Coordination Chemistry Reviews, 83 (1988) 137–167
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

RECENT STUDIES ON ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS

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(First received 28 November 1986; in final form 13 February 1987)

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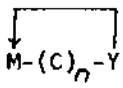
A. INTRODUCTION

Organometallic intramolecular-coordination compounds are shown in formula **1** where Y represents either a coordinating atom or group. The compounds mainly have N, P, As, O or S as the coordinating atom when Y is a coordinating atom, and generally tend to form a five-membered ring structure ($n = 3$ in formula **1**). When Y is a coordinating group, the compounds mainly have vinylene, π-allyl, cyclopentadienyl, or aryl as the coordinating group. These compounds are also generally stable when n is 3. In this review, the former compounds are termed σ-coordination compounds and the latter are π-coordination compounds.



M = metal
Y = coordinating atom or group
$n \geq 1$

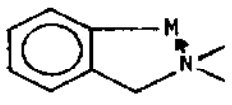
1

0010-8545/88/$10.85

In 1986, the author published a monograph [1] on organometallic intramolecular-coordination compounds by compiling his twelve reviews [2–13] and other articles until the end of 1984. This review is compiled mainly from articles published since 1985.

B. NITROGEN COMPOUNDS

Among the nitrogen, phosphorus, arsenic, oxygen, and sulfur compounds in the area of organometallic intramolecular-coordination compounds, there has been especial interest in the nitrogen compounds [14]. The cyclometalation reaction to form nitrogen compounds is fast and the isolation of these products relatively easy. These major nitrogen compounds are divided into ten groups depending on the nature of the ligand: benzylamines **2**, tolylamines **3**, benzamides **4**, ferrocenylmethylamines **5**, benzylideneamines **6**, azobenzenes **7**, phenyldiazene **8**, heteroaromatic compounds **9**, alkylamines **10** and imines **11**.



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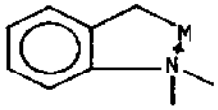

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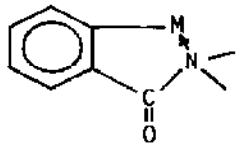

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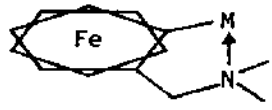

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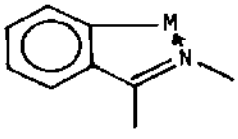

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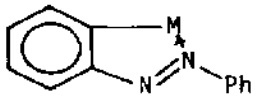

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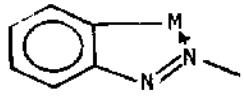

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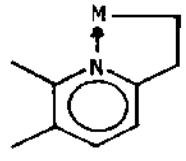

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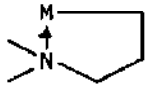

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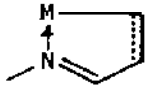

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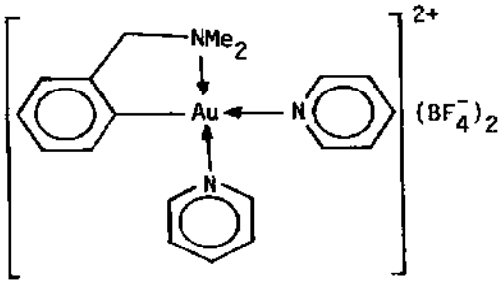
The benzylamines **2** have been reported with palladium [15–21], chromium [22,23], manganese [23], lithium [24,25], and gold [26] as the metal. Structures of palladium [15,18,19], chromium [22] and gold [26] compounds have been determined by X-ray diffraction studies, e.g. **12**.

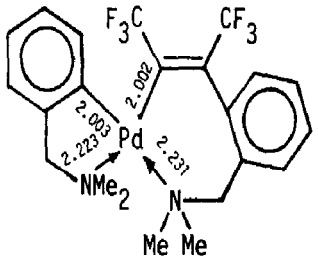


12

In organometallic intramolecular-coordination compounds, the five-membered ring is generally most stable because the ring size should have the most ideal geometry (bond angles and bond lengths) of all the possible ring sizes [13,14]. Generally the other membered rings are labile and the M–Y bonds are easily cleaved by other donor ligands such as amines and phosphines. The *cis*-benzylamine palladium compound with a seven-membered ring **13** reacts with PMe_2Ph to give **14** as the major product displacing the nitrogen atom of the seven-membered ring [19a]. However, reaction of the *trans* compound gives **16** as the major product displacing the nitrogen atom of the five-membered ring. Both products have been characterized by X-ray diffraction [19a]. It is evident that the seven-membered ring bond strengths are weaker than those of the five-membered ring from the data of Pd–C* and Pd–N bond lengths as shown in formulae **14** and **16**. The latter reaction is a very rare case since rings other than a five-membered ring are, usually, at first cleaved by donor compounds such as phosphines and amines [1]. The five-membered ring in the *cis*-compound **13** bonded with the hexafluorobutene moiety is almost as weak as the seven-membered ring in the same compound. Therefore, the author presumed that the five-membered ring in the *trans* form of the same compound might be weaker than the seven-membered ring, because the same seven-membered ring (Pd–N = 2.215 Å, Pd–C = 2.016 Å) in the compound having 8-methylquinoline bonded by hexafluorobut-2-yne shows stronger bonding than that in the five-membered ring of the above *cis*-compound **13** [19b].

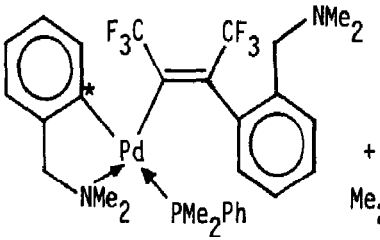
Compounds having a benzylamine carbon skeleton include [*o*,*o*′-bis[(dimethylamino)methyl]phenyl]metal compounds (metal = Ni [27,28], Pd [29] or Pt [28–32]) **17**, [2-(1′-dimethylamino)ethylphenyl]diphenylborane **18** [33], [1-(1′-dimethylamino)ethyl-2-naphthyl]diphenylborane **19** [33], and 8-(dimethylamino)-1-naphthylsilane **20** [34–36].

The compounds **17** with a tridentate ligand have a distorted square-planar (Pt) [29,31], square-pyramidal (Pt) [28] or octahedral (Ni) [27] geometry around the metal with the phenyl rings in the same plane as the N,N′,C



13

PMe_2Ph



major 14

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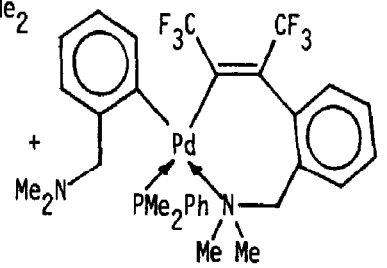
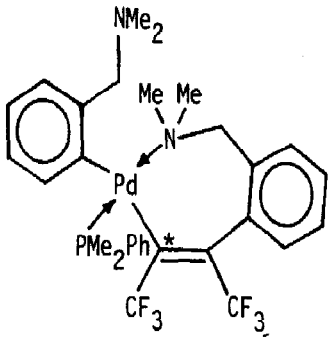


minor 15

Pd-N = 2.158 Å

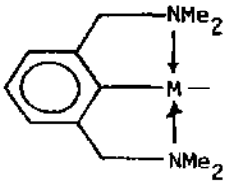
Pd-C*= 2.031 Å



16

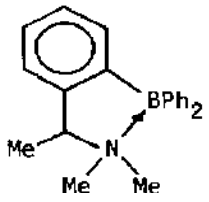
Pd-N = 2.226 Å

Pd-C*= 2.097 Å



M = Ni, Pd, Pt

17



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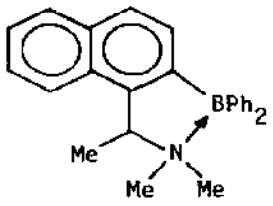

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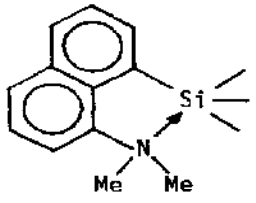


20

donor atom of the terdentate ligand and the metal. The square-planar platinum complex **21** reacts with methyl iodide to give the arenonium complex **22** [31]. The four-coordinate complex **22** also has square planar geometry, but the methylated phenyl ring makes a dihedral angle of 70.7° with the coordination plane of the complex [31], and the Pt–C1 bond length (2.293 Å) is longer than a Pt–phenyl bond (average Pt–phenyl 2.00 Å) [31,32].

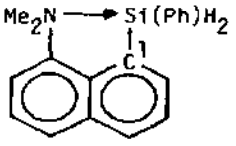
21

Pt-C^1 = 2.293 Å
Pt-C^2 = 2.005 Å

22

When the five-membered ring of 8-(dimethylaminonaphthyl)silyl **23** is compared with the six-membered ring of 8-(dimethylaminomethyl-naphthyl)silyl **24** one notes that the former Si–N bond is stronger than the

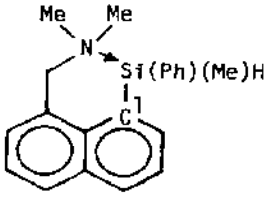
latter since the former is about 0.08 Å shorter, and the difference of the δ^{29}Si chemical shift in the former compound **23** to the chemical shift of a similar compound with no amino group, is larger than the corresponding difference in the latter compound **24** [36].



23

Si-N = 2.584 Å
Si-C = 1.881 Å

δ^{29}Si = -44.16 ppm
δ^{29}Si = -35.62 ppm(for 1-$C_{10}H_7(C_6H_5)SiH_2$)
$\Delta\delta^{29}$Si = 8.54 ppm

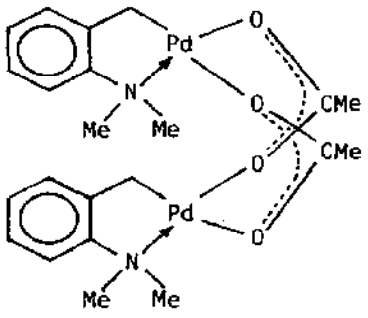


24

Si-N = 2.66 Å
Si-C = 1.88 Å

δ^{29}Si = -25.84 ppm
δ^{29}Si = -19.81 ppm(for 1-$C_{10}H_7(C_6H_5)Si(Me)H$)
$\Delta\delta^{29}$Si = 6.03 ppm

Concerning tolylamines **3** and aminoferrocenes **5**, there are [2-(dimethylamino)phenyl]methylpalladium **25** [37], and [(dimethylamino)methylferrocene palladium **26** [38,39]. The latter aminoferrocene is frequently used as an intermediate for organic syntheses [13,39].



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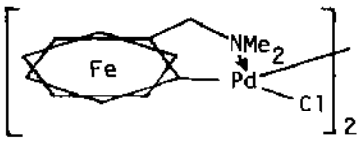

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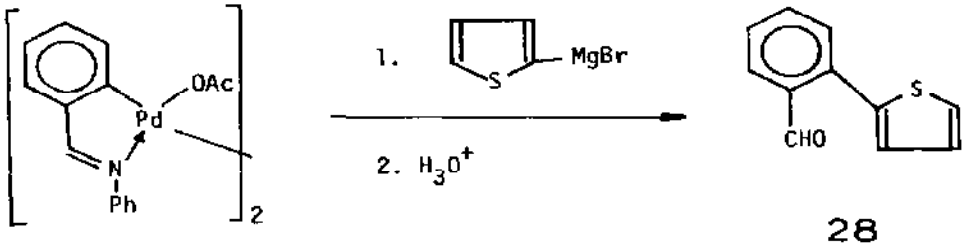
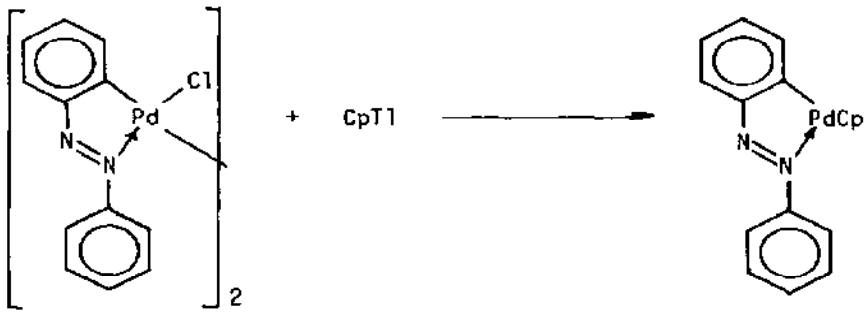
Benzylideneamines **6** [40–43] are used as intermediates for syntheses of *ortho*-derivatives of benzaldehyde. This synthetic method was developed by Murahashi et al. [44] in 1974. For example, benzylideneamine palladium **27** prepared from $Pd(OAc)_2$ and the condensation product of benzaldehyde and aniline, reacts with 2-thienylmagnesium bromide to give 2-(2-thienyl)benzaldehyde **28** [40] by the replacement of the metal with the 2-thienyl group.



27 28

Generally cyclometalated palladium compounds [45–48] are more reactive than the corresponding platinum compounds. For example, azobenzenepalladium compounds easily react with cyclopentadienylthallium to give the cyclopentadienylpalladium compound **30**. On the other hand, treatment of the azobenzeneplatinum compound **31** causes no reaction, but the carbonyl derivative **32**, obtained by reaction with carbon monoxide, immediately reacts with cyclopentadienylthallium to give cyclopentadienylplatinum compounds **33** [46].



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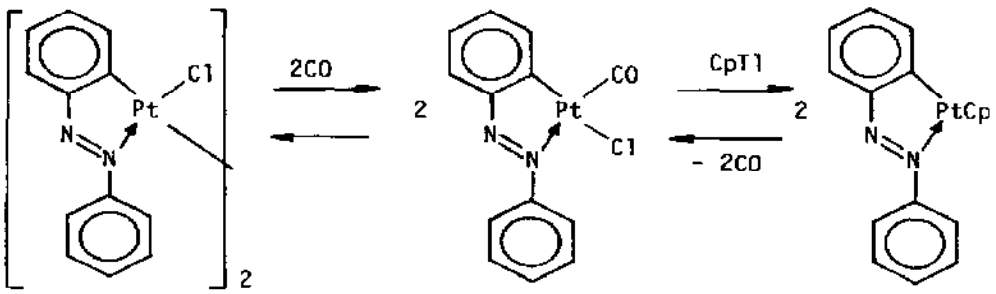
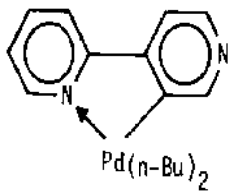


31 32 33

Heteroaromatic compounds **9** have been reported containing 2,4′-bipyridyl [49–53], quinoline [54–57] and phenanthroline compounds [52,53], e.g.,



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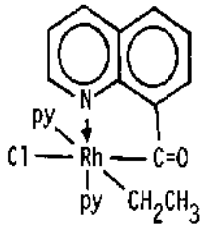

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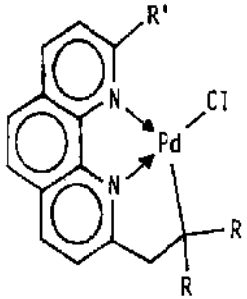

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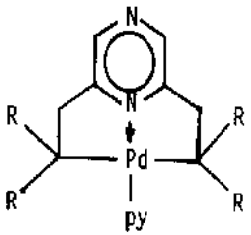
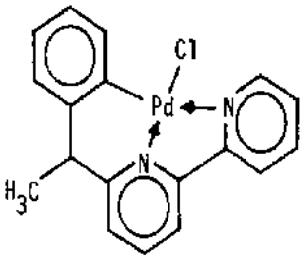
R = COOMe

R' = $CH_2CH(COOMe)_2$



R = COOMe

37



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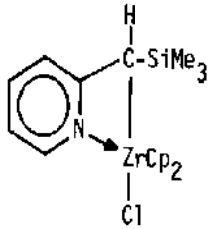
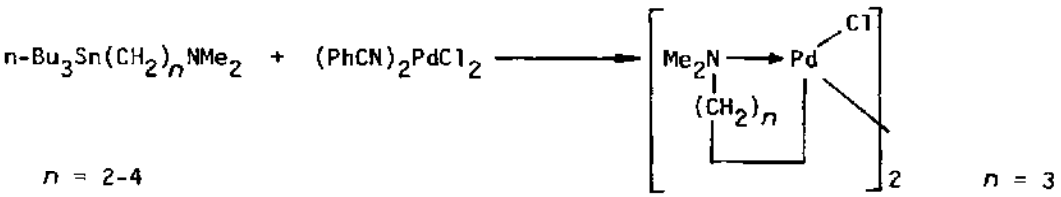


39

34 [49], **35** [56], and **36** [53], respectively. Other heteroaromatic compounds include pyrazine compounds [53], e.g. **37**, and pyridine compounds [58–60], e.g. **38** [59] and **39** [60].

The reaction of *N,N*-dimethylaminoalkyltri-n-butyltin (n-$Bu_3Sn(CH_2)_n NMe_2$; $n = 2$, 3, 4) with bis(benzonitrile)dichloropalladium gives only a cyclopalladated *N,N*-dimethylaminopropyl compound having a five-membered ring **40** ($n = 3$), but the reactions ($n = 2$ or 4) at room temperature, produced only palladium metal [57]. In the similar reaction of organotin esters ($Br_2Sn(CH_2)_nCOOMe$, $n = 1$, 2, 3), the formation of four- or six-membered rings is difficult [1]. Suggs and Lee [57] have determined the structure of *N,N*-dimethylaminopropylpalladium **40** and point out that it is possible that the conformations of organometallic five-membered rings seen in crystal structures such as **40** represent true energy minima and are not dominated by crystal packing [1].



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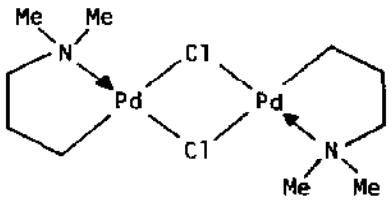
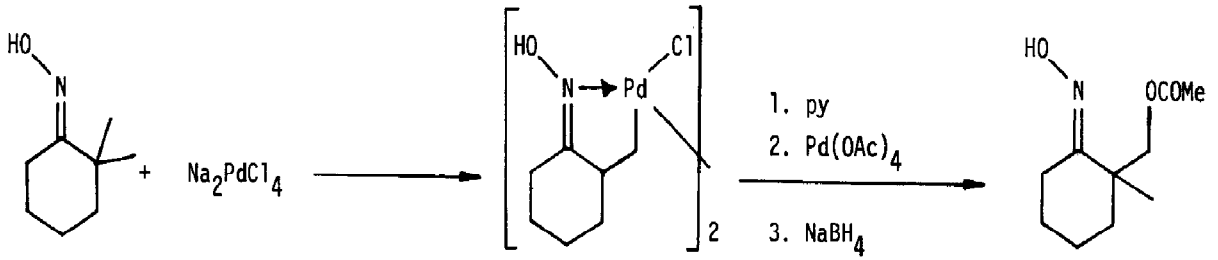


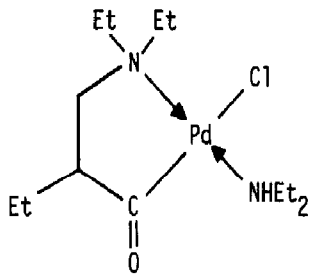
Pd-N = 2.085 Å
Pd-C = 1.998 Å (the sum of covalent radii is 2.08 Å)

Alkylamines **10**, other than **40**, have been reported for silicon [61], lithium [62], palladium [63], and manganese [64].

Concerning the imines **11** [65,66], cyclopalladation of oxime **41** has been reported, and the product **42** is easily converted to the derivative **43** having a functional group at the γ-position to the nitrogen atom by a replacement reaction at the palladium atom [65]. This reaction has been applied to the synthesis of a lupanone oxime derivative [65,66].



41 42 43



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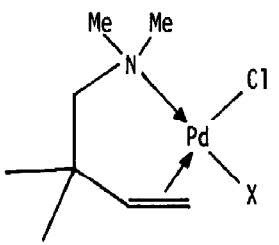


45

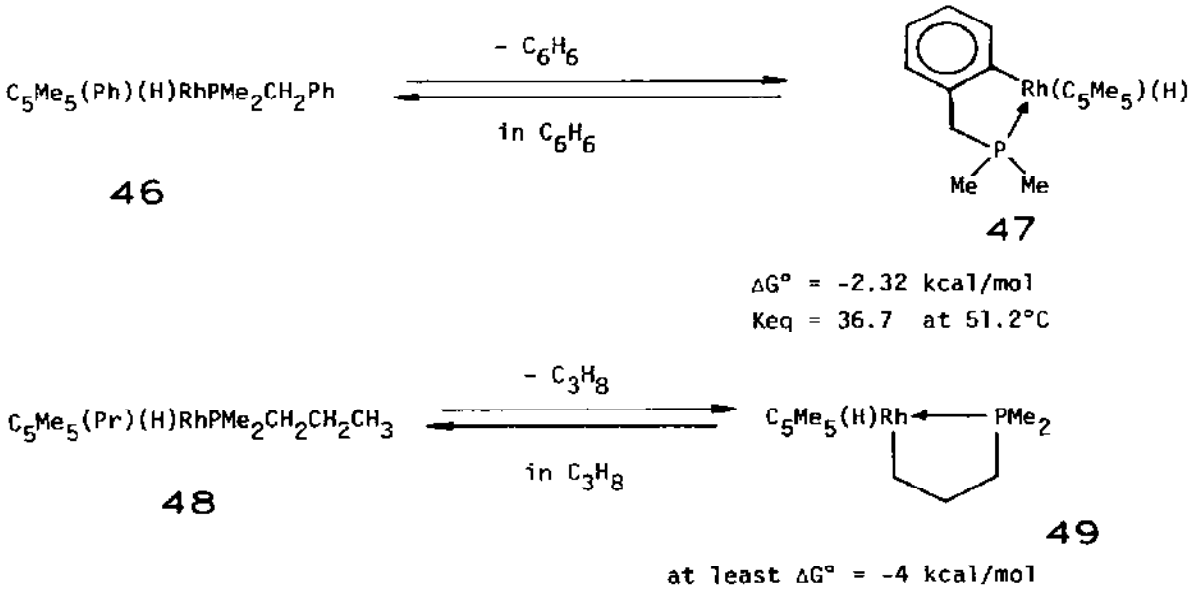
X = Cl, CH_2Cl, CH_2OEt, CH_3, CH_2OMe

Other nitrogen compounds include an aminoacyl compound **44** [67], *N*,*N*-dimethylaminobutenylpalladium **45** [68], etc. [20].

C. PHOSPHORUS COMPOUNDS

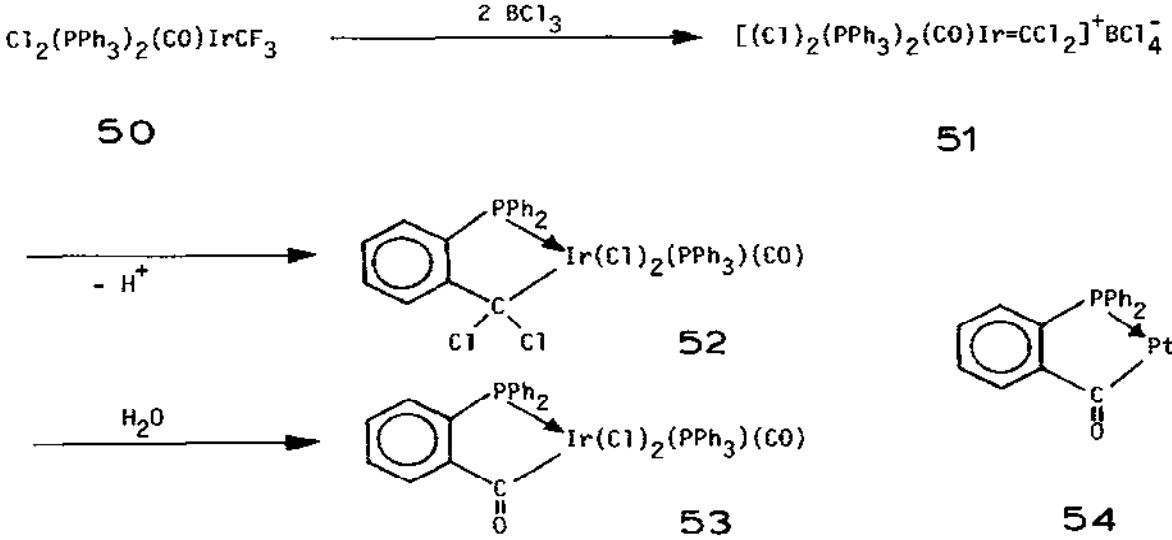
Phosphorus compounds have include benzylphosphines [69], tolylphosphines [60,70] and alkylphosphines [69,71] corresponding to the nitrogen compounds **2**, **3**, and **10**, respectively.

Jones and Feher [69] studied the kinetics and thermodynamics of intra- and intermolecular carbon–hydrogen bond activation by equilibration of both the benzylphosphine compound **46** and its cyclometalated analogue **47**, and the alkylphosphine **48** and its analogue **49**. A moderately high thermodynamic preference for intramolecular C–H bond activation was found for both aromatic and alkyl C–H bonds. On the other hand, in both cases the kinetics selectively favour inter- over intra-molecular reaction when neat solvent is the competing reactant. Therefore, unimolecular reaction to form small unstrained rings is favored over bimolecular reactions thermodynamically but not kinetically [69].

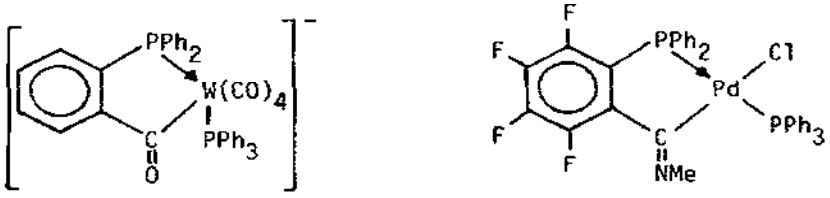


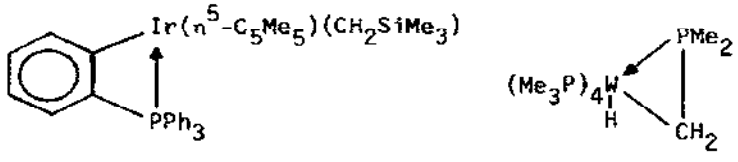
The reaction of the trifluoromethyliridium compound **50** with boron trichloride gives the cationic dichlorocarbene compound **51**, which immediately undergoes metallacycle formation by electrophilic attack of the CCl_2 ligand on a benzene ring of one PPh_3 ligand to give the cyclometalated *o*-dichloromethyl compound **52**. The two α-chlorine atoms of **52** are reactive, as demonstrated by the extreme moisture-sensitivity of **52**, which readily hydrolyses to the metallacyclic acyl compound **53** [72,73]. The

structures of **53** and the other acyl compound **54** [74] have been determined by X-ray diffraction [72,74].



The other five-membered ring phosphorus compounds include another acyl compound **55** [75] and imine **56** [76]. The other ring phosphorus compounds include the seven- **57** [71], eight- **58** [71], four- [77–79] (e.g. **59** [77]), and three- [80–82] (e.g. **60** [80]), etc. [83–86].

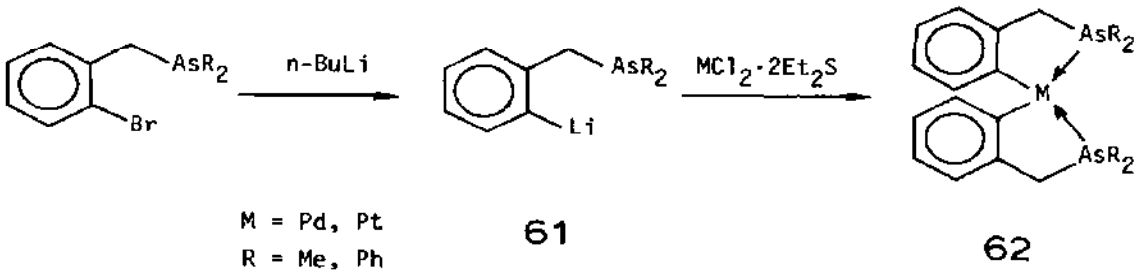


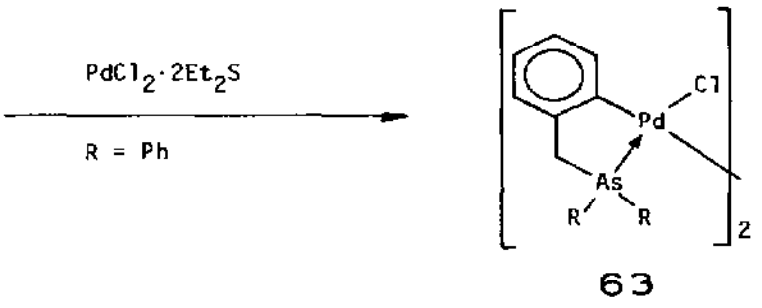


D. ARSENIC COMPOUNDS

The *ortho*-metalation reactivity of benzylarsines is lower than that of benzylamines **2** or benzylphosphines. Hence, active intermediates such as *o*-lithiobenzylarsines, prepared by lithiation of *o*-bromobenzylarsine, are often used as starting compounds.

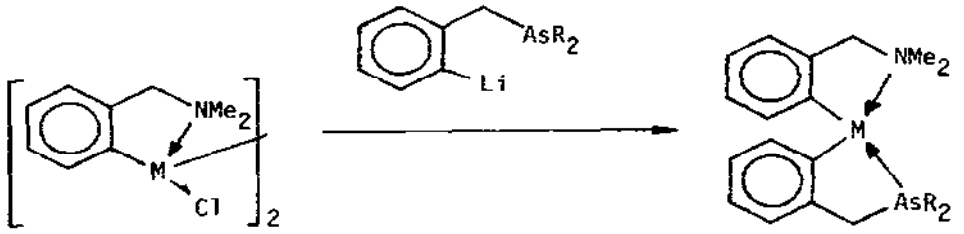
The *o*-lithiobenzyldiorganoarsines **61** react with palladium or platinum chloride to give the bicyclic benzylarsine compounds **62**, of which the diphenylarsine derivative **62** (R = Ph) are converted to chloro-bridged binuclear compounds **63** by reaction with palladium chloride. Further, reac-



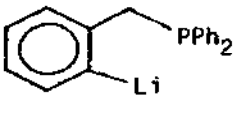


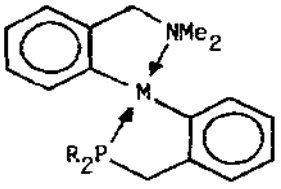
tions of the chloro-bridged compounds **63′** and **63″** with *o*-lithiobenzylamines or *o*-lithiobenzylphosphine form the asymmetric metallacycles **64**–**66** with two different donor atoms in the molecule [87].

The arsinetitanium compound coordinated with a cyclopentadienyl group **67** has been prepared by the replacement reaction of trimethylsilyl with trichlorotitanium [88].

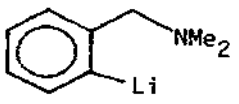


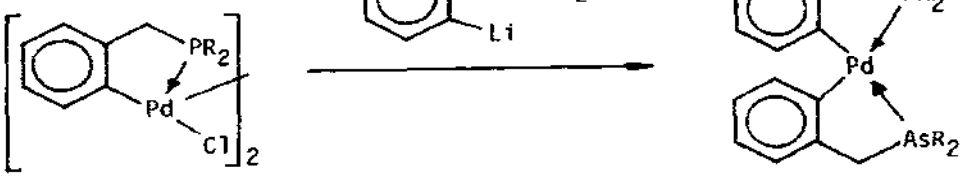
63′ 65



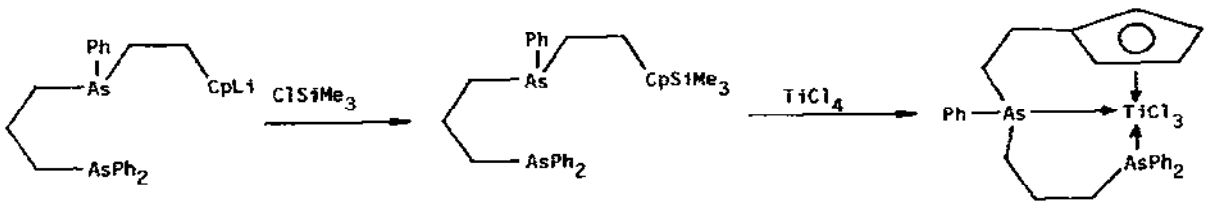


64





63″ R = Me, Ph M = Pd, Pt 66



67

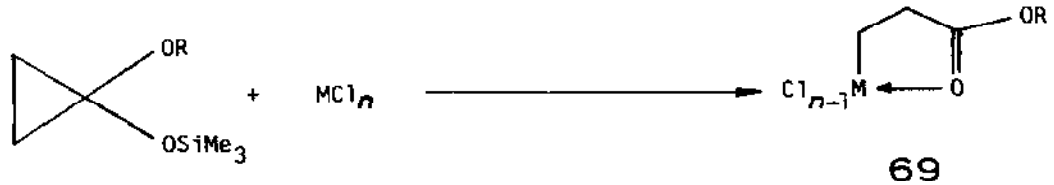
E. OXYGEN COMPOUNDS

Oxygen ligands consist mainly of two kinds of groups, i.e. carbonyl and alkoxy or aryloxy groups. The carbonyl groups are ester carbonyl, keto carbonyl, and, rarely, carboxylic acid carbonyl and aldehyde carbonyl as a ligand group.

The other specific example, sulfinyl group, is shown in formula **68** [89].

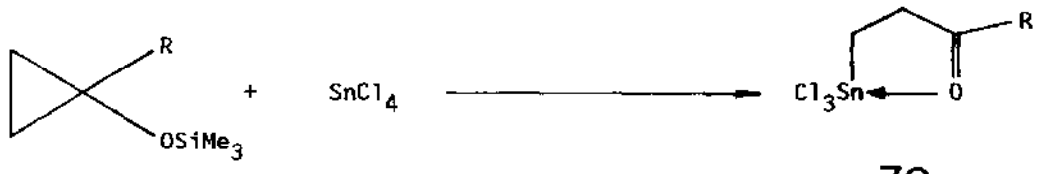
68

The ring-opening reaction of 1-siloxy-1-alkoxycyclopropane with main-group metal halides gives the chelate ester **69** [90,91]. On the other hand, the ring-opening reaction of 1-siloxy-1-alkyl (or aryl)cyclopropane gives the corresponding chelate ketones derivatives **70**. The subsequent treatment of the ketones **70** with dimethyl sulfoxide results in facile dehydrostannation to give a good yield of 2-methylene ketones **71** [92].

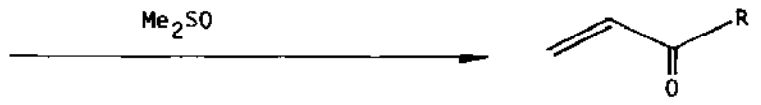


69

MCl_n = $TiCl_4$, $SnCl_4$, $SbCl_5$



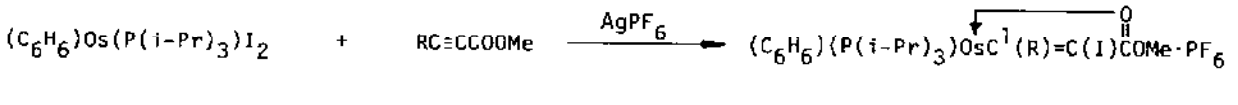
70



R = t-Bu, i-Pr, Ph, etc.

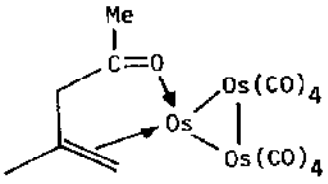
71

The reaction of a benzene osmium diiodide derivative with alkyne esters gives the five-membered metallacyclic compounds **72** by insertion of the alkyne into one of the Os–I bonds. The Os–C1 bond in the compound **72** is considered to be a canonical form with a metal–carbene bond, since the distance (2.02 Å) lies between that of an Os–C single and Os=C double bond [93].



72

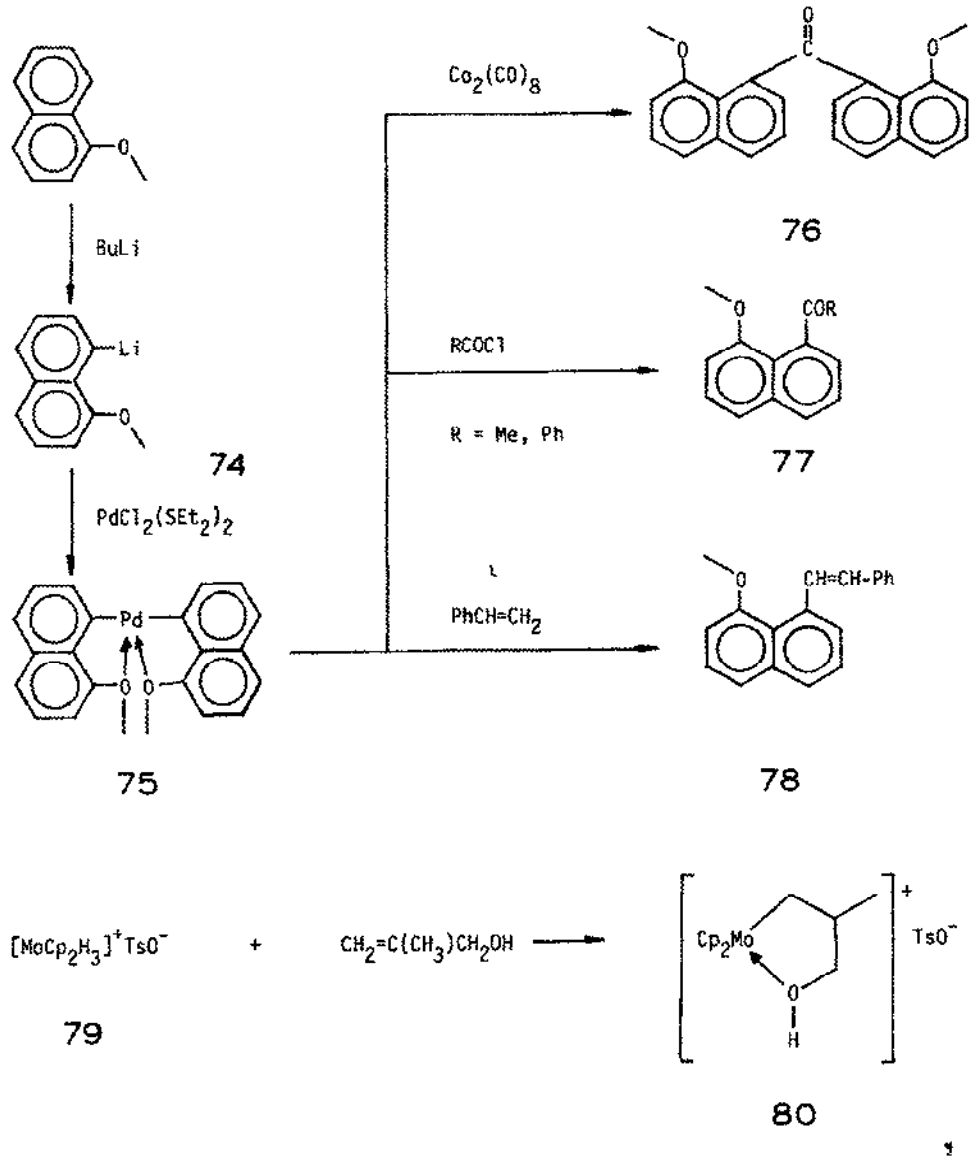
Other esters or ketones having a five-membered ring structure include molybdenum [94], ruthenium [95], tungsten [96,97], and tellurium compounds [98]. There is also a four-membered ring aldehyde [99] and a 5.5-membered ring ketone (e.g. **73** [100]).



73

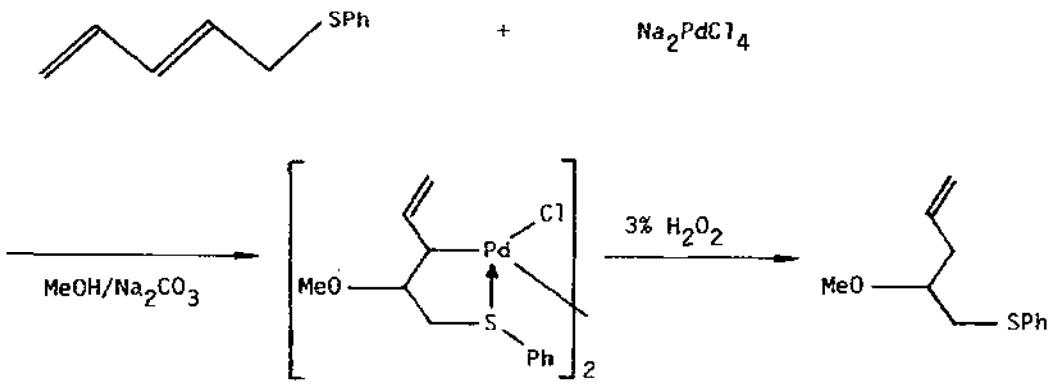
The ether oxygen is capable of coordination to a metal to form a chelate compound, but this metal–oxygen bond is rather labile since it reacts readily with a large variety of reagents. For example, the reaction between 1-methoxynaphthalene and n-butyllithium gives 8-lithio derivatives **74**. The lithium compound **74** reacts with $PdCl_2(SEt_2)_2$ to give the metal-exchange compound **75**. The chelate palladium compound **75** reacts readily with $Co_2(CO)_8$, acyl chloride, benzoyl chloride, styrene, etc. to give the 8-substituted derivatives **76**–**78** of 1-methoxynaphthalene, respectively [101].

Molybdenum cationic trihydride **79** reacts with 2-methylallyl alcohol to give the five-membered ring compound **80** with coordinated hydroxy oxygen at the terminal carbon atom [102].



F. SULFUR COMPOUNDS

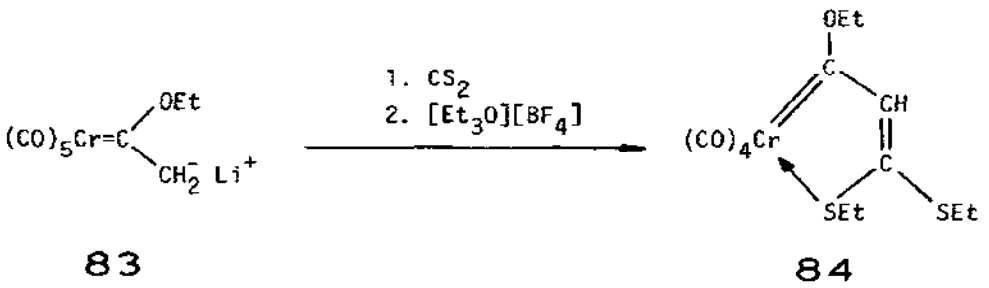
Alkyl- [103] or aryl-sulfides [104] also form cyclometalated compounds similar to the alkyloxy or aryloxy compounds described in the previous section. For example, pentadienylphenylsulfide reacts with sodium tetrachloropalladate(II) to give the chloro-bridged five-membered ring compound **81**, which is treated with hydrogen peroxide to give the demetalated compound **82** [104].



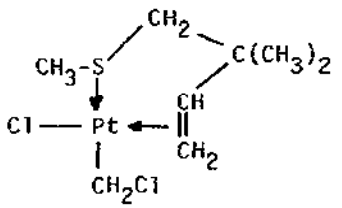
59% **81** 79% **82**

Another five-membered ring compound **84** is obtained by reaction of the carbene anion **83** with carbon disulfide and by ethylation [105].

Three-membered [106,107] and 5.5-membered ring compounds (e.g., **85** [108]) have also been reported, and the latter ring structure determined by X-ray crystal structure analysis [108].



83 **84**

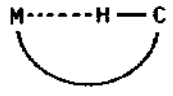


85

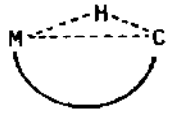
There have also been reports concerning antimony, halogen and hydrogen as the donor atom [1]. The hydrogen donor ligand contains a carbon–hydrogen–transition-metal bond. This kind of bond is not so strong as coordination bonds in the compounds described in previous sections, and it is considered to be an intramolecular interaction [1]. In the absence of any suitable lone pairs, the C–H bonding pair is donated to the metal in a two-electron, three-center bond [109].

These three-center M–H–C interactions [110] consist of an open form **86** (e.g. $[Ru(PPh_3)_3Cl_2]$ **88** [111]) and a closed form **87** (e.g. **89** [112]).

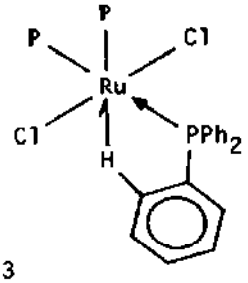
Recently, in extended-Hückel calculations on the cycloalkenyl metal compound, e.g. $[Fe(C_6H_9)(CO)_3]^+$ **90**, the M–H–C interaction is considered to be, electronically, a highly bent open system rather than a three-membered ring [110].



86

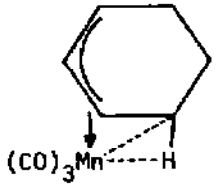


87

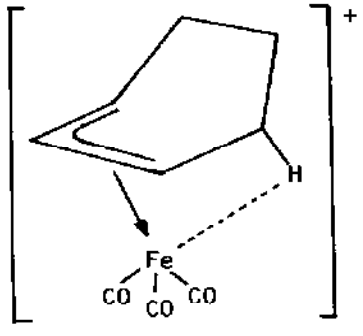


P = PPh_3

88



89



90

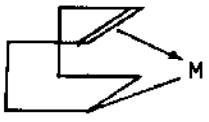
Transition metals capable of participating in the above M–H–C interaction include Ti [109], Cr [110], Mn [24,109,110], Fe [109], Co [24], Mo [109], Ru [113,114], Pd [109], Ta [109], Os [109,115] and Ir [109].

G. π-COORDINATION COMPOUNDS

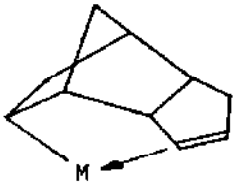
(i) Vinylene compounds

There are two types of vinylene compound $\overbrace{M-(C)_n-Y}$ (Y = vinylene group), i.e. σ, π-type (η^1, η^3-type) and π,π-type (η^2, η^2-type).

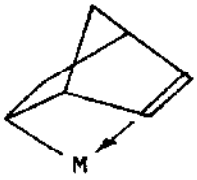
The former are mainly cyclooctenyl **91**, dicyclopentenyl **92**, and norbornenyl **93** compounds, and the latter are mainly cyclooctadienyl **94**, dicyclopentadienyl **95**, norbornadienyl **96** and cyclooctatetraenyl **97** metal compounds.



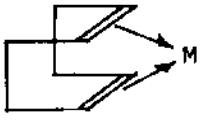
91



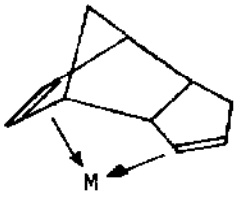
92



93



94



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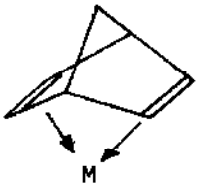
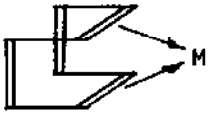


96

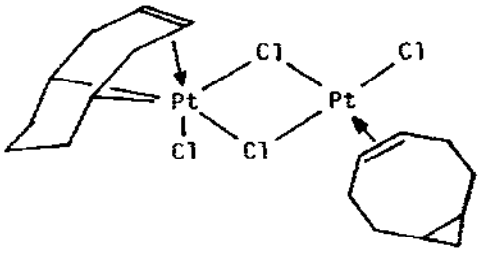


97

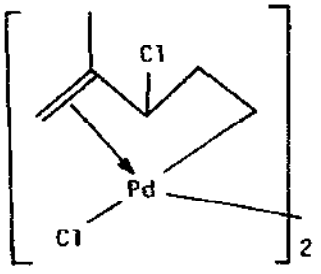
There are several reports of vinylene compounds containing metals: Ru [116] in **91**, Os [117] in **92** and **95**, Fe [22], Co [24], Rh [118,122], W [123], Re

[124], Ir [125] and Pt [126] in **94** [117], Os in **95** [117], Rh [122], W [123], Ir [127] and Pt [128] in **96**, and Ni [129], W [123] and Ir [127] in **97**.

Of these, the $\sigma,\pi(\eta^1,\eta^2)$ compounds having $n = 3$ in $\overset{\sigma}{M}-(C)_n-\overset{\pi}{Y}$ (Y = vinylene) are cyclooctenyl **91** and dicyclopentadienyl **92** compounds, and the others having $n = 3$ are e.g. cyclononenyl **98** [130], and pentenyl **99** compounds [131a].



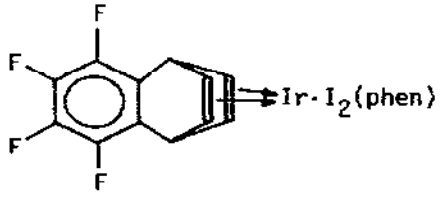
98



99

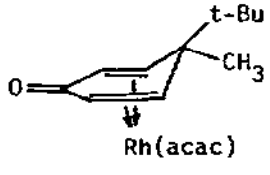
The $\pi,\pi(\eta^2,\eta^2)$-coordination compounds ($M(C{=}C{-}(C)_n{-}C{=}C)$ having $n = 2$, such as **94**, **95** and **97**, are stable. However, π,π-coordination compounds having $n = 1$ require a bridge such as norbornadiene **96** or tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene **100** or must form a semiquinone [132,133] (e.g. **101** [131]) to have stable metal–olefin π-bonds.

Another compound in this group is the η^2,η^4-compound, e.g. **102** [134,135].

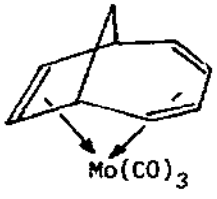


phen = 1,10-phenanthroline

100



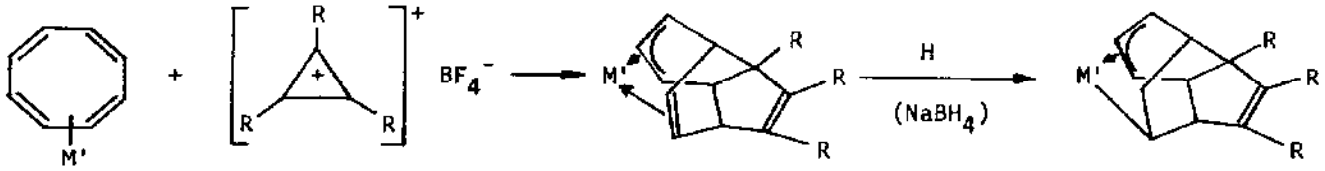
101



102

(ii) π-Allyl compounds

The π-allyl compounds $\overset{\diagdown}{M}-(C)_n-Y$ (Y = π-allyl group) are of two types, similar to the vinylene compounds, i.e. $\sigma,\pi(\eta^1,\eta^3)$-type and $\pi,\pi(\eta^3,\eta^3)$-type compounds, where $n = 1$ [136], 2 [137,138], 3 [139,140], 4 [141] or 5 [142–144]. Generally compounds with $n = 3$ are stable. For example, cyclooctatetraene reacts with cyclopropenium ion to yield the η^2,η^3-bonded product **103**, and subsequently reduction of compound **103** with sodium borohydride gives $\sigma,\pi(\eta^1,\eta^3)$-type compounds **104** ($n = 3$). The X-ray structure of **104** shows the ring-opened cyclopropenium ion which is bonded to the original cyclooctatetraene ring via three new carbon–carbon bonds [139].



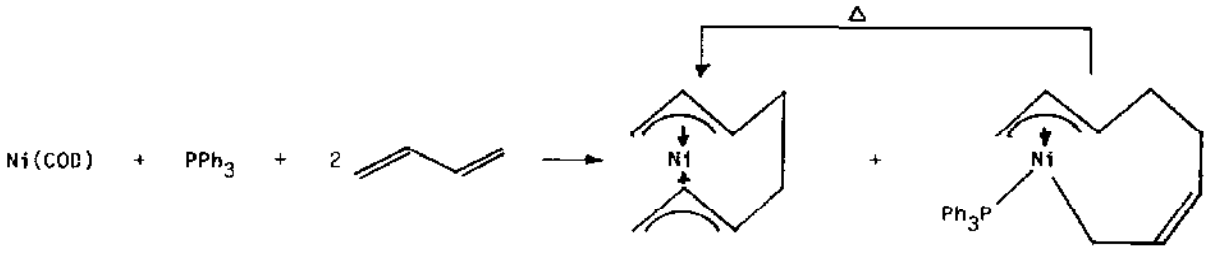
R = H, Ph

103

M' = $Fe(CO)_3$, $Ru(CO)_3$

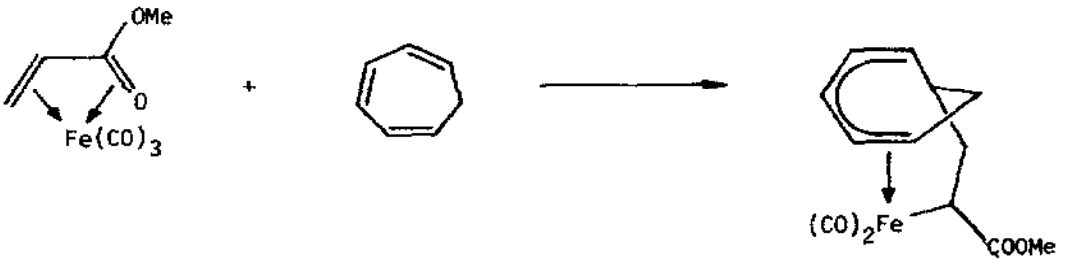
104

The reactions between butadiene or its derivatives and metal compounds such as bis(dibenzylideneacetone)palladium or cyclooctadienenickel give $\pi,\pi(\eta^3,\eta^3)$-type compounds (e.g. **105** [142]) by dimerization and isomerization of butadiene [24,142,144–146].



105 **106**

Other π,π-type compounds include η^2,η^3-coordination [139,143–148], e.g. **103** and η^1,η^5-coordination **107** (which is not a π-allyl compound). This is prepared by the carbonyliron-assisted coupling reaction of cycloheptatriene with methyl acrylate [140].

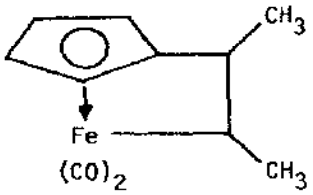


107

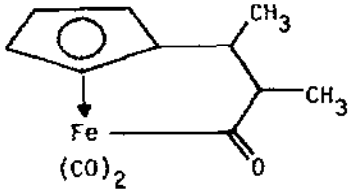
(iii) Cyclopentadienyl compounds

There are also two types of $\sigma,\pi(\eta^1,\eta^5)$- and $\pi,\pi(\eta^5,\eta^5)$-coordination compounds containing the cyclopentadienyl group ($\overbrace{M-(C)_n-}^{}Y$, (Y = cyclopentadienyl group). In the former σ,π-compounds $n = 1$ [149,150], 2 [151–153], 3 [153,154] or 4 [155]. Compounds with $n = 1$ or 2 are strained, but those with 3 or more are almost strain free.

Sterically hindered compounds having $n = 2$ in the formation reaction are susceptible to carbonyl insertion with carbon monoxide or the carbonyl of metal carbonyl compounds and then less hindered compounds with $n = 3$ are formed; e.g. the ring opening reaction product **108** between $Fe_2(CO)_9$ and 1,2-dimethylspiro[2.4]hepta-4,6-diene, and its carbonyl insertion product **109** [153].



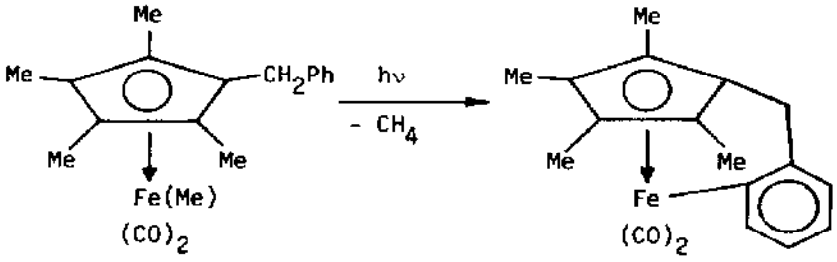
108



109

Near-UV irradiation of the benzylcyclopentadienyl iron compound **110** yields the cyclometalated product **111** ($n = 3$) by oxidative addition of the *ortho* C–H bond of the coordinated benzyl group with loss of methane [154]. Blaha et al. [154] propose a four-step process: (i) elimination of CO, (ii) oxidative addition of the *ortho* C–H bond, (iii) elimination of CH_4, and (iv) back reaction of CO. This process is presumed from the following evidence: PPh_3 or added CO at low concentration can efficiently capture the CO loss product and suppress the oxidation addition process completely, and the quantum efficiency for CO loss to yield the oxidative addition product

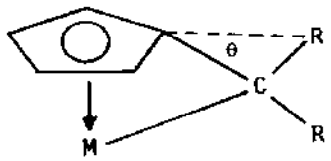
($\phi_{366nm} = 0.40$) is found to be nearly the same as the quantum efficiency for CO loss in the presence of PPh_3 to yield the substitution product (η^5-$C_5Me_4CH_2Ph$)Fe(CO)(PPh_3)Me ($\phi_{366nm} = 0.46$) [154].



110 111

Compounds with $n = 1$ in the cyclopentadienyl compounds **112** have been prepared by the reaction of 6,6-dimethyl- or 6,6-diphenylfulvene with bis(η-benzene)molybdenum, bis(η-benzene)tungsten or bis(η-toluene)titanium.

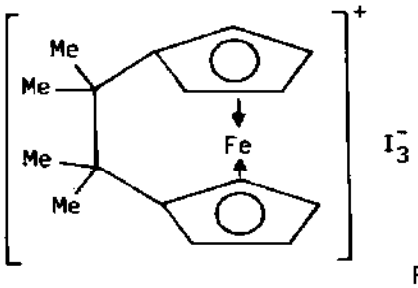
The X-ray crystal structure determinations of **112** reveal that the exocyclic carbon of the fulvene ligands is strongly bent ($\theta = 36$–$39°$) out of the plane of the C_5-ring carbon and bonds directly to the metal [149].



M = Ti, Mo, W
R = Me, Ph 112

The general formula of the π,π-type compounds is M(η^5-C_5–$(C)_n$–η^5-C_5) (M = Ti [156], Zr [156], Hf [1], Fe [157], Ru [1], Sn [1]; $n = 2$ [156–158], 3 [158–163], 4 [159,160,164] or 5 [159]). The [2]ferrocenophane (M = Fe, $n = 2$) has considerable strain and the two cyclopentadienyl rings are tilted 23–24°; the [3]ferrocenophane ($n = 3$) has only a small amount of strain and the rings are tilted 10°. The [4]- and [5]-ferrocenophanes have no strain [1].

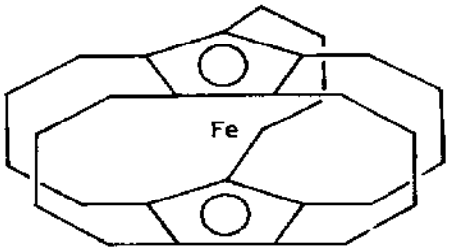
The two cyclopentadienyl rings of tetramethyl[2]ferrocenophanium triiodide **113** ($n = 2$) are tilted by 41° and the large tilt is considered to be due to the difference of the electronic states of the iron atom from the neutral [2]ferrocenophane [156].



Fe-I = 2.64 Å

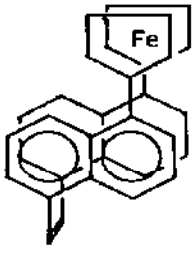
113

Hisatome et al. [164] have prepared the penta-bridged ferrocenophane (per-bridged ferrocenophane or superbridged ferrocenophane), [4.4.4.4.4](1,2,3,4,5)ferrocenophane **114** and determined the crystal structure.

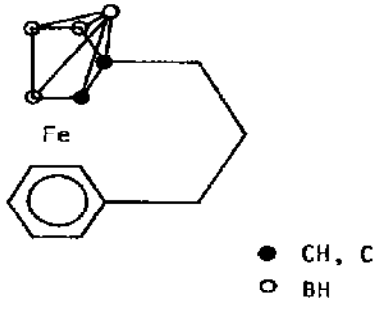


114

Other ferrocenophanes have been reported such as those having bis-(naphthyl)methylene bridges **115** [165] and also the ferrocenophane analog, trimethylene linked (arene)-ferracarbene **116** [166].

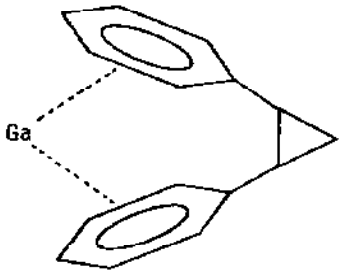


115



116

Other π-coordination compounds include the aryl compounds $\overset{\vee}{M}-(C)_n-Y$ (Y = aryl group). The metal atom is usually chromium. but molybdenum and tungsten [1], and gallium (e.g., **117** [167]) are known.



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ACKNOWLEDGMENT

The author express his gratitude to Dr. Sumio Chubachi for critical reading of the manuscript.

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