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Chemistry of 2-(diphenylphosphino)pyridine

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Abstract

The chemistry of 2-(diphenylphosphino)pyridine is discussed, including the preparation, structure, reactivity and catalytic behavior of this short-bite ligand in mono- or binuclear and cluster complexes.

Keywords: 2-(Diphenylphosphine)pyridine; Mononuclear cluster complexes; Binuclear cluster complexes

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List of abbreviations

COD	1,5-cyclooctadiene
dba	dibenzylideneacetone
dpmMe	1,1-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
form	*N,N'*-di-*p*-tolyformamidinate
2-Mepy	e-methylpyridine
mor	morpholine
pip	piperidine
PPDMe	3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine
[PPN]CN	bis(triphenylphosphoranylidene)ammonium nitrile
TBAC	tetra-*n*-butylammonium chloride
TBAH	tetra-*n*-butylammonium hexafluorophosphate
TBAN	tetra-*n*-butylammonium nitrate

1. Introduction

2-(Diphenylphosphino)pyridine (Ph_2Ppy) is an unsymmetrical bidentate ligand with a nitrogen donor atom and a phosphorus atom that can connect two identical or different metal centers [1]. It is also a rigid short-bite ligand because of the presence of the pyridyl ring, so it has small flexibility and can be used to stabilize binuclear complexes, especially heterobinuclear ones, by forming a metal–metal bond and acting as a bridging ligand [2]. The synthesis and reactivity of homo- and heterobinuclear complexes with bridging phosphine ligands have assumed considerable interest because of the novel structural and reactive features of these complexes, and their potential as catalysts [1]. In principle, in a heterobimetallic complex each metal center could undergo the reactions observed in the mononuclear compounds; in addition, when two metal atoms are held in close proximity by bridging ligands, novel modes of reactivity can be observed [3].

As well as working as a bridging ligand, Ph_2Ppy can also act as a monodentate ligand or as a chelating ligand.

Balch and co-workers initiated work on the chemistry of Ph_2Ppy in the early 1980s, and have made great progress in studying the synthesis, structure and reactivity of Ph_2Ppy-containing complexes.

Cotton and co-workers have used the Ph_2Ppy ligand to connect homobinuclear complexes containing a metal–metal multiple bond. Recently, Faraone and co-workers have reported synthesis of mono-bridging Ph_2Ppy binuclear complexes, which have some catalytic potential owing to small steric hindrance. We have found that the complex *trans*-$Fe(Ph_2Ppy)_2(CO)_3$ can act as a neutral organometallic tridentate ligand and react with metal compounds to yield a series of homo- and heterobinuclear complexes.

The present work reviews the synthesis, structure, reactivity and catalytic behavior of Ph_2Ppy complexes.

2. Complexes with monodentate Ph_2Ppy

The unsymmetrical ligand Ph_2Ppy can form monodentate complexes. The presence of two different donor atoms, nitrogen and phosphorus, creates two possibilities for coordination. However, the nitrogen atom is a stronger σ-donor and weaker π-acceptor than the phosphorus atom, so when a monodentate complex is prepared Ph_2Ppy usually binds via the phosphorus atom; no N monodentate complexes have yet been reported.

2.1. Preparation

Ph_2Ppy is similar to PPh_3 and should be capable of substitution for PPh_3 in any of the numerous complexes of the latter ligand [4]. So the synthesis of Ph_2Ppy monodentate P-bonded complexes resemble that of the PPh_3 analogues, which are usually formed from metal carbonyls, metal olefins, metal halides and several organometallic derivatives.

2.1.1. Substitution

Some ligands such as carbonyl, RNC, PhCN and olefin can be displaced by Ph_2Ppy, and the corresponding monodentate P-bonded complexes are obtained. The complexes shown in Table 1 are all prepared by substitution of the ligand L by Ph_2Ppy.

Similarly, the phosphine and amine ligands are also substituted by Ph_2Ppy (Eqs. (2.1), (2.2)) [17,18].

$$\mathrm{RhH(CO)(Ph_3P)_3 + Ph_2Ppy \rightarrow RhH(CO)(Ph_2Ppy)_3} \tag{2.1}$$

$$\mathrm{Ir(CO)_2Cl(}p\mathrm{\text{-}NH_2C_6H_4CH_3) + Ph_2Ppy \rightarrow Ir(CO)Cl(Ph_2Ppy)_2} \tag{2.2}$$

In short, ligand substitution is the most general method of preparing Ph_2Ppy P-bonded complexes.

2.1.2. Oxygen atom transfer

We have used the oxygen atom transfer reaction of $M(CO)_6$ ($M = Cr$, Mo, W) with TMNO (Me_3NO) in the presence of the Ph_2Ppy ligand in different solvents selectively to give Ph_2Ppy mono- or disubstituted products (Eq. (2.3)) [19].

The IR spectra suggest that the disubstituted complexes $M(CO)_4(Ph_2Ppy)_2$ ($M =$ Mo, W) possess cis structure, but that when $M = Cr$ a trans configuration is formed. It has been found that the best solvent is ether/acetonitrile (24 : 1) to give monosubstituted products. When $M = Cr$, a small quantity of trans disubstituted product is also formed.

Table 1
Ligand substitution reactions of Ph_2Ppy

Starting material	Product	Ref.
$M(CO)_x$ ($M = Fe$, Cr, Mo)	$M(CO)_{x-1}(Ph_2Ppy)$ ($M = Fe$, Cr, Mo)	[5]
$Re_2(CO)_{10}$	$Re_2(CO)_8(Ph_2Ppy)_2$	[5]
$Rh(chel)(CO)_2$	$Rh(chel)(CO)(Ph_2Ppy)$	[6]
(chel = acetylactonate or 8-hydroxyquinolinate)		
$(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)I_2$	$(\eta^5\text{-}C_5H_4CO_2CH_3)Co(Ph_2Ppy)I_2$	[7]
$(\eta^5\text{-}Cp)Rh(CO)_2$	$(\eta^5\text{-}Cp)Rh(CO)(Ph_2Ppy)$	[8]
$Fe(NO)_2(CO)_2$	$Fe(NO)_2(Ph_2Ppy)_2$	[9]
$AuCl(CO)$	$AuCl(Ph_2Ppy)$	[10]
$PdCl_2({}^tBuNC)_2$	*cis*-$PdCl_2({}^tBuNC)(Ph_2Ppy)$	[11]
$PdCl_2({}^tBuNC)_2$	*cis*- or *trans*-$PdCl_2(Ph_2Ppy)_2$	[12]
$[Pd_2(CNMe)_6]^{2+}$	$[Pd_2(CNMe)_4(Ph_2Ppy)_2]^{2+}$	[12]
$[Rh(CNMe)_4]^+$	$[Rh(CNMe)_2(Ph_2Ppy)_2]^+$	[13]
cis-$[Cr({}^tBuNC)_5(NO)]$	*cis*-$[Cr({}^tBuNC)_4(NO)(Ph_2Ppy)]$	[14]
$M(COD)X_2$ ($M = Pt$, Pd; $X = Cl$, I)	$M(Ph_2Ppy)_2X_2$ ($M = Pt$, Pd; $X = Cl$, I)	[1,15,16]
$PtMeX(COD)$ ($X = Me$, Cl, I)	$PtMeX(Ph_2Ppy)_2X_2$ ($X = Me$, Cl, I)	[16]

$$\mathrm{M\,(CO)_6 + Ph_2Ppy + Me_3NO} \begin{cases} \xrightarrow{\text{acetonitrile}} \mathrm{M\,(CO)_4\,(Ph_2Ppy)_2} \\ \xrightarrow[\text{ethyl ether/acetonitrile}]{} \mathrm{M\,(CO)_5\,(Ph_2Ppy)} \end{cases} \tag{2.3}$$

M=Cr, Mo, W

2.1.3. *Decomposition*

For some halide-bridged binuclear complexes, the halide bridges can be broken by Ph_2Ppy to give Ph_2Ppy P-bonded mononuclear products. Some reactions are shown in Eqs. (2.4)–(2.8) [1,4,20–24].

$$Pt_2Cl_6^{2-} + Ph_2Ppy \rightarrow cis\text{-}PtCl_2(Ph_2Ppy)_2 \tag{2.4}$$

$$\{Pd(\eta^3\text{-}CH_2CCH_3CH_2)Cl\}_2 + Ph_2Ppy \rightarrow Pd(\eta^3\text{-}CH_2CCH_3CH_2)(Ph_2Ppy)Cl \tag{2.5}$$

$$\{(1{,}5\text{-}COD)Rh(\mu\text{-}Cl)\}_2 + Ph_2Ppy \rightarrow (1{,}5\text{-}COD)Rh(Ph_2Ppy)Cl \tag{2.6}$$

$$\{Co(NO)_2I\}_2 + Ph_2Ppy \rightarrow ICo(NO)_2 \leftarrow PPh_2py \tag{2.7}$$

$$\{Rh(CO)_2(\mu\text{-}Cl)\}_2 + Ph_2Ppy \rightarrow Rh(CO)Cl(Ph_2Ppy)_2 \tag{2.8}$$

2.1.4. *Other methods*

Under mild conditions, reaction of hydrated MCl_2 (M = Co, Ni) and Ph_2Ppy with CO in the presence of zine powder yields $MCl_2(Ph_2Ppy)_2$ [25,26].

Ang and co-workers have obtained similar complexes from the reaction of cobalt or nickel salts with Ph_2Ppy in absolute solvents [27]. Inoguchi et al. have prepared the low polymers $[MCl \leftarrow PPh_2py]_n$ by the reaction of AgCl or CuCl with Ph_2Ppy in benzene. The configuration of $[AgCl \leftarrow PPh_2py]_n$ is a chlorobridged tetramer [28]. The dimer Ag_2 $(\mu\text{-}Ph_2Ppy)(Ph_2Ppy)_2(\mu\text{-}Cl)_2$ has also been obtained by the similar reaction in ethanol [29].

Alcock's study showed that $HAuCl_4$ could be reduced by Ph_2Ppy to give the complex $AuCl(Ph_2Ppy)$, which was also produced from AuCl(CO) by a substitution reaction [29].

Through a dismutation reaction, Roustan's group has obtained a Ph_2Ppy P-bonded complex accompanied by an iron chelate complex with Ph_2Ppy oxide (Eq. (2.9)) [9].

$$[Fe(NO)_2(THF)_n][BF_4] + Ph_2Ppy$$
$$\rightarrow Fe(NO)_2(Ph_2Ppy)_2 + [Fe(\eta\text{-}Ph_2PpyO)_3](BF_4)_2 \tag{2.9}$$

2.2. *Structure*

A number of molecular structures of P-bonded complexes have been determined, including $AuCl(Ph_2Ppy)$ [29], $Ag_2(\mu\text{-}Ph_2Ppy)(Ph_2Ppy)_2(\mu\text{-}Cl)_2$ [29], and the compound with chelating ring, $[Pt(Ph_2Ppy)_2X]^+$ (X = Me, Cl) [1,16,23].

^{31}P NMR spectra have shown that some square planar complexes with two Ph_2Ppy P-dentated ligands in solution possess two kinds of isomers, cis and trans. For example, $PtMeX(Ph_2Ppy)_2$ [16] is in cis configuration when X = Me, and adapts the trans configuration when X = Cl or I. Both cis and trans isomers exist for the complex $PdCl_2(Ph_2Ppy)_2$ [11].

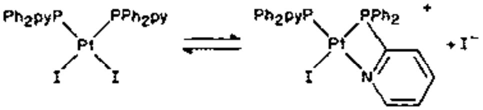
2.3. Reaction

The Ph_2Ppy P-dentated mononuclear complexes usually display good reactivities because of the presence of the uncoordinated nitrogen atom. On the one hand, the Ph_2Ppy ligand can act as a chelate ligand to give the four-membered chelate complexes. On the other hand, when an additional metal atom is present, further coordination through the nitrogen atom offers a route to form homo- and heterobinuclear complexes. This is one of the most important reactions of the Ph_2Ppy P-dentated mononuclear complexes. So the Ph_2Ppy P-dentated mononuclear complexes commonly acts as precursors in the synthesis of the bridging binuclear complexes.

2.3.1. Chelation

When no additional metal atom is present, a chelate four-membered ring may sometimes be formed because of the presence of the uncoordinated nitrogen atoms, although the strains are great in these Ph_2Ppy chelate complexes.

Balch and co-workers have observed rapid exchange between the cis and the chelated isomers in dichloromethane solution of $Pt(Ph_2Ppy)_2I_2$ at various temperatures (Eq. (2.10)), through the $^{31}P\{^1H\}$ NMR spectra.

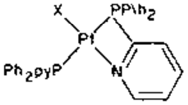


(2.10)

Low temperature favors ionic dissociation of the iodide ligand. However, the trans isomer is not involved in the process and the trans cation, **2.1**, is absent. This can be attributed to the operation of the trans effect, which selectively labilizes halo ligands trans to phosphine. The presence of halide abstractors favors the formation of chelate rings [15]. Some reactions are shown in Table 2.

Table 2
Some chelating reactions

Starting material $M(Ph_2Ppy)_2XX'$	Halide abstractor	Product *cis*-$[M(Ph_2Ppy)(\eta^2\text{-}Ph_2Ppy)X]Y$	Ref.
M = Pt, X = Me, X′ = Cl	NaY (Y = BPh_4, BF_4)	X = Me, Y = BPh_4, BF_4	[16]
M = Pt, X = X′ = Cl	$[Rh(CO)_2(\mu\text{-}Cl)]_2$	X = Cl, Y = $Rh(CO)_2Cl_2^-$	[1]
M = Pt, X = X′ = I	NH_4PF_6	X = I, Y = PF_6	[15]
M = Pd, X = X′ = Cl	$NH_4PF_6/AgNO_3$	X = Cl, Y = PF_6	[13]



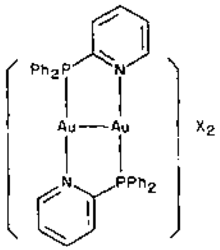
2.1

The Ph_2Ppy P-dentated complexes containing only one Ph_2Ppy ligand can also form a chelate ring (Eq. (2.11)) [11].

$$\mathrm{Rh(1{,}5\text{-}COD)(Ph_2Ppy)Cl + AgX \rightarrow [Rh(1{,}5\text{-}COD)(\eta^2\text{-}Ph_2Ppy)]^+X^-}$$

$$X = ClO_4^-,\ PF_6^- \tag{2.11}$$

Inoguchi et al. have reported that in the presence of AgX ($X = BF_4^-, PF_6^-$), $AuCl(Ph_2Ppy)$ produces Ph_2Ppy-bridged binuclear products, **2.2**, instead of chelate complexes [21].

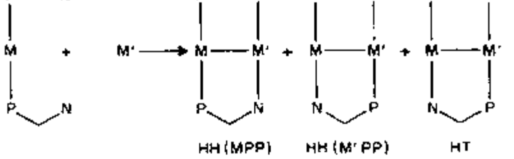


2.2

2.3.2. *Oxidative addition*

This is the most important reaction of the Ph_2Ppy P-dentated complexes. The uncoordinated nitrogen atom captures the additional metal atoms M′ to give binuclear complexes, and a metal–metal bond is formed because of the rigidity of the short-bite ligand Ph_2Ppy doesn't allow a large metal–metal distance. So Ph_2Ppy is a convenient building block for the construction of binuclear transition metal complexes [13].

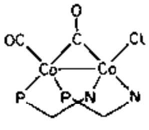
The general reaction is shown in Eq. (2.12) (HH, head-to-head configuration; HT, heat-to-tail).



(2.12)

2.3.3. *Reductive carbonylation*

This method, previously developed by us, can be used in Ph_2Ppy chemistry. Under mild conditions, the reactions of $M(Ph_2Ppy)_2Cl_2$ (M = Co, Ni) with CO in the presence of zinc powder gave **2.3**, **2.4** [25] and **2.5** [26], respectively. **2.3** and **2.4** are two bicobalt carbonyl complexes with mixed valence.



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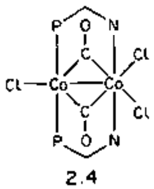
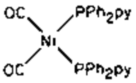


2.4



2.5

2.3.4. *Other reactions*

Faraone and co-workers have found that in the presence of PPh_3 the reaction of CO with $Rh(COD)(Ph_2Ppy)Cl$ gives *trans*-$Rh(Ph_2Ppy)(PPh_3)(CO)Cl$ by the replacement of COD with CO and PPh_3. However, when only CO was bubbled into the solution of $Rh(COD)(Ph_2Ppy)Cl$ in CH_2Cl_2, a carbonyl complex $Rh_2Cl_3(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)$ was isolated. Presumably the reactive involved the formation of the intermediate $[Rh(CO)_2(Ph_2Ppy)Cl]$ by the displacement of COD with CO from $Rh(COD)(Ph_2Ppy)Cl$. An intermolecular nucleophilic attack of the uncoordinated pyridine nitrogen atom on the 16-electron rhodium(I) center and loss of CO could be the subsequent reaction steps [11].

A stream of chlorine was bubbled into a solution of *trans*-$Ru(CO)_3(Ph_2Ppy)_2$ in CH_2Cl_2 at room temperature to produce *trans*-$Ru(CO)_2Cl_2(Ph_2Ppy)_2$ [30]. The IR spectra indicated complete transformation of the starting material into the ionic species $[Ru(CO)_3Cl(Ph_2Ppy)_2]^+Cl^-$, which then decarbonylated to give $Ru(CO)_2Cl_2(Ph_2Ppy)_2$.

In the presence of the proton acids, the uncoordinated pyridine nitrogen atom can be protonated (Eq. (2.13)) [11].

$$(1,5\text{-}COD)Rh(Ph_2Ppy)Cl + HPF_6 \rightarrow [(1,5\text{-}COD)Rh(Ph_2PpyH)Cl]PF_6 \tag{2.13}$$

The reaction of *trans*-$PtMeCl(Ph_2Ppy)_2$ with $SnCl_2$ generated a Pt—Sn bond [16]. A bromo analogue, $Pt(Ph_2Ppy)_2Br_2$ has been obtained from $Pt(Ph_2Ppy)_2Cl_2$ by metathesis with sodium bromide [1]. Autoxidation of $(Ph_2Ppy)_2CoCl_2$ may induce the formation of $(Ph_2P(O)py)_2CoCl_2$ when the former is crystallized from ethanol in air [31].

A copper(II) complex has been obtained by a metal exchange reaction as an unexpected product (Eq. (2.14)) [32].

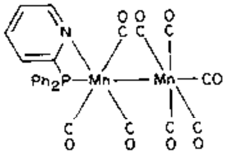
$$NiCl_2(Ph_2Ppy)_2 + CuC{\equiv}CPh \rightarrow [Cu(Ph_2Ppy)Cl(\mu\text{-}Cl)]_2 \tag{2.14}$$

3. Complexes with chelating Ph_2Ppy

3.1. *Synthesis*

Complexes with chelate Ph_2Ppy are commonly synthesized from the reaction of the Ph_2Ppy P-bonded complexes with halide abstractors (see Section 3.3). In addition, the addition of Ph_2Ppy can generate uranium and rhodium complexes containing chelate Ph_2Ppy. For example, the complexes $U(BH_4)_3(\eta^2\text{-}Ph_2Ppy)_2$, $UCl_3(\eta^5\text{-}Cp)(\eta^2\text{-}Ph_2Ppy)$ [33] and $[(1,5\text{-}COD)Rh(\eta^2\text{-}Ph_2Ppy)]X$ ($X = ClO_4$, PF_6) [11] have been formed respectively through the addition of $U(BH_4)_3(THF)_x$, $(\eta^5\text{-}Cp)UCl_3$, and $[Rh(1,5\text{-}COD)(solv)_2]X$ with Ph_2Ppy.

The reaction of $Pd(PhCN)_2Cl_2$ and $Pd(1,5\text{-}COD)Cl_2$ with equimolar Ph_2Ppy produced the complex with chelate ring $Pd(\eta^2\text{-}Ph_2Ppy)Cl_2$ [11], instead of the Ph_2Ppy P-dentated complexes. The reaction of $Mn_2(CO)_{10}$ with Ph_2Ppy gave a Ph_2Ppy chelate manganese carbonyl derivative, **3.1** [28]. In particular, when a saturated solution of chlorine in CH_2Cl_2 was added into a CH_2Cl_2 solution containing the cluster complex $[Ru(Ph_2Ppy)(CO)_3]_3$, a mononuclear complex $Ru(\eta^2\text{-}Ph_2Ppy)(CO)_2Cl_2$ was formed [20].


3.1

3.2. Structure

The structure of a number of Ph_2Ppy chelate complexes have been determined for the examples $Ru(\eta^2\text{-}Ph_2Ppy)(CO)Cl_2$ (**3.2**), $[Pt(\eta^2\text{-}Ph_2Ppy)(Ph_2Ppy)Cl]^+$ (**3.3**) and $[Pt(\eta^2\text{-}Ph_2Ppy)Ph_2Ppy)Me]^+$ (3.4) [20,1,16].

Because of the presence of the four-membered chelate ring, the phosphorus atom does not occupy the expected coordination site. Rather, it is pulled off-axis toward the pyridine nitrogen. Thus the angles at the central metal atoms between cis ligands deviate from the ideal value of 90°. The major deviation comes from P—M—N which is compressed to nearly 70°. The other three angles are opened up, so that the P—M—L angle (L is trans to the nitrogen atom) is over 100° and the other two angles are near to the ideal value of 90°.

Within the chelate ring there is also significant angular compression. All of the angles are compressed. Both the C—N—M and N—C—P angles are reduced from the ideal value of 120°, and the C—P—M angle is reduced below the expected value of 109.5°. Furthermore, the intrachelate P—C distance is longer than the extrachelate P—C distances (Table 3).

In the complex **3.4**, the Pt—P(1) distance is much longer than that of Pt—P(2). The longer bond is expected because of the trans influence of the methyl group.

There is also angular strain within the complex with two chelate rings, $U(BH_4)_3(\eta^2\text{-}Ph_2Ppy)_2$. The X-ray crystal structure of $U(BH_4)_3(\eta^2\text{-}Ph_2Ppy)_2$ shows N—U—P = 52.8°, B—U—N = 90.1°, P—U—P′ = 74.3° and N—U—N′ = 179.8°. These distortions arise from the presence of the tridentate equatorial BH_4 group [33].

Because of the high degree of angular distortion within the chelate rings, it is not

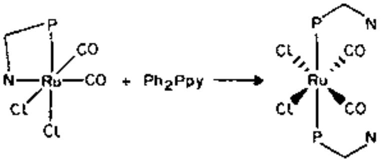
Table 3
Selected bond distances (Å) for Complexes **3.2**–**3.4**

Complex	Intrachelate P−C distance	P−C(Ph) distance	Intrachelate M−P distance	Extrachelate M−P distance	Ref.
3.2	1.859	1.812, 1.813	2.322	2.232	[20]
3.3	1.84	1.82, 1.82	2.223		[1]
3.4	1.81	1.78, 1.82	2.325	2.207	[16]

surprising that Ph_2Ppy has been found to act as a monodentate or bridging ligand more frequently than as a chelating ligand [20].

3.3. Reaction

Because of ring strain, Ph_2Ppy chelate complexes are unstable. It is easy to open the ring, and the nitrogen atom which is a weaker π-acceptor is expected to be more readily displaced from a low-valent metal than the phosphorus end of the bidentate ligand [20]. In this way a Ph_2Ppy P-dentated complex can be obtained (Eq. (3.1)). When an additional metal atom is present, a bridging binuclear complex may be formed (Eq. (3.2)) [11].



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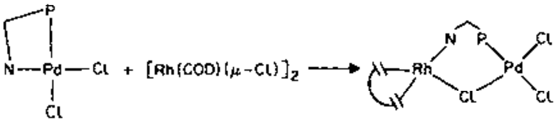


(3.2)

4. Complexes with bridging Ph_2Ppy

Bridged binuclear complexes using Ph_2Ppy to hold two metal atoms in close proximity have received considerable attention in recent years. Ph_2Ppy has a nitrogen atom positioned so that it can be bound to a second metal as a bridging ligand.

4.1. Complexes without metal–metal bonds

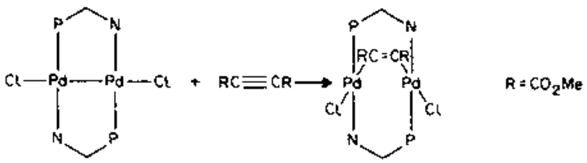
In this class there are compounds with one, two or three bridged Ph_2Ppy ligands. Owing to the rigidity of the pyridyl ring, the ligand may have difficulty in accommodating longer metal–metal (M−M) separations. Thus the kind of complex without a M—M bond is rare, and the steric factors usually confine the formation of the M—M bonds.

We have commented previously that Alcock et al. have synthesized $Ag_2(\mu\text{-}Ph_2Ppy)(Ph_2Ppy)_2(\mu\text{-}Cl)_2$, in which the Ag—Ag distance is 3.074 Å. The long Ag—Ag distance is caused by the presence of two bridging chloride atoms, producing weak interaction; moreover, the coordination of N with Ag is weak (Ag—N = 2.451 Å, Ag—P = 2.432 Å, Ag—N ≃ 2.04 Å), but the distance is shorter than the sum of the van der Waals radii [29].

Similarly, in the complex $Ag_2(\mu\text{-}Ph_2Ppy)_2(NO_3)_2(HT)$, the Ag—Ag distance (3.146 Å) is again indicative of the absence of a Ag—Ag bond [34].

Recently, Faraone and co-workers have found, during a study of PdRh heterobinuclear complexes containing only one Ph_2Ppy bridge, that the complex $(1,5\text{-}COD)RhPd(\mu\text{-}Cl)(\mu\text{-}Ph_2Ppy)Cl_2$ has no M—M bond. In this molecule, the Pd—Rh separation of 3.210 Å is too long to be considered indicative of a metal interaction and the complex is strongly tensioned as the Ph_2Ppy ligand is obliged to span the two metals separated by a long distance (the N—P separation is 2.72 Å) [11].

Mague has reported that $[Pd_2Cl_2(Ph_2Ppy)_2]$ reacts readily with electrophilic acetylenes to form a product in which the acetylenes appear to be bound as a dimetallated olefin and the Pd—Pd bond disappears (Eq. (4.1)) [18].



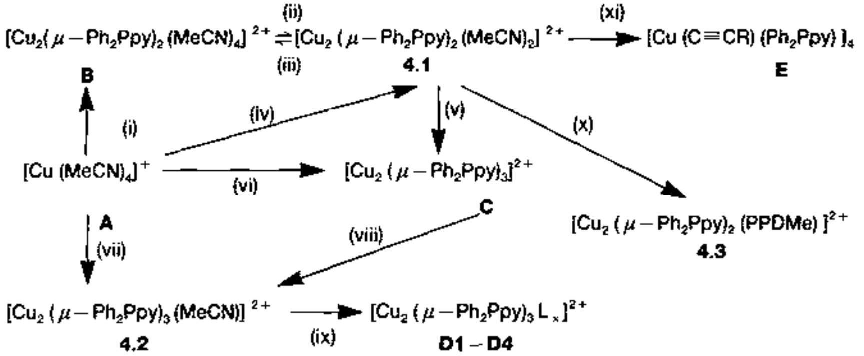
(4.1)

Binuclear copper(I) and copper(II) complexes form a significant group of derivatives in the coordination chemistry of copper which are currently receiving special attention, mainly because of studies related to the reactivity of dioxygen, not only in biological systems but also in catalytic oxidation and dioxygen-mediated processes [35,36].

Lastra and co-workers have synthesized the first copper(I) complexes containing Ph_2Ppy bridges and the scarcely known triple-bridged binuclear copper(I) complex (Scheme 1).

In complex **4.1** the two copper atoms are bridged by two Ph_2Ppy molecules in a HT arrangement, resulting in a rare staggered conformation of the eight-membered ring $Cu_2P_2N_2C_2$, whose factor is concerned with the coordination numbers of the central metal atoms, and the size or mode of binding of the other ligands which don't form part of the eight-membered ring. The Cu—Cu distance of 3.584 Å is indicative of no M—M bond [39].

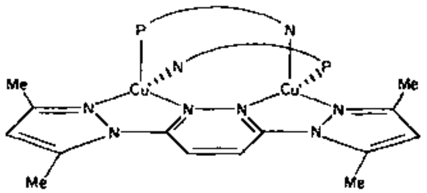
In complex **4.2** the Cu—Cu interaction is weak, or shown by the Cu—Cu separation of 2.721 Å, even though three bulky bridging Ph_2Ppy ligands should produce severe geometric constraints in a binuclear complex to hold the two metals in close proximity [37].



Scheme 1. (i) +Ph_2Ppy (MeCN, r.t.); (ii) −2MeCN (CH_2Cl_2, r.t.); (iii) MeCN solution; (iv) Ph_2Ppy (CH_2Cl_2, r.t.); (v) refluxing $CHCl_3$; (vi) +Ph_2Ppy (excess) (refluxing acetone); (vii) +Ph_2Ppy (excess) (refluxing MeCN); (viii) MeCN solution; (ix) +L, −MeCN ($x = 1$, L = 2-Mepy, **D1**; $x = 2$, L = $P(OMe)_3$, PMe_3, 4-Mepy, **D2–D4**) (CH_2Cl_2, r.t.) [37]; (x) +PPDMe (−MeCN) [35]; (xi) +HC≡CR (R = Ph, ${}^tBu$) (KOH excess) (CH_2Cl_2/MeOH) [38].

The lability of the MeCN ligand in complex **4.2**, as well as the presence of one coordinatively unsaturated copper atom, allows the displacement of the ligands L. When L = 2-MePy, the monosubstituted complex **D1** is the sole product formed, even when 2 molar equivalents of ligand are used. Steric as well as electronic properties of the methyl-substituted pyridine ligand are known to determine tri- or tetra-coordination geometries of copper(I) complexes. When the complex **C** is used as starting material instead of **4.2**, or, alternatively, an excess of ligand is added, a mixture of different derivatives is obtained probably owing to partial substitution of the labile bridging ligand Ph_2Ppy by the entering ligand [37].

The reaction of **4.1** with an equimolar amount of PPDMe gives product **4.3**, in which PPDMe acts as a dichelating tetradentate ligand [35]. The reaction of **4.1** with HC≡CR yields a copper cluster complex, **E** (see Section 5 for details) [38].



4.3

4.2. *Complexes with metal–metal bonds*

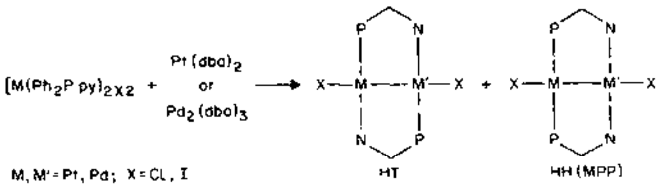
This class of complexes is the most important in Ph_2Ppy chemistry. The two sorts of donor atoms in Ph_2Ppy can stabilize metals in the lower oxidation state [39]. The rigidity of the short-bite Ph_2Ppy ligand forces the formation of the M—M bond when the two donor atoms coordinate with two metal atoms. Thus Ph_2Ppy is effective in stabilizing well defined homo- and heterobinuclear transition metal complexes [2,5]. In particular, one can prepare bridged heterobinuclear transition metal complexes in high yield [1,30]. So the binuclear transition metal complexes of Ph_2Ppy and their reaction chemistry have excited considerable interest in recent times.

4.2.1. *Synthesis*

4.2.1.1. Synthesis of heterobinuclear complexes. The study of heterobinuclear complexes is an important topic in organometallic chemistry. These complexes usually possess particular bonding patterns and may activate a series of small molecules, such as SO_2, CO and alkyne.

4.2.1.1.1. Oxidative addition. Heterobinuclear bridged complexes are usually obtained by conproportionation reactions. The first step leads to the formation of the monosubstituted derivative, with Ph_2Ppy being bonded to the metal by the phosphorus atom. The mononuclear complexes are expected to capture a second metal ion readily by coordination to the pyridine nitrogen. Then, the oxidative addition of the M−X bond to the metal center, a binuclear complex is formed.

Balch and co-workers have synthesized Pt(I) and Pd(I) homo- and heterobinuclear complexes with bridging Ph_2Ppy. These reactions are shown in Eq. (4.2) [12,15,30].



(4.2)

Both HH and HT isomers are obtained from this reaction. The difference in the configuration of the reactants induces different main products.

When M = Pt, if X = Cl the configuration of the main product is HT, but if X = I it is HH. When M = Pd, the main product is the HH isomer. This can be explained inasmuch as *trans*-$Pt(Ph_2Ppy)_2X_2$ reacts more readily than *cis*-$Pt(Ph_2Ppy)_2X_2$ with sources of platinum(0) or palladium(0) and, because of the orientation of the phosphine ligands, yields the HH(PPt) isomer under kinetic control. Thus $Pt(Ph_2Ppy)_2I_2$, with a detectable amount of trans isomer present, preferentially reacts through this isomer to yield the HH(PPt) isomer, but a part of the HH isomer can thermally convert into the HT isomer which is more stable thermodynamically. $Pt(Ph_2Ppy)_2Cl_2$, which in solution contains a negligible amount of trans isomer, is forced to use a different, slower pathway to form the HT isomer [15]. By these processes, $M_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ (HT) (M = Pt, Pd), $Pt_2(\mu\text{-}Ph_2Ppy)_2I_2$ (HH), $PtPd(\mu\text{-}Ph_2Ppy)_2Cl_2$ (HT), $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ (HH) etc. have been isolated.

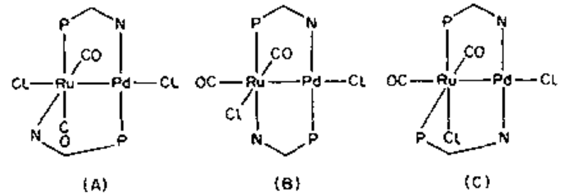
Recently, Suzuki's group have investigated these reactions. They found a dimeric HH isomer initially, which then isomerized to a HT isomer. The monomeric Pd(II) complexes in these dimerization and isomerization reactions reacted more rapidly than did the corresponding Pt(II) complexes. It seems that the dimerization occurs faster for each halo series of the Ph_2Ppy complexes, in the order of $Cl < Br < I$, while the order is reversed in isomerization, $Cl > Br > I$ [40,41].

Similarly, the oxidative addition of $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ with $Pd_2(dba)_3$ produces $PdRu(\mu\text{-}Ph_2Ppy)_2(CO)_2Cl_2$ (**4.4** and **4.5**). However, the reaction of *trans*-$Ru(Ph_2Ppy)_2(CO)_3$ with (1,5-COD)$PdCl_2$ forms the mixed products (Eq. (4.3)) [30].

$$\begin{aligned} &trans\text{-}Ru(Ph_2Ppy)_2(CO)_3 + (1,5\text{-}COD)PdCl_2 \\ &\rightarrow Pd_2(\mu\text{-}Ph_2Ppy)_2Cl_2 + Ru(\eta^2\text{-}Ph_2Ppy)(CO)_2Cl_2 + Ru(Ph_2Ppy)_2(CO)_2Cl_2 \\ &\quad + (\mathbf{4.4}) + (\mathbf{4.5}) \end{aligned} \tag{4.3}$$

The complex $Ru(Ph_2Ppy)_2(CO)_3$ in its lower oxidation states tends to be coordinatively saturated. This would inhibit access to the metal, and hence would slow down the analogous oxidative additions. In comparison with the similar reaction between $Ru(Ph_3P)_2(CO)_3$ and (1,5-COD)$PdCl_2$, it is found that a natural redox process would take effect in the previous reaction.

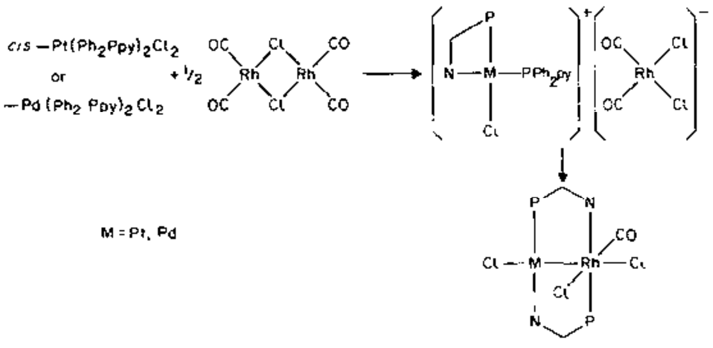
4.4 and **4.5** are isomers. The structure of **4.4** is (A); the structure of **4.5** is limited to (B) or (C), but there are insufficient data available to distinguish between these two possibilities.



Balch and co-workers have studied the synthesis of RhPd binuclear complexes. The reaction of $[Rh(Ph_2Ppy)_2(CNR)_2]X$ ($X = PF_6^-$, BPh_4^-) with $Pd(1,5\text{-}COD)Cl_2$ or $Pd(PhCN)_2Cl_2$ leads to the ionic complexes $[RhPd(\mu\text{-}Ph_2Ppy)_2(CNR)_2Cl_2]X$ [13,15]. However, the configurations are different, the former reaction yielding predominantly the HT species and the latter a mixture of nearly equal amounts of HH and HT isomer.

$^{31}P\{^1H\}$ NMR spectra have shown that the products depend on the leaving groups initially bound to palladium but are essentially independent of the anion (BPh_4^- or PF_6^-) that accompanies the rhodium cation. With a good leaving group on palladium, as is the case with $(PhCN)_2PdCl_2$, the reaction produces a significant quantity of the thermodynamically less stable HH isomer. However, with a chelated diolefin, which is more difficult to displace from palladium, the reaction proceeds to produce the thermodynamically favored HT isomer [13]. The reaction of $[Rh(MeCN)_4][BPh_4]$ with *trans*-$Pd(Ph_2Ppy)_2Cl_2$ yields the thermodynamically stable HT isomer [15].

The oxidative addition of (1,5-COD)$PdCl_2$ with *trans*-$Rh(Ph_2Ppy)_2(CO)Cl$ gives the neutral binuclear complex $RhPd(\mu\text{-}Ph_2Ppy)_2(CO)Cl_3$ (HT) [4,13,15,30]. However, the reaction between (1,5-COD)$PtCl_2$ and *trans*-$Rh(Ph_2Ppy)_2(CO)Cl$ pro-



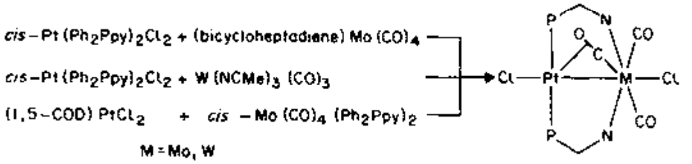
Scheme 2.

duces the homobinuclear complex $Rh_2(\mu\text{-}CO)(\mu\text{-}Ph_2Ppy)_2Cl_2$ (HT) and *cis*-$Pt(Ph_2Ppy)_2Cl_2$ instead of the desired heterobinuclear complex [1,4,23].

The reaction between $[Rh(\mu\text{-}Cl)(CO)_2]_2$ and $M(Ph_2Ppy)_2Cl_2$ (M = Pt, Pd) can yield $RhM(\mu\text{-}Ph_2Ppy)_2(CO)Cl_3$ (HT). Formally, this seems to improve an oxidative addition of the M—Cl bond to Rh(I), but in fact an ion pair mechanism is in action (see Scheme 2).

In this reaction an ion pair is obtained. This may be related to the ability of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ to abstract halide ions from metal complexes [42]. In addition to accomplishing the halide transfer, ionization also begins the process of reorientation of the phosphine ligand, and an isomeric cation with the pyridine nitrogen atom trans to the monodentate phosphine ligand is formed. This exact structure of the ion pair is unlikely to persist in solution. The plane of the chelating portion of the phosphinopyridine ligand along with coulombic and charge-transfer effects may serve to conduct the rhodium-containing anion toward the platinum atom, facilitating the formation of the binuclear compounds, PtRh and PdRh. The reaction to form the RhPt complex has been shown to be faster in benzene than it is in methanol, perhaps because ion pairing in the less polar solvents increases the probability of reaction between the cation and the anion [1,13].

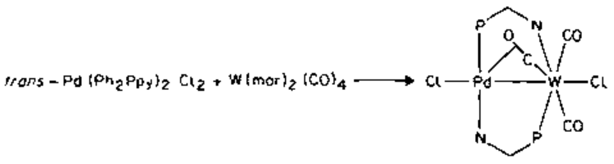
The M—X bonds can also achieve oxidative addition to the central metals of molybdenum(0) or tungsten(0) carbonyl complexes, forming a bridged carbonyl group (Eqs. (4.4)–(4.8)) [43–46].



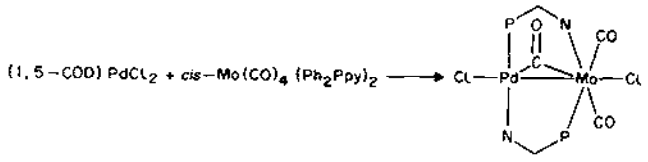
(4.4)–(4.6)

The iodine complex analogous to **4.6** is obtained by the oxidative addition of $Pd_2(dba)_3$ with $MoI_2(Ph_2Ppy)_2(CO)_3$ [46].

4.2.1.1.2. Coordination by organometallic multidentate ligand. Recently we have found that *trans*-$Fe(CO)_3(Ph_2Ppy)_2$ can react with metal halide or pseudohalide derivatives



(4.7)

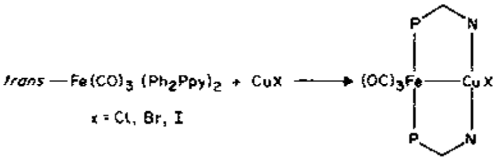


4.6

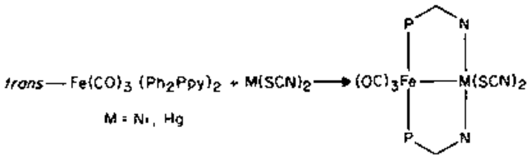
(4.8)

to give FeCu, FeNi, FeHg and FeRh heterobinuclear complexes acting as a neutral organometallic tridentate ligand (Eqs. (4.9)–(4.11)) [47].

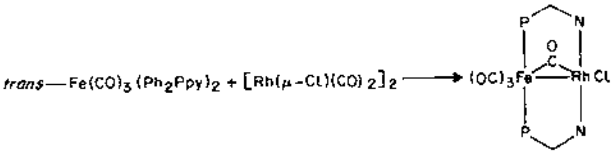
The structure of the FeHg complex has been determined. A donor-acceptor bond exists between Fe and Hg, and Hg is inclined to be a π-acceptor. The N—Hg separations are 2.595 Å and 2.867 Å, respectively, and in the range of the van der Waals radii. The Fe—Hg distance of 2.648 Å is longer than that of known FeHg complexes. The donor–acceptor bonds also exist in the FeCu, FeNi and FeRh complexes.



(4.9)



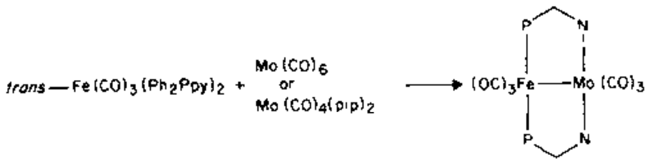
(4.10)



(4.11)

Our work has further shown that *trans*-Fe$(Ph_2Ppy)_2(CO)_3$ can displace three ligands in the Mo(0) mononuclear complex (Eq. (4.12)).

The FeMo complex is unstable in air. Attempts to prepare FeCr and FeW complexes by the same method have failed.



(4.12)

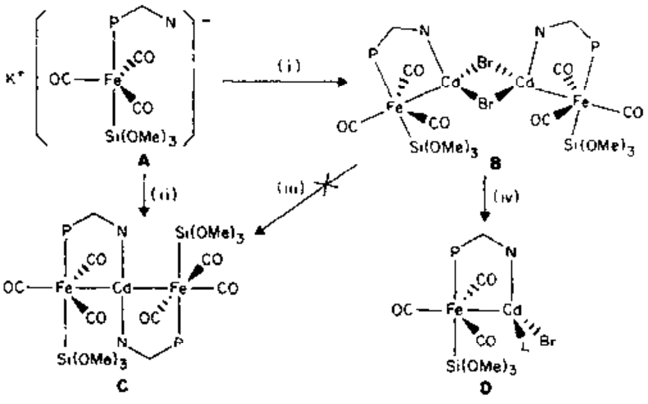
4.2.1.1.3. Substitution. Anionic silyl complexes readily undergo substitution with metal halides to yield polynuclear complexes. This kind of reaction, described in Scheme 3, has been reported by Fischer and co-workers [48].

The different outcome of the reactions of **A** with $CdBr_2$ and $CdCl_2$ is not due to a lack of splitting of the bromo bridges and formation of the monomeric 1 : 1 compound **D**. The reason may therefore be thermodynamic.

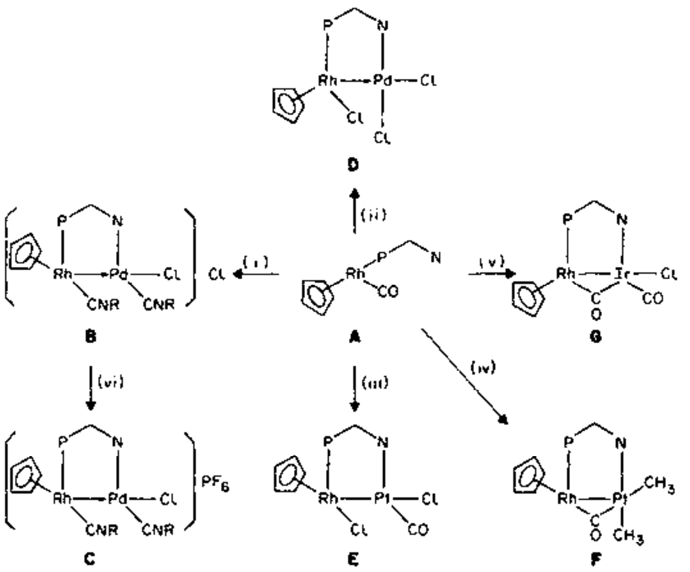
4.2.1.1.4. A complicated mechanism. Recently, Faraone and co-workers have studied the synthesis of Rh—M (M = Pd, Pt) heterobinuclear complexes containing one bridging Ph_2Ppy, and have proposed that steric factors may be determining the course of the reactions.

They have studied the reactions of Rh(η^5-Cp)(Ph_2Ppy)(CO) and Rh(1,5-COD)(Ph_2Ppy)Cl, respectively (Schemes 4 and 5) [3,8,11].

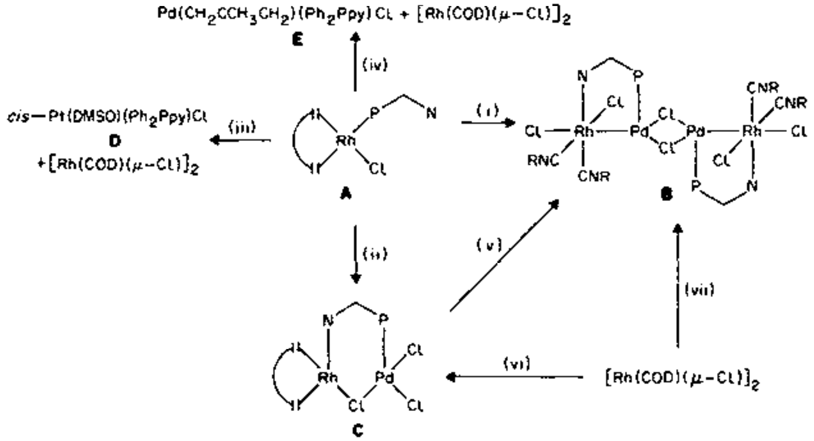
The reactions between **A** and d^8Pt(II), Pd(II) or Ir(I) complexes proceed by coordination of the pyridine nitrogen atom of **A** to the metal centers. The reactions appear to be strongly dependent on the presence of labile ligands (e.g. DMSO, COD) or of ligands with a strong trans-labilizing effect (e.g. alkyl group) bound to a palladium(II) or platinum(II) center. Steric factors and the possibility that the reaction occurs with concomitant movement of terminal ligands to the bridging site are very important in determining the course of the reaction and the nature of the products. The rigidity and the short-bite angle of the Ph_2Ppy ligand induces M—M bond formation. Steric interactions between the ligands coordinated to Pd(II) and Pt(II) and the ligands of the five-coordinated rhodium(I) center can give rise to



Scheme 3. (i) Excess $CdBr_2 \cdot 4H_2O$/THF, −KBr; (ii) excess $CdCl_2 \cdot 2.5H_2O$, −KCl; (iii) A; (iv) L = 4-picoline.



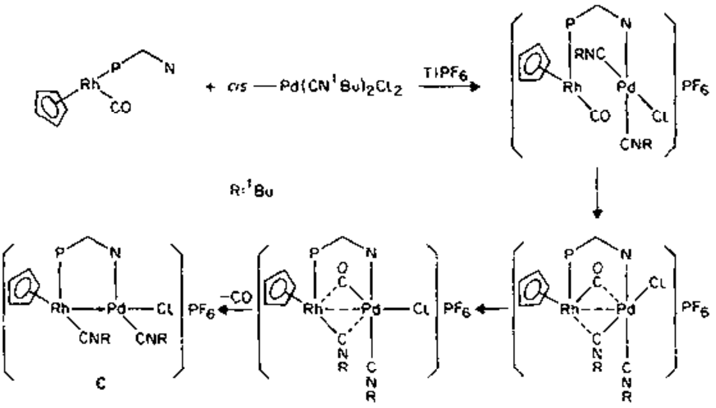
Scheme 4. (i) *cis*-Pd($CN^tBu)_2Cl_2$; (ii) Pd(COD)Cl_2; (iii) *cis*-Pd$(DMSO)_2Cl_2$; (iv) *cis*-Pd$(DMSO)_2(CH_3)_2$; (v) Ir$(CO)_2Cl(p\text{-}NH_2C_6H_4CH_3)$; (vi) $TlPF_6$.



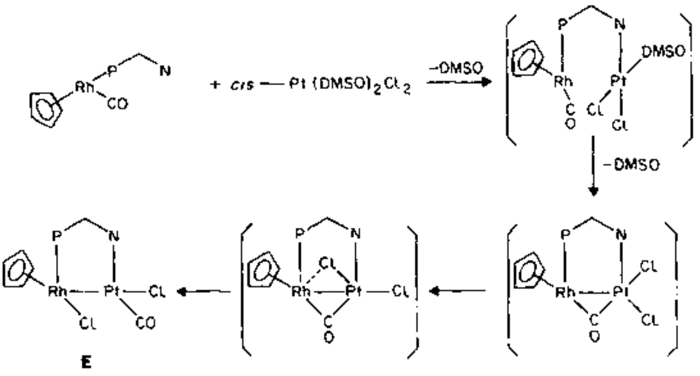
Scheme 5. (i) *cis*-Pd($CN^tBu)_2Cl_2$; (ii) Pd(COD)Cl_2 or Pd$(PhCN)_2Cl_2$; (iii) *cis*-Pt$(DMSO)_2Cl_2$; (iv) $[Pd(CH_2CCH_3CH_2)Cl]_2$; (v) ^tBuNC; (vi) Pd(η^2-$Ph_2Ppy)Cl_2$; (vii) *cis*-Pd($CN^tBu)(Ph_2Ppy)Cl_2$.

bridging coordination mode for terminal ligands and, in some cases, to transfer of ligands from one metal center to another. For example, the formation of **C** is shown in Scheme 6.

In particular, when transfer of a charged ligand occurs, the interaction involves oxidative addition (Scheme 7) [3].



Scheme 6.



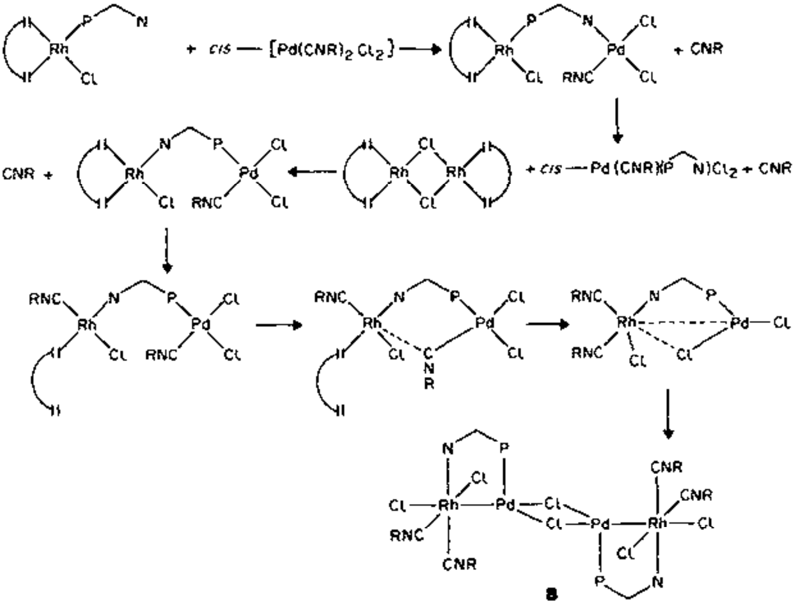
Scheme 7.

The reactions of Rh(1,5-COD)(Ph_2Ppy)Cl with Pd(II) or Pt(II), shown in Scheme 5, also proceed by coordination of the pyridine nitrogen atom [11].

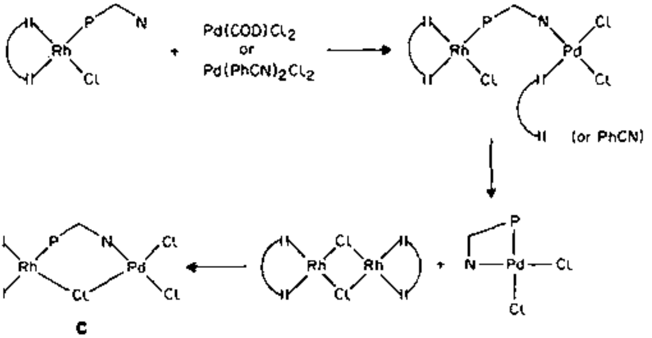
As a consequence of steric interactions between the hydrogens of the COD ligand and the phenyl groups of the bridged Ph_2Ppy ligand, the Rh—P bond in the rhodium–palladium intermediate is broken and the Ph_2Ppy ligand transfers from rhodium to palladium to form $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ and a Pd(II) complex. In the resulting Pd(II) complexes the Ph_2Ppy is bonded through the phosphorus or is chelated to the metal center. Since the Ph_2Ppy P-dentated or chelated complexes are active species, they can react with the second metal center to give stable heterobinuclear complexes. The subsequent reaction path appears to be strongly dependent on both the nature of the ligands bound to the Pd(II) center and the basicity of the Rh(I) center. Transfer of ligands from the Pd to the Rh atom can be achieved in the presence of the bridging ligand. If the Rh center is sufficiently basic, oxidative addition of the Pd—Cl bond across the Rh center can be observed. The oxidative addition process occurs by partial formation simultaneously of both the chloride bridge and the M—M bond. The rigidity and the short-bite angle of the Ph_2Ppy bridging ligand are very important in these processes, shown in Scheme 8 [11]. This process is supported by reaction (vii).

The process of (ii) is also similar to the above but, significantly, the oxidative addition of Pd—Cl across the rhodium center does not occur, probably owing to the low basicity of the rhodium(I) center and the presence of two bridging ligands (Scheme 9). Reaction (vi) provides support for this mechanism [11].

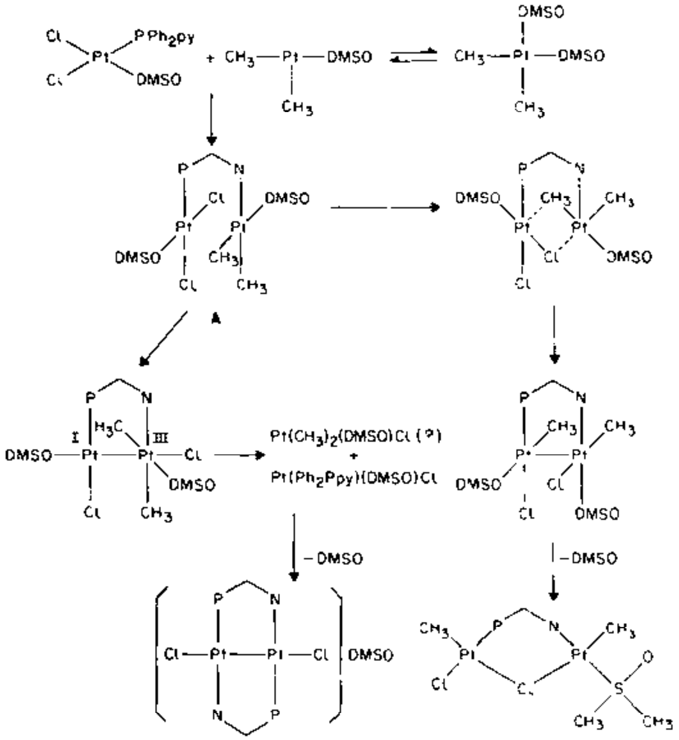
Similarly, the reaction between *cis*-$Pt(DMSO)(Ph_2Ppy)Cl_2$ and $Pt(CH_3)_2(DMSO)$ gives a product which is formed by a methyl-for-chloride exchange process. At the same time, a redox product is also isolated (Scheme 10) [49].



Scheme 8.



Scheme 9.



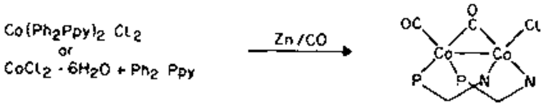
Scheme 10.

The product of the oxidative addition should be a very unstable Pt(I)—Pt(III) intermediate whose binuclear structure can be disrupted, breaking the Pt—N bond. Although steric requirements are an important determinant of the breaking of a metal–ligand bond when Ph_2Ppy is coordinated as a bridging ligand, the instability of the Pt(I)—Pt(III) intermediate should be due essentially to electronic factors. The most likely moiety derived from the Pt(I)—Pt(III) intermediate that gives complex **A** is the Pt(I) species [Pt(DMSO)(Ph_2Ppy)Cl]. An intermolecular nucleophilic attack of the pyridine N atom on the Pt(I) center, with concomitant displacement of DMSO, could lead to the binuclear complex **A**.

4.2.1.2. Synthesis of homobinuclear complexes. When homobinuclear complexes are bridged by the unsymmetrical ligand Ph_2Ppy the metal centers exhibit different character and reactivity. Studies of Ph_2Ppy-bridged homobinuclear complexes have therefore received considerable attention.

4.2.1.2.1. Mononuclear complexes as the starting species. The PtPt, PdPd and RhRh homobinuclear complexes with two bridged Ph_2Ppy may be obtained by oxidative addition (see Section 4.2.1.1).

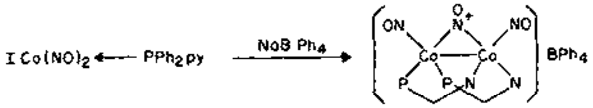
This kind of homobinuclear complex can also be formed by reductive carbonylation. We have prepared the first novel binuclear cobalt carbonyl complex with mixed valence (see Eq. (4.13)) [25,50]



(4.13)

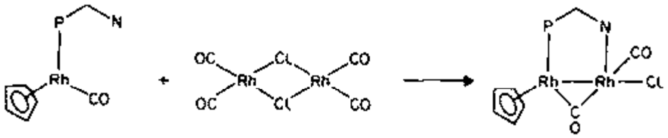
A possible mechanism is shown in Scheme 11.

Roustan et al. have prepared a dicobalt complex from a mononuclear complex in which a bridging nitrosyl group is present (Eq. (4.14)) [22]. However, when $AgBF_4$ is used as a halide abstractor, only the mononuclear complex $[Co(NO)_2(Ph_2Ppy)]^+$-BF_4^- is obtained. This is attributed to the fact that only $NaBPh_4$ can act simultaneously as a halide abstractor and a nitrosyl abstractor.



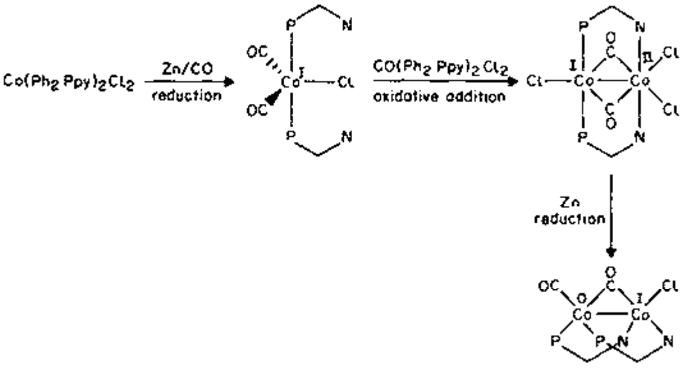
(4.14)

Faraone and co-workers have obtained the rhodium homobinuclear complex from $Rh(\eta^5\text{-}Cp)(CO)(Ph_2Ppy)$ (see Eq. (4.15)) [8]. The characters of the two Rh centers are different in the product.



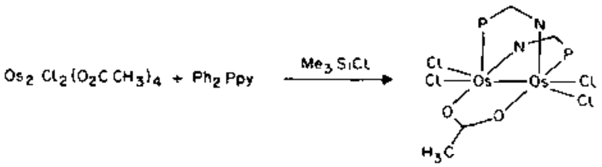
(4.15)

4.2.1.2.2. Homobinuclear complexes as the starting species. Cotton and co-workers have reported the synthesis of a series of homobinuclear complexes with Ph_2Ppy bridges.



Scheme 11.

4.2.1.2.2.1. Reduction. The quadruply-bonded Re_2^{6+} and triply-bonded Os_2^{6+} complexes can be reduced by the Ph_2Ppy ligand to give the Re_2^{4+} and Os_2^{5+} complexes with Ph_2Ppy bridges (an example is shown in Eq. (4.16)).

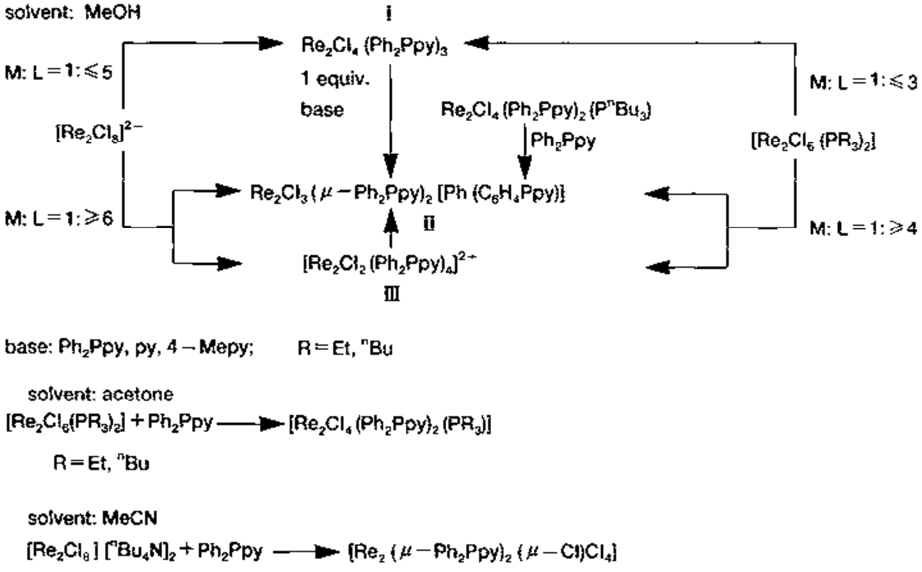


(4.16)

In the presence of a large excess of LiCl, the yield is increased from 30% to 75%. However, replacement of the remaining acetate ligand is impossible [51,52].

The reduction of the Re_2^{6+} core is interesting. The course of these reactions is markedly dependent upon the choice of solvent, the stoichiometry of the reactants and the reaction time (Scheme 12). From these reactions have been observed the first example of an *ortho*-metallation reaction occurring at a metal–metal multiple bond of the M_2L_8 type, and a rare example of a multiply-bonded dimetal unit complexed by four neutral bridging ligands [2,53].

Cotton and co-workers have studied the reaction of $[Re_2Cl_8]^{2-}$ with Ph_2Ppy in methanol with different stoichiometries. The results showed that both **I** and **III** can be regarded as "intermediates" in the formation of **II**, since both can be so converted under a variety of conditions. When other solvents are used, different products are obtained.



Scheme 12.

4.2.1.2.2.2. Disproportionation. Cotton's group have proposed that a disproportionation mechanism (via **4.7**) could be operative rather than the formation of **4.8** being a consequence of the direct phosphine-induced reduction of **4.7** (Scheme 13) [54,55].

4.2.1.2.2.3. Substitution. Cotton and co-workers have also prepared the quadruply-bonded Mo_2^{4+} complexes (Eqs. (4.17) and (4.18)) [56,57].

$$Mo_2(O_2CCF_3)_4 + Ph_2Ppy \xrightarrow{Me_3SiNCS} Mo_2(NCS)_4(\mu\text{-}Ph_2Ppy)_2 \tag{4.17}$$

$$Mo_2(O_2CCH_3)_4 + Ph_2Ppy \xrightarrow{Me_3SiCl} Mo_2Cl_4(\mu\text{-}Ph_2Ppy)_2 \tag{4.18}$$

Similarly, treatment of $[Mo_2(O_2CCMe_3)_3(MeCN)_2]BF_4$ with 1 equivalent of Ph_2Ppy, or $[Mo_2(O_2CCMe_3)_2(MeCN)_6]BF_4$ with 2 equivalent of Ph_2Ppy, yields $[Mo_2(O_2CCMe_3)_2(Ph_2Ppy)_2](BF_4)_2$ in which the two bridging ligands Ph_2Ppy are arranged in a cis position as shown by ^1H NMR [58].

However, further replacement of the remaining acetate ligand in the Rh_2^{4+} core has not been successful, even when Me_3SiCl or LiCl are used (see Eq. (4.19)) [52].

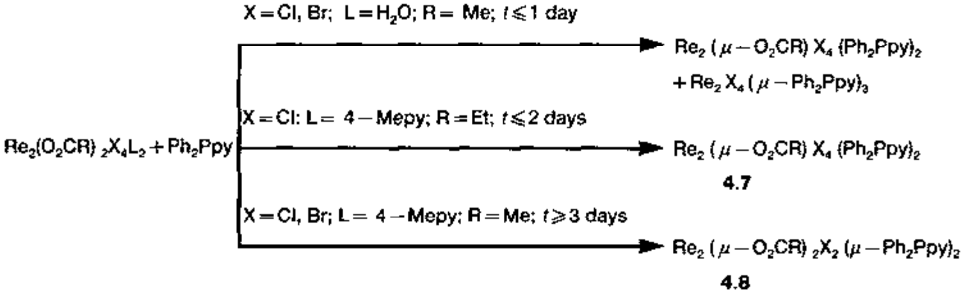
$$Rh_2(O_2CCH_3)_4(MeOH)_x \xrightarrow[LiCl/Me_3SiCl]{Ph_2Ppy} cis\text{-}Rh_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-}Ph_2Ppy)_2 \tag{4.19}$$

When $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ reacts with Ph_2Ppy, different products are obtained depending on the stoichiometry of the reagents [59]. When the mole ratio is 1 : 1, **4.9** is obtained, and **4.10** can be formed when the ratio is increased to 1 : 2 or 1 : 4. The $\overline{Rh-(form)_2-Rh}$ fragment remains stable.

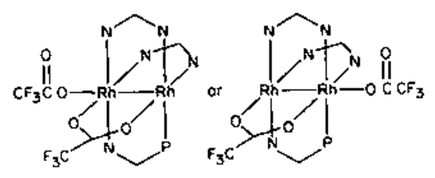
In different solvents, **4.9** and **4.10** dissociate in varying degrees. In acetonitrile, **4.9** behaves as a 1 : 1 electrolyte and **4.10** as a 1 : 2 electrolyte. In poorly or non-coordinating solvents, such as methanol, acetone, nitrobenzene or dichloromethane, **4.9** is poorly dissociated and **4.10** is only partially dissociated to a 1 : 1 electrolyte.

Cotton's group have proposed a possible mechanism operating during the reaction, on the basis of ^{31}P NMR spectroscopy (Scheme 14).

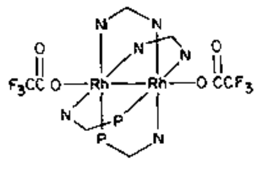
At 225 K a 1 : 1 adduct with a linear arrangement of the Rh—Rh—P atoms is formed when the ratio is 1 : 1, and the linear Rh—Rh—P can convert irreversibly to



Scheme 13.



4.9



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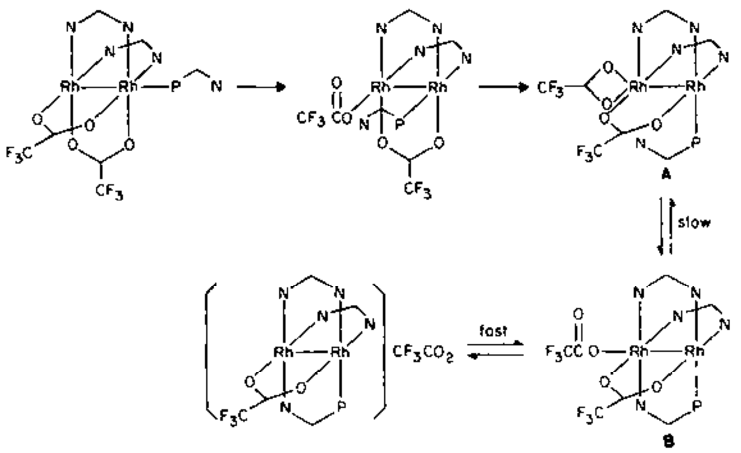


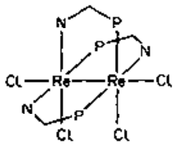
Scheme 14.

the bent one at 310 K. The equatorial isomer can undergo ring closure of the Rh—Rh—P—N fragment to form the species **B**. When 2 or 4 equivalent of Ph_2Ppy is added, the ^{31}P NMR spectra reveal the quantitative formation of a bisaxial adduct in which each phosphorus atom, axially coordinated to the rhodium, is also involved in a four-membered chelating ring. The reaction pattern could involve sequential axial coordination of Ph_2Ppy ligands through the phosphorus atoms with formation of the classical bisadducts followed or not by chelation of the pyridine nitrogen atoms. On warming to 310 K, the bisaxial adduct slowly isomerizes to give the equatorial isomer **4.10**.

4.2.2. Structure

In the binuclear complexes containing Ph_2Ppy bridging ligands, the number of Ph_2Ppy bridging ligands can change from one to four. Commonly, the number of Ph_2Ppy ligands is two, while complexes containing three or four Ph_2Ppy bridging ligands are rare. Cotton and co-workers have synthesized two novel complexes, **4.11** and **4.12**, in which the Re_2^{4+} unit is bridged by three or four Ph_2Ppy ligands [2,53]. A copper binuclear complex with three bridging Ph_2Ppy ligands, **4.13**, has also been obtained [35,37,39].

In both **4.11** and **4.12**, steric effects are introduced by the bulky Ph_2Ppy ligands. For example, in **4.12** the two Re—Cl bond lengths differ in spite of the similar



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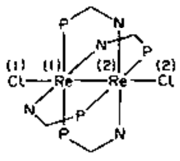
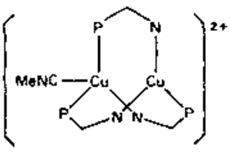


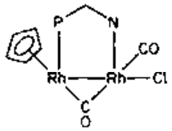
4.12



4.13

environments, and the Re(2)$-$Cl(2) bond is elongated owing to steric crowding. Otherwise, the bridging groups are arranged in a staggered mode because of the steric demands of these bulky ligands.

In binuclear complexes containing only one Ph_2Ppy ligand, the M$-$M bond may be lost (see Section 4.1), or the five-membered ring adopts a rather skewed configuration while the M$-$M bond is maintained. For example, in **4.14–4.16** the dihedral angles are 26.9°, 35.4° and 20.2°, respectively [3,8,11].



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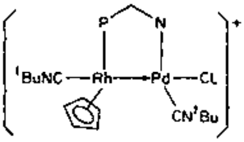

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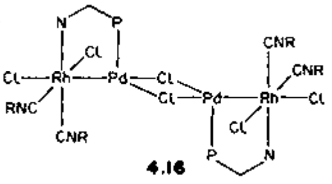


4.16

The complexes with two Ph_2Ppy bridging ligands possess two configurations, HH and HT, and on each metal atom the two ligands are arranged to be cis or trans to each other.

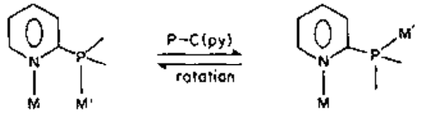
Generally, the binuclear complexes without other bridging ligands assume a trans,trans-HT configuration, such as $Pd_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ [12,60], $RhPd(\mu\text{-}Ph_2Ppy)_2(CO)Cl_3$, [4,13], $[Mo_2(\mu\text{-}Ph_2Ppy)_2(NCS)_4](THF)_2$ [57] etc. In all these complexes, the rigidity of the short-bite Ph_2Ppy ligand induces the formation of a M$-$M bond. Moreover, because the P$-$N distances are usually longer than the M$-$M separations, the MPCNM′ five-membered ring is skewed with a N$-$M$-$M′$-$P tersional angle larger than 10°.

The trans,trans-HH orientation is thermodynamically unstable and can transfer to HT configuration on heating, as for example in $PtPd(\mu\text{-}Ph_2Ppy)_2I_2$ [15].

The structure of **4.17** is different from that of **4.18**, although both Ru and Rh atoms are six-coordinate [30]. In **4.18** two bridging ligands adopt a HT arrangement and lie trans to one another on the Rh. In **4.17**, however, while the ligands are also arranged in a HT configuration, they are cis to each other on the Ru.

$Re_2Cl_4(\mu\text{-}Ph_2Ppy)_2(PEt_3)$ possesses the cis,cis-HT configuration [53].

Binuclear complexes with other bridging ligands usually have trans,trans-HT arrangements. Examples include $Rh_2(\mu\text{-}CO)(\mu\text{-}Ph_2Ppy)_2Cl_2$, which has a single atom bridge [4,23]; $Rh_2(\mu\text{-}RC{=}CR)(\mu\text{-}Ph_2Ppy)_2(CO)_2Cl_2$ ($R = CH_3CO_2$), which has a biatom bridge [61]; and $Rh_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}NO_3)(CO)Cl_3$, in which there is a triatom bridge [62]. The Ppy portion of these molecules is, as expected, planar. As this plane defines the direction of the pyridine lone pair, the metal atoms bound to nitrogen should lie in the Ppy plane. In fact, both metal atoms are very slightly out of this plane. As there should be no restriction to the rotation about the P—C(py) bond, the phosphorus-bound metal atom is not constrained to lie in the Ppy plane (Eq. (4.20)).



(4.20)

Lengthening of the M—M′ distance by rotation about the P—C(py) bond is, however, limited by the presence of the second Ph_2Ppy ligand. This leads to a skewing about the M—M′ axis of the rigid Ph_2Ppy ligand, and the two trans PMN units are not parallel to one another nor are they perpendicular to the plane containing M, M′ and other ligands [23].

In the complexes $MM'(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$ (M = Pt, Pd; M′ = Mo, W), the two bridging Ph_2Ppy ligands assume HH or HT arrangement and are trans to one another on the M atom, cis to one another on the M′ atom [43,45].

The location of the bridging carbonyl is of much interest. The crowding in these molecules may force one carbonyl group to lie over the M atom, and in that position it is likely to be acting as a weak π-donor to the somewhat electron-deficient 16-electron M atom. For example, complexes containing the Pt—M′ (M′ = Mo, W) bond have a semibridging carbonyl. Alternatively, the M—CO bond distance is within the known range for M-bridging carbonyls, the carbonyl can interact with these two metal atoms through σ–σ overlap and the two electrons of the carbonyl may be delocalized to form a bridging carbonyl: for example, the similar chloride or iodine complex of PdMo [47] and the chloride complex of PdW [45]. However, in complexes such as $PtRh(\mu\text{-}Ph_2Ppy)_2(CO)Cl_3$ [13], $PdRh(\mu\text{-}Ph_2Ppy)_2(CO)Cl_3$ [1,4,13] and $RuPd(\mu\text{-}Ph_2Ppy)_2(CO)_2Cl_2$ [30], which have similarly situated platinum and palladium atoms (each with a 16-electron count), there is no evidence for the presence of the similar bridging carbonyl. The major difference is probably the coordination number of the second metal atom. In the preceding complex the molybdenum and tungsten atoms are seven-coordinate, while in the latter complexes the rhodium and ruthenium atoms are only six-coordinate [45].

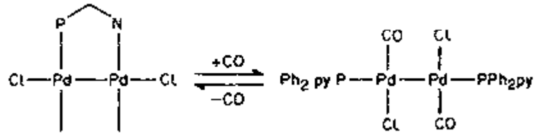
The cobalt binuclear complexes also possess novel structures. For example, both Co^0Co^I $(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$ [25,50] and $[Co_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}NO)(NO)_2]BPh_4$ have W-frame structures in which the two bridging Ph_2Ppy ligands are all in a HH arrangement [22]; and in the complex $Co_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)_2Cl_3$, which has two bridging carbonyls, the P—Co—P′ and N—Co—N′ angles are 173.8° and 177.2°, respectively [50].

For the binuclear complexes containing one or two triatom bridges, the two Ph_2Ppy ligands assume the HT arrangement and are cis to one another on every metal atom; for example, $Os_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}O_2CCH_3)Cl_4$ [51,52], $[Re_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}O_2CCH_2)_2Cl_2]^+$ [55], $Rh_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}O_2CCH_3)_2Cl_2$ [52], $Rh_2(form)_2(\mu\text{-}Ph_2Ppy)_2(O_2CCF_3)_2$ [59], etc. However, in $Mo_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}O_2CR)_2Cl_2$ the two N—Mo—P units are nearly linear (165.7°).

4.2.3. *Reaction*

There have been many studies on the reactions of Ph_2Ppy-bridged binuclear complexes with a M—M bond, some of which are very novel. However, attempts to insert small molecules such as CO, alkyne, cyanide or isocyanide into the M—M bond have proved unsuccessful.

4.2.3.1. Ring opening. The M—M bond is unreactive in Ph_2Ppy-bridged binuclear complexes, but these complexes do react with CO or RNC to give some ring opening products. One reason is the ease with which the pyridine nitrogen is displaced from the metal coordination plane. Another is the limited flexibility of the Ph_2Ppy ligand. This ligand lacks the articulation available to dppm which allows the M—M distance in its bridged complexes to vary from 2.2 to 3.5 Å. Ph_2Ppy, because of the planar nature of the pyridine ring and the short N—C distance, does not appear able to span the long end of M—M separations spanned by dppm. Consequently the M—M bond is not able to open up to form an A-frame structure (Eqs. (4.21)–(4.22)) [12]



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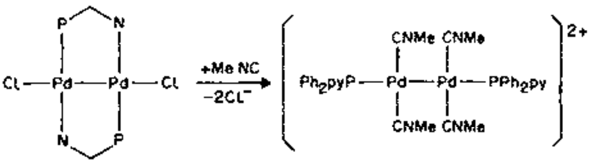


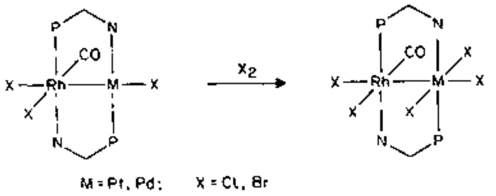
(4.22)

4.2.3.2. Ligand exchange. The bridging and terminal ligands in Ph_2Ppy-bridged complexes with a M—M bond can be displaced by other ligands.

It has been reported that the bridged Ph_2Ppy ligand can be successively displaced by diphosphine ligands dpmMe and dppm to give $Pd_2Cl_2(dpmMe)_2$ and $Pd_2Cl_2(dpmMe)(dppm)$ [64]. The bridging carbonyl ligands in both $Rh_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ [8,18] and $(\eta^5\text{-}Cp)Rh_2(\mu\text{-}Ph_2Ppy)(\mu\text{-}CO)(CO)Cl$ [61] can be displaced by SO_2 or alkynes with an electron-withdrawing group, such as COOR ($R=CH_3$, C_2H_5) or CF_3. Moreover, replacement of the terminal carbonyl by RNC can also occur on the complex $Rh_2(\mu\text{-}Ph_2Ppy)_2(CO)_2Cl_4$ [65].

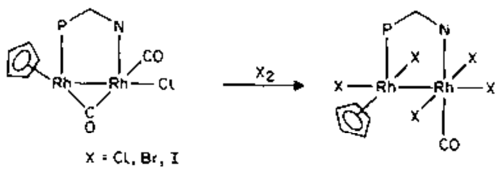
4.2.3.3. Addition. When an unsaturated center is present, addition of small molecules to the unsaturated center can occur. For example, the addition of CO to $Rh_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}RC{=}CR')Cl_2$ ($R=R'=CO_2CH_3$ or $R=CO_2CH_3$, $R'=H$) leads to the formation of $Rh_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}RC{=}CR')(CO)_2Cl_2$ [8,18], while the reactions of CO or SO_2 with $(\eta^5\text{-}Cp)Rh_2(\mu\text{-}Ph_2Ppy)(\mu\text{-}RC{=}CR')(CO)Cl$ ($R=R'=CO_2CH_3$ or $CO_2C_2H_5$) give the corresponding additive products $(\eta^5\text{-}Cp)Rh_2(\mu\text{-}Ph_2Ppy)(\mu\text{-}RC{=}CR')(CO)(L)Cl$ ($L=CO$ or SO_2) [61].

4.2.3.4. Oxidative addition. Halogens can oxidatively add to the unsaturated metal center, and the M—M bond is retained (Eq. (4.23)) [1,66].



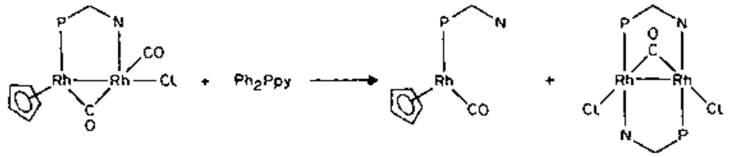
(4.23)

Faraone and co-workers have observed that (η^5-Cp)Rh_2(μ-Ph_2Ppy)(μ-CO)(CO)Cl has a 16-electron Rh(I) and an 18-electron Rh(I) center, which are very different in basicity and coordination number; but oxidative addition to one of the metals is not observed in reactions of this complex with halogens (Eq. (4.24)) [8]. This appears to be principally an electronic effect, in that the metal of lower oxidation state transfers some of its electron charge to the metal of higher oxidation state via the bridging ligand, and the electron density on the two metals is balanced before oxidative addition via the M—M bond [8].



(4.24)

4.2.3.5. Decomposition. In the presence of basic species such as Ph_2Ppy, py and PPh_3, binuclear complexes with one Ph_2Ppy bridge can decompose to give mononuclear complexes (Eqs. (4.25)–(4.27)) [3,67].



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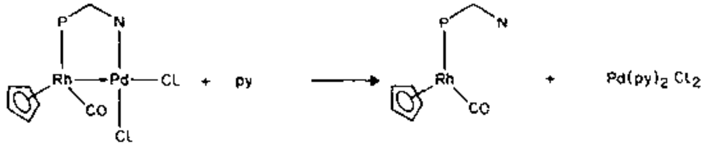

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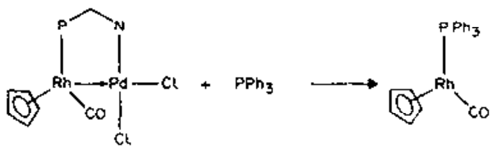
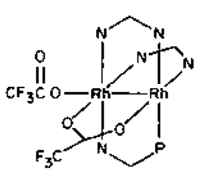


(4.27)

4.2.3.6. Displacement reaction. In the presence of some inorganic salts, poorly coordinated ligands can be displaced from Ph_2Ppy-bridged binuclear complexes. For example, Rotondo et al. have reported that in a polar solvent such as acetonitrile, **4.9** and **4.10** can dissociate and undergo displacement reactions in which one or both monoligated trifluoroacetate groups are replaced by X^- ligands ($X = Cl$, Br, I) [59].



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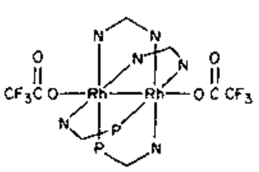
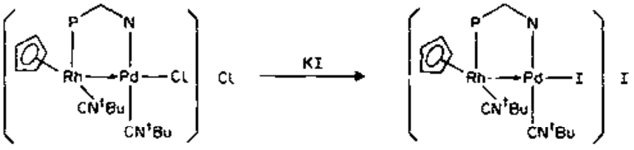


4.10

An analogous reaction occurs for the RhPd complexes containing one bridged Ph_2Ppy ligand (Eq. (28)) [3].



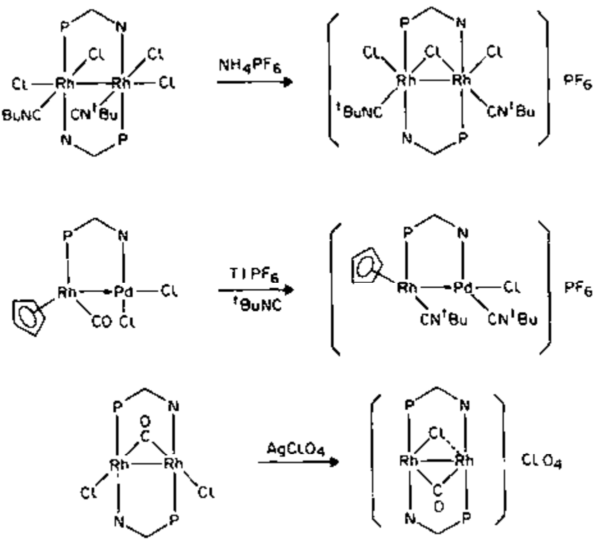
(4.28)

4.2.3.7. Ionization. In the presence of halide abstractors, terminal ligands such as Cl^- and $CO_2CF_3^-$ are easily drawn from the coordinative plane of the metal center, and various ionic species are formed. A number of examples are shown in Schemes 15 [3,18,65] and 16 [59].

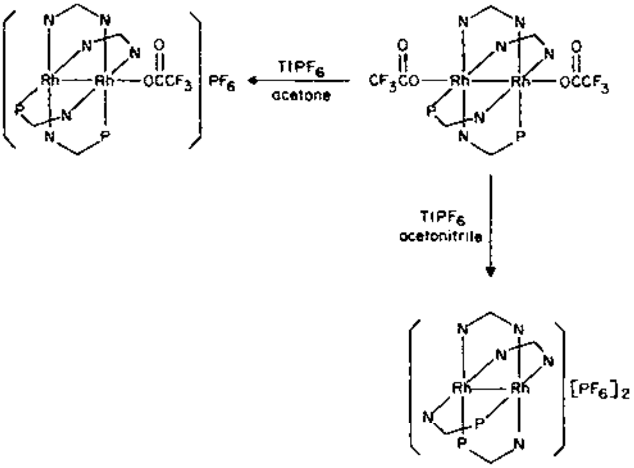
4.2.3.8. Electrochemical oxidation. Woods and co-workers have studied the electrochemical reaction of $Rh_2(\mu\text{-}CO)(\mu\text{-}Ph_2Ppy)_2Cl_2$ (Scheme 17) [65,68].

Though Cl^- is generally considered to be a better coordinating ligand for transition metals than NO_3^-, the binuclear Rh(I) species adds a Cl^- and a NO_3^- instead of two Cl^- ions. Even in the absence of an external source of Cl^-, oxidation of $Rh_2(\mu\text{-}CO)(\mu\text{-}Ph_2Ppy)_2Cl_2$ in CH_2Cl_2/TBAN still affords the same product. It is possible that the addition of the bridging NO_3^-, instead of a bridging Cl^- for instance, may result from the ability of the bridging nitrate to accommodate the twist angle imposed by the Ph_2Ppy ligands while still allowing each rhodium to have an electron count of 18 [68].

4.2.3.9. Other reactions. Balch et al. have found that $Pd_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ lacks the reactivity associated with the Pd—Pd bond, and the insertion of small molecules such as CO, SO_2 and RNC hasn't been explored [12]. However, $Pd_2(\mu\text{-}Ph_2Ppy)_2Cl_2$ can readily react with alkynes activated by an electron-withdrawing group, such as $RC{\equiv}CR$ ($R = CH_3CO_2$), to form the product **4.23**, in which the acetylene appears to be bound as a dimetallated olefin [18]. The reaction of $Pt_2(\mu\text{-}Ph_2Ppy)_2Br_2$ with $[IrBr_2(CO)_2]^-[Bu_4N]^+$ yields the PtIr complex **4.24** [18].



Scheme 15.



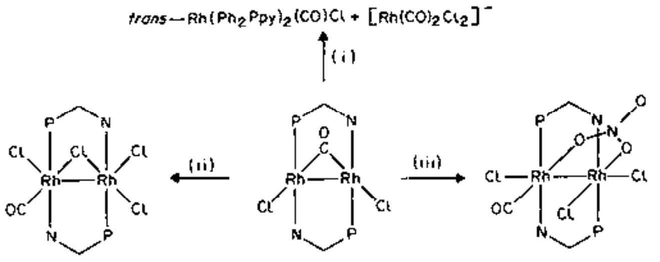
Scheme 16.

Addition of the sodium salt of the carbonyl metallate anions $[Mo(\eta^5\text{-}Cp)(CO)_3]^-$ to $(\eta^5\text{-}Cp)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2Ppy)Rh(CO)Cl$ gives the near-linear trinuclear complex **4.25**, in which the terminal chloride is replaced by the anion [67].

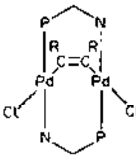
Walton et al. have found that the $Re_2(Ph_2Ppy)_2$ fragment remains in the reactions of $Re_2X_4(\mu\text{-}Ph_2Ppy)_2(PEt_3)$ with the carboxylate (Eq. (4.29)) [55].

$$Re_2X_4(\mu\text{-}Ph_2Ppy)_2(PEt_3) + MO_2CR \rightarrow Re_2X_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}O_2CR)_2$$

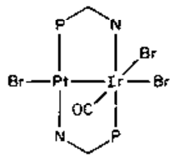
$$X = Cl, Br;\ R = CH_3, C_2H_5;\ M = Na, Li \qquad (4.29)$$



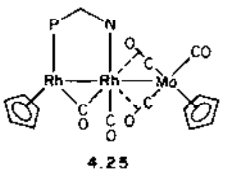
Scheme 17. (i) TBAC, CO; (ii) TBAH/TBAC, or an excess Cl_2; (iii) excess TBAC, $TBAN/CH_2Cl_2$, ox.



4.23



4.24



4.25

In these complexes, $Re_2Cl_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}O_2CR)_2$ can be very easily oxidized by $[(\eta^5\text{-}Cp)_2Fe]PF_6$ to give $[Re_2Cl_2(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}O_2CR)_2]PF_6$ [55].

5. Cluster complexes with Ph_2Ppy

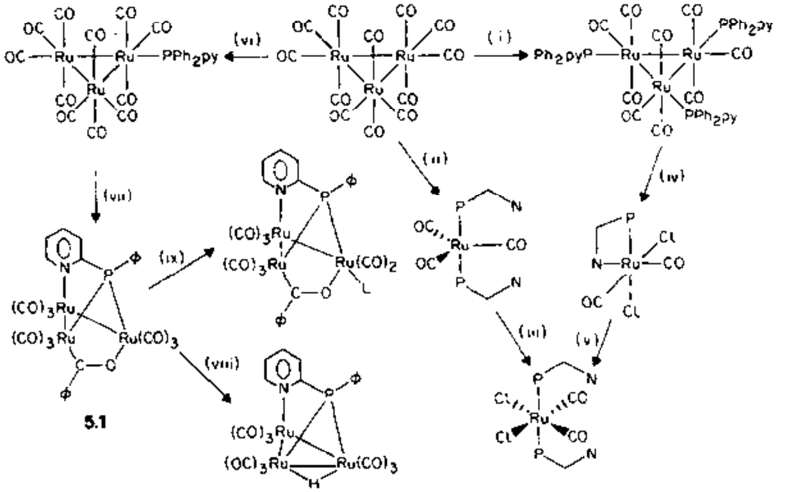
Cluster complexes are able to react with Ph_2Ppy to give some novel products. A number of reactions involving Ru_3 cluster complexes have been reported by Lugan and co-workers (Scheme 18) [30,69,70].

Using either sodium benzophenone ketyl or [PPN]CN can lead to the monosubstituted complex $Ru_3(CO)_{11}(Ph_2Ppy)$, selectively and quantitatively. The catalysts selectively promote the coordination of the phosphorus atom.

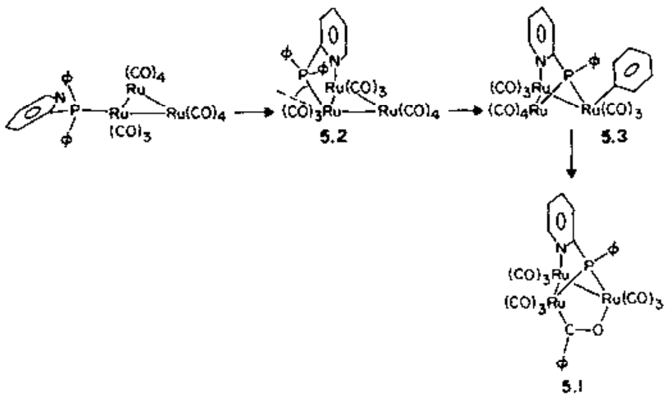
The formation of the 50-electron cluster **5.1** is described in Scheme 19.

In trimetal clusters, nitrogen ligands have shown a general tendency to coordinate at axial sites [71–73]. If this were to happen **5.2**, it would force the phosphorus atom into an axial position, known to be highly favorable for direct P—C bond cleavage at two metal centers. The oxidative cleavage of a P—C bond in Ph_2Ppy provides an organic fragment $P(C_6H_5)(C_5H_4N)$, which caps one face of the metal triangle through the bridging phosphido group, and spans the opening of the Ru(2)—Ru(3) edge to form **5.3** with a σ-bonded aryl group. In many cases, subsequent reductive elimination of benzene is favored, assuming a hydride ligand is available [74,75]. In the absence of any hydride here, the phenyl group undergoes migratory CO insertion to yield complex **5.1**, with an acyl group $C(O)C_6H_5$.

Complex **5.1** has exhibited high reactivity under mild conditions, which is related to a stereospecific labilizing effect of the acyl group to adjacent carbonyl ligands. For example, in the process (iv), phosphine ligands L stereospecifically substitute the carbonyl group at a cis position relative to the oxygen of the acyl group. When



Scheme 18. (i) $3Ph_2Ppy$, Δ; (ii) $6Ph_2Ppy$, hν; (iii) Cl_2; (iv) Cl_2; (v) Ph_2Ppy; (vi) [PPN]CN or sodium benzophenone ketyl; (vii) −CO (40 °C); (viii) H_2 (80 °C); (ix) L (25 °C) (L = PPh_3, Ph_2PH, Cy_2PH).



Scheme 19.

molecular hydrogen is bubbled through, the μ-acyl group is removed to give the monohydrido species $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}P(C_6H_5)(C_5H_4N))(CO)_9$ [69,70].

Lastra and co-workers have obtained novel tetranuclear copper(I) cluster complexes from a Cu(I) binuclear complex (Eq. (5.1)) [38].

$$[Cu_2(\mu\text{-}Ph_2Ppy)_2(MeCN)_2][BF_4]_2 + 4RC{\equiv}C^-$$
$$\rightarrow [Cu(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(Ph_2Ppy)]_4$$
$$R = Bu, Ph \qquad (5.1)$$

In the clusters, the bonding in the electron deficient "$Cu_3C{\equiv}CR$" moiety can be described as typical of a four-center two-electron system. Otherwise, in the

"$Cu_3C{\equiv}CR$" moiety there is a typical triple bond, and the metal–acetylide bonding can be considered to be of a pure σ-type. The Cu—Cu distances of 2.525–2.686 Å indicate weak or negligible M—M bonding interaction [39].

6. Complexes with deprotonated Ph_3Ppy

Cotton and co-workers have isolated a novel complex containing a tridentate bridging ligand Ph_2Ppy (Eq. (6.1)) [2,53].

$$\begin{aligned} &Re_2Cl_6(P^nBu_3)_2 \quad \text{or } Re_2Cl_8(N^nBu_4)_2 + 6Ph_2Ppy \\ &\quad \rightarrow Re_2Cl_3(\mu\text{-}Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy] \end{aligned} \tag{6.1}$$

The derivative of the triply-bonded Re_2^{4+} core is the product of ortho metallation at one of the phenyl rings. This is the first example of an ortho-metallation reaction occurring at a M—M multiple bond of the M_2L_8 skeleton. This result has an important bearing in the development of new reaction chemistry associated with dinuclear complexes containing multiple bonds. The Re—Re bond is a triple bond, there is no barrier to rotation, and a twist away from an eclipsed conformation does take place. Such a rotation appears to be necessary in order to prevent excessive strain in the three-point attachment of the ortho-metallated ligand. The Re—Re bond (2.336 Å) is longer than that in all previously characterized Re_2^{4+} dimers. This may be attributed to the axial chloride coordination and the skewed geometry of the molecule's core.

7. Catalytic behaviors

Transition metal complexes have been developed and utilized extensively as homogeneous catalysts owing to their high reactivity and selectivity [76]. Recently interest in binuclear complexes has arisen because it is anticipated that these will lead to advances in catalyst design. Complexes with two or more metal atoms can have advantages over a catalyst containing only a single metal. Small molecules, particularly those such as dinitrogen and nitrile that are difficult to reduce, may be more readily activated by attachment to several metal centers. In catalysts containing two metal centers, one may act to bind the substrate, while the second acts to feed or remove electrons from the first site. The presence of two metal atoms may facilitate multielectron redox reactions which cannot be handled by only a single metal atom.

Since the noble metals are scarce, studies on substitutes for non-noble metals are an important topic in the catalytic field. Bridging ligands such as Ph_2Ppy introduce the possibility of forming heterobinuclear complexes between noble and non-noble metals. Owing to the synergistic effect of adjacent metal centers, this kind of binuclear complex may be superior to the mononuclear complexes in some catalytic processes. We have studied the catalytic behavior of a number of Ph_2Ppy bridging heterobinuclear complexes [47]. Results of using these heterobinuclear complexes as homo-

Table 4
Activities and selectivities of catalytic effects of Fe—M complexes on carbonylation of ethanol to ethyl propionate

Complex	Conversion of ethanol (%)	Selectivity (%)	
		Ethyl ether	Ethyl propionate
$FeMo(Ph_2Ppy)_2(CO)_6$	88.5	81.3	18.7
$FeNi(Ph_2Ppy)_2(CO)_3(NCS)_2$	95.2	52.3	47.7
$FeRh(Ph_2Ppy)_2(CO)_4Cl$ (**7.1**)	92.4	48.0	52.0
$FeCu(Ph_2Ppy)_2(CO)_3Cl$	91.4	76.0	24.0
$FeHg(Ph_2Ppy)_2(CO)_3(SCN)_2$	94.4	73.2	26.8
$Rh(Ph_3P)_3Cl$[a]	96.5	52.4	47.6

Reaction conditions: temperature, 220°C; pressure, 35 kg cm^{-2}; time, 4 h; reagent ratio, ethanol : ethyl iodide : toluene = 86 : 61 : 95 (mmol); amount of catalyst, 0.060 mmol.

[a] Temperature, 180°C; amount of catalyst, 0.048 mmol.

geneous catalysts for carbonylation of ethanol to form ethyl propionate are given in Table 4. Evidently the Fe—Rh complex **7.1** is superior in activity and selectivity.

Comparison of the catalytic behaviors of **7.1** and $Rh(Ph_3P)_3Cl$ at different reaction temperatures (Table 5) shows that **7.1** is distinctly superior to $Rh(Ph_3P)_3Cl$ at 200°C for conversion of ethanol (99.5%) and selectivity to propionate (98.6%), although $Rh(Ph_3P)_3Cl$ has better activity at 160°C. Recently, it has been reported that some Fe—Rh bimetallic carbonyl clusters can act as molecular precursors for preparation of Fe—Rh bimetallic catalysts. These catalysts can be used to catalyze olefin hydroformylation and are effective for insertion of migratory CO. The Fe atom promotes migratory CO insertion at the Rh atom (Eq. (7.1)) [77].

Analogous synergistic behavior might be expected in our catalytic process. However, at lower reaction temperatures and because of the presence of the Fe atom, the oxidative addition of R towards the Rh atom is probably hindered, and this is the rate-determining step in the carbonylation of alcohols.

Table 5
Catalytic behaviors of Fe—Rh complex (**7.1**) and $Rh(Ph_3P)_3Cl$ at different reaction temperatures on carbonylation of ethanol to ethyl propionate

Temperature (°C)	Catalyst	Conversion of ethanol (%)	Selectivity (%)	
			Ethyl ether	Ethyl propionate
160	$Rh(Ph_3P)_3Cl$	46.9	61.6	38.4
	$FeRh(Ph_2Ppy)_2(CO)_4Cl$ (**7.1**)	38.9	66.1	33.9
180	$Rh(Ph_3P)_3Cl$	90.5	52.4	47.2
	$FeRh(Ph_2Ppy)_2(CO)_4Cl$ (**7.1**)	92.4	48.0	52.0
200	$Rh(Ph_3P)_3Cl$	96.4	32.3	67.7
	$FeRh(Ph_2Ppy)_2(CO)_4Cl$ (**7.1**)	99.5	1.4	98.6

(7.1)

Table 6
Comparison with CDT[a], selective hydrogenation

Catalyst	Reaction conditions			Results		
	Amount of catalyst (g)	Temperature (°C)	Pressure of H_2 (MPa)	Conversion CDT (%)	Selectivity (%)	
					CDE[b]	CDA[c]
Homogeneous	0.035	170	20	92.5	93.2	6.8
Heterogeneous	1[d]	110	20	89.4[e]	84.2	15.8

[a] Cyclododecatriene; [b] cyclododecaene (the main product in the reaction); [c] cyclododecane (the by-product). [d] Amount of PdMo complex in heterogeneous catalyst, 7%. [e] Mean value over ten times.

The Ph_2Ppy bridging binuclear complexes also have an advantage over the cluster complexes, in that the latter are easily decomposed during catalytic reactions, while in the former the bridging ligands can act as an "anchor" to maintain the integration of the binuclear catalytic units. The simple structures make it possible to use this kind of complex to study catalytic mechanisms, acting as models of cluster complexes.

There have been several attempts to overcome the difficulty of separating reactants and products from transition metal complexes in homogeneous catalyst systems. For example, using reverse osmosis with selectivity permeable membranes allows permeation of small molecules but retention of metal complexes. Two-phase systems have also been used, in which the metal complex acts as its own phase transfer catalyst. The best studied procedure involves "heterogenising" homogeneous catalysts by anchoring them to supports. Zhao et al. [78] have obtained the $PdMo(\mu\text{-}CO)(\mu\text{-}Ph_2Ppy)_2(CO)_2Cl_2$ heterogeneous catalyst from the cross-linking of 2-(diphenylphosphino)pyridine-4-methenyl polystyrene resin, and have compared this with the corresponding homogeneous catalyst $PdMo(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)_2Cl_2$ on catalytic hydrogenation to 1,5,9-cyclododecatriene (Table 6).

As shown in Table 6, the homogeneous catalysts have high selectivity and conversion in the hydrogenation of 1,5,9-cyclododecatriene. The immobilized catalyst has poor selectivity, but the conversion is similar. Thus the study of these heterogeneous catalysts is of great interest [78].

8. Summary

This review article has discussed progress in the field of Ph_2Ppy chemistry, in terms of synthesis, structure and reactivity. Many novel complexes have been obtained from the bridging ligand Ph_2Ppy. In particular, the utilization of Ph_2Ppy

in bridging bimetal complexes has promoted the study of binuclear, and especially heterobinuclear complexes.

As the rigidity of the Ph_2Ppy ligand usually induces formation of a metal–metal bond, it should be possible to obtain even more structural binuclear complexes with metal–metal bonds by incorporating pairs of two different metals, including main, transition and rare earth metals.

Our results have shown that *trans*-$Fe(Ph_2Ppy)_2(CO)_3$ can act as a neutral organometallic tridentate ligand to yield, easily, a binuclear complex with a Fe—M bond. Similarly, another ligand, *trans*-$M(O)L_n(\overset{\frown}{P\quad X})_2$($L = CO$ or CNR, M = Fe, Os, Cr, Mo, W; X = O, S, N, P, As), can also be expected to be an effective organometallic polydentate ligand and provide a simple method for preparing binuclear complexes, and particularly heterobinuclear complexes.

Investigations to date have concentrated on the metal atoms, but in fact the bridging ligand has been activated. For example, an ortho-metallation reaction occurs at one of the phenyl rings of the bridging Ph_2Ppy ligand [2,53]. It is to be expected that interesting reactions will be found to occur on the bridging ligands.

The Ph_2Ppy bridging binuclear complexes display catalytic activity when used as homogeneous or heterogeneous catalysts [47,78,79]. In particular, the Ph_2Ppy mono-bridging binuclear complexes may possess high catalytic reactivities owing to low steric hindrance [3,11,49]. We anticipate that more effective homo- or heterogeneous catalysts will be found through further study of Ph_2Ppy chemistry.

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