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Transition metals in organic synthesis. Annual Survey covering the year 1991 *

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Contents

1. General comments

This Annual Survey covers the literature for 1991 dealing with the use of transition metal intermediates for organic synthetic transformations. It is not a comprehensive review but is limited to reports of discrete systems that lead to at least moderate yields of organic compounds, or that allow unique organic transformations, even if low yields are obtained. Catalytic reactions that lead cleanly to a major product and do not involve extreme conditions are also included. This is not a critical review, but rather a listing of the papers published in the title area.

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* Reprints are not available. For previous Annual Survey see *J. Organomet. Chem.*, *422* (1992) 301.

0022-328X/93/$6.00

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 effected than the metal causing it. Oxidation, reduction, and hydroformylation reactions are specifically excluded, and will be covered in a different annual survey. 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.

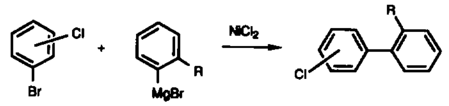
2. Carbon–carbon bond forming reactions

2.1. Alkylations

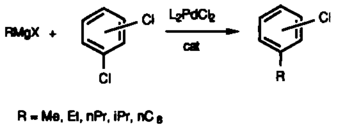
2.1.1. Alkylation of organic halides, tosylates, triflates, acetates, and epoxides

The main stages of the cross-coupling of organometallic compounds with organic halides catalyzed by nickel and palladium complexes has been reviewed (100 references) [1]. Nickel chloride (eqn. (1) [2]) and (bis)phosphine palladium chloride (eqn. (2) [3]) catalyzed the coupling of polyhalogenated arenes with Grignard reagents. Sterically hindered (neopentyl) iodides were alkylated by Grignard reagents in the presence of dppf $NiCl_2$ catalysts (eqn. (3) [4]). Related nickel(II) complexes catalyzed the coupling of vinyl halides to 2-metallated allylamines, to give dienes, which were used in Diels–Alder reactions (eqn. (4) [5]).

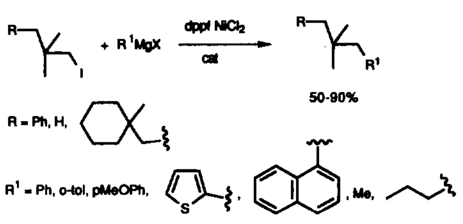
(Equation 1)



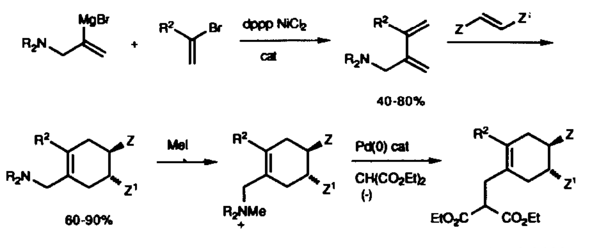
(Equation 2)



(Equation 3)

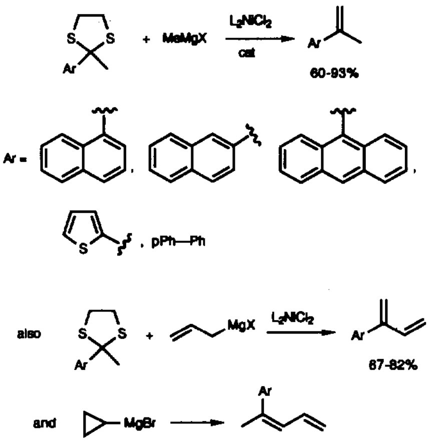


(Equation 4)

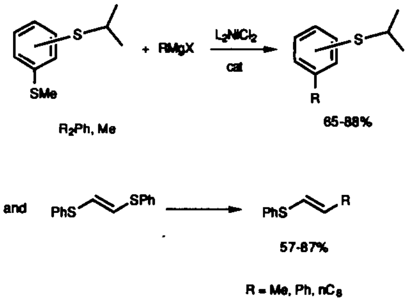


Thioketals (eqn. (5) [6]) and both aryl and vinyl sulfides (eqn. (6) [7]) were alkylated by Grignard reagents in the presence of nickel(II) catalysts.

(Equation 5)

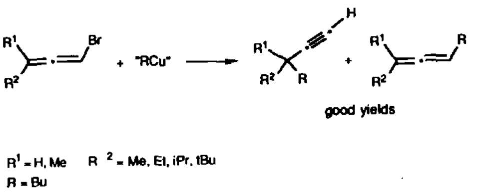


(Equation 6)

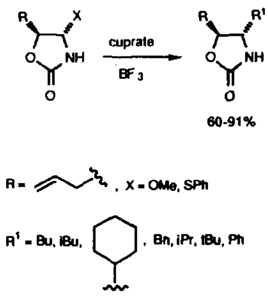


Organocopper complexes efficiently alkylated a variety of organic halides. Allenic bromides were alkylated by organocopper complexes to give both alkylated allenes and alkynes (eqn. (7) [8]). α-Heterooxazolidinones were alkylated with retention by organocopper complexes (eqn. (8) [9]). Allyl silanes were prepared by the alkylation of trimethylsilylmethyl iodide with vinyl copper species (eqn. (9) [10]). Enol triflates were alkylated by a variety of organometallics including copper reagents (eqn. (10) [11]).

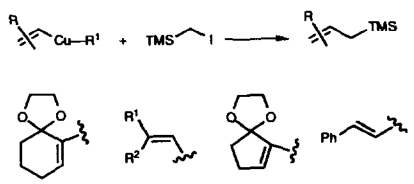
(Equation 7)



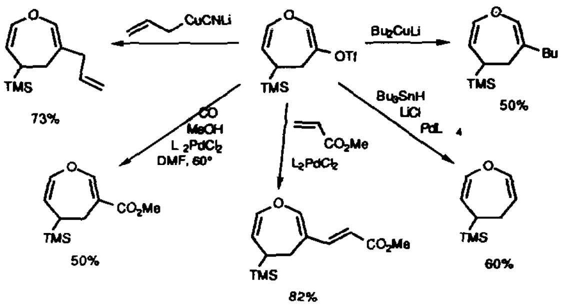
(Equation 8)



(Equation 9)

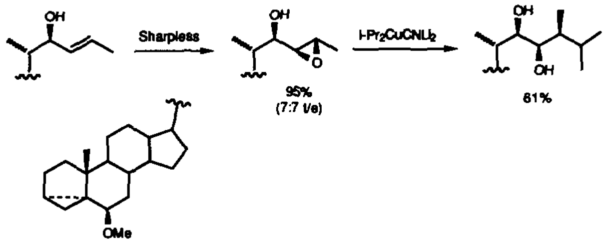


(Equation 10)

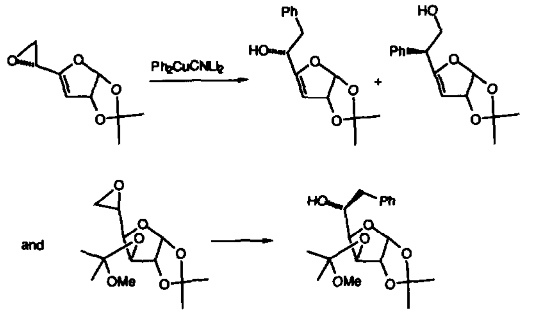


Cyanocuprates opened epoxides stereoselectively (eqn. (11) [12] and eqn. (12) [13]). Organocuprates having functional groups were prepared from activated copper, or from organozinc reagents, and were coupled to organic halides (eqn. (13) [14], eqn. (14) [15], eqn. (15) [16], and eqn. (16) [17]).

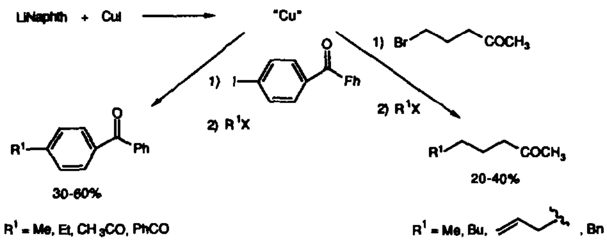
(Equation 11)



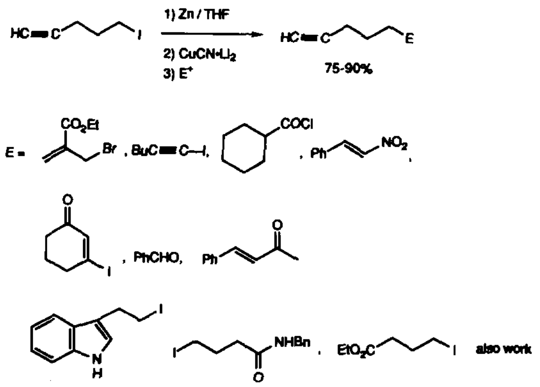
(Equation 12)



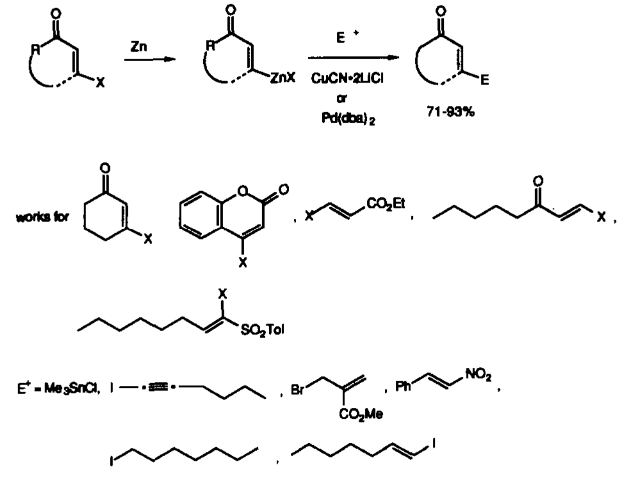
(Equation 13)



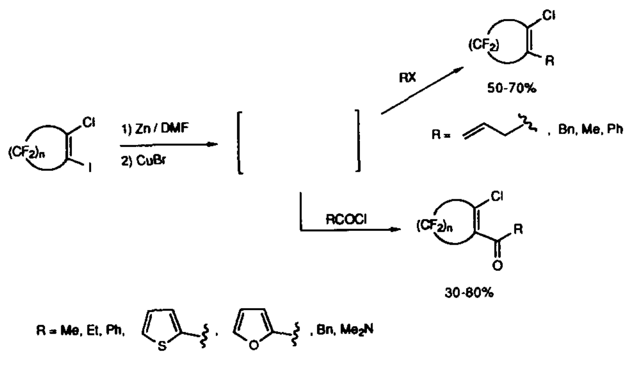
(Equation 14)



(Equation 15)

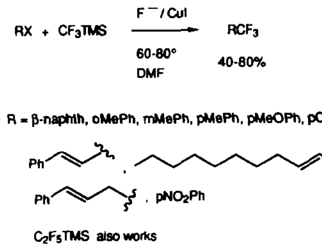


(Equation 16)



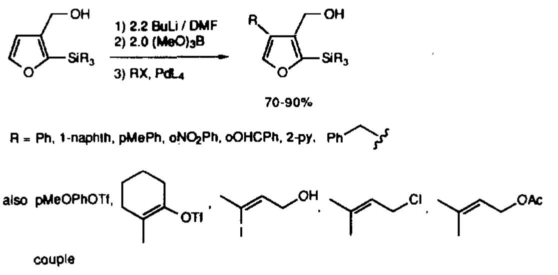
Halides were trifluoromethylated by CF_3TMS by treatment with fluoride in the presence of copper(I) iodide (eqn. (17) [18]) or by the treatment with trifluoroacetate in the presence of copper(I) iodide [19]. Muscalure was synthesized by the copper catalyzed cross coupling reaction of n-pentylmagnesium bromide with oleyl tosylate [20].

(Equation 17)

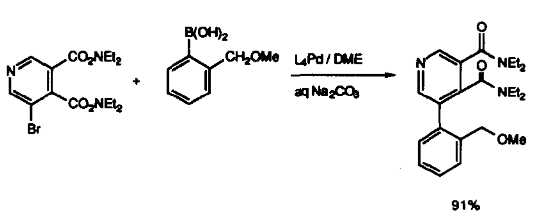


Oxidative addition–transmetallation processes have finally been "discovered" by synthetic organic chemists, and have been the subject of an explosion of papers, not withstanding the fact that the processes have been known for years. Synthetic studies via the cross coupling reaction of organoboron derivatives with organic halides is the subject of a review [21]. Aryl and 1-alkenyl triflates were coupled to 1-alkenyl boron compounds in the presence of palladium catalysts and potassium phosphate [22]. 2-Silyl-3-hydroxymethyl furans were lithiated, transmetallated to boron, then coupled to organic halides (eqn. (18) [23]). Halopyridines were converted to phenylpyridines by treatment with diethyl phenyl borate in the presence of palladium catalysts [24], and by phenyl boronic acids (eqn. (19) [25]). Arylboronic acids also arylated iodoglycals (eqn. (20) [26]), aryl halides (eqn. (21) [27]), and heteroaryl halides (eqn. (22) [28]) in the presence of palladium(0) catalysts.

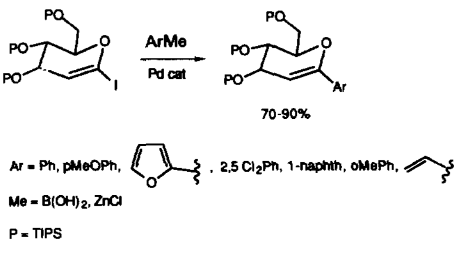
(Equation 18)



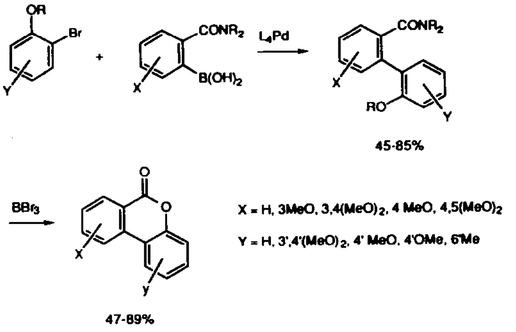
(Equation 19)



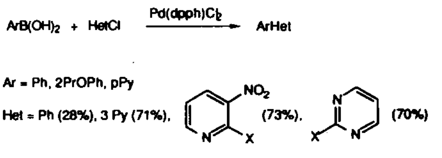
(Equation 20)



(Equation 21)

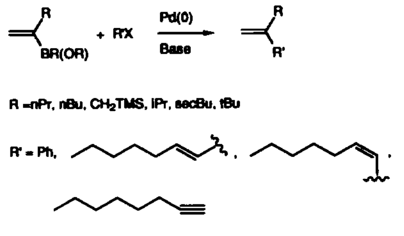


(Equation 22)

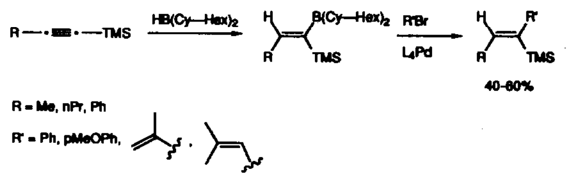


Vinyl boranes were also coupled to halides using palladium catalysis (eqn. (23) [24], eqn. (24) [30], and eqn. (25) [31]). Polycyclic aromatic compounds were synthesized by the palladium(0) catalyzed coupling of an aryl iodide with an aryl boronic acid (eqn. (26) [32]). (1Z,3E)-1-Phenyl-1,3-octadiene was synthesized by the coupling of 1-alkenyl-boronates with vinyl halides [33]. Palladium also catalyzed the coupling of aryl halides with arylboronic acids in water [34].

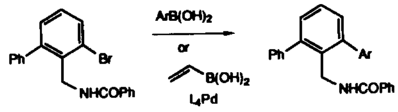
(Equation 23)



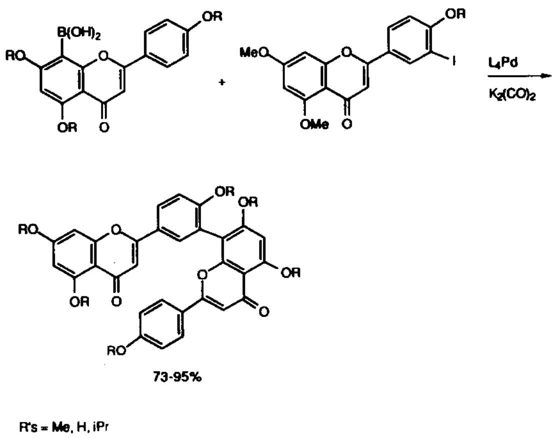
(Equation 24)



(Equation 25)

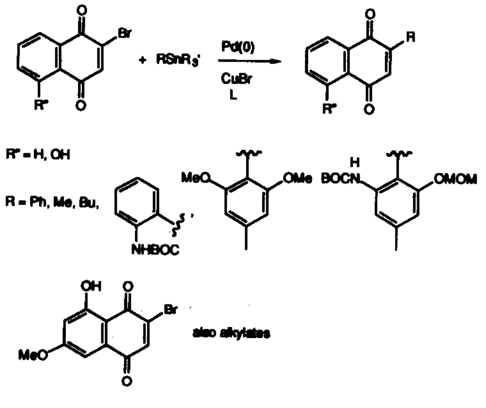


(Equation 26)

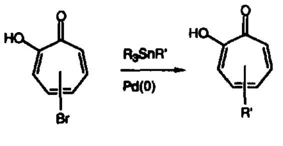


Transmetallation from tin and zinc to palladium remained a popular pursuit this year. Haloquinones were alkylated by organotin reagents in the presence of palladium(0) catalysis (eqn. (27) [35]), as were bromotropanones (eqn. (28) [36]). Cyclobutene diones were annellated to isoquinolines using palladium catalyzed tin coupling reaction (eqn. (29) [37]). α-Stannyl silylenol ethers were alkylated by halides in the presence of palladium catalysts (eqn. (30) [38]). The effect of ligands on the Stille coupling of organic halides and triflates to vinyl tin reagents was studied (eqn. (31) [39]). Tris-(2-furyl)phosphine was the best ligand.

(Equation 27)

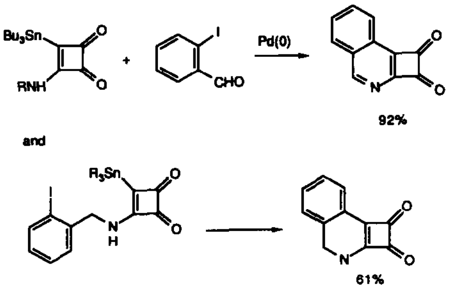


(Equation 28)

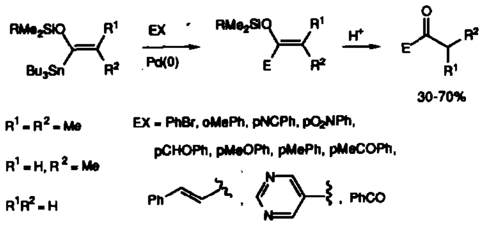


R' = vinyl and aryl gps.

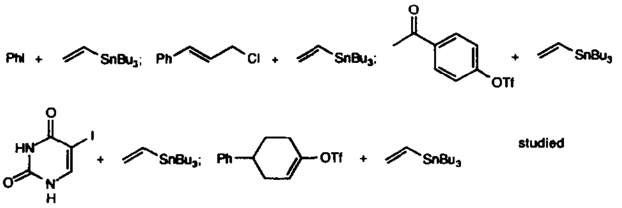
(Equation 29)



(Equation 30)

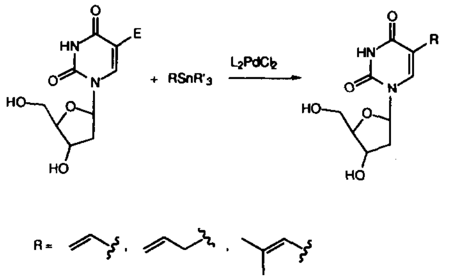


(Equation 31)

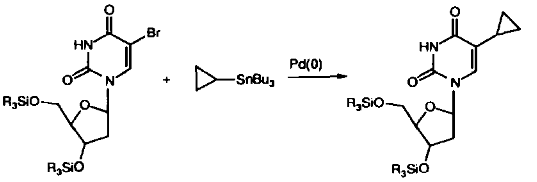


The cross coupling of nucleoside halides with organostannanes catalyzed by palladium(0) is becoming increasingly utilized (eqn. (32) [40], eqn. (33) [41], eqn. (34) [42], and eqn. (35) [43]).

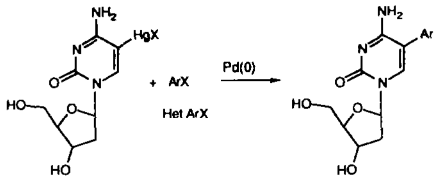
(Equation 32)



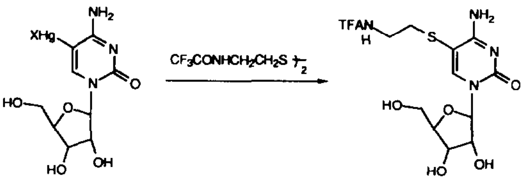
(Equation 33)



(Equation 34)

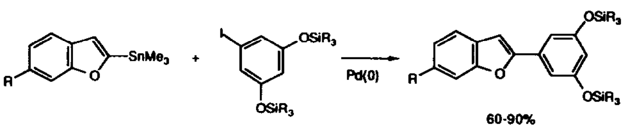


(Equation 35)

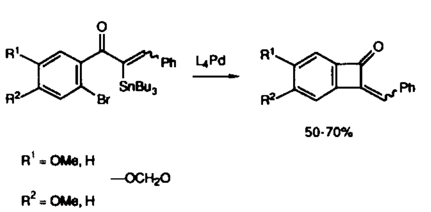


Aryl iodides coupled to 2-stannyl benzofurans in the presence of palladium(0) catalyst (eqn. (36) [44]). 2-Methylenebenzocyclobutanones were made by intramolecular coupling (eqn. (37) [45]). Zearelenone was synthesized in a aryl iodide–vinyl tin coupling process (eqn. (38) [46]).

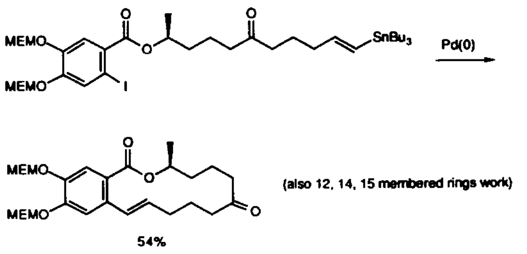
(Equation 36)



(Equation 37)

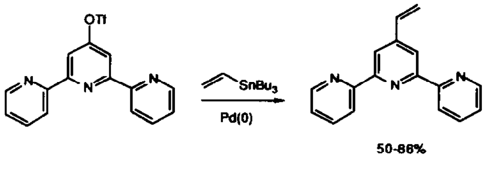


(Equation 38)

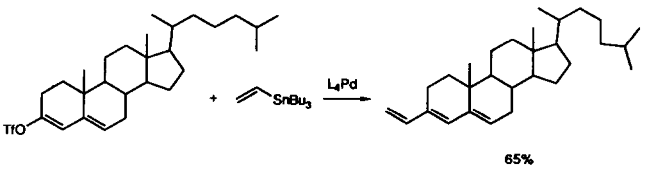


4-t-Butyl-1-vinylcyclohexane was synthesized by the palladium(0) catalyzed vinylation of the corresponding triflate with vinyl tin [47]. Aryl (eqn. (39) [48]) and dienyl (eqn. (40) [49]) triflates were similarly vinylated. A new annellation strategy involving vinyl tin/enol triflate coupling has been developed (eqn. (41) [50] and eqn. (42) [51]). Triflates of β-ketoesters were also alkylated by tin reagents in the presence of palladium(0) catalysts (eqn. (43) [52]). Arylation of vinyl (eqn. (44) [53]) and aryl triflates (eqn. (45) [54]) has also been developed.

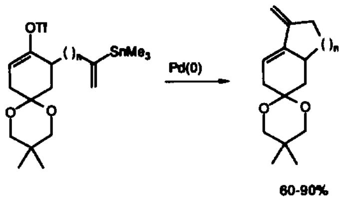
(Equation 39)



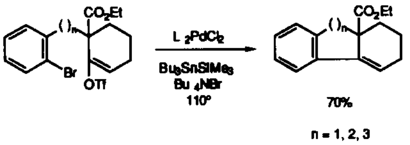
(Equation 40)



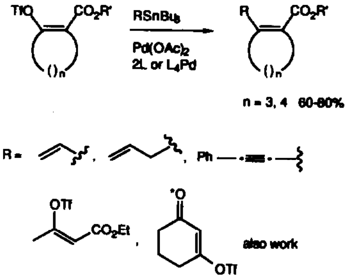
(Equation 41)



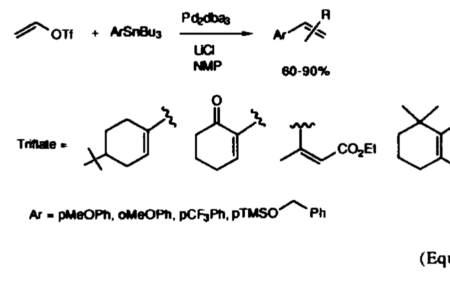
(Equation 42)



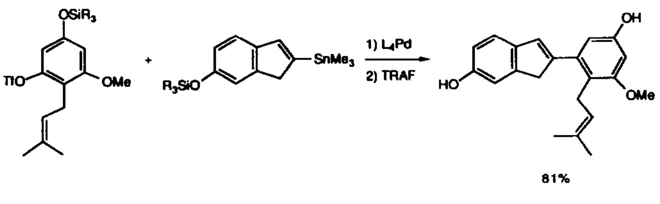
(Equation 43)



(Equation 44)

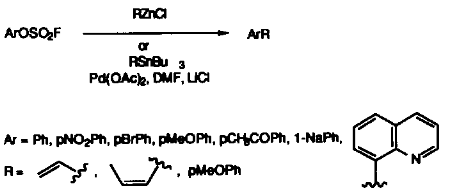


(Equation 45)

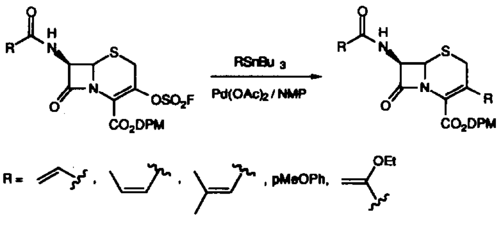


Fluorosulfonates (eqn. (46) [55] and eqn. (47) [56,57]), enol mesylates (eqn. (48) [58]), and aryldiazonium salts are also alkylated by alkyl tin reagents in the presence of palladium(0) complexes [59].

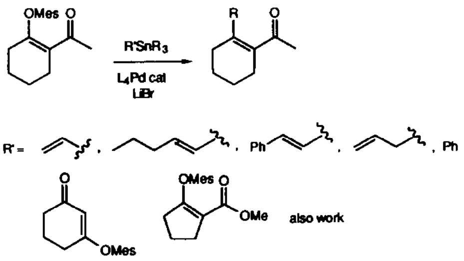
(Equation 46)



(Equation 47)

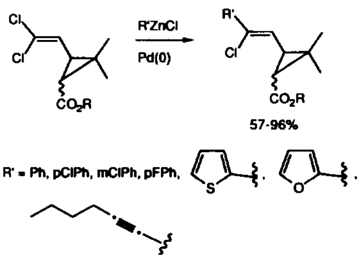


(Equation 48)

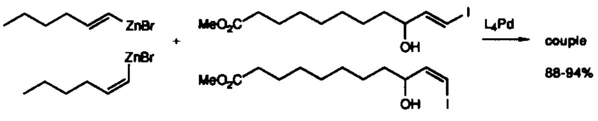


Vinyl halides were coupled to alkyl zinc reagents with palladium catalysis (eqn. (49) [60] and eqn. (50) [61]). Aryl halides were also coupled to vinyl zinc reagent under similar conditions (eqn. (51) [62]). This coupling was used with highly functionalized compound (eqn. (52) [63]). Vinyl triflates were coupled to vinyl tin reagents using palladium catalysis (eqn. (53) [64]). Benzofurans were made in a palladium catalyzed tandem coupling process (eqn. (54) [65]).

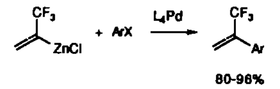
(Equation 49)



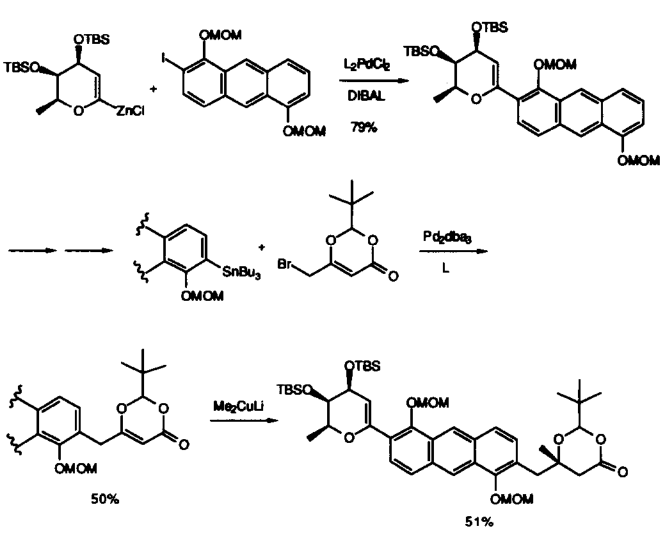
(Equation 50)



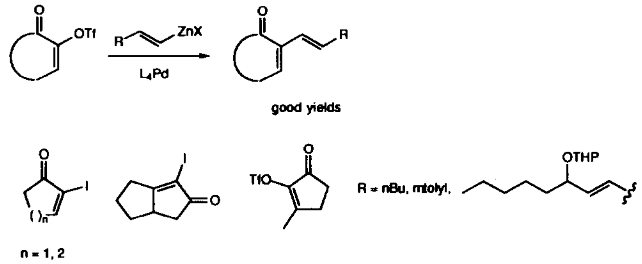
(Equation 51)



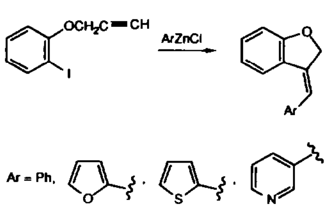
(Equation 52)



(Equation 53)

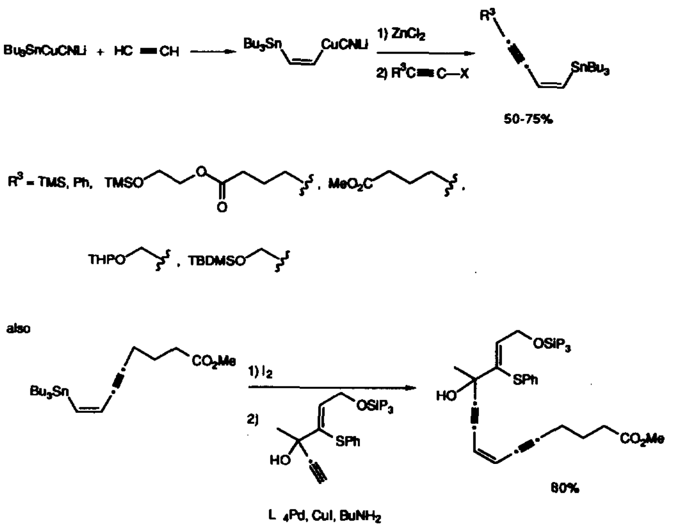


(Equation 54)

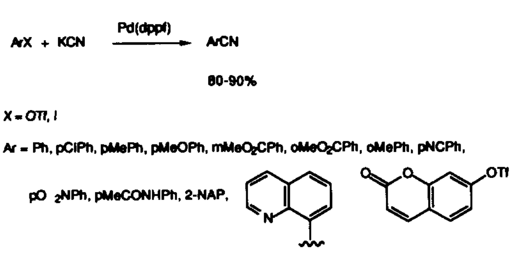


Conjugated enynes were built up using a variety of coupling processes (eqn. (55) [66]). Palladium(0) complexes catalyzed the conversion of aryl halides and triflates to aryl cyanides (eqn. (56) [67]). Palladium(0) catalyzed the coupling of aryl thallium compounds with vinyl tin reagents (eqn. (57) [68]). *Ortho*-palladated aromatics were alkylated by treating with excess alkyl iodides (eqn. (58) [69]).

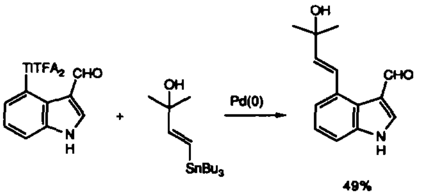
(Equation 55)



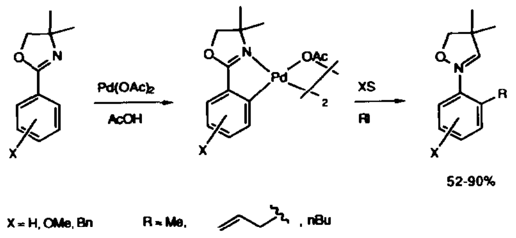
(Equation 56)



(Equation 57)

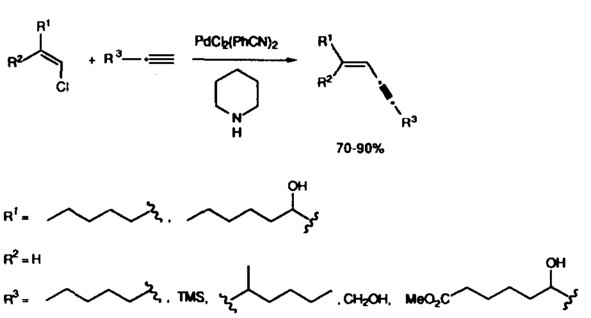


(Equation 58)

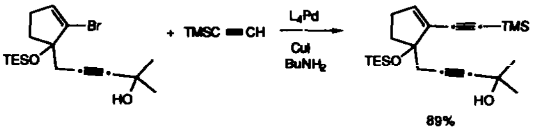


With the advent of ene–diyne antitumor agents, the palladium catalyzed coupling of alkynes with vinyl halides has undergone explosive growth. This reaction works well with simple vinyl halides (eqn. (59) [70] and eqn. (60) [71]) and with heteroaromatic halides (eqn. (61) [72], eqn. (62) [73], eqn. (63) [74], eqn. (64) [75], and eqn. (65) [76]). Tertiary allylic alcohols are tolerated (eqn. (66) [77]).

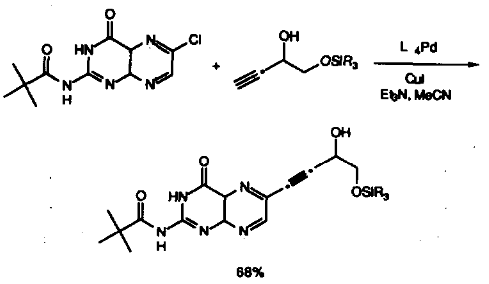
(Equation 59)



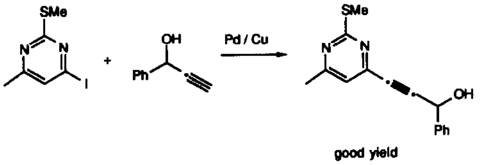
(Equation 60)



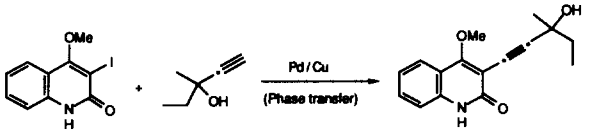
(Equation 61)



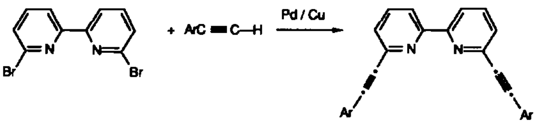
(Equation 62)



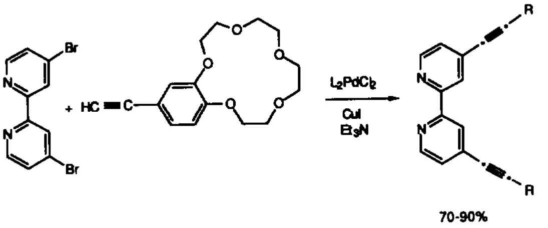
(Equation 63)



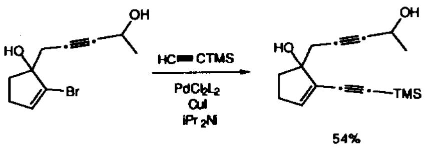
(Equation 64)



(Equation 65)

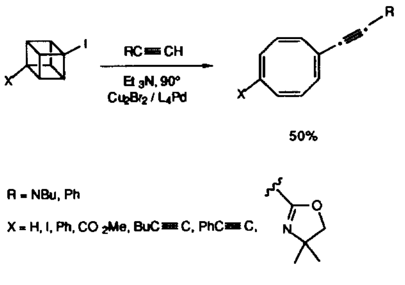


(Equation 66)

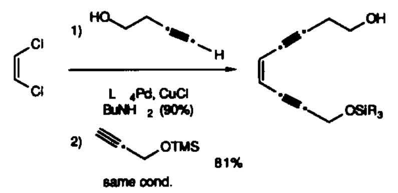


Attempted alkynation of an iodocubane led to rearrangement (eqn. (67) [78]). Palladium on carbon catalyzed the coupling of aryl bromides with terminal alkynes [79]. Unsymmetrical ene diynes were prepared by sequential coupling of two different alkynes to 1,2-dichloroethene (eqn. (68) [80]). This worked in more complex systems as well (eqn. (69) [81], eqn. (70) [82], eqn. (71) [83], eqn. (72) [84], eqn. (73) [85], and eqn. (74) [86]).

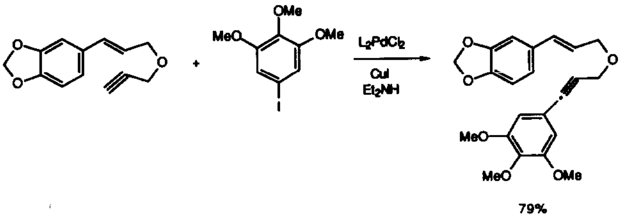
(Equation 67)



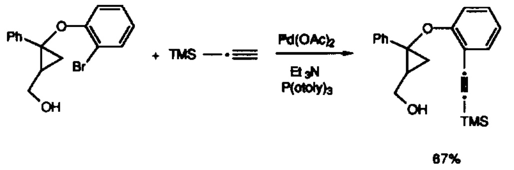
(Equation 68)



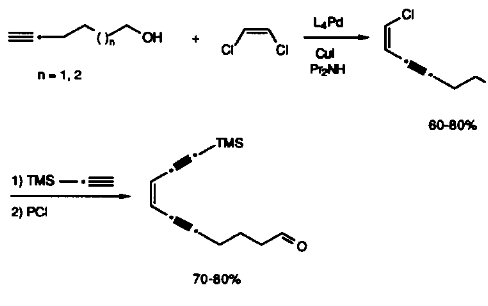
(Equation 69)



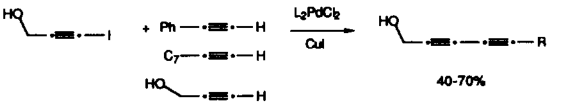
(Equation 70)



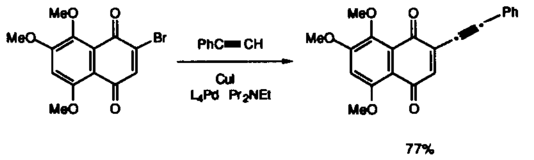
(Equation 71)



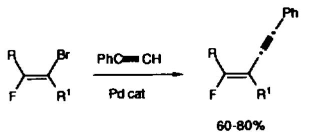
(Equation 72)



(Equation 73)

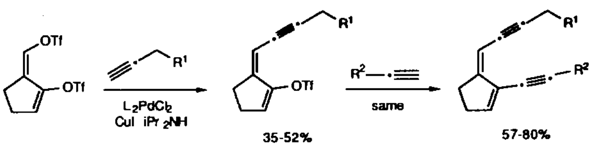


(Equation 74)



Vinyl triflates are also alkynylated using palladium/copper catalysis (eqn. (75) [87,88], eqn. (76) [89], and eqn. (77) [90]).

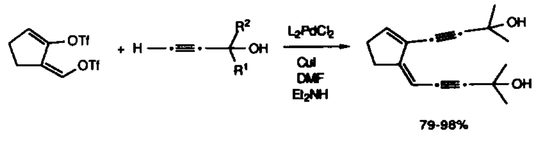
(Equation 75)



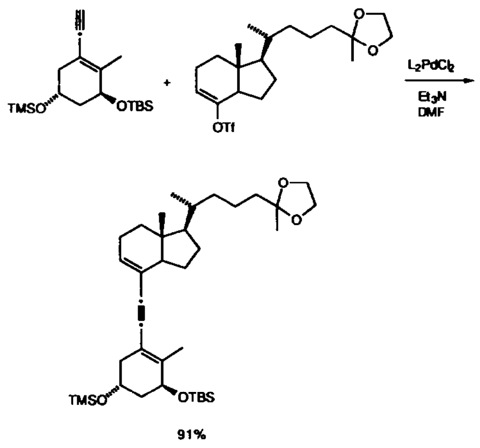
R^1 = OTHP, OSiR₃, CH_2OH, TMS, CH_2CH_2OH

R^2 = TMS, $TMSCH_2$, nBu, CH_2CH_2OH, $(CH_2)_3OH$

(Equation 76)

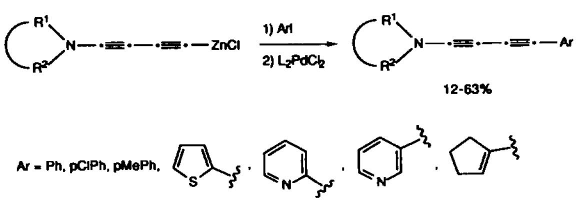


(Equation 77)

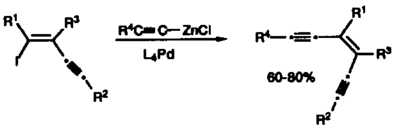


Alkynyl zinc reagents were alkylated by aryl halides in the presence of palladium catalysis (eqn. (78) [91]), and by vinyl iodides (eqn. (79) [92], eqn. (80) [93] and eqn. (81) [94]).

(Equation 78)



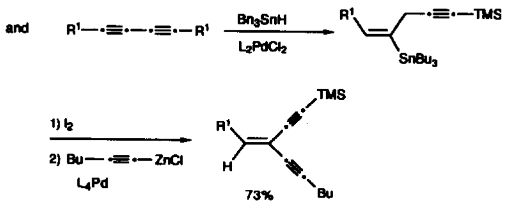
(Equation 79)



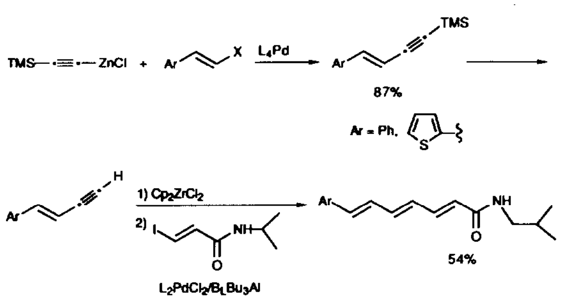
R^1 = C_6, Me, H R^3 = H, Me

R^2 = TMS R^4 = Bu, Ph, TMS

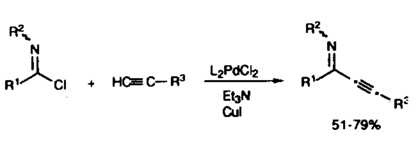
(Equation 80)



(Equation 81)

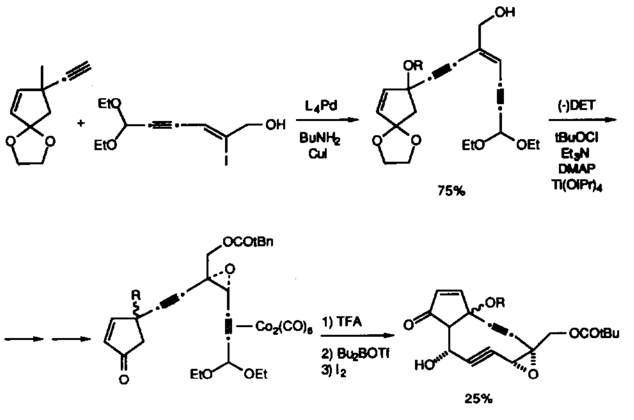


(Equation 82)

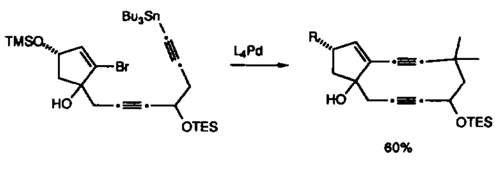


The chemistry and biology of the enediyne anticancer antibiotics has been reviewed (136 references) [95]. This review contains many references to ene–yne coupling processes. There are several examples of the use of this coupling reaction for the synthesis of enediyne compounds (eqn. (83) [96], eqn. (84) [97], and eqn. (85) [98,99]). This chemistry has also been applied to the synthesis of polyether antibiotics (eqn. (86) [100]). It also has been used to provide starting materials for diazo insertion reactions (eqn. (87) [101]).

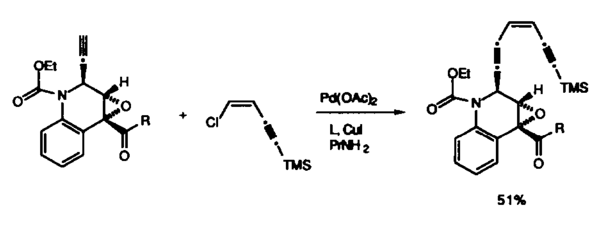
(Equation 83)



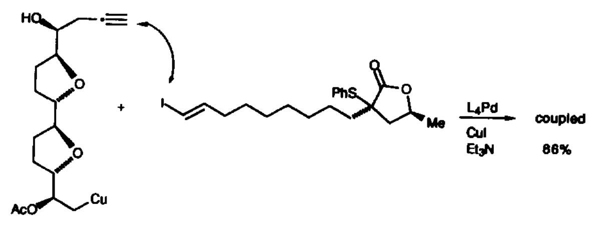
(Equation 84)



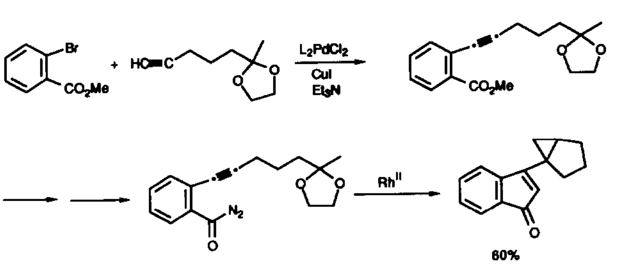
(Equation 85)



(Equation 86)

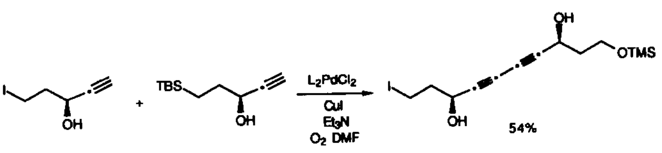


(Equation 87)



Terminal alkynes were unsymmetrically coupled by palladium/copper catalysts (eqn. (88) [102]). Iodoalkynes also coupled to alkynes to give 1,3-diynes using the same catalyst (eqn. (89) [103]). Bicyclic ketones were synthesized by electroreductive coupling of bromocycloalkenones in the presence of cobalt and nickel catalysts (eqn. (90) [104]). Alkylmanganese complexes coupled to β-chloroalkenyl ketones (eqn. (91) [105]).

(Equation 88)

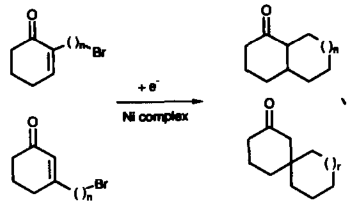


(Equation 89)

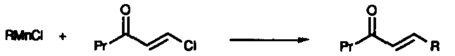
$$HOCH_2C{\equiv}CCl + PhC{\equiv}CH \xrightarrow{Pd/Cu} PhC{\equiv}C{-}C{\equiv}C{-}CH_2OH$$

79%

(Equation 90)



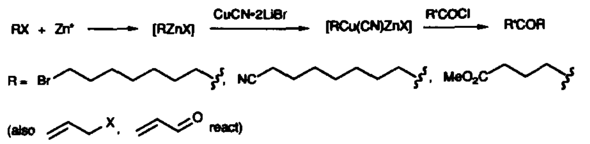
(Equation 91)



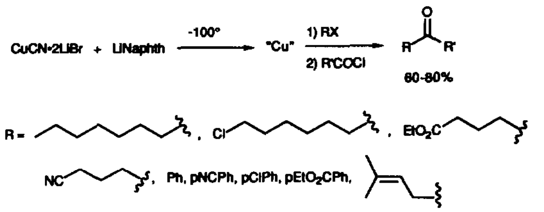
2.1.2. *Alkylation of acid derivatives*

Acid chlorides were alkylated by functionalized organocopper reagents prepared from organozinc reagents (eqn. (92) [106]) or by copper cyanide reduced with sodium napththalenide (eqn. (93) [107]). Organocopper reagents alkylated N-acylpyridinium compounds in the 4-position (eqn. (94) [108,109]).

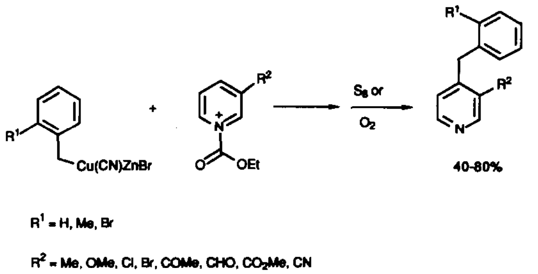
(Equation 92)



(Equation 93)

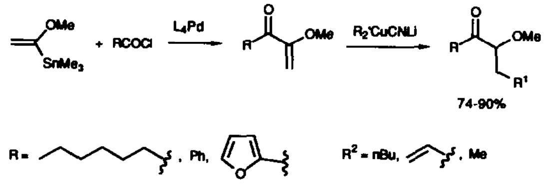


(Equation 94)

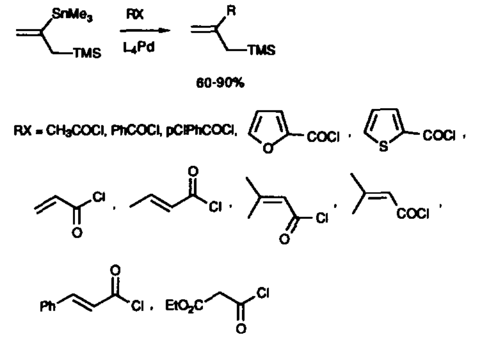


Palladium(0) complexes catalyzed the alkylation of acid chlorides by organostannanes (eqn. (95) [110], eqn. (96) [111], eqn. (97) [112], eqn. (98) [113], eqn. (99) [114], and eqn. (100) [115]). Palladium(0) complexes also catalyzed the alkylation of acid chlorides by cyclopropanone ketals (eqn. (101) [116]).

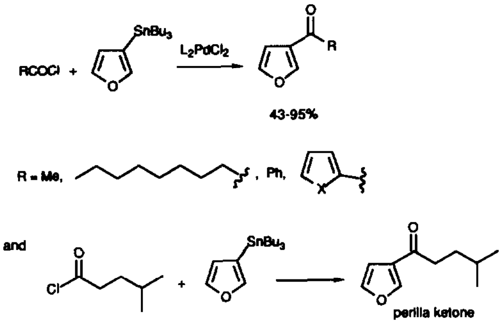
(Equation 95)



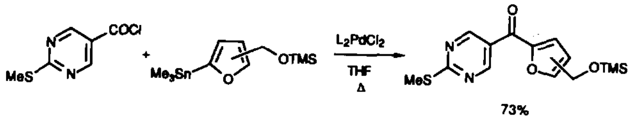
(Equation 96)



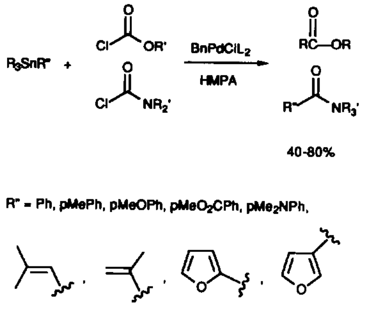
(Equation 97)



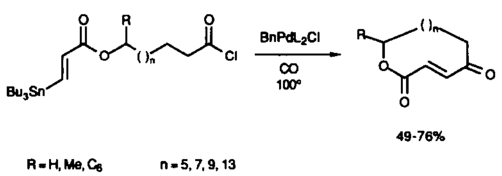
(Equation 98)



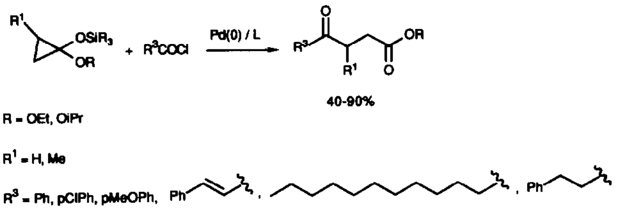
(Equation 99)



(Equation 100)

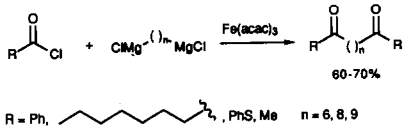


(Equation 101)

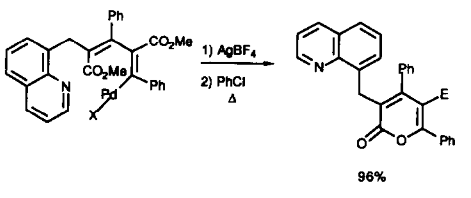


Digrignard reagents were bis acylated by acid chlorides in the presence of iron(III) acetylacetonate catalysts (eqn. (102) [117]). Pyrones were formed by insertion of vinyl palladium species into adjacent ester groups (eqn. (103) [118]).

(Equation 102)



(Equation 103)

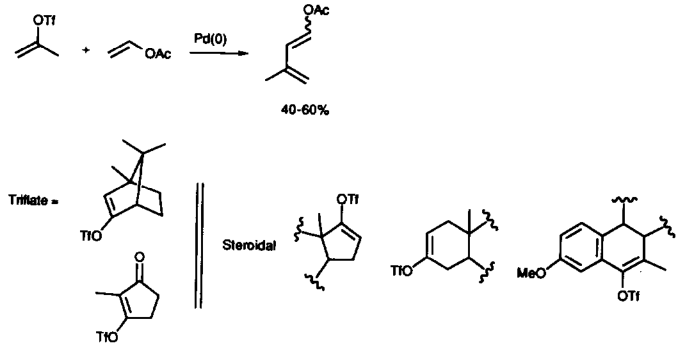


2.1.3. Alkylation of olefins

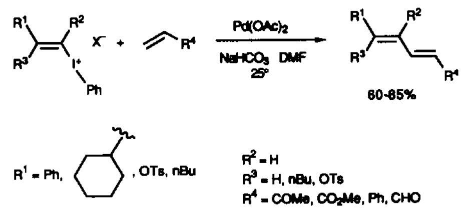
The Heck reaction (palladium catalyzed oxidative addition/olefin insertion) remained a popular way to alkylate olefins. The palladium catalyzed arylation and vinylation of olefins was the subject of a review (18 references) [119], as was palladium-mediated arylation of enol ethers (127 references) [120]. Palladium catalyzed arylation and vinylation of cyclic alkenes was the topic of a dissertation [121]. The dramatic effect of adding quatermary ammonium halides to Heck reactions has been investigated electrochemically [122]. It was found that halides stabilize palladium(0) complexes and prevent catalyst deactivation particularly in ligandless systems. In the palladium catalyzed arylation of styrene by iodobenzene, β-elimination was found to be the rate limiting step [123].

1-Acetoxydienes were synthesized by the palladium catalyzed coupling of vinyl acetates with vinyl triflates (eqn. (104) [124]). Vinyliodonium salts alkylated olefins to give dienes (eqn. (105) [125]). 1-Azadienes were prepared by the palladium catalyzed olefination of imidoylhalide (eqn. (106) [126]).

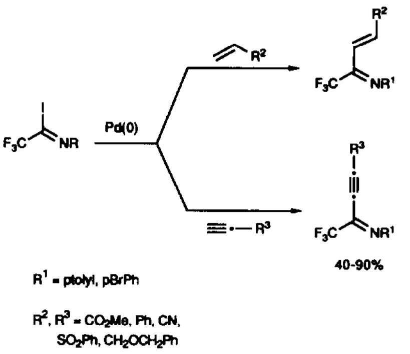
(Equation 104)



(Equation 105)

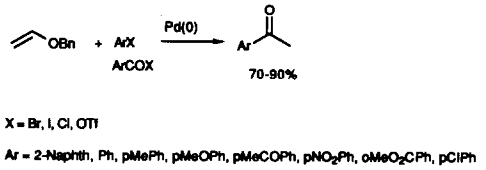


(Equation 106)

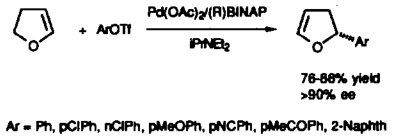


Electron rich olefins were arylated by aryl halides and triflates in the presence of palladium(0) catalysts (eqn. (107) [127], eqn. (108) [128], and eqn. (109) [129]).

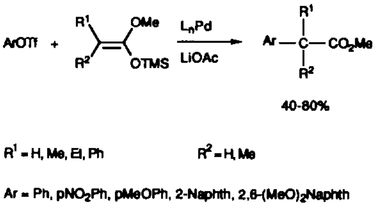
(Equation 107)



(Equation 108)

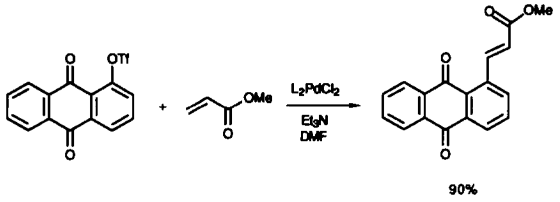


(Equation 109)

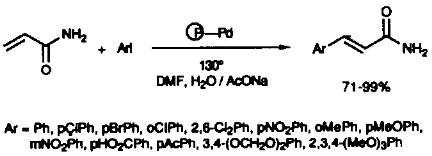


Electron deficient olefins (eqn. (110) [130] and eqn. (111) [131]) and σ-acetamidoacrylates (eqn. (112) [132,133] and eqn. (113) [134]) were arylated using the Heck reaction.

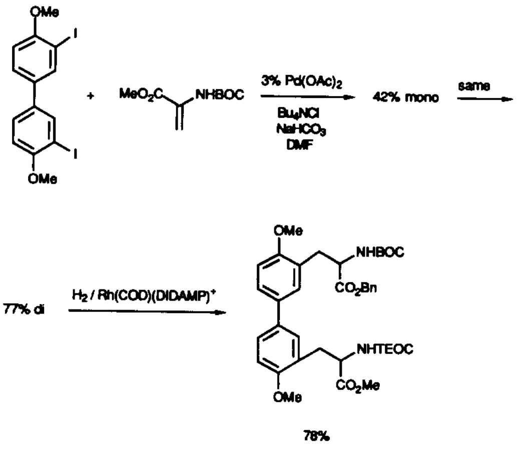
(Equation 110)



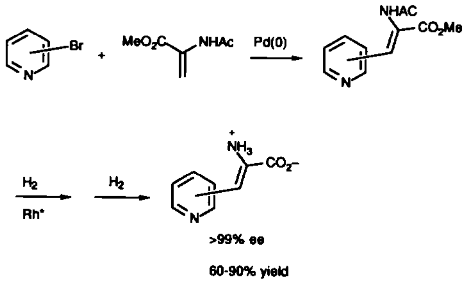
(Equation 111)



(Equation 112)

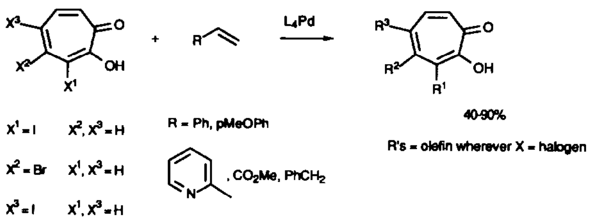


(Equation 113)

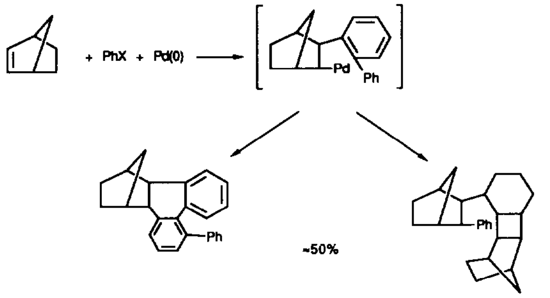


Halogenated tropanones were olefinated using Heck chemistry (eqn. (114) [135]). Multiple insertions were observed in the palladium(0) catalyzed arylation of norbornene (eqn. (115) [136]). Palladium also catalyzed an unusual iodoalkylation of alkenes (eqn. (116) [137]).

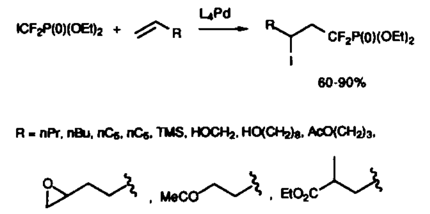
(Equation 114)



(Equation 115)

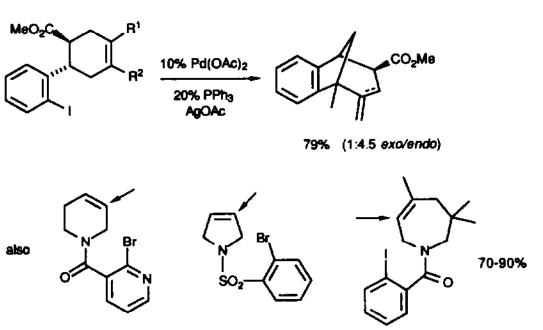


(Equation 116)

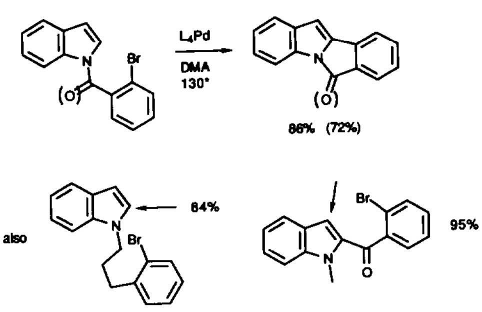


Intramolecular Heck reactions were also extensively used for cyclization, particularly in alkaloid synthesis (eqn. (117) [138], eqn. (118) [139], eqn. (119) [140], eqn. (120) [141], eqn. (121) [142], eqn. (122) [143], and eqn. (123) [144]). Thallium salts suppressed alkene isomerization products from intramolecular Heck reactions [145].

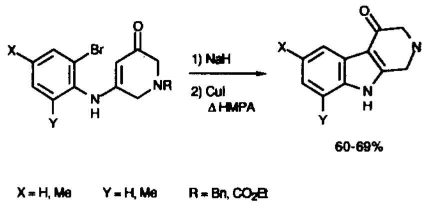
(Equation 117)



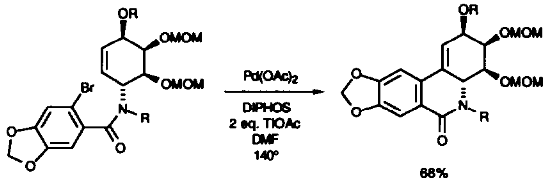
(Equation 118)



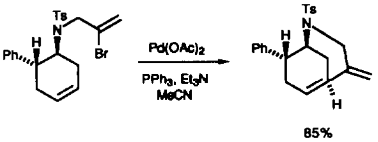
(Equation 119)



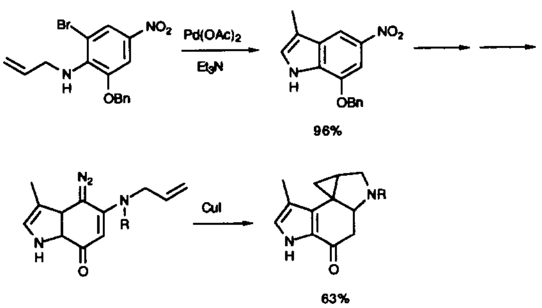
(Equation 120)



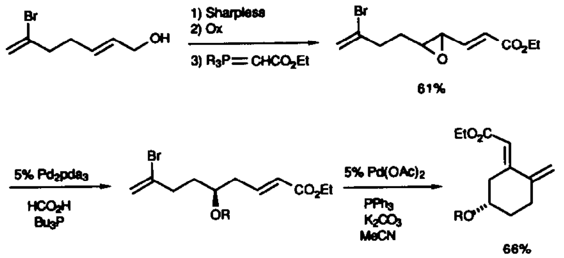
(Equation 121)



(Equation 122)

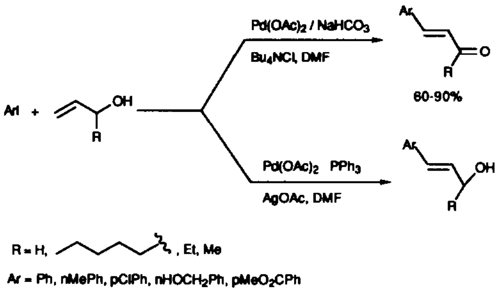


(Equation 123)

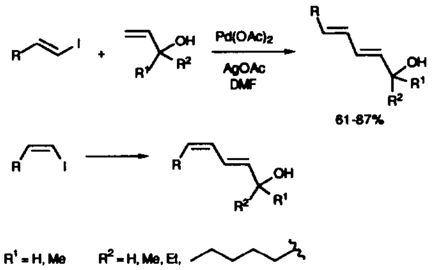


Heck arylation of allylic alcohols produces carbonyl compounds if β-elimination is possible (eqn. (124) [146], eqn. (125) [147], eqn. (126) [148], and eqn. (127) [149]).

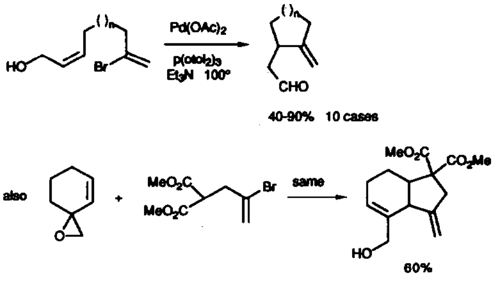
(Equation 124)



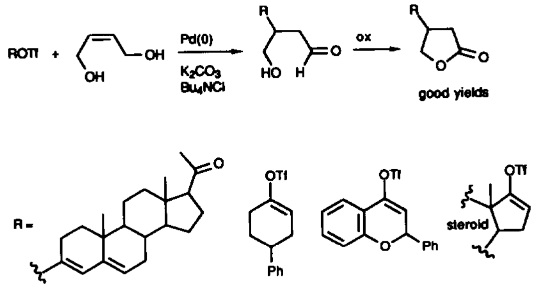
(Equation 125)



(Equation 126)

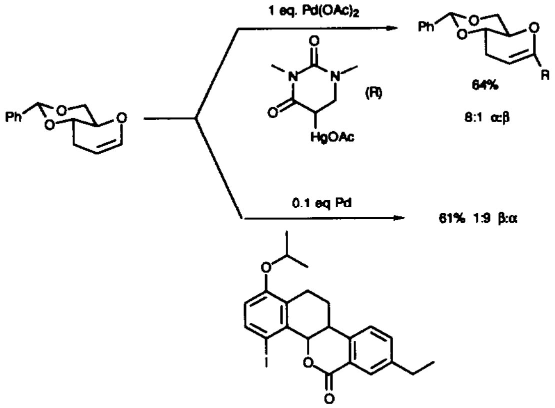


(Equation 127)

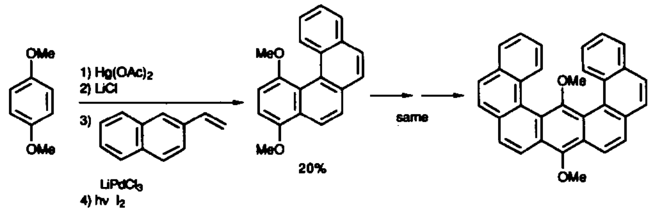


Transmetallation from mercury (eqn. (128) [150] and eqn. (129) [151]) and boron (eqn. (130) [152]), as well as direct metallation (eqn. (131) [153]) and cyclopalladation (review, 15 references) [154] have all been used to produce σ-alkyl palladium complexes for olefination.

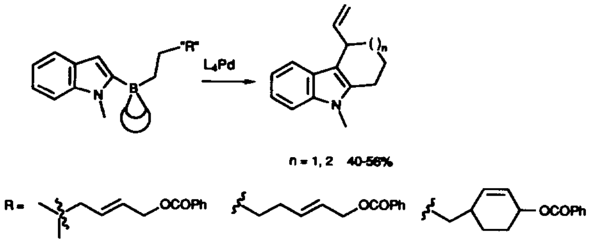
(Equation 128)



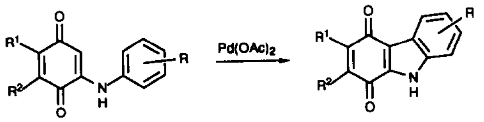
(Equation 129)



(Equation 130)

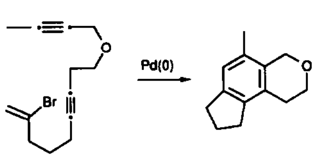


(Equation 131)

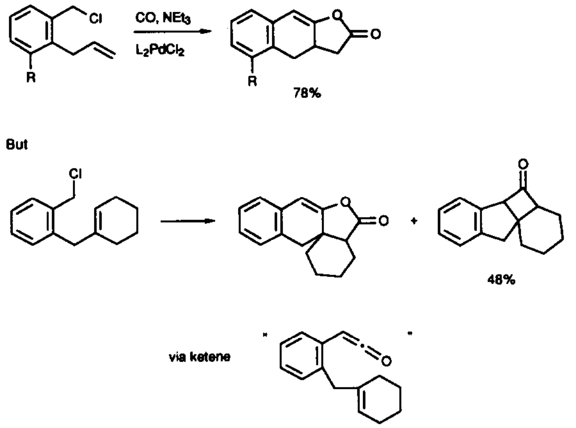


Multiple insertion "cascade" cyclizations have become increasingly popular, and many interesting cyclizations have been achieved (eqn. (132) [155], eqn. (133) [156], eqn. (134) [157], eqn. (135) [158], eqn. (136) [159], and eqn. (137) [160]).

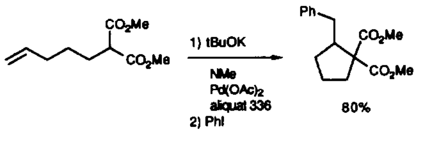
(Equation 132)



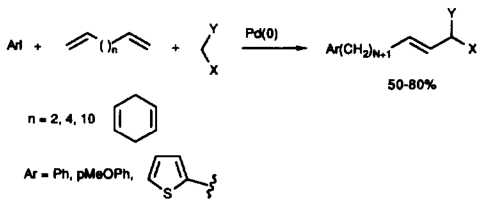
(Equation 133)



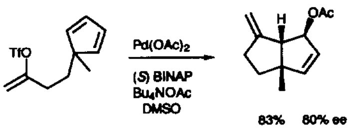
(Equation 134)



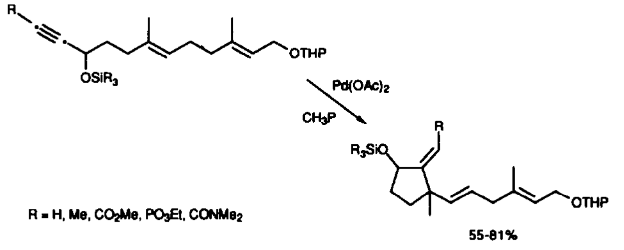
(Equation 135)



(Equation 136)

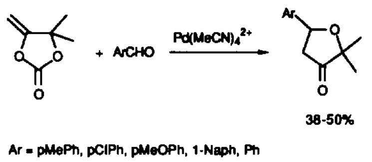


(Equation 137)

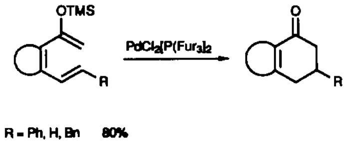


Palladium(II) catalyzed the alkylation of ene carbonates by aldehydes (eqn. (138) [161]), and the rearrangement of 2-silyloxy-1,3,5-hexatrienes (eqn. (139) [162]).

(Equation 138)

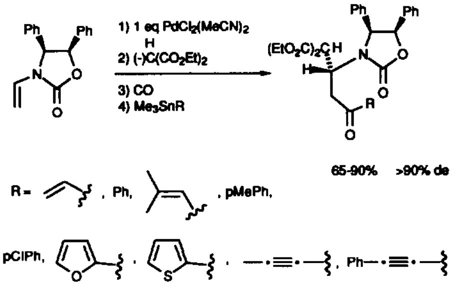


(Equation 139)

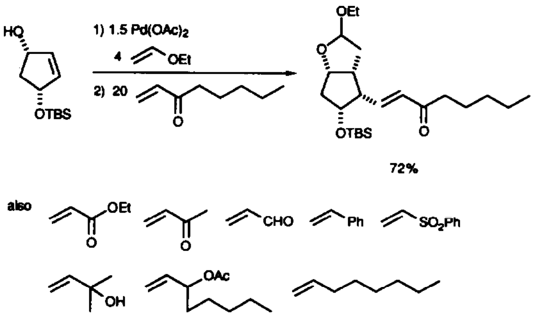


Palladium(II) complexes catalyzed the alkylation of olefins by stabilized carbanions. This chemistry was used to synthesize a relay to thienamycin [163]. Optically active ene-carbamates were efficiently alkylated and acylated utilizing palladium(II) salts (eqn. (140) [164]). A very nice synthesis of prostacyclin analogs used alkylation of an olefin as a key step (eqn. (141) [165]). Enolates alkylated the olefin of platinum or iridium complexed C-allyl glycine and C-vinyl glycine [166]. Rhodium(I) complexes catalyzed the alkylation of terpenes by enolates (eqn. (142) [167]).

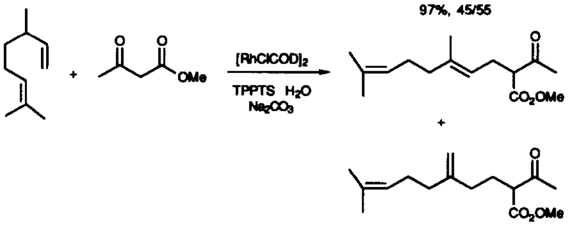
(Equation 140)



(Equation 141)

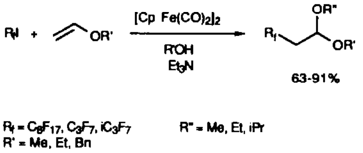


(Equation 142)

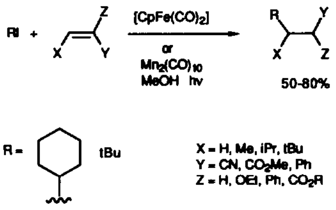


Iron complexes catalyzed the addition of alkyl iodides to alkenes (eqn. (143) [168] and eqn. (144) [169]). Copper (eqn. (145) [170]) and manganese complexes (eqn. (146) [171]) catalyzed radical cyclization processes.

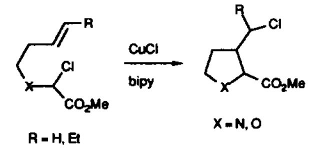
(Equation 143)



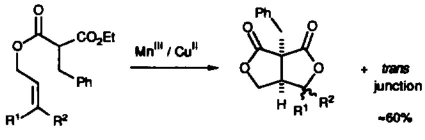
(Equation 144)



(Equation 145)

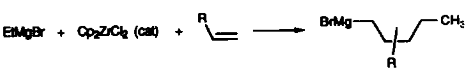


(Equation 146)

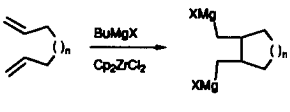


Zirconocene dichloride catalyzed the addition of ethyl magnesium bromide to alkenes (eqn. (137) [172], eqn. (148) [173], and eqn. (149) [174]). Zirconium complexes of benzynes inserted olefins (eqn. (150) [175] and eqn. (151) [176]).

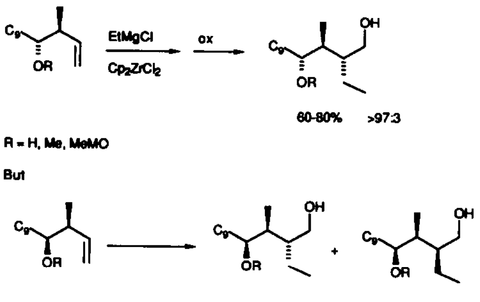
(Equation 147)



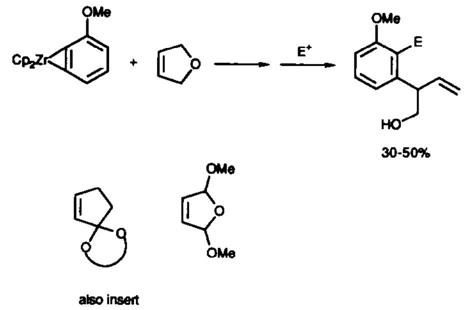
(Equation 148)



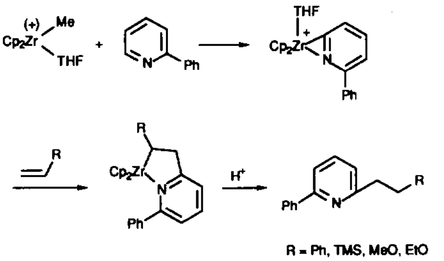
(Equation 149)



(Equation 150)



(Equation 151)

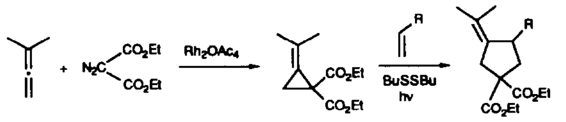


2.1.4. Decomposition of diazoalkanes and other cyclopropanations

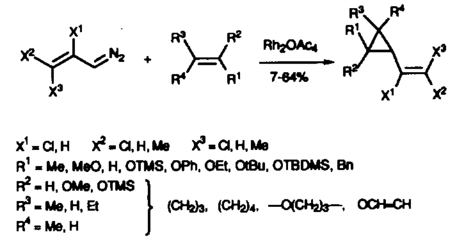
A number of reviews dealing with cyclopropanations and metal catalyzed decomposition of diazo compounds have appeared. These include: *Transition Metal Carbene Complexes in Cyclopropanation* (30 references) [177]; *Chiral Catalysts for Enantioselective Carbenoid Cyclopropanation Reactions* (37 references) [178]; *Rhodium(II) Catalyzed Reactions of Diazocarbonyl Compounds* (151 references) [179]; *Carbenoid Cyclizations* (28 references) [180]; *Metal Salt Catalyzed Carbenoids* (dissertation) [181].

Rhodium(II) salts were the most extensively studied catalysts for cyclopropanation via decomposition of diazocompounds. Recoverable catalysts were prepared by making soluble polyethylenecarboxylate-supported rhodium catalysts [182]. A rhodium-porphyrin catalyst with four BINAP ligands around the periphery catalyzed the cyclopropanation of styrene, β-methyl styrene, and allyl benzene by ethyl diazoacetate with 2.3 to 7.8 syn to anti ratios and 10–45% enantiomeric excess in the syn manifold and 0–60% enantiomeric excess in the anti [183]. Allenes cyclopropanated on the unsubstituted olefin when treated with diazomalonate and a rhodium(II) catalyst (eqn. (152) [184]). Unsaturated diazo compounds cyclopropanated a wide range of olefins (eqn. (153) [185] and eqn. (154) [186]). With dienes as substrates ring expansion-rearrangements occurred (eqn. (155) [187] and eqn. (156) [188]).

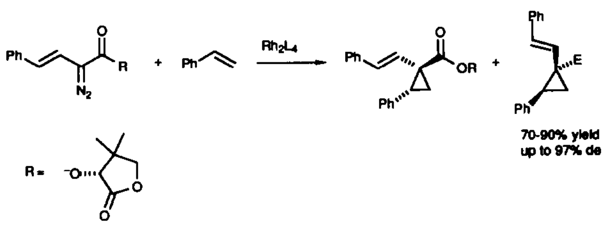
(Equation 152)



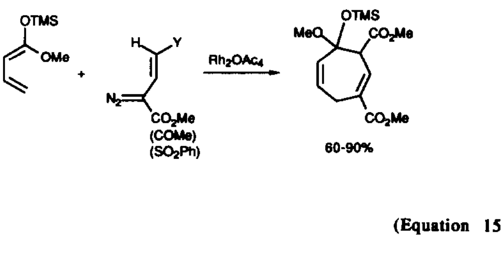
(Equation 153)



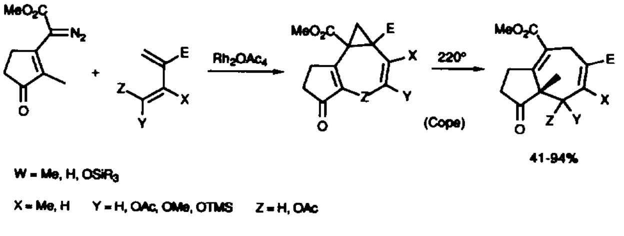
(Equation 154)



(Equation 155)

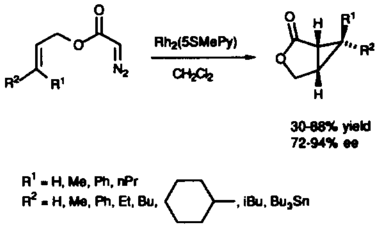


(Equation 156)

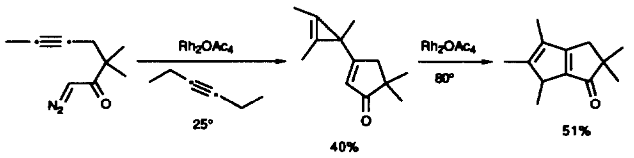


Intramolecular cyclopropanations were also developed (eqn. (157) [189], eqn. (158) [190], eqn. (159) [191], and eqn. (160) [192]).

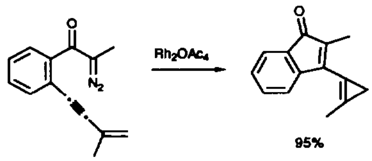
(Equation 157)



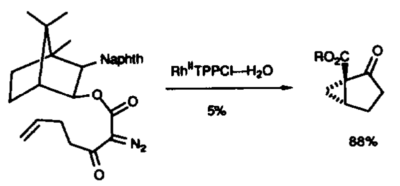
(Equation 158)



(Equation 159)

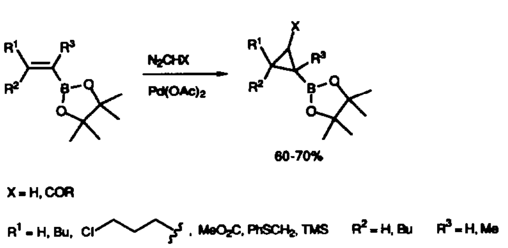


(Equation 160)

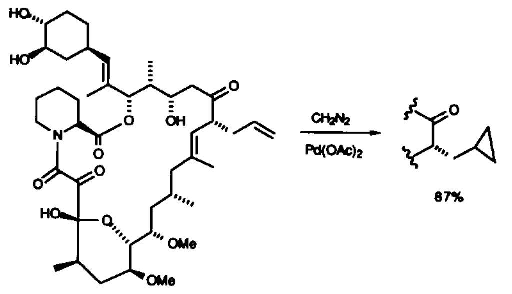


Palladium acetate (eqn. (161) [193], eqn. (162) [194], and eqn. (163) [195]) also catalyzed the cyclopropanation of olefins by diazocompounds. Chiral bis oxazoline copper catalysts cyclopropanated dienes with high enantiomeric excess (eqn. (164) [196]).

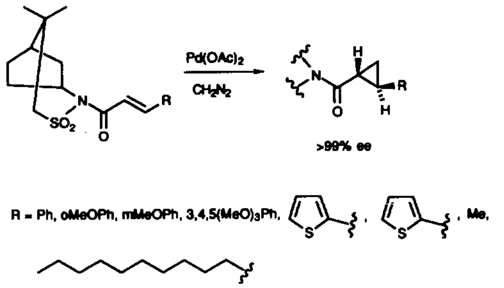
(Equation 161)



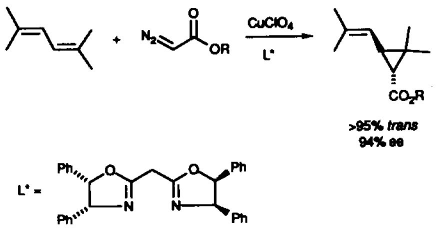
(Equation 162)



(Equation 163)

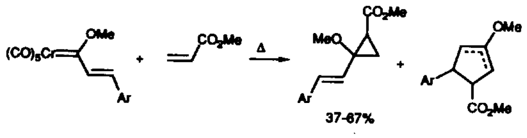


(Equation 164)

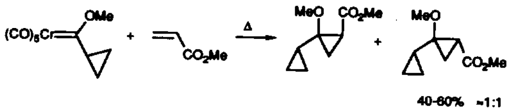


The thermal reaction of unsaturated (eqn. (165) [197]) or cyclopropyl chromium carbene complexes (eqn. (166) [198]) with electron poor olefins gave modest yields of cyclopropanation. Group VI carbene complexes cyclopropanated dienes efficiently (eqn. (167) [199] and eqn. (168) [200]).

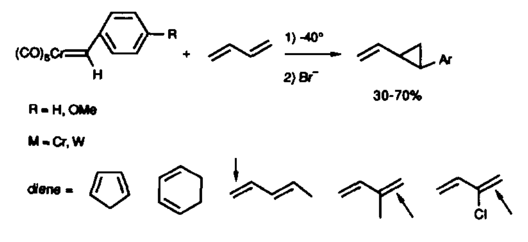
(Equation 165)



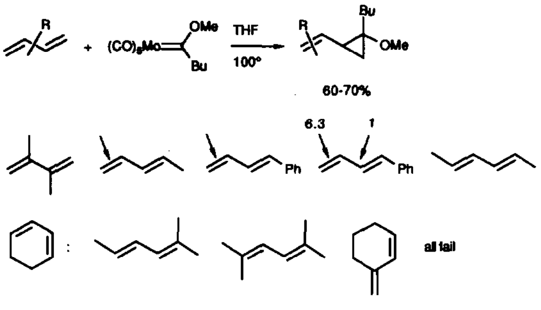
(Equation 166)



(Equation 167)

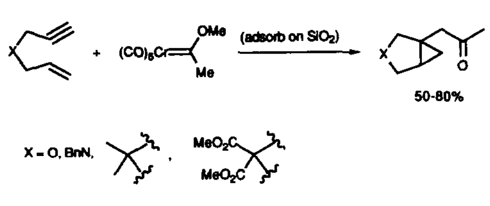


(Equation 168)

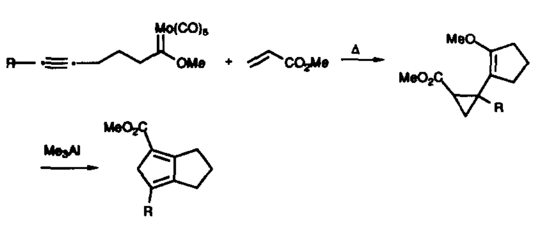


Group VI carbene complexes also participate in multiple insertion/metathesis/cyclopropanation processes, which generate multiple rings in a single reaction (eqn. (169) [201], eqn. (170) [202], eqn. (171) [203], eqn. (172) [204], and eqn. (173) [205]).

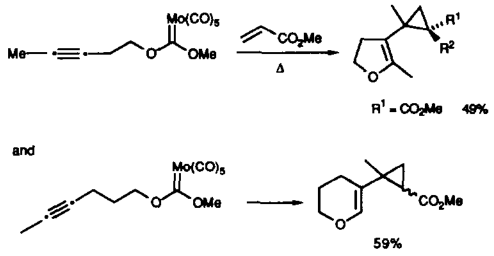
(Equation 169)



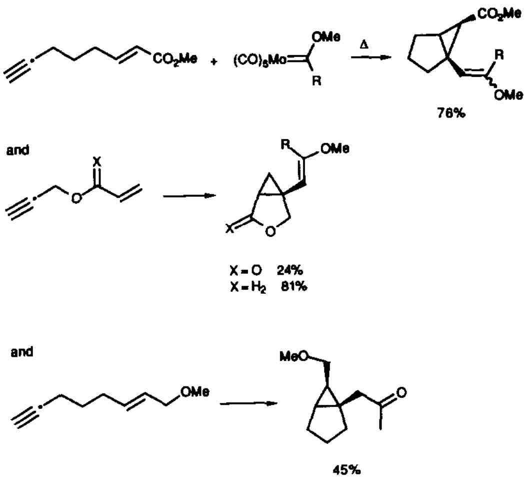
(Equation 170)



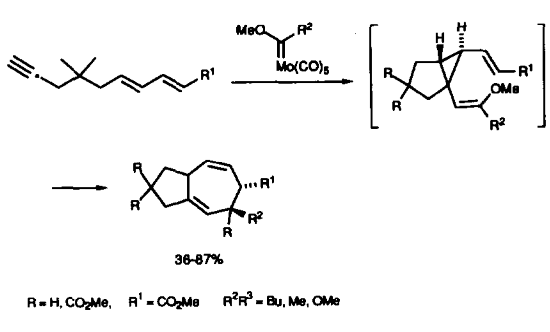
(Equation 171)



(Equation 172)

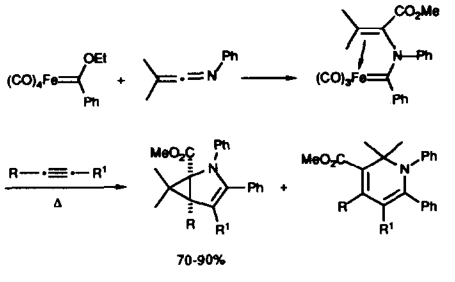


(Equation 173)



A detailed study of the mechanism of asymmetric cyclopropanation of alkenes by optically active cationic iron carbene complexes has appeared [206]. Iron Fischer-type carbene complexes underwent reaction with ketenimines, followed by alkynes to give nitrogen heterocycles (eqn. (174) [207]). Nickel acetylacetonate catalyzed the cyclopropanation of nonactivated alkenes by α-sulfonyl carbanions [208,209].

(Equation 174)

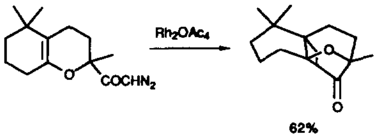


R = Me, Ph, CO$_2$Me

R^1 = Me, H, CO$_2$Me

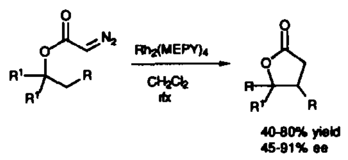
Rhodium(II) acetate catalyzed an intramolecular cyclopropanation to produce a bridged polycyclic system (eqn. (175) [210]).

(Equation 175)



Rhodium(II) acetate also catalyzed diazo decompositions to give C–H insertion products. Cyclopentene construction by rhodium-catalyzed intramolecular C–H insertion was reviewed (28 references) [211]. Lactones were formed this way (eqn. (176) [212] and eqn. (177) [213]). Selectivity in intramolecular insertions has also been probed in detail (eqn. (178) [214] and eqn. (179) [215]). Cyclopentenones (eqn. (180) [216,217]), and cyclohexenones (eqn. (181) [218]) were prepared by C–H insertion processes, as were bridged bicyclic lactones (eqn. (182) [219]).

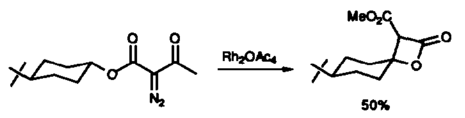
(Equation 176)



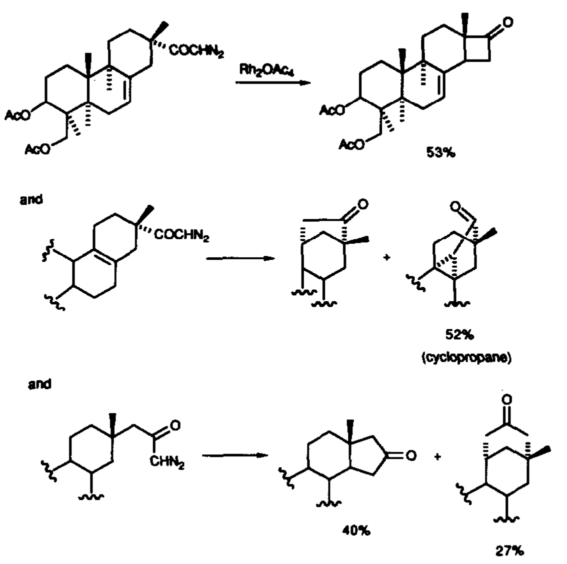
(MEPY = Methyl-2-pyrrolidone-5(S) carboxylate

R = MeO, OEt, BnO, Ph R^1 = H, Me

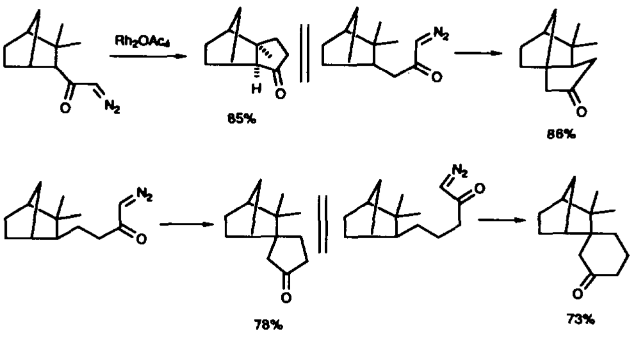
(Equation 177)



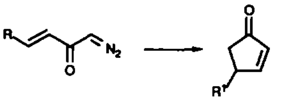
(Equation 178)



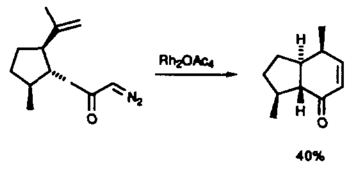
(Equation 179)



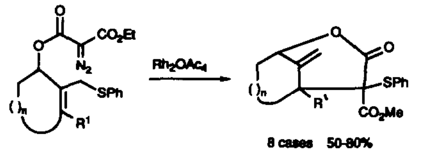
(Equation 180)



(Equation 181)

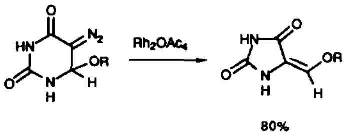


(Equation 182)

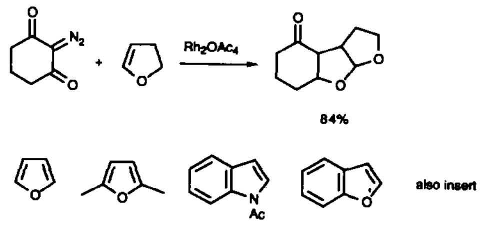


Other rhodium(II) catalyzed insertions are shown in eqn. (183) [220], eqn. (184) [221], eqn. (185) [222], eqn. (186) [223], and eqn. (187) [224]. Palladium acetate also catalyzed CH insertion of diazo compounds (eqn. (188) [225]).

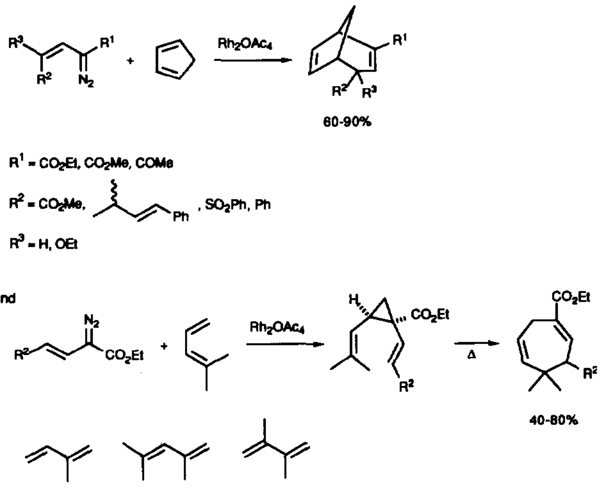
(Equation 183)



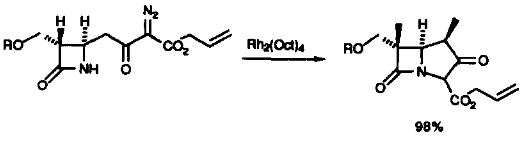
(Equation 184)



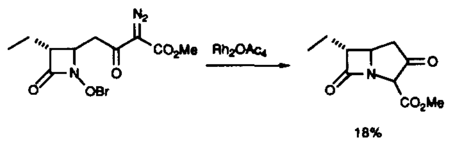
(Equation 185)



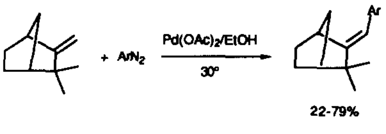
(Equation 186)



(Equation 187)



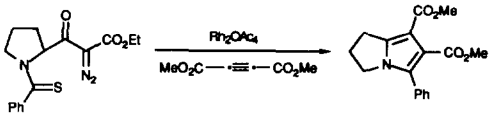
(Equation 188)



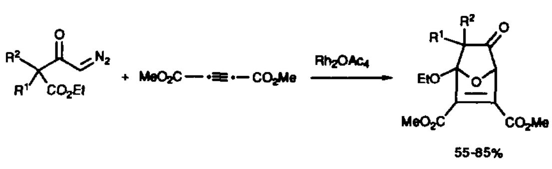
Ar = Ph, pMePh, mMePh, mMeOPh, pMeOPh, pClPh, oClPh, pBrPh, nNO$_2$Ph, pNO$_2$Ph, 2,4Cl$_2$Ph

Ylide formation from reactions of carbenes and carbenoids with heteroatom lone pairs has been reviewed (332 references) [226] as has the generation and utilization of carbonyl ylides via the tandem cyclization–cycloaddition method [227]. For examples, see eqn. (189) [228] and eqn. (190) [229]. Tandem cyclization reactions of rhodium carbenoids and its application for the synthesis of heterocyclic compounds was the topic of a dissertation [230]. In the rhodium(II) catalyzed cascade cyclization in eqn. (191), rhodium failed to insert into an alkyne [231].

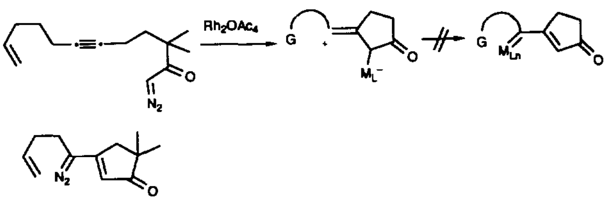
(Equation 189)



(Equation 190)



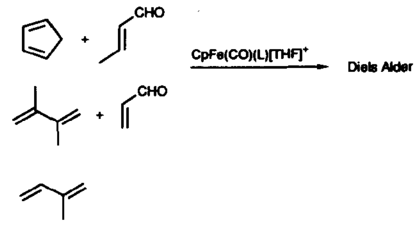
(Equation 191)



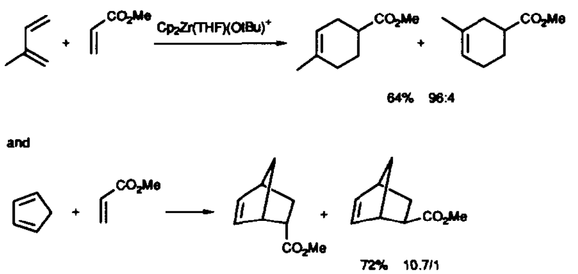
2.1.5. Cycloaddition reactions

Cationic iron (eqn. (192) [232]) and zirconium (eqn. (193) [233]) catalyzed Diels–Alder reactions. Reduced cobalt complexes catalyzed asymmetric homo Diels–Alder reactions in the presence of chiral ligands (eqn. (194) [234]). Chromium cycloheptatriene complexes underwent 6 + 2 cycloaddition with alkynes (eqn. (195) [235]) and alkenes (eqn. (196) [236]), while manganese pentadienyl complexes underwent 6 + 4 cycloaddition with dienes (eqn. (197) [237]).

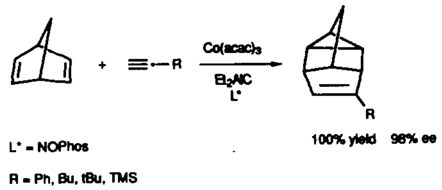
(Equation 192)



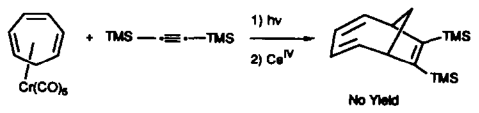
(Equation 193)



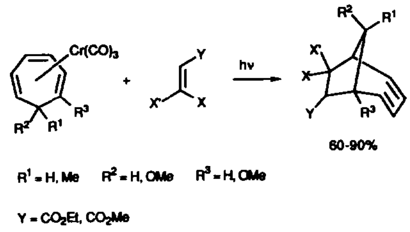
(Equation 194)



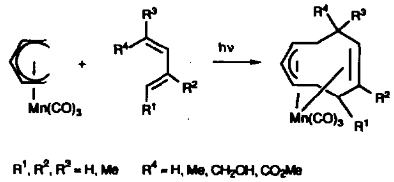
(Equation 195)



(Equation 196)

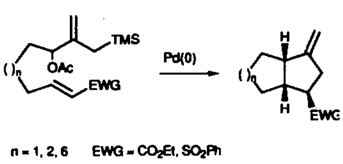


(Equation 197)

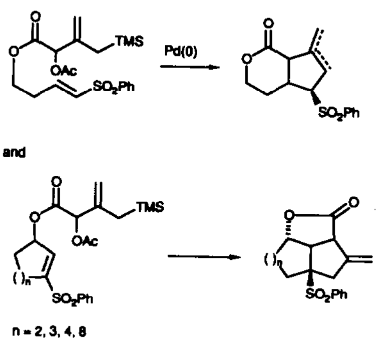


Intramolecular palladium-catalyzed trimethylennmethane cycloaddition was the topic of a dissertation [238]. Full papers on this topic has also appeared (eqn. (198) [239] and eqn. (199) [240]). Intermolecular versions were also useful (eqn. (200) [241]). Palladium also catalyzed cycloadditions of methylenecyclopropanes (eqn. (201) [242]) and methylenethiaranes (eqn. (202) [243]).

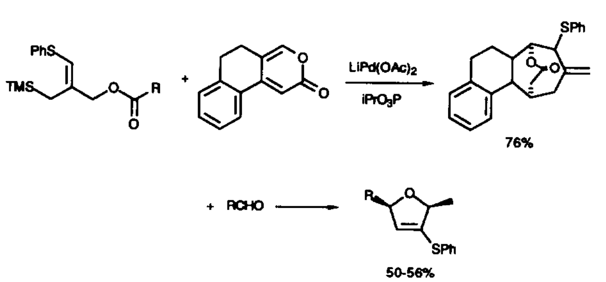
(Equation 198)



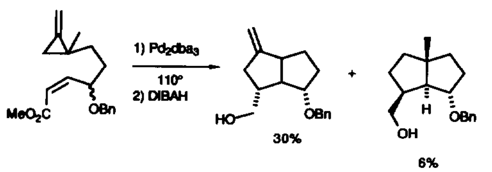
(Equation 199)



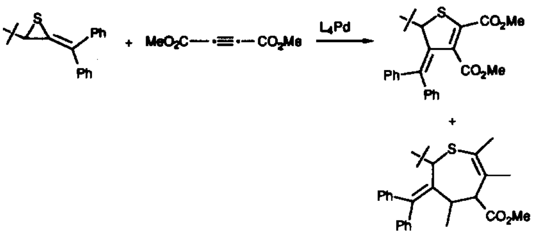
(Equation 200)



(Equation 201)

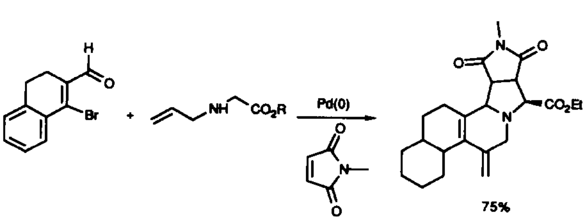


(Equation 202)

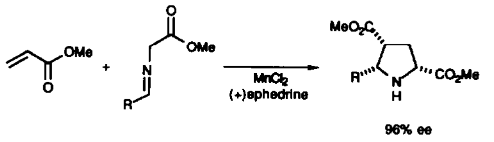


Palladium (eqn. (203) [244]) and manganese (eqn. (204) [245]) catalyzed 1,3-dipolar cycloadditions. The [3 + 2] cycloaddition reactions of allylstannanes with α,β-unsaturated acyliron complexes have been reviewed (91 referenced) [246]. The response of yields to the position and steric environment of the oxygenation in the nickel mediated [2 + 2 + 2] cocyclization of hepta-1,6-diyne and alkynols was examined [247]. Palladium catalyzed enyne cyclizations which involved metathesis processes (eqn. (205) [248] and eqn. (206) [249]).

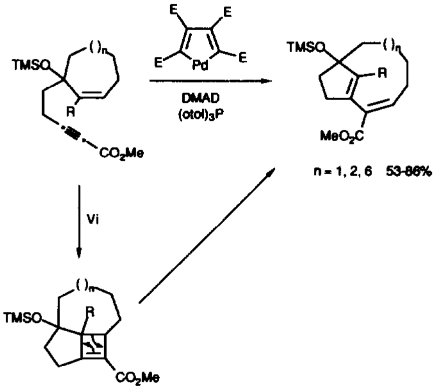
(Equation 203)



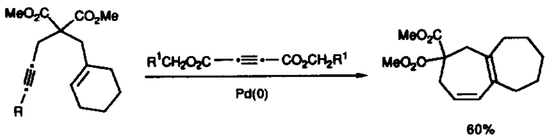
(Equation 204)



(Equation 205)



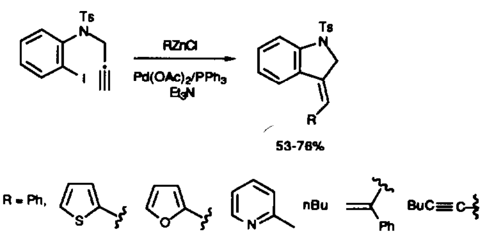
(Equation 206)



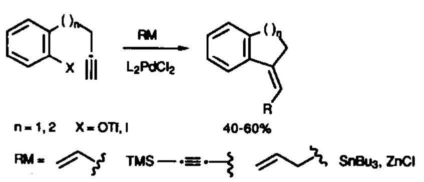
2.1.6. *Alkylation of alkynes*

Palladium(0) catalyzed the intramolecular alkylation of alkynes by aryl halides (eqn. (207) [250] and eqn. (208) [251]). Insertion of two alkynes produced arenes (eqn. (209) [252]). A spectacular alkyne insertion/cascade cyclization has been achieved (eqn. (210) [253]). Palladium(0) complexes catalyzed the alkylation of alkynes by enolates (eqn. (211) [254]), and by aryl halides followed by enolates (eqn. (212) [255]). Allenes also were alkylated by this same insertion–alkylation sequence (eqn. (213) [256] and eqn. (214) [257]). Homologation was achieved using palladium(0) catalyzed oxidative addition/insertion/transmetallation processes (eqn. (215) [258] and eqn. (216) [259]).

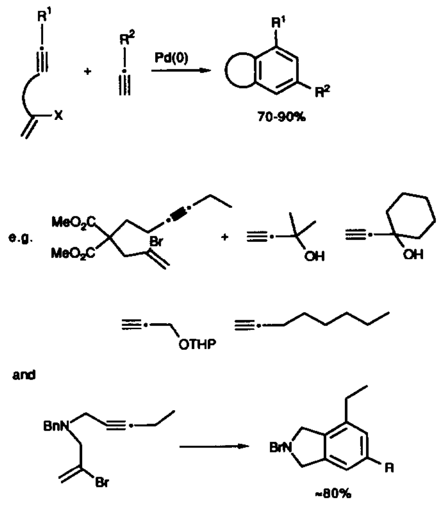
(Equation 207)



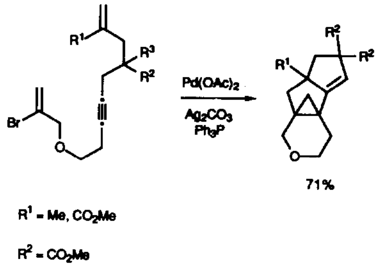
(Equation 208)



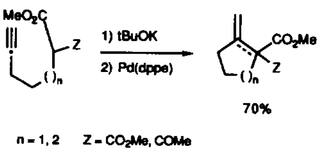
(Equation 209)



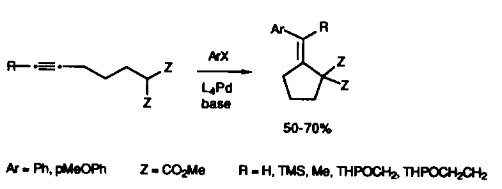
(Equation 210)



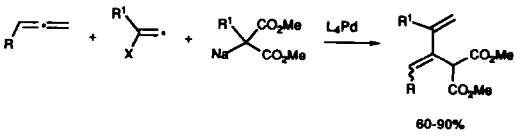
(Equation 211)



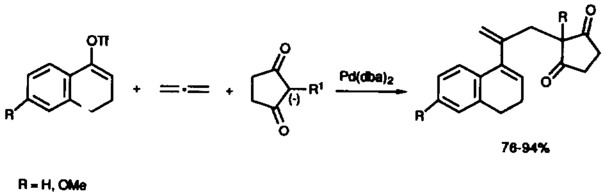
(Equation 212)



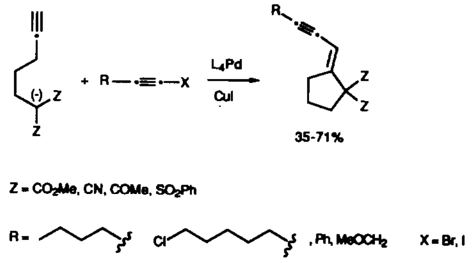
(Equation 213)



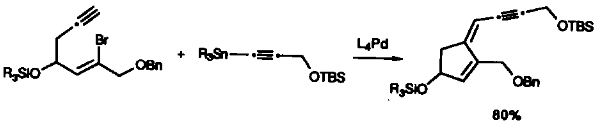
(Equation 214)



(Equation 215)

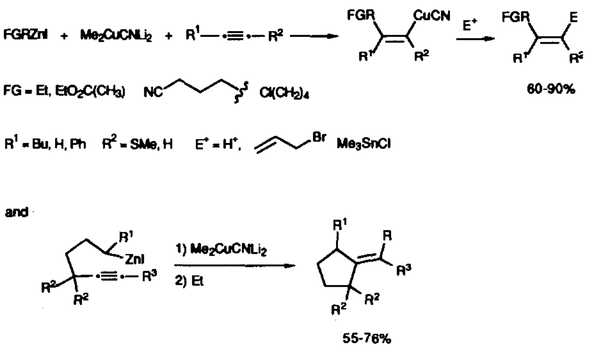


(Equation 216)

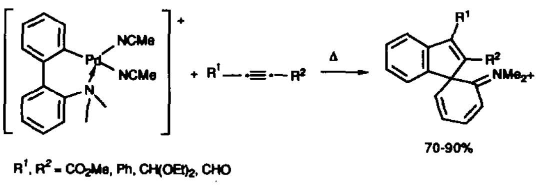


Alkynes were "carbocuprated" by functionalized organozinc reagents in the presence of (dimethyl)(cyano)cuprates (eqn. (217) [260]). Palladium(0)/copper(I) systems catalyzed the alkylation of terminal alkynes by fluorinated vinyl iodides [261]. Reactions of cyclopalladated compounds with alkynes have been reviewed (56 references) [262] (eqn. (218) [263]). Alkynes were alkylated by alkynyl tins using palladium catalysts (eqn. (219) [264]). Organolithium reagents alkylated alkynylzirconium complexes (eqn. (220) [265]). Alkynes were alkylated by zirconium benzyne complexes (eqn. (221) [266]). Alkynes were alkylated by 2thienoyliron complexes (eqn. (222) [267]).

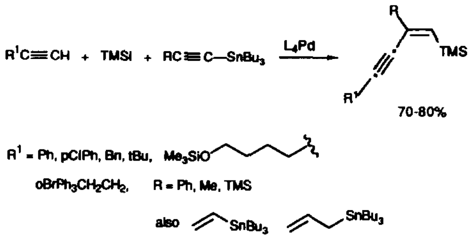
(Equation 217)



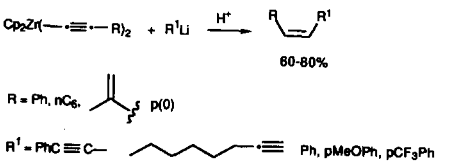
(Equation 218)



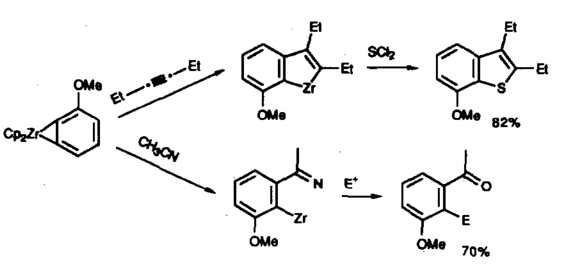
(Equation 219)



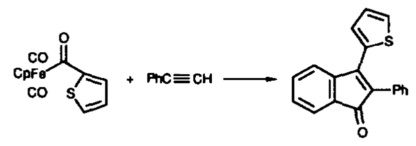
(Equation 220)



(Equation 221)



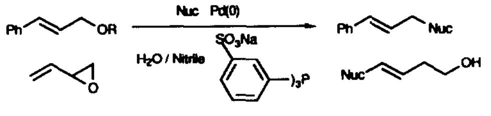
(Equation 222)



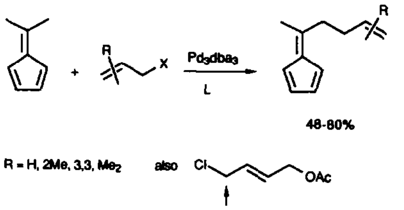
2.1.7. Alkylation of allyl, propargyl, and allenyl systems

Palladium catalyzed allylic alkylation continued to be actively investigated. Phase transfer conditions for the alkylation of allyl acetates and chlorides by stabilized enolates using palladium catalysts have been developed [268] (eqn. (223) [269]). The regioselectivity of palladium(0) catalyzed reactions of nucleophiles with cyclopropyl group containing allyl esters has been studied [270]. Palladium(0) catalyzed the alkylation of allyl halides by dimethylfulvene (eqn. (224) [271]). Cyclic allyl acetates were alkylated by acetonitrile anion generated by palladium(0) catalyzed decomposition of allyl carbonates (eqn. (225) [272]). Palladium(0) complexes catalyzed the C-allylation of cyclic β-diketones by allyl acetate in acid mediums [273].

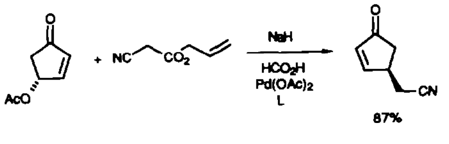
(Equation 223)



(Equation 224)

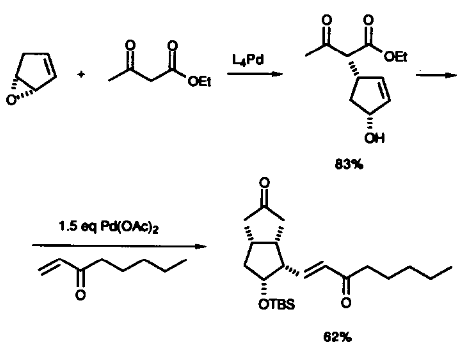


(Equation 225)

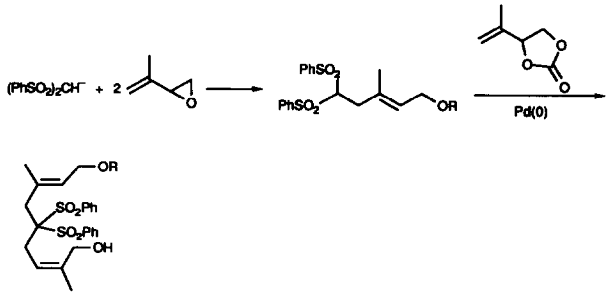


Palladium(0) also catalyzed the alkylation of allyl epoxides by stabilized carbanions (eqn. (226) [274] and eqn. (227) [275]).

(Equation 226)

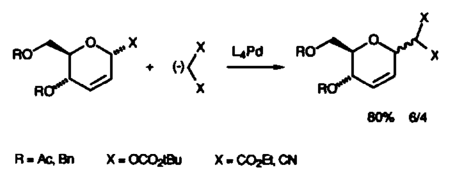


(Equation 227)

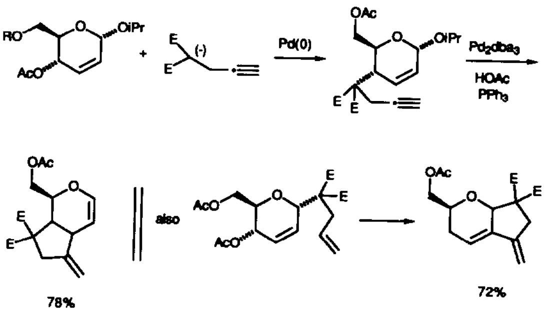


Palladium(0) catalyzed alkylation of allylic acetates has found applications in the synthesis of C-glycosides (eqn. (228) [276], eqn. (229) [277], and eqn. (230) [278]).

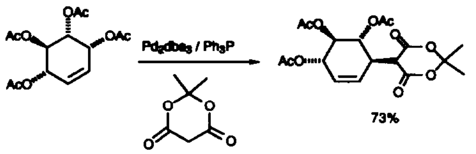
(Equation 228)



(Equation 229)

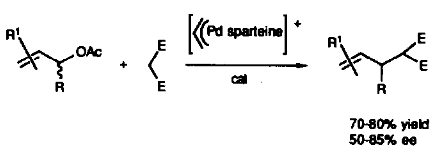


(Equation 230)

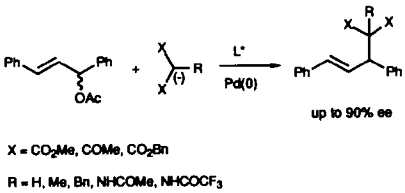


Asymmetric inductions in palladium catalyzed allylic alkylations has been achieved by using chiral ligands (eqn. (231) [279], eqn. (232) [280], eqn. (233) [281], and eqn. (234) [282]).

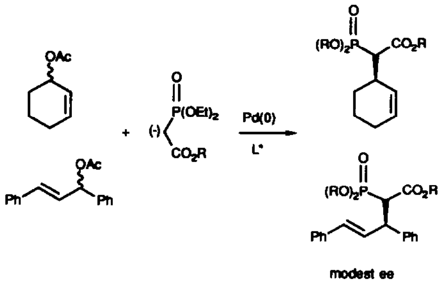
(Equation 231)



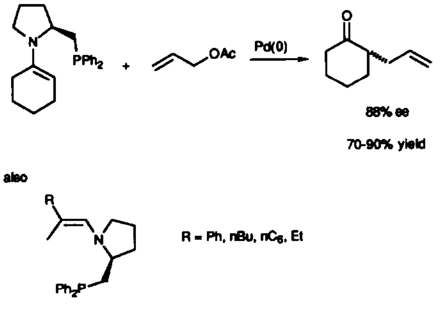
(Equation 232)



(Equation 233)

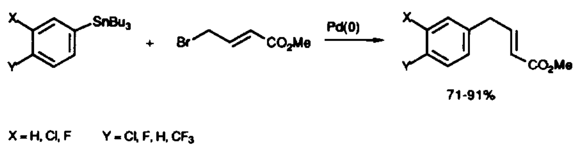


(Equation 234)

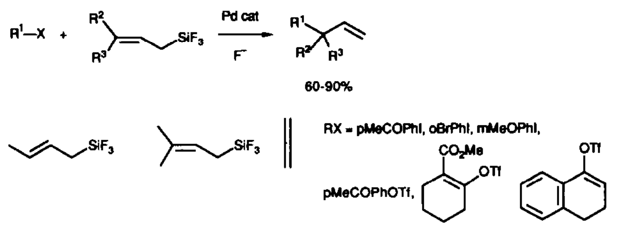


Palladium(0) also catalyzed allylation by transmetallation from tin (eqn. (235) [283]), silicon (eqn. (236) [284]) and boron (eqn. (237) [285]), as well as reduction (eqn. (238) [286]) and rearrangement/insertion reactions (eqn. (239) [287] and eqn. (240) [288]).

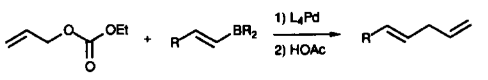
(Equation 235)



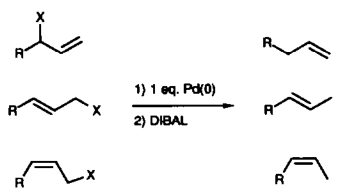
(Equation 236)



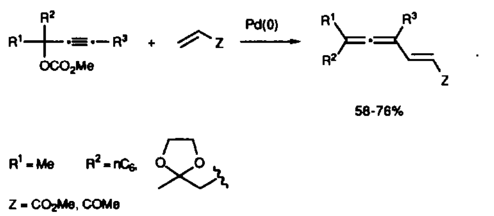
(Equation 237)



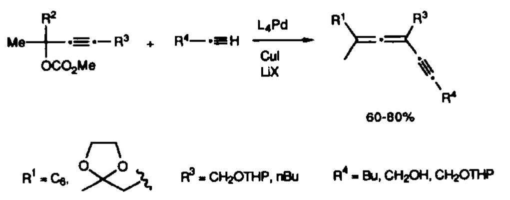
(Equation 238)



(Equation 239)

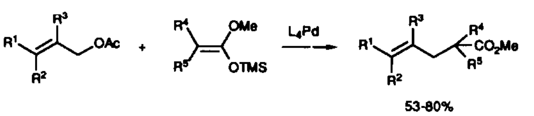


(Equation 240)

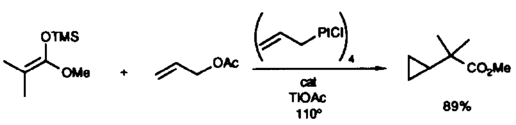


Silylketene acetals attacked allyl acetates at the less substituted carbon in the presence of palladium catalysts (eqn. (241) [289]), but at the central carbon with a platinum catalyst (eqn. (242) [290]).

(Equation 241)

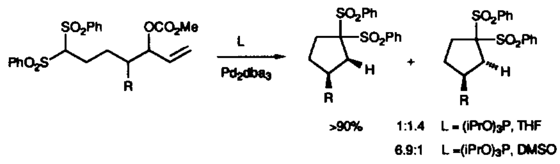


(Equation 242)

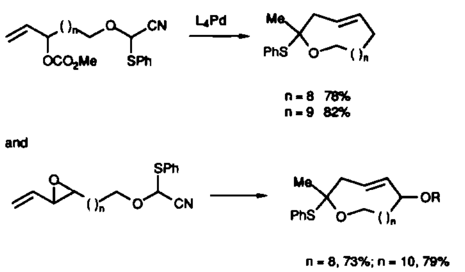


Palladium catalyzed allylic alkylation was useful for several cyclizations (eqn. (243) [291], eqn. (244) [292], eqn. (245) [293], and eqn. (246) [294]). This process could be truncated by a transmetallation leading to increased functionalization (eqn. (247) [295]).

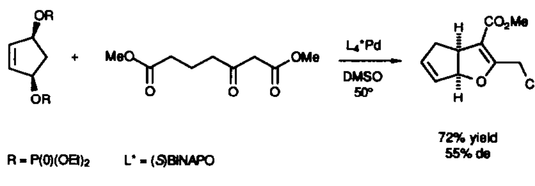
(Equation 243)



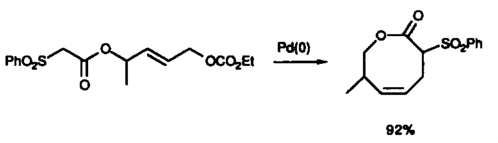
(Equation 244)



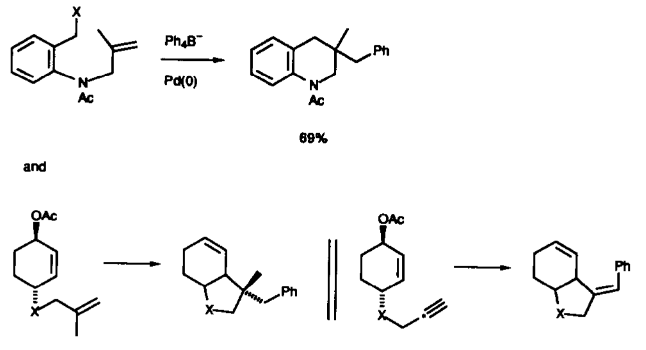
(Equation 245)



(Equation 246)

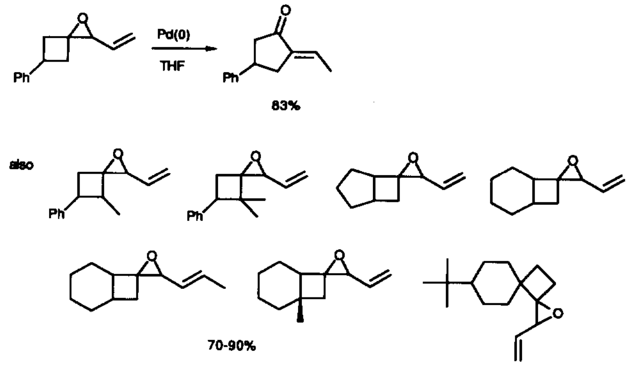


(Equation 247)

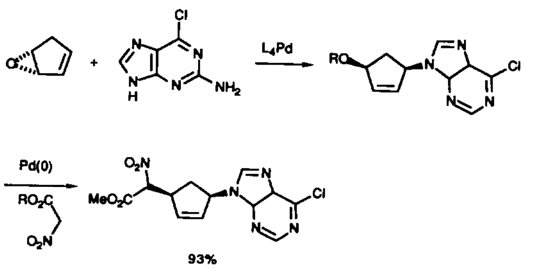


Palladium(0) catalyzed the rearrangements of allyl epoxides (eqn. (248) [296]), nucleoside synthesis (eqn. (249) [297]), diene cyclization (eqn. (250) [298]) and deprotection (eqn. (251) [299]).

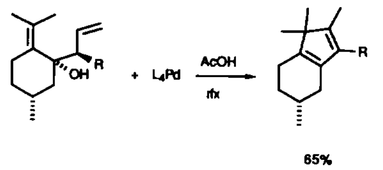
(Equation 248)



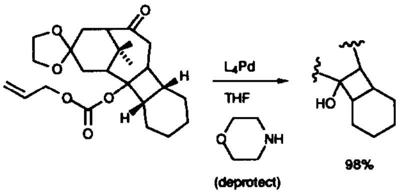
(Equation 249)



(Equation 250)

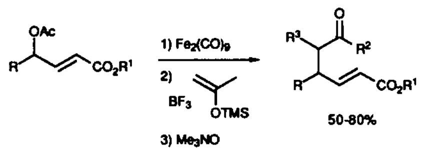


(Equation 251)

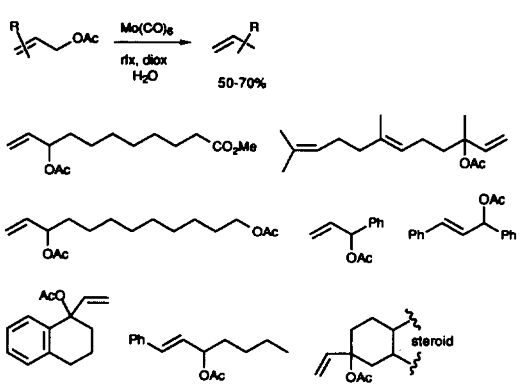


Iron catalyzed the alkylation of allyl acetates by silyl enol ethers (eqn. (252) [300]). Molybdenum carbonyl catalyzed the reduction of allyl acetals (eqn. (253) [301]).

(Equation 252)

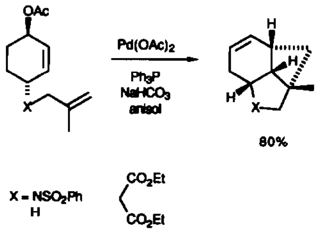


(Equation 253)

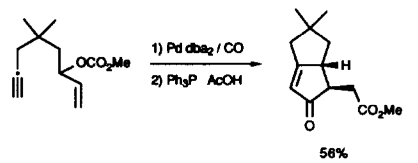


Palladium(0) catalyzed a number of fantastic multiple insertion/cascade cyclizations, starting from allyl acetates (eqn. (254) [302], eqn. (255) [303], eqn. (256) [304], eqn. (257) [305], eqn. (258) [306], and eqn. (259) [307]).

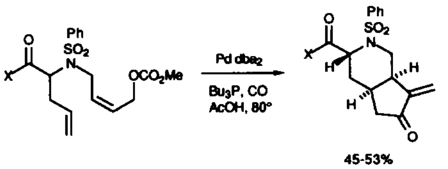
(Equation 254)



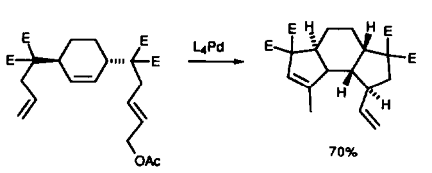
(Equation 255)



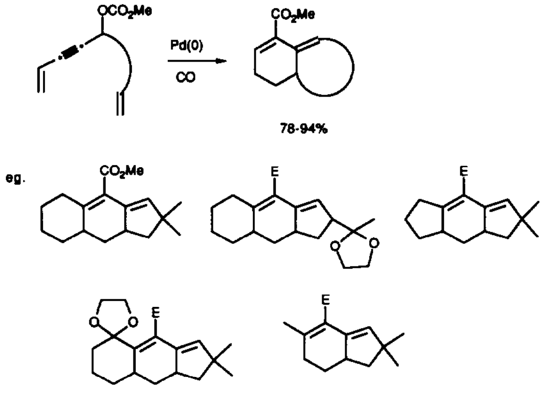
(Equation 256)



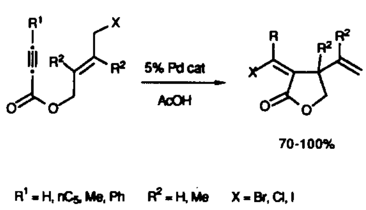
(Equation 257)



(Equation 258)

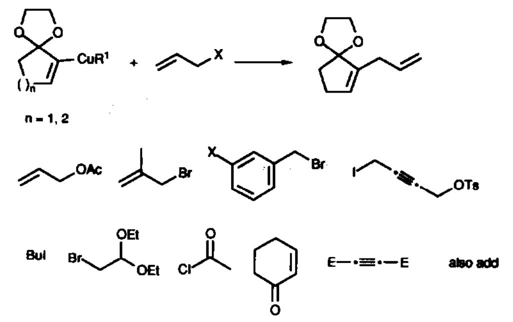


(Equation 259)

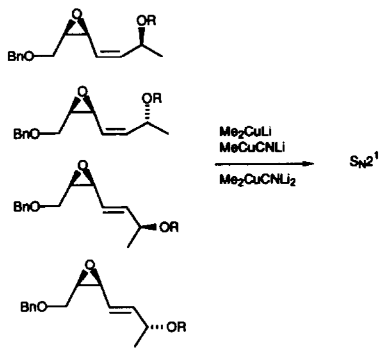


Vinyl cuprates alkylated allyl and propargyl compounds (eqn. (260)] [308]. The diastereodifferentiation in the alkylation of allyl epoxides by cuprates was studied (eqn. (261) [309]). Bis-propargyl halides or tosylates were dialkylated to dienes by organozinc reagents in the presence of copper cyanide (eqn. (262) [310]).

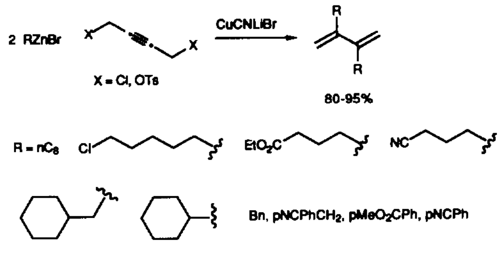
(Equation 260)



(Equation 261)

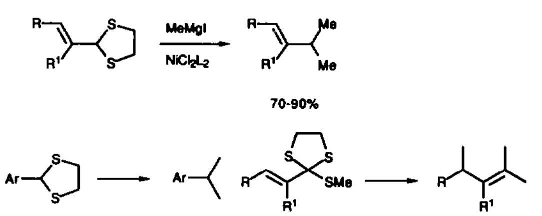


(Equation 262)

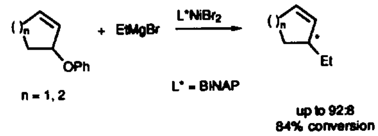


Nickel(II) complexes catalyzed the alkylation of allyl dithio ethers (eqn. (263) [311]), and allyl ethers (eqn. (264) [312]) by Grignard reagents. Copper(I) catalyzed the alkylation of allyl chlorides or phosphonates by alkyltitanium alkoxides in "clean S_N2" *anti* sense (eqn. (265) [313]). Zirconocene dichloride catalyzed the alkylation of allyl alcohols by Grignard reagents (eqn. (266) [314]).

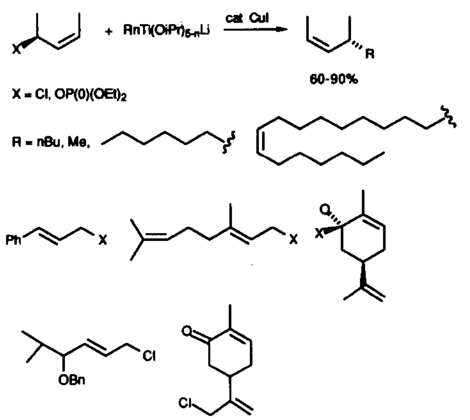
(Equation 263)



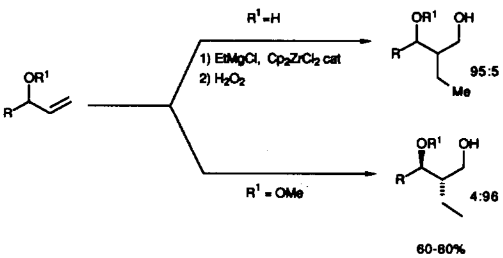
(Equation 264)



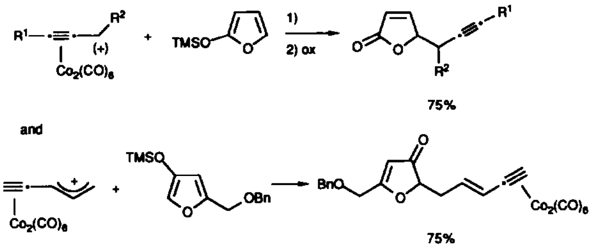
(Equation 265)



(Equation 266)

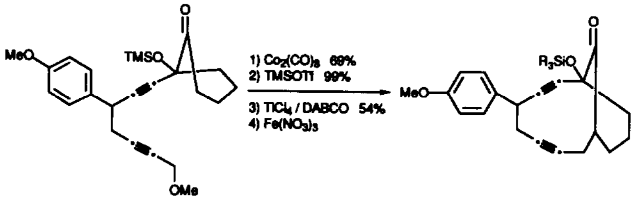


(Equation 267)

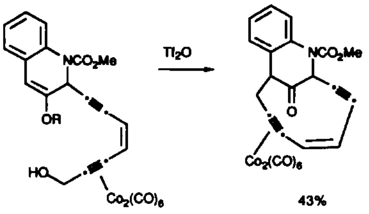


Cobalt-stabilized propargyl cations were alkylated by enol ethers (eqn. (267) [315], eqn. (268) [316], eqn. (269a) [317a], and eqn. (269b) [317b]). Cobalt complexed propargyl aldehydes were alkylated by silylketene thioacetals (eqn. (270) [318]).

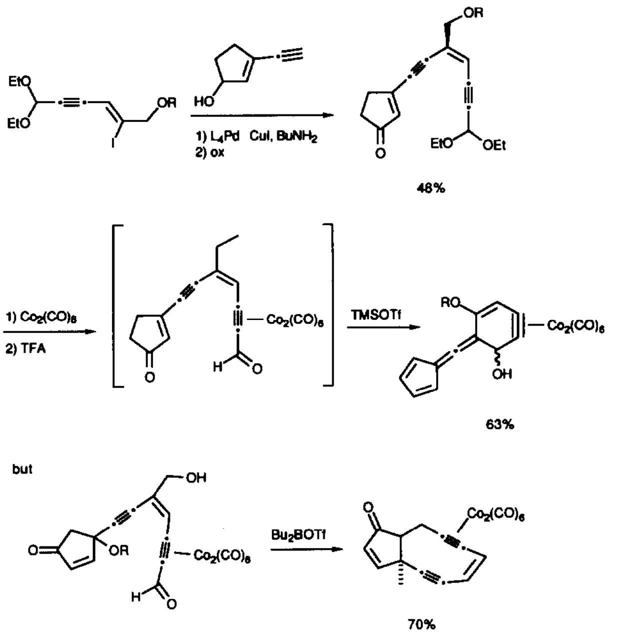
(Equation 268)



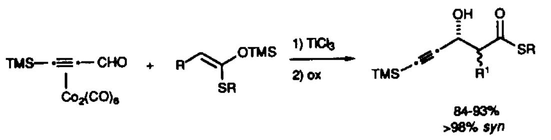
(Equation 269a)



(Equation 269b)



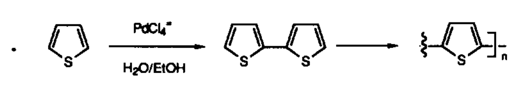
(Equation 270)



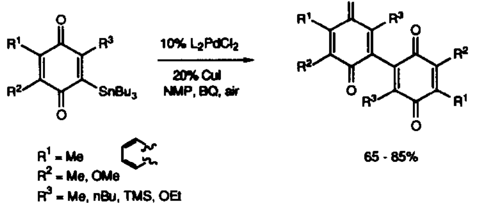
2.1.8. Coupling reactions

Regio- and stereoselective aryl coupling using transition metals has been reviewed (21 references) [319]. Palladium mediated couplings for the synthesis of rotenoids was the subject of a dissertation [320]. Biaryls were synthesized by the coupling of aryl halides using palladium catalysts in the presenced of tertiary amines [321]. Thiophene was dimerized then oligomerized when treated with chloropalladate in aqueous ethanol (eqn. (271) [322]). Stannyl quinones were coupled by palladium/copper catalyst systems (eqn. (272) [323]). Intramolecular coupling of aryl iodides was achieved using palladium(0) catalysts and hexamethylditin (eqn. (273) [324]), while palladium(0) catalyzed the coupling of vinyl iodides via their zinc derivative (eqn. (274) [325]).

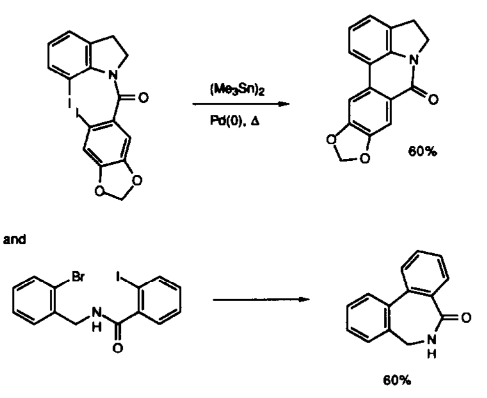
(Equation 271)



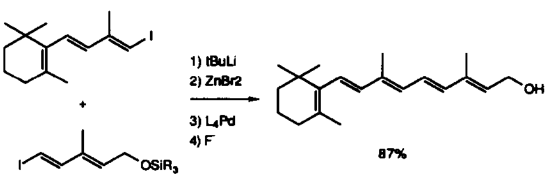
(Equation 272)



(Equation 273)

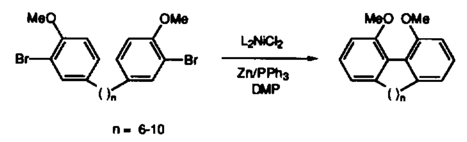


(Equation 274)

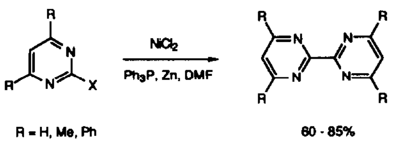


Aryl chlorides were electrochemically reductively coupled to biaryls using a nickel(II) chloride bisphosphine catalyst [326]. Nickel species reduced by zinc also coupled aryl halides (eqn. (275) [327] and eqn. (276) [328]).

(Equation 275)

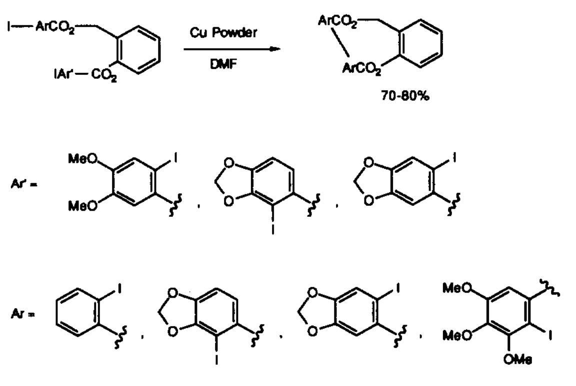


(Equation 276)



Highly stereoselective asymmetric synthesis of axially dissymmetric diphenic acids via intramolecular Ullmann reaction was the subject of a review (49 references) [329]. Unsymmetrical Ullmann coupling was achieved by "templating" the process (eqn. (277) [330]), or by oxidatively coupling unsymmetrical (bis) aryl copper complexes at low temperature (eqn. (278) [331]). *Gem*-dibromoalkenes were coupled to 1,2,3-trienes by zinc/copper (eqn. (279) [332]). Copper coupled selenoamides to (bis)aminoolefins (eqn. (280) [333]).

(Equation 277)



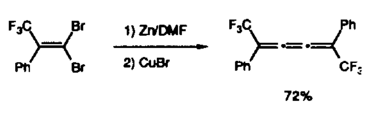
(Equation 278)

$$\mathrm{ArLi + CuCN} \xrightarrow{-78°} \mathrm{ArCu(CN)Li} \xrightarrow[-125°]{\mathrm{Ar'Li}} \xrightarrow[-125°]{\mathrm{O_2}} \mathrm{Ar\,Ar'}$$

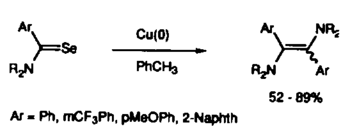
high yields
>96:4
78-90%

Ar = Ph, oMeOPh, mMeOPh, pMeOPh, 2Cl, 4CF$_3$Ph, 1-Naphth
Ar' = oMeOPh, pMeOPh, oMePh, 3F, 4MePh

(Equation 279)

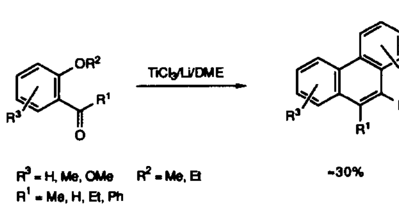


(Equation 280)

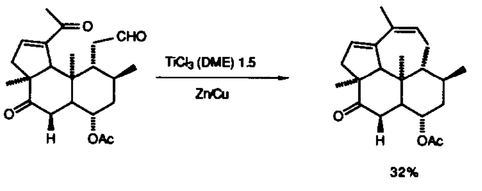


Low valent titanium species and their application to organic synthesis has been reviewed (204 references) [334], as had *Ambrene diterpene synthesis* using titanium induced carbonyl coupling reactions (44 references) [335]. Ultrasound has been found to accelerate the McMurray coupling reaction [336]. Low valent titanium was used to couple benzoic acid halides and esters to stilbenes [337]. Aromatic nitriles were reductively coupled to 1,2-diaryl ethanones by TiCl$_4$/Zn [338]. McMurray coupling of dicarbonyl compounds was accomplished by TiCl$_3$/K–C$_8$ (potassium–graphite) intercolate [339]. (This paper neglected to cite the extensive work of Furstner in the area.) McMurray coupling was not restricted to simple ketones, as evidenced by the examples in eqn. (281) [340,341], eqn. (282) [342], eqn. (283) [343], and eqn. (284) [344]. Optically active 1,2-diphenylethylene diamine was synthesized by the titanium induced coupling of the appropriate D-camphor ketimine (eqn. (285) [345]).

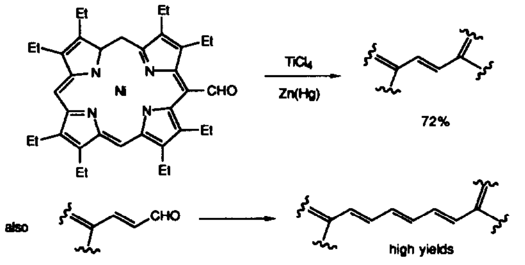
(Equation 281)



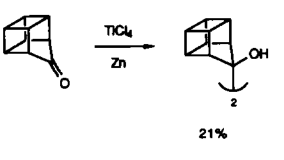
(Equation 282)



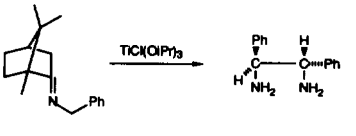
(Equation 283)



(Equation 284)

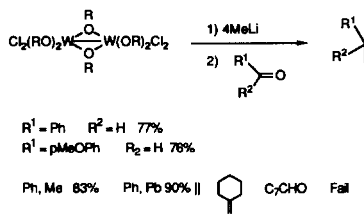


(Equation 285)

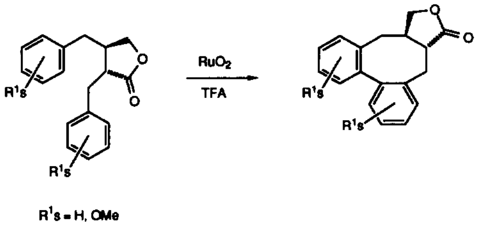


Dimeric tungsten alkoxychlorides effected a methylative reductivedimerization of ketones (eqn. (286) [346]). The coupling of alkynes with alkynes, isonitriles and carbon monoxide by complexes of molybdenum, niobium and tantalum was the topic of a dissertation [347]. Palladium(II) acetate oxidatively coupled benzopyranones to benzene [348]. Ruthenium dioxide in trifluoroacetic acid oxidatively coupled aryls (eqn. (287) [349]).

(Equation 286)



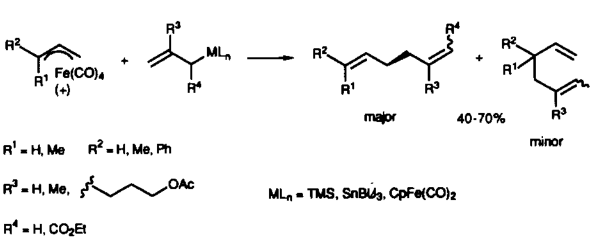
(Equation 287)



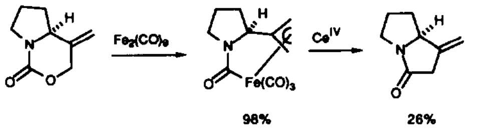
2.1.9. *Alkylation of π-allyl complexes*

The allylnickel chemistry of optically active 2-alkenyl-1,3-dioxolan-5-ones was the topic of a dissertation [350]. A theoretical study of palladium(0) catalyzed substitution on σ-allenic and allylic derivatives has appeared [351]. Palladium catalyzed allylic alkylations of propen-2-yl acetates using chiral η^3-allyl complexes as catalysts were studied by NMR and crystallographic techniques [351]. Cationic η^3-allyliron complexes were alkylated by η^1-allylmetal complexes (eqn. (288) [353]). α-Methylene lactones were deoxygenated via π-allyliron complexes (eqn. (289) [354]). Trimethylsilyloxy π-allyliron complexes underwent reaction with both nucleophiles and electrophiles (eqn. (290) [355]).

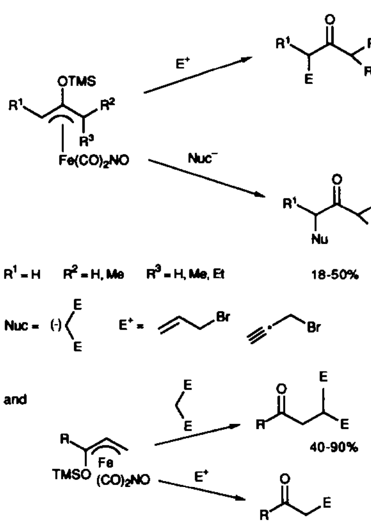
(Equation 288)



(Equation 289)

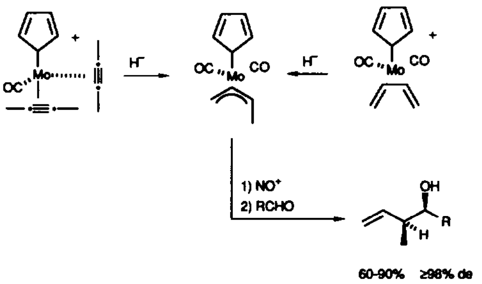


(Equation 290)

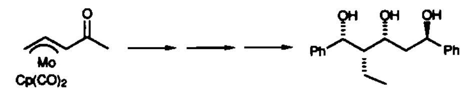


Chiral π-allylmolybdenum complexes were used to alkylate aldehydes with high de (eqn. (291) [356]). Other uses of π-allyl molybdenum complexes in synthesis are seen in eqn. (292) (reported several times last year) [357], eqn. (293) [358], eqn. (294) [359], and eqn. (295) [360].

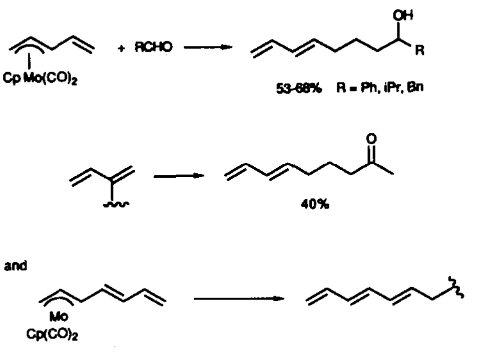
(Equation 291)



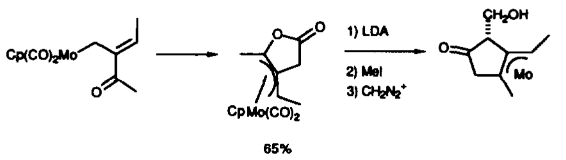
(Equation 292)



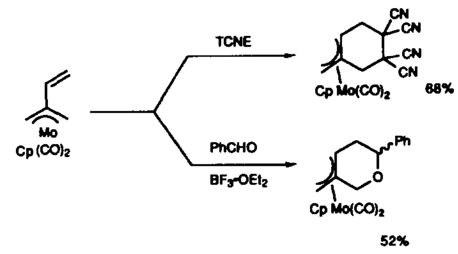
(Equation 293)



(Equation 294)



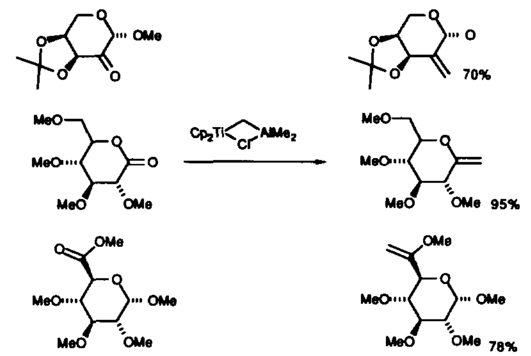
(Equation 295)



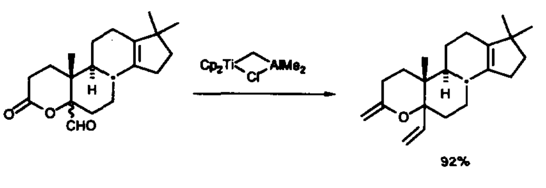
2.1.10. Alkylation of carbonyl compounds

Tebbe's reagent ("Cp_2TiCH_2") was compared to Wittig's reagent (Ph_3PCH_2) for ketone methylenation. Tebbe's proved better, particularly for hindered or enolizable ketones [361]. Sugar esters, lactones and uloses were efficiently methylenated by Tebbe's reagent (eqn. (296) [362]) as were polycyclic lactones (eqn. (297) [363]). Ketones were converted to dienes by titanacyclobutenes (eqn. (298) [364]). Other efficient methylenating reagents are shown in eqn. (299) [365], eqn. (300) [366], and eqn. (301) [367]. Reduced niobium species coupled aldehydes (eqn. (302) [368]).

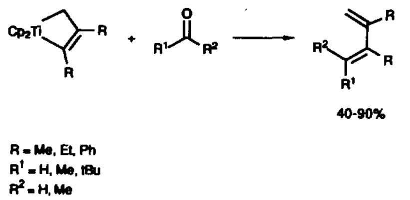
(Equation 296)



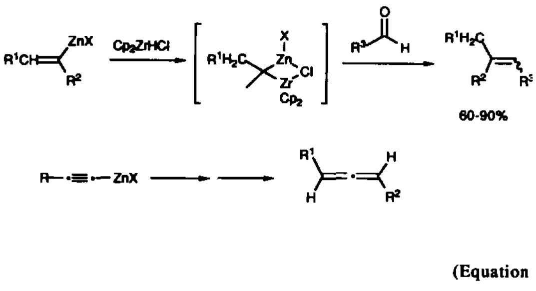
(Equation 297)



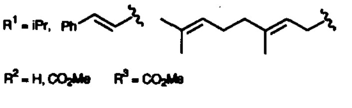
(Equation 298)



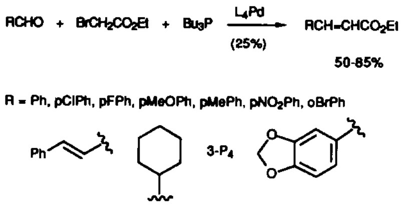
(Equation 299)



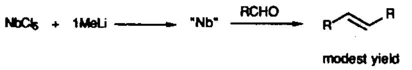
(Equation 300)



(Equation 301)

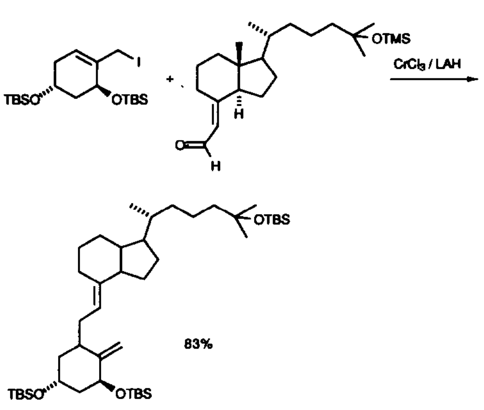


(Equation 302)

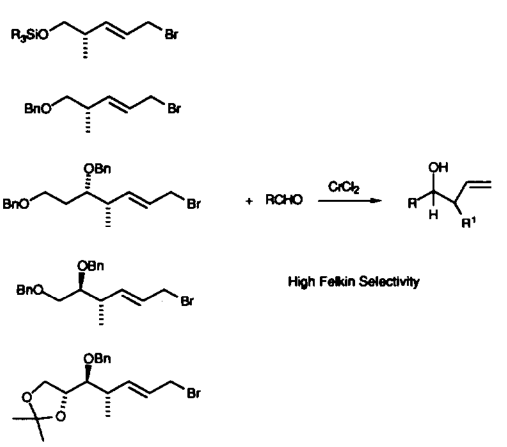


Chromous chloride reductively alkylated aldehydes with allylic halides (eqn. (303) [369]) with high Felkin selectivity (eqn. (304) [370]). Methyl chromium(III) species alkylated aldehydes and α or β oxo ketones but not simple ketones (eqn. (305) [371]). Ketones were alkylated by α haloesters or nitriles by electrochemical reduction at a zinc anode using a nickel(II) catalyst (eqn. (306) [372]). Vinyl tantalum complexes alkylated ketones (eqn. (307) [373]).

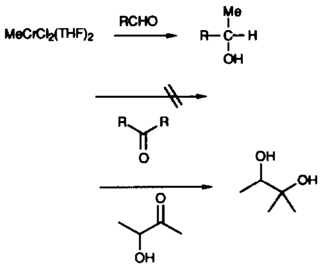
(Equation 303)



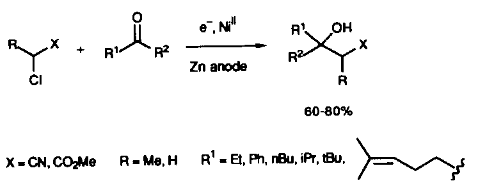
(Equation 304)



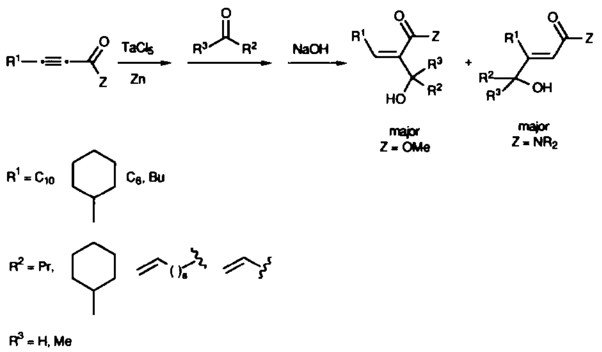
(Equation 305)



(Equation 306)

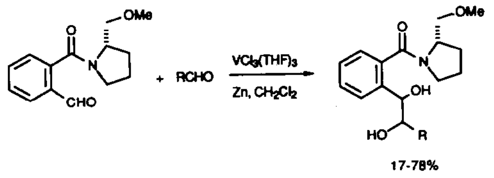


(Equation 307)

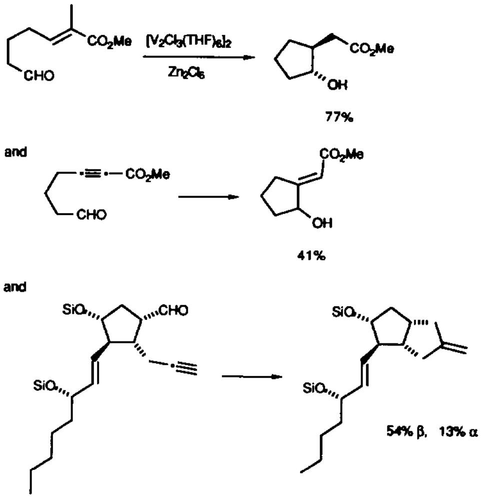


Reduced vanadium species cross coupled aldehydes (eqn. (308) [374]) and promoted the intramolecular alkylation of aldehydes by olefins (eqn. (309) [375]). Vanadium oxychlorides ring opened cyclobutanones and coupled them to olefins (eqn. (310) [376]).

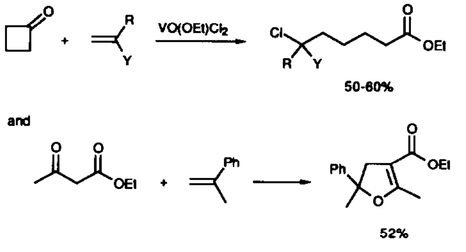
(Equation 308)



(Equation 309)

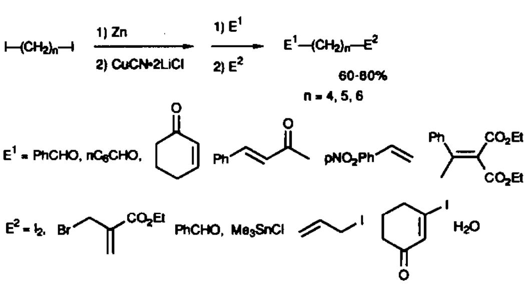


(Equation 310)

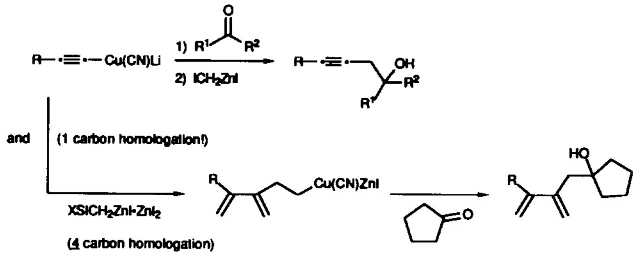


Functionalized organocopper species alkylated carbonyl compounds (eqn. (311) [377] and eqn. (312) [378]). Allyl copper complexes alkylated chiral imines with high diastereoselectivity (eqn. (313) [379]). Cyclopentadienyliron σ-allyl complexes alkylated aldehydes [380] and ketones (eqn. (314) [381]).

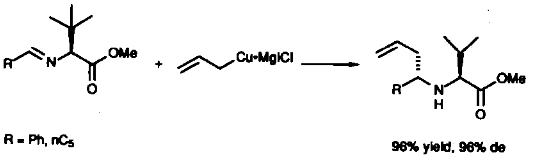
(Equation 311)



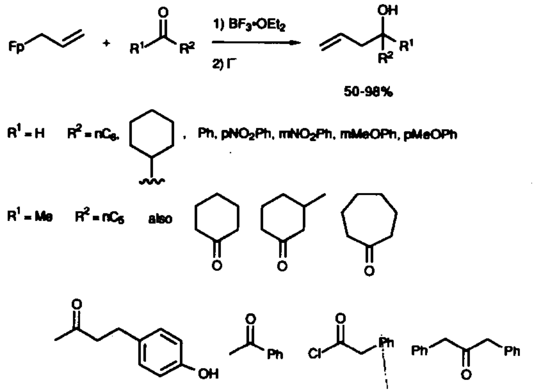
(Equation 312)



(Equation 313)

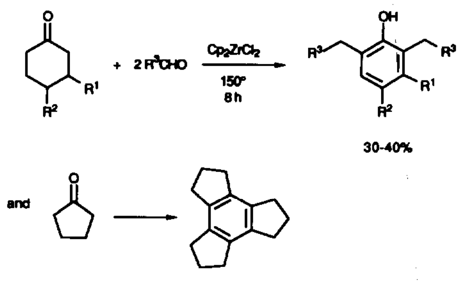


(Equation 314)

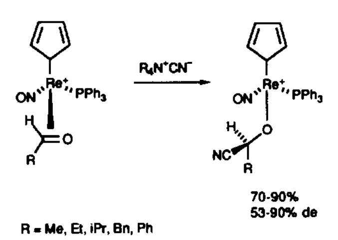


Chiral ferrocenylphosphine ligands in combination with gold(I), catalyzed the asymmetric aldol reaction [382]. Zirconocene dichloride did strange things to ketones and aldehydes (eqn. (315) [383]). Cyanide added to rhenium-complexed aldehydes with high diastereoselectivity (eqn. (316) [384]). Palladium catalyzed the alkylation of α-hydroxy ketones by allylic alcohols (eqn. (317) [385]).

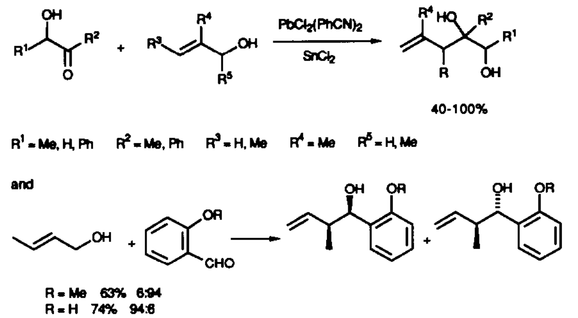
(Equation 315)



(Equation 316)



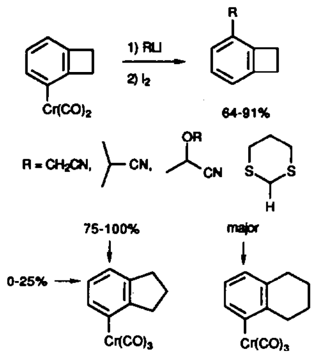
(Equation 317)



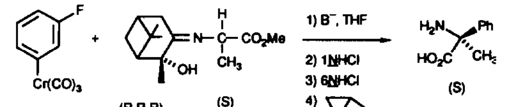
2.1.11. Alkylation of aromatic compounds

Reviews entitled *Tricarbonyl(η^6-arene)chromium Complexes in Organic Synthesis* (112 references) [386], *The study of catalyst effects on the complexation of arenes with chromium .hexacarbonyl. An overview* (15 references) [387] and *New methods of arene–carbon bond formation by aromatic nucleophilic substitution reactions* (84 references) [388] have appeared. Chromium-complexed benzocyclobutanes and benzocyclopentanes were alkylated by branched carbanions (eqn. (318) [389]). Optically active α-methyl phenyl glycine was synthesized by alkylation of chromium complexed fluorobenzene (eqn. (319) [390,391]). Complexed fluorotoluene was dialkylated by cyanocarbon carbanions (eqn. (320) [392]).

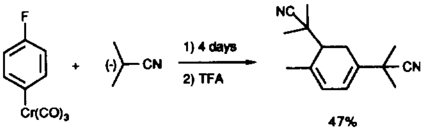
(Equation 318)



(Equation 319)

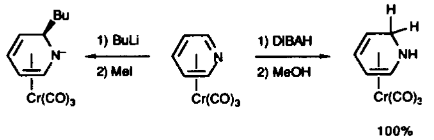


(Equation 320)

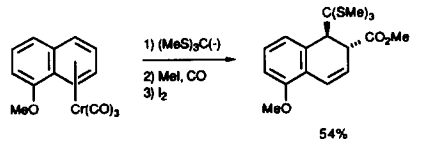


Chromium-complexed pyridine underwent nucleophilic attack (eqn. (321) [393]). Chromium complexed 1-methoxynaphthalene was alkylated/acylated (eqn. (322) [394]). Chromium complexed phenyl oxazolines or benzaldehyde imines underwent clean *ortho* alkylation (eqn. (323) [395]) as well as trialkylation (eqn. (324) [396]).

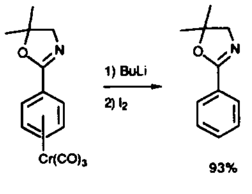
(Equation 321)



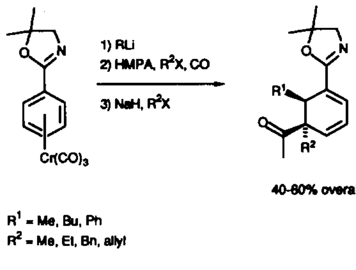
(Equation 322)



(Equation 323)

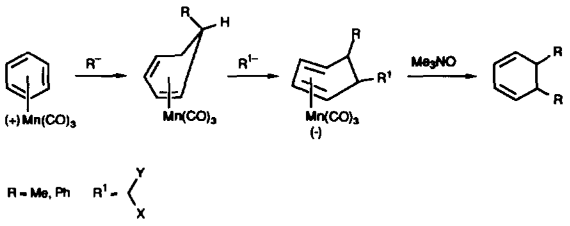


(Equation 324)

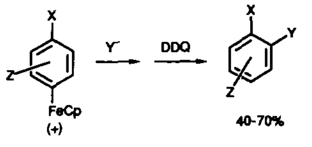


Cationic manganese arene complexes were dialkylated (eqn. (325) [397]). Dimethyldioxirane efficiently decomplexed chromium from chromium arene complexes [398]. The regio- and diastereoselective addition of nucleophiles to electron-rich (η^5-pentadienyl)iron complexes was the topic of a dissertation [399]. Cationic iron arene complexes were alkylated (eqn. (326) [400]).

(Equation 325)



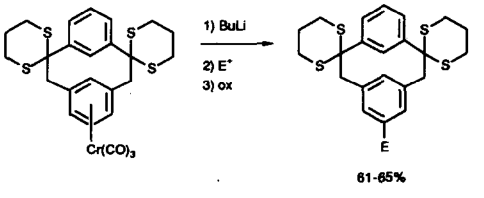
(Equation 326)



$X = NO_2$, Cl, pTs, tBu Z = H, 4Me, 4Cl $Y = {}^-CH_2NO_2$, $PhC\equiv C(-)$ $^-CH_2CN$, nBu, $^-CHCl_2$, $^-CCl_3$

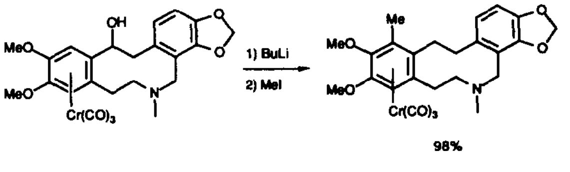
Chromium complexed arenes were cleanly lithiated and then functionalized with electrophiles (eqn. (327) [401], eqn. (328) [402], eqn. (329) [403], and eqn. (330) [404].

(Equation 327)

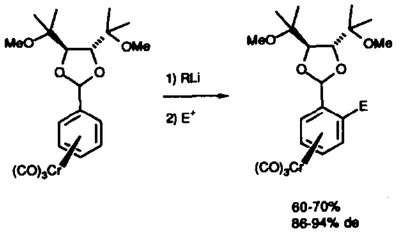


E = TMS, CO_2Et

(Equation 328)

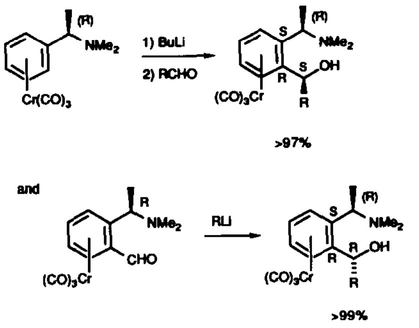


(Equation 329)



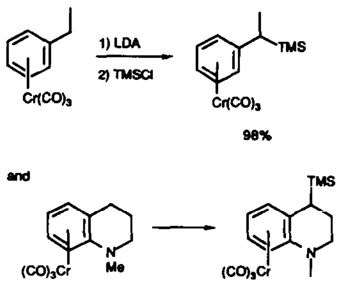
E = TMSCl, MeI, Bu_3SnCl, Ph_2PCl, Br^+

(Equation 330)

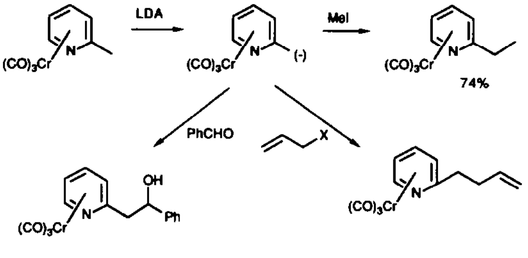


Complexation of arenes to chromium also activates benzylic positions. Synthetic applications of chromium tricarbonyl stabilized benzylic carbanions has been reviewed (66 references) [405]. Functionalization of benzylic positions by deprotonation/reaction with electrophiles is efficient and selective (eqn. (331) [406], eqn. (332) [407], eqn. (333) [408], and eqn. (334) [409]). This could be accomplished by anodic reduction of complexed methyl phenyl acetate [410]. Deprotonation of complexed allyl benzene followed by reaction with aldehydes gave thermodynamic products with sodium or potassium counter ions and kinetic products with lithium counter ions (eqn. (335) [411]).

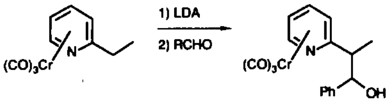
(Equation 331)



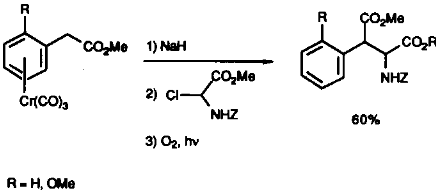
(Equation 332)



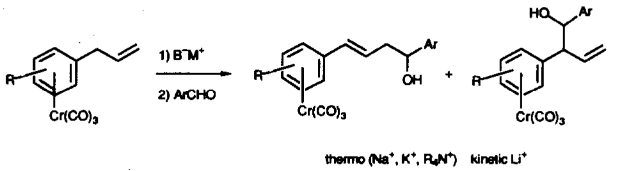
(Equation 333)



(Equation 334)

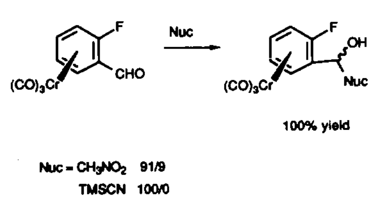


(Equation 335)

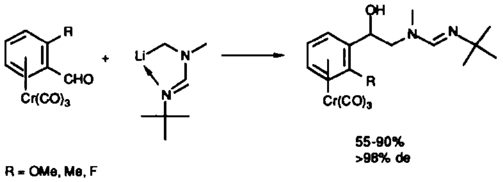


Chromium complexed aldehydes underwent nucleophilic attack with a high degree of stereoselectivity (eqn. (336) [412], eqn. (337) [413], and eqn. (338) [414]. Chromium complexed benzocyclobutanones underwent unusual reaction chemistry (eqn. (339) [415], eqn. (340) [416], and eqn. (341) [417]).

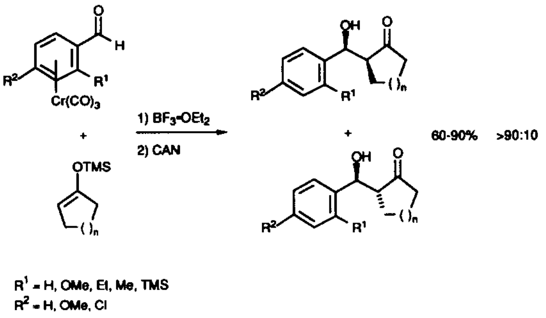
(Equation 336)



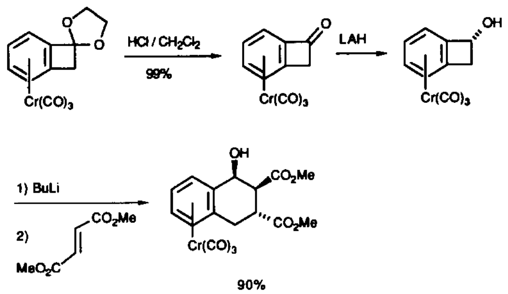
(Equation 337)



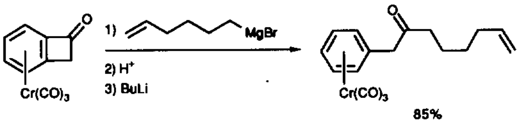
(Equation 338)



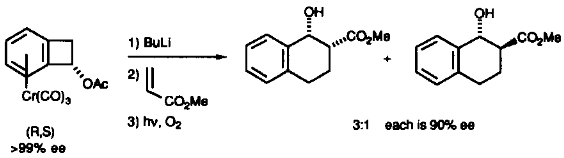
(Equation 339)



(Equation 340)

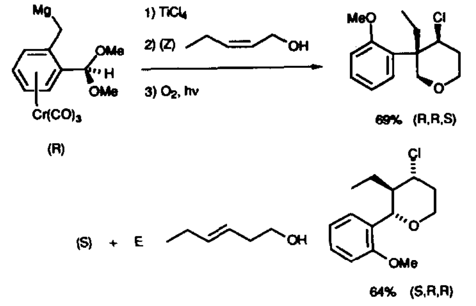


(Equation 341)

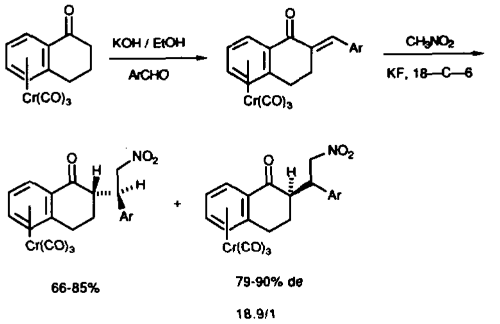


Other reactions of complexed arenes, remote from the arene group, are shown in eqn. (342) [418,419], eqn. (343) [420], and eqn. (344) [421]. Arenechromium chemistry has been used extensively in the synthesis of complex natural products (eqn. (345) [422,423] and eqn. (346) [424]).

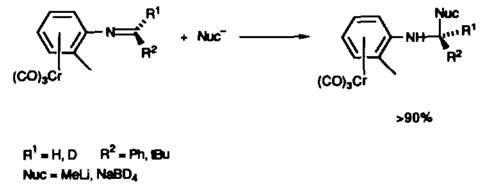
(Equation 342)



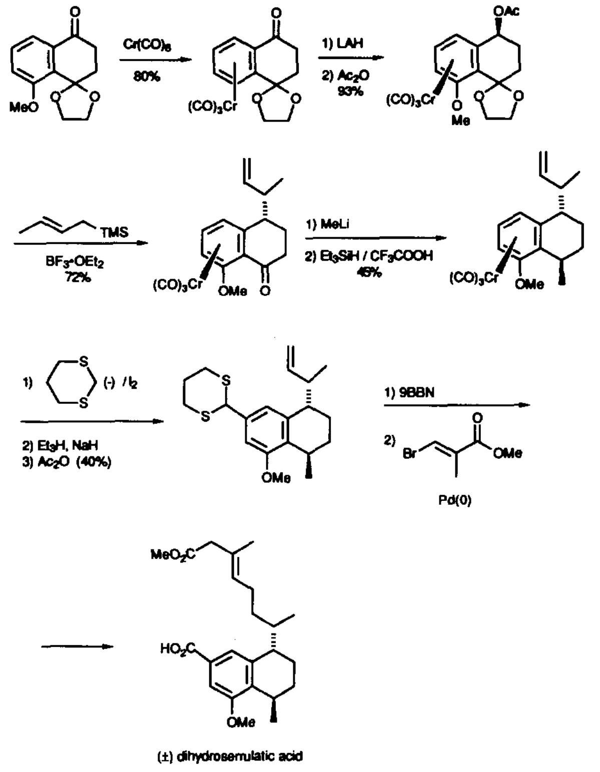
(Equation 343)



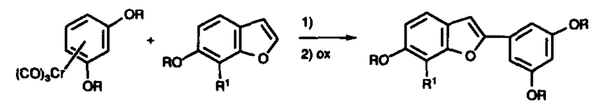
(Equation 344)



(Equation 345)

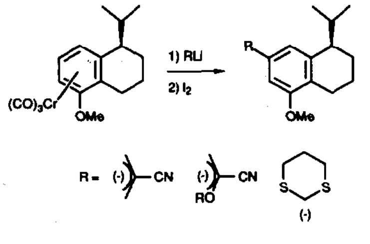


(Equation 346)

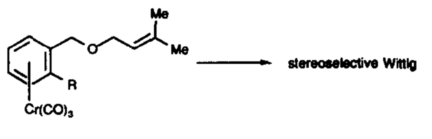


Chromium complexed arenes underwent direct alkylation (eqn. (237) [425]), and Wittig rearrangement (eqn. (348) [426]). The methyl benzoate chromium tricarbonyl complex catalyzed the 1,4 hydrogenation of exocyclic dienes (eqn. (349) [427] and eqn. (350) [428]). The arene chromium tricarbonyl fragment was used as a chiral auxilliary in the synthesis of β-lactams (eqn. (351) [429]).

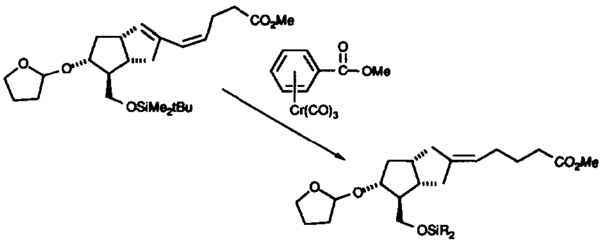
(Equation 347)



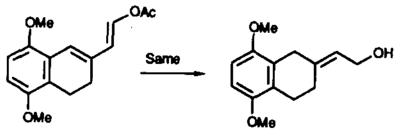
(Equation 348)



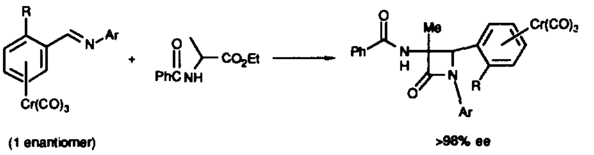
(Equation 349)



(Equation 350)

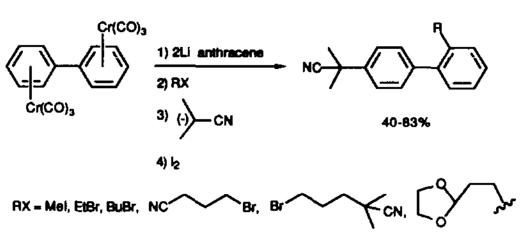


(Equation 351)

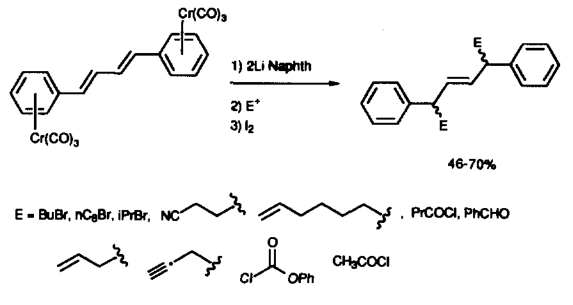


Biphenyl (eqn. (352) [430]) and 1,4-diphenylbutadiene (bis) chromium arene complexes (eqn. (353) [431]) were reduced then alkylated.

(Equation 352)



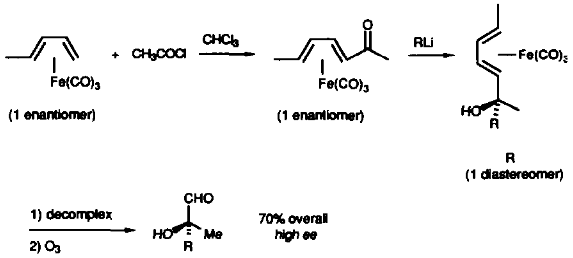
(Equation 353)



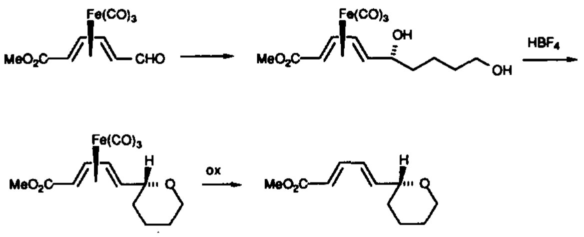
2.1.12. *Alkylation of dienyl and diene complexes*

A review entitled *Transition Metal Diene Complexes in Organic Synthesis. Part 5. Application of Iron-Diene Complexes to Natural Product Synthesis* has appeared [432]. Complexation to iron carbonyl has been extensively used to protect diene portions of unsaturated carbonyl compounds during chemical reactions of the carbonyl group (eqn. (354) [433], eqn. (355) [434], eqn. (356) [435], eqn. (357) [436], eqn. (358) [437], eqn. (359) [438], eqn. (360) [439], eqn. (361) [440], and eqn. (362) [441]).

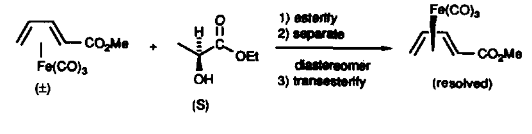
(Equation 354)



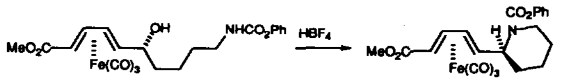
(Equation 355)



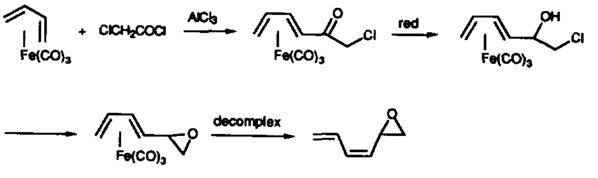
(Equation 356)



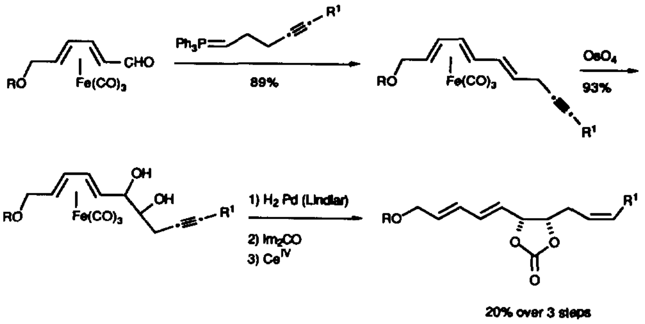
(Equation 357)



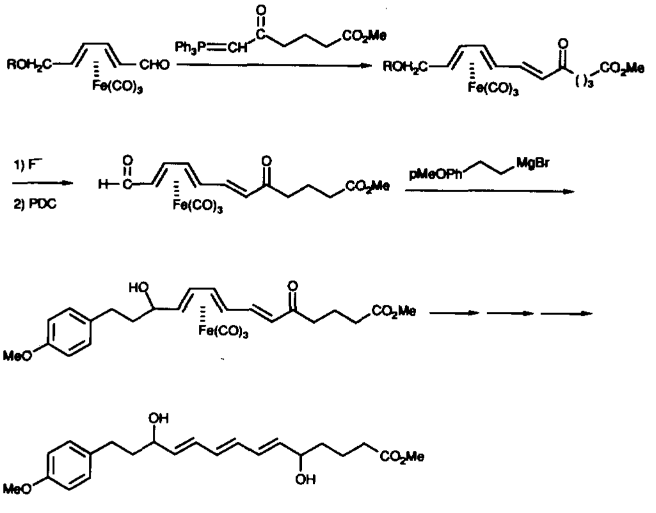
(Equation 358)



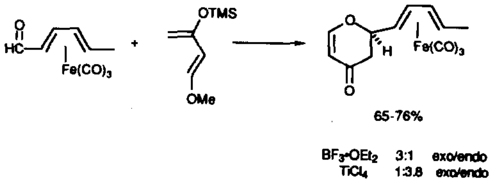
(Equation 359)



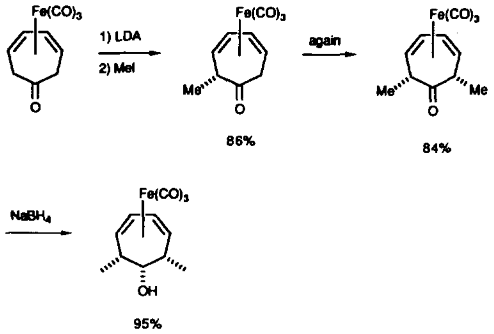
(Equation 360)



(Equation 361)

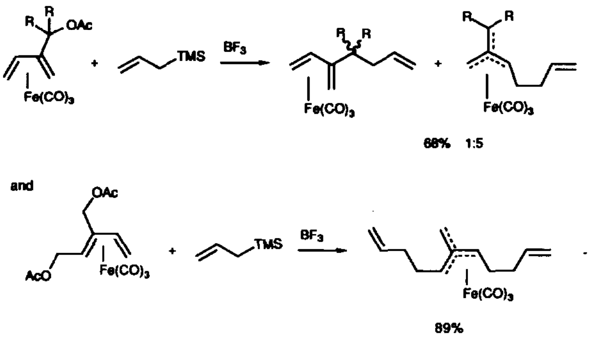


(Equation 362)

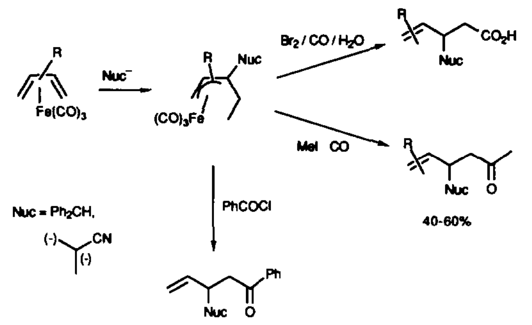


Allylsilanes underwent reaction with appropriate diene complexes to give trimethylene methanes (eqn. (363) [442,443]). Diene iron complexes also underwent nucleophilic attack, generating η^3-allyl complexes, which were further functionalized (eqn. (364) [444,445]).

(Equation 363)

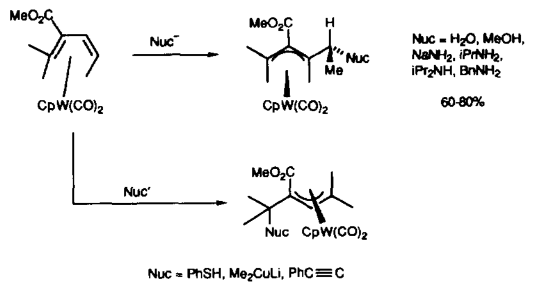


(Equation 364)

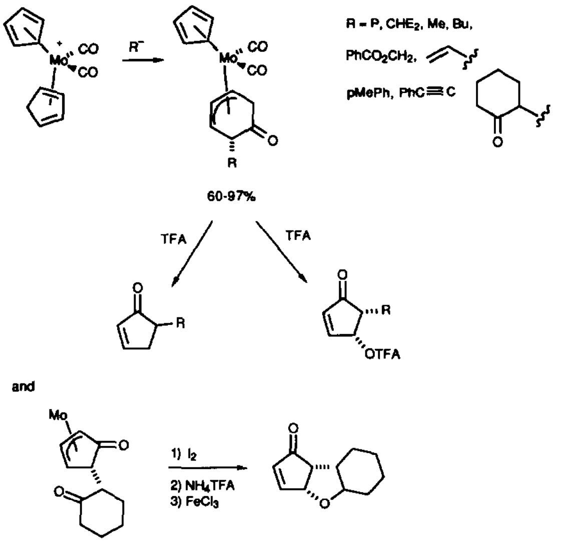


Tungstem diene (eqn. (365) [446]) and molybdenum dienone complexes (eqn. (366) [447]) also underwent nucleophilic attack.

(Equation 365)

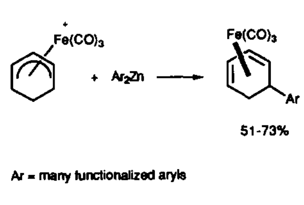


(Equation 366)

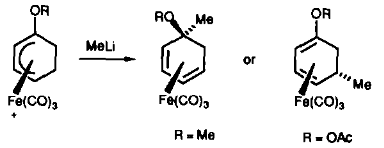


Reactions of nucleophiles with cationic dienyl complexes have been much more extensively studied. Cyclohexadienyliron complexes were alkylated by diarylzinc reagents (eqn. (367) [448]), methyllithium (eqn. (368) [449]) as well as more complex anions (eqn. (369) [450]). This chemistry has been used in the synthesis of isoquinuclidines (eqn. (370) [451]), indole alkaloids (eqn. (371) [452]) and isoquinoline alkaloids (eqn. (372) [453]). Alkylcadmium (eqn. (373) [454]) and functionalized organocopper species (eqn. (374) [455]) also alkylated dienyl complexes.

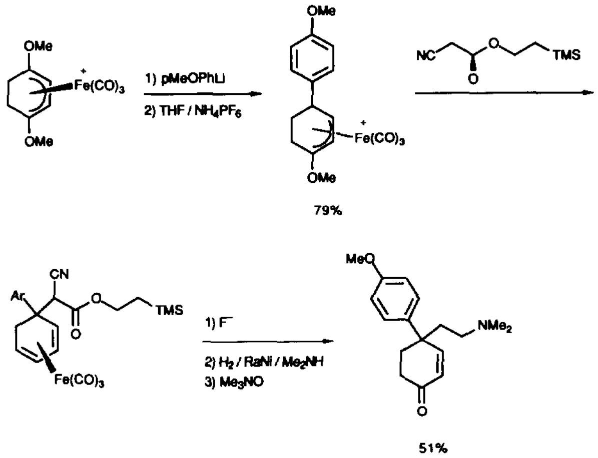
(Equation 367)



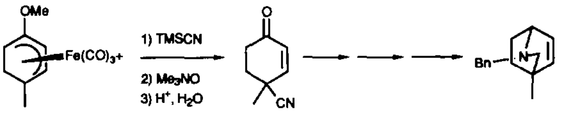
(Equation 368)



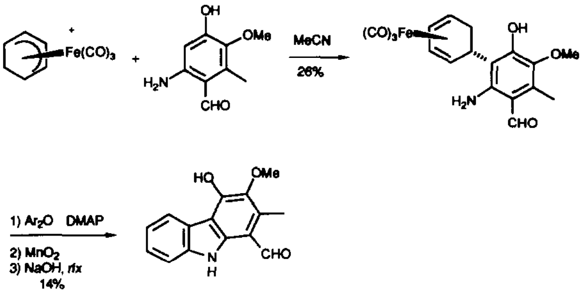
(Equation 369)



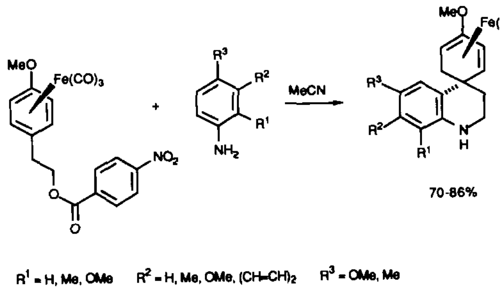
(Equation 370)



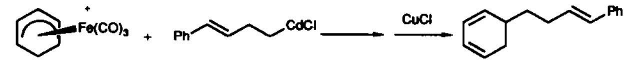
(Equation 371)



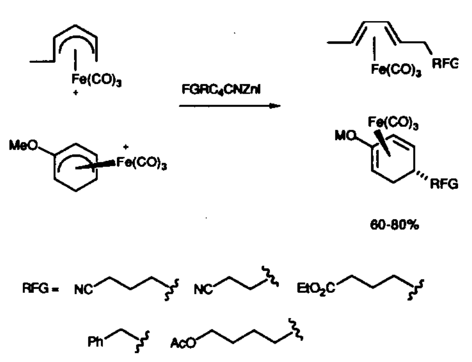
(Equation 372)



(Equation 373)

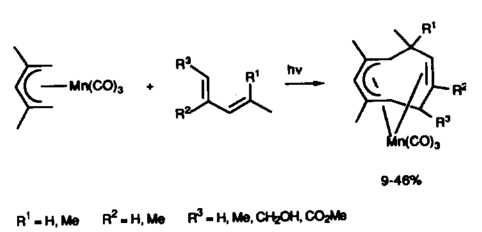


(Equation 374)



A dissertation dealing with nucleophilic attack on η^5-dienylmanganese tricarbonyl complexes has appeared [456]. Manganese dienyl complexes underwent photochemical cycloaddition with dienes in low yield (eqn. (375) [457]).

(Equation 375)



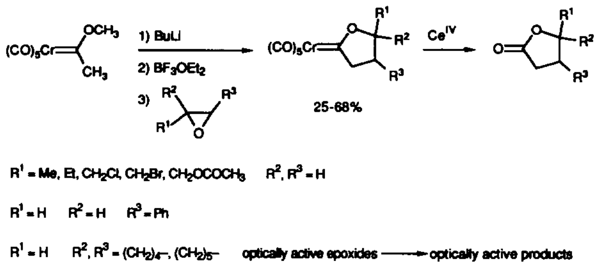
2.1.13. *Metal / carbene reactions*

Metal carbene complex chemistry remained an active area for research, and a large number of reviews and dissertations on the subject appeared this year. A list follows:

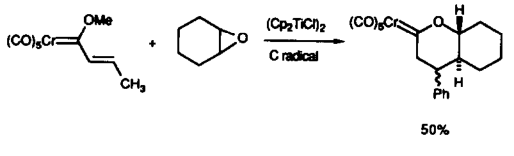
Benzannulation Reactions Employing Fischeri Carbene Complexes [458];
Development of Carbene Complexes of Iron as New Reagents for Synthetic Organic Chemistry [459];
Metallacycle and Metallacycle-Carbene Complexes: Synthesis, Structure, Relativity and Mechanistic Studies [460];
Carbene Complexes of Chromium Bearing Nitrogen Substituents [461];
Application of Fischer-type Metal Carbene Complexes to Organic Synthesis [462];
Mechanistic Studies of Enantioselective Carbene Transfer Reactions of the Chiral-at-Iron Carbene Complexes [463];
Studies in the Synthesis of Metal-Nitrenoids and the Pericyclic Reactions of Cyclopropylcarbene Chromium Complexes [464];
Synthetic and Mechanistic Studies of Reactions of Organometallic Carbene Complexes with Enynes [465];
Organometallic Chemistry of Vinylidene and Related Unsaturated Carbenes [466];
Chromium Aminocarbene Complexes in Organic Synthesis [467];
Cyclization Reactions Involving Carbene Complexes in the Inner Sphere of Transition Metals [468];
Cyclization Reactions Occurring in the Inner Coordination Sphere of Transition Metals with the Participation of Carbene Complexes [469].

Several procedures for elaborating chromium carbene complexes have been developed (eqn. (376) [470,471], eqn. (377) [472], and eqn. (378) [473]).

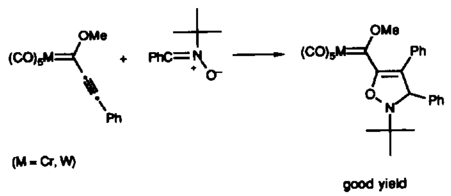
(Equation 376)



(Equation 377)

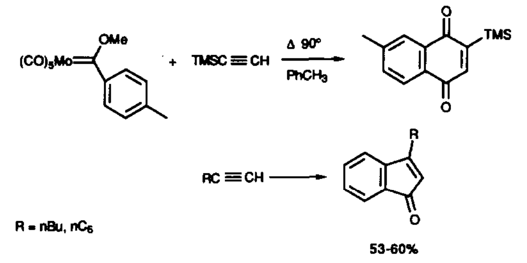


(Equation 378)

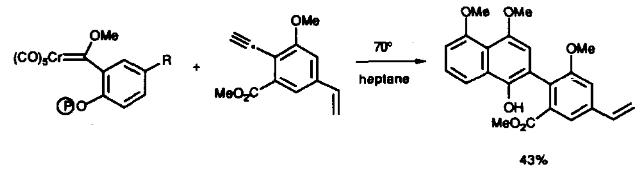


The thermal benzannulation (Dötz) reaction continues to be utilized to synthesize naphthoquinones and related derivatives (eqn. (379) [474], eqn. (380) [475], eqn. (381) [476], and eqn. (382) [477]). A full paper on the response of this reaction to variations in substrate structures has appeared (eqn. (383) [478]).

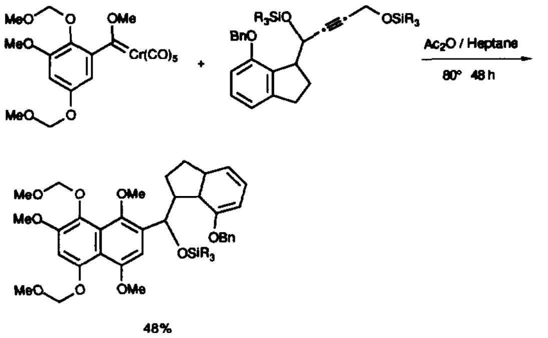
(Equation 379)



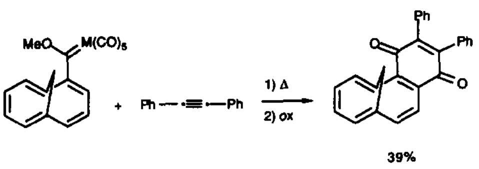
(Equation 380)



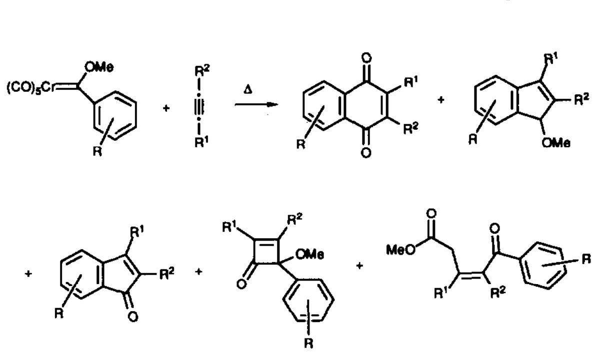
(Equation 381)



(Equation 382)

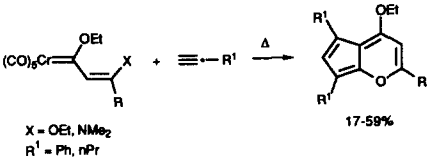


(Equation 383)

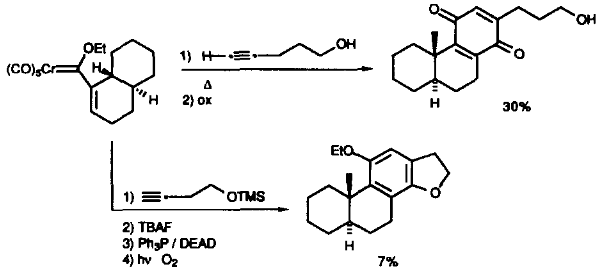


Other less straightforward uses are shown in eqn. (384) [479], eqn. (385) [480], eqn. (386) [481], eqn. (387) [482], and eqn. (388) [483].

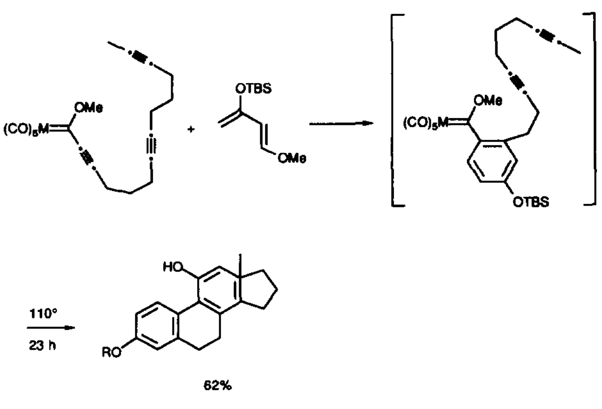
(Equation 384)



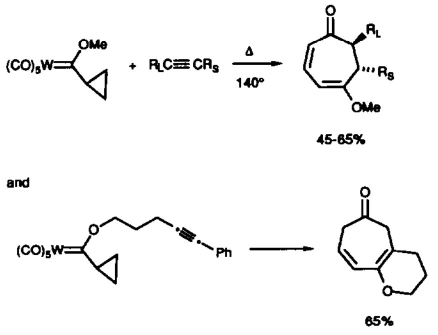
(Equation 385)



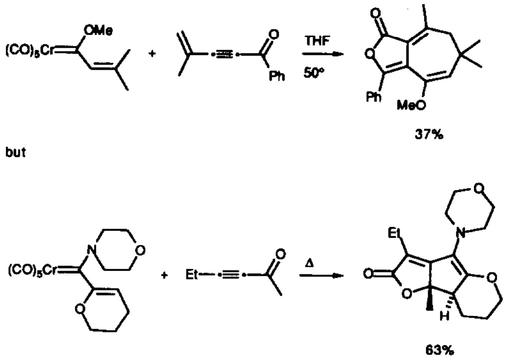
(Equation 386)



(Equation 387)

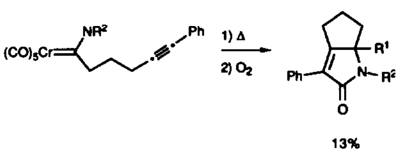


(Equation 388)

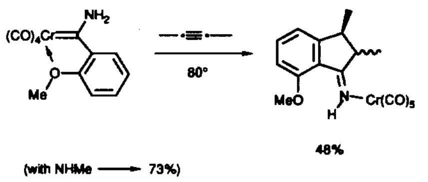


Aminocarbene complexes give five- rather than six-membered rings (eqn. (389) [484], eqn. (390) [485], and eqn. (391) [486]).

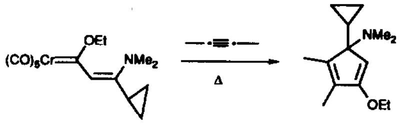
(Equation 389)



(Equation 390)

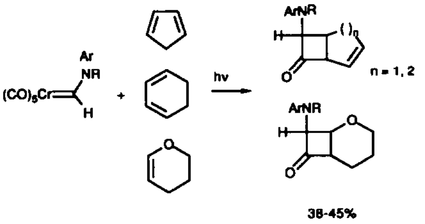


(Equation 391)

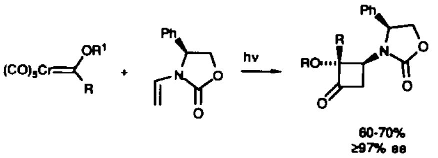


Photochemical reactions of chromium carbene complexes generate ketene-like species. This has been used to synthesize cyclobutenones (eqn. (392) [487]) and (eqn. (393) [488]), to compare the stereoselectivity of free ketenes (generated from acid chlorides) to photogenerated ketenes (from carbene complexes) in their reactions with imines to produce β-lactams [489], and to generate and intramolecularly trap vinylketenes to give a photo (Hege–Dötz) reaction (eqn. (394) [490]).

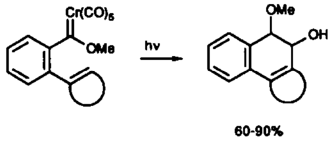
(Equation 392)



(Equation 393)

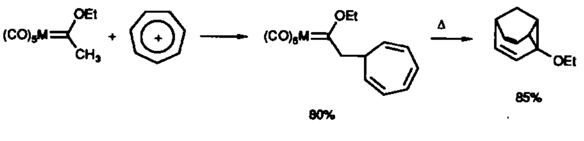


(Equation 394)

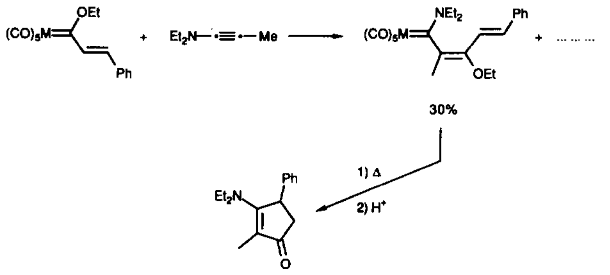


Carbene complexes reacted with tropylium ions to give elaborated carbenes, which annulated intramolecularly (eqn. (395) [491]). Ynamines inserted into alkoxycarbene complexes to give complex mixtures of which also underwent intramolecular homologation (eqn. (396) [492]). Alkoxy carbene complexes combined sequentially with allenes, then alkynes to give methylenecyclopentenes (eqn. (397) [493]). Polyunsaturated carbene complexes cyclized when heated (eqn. (398) [494]).

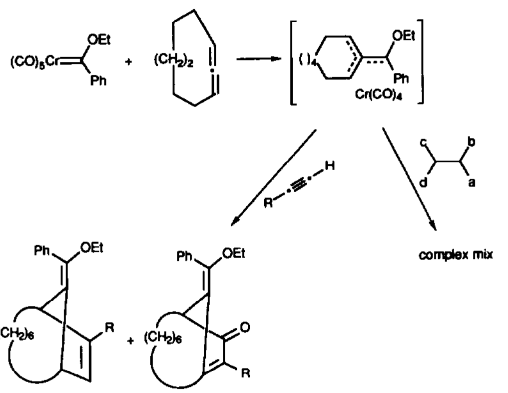
(Equation 395)



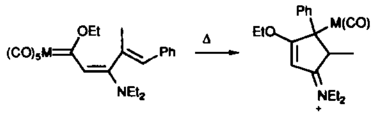
(Equation 396)



(Equation 397)

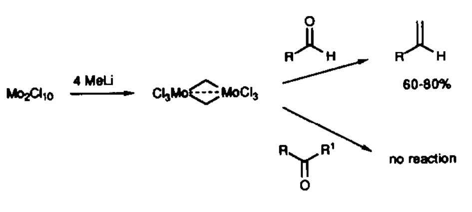


(Equation 398)

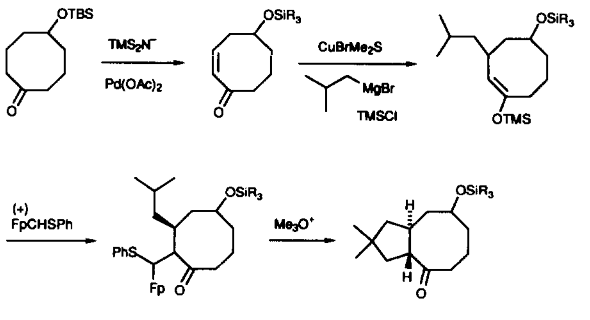


Bridging methylene molybdenum complexes methylenated aldehydes but not ketones (eqn. (399) [495]). Iron carbene complexes inserted at C–H bonds (eqn. (400) [496]).

(Equation 399)



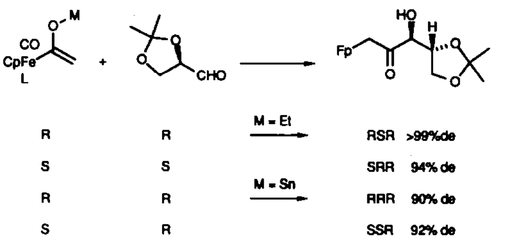
(Equation 400)



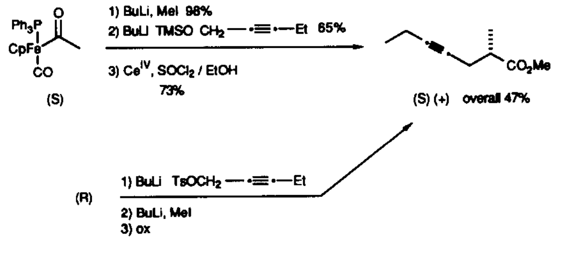
2.1.14. *Alkylation of metal acyl enolates*

The results of the two papers on this topic are present in eqn. (401) [497] and eqn. (402) [498].

(Equation 401)



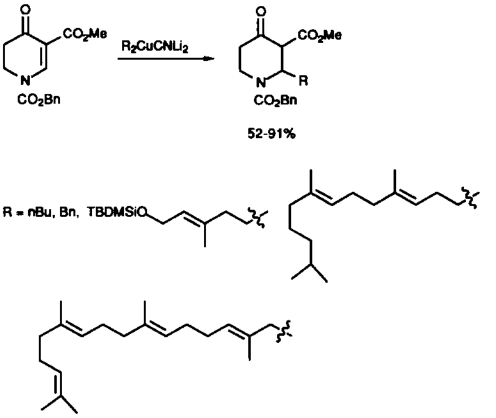
(Equation 402)



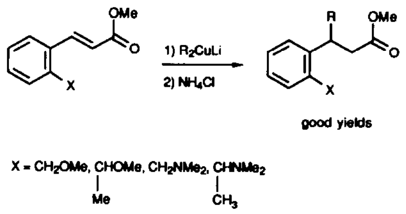
2.2. *Conjugate addition*

Low temperature NMR studies of the addition of $(R_3Si)_3CuLi_2$ and $(Me_3Sn)_3CuLi_2$ to cyclohexenone gave evidence of π-complexation [499]. Functionalized enones were cleanly 1,4-alkylated by organocuprates (eqn. (403) [500] and eqn. (404) [501]). Functionalized organocuprates also efficiently 1,4-alkylated conjugated enones (eqn. (405) [502] and eqn. (406) [503]). This chemistry was used in the synthesis of prostaglandins (eqn. (407) [504] and eqn. (408) [505]).

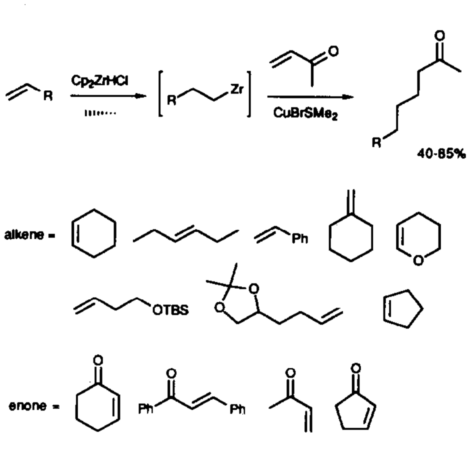
(Equation 403)



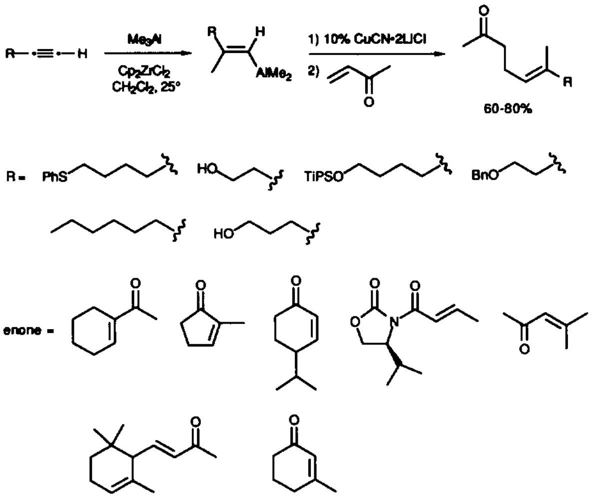
(Equation 404)



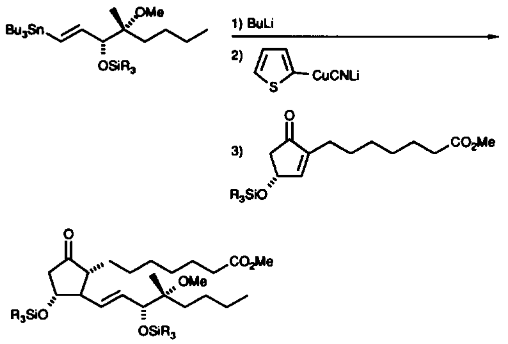
(Equation 405)



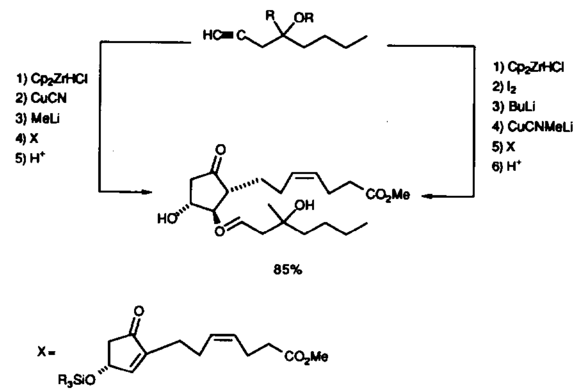
(Equation 406)



(Equation 407)

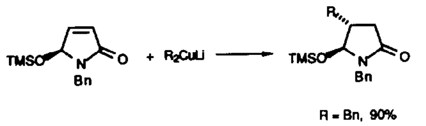


(Equation 408)

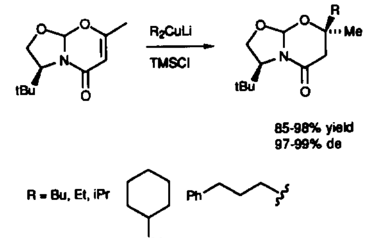


Asymmetric conjugate addition was very popular this year, with several different approaches being successful. The most popular was conjugate addition to chiral substrates (eqn. (409) [506], eqn. (410) [507], eqn. (411) [508], eqn. (412) [509], eqn. (413) [510], eqn. (414) [511,512], and eqn. (415) [513]).

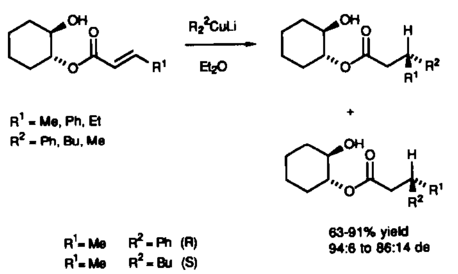
(Equation 409)



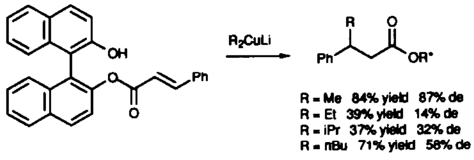
(Equation 410)



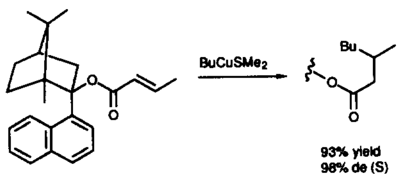
(Equation 411)



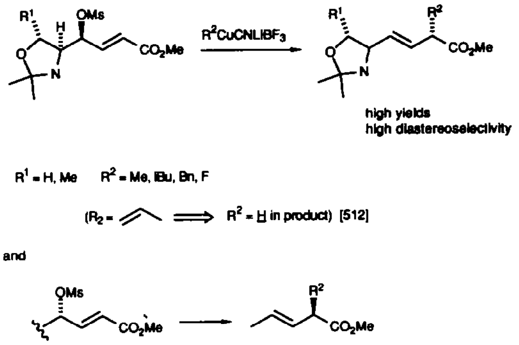
(Equation 412)



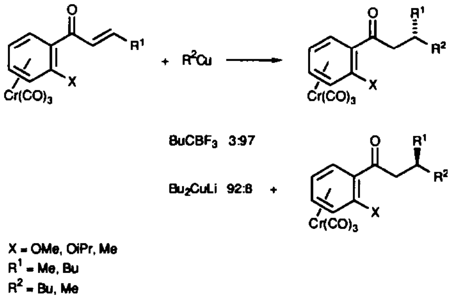
(Equation 413)



(Equation 414)

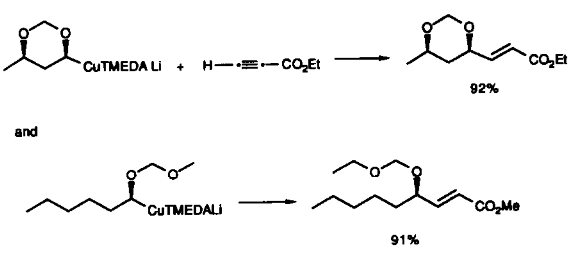


(Equation 415)

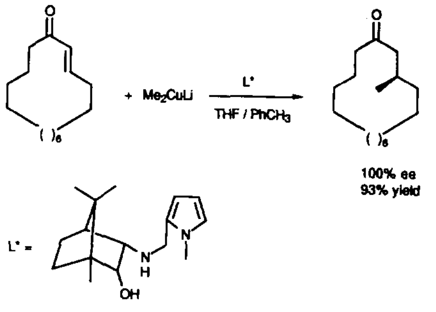


Optically active copper species added to ynones (eqn. (416) [514]). The use of optically active ligands was also efficient. The synthesis of R(−) muscone in this way (eqn. (417) was the subject of three papers this year [515–517]) and at least one last year, all by the same group with the same ligand and substrate! Other systems are seen in eqn. (418) [518], eqn. (419) [519], and eqn. (420) [520].

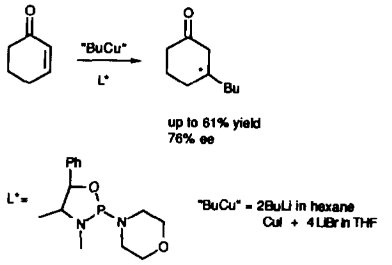
(Equation 416)



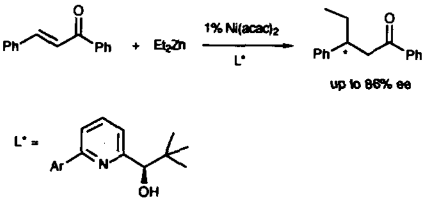
(Equation 417)



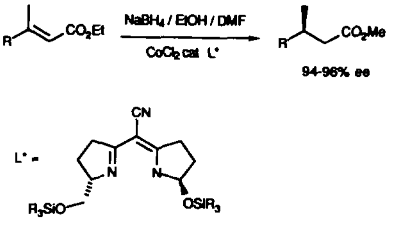
(Equation 418)



(Equation 419)

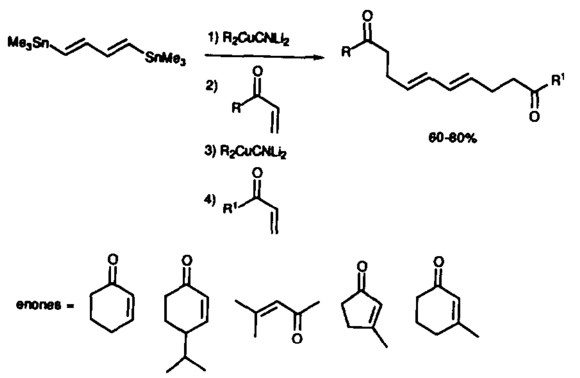


(Equation 420)

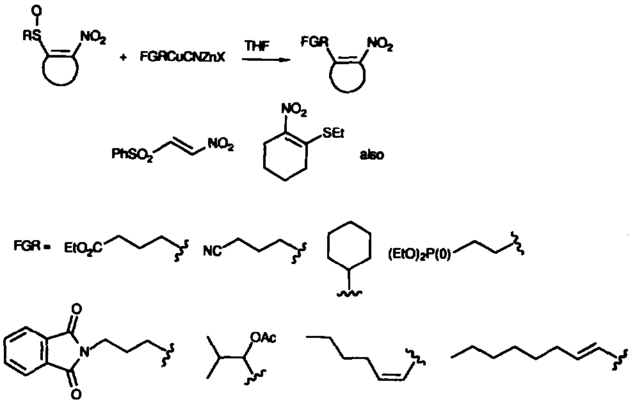


More complex conjugate additions are also possible (eqn. (421) [521] and eqn. (422) [522]). The enolate resulting from conjugate addition could be trapped as the silylenol ether by treatment with TMS chloride in the presence of lithium iodide (eqn. (423) [523]). Cuprates added 1,6 to ynenones (eqn. (424) [524]). Rhodium(I) complexes catalyzed the 1,4-addition of ω-enones to α,β-unsaturated ketones (eqn. (425) [525]). 1,4-Additions to enones was effected by nickel π-allyl species in a somewhat convoluted but useful manner (eqn. (426) [526]). Palladium(0) catlayzed the conjugate addition of iodopyrimidines to α,βunsaturated ketones [527]. Allyl manganese compounds added diastereospecifically to α,β-unsaturated esters [528].

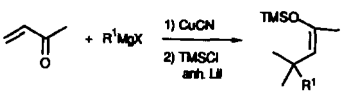
(Equation 421)



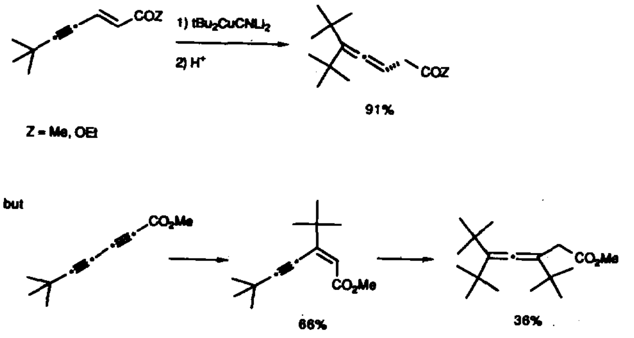
(Equation 422)



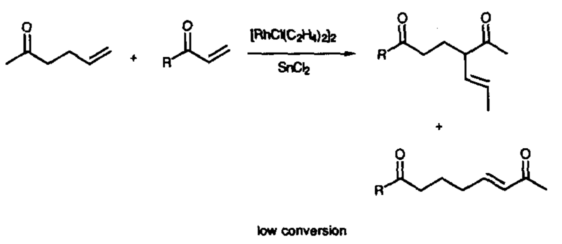
(Equation 423)



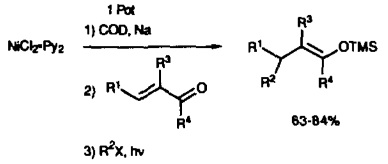
(Equation 424)



(Equation 425)



(Equation 426)



2.3. *Acylation reactions (excluding hydroformylation)*

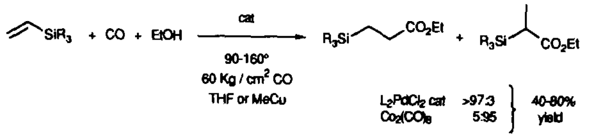
The following general reviews and dissertations dealing with acylation/carboxylation chemistry have been published:

Carbon Monoxide Activation by Homogeneous Catalysts	[529];
Carbonylation. Direct Synthesis of Carbonyl Compounds	[530];
Advances in Catalytic Carbonylation with Transition Metal Complexes in Homogeneous Phase	[531];
Asymmetric Hydroformylation in the Synthesis of Pharmaceuticals	[532];
Chelation-Controlled Carbonylations Catalyzed by Group VIII Transition Metal Complexes	[533];
Carbonylation of Formaldehyde and Its Derivatives	[534];
Cyclocarbonylation Catalyzed by Palladium Complexes	[535];
CIR-FTIR Studies of Palladium-Catalyzed Carboalkoxylation Reactions	[536];
Mechanisms of Double and Single Carbonylation Reactions Catalyzed by Palladium Complexes	[537];
Total Synthesis of (±) Jatrophone and Its Epimer via a Key Palladium-Catalyzed Carbonylative Coupling	[538].

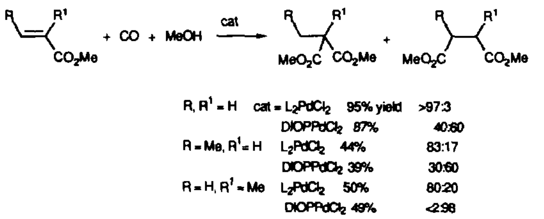
2.3.1. *Carbonylation of alkenes and arenes*

The effect of temperature and pressure on the palladium catalyzed carbonylation of 1,5-cyclooctadiene was examined [539]. Asymmetric hydroformylation of styrenes using chiral phosphine/platinum/tin complex catalysts (4:1 branched to normal ≈ 100% ee) [540] and of acylamino acrylates by rhodium/DIPO catalysts (≈ 60% ee) [591] has been developed. Monoterpenes were selectively hydroformylated using rhodium/phosphine catalysts [542]. *para*-substituted 2-phenylpropenes were asymmetrically hydroformylated by palladium/DIOP systems [543]. The regioselectivity of the hydrocarboxylation of vinyl silanes strongly depended on the catalyst (eqn. (427) [544]), as did the regioselectivity for hydroesterification of acrylic acid esters (eqn. (428) [545]). Cobalt carbonyl catalyzed the hydrocarboxylations of unsaturated cyclic amines (eqn. (429) [546]). Palladium acetate catalyzed the carbonylative polymerization of ethene (eqn. (430) [547]).

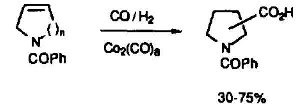
(Equation 427)



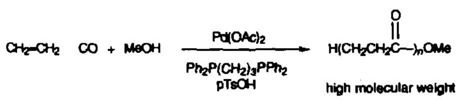
(Equation 428)



(Equation 429)

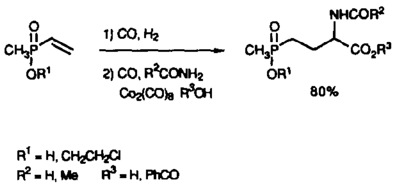


(Equation 430)

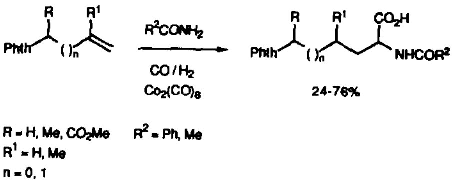


Olefins were efficiently amidocarbonylated using cobalt carbonyl catalysts (eqn. (431) [548], eqn. (432) [549], and eqn. (433) [550]).

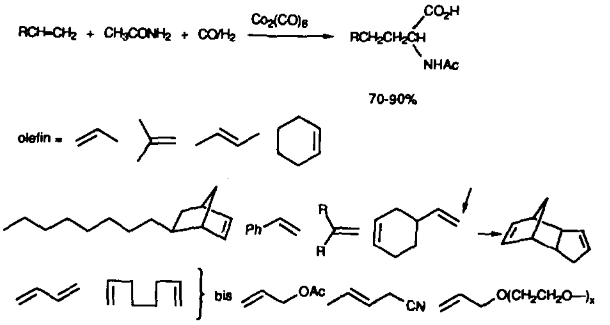
(Equation 431)



(Equation 432)

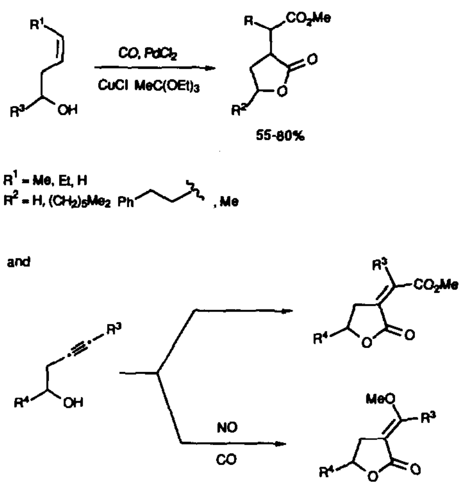


(Equation 433)

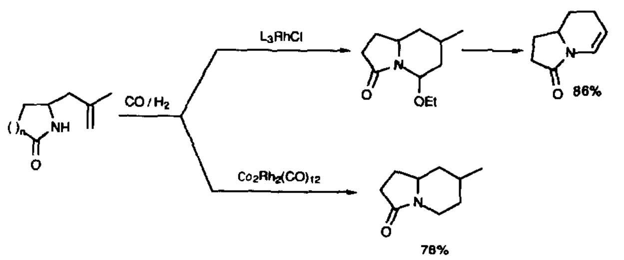


Hydroxyalkenes (eqn. (434) [551]) and aminoalkenes (eqn. (435) [552], eqn. (436) [553], and eqn. (437) [554]) were intramolecularly acylated.

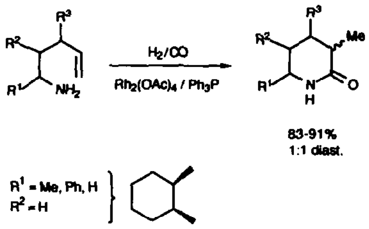
(Equation 434)



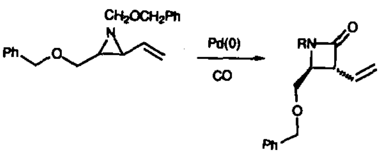
(Equation 435)



(Equation 436)

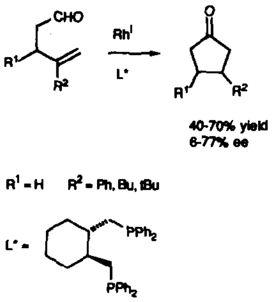


(Equation 437)

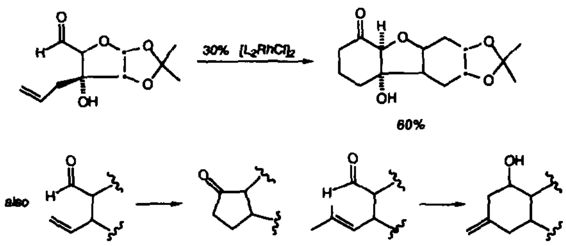


Rhodium(I) complexes catalyzed the intramolecular addition of aldehydes to alkenes (eqn. (438) [555] and eqn. (439) [556]). Other acylations of olefins are seen in eqn. (440) [557], eqn. (441) [558], and eqn. (442) [559].

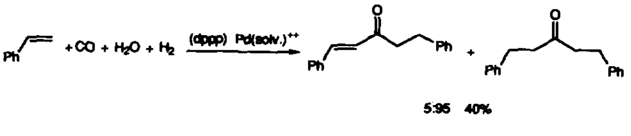
(Equation 438)



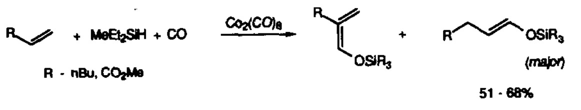
(Equation 439)



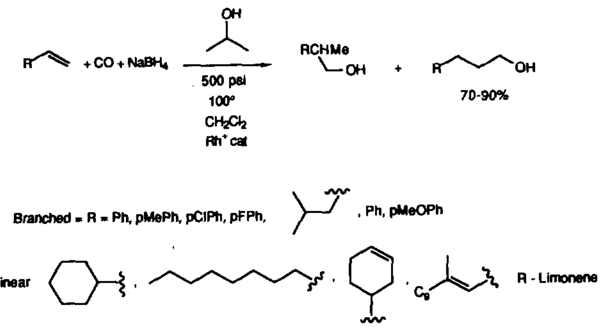
(Equation 440)



(Equation 441)



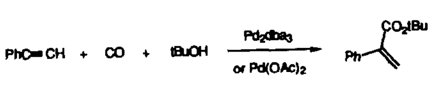
(Equation 442)



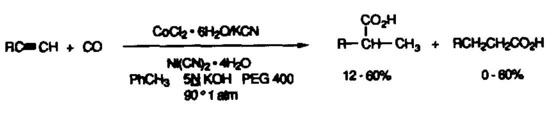
2.3.2. *Carbonylation of alkynes (including the Pauson–Khand reaction)*

Ruthenium-Catalyzed Additions to Alkynes: Synthesis of Activated Esters and Their Use in Acylation Reactions was the subject of a review (57 references) [560]. Palladium catalyzed the acylation of alkynes to branched t-butyl esters (eqn. (443) [561]). Mixed cobalt/nickel catalysts gave reductive carbonylation products (eqn. (444) [562]). Cyclic propargyl alcohols and alkynes lacking propargylic hydrogens underwent double carbonylation (eqn. (445) [563]). Allenes were acylated by manganese carbonyl/methyl iodide (eqn. (446) [564]). Alkynes were cyclo dicarbonylated to butenolides by rhodium catalysts (eqn. (447) [565]). The same complex catalyzed the cross hydrocarbonylation of 1-alkynes with ethene (eqn. (448) [566]).

(Equation 443)

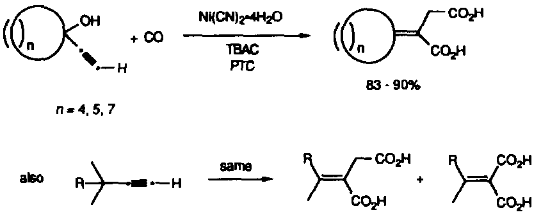


(Equation 444)

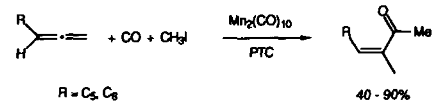


R = Ph, pMePh, piBuPh, pPhCOPh, pMeOPh

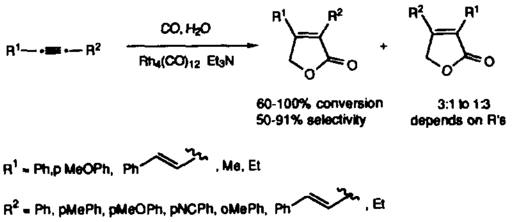
(Equation 445)



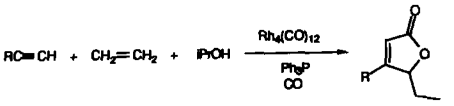
(Equation 446)



(Equation 447)

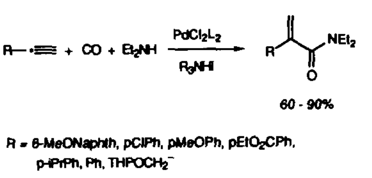


(Equation 448)

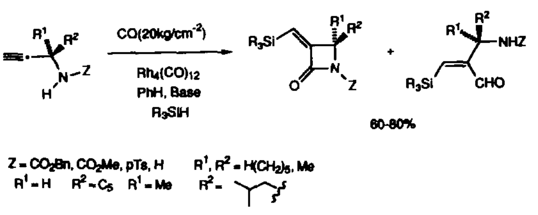


Palladium catalyzed the inter- (eqn. (449) [567]) and intramolecular (eqn. (450) [568]) aminocarbonylation of alkynes. Cobalt carbonyl converted phenylacetylenes to indanones (eqn. (451) [569]). Iron pentacarbonyl cyclized diynes to cyclopentadienones and enynes to cyclopentenones (eqn. (452) [570]). Zirconocene effected a similar transformation stepwise (eqn. (453) [571]).

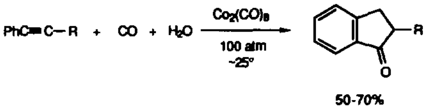
(Equation 449)



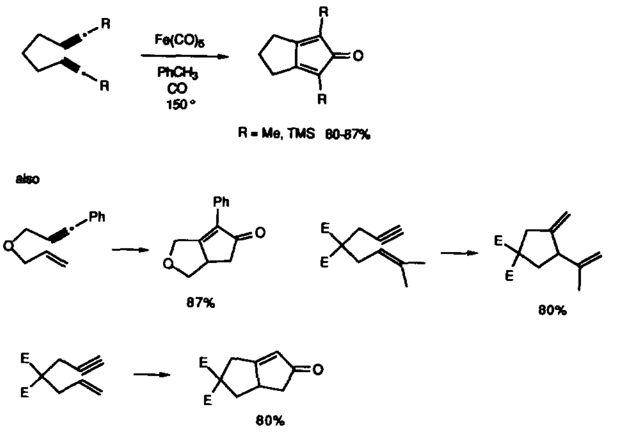
(Equation 450)



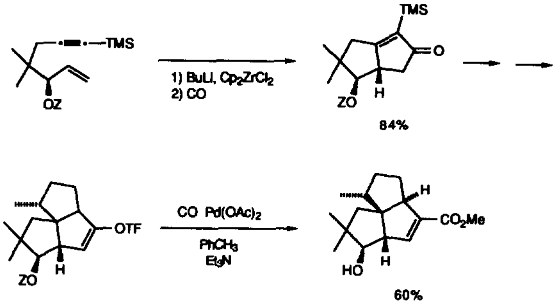
(Equation 451)



(Equation 452)

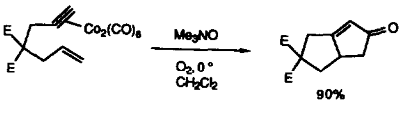


(Equation 453)

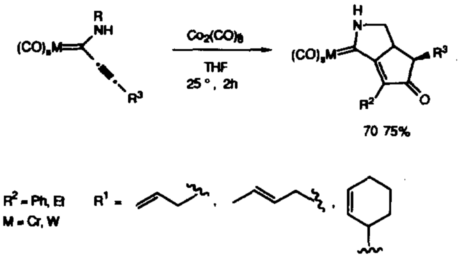


The Pauson–Khand cycloaddition reactions for synthesis of cyclopentenones has been reviewed (79 references) [572]. Trimethyl amine oxide dramatically accelerated this process (eqn. (454) [573]) as did the use of alkynyl chromium carbene complexes (eqn. (455) [574]). The regiochemistry of the Pauson–Khand reaction could be ligand controlled, with the homoallylic position being most effective (eqn. (456) [575]). The reaction has found extensive use in synthesis (eqn. (457) [576], eqn. (458) [577], eqn. (459) [578], eqn. (460) [579], and eqn. (461) [580]).

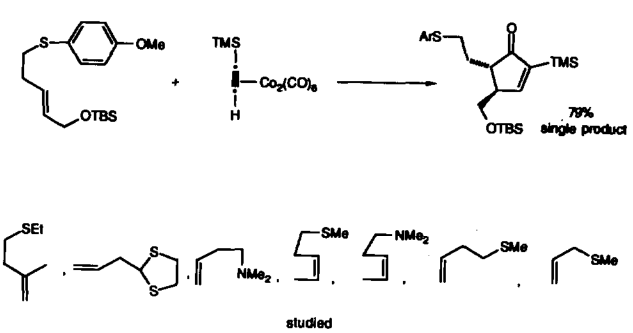
(Equation 454)



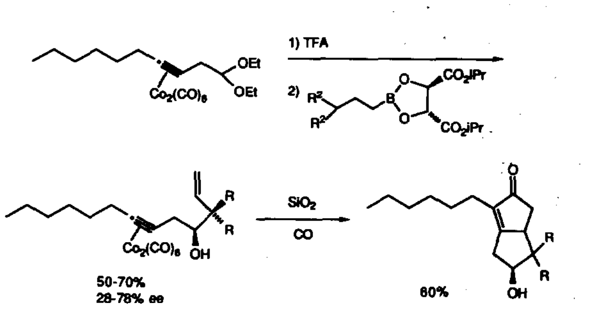
(Equation 455)



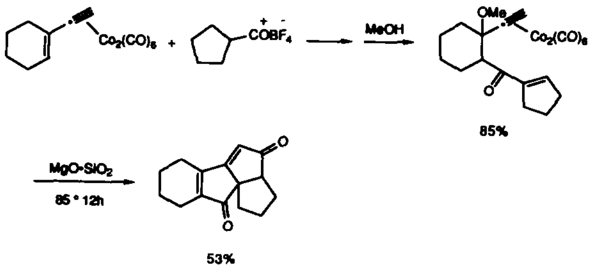
(Equation 456)



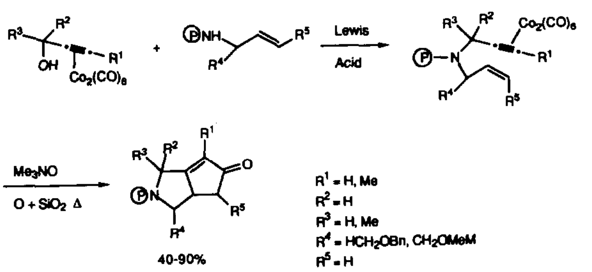
(Equation 457)



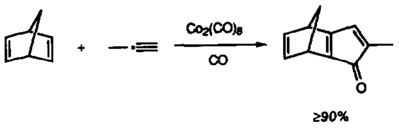
(Equation 458)



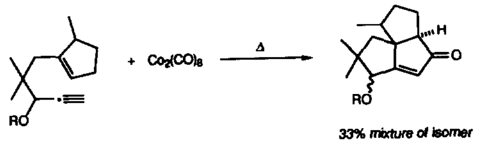
(Equation 459)



(Equation 460)



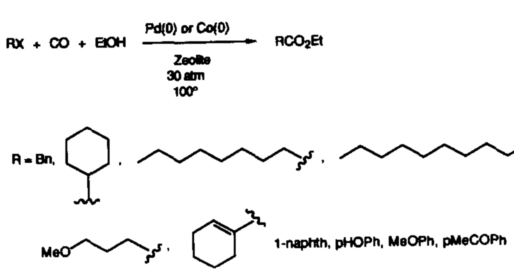
(Equation 461)



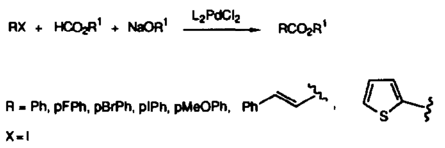
2.3.3. Carbonylation of halides and triflates

Organic halides were converted to esters over cobalt or palladium catalysts on zeolites (eqn. (462) [581,582]). Formate esters were used as a source of carbon monoxide in the carbonylation of halides (eqn. (463) [583]). Palladium(0) complexes catalyzed the carbonylation of chloropyrazines (eqn. (464) [584]), and chlorobenzene chromium complexes (eqn. (465) [585]). Aryl halides were trifluoroacylated via their copper derivatives (eqn. (466) [586]). Gem dihalides were carboxylated (eqn. (467) [587]) and aminoacylated (eqn. (468) [588]) over cobalt catalysts. (2-Bromoethyl)benzene was converted to a lactone by double carbonylation using a cobalt catalyst (eqn. (469) [589]). 4Pyridone esters were prepared by the carbonylative coupling of bromoaminoacrylates with alkynes (eqn. (470) [590]).

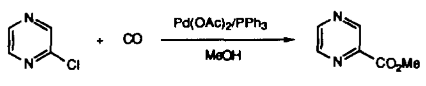
(Equation 462)



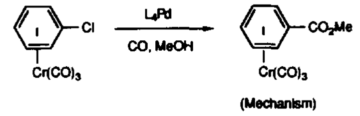
(Equation 463)



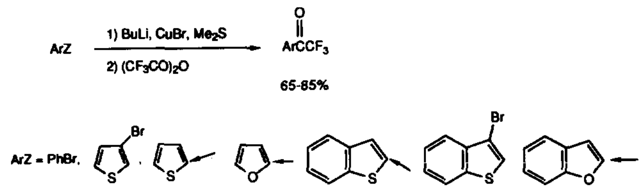
(Equation 464)



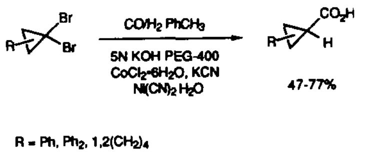
(Equation 465)



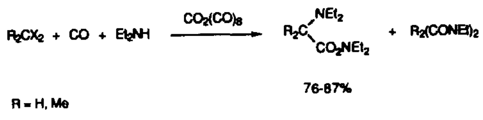
(Equation 466)



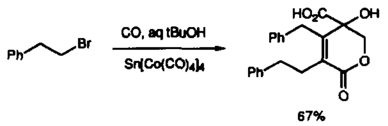
(Equation 467)



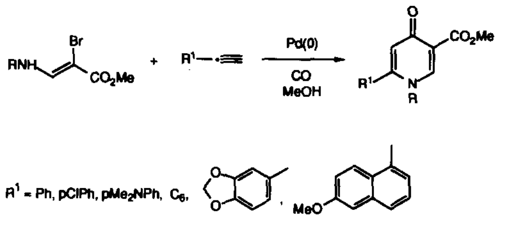
(Equation 468)



(Equation 469)

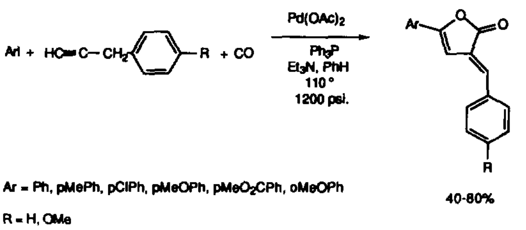


(Equation 470)

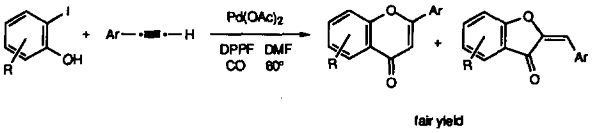


Lactones (eqn. (471) [591], eqn. (472) [592], and eqn. (473) [593]), amides (eqn. (474) [594]), and pyridones (eqn. (475) [595]) were all synthesized by the carbonylation of halides.

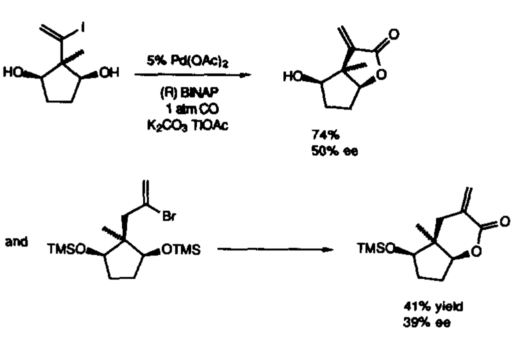
(Equation 471)



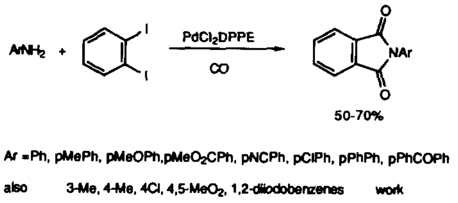
(Equation 472)



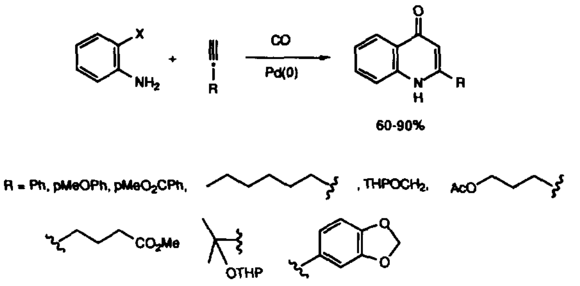
(Equation 473)



(Equation 474)

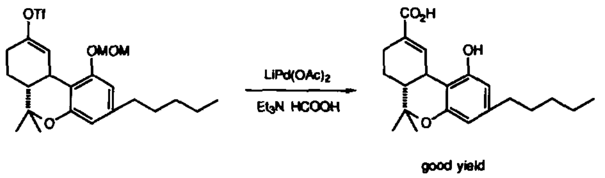


(Equation 475)

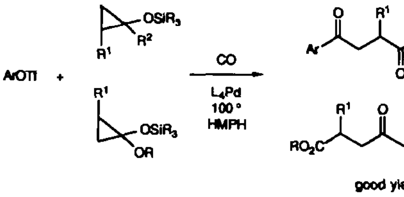


Palladium(0) complexes catalyzed the carbonylation (eqn. (476) [596]) and carbonylative coupling (eqn. (477) [597], eqn. (478) [598], and eqn. (479) [599]) of triflates. Cobalt complexes catalyzed the carbonylation of sulfonates (eqn. (480) [600]). Palladium complexes catalyzed the carbonylative coupling of boranes (eqn. (481) [601] and eqn. (482) [602]).

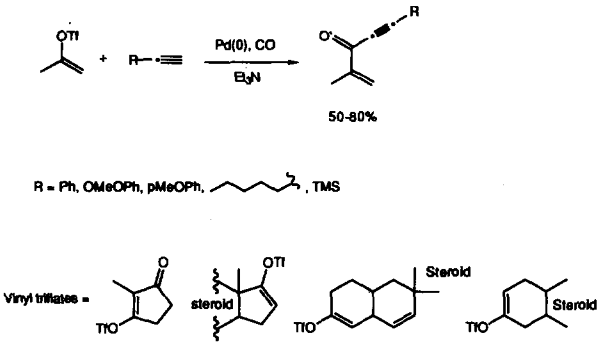
(Equation 476)



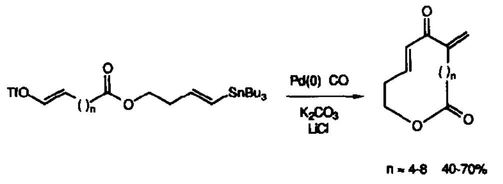
(Equation 477)



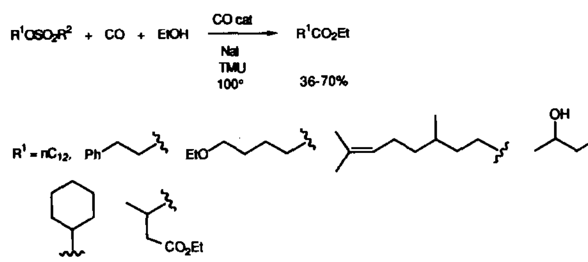
(Equation 478)



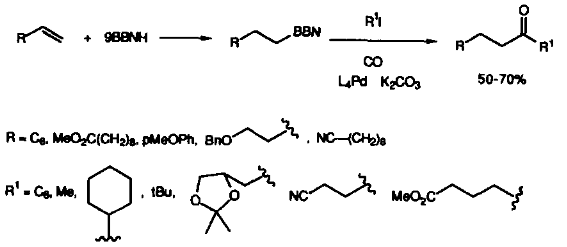
(Equation 479)



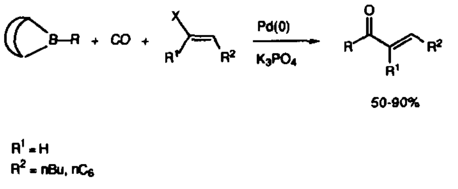
(Equation 480)



(Equation 481)



(Equation 482)



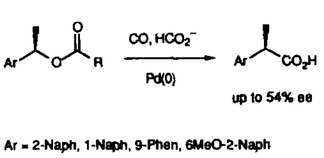
2.3.4. Carbonylation of nitrogen compounds

Allylamine was carbonylated in very low yield to give a mixture of products [603]. The reductive carbonylation of nitroaromatics to isocyanates with palladium catalysts [604] and rhodium catalysts [605] as well as the ruthenium catalyzed reductive carbonylation of aromatic nitro compounds to arenes [606], has been reported.

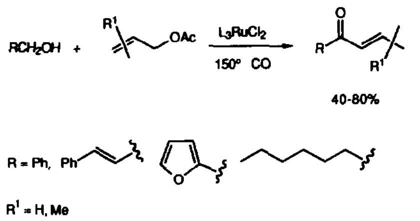
2.3.5. Carbonylation of oxygen compounds

Carbonylation of allylic compounds and cross double carbonylation of amines and alcohols using palladium and rhodium catalysts has been reviewed (42 references) [607]. Optically active benzyl carbonates were carboxylated in modest enantiomeric excess using palladium catalysts (eqn. (483) [608]). Allyl acetates were acylated by alcohols using ruthenium catalysts (eqn. (484) [609]). Propargyl carbonates were carbonylated to allenyl ketones using palladium catalysis (eqn. (485) [610]). Allyl ethers were carbonylated equally well by homogeneous and heterogeneous palladium catalysts [611]. Aromatic aldehydes were carbonylated to phenyl acetic acid derivatives by palladium-phosphinehydrogen chloride systems [612]. Tetrahydrofuran was ring opened and carbonylated by manganese carbonyl triflates (eqn. (486) [613]). Diphenyl allyl acetates were cycloacylated to naphthols by palladium catalysts (eqn. (487) [614]).

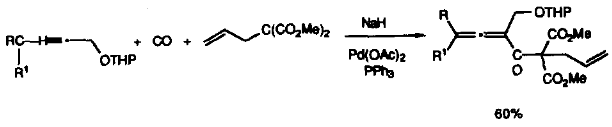
(Equation 483)



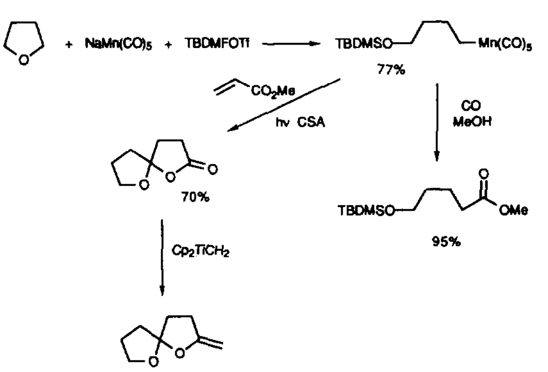
(Equation 484)



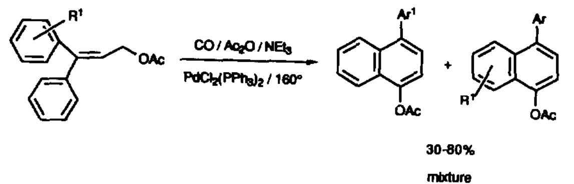
(Equation 485)



(Equation 486)



(Equation 487)

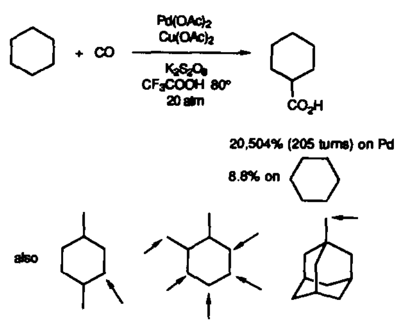


Ar = Ph, pMePh, 2-furyl, pMeOPh
Ar¹ = Ph, pMePh, pCF₃Ph, 3,5-Cl₂Ph, 3,5-Me₂Ph

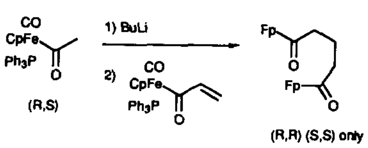
2.3.6. *Miscellaneous carbonylations*

Palladium acetate/copper acetate/oxidizing agent systems carboxylated cyclohexane [615] and alkylated cyclohexanes (eqn. (488) [616]). Iron acyl complexes added to iron α,β-unsaturated acyl complexes (eqn. (489) [617]). Palladium catalyzed the carbonylation of silyl allyl carbonates (eqn. (490) [618]), cyclopalladated arenes (eqn. (491) [619]), and dienyl acetates (eqn. (492) [620] and eqn. (493) [621]). Cyclopentenones were made by the carbonylation of zirconacyclopentanes (eqn. (494) [622]).

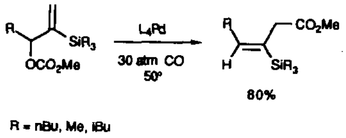
(Equation 488)



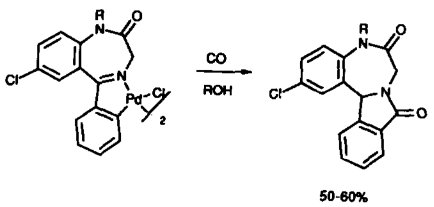
(Equation 489)



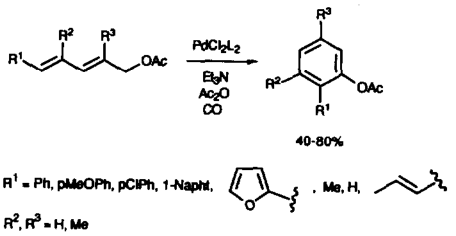
(Equation 490)



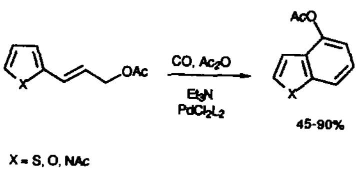
(Equation 491)



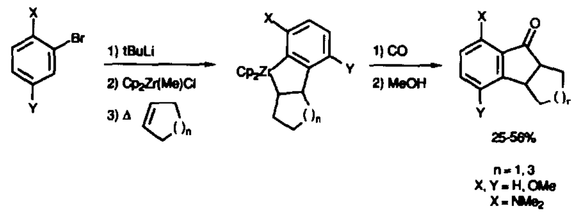
(Equation 492)



(Equation 493)



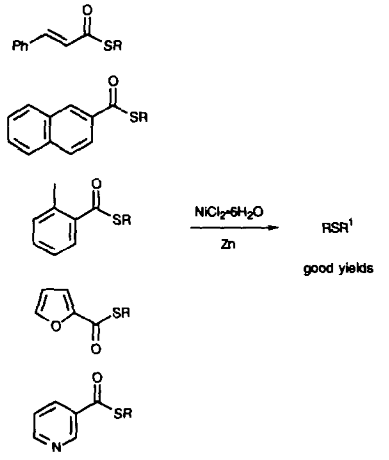
(Equation 494)



2.3.7. *Decarbonylation reactions*

A dissertation dealing with mechanistic studies on rhodium(I) catalyzed decarbonylation reactions of acid chlorides has appeared. Thioesters were decarbonylated to dithiols by nickel(II) chloride/zinc (eqn. (495) [624]).

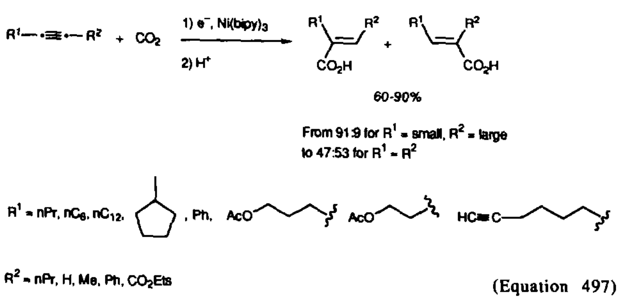
(Equation 495)



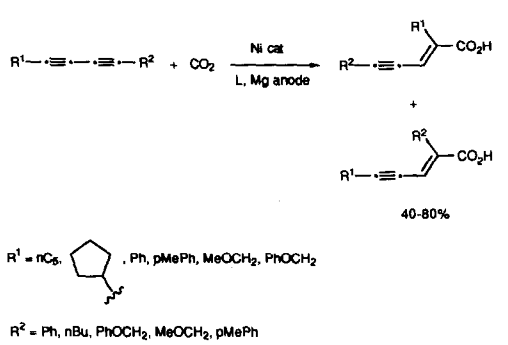
2.3.8. *Reactions of carbon dioxide*

A review entitled *Chemical Utilizations of Carbon Dioxide. Synthesis of Unsaturated Lactones* (3 references) has appeared [625], as has one dealing with carbon dioxide as a C-1-synthon in catalytic syntheses (19 references) [626]. Alkynes were carboxylated by carbon dioxide under electrochemical reduction in the presence of nickel catalysts (eqn. (496) [627]), as were diynes (eqn. (497) [628]). Palladium catalyzed the carboxylation of alkynes (eqn. (498) [629]) and dienes (eqn. (499) [630]), while ruthenium complexes catalyzed the carboxylation of enynes (eqn. (500) [631]). Alkynes were used to carry the carbonylation of amines by carbon dioxide (eqn. (501) [632]).

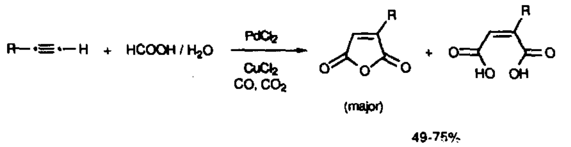
(Equation 496)



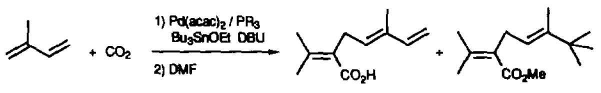
(Equation 497)



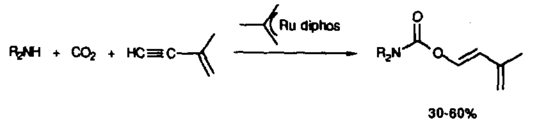
(Equation 498)



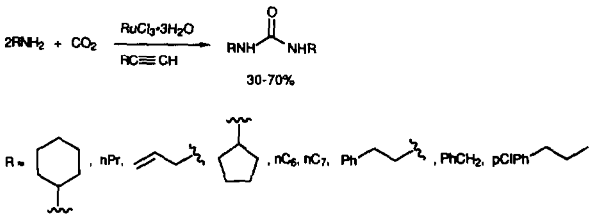
(Equation 499)



(Equation 500)

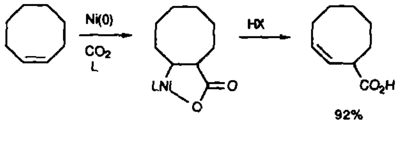


(Equation 501)

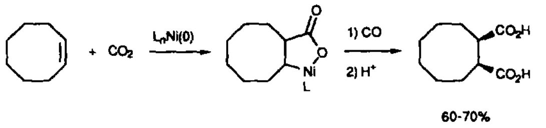


Low valent nickel incorporated carbon dioxide into a number of substrates (eqn. (502) [633], eqn. (503) [634], eqn. (504) [635], and eqn. (505) [636]). Palladium (0) complexes decarboxylated allyl carbonates (eqn. (506) [637]).

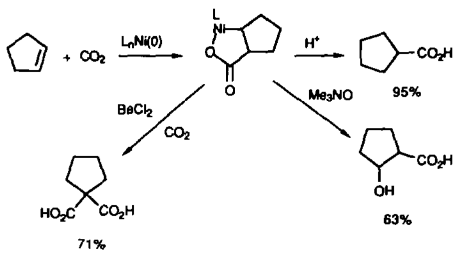
(Equation 502)



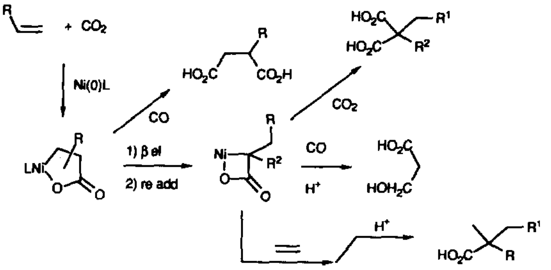
(Equation 503)



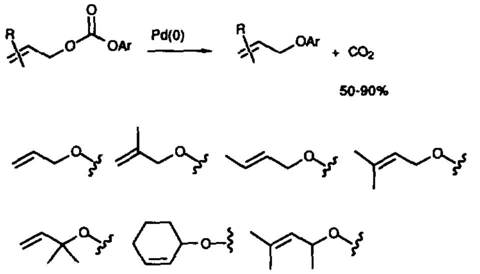
(Equation 504)



(Equation 505)



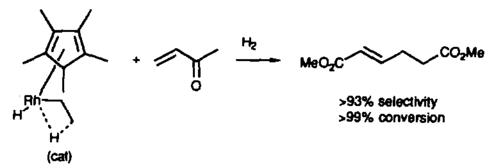
(Equation 506)



2.4. *Oligomerization (including cyclotrimerization of alkynes, and metathesis polymerization)*

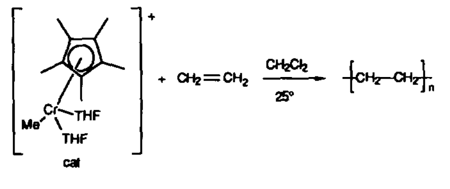
A dissertation dealing with ethylene dimerization catalyzed by rhodium supported on oxide surfaces has appeared [638]. Square planar nickel complexes [639], nickel formazanates [640], silica supported molybdenum catalysts derived from Mo(NMe2)3 [641], and nickel(II), palladium(II), and platinum(II) phosphine complexes [642] all catalyzed ethylene dimerization. Nickel aminophosphinite complexes dimerized conjugated dienes [643]. Rhodium (ethyl) (ethylene) complexes catalyzed the efficient tail to tail dimerization of methyl acrylate (eqn. (507) [644]). Low valent titanium complexes catalyzed the oligomerization of methylene cyclopropene, and its cocyclooligomerization with conjugated dienes [645].

(Equation 507)

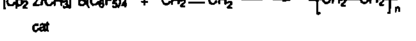


The oligomerization of α-olefins to higher linear oligomers has been reviewed (447 references) [646]. Olefins were polymerized by vanadium containing polyhedral oligometallasilsesquioxanes [647]. Cationic chromium complexes (eqn. (508) [648]) and zirconium complexes (eqn. (509) [649] and eqn. (510) [650]) polymerized ethene and propene. Palladium(0) complexes catalyzed the oligomerization of 1,2-distannyl ethene with dibromothiophenes (eqn. (511) [651]). Enantioselective telomerization of 1,3-dienes has been reviewed (23 references) [625].

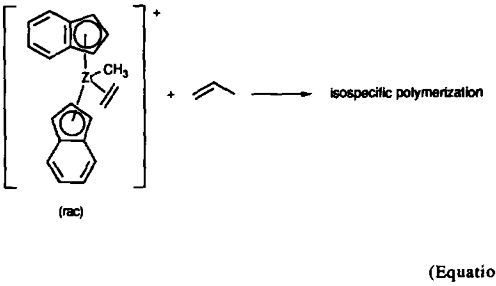
(Equation 508)



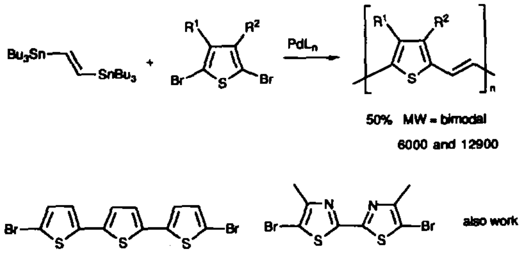
(Equation 509)



(Equation 510)

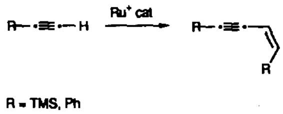


(Equation 511)

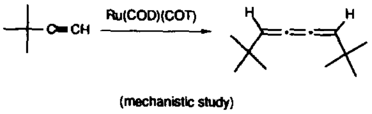


Alkynes were dimerized by ruthenium catalysts (eqn. (512) [653,654] and eqn. (513) [655]), while α,β-unsaturated ketones were tail to tail dimerized by rhodium catalysts (eqn. (514) [656]). Ruthenium catalysts codimerized alkynes with alkenes (eqn. (515) [657]) while titanacyclopentenes codimerized isoprene and ethylene (eqn. (516) [658]). Palladium complexes catalyzed the cooligomerization of alkynes and alkenes (eqn. (517) [659] and eqn. (518) [660]).

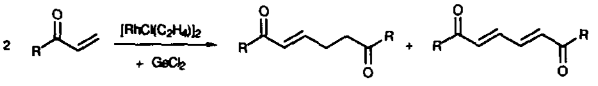
(Equation 512)



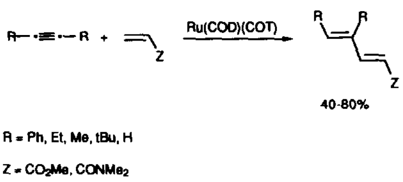
(Equation 513)



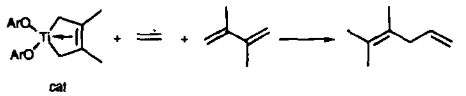
(Equation 514)



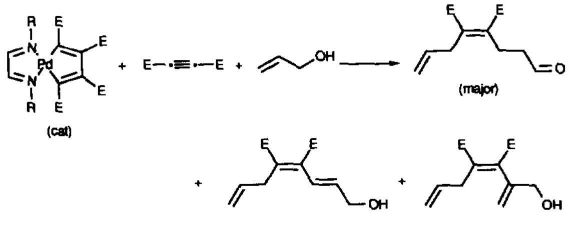
(Equation 515)



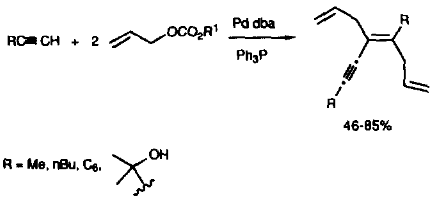
(Equation 516)



(Equation 517)

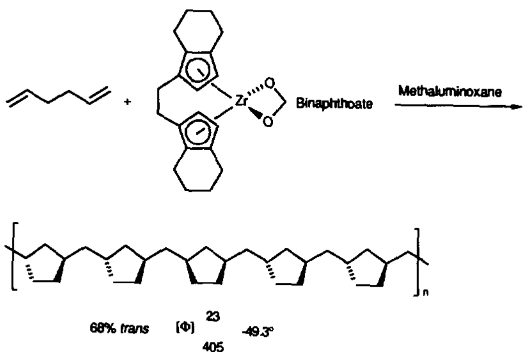


(Equation 518)

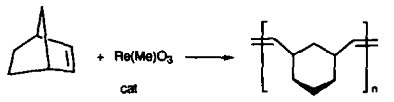


Optically active (bis) indenylzirconium complexes polymerized 1,5-hexdienes very stereoselectively (eqn. (519) [661]). Simple methyl rhenium oxo species were efficient ROMP catalysts (eqn. (520) [662]). Chiral polyacetylenes were synthesized by tungsten catalyzed ROMP polymerization of cyclooctatetraenes with chiral side chains (eqn. (521) [663]). Tungsten(VI) chloride cooligomerized norbornene and phenyl acetylene (eqn. (522) [664]). ROMP polymerization of functionalized bridge bicyclic dienes led to highly functionalized oligomers (eqn. (523) [665]).

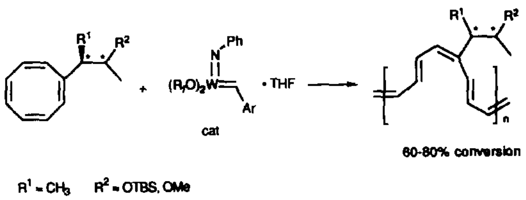
(Equation 519)



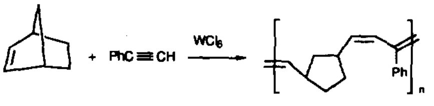
(Equation 520)



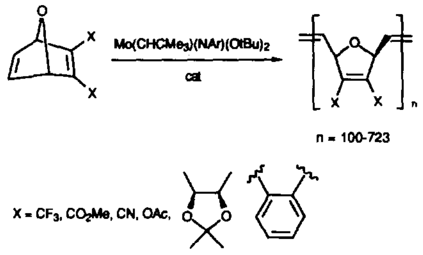
(Equation 521)



(Equation 522)

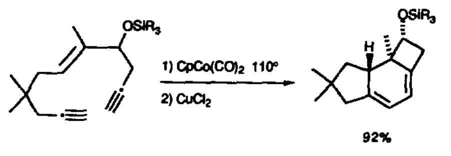


(Equation 523)

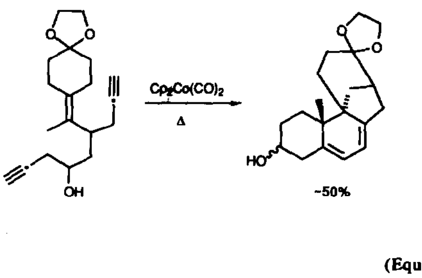


Cyclopentadienyl cobalt dicarbonyl catalyzed a number of cyclotrimerization reactions of alkynes, and alkene/alkyne cocyclotrimerizations (eqn. (524) [666], eqn. (525) [667], eqn. (526) [668], and eqn. (527) [669]).

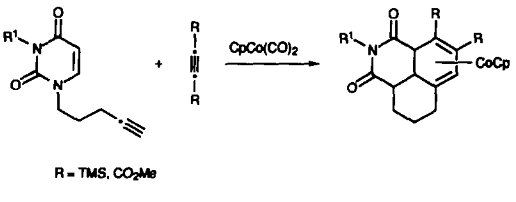
(Equation 524)



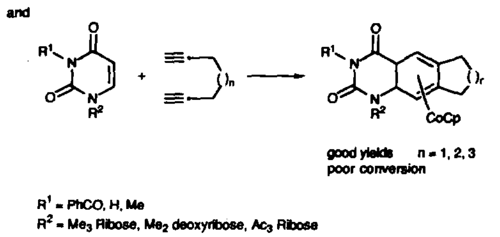
(Equation 525)



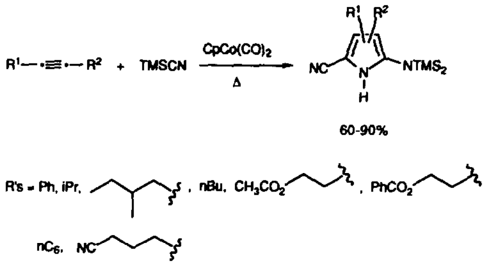
(Equation 526)



(Equation 527)

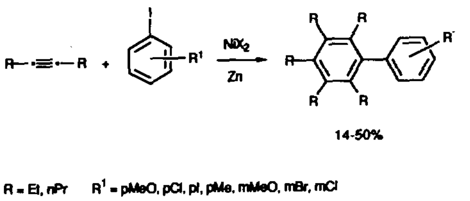


(Equation 528)

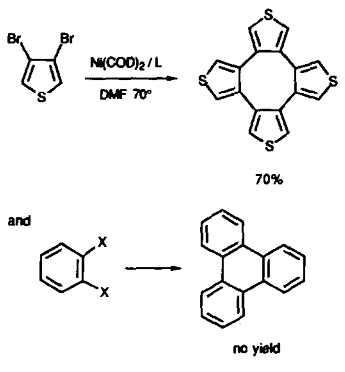


Reduced nickel species cyclooligomerized unsaturated species (eqn. (529) [670], eqn. (530) [671], eqn. (531) [672], and eqn. (532) [673]).

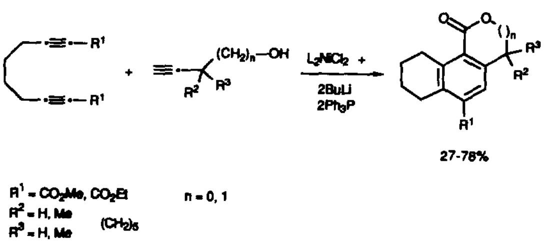
(Equation 529)



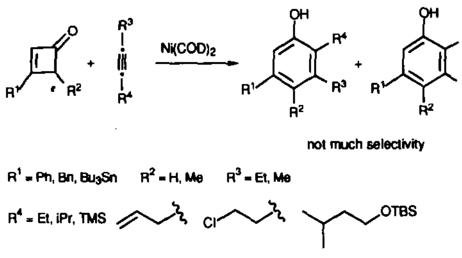
(Equation 530)



(Equation 531)

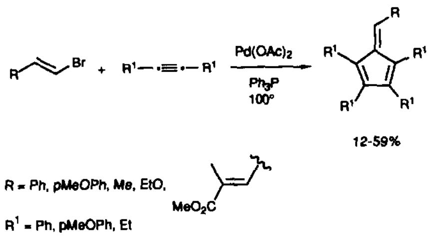


(Equation 532)

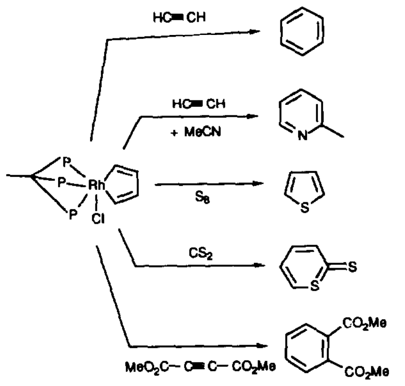


Other cyclooligomerizations are shown in eqn. (533) [674] and eqn. (534) [675]. Niobium(V) chloride catalyzed the cocyclotrimerization of phenyl acetylenes and hexynes [676]. Rhodium chloride/aliquat 336 catalyzed the cooligomerization of phenylated diynes [677], while rhodium(+) phosphine complexes oligomerized phenylacetylene [678].

(Equation 533)

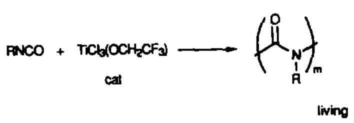


(Equation 534)

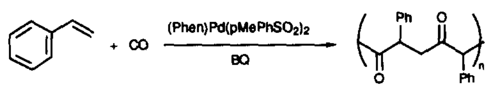


Titanium(IV) complexes catalyzed the living polymerization of isocyanates (eqn. (535) [679]). The mode of chain growth for the cooligomerization of styrene and carbon monoxide was studied (eqn. (536) [686]).

(Equation 535)



(Equation 536)



2.5. *Rearrangements*

2.5.1. *Metathesis*

The following reviews and dissertations dealing with olefin metathesis have appeared:

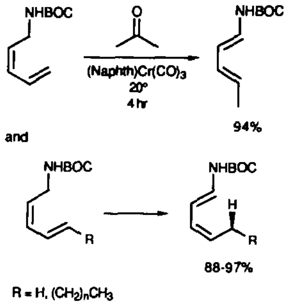
The Stereochemistry of Metathesis of Acyclic and Cyclic Olefins (23 references)	[681];
Metathesis of Functionalized Acyclic Olefins (49 references)	[682];
General Properties of Supported Metathesis Catalysts (47 references)	[683];
Novel Supported Catalysts for Terminal Alkene Metathesis (35 references)	[684];
Catalysts for the Homogeneous Metathesis of Functionalized Olefins (43 references)	[685];
Metathesis of Alkynes (58 references)	[686];
"Photochemical" Azo Metathesis by Tungsten Carbenes. Generation of Low-Valent Tungsten Nitrenes	[687].

New olefin metathesis catalyst systems involving anchoring molybdenum dioxo(acetylacetonate) to alumina [688], tungsten carbonyls [689], heteropolytungstate and molybdates on silica [690], Re_2O_7/Al_2O_3 [691], tungsten/tin/aluminum [692], and dinitrosylmolybdenum complexes [693] have all been developed.

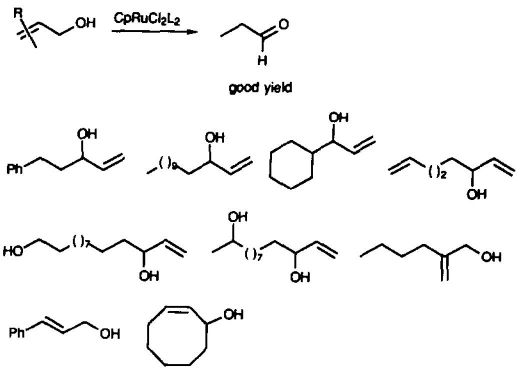
2.5.2. *Olefin isomerization*

Palladium(II) dithio-β-diketonate complexes catalyzed the isomerization of α-olefins in the presence of alkylaluminum cocatalyst [694]. Catalytic asymmetric hydrogen migration of allylamines has been reviewed (69 references) [695]. Arene chromium complexes catalyzed the rearrangement of allylic diene amines to dienamines (eqn. (537) [696]). Ruthenium complexes rearranged allyl alcohols to aldehydes (eqn. (538) [697]) while cationic rhodium complexes rearranged allyl alcohols to enols, which were quite stable [eqn. (539)]) [698]. Iridium hydride complexes rearranged propargyl amines to ketones (eqn. (540) [699]).

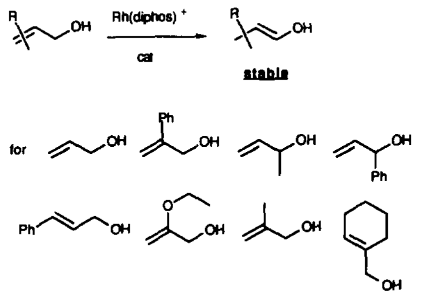
(Equation 537)



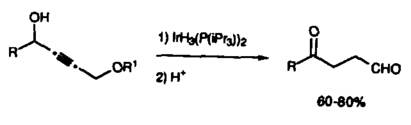
(Equation 538)



(Equation 539)



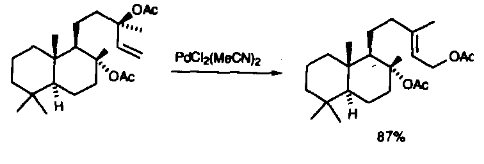
(Equation 540)



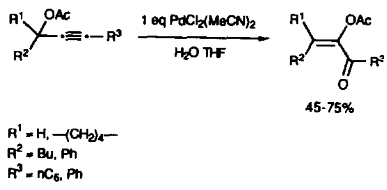
2.5.3. Rearrangement of allylic and propargylic compounds

Palladium(II) complexes catalyzed the allylic transposition of allyl acetates (eqn. (541) [700]) propargyl acetates (eqn. (542) [701]), Sallyl dithiocarbamates (eqn. (543) [702]), and *o*-allyloximes (eqn. (544) [703]). Chromium complexed benzylallyl ethers underwent rearrangement when treated with butyllithium (eqn. (545) [704]).

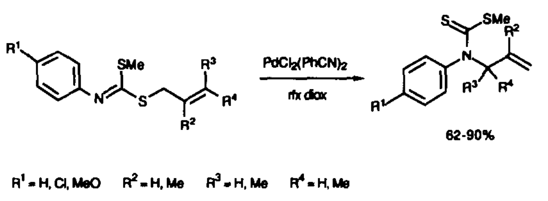
(Equation 541)



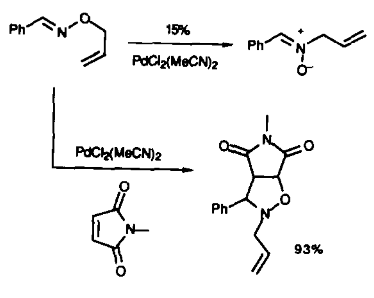
(Equation 542)



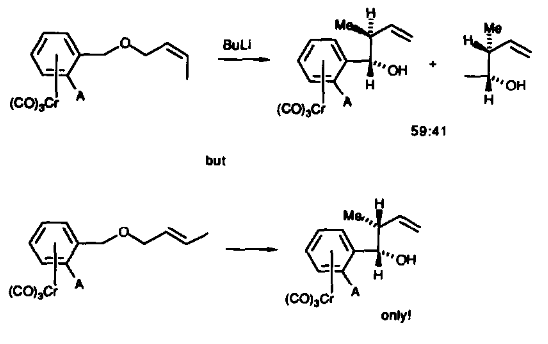
(Equation 543)



(Equation 544)



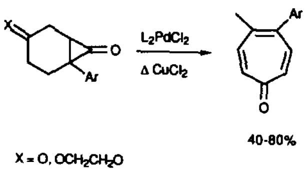
(Equation 545)



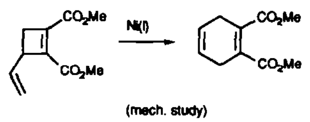
2.5.4. Skeletal rearrangements

Reviews dealing with transition metal (Pd and Ni) catalyzed cycloisomerization of enynes have appeared ([705] (40 references) and [706] (11 references)). Miscellaneous skeletal rearrangements are presented in eqn. (546) [707], eqn. (547) [708], eqn. (548) [709], eqn. (549) [710], eqn. (550) [711], and eqn. (551) [712].

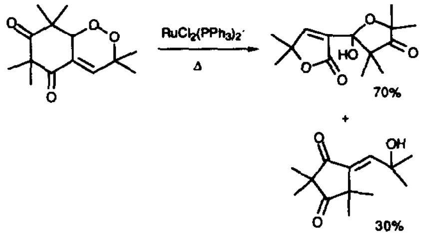
(Equation 546)



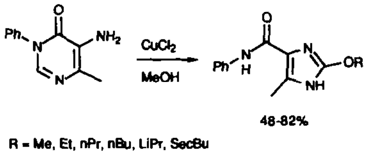
(Equation 547)



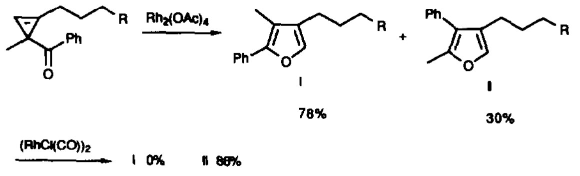
(Equation 548)



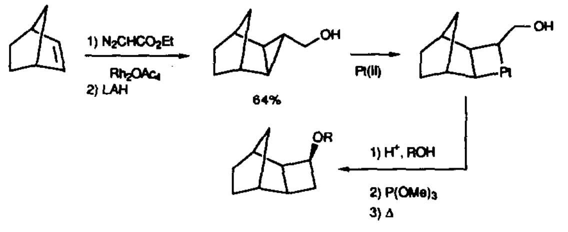
(Equation 549)



(Equation 550)



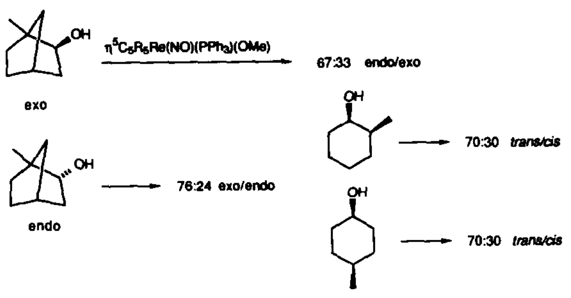
(Equation 551)



2.5.5. Miscellaneous rearrangements

Epoxides were isomerized to aldehydes by $Sn[Co(CO)_4]_4$ [714a]. Rhenium complexes catalyzed the epimerization of secondary alcohols (eqn. (552) [713]).

(Equation 552)

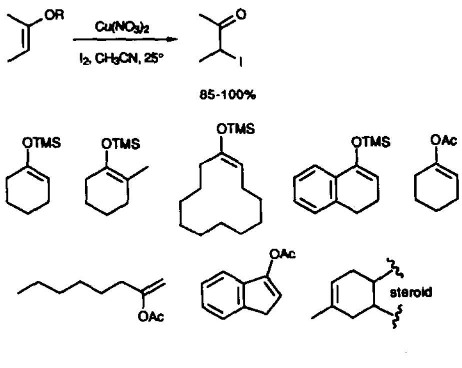


3. Functional group preparations

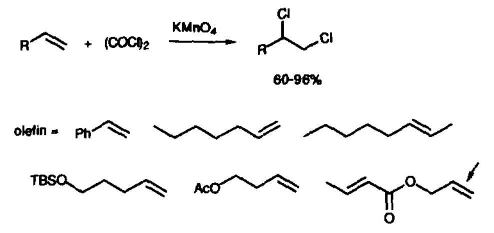
3.1. Halides

Enol ethers were converted to α-iodoketones by iodine/copper(II) nitrate (eqn. (553) [714b]). Alkenes were converted 1,2-dichlorides by oxallyl chloride and potassium permanganate (eqn. (554) [715]). O-Bromo-N-allylanilines were converted to 4-iodoindoles via zirconium chemistry (eqn. (555) [716]). Cyclopropyl ketones were chlorinatively ring-opened by molybdenum pentachloride (eqn. (556) [717]).

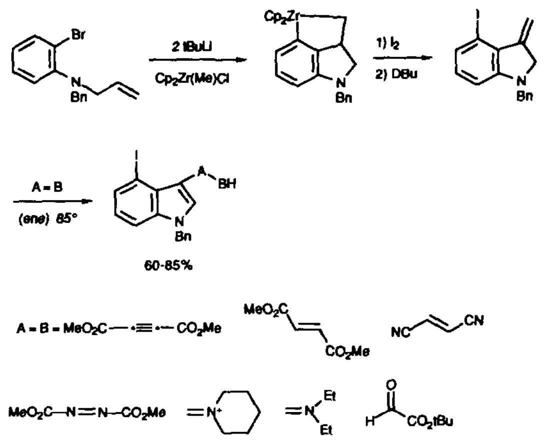
(Equation 553)



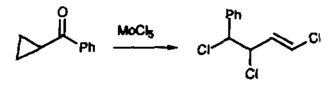
(Equation 554)



(Equation 555)



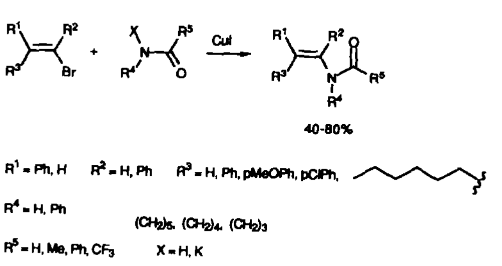
(Equation 556)



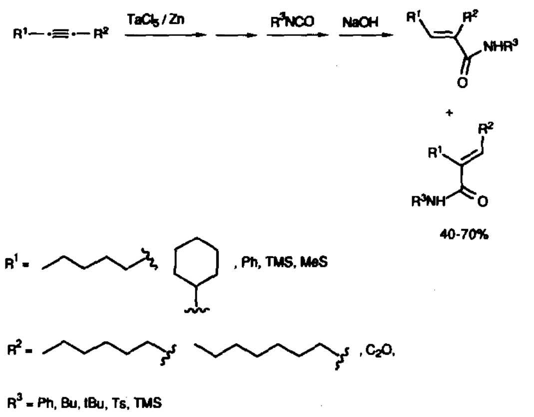
3.2. Amides and nitriles

A dissertation dealing with amino acid bis amides from 5-aminoisoxazoles-transmetallations of organostannanes via higher-order cyanocuprates has appeared [718]. Copper(I) iodide coupled vinyl bromides with amides to give enamides (eqn. (557) [719]). Alkynes were converted to α,β-unsaturated amides by reaction with reduced tantalum species and isocyanates (eqn. (558) [720]). Nickel(0) complexes catalyzed the reaction of ω-olefinic amides with isocyanates to give bis-amides (eqn. (559) [721]).

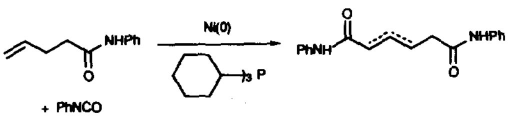
(Equation 557)



(Equation 558)



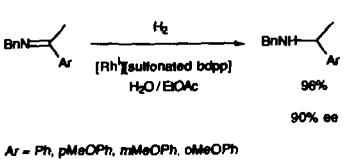
(Equation 559)



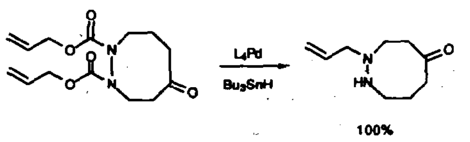
3.3. Amines and alcohols

A review entitled *Amination Reagent. Lithium Diamido Cuprate* has appeared (3 references) [722]. Aromatic nitro compounds were reduced to anilines by $Rh_4(CO)_{12}$-9,10-diaminoanthracene catalysts [723] and by polymer-bound palladium acetate [724]. Imines were reduced to amines asymmetrically by rhodium(I) complexes of chiral bidentate phosphines with up to 69% enantiomeric excess [725]. The reaction could be carried out in aqueous solvents using sulfonated bdpp as the ligand (eqn. (560) [726]). O-Allyl carbamates were deprotected to the free amine by palladium(0) catalysts and tin hydrides (eqn. (561) [727] and eqn. (562) [728]). Palladium also catalyzed the amination of allylic carbonates [729].

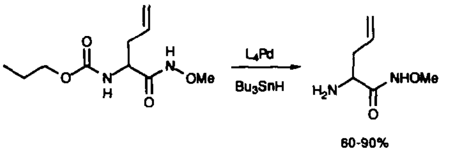
(Equation 560)



(Equation 561)

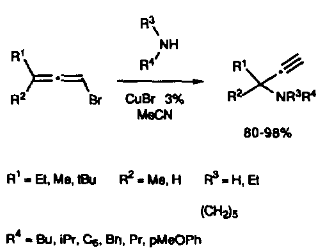


(Equation 562)

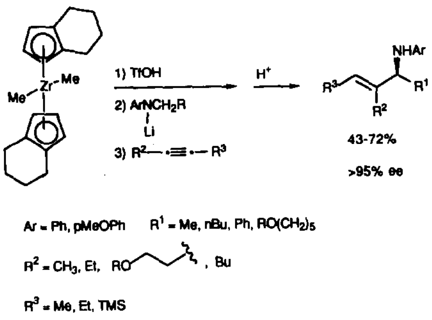


Allenyl bromides were converted to propargyl amines using copper(I) bromide (eqn. (563) [730]). Optically active zirconocene derivatives were used to synthesize allyl amines (eqn. (564) [731]). Nitriles were reductively coupled to give secondary amines by rhodium on alumina (eqn. (565) [732]).

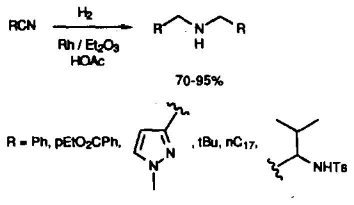
(Equation 563)



(Equation 564)

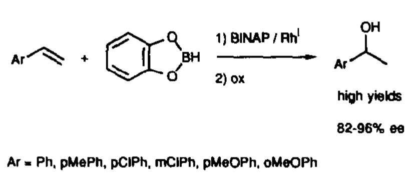


(Equation 565)

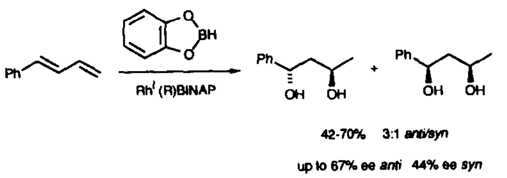


Transition Metal Promoted Hydroborations of Alkenes, Emerging Methodology for Organic Transformations is the title of a review (63 references) [733]. This process was accelerated by electron-withdrawing groups, and metal complexation determined stereoselectivity [734]. The asymmetric hydroboration of norbornene, indene, α-methyl styrene and 2,3,3-trimethylbut-1-ene using rhodium(I) catalysts and diop as ligand gave very modest enantiomeric excesses (27%) [735]. The use of BINAP gave much better enantiomeric excesses with styrenes (eqn. (566) [736]). Phenylbutadienes were dihydroxylated (eqn. (567) [737]). B,γ-unsaturated amides were regioselectively hydroborated (eqn. (568) [738]).

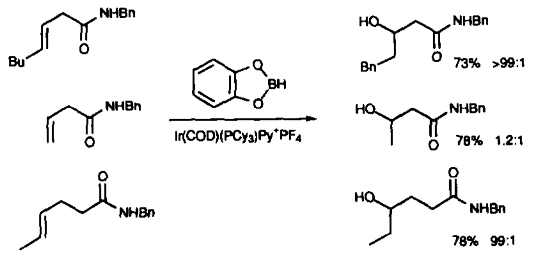
(Equation 566)



(Equation 567)

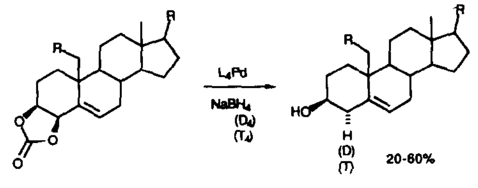


(Equation 568)

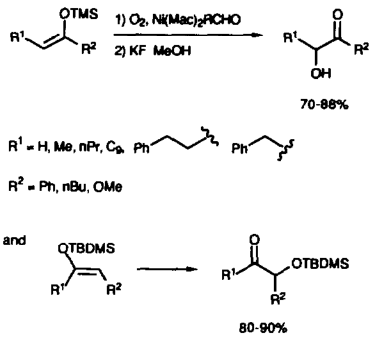


Selective hydrogenolysis of benzyl and carbobenzyloxy protecting groups for hydroxyl and amino functions has been reviewed (16 references) [739]. Allyl carbonates were reduced to homoallyl alcohols by borohydride and palladium(0) catalysts (eqn. (569) [740]). Nickel complexes catalyzed the α oxidation of silylenol ethers (eqn. (570) [741]). Carboxylic acids underwent remote oxidation with platinum(IV) (eqn. (571) [742]).

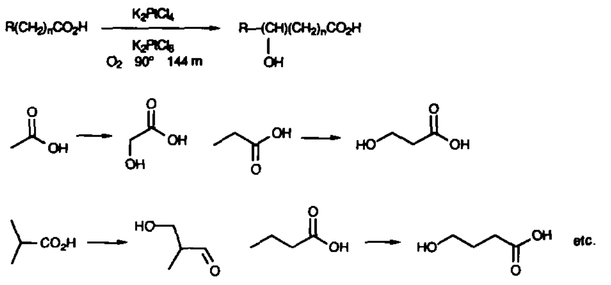
(Equation 569)



(Equation 570)

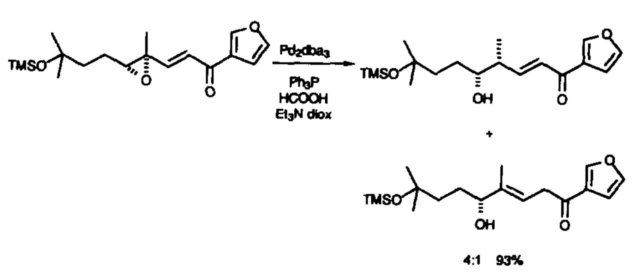


(Equation 571)

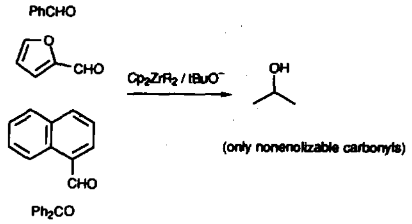


Catalytic enantioselective hydrogenation of ketones and imines using platinum-metal complexes has been reviewed (40 references) [743]. Cationic iridium complexes catalyzed the asymmetric hydrogenation of α-amino ketones [744]. Palladium(0) complexes catalyzed the reduction of epoxides to alcohols (eqn. (572) [745]). Nonenolizable ketones and aldehydes were reduced by zirconocene dialkyls (eqn. (573) [746]). Dihydropyridine iron acyl complexes were NADH mimics (eqn. (574) [747]). Ketones were reduced to optically active alcohols by silanes and chiral rhodium complexes (eqn. (575) [748]). Esters were reduced to alcohols by titanocene dialkyls/silanes (eqn. (576) [749]).

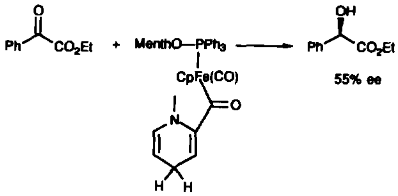
(Equation 572)



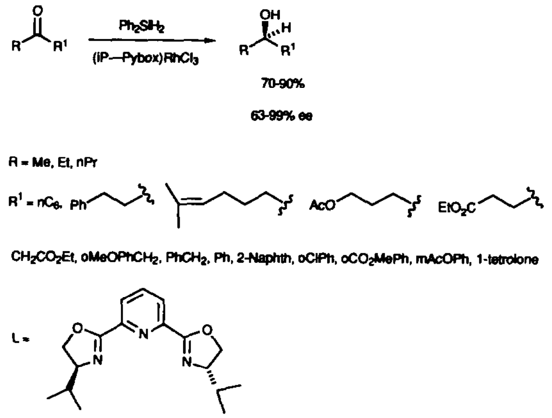
(Equation 573)



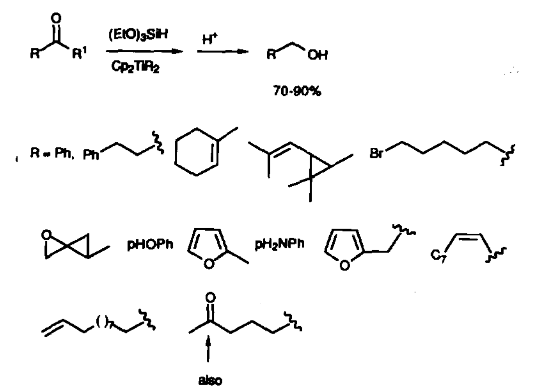
(Equation 574)



(Equation 575)

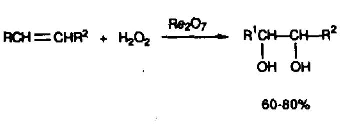


(Equation 576)

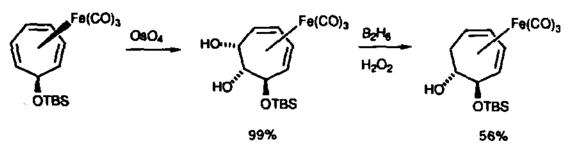


Asymmetric osmium tetroxide oxidation with 2,2′-bipyrrolidine ligands was reviewed (3 references) [750]. Olefins were cis dihydroxylated by Re_2O_7/H_2O_2 (eqn. (577) [751]), and osmium tetroxide (eqn. (578) [752]), while this reagent tetrahydroxylated dienes (eqn. (579) [753]). Asymmetric dihydroxylations of alkenes using osmium tetroxide/alkaloid ligands continued its development [7541 and [755]. Bis epoxides were converted to 1,2-diols by reaction with copper catalyzed Grignard reagent (eqn. (580) [756]).

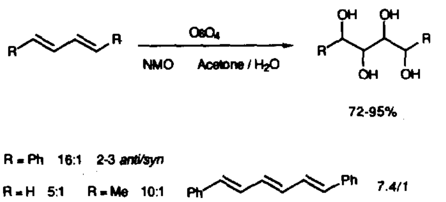
(Equation 577)



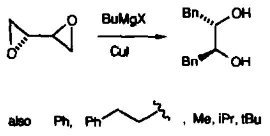
(Equation 578)



(Equation 579)

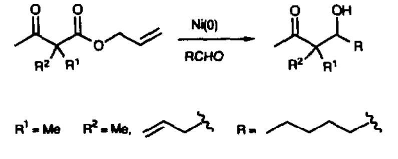


(Equation 580)

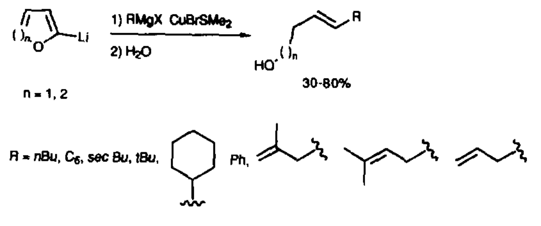


Nickel(0) complexes catalyzed the alkylation of aldehydes by βdicarbonyl allyl carbonates (eqn. (581) [757]). Grignard reagents ring opened lithiated dihydrofurans and pyrans (eqn. (582) [758]).

(Equation 581)



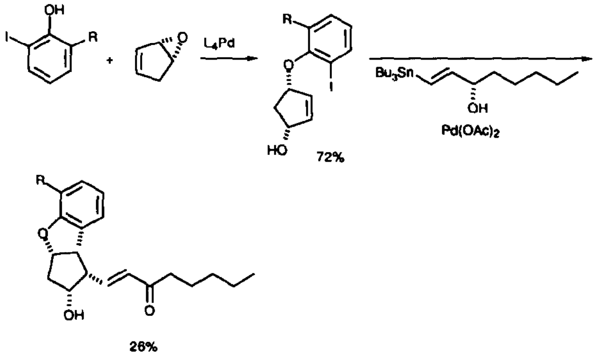
(Equation 582)



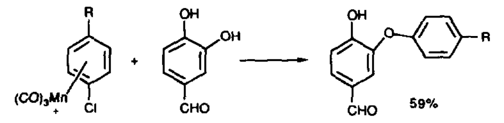
3.4. Ethers, esters, and acids

Procedures to control the regiochemistry of palladium catalyzed etherification of allylic acetates have been developed [759]. Palladium complexes catalyzed the attack of phenols on allyl epoxides (eqn. (583) [760]). Manganese-complexed chlorobenzenes were alkoxylated by phenols (eqn. (584) [761]). Oxidation of σ-alkylpalladium(II) complexes produced ethers (eqn. (585) [762]). Ketals were reduced to ethers by zirconium hydrides (eqn. (586) [763]).

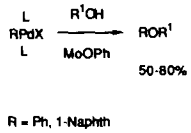
(Equation 583)



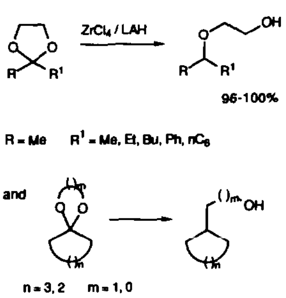
(Equation 584)



(Equation 585)

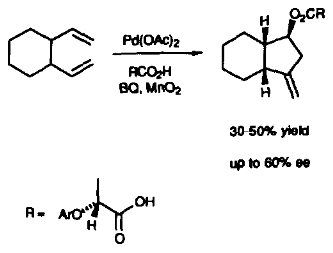


(Equation 586)

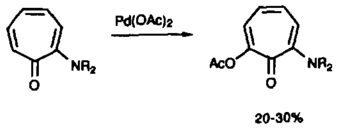


Palladium catalyzed benzylic acetoxylation was purely heterogeneously catalyzed even when homogeneous palladium catalyst precursors were used [764]. The activity and selectivity of acetoxylation of cyclic conjugated dienes over Group VIII metal catalysts has been studied [765]. Acetoxylations of cyclohexene by copper acetate in the presence of amino acids proceeded with up to 30% enantiomeric excess [766]. Sulfonylquinones were used to promote the palladium catalyzed 1,4-acetoxylation of dienes, improving the rate and the stereoselectivity [767]. Palladium(II) catalyzed the acetoxy cyclization of 1,5-dienes (eqn. (587) [768,769]). Palladium catalyzed the acetoxylation of α-aminotropanone (eqn. (588) [770]).

(Equation 587)

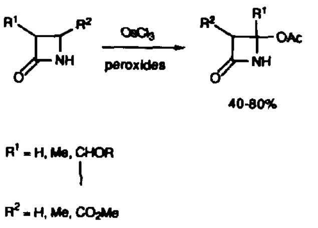


(Equation 588)

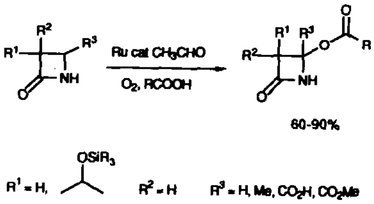


β-Lactams were acetoxylated a to nitrogen by OsCl$_3$/peroxides (eqn. (589) [771]), ruthenium catalyst (eqn. (590) [772]) and copper acetate (eqn. (591) [773]). Nickel(II) complexes catalyzed Baeyer–Villiger oxidation of ketones (eqn. (592) [774]). Ruthenium complexes catalyzed the reductive coupling of aroyl chlorides (eqn. (593) [775]).

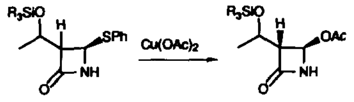
(Equation 589)



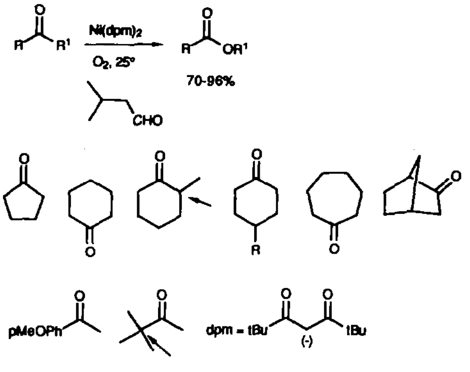
(Equation 590)



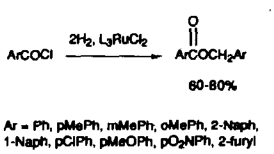
(Equation 591)



(Equation 592)



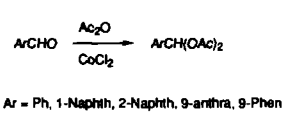
(Equation 593)



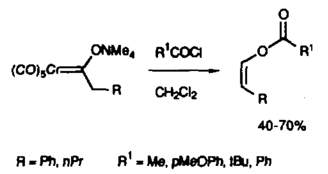
Cobalt(II) chloride catalyzed the conversion of aryl aldehydes to acetals (eqn. (594) [776]). Chromium acylate complexes were converted to enol acetates by acid chlorides (eqn. (595) [777]). Rhodium and iridium(I)-

complexes were used to promote peptide coupling (eqn. (596) [778]). Nickel(II) complexes catalyzed the oxidation of aldehydes to acids (eqn. (597) [779]).

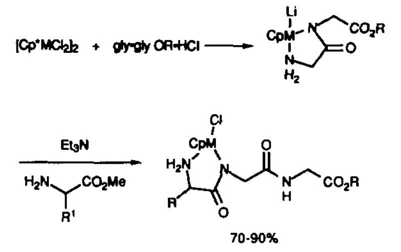
(Equation 594)



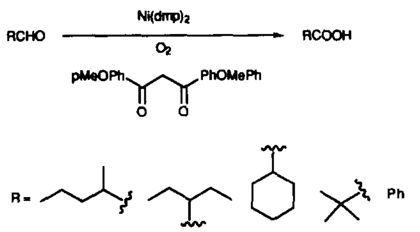
(Equation 595)



(Equation 596)



(Equation 597)



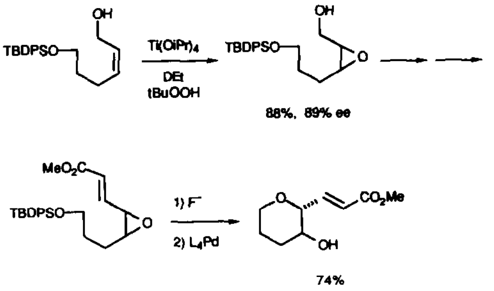
3.5. Heterocycles

Asymmetric epoxidation of olefin continues to be a very active area for research. The following reviews on this topic have appeared:

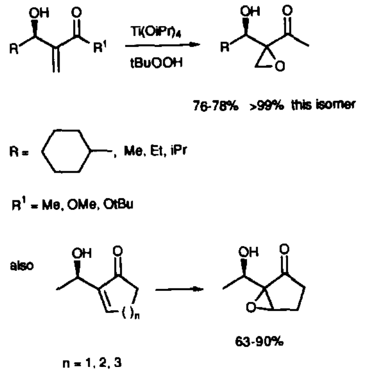
Asymmetric Epoxidation (242 references) [780];
Catalytic, Enantioselective Epoxidation of Simple Olefins (11 references) [781];
A Revolution in Organic Synthesis. Discovery of Asymmetric Epoxidation (17 references) [782];
Metal-Mediated Enantioselective Access to Simple Oxiranes. Prochiral and Chiral Recognition (37 references) [783];
Applications of Some Chiral, β-Ketophosphonate Transition Metal Complexes in Epoxidation Catalysis [784].

The effect of hydroperoxide structure on the enantioselectivity of the Sharpless epoxidation of 3-methyl-2-buten-1-ol has been studied [785]. Sharpless asymmetric epoxidation figures extensively in complex syntheses (eqn. (598) [786], eqn. (599) [787,788], eqn. (600) [789], and eqn. (601) [790]). Functionalized allyl alcohols also underwent this reaction (eqn. (602) [791], eqn. (603) [792], and eqn. (604) [793]. Titanium(IV) t-butoxide was much less efficient than the isopropoxide for Sharpless kinetic resolution of racemic secondary alcohols [794].

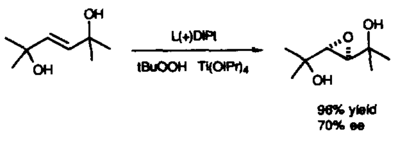
(Equation 598)



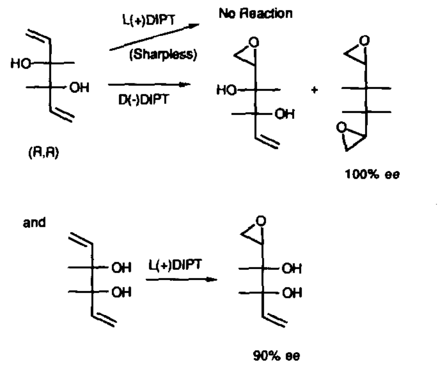
(Equation 599)



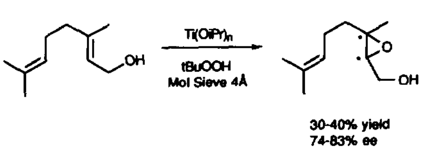
(Equation 600)



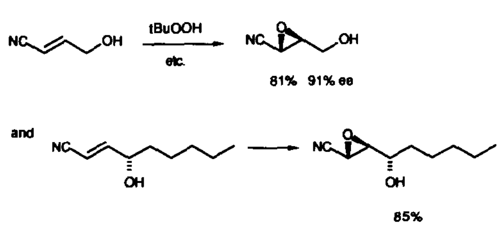
(Equation 601)



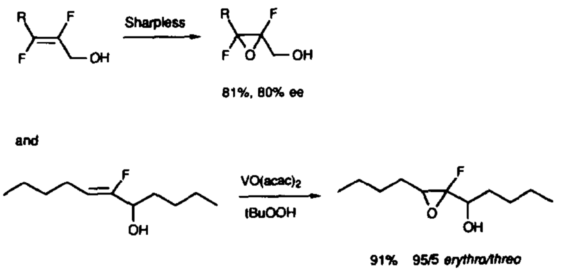
(Equation 602)



(Equation 603)

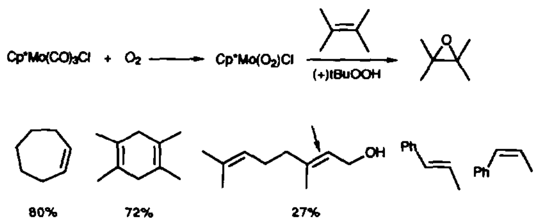


(Equation 604)

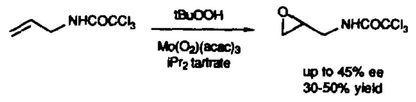


Molybdenum peroxo compounds catalyzed the epoxidation of olefins (eqn. (605) [795] and eqn. (606) [796]).

(Equation 605)

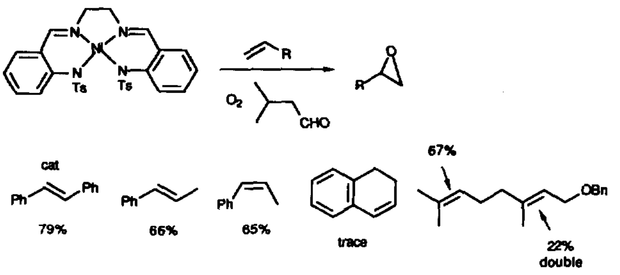


(Equation 606)

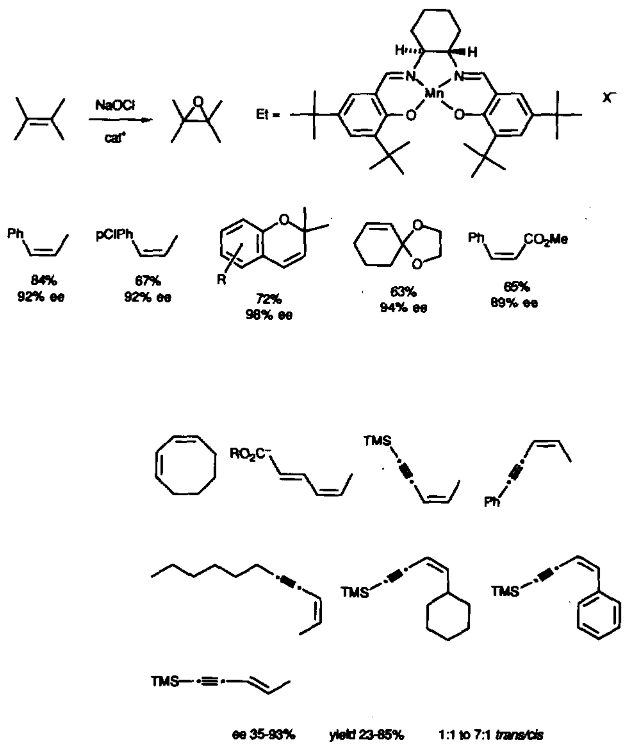


Cobalt Shiff base complexes catalyzed the epoxidation of olefins [797], as did nickel salen complexes (eqn. (607) [798]). Optically active manganese salen complexes were efficient asymmetric epoxidation catalysts (eqn. (608) [799–801] and eqn. (609) [802]).

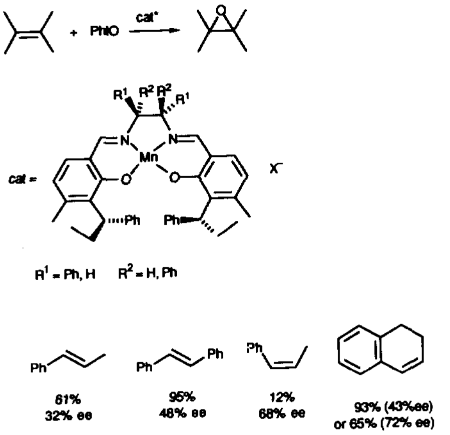
(Equation 607)



(Equation 608)

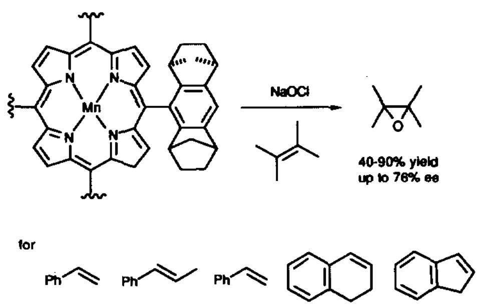


(Equation 609)

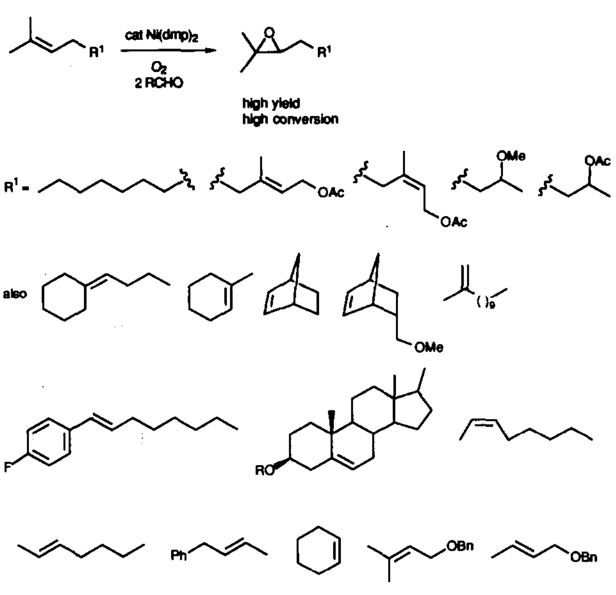


Metal Complex / Iodosobenzene Active Species for Oxidation was the topic of a review (5 references) [803]. Optically active porphyrin-manganese complexes catalyzed the olefin epoxidation (eqn. (610) [804]), as did nickel(II), β-diketonate complexes (eqn. (611) [805, 806]), nickel bipyridine complexes (eqn. (612) [807]), and iron cyclams (eqn. (613) [808]).

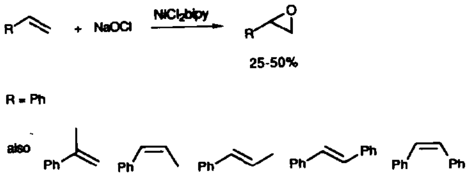
(Equation 610)



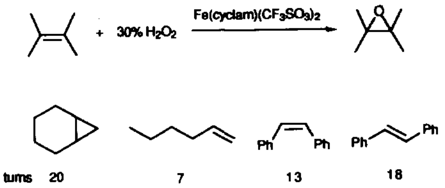
(Equation 611)



(Equation 612)

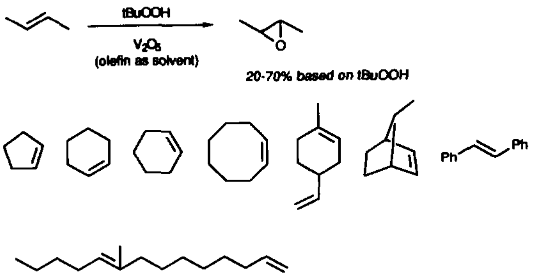


(Equation 613)

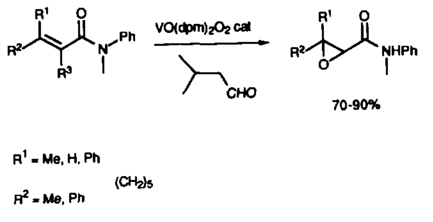


Olefin epoxidation was also catalyzed by vanadium oxo species (eqn. (614) [809] and eqn. (615) [810]) and simple rhenium oxo species (eqn. (616) [811]). Copper catalyzed the aziridination of alkenes (eqn. (617) [812]).

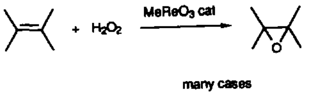
(Equation 614)



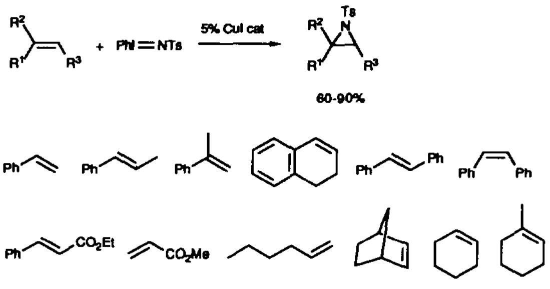
(Equation 615)



(Equation 616)

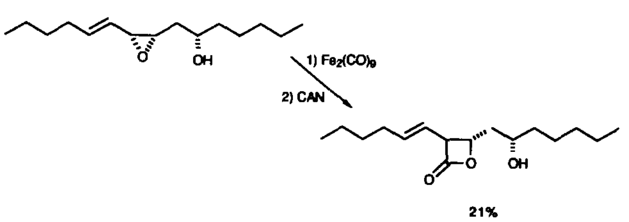


(Equation 617)

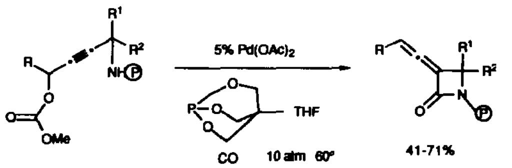


A β-lactone natural product was synthesized using iron carbonyl chemistry (eqn. (618) [813,814]). Asymmetric synthesis of azetidinones was reviewed [815]. β-Lactams were synthesized using palladium (eqn. (619) [816]), chromium (eqn. (620) [817]), and cobalt chemistry (eqn. (621) [818]).

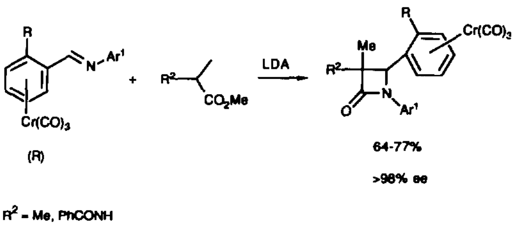
(Equation 618)



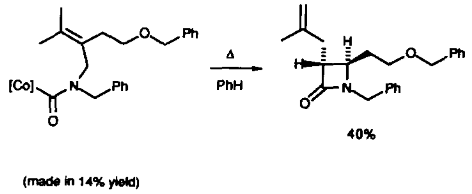
(Equation 619)



(Equation 620)

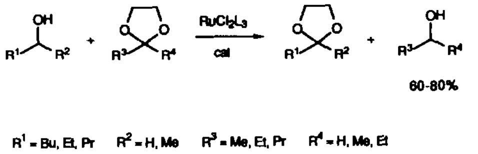


(Equation 621)

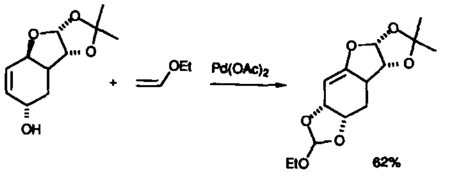


Rhenium(II) complexes catalyzed the trans acetylization reaction (eqn. (622) [819]). Palladium(II) catalyzed several forming reactions (eqn. (623) [820], eqn. (624) [821], and eqn. (625) [822]).

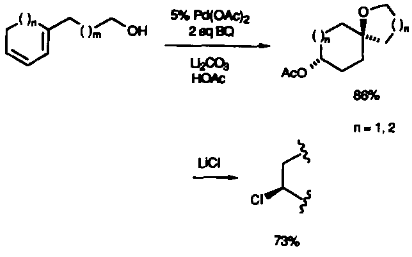
(Equation 622)



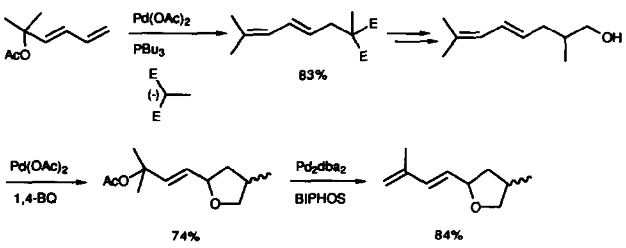
(Equation 623)



(Equation 624)

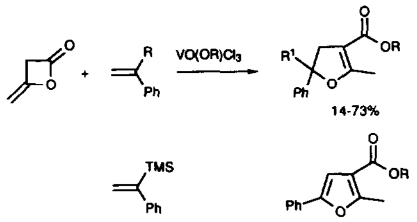


(Equation 625)

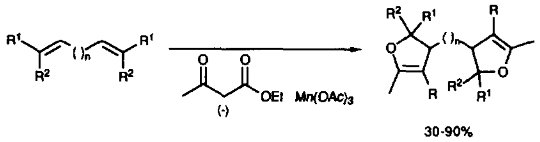


Dihydrofurans were made by the reaction of ketene dimer with olefins (eqn. (626) [823]), manganese catalyzed cyclization of diolefins (eqn. (627) [824]) and the condensation of isonitriles with α-halo ketones (eqn. (628) [825]).

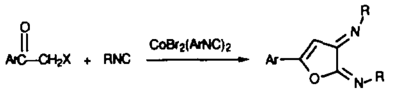
(Equation 626)



(Equation 627)



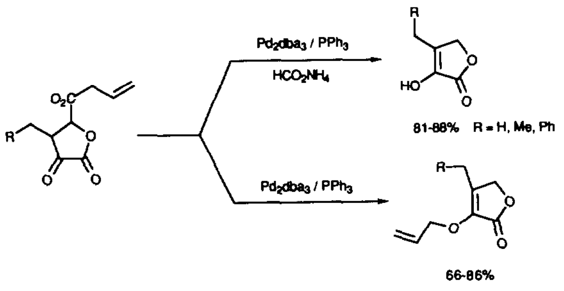
(Equation 628)



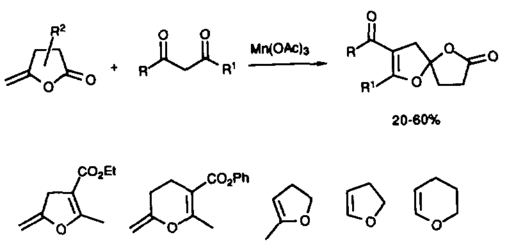
Ar = Ph, pMePh, pPhPh, pMeOPh, pNO$_2$Ph

Five-membered lactones were synthesized by a number of different organometallic routes (eqn. (629) [826], eqn. (630) [827], eqn. (631) [828], eqn. (632) [829], eqn. (633) [830], and eqn. (634) [831]).

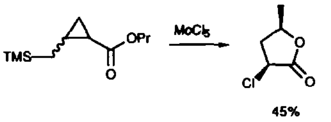
(Equation 629)



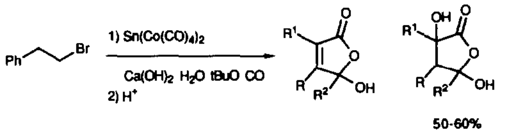
(Equation 630)



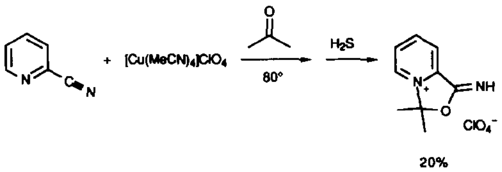
(Equation 631)



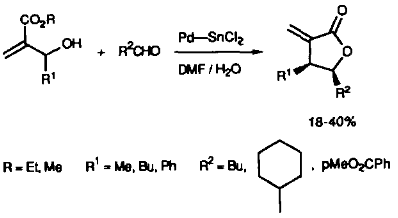
(Equation 632)



(Equation 633)

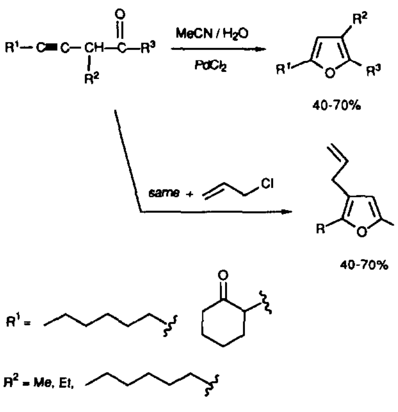


(Equation 634)

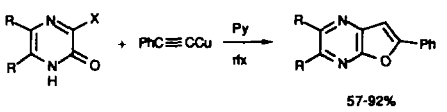


Furans were synthesized by palladium catalyzed cyclization of βynones (eqn. (635) [832]), copper acetylide reaction with halopyrimidines (eqn. (636) [833]), and McMurray coupling (eqn. (637) [834]).

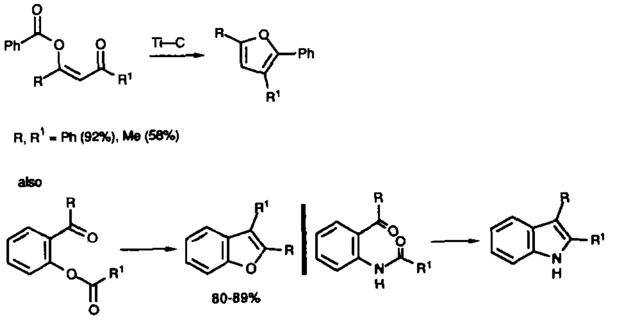
(Equation 635)



(Equation 636)

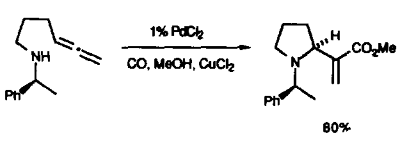


(Equation 637)

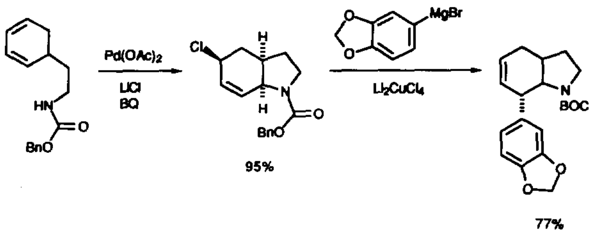


Pyrrolidines were made by palladium catalyzed cyclizations (eqn. (638) [835], eqn. (639) [836], eqn. (640) [837], and eqn. (641) [838]).

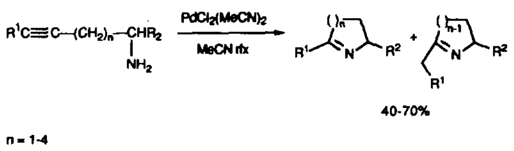
(Equation 638)



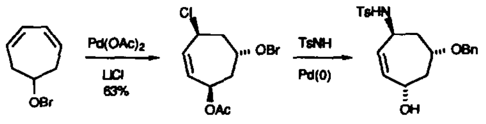
(Equation 639)



(Equation 640)

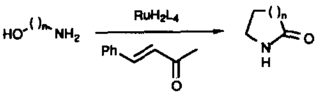


(Equation 641)

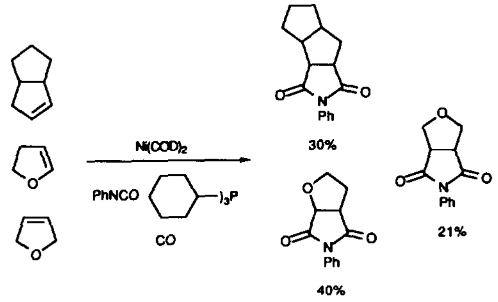


1,4- and 1,5-aminoalcohols were cyclized to lactams by ruthenium complexes (eqn. (642) [839]). Nickel(0) complexes cyclized olefins, isocyanates, and carbon monoxide to imides (eqn. (643) [840]). Copper(I) cyclized propargyl alcohols and isocyanates to give oxazolidinones (eqn. (644) [841]). Diols were converted to oxazolidinones by reaction with isocyanates in the presence of palladium catalysts (eqn. (645) [842]).

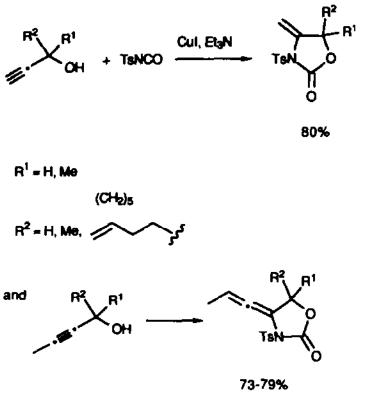
(Equation 642)



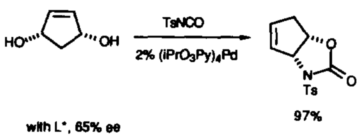
(Equation 643)



(Equation 644)

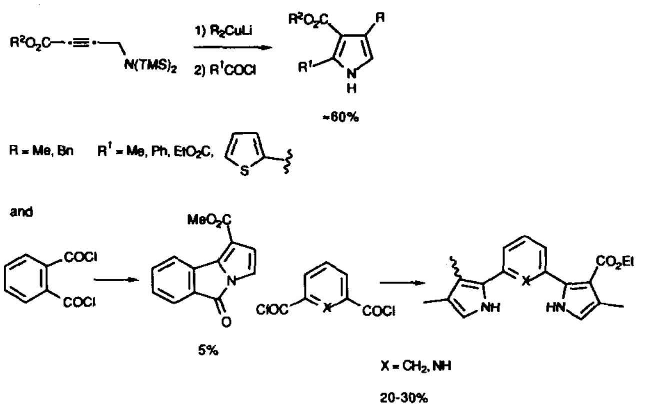


(Equation 645)

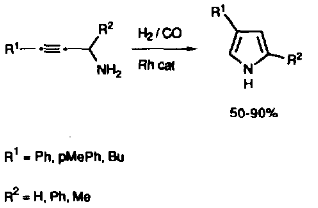


Pyrroles were synthesized by the reaction of propargyl amines, organocopper complexes and acid chlorides (eqn. (646) [843]), by the rhodium catalyzed carbonylation of propargyl amines (eqn. (647) [844]), and by unusual zirconium chemistry (eqn. (648) [845]).

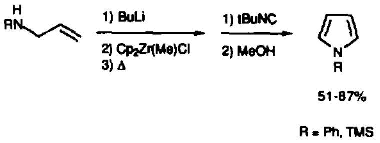
(Equation 646)



(Equation 647)

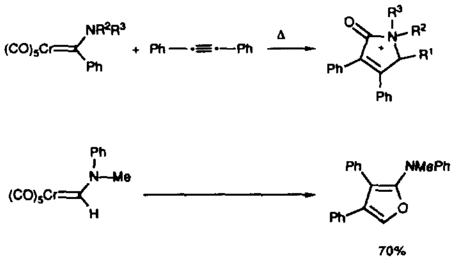


(Equation 648)

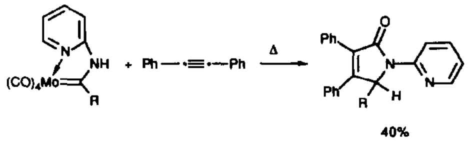


Chromium carbene complexes were used to synthesize a variety of five-membered nitrogen heterocycles (eqn. (649) [846], eqn. (650) [847], eqn. (651) [848], eqn. (652) [849], and eqn. (653) [850]).

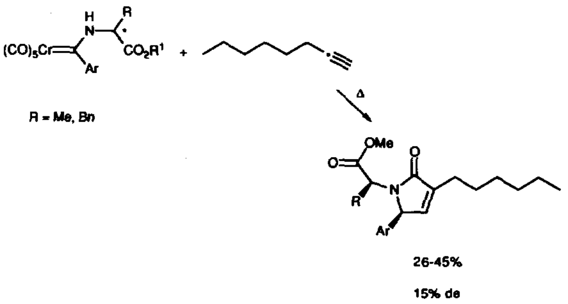
(Equation 649)



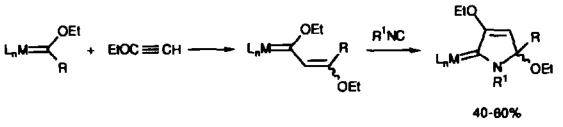
(Equation 650)



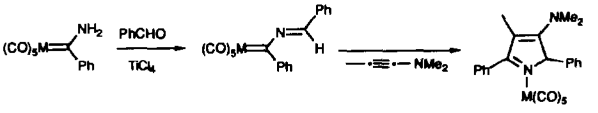
(Equation 651)



(Equation 652)

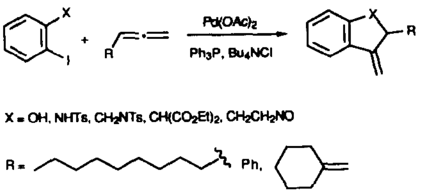


(Equation 653)

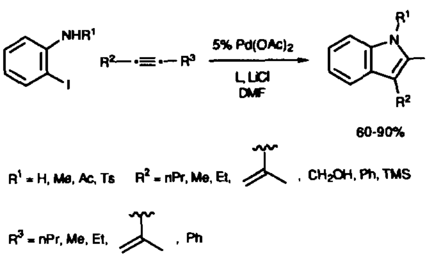


Indoles were synthesized by palladium catalyzed cyclization (eqn. (654) [851] and eqn. (655) [852]), ruthenium catalyzed cyclization (eqn. (656) [853]), and direct palladation (eqn. (657) [854] and eqn. (658) [855]). Other nitrogen heterocycles were synthesized as in eqn. (659) [856] and eqn. (660) [857].

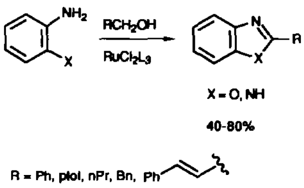
(Equation 654)



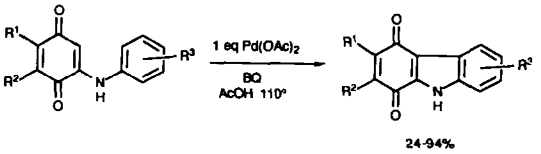
(Equation 655)



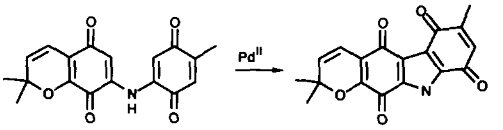
(Equation 656)



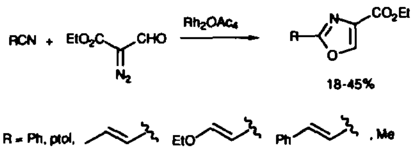
(Equation 657)



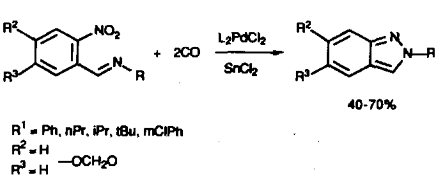
(Equation 658)



(Equation 659)

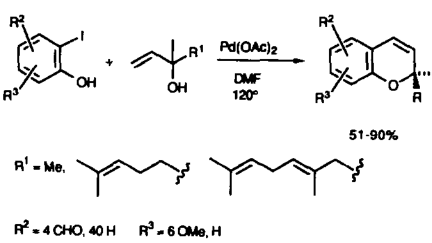


(Equation 660)

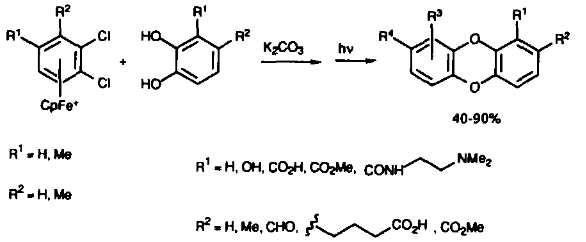


Six-membered oxygen heterocycles were made by palladium catalyzed cyclization (eqn. (661) [858]), and by nucleophilic attack on cationic π-arene iron complexes (eqn. (662) [859]).

(Equation 661)

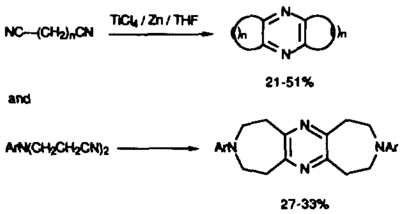


(Equation 662)

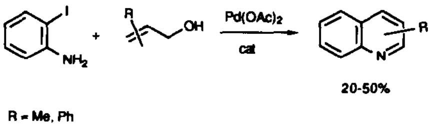


Organocobalt-catalyzed synthesis of pyridines has been reviewed (9 references) [860]. Pyrazines were prepared by low valent titanium coupling of dinitriles (eqn. (663) [861]). Quinolines resulted from palladium catalyzed reactions (eqn. (664) [862] and eqn. (665) [863]). Piperidones were prepared by the ruthenium tetroxide oxidation of piperidines [864], and by nickel (eqn. (666) [865]) and rhodium (eqn. (667) [866]) catalyzed cyclizations. Malononitrile was cyclotrimerized by nickel complexes (eqn. (668) [867]).

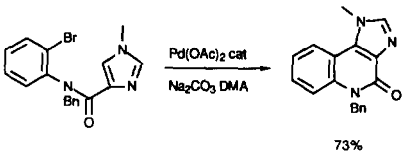
(Equation 663)



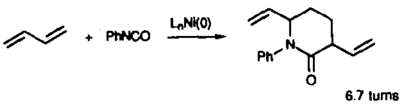
(Equation 664)



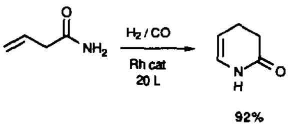
(Equation 665)



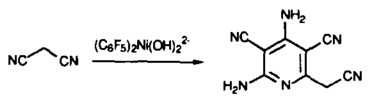
(Equation 666)



(Equation 667)

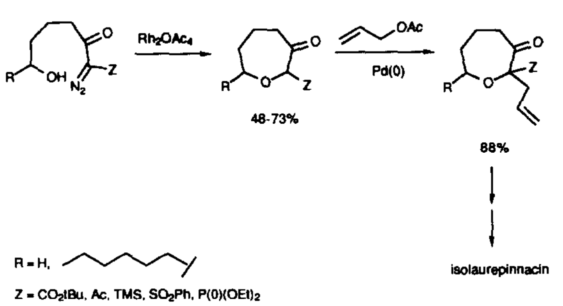


(Equation 668)

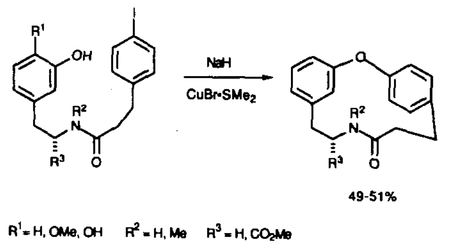


Oxapines (eqn. (669) [868,869]) and perhydroazepines [870,871] were synthesized using transition metal catalysts. The macrocyclic lactam in eqn. (670) was made by an Ullmann-type coupling reaction [872].

(Equation 669)

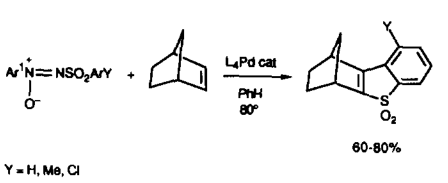


(Equation 670)

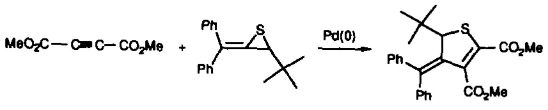


Dissertations dealing with the synthesis of heterocycles via palladiumcatalyzed heteroannulation of dienes [873], and the synthesis of macrolides via organopalladium chemistry — application to the synthesis of zearalenone [874] have appeared. Palladium also catalyzed the synthesis of sulfur heterocycles (eqn. (671) [875] and eqn. (672) [876]). Other strange heterocycles are seen in eqn. (673) [877] and eqn. (674) [878].

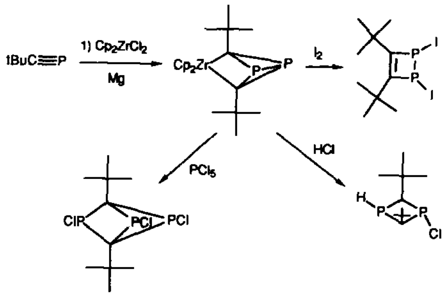
(Equation 671)



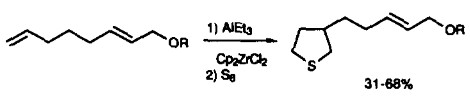
(Equation 672)



(Equation 673)



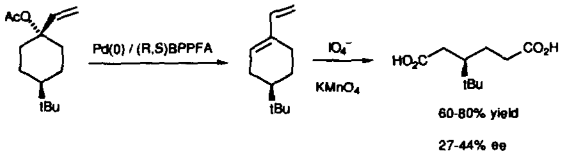
(Equation 674)



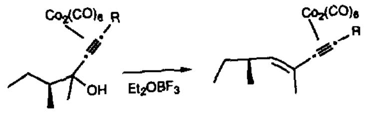
3.6. Alkenes and alkanes

Chiral palladium(0) complexes catalyzed the asymmetric elimination of acetic acid from allyl acetates (eqn. (675) [879]). Cobalt complexes of propargyl alcohols were cleanly dehydrated to enynes (eqn. (676) [880]). Cyclohexenones were aromatized by vanadium oxo species (eqn. (677) [881]).

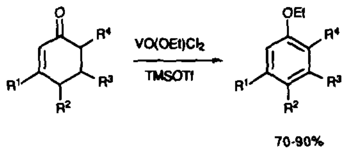
(Equation 675)



(Equation 676)

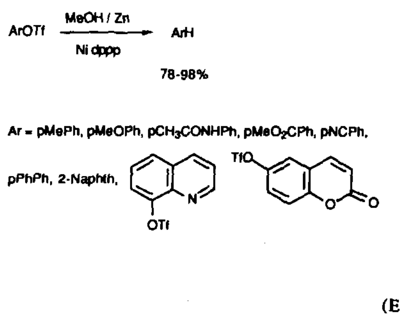


(Equation 677)



Aryl triflates were reduced to arenes by zinc/nickel(0) complexes (eqn. (678) [882]). Aryl chlorides were reduced by rhodium hydride complexes under phase transfer conditions (eqn. (679) [883]). Aryl iodides were reduced by iron carbonyl hydrides (eqn. (680) [884]). Vinyl halides were reduced by tin hydrides in the presence of palladium catalysts (eqn. (681) [885]). Allyl acetates were deacetoxylated by molybdenum hexacarbonyl (eqn. (682) [886]). Chromium complexed aryl ethers were reduced by lithium aluminum hydride (eqn. (683) [887]).

(Equation 678)



(Equation 679)

$$\mathrm{ArCl} + \mathrm{H_2} \xrightarrow[\mathrm{PhCH_3 / NaOH}]{[(\mathrm{Cy_3P})_3\mathrm{Rh(H)Cl_2}]} \mathrm{ArH}$$

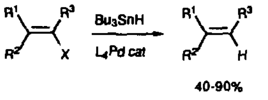
high yields

Ar = Ph, 1-Naphth, pMePh, mMePh, oMePh, pH_2NPh, pMeOPh, pCF_3Ph, pHO_2CPh

(Equation 680)

$$\mathrm{ArI} + \mathrm{KFe(H)(CO)_4} \xrightarrow{\mathrm{MeOH / H_2O}} \mathrm{ArH}$$

(Equation 681)



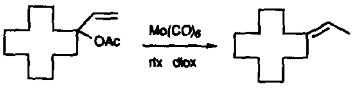
R^1 = nC_{10}, nC_5, H, tBu, C_6F_{13}

R^2 = H, C_{10} R^3 = H, TMS, nC_5, nC_{10}, $Ph(CH_2)_5$

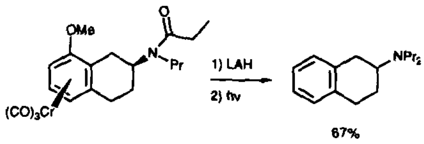
X = Br, I

also $\mathrm{ArI} \longrightarrow \mathrm{ArH}$

(Equation 682)

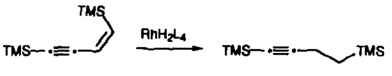


(Equation 683)



Rhodium complexes catalyzed the reduction of enynes to alkynes (eqn. (684) [888]). Palladium(0) catalysts with formate reduced α,β-unsaturated enones in a conjugate fashion [889]. Iridium pentahydrides converted diynones to tetraenones (eqn. (685) [890]).

(Equation 684)



(Equation 685)

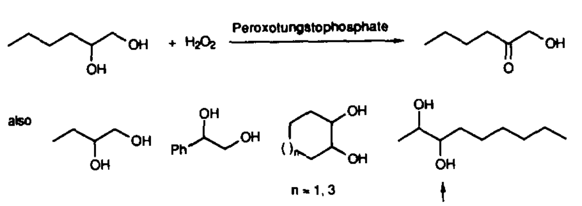
R = Me, Et, nPr, nBu

3.7. *Ketones and aldehydes*

Oxidation of alcohols and diols by peroxometal complexes has been reviewed (7 references) [891]. Alcohols were oxidized to ketones by hydrogen peroxide with

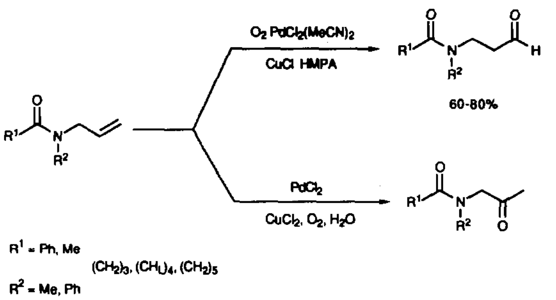
$[PO_4[W(O)CO_2)_2]_4]^{3-}(R^1_4N)_3^+$ [892]. Primary alcohols and aldehydes were oxidized to acids. Diols were oxidized to hydroxyketones by hydrogen peroxide peroxotungstophosphates (eqn. (686) [893]). Primary alcohols were oxidized to aldehydes by hypochlorite in the presence of ruthenium(III) chloride [894]. Benzyl alcohol was oxidized to benzaldehyde by air using $RuCl(OAc)(PPh_3)_3$ with hydroquinone/cobalt salen as cocatalysts [895]. Ruthenium(II) complexes also catalyzed the oxidation of other alcohols [896] and α-hydroxyacids to α-ketoacids [897].

(Equation 686)

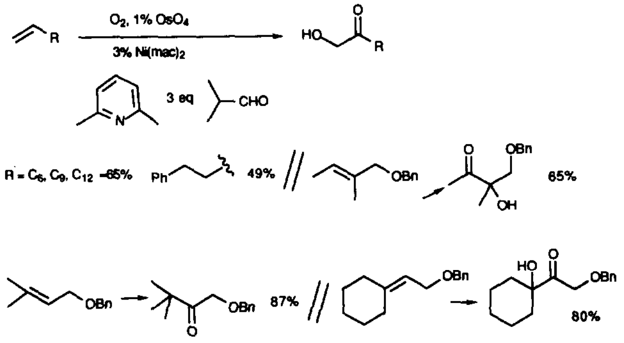


A "true" heterogeneous Wacker catalyst was prepared by exchanging $Pd(NH_3)_4^{2+}$ and Cu^{2+} into y-type zeolites [898]. The regioselectivity of Wacker oxidation of N-allyl amides was controlled by reaction conditions (eqn. (687) [899]). Nickel/osmium/oxygen systems oxidized alkenes to α-hydroxyketones (eqn. (688) [900]).

(Equation 687)

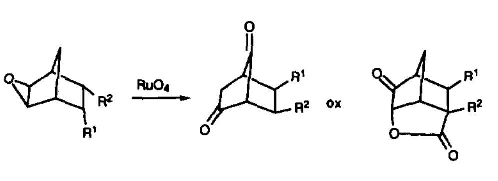


(Equation 688)

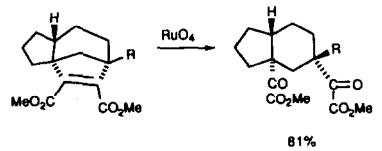


Other oxidative processes giving ketones are shown in eqn. (689) [901], eqn. (690) [902], eqn. (691) [903], and eqn. (692) [904].

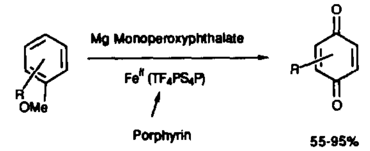
(Equation 689)



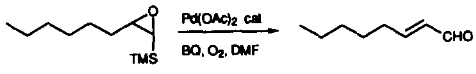
(Equation 690)



(Equation 691)

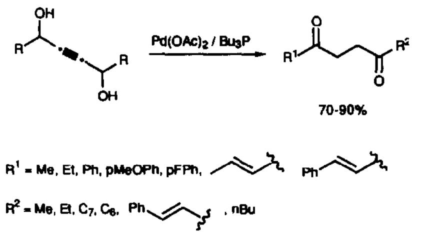


(Equation 692)

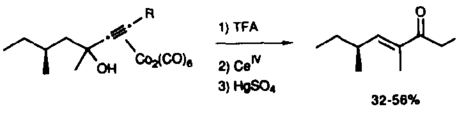


Other unusual approaches to ketones and aldehydes are shown in eqn. (693) [905], eqn. (694) [906], eqn. (695) [907], and eqn. (696) [908].

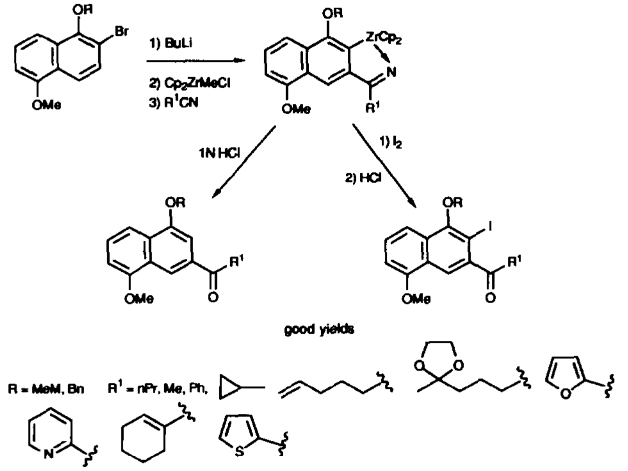
(Equation 693)



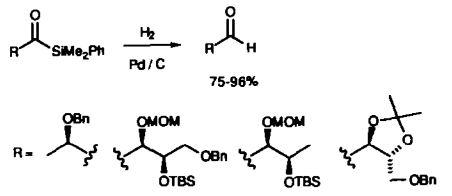
(Equation 694)



(Equation 695)



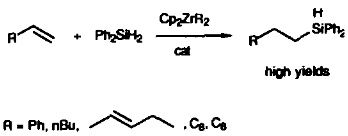
(Equation 696)



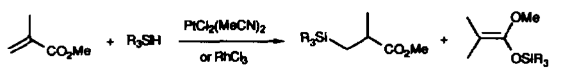
3.8. Organosilanes

The hydrosilylation of alkenes was catalyzed by zirconium complexes (eqn. (697) [909,910]), platinum and rhodium complexes (eqn. (698) [911] and eqn. (699) [912]), and by palladium complexes (eqn. (700) [913]).

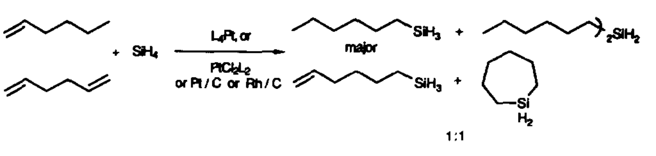
(Equation 697)



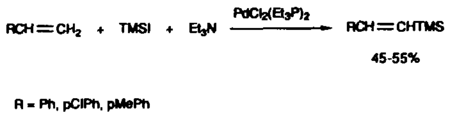
(Equation 698)



(Equation 699)

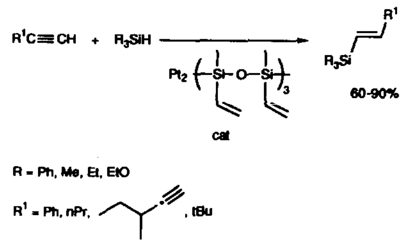


(Equation 700)

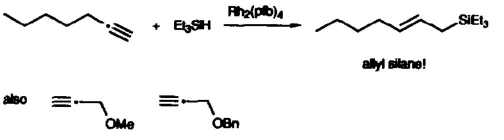


Alkynes were hydrosilylated to vinyl silanes over platinum silyloxy catalysis (eqn. (701) [914]), and rhodium catalysts (eqn. (702) [915]). The same products were made by palladium(0) catalyzed silylstannylation (eqn. (703) [916]). With rhodium(acac) catalyst, internal silylation was observed (eqn. (704) [917]).

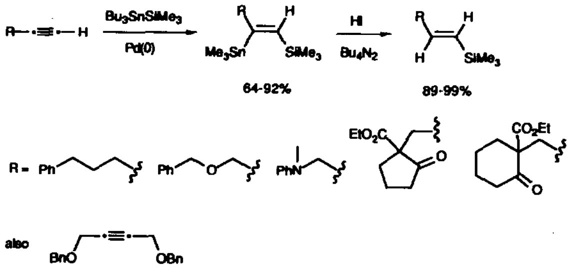
(Equation 701)



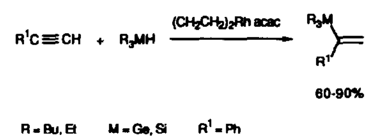
(Equation 702)



(Equation 703)

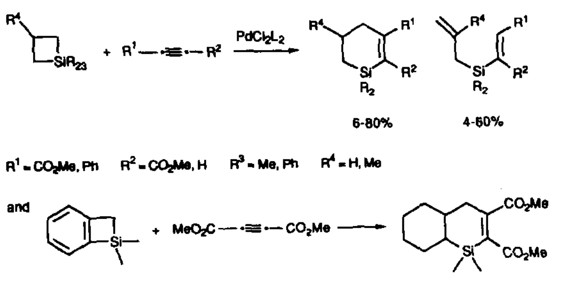


(Equation 704)

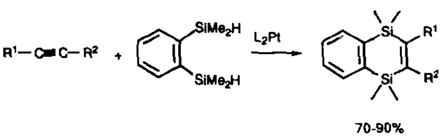


Alkynes were also cyclosilylated (eqn. (705) [918] and eqn. (706) [919]) and polylsilylated (eqn. (707) [920] and eqn. (708) [921]).

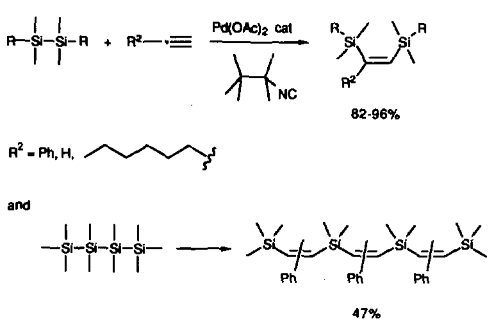
(Equation 705)



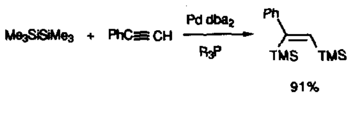
(Equation 706)



(Equation 707)

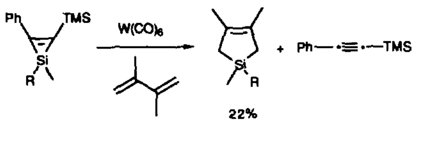


(Equation 708)

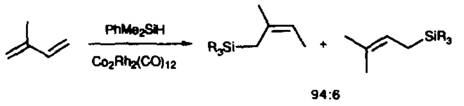


Dienes were readily hydrosilylated (eqn. (709) [922] and eqn. (710) [923]), as were allenes (eqn. (711) [924]).

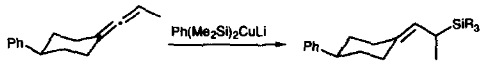
(Equation 709)



(Equation 710)

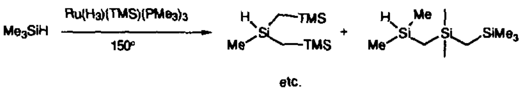


(Equation 711)

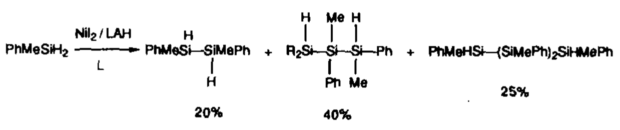


Ruthenium (eqn. (712) [925]) and nickel complexes (eqn. (713) [926]) catalyzed the oligomerization of silanes, while palladium(II) acetate catalyzed the co-oligomerization of silanes with isonitriles (eqn. (714) [927]).

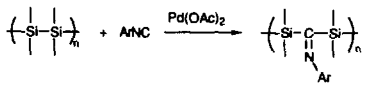
(Equation 712)



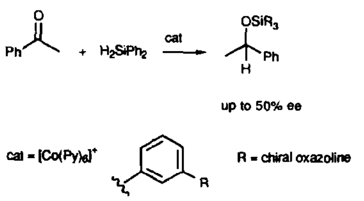
(Equation 713)



(Equation 714)

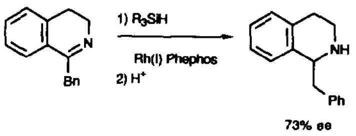


(Equation 715)

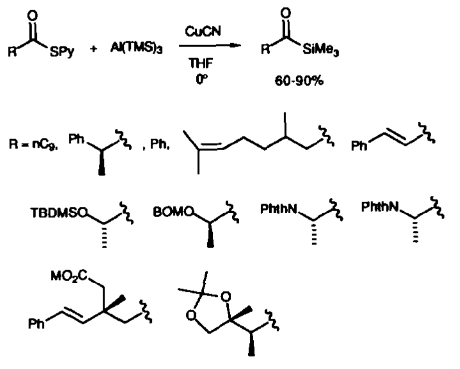


Chiral cobalt (eqn. (715) [928]) and rhodium (eqn. (716) [929,930]) complexes catalyzed the asymmetric hydrosilylation of ketones and imines. Acyl silanes were prepared using copper catalysts (eqn. (717) [931]). Cobalt catalyzed the silylcarbonylation of cyclic orthoesters (eqn. (718) [932]).

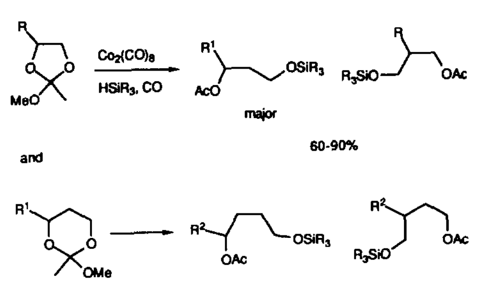
(Equation 716)



(Equation 717)



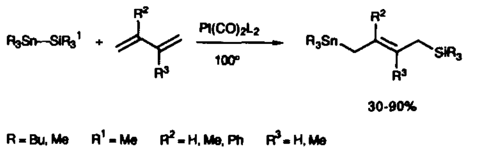
(Equation 718)



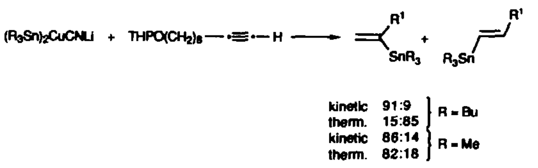
3.9. Miscellaneous

Transition Metal Catalyzed Silylmetallation of Acetylenes — Selective Synthesis of Vinyl Stannanes and Vinyl Silanes was the topic of a dissertation [933]. Transition metals figured extensively in the synthesis of organostannanes (eqn. (719) [934], eqn. (720) [935], eqn. (721) [936], eqn. (722) [937], eqn. (723) [938], and eqn. (724) [939]). Similar chemistry was used to synthesize organogermanes (eqn. (725) [940]).

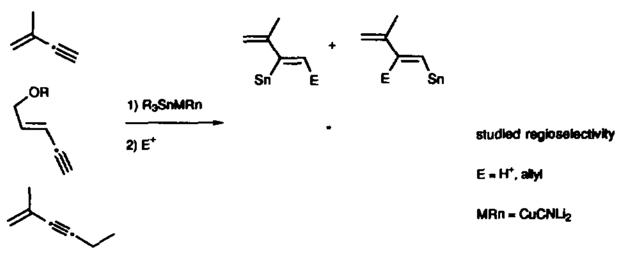
(Equation 719)



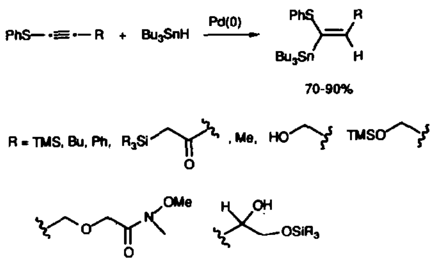
(Equation 720)



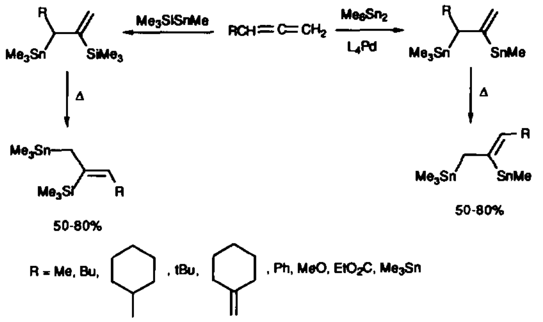
(Equation 721)



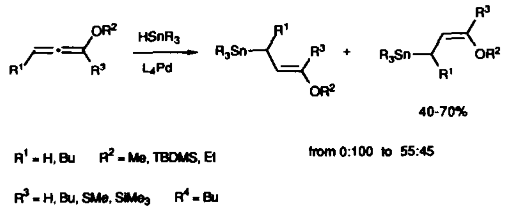
(Equation 722)



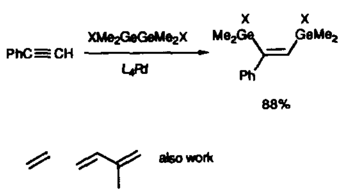
(Equation 723)



(Equation 724)

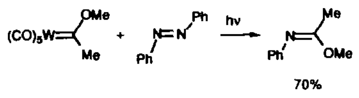


(Equation 725)

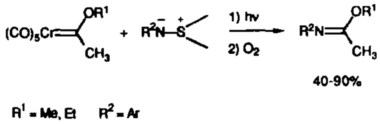


Imidates were synthesized via Group VI carbene complex chemistry (eqn. (726) [941] and eqn. (727) [942]). Ketenimines were produced in the reaction of cobalt isonitriles with diazo compound (eqn. (728) [943]). Tetraazamacrocyclic amines could be monoalkylated by selective complexation to chromium [944]. Palladium catalyzed the reduction of α,β-unsaturated nitro compounds to oximes by ammonium formate [945] while nitro compounds were reduced to azo compounds by titanocene chloride [946].

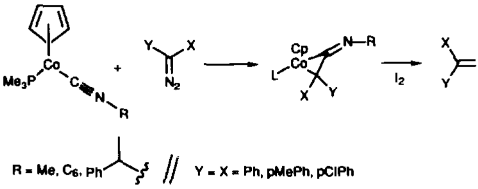
(Equation 726)



(Equation 727)

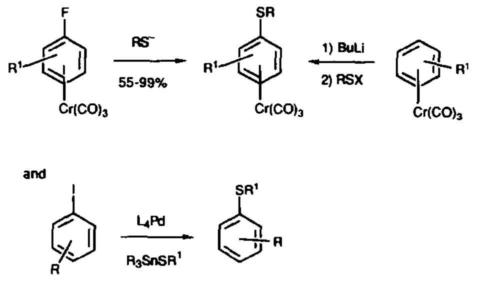


(Equation 728)

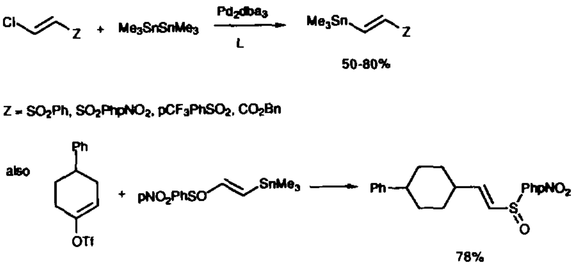


Chromium thiophenol complexes were synthesized by several routes (eqn. (729) [947]). Other processes involving sulfur chemistry are shown in eqn. (730) [948], eqn. (731) [949], eqn. (732) [950], and eqn. (733) [951].

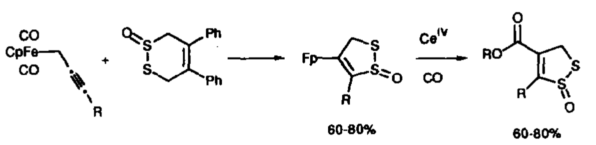
(Equation 729)



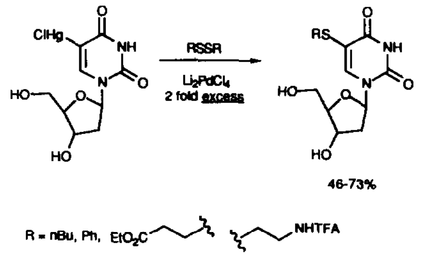
(Equation 730)



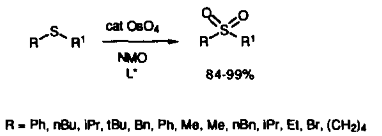
(Equation 731)



(Equation 732)

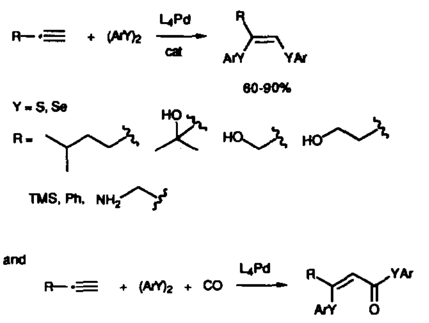


(Equation 733)

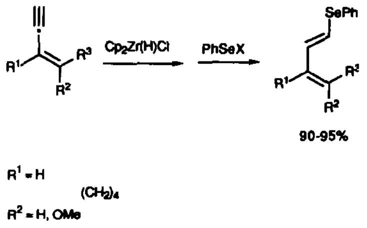


The Binary Reagent PhSeSePh–CuOTf — A Useful Phenylselenating Reagent was the topic of a review [952]. Organoselenium compounds were made by palladium (eqn. (734) [953]) and zirconium mediated processes (eqn. (735) [954]). An efficient hydrozirconation reagent was generated by the reaction of zirconocene dichloride with t-butyl Grignard reagent (eqn. (736) [955]).

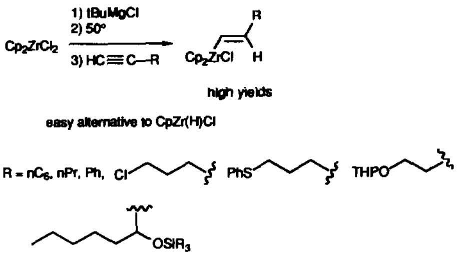
(Equation 734)



(Equation 735)

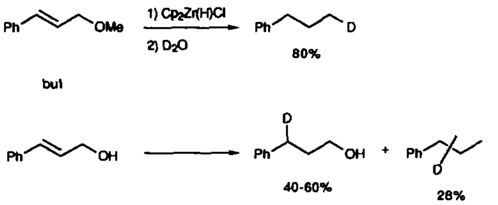


(Equation 736)



Allyl alcohols and ethers were deuterated using zirconium chemistry (eqn. (737) [956]). Rhodium, ruthenium [957] and platinum [958] catalysts were used to introduce tritium into organic compounds.

(Equation 737)



4. Reviews

The following reviews and dissertations have appeared:

Synthesis of Cyclobutane and Cyclopentane Derivatives Using Homogeneous Metal Complex Catalysts (152 references)	[959];
Stoichiometric and Catalytic Functionalization Reactions of Alkynes at Transition Metal Complexes Stabilized by Tripodal Polyphosphine Ligands (6 references)	[960];
Reflection on Organotransition Metal Chemistry (no references)	[961];
Cobalt-Mediated Alkylation of Electron-Rich Oxygen Heterocycles	[962];
Oxidation and Condensation of Alcohols Catalyzed by Ruthenium Complexes (66 references)	[963];
Homogeneous Catalysis of Organic Reactions by Transition Metal Complexes (132 references)	[964];
Metal Complex Catalysis	[965];
Transition-Metal-Promoted Hydroborations of Alkenes, Emerging Methodology for Organic Transformations (65 references)	[966];
Advances in Organometallic Chemistry	[967];
Organometallic Models and Mechanisms (Part B)	[968];
Organometallic Compounds: Syntheses and Applications	[969];
Advances in Metal-Organic Chemistry, Vol. 2	[970];
A Brief History of Organometallic Chemistry in Australia and New Zealand (> 461 references)	[971];
Heterogeneous Catalysis: A Molecular Perspective (12 references)	[972];
Transition Metals in Organic Synthesis: Hydroformylation, Reduction, and Oxidation: Annual Survey Covering the Year 1989 (879 references)	[973];
Selectivity and Homogeneous Transition Metal Catalysis (40 references)	[974];
Investigations Into the Transition Metal Catalyzed Cyclization of Unsaturated α-Monochloro Esters, Acids, and Olefinic Polychloromethyl Derivatives	[975];
Organometallics in Synthesis (> 287 references)	[976];
Homogeneous Catalysis by Transition-Metal Complexes (86 references)	[977];
New Reactions via Complexation of Organo metallic Compounds (12 references)	[978];
Complexes as Catalysts in Organic Chemistry and Biomechanics (10 references)	[979];

The Chemistry of Diene Tricarbonyl Trimethylphosphite Chromium(0) Complexes [1024];
Reactivity of Manganese and Tungsten Carbyne Complexes with Unsaturated Organic Substrates [1025];
Stereochemistry and Catalysis with Zirconium Complexes (17 references) [1026];
Titanium Complex with Chiral 1,4-Diol (6 references) [1027];
Tantalum-Alkyne Complexes “Low-Valent Tantalum ($TaCl_5$–Zn) (6 references) [1028];
Organomanganese Complexes in Organic Synthesis [1029];
Recent Advances in the Chemistry of Metal–Carbon Triple Bonds (213 references) [1030];
Ruthenium Complex-Catalyzed Novel Organic Synthesis via Formyl Carbon–Hydrogen Bond Activation (14 references) [1031];
Coupling of C_1 Ligands: Organometallic Model Reactions (> 10 references) [1032];
Metal-Macrocycle Complexes in Catalysis (90 references) [1033];
Helices, Supramolecular Chemistry and Metal Induced Self Organization (> 13 references) [1034];
Application of Metal Imido Clusters to Chemical-Catalytic Reaction (24 references) [1035];
Metal Vapor Synthesis (17 references) [1036];
Photo-Induced Homogeneous Catalysis (27 references) [1037];
Metal-Mediated Reactions in Nucleoside Synthesis [1038];
Peroxo Complexes of Transition Metals in the Oxidation of Organic Substrates: Some Examples of Selectivity (57 references) [1039];
Transition Metal Chemistry of Cumulenes and Strained Cyclopropene-Containing Molecules [1040];
The Transition Metal-Promoted Conversion of Dichlorovinylcyclobutanes to Cyclohexadienes [1041];
Synthesis of Alkan-2-ones by Dirhodium-Mediated Four Carbon Coupling [1042];
Synthesis of Cyclobutane and Cyclopentane Compounds Using Homogeneous Metal Complex Catalysts (152 references) [1043];
Organometallic and Homogeneous Catalytic Chemistry of Rhodium and Iridium (511 references) [1044];
Synthetic Reactions with Organocopper Reagents (45 references) [1045];
Hydride-Mediated Homogeneous Catalysis. Catalytic Reductions of α,β-Unsaturated Ketones Using Soluble Copper(I) Hydride Complexes [1046];
Highly Selective Synthesis of (E)-Alkene Isosteric Dipeptides with High Optical Purity via Organocyanocopper–Boron Trifluoride Mediated Reaction [1047];
Synthetic Studies Toward Optically Active Anthracyclinones. II. Allylic Cyanocuprates in Synthesis [1048];
S_N2' Additions of Cuprates to Acyclic Vinyloxiranes: A Strategy for the Synthesis of Polyketide Natural Products [1049];
New Tools in Synthetic Organocopper Chemistry (54 references) [1050];
Activation of Carbon–Hydrogen Bonds in Alkanes (15 references) [1051];
Activation of Carbon–carbon Bonds in Saturated Hydrocarbons by Metal Complexes (158 references) [1052];
Activation of CH Bond by Metal Complexes (340 references) [1053];
Metal Complexes as Catalysts for Oxygenation of Organic Compounds [1054];
Nonporphyrinic Metal Complex-Catalyzed Reactions of Iodosylbenzene with Olefins [1055];
Activation of Molecular Oxygen by Transition Metal Complexes (42 references) [1056];
Catalytic Oxygenation of Alkenes by Phosphino-Complexes of Rhodium and Ruthenium (24 references) [1057];
Asymmetric Synthesis via Iron Acyl Complexes [1058];
Applications of Organoiron in Organic Synthesis (24 references) [1059];
The Chemistry of Anionic Iron Olefin Complexes and the Synthesis of Palladium Enolate Complexes [1060];
Iron Acyl Complexes in Synthesis [1061];
Catalyst for Carbon–Carbon Bond Forming Reactions. (1,2,5,6-η-Cyclooctadiene)(1,6-η-Cyclooctatriene)ruthenium(0) [Ru(COD)(COT)] (14 references) [1062];
New Chemical and Stereochemical Applications of Organoiron Complexes (many references) [1063];
Transition Metal-Diene Complexes in Organic Synthesis. Part 8. Iron-Mediated Approach to the Discorhabdin and Prianosin Alkaloids [1064];
An Organoiron Approach to Dihydrodioscorine [1065];
Carbon–Carbon Bond Formation via Carbon-Centered Radicals Generated from Dicarbonyl(η^5-Cyclopentadienyl)Organoiron Complexes [1066];
Acetylenes and Diazo Ketones in Organic Synthesis. Can a Synthetic Organic Chemist Avoid Organometallic Chemistry? (> 45 references) [1067];

Studies on Novel Catalytic Reactions Using Transition Metal Complexes (19 references) [980];
Metal-Catalyzed Reactions in Organic Chemistry [981];
Organometallic Approaches to the Synthesis of Tridachiapyrones [982];
Chemistry and Synthetic Utility of Metal Complexed Indoles (> 40 references) [983];
Displacement of Aliphatic Nitro Groups by Carbon and Heteroatom Nucleophiles (64 references) [984];
Lipoxins, and Related Eiconosides; Biosynthesis, Biological Properties, and Chemical Synthesis (129 references) [985];
New Cyclization Reactions Mediated by Nickel Complexes (6 references) [986];
Look What Palladium Catalyzes (40 references) [987];
Palladium-Mediated Cyclizations [988];
Transition Metal-Mediated Bond Activation Studies: Homogeneous Bond Activation of 8-Substituted Quinolines by Rhodium(I) and Iridium(I) Complexes, and of Neophyl Derivatives by Platinum(II) Complexes [989];
The Atom Economy: A Search for Synthetic Efficiency (> 81 references) [990];
Directed Ortho Metalation and Palladium Catalyzed Aryl–Aryl Cross-Coupling Reactions. Synthesis of Heteroaromatics and Alkaloids [991];
Functionalization of Heterocycles by Ni and Pd Catalyzed Reactions (228 references) [992];
trans-Bis(5-acyloxy-1,2,3-η^3-cyclohexenyl)-palladium Complexes by Palladium(II) Promoted Additions to 1,4-cyclohexadienes. Synthesis and Reactions [993];
Organopalladium Complexes in Organic Synthesis [994];
Palladium-Catalyzed Cyclization of Oxyhexatrienes [995];
Palladium-Catalyzed Hydrogenolysis of Allylic Compounds with Formic Acid. Its Application to Organic Synthesis (29 references) [996];
C8-Substituted Derivatives of 2-(dipropylamino)tetralin: Palladium-Catalyzed Synthesis and Interactions with 5-HT$_{1A}$-Receptors [997];
Palladium Mediated Cyclization Reactions: Evidence for Spirocyclic Intermediate Species for the Annulation of Aryl Groups [998];
Asymmetric Synthesis with Palladium Catalysts (6 references) [999];
Palladium-Catalyzed Approaches to the Ergot Alkaloids. 2. Captodative Allenes from Chromium-Carbene Complexes [1000];
Organic Synthesis via Palladium Coupling Reactions [1001];
Group 10 Transition Metal-Catalyzed Carbon–Carbon Bond Forming Reactions [1002];
Platinum-Group Metal Catalysis in the Synthesis of Chemicals from Synthesis Gas (> 301 references) [1003];
Organometallic and Homogeneous Catalytic Chemistry of Palladium and Platinum (> 408 references) [1004];
Organopalladium Approaches to Prostaglandins [1005];
Enantioselective Synthesis Using Chiral Heterogeneous Catalysts (119 references) [1006];
The Chiral Auxilliary $[(C_5H_5)Fe(CO)(PPh_3)]$ for Asymmetric Synthesis (48 references) [1007];
Enantioselective Catalysis with Metal Complexes Containing Heterocyclic Ligands [1008];
Design of New Catalytic Reactions and Catalytic Asymmetric Synthesis (18 references) [1009];
Synthesis of Chiral Catalysts and Their Application to Asymmetric Cross-Coupling Reactions and Selective Hydrogenation [1010];
Asymmetric Synthesis via Iron Acyl Complexes [1011];
Optically Active Sulfoxides and Low-Valent Titanium in Asymmetric Synthesis of Natural Products (18 references) [1012];
Enantioselective Catalysis with Transition Metal Compound [1013];
Asymmetric Synthesis with Chiral Metal complexes as Catalysts (45 references) [1014];
The Synthesis, Structure, and Reactivity of Chiral Rhenium Ketone Complexes [1015];
Chirality Recognition in Synthesis (21 references) [1016];
The Asymmetric Alkylations of Chiral Transition Metal Complexes of (+)-Camphor Imine [1017];
Reagent for Asymmetric Cross-Coupling (Chiral Ferrocenylphosphine-palladium Complex) (6 references) [1018];
Acetylenes and Diazoketones in Organic Synthesis (42 references) [1019];
Aminocarbene Complexes of Chromium and Molybdenum: Initiators for Cascade Reactions with Alkynes Leading to Heterocyclic Compounds via Nitrogen Ylides (60 references) [1020];
Cyclization of Hexene Over $LMo(CO)_5$–$TiCl_4$ Catalyst System [1021];
Synthesis and Electrophilic Reactions of Molybdenum Formyl Complexes [1022];
Synthesis and Reactivity of Tantalum and Tungsten Alkyne Complexes: Models for Alkyne Cyclization [1023];

Cp_2MCl_2–AgX (M = Zr, Hf) (7 references) [1068]; Catalytic Reduction of Carbon Dioxide by Dihydrogen in the presence of Transition Metal Complexes [1069].

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