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ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS CONTAINING A PHOSPHORUS DONOR LIGAND

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CONTENTS

A. INTRODUCTION

Organometallic intramolecular-coordination compounds can be classified into two groups, those which contain σ-coordinated and those which contain π-coordinated organometallic groups, in addition to the carbon—metal bond that is also present in the ligand [1]. Since about 1955 a great many articles concerning the latter compounds have been reported. The number of articles concerning the former compounds has increased since 1970, and many reports concerning nitrogen and phosphorus donor ligands have recently been published.

Parshall [2], Dehand and Pfeffer [3], and Bruce [4] have also reported articles concerning mainly nitrogen and phosphorus donor ligands in their reviews regarding organometallic intramolecular-coordination compounds, but a review summarizing only phosphorus donor ligands has not yet been published.

Reviews regarding organometallic intramolecular-coordination compounds containing a carbonyl oxygen [1,5], sulfur [6] or nitrogen [7] donor ligand have appeared. All of these stressed the fact that organometallic intramolecular-coordination compounds are generally prone to form a five-membered ring structure.

The purpose of the present review is to survey articles concerning organometallic intramolecular-coordination compounds containing a phosphorus donor ligand and to show that these compounds are also prone to form a five-membered ring structure. We also discuss, critically, these compounds in comparison with other organometallic intramolecular-coordination compounds containing a nitrogen donor ligand [7], a ligand which also belongs to group V. The literature has been covered to 31 July 1979.

B. FIVE-MEMBERED RING COMPOUNDS

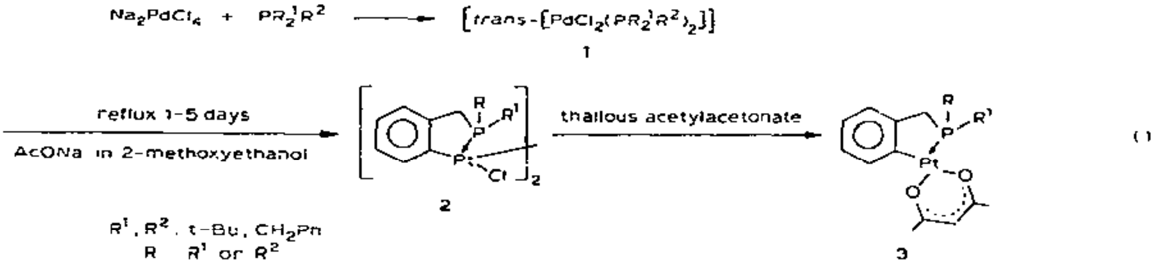
Organometallic intramolecular-coordination compounds, except for π-coordinated compounds are generally prone to form a five-membered ring structure which has less strain. Almost all compounds containing an oxygen [1,5], or nitrogen [7] donor ligand, whose atoms have no electron in the *d* orbital, form the five-membered ring structure. However, organometallic intramolecular-coordination compounds having sulfur [6] or phosphorus donor ligands [6], whose metal atoms have electrons in the *d* orbitals, show an increasing tendency to form three-membered rings [7a] or four-membered rings as described in Section C. This is the degree of freedom in compounds having *d*-electrons and is higher than that of compounds having only *s* and *p* electrons such as the compounds containing a nitrogen or oxygen donor ligand.

However, organometallic intramolecular-coordination compounds containing a phosphorus donor ligand are still prone to form a five-membered ring structure, with various kinds of metals and ring members such as aliphatic, olefinic and aromatic moieties. The five-membered ring structure is the most strain free and more stable than other ring structures.

In organometallic intramolecular-coordination compounds containing phosphorus, five-membered ring compounds are mainly reaction products of metal compounds with benzylphosphine, tolylphosphine, benzoyl compounds, alicyclic compounds, or the like, as described below.

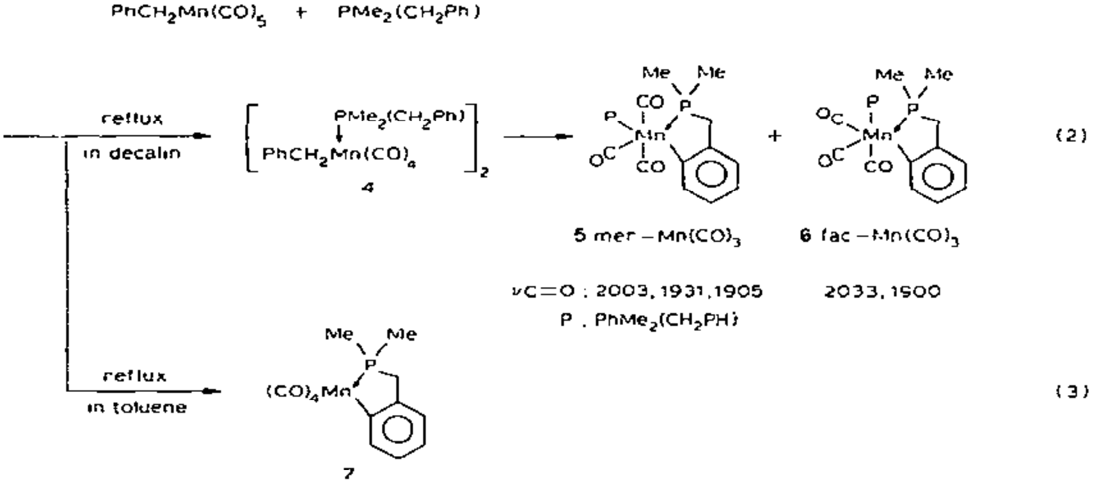
(i) Benzyl compounds

Orthometalation reactions with benzylphosphine yield cyclometalated compounds via an intermediate compound which has a coordination bond between the metal and phosphorus donor atom. The amine orthometalation reaction [7b—d] proceeds readily via a very unstable intermediate, which is a molecular complex between metal and nitrogen, generally not capable of being isolated. But, in the case of phosphines, orthometalation usually proceeds via a stable intermediate and the reactivity of phosphines is lower. The reason for the above difference is clear. Generally the orthometalation reaction proceeds via an electrophilic mechanism [2,7b,7e,7f], but the electrophilicity of the metal coordinated by the phosphorus atom is lower than that of the metal coordinated by the nitrogen because the electronegativity of nitrogen is larger than that of phosphorus.

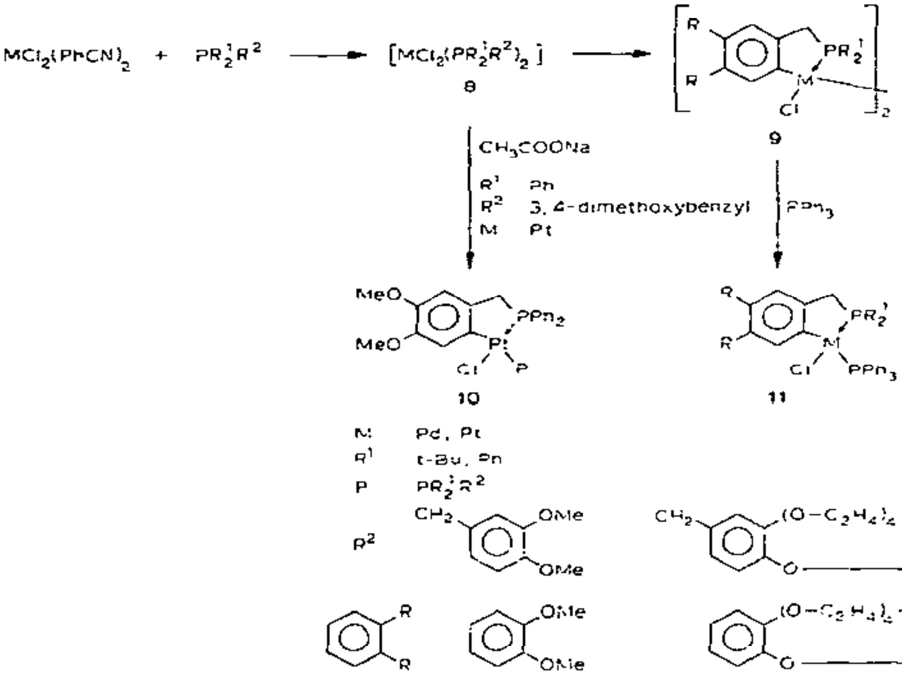


For example, orthometalation [8] of benzyl phosphine showed low reactivity and gave the stable intermediate **1**. The orthometalated chloro-bridged products **2** were obtained by heating **1** for a long time in the presence of sodium acetate as a promoter for internal metalation. The ^{31}P NMR resonance of **2** shows a marked shift (e.g. from $\delta = -33.8$ (free ligand; R, R^1 = t-Bu, $R^2 = CH_2Ph$) to $\delta = -102.1$ (**2**)) through coordination of phosphine to the metal atom. Treatment of **2** with thallous acetylacetonate gave the palladium acetylacetonate by chloride bridged cleavage.

Manganese carbonyl reacted with benzyldimethylphosphine in decalin to give two orthometalated isomers (**5**, **6**) via an intermediate (**4**) binuclear compound; however, orthometalation in toluene gave one kind of cyclometalated compound **7** having one phosphine group [9]. Under similar conditions, reaction with dimethylphenylphosphine afforded only the molecular complex $Mn(CH_2Ph)(CO)_4(PMe_2Ph)$ similar to intermediate **4**. The formation of a five-membered ring is easier than that of a four-membered ring formed by orthometalation of phenylphosphine as described in Section B.

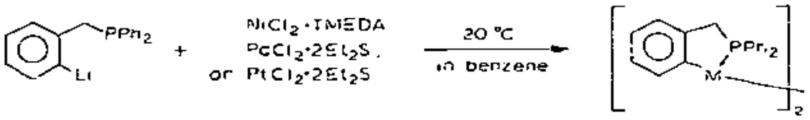


The reactivity [10] of benzylphosphines having methoxy or crown ether groups at the benzene 3 or 4 position is higher than that of unsubstituted benzylphosphine. Orthometalation of these benzylphosphine derivatives proceeds easily to give the chloro-bridged compounds **9** via intermediates **8**. However, in the case of the reaction of 3,4-dimethoxybenzylphosphine with platinum chloride, orthometalation gave no chloro-bridged dimer **9** but rather the monomeric compound **10** via the intermediate compound **8**. The chloro-bridged compounds **9** reacted further by bridge cleavage, with phosphine to give the compounds **11** similar to **10**.



(4)

Benzylphosphines having lithium at the *ortho* position are highly reactive, and orthometalation proceeds very easily even at room temperature, without isolation of intermediate, to afford the orthometalated compound 12 [11]. The UV spectrum of 12 (M = Ni, Pd) infers a square-planar structure and the ^{31}P NMR spectrum of 12 (M = Pd, Pt) indicates the presence of both *cis* and *trans* isomers [11].



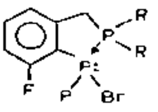
(5)

12

M	UV	^{31}P
Ni	450 nm, 371 nm (in $CHCl_3$)	29.2 ppm
Pd	420 nm (in benzene)	40.9 ppm 20.0 ppm
Pt		42.8 ppm 15.5 ppm

In the case of the reaction of (*o*-lithiobenzyl)diphenylphosphine with the chloro-bridged palladium compound **2** (R, R^1 : t-Bu) in eqn. (1), the *cis* isomer of the dibutyl derivative of **12** was isolated and the ^{31}P NMR spectrum exhibited resonances at δ 39.1 p.p.m. (PPh_2) and δ 81.6 p.p.m. (P(t-Bu)$_2$).

Recently, Hietkamp and co-workers [12] examined the orthometalation reactivity of metal halides ($[(COT)_2IrCl]_2$, $[(COT)_2RhCl]_2$, $PdCl_2$ and $PtCl_2(PhCN)_2$) with benzylphosphines. They discovered that the reactivity appears to decrease in the order of $Ir^I > Rh^I >> Pd^{II} \sim Pt^{II}$. Among these metal compounds, those of iridium and rhodium also show the same order in the orthometalation of azo compounds or imines [13]. These workers [12] examined the electronic preference for orthometalation by reaction of the benzylphosphines m-$FC_6H_4CH_2PR_2$ (R = cyclohexyl, t-butyl) with the above metal halides. They consequently presumed that for Ir^I and Rh^I a nucleophilic mechanism operates, since the main product (80%) contained the fluoro substituent *ortho* to the metalated carbon atom and the side product (20%) contained the fluorine atom *para* to the metalated carbon atom. In contrast, the metalated palladium complex appeared to be exclusively *para*-substituted; hence for Pd^{II} the usual electrophilic mechanism [2,7b,7d] operates. However no decision could be made for Pt^{II} because there are many products such as *ortho*, *para*-substituted mono-metalated and dimetalated species (e.g. **13** and **14**) produced in small amounts by orthometalation reactions at high temperature.



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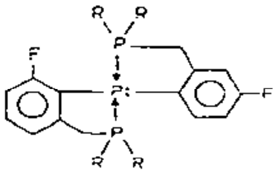
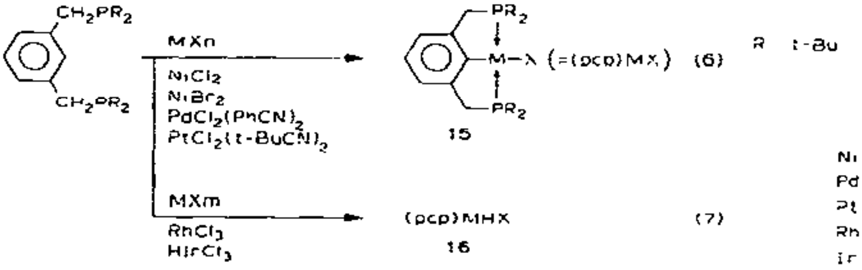


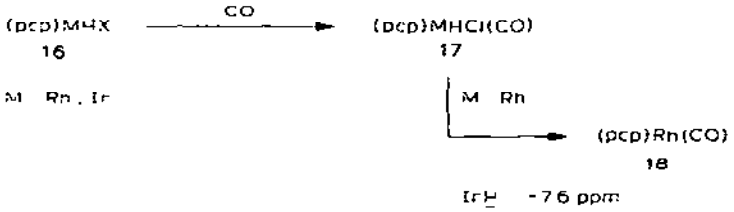
14

m-Xylenediphosphine is more reactive than benzylphosphine and reacts selectively with metal halides at the position *ortho* to both phosphine groups to afford cyclometalated tridentate **15** [14]. Orthometalation usually occurs via substitution of the hydrogen of the benzene ring by metals such as Ni, Pd and Pt as shown in eqn. (6), but, in the case of rhodium and iridium orthometalation occurs via insertion at the *ortho* phenyl hydrogen position as shown in eqn. (7), to give five coordinated square pyramidal compounds [15].



	^{31}P	MH
Ni	74.65	
Pd	72.5	
Pt	64.95	
Rh	71.9	−27.5
Ir	67.5	−43.0

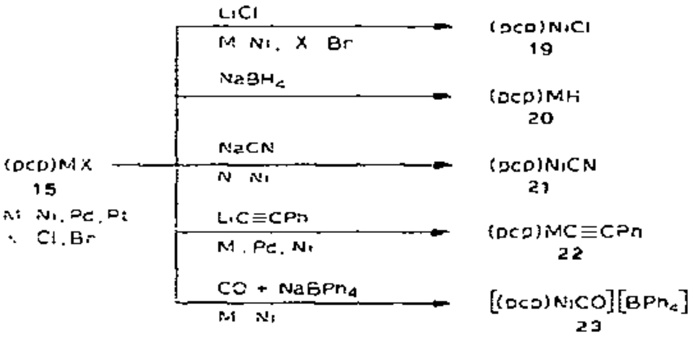
When the metal hydride **16** reacted with carbon monoxide, the iridium species **16** rapidly gave the carbonyl compound **17**, whilst the rhodium hydride **16** probably gave the adduct **17** which is unstable and easily loses the elements of hydrogen chloride to give the rhodium carbonyl **18**.



16 17 18

(8)

The tridentate structure of **15** and **16**, obtained by orthometalation as shown in eqns. (6) and (7), is so stable that **15** or **16** react with carbon monoxide, lithium chloride, sodium borohydride, sodium cyanide, or phenylacetylide in the presence of sodium tetraphenylborate to give the corresponding substituted compounds **17**—**23** without breaking the tridentate structure.



15 19 20 21 22 23

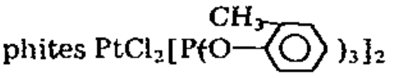
(9) (10) (11) (12) (13)

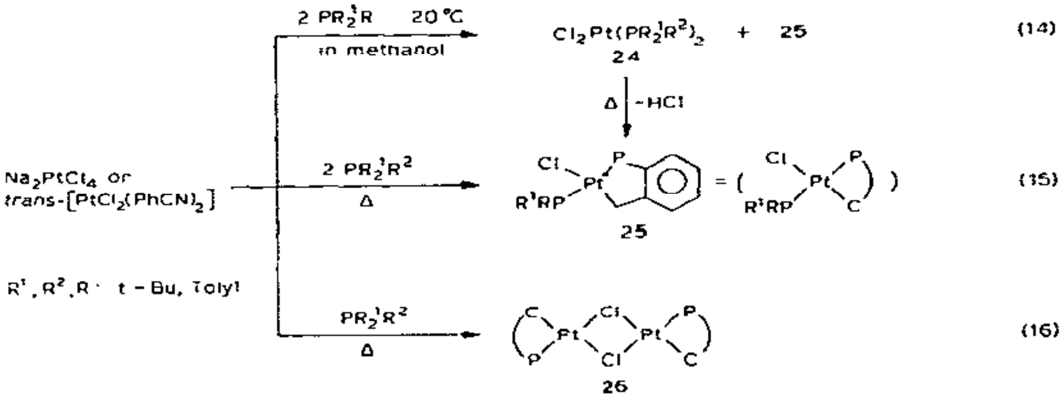
m-Xylenediphosphine also reacts with hydrated ferrous chloride to give the orthometalated tridentate compound (μFe--P = 347 cm^{-1}) [16].

(ii) o-Tolyl compounds

o-Tolylphosphines also react with metal compounds to give cyclometalated ring compounds via intermediates which have a coordination bond between metal and phosphorus donor atom. These are similar to orthometalated compounds obtained via intermediates through reaction of benzylphosphines with metal compounds as described in the previous section. *o*-Tolylphosphines yield cyclometalated compounds more easily than benzylphosphines [8].

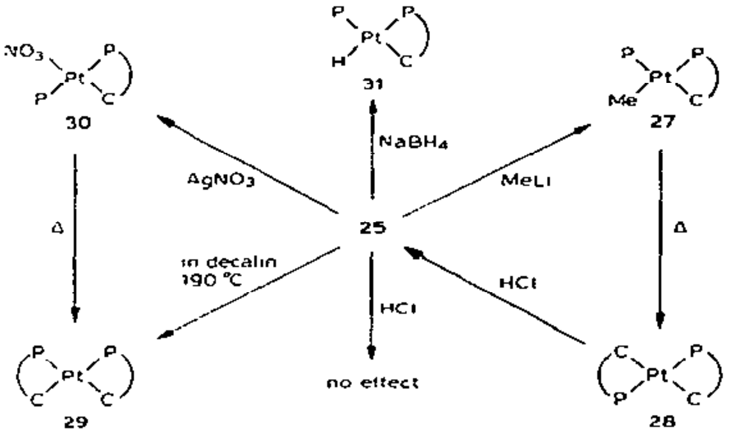
The difference in ease of intermediate formation between benzylphosphine and *o*-tolylphosphine would be small in the first step, and there must be some difference in the second step. In the second step, with benzylphosphine, cyclometalation proceeds by substitution of metal for one inert hydrogen of the benzene ring. With *o*-tolylphosphine on the other hand, cyclometalation proceeds by substitution of metal for one relatively reactive methyl hydrogen of the *o*-tolyl group. The difference of reactivity between benzylphosphine and tolylphosphine in the cyclometalation is considered to be due to the difference in substitution reactivity.

The cyclometalation of *o*-tolylphosphine to give a five-membered ring compound proceeds more easily than orthometalation of *o*-tolylphosphine to give a four-membered ring compound (Section B). Moreover, the phosphites  $PtCl_2[P(O-C_6H_4CH_3)_3]_2$ (X = Cl, Br or I) [17], gave five-membered ring compounds (such as shown in eqns. (51,52) by orthometalation despite the fact that the phosphite has a reactive *o*-tolylmethyl for cyclometalation such as *o*-tolylphosphine in eqn. (15). These reactions also show that the formation of a five-membered ring structure is easier than that of a four- or six-membered ring structure. To predict the structure of such products of these reactions, the ease of formation of a five-membered ring should be considered first rather than the reactivities of the functional groups in the compounds.



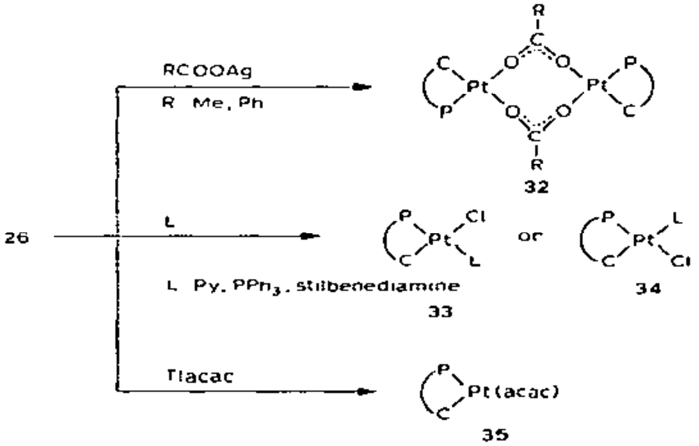
o-Tolylphosphine is more reactive than benzylphosphine; however, *o*-tolylphosphine reacted with platinum chloride at room temperature to give the intermediate 24 in addition to the cyclometalated compound 25; 24 converted to 25 easily on heating [18].

The complex 25 is obtained in high yield when a mixture of *o*-tolylphosphine (2 molar equiv.) and platinum halide is heated, but chloro-bridged binuclear compound 26 is also formed in high yield when an equimolar mixture of both raw materials is heated. Complex 25 is a very stable ring compound; for example, 25 is unaffected by treatment with dry hydrogen chloride at room temperature or by heating in boiling 2-methoxyethanol (b.p. 124°C) for 20 h. However on heating 25 in decalin at ca. 190°C for 6 days, 29 *cis*[Pt(P—C)$_2$] is formed.



Treatment of 25 with silver nitrate, sodium borohydride or methyl-lithium gives the corresponding nitrate 30, hydrogenate 31 [19] or methylate complex 27, respectively. The *cis* complex 29 is also obtained by heating the nitrate 30, but *trans* complex 28 is obtained by heating the methylated complex 27.

In addition, treatment of chloro-bridged compound 26 with silver carboxylate, pyridine, phosphine, stilbenediamine and thallous acetylacetonate gave the corresponding chloro-bridge cleaved compounds (32—35) as shown in eqns. (17—19).



(17)

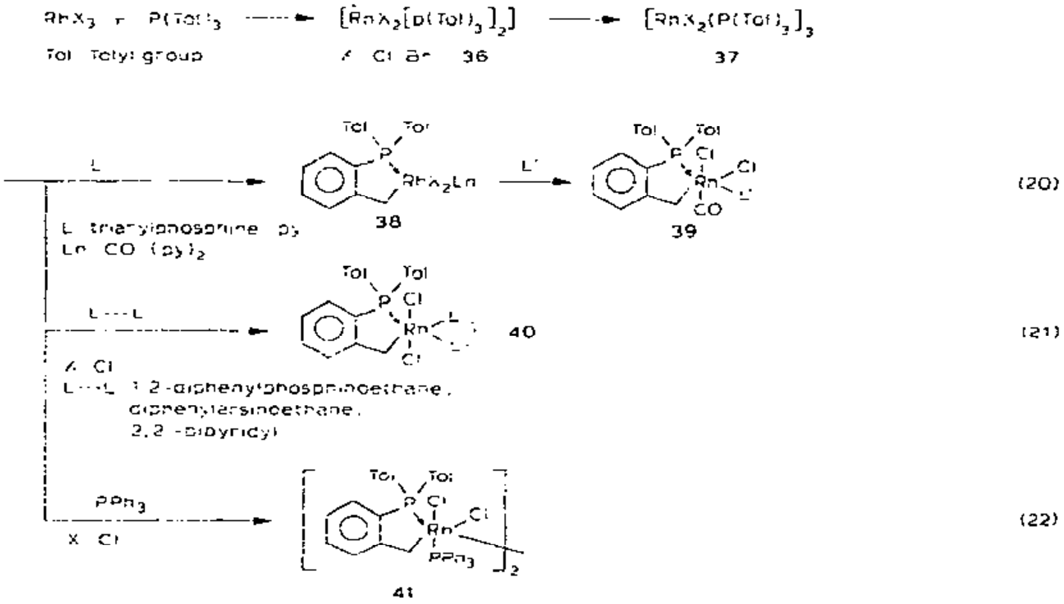
(18)

(19)

In eqns. (14) and (15), *trans*-[PtCl$_2$[P(*o*-tolyl)$_2$Ph]$_2$] (intermediate 24), gave cyclometalated 25; however, similar treatment in the presence of lithium bromide or sodium iodide gave the corresponding bromide or iodide derivatives of 25 [20,21]. The rate of the metalation reaction is increased slightly by lithium bromide and in the presence of sodium iodide is complete after a short time. From these data, Shaw and co-workers [20,21] indicated "generally, the tendency to internal metalation increases in the order of anionic ligands Cl < Br < I". This should be considered as the order of metal—halogen bond strength, because these cyclometalation reactions proceed by elimination of hydrogen halides obtained from the reaction of a methyl hydrogen with the halogens bound to the metals.

The *o*-tolylphosphines also reacted with palladium compounds to afford cyclometalated bridged compounds, similar to 26 (in eqn. 16), which afforded mononuclear species by halo-bridge cleavage using various ligands as shown in eqns. (17--19) [21a].

Rhodium halides reacted with *o*-tolylphosphines to give cyclometalated compounds [22]. The reaction at room temperature gave only the *trans*-planar intermediate 36, but on heating, gave initially a trimeric complex of apparent formula $[RhCl_2[P(o\text{-tolyl})_3]]_3$ 37 and finally a monomeric complex of apparent formula $RhCl[P(tolyl)_3]_2$, described later in section E. Compound 37 is presumed to be a cyclometalated compound such as 25 [22]. Treatment of 37 with carbon monoxide, pyridine, phosphine, arsine, bipyridyl, etc. gave mainly the corresponding six-coordinate compounds 38—41 in eqns. (20—22).



Reaction with carbon monoxide gave the five-coordinate compound 38, which gave the six-coordinate compound by treatment with triarylphosphine or pyridine (eqn. [20]). Direct treatment of 37 with triphenylphosphine gave the chloro-bridged compound 41 (eqn. [22]). The crystal structure

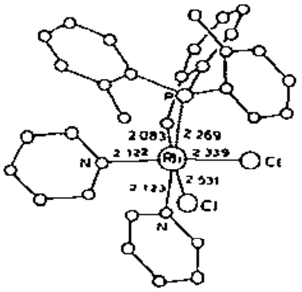


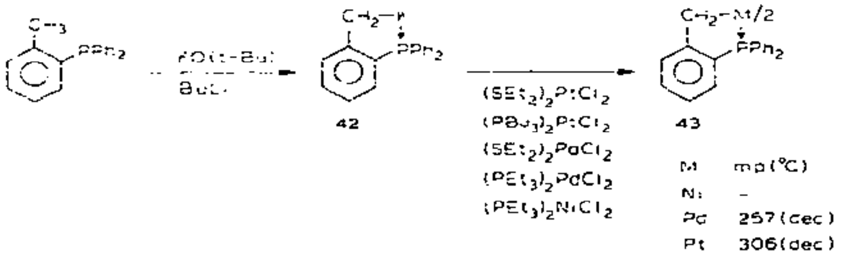
Fig. 1. The structure of dichloro-dipyridine-[*o*-(di-*o*-tolylphosphino)benzyl]rhodium(III)-0.61 chloroform, 38.

of the dichlorodipyridine compound 38 has been determined by a three-dimensional X-ray analysis [23].

While pyridine and Cl atoms are in *cis* positions to each other, the phosphorous atom is *trans* to one pyridine, the carbon atom is *trans* to one of the Cl atoms, and one pyridine is *trans* to one Cl atom. The *trans* influence exerted by a saturated carbon ligand is evidenced by the significant difference between the Rh—Cl bond lengths; chlorine *trans* to pyridine (Rh—Cl = 2.339 Å), the other *trans* to the benzyl carbon (Rh—Cl = 2.531 Å).

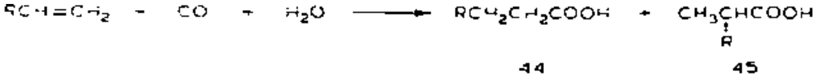
Methylmanganese pentacarbonyl is relatively reactive, and cyclometalation of tris(*o*-tolyl)phosphine with this metal carbonyl gave an internal metalated carbonyl product directly at temperatures considerably below those required for the metalation of the other compounds [24].

Potassium t-butoxide reacted with *o*-tolylphosphine in the presence of n-butyl-lithium to give the cyclometalated potassium complex 42, an air-unstable powder [25]. Treatment of 42 with $(SEt_2)_2PtCl_2$, etc., gave bimetallic compounds 43, in which the transition-metal—carbon bond is stabilized by chelation with a phosphorus atom. The platinum compound 43 is assigned *cis* on the basis of the Pt—H coupling constant (75 Hz) [26].



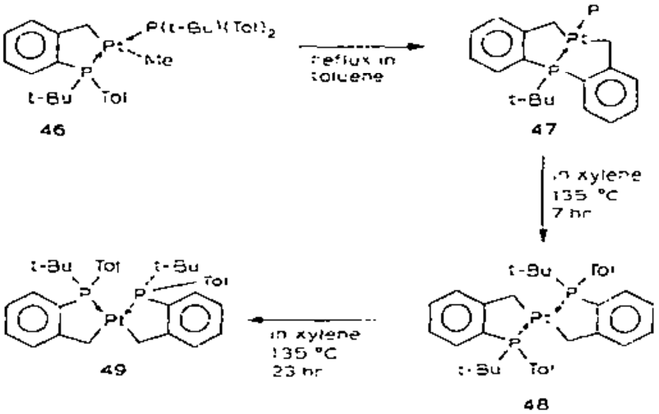
(23)

The hydratocarbonylation reaction of olefins with carbon monoxide and water gave saturated carboxylic acids [27], using a palladium—phosphine complex as a catalyst (eqn. [24]). Esters are produced [28], if alcohols are used in place of water. These palladium—phosphine catalyzed systems have advantages in rate and selectivity over the earlier palladium complexes without phosphines [29]. Fenton [30] proposed a mechanism of catalyst action via cyclometalation of *o*-tolylphosphine or phenylphosphine (described in Section C) for this hydratocarbonylation (eqn. [24]).



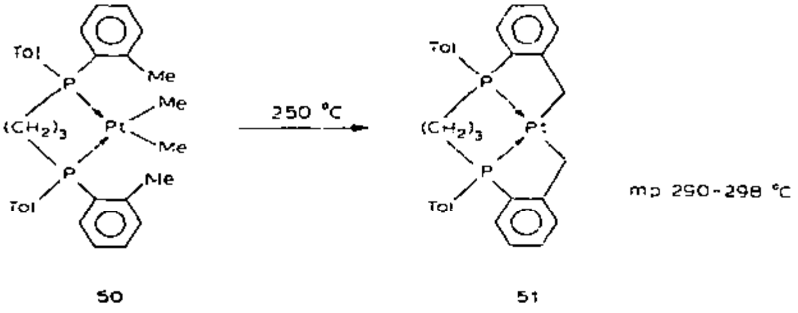
$$RCH{=}CH_2 + CO + H_2O \longrightarrow \underset{44}{RCH_2CH_2COOH} + \underset{45}{CH_3\underset{R}{C}HCOOH} \qquad (24)$$

The platinum five-membered ring compound 46, obtained from *o*-tolylphosphines, on heating in toluene [31] gave the tridentate compound 47 by cyclometalation of another phosphine bonded to the metal.



When 47 was heated in refluxing xylene it isomerised to the *trans*-isomer 48 but it contained a small amount of the *cis*-isomer 49. Prolonged heating increased the proportion of the *cis*-isomer to ca. 20% [18]. The structures of the three isomers were determined by X-ray diffraction. All are square-planar. The bond length of the intramolecular-coordinated Pt—P bond is ca. 0.1 Å shorter than that of the intermolecular Pt—P bond of 47.

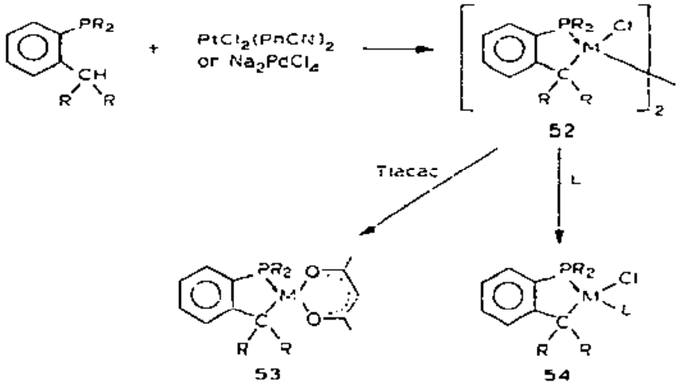
On pyrolysis at 250° C, di-*o*-tolylphosphine dimethylplatinum 50 lost 2 mol equiv. of methane and gave the tetradentate 51 having two rings. Complex 51 is extremely stable thermally and melts with decomposition at 290—298°C [32].



(25)

o-Tolylphosphine methyl derivatives react with metal compounds in a fashion analogous to the *o*-tolylphosphine compounds mentioned above to give cyclometalated methyl derivatives. These products are also produced from *o*-styrylphosphine.

The former reaction is a substitution reaction of the methyl derivatives, but the latter is an addition reaction of the metal compounds to vinyl olefin.



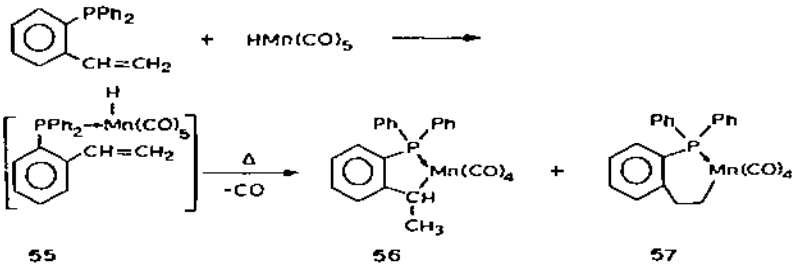
(26)

R t-Bu, Ph
R^{1-3} H, Me
L py, PPh_3, Me_2PhAs

For example, *o*-ethylphenylphosphine, *o*-isopropylphenylphosphine, etc. easily reacted with metal compounds such as platinum chloride and palladium chloride to give chloro-bridged compounds 52. Furthermore, the reaction of 52 [33,34] with pyridine, triphenylphosphine, dimethylarsine or thallous acetylacetonate gave the conventional bridge split compounds 53 and 54.

In eqn. (26), there are three possible metalation positions on the tolylphosphine derivatives by which four-, five- or six-membered rings may be formed; however, orthometalation at the phenyl ring (through which a four-membered ring may be formed) and the substitution reaction at the terminal methyl group (by which a six-membered ring may be formed) do not proceed.

In the case of *o*-styrylphosphine, the terminal vinyl hydrogen is reactive. The six-membered ring compound 57 was formed as a minor product; however, the sterically favoured five-membered ring compound 56 was the main product [35]. Both 56 and 57 are formed by the addition reaction of manganese and hydride to the vinyl group via intermediate 55, the direction of addition being Markownikoff and anti-Markownikoff, respectively.



(27)

Product 56 is found to have a strainless ring structure as shown in Fig. 2 by three-dimensional X-ray data [36].

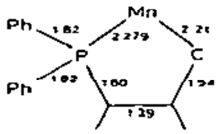
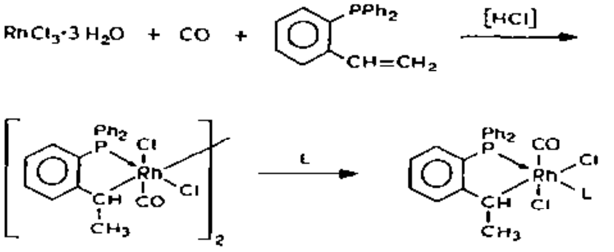


Fig. 2. Bond distances within the five-membered chelate ring about the manganese atom of 56.

Hydrated rhodium(III) chloride was treated first with carbon monoxide, and then heated with *o*-styryldiphenylphosphine to form the chloro-bridged cyclometalated 58 by addition of HCl to the double bond of coordinated *o*-styryldiphenylphosphine. The hydrogen chloride was undoubtedly both formed when hydrated $RhCl_3$ was dissolved in alcohol as a solvent, and also when this solution was carbonylated [37]. The reaction of 58 with phosphines afforded the chloro-bridge fission product 59.



58

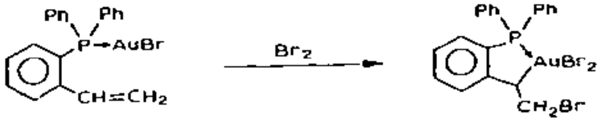
59

L . PPh_3, PPh_2Me, $PPhMe_2$

(28)

Reaction of *o*-styryldiphenylphosphine (sp) with $M_3(CO)_{12}$ (M = Fe, Ru) gave the mono-olefin chelate complexes $M(CO)_3$ (sp) [38], which have an intra-π-coordination bond (see Section E). Treatment of the chelate complex with hydrogen halide gives an octahedral cyclometalated complex similar to 59. The structure of the ruthenium bromide complex is found to be octahedrally coordinated by three fac-carbonyl groups according to a single-crystal X-ray analysis [39].

A molecular complex of gold bromide and *o*-styryldiphenylphosphine reacted with bromine to yield the cyclometalated compound 60. This product, also confirmed by a single-crystal X-ray study, possesses a ring and a square-planar structure [40].

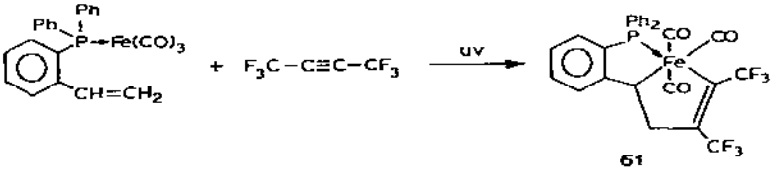


60

(29)

On the other hand, reaction of bromine with the molecular complex obtained by reaction of platinum bromide and *o*-styryldiphenylphosphine gave an octahedral bromo-bridged dimer having a five-membered ring similar to 60 [41].

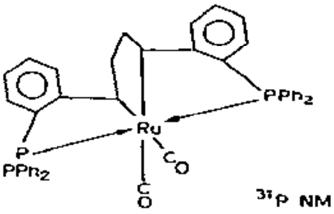
The *o*-styryldiphenylphosphine metal complex yields a ring compound upon photochemical reaction. For example, hexafluoro-but-2-yne reacted under UV irradiation with tricarbonyl(diphenyl-*o*-styrylphosphine)iron to give the tridentate compound 61, in which the acetylene links the iron and vinyl group [42].



61

(30)

The reaction [43] of *o*-styryldiphenylphosphine with $Ru_3(CO)_3$ in refluxing n-nonane gave the octahedral tetradenate complex 62 containing a puckered ruthenacyclopentane ring formed by the coupling of two vinyl residues at the β-carbon atoms. In addition intramolecular-π-coordination products, described later in Section E, were also obtained.

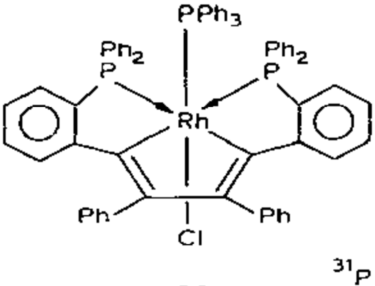


^{31}P NMR : 64.1 ppm

62

The proton-decoupled ^{31}P NMR spectrum of 62 shows a singlet, as expected for two equivalent mutually *trans* phosphorus atoms.

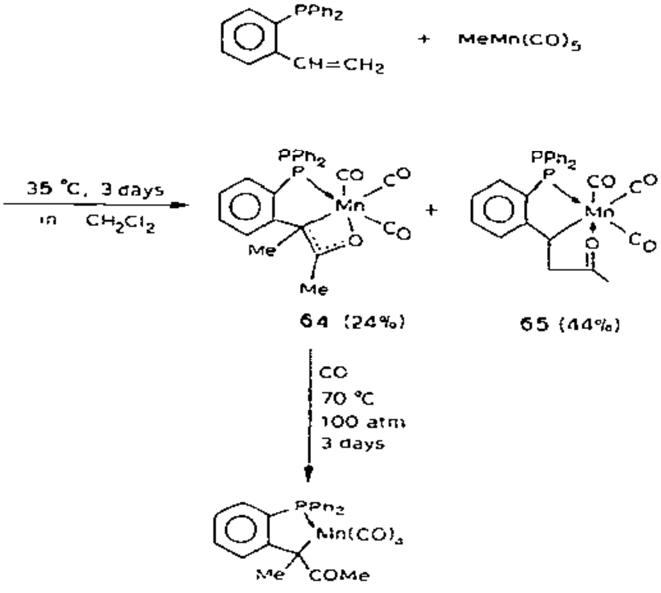
A similarly dimerized tetradentate complex 63 was obtained in high yield by reaction of *o*-[Ph_2P—C_6H_4—C≡C—Ph] with $RhCl(PPh_3)_3$ [44].



63

^{31}P NMR : −8.7 ppm
^{J}RhP(a): 94 Hz
^{J}RhP(a)-P: 29 Hz

Methylmanganese pentacarbonyl reacts with *o*-styryldiphenylphosphine, but does not afford the normal five-membered ring compound similar to 56 (eqn. (27)) by addition to a vinyl group, but rather, a delocalised pseudo-π-allylic π-oxopropenyl complex 64 and oxobutyl complex 65 by the reaction of α- or β-carbon of the vinyl group with the methyl carbonyl group (formed by carbonyl insertion to Mn—Me bond or by methyl migration to carbonyl) [45—47].

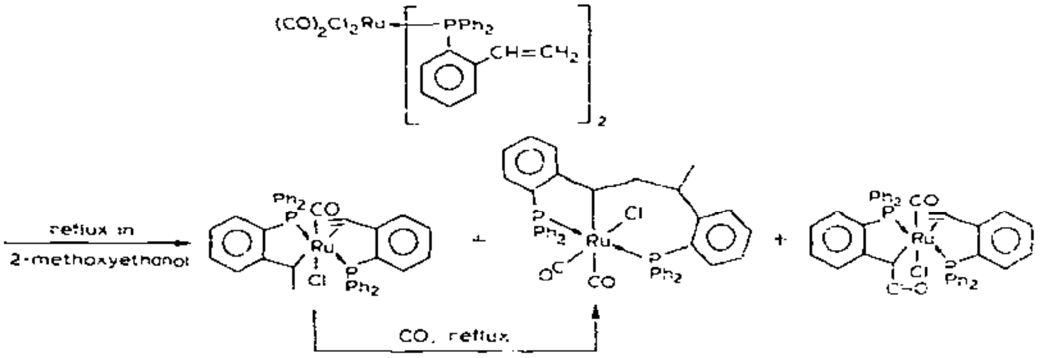


66

(31)

The former π-oxopropenyl complex 64 reacts with carbon monoxide to give the normal five-membered ring compound 66 by fission of the pseudo-π-allylic π-oxopropenyl—manganese bond. The structures of 64 and 65 were determined by three-dimensional X-ray analysis [46,47]. In 64 [47], coordination at the manganese atom is essentially a distorted octahedron, within the π-oxopropenyl moiety, the C—C and C—O distances [1.427 and 1.295 Å, respectively) are intermediate between their respective single- and double-bond distances, confirming the formulation as a delocalized π-bonded system. In 65 [46], the manganese atom is also octahedrally coordinated, the bond distances to the oxobutyl substituent being as expected for Mn—C (2.146 Å) and Mn—O (2.067 Å) σ-bonds.

The reaction of *o*-styryldiphenylphosphine with a metal compound usually requires the addition of species such as hydrogen halide to the vinyl group in order to cyclometalate as shown in eqn. (28). But, in the case of eqn. (32), there are no strong addition species, and reaction gives compound 67 as a main product, having the usual ring but containing another ring with an intramolecular π-bond, described later in Section E, together with small amounts of two compounds 68 and 69 [48]. 68 having five- and seven-membered rings, formed by coupling two vinyl groups, was also produced by heating the main product 67 under CO pressure.



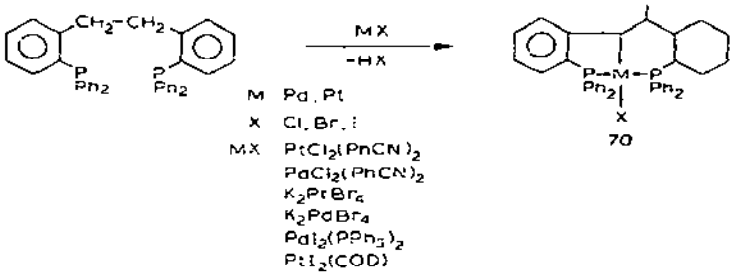
67 (60%) 68 (18%) 69 (5%)

(32)

69 is the oxide of the main product 67. The formation of these products 67 and 68 is thought to involve the reaction between the starting compound $(CO)_2Cl_2Ru{-}(PPh_2C_6H_4{-}CH{=}CH_2)$ and 2-methoxyethanol as a solvent to give intermediate ruthenium(II) hydride complexes [48].

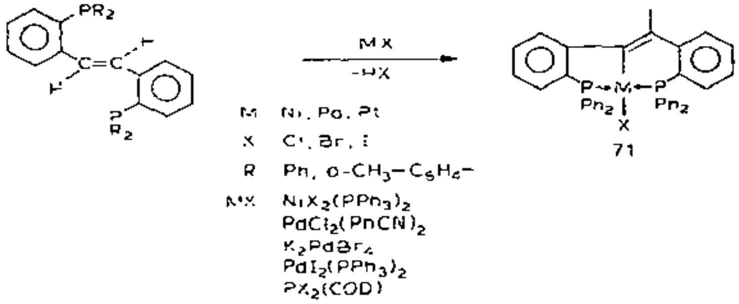
Other studies include reaction of *o*-styryldiphenylphosphine with platinum compounds [49], in which it was not clear whether five-membered rings such as 56 or six-membered rings such as 57 were present.

2,2'-Bis(diphenylphosphino)dibenzyl or 2,2'-bis(diphenylphosphino)stilbene react with metal halides [50,51] to give the cyclometalated tridentate compounds having five- and six-membered rings 70 or 71, accompanied by elimination of hydrogen halide. Reaction of the stilbene above with $PtMe_2$-(COD) (COD = 1,5-cyclooctadiene) gave the methyl derivative (71, X = Me) instead of the metal halide.



70

(33)



71

(34)

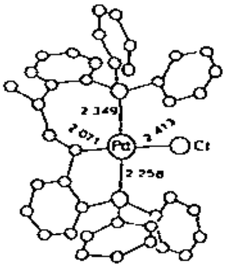


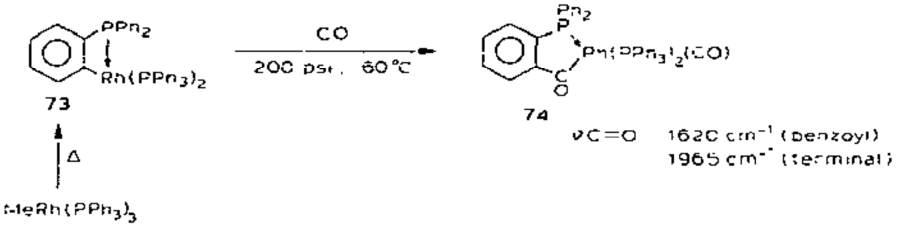
Fig. 3. The structure of 1,3-bis[*o*-diphenylphosphino)phenyl]-2-buten-1-yl]chloropalladium(II), 72.

The crystal structure of 71 (M = Pt, X = Cl) has been determined by three-dimensional X-ray analysis [50,52]. Coordination at the central platinum atom is essentially square planar. As expected, there is also a marked structural *trans* effect in this complex [53]. The Pt—Cl distance (2.377 Å) is very much longer than the Pt—Cl distance of 2.294 Å found for *trans*-$[PtCl_2[P(CH_2CH_3)_3]_2]$ [54].

1,3-Bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene reacts with palladium chloride to give a chelate η^1-allyl complex 72 in which the double bond has migrated from the 1- to the 2-position in the carbon chain [55]. The coordination about the central palladium atom is also essentially square planar with the two phosphorus atoms of the tridentate ligand being mutually *trans*. The Pd—Cl distance of 2.413 Å is significantly longer than the corresponding distances in K_2PdCl_4 (2.313 Å, Cl *trans* to Cl) [56] and provides additional evidence for the well-known *trans*-bond weakening influence of a σ-bonded carbon atom [53].

(iii) Benzoyl compounds

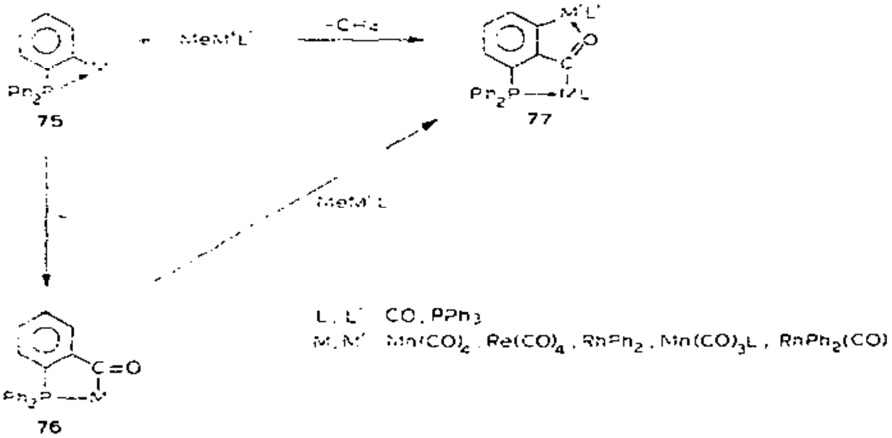
The author has reported organometallic intramolecular-coordination compounds having a benzoyl group, in which the ligand atom is O [1,5] or N [7]. Organometallic intramolecular-coordination compounds containing a phosphorus donor ligand often possess a benzoyl group synthesized by carbonyl insertion into the relatively unstable four-membered ring compound (e.g. 73, obtained by the orthometalation reaction of phenylphosphine [57]). Similarly they are obtained by cyclometalation with *o*-phosphinobenzaldehyde, etc.



(35)

In the reaction of phenyltris(triphenylphosphine)rhodium with carbon monoxide, the metal carbonyl bond (νCO = 1960 cm^{-1}) is formed at very low temperature (e.g. —40 to —20°C), but carbonyl insertion occurs at room temperature, forming a benzoyl complex $Ph_3PRhCOPh$ (νCO = 1625 cm^{-1}). Insertion is a slow step compared to CO coordination and CO coordination occurs readily at temperatures at which insertion does not take place at a measurable rate [58—60]. The reaction of $(Ph_3P)_3RhMe$ and CO at very low temperature gave only a carbonyl compound having a terminal carbonyl bond. However upon warming methyltris(triphenylphosphine)rhodium under CO pressure, complex 74 was obtained accompanied by elimination of CH_4, probably via the reaction path shown in eqn. (35) [57].

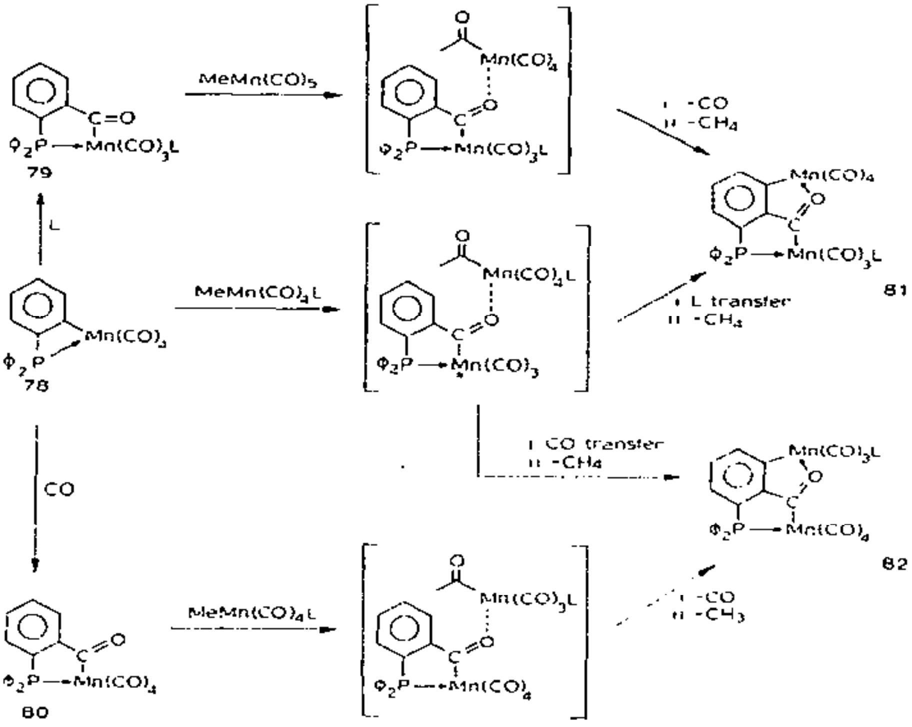
In the four-membered ring compounds obtained by orthometalation, the carbonyl insertion reaction proceeds in the presence of a ligand, e.g. triphenylphosphine, without carbon monoxide when the ring compounds have carbonyl groups, to give the benzoylphosphine compound 76 [24,61]. Attempted decarbonylation of 76 at 126°C in octane solution, led only to 10% of the decarbonylated product 75 with recovery of 85% of 76 (M = Mn-$(CO)_4$) after 1.5 h. From this evidence, Kaesz and co-workers [24] also considered that the five-membered ring compound 76 must be regarded as relatively more stable than the four-membered ring compound 75.



L, L' CO, PPh_3
M, M' $Mn(CO)_4$, $Re(CO)_4$, $RhPh_2$, $Mn(CO)_3L$, $RhPh_2(CO)$

(36)

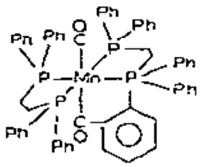
76 reacted further with methyl metal carbonyl to give the secondary cyclometalated compound 77 having two five-membered rings [61]. The secondary metalated compounds 77 were obtained directly by reaction of 75 with methyl metal carbonyl compounds [61—63]. McKinney and Kaesz [61] have suggested the reaction mechanism shown in Scheme I. Reaction of the acyl derivatives 79 or 80 with metal carbonyl proceeds at a relatively low temperature (ca. 90°C), but the primary metalation product 78 requires the higher temperature (ca. 110°C) because it must proceed via carbonyl insertion. In the reaction of acyl derivatives 79, 80, the first step is the coordination of the carbonyl oxygen to the metal, but, in the primary metalation



Scheme I

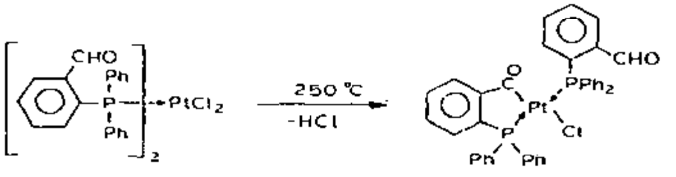
product **78**, coordination of the carbonyl oxygen to the metal occurs via the carbonyl insertion reaction. Subsequently, the acyl derivatives coordinate to the manganese atom, followed by decarbonylation and demethanation, to give the secondary metalated compounds **81**, **82**. On the other hand, the primary metalated compound similarly coordinated to manganese, followed by transfer of the ligand and demethanation without decarbonylation, also gives 81, 82 [61]. The structures of many secondary metalated compounds **81**, **82**, shown in the general formula **77**, were determined by X-ray diffraction studies [63—66]. These compounds contain an extended planar tricyclic ring system which includes both metal atoms and the bridging ligand of two rings.

Reaction [67] of $Mn_2(CO)_{10}$ with $Ph_2PCH_2CH_2PPh_2$ (dpe) gave $[Mn(CO)(dpe)_2Mn(CO)_5]$ **83** as a major product, together with a small amount of the carbonyl insertion compound $[Mn(CO)(COC_6H_4P(Ph)CH_2CH_2PPh_2)(dpe)]$ **84**, etc. **84** is presumed to be formed when the basic $[Mn(CO)_5]^-$ ion abstracts an *ortho* proton from one phenyl ring in $[Mn(CO)_2(dpe)_2]^+$ followed by a nucleophilic attack of the carbanion on the adjacent carbonyl group. **84** is also obtained in better yield when the major product **83** is refluxed in xylene. The X-ray structure [67] of **84** involves an octahedral manganese atom with four P atoms in an approximate square plane.



84

Vacuum thermolysis [68] of *cis*-$PtCl_2[PPh_2(o—C_6H_4CHO)]_2$, easily prepared from *o*-diphenylphosphinobenzaldehyde and K_2PtCl_4, resulted in rapid and quantitative formation of the cyclometalated compound 85 by intramolecular elimination of HCl from a metal-aldehyde complex.

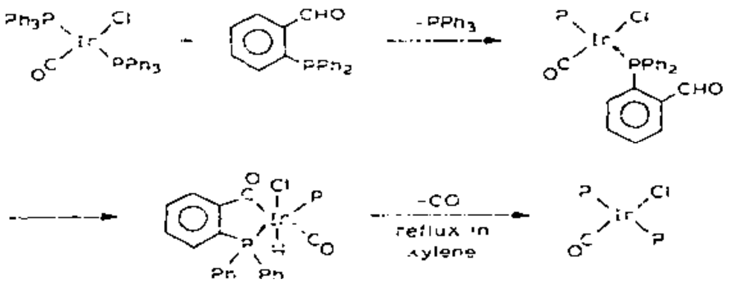


85

(37)

This thermolysis is presumed to occur via two paths: oxidative addition of the C—H bond followed by reductive elimination of HCl, or direct electrophilic attack on the formyl group by platinum(II) with displacement of a proton [68].

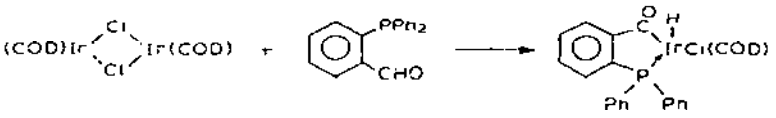
In contrast to the platinum(II) reaction, treatment of *o*-diphenylphosphinobenzaldehyde with nucleophilic iridium(I) complexes results in oxidative addition affording hydride 86 without intramolecular elimination of HCl [68].



86

(38)

Reaction with the chloro-bridged 1,5-cyclooctadiene iridium complex gave the thermally unstable acyl hydrido olefin complex 87 by bridge cleavage-oxidative addition.

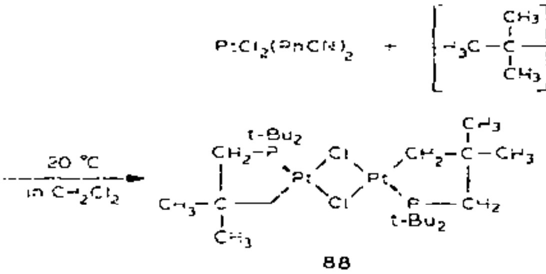


87

(39)

(iv) Alicyclic compounds

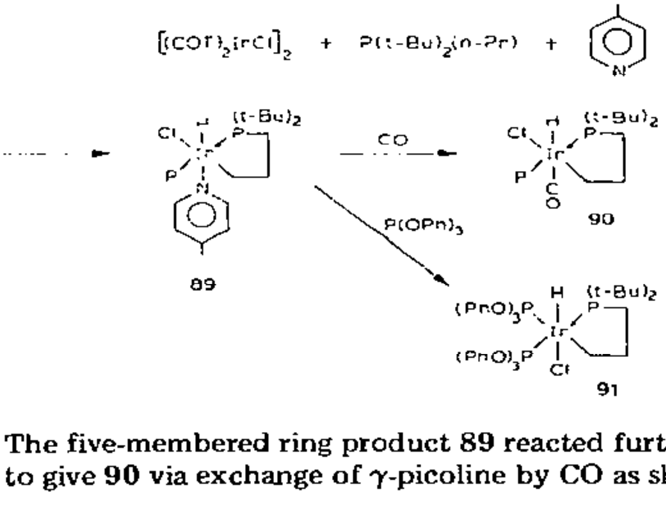
Five-membered organometallic intramolecular-coordination ring structures containing an aromatic ring were described in the previous sections. Five-membered rings having an aliphatic chain are also formed. For example, reaction of di-t-butyl(neopentyl)phosphine with $PtCl_2(PhCN)_2$ at room temperature provided a white complex whose structure was characterised by X-ray diffraction methods and found to contain chloro-bridged binuclear metalated neopentyl groups [69].



(40)

The phosphine, as a starting material, has two t-butyl groups and one neopentyl group, but, the ring structure of the product 88 is formed by the neopentyl group, not by the t-butyl group which could form a four-membered ring structure. This is evidence that the formation of a five-membered ring structure is also easier than that of a four-membered ring structure in aliphatic compounds. The coordination geometry of the platinum atom is planar [69].

Di(t-butyl)-n-propylphosphine upon reaction with $[(COT)_2IrCl]_2$ in the presence of γ-picoline or acetonitrile yields predominantly a cyclometalated product 89 [70].

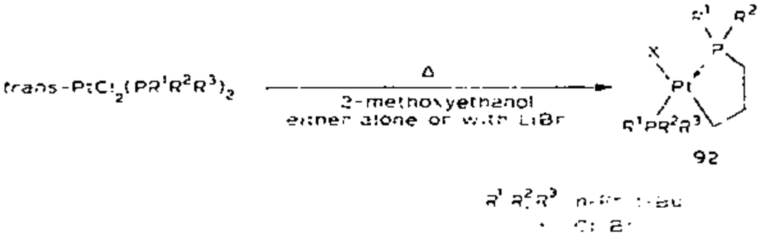


(41)

(42)

The five-membered ring product 89 reacted further with carbon monoxide to give 90 via exchange of γ-picoline by CO as shown in eqn. (41); however, reaction with triphenylphosphite gave **91**, in which the two phosphites were *cis*, by rearrangement around the metal. It is considered that the aliphatic five-membered ring is stable because no ring fission occurred under reaction with a ligand such as carbon monoxide or phosphite.

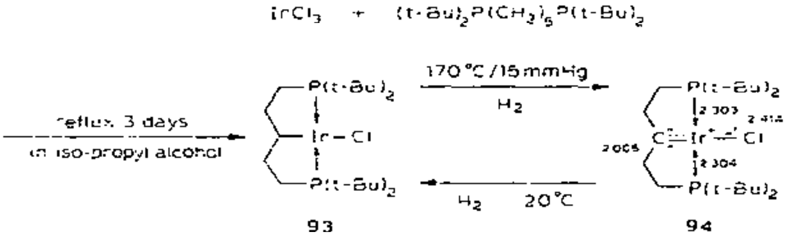
On heating, tri-n-propylphosphine platinum compound is believed to give the cyclometalated compound **92** having the same ring as **89—91**, in which the two phosphorus nuclei are mutually *trans* (cf. NMR data, ^2J(P P) = 396.5 Hz), but Shaw and co-workers [20,21] could not confirm by NMR whether the compound has a five- or four-membered ring.



(43)

Chloro-bridged diplatinum(II) complexes of the type [$Pt_2Cl_4L_2$] (L = PPr_3, $P(t\text{-}Bu)_3$, $P(t\text{-}Bu)Pr_2$, $P(t\text{-}Bu)_2Pr$, $PPrPh_2$, PPr_2Ph or $P(t\text{-}Bu)Ph_2$), underwent a regiospecific hydrogen—deuterium exchange in an aqueous (D_2O) acetic acid (CH_3COOD) medium to give complexes containing deuterium in the alkyl groups of the tertiary phosphine moiety [71]. The steric requirements of the tertiary phosphine have a marked influence on both the rate and position of deuterium incorporation. The results presented show that, in internal metalation reactions of platinum, the ease of ring formation decreases in the order five-membered > six-membered > four-membered rings. Kiffen et al. [71] pointed out "it is suggested that in such reactions steric rather than electronic factors are dominant".

Treatment [72] of hydrated iridium chloride with the diphosphine $t\text{-}Bu_2P\text{—}(CH_2)_5\text{—}P(t\text{-}Bu)_2$ gave the tridentate compound **93** having two five-membered rings. When **93** is heated under reduced pressure, an unusual ylide or carbene complex **94** is produced by elimination of hydrogen, the structure of which is determined by X-ray diffraction [72].



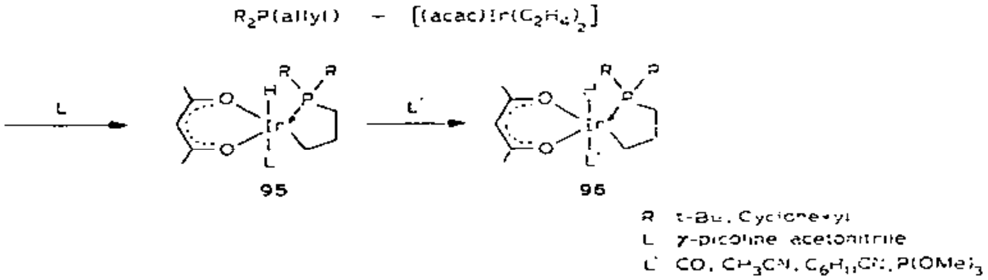
(44)

The Ir—C bond length of 2.006 Å is shorter than that found (2.16 [73] and 2.10 Å [74]) in octahedral iridium(II) complexes having a saturated carbon atom *trans* to Cl [72]. The ^{13}C NMR evidence [75] (δ(C_6D_6) 66.6) is against a pure carbene structure and favours substantial contribution from the ylide form [72]. The loss of dihydrogen from **93** is reversible since a benzene solution of **94** under dihydrogen at room temperature gives back the hydride **93**.

Rhodium chloride trihydride reacts with t-Bu_2P—$(CH_2)_5$—P(t-Bu)$_2$ to give the tridentate rhodium complex similar to **93** [76]. The occurrence and stereochemistry of a rapid reversible C—H fission in **93** is established by NMR spectroscopy, including triple resonance INDOR, and by X-ray crystallography.

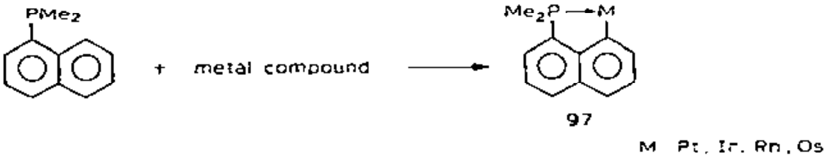
(v) Miscellaneous compounds

Allylphosphines react with various iridium complexes (e.g. acetylacetone iridium complex [77], cyclooctene iridium complex [78], etc.) to give olefinic ring compounds, e.g. **95**. This ring structure is stable because the ligand exchange reaction with other ligands such as carbon monoxide, occurs without fission of the ring structure to give **96**.



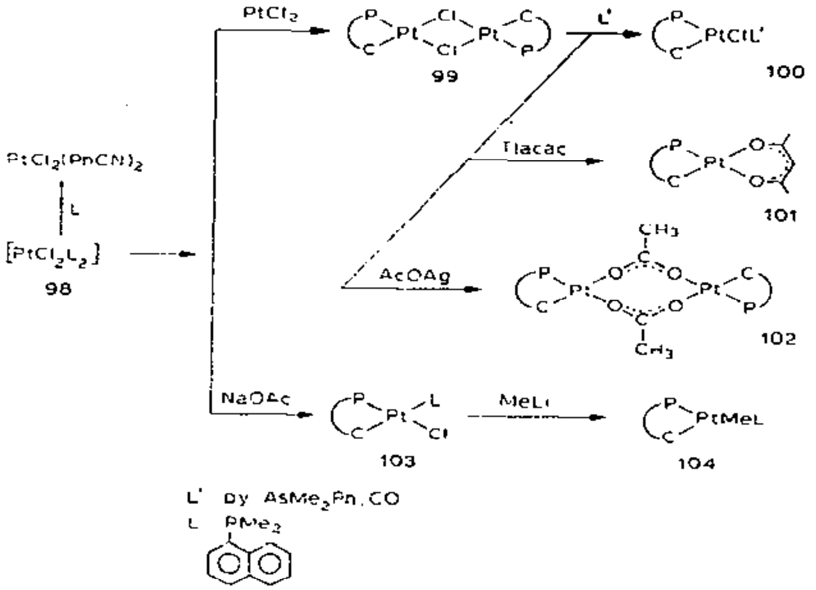
(45)

As shown in eqn. (46), dimethyl(1-naphthyl)phosphine reacts with metal halides such as platinum [79], iridium [80], rhodium [80] and osmium [81] to give the five-membered ring compound **97** by selective reaction at the peri position.



(46)

For example [79], dimethyl(1-naphthyl)phosphine reacts with $PtCl_2$-$(PhCN)_2$ to afford the molecular complex **98**, and prolonged heating of **98** with platinum halide affords the chloro-bridged compound **99**. The reaction of **98** with pyridine, carbon monoxide, dimethylphenylarsine, thallous acetylacetonate, silver acetate, etc., gave the corresponding chloro-bridged cleavage reaction products **100**—**102**.



(47)

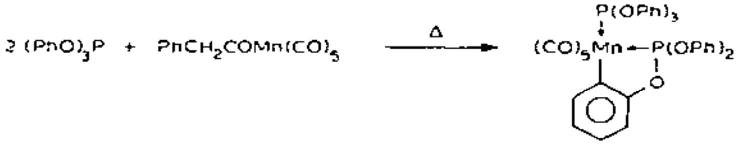
(48)

(49)

(50)

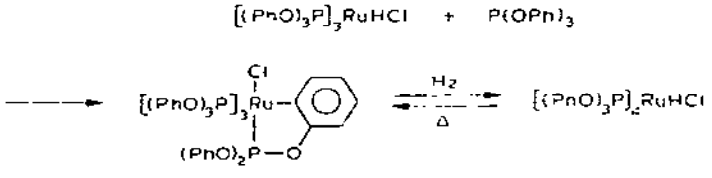
However, heating **98** in the presence of sodium acetate easily affords the cyclometalated compound **103**, which reacts with methyl lithium to afford the methylated compound **104** by substitution of halogen in **103** with methyl.

The phosphite metal compounds, e.g. **105**, **106**, obtained from triarylphosphite, also contain five-membered rings with an M ← P bond. However, as the ring contains another element besides carbon, metal and phosphorus, these compounds do not strictly belong to organometallic intramolecular-coordination compounds [1,6,7,81a] as shown below in formula **120**, but in a broad sense could be regarded as organometallic intramolecular-coordination compounds in which the P—O bond is a ligand group (Y in **120**). These compounds have been synthesized by reaction of triarylphosphite with a metal compound, by heating the molecular complex obtained by reaction of triarylphosphite with metal compound, or by reaction of the above molecular complex with another triarylphosphite. For example, reaction of triphenylphosphite with manganese carbonyl gave the cyclometalated compound **105** [82]. The ruthenium compound obtained by reaction with triarylphosphite, reacted with triphenylphosphite to give the cyclometalated compound **106**, in which the ring was opened to give **107** by hydrogenation; **107** reverts to **106** upon heating [83,84].



(51)

105



106 107

(52)

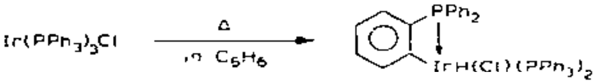
Many compounds having five-membered rings such as **110** have been reported with Pd [85], Pt [85,86], Ru [87–91], Co [84,92,93], Fe [94], Mn [24], Ir [95–100], Rh [101], Os [102], etc., and, of these compounds, structures of iridium [96–98,100] and rhodium compounds [90] have been determined by X-ray diffraction.

C. FOUR-MEMBERED RING COMPOUNDS

As described in the previous section, organometallic intramolecular-coordination compounds usually contain a five-membered ring, and this tendency for compounds containing an oxygen [102a] or nitrogen donor ligand [102b] is higher than that of compounds containing a sulfur [102c] or phosphorus donor ligand. For the latter compounds having *d* orbitals, formation of other rings is less difficult because the degree of freedom of the intramolecular bond in the latter compounds is higher than that of the freedom in the former compounds, owing to the additional *d* orbitals and their hybrid orbitals with *s* and *p* orbitals [102d,102e].

In a previous review [6] of these organometallic intramolecular-coordination compounds containing a sulfur donor ligand, it was reported that these compounds formed mainly five-membered rings and some three-membered rings, etc. However, organometallic intramolecular-coordination compounds containing a phosphorus donor ligand frequently contain four-membered rings.

The formation of a four-membered ring is not usually an easy process compared to that of a five-membered ring, since presumably the four-membered ring structure has more strain than the five-membered; however, when there are no possibilities for formation of a five-membered ring in the reaction of phenylphosphines with a metal compound or pyrolysis of a metal complex containing phenylphosphine (mainly triphenylphosphine), then the four-membered ring compound is formed by the orthometalation reaction.



108

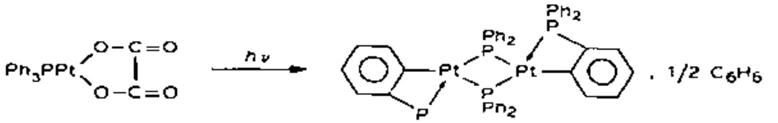
(53)

For example, chloro-tri(triphenylphosphine)iridium [103] was heated in benzene to give the cyclometalated compound **108** in which the iridium metal substituted a phenyl hydrogen. Reaction of the deuterated complex

$Ir[P(C_6D_5)_3]_3Cl$ gave the deuteride, in which the metal is bonded by deuterium, showing strong bands due to ν(Ir—D) at 1600 cm^{-1} and 1540 cm^{-1}, and indicating that deuterium has been extracted from coordinated triphenylphosphine. An intense band in the IR spectrum of **108** at 728 cm^{-1}, is assigned to the C—H out-of-plane deformation mode of an *ortho*-disubstituted benzene.

Four-membered rings are obtained by heating phenylphosphine—metal complexes containing Ir [104—107], Pt [20,21,108,109], Ru [89,110], Mn [24,111], Rh [112], Fe [113], etc.

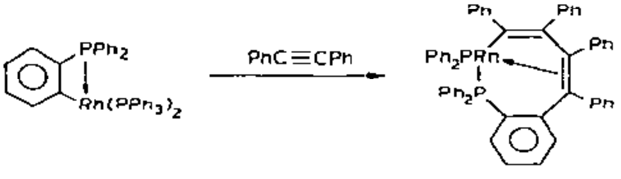
Phenylphosphine metal complexes yield four-membered ring compounds by orthometalation under irradiation with ultraviolet light [114,115]. For example, as shown in eqn. [54], oxalatobis(triphenylphosphine)platinum(II) [114] reacts photochemically to give the diphenylphosphido-bridged dimeric complex **110**.



109 110 δ(C—H) 725 cm^{-1}

(54)

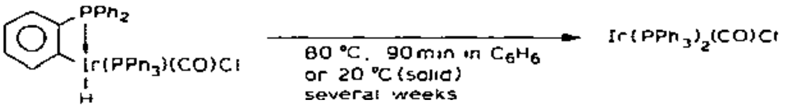
Because of the low stability of orthometalated four-membered rings compared with five-membered rings e.g., benzoyl compounds as described in Section B(iii) the four-membered ring undergoes carbonyl insertion upon reaction with carbon monoxide. Moreover, other species can insert in these compounds, e.g. diphenylacetylene [115] and hexafluorobut-2-yne [89]. The latter are bis-insertion reactions as shown in eqn. (55). On the basis of an X-ray study [115] on **111**, the coordination about the Rh atom is distorted square-planar.



111

(55)

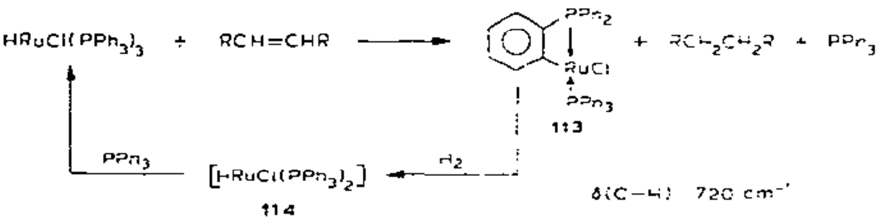
The reverse reaction [107,116] for opening the four-membered ring is found in a phenylphosphine—iridium complex as shown in eqn. (56). The orthometalated derivatives **112** of phenylphosphine gave the ring-opened phenylphosphine—iridium complex on heating or on standing for a long time at room temperature [107].



112

(56)

Phenylphosphineruthenium hydrides are used as catalysts for catalytic hydrogenation or stoichiometric hydrogenation [117,118]. For example, in the reaction of $HRuCl(PPh_3)_3$ with olefins (eqn. (57)), the olefins are hydrogenated by two hydrogens, one from the hydride and the other from the phenyl hydrogen in the orthometalation reaction. The orthometalated four-membered ring compound reacted with H_2 probably via a $Ru^{IV}H_2$ to give $HRuCl(PPh_3)_2$ **114** (not isolated); addition of phosphine regenerates the starting phenylphosphine—ruthenium complex.

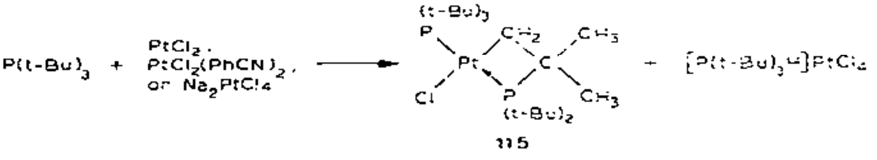


(57)

However, the stoichiometric process is unimportant in hydrogenations catalyzed by $HRuCl(PPh_3)_3$ under H_2, which are very much more rapid. Spectrophotometric data indicate that both the stoichiometric and catalytic hydrogenations probably proceed via the same alkyl intermediate but the subsequent hydrogenolysis step is faster than the intramolecular hydrogen transfer step. Regeneration of the hydride by the reverse reaction is also slower than the catalytic hydrogenations [117].

Other four-membered ring compounds derived from phenylphosphine compounds [57,109,111,113,119—126] have been reported and some X-ray diffraction studies [109,111] have appeared.

There are many articles concerning four-membered rings obtained by orthometalation of phenylphosphine; however, several reports were published concerning four-membered ring compounds produced by cyclometalation of aliphatic phosphines. For example, reaction [127] of butylphosphine with platinum chloride, gave the internally metalated four-membered ring complex **115**, in which the position of the two phosphorus nuclei are *trans* [128,129] to each other from ^{31}P NMR data ($^2J(P—P') = 382, 383$).



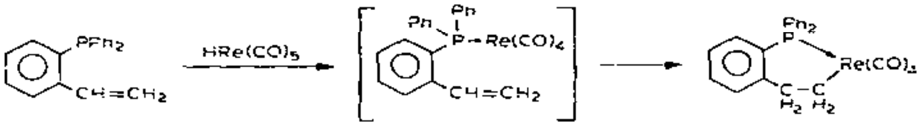
(58)

Palladium compounds such as $Pd(PhCN)_2$, $PdCl_2(COD)$ and Na_2PdCl_4 also gave cyclometalated products similar to **115** [127].

Other aliphatic four-membered ring compounds were reported using butylphosphine [130], isopropylphosphine [131], ethylphosphine [132], etc. [133].

D. SIX-MEMBERED RING COMPOUNDS

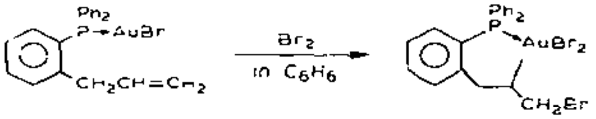
A few six-membered (intramolecular-coordination rings containing a phosphorus donor ligand) have been reported. In the reaction of *o*-styryldiphenylphosphine with metal compounds, manganese carbonyl, as shown in eqn. (27), gave predominantly a five-membered ring **56** by Markownikoff addition described in Section B, but rhenium carbonyl gave the six-membered ring **117** via intermediate **116** by anti-Markownikoff addition [35].



116 117 (59)

Bennett and Watt [35] presumed the reason for the difference between these two reactions might be related to the fact that $HRe(CO)_5$ is a weaker acid than $HMn(CO)_5$ [134], so that addition in the sense $H^+—M^-$ will be favoured for the lighter element.

The (*o*-allylphenyl)diphenylphosphine gold complex reacts with bromine to give the cyclometalated complex **118** having a six-membered ring [40], whose structure was determined by a single crystal X-ray study [40].

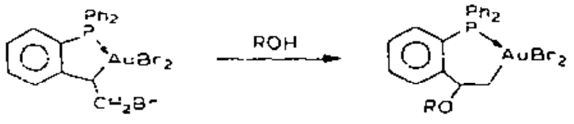


118 (60)

118 contains a planar-coordinated gold atom, attached to the *β*-carbon atom of the side chain to give a six-membered ring having a twist-boat conformation.

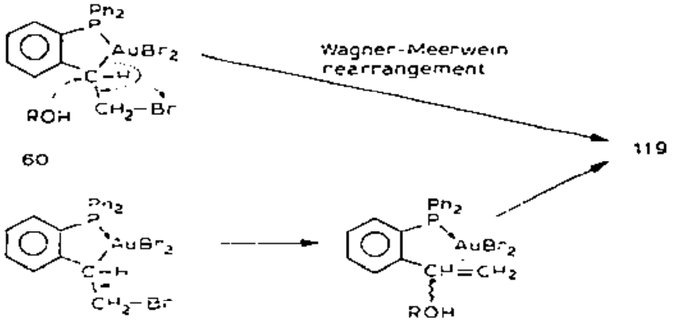
The complex between platinum bromide and (*o*-allylphenyl)diphenylphosphine also gave upon reaction with bromine [41] a six-coordinate bromide-bridge compound having the same six-membered ring as **118**.

The five-membered ring compound **60**, described in eqn. (29), reacted with alcohol or water to give the six-membered ring compound **119** [135].



60 119 R H, Me, Et (61)

Bennett and co-workers [135] presumed that the ring expansion accompanying nucleophilic substitution of Br by alkoxy or hydroxy groups bears an obvious resemblance to the Wagner-Meerwein rearrangements occurring in ring expansions of cycloalkanecarbinyl systems [136]. A similar mechanism involving a Wagner-Meerwein shift of the metal atom could be operative in the present case. An alternative possibility [137] involves initial *cis* elimination of $AuBr_3$ followed by nucleophilic attack on the resulting coordinated double bond.

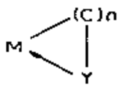


Scheme II

Other six-membered ring compounds include the compound [138] produced from π-coordination compounds, etc. [139].

E. UNSATURATED COMPOUNDS

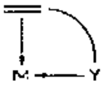
Organometallic intramolecular-coordination compounds are defined in formula **120**, and are classified into two groups, σ-coordination and π-coordination with respect to Y in **120**.



120

121

122

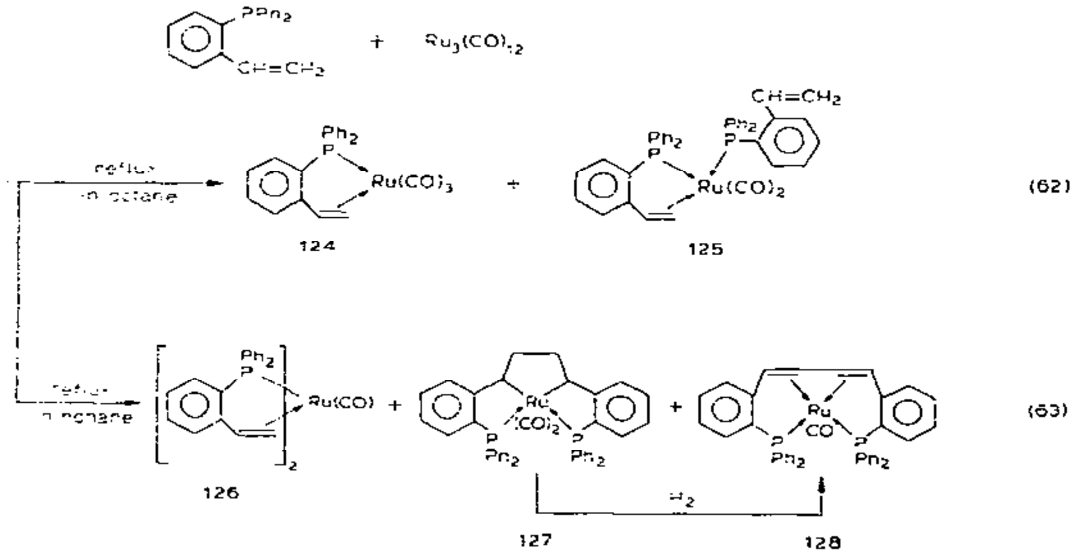


123

M metal
Y coordinating atom or group
n ≥1

The π-coordination compounds are predominantly compounds of the types **121** and **122**, in which the M—Y bond is a π-bond and the M—C bond is a σ-bond (**121**) or a π-bond (**122**). However, most of the σ-coordination compounds have a σ M—C bond and very few have a π M—C bond, shown as **123**. A few reports concerning the latter compounds were reported in a review [1—7,140] on organometallic intramolecular-coordination compounds. There are many reports concerning the latter compounds amongst intramolecular-coordination compounds containing a phosphorus donor ligand.

In the reaction between *o*-styryldiphenylphosphine and a metal complex as described in eqns. (27—29, 31), the five-membered ring compounds can be formed by cyclometalation when addition species such as halogen and hydrogen are in the reaction system. But, when there is no addition species, the vinyl bond may form a π-coordination bond to give compounds with a ring structure which could be defined as a 5.5-membered ring compound, e.g. compounds **124**—**126**, **128** [43].

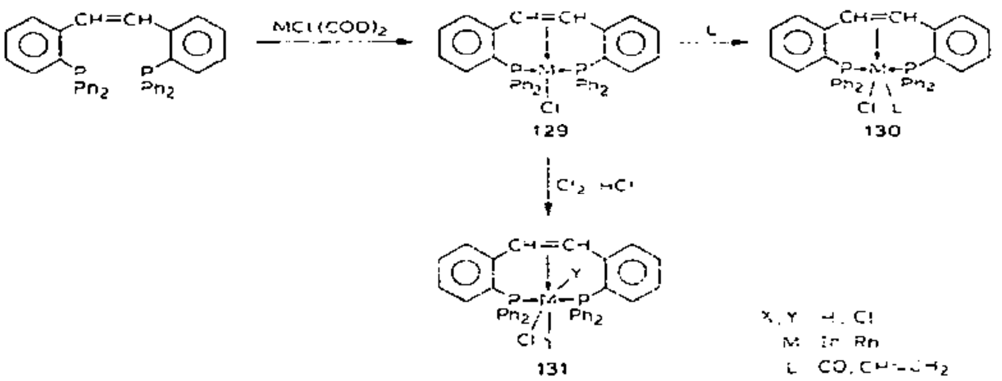


In eqns. (62) and (63), reaction at a higher temperature gave the decarbonylation product (**126**) of **125**, and dimerization products (**127**, **128**) of *o*-styryldiphenylphosphine [43].

Many cyclometalated π-complexes having a 5.5-membered ring such as **124**—**126** were reported containing Fe [38,43], Pt [141,142], Cr [143,144], Mo [143,144] and W [143,144] besides Ru [145] and Rh [146]. X-ray diffraction studies (Fe [38] and Pt [141]) have been reported.

When the reaction of *o*-styryldiphenylphosphine with metal compounds is carried out in a solvent such as methoxyethanol without the presence of strong addition species such as halogen or metal hydride, five-membered rings are obtained. In addition another compound is obtained, shown in **67** and **69** [48] having a five-membered ring together with a cyclometalated π-bond in the same compound (described in Section B.).

Bis-(*o*-diphenylphosphino)stilbene, as shown in eqn. (64), reacted with metal compounds to give tridentate **129** having a π-bond [51], and the four-coordinate compound **129** gave a five- (**130**) or six-coordinate compound (**131**) by reaction with CO, $CH_2{=}CH_2$, Cl_2, HCl, etc. [147].

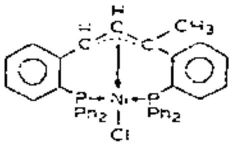


(54)

The structure of **129** was determined by X-ray structure analysis; the stereochemistry about the metal atom is essentially square-planar, and the Rh—C distances between metal and olefinic carbons are equal within experimental error (2.117, 2.110 Å).

When tolylphosphine reacts with a rhodium halide for a long time (eqn. (20)), the rhodium compound similar to **129** is obtained via intermediates **36** and **37**, by formation of stilbene dimerized tolylphosphine [22].

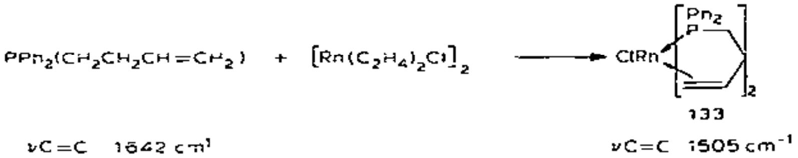
The reaction of *o*-styryldiphenylphosphine and hydrated rhodium(III) chloride in 2-methoxyethanol gave bis-1,3-[*o*-diphenylphosphino)phenyl]-*trans*-1-butene, which is the tridentate rhodium π-complex similar to **129** [148]. But, the reaction [55] of 1,3-bis[(*o*-diphenylphosphino)phenyl]-*trans*-1-butene and $NiCl_2(MeOCH_2CH_2OMe)$ gave the η^3-allyl tridentate complex **132**. Reaction with rhodium(III) chloride instead of the nickel compound also gave the similar η^3-allyl rhodium compound to **132**. The overall stereochemistry of this rhodium dichloride complex is found to be essentially octahedral about the central Rh^{III} atom [148a].



132

Other tridentate π-complexes are produced by the insertion of acetylene compounds [89,116] with the four-membered ring compound obtained by orthometalation of triphenylphosphine, e.g. as described in eqn. (55).

Alkenylphosphines [149—152] such as $PPh_2(CH_2CH_2CH{=}CH_2)$ react with metal complexes (e.g. $[Rh(C_2H_4)_2Cl]_2$, $Ir_2Cl_2(COT)_4$ and $Rh_2Cl_2(COD)_2$) to give olefin-π-complexes such as **133**, which have a 5.5 membered ring. The free olefin (ν C=C) of the starting phosphine was observed at ca. 1640 cm^{-1}, but lies at 1480—1540 cm^{-1} when coordinated.



(65)

The structure of 133 was determined by three-dimensional X-ray diffractometer techniques [149]. The coordination around the Rh(I) atom is best described as trigonal bipyramidal with one phosphorus and the midpoints of the two olefinic groups forming the equatorial plane, which lies 0.13 Å toward the Cl atom from Rh(I).

Other π-complexes containing alkenylphosphine [153—156] similar to 133, cyclobutadienyl [157], cyclopentadienyl [158,159], η^6-arene chelate compound [44], etc. [41,76,160,161], are reported.

F. MISCELLANEOUS COMPOUNDS

A few three-membered ring compounds [162—165] containing a phosphorus donor ligand have been reported. The reaction between 1-lithium 2-phenyl-1,2-dicarbaclosododecaborane (12) and *trans*-dichloro-bis(tri-n-propylphosphine)platinum(II) gave 1-[(P(n-Pr)$_3$$\underline{\text{Pt}^{II}(\text{P(n-Pr)}_2\text{C}}HCH_2CH_3$)]-2-C$_6H_5$-1,2-($\sigma$-B$_{10}C_2H_{10}$) 134, whose structure was determined by an X-ray diffraction study [162]. The platinum and the four-coordinate atoms are coplanar, and the carbon and phosphorus atoms of the three-membered ring are nearly equidistant from Pt(Pt—P = 2.20 Å, Pt—C = 2.17 Å).

The P—C bond of the three membered ring is presumed to have a significant amount of double-bond character because the P—C distance of 1.76 Å is shorter than other P—C distances which range from 1.82 to 1.89 Å [162].

G. CONCLUDING REMARKS

Organometallic intramolecular-coordination compounds containing a phosphorus donor ligand such as benzyl, tolyl, benzoyl and alicyclic compound are prone to form five-membered rings.

The stability of the ring decreases in the order five- > six- > four-membered ring [71], hence, very few four-membered ring compounds containing a nitrogen donor ligand are reported [166—168]; however, many four-membered ring compounds containing a phosphorus donor ligand were reported. This difference is presumed to be due to *d* orbital participation by phosphorus compared with nitrogen which has only *s* and *p* orbitals.

Organometallic intramolecular-coordination compounds containing a phosphorus donor ligand can easily form a stable π-bond at the M—C bond. Many of these π-complexes were reported to form a 5.5-membered ring structure.

The orthometalation of phosphines is much less reactive than that of amines [7c]. Completion of orthometalation of the phosphine usually requires heating the intermediate for a long time because the intermediate is very stable [8]. The difference in reactivity is presumed to be due to electronic differences [102d] between the two ligand atoms coordinated to metal at the first step of orthometalation.

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