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ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS CONTAINING A DIOLEFIN DONOR LIGAND

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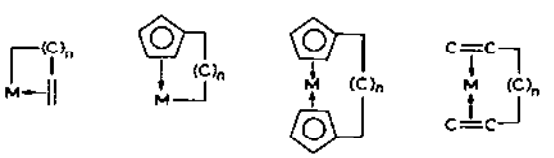
A. INTRODUCTION

Organometallic intramolecular-coordination compounds ($\overbrace{M-(C)_n-Y}$; M = metal; Y = coordinating atom or group; $n \geqslant 1$) have been classified mainly into three kinds; σ,σ type, σ,π type (in which the M—C bond is a σ-bond and the M—Y bond is a σ- or π-bond) and π,π type coordination compounds (in which both the bonds are π-bonds). Parshall [1], Prokof'ev et al. [2], Nonoyama [3], Dehand and Pfeffer [4], Bruce [5] and Omae [6–12]



1 (σ,π) 2 (σ,π) 2′ (π,π) 3 (π,π)

have reviewed the σ,σ type which involve chelate compounds having transition metal–carbon σ-bonds, cyclometallated compounds, or organometallic intramolecular-coordination compounds. In these compounds Y is selected

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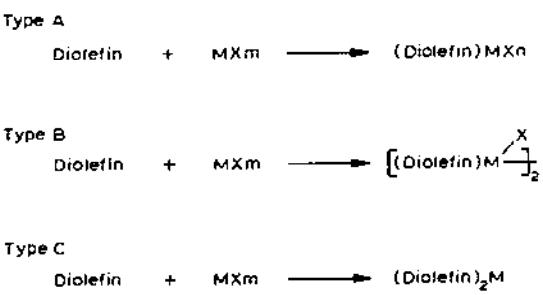
predominantly from five elements: N, P and As in Group VB and O and S in Group VIB. They tend to form a five-membered ring structure [6–12]. The σ,π and π,π type coordination compounds have also been reported in many reviews [13–24] and monographs [25,26]. The author has reviewed organometallic intramolecular-coordination compounds containing a carbon–carbon double bond donor ligand [27] (σ,π type) and a cyclopentadienyl donor ligand [28] (σ,π and π,π type). In the former review, it was pointed out that the intramolecular-coordination compounds **1** having a carbon–carbon double bond tend to form easily a 5.5-membered ring structure ($n = 3$) sterically free from strain and in the latter review it was shown that the σ,π type and π,π type cyclopentadienyl compounds (**2** and **2'**), where n is 3 or 4, are almost strain-free. Here we are interested in other π,π type coordination compounds having a simple diolefin donor ligand as shown in formula **3** ($n \geqslant 1$), and discuss their structural characteristics, synthetic methods, X-ray data, reaction mechanisms, chemical properties etc.

This review does not include intramolecular-coordination compounds having a delocalized π-bond such as π-allyl, phenyl or cyclopentadienyl, and the butadiene compounds **3** ($n = 0$), because of their ability to form a mainly delocalized π-bond.

B. SCOPE

Organometallic intramolecular-coordination compounds containing a diolefin donor ligand as shown in formula **3** are primarily metal compounds of 1,5-cyclooctadiene ($n = 2$), dicyclopentadiene ($n = 2$), norbornadiene ($n = 1$) or cyclooctatetraene ($n = 2$).

These compounds can be classified into three types in accordance with the structures of reaction products. With respect to the reactions of diolefins



with MX_m, the type of products derived depends predominantly on the nature of M and X_m rather than the reaction conditions. In the case of type B, the products form a bridge, with X_m restricted to substances, e.g.,

chloride, sulfide, etc. which are capable of forming a bridge. For example, when the diolefin is 1,5-cyclooctadiene, in type A M = Pd, Pt, Ru, W, Mo, Fe, Cr, Co, Ni, Re or Rh; while in type B, M = Cu, Ir, or Rh; hence only Rh is involved in both types. However, the rhodium compound for type A should not be rhodium halide which is capable of forming the bridge compound in type B. In the case of type C, the products should be prepared by substitution of four ligands at the same time. For example, $M(acac)_2$ having four coordination bonds is used as MX_m, and M(cyclododecatriene) having three π-coordination bonds is also used in type C. In this manner, the kind of MX_m for type B and C are limited considerably. The majority of products are of type A. $(Diolefin)_2M$ obtained as type C, are also easily prepared by the reaction of $(diolefin)MX_n$ with the diolefin under UV irradiation.

The diolefin metal compounds prepared in this manner react with amines, phosphines, acetylacetones, olefins, halides, acetates, potassium superoxide, etc. to afford new diolefin metal compounds by ligand exchange reactions without fission of the intramolecular-coordination bonds. All these diolefin metal compounds show large spectroscopic shifts due to coordination of the diolefin to the metal, e.g., 100–150 cm^{-1} in IR $\nu C{=}C$ or ca. 1 ppm on ^1H NMR, compared with the free diolefins.

The coordination bond of organometallic intramolecular-coordination compounds containing a ligand with two carbon–carbon double bond donors, is fairly stable, and ligand exchange reactions with other ligands proceeds without cleavage of the intramolecular coordination bonds. However, some of these compounds can undergo ligand exchange reactions with other olefins to produce different olefin metal compounds.

The reactions of the two double bonds in the formation of intramolecular-coordination compounds containing a diolefin donor ligand proceed in two stages, based on the isolation of an intermediate at low temperature, in which only one double bond coordinates to the metal.

The compounds, in which $n = 2$, are generally stable because the double bond midpoint–metal–double bond midpoint bite angle(α) of these metal compounds is close to 90°, suitable for forming tetrahedral, trigonal-bipyramidal or square-planar coordination structures.

On the other hand, when the two double bonds are located near to each other ($n = 1$) the bite angle α is narrow, e.g., that of norbornadiene is ca. 70°. However, these norbornadiene compounds generally have a bridge carbon atom which links the two double bonds, and which allows the two double bonds to locate favorably for coordination to a metal. This suppresses delocalization of the double bond which will give a narrower bite angle than 70°, for formation of stable intramolecular-coordination compounds. However, under certain circumstances the reaction proceeds to

broaden the bite angle α of the products.

The double bond lengths of these compounds are 1.33–1.44 Å, slightly long compared to the normal double bond length.

C. CYCLOOCTADIENE COMPOUNDS

1,5-Cyclooctadiene (COD) metal compounds, where n is 2, have been studied very extensively. These compounds were synthesized by reactions of COD with metal halides [29–33], metal carbonyls [29,34–44], cuprous triflate-benzene [45], π-tolyl [46], phosphine [47] or metal hydride [48] as shown in eq. (1), that is, type A.

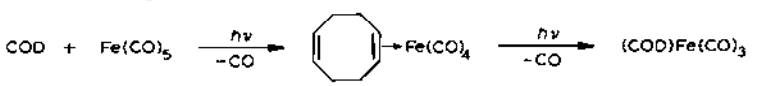
Type A

4 (COD)MXn (1)

MXm : Na_2PdCl_4[29], $(PhCN)_2PdCl_2$[29], K_2PtCl_4[30,31], [K_2PtCl_4 + KI][32], $RuCl_3$[33], $W(CO)_6$[34-36], $(CH_3CN)_3W(CO)_3$[37], $Mo(CO)_6$[33-36], $Fe(CO)_5$[35,38], $Fe_3(CO)_{12}$[39,40], $Cr(CO)_6$[35,36,41], $Ru(CO)_4(GeMe_3)_2$[42,43], $Cr(CO)_5(P(OMe)_3)$[41], $CpCo(CO)_2$[44], $[CuOSO_3CF_3]_2 \cdot C_6H_6$[45], $(C_6F_6)_2Ni(Tol)$[46], $(Ph_3P)_2RhC_6H_4PPh_2$[47], $(Ph_3P)_2ReH_7$[48]

MXn : $PdCl_2$, $PtCl_2$, PtI_2, $RuCl_2$
$W(CO)_4$, $Mo(CO)_4$, $Fe(CO)_3$
$Cr(CO)_4$, $Ru(CO)_2(GeMe_3)_2$
CoCp, $Cu(OSO_2CF_3)$, $Ni(C_6F_6)_2$,
$(PPh_3)RhC_6H_4PPh_2$, $(Ph_3P)_2ReH_3$

$(COD)Fe(CO)_3$ was produced by reactions of COD with $Fe_3(CO)_{12}$ [39,40], or $Fe(CO)_5$ [35], and was reported as a liquid (n_D^{20} 1.5765) or an unstable solid melting just below room temperature. Later, Gustoff and Hogen [38] reinvestigated this reaction: illumination of $Fe(CO)_5$ and COD yielded $(COD)Fe(CO)_4$ as an unstable oil (n_D^{20} 1.575) when only about a third of the $Fe(CO)_5$ reacted. Similarly to $(COD)Fe(CO)_3$, this product could be recrystallized from pentane at $-120°C$ and its structure is supported by degradation with $Ce(NH_4)_2(NO_3)_6$, elemental analyses, IR, NMR, and mass spectral data.



(2)

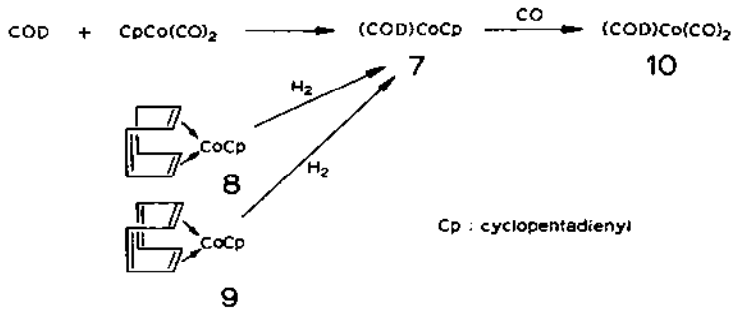
5

n_D^{20} 1.575
τ 4.53 ppm (2H)
τ 6.8 ppm (2H)
τ 7.9 ppm (8H)

6

mp 90–90.5 °C
–
τ 6.6 ppm (4H)
τ 8.0 ppm (8H)

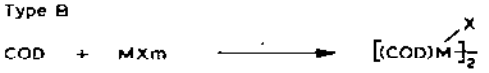
Extended irradiation of $Fe(CO)_5$ with COD yielded $(COD)Fe(CO)_3$ as stable orange crystals (m.p. 90–90.5°C) as shown in eqn. (2). Therefore, we suppose the liquid product to be mainly $(COD)Fe(CO)_4$ (**5**). Eqn. (2) is consistent with the view that these intramolecular-coordination compounds containing a diolefin donor ligand are produced in two stages.



Scheme 1

COD metal compounds **4** obtained in this manner form a tub configuration (i.e. boat configuration) as shown in eqn. (1). (Cyclooctatriene)- or (cyclooctatetraene)cyclopentadienecobalt dicarbonyl are compounds having one or two additional carbon–carbon double bonds, compared with COD. (COD)CoCp **7** having the tub configuration was prepared by reaction of COD with cyclopentadienecobalt dicarbonyl [44], and **7** was also derived by hydrogenation of the cyclooctatrienecobalt compound **8** or cyclooctatetraenecobalt compound **9** [49]. Further, the reaction of **7** with carbon monoxide affords dicarbonyl compound **10** by displacement of the cyclopentadienyl moeity. This reaction shows the high stability of 1,5-cyclooctadiene metal compounds in that the bond between COD and metal is more stable than that between cyclopentadienyl and metal.

Type B



(3)

11

MXm : $CuCl$[50, 51], $CuCl_2$[50,51], $RhCl_3$[52-54], Na_2IrCl_6[54]
MX : RhCl, IrCl, CuCl

In the cases where MX_m in eqn. (1) are copper [50,51], rhodium [52–55], or iridium halides [55], the reaction affords not $(COD)MX_n$ type compounds but halo-bridged compounds **11** as shown in eqn. (3), that is, type B. For example, cuprous chloride dissolved in 0.18 N hydrochloric acid, and added to COD yielded the cuprous compound **11** after 10 min shaking [50,51]. The

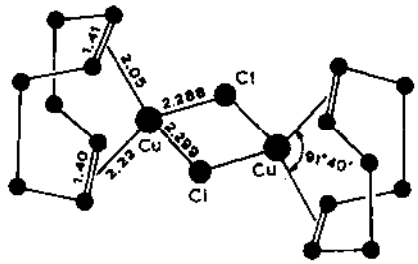


Fig. 1. Structure of $[(COD)CuCl]_2$.

structure of this compound was determined by X-ray diffraction [50]. It is a centro-symmetric chloro-bridged compound, where the COD molecule is in the tub configuration. The copper atoms are quasi-tetrahedrally bonded to two chlorine atoms and to the two double bonds of a COD molecule (Fig. 1).

$$COD + Fe \rightarrow \underset{\mathbf{12}}{(COD)_2Fe} \tag{4}$$

An iron COD compound can be prepared by direct reaction of metal with COD [56,57] under vacuum (eqn. 4), e.g., the reaction is carried out in a rotary apparatus with COD at $-120°C$ and the vapor pressure of iron less than 10^{-1} torr. The brown crystalline product, $(COD)_2Fe$, was labile and rapidly decomposed to metallic iron above $-20°C$ or caught fire in the air. When it was treated with trifluorophosphine at $-30°C$ in n-hexane, $(COD)Fe(PF_3)_3$ was formed; similarly cyclooctatetraene (COT) reacts with the compound at $-30°C$ to form $(COT)_2Fe$ [56].

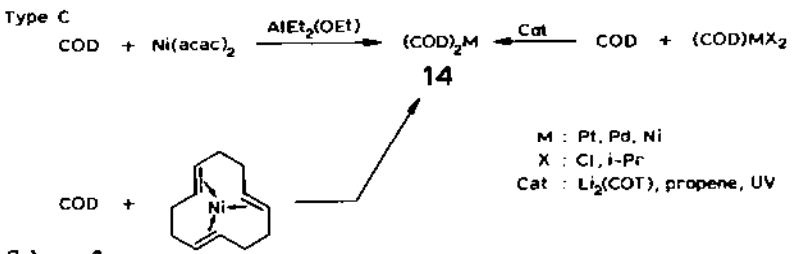
$$COD + M + L \rightarrow \underset{\mathbf{13}}{(COD)MLn} \tag{5}$$

M: Fe [57], Cr [58,58a]
L: CO, PF_3, $P(OMe)_3$
MLn: $Cr(CO)_4$, $Cr(PF_3)_4$, $Fe(P(OMe)_3)_3$

In the presence of strong electron donors such as phosphite [57], phosphine [58,58a] or carbon monoxide [58,58a], a metal is capable of reacting directly with COD to afford a stable COD compound **13**, corresponding to **4** (eqn. 1), as shown in eqn. (5); e.g. the reaction of chromium with COD in the presence of CO affords $(COD)Cr(CO)_4$, which is also prepared by reaction of $Cr(CO)_6$ with COD in eqn. (1). Therefore, these components of (M + L) and the ML_n moiety correspond to MX_m and MX_n in eqn. (1), respectively. This reaction proceeds by activating the metal by coordination

of the strong electron donor L, but L as an activator is capable of further reacting with the product; hence the selectivity of this reaction is not high. Further, generally, these direct reactions require a temperature lower than $-100°C$ and high vacuum for evaporation of the metal.

The bis(cyclooctadiene) metals, prepared by direct reaction as shown in eqn. (4), are usually synthesized in good yield in two stages by reaction of COD metal halides [59] or COD metal alkyls [60] with another molecule of COD in the presence of a catalyst such as Li_2(COT), propene or ultraviolet light. They can also be prepared in one step by reaction of COD with nickel acetylacetonate [61] in the presence of $AlEt_2$(OEt) or with cyclododecatriene nickel (Scheme 2) [62,63].

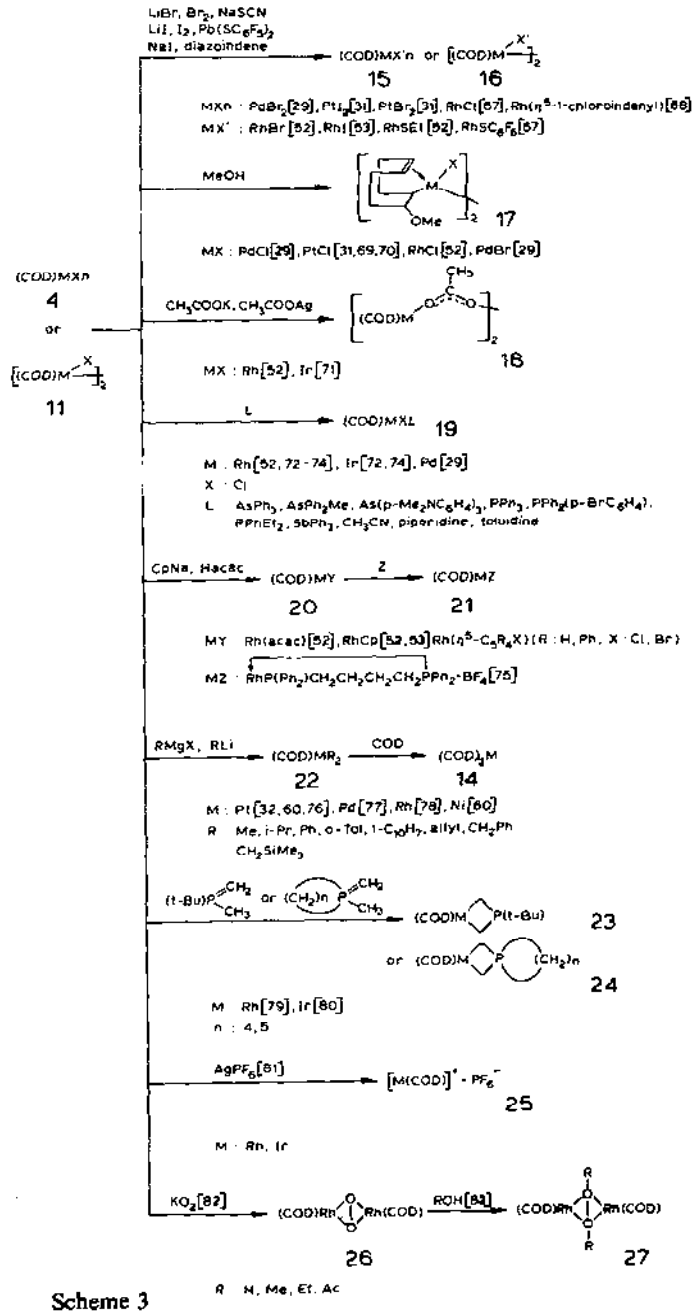


Scheme 2

Other synthetic procedures for COD metal compounds, e.g., (1,5-cyclooctadiene)cyclopentadienyl metal compounds from metalocenes [64–66], have also been reported. These COD metal compounds generally fall into three types $(COD)MX_n$, **4**, $[(COD)MX]_2$, **11** and $(COD)_2M$, **14**, prepared by reactions described in eqns. (1) and (3) and Scheme 2. These were converted easily to their derivatives by reactions with various reagents as shown in Schemes 3 and 4 and eqn. (6).

For example, reactions of **4** or **11** with lithium bromide, sodium iodide, lithium iodide, bromine, iodine, sodium thiocyanate, pentafluorophenylthiolate, diazoindene, etc. afford substituted products **15** or **16**. Reactions with alcohols in the presence of a base afford a σ,π type coordination compound **17** (i.e. compound **1**) by bonding of both the alkoxy group and metal to one double bond in COD [27]. Treatment with acetates gives the acetate bridged compounds **18**. Treatment with electron donors such as phosphines, amines, arsine or stilbine gives the single ligand substituted compounds **19** by ligand exchange reaction. On the other hand, treatment with cyclopentadienyl compounds, acetylacetone or diazocyclopentadienide gives two ligand exchanged products **20**. As the bond of COD to metal in **20** is stronger than that of acac, further reaction with bis(diphosphino)butane yields the product **21** with displacement of acac [75].

Grignard reagents or organolithium compounds easily react with **4** or **11**



Scheme 3

to afford the alkyl, aryl or allyl derivatives **22**. The dialkyl compounds **22** give $(COD)_2M$, **14**, by reaction with an excess of COD under UV irradiation as shown in Scheme 2.

Reactions of **11** with alkyl olefins [83] or cyclic olefins [84,85] in the presence of Grignard reagents, easily afford COD metal olefin derivatives, e.g., reaction of $[(COD)RhCl]_2$ with 1,3,5-cyclooctatriene in the presence of isopropyl Grignard reagent affords (1,5-cyclooctadiene)-η^5-1,2,3,4,5-cyclooctadienylrhodium [86] (cpd. **45** in Table 1). This reaction probably proceeds via a dialkyl compound **22** which is the product of the reactions with Grignard reagents.

Treatment of the diisopropylplatinum compounds **22** ($MR_2 = Pt(i\text{-}Pr)_2$) with various kinds of fluorocarbons under UV irradiation, also affords the fluorine compounds where the fluoride substitutes the two alkyl groups [87]. For example, treatment with tetra-fluoroethylene gives the dimerized product ($(COD)Pt\overline{CF_2CF_2CF_2CF_2}$) having a five membered ring.

In the reaction with methylmethylenephosphorane, the compounds **4** afford the four-membered ring compounds **23** and **24** bonded with both the methylene and methyl groups [79,80]. Reaction with silver hexafluorophosphine [81] gives the ionic compound **25**.

Potassium superoxide [82] reacts easily with halo-bridge compounds **11** to give the dioxygen-bridge compound **26**, and **26** is also easily converted to the other bridged compounds, e.g. the alkoxy-bridge compound **27** by treatment with an alcohol. Potassium superoxide is a good reagent for bridge formation and the dioxygen-bridged product is also a good reagent for formation of other bridged compounds such as alkoxy, hydroxy, chloro, acetoxy, etc.

$$Pt(COD)_2 + Olefin \rightarrow \underset{\mathbf{28}}{(COD)Pt(Olefin)_n} \qquad (6)$$

$n = 1$: dimethyl fumalate, diethyl fumalate, maleic acid, pyran (**53** in Table 1), benzo-1,4-quinone (**55** in Table 1)
$n = 2$: methylvinylketone

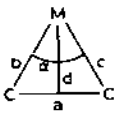
Bis(1,5-cyclooctadiene) metal compounds **14** are easily converted to COD metal compounds by substitution of olefins, allyls, ketones, acetylenes, etc. for one COD. For example, the platinum compound $Pt(COD)_2$ affords three or four coordinate compounds. The three coordinate compounds are the mono-substituted products of $Pt(COD)_2$ with monoolefins ($n = 1$) such as fumarate, or maleic anhydride [88], and pyran [89] as diolefin ($n = 1$), and the four coordinate compounds are monosubstituted with the diolefin of benzo-1,4-quinone ($n = 1$) [90] and the disubstituted compound

$$\left((COD)Pt \leftarrow \begin{bmatrix} CH \\ \| \\ CHCOMe \end{bmatrix}_2, \quad (n = 2)\right)$$

with methylvinylketone [91].

TABLE 1

Selected mean distances (Å) and angles (deg) for some COD metal compounds



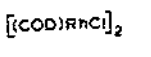
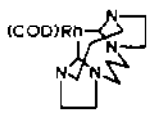
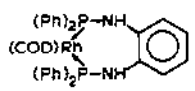
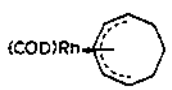
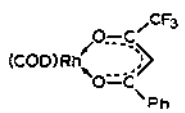
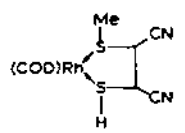
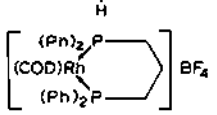
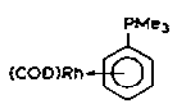
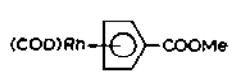
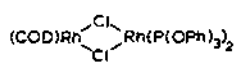
Compound		*a*	$(b+c)/2$	*d*	α	Ref.
	**42**	1.44	2.12	2.00 [a]	90	103, 104
	**43**		2.196			105
	**44**	1.398	2.256	2.145 [a]		106
	**45**	1.42	2.23	2.11 [a]		86
	**46**	1.403	2.118	1.999 [a]		107
	**47**	1.40		2.08		108
	**48**	1.335	2.242	2.140 [a]		109
	**49**	1.34	2.18	2.08 [a]		110
	**50**	1.388	2.115	1.998 [a]		111
	51	1.41	2.094	1.97 [a]		112
	**52**	1.43	2.10	1.98 [a]		113

TABLE 1 (continued)

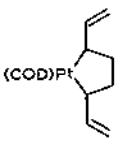
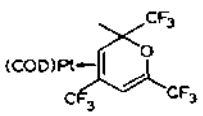
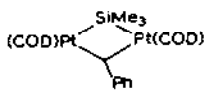
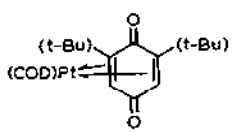
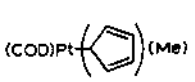
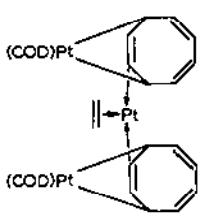
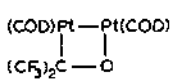
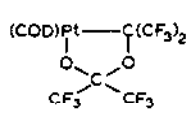
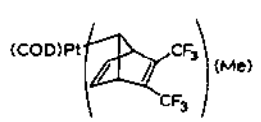
Compound		*a*	*(b + c)/2*	*d*	*α*	Ref.
	**41**	1.42	2.29	2.18		100, 101
	**53**	1.37	2.244	2.14 [a]	85.7	89
	**54**	1.40	2.243	2.131		114
	**55**	1.397	2.182	2.068 [a]	86.1	90
	**56**	1.384	2.229	2.119	85.6	115
	**57**	1.38	2.21	2.11	85.7	116
	**58**	1.37	2.25	2.16	86.1	117
	**59**	1.43	2.22	2.10	86.7	117
	**60**	1.35	2.257	2.15 [a]		118

TABLE 1 (continued)

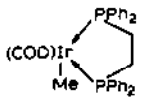
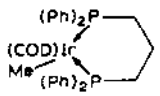
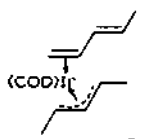
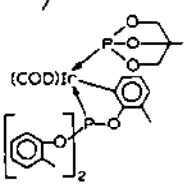
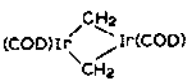
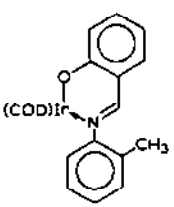
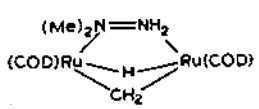
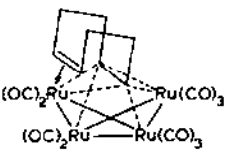
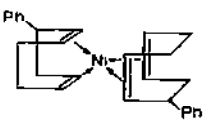
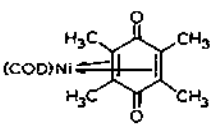
Compound		*a*	(*b* + *c*)/2	*d*	α	Ref.
	**61**	1.417		2.059	84.0	119
	**62**	1.434		2.080	83.2	120
	**63**		2.20			121
	**64**	1.43	2.21	2.09 [a]		122
$(COD)Ir(Me)(PPrnMe_2)_2$	**65**	1.374		2.098	86.4	123
	**66**		2.20			124
	**67**	1.422		2.002	88.0	125
$(COD)RuC_6H_6$	**68**	1.414	2.138	2.018 [a]		126
$(COD)Ru(N{=}NMe_2)_3$	**69**	1.41	2.16	2.04 [a]		127
	**70**	1.42	2.18	2.06 [a]		128, 129
$(COD)Ru(py)_2(Cl)H$	**71**	1.400	2.168	2.052 [a]	86.5	130

TABLE 1 (continued)

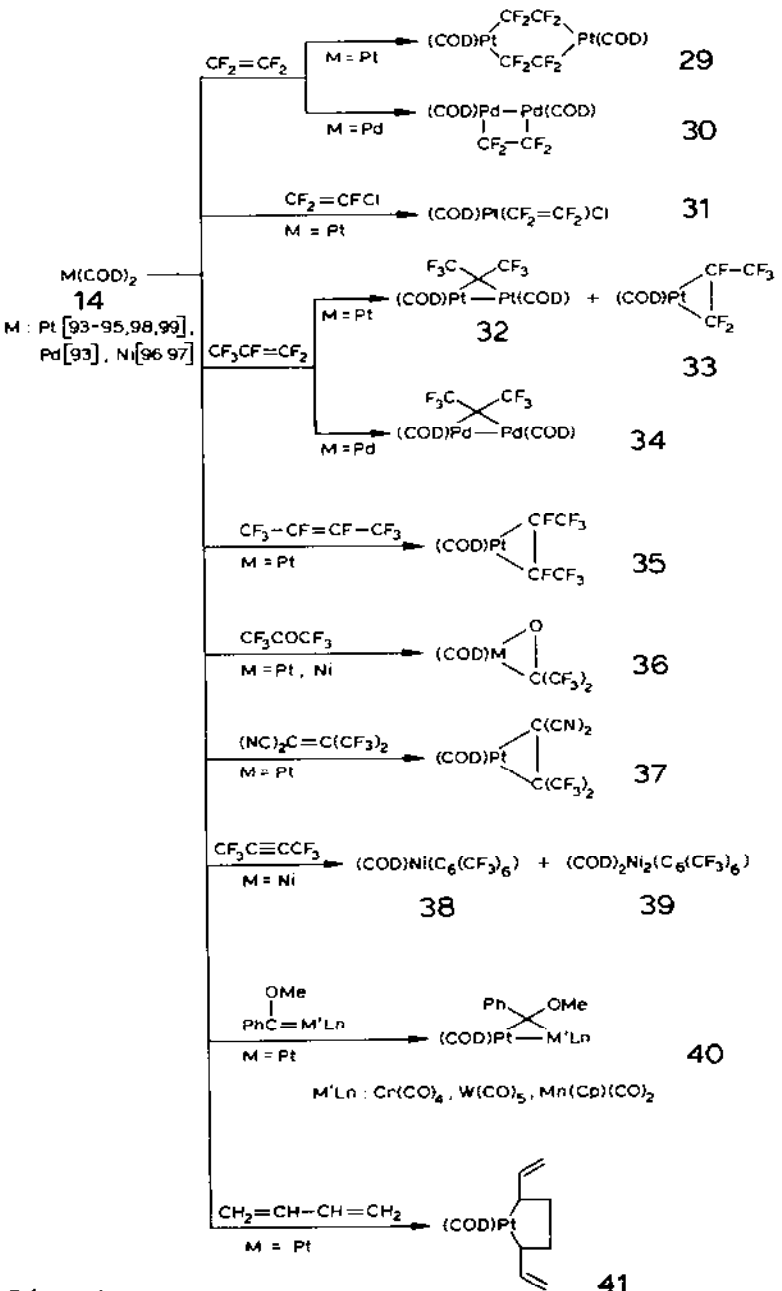
Compound		a	(b + c)/2	d	α	Ref.
(COD)Ru(Cl)$_2$(hexylamine)$_2$	72	1.389	2.179	2.065	85.9	131
	73	1.43	2.23	2.11 [a]		132, 133
(COD)$_2$Ni	74	1.38 ~ 1.39	2.11 ~ 2.13			61
	75	1.387	2.138	2.023 [a]		134
	76	1.33	2.10	1.99 [a]	93.6	135
[(COD)$_2$Ag]$^{\oplus}$BF$_4^{\ominus}$	77	1.34	2.50			136
[(COD)CuCl]$_2$	78	1.41	2.14		91.4	50
(COD)PdCl$_2$	79	1.39		2.095	86.3	137
	80	1.383	2.262	2.154		138

[a] Calculated from the values of a, b and c by the author.

Addition of an excess of allylic halide to Pt(COD)$_2$ yields the σ-allyl compounds (COD)PtX(σ-allyl) (X = Cl, Br; allyl = C_3H_5, 2-Me-C_3H_4 or 3-PhC_3H_4) [92]; however, further addition of silver tetrafluoroborate yields the π-allyl compound [(COD)Pt(η^3-allyl)]$\cdot$ BF_4 by halide-anion abstraction.

In the reaction of (COD)$_2$M with fluoro-olefins [93], fluoroketone [94–96], fluoroacetylene [97], metal carbene compounds [98,99] or butadiene

[100–102], the simple substitution product is not obtained; instead various kinds of metal–metal compounds or ring metal compounds are produced as shown in Scheme 4.



Scheme 4

Many COD metal compounds have been studied by three-dimensional X-ray structure analysis. Crystal data for their double bond length (a), metal–carbon distance ($(b+c)/2$), metal and double bond midpoint distance (d), and the double bond midpoint and metal and double bond midpoint "bite" angle (α) are shown in Table 1. Compounds **42–80** form a tub configuration, and the carbon–carbon double bond length coordinated to the metal is slightly longer (1.33–1.44 Å) than that of a free double bond. These bond lengths (a) are similar to those of ordinary monoolefin metal compounds or σ,π-coordination compounds **1**. The bond lengths (d) between metal and the midpoint of the carbon–carbon double bond are also similar to those of the above olefins. Further, most of the bite angles (α) in compounds **42–80** are close to 90° which is suitable for octahedral, trigonal-bipyramidal or square-planar coordination even though there are also a few compounds of metals such as Ni, Cu or Ag which are tetrahedral (Table 1). Hence generally this evidence indicates that these tub configurations are almost strain-free.

Crystal, IR, Raman, ^{1}H NMR, and ^{13}C NMR data for (COD)$PdCl_2$, (1,4-cyclooctadiene)$PdCl_2$ and (1,5-cyclononadiene)$PdCl_2$, are shown in Ta-

TABLE 2

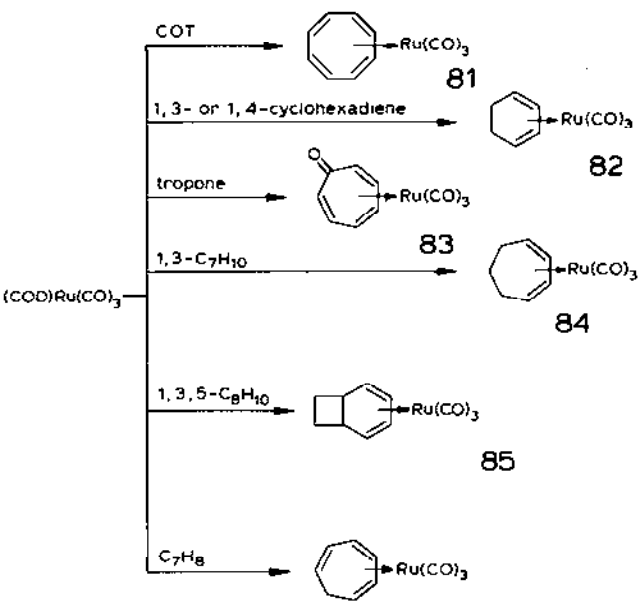
Crystal, IR, Raman, and NMR data for palladium dichloride complexes of COD, 1,5-cyclononadiene and 1,4-cyclooctadiene

	(COD)$PdCl_2$	(1,5-CND)$PdCl_2$	(1,4-COD)$PdCl_2$
d [c]	2.092	2.099	2.122
	2.097	2.130	2.100
α [c]	86.3	92.3	81.6
a [c]	1.39	1.37	1.38
	1.38	1.39	1.37
νC=C	1515	1525	1518
(Free diene νC=C)	(1650) [d]	(1650)	(1640) [d]
$\Delta\nu$C=C [a]	−135	−125	−122
Olefinic proton (ppm)	6.30(br)	6.75–6.5(br)	6.3–5.9 5.4(q, $J \approx 7$ Hz)
(Free olefinic proton)	(5.5(br))	(5.9–5.6(m))	(5.8–5.5(q, $J \approx 5$ Hz)) (5.5–5.1(m))
$\Delta\delta$ [b]	0.8	ca. 1	0.8, −0.25
Olefinic carbon	116.6	116.4, 115.4	118.9, 76.6
(Free olefinic carbon)	(128.3)	(130.9, 129.8)	(128.4, 130)
$\Delta\delta$ [c]	−11.7	−14.5	−9.5, −53.8

[a] Shifts in ν(C=C) on coordination. [b] Hydrogen coordination shift. [c] Carbon coordination shift. [d] Raman results. [e] See Table 1.

ble 2 [137]. The spectroscopic data are almost the same for (COD)$PdCl_2$ and (1,5-CND)$PdCl_2$ in which the number of carbon linked to double bonds is two ($n = 2$ in **3**). However, in (1,4-cyclooctadiene)$PdCl_2$, where n is one, the double bond midpoint and metal and double bond midpoint bite angle α is narrower by about 10° than the usual 90°; this compound shows abnormal shifts in its ^1H NMR and ^{13}C NMR spectra. From these data, Retting et al. [137] presumed that this compound forms a homoallylic structure. This evidence suggests that simple bond formation in these compounds where n is 1, is not easy.

COD metal compounds are easily prepared and converted to their derivatives by ligand exchange reactions as shown in eqns. (1–6) in Schemes 1–4. They are relatively stable because these reactions are carried out without fission of the two COD π-bonds to the metal and yet are relatively reactive to conventional organic compounds having stable carbon–carbon covalent bonds. Therefore, COD metal compounds are capable of being utilized as intermediates for organic syntheses. For example, cycloolefin ruthenium compounds (**81**–**86**) (Scheme 5) were prepared by displacement reactions of



Scheme 5

COD ruthenium carbonyl with cycloolefins [139,140]. This reaction proved to be very simple; refluxing (COD)$Ru(CO)_3$ and olefin in benzene for a short time (less than 30 min) afforded a high purity product in high yield.

Many other reports [141–184b] such as those discussing hydrogenation catalysts [149,160], spectroscopic data [151,181,182], syntheses of cycloal-

kanes [150] or cyclohexanones [148], etc. on COD metal compounds have been published.

D. DICYCLOPENTADIENE COMPOUNDS

Dicyclopentadiene (DCP), in which the number of carbon atoms linked between two carbon–carbon double bonds is two, also reacts easily with metal halides, metal carbonyls, metal thiocyanates, or metal thioalkyl to afford the cyclopentadienyl metal compounds **87** or **88** as shown in eqns. (7)

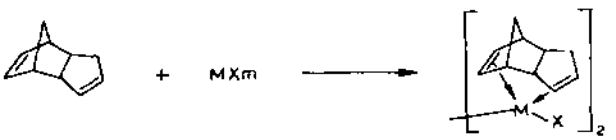
Type A

(7)

87 (DCP)MXn

MXm : Na_2PdCl_4[29,69], K_2PtCl_4[31, 69, 185], $(CH_3CN)_3W(CO)_3$[37]
MXn : $PdCl_2$, $PtCl_2$, $W(CO)_4$

Type B



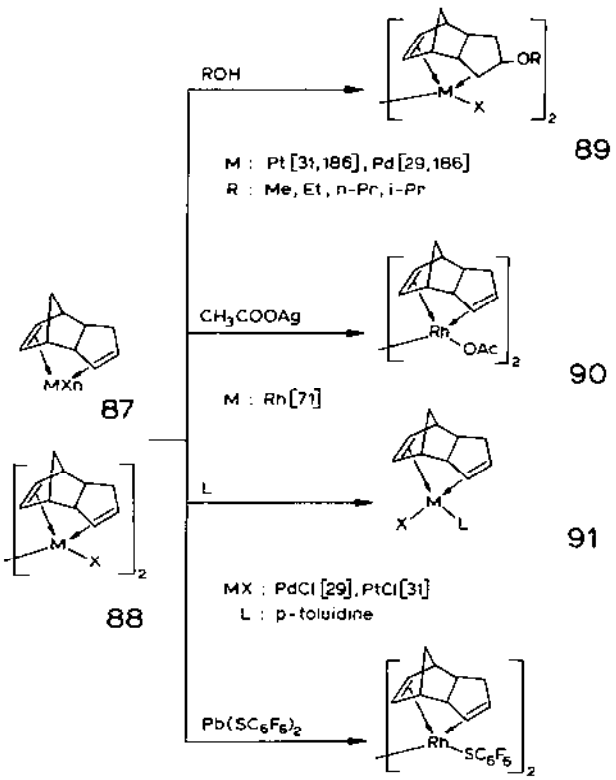
(8)

88

MXm : $RhCl_3$[52,71], $Pt(SCN)_2$[31], $Pt(SEt)_2$[31]
MX : RhCl, Pt(SCN), PtSEt

(type A) or (8) (type B). Further these products react with alcohols, silver acetate, amines or pentafluorophenylthiolate to give the corresponding derivatives **89**–**92** by substitution for halogen, carbonyl, etc. (Scheme 6). These reactions proceed similarly to the reactions of COD as shown in Scheme 3. However, in Scheme 6, the alkoxy compounds **89** obtained by reaction of the bridged compound **88** with alcohols, are also prepared easily by direct reaction of DCP with metal halide in an alcohol.

The molecular structure of dicyclopentadiene palladium dichloride was determined by single-crystal X-ray diffraction studies [187]. The structure shows that both of the double bond midpoints are at normal distances from the central palladium (2.13 and 2.10 Å), similar to that (2.095 Å) of $(COD)PdCl_2$ **79** in Table 1; however, the double bond midpoint–Pd–double bond bite angle α (92.5°) is slightly larger than that (86.3°) of **79**. Both



Scheme 6

angles may be regarded as being close to 90°, suitable for square-planar coordination structure.

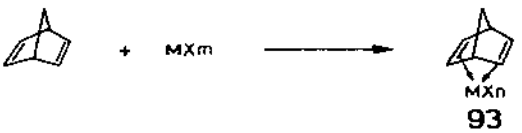
These dicylopentadiene metal compounds having an intramolecular-coordination bond such as **87–92** were first reported in 1957 by Chatt et al. [29,31], but, in 1908, Hofmann and Narbutt [187a] had found the same type of compound e.g. $(C_{10}H_{12}OMe)PtCl$, or $[C_{10}H_{12}OMePtCl]_2$ (**89** (R : Me)) without knowing of the intramolecular-coordination. These compounds were rediscovered fifty years later.

Other articles regarding dicyclopentadienyl metal compounds have also appeared [175–177,183a].

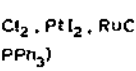
E. NORBORNADIENE COMPOUNDS

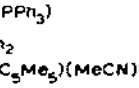
Norbornadiene (NBD) metal compounds **93**, **94** are easily prepared by reaction of norbornadiene with metal halide, metal carbonyl, etc. as shown in eqns. (9) (type A) and 10 (type B). NBD metal compounds **93**, **94** also react with silver acetate, silver hexafluorophosphine, Grignard reagents, phosphines, amines, acetylacetonates, cyclopentadienyl compounds, etc. to

Type A



93 (NBR)MXn (9)

MXm : $Fe(CO)_5$[188], $Mo(CO)_6$[188], $H(C_2H_4PtCl_3)$[189], (K_2PtCl_4 + NaI)[189, 32]
$(PhCN)_2PdCl_2$[189, 190], K_2PtCl_4[69], $(CH_3CN)_3W(CO)_3$[37], Na_2PdCl_4[69]
$(C_6F_5)_2Ni(\eta^6\text{-}C_6H_5CH_3)$ [46],  [47]
$[Rh(C_5Me_5)(MeCN)][PF_6]_2$[190], $[Ir(C_5Me_5)(MeCN)][PF_6]_2$[190], $RuCl_2(PPh_3)_4$[191]

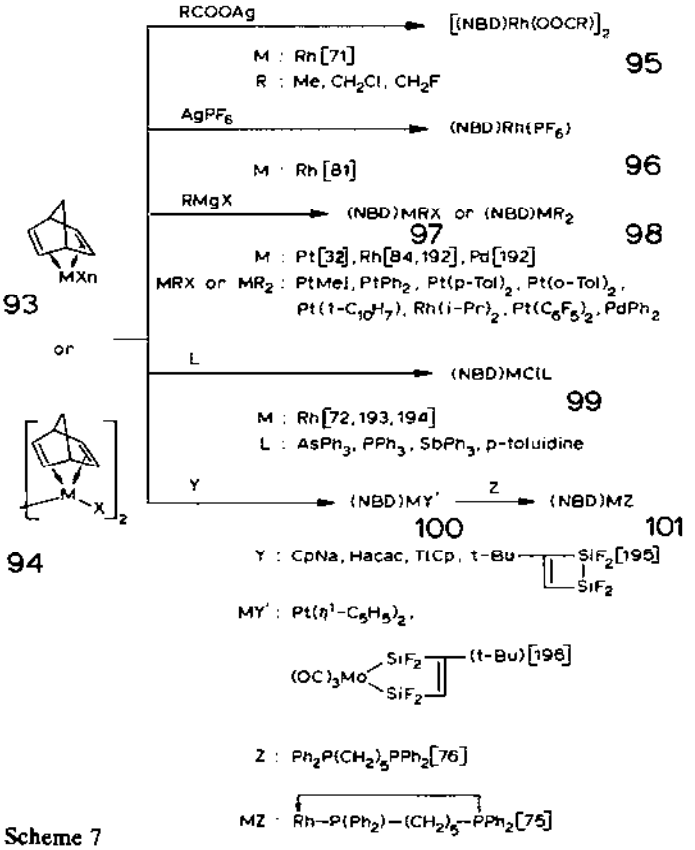
MXn : $Fe(CO)_3$, $Mo(CO)_4$, $PtCl_2$, PtI_2, $RuCl_2(PPh_3)_2$, $PdCl_2$,
$W(CO)_4$, $Ni(C_6F_5)_2$, 
$Rh(C_5Me_5)(MeCN)(PF_6)_2$, $Ir(C_5Me_5)(MeCN)(PF_6)_2$

Type B

94 (10)

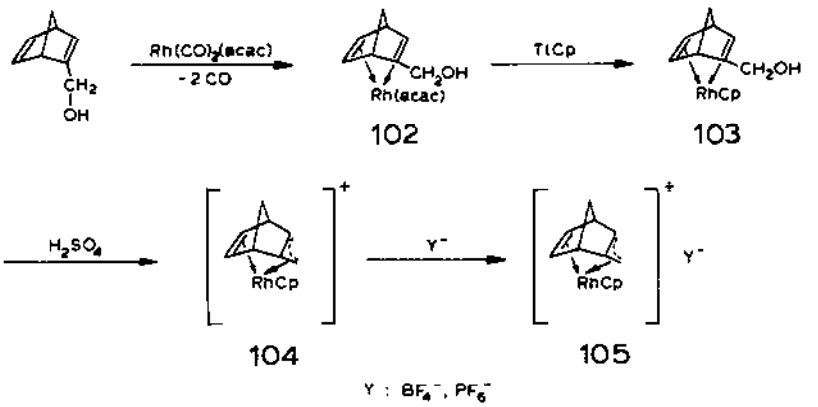
MXm : Na_2IrCl_6[56], $RhCl_3$[74]
MXn : IrCl, RhCl

afford the derivatives (Scheme 7) also similar to the reaction of COD (Scheme 3). However, NBD metal compounds **93**, **94** in which the number of carbon atoms linked between the two double bonds is one, differ from COD or DCP. The compound whose structure lacks the methylene bridge of NBD is 1,4-cyclohexadiene, but this does not usually react with metal compounds without migration of the double bond to the 1,3-diene. Very few 1,4-cyclohexadiene compounds react with metal compounds to afford 1,4-cyclohexadiene metal compounds. Hence, the author presumes that the reactivity of NBD with metal compounds and the stability of NBD metal compounds are attributable to the presence of the methylene bridge, the bridge bond suppresses the migration of the double bond and lets two double bonds locate favorably for coordination to a metal in comparison to 1,4-cyclohexadiene. However, the double bond midpoint and metal and double bond midpoint bite angle α of these NBD metal compounds is ca. 70° (Table 3) and the bite angle α is narrower by 20° than those of COD or DCP metal compounds. Therefore the bite angle α is sometimes broadened.



Scheme 7

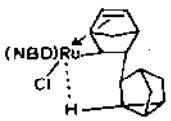
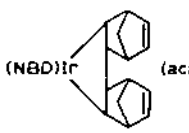
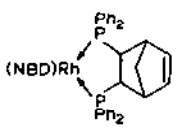
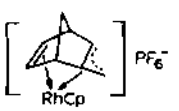
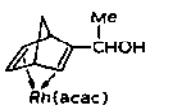
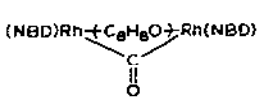
For example, as shown in eqn. (11), hydroxymethylnorbornadiene reacts with rhodium carbonyl, and then with thallous cyclopentadienide to afford (2-hydroxymethylnorbornadiene)cyclopentadienylrhodium **103** [197,198]. Further treatment of **103** with sulfuric acid offers the stable η^3-allyl cationic



(11)

TABLE 3

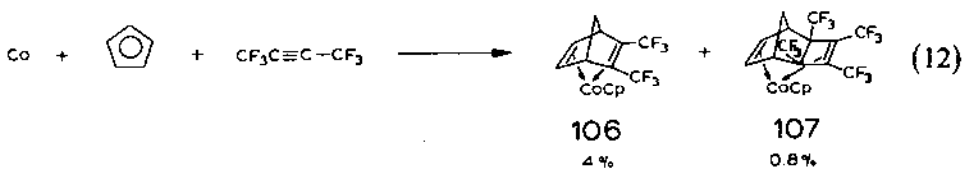
Selected mean distances (Å) and angles (deg) for some NBD metal complexes

Compounds		a [a]	$(b+c)/2$ [a]	d [a]	α [a]	Ref.
(NBD)Ru(Cl)$_2$(piperidine)	**108**	1.389	2.185	2.072	69.7	131
(NBD)Ru(Cl)$_2$(PPh$_3$)$_2$	**109**	1.41	2.205	2.09 [b]		191
	**110**	1.411	2.156	2.037 [b]	69.8	200
(NBD)Ir(SnCl$_3$)(PMe$_2$Ph)$_2$	**111**	1.398	2.209	2.096	67.57	201
(NBD)Ir(Cl)$_2$(C$_6$H$_5$NH$_2$)$_2$	**112**	1.385	2.179	2.237	70.0	202
	**113**			2.130		203
	**114**	1.367	2.202	2.092		204
	**115**	1.39	2.18			197
	**116**	1.405	2.107	1.987 [b]		205
	**117**			2.15		206
(NBD)PdCl$_2$	**118**		2.22			207

[a] See Table 1.

[b] Calculated from the values of a, b and c by the author.

compound **104**, which can be isolated as PF_6^- or BF_4^- salts [197]. The structure of the PF_6^- salt **105** (**115** in Table 3) is supported by a single-crystal X-ray diffraction study [197]. Koridze et al. [197] show no data regarding the angle α of **105**, but it is considered that the angle is broadened compared with **102** or **103** because the center of η^3-allyl group is located at the outer side of the double bond midpoint of **102** or **103**. The reaction [199] of cobalt vapor and cyclopentadiene with hexafluorobutyne yields the NBD metal compound **106** formed by the cycloaddition of a hexafluorobutyne to cyclopentadiene, and the further cycloaddition product **107** (considered to have a normal bite angle α) plus a variety of fluorocarboncobalt compounds such as $CpCo(\eta^4\text{-}(CH(CF_3)=C(CF_3)-C(CF_3)=CH(CF_3)))$ and $Cp_3Co_3(CF_3C{\equiv}CCF_3)$ (eq. 12).



(12)

106 4%

107 0.8%

As two double bonds of norbornadiene are located near each other, nortricycle compounds, where the two double bonds are bonded to each other, are formed in the reaction of norbornadiene metal compounds, e.g., in reduction of $(NBD)RuCl_2$ by means of zinc powder in the presence of norbornadiene, which affords the compounds (**110** in Table 3) having three norbornadiene moieties one of which forms a nortricycle [200].

The formation of these expanded products such as **104** (or **105**) or **107** shows that norbornadiene metal compounds ($n = 1$ in formula 3) have slight strain due to their narrower bite angle α, but their intramolecular π-bonds are relatively stable because fission did not occur during the ligand exchange reactions (Scheme 7).

X-ray diffraction studies on NBD metal compounds are shown in Table 3 and many other articles [175–177,180–184,208–231] concerning NBD metal compounds have been reported.

F. CYCLOOCTATETRAENE COMPOUNDS

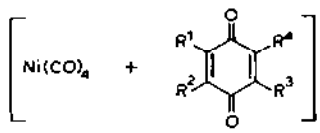
Reactions of cyclooctatetraene (COT) similar to the reactions of COD, DCP or NBD, also afford COT metal compounds (**119–122**, eqns. (13) (type A), 14 (type B) and 15 (type C)). The COT metal compounds also form a tub configuration. However, COT has two more double bonds than COD, capable of coordinating to another metal to form sandwich type compounds

120 as shown in eqn. (13) (type A). The dimetal compounds **120** can be prepared by heating the monometal compound **123** or by reaction of **123**

Type A

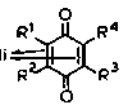
(13)

MXm : $CpCo(CO)_2$[49, 232, 233], $Fe(CO)_5$[234-240], $CpRh(CO)_2$[241]
$[Cu(CF_3SO_3)]_2{\cdot}C_6H_6$[45], $(K_2PtCl_4 + NaI)$[32],



(R^{1-4} : H, Me)[178, 242]

MXn : CpCo, $Fe(CO)_3$, $Fe_2(CO)_7$, PtI_2
$(XnM(COT))MXn$: $Fe(CO)_3$, CoCp, RhCp, Ni



Type B

(14)

MXm : $RhCl_3$[243, 244], $(cyclooctene)_2RhCl$[244]
MX : RhCl

121

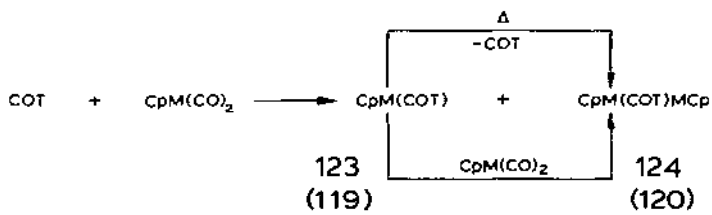
Method C

(15)

MXm : (cyclododecatriene)Ni[63], $Ni(acac)_2$[61, 62]

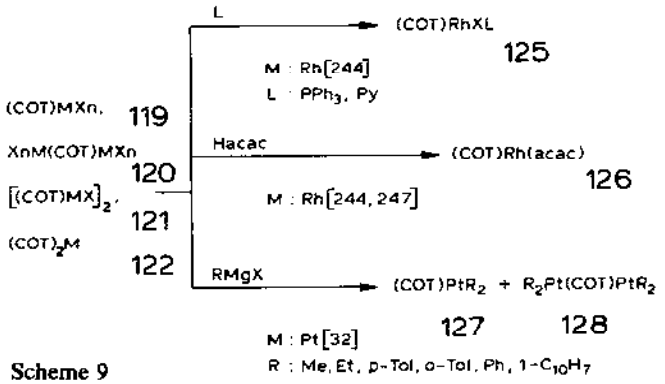
122

with another metal carbonyl, in addition to the conventional reaction (eqn. 13) as shown in Scheme 8 [233,241,244–246].



Scheme 8 M : Co, Rh

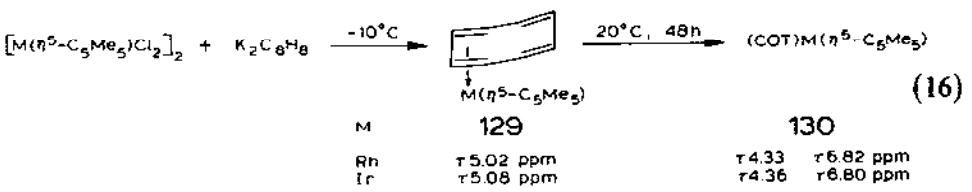
The COT metal compounds (**119–122**) obtained by the reactions shown in eqns. (13–15) also react with phosphines, amines, acetylacetone or Grignard reagents, etc. to afford derivatives as shown in Scheme 9, analogous to Scheme 3.



Scheme 9

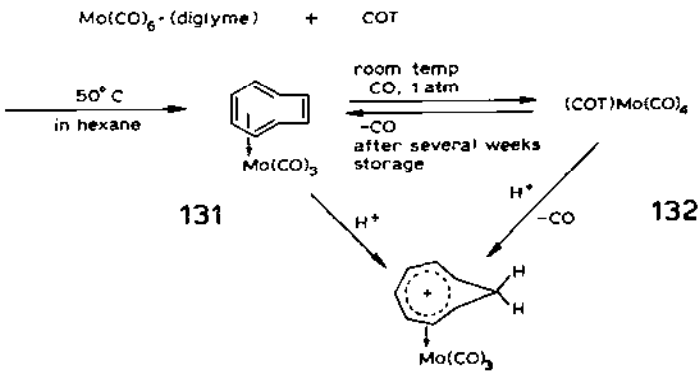
Most of the COD compounds have a tub configuration of the 1,5-diene coordination to the metal as shown in Table 1. However, in the case of COT, besides the tub configuration (**119**) analogous to COD, the sandwich structure (**120**), delocalized 1,3-diene coordination compounds, η^8-coordination compounds, etc. have been reported [25,26,248]. For example, the structure of cyclooctatetraeneiron tricarbonyl in the solid state, was determined not to be the conventional η^4-1,2,5,6-coordination (**119**) described above, but the delocalized η^4-1,2,3,4-coordination compound (i.e. **129** coordination type compounds described below) by X-ray diffraction [249]; however, in solution, it forms the η^4-1,2,5,6-coordination state at room temperature, and at -100°C or below again η^4-1,2,3,4-coordination as determined by NMR or IR spectra [234–240].

In the reaction of pentamethylcyclopentadienyl metal compounds with cyclooctatetraene dipotassium at a low temperature as shown in eqn. (16), the η^4-1,2,3,4-cyclooctatetraene compound **129** was formed. A low-energy barrier to the fluxional behavior of the C_8H_8 ring makes all eight protons equivalent (at τ 5.08 ppm (singlet)) on the NMR timescale even at low temperatures. It isomerized to η^4-1,2,5,6-cyclooctatetraene **130** when warmed in solution [248].



(16)

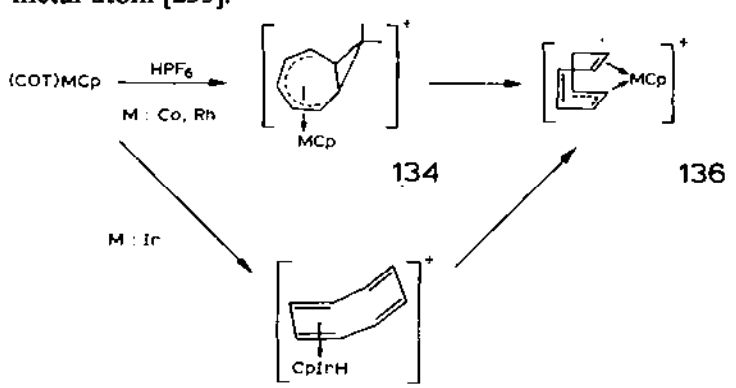
The reaction of diglyme-molybdenum hexacarbonyl with COT affords a η^6-1,2,3,4,5,6-cyclooctatetraene molybdenum compound **131** [250,251] which reacts with carbon monoxide at 1 atm. and at room temperature to give the tetracarbonyl compound **132** having the conventional tub configuration. Compound **132** is moderately stable as a solid, tending to lose some CO after several weeks' storage. These reactions also proceed with cyclooctatriene in place of cyclooctatetraene [251,252]. The dissolution of **132** in H_2SO_4 was accompanied by immediate evolution of CO, with formation of the homoaromatic monohomotropyliummolybdenum tricarbonyl species **133**, identical in all aspects with the product from protonation of cyclooctatetraenemolybdenum tricarbonyl **131**.



Scheme 10

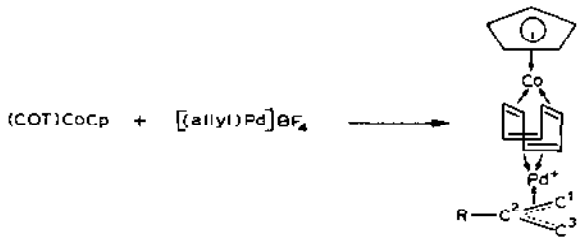
133

The protonation of iridium, rhodium or cobalt compounds ((COT)MCp) affords the η^3-allyl compound **136**. In the case where the metal is cobalt or rhodium, a bicyclic cation **134** is initially produced; this subsequently undergoes isomerization to the monocyclic form **136**. At low temperature, protonation of the iridium compound yields a metal hydride intermediate species **135** bound through a coordinating 1,3-diene unit to the protonated metal atom [253].



Scheme 11

Cyclooctatetraenecobalt cyclopentadiene reacts with allylpalladium tetrafluoroborate [254] to afford the palladium compound **137** having a pseudo-tripledecker structure. The tub-shaped cyclooctatetraene coordinates by a set of two double bonds each to two different metals which are coordinated by two different organic moieties as shown in eqn. (17).



(17)

R	H (ppm)	CH_3 (ppm)
Cp	87.4	87.5
COT/Co	71.7	71.7
COT/Pd	122.8	122.5
Allyl(C^1,C^3)	77.1	76.3
C^2	124.9	141.4
Me	-	22.9

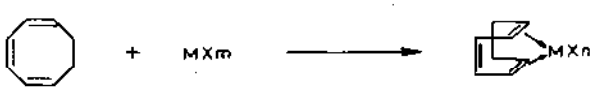
137

In contrast to COD, COT metal compounds are capable of forming many derivatives with various structures such as **119**, **120**, **129**, **133**, **134**, **136** and **137**. However, it is apparent that the nature of the metal and the other ligands strongly influence the mode of coordination of COT. However, the precise electronic or steric reasons are not yet clear [248]. Further studies in this field is desirable.

If COT has a phenyl group substituent, it reacts with metal compounds to afford the phenyl derivatives of **119** and **120** (eqn. 13) [255].

Cyclooctatriene has one more double bond than COD and one less than COT. This compound reacts to afford **138** having a tub configuration as shown in eqn. (18), but does not afford sandwich type compounds such as **120** which can be derived from COT.

Type A



(18)

138 (COT')MXn

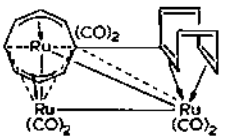
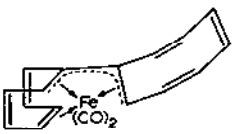
MXm : $Fe(CO)_5$ [256], $Fe_2(CO)_9$ [256], $CpCo(CO)_2$ [49]

MXn : $Fe(CO)_3$, CoCp

Crystal data for COT metal compounds are shown in Table 4.

TABLE 4

Selected mean distances (Å) and angles (deg) for some COT metal complexes

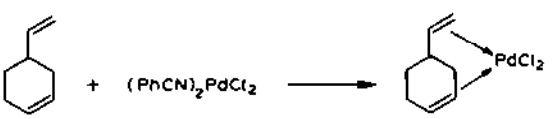
Compound		a [a]	$(b+c)/2$ [a]	d [a]	α [a]	Ref.
	**139**	1.42	2.25	2.11	84	257
	**140**	1.418	2.129	2.007	86.2	257

[a] See Table 1.

Other articles regarding COT metal compounds have also been published [175–178,182,258–264].

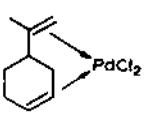
G. MISCELLANEOUS COMPOUNDS

4-Vinylcyclohexane is a compound in which the number of carbon atoms (2) linking two double bonds is the same as COD, DCP and COT. It also forms easily the intramolecular-coordination compound **141** as shown in eqn. (19) [265] (type A).

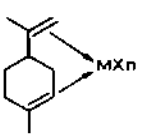


(19)

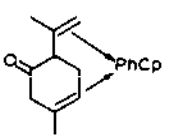
141



142



143



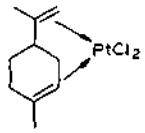
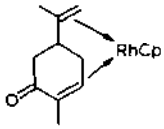
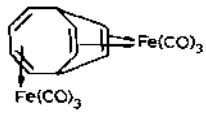
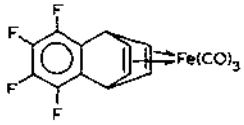
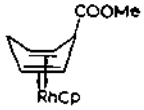
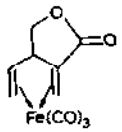
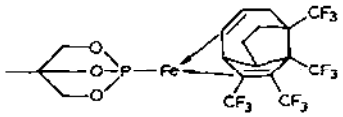
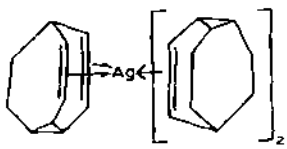
144

MXn : RhCp, $PtCl_2$

4-Isopropylcyclohexene, limonene and carbone metal compounds (**142** [265],

TABLE 5

Selected mean distances (Å) and angles (deg) for some miscellaneous metal complexes

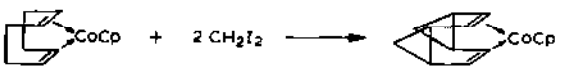
Compound		a [a]	$(b+c)/2$ [a]	d [a]	α [a]	Ref.
	**142**		2.20	2.14	92.8	265, 267
	**144**	1.42	2.183	2.07 [b]		268
	**168**	1.40	2.150	2.04 [b]		303
	**162**	1.39		2.15		289
	**166**	1.40	2.132	2.02 [b]		297
	**169**	1.386	2.156	2.042 [b]		295
	**170**	1.413	2.158	2.039 [b]		304
	**171**	1.34	2.74	2.66 [b]		305

[a] See Table 1.

[b] Calculated from the values of a, b and c by the author.

143 [266,267] and **144** [266,268]), analogous to the 4-vinylcyclohexene metal compound **141**, have also been isolated and the structures of the limonene and carbone metal compounds (**143** and **144**) determined by X-ray diffraction studies [267,268] (Table 5).

The COT metal compound reacts with excess Simmons–Smith reagent to yield the COD metal compound **145** having two cyclopropyl rings *syn* to the metal retaining a tub configuration [269,270]. On the other hand, the cyclooctatriene having a monocyclopropyl ring obtained by reaction of COT with the Simmons–Smith reagent, reacts with metal carbonyl to give the monocyclopropyl metal compound **146** [271–273].

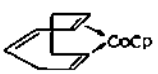


(20)

145

MXn : $Mo(CO)_4$, $Fe(CO)_3$

146



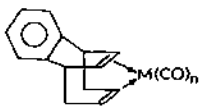
147

MXn : CoCp, $PdCl_2$

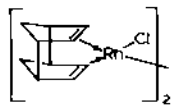
148

The reaction of cyclopentadienylcobalt dicarbonyl with bicyclo[6.1.0]nona-2,4,6-triene affords the ring-expanded compound **147** [274]. Its hydrogenation proceeds selectively at the uncoordinated double bonds to give the compounds **148** (MX_n = CoCp). One of the latter type compounds (**148**; $MX_n = PdCl_2$) [274] is also prepared directly by the ring expansion reaction of dichlorobis(benzonitrile)palladium(II) with dicyclo[6.1.0]non-4-ene obtained by the Simmons–Smith reaction of COD [275].

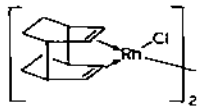
Other compounds with $n = 2$ of general formula **3** are *anti*-7,8-benzotricyclo[4.2.0.$0^{2,5}$]deca-3,7,9-triene iron, molybdenum or chromium compounds **149** [276], *syn*-tricyclo[4.2.1.$1^{2,5}$]deca-3,7-diene rhodium **150** [277], octahydro[0,0]paracyclophane rhodium **151** [278], endo-*anti*-tricyclo [4.2.2.$0^{2,5}$]decadiene-(3.9) metal **152** [279,280], tricyclo[4.2.2.$0^{2,5}$]decatriene palladium dichloride **153** [281], 1,5-hexadiene palladium dichloride **154** [282,283] and all-*trans*-cyclodecatriene-(1,5,9)-nickel or copper triflate **155** [45,62,63,283], etc. [283a,283b].



149

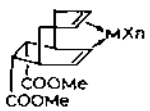


150

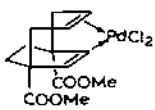


151

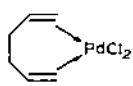
M(CO)n : $Mo(CO)_4$, $Cr(CO)_4$, $Fe(CO)_3$



152



153



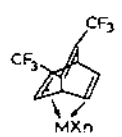
154

155

MXn : $AgNO_3$, $PdCl_2$

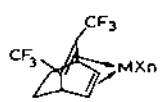
MX : Ni, Cu, CF_3SO_3

In general formula **3**, the compounds ($n = 1$) forming a bridge such as NBD yield stable metal compounds, e.g. bicyclo[2.2.2]octatriene metal compounds **156**, **157** [284], tricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene(hexafluoropentan-2,4-dionato)rhodium **158** [285], bicyclo[3.2.2]nona-2,6,8-triene-4-ol iron tricarbonyl **159** [286], bicyclo[3.2.1]octa-1,5-diene ruthenium tricarbonyl **160** [139], octano-bridge 7-oxanorbornadiene rhodium compound **161** [287], benzobicyclo[2.2.2]octatriene compounds **162** [288–291] and Dewar hexamethylbenzene metal compounds **163** [292–294].



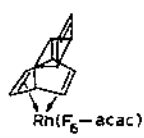
156

MXn : $Fe(CO)_3$, CoCp, $Mo(CO)_4$



157

MXn : $Fe(CO)_3$, CoCp, $Mo(CO)_4$



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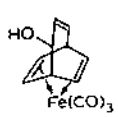
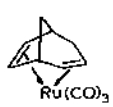


159



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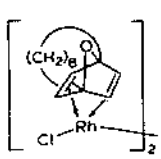
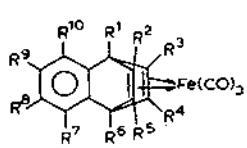
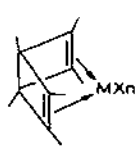


161



162

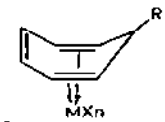
R^1–R^6 : H, Me
R^7–R^{10} : Br, F



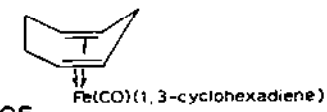
163

MXn : $Cr(CO)_4$, $Mo(CO)_4$, $W(CO)_4$, $PdCl_2$

Non-bridged compounds [295–298], in which n is 1 of general formula **3**, are cycloheptatriene metal compounds **164** [299,300], 1,4-cycloheptadiene iron compound **165** [301], 1,4-cyclohexadiene **166** [297], 1,4-hexadiene, **167** [295–298], etc. [302–308] and these usually isomerizes easily to 1,3-diene delocalized coordination type compounds. For example, 1,4-cyclohexadiene is capable of reacting with a rhodium compound to afford the metal compound **166** and the structure was determined by X-ray diffraction;

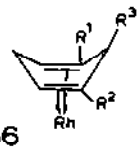


164



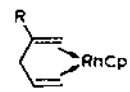
165

MXn : Rh(acac), $Mo(CO)_3$, $Cr(CO)_3$
R : H, OMe, Ph



166

R^1–R^3 : H, Me, COOMe



167

R : H, Me

however, it also isomerizes easily to the 1,3-diene isomer on heating.

Some X-ray diffraction studies are shown in Table 5.

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