Coordination Chemistry Reviews, 53 (1984) 261–291
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS CONTAINING A π-ALLYL DONOR LIGAND

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(First received 14 March 1983; in final form 5 July 1983)

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A. INTRODUCTION

Organometallic intramolecular-coordination compounds $\overset{\longleftarrow}{\mathrm{M{-}(C)_{\mathit{n}}{-}Y}}$ (M = metal; Y = coordinating atom or group; $n \geqslant 1$) [1] are classified into two groups. One contains a σ-coordination bond and the other contains a π-coordinate bond, linking Y to the metal atom. These are tentatively named as σ-coordination compounds and π-coordination compounds respectively, in this review. The author, hitherto, has summarized compounds having N [2,3], S [4], O [5–7], P [8] or As [9] as the donor atom for the σ-coordination compounds, and those having a cyclopentadienyl [10], or carbon–carbon double bond [11,12] as the donor group for π-coordination compounds. It is

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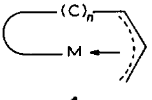
pointed out that the σ-coordination compounds having $n = 3$ are stabilized by a five-membered ring structure, while π-coordination compounds having $n = 3$ and a carbon–carbon double bond donor ligand [11] or a cyclopentadienyl donor ligand [10], also form stable compounds.

This review deals with compounds containing a π-allyl group as Y, as shown in general formula **1**, and includes η^2-ethylenic-η^3-allyl or bis π-allyl type compounds, where the M–C bond is also either a η^2-ethylenic or π-allyl coordination bond. The syntheses, reactivities, reaction mechanisms and structures of these compounds are summarized herein.



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B. 1-σ-4,5,6-η^3-ALLYL METAL COMPOUNDS

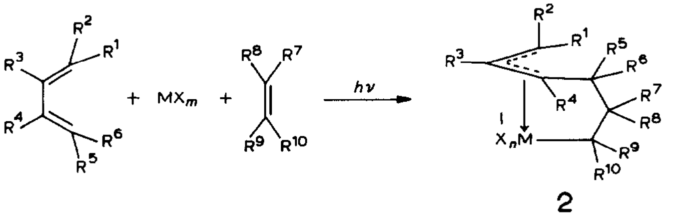
Organometallic intramolecular-coordination compounds containing a π-allyl donor ligand are shown in **1**. Of these, most of the compounds that have been synthesized are those with $n = 3$, that is, 1-σ-4,5,6-η^3-allyl metal compounds; they are relatively strain free and stable. Their syntheses are generally easy compared with the other types of compounds described in the next section.

The 1-σ-4,5,6-η^3-allyl metal compounds are usually synthesized by diolefin monoolefin reactions, diolefin acetylene reactions, cyclopolyolefin reductions, cyclopropane ring opening and carbonylations, etc.

(i) Diolefin monoolefin reactions and diolefin acetylene reactions

The reactions of diolefin, monoolefin and metal compounds under ultraviolet irradiation afford 1-σ-4,5,6-η^3-allyl metal compounds, **2**, i.e. σ, π-allyl metal compounds having $n = 3$ in **1**, where the diolefin and the monoolefin are bonded as shown in eqn. 1.

It is considered that two components of three react in advance to yield the metal π-complex, then the complex reacts with the residual component (eqns. (1–4)). For example, iron pentacarbonyl, methylacrylate and a diene



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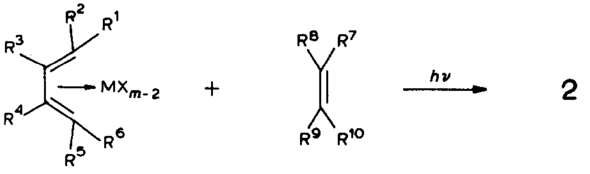
(1)



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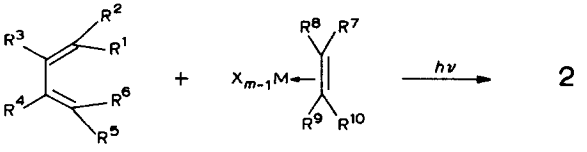

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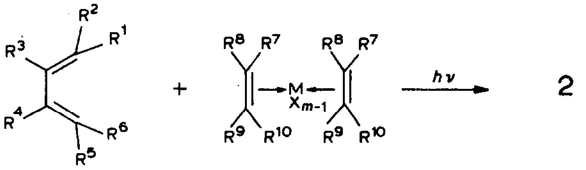
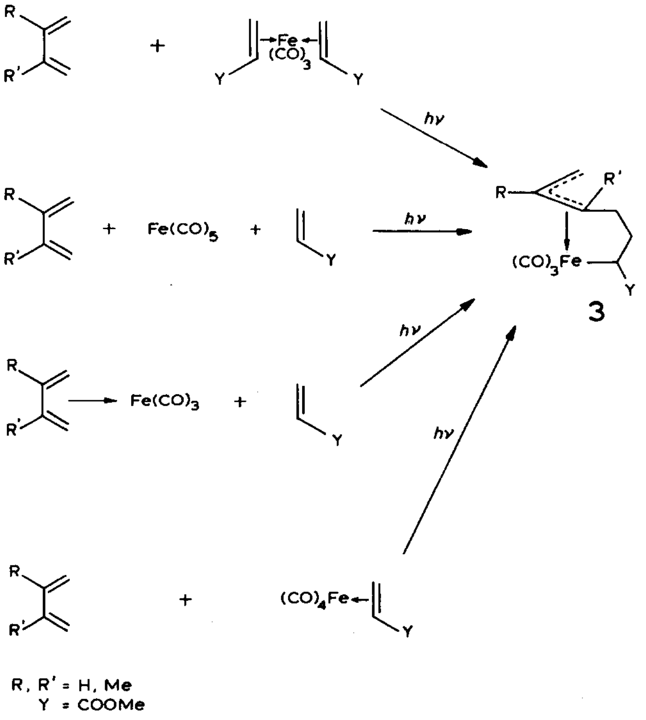


(4)

(2,3-dimethylbutadiene, isoprene or butadiene) mixtures react photochemically to afford 1-σ-4,5,6-η^3-allyl metal compounds **3** [13,14] (Scheme 1).

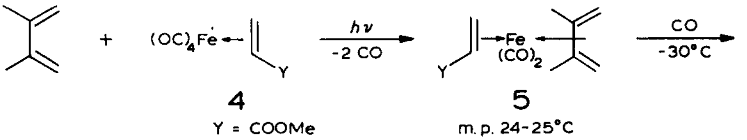
As shown in Scheme 1, **3** is also obtained by the reaction of tricar-



Scheme 1

bonyl(bis(η^2-methylacrylate))iron with diene or reaction of tetracarbonyl(η^2-methylacrylate)iron with diene.

Recently, Grevels and Schneider [15] isolated the intermediate **5** in which the iron carbonyl is coordinated by both diene and methylacrylate (eqn. (5)). Compound **5** reacts with carbon monoxide at ca. −30°C to afford **3**. Hence, the 1-σ-4,5,6-η^3-allyl metal compounds **3** occur first via formation of η^2- or η^4-coordination compounds of iron carbonyl with monoolefin or diene. Subsequently tricarbonyl(η^2-monoolefin-η^4-diene)iron **5** is coordinated by both diene and monoolefin, and finally there is thermal C–C coupling of the ligands with re-uptake of one carbon monoxide (eqn. (5)) [15].



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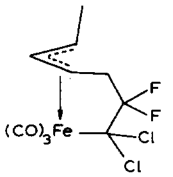
Kerber and Koerner von Gustorf [16], with 1,1-dichloro-2,2-difluoroethylene as a monoolefin, synthesized σ,π-allyl compounds **6** similar to **3**, and they proposed a mechanism in which the last step to the σ,π-allyl compounds occurs via $\pi \rightarrow \sigma$ ligand rearrangements accompanied by carbon monoxide reattachment as shown in eqn. (6). The σ,π-allyl and octahedral structure of a butadiene compound **3** was determined by an X-ray diffraction study (Fig. 1) [13].



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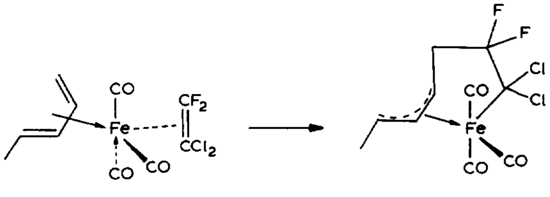

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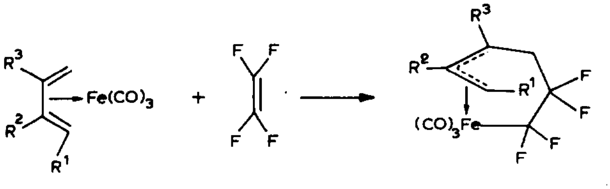
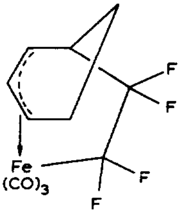
(6)

Tetrafluoroethylene also reacts with various kinds of tricarbonyl(η^4-diene)iron compounds **8** to give the 1-σ-4,5,6-η^3-allyl metal compounds **9** [17,18] while cyclohexa-1,3-diene or bicyclo[4.2.0]octa-1,3-diene as a diene affords analogously the σ,π-allyl compound **10** or **11** (eqn. (7)) [17]. Further, hexafluoropropene reacts as monoolefin with tricarbonyl(η^4-diene)iron or



8 R¹, R², R³ = H, Me 9

(7)



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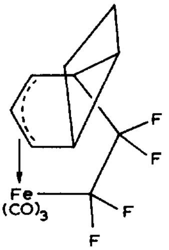

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tricarbonyl(η^4-diene)ruthenium to afford σ,π-allyl compounds **12** or **13** similar to the above σ,π-allyl compounds. The structure of the isoprene

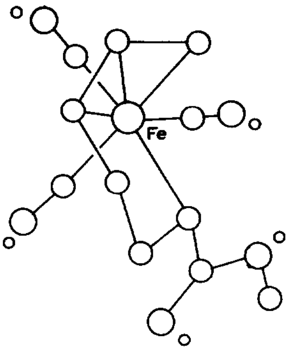
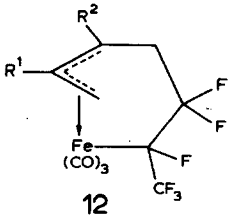


Fig. 1. Structure of reaction product of butadiene, methyl acrylate and pentacarbonyliron.



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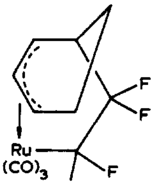
R¹, R² = H, Me



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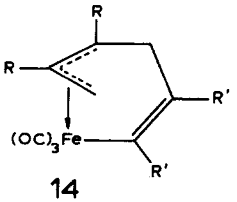


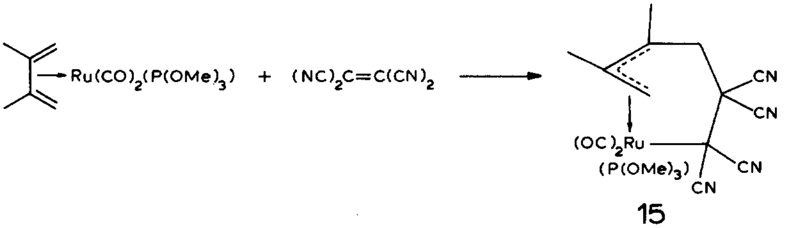
14

R = H, Me
R' = H, CF₃

compound (**12**, $R^1 = Me$, $R^2 = H$) was also determined by single crystal X-ray diffraction [18,19].

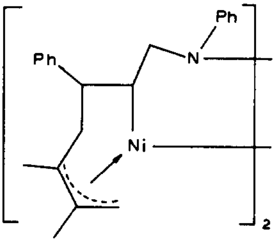
Acetylene in place of the monoolefin also reacts with diene–metal compounds to form the 1-σ-4,5,6-η^3-allyl metal compounds having a double bond, e.g., hexafluorobut-2-yne or 3,3,3-trifluoroprop-1-yne reacts with carbonyl(η^4-diene)iron to afford the σ,π-allyl compounds **14** [20–22].

Tetracyanoethylene as monoolefin also reacts with η^4-diene metal compounds to yield the σ,π-allyl compound **15** (eqn. (8)) [23].



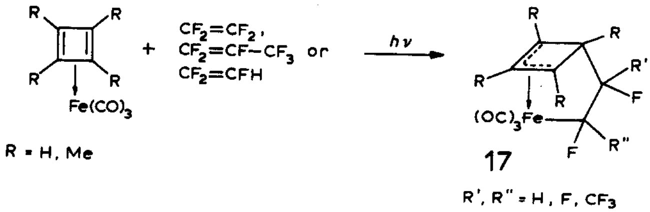
(8)

The reaction of cinnamaldehydaniline (as monoolefin) and 2,3-dimethylbutadiene with bis(1,5-cyclooctadiene)nickel gives the σ,π-allyl dimer **16**, the structure of which has been determined by X-ray diffraction [24].



16

Cyclobutadiene, as an active diene, is also capable of affording the 1-σ-4,5,6-η^3-allyl metal compound **17** [18,25–27] by reaction of its iron carbonyl with fluoroethylene. Tricarbonyl(η^4-cyclobutadiene)iron is capable of reaction with hexafluorobuta-1,3-diene, but, since both components are a diene, the former acts as a monoolefin to give **18** involving 1,3-fluorine shift. Trifluoroethylene as a monoolefin affords a normal 1-σ-4,5,6-η^3-allyl metal



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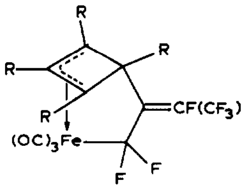

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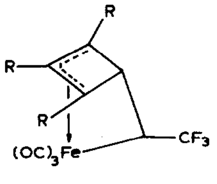


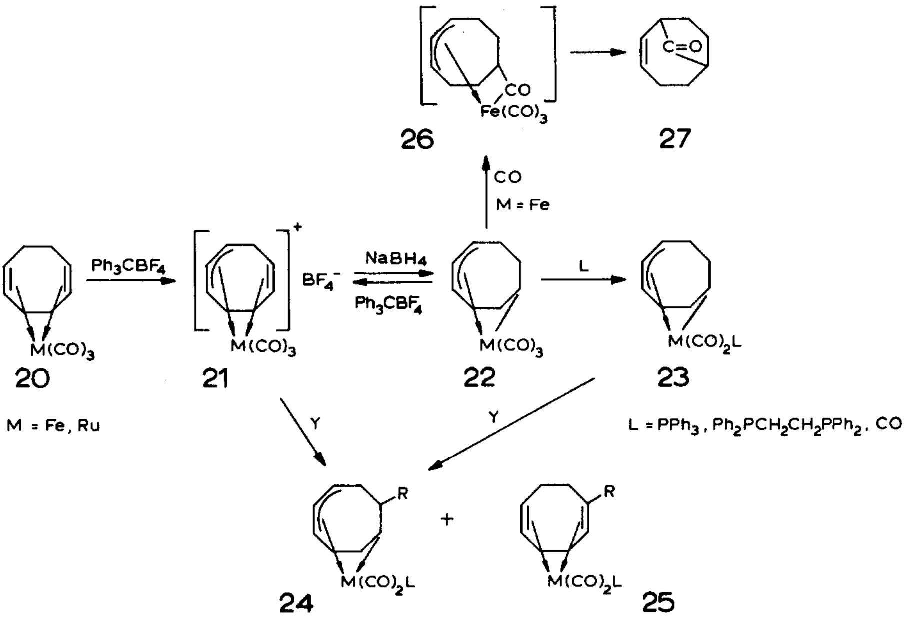
19

compound **17** plus 1-σ-3,4,5-η^3-allyl metal compound **19** as a second unusual product [25].

The photochemical reaction of monosubstituted cyclobutadieneiron tricarbonyl with propyne affords only intermediate 1-σ-4,5,6-η^3-allyl metal type compounds **17** having a monoolefin bond as deduced from toluene derivatives as products [28].

(ii) Cyclopolyolefin reductions

1-σ-4,5,6-η^3-Allyl metal compounds are also synthesized by reduction of cyclopolyolefin metal compounds, e.g. tricarbonyl(cycloocta-1,5-diene) metal compounds **20** react with triphenylmethyl tetrafluoroborate to afford tri-



Y = NaCN, NaCH(COOEt)$_2$, NaCPh(COOEt)$_2$, MeMgI, (CH=CHCH$_2$)MgBr, CH$_3$O$^-$, N$_3$
R = CN, Me, CH$_2$=CH−CH$_2$, CH(COOEt)$_2$, CPh(COOEt)$_2$, N$_3$, OMe

Scheme 2

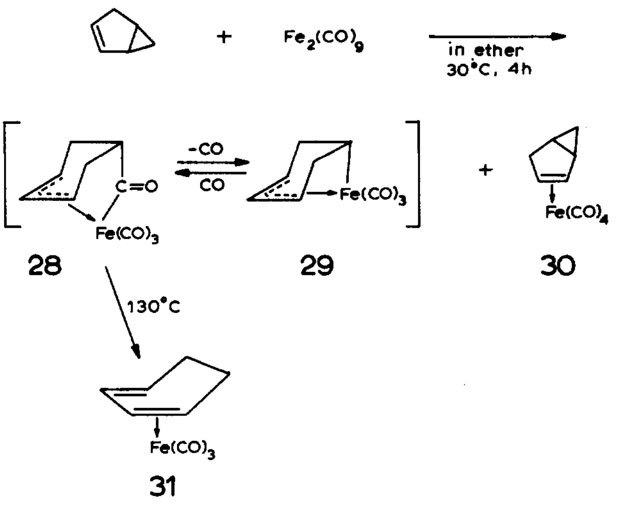
carbonyl(1,2-η^2-4,5,6-η^3-cyclooctadienyl) metal **21** described below by hydride-ion abstraction. Subsequently 1-σ-4,5,6-η^3-allyl metal compounds **22** are obtained by reduction of **21** with sodium borohydride [29–31]. The σ,π-allyl metal compounds **22** are very stable because they are capable of reacting with a phosphine such as triphenylphosphine or 1,2-bis(diphenylphosphino)ethane through ligand exchange of one carbonyl with another ligand to give compound **23** without cleavage of the transition metal–carbon σ bond and no further replacement of CO or cleavage of the organic group occurred on treating **22** with excess triphenylphosphine in cyclohexane under reflux for 8 h. Both of the η^2-ethylenic-η^3-allyl metal compounds **21** and σ,η^3-allyl metal compound **23** react with sodium cyanide, sodium pentane-2,4-dionate, or the like to give a mixture of σ,η^3-allyl **24** and bis(η^2-ethylenic)metal compound **25**. The structure of the ruthenium product **24** ($M(CO)_2L = Ru(CO)_3$, $R = CN$) from sodium cyanide was determined by X-ray diffraction [21]; this may also be regarded as an octahedral complex of ruthenium(II) (d^6) with two CO groups *trans* to a bidentate η^3-allyl group and with the third CO unique and *trans* to the ruthenium–carbon σ-bond [30,32]. On the other hand, the reaction of σ,π-allyl compounds with carbon monoxide at high pressure (85 atm.) for a long time (50 h) affords the *trans*-annular ketone **27** by fission of the σ,π-allyl intramolecular-coordination bond and carbonyl insertion [29,30,33,34].

(iii) Cyclopropane ring opening and carbonylation

Cycloolefins having a cyclopropane ring react with metal carbonyl to yield 1-σ-4,5,6-η^3-allyl metal compounds by simultaneous cyclopropane ring opening reactions and carbonylation.

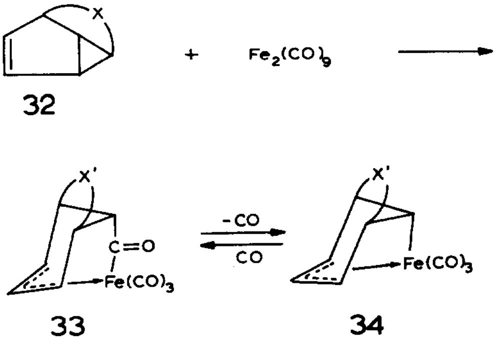
For example, reaction of bicyclo[3.1.0]hex-2-ene with diiron nonacarbonyl affords cyclopropane ring opening reaction product **29**, carbonyl insertion product **28**, and η^2-cyclopentenyliron compound **30** as a minor product (the ratio of **30** to **28** is 1 : 10) [35]. The carbonyl insertion product **28** is decomposed at 130°C ($t_{1/2}$, ca. 4 h) to yield the η^4-cyclohexadienyliron compound **31** whose formation is presumed to proceed via **29** by decarbonylation [35]. From these reaction products and the diolefin monoolefin reaction mechanism described above, the author presumes that firstly formation of η^2-cyclopentenyliron compound **30** occurs, then cyclopropane ring opening and finally carbonyl insertion, or then simultaneous cyclopropane ring opening and carbonyl insertion.

Tricyclic compounds having the bicyclo[3.1.0]hex-2-ene moiety (eqn. (10)) and the bond –X–, **32**, also react with diiron nonacarbonyl to give both cyclopropane ring opening (**34**) and carbonyl insertion (**33**) [36–38]. The latter product is obtained directly by carbonylation of **34**. The carbonyl



(10)

inserted structure of the isobullvalene derivative (**33b**) was determined by X-ray analysis [36].

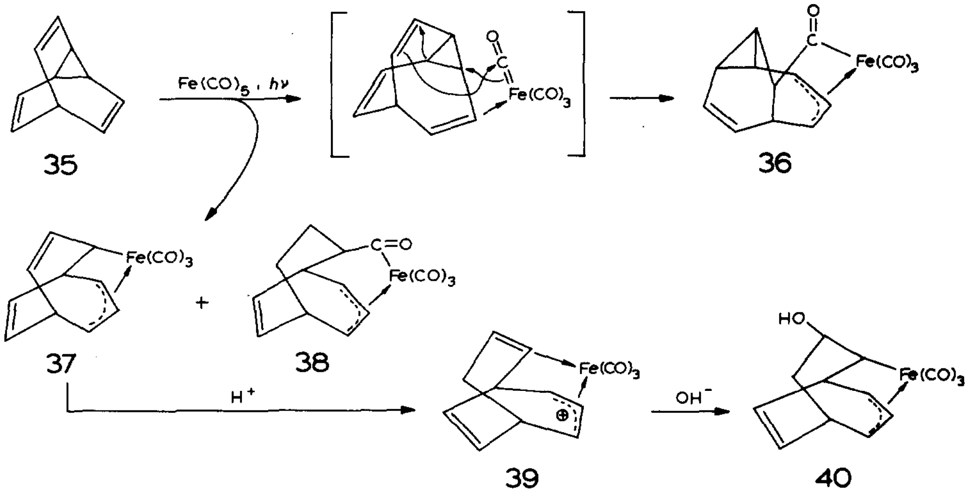


(11)

(11)

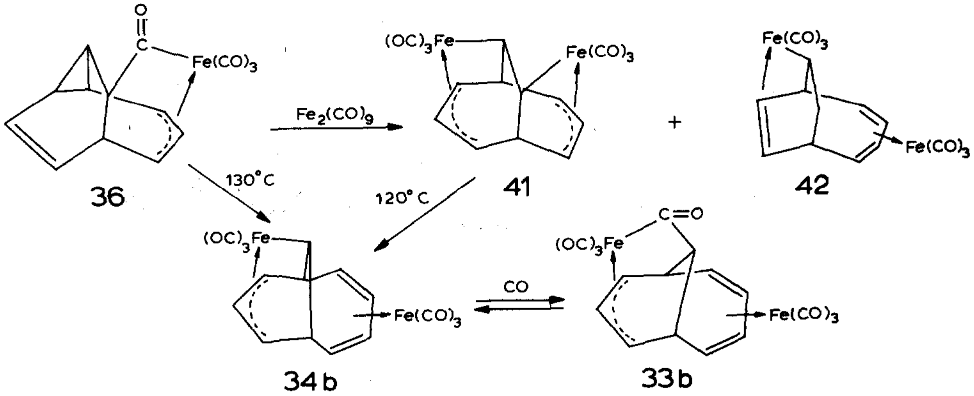
Homosemibullvalen	(32a)	X = $-CH{=}CH-CH_2-$
(Tricyclo[4.3.0.0^{2,9}]nona-3,7-diene)	(33,34a)	X' = $-CH{=}CH-CH_2-$
Isobullvalen	(32b)	X = $-CH{=}CH-CH{=}CH-$
(Tricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene)	(33b,34b)	X' = $\underset{\mathrm{Fe(CO)_3}}{-CH{=}CH-CH{=}CH-}$
Semibullvalen	(32c)	X = $-CH{=}CH-$
(Tricyclo[3.3.0.0^{2,8}]octa-3,6-diene)	(33c,34c)	X' = $\underset{\mathrm{Fe(CO)_3}}{-CH{=}CH-}$

Bicyclo[4.1.0]hept-2-ene [35] or *cis,cis*-bishomobenzene [39] having a cyclopropane ring also affords similar products to **28**, **29**, **33** or **34** by reaction with iron carbonyl. On the other hand, photochemical reaction of bullvalene **35** with iron pentacarbonyl in moist benzene yields cyclopropane ring opening and carbonylation product **36** and hydroxy compound **40** obtained by action of water as shown in Scheme 3 [40]. This carbonyl



Scheme 3

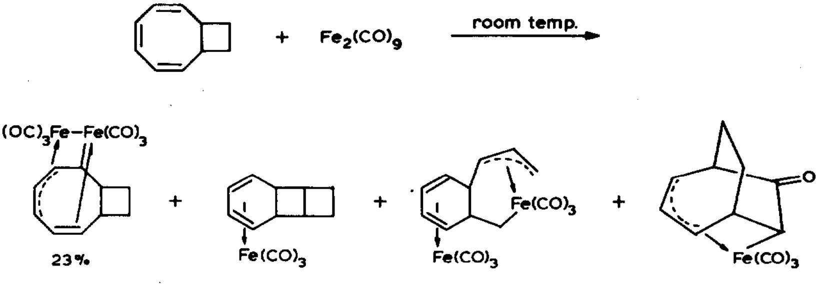
inserted product **36** further reacts with diiron nonacarbonyl in ether to give the binuclear[3.3.2]-compound **41** and the [4.2.2]-compound **42**. At 130°C, **36** rearranges smoothly to the [4.3.1] system **34b**, which under CO pressure forms the corresponding **33b** [40]. **41** is also obtained by reaction of bullvalene with diiron nonacarbonyl [41] and **41** is capable of being converted to **34b** by heating at 120°C.



Scheme 4

(iv) *Miscellaneous reactions*

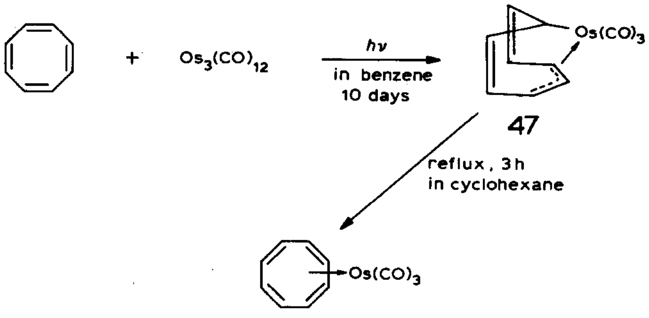
Cyclopolyolefin having cyclobutane in place of a cyclopropane will afford 1-σ-4,5,6-η^3-allyl metal compounds without carbonyl insertion, but, the yield is very low since the ring-opening reactivity is low. For example the reaction [42] of *cis*-bicyclo[6.2.0]deca-2,4,6-triene with diiron nonacarbonyl affords several products such as Fe–Fe bonded compound **43** and η^4-cyclohexadienyliron compound **44**. The structures of 1-σ-4,5,6-η^3-allyl iron compound **45** and 1-σ-3,4,5-η^3-allyl metal compound **46** have been confirmed by X-ray crystallography [43a,43b].



43 44 45 46

(12)

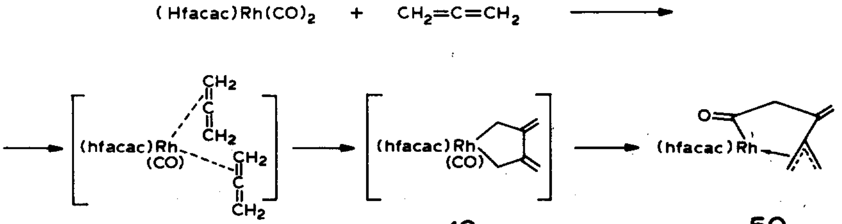
Cyclooctatetraene reacts with dodecacarbonyltriosmium in benzene for ten days under ultraviolet irradiation to yield the transannular σ,π-allyl metal compound **47**, which produces on heating the η^4-cyclooctatetraene osmium compound **48** [44].



48

(13)

In addition, the compound having $n = 3$ in **1** is obtained by reaction of allene with metal carbonyl [45,46]. Borrini and Ingrosso [46] proposed that this reaction proceeds via the metallocyclic intermediate **49** containing



49 50

(14)

3,4-dimethylenerhodacyclopentane formed by bimolecular addition of allene, and followed by carbonyl insertion to yield **50**.

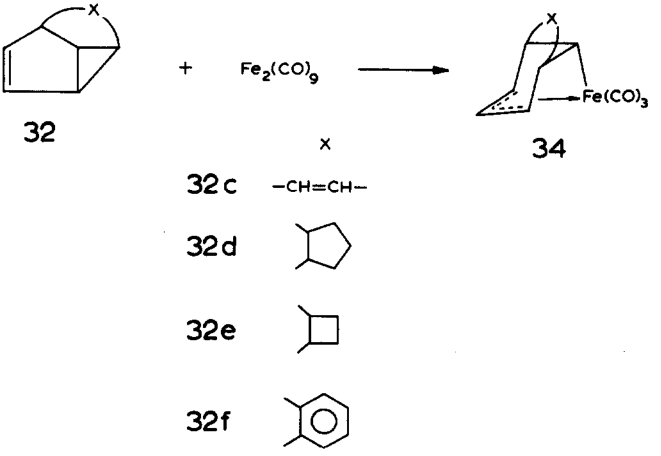
Moreover, in other studies of compounds having $n = 3$ in **1**, carbonyl insertion of cycloolefin metal compounds [47,48], etc. [49,50] have been reported.

C. 1-σ-3,4,5-η^3-ALLYL METAL COMPOUNDS

The compounds **1** ($n = 2$) are synthesized by cyclopropane ring opening reactions and cyclopolyolefin reductions as shown above. In addition they are synthesized by cyclodiolefin carbonylations, 1,3-cycloadditions, or reductions of η^2-ethylenic-η^3-allyl metal compounds.

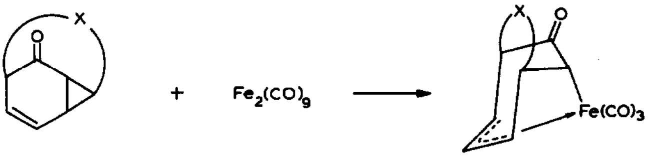
(i) Cyclopropane ring opening reactions

As shown in eqns. (10) and (11) and in Schemes 3 and 4, a cycloolefin containing a cyclopropane ring reacts with metal carbonyl to afford **1** ($n = 2$) either by cyclopropane ring opening, or simultaneous carbonyl insertion followed by decarbonylation. Cycloolefins having a tendency to afford products without an inserted carbonyl group are semibullvalene **32c** [51–53], 3,6-endo-tetracyclo$[5.3.0^{2,10}0^{3,6}]$decene-8 **32d** [54], 3,7-endo-tetracyclo$[6.3.0^{2,11}0^{3,7}]$undecene-9 **32e** [54] or benzosemibullvallene **32f** [54], which have a carbon–carbon double or cyclic bond as X (eqn. (15)).



(15)

When barbaralone **51** containing a skeleton larger by a carbonyl group than the bicyclo[3.1.0]hex-2-ene in **32**, reacts with diiron nonacarbonyl, the product **52** has a seven-membered ring containing the carbonyl group by cyclopropane ring opening [55] (see X-ray structure analysis of **52** [56]).



51 52 (16)

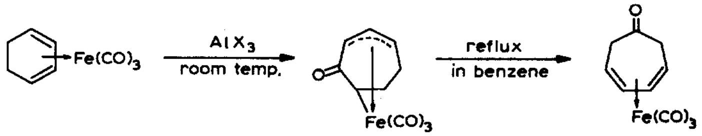
barbaralone, X = —CH=CH—

Other examples of cyclopropane ring opening reactions to give 1-σ-3,4,5-η^3-allyl metal compounds are reaction of tetracyclo[4.4.$0^{5,7}0^{2,10}$]deca-3,8-diene [57], 3-methoxy-4-azatricyclo[3.3.2.$0^{2,8}$]deca-3,6,9-triene [58], 4-methylenedispiro[2.1.2.3]decane [59], etc. [60], with iron carbonyl.

(ii) Cyclodiolefin carbonylations

η^4-Cyclodiolefin metal carbonyls react with intramolecular carbonyl or carbon monoxide in the presence of a Lewis acid to yield σ,π-allyl metal compounds with an inserted carbonyl group.

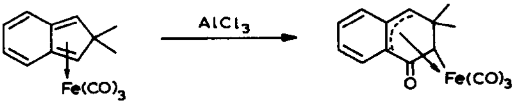
For example, reaction of tricarbonyl(η^4-cyclohexadiene)iron **53** with aluminium halide gives tricarbonyl(2,3,4-η^3-7-σ-cycloheptenediyl-1-one)iron **54** by ring expansion and carbonyl insertion [60–62]. Heating **54** in benzene produces the tricarbonyl(η^4-cyclohepta-2,4-diene-1-one)iron **55**. Tricarbonyl(η^4-cyclohexa-1,3-diene)iron **53** interacts reversibly with AlX_3(X = Cl or Br) over a period of several hours to give an adduct $(CO)_3C_6H_8Fe \rightarrow AlX_3$. However, when a solution of **53** containing two equivalents of AlX_3 is stirred under nitrogen in CH_2Cl_2 at room temperature for two days, carbonyl inserted σ,π-allyl metal compound **54** is obtained in low yield (ca. 9%). If the same reaction is carried out under one atmosphere of CO, the yield increases markedly to ca. 55% [61].



53 54 55 (17)

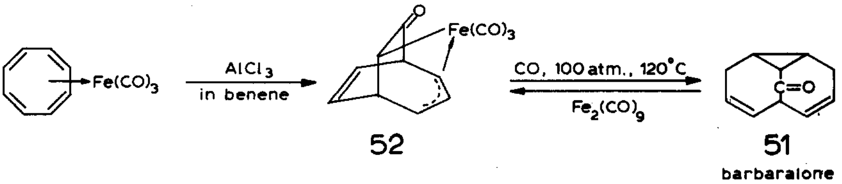
X = Cl, Br

Tricarbonyl(η^4-isoindene)iron having a η^4-cyclopentadienyl ring **56** reacts with aluminium chloride to give the ring expansion product **57** by carbonyl insertion [63]. But, treatment of aluminium chloride with tricarbonyl(η^4-



56 57 (18)

cyclooctatetraene)iron having a large polyolefin ring does not proceed by a ring expansion reaction with simple carbonyl insertion, but by transannular carbonylation (eqn. (19)) [62,64,65a]. Johnson and co-workers [65a] clarified the reason for this observation by IR spectroscopy; these reactions require two moles of aluminium halide [62] (eqns. (17)–(19)) for the formation of molecular compounds between metal and AlX_3 and also between the inserted carbonyl oxygen and AlX_3 as intermediates. The transannular carbonylation product **52** is the same product of the reaction between barbaralone and diiron nonacarbonyl (eqn. (16)) and its reverse reaction is favored for preparation of barbaralone **51** because the reaction of **52** with carbon monoxide under pressure produces **51** in high yield (eqn. (19)) [65b].

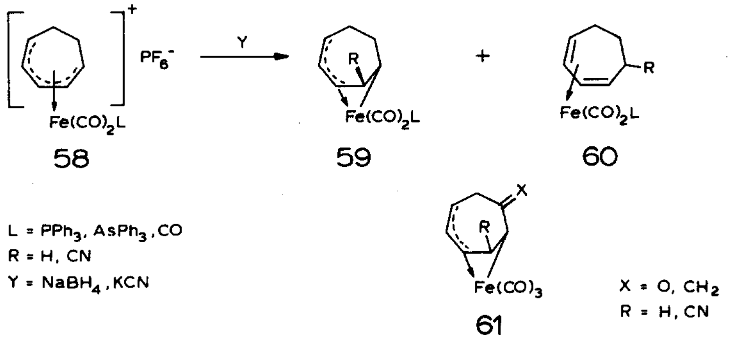


(19)

(iii) Cyclopolyolefin reductions

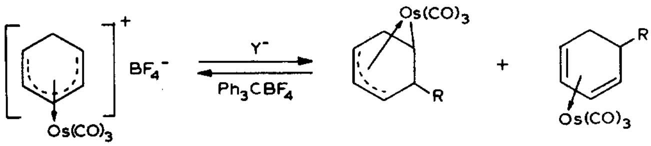
As shown in Scheme 2, the reduction of a cyclopolyolefin having an eight-membered ring yields 1-σ-4,5,6-η^3-allyl metal compounds; however, the reduction of cyclopolyolefins having a seven- or six-membered ring gives 1-σ-3,4,5-η^3-allyl metal compounds.

In the case of cycloheptadieneyliron cations having a seven-membered ring, **58** (L = PPh_3, $AsPh_3$) reaction with sodium borohydride or potassium cyanide affords solely 1-σ-3,4,5-η^3-allyl metal compounds **59**; however, where L in **58** is carbonyl, the reaction yields mixtures of **59** and η^4-cycloheptadienyl iron compound **60**, with the proportion being dependent both on reaction conditions and nucleophile [66]. Tricarbonyl(η^4-tropone- or η^4-heptafulvene)iron also affords the σ,π-allyl metal compounds **61** similar to **59** [67].



(20)

Reduction of the η^5-cyclohexadienyl osmium cation **62** having a six-membered ring with sodium borohydride in water yields two products in approximately equal amounts (eqn. (21)). These could not be isolated by chromatography, but were identified as the σ,π-allyl metal compounds **63** and 1,3-diene compound **64** by ^{1}H NMR, mass and IR spectra. The reaction of these products with trityl cation regenerates only the starting cation **62**. Refluxing the mixture in hexane for 5 h results in isomerization of the σ,π-allyl product to 1,3-diene compounds **64**, presumably by a hydrogen atom migration via the endo face of the coordinated ligand [68]. The same



(21)

62

Y$^-$ = BF$_4$, CN$^-$
R = H, CN

63
(R = H)

64
(R = H)

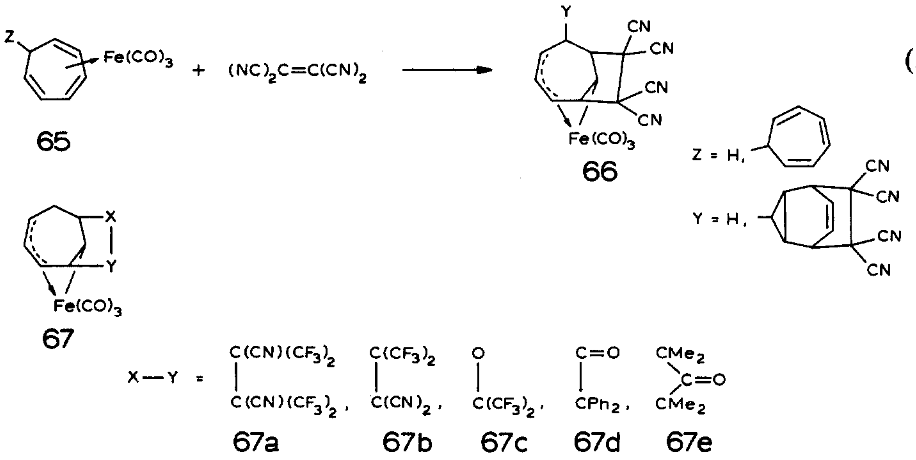
center allyl	4.94 ppm inner	5.50 ppm
out of the allyl	4.62 ppm outer	3.28 ppm
exo methylene	3.00 ppm methylene	1.56 ppm
σ-bond-metal	0.94 ppm	

type of isomerization of seven-membered σ,π-allyl derivatives **59** requires more vigorous reaction conditions (120°C, 15 h [66]) than those for the six-membered compound **63**. Burrows et al. [68] pointed out that the more facile rearrangement in the case of the 6-membered complex probably reflects the lower stability of the σ,π-allyl conformation for the six- over the seven-membered ring. The reaction of **62** with cyanide ion also results in the formation of the σ,π-allyl product **63** together with the corresponding 1,3-diene product **64** in the ratio 3/1. However, all other nucleophiles such as alcohols, thiols, amines, phosphines or carbon nucleophiles other than cyanide ion, yielded only the 1,3-diene product **64** [68].

(iv) 1,3-Cycloadditions

Reactions of η^4-cycloheptotriene or η^4-cyclooctatetraene metal compounds with systems such as tetracyanoethylene(TCNE) and hexafluoroacetone, having a double bond afford σ,π-allyl compounds by 1,3-cycloaddition.

Tricarbonyl(η^4-cycloheptatriene)iron reacts with TCNE to afford σ,π-allyl iron compounds **66** by 1,3-cycloaddition of TCNE to the cycloheptatriene ring [69–72]. The structure of tricarbonyl(cycloheptatriene)iron-TCNE-1,3-adduct **66**(Z = H) was determined by single-crystal X-ray [69,70]. On the other hand, in the reaction of bis-cycloheptatriene iron compounds with TCNE, TCNE reacts first by 1,4-addition with the cycloheptatriene moiety



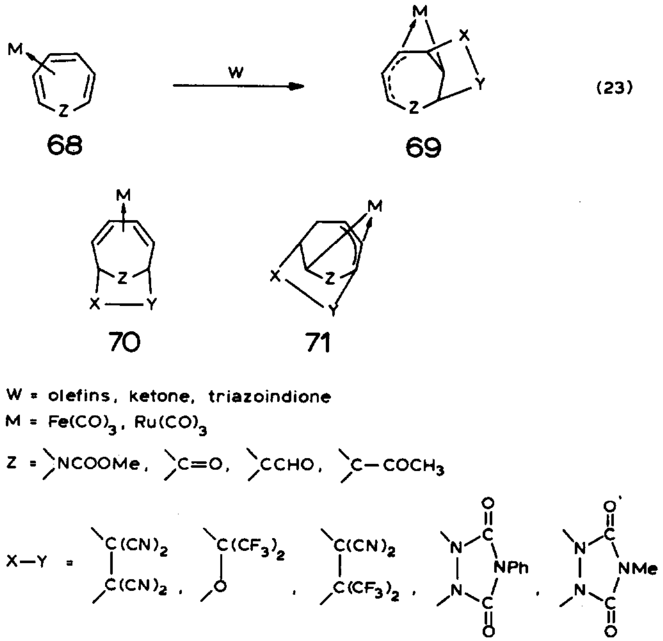
(22)

not bonded with iron; then, the excess TCNE reacts with the metalated cycloheptatriene moiety to afford the 1,3-adduct [72]. 1,2-Dicyano-1,2-bis(trifluoromethyl)ethylene, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, hexafluoroacetone [73] or diphenylketene also react in place of TCNE [74], with tricarbonyl(η^4-cycloheptatriene)iron to afford the corresponding 1,3-adducts (**67a–67d**). Further, the 2-oxallyl-Fe(II) cation obtained from 2,4-dibromo-2,4-dimethylpentane-3-one and diiron nonacarbonyl, having no double bond such as TCNE, also affords the 1,3-addition product **67e** [75] (see X-ray structure analysis of **67e** [75]).

The iron or ruthenium carbonyls of acetylcycloheptatriene [76], formylcycloheptatriene [77], *N*-methoxycarbonyl-1H-azepine [80], or tropone [76,78,79] (as the derivatives of cycloheptatriene), also react with a compound having a double bond such as TCNE, hexafluoroacetone, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, *N*-phenyltriazolinedione [77] or *N*-methyltriazolinedione [78] to give exo-1,3-adducts **69**. However, with the azepine–iron system [80], a 1,6-adduct **70** is also obtained. The 1,3-tetracyanoethylene adduct of the cycloheptatrienenoneiron compound readily isomerizes to a 1,5-adduct **71** in solution [80].

The structure of the 1,3-cycloaddition product between tricarbonyl(cycloheptatrienone)iron and *N*-methyltriazolinedione has been determined by X-ray analysis [78].

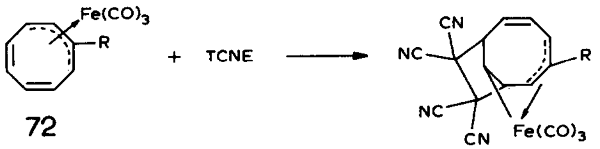
Tricarbonyl(η^4-cyclooctatetraene)iron [73] or its derivatives **72** [81] react by 1,3-cycloaddition with TCNE to afford the σ,π-allyl metal compounds **73** similar to the above reactions of cycloheptatriene. The site of initial attack by the electrophile is markedly influenced by electronic factors. With respect to carbomethoxy substitution, this electron-withdrawing group directs the electrophile preferentially at α and β positions to the substituent. With the methyl (electron-donating) group, the electrophile attacks at the γ and δ ring carbon [81].



68 69 70 71

W = olefins, ketone, triazoindione
M = Fe(CO)$_3$, Ru(CO)$_3$
Z = >NCOOMe, >C=O, >CCHO, >C—COCH$_3$
X—Y =

(23)



72

73

R = Me, Ph, COOMe, OMe

(24)

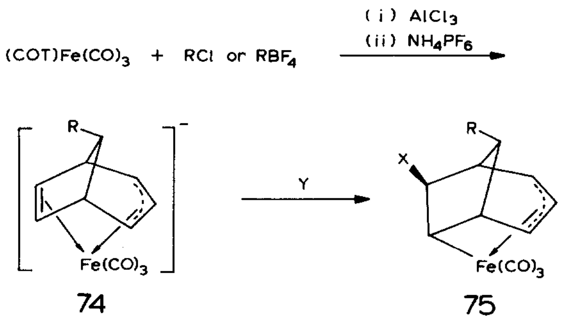
(v) *Reduction of η^2-ethylenic-η^3-allyl metal compounds*

The η^2-ethylenic-η^3-allyl metal compounds described above (Schemes 2, 3) are capable of yielding σ,π-allyl metal compounds by attack of a nucleophile on the double bond.

For example, treatment of tricarbonyl(η^4-cyclooctatetraene)iron with acetyl tetrafluoroborate in the presence of aluminium chloride, followed by addition of ammonium hexafluorophosphate, affords the η^2,η^3-bicyclo-[3.2.1]octadienyl metal cation **74**; this then reacts with sodium tetrahydroborate, or sodium cyanide to give the σ,π-allyl products **75** by exo addition [82].

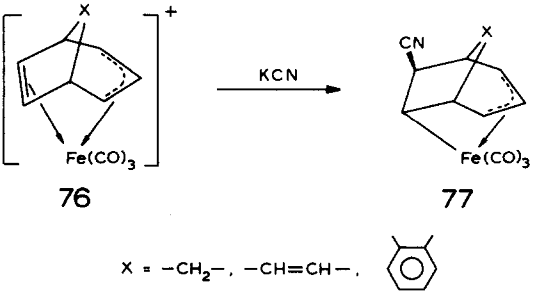
Nucleophilic attack of CN$^-$ not only on methylene, but also, ethylene or *o*-phenylene bridged bicyclodienyliron tricarbonyl tetrafluoroborates, results also in σ,π-allyl compounds **77** by exo addition [83].

With ruthenium compounds such as (COD)Ru(CO)$_3$ [84] (COD =



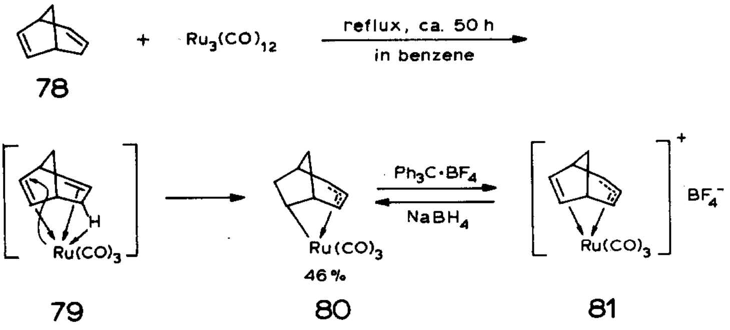
R = CH$_3$CO, PhCO
Y = NaBH$_4$, LiBD$_4$, NaCN
X = H, D, CN

(25)



(26)

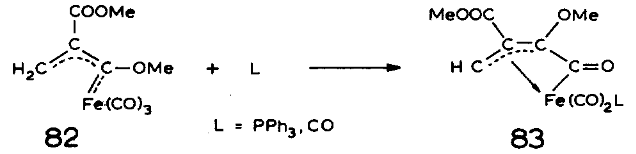
cyclooctadiene) and dodecacarbonyltriruthenium [85] (eqn. (27)), reaction directly with bicyclo[3.2.1]octa-2,6-diene **78** affords the σ,π-allyl metal compounds **80**. Via reaction with (COD)Ru(CO)$_3$, the diene metal compound **79** is also isolated. From the results of a reaction with their deuterium labelled compound Domingos et al. [85] proposed that this reaction (eqn. (27)) proceeds with a hydride transfer mechanism. Conversely, **80** undergoes hydride-ion abstraction with trityl tetrafluoroborate to yield the monocation compound **81**. Treatment of **81** with sodium tetrahydroborate reproduces the initial σ,π-allyl compound **80** [85].



(27)

D. 1-σ-l,m,n-η^3-ALLYL METAL COMPOUNDS

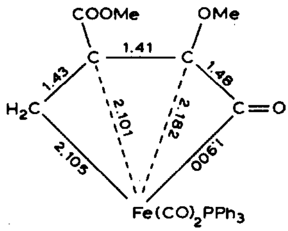
Very few 1-σ-2,3,4-η^3-allyl metal ($n = 1$ in **1**) carbonyl insertion compounds have been reported. The insertion compound **83** (eqn. (28)), is prepared by ligand exchange reaction of (η^3-vinylcarbene)iron compound **82** with triphenylphosphine or carbon monoxide in methylene dichloride at room temperature [86–88]. The (η^3-allyl + η^1-acyl)Fe^{II} structure of the triphenylphosphine product **84**(**83**, L = PPh_3) was determined by X-ray analysis [86,87].



82

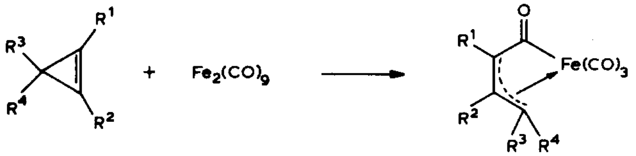
83

(28)



84

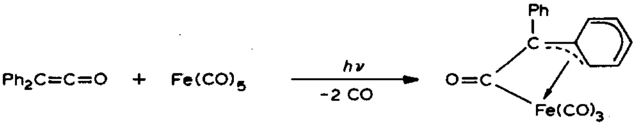
Cyclopropene compounds react with diiron nonacarbonyl to afford σ,π-allyl acyl iron compounds **85** in good yield by ring-opening and carbonylation reactions [89,90]. Such σ,π-allyl metal compounds are also prepared by photolysis of diphenylketene with iron pentacarbonyl, as established by X-ray diffraction [91–93].



85

(29)

R^1 = H, Me, COMe, CMe, i-Pr, t-Bu, C_6H_{11}, Ph, COOMe, n-Pr, $CH{=}CMe_2$
R^2 = H, Me, COMe, $CH{=}CMe_2$, Ph, COOMe, n-Pr, i-Pr
R^3, R^4 = H, Me

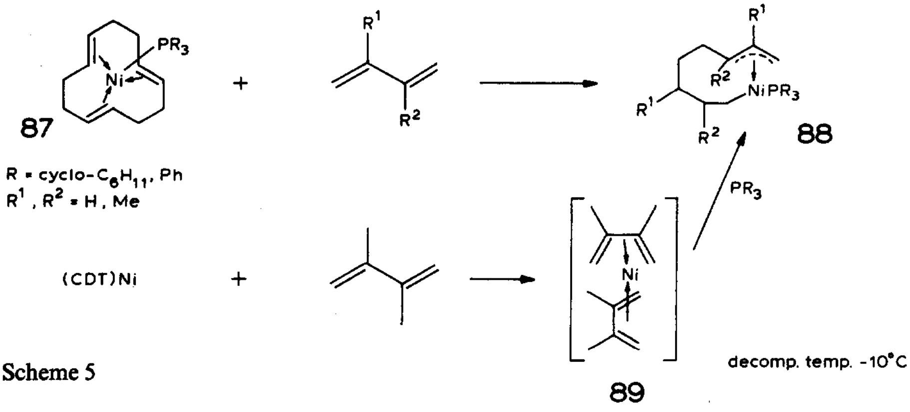


86

(30)

Isolation of another type of σ,π-allyl metal compound having $n = 1$ in **1** is difficult; the presence of such compounds is identified only by ^1H NMR, ^{13}C NMR or IR spectra in reaction solutions such as protonation [94–96] of butadieneiron tricarbonyl, etc. [54,97–100].

The dimerization of butadiene or its methyl substituted derivatives such as isoprene, *trans*-piperylene or 2,3-dimethylbutadiene with cyclododecatriene(triphenylphosphine)nickel **87** affords the σ,π-allyl nickel compound **88** having $n = 5$ in **1** (Scheme 5) [101–104]. Cyclododecatrienenickel reacts with 2,3-dimethylbutadiene at a low temperature (−15°C) to yield bis(2,3-dimethylbutadiene)nickel **89**, and further reacts with phosphine to produce the σ,π-allyl nickel compound **88**. Hence, formation of the σ,π-allyl nickel compounds **88** is presumed to occur via dimerization of the bis(butadiene) (or its derivatives) nickel **89** (which is known to form a tetrahedral structure by ^{13}C NMR study [103]). The structure of bis(isoprene)nickel cyclohexylphosphine **88**($R^1 = CH_3$, $R^2 = H$) was determined by X-ray diffraction [102].

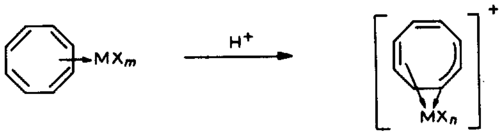


Scheme 5

E. 1,2-η^2-ETHYLENIC-*l*,*m*,*n*-η^3-ALLYL METAL COMPOUNDS

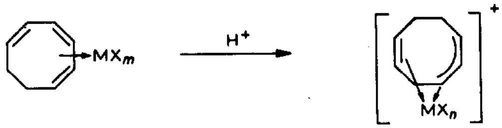
Cyclooctatetraene, cyclooctatriene or cyclooctadiene metal compounds afford η^2-ethylenic-η^3-allyl metal compounds **90–92** by protonation or hydride-ion abstraction as shown in eqns. (31)–(33).

Protonation of Ru(arene)(COT) (arene = mesitylene, hexamethylbenzene or t-butylbenzene) with hydrogen hexafluorophosphate or hydrogen tetrafluoroborate provides $[Ru(\eta^5\text{-}C_8H_9)(arene)]^+$ cations **93** which can be isolated as PF_6 or BF_4 salts. The cations **93** isomerize on warming in organic solvents to the η^2-ethylenic-η^3-allyl ruthenium cations having an uncoordinated double bond **94**. The structure of the mesitylene derivative **94** was determined from single-crystal X-ray data [105].



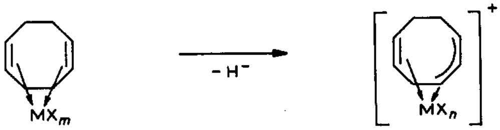
90

(31)



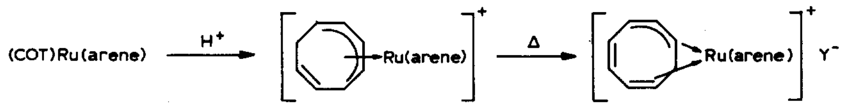
91

(32)



92

(33)



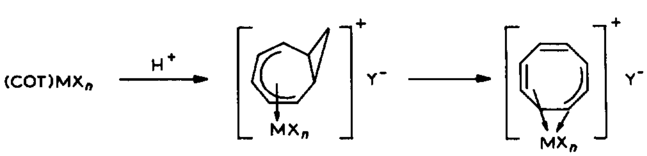
93

94

(34)

Y = PF$_6$, PF$_4$
(arene) = mesitylene, hexamethylbenzene, t-butylbenzene

The ruthenium, cobalt, rhodium, iridium [106,107] and osmium [108] η^2-olefinic-η^3-allyl metal compounds have been prepared. For example, protonation of η^5-cyclooctatetraene(η^5-cyclopentadienyl)cobalt in trifluoroacetic acid initially yielded two isomeric forms of the protonated species $[(C_8H_9)Co(Cp)]^+$, namely η^5-bicyclic cobalt compound **95** and η^2-olefinic-η^3-allyl metal compound **96**, in ca. 1 : 1 ratio. After 48 h in solution isomer **95** isomerized irreversibly to **96**, which is also obtained as the only product of the reaction (35) [106]. NMR spectral studies [109] have demonstrated



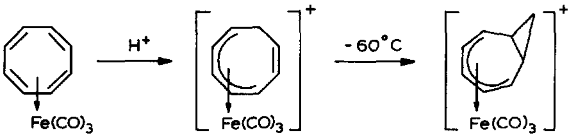
95

96

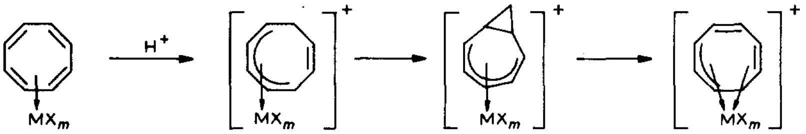
(35)

MX$_n$ = CoCp, RhCp, IrCp, Os(CO)$_3$, Ru(CO)$_3$
Y = PF$_6^-$

that at low temperatures proton attack on tricarbonyl(η^4-cyclooctatetraene)iron generates tricarbonyl(η^5-cyclooctatrienylium)iron **98** which rearranges to η^5-bicyclo[5.1.0]octadienylium(tricarbonyl)iron **99** at −60°C. Hence, it is proposed that formation of η^2-olefinic-η^3-allyl metal compounds from COT metal complexes by protonation proceeds via η^5-cyclooctatrienylium metal **101** and η^5-biscyclooctadienylium metal intermediate **102** as shown in eqn. (37) [106].

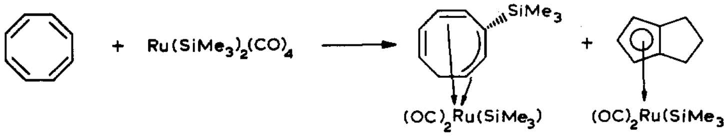


97 98 99 (36)



100 101 102 103 (37)

Cyclooctatetraene reacts with tetracarbonyl(bis-trimethylsilyl)ruthenium in hexane at reflux temperature to give the trimethylsilyl migration product **105** and ring-closed tetrahydropentalenyl compound **106** (eqn. (38)). The molecular structure of the former η^2-olefinic-η^3-allyl metal compound **105** has been established by a single-crystal X-ray diffraction study [110].

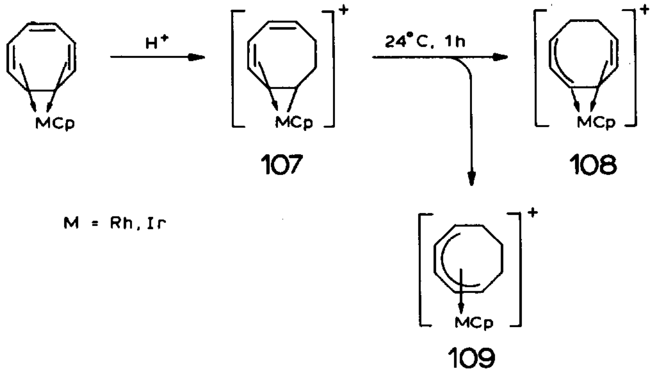


104 105 106 (38)

As shown in eqn. (25), tricarbonyl(η^4-cyclooctatetraene)iron reacts with acetyl or benzoyl compounds to give η^2-ethylenic-η^3-allyl metal compound **74** having a bridge formed by a carbon of the cyclooctatetraene. X-ray diffraction studies have established the molecular structure of the acetyl hexafluorophosphate salt **74** [111].

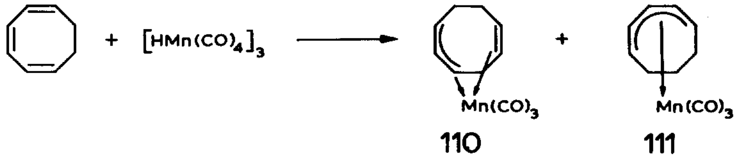
In addition, methyl or methylol derivatives of COT also afford η^2-ethylenic-η^3-allyl metal compounds [112–114].

Protonation of cyclooctatriene metal compounds gives η^2-ethylenic-η^3-allyl metal compounds having no uncoordinated double bond. This behaviour is different from that of the cyclooctatetraene metal compounds shown by eqns. (34)–(37), e.g., the protonations of cyclooctatriene(cyclopentadienyl)rhodium or iridium first yields σ,π-cationic compound **107** and subsequent prototropic rearrangements yield both η^2-ethylenic-η^3-allyl **108** and η^5-cyclooctadienyl compound **109** [115,116].



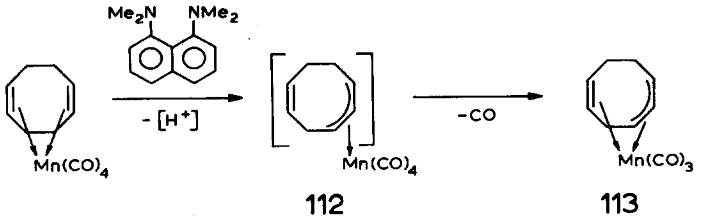
(39)

Treatment of cyclooctatriene with metal hydride also yields neutral η^2-ethylenic-η^3-allyl **110** and η^5-cyclooctadienyl compound **111** by hydrometalation (eqn. (40)) [117].



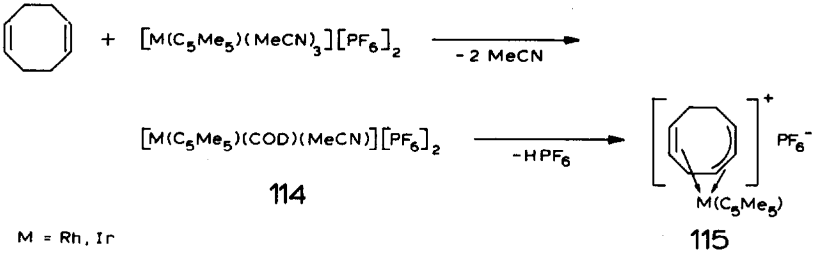
(40)

On the other hand, cycloocta-1,5-diene, or its metalated compound reacts with a deprotonation reagent such as amine or tetrafluorophosphorus salt to afford η^2-ethylenic-η^3-allyl metal compounds. In reaction of tricarbonyl(η^4-cycloocta-1,5-diene)manganese with 1,8-bis(dimethylamino)naphthalene, the amine initially removes a proton from the cycloocta-1,5-diene manganese compound to give the η^3-allyl manganese compound **112** which then releases carbon monoxide to give the η^2-ethylenic-η^3-allyl manganese compound **113** [118].



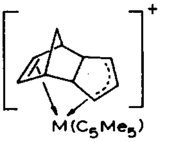
(41)

Both $[M(C_5Me_5)(MeCN)_3][PF_6]_2$ and $[M(C_5Me_5)(Me_2CO)_3][PF_6]_2$ (M = Rh or Ir) act as deprotonation and metalation reagents [119]. They react directly with cycloocta-1,5-diene to afford the η^2-ethylenic-η^3-allyl compounds **115** [119]. The former $[M(C_5Me_5)(MeCN)_3][PF_6]_2$ is a less active deprotonation reagent than the latter $[M(C_5Me_5)(Me_2CO)_3][PF_6]_2$. In reactions with the former reagent, ^1H NMR data lead to the conclusion that the intermediate is **114** which subsequently undergoes spontaneous deprotonation to give **115** [119].



114 **115** (42)

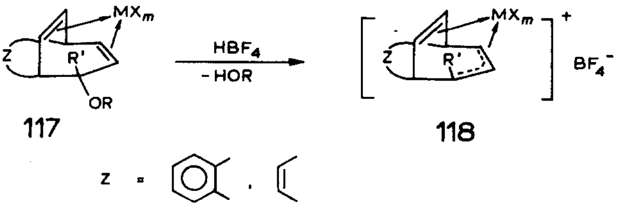
Dicyclopentadiene also affords η^2-ethylenic-η^3-allyl metal compounds **116** similar to **115** by reaction with these deprotonation reagents [119]. Bis(triphenylphosphine)carbon ($(Ph_3P)_2C$) also gives the η^2-ethylenic-η^3-allyl metal compound by reaction with cycloocta-1,5-dieneiridium hexafluorophosphate [120].



116 M = Rh, Ir

The hydride abstraction reagent trityl fluoroborate reacts with equimolar cycloocta-1,5-diene(cyclopentadienyl)cobalt to give the η^2-ethylenic-η^3-allyl metal cation similar to **115**, but reaction with cycloocta-1,5-diene(cyclopentadienyl)rhodium [121] or iridium [122] gives the neutral η^2-ethylenic-η^3-allyl metal compounds (e.g. $Ph_3C \cdot C_5H_4RhC_8H_{12}$, in which the cyclopentadienyl ring has undergone an electrophilic substitution).

Trityl fluoroborate reacts with bicyclic σ,π-allyl metal compound **80** to give η^2-ethylenic-η^3-allyl metal compound **81** (eqn. (27)). When the bicyclo[3.2.1]octadiene **78** is heated in methylcyclohexane solution in the presence of iron pentacarbonyl, the neutral η^2-ethylenic-η^3-allyl metal compound is formed. The molecular structure of the η^2-olefinic-η^3-allyl iron carbonyl cation (metal in **81** is iron) prepared by treatment of the neutral compound with trityl fluoroborate, was determined by X-ray diffraction [123].

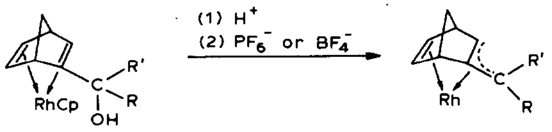


117 **118** (43)

R = H, Me
R' = H, Me
MX_m = $Fe(CO)_3$

Reaction of bicyclo[3.2.2] alcohols or their methyl ether with diiron nonacarbonyl yields the corresponding dienyl iron tricarbonyl **117** which upon tetrafluoroboric acid treatment yields the η^2-ethylenic-η^3-allyliron tricarbonyl cation **118** [83,124–126].

As pointed out in a previous review [12], the norbornadiene metal compounds **119** have a narrow olefin midpoint–metal–olefin midpoint bite angle. The removal of a hydroxy group from **119** forms a π-allyl group at the outer side of the norbornadiene ring [127,128]. The structure of this η^2-ethylenic-η^3-allyl rhodium hexafluorophosphoric salt is supported by a single-crystal X-ray diffraction study [128].



119 120

(44)

R, R' = H, Me, Ph, ferrocenyl

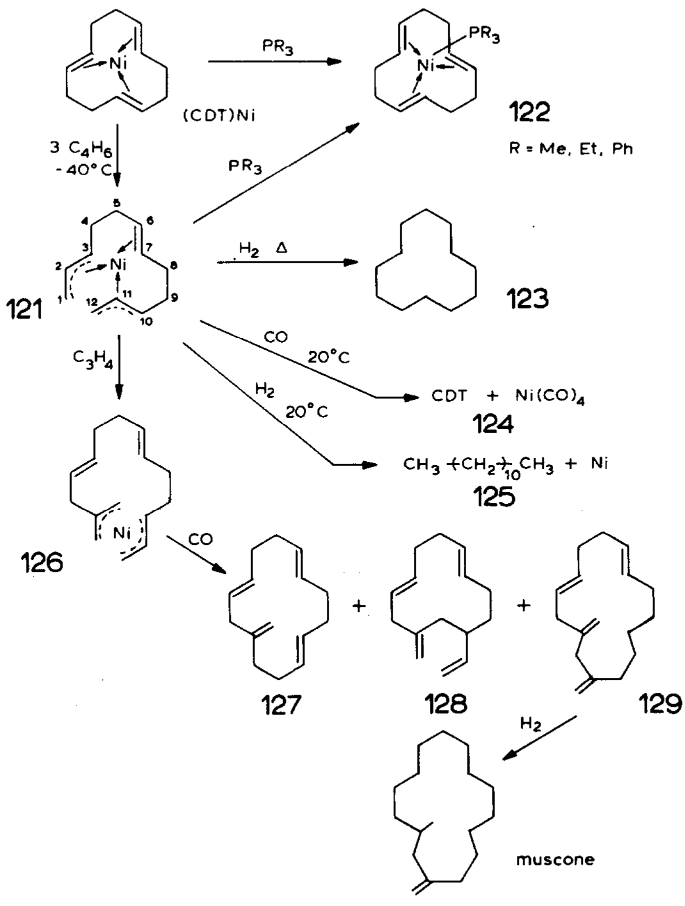
Other η^2-ethylenic-η^3-allyl metal compounds are involved in metal complex catalyzed 1,4-polymerization of butadiene [129], etc. [130].

F. 1,2,3-η^3-ALLYL-*l*,*m*,*n*-η^3-ALLYL METAL COMPOUNDS

Compounds having two π-allyl bonds, i.e., 1,2,3-η^3-allyl-*l*,*m*,*n*-η^3-allyl metal compounds have been reported. For example, all *trans*-cyclododecatriene(1,5,9)nickel(0) reacts by the replacement of butadiene trimer for the cyclododecatriene ligand with a triple molar quantity of the butadiene at −40°C to afford the compound **121** having two π-allyl coordination bonds at 1,2,3 and 10,11,12 and one olefinic π-bond at 6,7-positions. Further, **121** reacts by cyclization with phosphine to yield all *trans*-cyclododecatriene(1,5,9)nickel phosphine **122**.

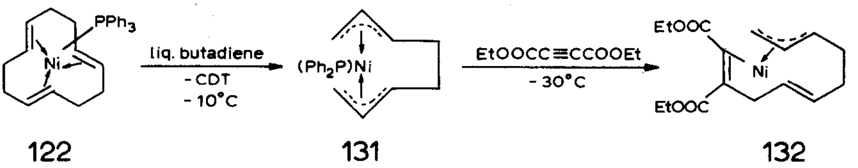
In place of the phosphine, reactions with hydrogen or carbon monoxide yield cyclododecane, n-dodecane or cyclododecatriene, **123**–**125** [131–136]. In addition, the reaction with allene yields cyclic olefins **127**–**129** via bis-π-allyl **126**, and on hydrogenation **129** gives muscone **130** having a strong musk odour [137].

The triphenylphosphine adduct of cyclododecatrienenickel **122** reacts with liquid butadiene at −10°C to yield the α,ω-bis-π-allyl-C_8 nickel compound **131** by dimerization of butadiene [138–141]. Further, the reaction of **131** with acetylenedicarboxylic acid diethylester at −30°C produces the σ,π-allyl compound **132** by insertion of the ester in one π-allyl coordination bond. Other examples of α,ω-bis-π-allyl-C_8 metal compounds are isolated as zirconium cyclooctatetraene derivatives from the butadiene dimerization reaction [142].



Scheme 6

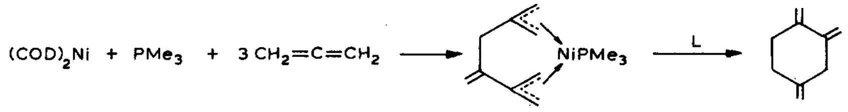
In place of a nickel compound, ruthenium trichloride reacts with butadiene in 2-methoxyethanol at 90°C to give a bis-π-allyl compound similar to **121** [132,134,137], and the crystal structure of the dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV) was determined by X-ray diffraction measurements [133].



(45)

In place of butadiene, allene reacts with the nickel compound in the presence of phosphine (eqn. (46)), or directly with nickel diphosphine-

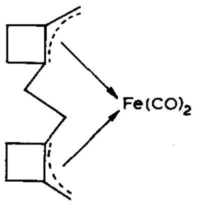
($Ni[P(C_6H_{11})_3]_2$) or nickel diphosphite ($Ni[P\text{-}(OC_6H_4\text{-}o\text{-}C_6H_5)_3]_2$) to yield the bis-π-allyl compound **133** with an allene trimer. Further reaction of **133** [143] with triphenylphosphine or carbon monoxide forms demetalated 1,2,4-trimethylenecyclohexane **134** [144].



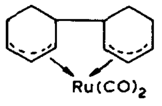
(46)

133 134

L = PPh_3, CO



135



136

The other bis-π-allyl metal compounds are 1,2-dimethylcyclobutane **135** [145] 1,3-cyclohexadiene metal compound **136** [146], etc. [147–149].

G. CONCLUDING REMARKS

Among the organometallic intramolecular-coordination compounds containing a π-allyl donor ligand **1**, many compounds having $n = 3$ have been synthesized and are found to be relatively strain-free and stable. Most of the others involve $n = 2$; very few have $n = 1$, 5 or 7. The rest are η^2-ethylenic-η^3-allyl or bis-π-allyl compounds.

The majority of these compounds contain iron, ruthenium, nickel and osmium. Very few compounds involve rhodium, cobalt, iridium, manganese, or molybdenum.

Compounds are synthesized by diolefin monoolefin reactions, cyclopolyolefin reductions, cyclopropane ring openings and carbonylations, cyclopolyolefin carbonylations, 1,3-cycloadditions, etc. These π-allyl metal compounds are usually produced via metal olefin π-complex intermediates such as **4**, **5**, **7**, **30** and **79**.

ACKNOWLEDGEMENT

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

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