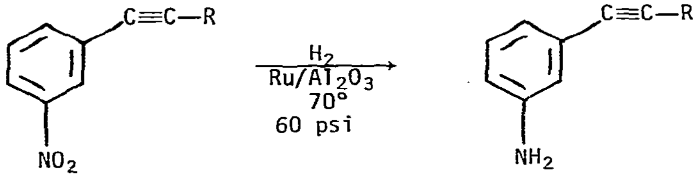
K. Nitrogen Compounds

Nitroarenes were reduced to arylamines by sodium borohydride and copper(II) acetylacetonate in very high yield. Many functional groups were tolerated (eq. 280) [599]. Aromatic nitro groups were reduced in the presence of alkynes by



(280)

R = H, 4-Cl, 3-Cl, 2-Cl, 4-Me, 3-Me, 2-Me, 4-OMe, 3-OMe, 2-OMe

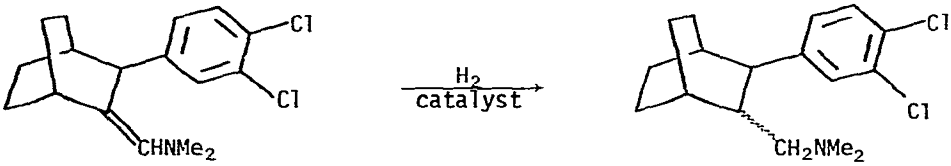


(281)

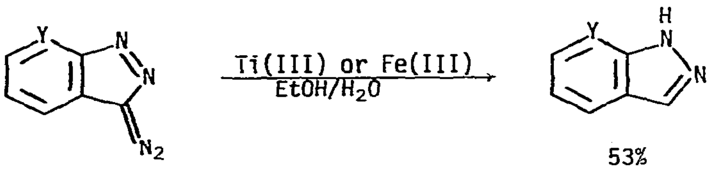
hydrogenation over 5% Ru on Al_2O_3 (eq. 281) [600]. Cobalt polysulfide and ruthenium sulfide catalysts showed similar selectivity [601].

Addition of triethylamine to $RhCl(PPh_3)_3$ produced a very active catalyst for the reduction of aromatic nitro compounds to aryl amines [602]. Nitrobenzene was reduced to aniline by CO and H_2O in the presence of $Rh_6(CO)_{16}$ as a catalyst. The hydrogen source was claimed to be the water gas shift reaction [603]. Nitrobenzene was reduced to aniline at room temperature and one atmosphere of hydrogen in the presence of $Pd(acac)_2$-pyridine. The complex $Pd(acac)H(PhNO_2)py$ was isolable from the reaction [604]. Isopropanol reduced nitrobenzene to aniline in the presence of $RhCl(PPh_3)_3$ or $RuCl_2(PPh_3)_3$ and KOH [605]. Nitrobenzene was reduced to aniline under homogeneous conditions using $PdCl_2(PhCN)_2$ as a catalyst [606]. Diacid complexes of cerium catalyzed the same reduction [607], as did $CuBr(PPh_3)_3$[608].

Imines were reduced stereoselectively cis by platinum catalysts in polar solvents; in contrast palladium and supported catalyst reduced them preferentially trans (eq. 282) [609]. Heterocyclic diazocompounds were reduced by titanium(III) or iron(III) salts in ethanol/water (eqs. 283, 284) [610].

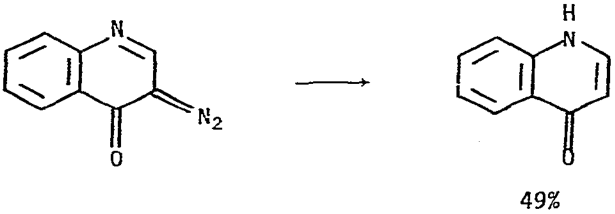


(282)



(283)

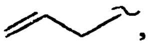
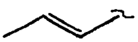
Y = CH, N



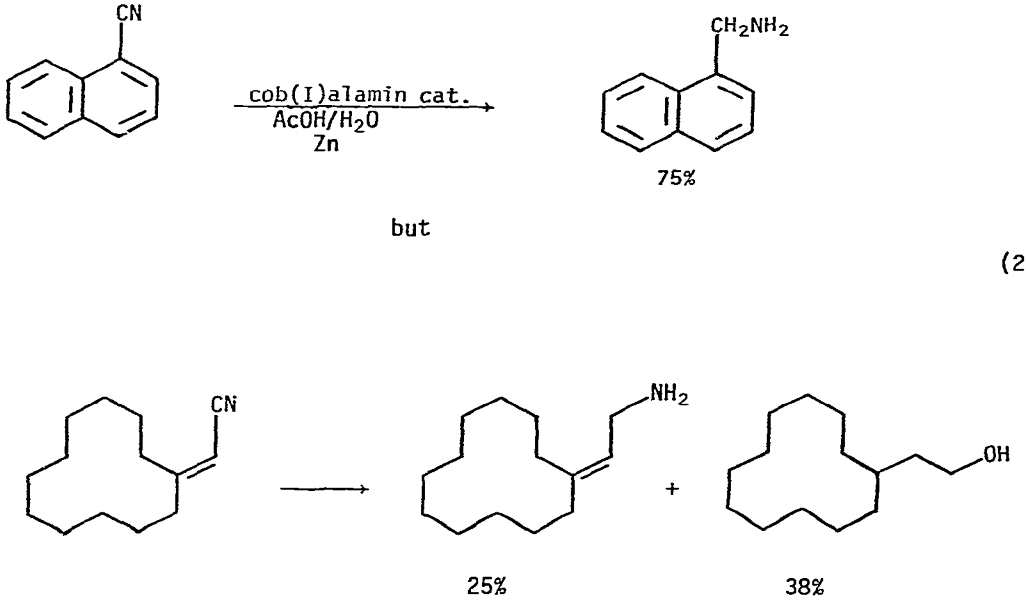
(284)

Nitriles were reduced to amines by hydrogen using $RhH(P\text{-}i\text{-}Pr_3)_3$ as a catalyst (eq. 285) [611]. Nitriles were reduced in a stepwise fashion on the face of an

$$RC{\equiv}N \; + \; H_2 \xrightarrow{RhH(i\text{-}Pr_3P)_3} \underset{70\text{-}100\%}{RCH_2NH_2} \qquad (285)$$

R = n-Bu, i-Pr, t-Bu, $PhCH_2$, , , Ph-

$Fe_3(CO)_9$ cluster catalyst [612]. Aldononitriles of aldoses were reduced by hydrogen over a $Pd/BaSO_4$ catalyst [613]. Conjugated nitriles were reduced to benzyl or allylamines by zinc in the presence of cob(I)alamin catalysts (eq. 286) [614].



(286)

The role of isocyanide insertion reactions in cluster catalyzed hydrogenation of isocyanides was examined [615]. The reduction of isocyanides by hydrogen in the presence of Cp_2ZrH_2 was studied as a model for carbon monoxide reduction [616].

L. Halides, Allyl Ethers

Iron pentacarbonyl reduced α-bromoketones to ketones when refluxed in xylene.

The yields were 45-68%. A free radical mechanism was favored [617]. Aromatic halides were reduced to hydrocarbons by sodium borohydride in the presence of catalytic amounts of nickel(0) complexes (eq. 287) [618]. Nickel boride catalyzed the dechlorination of several organochlorine pesticides including lindane, heptachlor, and chlordane [619]. Polychlorinated alkanes were reduced by iron pentacarbonyl by a radical process [620]. Halides were reduced to hydrocarbons by Cp_2MoH_2. With chiral substrates the reaction went with retention (eq. 288) [621].

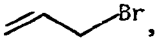
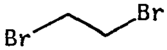
$$\mathrm{ArI} + \mathrm{NaBH_4} \xrightarrow[\mathrm{DMF}\ 70°]{\mathrm{L_3Ni\ cat.}} \mathrm{ArH} \qquad (287)$$

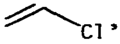
Ar = H, p-Cl, p-COOMe--high yields

Ar = p-OMe, p-CN, p-Me, p-NO_2, p-OH, p-NH_2--low yields

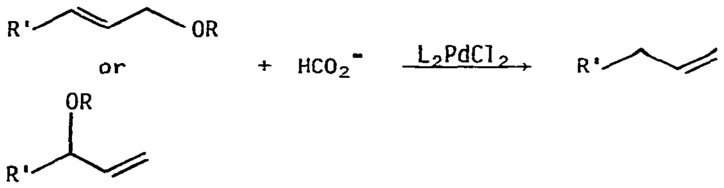
$$\mathrm{Cp_2MoH_2} + \mathrm{RX} \longrightarrow \mathrm{RH} \qquad (288)$$

1 hr RX = CF_3I, CH_3I, CH_2I_2, CH_2Br_2, MeO_2CCH_2I, $NCCH_2Br$, MeO_2CCH_2Br, $CHCl_3$

1 day RX = EtI, n-PrI, i-PrI, , , $PhCH_2Br$, CH_2Cl_2, MeO_2CCH_2Cl, $NCCH_2Cl$, $PhCHCl_2$

No reaction RX = PhI, EtBr, n-BuCl, , $PhCH_2Cl$

Acid chlorides were reduced to aldehydes with no overreduction by $(Ph_3P)_2CuBH_4$ [622]. The mechanism of the reduction of allylic ethers and acetates by organocuprates has been studied [623]. Allyl acetates and allyl phenyl ethers were converted to terminal olefins by reaction with ammonium formate and a palladium(II) catalyst (eq. 289) [624].

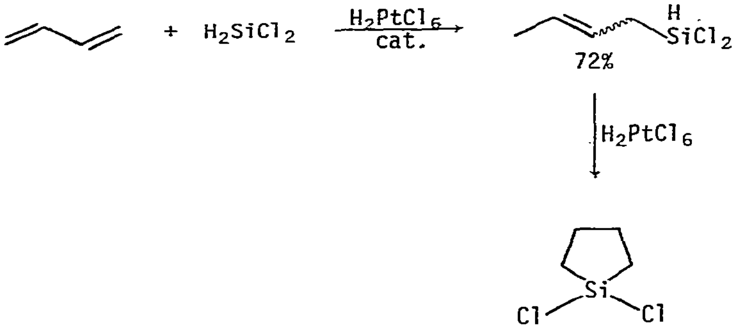


(289)

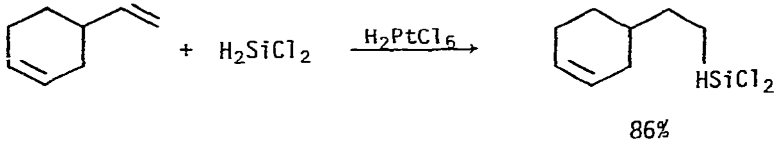
R = Ph, CH_3CO

M. Reduction by Hydrosilation

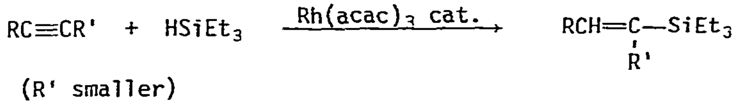
Homogeneous catalysis of hydrosilation by transition metals has been reviewed (59 references) [625]. Hydrosilation of norbornene systems catalyzed by nickel(II) phosphine complexes has been studied [626]. The stereoselectivity of the hydrosilation of substituted cyclohexanones catalyzed by $RhCl(PPh_3)_3$ under homogeneous conditions and by silicon bound phosphine rhodium(I) complexes under heterogeneous conditions was similar [627]. Butadiene underwent almost exclusive 1,4 addition when treated with H_2SiCl_2 and H_2PtCl_6 as catalyst. Nonconjugated dienes underwent 1,2 additions (eqs. 290,291) [628]. Allylamine was hydrosilated to mixtures of γ and β-aminopropyl(triethoxy)silane in the presence of H_2PtCl_6 and phosphines or arsines [629]. Alkynes (eq. 292), dienes (eq. 293), olefins (eq. 294), and conjugated aldehydes (eq. 295) were hydrosilated using $Rh(acac)_3$ as a catalyst [630].



(290)



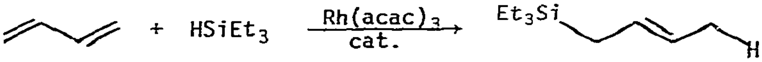
(291)



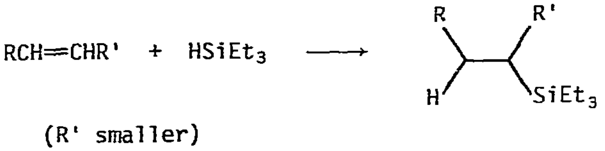
$$RC\equiv CR' + HSiEt_3 \xrightarrow{Rh(acac)_3\ cat.} RCH{=}\underset{R'}{C}{-}SiEt_3$$

(R' smaller)

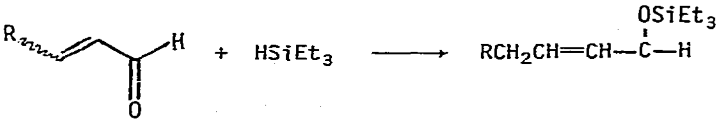
(292)



(293)



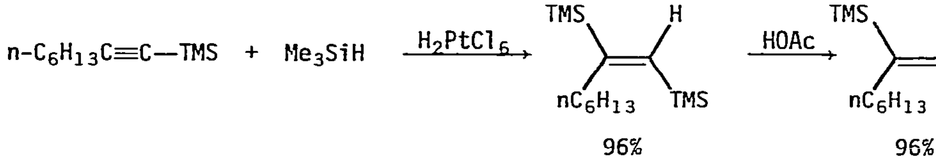
(294)



$$RCH_2CH{=}CH{-}\overset{OSiEt_3}{C}{-}H$$

(295)

Isoprene was hydrosilated by $(EtO)_3SiH$ in the presence of cocondensed Ni, Co, or Fe vapor [631]. 2-(Trimethylsilyl)-1-alkenes were prepared by platinum catalyzed hydrosilation of a trimethylsilylacetylene followed by desilation (eq. 296) [632].



(296)

N. Miscellaneous Reviews

The following reviews dealing with reduction have appeared:

Catalytic Reductions using Carbon Monoxide and Water in Place of Hydrogen. (19 references) [633]

Highly Stereoselective Hydrogenations with Group VIII Transition Metal Catalysts. (54 references) [634]

Reduction of Organic Compounds with Low-Valent Species of Group IVB, VB, and VIB Metals. (172 references) [635]

Catalytic Hydrogenation in Organic Synthesis--Procedures and Commentary. (191 pages) [636]

Hydrogenation Reactions Catalyzed by Transition Metal Complexes. (548 references) [637]

Metal Catalyzed-Borohydride Reducing Systems for Organofunctional Groups. (41 references) [638]

Reductions with Covalent Borohydride Complexes. (5 references) [639]

Cationic Ionic Hydrogenation. (58 references) [640]

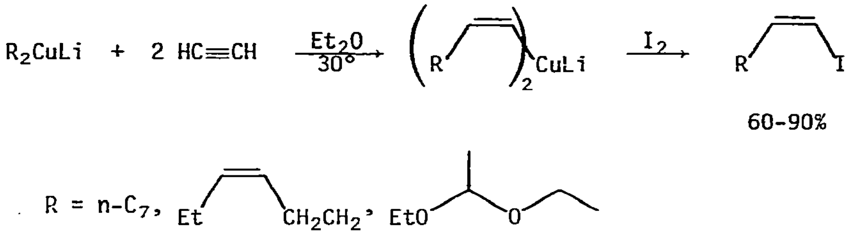
Catalytic Homogeneous Hydrogenations Using Micellar and Phase Transfer Reaction Conditions. (16 references) [641]

Part I. The Intramolecular Cyclization of Organoaluminum Compounds. Part 2. Reduction Using Low-Valent Titanium and Zirconium Complexes. (136 pages) [642]

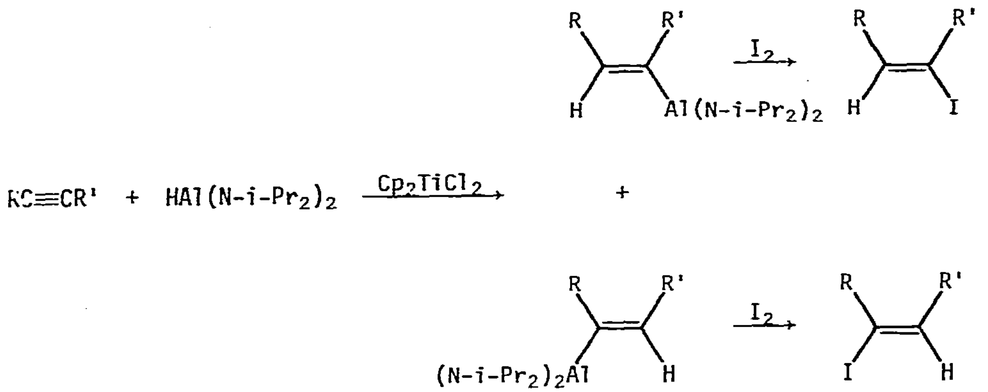
V. Functional Group Preparations

A. Halides

cis-Vinyl iodides were prepared from acetylene by alkylation with an organocuprate followed by reaction with iodine (eq. 297) [643]. Hydroalumination of alkynes by $HAl(N\text{-}i\text{-}Pr_2)_2$ catalyzed with Cp_2TiCl_2, followed by iodine cleavage of the alane led to similar products (eq. 298) [644]. Iron(III) chloride reacted with acetylenes in the presence of a hydrogen source to give vinyl chlorides in a nonregio- and nonstereoselective fashion [645].



(297)

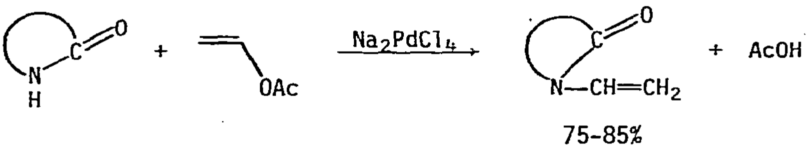


(298)

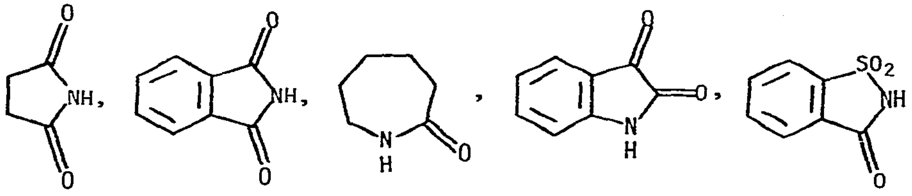
Chlorobenzene was halogenated by iron(III) chloride [646]. Aromatic, alkynyl and alkenyl nickel(II) complexes were cleaved by N-bromosuccinimide to the corresponding organic bromides [647]. The conversion of Zeiss' salt to 2-chloroethanol by reaction with chlorine in water was studied [648].

B. Amides, Nitriles

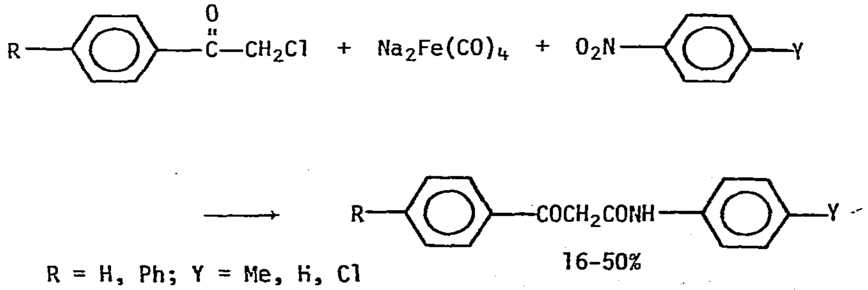
Lactams and imides were vinylated by reaction with vinyl acetate in the presence of Na_2PdCl_4 (eq. 299) [649]. α-Chloroacetophenones were converted to amides by reaction with nitroaromatics and $Na_2Fe(CO)_4$ (eq. 300) [650].



(299)



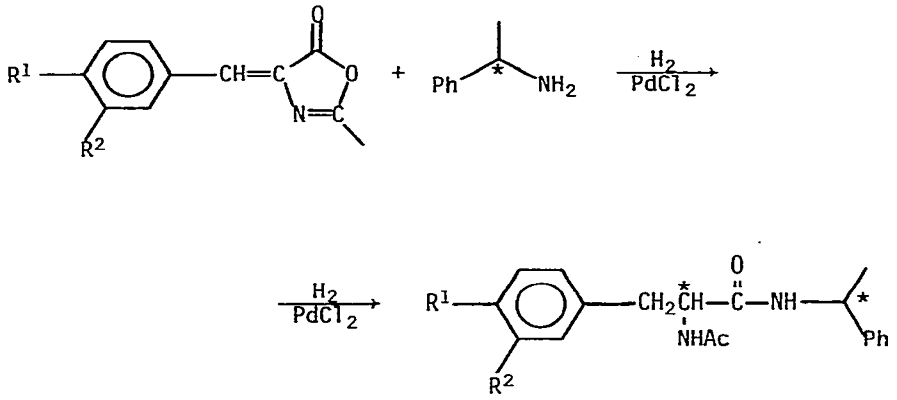
work



(300)

R = H, Ph; Y = Me, H, Cl

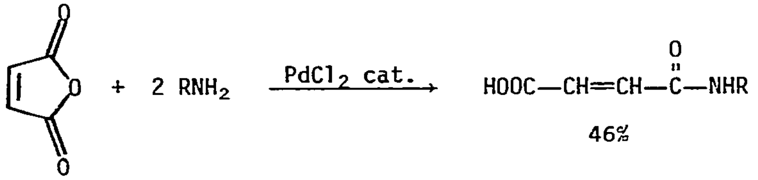
Azlactones were converted to chiral amides by reduction using palladium(II) chloride as a catalyst in the presence of optically active α-phenethylamine (eq. 301) [651]. Maleic anhydride was converted to maleic acid monoamides by reaction with amines in the presence of palladium(II) chloride (eq. 302) [652].



(301)

63% yield
60% diastereomeric excess

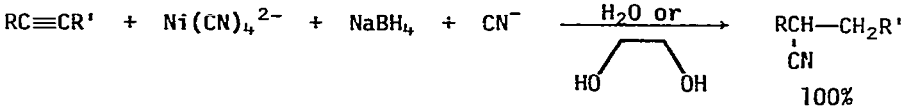
R^1 = OAc, OMe
R^2 = H



46%

(302)

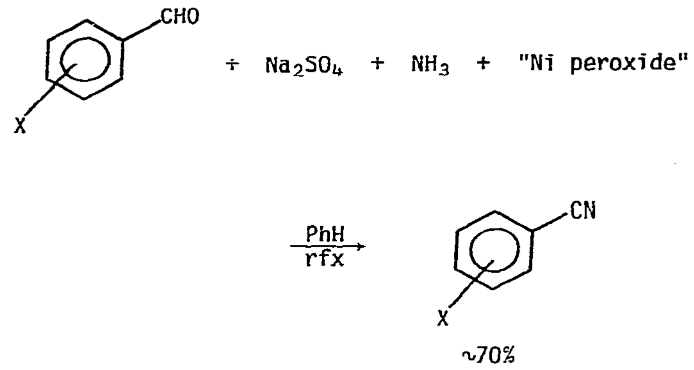
Alkynes were converted to saturated nitriles by reaction with $Ni(CN)_4^{=}$, sodium borohydride and cyanide ion (eq. 303) [653]. Aromatic aldehydes and saturated aldehydes were converted to the corresponding nitrile by oxidative amination (eq. 304) [654]. Aromatic halides were converted to nitriles by reaction with



$$RC{\equiv}CR' + Ni(CN)_4^{2-} + NaBH_4 + CN^- \xrightarrow{H_2O \text{ or } HOCH_2CH_2OH} \underset{CN}{RCH}-CH_2R' \quad (303)$$

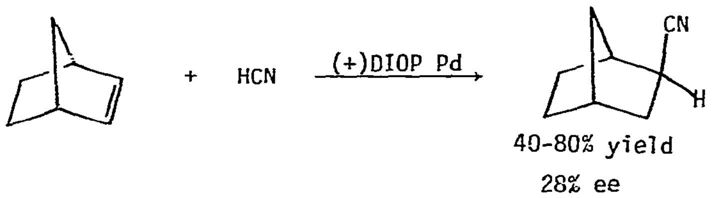
100%

R = Ph, $PhCH_2CH_2$
R' = H, Et



(304)

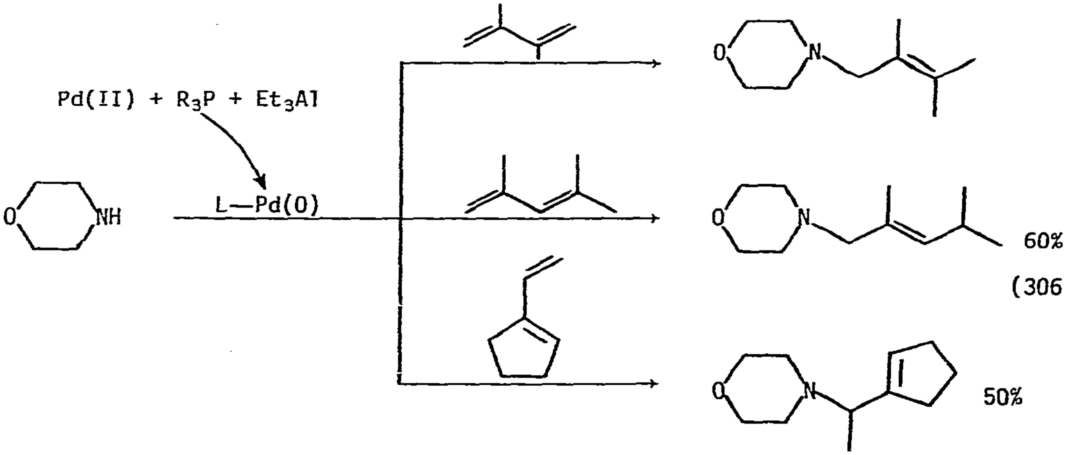
cyanide and nickel(0) catalysts under phase transfer conditions [655]. Chiral palladium(0) complexes (DIOP) catalyzed the asymmetric hydrocyanation of norbornene (eq. 305) and norbornadiene [656].



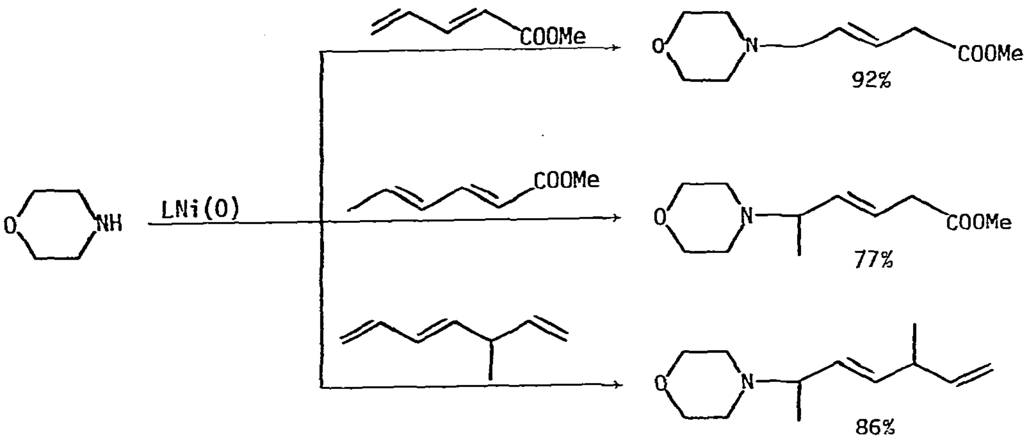
(305)

C. Amines, Alcohols

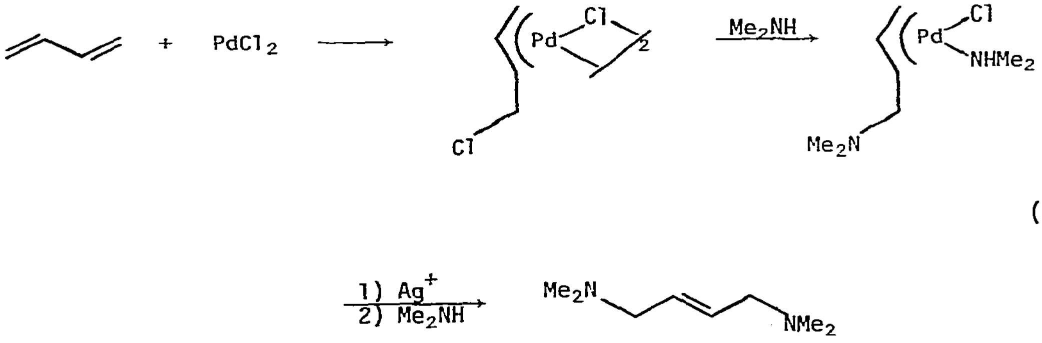
A number of conjugated dienes were aminated in the presence of nickel(0) or palladium(0) complexes (eqs. 306, 307) [657]. Butadiene was converted to 1,4-bis dimethylaminobut-2-ene by dimethylamine and palladium(II) chloride (eq. 308) [658]. Allylic acetates were aminated by an ammonia equivalent in



(306)

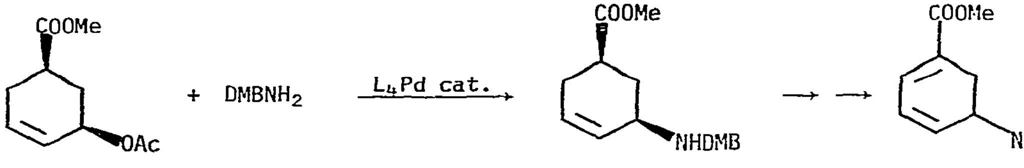


(307)

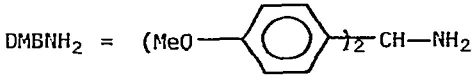


(308)

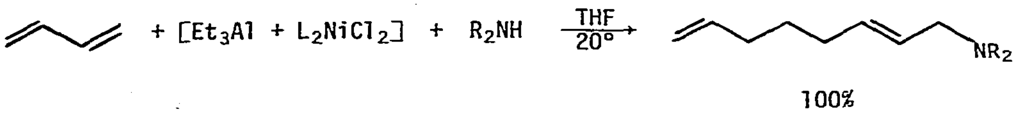
the presence of $L_4Pd(0)$ catalysts. (±) Gabaculine was synthesized in this manner (eq. 309) [659]. Butadiene was aminated and dimerized by treatment with secondary amines and nickel(0) catalysts (eq. 310) [660]. Cationic cyclohexadienyl iron complexes were aminated by aromatic amines and phthalimide (eq. 311) [661].



(309)

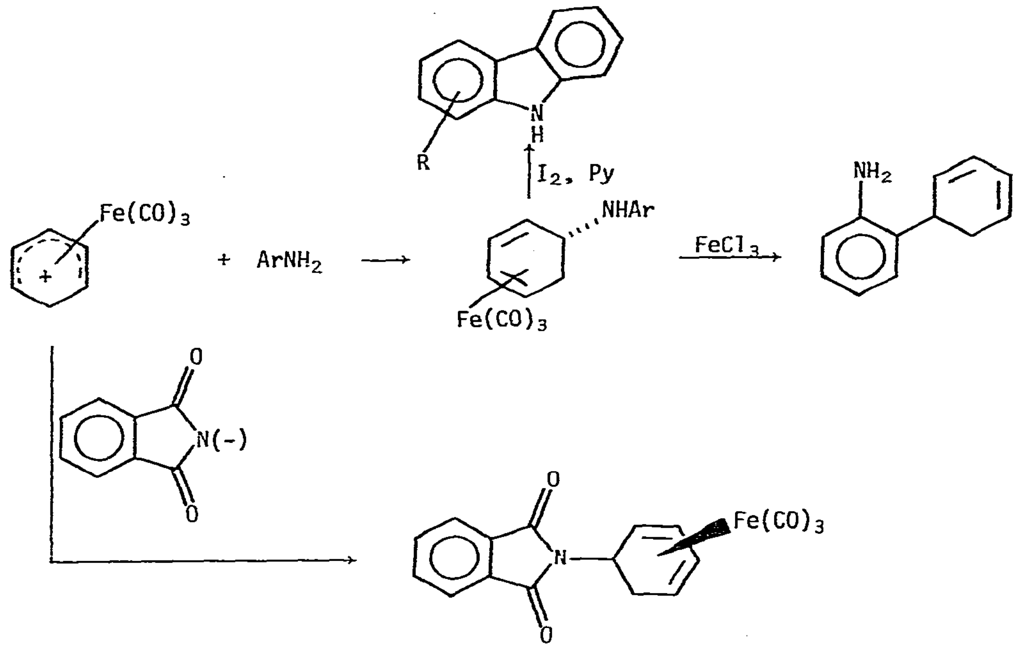


(NH$_3$ equivalent HCOOH cleaves)



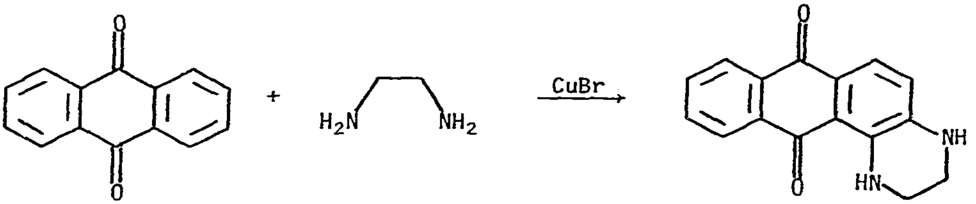
(310)

turnover > 400

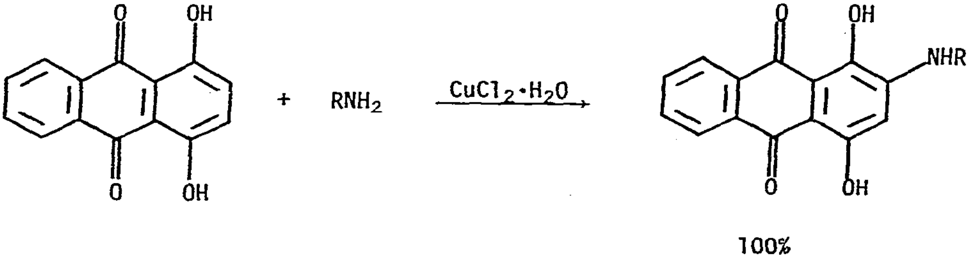


(311)

The Ullman condensation reaction of haloanthraquinones with amines has been reviewed (42 references) [662]. Anthraquinone reacted with ethylene diamine in the presence of copper(I) bromide catalyst to produce diaminated product (eq. 312) [663]. Copper(I) or copper(II) chloride catalyzed the amination of 1,4-dihydroxyanthraquinone (eq. 313) [664]. 5,8-Dihydroxy-1,4-naphthoquinone underwent preferential β-amination under these conditions [665].



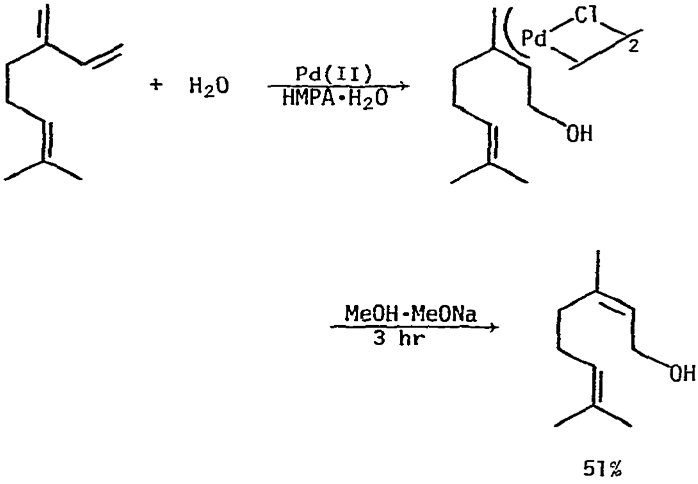
(312)



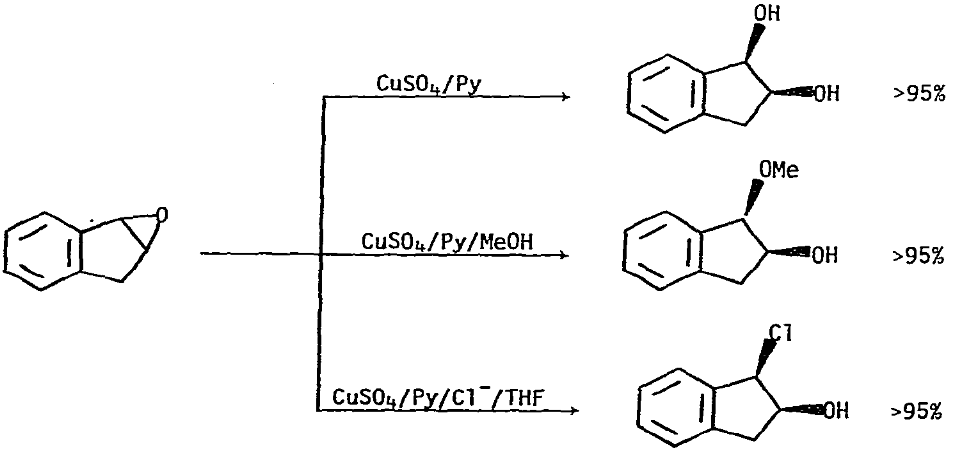
(313)

Ketones and aldehydes were reductively aminated by ammonia in the presence of a rhodium glyoxime complex [666]. Acetone was reductively aminated by aniline in the presence of commercial copper based catalysts [667]. Tri-n-butylamine reacted with 2,4-dinitrophenylhydrazine, Pd black and HCl at 200° to produce 98% di-n-butylamine and 92% 2,4-dinitrophenylhydrazone of butyraldehyde [668]. Amino groups in polypeptides were protected with β-haloalkyoxycarbonyl groups, which were readily cleaved by the supernucleophiles, cobalt(I)-phthalocyanines [669]. Primary and secondary amines were arylated by aryl halides in the presence of copper catalysts [670].

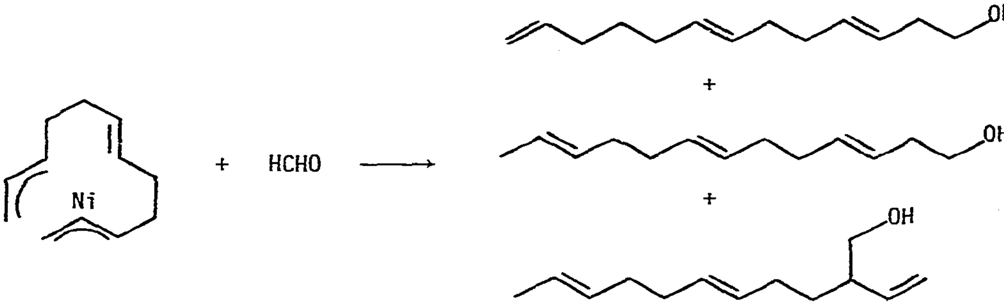
Nerol was prepared by palladium(II) assisted hydroxylation of the corresponding triene. The terminal olefin was selectively oxygenated (eq. 314) [671]. Epoxides were opened to diols, α-methoxy alcohols or chlorohydrins by copper(II) sulfate (eq. 315) [672]. Paraformaldehyde reacted with the bis π-allylnickel complex of 1,6,11-dodecatriene to give linear alcohols (eq. 316) [673]. Hydroperoxides reacted with iron(II) sulfate/copper(II) acetate to produce unsaturated alcohols by a radical process (eq. 317) [674]. Hydroboration of terminal olefins by $LiBH_4$ was catalyzed by Cp_2TiCl_2. The resulting boranes were oxidatively cleaved to terminal alcohols [675].



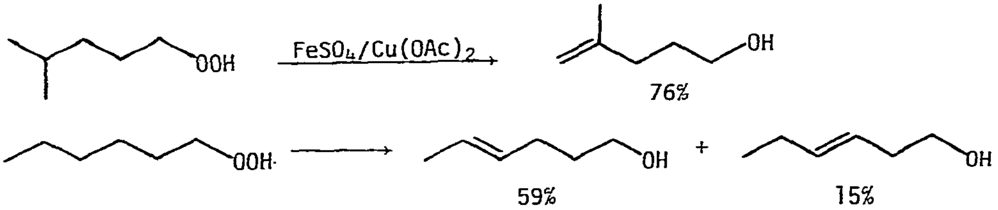
(314)



(315)



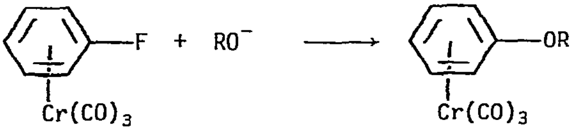
(316)



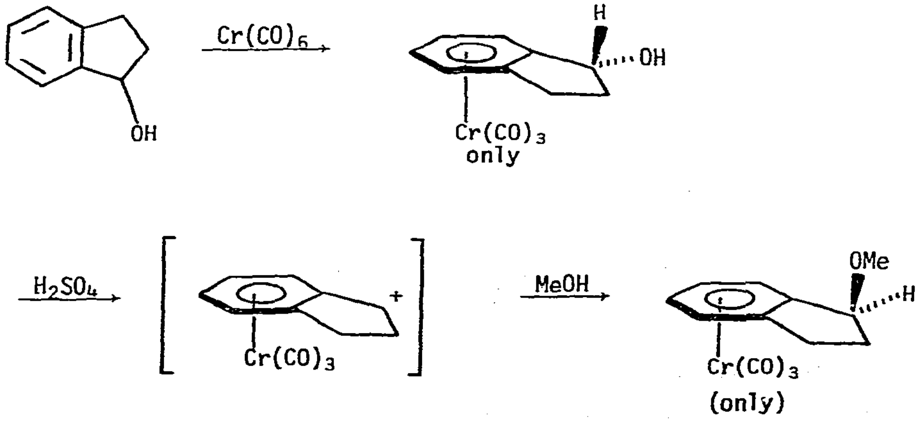
(317)

D. Ethers, Esters, Acids

Chromium tricarbonyl complexes of fluorobenzene were converted to ethers by reaction with alkoxide. With the appropriate alkoxide the reaction was catalytic in chromium (eq. 318) [676]. Indanols were stereospecifically converted to ethers by complexation to chromium, formation of the chromium stabilized carbonium ion, and reaction with methanol exclusively from the face opposite chromium (eq. 319) [677]. Irradiation of primary or secondary alcohols in THF



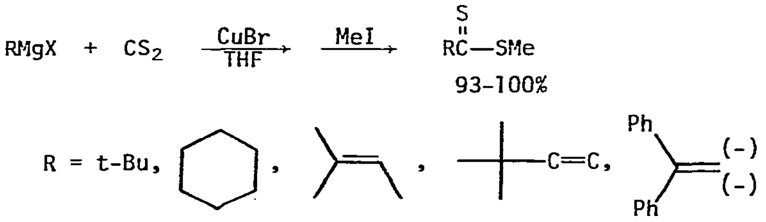
(318)



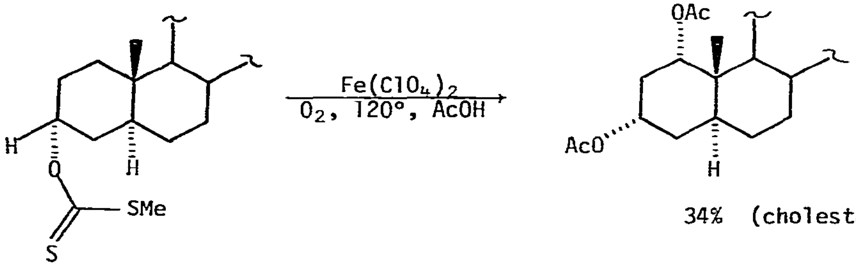
(319)

in the presence of iron(III) chloride produced the corresponding tetrahydro-2-furyl ethers [678]. Allyl alcohols were converted to silylenol ethers by reaction with trimethylsilyl chloride in the presence of $RuH_2(PPh_3)_4$. The reaction involved rearrangement of the allylic alcohol to the enol [679]. Butadiene was converted to 1,4-diacetoxy-2-butene by reaction with acetic acid over a palladium-tellurium-carbon catalyst [680].

Anhydrous iron(III) chloride catalyzed the esterification of carboxylic acids in refluxing alcohol [681]. Transesterification reactions were catalyzed by copper(I) alkoxide phosphine complexes $[ROCu(PPh_3)_n]$[682]. Oxiranes were converted to β-hydroxy esters by reaction with $Co_2(CO)_8$ and carbon monoxide in methanol [683]. Thioesters were available from the copper catalyzed reaction of Grignard reagents with carbon disulfide (eq. 320) [684]. Steroidal dithiocarbonates produced diacetates upon reaction with iron(II) perchlorate and oxygen in acetic acid (eq. 321) [685]. Aldehydes (RCHO) condensed to self esters (RCO_2CH_2R) when reacted with $RuH_2(PPh_3)_4$ [686].



(320)

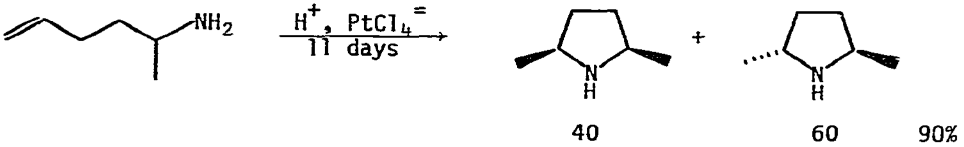


(321)

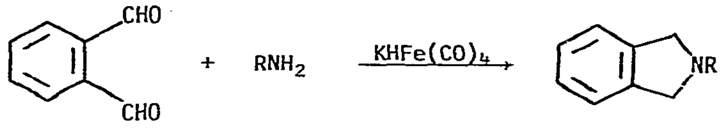
34% (cholestane ring system)

E. Heterocycles

ω-Olefinic amines cyclized when reacted with $PtCl_4^{=}$ in acidic aqueous solution. The reaction was very slow taking from 8 to 67 days (eq. 322) [687]. Aromatic dialdehydes were reductively aminated by primary amines in the presence of $KHFe(CO)_4$ (eq. 323) [688]. (±)Catheranthine was synthesized using two



(322)

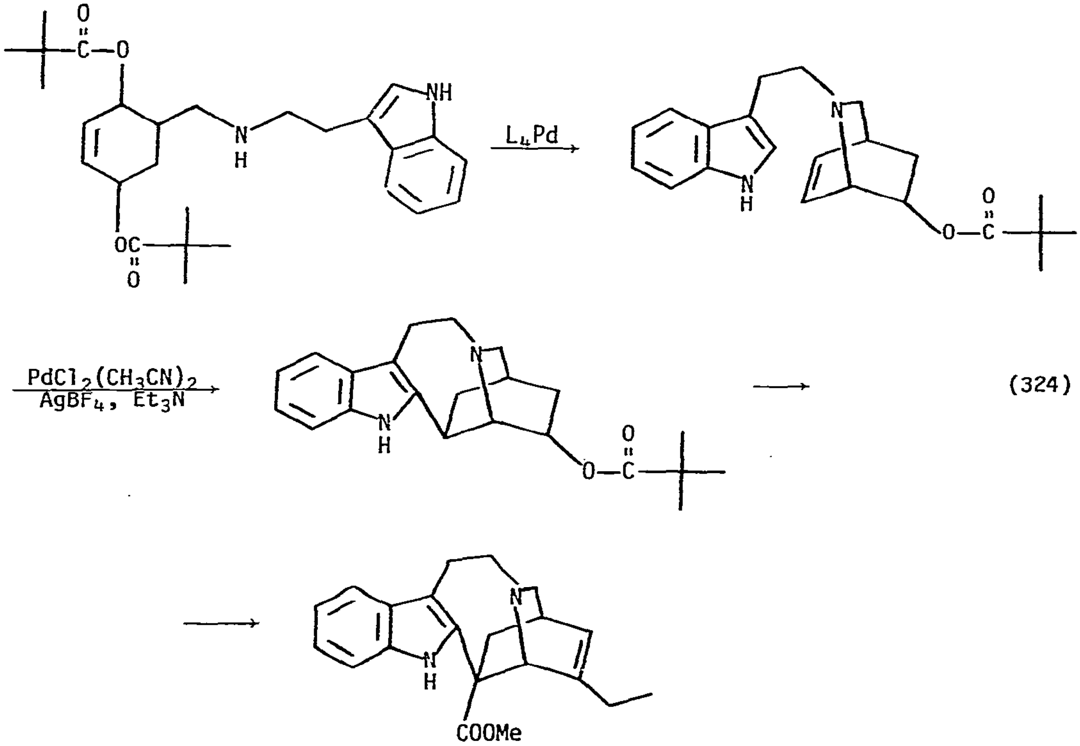


(323)

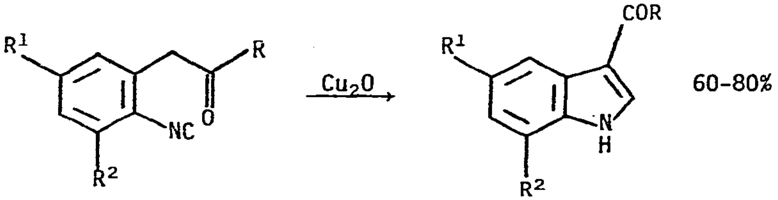
R = Me, $PhCH_2$, furfuryl, aryl

palladium assisted ring closures (eq. 324) [689]. The general approach has been described in detail [690].

Indoles were prepared by the reaction of (o-isonitrile)benzyl ketones with copper(I) oxide (eq. 325) [691,692]. Indoles, quinolines and benzazopines were prepared from o-haloanilines containing unsaturated alkyl groups



(324)



(325)

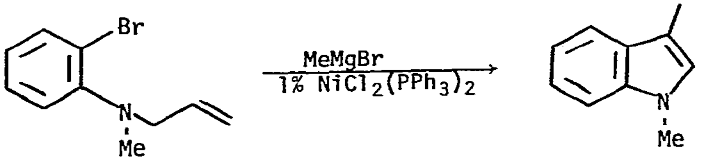
R = Me, n-Pr, i-Bu, n-C_7, Ph, t-Bu

R^1 = H, Me

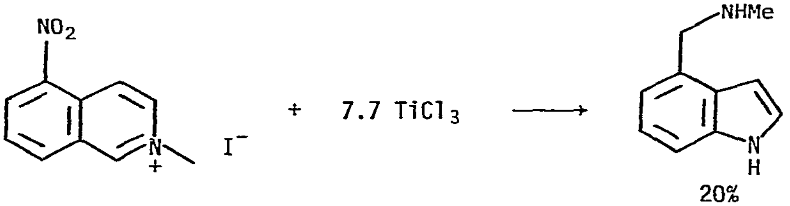
R^2 = H, Me

on nitrogen by reaction with Ni(0) complexes (eq. 326) [693]. N-Methylisoquinoline salts contracted to indoles upon reaction with titanium(III) chloride (eq. 327) [694].

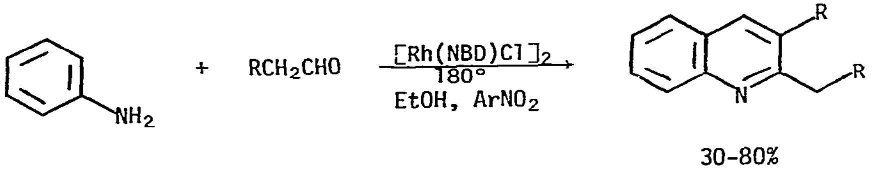
Anilines reacted with aldehydes in the presence of $[Rh(NBD)Cl]_2$ as a catalyst to produce 2,3-disubstituted quinolines (eq. 328) [695]. Aniline reacted with ethene in the presence of rhodium(III) chloride and phosphine to give mixtures of 2-methylquinoline and N-ethylaniline [696]. More unusual heterocyclic syntheses are shown in equations 329 [697], 330 [698], 331 [699], and 332 [700].



(326)

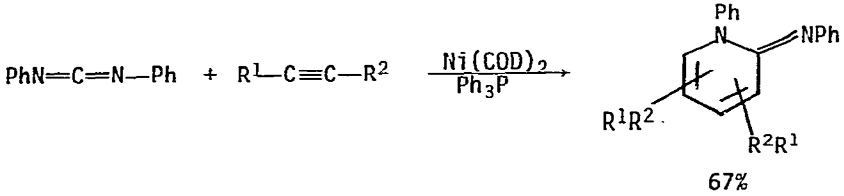


(327)



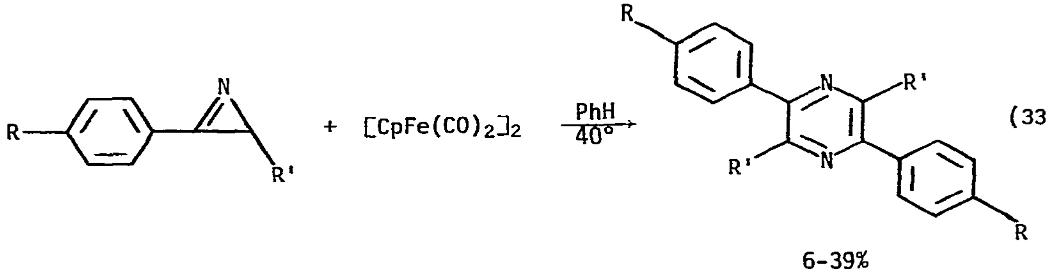
(328)

R = H, Me, Et-



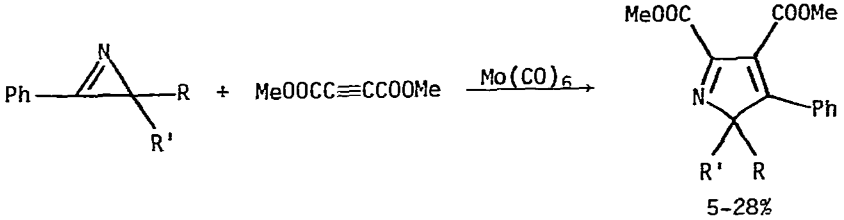
(329)

R^1 = Ph, Et
R^2 = Ph, Et, COOEt

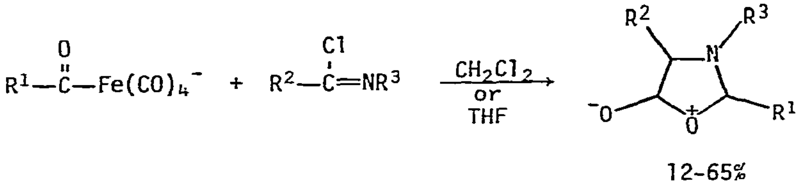


(330)

R = H, Br
R' = H, CHO



(331)



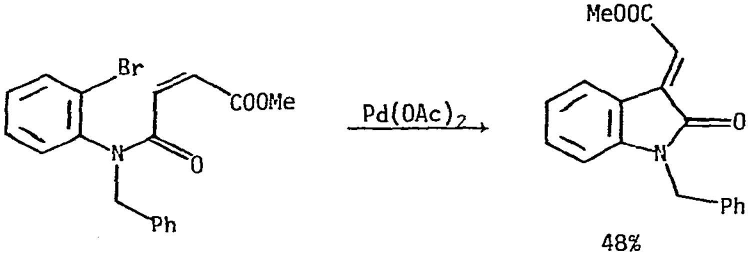
(332)

R^1 = Ph-, p-anisyl, 2-furyl, Me

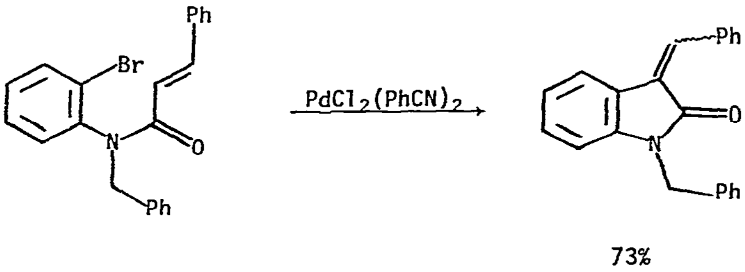
R^2 = Ph, p-BrPh, Et, 2-furyl

R^3 = p-tolyl, Ph, p-ClPh, Me, p-anisyl

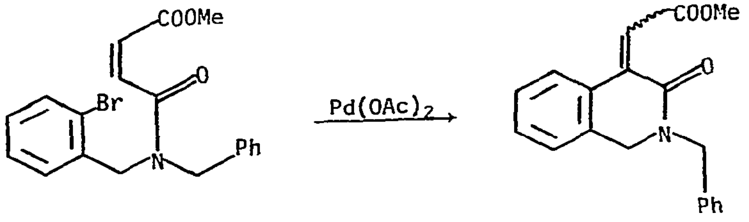
Unsaturated amides of o-bromoaniline cyclized to oxindoles or isoquinolones upon reaction with catalytic amounts of palladium(II) salts (eqs. 333-336) [701]. An unusual rearrangement was noted in this type of reaction (eq. 337) [702]. β-Lactams were made by the Pd(0) catalyzed cyclization-carbonylation of (bromo)-allylamines (eq. 338) [703]. Polycyclic ring systems were prepared by a similar reaction (eq. 339) [704]. Palladium(II) acetate catalyzed the cyclization of N-benzoyl indole derivatives (eq. 340) [705]. Penams were synthesized by a copper(I) mediated cyclization (eq. 341)[706]. N-chlorocarboxamides cyclized when treated with chromium(II) chloride (eq. 342) [707].



(333)

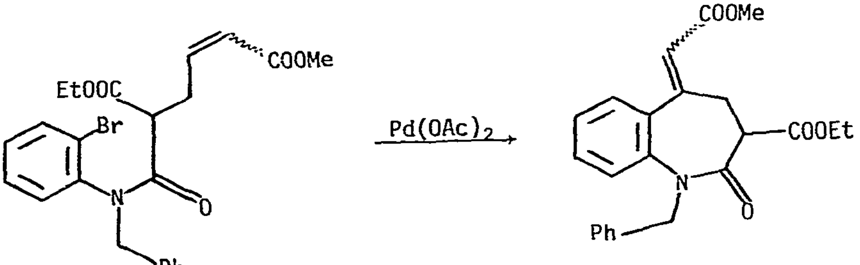


(334)



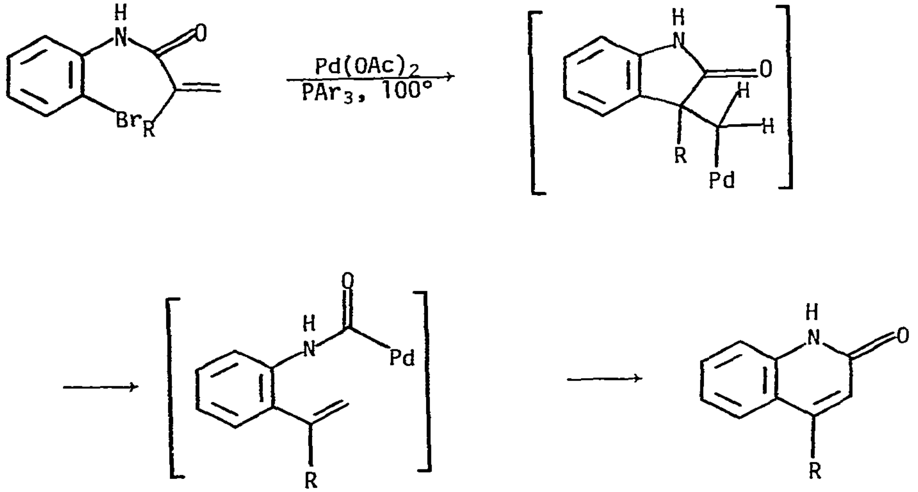
47%

(335)

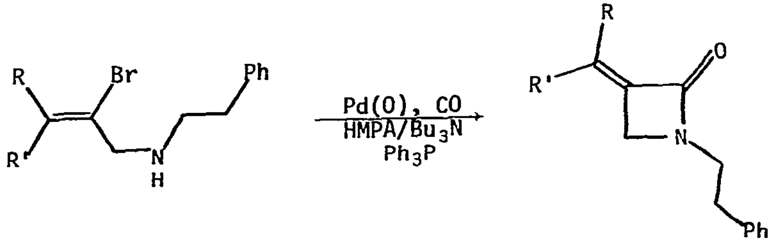


38%

(336)

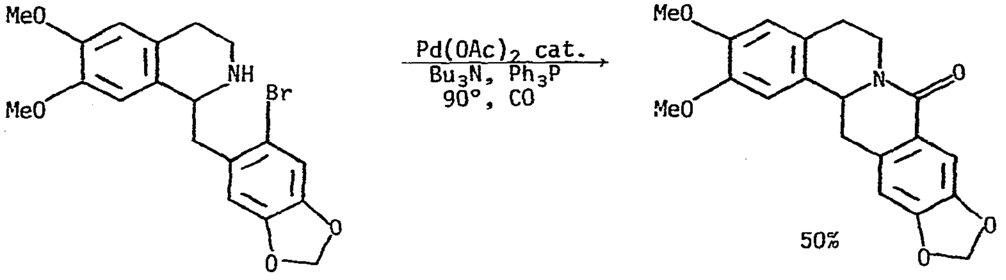


(337)

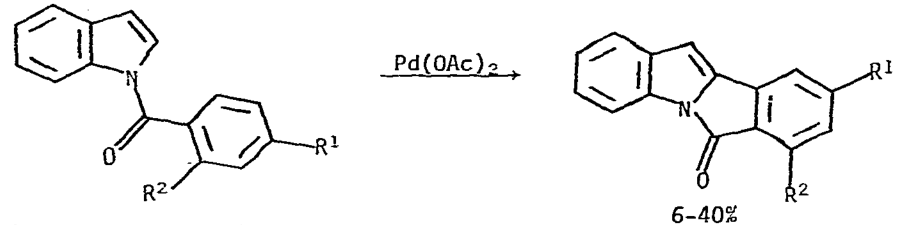


40-90%

(338)

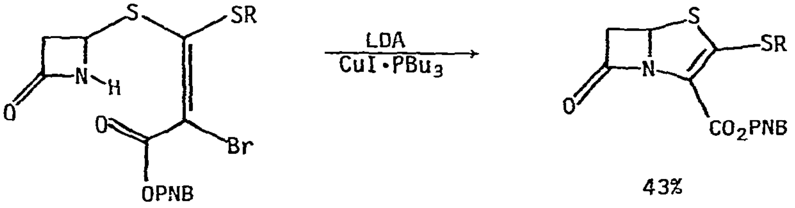


(339)

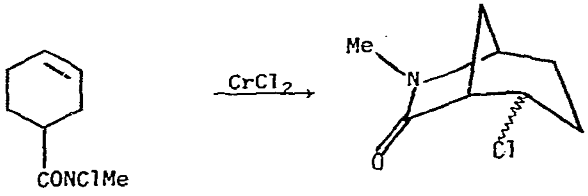


(340)

R^1 = H, Cl, CH_3; R^2 = H, CH_3, Cl

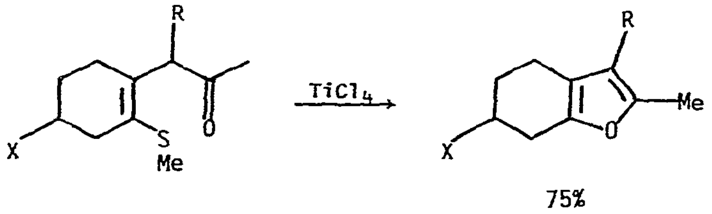


(341)



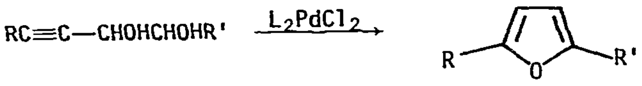
(342)

γ-Ketothioenol ethers cyclized to furans when treated with titanium tetrachloride (eq. 343) [708]. Furans were produced from α-acetylene glycol by reaction with L_2PdCl_2 (eq. 344) [709]. Chiral cobalt complexes converted chloro-



(343)

X = H, Me
R = Me, Et

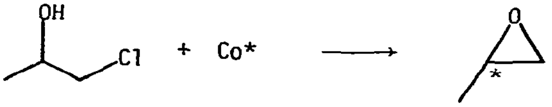


(344)

40-90%

R = Me, Et
R' = Ph, $HC\equiv C$—, $MeC\equiv C$—, $EtC=C$

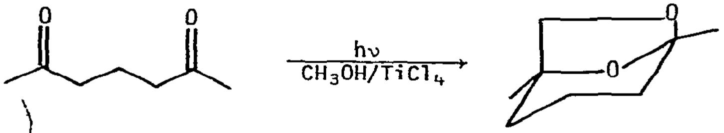
hydrins to epoxides in up to 35% optical purity (eq. 345) [710]. Heptane-2,6-dione was converted to frontalin by irradiation in the presence of titanium tetrachloride (eq. 346) [711]. Tetrahydrofurans and pyrans were prepared from 1,5-dienes and phenylselenyl cyanide and copper(II) chloride (eq. 347) [712].



(345)

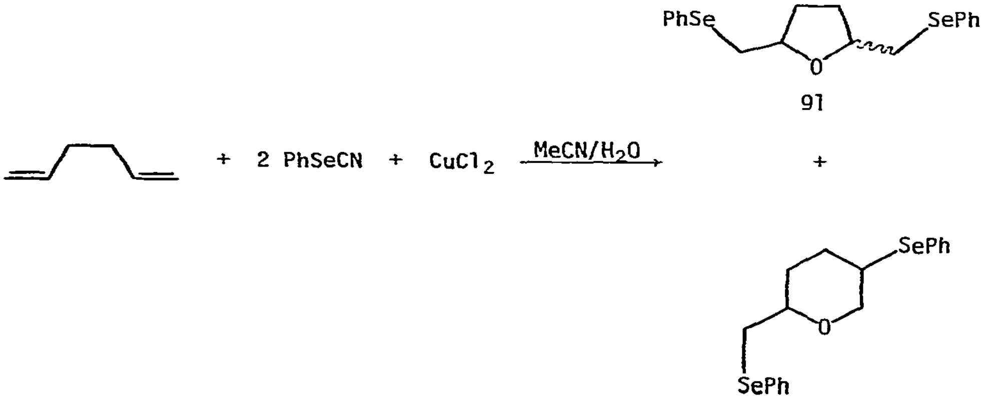
<35% optical purity

Co* = N,N'-disalicyliden-(1R,2R)-1,2-cyclohexandiaminatocobalt(II)



(346)

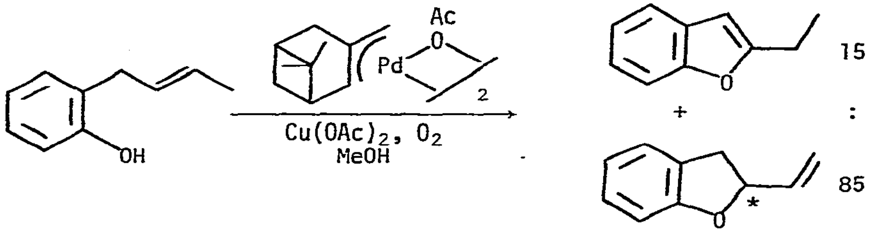
58%



(347)

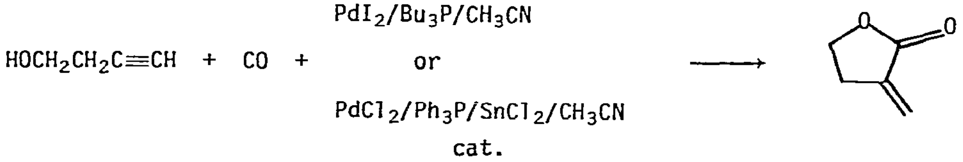
Chiral 2-substituted dehydrobenzofurans were prepared by cyclization of o-allylphenols with chiral π-allylpalladium halide catalysts (eq. 348) [713].

The full experimental details, including a detailed kinetic and mechanistic study, of the palladium(II) catalyzed conversion of acetylenic alcohols to α-methylene lactones has appeared (eq. 349) [714]. Butenolides were synthesized by the reaction of iodoalkenols with carbon monoxide and palladium(0) catalysts (eq. 350) [715]. Styrenes reacted with palladium complexes of aryl carboxylic acids to give dihydroisocoumarins (eq. 351) [716]. Propargyl alcohols were converted to butenolides or dihydrofurans by reaction with Grignard reagents followed by reaction of the thus-formed vinyl magnesium halide with the appropriate electrophile (eq. 352) [717]. Olefins reacted with dihaloacetic acids

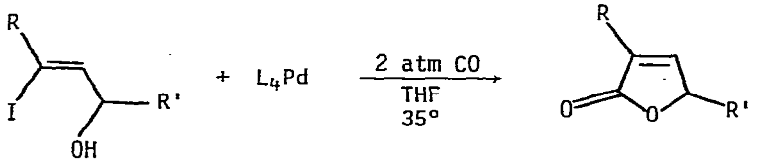


(348)

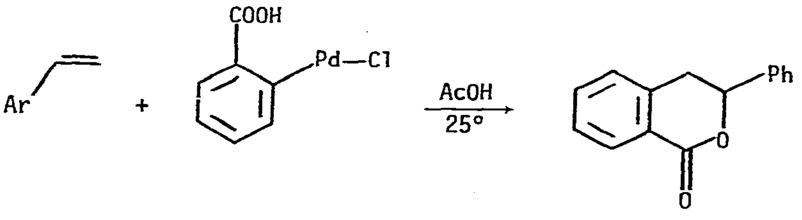
$[\alpha]_D^{25} = 3.42°$



(349)

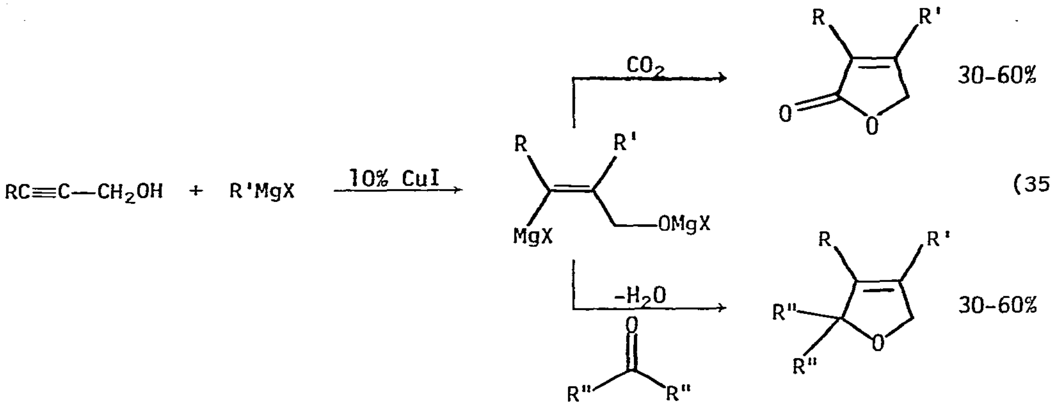


(350)



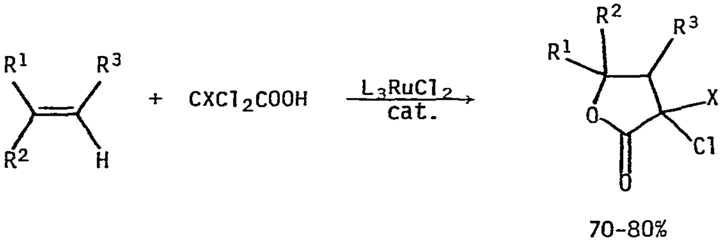
(351)

29-83%



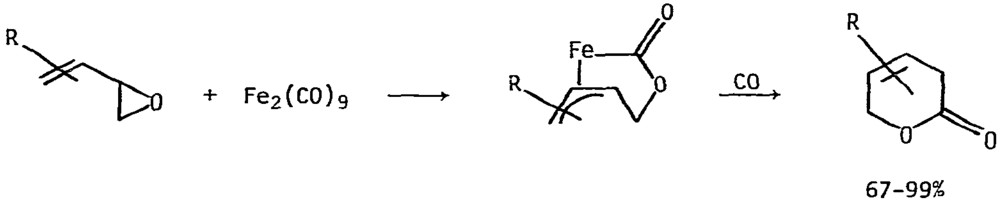
(352)

in the presence of L_3RuCl_2 to produce α halolactones (eq. 353) [718]. 1,3-Diene monoxides reacted with $Fe_2(CO)_9$ to produce unsaturated lactones (eq. 354) [719]. Carbon dioxide reacted with <u>bis</u>-π-allylnickel halides complexes to produce butyrolactones (eq. 355) [720].

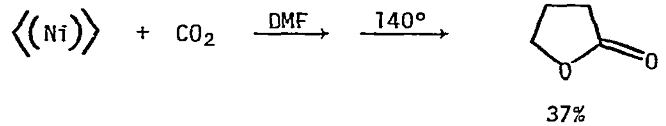


(353)

X = H, Cl



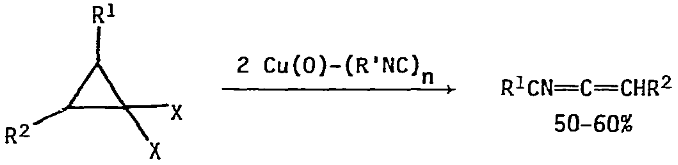
(354)



(355)

F. Miscellaneous

Gem-dihalocyclopropanes were converted to allenes by reaction with copper(0)-isonitrile complexes (eq. 356) [721]. Rhodium(III) chloride-phosphine complexes dehydrated 1,3-diols to allylic alcohols and ketones [722]. Molybdenum hexacarbonyl on alumina dehalogenated α-bromoaryl ketones [723]. Chromium(II) complexes dehalogenated α-haloketones without competing reductive elimination [724].

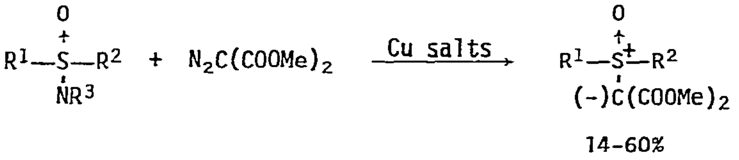


(356)

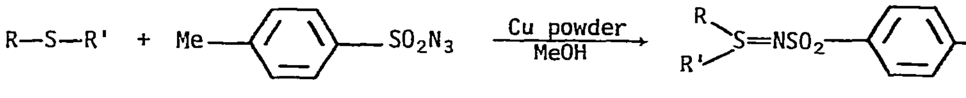
R' = n-hex, t-Bu
$R^1 = R^2 = (CH_2)_6$
$R^2 = H$

Azidoformates reacted with allyl ethers in the presence of palladium complexes to produce N-carbalkoxyimines (eq. 357) [725]. Oxosulfonium ylids were produced in the copper-catalyzed reaction of methyl diazomalonate with sulfoximides (eq. 358) [726]. Organic sulfides reacted with p-toluenesulfonyl azide to produce sulfilimines in the presence of copper powder (eq. 359) [727]. β-Ketoesters were prepared in the reaction of α-diazoesters with rhodium(II) acetate (eq. 360) [728].

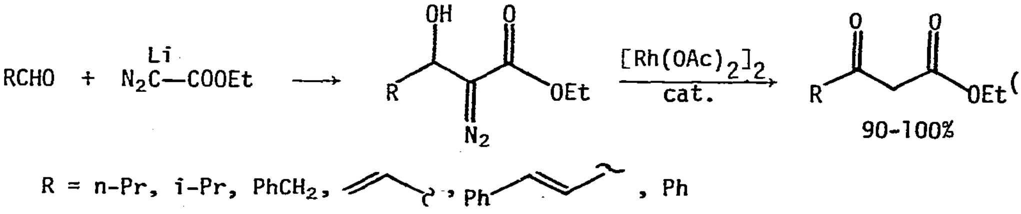
(357)



(358)

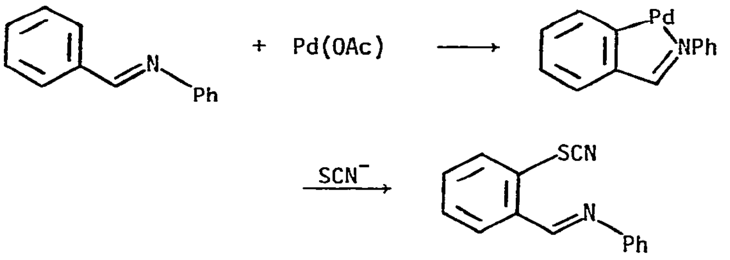


(359)

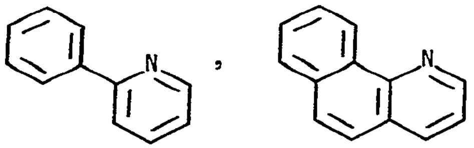


(360)

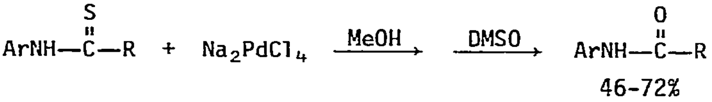
Benzene and nitromethane reacted to form α-nitrotoluene when manganese(II) was electrochemically oxidized to manganese(III) in the presence of these substrates [729]. The thiocyanate group was introduced into aromatic nitrogen containing compounds by ortho palladation followed by reaction with thiocyanate (eq. 361) [730]. Thioamides were converted to amides by reaction with sodium chloropalladate in methanol, followed by DMSO (eq. 362) [731]. Racemic arene tricarbonyl complexes of aromatic aldehydes were resolved by formation of the semioxamazones derived from (-)-(S)-α-phenethylamine [732]. Alcohols added 1,4 to phenylazostilbene in the presence of iron or copper catalysts (eq. 363) [733]. Polycyclic aromatic thiophenes were hydrodesulfurized by reaction with sulfided cobalt(II) oxide-molybdenum(VI) oxide/γ-alumina [734]. Tertiary amines were converted to secondary amines when treated with Pd black and thiolates at 200° (eq. 364) [735].



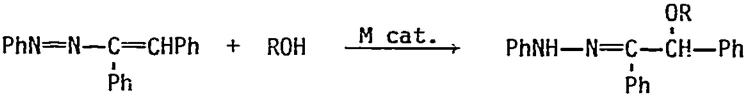
(361)



react similarly



$$\mathrm{ArNH{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}R} + \mathrm{Na_2PdCl_4} \xrightarrow{\mathrm{MeOH}} \xrightarrow{\mathrm{DMSO}} \underset{46\text{-}72\%}{\mathrm{ArNH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R}} \qquad (362)$$



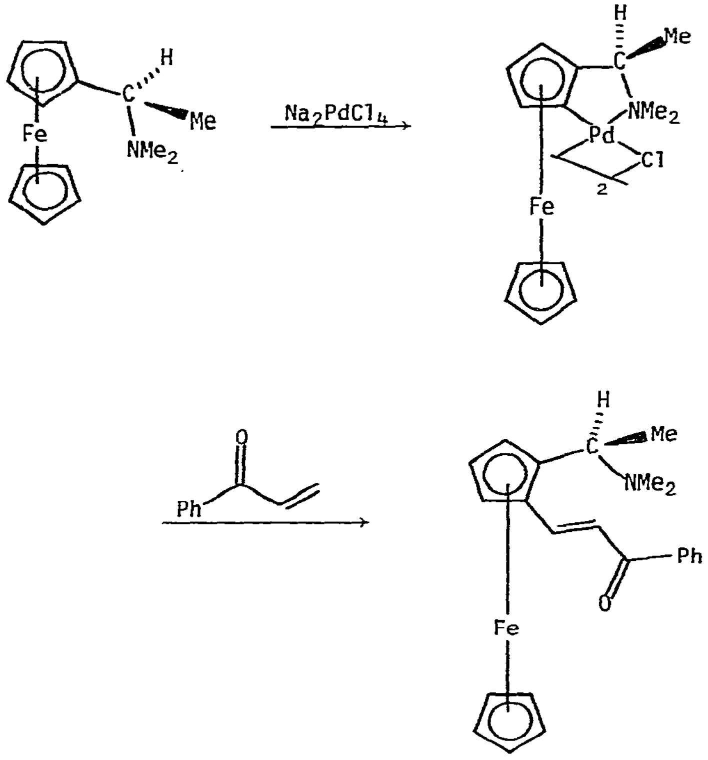
$$\mathrm{PhN{=}N{-}\underset{\displaystyle Ph}{C}{=}CHPh} + \mathrm{ROH} \xrightarrow{\text{M cat.}} \mathrm{PhNH{-}N{=}\underset{\displaystyle Ph}{C}{-}\overset{\displaystyle OR}{CH}{-}Ph} \qquad (363)$$

$M = CuSO_4 \cdot 5H_2O,\ CuCl_2 \cdot 2H_2O,\ FeSO_4 \cdot 7H_2O,\ Fe_2(SO_4)_3 \cdot mH_2O$

$$R^1R^2R^3N + R^4SNa \xrightarrow[\text{2) } H_3O^+]{\text{1) Pd black, } 200^\circ} R^4SR^1 + R^2R^3NH \qquad (364)$$

3° > 2° > 1° for R^1

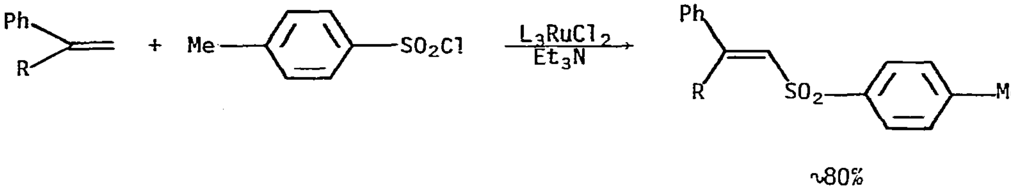
Monosubstituted terminal olefins were converted to the corresponding π-allylpalladium chloride complexes in 41-92% yield by irradiation of the olefin and t-butyl hypochloride, followed by treatment with $PdCl_2$, NaCl, MeOH and H_2O under CO [736]. Triphenylphosphine reacted with styrene in acetic acid in the presence of palladium(II) acetate to give 94% stilbene. The phenyl group was derived from the phosphine [737]. Ethyllithium was produced in the reaction of lithium with $(COD)_2Ni$ followed by hydrogen and ethylene [738]. Optically active 1-dimethylaminoferrocenes were ortho palladated, then treated with conjugated enones to give 1,2-disubstituted ferrocene derivatives (eq.365) [739].



(365)

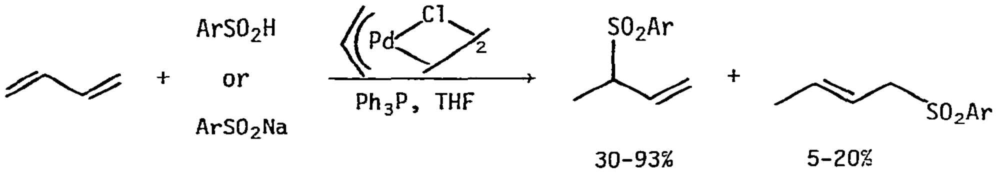
Chelating diphosphine complexes of iron(0) cleave a variety of C—H bonds including those of primary acetylenes, activated methyl groups, and aromatic and other sp^2 hybridized systems [740]. Cyclic ketazines were cleaved to cycloalkenes and cycloalkanones when treated with t-butylhydroperoxide and molybdenum(V) chloride or molybdenum carbonyl [741]. Aryl halides reacted with $CuSC_6F_5$ to produce aryl-perfluoroarylsulfides Ar—S—C_6F_5[742]. Steroidal epoxides were ring opened to the corresponding chlorohydrins by dichloro-bis (benzonitrile)palladium(II). The reaction was most efficient for 4,5-oxido-3-ketosteroids, giving yields of 80-95% [743].

Styrenes reacted with p-toluenesulfonyl chloride in the presence of L_3RuCl_2 as catalyst to give vinyl sulfones (eq. 366) [744]. Conjugated dienes reacted

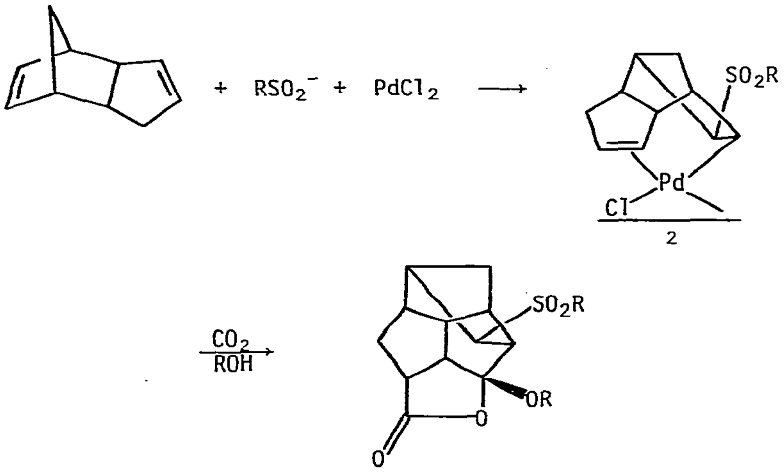


(366)

with sulfinic acids or their sodium salts using π-allylpalladium chloride and phosphine as catalysts to give allylsulfones (eq. 367) [745]. Chelating diolefin palladium(II) complexes reacted in a similar fashion (eq. 368) [746].

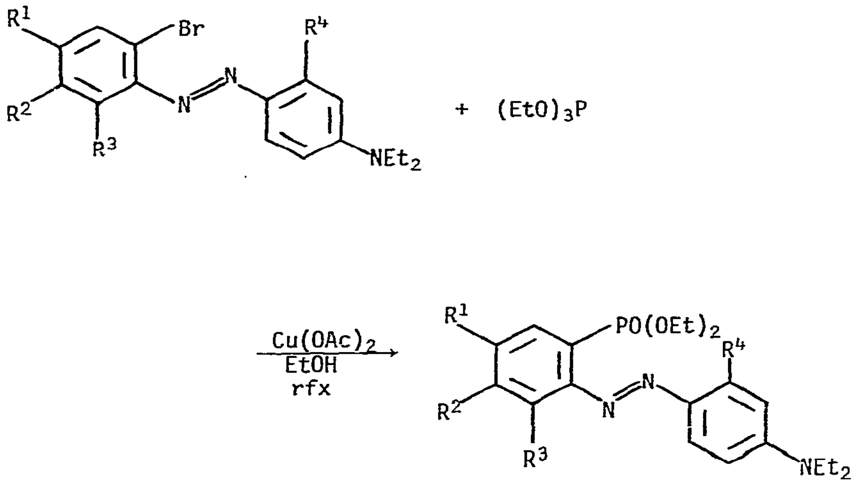


(367)



(368)

Nickel(II) complexes of the lactam of lysine racemized (the lysine) when treated with ethoxide in refluxing ethanol. By seeding with crystals of enantiomerically pure nickel complex, one enantiomer of lysine could be obtained. By running the undesired enantiomer through the above sequence again, racemic lysine could be converted to a single enantiomer [747]. Olefins reacted with diphenyl diselenide in the presence of copper(II) acetate to produce α-acetoxy phenylselenides [748]. Perfluoroalkyl iodides α-added to isocyanides in the presence of copper powder as catalyst [749]. Copper(II) acetate catalyzed the reaction of triethylphosphite with bromo-azobenzenes (eq. 369) [750]. Benzene was converted to mixtures of monosubstituted linear alkylbenzenes



(369)

with one to five carbon atoms by reaction with hydrogen and carbon monoxide (CO, 100 atm) and a $W(CO)_6/AlCl_3$ catalyst at 200°[751].

VI. Reviews

The following reviews have appeared:

Organometallic Compounds of the Transition Metals. (719 references) [752]
Transition Metal Chemistry. (Dissertation) [753]
Fine Chemistry and Catalysis. (~100 references) [754]

Organotransition Metal Compounds as Intermediates in Homogeneous Catalytic Reactions. (35 references) [755]

Synthesis of Fine Chemicals with Noble Metal Catalysts. (15 references) [756]

Transition Metals in Organic Synthesis. Annual Survey Covering the Year 1978. (750 references) [757]

Organometallics in Synthesis. (215 references) [758]

Organic Syntheses via the Polybromo Ketone-Iron Carbonyl Reaction. (40 references) [759]

Stereo- and Regiospecificity in Organic Synthesis Promoted by Metal Ions. (26 references) [760]

Regiocontrolled Aromatic Palladation. A Biogenetic-Type Synthesis of Salutaridine. (253 pages) [761]

Synthetic Applications of Organonickel Complexes in Organic Chemistry. (262 references) [762]

Selective Carbon-Carbon Bond Formation via Transition Metal Catalysis: Is Nickel or Palladium Better than Copper? (59 references) [763]

Carbopalladation and Subsequent Transformations of Olefinic Amines and Sulfides. (285 pages) [764]

Organic Syntheses Applied with Titanium and Zirconium. (50 references) [765]

Organic Syntheses with Copper Reagents. (73 references) [766]

New Applications of Organocopper Intermediates in Organic Synthesis. (231 pages) [767]

Advance in Organic Syntheses Applied with Palladium, Nickel and Rhodium as Catalysts. (21 references) [768]

Palladium Catalysis in Natural Products Synthesis. (23 references) [769]

Selectivity in the Design of the Total Synthesis of Natural Products. (19 references) [770]

New Approaches in Asymmetric Synthesis. (306 references) [771]

Recent Advances in Asymmetric Synthesis. (235 references) [772]

Asymmetric Synthesis. (86 references) [773]

Optical Induction in Organo-Transition Metal Compounds and Asymmetric Catalysis. (85 references) [774]

Industrial Use of Catalysts for Asymmetric Syntheses. (28 references) [775]

Catalytic Chiral Synthesis. (77 references) [776]

The Organic Chemistry of Iron. (673 pages) [777]

Reactions of Iron(0) Carbonyls with Olefins and Strained Ring Systems. (106 pages) [778]

Arene Complexes in Organic Synthesis. (100 references) [779]

The Potential Utility of Transition Metal-Alkyne Complexes and Derived Cluster Compounds as Reagents in Organic Synthesis. (100 references) [780]

Transmetalation Reactions in Organic Synthesis. (302 pages) [781]

New Applications of Organomercury, -Palladium, and -Rhodium Compounds in Organic Synthesis. (34 references) [782]

Organic Synthesis by Means of Metal Clusters. (86 references) [783]

Metal Clusters of Osmium and Their Potential in Homogeneous Catalysts. (17 references) [784]

Alkylidene Complexes of Niobium and Tantalum. (53 references) [785]

Transition Metal Carbene Complexes in Organic Synthesis. (30 references) [786]

Phosphine Complexes of Rh as Homogeneous Catalysts. (29 references) [787]

Rhodium and Ruthenium Catalysis in Organic Synthesis. (153 pages) [788]

Iridium Compounds in Catalysis. (30 references) [789]

Homogeneous Catalysis in Technology. (no references) [790]

Studies of Bond Cleavages by Nickel(0) Complexes. (146 pages) [791]

Electrochemistry of Transition Metal Organometallic Compounds. (many references) [792]

Studies on the Use of Synthetic Zeolites in Catalysis. (44 references) [793]

Polymer Supports in Organic Synthesis. (no references) [794]

Heterogenized Homogeneous Catalysts. (117 references) [795]

Immobilized Metal Complexes for Organic Synthesis. (60 references) [796]

Organic Synthesis Using Supported Reagents. Part I. (68 references) [797]

Silica-Supported Bidentate Phosphine Ligands for Rhodium(I) Catalysts. (172 pages) [798]

Catalyzed Reactions of Alkynes by Polystyrene-Supported Molybdenum. (222 pages) [799]

Metal Vapor Chemistry Related to Molecular Metals. (20 references) [800]

Heterogeneous Metal Complex Catalysts. (203 references) [801]

Metal Cluster Complexes and Heterogeneous Catalysis. A Heterdox View. (74 references) [802]

Catalytic Reactions with Hydrosilane and CO. (48 references) [803]

New Synthesis Methods. 30. Catalytic Reactions with Hydrosilane and Carbon Monoxide. (48 references) [804]

Mechanism of Oxidative Addition of Organic Halides to Group VIII Transition Metal Complexes. (15 references) [805]

Organometallic Elimination Mechanisms: Studies on Osmium Alkyls and Hydrides. (68 references) [806]

Activation of Alkanes by Transition Metal Complexes. (31 references) [807]

Activation of Carbon-Hydrogen Bonds by Some Derivatives of bis(Cyclopentadienyl)-zirconium(IV). (103 pages) [808]

Carbonyls. [809]

REFERENCES

1. H. Onoue, M. Narisada, S. Uyeo, H. Matsamura, K. Okada, T. Yano and W. Nagata, Tetrahedron Lett., 3867 (1979).
2. F. Babudri, L. DiNunno, S. Florio, G. Marchese and F. Naso, J. Organomet. Chem., 166, 265 (1979)
3. S. Terashima, C. C. Tseng, and K. Koga, Chem. Pharm. Bull., 27, 747 (1979).
4. J. E. Maansson, T. Olsson, and O. Wennerstrom, Acta Chem. Scand. B, B33, 307 (1979).
5. F. A. Ziegler and C. Chan Tam, J. Org. Chem., 44, 3428 (1979).
6. Y. Kobayashi, K. Yamamoto, and I. Kumadaki, Tetrahedron Lett., 4071 (1979).
7. P. Savignac, A. Breque, and F. Mathey, Synth. Commun., 9, 487 (1979).
8. P. Savignac, A. Breque, F. Mathey and J. M. Varlet, Synth. Commun., 9, 287 (1979).
9. R. H. Schwartz and J. San Filippo, Jr., J. Org. Chem., 44, 2705 (1979).
10. G. H. Posner and K. A. Babiak, J. Organomet. Chem., 177, 299 (1979).
11. P. Mueller and N. T. M. Phuong, Tetrahedron Lett., 4727 (1978).
12. D. Cabaret, N. Maigrot and Z. Welvart, J. Organomet. Chem., 182, 257 (1979).
13. C. V. Maffeo, G. Marchese, F. Naso, and L. Ronzini, JCS Perkin I, 92 (1979).
14. G. H. Posner and C. M. Lentz, J. Amer. Chem. Soc., 101, 934 (1979).
15. G. A. Mora-Lopez, Ing. Cienc Quim., 3, 43 (1979). [Chem. Abstr., 91, 123375n (1979)]
16. H. Bross, R. Schneider, and H. Hopf, Tetrahedron Lett., 2129 (1979).
17. K. Kondo and S-i Murahashi, Tetrahedron Lett., 1237 (1979).
18. H. R. Allcock and P. J. Harris, J. Amer. Chem. Soc., 101, 6221 (1979).
19. Y. Butsugan, I. Kadosaka, and S. Araki, Chem. Lett., 527 (1979).
20. K. Yamada, Y. Yano, N. Miyaura, and A. Suzuki, Bull. Chem. Soc. Japan, 52, 275 (1979).
21. Y. Yamamoto and K. Maruyama, Yuki Gosei Kaguki Kyokaishi, 37, 641 (1979). [Chem. Abstr., 91, 192224z (1979)]
22. K. Tamao, T. Hayashi, H. Matsumoto, H. Yamamoto, and M. Kumada, Tetrahedron Lett., 2155 (1979).
23. G. Consiglio, O. Piccolo, and F. Morandini, J. Organomet. Chem., 177, C13 (1979).

24. A. Hosomi, M. Saito, and H. Sakurai, Tetrahedron Lett., 429 (1979).
25. H. Okamura, M. Miura and H. Takei, Tetrahedron Lett., 43 (1979).
26. T. T. Tsou and J. K. Kochi, J. Amer. Chem. Soc., **101**, 6319 (1979).
27. T. Hayashi, M. Konishi, and M. Kumada, Tetrahedron Lett., 1871 (1979).
28. S-i Murahashi, M. Yamamura, K-i Yanagisawa, N. Mita, and K. Kondo, J. Org. Chem., **44**, 2408 (1979).
29. N. Cong-Danh, J-P. Beaucourt, and L. Pichat, Tetrahedron Lett., 3159 (1979).
30. J. F. Fauvarque and A. Jutand, J. Organomet. Chem., **177**, 273 (1979).
31. H. Yamanaka, M. Shiraiwa, K. Edo, and T. Sakamoto, Chem. Pharm. Bull., **27**, 270 (1979).
32. N. Miyaura, K. Yamada, and A. Suzuki, Tetrahedron Lett., 3437 (1979).
33. N. Miyaura and A. Suzuki, JCS Chem. Commun., 866 (1979).
34. D. Milstein and J. K. Stille, J. Amer. Chem. Soc., **101**, 4992 (1979).
35. D. Milstein and J. K. Stille, J. Amer. Chem. Soc., **101**, 4981 (1979).
36. M. Veber, K. N. V. Duong, F. Gaudemer, and A. Gaudemer, J. Organomet. Chem., **177**, 231 (1979).
37. J. Marquet and M. Moreno-Manas, Synthesis, 348 (1979).
38. K. Maruyama, T. Ito, and A. Yamamoto, Bull. Chem. Soc. Japan, **52**, 849 (1979).
39. A. S. Narula, Tetrahedron Lett., 1921 (1979).
40. I. Paterson and I. Fleming, Tetrahedron Lett., 995 (1979).
41. I. Paterson and I. Fleming, Tetrahedron Lett., 2179 (1979).
42. K. Yamamoto, M. Ohta and J. Tsuji, Chem. Lett., 713 (1979).
43. J. Cornforth, A. F. Sierakowski, and T. W. Wallace, JCS Chem. Commun., 294 (1979).
44. D. Milstein and J. K. Stille, J. Org. Chem., **44**, 1613 (1979).
45. H. Gopal and C. Tamborski, J. Fluorine Chem., **13**, 337 (1979).
46. F. Sato, H. Kodama, Y. Tomuro, and M. Sato, Chem. Lett., 623 (1979).
47. R. F. Heck, Accts. Chem. Res., **12**, 146 (1979).
48. J. E. Plevyak, J. E. Dickerson and R. F. Heck, J. Org. Chem., **44**, 4078 (1979).
49. I. Arai and G. Doyles Daves, Jr., J. Org. Chem., **44**, 21 (1979).
50. Y. Tamaru, Y. Yamada, and Z-i Yoshida, Tetrahedron, **35**, 329 (1979).
51. C. F. Bigge, P. Kalarites, and M. P. Mertes, Tetrahedron Lett., 1653 (1979).
52. B. M. Trost and Y. Tanigawa, J. Amer. Chem. Soc., **101**, 4743 (1979).
53. N-T Luong-Thi and H. Riviere, Tetrahedron Lett., 4657 (1979).
54. E. Wenkert, E. L. Michelotti, and C. S. Swindell, J. Amer. Chem. Soc., **101**, 2246 (1979).
55. H. Horino and N. Inoue, Tetrahedron Lett., 2403 (1979).
56. A. Heumann, M. Reglier, and B. Waegell, Angew. Chem. Int. Ed., **18**, 866 (1979).
57. A. Heumann, M. Reglier, and B. Waegell, Angew. Chem. Int. Ed., **18**, 867 (1979).
58. B. M. Trost and D. M. T. Chan, J. Amer. Chem. Soc., **101**, 6429 (1979).
59. O. Maruyama, M. Yoshidomi, Y. Fujiwara, and H. Taniguchi, Chem. Lett., 1229 (1979).

60. A. D. Ryabov and A. K. Yatsimirskii, *Kinet. Katal.*, **20**, 106 (1979).
61. A. K. Yatsimirskii, A. Ryabov, and I. V. Berezin, *J. Mol. Catal.*, **5**, 399 (1979).
62. V. E. Taraban'ko, I. V. Kozhevnikov, and K. I. Matveev, *Kinet. Katal.*, **19**, 1160 (1978).
63. P. Hong and H. Yamazaki, *Chem. Lett.*, 1335 (1979).
64. E. R. Evitt and R. G. Bergman, *J. Amer. Chem. Soc.*, **101**, 3973 (1979).
65. H. Kurosawa and N. Asada, *Tetrahedron Lett.*, 255 (1979).
66. K. Hirai, N. Ishii, H. Suzuki, Y. Moro-Oka, and T. Ikawa, *Chem. Lett.*, 1113 (1979).
67. J. P. Haudegond, Y. Chauvin, D. Commereuc, *J. Org. Chem.*, **44**, 3063 (1979).
68. A. J. Pearson, *JCS Perkin I*, 1255 (1979).
69. L. F. Kelley, A. S. Narula, and A. J. Birch, *Tetrahedron Lett.*, 4107 (1979).
70. H. Westmijze, H. Kleijn, and P. Vermeer, *J. Organomet. Chem.*, **172**, 377 (1979).
71. M. Julia, L. Saussine, and G. LeThullier, *J. Organomet. Chem.*, **174**, 359 (1979).
72. J-L. Fabre, M. Julia, B. Mansour, and Saussine, *J. Organomet. Chem.*, **177**, 221 (1979).
73. M. Julia, G. LeThullier, and L. Saussine, *J. Organomet. Chem.*, **177**, 211 (1979).
74. S. Brandt and P. Helquist, *J. Amer. Chem. Soc.*, **101**, 6973 (1979).
75. C. P. Casey, S. W. Polichnouski, A. J. Schusterman, and C. R. Jones, *J. Amer. Chem. Soc.*, **101**, 7282 (1979).
76. H. Kanai and N. Hiraki, *Chem. Lett.*, 761 (1979).
77. N. Kawabata, I. Kamemura, and M. Naka. *J. Amer. Chem. Soc.*, **101**, 2139 (1979).
78. J. J.Barber, C. Willis, and G.M. Whitesides, *J. Org. Chem.*, **44**, 3603 (1979).
79. T. Saito, A. Itoh, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 3519 (1979).
80. G. Erker and K. Kropp, *J. Amer. Chem. Soc.*, **101**, 3659 (1979).
81. B. E. Marijanoff, *J. Org. Chem.*, **44**, 4410 (1979).
82. T. Nagase, T. Akitani, and Y. Yoneda, *Sumitomo Kagaku Tokushugo*, 9 (1978); *Chem. Abstr.*, **90**, 54510t (1979).
83. R. Noyori, M. Nishizawa, F. Shimizu, Y. Hayakawa, K. Maruoka, S. Hashimoto, and H. Yamamoto, *J. Amer. Chem. Soc.*, **101**, 220 (1979).
84. B. M. Trost and M. T. D. Chan, *J. Amer. Chem. Soc.*, **101**, 6429 (1979).
85. T. S. Abram and R. Baker, *JCS Chem. Commun.*, 267 (1979).
86. J. P. Genet, and J. Ficinl, *Tetrahedron Lett.*, 1499 (1979).
87. T-a. Mitsudo, K. Kokuryo, T. Shinsugi, Y. Nakagawa, Y. Watanabe, and Y. Takegami, *J. Org. Chem.*, **44**, 4492 (1979).
88. M. Catellani, G. P. Chiusoli, E. Pradi, and G. Salerno, *J. Organomet. Chem.*, **177**, C29 (1979).

89. A. Alexakis, G. Cahiez, and J. F. Normant, *J. Organomet. Chem.*, **177**, 293 (1979).
90. A. Alexakis, G. Cahiez, and J. F. Normant, *Synthesis*, 826 (1979).
91. J. F. Normant, *Pure Appl. Chem.*, **50**, 709 (1978).
92. H. Kleijn, H. Westmijze, A. Schaap, H. J. T. Bos, and P. Vermeer, *Rec. Trav. Chim.*, **98**, 209 (1979).
93. J-G. Duboudin and B. Jousseaume, *Synth. Commun.*, **9**, 53 (1979).
94. A. Marfat, P. R. McGuirk, and P. Helquist, *J. Org. Chem.*, **44**, 1345 (1979).
95. A. Marfat, P. R. McGuirk, and P. Helquist, *J. Org. Chem.*, **44**, 3888 (1979).
96. B. B. Snider, R. S. E. Conn and M. Karras, *Tetrahedron Lett.*, 1679 (1979).
97. K. Kaneda, Y. Uchiyama, Y. Fujiwara, T. Imanaka, and S. Teranishi, *J. Org. Chem.*, **44**, 55 (1979).
98. P. Hong, B-R. Cho, and H. Yamazaki, *Chem. Lett.*, 339 (1979).
99. E-i. Negishi, D. E. Van Horn, A. O. King, and N. Okukado, *Synthesis*, 501 (1979).
100. B. B. Snider and M. Karras, *J. Organomet. Chem.*, **179**, C37 (1979).
101. H. Westmijze and P. Vermeer, *Synthesis*, 390 (1979).
102. H. Kleijn, C. J. Elsevier, H. Westmijze, J. Meijer and P. Vermeer, *Tetrahedron Lett.*, 3101 (1979).
103. G. Balme, M. Malacria, and J. Gore, *Tetrahedron Lett.*, 7 (1979).
104. P. Baret, E. Barreiro, A. E.Greene, J-L. Lucke, M-A. Teixeira, and P. Crabbe, *Tetrahedron*, **35**, 2931 (1979).
105. F. Delbecq, R. Baudony, and J. Gore, *Nouv. J. Chem.*, **3**, 321 (1979).
106. J. G. Duboudin and B. Jousseaume, *J. Organomet. Chem.*, **168**, 1 (1979).
107. J. G. Duboudin, B. Jousseaume, and A. Bonakdar, *J. Organomet. Chem.*, **168**, 227 (1979).
108. H. D. Verkruijsse and M. Hasselaar, *Synthesis*, 292 (1979).
109. M. Julia, A. Righini, J-N. Verpeaux, *Tetrahedron Lett.*, 2393 (1979).
110. C. Gallina and P. G. Ciattini, *J. Amer. Chem. Soc.*, **101**, 1035 (1979).
111. V. Calo, L. Lopez, G. Marchese and G. Pesce, *Tetrahedron Lett.*, 3873 (1979).
112. G. Cassani, P. Massardo, and P. Piccardi, *Tetrahedron Lett.*, 633 (1979).
113. H. Kleijn, H. Westmijze, K. Kruithof, and P. Vermeer, *Rec. Trav. Chim.*, **98**, 27 (1979).
114. Y. Gendreau and J. F. Normant, *Tetrahedron*, **35**, 1517 (1979).
115. J. F. Normant, A. Commercon, Y. Gendreau, M. Bourgain, and J. Villieras, *Bull. Soc. Chim. Fr.*, II, 309 (1979).
116. Y. Gendreau and J. F. Normant, *Bull. Soc. Chim. Fr.*, II, 305 (1979).
117. H. Okamura and H. Takei, *Tetrahedron Lett.*, 3425 (1979).
118. J. L. Roustan, J. Y. Merour and F. Houlihan, *Tetrahedron Lett.*, 3721 (1979).
119. A. J. Chalk and S. A. Magennis, *Catal. Org. Synth.*, 139 (1977).
120. D. C. Brown, S. A. Nichols, A. Bruce Gilpin, and D. W. Thompson, *J. Org. Chem.*, **44**, 3457 (1979).

121. P. J. Wittek, T. Kai Liao, and C. Chung Cheng, *J. Org. Chem.*, **44**, 870 (1979).
122. K. Takagi, N. Hayama, and S. Inokawa, *Chem. Lett.*, 917 (1979).
123. R. D. Rieke and L. D. Rhyne, *J. Org. Chem.*, **44**, 3445 (1979).
124. T. T. Tsou and J. K. Kochi, *J. Amer. Chem. Soc.*, **101**, 7547 (1979).
125. B. Ortiz, A. Sandoval, and F. Walls, *Rev. Latinoam. Quim.*, **9**, 197 (1978).
126. H. Inoue, M. Suzuki and N. Fujimoto, *J. Org. Chem.*, **44**, 1722 (1979).
127. H. Ledon, I. Tkatchenko, and D. Young, *Tetrahedron Lett.*, 173 (1979).
128. S. Nakanishi, T. Shundo, T. Nishibuchi, and Y. Otsuji, *Chem. Lett.*, 955 (1979).
129. J. R. Fritch, K.P.C.Vollhardt, M. R. Thompson, and V. W. Day, *J. Amer. Chem. Soc.*, **101**, 2768 (1979).
130. J-i. Yoshida, K. Tamao, T. Kakui, and M. Kumada, *Tetrahedron Lett.*, 1141 (1979).
131. V. V. Ramana Rao, Ch. V. Kumar, and D. Devaprabhakara, *J. Organomet. Chem.*, **179**, C7 (1979).
132. G. Oehme and H. Pracejus, *Tetrahedron Lett.*, 343 (1979).
133. A. Hosomi, H. Hashimoto, H. Kobayashi, and H. Sakurai, *Chem. Lett.*, 245 (1979).
134. J. Luechetti, J. Remion and A. Krief, *Comptes Rend., C*, **288**, 553 (1979).
135. A. Suzuki and N. Miyaura, *Kagaku (Kyoto)*, **34**, 322 (1979); *Chem. Abstr.*, **91**, 175410q (1979).
136. B. M. Trost and F. W. Gowland, *J. Org. Chem.*, **44**, 3448 (1979).
137. B. M. Trost and T. P. Klun, *J. Amer. Chem. Soc.*, **101**, 6756 (1979).
138. B. M. Trost and T. R. Verhoeven, *J. Amer. Chem. Soc.*, **101**, 1595 (1979).
139. B. M. Trost and D. M. T. Chan, *J. Amer. Chem. Soc.*, **101**, 6432 (1979).
140. Y. Ito, A. Aoyama, T. Hirao, A. Mochizuki and T. Saegusa, *J. Amer. Chem. Soc.*, **101**, 494 (1979).
141. H. Kurosawa, *JCS Dalton*, 939 (1979).
142. Y. Castanet and F. Petit, *Tetrahedron Lett.*, 3221 (1979).
143. G. Balavoine, C. Eskenazi, and M. Guillemot, *JCS Chem. Commun.*, 1109 (1979).
144. D. Seebach and W. Langer, *Helv. Chim. Acta*, **62**, 1701 (1979).
145. K. Irie, A. Imazawa, K-i. Watanabe, *Chem. Lett.*, 1401 (1979).
146. M. Yamaguchi, M. Murakami, and T. Mukaiyama, *Chem. Lett.*, 957 (1979).
147. C. Walsselman and M. Tordeux, *J. Org. Chem.*, **44**, 4219 (1979).
148. G. Simonneaux and G. Jaouen, *Tetrahedron*, **35**, 2249 (1979).
149. S. Cacchi, F. Latorre, and D. Misiti, *Chim. Ind. (Milan)*, **60**, 715 (1978); *Chem. Abstr.*, **90**, 87731u (1979).
150. Y. Kojima, S. Wakita and N. Kato, *Tetrahedron Lett.*, 4577 (1979).
151. C. Huynh, F. Derguini-Boumechal and G. Linstrumelle, *Tetrahedron Lett.*, 1503 (1979).
152. K. Mori and S. Tamada, *Tetrahedron*, **35**, 1279 (1979).
153. G. Teutsch and A. Belanger, *Tetrahedron Lett.*, 2051 (1979).

154. M. A. W. Finch, T. V. Lee, S. M. Roberts, and R. F. Newton, *JCS Chem. Commun.*, 677 (1979).

155. R. J. Cave, C. C. Howard, G. Klinkert, R. F. Newton, D. P. Reynolds, A. H. Wadsworth, and S. M. Roberts, *JCS Perkin I*, 2954 (1979).

156. I. V. Kozhevnikov and K. F. Matveev, *Russ. Chem. Rev.*, 649 (1978).

157. A. J. Schouten, D. Noordegraaf, A. P. Jekel, and G. Challa, *J. Mol. Catal.*, **5**, 331 (1979).

158. G. Davies, M. F. El-Shazly, D. R. Kozlowski, C. E. Kramer, M. W. Rupich, and R. W. Slaven, *Adv. Chem. Ser.*, **173**, 178 (1979).

159. I. V. Kozhevnikov, S. A. Tuzovskaya, V. P. Lopatinskii, V. M. Sutyagin, O. V. Rotar, and K. I. Matveev, *React. Kinet. Catal. Lett.*, **9**, 287 (1978).

160. Y. Kobayashi, T. Taguchi, and T. Morikawa, *Tetrahedron Lett.*, 3555 (1978).

161. L. Lombardo and F. Sondheimer, *J. Chem. Res. (S)*, 454 (1978).

162. M. F. Semmelhack, G. R. Clark, R. Farina and M. Saeman, *J. Amer. Chem. Soc.*, **101**, 217 (1979).

163. M. F. Semmelhack, J. Bisaha, and M. Czarny, *J. Amer. Chem. Soc.*, **101**, 768 (1979).

164. M. F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, *J. Amer. Chem. Soc.*, **101**, 3535 (1979).

165. M. F. Semmelhack, J. J. Harrison, and Y. Thebtaranonth, *J. Org. Chem.*, **44**, 3275 (1979).

166. C. A. L. Mahaffy and P. L. Pauson, *J. Chem. Res., Synop*, 126 (1979).

167. C. Heathcock, T. C. Germroth, and S. L.Graham, *J. Org. Chem.*, **44**, 4481 (1979).

168. M. Schwarz, N. Wakabayashi, and E. G. Thing, *Org. Prep. Proced. Int.*, **11**, 97 (1979); *Chem. Abstr.*, **91**, 39658z (1979).

169. R. D. Clark, *Synth. Commun.*, **9**, 325 (1979).

170. G. Stork and E. W. Logusch, *Tetrahedron Lett.*, 3361 (1979).

171. E. W. Logusch, *Tetrahedron Lett.*, 3365 (1979).

172. B. R. Davis and S. J. Johnson, *JCS Perkin I*, 2840 (1979).

173. M. B. Floyd and M. J. Weiss, *J. Org. Chem.*, **44**, 71 (1979).

174. R. K. Boeckman, Jr. and K. J. Bruza, *J. Org. Chem.*, **44**, 4781 (1979).

175. J. Ficini, P. Kahn, S. Falon, and A. M. Touzin, *Tetrahedron Lett.*, 67 (1979).

176. D. B. Ledlie and G. Miller, *J. Org. Chem.*, **44**, 1006 (1979).

177. C. Huynh and G. Linstrumelle, *Tetrahedron Lett.*, 1073 (1979).

178. F. Sato, T. Oikawa, and M. Sato, *Chem. Lett.*, 167 (1979).

179. R. Davis and K. G. Untch, *J. Org. Chem.*, **44**, 3755 (1979).

180. K. K. Heng and R. A. J. Smith, *Tetrahedron*, **35**, 425 (1979).

181. P. Miginiac, G. Daviand, and F. Gerard, *Tetrahedron Lett.*, 1811 (1979).

182. Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Org. Chem.*, **44**, 1744 (1979).

183. A. G. Schultz, J. D. Godfrey, E. V. Arnold, and J. Clardy, *J. Amer. Chem. Soc.*, **101**, 1276 (1979).

184. S. Mubarik Ali, M. A. W. Finch, S. M. Roberts, and R.F. Newton, *JCS Chem. Comm.*, 679 (1979).

185. C. P. Casey and M. C. Cesa, J. Amer. Chem. Soc., 101, 4236 (1979).
186. J. Berlan, J-P. Battioni, and K. Koosha, Bull. Soc. Chim. Fr. (II), 183 (1979).
187. R. A. J. Smith and D. J. Hannah, Tetrahedron, 35, 1183 (1979).
188. J. P. Marino and D. M. Floyd, Tetrahedron Lett., 675 (1979).
189. J. P. Marino and N. Hatanaka, J. Org. Chem., 44, 4467 (1979).
190. J. J. Eisch and J. E. Galle, J. Org. Chem., 44, 3277 (1979).
191. C. Chuit, R. Sauvetre, D. Masure and J. F. Normant, Tetrahedron, 35, 2645 (1979).
192. F.-W. Sum and L. Weiler, Can. J. Chem., 57, 1431 (1979).
193. H. Johansen and K. Udheim, Acta. Chem. Scand. B, 33, 460 (1979).
194. R. Pardo, J-P. Zahora, and M. Santelli, Tetrahedron Lett., 4557 (1979).
195. C. H. Chao, D. W. Hart, R. Bau, and R. F. Heck, J. Organomet. Chem., 179, 301 (1979).
196. S. Cacchi, F. LaTorre, and D. Misiti, Tetrahedron Lett., 4591 (1979).
197. M. Pardhasaradhi and B. M. Choudary, Ind. J. Chem., Sect. B. 17B, 79 (1979).
198. R. L. Pruett, Adv. Organomet. Chem., 17, 1 (1979).
199. J. Hjortkjaer, J. Mol. Catal., 5, 377 (1979).
200. V. M. Ushakov, Deposited Doc., 280 (1978); Chem. Abstr., 91, 192508v (1979).
201. V. M. Ushakov, D. B. Kazarnovskaya, L. L. Klinova, and N. M. Malygina, Neftekhimiya, 19, 62 (1979); Chem. Abstr., 90, 186438k (1979).
202. G. Gregorio, G. Montrasi, M. Tampieri, P. Cavalieri d'Oro, G. Pagani, and A. Andreetta, Symp. Rhodium Homogeneous Catal., 121 (1978); Chem. Abstr., 90, 38251d (1979).
203. R. H. Crabtree and H. Felkin, J. Mol. Catal., 5, 75 (1979).
204. W. Strohmeier and M. Michel, Symp. Rhodium Homogeneous Catal., 104 (1978); Chem. Abstr., 90, 71705c (1979).
205. R. B. Borisov, V. Yu. Gankin, and V. A. Rybakov, Zh. Prikl. Khim., 52, 625 (1979); Chem. Abstr., 91, 4930e (1979).
206. T. Hayashi, M. Tanaka, and I. Ogata, J. Mol. Catal., 6, 1 (1979).
207. R. B. King, A. D. King, Jr., and M. Z. Iqbal, J. Amer. Chem. Soc., 101, 4893 (1979).
208. K. Bott, Symp. Rhodium Homogeneous Catal., 106 (1978); Chem. Abstr., 90, 54623g (1979).
209. D. Bondoux, D. Houalla, B. Mentzen, C. Pradat, J. Riess, I. Tkatchenko, and R. Wolf, Symp. Rhodium Homogeneous Catal., 1 (1978); Chem. Abstr., 90, 121718g (1979).
210. K. Murata, A. Matsudo, K-i. Bando, and Y. Sugi, JCS Chem. Commun., 785 (1979).
211. Y. Kawabata, T. Hayashi, and I. Ogata, JCS Chem. Commun., 462 (1979).
212. Y. Watanabe, T-a. Mitsudo, Y. Yasunori, J. Kikuchi, and Y. Takegami, Bull. Chem. Soc. Japan, 52, 2735 (1979).
213. T. Hayashi, M. Tanaka, Y, Iheda, and I. Ogata, Bull. Chem. Soc. Japan, 52, 2605 (1979).

214. V. Schurig, *J. Mol. Catal.*, **6**, 75 (1979).

215. A. Stefani, D. Tatone, and P. Pino, *Helv. Chim. Acta*, **62**, 1098 (1979).

216. F. Piacenti, G. Menchi, P. Frediani, U. Matteoli, and C. Botteghi, *Chim. Ind. (Milan)*, **60**, 808 (1978); *Chem. Abstr.*, **90**, 86616y (1979).

217. S. Fritschel, J. J. H. Ackerman, T. Keyser, and J. K. Stille, *J. Org. Chem.*, **44**, 3152 (1979).

218. G. Gubitosa, H. H. Brintzinger, *Colloq. Int. CNRS*, **281**, 173 (1978); *Chem. Abstr.*, **91**, 174442q (1979).

219. T. Mason, D. Grote, B. Trivedi, *Catal. Org. Synth.*, 165 (1977); *Chem. Abstr.*, **91**, 123358j (1979).

220. M. Ichikawa, *J. Catal.*, **56**, 127 (1979).

221. M. Ichikawa, *J. Catal.*, **59**, 67 (1979).

222. M. O. Farrell, C. H. Van Dyke, L. J. Boucher, and S. J. Metlin, *J. Organomet. Chem.*, **169**, 199 (1979).

223. A. M. Lennertz, J. Laege, M. J. Mirbach, and A. Saus, *J. Organomet. Chem.*, **171**, 203 (1979).

224. G. Mignani, H. Patin, and R. Dabard, *J. Organomet. Chem.*, **169**, C19 (1979).

225. J. W. Suggs, *J. Amer. Chem. Soc.*, **101**, 489 (1979).

226. G. Cavinato and L. Toniolo, *J. Mol. Catal.*, **6**, 111 (1979).

227. G. Cavinato and L. Toniolo, *Chimia*, **33**, 286 (1979).

228. R. Bardi, A. Del Pra, A. M. Piazzesi, and L. Toniolo. *Inorg. Chim. Acta*, **35**, L345 (1979).

229. D. E. Morris, G. V. Johnson, *Symp. Rhodium Homogeneous Catal.*, 113 (1978); *Chem. Abstr.*, **90**, 38250c (1979).

230. A. L. Lapidus, D. Pirozhkov, A. R. Sharipova, and K. V. Puzitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 371 (1979); *Chem. Abstr.*, **90**, 186311p (1979).

231. A. Lapidus, S. D. Pirozhkov, A. R. Sharipova, and A. N. Detyak, *Neftekhimiya*, **19**, 433 (1979); *Chem. Abstr.*, **91**, 107643t (1979).

232. J. K. Stille and R. Divakaruni, *J. Org. Chem.*, **44**, 3474 (1979).

233. R. S. Divakaruni, *Diss. Abstr. Int. B*, **39**, 5923 (1979); *Chem. Abstr.*, **91**, 157217c (1979).

234. G. Cometti and G. P. Chiusoli, *J. Organomet. Chem.*, **181**, C14 (1979).

235. D. B. Carr, J. Schwartz, *J. Amer. Chem. Soc.*, **101**, 3521 (1979).

236. N. G. Mekhryakova, L. G. Bruk, O. L. Kaliya, O. N. Temkin, A. Yu. Prudnikov, *Kinet. Katal.*, **20**, 629 (1979); *Chem. Abstr.*, **91**, 90814z (1979).

237. I. A. Orlova, N. F. Alekseeva, A. D. Troitskaya, and O. N. Temkin, *Zh. Obshch. Khim.*, **49**, 1601 (1979); *Chem. Abstr.*, **91**, 210506z (1979).

238. K. Tamao, T. Kakui, and M. Kumada, *Tetrahedron Lett.*, 619 (1979).

239. T. F. Murray, *Diss. Abstr. Int. B*, **39**, 4342 (1979); *Chem. Abstr.*, **90**, 203455h (1979).

240. H. Alper and J. K. Currie, *Tetrahedron Lett.*, 2664 (1979).

241. J. Y. Merour, J. L. Roustan, C. Charrier, J. Benaim, J. Collin, and P. Cadiot. *J. Organomet. Chem.*, **168**, 337 (1979).

242. Y. Inoue, T. Hibi, M. Satake, and H. Hashimoto, *JCS Chem. Comm.*, 982 (1979).

243. R. Santi, M. Marchi, *J. Organomet. Chem.*, **182**, 117 (1979).

244. J. J. Brunet, C. Sidot, B. Loubinoux, and P. Caubere, *J. Org. Chem.*, **44**, 2199 (1979).

245. Y. Kimura, Y. Tomita, S. Nakanishi, and Y. Otsuji, *Chem. Lett.*, 321 (1979).

246. C. Cahiez, A. Alexakis, and J. F. Normant, *Synth. Commun.*, 639 (1979).

247. M. Yamashita, S. Yamamura, M. Kurumoto, and R. Suemitsu, *Chem. Lett.*, 1067 (1979).

248. R. C. Cookson and G. Farquharson, *Tetrahedron Lett.*, 1255 (1979).

249. J. Bergman and L. Engman, *J. Organomet. Chem.*, **175**, 233 (1977)

250. B. K. Nefedev, V. I. Manov-Yuvenskii, *Bull. Akad. Nauk SSSR*, **27**, 2066 (1978).

251. G. A. Razuvaeva, B. K. Nefedov, V. I. Manov-Yuvenskii, L. V. Gorbunova, N. N. Vavilina, A. L. Chimishkyan, and A. V. Smetanin, *Bull. Akad. Nauk SSSR*, **27**, 2294 (1978).

252. B. N. Nefedov, V. I. Manov-Yuvenskii, *Bull. Akad. Nauk SSSR*, **28**, 540 (1979).

253. S. S. Novikov, B. K. Nefedov, V. I. Manov-Yuvenskii, B. F. Dzhurinskii, A. L. Chimishkyan, A. V. Smetanin, G. V. Lysanova, E. M. Reznik, and L. Z. Gokhman, *Dokl. Akad. Nauk SSSR*, **247**, 125 (1979); *Chem. Abstr.*, **91**, 211010v (1979).

254. K. Unverferth, R. Hontsch, and K. Schwetlick, *J. Pract. Chem.*, **321**, 586 (1979).

255. H. Tietz, K. Unverferth, D. Sagasser, and K. Schwetlick, *Z. Chem.*, **19**, 304 (1979).

256. T. Sakakibara and H. Alper, *JCS Chem. Commun.*, 458 (1979).

257. L. Toniolo, *Inorg. Chim. Acta*, **35**, L367 (1979).

258. V. M. Dzhemilev, R. N. Fakhretdinov, A. G. Telin, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2158 (1979).

259. D. Forster, *Adv. Organomet. Chem.*, **17**, 255 (1979).

260. T. Mizoroki, T. Matsumoto, and A. Ozaki, *Bull. Chem. Soc. Japan*, **52**, 479 (1979).

261. N. Takahashi, Y. Orikasa, and T. Yashima, *J. Catal.*, **59**, 61 (1979).

262. F. Rivetti and U. Romano, *J. Organomet. Chem.*, **174**, 221 (1979).

263. J. E. Hallgren and R. O. Matthews, *J. Organomet. Chem.*, **175**, 135 (1979).

264. J. A. Roth and M. Orchin, *J. Organomet. Chem.*, **172**, C27 (1979).

265. S. Murai, T. Kato, N. Sonada, Y. Seki and K. Kawamoto, *Angew. Chem. IE.*, **18**, 393 (1979).

266. H. Alper, B. Marchand and M. Tanaka, *Can. J. Chem.*, **57**, 598 (1979).

267. F. Sato, Y. Mori, and M. Sato, *Chem. Lett.*, 1337 (1978).

268. T.-Y. Luh, *J. Organomet. Chem.*, **174**, 169 (1979).

269. K. Maruyama, T. Shio, and Y. Yamamoto, *Bull. Chem. Soc. Japan*, **52**, 1877 (1979)

270. C. P. Chiusoli, G. Salerno, E. Bergamaschi, G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *J. Organomet. Chem.*, **177**, 245 (1979).

271. E. A. Kelley, G. A. Wright, and P. M. Maitlis, *JCS Dalton*, 179 (1979).

272. B. E. Foulger, F-W. Grevels, D. Hess, E. A. Koerner von Gustorf and J. Leitich, JCS Dalton, 1451 (1979).

273. C. D. Wood and R. R. Schrock, J. Amer. Chem. Soc., 101, 5421 (1979).

274. U. M. Dzhemilev, A. Z. Yakupova, and G. A. Tolstikov, J. Org. Chem. USSR, 15, 1037 (1979).

275. J. Thivolle-Cazat and I. Tkatchenko, JCS Chem. Comm., 377 (1979).

276. M. Murakami and S. Nishida, Chem. Lett., 931 (1979).

277. D. Huchette, J. Nicole, and F. Petit, Tetrahedron Lett., 1035 (1979).

278. D. Ballivet-Tkatchenko, M. Riveccie, and N. El Murr, J. Amer. Chem. Soc., 101, 2764 (1979).

279. U. M. Dzhemilev, G. M. Latypov, G. A. Tolstikov, and O. S. Vostrikova, Bull. Akad. Nauk SSSR, 28, 509 (1979).

280. I. Mochida, K. Kitagawa, H. Fujitsu, and K. Takeshitia, J. Catal., 54, 175 (1978).

281. H. Tom Dieck and A. Kinzel, Angew. Chem. IE, 18, 324 (1979).

282. B. Bogdanovic, Adv. Organomet. Chem., 17, 105 (1979).

283. F. Brille, J. Kluth, and H. Schenkluhn, J. Mol. Catal., 5, 27 (1979).

284. F. Brille, P. Heimbach, J. Kluth, and H. Schenkluhn, Angew. Chem. IE., 18, 400 (1979).

285. K. Sporka, J. Hanika, V. Ruzicka, Sb. Vys. Sk. Chem.-Technol. Praze, Org. Chem. Technol., C25, 43 (1978); Chem. Abstr., 92, 6583p (1979).

286. U. M. Dzhemilev, L. Yu. Gubaidullin, and G. A. Tolstikov, Bull. Akad. Nauk SSSR, 28, 102 (1979).

287. A. C. L. Su, Symp. Rhodium Homogeneous Catal., Proc., 128 (1978); Chem. Abstr., 90, 91246d (1979).

288. V. M. Vdovin, A. B. Amerik, V. A. Poletaev, Iz.Akad. Nauk SSSR, Ser. Khim., 12, 2781 (1978); Chem. Abstr., 90, 103468w (1979).

289. X. Cochet, A. Mortreux, F. Petit, C.R. Hebd. Seances Acad. Sci., Ser. C, 288, 105 (1979).

290. F. G. Yusupova, G. A. Gailyunas, I. I. Furlei, A. A. Panasenko, V. D. Sheludyakov, G. A. Tolstikova, V. P. Yur'ev, Bull. Akad. Nauk SSSR, 28, 552 (1979).

291. A. Busch, P. Heimbach, R.-V. Meyer, and H. Schenkluhn, J. Chem. Res., 228 (1979).

292. T. Mandai, H. Yasuda, M. Kaito, J. Tsuji, R. Yamaoka and H. Fukami, Tetrahedron, 35, 309 (1979).

293. J. Tsuji, T. Yamakawa and T. Mandai, Tetrahedron Lett., 3741 (1979).

294. T. Takahashi, K. Kasuga, M. Takahashi, and J. Tsuji, J. Amer. Chem. Soc., 101, 5072 (1979).

295. J. Tsuji, Y. Kobayashi, and I. Shimizu, Tetrahedron Lett., 39 (1979).

296. J. Tsuji, I. Shimizu, H. Suzuki, and Y. Naito, J. Amer. Chem. Soc., 101, 5070 (1979).

297. B. A. Patel, L-Chang Kao, N. A. Cortese, J. V. Vinkiewicz, and R. F. Heck, J. Org. Chem., 44, 918 (1979).

298. J. Tsuji, K. Kasuga, and T. Takahashi, Bull. Chem. Soc. Japan, 52, 216 (1979).

299. U. M. Kzhemilev, L. Yu. Gubaidullin, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 915 (1979); Chem. Abstr., 91, 56491g (1979).

300. R. Baker and M. J. Crimmin, JCS Perkin I, 1264 (1979).

301. U. M. Dzhemilev, L-Yu. Gubaidullin, and G. A. Tolstikov, Bull. Akad. Nauk SSSR, 27, 2284 (1978); Chem. Abstr., 90, 121386x (1979).

302. N. Hao, J. F. Sawyer, B. G. Sayer, and M. J. McGlinchey, J. Amer. Chem. Soc., 101, 2203 (1979).

303. J. D. Fellman, G. A. Rupprecht, and R. R. Schrock, J. Amer. Chem. Soc., 101, 5099 (1979).

304. T. Matsuda, H. Miura, K. Sugiyama, N. Ohno, S. Keino, and A. Kaise, JCS Faraday Trans. 1, 75, 1513 (1979).

305. M. Ennis, R. Foley, A. R. Manning, J. Organomet. Chem., 166, C18 (1979).

306. U. M. Dzhemilev, R. I. Khusnutdinov, D. K. Galeev, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 910 (1979); Chem. Abstr., 91, 38982p (1979).

307. W. Keim, B. Hoffmann, R. Lodewick, M. Peuckert, G. Schmitt, J. Fleischhauer, and U. Meier, J. Mol. Catal., 6, 79 (1979).

308. E. A. Mintz, M. D. Rausch, J. Organomet. Chem., 171, 345 (1979).

309. K. Mizuno, J. Ogawa, M. Kamura, and Y. Otsuji, Chem. Lett., 731 (1979).

310. G. Giacomelli, A. M. Caporusso, and L. Lardicci, J. Org. Chem., 44, 231 (1979).

311. A. M. Caporusso, G. Giacomelli and L. Lardicci, J. Org. Chem., 44, 1496 (1979).

312. A. M. Caporusso, G. Giampaolo and L. Lardicci, JCS Perkin I, 3139 (1979).

313. G. Giacomelli, F. Marcacci, A. M. Caporusso, and L. Lardicci, Tetrahedron Lett., 3217 (1979).

314. I. U. Khand, P. L. Pauson, J. A. M. Habib, J. Chem. Res. (S), 348 (1978); Chem. Abstr., 90, 103690n (1979).

315. P. L. Pauson and I. U. Khand, Heterocycles, 11, 59 (1978).

316. R. L. Funk and K. P. C. Vollhardt, J. Amer. Chem. Soc., 101, 215 (1979).

317. R. L. Funk, Diss. Abstr. Int. B, 40, 245 (1979).

318. A. J. Carty, N. J. Taylor, and D. K. Johnson, J. Amer. Chem. Soc., 101, 5422 (1979).

319. S. Ceriotti, G. Longoni, P. Chini, J. Organomet. Chem., 174, C27 (1979).

320. K. Kaneda, T. Uchiyama, Y. Fujiwara, T. Imanaka, and S. Teranishi, J. Org. Chem., 44, 55 (1979).

321. H. Dumas, J. Levisalles, H. Rudler, J. Organomet. Chem., 177, 239 (1979).

322. N. Calderon, J. P. Lawrence, E. A. Ofstead, Adv. Organomet. Chem., 17, 449 (1979).

323. M. Leconte and J. M. Basset, Nouv. J. Chim., 3, 429 (1979).

324. F. N. Tebbe, G. W. Parshall and D. W. Ovenall, J. Amer. Chem. Soc., 101, 5074 (1979).

325. N. B. Bespalova, L. V. Efstifeev, Nov. Aspekty Neftekhim. Sinteza, 19 (1978); Chem. Abstr., 90, 167951f (1979).

326. J. A. K. DuPlessis and P. J. Heenop, S. Afr. J. Chem., 32, 1 (1979); Chem. Abstr., 91, 211565e (1979).

327. N. B. Bespalova, E. P. Babich, V. M. Vdovin, Bull. Akad. Nauk SSSR, 28, 1314 (1979).

328. F. Garnier, P. Krausz and J-E. Dubois, J. Organomet. Chem., 170, 195 (1979).

329. K. Tanaka, K-i. Tanaka, and K. Miyahara, JCS Chem. Comm., 314 (1979).

330. J. C. Mol, E. F. G. Woerlee, JCS Chem. Comm., 330 (1979).

331. J. Engelhardt, React. Kinet. Catal. Lett., 11, 229 (1979); Chem. Abstr., 91, 91086a (1979).

332. K. J. Ivin, G. Lapienis, and J. J. Rovang, JCS Chem. Comm., 1068 (1979).

333. A. E. Stevens, and J. L. Beauchamp. J. Amer. Chem. Soc., 101, 6449 (1979).

334. R. H. Grubbs, Inorg. Chem., 18, 2623 (1979).

335. R. H. Grubbs and C. R. Hoppin, J. Amer. Chem. Soc., 101, 1499 (1979).

336. B. A. Dolgoplosk, I. A.Oreshkin, S. A. Smirnov, I. A. Kop'eva, and E. I. Tinyakova, Eur. Polym. J., 15, 237 (1979); Chem. Abstr., 91, 175471k (1979).

337. R. G. Salomon, D. J. Coughlin, and E. M. Easler, J. Amer. Chem. Soc., 101, 3961 (1979).

338. J. R. Fritch, K. P. C. Vollhardt, Angew. Chem., 91, 439 (1979).

339. S. Deverajan, D. R. M. Walton and G. J. Leigh, J. Organomet. Chem., 181, 99 (1979).

340. M. Gilet, A. Mortreux, J. Nicole, and F. Petit, JCS Chem. Comm., 521 (1979).

341. M. Tuner, J. Von Jouanne, H. D. Brauer, and H. Kelm, J. Mol. Catal., 5, 425 (1979).

342. M. Tuner, J. Von Jouanne, H. D. Brauer, and H. Kelm, J. Mol. Catal., 5, 433 (1979).

343. M. Tuner, J. Von Jouanne, and H. Kelm, J. Mol. Catal., 5, 447 (1979).

344. G. Messina, R. Moraglia, and L. Lorenzoni, Chim. Ind. (Milan), 61, 106 (1979).

345. E. O. Sherman, Jr., and M. Olson, J. Organomet. Chem., 172, C13 (1979).

346. L. G. Bruk, O. N. Temkin, Z. V. Goncharova, I. S. Ustenko, V. R. Flid, React. Kinet. Catal. Lett., 9, 303 (1978); Chem. Abstr., 90, 167943e (1979).

347. T. Onishi, Y. Fujita, and T. Nishida. Chem. Lett., 765 (1979).

348. D. H. R. Barton, S. G. Davies and W. B. Motherwell, Synthesis, 265 (1979).

349. M. Franck-Neumann and F. Brion, Angew. Chem. IE, 18, 688 (1979).

350. A. Claesson, L-I. Olsson, JCS Chem. Comm., 524 (1979).

351. B. M. Trost, T. R. Verhoeven, and J. M. Fortunak, Tetrahedron Lett., 2301 (1979).

352. Y. Yamada, K. Mukai, H. Yoshioka, Y. Tamura, and Z.-i. Toshida, Tetrahedron Lett., 5015 (1979).

353. L. E. Overman and F. M. Knoll, Tetrahedron Lett., 321 (1979).

354. G. Balavoine and F. Guibe, Tetrahedron Lett., 3949 (1979).

355. M. Catellani, C. P. Chiusoli, G. Salerno, Symp. Rhodium Homogeneous Catal., Proc., 136 (1978); Chem. Abstr., **90**, 54427w (1979).
356. J. L. Kachinski, Diss. Abstr. Int. B, **39**, 3332 (1979).
357. Y. Sasson, A. Zoran, and J. Blum, J. Mol. Catal., **6**, 289 (1979).
358. T. Yamamoto, J. Ishizu, and A. Yamamoto, Chem. Lett., 991 (1979).
359. H. Suzuki, Y. Koyama, M. Moro-oka, and T. Ikawa, Tetrahedron Lett., 1415 (1979)
360. M. Suzuki, Y. Oda and R. Noyori, J. Amer. Chem. Soc., **101**, 1623 (1979).
361. M. Aresta, R. Greco, and D. Petruzzelli, Synth. React. Inorg. Met.-Org. Chem., **9**, 157 (1979); Chem. Abstr., **91**, 5338e (1979).
362. M. Aresta, R. Greco, Synth. React. Inorg. Met.-Org. Chem., **9**, 377 (1979); Chem. Abstr., **91**, 140973y (1979).
363. R. Noyori, Adv. Chem. Ser., 173 (1979).
364. O. V. Bragin, Z. Karpinski, K. Matusek, Z. Paal, and P. Tetenyi, J. Catal., **56**, 219 (1979).
365. M. Murakami and S. Nishida, Chem. Lett., 927 (1979).
366. T. Miyashi, T. Nakajo, H. Kawamoto, K. Akivama, and T. Mukai, Tetrahedron Lett., 151 (1979).
367. M. Sohn, J. Blum, and J. Halpern, J. Amer. Chem. Soc., **101**, 2694 (1979).
368. M. J. Chen, H. M. Feder, Inorg. Chem., **18**, 1864 (1979).
369. R. B. King and E. M. Sweet, J. Org. Chem., **44**, 385 (1979).
370. R. B. King and S. Ikai, Inorg. Chem., **18**, 949 (1979).
371. P. A Grutsch and C. Kutal, J. Amer. Chem. Soc., **101**, 4228 (1979).
372. R. J. Al-Essa, R. J. Puddephatt, and M. A. Quyser, Inorg. Chim. Acta, **34**, L187 (1979).
373. E. Mincione, G. Ortaggi, and A. Sirna, J. Org. Chem., **44**, 2320 (1979).
374. C. B. Chapelo, M. A. W. Finch, T. V. Lee, and S. M. Roberts, JCS Chem. Comm., 676 (1979).
375. K. Formanek, J. P. Aune, M. Jouffret, and J. Metzger, Nouv. J. Chim., **3**, 311 (1979).
376. a. S. Yoshikawa, M. Saburi, and M. Yamaguchi, Pure Appl. Chem., **50**, 915 (1978).
    b. S. E. Jacobson, D. A. Muccigrosso, and F. Mares, J. Org. Chem., **44**, 921 (1979).
377. M. Bertrand, G. Gil, and J. Viela, Tetrahedron Lett., 1595 (1979).
378. M. P. Doyle, W. J. Patrie, and S. B. Williams, J. Org. Chem., **44**, 2955 (1979).
379. M. Schroeder and W. P. Griffith, JCS Chem. Comm., 59 (1979).
380. K. Ohkubo, T. Ohgushi, and K. Yoshinaga, J. Coord. Chem., **8**, 195 (1979).
381. K. Ohkubo, T. Shoji, and K. Yoshinaga, J.Catal., **54**, 166 (1978).
382. C. Fragale, M. Gargano, and M. Rossi, J. Mol. Catal., **5**, 65 (1979).
383. E. J. Corey, G. Schmidt, Tetrahedron Lett., 399 (1979).
384. P. Mueller and J. Blanc, Helv. Chim. Acta, **62**, 1980 (1979).
385. R. A. D. Wentworth, Inorg. Chim. Acta, **36**, 37 (1979).
386. P. S. Radhakrishnamurti and B. Sahu, Indian J. Chem., Sect. A, **17A**, 95 (1979).

387. B. S. Tovrog, S. E. Diamond, and F. Mares, *J. Amer. Chem. Soc.*, **101**, 5067 (1979).

388. S. Rajan and D. Ramesh, *J. Org. Chem.*, **44**, 138 (1979).

389. Y. Tamaru, Y. Yamamoto, Y. Yamada, and Z-i. Yoshida, *Tetrahedron Lett.*, 1401 (1979).

391. G. Descotes, J-C. Martin, D. Sinow, T-c. Dung, *Bull. Soc. Chim. Fr.*, II-61 (1979).

392. Y. R. Rao, K. C. Rajanna, and P. K. Saiprakash, *Indian J. Chem., Sect. A*, **17A**, 297 (1979).

393. R. Grigg, T. R. B. Mitchell, and S. Sutthivaiyakit, *Tetrahedron Lett.*, 1067 (1979).

394. J. K. Stille and R. Divakaruni, *J. Organomet. Chem.*, **169**, 239 (1979).

395. J. E. Bäckvall, B. Akermark, and S. O. Ljunggren, *J. Amer. Chem. Soc.*, **101**, 2411 (1979).

396. L. Forni, G. Gilardi, and G. Terzoni, *Chim. Ind. (Milan)*, **60**, 798 (1978).

397. A. B. Svetlova, S. M. Brailovskii, and O. N. Temkin, *Kinet. Katal.*, **19**, 1588 (1978).

398. M. Hirano and T. Morimoto, *J. Chem. Res., Synop.*, 104 (1979).

399. R. Ugo, *Colloq. Int. C.N.R.S. 1977*, **281**, 133 (1978); *Chem. Abstr.*, **91**, 210392j (1979).

400. S. Uemura, A. Toshimitsu, T. Aoai, M. Okano, *JCS Chem. Comm.*, 610 (1979)

401. M. Nakayama, S. Shinke, Y. Matsushita, S. Ohira, and S. Hayashi, *Bull. Chem. Soc. Japan*, **52**, 184 (1979).

402. C. Guizard, H. Cheradame, Y. Brunel, and C. G. Beguin, *J. Fluorine Chem.*, **13**, 175 (1979).

403. W. J. Rodewald, Z. Bonczya-Tomaszewski, *Tetrahedron Lett.*, 3119 (1979).

404. S. Schwarz, C. Carl, and H. Schick, *Z. Chem.*, **18**, 401 (1978).

405. G. Sosnovsky, G. A. Karas, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **33B**, 1165 (1978).

406. W. B. Sheats, L. K. Olli, J. T. Lundeen, R. Justus, and W. G. Nigh, *J. Org. Chem.*, **44**, 4075 (1979).

407. T. Itoh, K. Jitsuokawa, K. Kaneda, and S. Teranishi, *J. Amer. Chem. Soc.*, **101**, 159 (1979).

408. R. B. Dehnel and G. H. Whitham, *JCS Perkin Trans. I*, 953 (1979).

409. E. D. Mihelich, *Tetrahedron Lett.*, 4729 (1979).

410. B. E. Rossiter, T. R. Verhoeven, and K. B. Sharpless, *Tetrahedron Lett.*, 4733 (1979).

411. V. N. Sapunov, I. Yu. Litvintsev, V. G. Sharykin, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **21**, 1583 (1978); *Chem. Abstr.*, **91**, 19458f (1979).

412. Y. Ishii, Y. Matoba, H. Ito, A. Muguruma, K. Oda, and M. Ogawa, *Sekiyu Gakkaishi*, **21**, 410 (1978); *Chem. Abstr.*, **90**, 121303t (1979).

413. V. N. Sapunov, I. Yu. Litvintsev, T. T. Avakyan, L. P. Karpenko, V. M. Smagin, B. R. Serebryakov, and N. N. Lebedev, *Kinet. Katal.*, **19**, 1477 (1978).

414. V. N. Sapunov, I. Yu. Litvintsev, T. T. Avakyan, L. P. Karpenko, V. M. Smagin, B. R. Serebryakov, and N. N. Lebedev, *Kinet. Katal.*, **19**, 1482 (1978).

415. S. Tanielyan, S. Ivanov, R. Boeva, *Neftekhimiya*, **18**, 760 (1978); *Chem. Abstr.*, **90**, 71966p (1979).

416. I. Stovcikova, E. J. Mistrik, *Petrochemia*, **18**, 186 (1978); *Chem. Abstr.*, **91**, 56716j (1979).

417. L. Sumegi, I. P. Hajdu, I. Nemes, and A. Gedra, *React. Kinet. Catal. Lett.*, **12**, 57 (1979).

418. L. Sumegi, I. Nemes, P. Hajdu, and D. Gal, *Magy. Kem. Foly.*, **85**, 14 (1979); *Chem. Abstr.*, **90**, 151302j (1979).

419. J. Sobczak, J. J. Ziolkowski, *React. Kinet. Catal. Lett.*, **11**, 359 (1979).

420. J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Amer. Chem. Soc.*, **101**, 1032 (1979).

421. A. F. Noels, A. J. Hubert, and P. Teyssie, *J. Organomet. Chem.*, **166**, 79 (1979).

422. R. Tang, F. Mares, N. Neary, and D. E. Smith, *JCS Chem. Comm.*, 274 (1979).

423. H. B. Kagan, H. Mimoun, C. Mark, and V. Schurig, *Angew. Chem. IE*, **18**, 485 (1979).

424. K. Tani, M. Hanafusa and S. Otsuka, *Tetrahedron Lett.*, 3017 (1979).

425. A. Yasuda, S. Tanaka, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Japan*, **52**, 1752 (1979).

426. I. Ahmad and C. M. Ashraf, *Indian J. Chem., Sect. A.*, **17A**, 302 (1979).

427. I. Ahmad, M. A. Beg, *Indian J. Chem., Sect. A.*, **17A**, 186 (1979).

428. K. Nakagawa, S. Mineo, S. Kawamura, M. Horikawa, T. Tokumoto and O. Mori, *Synth. Commun.*, **9**, 529 (1979).

429. P. S. Radhakrishnamurti, D. K. Mahapatro, *Indian J. Chem., Sect. A.*, **18A**, 53 (1979).

430. C. P. Murthy, B. Sethuram, and T. Rao, *Indian J. Chem., Sect. A.*, **17A**, 48 (1979).

431. P. S. Radhakrishnamurti and B. Sahu, *Indian J. Chem., Sect. A.*, **17A**, 93 (1979).

432. W. K. Rybak, J. Sobczak, T. Szymanska-Buzar, and J. J. Ziolkowski, *Proc. Conf. Coord. Chem.*, **6**, 219 (1976); *Chem. Abstr.*, **90**, 71236a (1979).

433. V. P. Tret'yakov, E. S. Rudakov, A. A. Galenin, and A. N. Osetskii, *Dokl. Akad. Nauk SSSR*, **245**, 1135 (1979).

434. T. Endo and J. Zemlicka, *J. Org. Chem.*, **44**, 3652 (1979).

435. H. Yukimasa, H. Sawai, and T. Takizawa, *Chem. Pharm. Bull.*, **27**, 551 (1979).

436. K. Schug and C. P. Guengerich, *J. Amer. Chem. Soc.*, **101**, 235 (1979).

437. M. K. Starchevskii, M. N. Vargaftik, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 242 (1979); *Chem. Abstr.*, **90**, 121096c (1979).

438. K. Maruyama, H. Tsukube, and T. Araki, *Chem. Lett.*, 499 (1979).

439. D. L. Evans, D. K. Minster, U. Jordis, S. M. Hecht, A. L. Mazzu, Jr., and A. I. Meyers, *J. Org. Chem.*, **44**, 497 (1979).

440. T. Kurata, *Yukagaku*, **28**, 407 (1979); *Chem. Abstr.*, **91**, 141012w (1979).

441. B. Siegel and J. Lanphear, *J. Amer. Chem. Soc.*, **101**, 2221 (1979).

442. F. DiFuria and G. Modena, *Recl. Trav. Chim. Pays-Bas*, **98**, 181 (1979); *Chem. Abstr.*, **91**, 19476k (1979).

443. W. Brown, *Diss. Abstr. Int. B*, **39**, 4367 (1979).

444. J. Davidson, *Catalysis (London)*, **2**, 198 (1978).

445. G. Webb, *Catalysis (London)*, **2**, 145 (1978).

446. R. G. Nuzzo, D. Feitler, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **101**, 3683 (1979).

447. J. Halpern, A. S. C. Chan, D. P. Riley and J. J. Pluth, *Adv. Chem. Ser.*, **173**, 16 (1979).

448. R. Uson, L. A. Oro, M. A. Garralda, M. Carmen Claver, and P. Lahuerta, *Transition Met. Chem.*, **4**, 55 (1979); *Chem. Abstr.*, **91**, 5337d (1979).

449. O. V. Bragin, E. G. Khelkovskaya-Sergeeva, and A. L. Liberman, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1037 (1979); *Chem. Abstr.*, **91**, 56407j (1979).

450. R. L. Augustine, R. J. Pellet, *JCS Dalton Trans.*, 832 (1979).

451. M.H.J.M. DeCroon, P.F.M.T. Van Nisselrooij, H.J.A.M. Kuipers, and J.W.E. Coenen, *J. Mol. Catal.*, **4**, 325 (1978).

452. H. C. Clark, C. Billard, and C. S. Wong, *J. Organomet. Chem.*, **173**, 341 (1979).

453. R. H. Crabtree, H. Felkin, T. Fillebeen-Khan, and G. E. Morris, *J. Organomet. Chem.*, **168**, 183 (1979).

454. C. Rousseau, M. Evrard, and F. Petit, *J. Mol. Catal.*, **5**, 163 (1979).

455. S. Imaizumi, Y. Senda, J. Ishiyama, K. Gohke, S. Komatsu, M. Uragami, M. Satoh, and H. Nakajima, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku*, **32**, 171 (1978); *Chem. Abstr.*, **91**, 157126x (1979).

456. S. A. Fonda and G. L. Rempel, *Inorg. Chem.*, **18**, 1 (1979).

457. H. Singer, E. Hademer, U. Oehmichen and P. Dixneuf, *J. Organomet. Chem.*, **178**, C13 (1979).

458. S. Komiya, A. Yamamoto, *J. Mol. Catal.*, **5**, 279 (1979).

459. S-K. Chung, *J. Org. Chem.*, **44**, 1014 (1979).

460. G. Carturan, A. Scrivanti, and M. Graziani, *J. Mol. Catal.*, **5**, 139 (1979).

461. G. Dozzi, S. Cucinella, A. Mazzei, *J. Organomet. Chem.*, **164**, 1 (1979).

462. E. C. Ashby and S. A. Noding, *J. Org. Chem.*, **44**, 4364 (1979).

463. M. V. Klynev, B. G. Rogachev, and M. L. Khidekel, *Bull. Akad. Nauk SSSR*, **27**, 2344 (1978).

464. A. W. Messing, F. P. Ross, A. W. Norman, and W. H. Okamura, *Tetrahedron Lett.*, 3635 (1978).

465. K. Tsukada, K. Aika, and A. Ozaki, *Nippon Kagaku Kaishi*, 703 (1979); *Chem. Abstr.*, **91**, 107334t (1979).

466. D. R. Anderson, *Diss. Abstr. Int. B.*, **39**, 5941 (1979).

467. E. L. Muetterties, *Pure Appl. Chem.*, **50**, 941 (1978).

468. C. U. Pittman, Jr., R. C. Ryan, and J. McGee, *J. Organomet. Chem.*, **178**, C43 (1979).

469. A. Sisak and F. Ungvary, Acta. Chim. Acad. Sci. Hung., 99, 209 (1979); Chem. Abstr., 92, 21695v (1979).

470. M. Terasawa, H. Yamamoto, K. Kaneda, T. Imanaka, and S. Teranishi, J. Catal., 57, 315 (1979).

471. D. L. Reger, C. J. Coleman, and P. J. McElligott, J. Organomet. Chem., 171, 73 (1979).

472. J. K. Crandall and W. R. Heitmann, J. Org. Chem., 44, 3471 (1979).

473. E. C. Ashby and S. R. Noding, J. Organomet. Chem., 177, 117 (1979).

474. G. Strukul and G. Carturan, Inorg. Chim. Acta, 35, 99 (1979).

475. A. A. Leslie Gunatilaka, A. F. Mateos, JCS Perkin I, 935 (1979).

476. N. M. Nazarova, S. R. Sergienko , M. A. Annamuradov, L. Kh, Freidlin, and V. A. Petukhov, Neftekhimiya, 19, 366 (1979); Chem. Abstr., 91, 107251p (1979).

477. J. G. Van Ommen, P. Mars, and P. J. Gellings, J. Mol. Catal., 6, 145 (1979).

478. D. L. Reger and M. M. Habib, J. Mol. Catal., 4, 315 (1978).

479. K. Kawakami, T. Mizoroki, and A. Ozaki, J. Mol. Catal., 5, 175 (1979).

480. V. M. Frolov, O. P. Parenago, L. P. Shuikina, Kinet. Katal., 19, 1608 (1978).

481. T. E. Zhesko, Yu. N. Kukushkin, N. S. Barinov, V. P. Kotel'nikov, A. G. Ninitina, and V. P. Spevak, Koord. Khim., 5, 423 (1979).

482. M. M. Habib, Diss. Abstr. Int. B, 39, 5371 (1979).

483. E. L. Muetterties and J. R. Bleeke, Accts. Chem. Res., 12, 324 (1979).

484. P. M. Maitlis, Adv. Chem. Ser., 173, 31 (1979).

485. E. L. Muetterties, H. Schaeffer, R. I. Mink, M. Y. Darensbourg, M. Millar, T. Groshens, K. J. Klabunde, Inorg. Chem., 18, 883 (1979).

486. P. Patnaik and S. Sarkar, J. Indian Chem. Soc., 56, 266 (1979).

487. S. Siegel and N. Garti, Catal. Org. Synth., (Conf.), 6th, 1976, 9-23; Chem. Abstr., 91, 91260c (1979).

488. M. A. Bennett, T-N, Huang and T. W. Turney, JCS Chem. Comm., 312 (1979).

489. G.-C. Wang, Hua Hsueh Tung Pao, 16 (1979); Chem. Abstr., 90, 167368w (1979).

490. Y. Sugi, Yuki Gosei Kagaku Kyokaishi, 37, 71 (1979); Chem. Abstr., 90, 187300w (1979).

491. S. Hathaway, Diss. Abstr. Int. B, 39, 3330 (1979).

492. Y. Sugi, Tokoshi Nyusu, Kagaku Kogyo Shiryo, 13, 109 (1978); Chem. Abstr., 91, 20994j (1979).

493. M. D. Fryzuk, Diss. Abstr. Int. B, 40, 751 (1979).

494. R. B. King, J. Bakos, C. D. Hoff, and L. Marko, J. Org. Chem., 44, 3095 (1979).

495. R. B. King, J. Bakos, C. D. Hoff, L. Marko, J. Org. Chem., 44, 1729 (1979).

496. Z. Nagy-Magos, S. Vastag, B. Heil, and L. Marko, J. Organomet. Chem., 171, 97 (1979).

497. H. Brunner and W. Pieronczyk, Angew. Chem. IE, 18, 620 (1979).

498. M. Lauer, O. Samuel, and H. B. Kagan, J. Organomet. Chem., 177, 309 (1979).

499. T. H. Johnson, D. K. Pretzer, S. Thomen, V. J. K. Chaffin, and G. Rangarajan, J. Org. Chem., 44, 1878 (1979).

500. A. D. Calhoun, W. J. Kobas, T. A. Nile, and C. A. Smith, J. Organomet. Chem., **170**, 175 (1979).

501. K. Achiwa, Tennen Yuki Kagobutsu Toronkai Koen Yoshishu, 21st, 275 (1978); Chem. Abstr., **90**, 86122j (1979).

502. K. Achiwa, Heterocycles, **12**, 515 (1979).

503. M. Kumada and T. Hayashi, Symp. Rhodium Homogeneous Catal., Proc., 157 (1978); Chem. Abstr., **90**, 121760q (1979).

504. K. Onuma, T. Ito, and A. Nakamura, Chem. Lett., 905 (1979).

505. K-i. Onuma, T. Ito, and A. Nakamura, Tetrahedron Lett., 3163 (1979).

506. Y. Sugi and W. R. Cullen, Chem. Lett., 39 (1979).

507. D. Lafont, D. Sinou, and G. Descotes, J. Organomet. Chem., **169**, 87 (1979).

508. R. Selke, G. Pracejus and H. Pracejus, Symp. Rhodium Homogeneous Catal., Proc., 143 (1978); Chem. Abstr., **90**, 87859s (1979).

509. E. Cesarotti, R. Ugo and H. B. Kagan, Angew. Chem. IE, **18**, 779 (1979).

510. M. D. Fryzuk and B. Bosnich, J. Amer. Chem. Soc., **101**, 3043 (1979).

511. U. Hengartner, D. Valentine, Jr., K. K. Johnson, M. E. Larschied, F. Pigott, F. Scheidl, J. W. Scott, R. C. Sun, J. M. Townsend, and T. H. Williams, J. Org. Chem., **44**, 3741 (1979).

512. A. Fischli and D. Suss, Helv. Chim. Acta, **62**, 48 (1979).

513. A. Fischli and D. Suss, Helv. Chim. Acta, **62**, 2361 (1979).

514. V. Schurig, Symp. Rhodium Homogeneous Catal., Proc., **140**, 1978; Chem. Abstr., **90**, 102838e (1979).

515. J. M. Brown, P. A. Chaloner, G. Descotes, R. Glaser, D. Lafont, D. Sinou, JCS Chem. Comm., 611 (1979).

516. J. M. Brown and P. A. Chaloner, JCS Chem. Comm., 613 (1979).

517. J. M. Brown and B. A. Murrer, Tetrahedron Lett., 4859 (1979).

518. R. Glaser, S. Geresh, M. Twaik and N. L. Benoiton, Tetrahedron, **34**, 3617 (1978).

519. I. Ojima, T. Kogure and N. Yoda, Chem. Lett., 495 (1979).

520. I. Ojima and T. Kogure, Chem. Lett., 641 (1979).

521. K. Achiwa, Y. Ohga, and Y. Iitaka. Chem. Lett., 865 (1979).

522. W. Christofel and B. D. Vineyard, J. Amer. Chem. Soc., **101**, 4406 (1979).

523. L. M. Koroleva, E. V. Borisov, V. K. Latov, and V. M. Belikov, Bull. Akad. Nauk SSSR, **27**, 1542 (1979).

524. M. Fiorini and G. M. Giongo, J. Mol. Catal., **5**, 303 (1979).

525. W.H. Krause,React. Kinet. Catal. Lett., **10**, 243 (1979).

526. H. B. Kagan, T. Yamagishi, J. C. Motte, and R. Setton, Israel J. Chem., **17**, 224 (1978).

527. A. Tai, H. Watanabe, and T. Harada, Bull. Chem. Soc. Japan, **52**, 1468 (1979).

528. K. Ito, T. Harada, A. Tai, and Y. Izumi, Chem. Lett., 1049 (1979).

529. A. Hoek, W.M.H. Sachtler, J. Catal., **58**, 276 (1979).

530. E. I. Klabunovskii, A. A. Vedenyapin, Yu. S. Airapetov, and Ya. D. Fridman, React. Kinet. Catal. Lett., **9**, 73 (1978).

531. Y. Orito, S. Imai and S. Niwa, *Nippon Kagaku Kaishi*, 1118 (1979); *Chem. Abstr.*, **91**, 192483h (1979).

532. Y. Orito, S. Imai, S. Niwa and G. H. Nguyen, *Yuki Gosei Kagaku Kyokaishi*, **37**, 173 (1979); *Chem. Abstr.*, **91**, 140487t (1979).

533. S. Lee, T. Kanmera, H. Aoyagi, and N. Izumiya, *Int. J. Pept. Protein Res.*, **13**, 207 (1979); *Chem. Abstr.*, 91, 91945e (1979).

534. E. S. Neupokoeva, E. I. Karpeiskaya, L. F. Godunova, and E. I. Klabunovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 146 (1979); *Chem. Abstr.*, **91**, 21020a (1979).

535. H. B. Kagan, J. F. Peyronel and T. Yamagishi, *Adv. Chem. Ser.*, **173**, 50 (1979).

536. K. Ohkubo, M. Setoguchi, and K. Yoshinaga, *Inorg. Nucl. Chem. Lett.*, **15**, 235 (1979); *Chem. Abstr.*, **91**, 123310n (1979).

537. T. Hayashi, A. Katsumura, M. Konishi, and M. Kumada, *Tetrahedron Lett.*, 425 (1979).

538. C. H. Brubaker, Jr., *Catal. Org. Synth., (Conf.), 6th, 1976,* 25 (1977); *Chem. Abstr.*, **91**, 90627r (1979).

539. M. S. Jarrell, *Diss. Abstr. Int. B*, **39**, 2900 (1978).

540. J. Lieto, *Diss. Abstr. Int. B,* **40**, 848 (1979).

541. N. L. Holy, *J. Org. Chem.*, **44**, 239 (1979).

542. S. Lamalle, A. Mortreux, M. Evrard, F. Petit, J. Grimblot, and J. P. Bonnelle, *J. Mol. Catal.*, **6**, 11 (1979).

543. B-H. Chang, R. H. Grubbs, and C. H. Brubaker, *J. Organomet. Chem.*, **172**, 81 (1979).

544. J. M. Brown and H. Molinari, *Tetrahedron Lett.*, 2933 (1979).

545. T. J. Pinnavaia, R. Raythatha, J. Guo-Shu Lee, L. J. Hallorn, J. F. Hoffman, *J. Amer. Chem. Soc.*, **101**, 6891 (1979).

546. Z. Kozak and M. Capka, *Coll. Czech. Chem. Comm.*, **44**, 2624 (1979).

547. V. Sharf, A. S. Gurovets, L. P. Finn, I. B. Slinyakova, V. N. Krutii, L-Kh. Freidlin, *Bull. Akad. Nauk SSSR*, **28**, 93 (1979).

548. R. J. Card, C. E. Liesner, and D. C. Neckers, *J. Org. Chem.*, **44**, 1095 (1979).

549. R. J. Card and D. C. Neckers, *Israel J. Chem.*, **17**, 269 (1978).

550. H. Dupin, J. Sabadie, D. Barthomeuf, and J. E. Germain, *Bull. Soc. Chim. Fr.*, 86 (1979).

551. D. J. Baker and J. C. Bailar, Jr., *Catal. Org. Synth., (Conf.), 6th 1976,* 1-8; *Chem. Abstr.*, **91**, 123343a (1979).

552. Y-Z. Zhou and Y-Y. Chiang, *Kao Fen Tzu T'ung Hsun*, 97 (1979); *Chem. Abstr.*, **91**, 139850z (1979).

553. S. G. Gagarin, A. Vol-Epshtein, V. P. Shifrin, V. S. Kortov, M. B. Shpil'berg, and S. S. Makar'ev, *Kinet. Katal.*, **19**, 961 (1978).

554. A. S. Al-Ammar and G. Webb, *JCS Faraday Trans. I.*, **75**, 1900 (1979).

555. N. G. McDuffie, *J. Catal.*, **57**, 193 (1979).

556. R. D. Sanner, R. G. Austin, M. S. Wrighton, W. D. Honnick, and C. U. Pittman, *Inorg. Chem.*, **18**, 928 (1979).

557. A. Brenner, *JCS Chem. Comm.*, 251 (1979).

558. P. Perkins and K.P.C. Vollhardt, J. Amer. Chem. Soc., 101, 3985 (1979).
559. R. Drago and J. H. Gaul, Inorg. Chem., 18, 2019 (1979).
560. W. Supinski, I. Creslowska and S. Malinowski, J. Organomet. Chem., 182, C33 (1979).
561. F. Sato, H. Ishikawa, T. Takahashi, M. Miura, and M. Sato, Tetrahedron Lett., 3745 (1979).
562. B. Gates, R. Pierantozzi, K. J. McQuade, M. Wolf, H. Knozingh, W. Ruhmann, J. Amer. Chem. Soc., 101, 5437 (1979).
563. D. Beaupere, P. Bauer, and R. Uzan, Can. J. Chem., 57, 218 (1979).
564. L. Mordenti, J. J. Brunet, and P. Caubere, J. Org. Chem., 44, 2203 (1979).
565. D. L. Reger, M. M. Habib, and D. J. Fauth, Tetrahedron Lett., 115 (1979).
566. W. S. Millman and G. V. Smith, Catal. Org. Synth., (Conf.) 6th 1976, 33; Chem. Abstr., 91, 107432y (1979).
567. E. J. Ucciani, G. Cecchi, G. Mallet, Rev. Fr. Corps Gras, 26, 225 (1979); Chem. Abstr., 91, 140049b (1979).
568. P. M. Lausarot, G. A. Vaglio, and M. Valle, Gazz. Chim. Ital., 109, 127 (1979).
569. B. R. James and D. Mahajan, Can. J. Chem., 57, 180 (1979).
570. T. Nishio and Y. Omote, Chem. Lett., 1223 (1979).
571. S. Vastag, B. Heil, and L. Marko, J. Mol. Catal., 5, 189 (1979).
572. G. Mestroni, A. Camus, R. Spogliarich, and G. Zassinovich, Symp. Rhodium Homogeneous Catal., (Proc.), 69 (1978); Chem. Abstr., 90, 71474b (1979).
573. W. Strohmeier and L. Weigelt, J. Organomet. Chem., 171, 121 (1979).
574. O. L. DeOchoa and R. A. Sanchez-Delgado; J. Mol. Catal., 6, 303 (1979).
575. Y. Sugi, A. Matsuda, K. Bando, K. Murata, Chem. Lett., 363 (1979).
576. G. R. Newkome and J. M. Roper, J. Org. Chem., 44, 502 (1979).
577. B. Heil, S. Tőrös, J. Bakos, and L. Marko, J. Organomet. Chem., 175, 229 (1979).
578. J-L. Lucke and A. L. Gemal, J. Amer. Chem. Soc., 101, 5848 (1979).
579. G. Paolucci, S. Cacchi, and L. Caglioti, JCS Perkin I, 1129 (1979).
580. E. L. Muetterties and J. Stein, Chem. Rev., 79, 479 (1979).
581. P. J. Denny and D. A. Whan, Catalysis (London), 2, 46 (1978).
582. M. W. Edens, Diss. Abstr. Int. B, 39, 3329 (1979).
583. S. M. Neumann, Diss. Abstr. Int. B, 39, 4897 (1979).
584. J. S. Bradley, J. Amer. Chem. Soc., 101, 7419 (1979).
585. J. G. Ekerdt and A. T. Bell, J. Catal., 58, 170 (1979).
586. J. R. Sweet, W. A. G. Graham, J. Organomet. Chem., 173, C9 (1979).
587. A. P. Kouwenhoven, M. J. Doyle, C. A. Schaap, and B. Van Oort, J. Organomet. Chem., 174, C55 (1979).
588. P. T. Wolczanski, R. S. Threlkel, J. E. Bercaw, J. Amer. Chem. Soc., 101, 218 (1979).
589. R. Spogliarich, G. Zassinovich, G. Mestroni, and M. Graziani, J. Organometl. Chem., 179, C45 (1979).

590. G. Zassinovich, G. Mestroni, and A. Camus, *J. Organomet. Chem.*, **168**, C37 (1979).

591. V. Z. Sharf, E. A. Mistryukov, L. Kh. Freidlin, I. S. Portyakova, and V. N. Krutii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1411 (1979); *Chem. Abstr.*, **91**, 123152n (1979).

592. A. Camus, G. Mestroni, G. Zassinovich, *J. Mol. Catal.*, **6**, 231 (1979).

593. S. Rajagopal, S. Vancheesan, J. Rajaram, J. C. Kuriacose, *Indian J. Chem., Sect. B*, **18B**, 293 (1979).

594. B. El.Amin, G. M. Anantharamaian, G. P. Royer, and G. E. Means, *J. Org. Chem.*, **44**, 3442 (1979).

595. K. M. Sivanandaiah, S. Gurusiddappa, *J. Chem. Res., Synop.*, 108 (1979); *Chem. Abstr.*, **91**, 141203j (1979).

596. G. Brieger, T. J. Nestrick, and T-H. Fu, *J. Org. Chem.*, **44**, 1876 (1979).

597. M. J. Andrews, C. N. Pillai, *Indian J. Chem., Sect. B*, **16B**, 465 (1978).

598. L. Horner, H. Ziegler and H. D. Ruprecht, *Liebigs Ann. Chem.*, 341 (1979); *Chem. Abstr.*, **91**, 4888x (1979).

599. K. Hanaya, T. Muramatsu, H. Kudo, and Y. L. Chow, *JCS Perkin I*, 2409 (1979).

600. A. Onopchenko, E. T. Sabourin, C. M. Selwitz, *J. Org. Chem.*, **44**, 1233 (1979).

601. A. Onopchenko, E. T. Sabourin, and C. M. Selwitz, *J. Org. Chem.*, **44**, 3671 (1979).

602. P. Kvintovics, B. Heil, and L. Marko, *Adv. Chem. Ser.*, **173**, 26 (1979).

603. R. C. Ryan, G. M. Wilemon, M. P. Dalsanto, and C. U. Pittman, Jr., *J. Mol. Catal.*, **5**, 319 (1979).

604. M. C. Datta, C. R. Saha, D. Sen, *J. Appl. Chem. Biotechnol.*, **28**, 709 (1978); *Chem. Abstr.*, **91**, 74282u (1979).

605. V. Z. Sharf, L. Kh. Freidlin, B. M. Savchenko, V. N. Krutii, *Izv. Akad. Nauk SSSR, Ser. Khim*, 1134 (1979); *Chem. Abstr.*, **91**, 91268m (1979).

606. T. Banerjee, T. Mondal, C. R. Saha, *Chem. Ind. (London)*, 212 (1979).

607. A. D. Shebaldova, T. A. Bol'shinskova, V. N. Kravtsova, M. L. Khidekel, V. P. Khramov, T. V. Zakharova, A. V. Lapitskaya, and S. B. Pirkes, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1104 (1979); *Chem. Abstr.*, **91**, 174930x (1979).

608. M. C. Datta, C. R. Saha, and D. Sen, *J. Chem. Technol. Biotechnol.*, **29**, 88 (1979); *Chem. Abstr.*, **92**, 21783x (1979).

609. D. C. Horwell, G. H. Timms, *Synth. Commun.*, **9**, 223 (1979).

610. B. Stanovnik, M. Tisler, M. Kocevar, B. Koren, M. Bester, and V. Koervmainer, *Synthesis*, 194 (1979).

611. T. Yoshida, T. Okano, and S. Otsuka, *JCS Chem. Comm.*, 870 (1979).

612. H. D. Kaesz, M. A. Andrews, C. Knobler, *Colloq. Int. C.N.R.S. 1977*, **281**, 211 (1978); *Chem. Abstr.*, **91**, 210625n (1979).

613. A. S. Serianni, H. A. Nunez, and R. Barker, *Carbohydr. Res.*, **72**, 71 (1979).

614. A. Fischli, *Helv. Chim. Acta*, **62**, 882 (1979).

615. R. D. Adams and N. M. Golembeski, *J. Amer. Chem. Soc.*, **101**, 2579 (1979).

616. P. T. Wolczanski and John E. Bercaw, *J. Amer. Chem. Soc.*, **101**, 6450 (1979).

617. T-Yau. Luh, C. Hung Lai, K. Lon Lei and S. W. Tam, *J. Org. Chem.*, **44**, 641 (1979).

618. S-T. Lin and J. A. Roth, *J. Org. Chem.*, **44**, 309 (1979).

619. W. H. Dennis, Jr., and W. J. Cooper, *Ventron Alembic*, **9**, 4 (1977); *Chem. Abstr.*, **91**, 55609q (1979).

620. T. T. Vasil'eva, N. V. Kruglova, and T. V. Tarasova, *Izv. Akad. Nauk SSSR, Ser Khim.*, 1543 (1979); *Chem. Abstr.*, **91**, 174753s (1979).

621. A. Nakamura, *J. Organomet. Chem.*, **164**, 183 (1979).

622. G. W. J. Fleet and P. J. C. Harding, *Tetrahedron Lett.*, 975 (1979).

623. A. Claesson and C. Sahlberg, *J. Organomet. Chem.*, **170**, 355 (1979).

624. J. Tsuji and T. Yamakawa, *Tetrahedron Lett.*, 613 (1979).

625. J. L. Speier, *Adv. Organomet. Chem.*, **17**, 407 (1979).

626. V. P. Yur'ev, I. M. Salimgareeva, V. V. Kaverin, K. M. Khalilov and A. A. Panasenko, *J. Organomet. Chem.*, **171**, 167 (1979).

627. J-i. Ishiyama, Y. Senda, I. Shinoda, and S. Imaizumi, *Bull. Chem. Soc. Japan*, **52**, 2353 (1979).

628. R. A. Benkeser, E. C. Mozdzen, W. C. Muench, R. T. Roche, and M. P. Siklasi, *J. Org. Chem.*, **44**, 1370 (1979).

629. V. Vybiral, P. Svoboda, and J. Hetflejs, *Collect. Czech. Chem. Commun.*, **44**, 866 (1979); *Chem. Abstr.*, 91, 57092q (1979).

630. A. J. Cornish, M. F. Lappert, G. Filatous, and T. A. Nile, *J. Organomet. Chem.*, **172**, 153 (1979).

631. A. J. Cornish, M. F. Lappert, J. J. Macquitty, and R. K. Maskell, *J. Organomet. Chem.*, **177**, 153 (1979).

632. P. F. Hudrlik, R. H. Schwartz, and J. C. Hogan, *J. Org. Chem.*, **44**, 155 (1979).

633. R. Pettit, K. Cann, T. Cole, C. H. Mauldin, and W. Slegeir, *Adv. Chem. Ser.*, **173**, 121 (1979).

634. S. Nishimura, *Yuki Gosei Kagaku Kyokaishi*, **36**, 268 (1978); *Chem. Abstr.*, **90**, 136844u (1979).

635. T. L. Ho, *Synthesis*, 1 (1979).

636. M. Freifelder, *Catalytic Hydrogenation in Organic Synthesis Procedures and Commentary*, Wiley, New York, NY (1978).

637. E. R. James, *Adv. Organomet. Chem.*, **17**, 319 (1979).

638. Thiokol, *Ventron Alembic*, **15**, 3 (1979); *Chem. Abstr.*, **91**, 122953n (1979).

639. T. N. Sorrell, *Ventron Alembic*, **16**, 1 (1979); *Chem. Abstr.*, **91**, 174271h (1979).

640. M. I. Kalinkin, G. D. Kolomnikova, Z. N. Parnes, nad D. N. Kursanov, *Russ. Chem. Rev.*, **48**, 332 (1979).

641. D. L. Reger and M. M. Habib, *Adv. Chem. Ser.*, **173**, 43 (1979).

642. P-W. Chum, *Diss. Abstr. Int. B*, **39**, 2303 (1978).

643. A. Alexakis, G. Cahiez, and J. F. Normant, *J. Organomet. Chem.*, **177**, 293 (1979).

644. E. C. Ashby and S. R. Noding, *J. Organomet. Chem.*, **177**, 117 (1979).

645. D. Cassagne, M. Gillet, and J. Braun, *Bull. Soc. Chim. Fr.*, 140 (1979).

646. R. Commandeur, H. Mathais, B. Raynier, and B. Waegell, *Nouv. J. Chim.*, **3**, 385 (1979).

647. K. Oguro, M. Wada, and N. Sonoda, *J. Organomet. Chem.*, **165**, C13 (1979).

648. J. Halpern and R. A. Jewsburg, *J. Organomet. Chem.*, **181**, 223 (1979).

649. E. Bayer and K. Geckeler, *Angew. Chem. IE*, **18**, 533 (1979).

650. Y. Watanabe, K. Taniguchi, M. Suga, T-a. Mitsudo, and Y. Takegami, *Bull. Chem. Soc. Japan*, **52**, 1869 (1979).

651. E. S. Neupokoeva, E. I. Karpeiskaya, L. F. Godunova, and E. I. Klabundovskii, *Bull. Akad, Nauk SSSR*, **28**, 129 (1979).

652. S. Paraskewas and L. Lapatsanis, *Synthesis*, 457 (1979).

653. T. Funabiki and Y. Yamazaki, *JCS Chem. Comm.*, 1110 (1979).

654. K. Nakagawa, S. Mineo, S. Kawamura, H. Horikawa, T. Tokumoto, and O. Mori, *Synth. Commun.*, **9**, 529 (1979).

655. L. Cassar, M. Foa, F. Montanari, G. P. Marinelli, *J. Organomet. Chem.*, **173**, 335 (1979).

656. P. S. Elmes and W. R. Jackson, *J. Amer. Chem. Soc.*, **101**, 6128 (1979).

657. U. M. Dzhemilev, A. Z. Yakupova, S. K. Minsker and G. A. Tolstikov, *J. Org. Chem., USSR*, **15**, 1041 (1979).

658. B. Akermark, J. E. Backvall, A. Lowenborg, and K. Zetterberg, *J. Organomet. Chem.*, **166**, C33 (1979).

659. B. M. Trost and E. Keinan, *J. Org. Chem.*, **44**, 3451 (1979).

660. B. Akermark, G. Akermark, C. Moberg, C. Bjorklund, and K. Siirala-Hansen, *J. Organomet. Chem.*, **164**, 97 (1979).

661. A. J. Birch, A. J. Liepa, and G. R. Stephenson, *Tetrahedron Lett.*, 3565 (1979).

662. M. Hida, *Yuki Gosei Kagaku Kyokaishi*, **37**, 207 (1979); *Chem. Abstr.*, **91**, 19200r (1979).

663. S. Arai, A. Tanaka, M. Hida, and T. Yamagishi, *Bull. Chem. Soc. Japan*, **52**, 1731 (1979).

664. M. Matsuoka, Y. Makino, K. Yoshida, and T. Kitao, *Chem. Lett.*, 219 (1979).

665. M. Matsuoka, T. Takei, and T. Kitao, *Chem. Lett.*, 627 (1979).

666. M. V. Klyuev and M. L. Khidekel, *Symp. Rhodium Homogeneous Catal., (Proc).*, 1978, 64; *Chem. Abstr.*, **90**, 86815n (1979).

667. J. Volf, J. Pasek, *Chem. Prum.*, **28**, 464 (1978); *Chem. Abstr.*, **90**, 86892k (1979).

668. S. Murahashi and T. Watanabe, *J. Amer. Chem. Soc.*, **101**, 7429 (1979).

669. H. Eckert and I. Ugi, *Liebigs Ann. Chem.*, 278 (1979); *Chem Abstr.*, **90**, 204485e (1979).

670. T. Yamamoto, *Synth. Commun.*, **9**, 219 (1979).

671. M. Takahashi, H. Suzuki, Y. Moro-oka, and T. Ikawa, *Chem. Lett.*, 53 (1979).

672. M. Imuta and H. Ziffer, *J. Amer. Chem. Soc.*, **101**, 3990 (1979).

673. J. Thivolle-Cazat and I. Tkatchenko, *Tetrahedron Lett.*, 345 (1979).

674. Z. Cekovic, L. Dimitrizevic, G. Djokic, and T. Srnic, *Tetrahedron*, **35**, 2021 (1979).

675. K. Isagawa, H. Sano, M. Hattori, and Y. Otsuji, *Chem. Lett.*, 1069 (1979).

676. C. A. L. Mahaffy and P. L. Pauson, *J. Chem. Res.*, 128 (1979).

677. S. Top, A. Meyer and G. Jaouen, *Tetrahedron Lett.*, 3537 (1979).

678. H. Kurokawa, T. Ishigami, K. Morimoto, and A. Sugimori, *Bull. Chem. Soc. Japan,* **52**, 959 (1979).

679. H. Suzuki, Y. Koyama, Y. Morooka, and T. Ikawa, *Tetrahedron Lett.*, 1415 (1979).

680. K. Takehira, H. Mimoun, and I. Seree De Roch, *J. Catal.*, **58**, 155 (1979).

681. G. R. Mallavarapu and K. Narasimhan, *Indian J. Chem.*, **16B**, 725 (1978).

682. M. Kubota, T. Yamamoto and A. Yamamoto, *Bull. Chem. Soc. Japan*, **52**, 146 (1979).

683. Y. Kawabata, M. Tanaka, T. Hayashi, and I. Ogata, *Nippon Kagaku Kaishi*, 635 (1979); *Chem. Abstr.*, **92**, 6320a (1979).

684. H. Westmijze, H. Kleijn, J. Meijer and P. Vermeer, *Synthesis*, 432 (1979).

685. H. Patin and G. Mignani, *JCS Chem. Comm.*, 685 (1979).

686. T. Ito and A. Yamamoto, *Ventron Alembic*, **16**, 2 (1979); *Chem. Abstr.*, **91**, 192782e (1979).

687. J. Ambuehl, P. S. Pregosin, L. M. Venanzi, G. Consiglio, F. Bachechi, and L. Zambonelli, *J. Organomet. Chem.*, **181**, 255 (1979).

688. Y. Watanabe, S. C. Shim, H. Uchida, T. Mitsudo, and Y. Takegami, *Tetrahedron*, **35**, 1433 (1979).

689. B. M. Trost, S. A. Godleski, and J. L. Belletire, *J. Org. Chem.*, **44**, 2054 (1979).

690. B. M. Trost, *Pure Appl. Chem.*, **51**, 787 (1979).

691. Y. Ito, K. Kobayashi, and T. Saegusa, *J. Org. Chem.*, **44**, 2030 (1979).

692. Y. Ito, K. Kobayashi, and T. Saegusa, *Tetrahedron Lett.*, 1039 (1979).

693. M. Mori, S. Kudo, and Y. Ban, *JCS Perkin Trans. I*, 771 (1979).

694. M. Somei, F. Yamada, C. Kaneko, *Chem. Lett.*, 943 (1979).

695. Y. Watanabe, M. Yamamoto, S. Shim, T. Mitsudo, and Y. Takegami, *Chem. Lett.*, 1025 (1979).

696. S. E. Diamond, A. Szalkiewicz, and F. Mares, *J. Amer. Chem. Soc.*, **101**, 490 (1979).

697. H. Hoberg and G Burkhart, *Synthesis*, 524 (1979).

698. H. Alper and T. Sakakibara, *Can. J. Chem.*, **57**, 1541 (1979).

699. A. Inada, H. Heimgartner, and H. Smid, *Tetrahedron Lett.*, 2983 (1979).

700. H. Alper and M. Tanaka, *J. Amer. Chem. Soc.*, **101**, 4245 (1979).

701. M. Mori and Y. Ban, *Tetrahedron Lett.*, 1133 (1979).

702. M. O. Terpko and R. F. Heck, *J. Amer. Chem. Soc.*, **101**, 5281 (1979).

703. M. Mori, K. Chiba, M. Okita, and Y. Ban, *JCS Chem. Comm.*, 698 (1979).

704. G. D. Pandey and K. P. Tiwari, *Synth. Commun.*, **9**, 895 (1979).

705. T. Itahara, *Synthesis*, 151 (1979).

706. F. DiNinno, E. V. Linek, and B. G. Christensen, *J. Amer. Chem. Soc.*, **101**, 2210 (1979).

707. R. Cote, J. Lessard, P. Mackiewicz, R. Furstoss, and B. Baegell, *Colloq. Int. C.N.R.S., 1977,* 278, 395 (1978); *Chem. Abstr.*, **91**, 192860d (1979).

708. S. Kano, Y. Tanaka, S. Hibino, and S. Shibuya, *JCS Chem. Comm.*, 238 (1979).

709. S. Galaj, Y. Guichon, Y-L. Pascal, *C.R. Hebd. Seances Acad. Sci., Ser. C,* **288**, 541 (1979).

710. T. Takeichi, M. Ishimori, and T. Tsuruta, *Bull. Chem. Soc. Japan,* **52**, 2614 (1979).

711. T. Sato, S. Yamaguchi, and H. Kaneko, *Tetrahedron Lett.*, 1863 (1979).

712. S. Uemura, A. Tashimitsu, T. Aoai, and M. Okano, *Chem. Lett.*, 1359 (1979).

713. T. Hosokawa, T. Uno, and S. Murahashi, *JCS Chem. Comm.*, 475 (1979).

714. T. F. Murray and J. R. Norton, *J. Amer. Chem. Soc.*, **101**, 4107 (1979).

715. A. Cowell and J. K. Stille, *Tetrahedron Lett.*, 133 (1979).

716. H. Horino and N. Inoue, *Heterocycles,* **11**, 281 (1979).

717. J. G. Duboudin and B. Jousseaume, *J. Organomet. Chem.*, **168**, 233 (1979).

718. H. Matsumoto, K. Ohkawa, S. Ikemori, T. Nakano, and Y. Nagai, *Chem. Lett.*, 1011 (1979).

719. R. Aumann, H. Ring, C. Kruger, and R. Goddard, *Chem. Ber.*, **112**, 3644 (1979).

720. T. Tsuda, Y. Chujo, and T. Saegusa, *Synth. Commun.*, **9**, 427 (1979).

721. A. Ballatore, M. P. Crozet, and J-M. Surzur, *Tetrahedron Lett.*, 3077 (1979).

722. K. Felfoldi, A. Molnar, M. Bartok, *Symp. Rhodium Homogeneous Catal., (Proc.)*, 38 (1978); *Chem. Abstr.*, **90**, 54158j (1979).

723. H. Alper and L. Pattee, *J. Org. Chem.,* **44**, 2568 (1979).

724. G. B. V. Subramanian, K. N. Ganesh, V. K. Mahajan, and U. Majumdar, *Indian J. Chem., Sect. B*, **16B**, 763 (1978).

725. T. Migita, M. Chiba, M. Kosugi, and S. Nakaido, *Chem. Lett.*, 1403 (1978).

726. N. Furukawa, F. Takahashi, T. Yoshimura, and S. Oae, *Tetrahedron*, **35**, 317 (1979).

727. P. Svoronos and V. Horak, *Synthesis*, 596 (1979).

728. R. Pellicciari, R. Fringuelli, P. Ceccherelli, and E. Sisan, *JCS Chem. Comm.*, 959 (1979).

729. A. J. Bellamy, *Acta Chem. Scand., B*, **33**, 208 (1979).

730. R. C. Davis, T. J. Grinter, D. Leaver, and R. M. O'Neil, *Tetrahedron Lett.*, 3338 (1979).

731. H. Alper and J. K. Currie, *J. Organomet. Chem.*, **168**, 369 (1979).

732. A. Solladie-Cavallo, G. Solladie, and E. Tsamo, *J. Org. Chem.*, **44**, 4189 (1979).

733. O. Attanasi, P. Battistoni, and G. Fava, *Synth. Commun.*, **9**, 465 (1979).

734. N. K. Nag, A. V. Sapre, D. H. Broderick, and B. C. Gates, *J. Catal.*, **57**, 509 (1979).

735. S-i. Murahashi and T. Yano, *JCS Chem. Comm.*, 270 (1979).

736. R. C. Larock and J. P. Burkhart, *Synth. Commun.*, **9**, 659 (1979).

737. K. Kikukawa, M. Takagi, and T. Matsuda, *Bull. Chem. Soc. Japan*, **52**, 1493 (1979).

738. K. Jonas and K. R. Poerschke, *Angew. Chem.*, **91**, 521 (1979).

739. A. Kasahara, T. Izumi, and H. Watabe, *Bull. Chem. Soc. Japan*, **52**, 957 (1979).

740. S. D. Ittel, C. A. Tolman, A. D. English, and J. P. Jesson, *Adv. Chem. Ser.*, **173**, 67 (1979).

741. U. M. Dzhemilev, N. S. Vostrikov, G. A. Tolstikov, and S. R. Rafikov, *Dokl. Akad. Nauk SSSR*, **244**, 369 (1979); *Chem. Abstr.*, **90**, 137295c (1979).

742. L. J. Johnston and M. E. Peach, *J. Fluorine Chem.*, **13**, 41 (1979).

743. E. Mincione, G. Ortaggi, and A. Sirna, *J. Org. Chem.*, **44**, 1569 (1979).

744. N. Kamigata, H. Sawada, M. Kobayashi, *Chem. Lett.*, 159 (1979).

745. M. Julia, M.Nel, and L. Saussine, *J. Organomet. Chem.*, **181**, C17 (1979).

746. Y. Tamaru and Z-i. Yoshida, *J. Org. Chem.*, **44**, 1188 (1979).

747. W. J. Boyle, Jr., S. Sifniades, and J. F. Van Peppen, *J. Org. Chem.*, **44**, 4841 (1979).

748. N. Miyoshi, Y. Ohno, K. Kondo, S.Murai, and N. Sonada, *Chem. Lett.*, 1309 (1979).

749. C. Wakselman and M. Tordeux, *J. Org. Chem.*, **44**, 4219 (1979).

750. N. Hall and R. Price, *JCS Perkin I*, 2634 (1979).

751. G. Henrici-Olive and S. Olive, *Angew. Chem. IE*, **18**, 77 (1979).

752. D.S.C. Black, W. R. Jackson, and J. M. Swan, *Compr. Org. Chem.*, **3**, 1127 (1979); *Chem. Abstr.*, **91**, 5275g (1979).

753. D. J. Fauth, *Diss. Abstr. Int. B*, **39**, 5910 (1979).

754. P. Pino, G. Consiglio, and A. Stefani, *Chim. Ind. (Milan)*, **61**, 27 (1979).

755. G. Wilke, *Pure Appl. Chem.*, **50**, 677 (1978).

756. P. N. Rylander, *Chim. Ind. (Milan)*, **60**, 828 (1978).

757. L. S. Hegedus, *J.Organomet. Chem.*, **180**, 301 (1979).

758. D. J. Thompson and K. Smith, *Gen. Synth. Methods*, **2**, 153 (1979).

759. R. Noyori, *Accts. Chem. Res.*, **12**, 61 (1979).

760. A. M. Sargeson, *Pure Appl. Chem.*, **50**, 905 (1978).

761. R. V. Nelson, *Diss. Abstr. Int. B.*, **40**, 254 (1979).

762. G. P. Chiusoli and G. Salerno, *Adv. Organomet. Chem.*, **17**, 195 (1979).

763. E. Negishi, *Aspects Mech. Organomet. Chem.*, 285 (1978); *Chem. Abstr.*, **90**, 185801m (1979).

764. R. A. Kjonaas, *Diss. Abstr. Int. B*, **39**, 4354 (1979).

765. Y. Otsuji and K. Isagawa, *Kagaku (Kyoto)*, **33**, 781 (1978); *Chem. Abstr.*, **91**, 139845b (1979).

766. F. Naso, *Chim. Ind. (Milan)*, **61**, 473 (1979).

767. A. Marfat, *Diss. Abstr. Int. B*, **39**, 4896 (1979).

768. R. Oda, *Kagaku (Kyoto)*, **33**, 857 (1978); *Chem. Abstr.*, **91**, 174263g (1979).

769. J. Tsuji, *Pure Appl. Chem.*, **51**, 1235 (1979).

770. B. M. Trost, *Pure Appl. Chem.*, **51**, 787 (1979).

771. H. B. Kagan and J. C. Fiaud, *Top. Stereochem.*, **10**, 175 (1978); *Chem. Abstr.*, **90**, 71255f (1979).

772. J. W. ApSimon and R. P. Seguin, *Tetrahedron*, **35**, 2797 (1979).

773. D. Valentine, Jr., and J. W. Scott, *Annu. Rep. Med. Chem.*, **13**, 282 (1978); *Chem. Abstr.*, **91**, 73715a (1979).

774. H. Brunner, *Accts. Chem. Res.*, **12**, 250 (1979).

775. A. Nakmura and N. Oguni, *Kagaku Kojo*, **22**, 41 (1978); *Chem. Abstr.*, **91**, 38285p (1979).

776. R. Pearce, *Catalysis (London)*, **2**, 176 (1978).

777. K. Von Gustorf, F. W. Grevels, and I. Fischler, *The Organic Chemistry of Iron*, Academic Press, New York, NY (1978).

778. F. P. Lamm, *Diss. Abstr. Int. B*, **40**, 1171 (1979).

779. G. Jaouen, *Org. Chem. (N.Y.)*, **33**, 65 (1978); *Chem. Abstr.*, **91**, 73717c (1979).

780. K. M. Nicholas, M. O. Nestle, and D. Seyferth, *Org. Chem. (N.Y.)*, **33**, 1 (1978); *Chem. Abstr.*, **91**, 73716b (1979).

781. D. B. Carr, *Diss. Abstr. Int. B*, **39**, 2800 (1978).

782. R. C. Larock, *Aspects Mech. Organomet. Chem., (Proc. Symp.)*, 251 (1978); *Chem. Abstr.*, **90**, 185800k (1979).

783. Y. Ishii, *Yuki Gosei Kagaku Kyokaishi*, **36**, 797 (1978); *Chem. Abstr.*, **90**, 72248t (1979).

784. B. F. G. Johnson, *Colloq. Int. C.N.R.S.*, **281**, 101 (1977); *Chem. Abstr.*, **91**, 210391h (1979).

785. R. R. Schrock, *Accts. Chem. Res.*, **12**, 98 (1979).

786. C. P. Casey, *Adv. Pestic. Sci., Plenary Lect. Symp. Pap. Int. Congr. Pestic. Chem., 4th*, **2**, 148 (1978); *Chem. Abstr.*, **91**, 123765q (1979).

787. L. Marko, *Pure Appl. Chem.*, **51**, 2211 (1979).

788. J. M. Reuter, *Diss. Abstr. Int. B*, **39**, 2811 (1978).

789. R. Crabtree, *Accts. Chem. Res.*, **12**, 331 (1979).

790. Anon, *Nachr. Chem., Tech. Lab.*, **27**, 257 (1979); *Chem. Abstr.*, **91**, 55594f (1979).

791. K. R. Im, *Diss. Abstr. Int. B*, **39**, 2309 (1978).

792. D. DeMontauzon, R. Poilblanc, P. Lemoine, and M. Gross, *Electrochim. Acta*, **23**, 1247 (1978); *Chem. Abstr.*, **91**, 39549q (1979).

793. Kh. M. Minachev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2665 (1978); *Chem. Abstr.*, **90**, 120456h (1979).

794. C. U. Pittman, Jr., *Polym. News*, **5**, 76 (1978); *Chem Abstr.*, **90**, 120455g (1979).

795. M. S. Scurrell, *Catalysis (London)*, **2**, 215 (1978).

796. N. Toshima, *Yuki Gosei Kagaku Kyokaishi*, **36**, 909 (1978); *Chem. Abstr.*, **90**, 104033n (1979).

797. A. McKillop and D. W. Young, *Synthesis*, 401 (1979).

798. M. K. Neuberg, *Diss. Abstr. Int. B*, **39**, 5929 (1979).

799. S. Vatanatham. *Diss. Abstr. Int. B*, **39**, 5915 (1979).

800. K. J. Klabunde, R. G. Gastinger, T. J. Groshens, and M. Brezinski, *NATO Conf. Ser., (Ser.), 6*, **1**, 81 (1978); *Chem. Abstr.*, **91**, 123766r (1979).

801. A. Ya Yujja and G. V. Lisichkin, *Russ. Chem. Rev.*, **47**, 751 (1979).

802. M. Moskovits, *Accts. Chem. Res.*, **12**, 229 (1979).

803. S. Murai and N. Sonada, *Angew. Chem. IE,* **18**, 837 (1979).

804. S. Murai and N. Sonada, *Angew. Chem.*, **91**, 896 (1979).

805. J. K. Stille, *Ann. N.Y. Acad. Sci.*, **295**, 52 (1977); *Chem. Abstr.*, **90**, 151121z (1979).

806. J. R. Norton, *Accts. Chem. Res.*, **12**, 139 (1979).

807. A. E. Shilov, *Pure Appl. Chem.*, **50**, 725 (1978).

808. D. K. Erwin, *Diss. Abstr. Int. B*, **39**, 5371 (1979).

809. F. S. Wagner, *Kirk-Othmer Encycl. Chem. Technol., 3rd Ed.*, **4**, 794 (1978); *Chem. Abstr.*, **91**, 5260y (1979).