

# 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	<i>N,N'</i> -di- <i>p</i> -tolylformamidinate
2-Mepy	<i>e</i> -methylpyridine
mor	morpholine
pip	piperidine
PPDMe	3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine
[PPN]CN	bis(triphenylphosphoranylidene)ammonium nitrile
TBAC	tetra- <i>n</i> -butylammonium chloride
TBAH	tetra- <i>n</i> -butylammonium hexafluorophosphate
TBAN	tetra- <i>n</i> -butylammonium nitrate

## 1. Introduction

2-(Diphenylphosphino)pyridine ( $\text{Ph}_2\text{Ppy}$ ) 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,  $\text{Ph}_2\text{Ppy}$  can also act as a monodentate ligand or as a chelating ligand.

Balch and co-workers initiated work on the chemistry of  $\text{Ph}_2\text{Ppy}$  in the early 1980s, and have made great progress in studying the synthesis, structure and reactivity of  $\text{Ph}_2\text{Ppy}$ -containing complexes.

Cotton and co-workers have used the  $\text{Ph}_2\text{Ppy}$  ligand to connect homobinuclear complexes containing a metal–metal multiple bond. Recently, Faraone and co-workers have reported synthesis of mono-bridging  $\text{Ph}_2\text{Ppy}$  binuclear complexes, which have some catalytic potential owing to small steric hindrance. We have found that the complex *trans*- $\text{Fe}(\text{Ph}_2\text{Ppy})_2(\text{CO})_3$  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  $\text{Ph}_2\text{Ppy}$  complexes.

## 2. Complexes with monodentate $\text{Ph}_2\text{Ppy}$

The unsymmetrical ligand  $\text{Ph}_2\text{Ppy}$  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  $\sigma$ -donor and weaker  $\pi$ -acceptor than the phosphorus atom, so when a monodentate complex is prepared  $\text{Ph}_2\text{Ppy}$  usually binds via the phosphorus atom; no N monodentate complexes have yet been reported.

### 2.1. Preparation

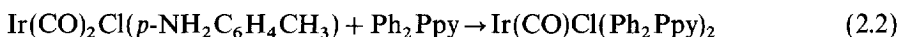
$\text{Ph}_2\text{Ppy}$  is similar to  $\text{PPh}_3$  and should be capable of substitution for  $\text{PPh}_3$  in any of the numerous complexes of the latter ligand [4]. So the synthesis of  $\text{Ph}_2\text{Ppy}$  monodentate P-bonded complexes resemble that of the  $\text{PPh}_3$  analogues, which are

usually formed from metal carbonyls, metal olefins, metal halides and several organo-metallic derivatives.

### 2.1.1. Substitution

Some ligands such as carbonyl, RNC, PhCN and olefin can be displaced by Ph<sub>2</sub>Ppy, 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<sub>2</sub>Ppy.

Similarly, the phosphine and amine ligands are also substituted by Ph<sub>2</sub>Ppy (Eqs. (2.1), (2.2)) [17,18].



In short, ligand substitution is the most general method of preparing Ph<sub>2</sub>Ppy P-bonded complexes.

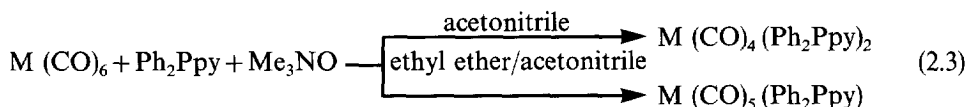
### 2.1.2. Oxygen atom transfer

We have used the oxygen atom transfer reaction of M(CO)<sub>6</sub> (M = Cr, Mo, W) with TMNO (Me<sub>3</sub>NO) in the presence of the Ph<sub>2</sub>Ppy ligand in different solvents selectively to give Ph<sub>2</sub>Ppy mono- or disubstituted products (Eq. (2.3)) [19].

The IR spectra suggest that the disubstituted complexes M(CO)<sub>4</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub> (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<sub>2</sub>Ppy

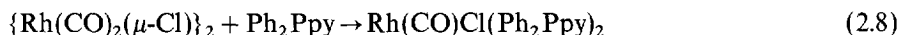
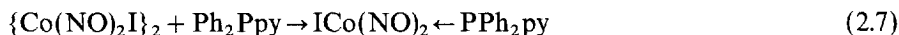
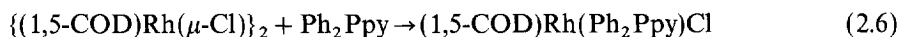
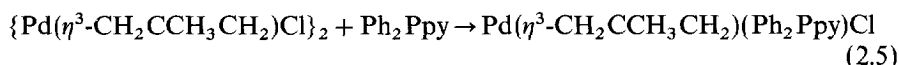
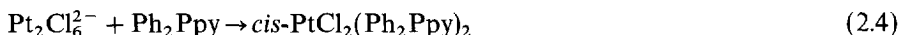
Starting material	Product	Ref.
M(CO) <sub>x</sub> (M = Fe, Cr, Mo)	M(CO) <sub>x-1</sub> (Ph <sub>2</sub> Ppy) (M = Fe, Cr, Mo)	[5]
Re <sub>2</sub> (CO) <sub>10</sub>	Re <sub>2</sub> (CO) <sub>8</sub> (Ph <sub>2</sub> Ppy) <sub>2</sub>	[5]
Rh(chel)(CO) <sub>2</sub> (chel = acetylacetonate or 8-hydroxyquinolate)	Rh(chel)(CO)(Ph <sub>2</sub> Ppy)	[6]
(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>3</sub> )Co(CO)I <sub>2</sub>	(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>3</sub> )Co(Ph <sub>2</sub> Ppy)I <sub>2</sub>	[7]
(η <sup>5</sup> -Cp)Rh(CO) <sub>2</sub>	(η <sup>5</sup> -Cp)Rh(CO)(Ph <sub>2</sub> Ppy)	[8]
Fe(NO) <sub>2</sub> (CO) <sub>2</sub>	Fe(NO) <sub>2</sub> (Ph <sub>2</sub> Ppy) <sub>2</sub>	[9]
AuCl(CO)	AuCl(Ph <sub>2</sub> Ppy)	[10]
PdCl <sub>2</sub> ( <sup>t</sup> BuNC) <sub>2</sub>	cis-PdCl <sub>2</sub> ( <sup>t</sup> BuNC)(Ph <sub>2</sub> Ppy)	[11]
PdCl <sub>2</sub> ( <sup>t</sup> BuNC) <sub>2</sub>	cis- or trans-PdCl <sub>2</sub> (Ph <sub>2</sub> Ppy) <sub>2</sub>	[12]
[Pd <sub>2</sub> (CNMe) <sub>6</sub> ] <sup>2+</sup>	[Pd <sub>2</sub> (CNMe) <sub>4</sub> (Ph <sub>2</sub> Ppy) <sub>2</sub> ] <sup>2+</sup>	[12]
[Rh(CNMe) <sub>4</sub> ] <sup>+</sup>	[Rh(CNMe) <sub>2</sub> (Ph <sub>2</sub> Ppy) <sub>2</sub> ] <sup>+</sup>	[13]
cis-[Cr( <sup>t</sup> BuNC) <sub>5</sub> (NO)]	cis-[Cr( <sup>t</sup> BuNC) <sub>4</sub> (NO)(Ph <sub>2</sub> Ppy)]	[14]
M(COD)X <sub>2</sub> (M = Pt, Pd; X = Cl, I)	M(Ph <sub>2</sub> Ppy) <sub>2</sub> X <sub>2</sub> (M = Pt, Pd; X = Cl, I)	[1,15,16]
PtMeX(COD) (X = Me, Cl, I)	PtMeX(Ph <sub>2</sub> Ppy) <sub>2</sub> X <sub>2</sub> (X = Me, Cl, I)	[16]



M=Cr, Mo, W

### 2.1.3. Decomposition

For some halide-bridged binuclear complexes, the halide bridges can be broken by  $\text{Ph}_2\text{Ppy}$  to give  $\text{Ph}_2\text{Ppy}$  P-bonded mononuclear products. Some reactions are shown in Eqs. (2.4)–(2.8) [1,4,20–24].



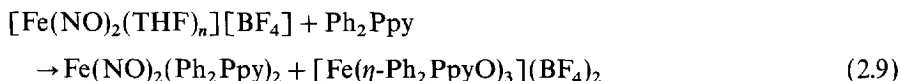
### 2.1.4. Other methods

Under mild conditions, reaction of hydrated  $\text{MCl}_2$  (M = Co, Ni) and  $\text{Ph}_2\text{Ppy}$  with CO in the presence of zinc powder yields  $\text{MCl}_2(\text{Ph}_2\text{Ppy})_2$  [25,26].

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

Alcock's study showed that  $\text{HAuCl}_4$  could be reduced by  $\text{Ph}_2\text{Ppy}$  to give the complex  $\text{AuCl}(\text{Ph}_2\text{Ppy})$ , which was also produced from  $\text{AuCl}(\text{CO})$  by a substitution reaction [29].

Through a dismutation reaction, Roustan's group has obtained a  $\text{Ph}_2\text{Ppy}$  P-bonded complex accompanied by an iron chelate complex with  $\text{Ph}_2\text{Ppy}$  oxide (Eq. (2.9)) [9].



## 2.2. Structure

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

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

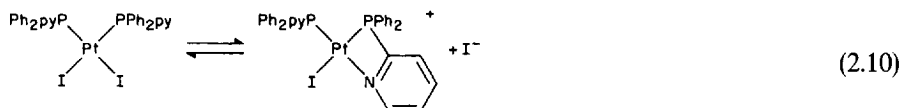
### 2.3. Reaction

The  $\text{Ph}_2\text{Ppy}$  P-dentated mononuclear complexes usually display good reactivities because of the presence of the uncoordinated nitrogen atom. On the one hand, the  $\text{Ph}_2\text{Ppy}$  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  $\text{Ph}_2\text{Ppy}$  P-dentated mononuclear complexes. So the  $\text{Ph}_2\text{Ppy}$  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  $\text{Ph}_2\text{Ppy}$  chelate complexes.

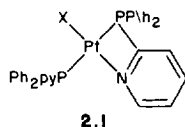
Balch and co-workers have observed rapid exchange between the cis and the chelated isomers in dichloromethane solution of  $\text{Pt}(\text{Ph}_2\text{Ppy})_2\text{I}_2$  at various temperatures (Eq. (2.10)), through the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra.



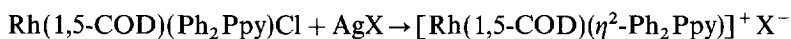
Low temperature favors ionic dissociation of the iodide ligand. However, the trans isomer is not involved in the process and the trans cation, **2.1**, is absent. This can be attributed to the operation of the trans effect, which selectively labilizes halo ligands trans to phosphine. The presence of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

Table 2  
Some chelating reactions

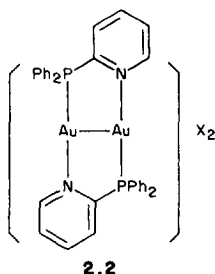
Starting material $\text{M}(\text{Ph}_2\text{Ppy})_2\text{XX}'$	Halide abstractor	Product $\text{cis-}[\text{M}(\text{Ph}_2\text{Ppy})(\eta^2\text{-Ph}_2\text{Ppy})\text{X}]\text{Y}$	Ref.
$\text{M} = \text{Pt}, \text{X} = \text{Me}, \text{X}' = \text{Cl}$	$\text{NaY} (\text{Y} = \text{BPh}_4, \text{BF}_4)$	$\text{X} = \text{Me}, \text{Y} = \text{BPh}_4, \text{BF}_4$	[16]
$\text{M} = \text{Pt}, \text{X} = \text{X}' = \text{Cl}$	$[\text{Rh}(\text{CO})_2(\mu\text{-Cl})]_2$	$\text{X} = \text{Cl}, \text{Y} = \text{Rh}(\text{CO})_2\text{Cl}_2^-$	[1]
$\text{M} = \text{Pt}, \text{X} = \text{X}' = \text{I}$	$\text{NH}_4\text{PF}_6$	$\text{X} = \text{I}, \text{Y} = \text{PF}_6$	[15]
$\text{M} = \text{Pd}, \text{X} = \text{X}' = \text{Cl}$	$\text{NH}_4\text{PF}_6/\text{AgNO}_3$	$\text{X} = \text{Cl}, \text{Y} = \text{PF}_6$	[13]



The  $\text{Ph}_2\text{Ppy}$  P-dentated complexes containing only one  $\text{Ph}_2\text{Ppy}$  ligand can also form a chelate ring (Eq. (2.11)) [11].



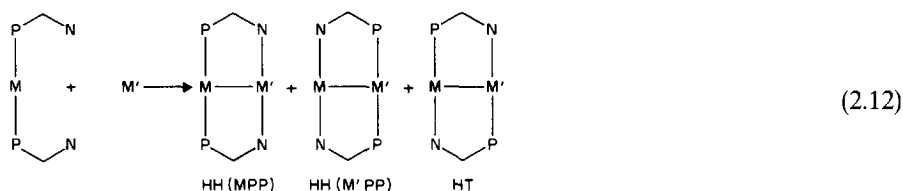
Inoguchi et al. have reported that in the presence of  $\text{AgX}$  ( $\text{X} = \text{BF}_4^-, \text{PF}_6^-$ ),  $\text{AuCl}(\text{Ph}_2\text{Ppy})$  produces  $\text{Ph}_2\text{Ppy}$ -bridged binuclear products, **2.2**, instead of chelate complexes [21].



### 2.3.2. Oxidative addition

This is the most important reaction of the  $\text{Ph}_2\text{Ppy}$  P-dentated complexes. The uncoordinated nitrogen atom captures the additional metal atoms  $\text{M}'$  to give binuclear complexes, and a metal–metal bond is formed because of the rigidity of the short-bite ligand  $\text{Ph}_2\text{Ppy}$  doesn't allow a large metal–metal distance. So  $\text{Ph}_2\text{Ppy}$  is a convenient building block for the construction of binuclear transition metal complexes [13].

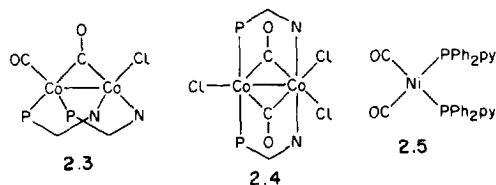
The general reaction is shown in Eq. (2.12) (HH, head-to-head configuration; HT, heat-to-tail).



### 2.3.3. Reductive carbonylation

This method, previously developed by us, can be used in  $\text{Ph}_2\text{Ppy}$  chemistry. Under mild conditions, the reactions of  $\text{M}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$  ( $\text{M} = \text{Co}, \text{Ni}$ ) with  $\text{CO}$  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.

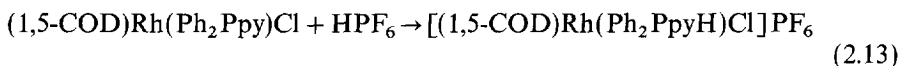


#### 2.3.4. Other reactions

Faraone and co-workers have found that in the presence of  $\text{PPh}_3$  the reaction of CO with  $\text{Rh}(\text{COD})(\text{Ph}_2\text{Ppy})\text{Cl}$  gives *trans*- $\text{Rh}(\text{Ph}_2\text{Ppy})(\text{PPh}_3)(\text{CO})\text{Cl}$  by the replacement of COD with CO and  $\text{PPh}_3$ . However, when only CO was bubbled into the solution of  $\text{Rh}(\text{COD})(\text{Ph}_2\text{Ppy})\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$ , a carbonyl complex  $\text{Rh}_2\text{Cl}_3(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-CO})$  was isolated. Presumably the reactive involved the formation of the intermediate  $[\text{Rh}(\text{CO})_2(\text{Ph}_2\text{Ppy})\text{Cl}]$  by the displacement of COD with CO from  $\text{Rh}(\text{COD})(\text{Ph}_2\text{Ppy})\text{Cl}$ . 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].

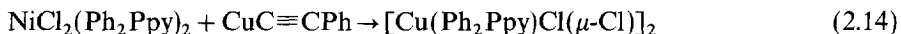
A stream of chlorine was bubbled into a solution of *trans*- $\text{Ru}(\text{CO})_3(\text{Ph}_2\text{Ppy})_2$  in  $\text{CH}_2\text{Cl}_2$  at room temperature to produce *trans*- $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_2$  [30]. The IR spectra indicated complete transformation of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

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



The reaction of *trans*- $\text{PtMeCl}(\text{Ph}_2\text{Ppy})_2$  with  $\text{SnCl}_2$  generated a Pt–Sn bond [16]. A bromo analogue,  $\text{Pt}(\text{Ph}_2\text{Ppy})_2\text{Br}_2$  has been obtained from  $\text{Pt}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$  by metathesis with sodium bromide [1]. Autoxidation of  $(\text{Ph}_2\text{Ppy})_2\text{CoCl}_2$  may induce the formation of  $(\text{Ph}_2\text{P}(\text{O})\text{py})_2\text{CoCl}_2$  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].



### 3. Complexes with chelating $\text{Ph}_2\text{Ppy}$

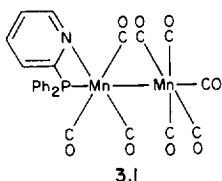
#### 3.1. Synthesis

Complexes with chelate  $\text{Ph}_2\text{Ppy}$  are commonly synthesized from the reaction of the  $\text{Ph}_2\text{Ppy}$  P-bonded complexes with halide abstractors (see Section 3.3). In



addition, the addition of  $\text{Ph}_2\text{Ppy}$  can generate uranium and rhodium complexes containing chelate  $\text{Ph}_2\text{Ppy}$ . For example, the complexes  $\text{U}(\text{BH}_4)_3(\eta^2\text{-Ph}_2\text{Ppy})_2$ ,  $\text{UCl}_3(\eta^5\text{-Cp})(\eta^2\text{-Ph}_2\text{Ppy})$  [33] and  $[(1,5\text{-COD})\text{Rh}(\eta^2\text{-Ph}_2\text{Ppy})]\text{X}$  ( $\text{X} = \text{ClO}_4$ ,  $\text{PF}_6$ ) [11] have been formed respectively through the addition of  $\text{U}(\text{BH}_4)_3(\text{THF})_x$ ,  $(\eta^5\text{-Cp})\text{UCl}_3$ , and  $[\text{Rh}(1,5\text{-COD})(\text{solv})_2]\text{X}$  with  $\text{Ph}_2\text{Ppy}$ .

The reaction of  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  and  $\text{Pd}(1,5\text{-COD})\text{Cl}_2$  with equimolar  $\text{Ph}_2\text{Ppy}$  produced the complex with chelate ring  $\text{Pd}(\eta^2\text{-Ph}_2\text{Ppy})\text{Cl}_2$  [11], instead of the  $\text{Ph}_2\text{Ppy}$  P-dentated complexes. The reaction of  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{Ph}_2\text{Ppy}$  gave a  $\text{Ph}_2\text{Ppy}$  chelate manganese carbonyl derivative, **3.1** [28]. In particular, when a saturated solution of chlorine in  $\text{CH}_2\text{Cl}_2$  was added into a  $\text{CH}_2\text{Cl}_2$  solution containing the cluster complex  $[\text{Ru}(\text{Ph}_2\text{Ppy})(\text{CO})_3]_3$ , a mononuclear complex  $\text{Ru}(\eta^2\text{-Ph}_2\text{Ppy})(\text{CO})_2\text{Cl}_2$  was formed [20].



### 3.2. Structure

The structure of a number of  $\text{Ph}_2\text{Ppy}$  chelate complexes have been determined for the examples  $\text{Ru}(\eta^2\text{-Ph}_2\text{Ppy})(\text{CO})\text{Cl}_2$  (**3.2**),  $[\text{Pt}(\eta^2\text{-Ph}_2\text{Ppy})(\text{Ph}_2\text{Ppy})\text{Cl}]^+$  (**3.3**) and  $[\text{Pt}(\eta^2\text{-Ph}_2\text{Ppy})\text{Ph}_2\text{Ppy}]\text{Me}]^+$  (**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  $90^\circ$ . The major deviation comes from  $\text{P-M-N}$  which is compressed to nearly  $70^\circ$ . The other three angles are opened up, so that the  $\text{P-M-L}$  angle ( $\text{L}$  is trans to the nitrogen atom) is over  $100^\circ$  and the other two angles are near to the ideal value of  $90^\circ$ .

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

In the complex **3.4**, the  $\text{Pt-P}(1)$  distance is much longer than that of  $\text{Pt-P}(2)$ . 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,  $\text{U}(\text{BH}_4)_3(\eta^2\text{-Ph}_2\text{Ppy})_2$ . The X-ray crystal structure of  $\text{U}(\text{BH}_4)_3(\eta^2\text{-Ph}_2\text{Ppy})_2$  shows  $\text{N-U-P} = 52.8^\circ$ ,  $\text{B-U-N} = 90.1^\circ$ ,  $\text{P-U-P}' = 74.3^\circ$  and  $\text{N-U-N}' = 179.8^\circ$ . These distortions arise from the presence of the tridentate equatorial  $\text{BH}_4$  group [33].

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

Table 3

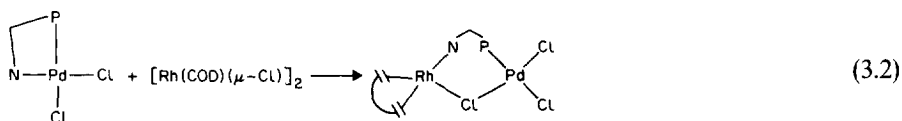
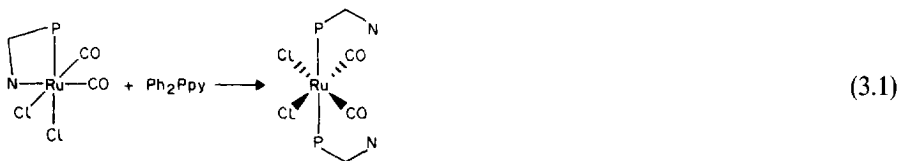
Selected bond distances (Å) for Complexes 3.2–3.4

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<sub>2</sub>Ppy 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<sub>2</sub>Ppy chelate complexes are unstable. It is easy to open the ring, and the nitrogen atom which is a weaker  $\pi$ -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<sub>2</sub>Ppy 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].



## 4. Complexes with bridging Ph<sub>2</sub>Ppy

Bridged binuclear complexes using Ph<sub>2</sub>Ppy to hold two metal atoms in close proximity have received considerable attention in recent years. Ph<sub>2</sub>Ppy 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<sub>2</sub>Ppy 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

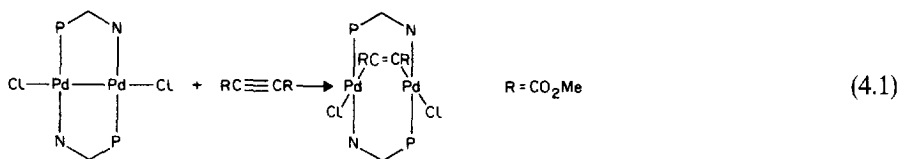
a M—M bond is rare, and the steric factors usually confine the formation of the M—M bonds.

We have commented previously that Alcock et al. have synthesized  $\text{Ag}_2(\mu\text{-Ph}_2\text{Ppy})(\text{Ph}_2\text{Ppy})_2(\mu\text{-Cl})_2$ , 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  $\approx$  2.04 Å), but the distance is shorter than the sum of the van der Waals radii [29].

Similarly, in the complex  $\text{Ag}_2(\mu\text{-Ph}_2\text{Ppy})_2(\text{NO}_3)_2(\text{HT})$ , 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  $\text{Ph}_2\text{Ppy}$  bridge, that the complex  $(1,5\text{-COD})\text{RhPd}(\mu\text{-Cl})(\mu\text{-Ph}_2\text{Ppy})\text{Cl}_2$  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  $\text{Ph}_2\text{Ppy}$  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  $[\text{Pd}_2\text{Cl}_2(\text{Ph}_2\text{Ppy})_2]$  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].

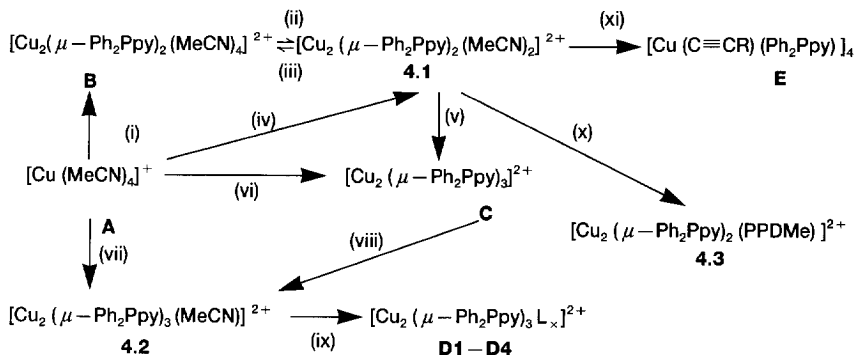


Binuclear copper(I) and copper(II) complexes form a significant group of derivatives in the coordination chemistry of copper which are currently receiving special attention, mainly because of studies related to the reactivity of dioxygen, not only in biological systems but also in catalytic oxidation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

Lastra and co-workers have synthesized the first copper(I) complexes containing  $\text{Ph}_2\text{Ppy}$  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  $\text{Ph}_2\text{Ppy}$  molecules in a HT arrangement, resulting in a rare staggered conformation of the eight-membered ring  $\text{Cu}_2\text{P}_2\text{N}_2\text{C}_2$ , 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].

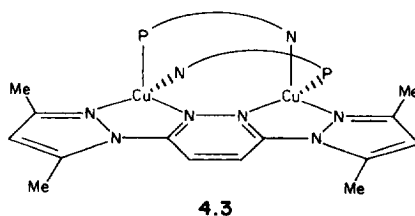
In complex **4.2** the Cu—Cu interaction is weak, or shown by the Cu—Cu separation of 2.721 Å, even though three bulky bridging  $\text{Ph}_2\text{Ppy}$  ligands should produce severe geometric constraints in a binuclear complex to hold the two metals in close proximity [37].



Scheme 1. (i) + Ph<sub>2</sub>Ppy (MeCN, r.t.); (ii) – 2MeCN (CH<sub>2</sub>Cl<sub>2</sub>, r.t.); (iii) MeCN solution; (iv) Ph<sub>2</sub>Ppy (CH<sub>2</sub>Cl<sub>2</sub>, r.t.); (v) refluxing CHCl<sub>3</sub>; (vi) + Ph<sub>2</sub>Ppy (excess) (refluxing acetone); (vii) + Ph<sub>2</sub>Ppy (excess) (refluxing MeCN); (viii) MeCN solution; (ix) + L, – MeCN (x = 1, L = 2-Mepy, **D1**; x = 2, L = P(OMe)<sub>3</sub>, PMe<sub>3</sub>, 4-Mepy, **D2–D4**) (CH<sub>2</sub>Cl<sub>2</sub>, r.t.) [37]; (x) + PPDMe (– MeCN) [35]; (xi) + HC≡CR (R = Ph, <sup>t</sup>Bu) (KOH excess) (CH<sub>2</sub>Cl<sub>2</sub>/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<sub>2</sub>Ppy 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].



#### 4.2. Complexes with metal–metal bonds

This class of complexes is the most important in Ph<sub>2</sub>Ppy chemistry. The two sorts of donor atoms in Ph<sub>2</sub>Ppy can stabilize metals in the lower oxidation state [39]. The rigidity of the short-bite Ph<sub>2</sub>Ppy ligand forces the formation of the M–M bond when the two donor atoms coordinate with two metal atoms. Thus Ph<sub>2</sub>Ppy is effective in stabilizing well defined homo- and heterobinuclear transition metal

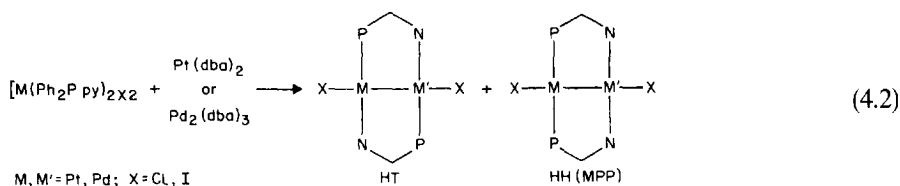
complexes [2,5]. In particular, one can prepare bridged heterobinuclear transition metal complexes in high yield [1,30]. So the binuclear transition metal complexes of  $\text{Ph}_2\text{Ppy}$  and their reaction chemistry have excited considerable interest in recent times.

#### 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  $\text{SO}_2$ , 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  $\text{Ph}_2\text{Ppy}$  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  $\text{M}-\text{X}$  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  $\text{Ph}_2\text{Ppy}$ . These reactions are shown in Eq. (4.2) [12,15,30].



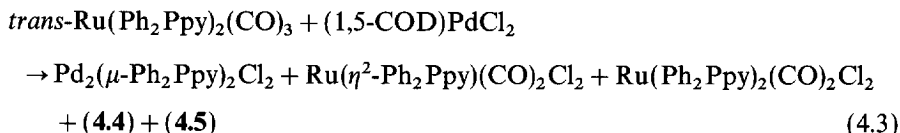
Both HH and HT isomers are obtained from this reaction. The difference in the configuration of the reactants induces different main products.

When  $\text{M} = \text{Pt}$ , if  $\text{X} = \text{Cl}$  the configuration of the main product is HT, but if  $\text{X} = \text{I}$  it is HH. When  $\text{M} = \text{Pd}$ , the main product is the HH isomer. This can be explained inasmuch as *trans*- $\text{Pt}(\text{Ph}_2\text{Ppy})_2\text{X}_2$  reacts more readily than *cis*- $\text{Pt}(\text{Ph}_2\text{Ppy})_2\text{X}_2$  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  $\text{Pt}(\text{Ph}_2\text{Ppy})_2\text{I}_2$ , 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.  $\text{Pt}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$ , 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,  $\text{M}_2(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_2$  (HT) ( $\text{M} = \text{Pt, Pd}$ ),  $\text{Pt}_2(\mu\text{-Ph}_2\text{Ppy})_2\text{I}_2$  (HH),  $\text{PtPd}(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_2$  (HT),  $\text{PtPd}(\mu\text{-Ph}_2\text{Ppy})_2\text{I}_2$  (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

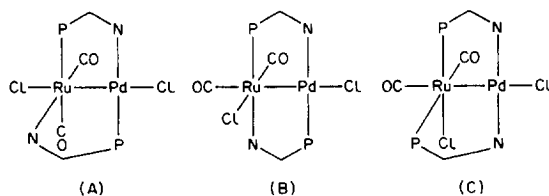
faster for each halo series of the  $\text{Ph}_2\text{Ppy}$  complexes, in the order of  $\text{Cl} < \text{Br} < \text{I}$ , while the order is reversed in isomerization,  $\text{Cl} > \text{Br} > \text{I}$  [40,41].

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



The complex  $\text{Ru}(\text{Ph}_2\text{Ppy})_2(\text{CO})_3$  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  $\text{Ru}(\text{Ph}_3\text{P})_2(\text{CO})_3$  and  $(1,5\text{-COD})\text{PdCl}_2$ , it is found that a natural redox process would take effect in the previous reaction.

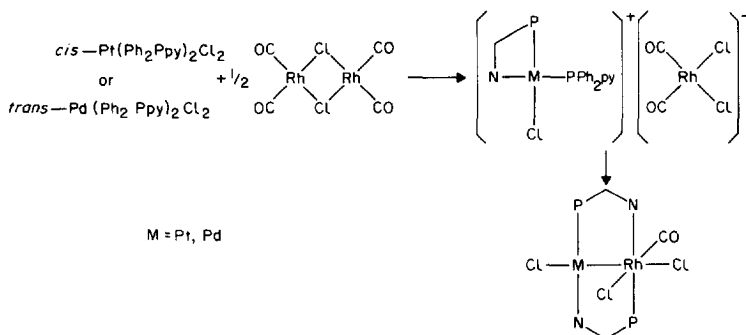
**4.4** and **4.5** are isomers. The structure of **4.4** is (A); the structure of **4.5** is limited to (B) or (C), but there are insufficient data available to distinguish between these two possibilities.



Balch and co-workers have studied the synthesis of RhPd binuclear complexes. The reaction of  $[\text{Rh}(\text{Ph}_2\text{Ppy})_2(\text{CNR})_2]\text{X}$  ( $\text{X} = \text{PF}_6^-, \text{BPh}_4^-$ ) with  $\text{Pd}(1,5\text{-COD})\text{Cl}_2$  or  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$  leads to the ionic complexes  $[\text{RhPd}(\mu\text{-Ph}_2\text{Ppy})_2(\text{CNR})_2\text{Cl}_2]\text{X}$  [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.

$^{31}\text{P}\{^1\text{H}\}$  NMR spectra have shown that the products depend on the leaving groups initially bound to palladium but are essentially independent of the anion ( $\text{BPh}_4^-$  or  $\text{PF}_6^-$ ) that accompanies the rhodium cation. With a good leaving group on palladium, as is the case with  $(\text{PhCN})_2\text{PdCl}_2$ , 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  $[\text{Rh}(\text{MeCN})_4][\text{BPh}_4^-]$  with *trans*- $\text{Pd}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$  yields the thermodynamically stable HT isomer [15].

The oxidative addition of  $(1,5\text{-COD})\text{PdCl}_2$  with *trans*- $\text{Rh}(\text{Ph}_2\text{Ppy})_2(\text{CO})\text{Cl}$  gives the neutral binuclear complex  $\text{RhPd}(\mu\text{-Ph}_2\text{Ppy})_2(\text{CO})\text{Cl}_3$  (HT) [4,13,15,30]. However, the reaction between  $(1,5\text{-COD})\text{PtCl}_2$  and *trans*- $\text{Rh}(\text{Ph}_2\text{Ppy})_2(\text{CO})\text{Cl}$  pro-



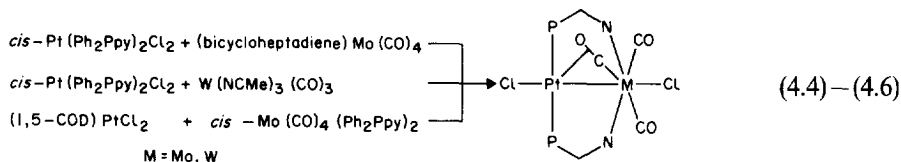
Scheme 2.

duces the homobinuclear complex  $\text{Rh}_2(\mu\text{-CO})(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_2$  (HT) and  $\text{cis-Pt}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$  instead of the desired heterobinuclear complex [1,4,23].

The reaction between  $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$  and  $\text{M}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$  ( $M = \text{Pt}, \text{Pd}$ ) can yield  $\text{RhM}(\mu\text{-Ph}_2\text{Ppy})_2(\text{CO})\text{Cl}_3$  (HT). Formally, this seems to improve an oxidative addition of the  $\text{M}-\text{Cl}$  bond to  $\text{Rh}(\text{I})$ , but in fact an ion pair mechanism is in action (see Scheme 2).

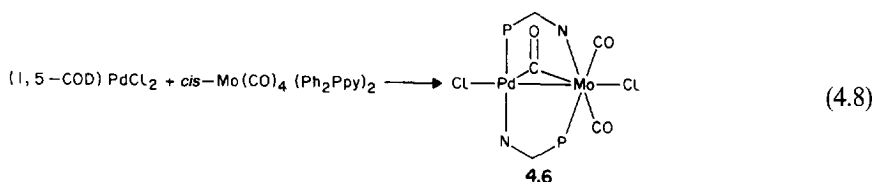
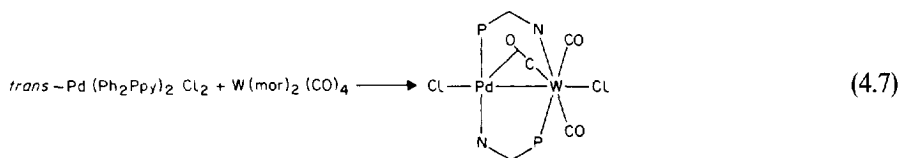
In this reaction an ion pair is obtained. This may be related to the ability of  $\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4$  to abstract halide ions from metal complexes [42]. In addition to accomplishing the halide transfer, ionization also begins the process of reorientation of the phosphine ligand, 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,  $\text{PtRh}$  and  $\text{PdRh}$ . The reaction to form the  $\text{RhPt}$  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  $\text{M}-\text{X}$  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].



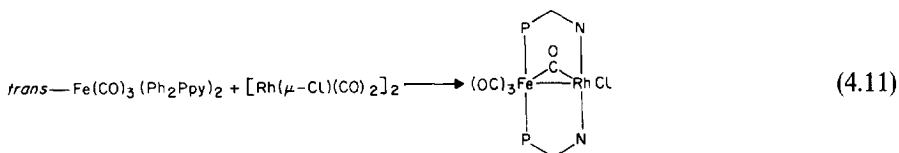
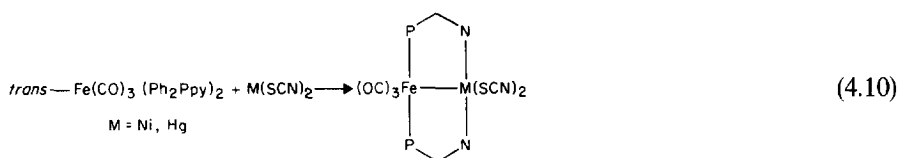
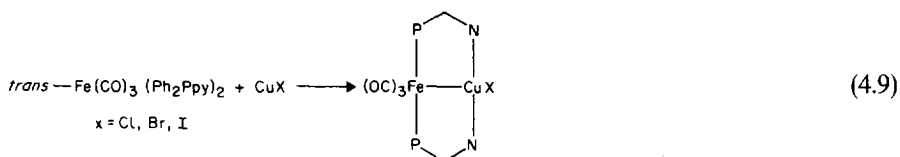
The iodine complex analogous to 4.6 is obtained by the oxidative addition of  $\text{Pd}_2(\text{dba})_3$  with  $\text{MoI}_2(\text{Ph}_2\text{Ppy})_2(\text{CO})_3$  [46].

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



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

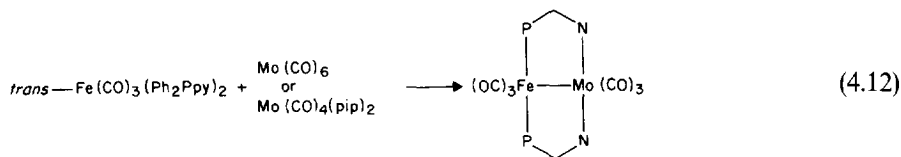
The structure of the FeHg complex has been determined. A donor-acceptor bond exists between Fe and Hg, and Hg is inclined to be a  $\pi$ -acceptor. The N–Hg separations are 2.595 Å and 2.867 Å, respectively, and in the range of the van der Waals radii. The Fe–Hg distance of 2.648 Å is longer than that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



Our work has further shown that  $\text{trans-Fe}(\text{Ph}_2\text{Ppy})_2(\text{CO})_3$  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.





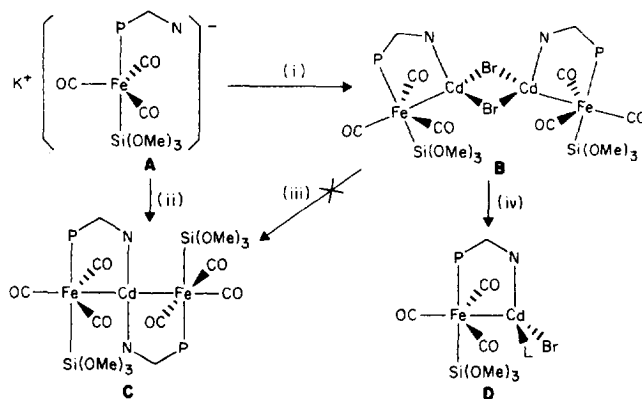
4.2.1.1.3. *Substitution.* Anionic silyl complexes readily undergo substitution with metal halides to yield polynuclear complexes. This kind of reaction, described in Scheme 3, has been reported by Fischer and co-workers [48].

The different outcome of the reactions of **A** with  $\text{CdBr}_2$  and  $\text{CdCl}_2$  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.

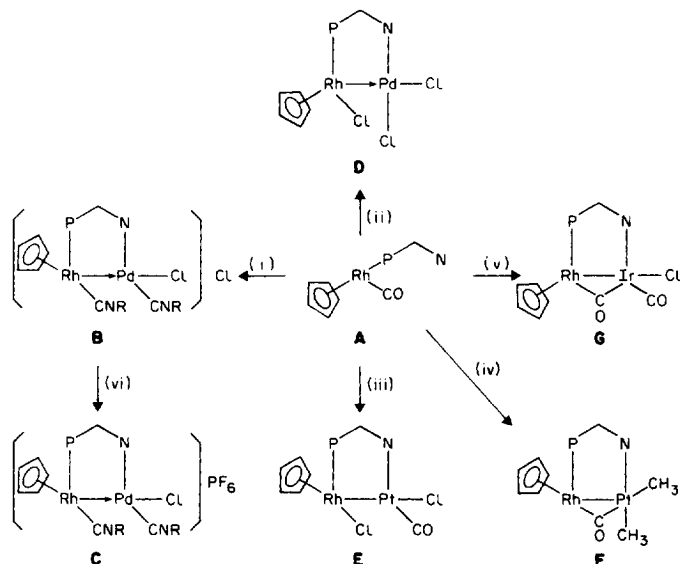
4.2.1.1.4. *A complicated mechanism.* Recently, Faraone and co-workers have studied the synthesis of  $\text{Rh-M}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) heterobinuclear complexes containing one bridging  $\text{Ph}_2\text{Ppy}$ , and have proposed that steric factors may be determining the course of the reactions.

They have studied the reactions of  $\text{Rh}(\eta^5\text{-Cp})(\text{Ph}_2\text{Ppy})(\text{CO})$  and  $\text{Rh}(1,5\text{-COD})(\text{Ph}_2\text{Ppy})\text{Cl}$ , respectively (Schemes 4 and 5) [3,8,11].

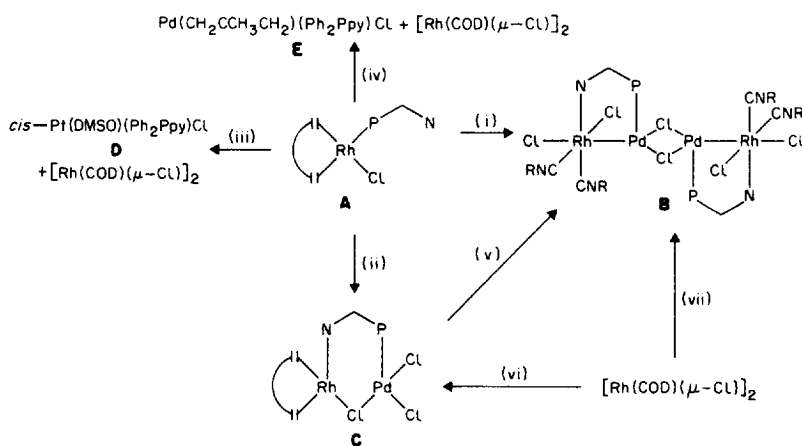
The reactions between **A** and  $\text{d}^8\text{Pt(II)}$ ,  $\text{Pd(II)}$  or  $\text{Ir(I)}$  complexes proceed by coordination of the pyridine nitrogen atom of **A** to the metal centers. The reactions appear to be strongly dependent on the presence of labile ligands (e.g.  $\text{DMSO}$ ,  $\text{COD}$ ) 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  $\text{Ph}_2\text{Ppy}$  ligand induces  $\text{M-M}$  bond formation. Steric interactions between the ligands coordinated to  $\text{Pd(II)}$  and  $\text{Pt(II)}$  and the ligands of the five-coordinated rhodium(I) center can give rise to



Scheme 3. (i) Excess  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}/\text{THF}$ ,  $-\text{KBr}$ ; (ii) excess  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ,  $-\text{KCl}$ ; (iii) **A**; (iv)  $\text{L} = 4\text{-picoline}$ .



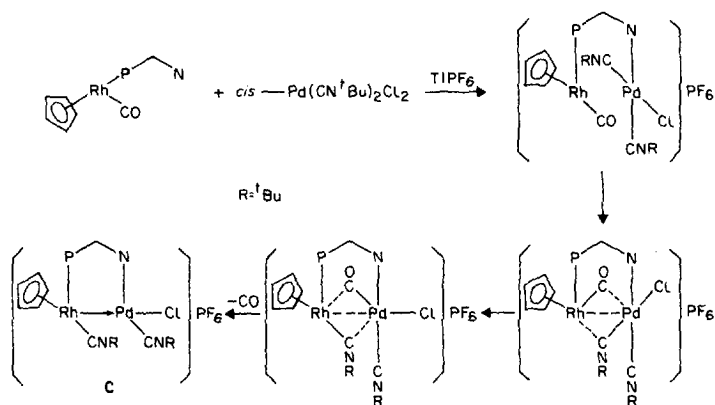
Scheme 4. (i) *cis*-Pd(CN<sup>t</sup>Bu)<sub>2</sub>Cl<sub>2</sub>; (ii) Pd(COD)Cl<sub>2</sub>; (iii) *cis*-Pd(DMSO)<sub>2</sub>Cl<sub>2</sub>; (iv) *cis*-Pd(DMSO)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>; (v) Ir(CO)<sub>2</sub>Cl(*p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>); (vi) TlPF<sub>6</sub>.



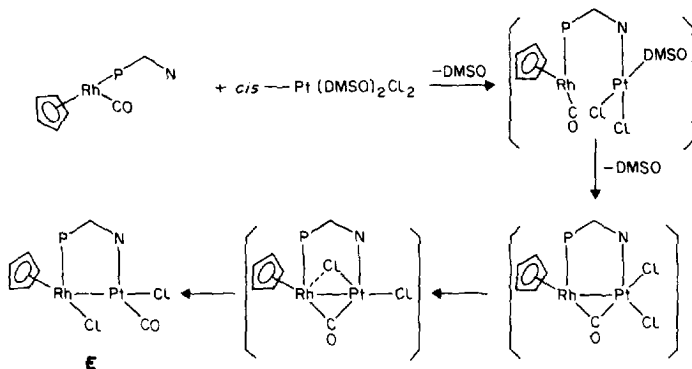
Scheme 5. (i) *cis*-Pd(CN<sup>t</sup>Bu)<sub>2</sub>Cl<sub>2</sub>; (ii) Pd(COD)Cl<sub>2</sub> or Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>; (iii) *cis*-Pt(DMSO)<sub>2</sub>Cl<sub>2</sub>; (iv) [Pd(CH<sub>2</sub>CCH<sub>3</sub>CH<sub>2</sub>)Cl]<sub>2</sub>; (v) <sup>t</sup>BuNC; (vi) Pd(η<sup>2</sup>-Ph<sub>2</sub>Ppy)Cl<sub>2</sub>; (vii) *cis*-Pd(CN<sup>t</sup>Bu)(Ph<sub>2</sub>Ppy)Cl<sub>2</sub>.

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.

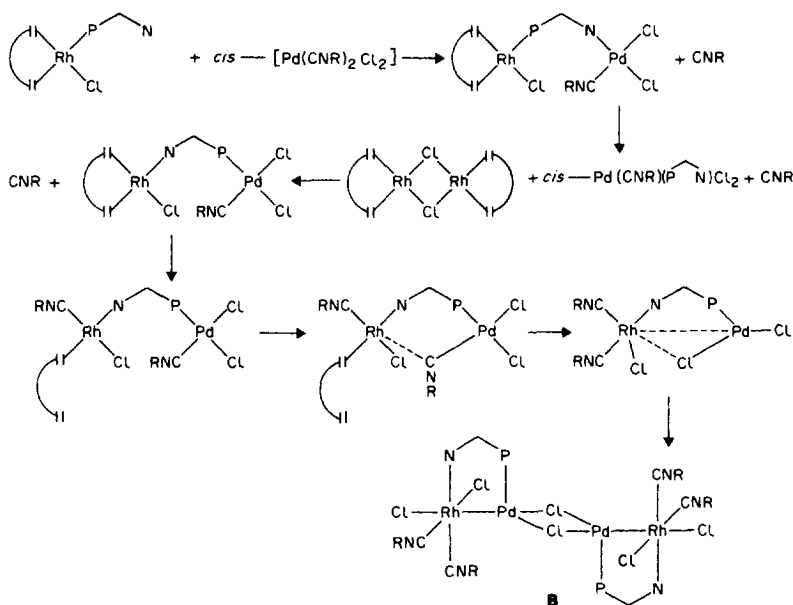
The reactions of  $\text{Rh}(1,5\text{-COD})(\text{Ph}_2\text{Ppy})\text{Cl}$  with  $\text{Pd}(\text{II})$  or  $\text{Pt}(\text{II})$ , shown in Scheme 5, also proceed by coordination of the pyridine nitrogen atom [11].

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

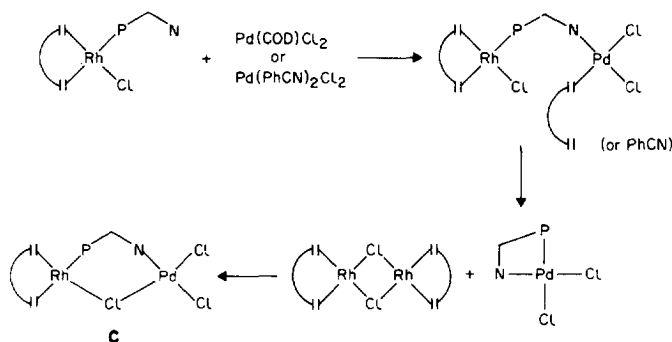
chloride bridge and the M–M bond. The rigidity and the short-bite angle of the  $\text{Ph}_2\text{Ppy}$  bridging ligand are very important in these processes, shown in Scheme 8 [11]. This process is supported by reaction (vii).

The process of (ii) is also similar to the above but, significantly, the oxidative addition of  $\text{Pd}-\text{Cl}$  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].

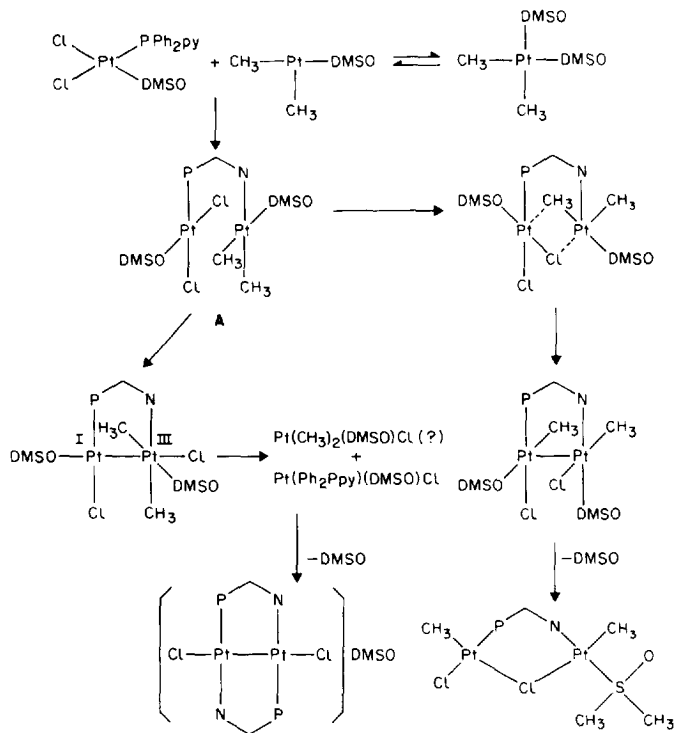
Similarly, the reaction between  $\text{cis-Pt}(\text{DMSO})(\text{Ph}_2\text{Ppy})\text{Cl}_2$  and  $\text{Pt}(\text{CH}_3)_2(\text{DMSO})$  gives a product which is formed by a methyl-for-chloride exchange process. At the same time, a redox product is also isolated (Scheme 10) [49].



Scheme 8.



Scheme 9.



Scheme 10.

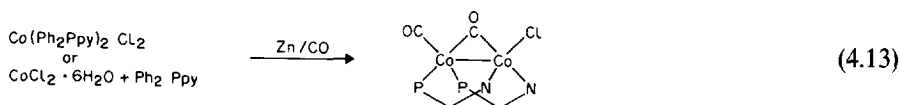
The product of the oxidative addition should be a very unstable Pt(I)–Pt(III) intermediate whose binuclear structure can be disrupted, breaking the Pt–N bond. Although steric requirements are an important determinant of the breaking of a metal–ligand bond when  $\text{Ph}_2\text{Ppy}$  is coordinated 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  $[\text{Pt}(\text{DMSO})(\text{Ph}_2\text{Ppy})\text{Cl}]$ . 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  $\text{Ph}_2\text{Ppy}$  the metal centers exhibit different character and reactivity. Studies of  $\text{Ph}_2\text{Ppy}$ -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  $\text{Ph}_2\text{Ppy}$  may be obtained by oxidative addition (see Section 4.2.1.1).

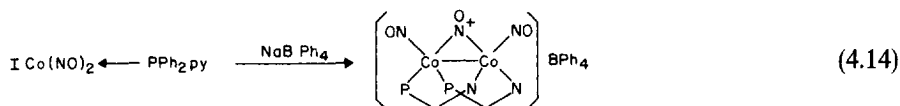
This kind of homobinuclear complex can also be formed by reductive carbonyla-

tion. We have prepared the first novel binuclear cobalt carbonyl complex with mixed valence (see Eq. (4.13)) [25,50]

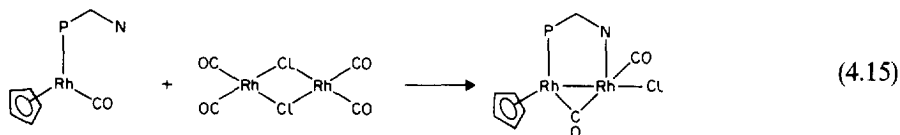


A possible mechanism is shown in Scheme 11.

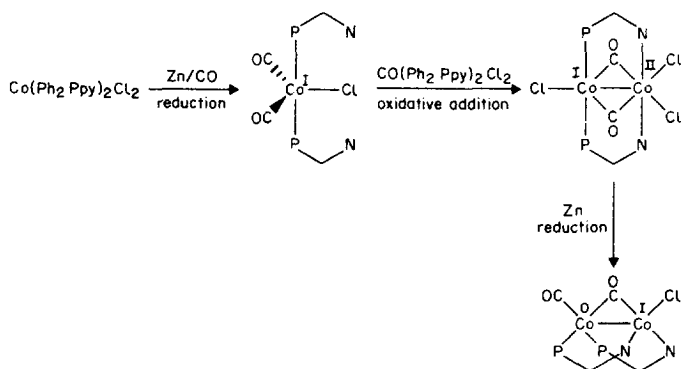
Roustan et al. have prepared a dicobalt complex from a mononuclear complex in which a bridging nitrosyl group is present (Eq. (4.14)) [22]. However, when  $\text{AgBF}_4$  is used as a halide abstractor, only the mononuclear complex  $[\text{Co}(\text{NO})_2(\text{Ph}_2\text{Ppy})]^+ \text{BF}_4^-$  is obtained. This is attributed to the fact that only  $\text{NaBPh}_4$  can act simultaneously as a halide abstractor and a nitrosyl abstractor.



Faraone and co-workers have obtained the rhodium homobinuclear complex from  $\text{Rh}(\eta^5\text{-Cp})(\text{CO})(\text{Ph}_2\text{Ppy})$  (see Eq. (4.15)) [8]. The characters of the two Rh centers are different in the product.

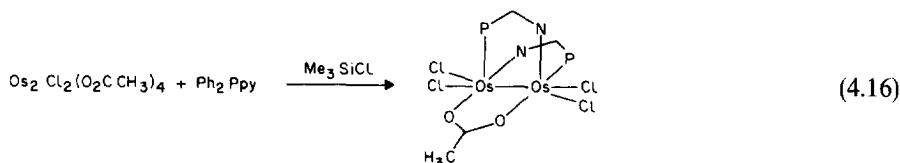


4.2.1.2.2. *Homobinuclear complexes as the starting species.* Cotton and co-workers have reported the synthesis of a series of homobinuclear complexes with  $\text{Ph}_2\text{Ppy}$  bridges.



Scheme 11.

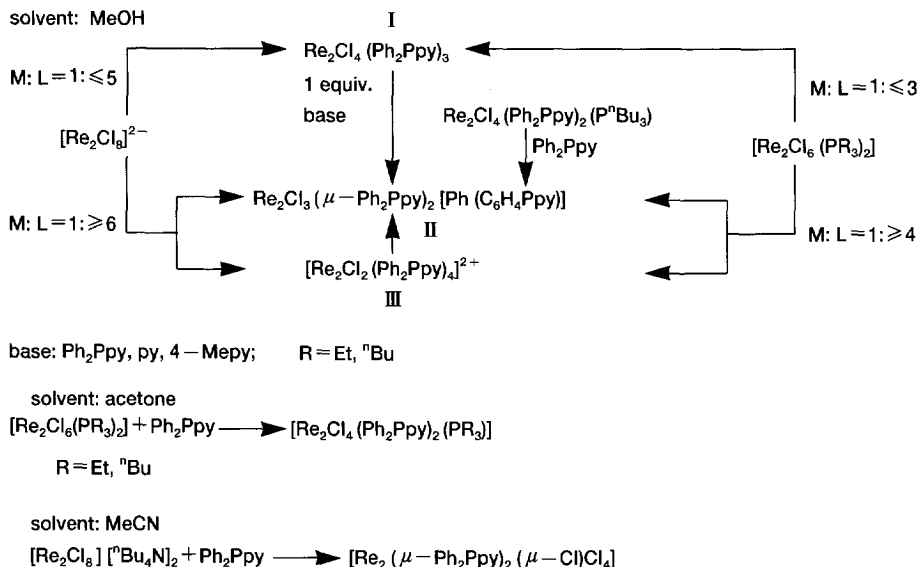
4.2.1.2.2.1. *Reduction.* The quadruply-bonded  $\text{Re}_2^{6+}$  and triply-bonded  $\text{Os}_2^{6+}$  complexes can be reduced by the  $\text{Ph}_2\text{Ppy}$  ligand to give the  $\text{Re}_2^{4+}$  and  $\text{Os}_2^{5+}$  complexes with  $\text{Ph}_2\text{Ppy}$  bridges (an example is shown in Eq. (4.16)).



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

The reduction of the  $\text{Re}_2^{6+}$  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  $\text{M}_2\text{L}_8$  type, and a rare example of a multiply-bonded dimetal unit complexed by four neutral bridging ligands [2,53].

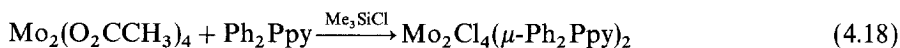
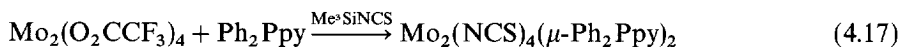
Cotton and co-workers have studied the reaction of  $[\text{Re}_2\text{Cl}_8]^{2-}$  with  $\text{Ph}_2\text{Ppy}$  in methanol with different stoichiometries. The results showed that both **I** and **III** can be regarded as “intermediates” in the formation of **II**, since both can be so converted under a variety of conditions. When other solvents are used, different products are obtained.



Scheme 12.

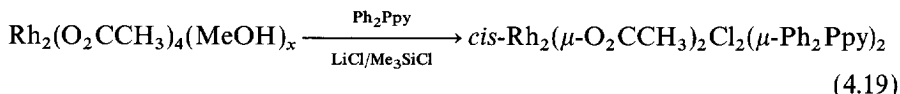
4.2.1.2.2.2. *Disproportionation*. Cotton's group have proposed that a disproportionation mechanism (via **4.7**) could be operative rather than the formation of **4.8** being a consequence of the direct phosphine-induced reduction of **4.7** (Scheme 13) [54,55].

4.2.1.2.2.3. *Substitution*. Cotton and co-workers have also prepared the quadruply-bonded  $\text{Mo}_2^{4+}$  complexes (Eqs. (4.17) and (4.18)) [56,57].



Similarly, treatment of  $[\text{Mo}_2(\text{O}_2\text{CCMe}_3)_3(\text{MeCN})_2]\text{BF}_4$  with 1 equivalent of  $\text{Ph}_2\text{Ppy}$ , or  $[\text{Mo}_2(\text{O}_2\text{CCMe}_3)_2(\text{MeCN})_6]\text{BF}_4$  with 2 equivalent of  $\text{Ph}_2\text{Ppy}$ , yields  $[\text{Mo}_2(\text{O}_2\text{CCMe}_3)_2(\text{Ph}_2\text{Ppy})_2](\text{BF}_4)_2$  in which the two bridging ligands  $\text{Ph}_2\text{Ppy}$  are arranged in a cis position as shown by  $^1\text{H}$  NMR [58].

However, further replacement of the remaining acetate ligand in the  $\text{Rh}_2^{4+}$  core has not been successful, even when  $\text{Me}_3\text{SiCl}$  or  $\text{LiCl}$  are used (see Eq. (4.19)) [52].

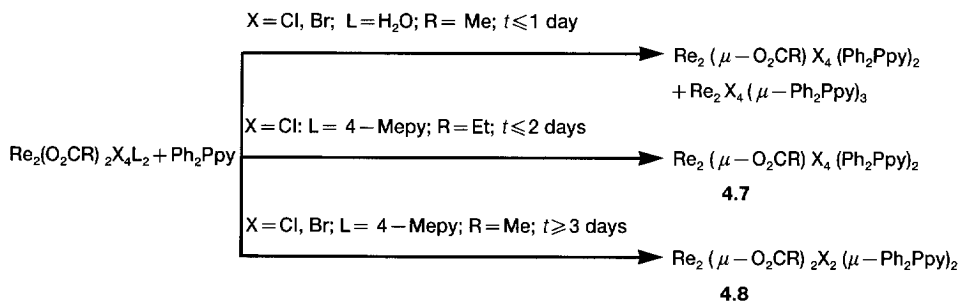


When  $\text{Rh}_2(\text{form})_2(\text{O}_2\text{CCF}_3)_2(\text{H}_2\text{O})_2$  reacts with  $\text{Ph}_2\text{Ppy}$ , different products are obtained depending on the stoichiometry of the reagents [59]. When the mole ratio is 1:1, **4.9** is obtained, and **4.10** can be formed when the ratio is increased to 1:2 or 1:4. The  $\text{Rh}-(\text{form})_2-\text{Rh}$  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.

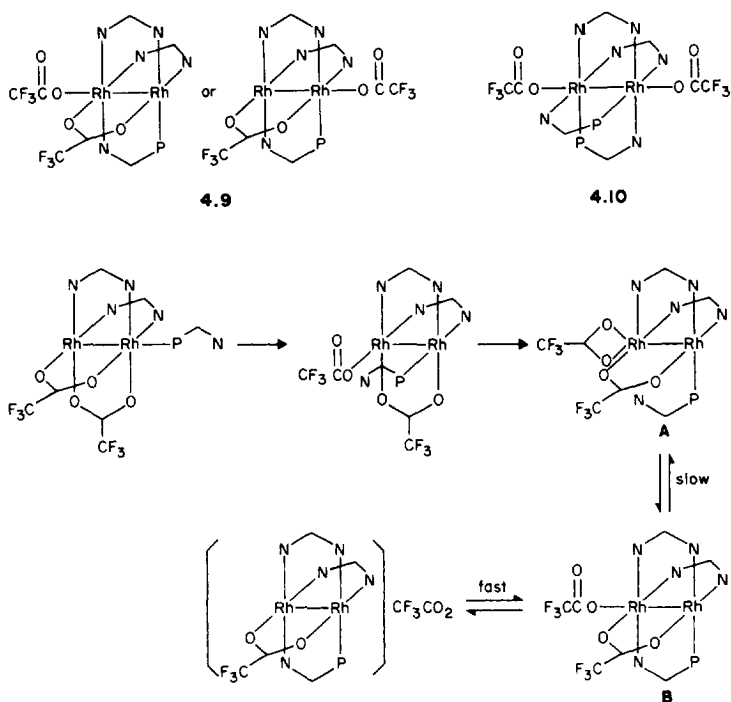
Cotton's group have proposed a possible mechanism operating during the reaction, on the basis of  $^{31}\text{P}$  NMR spectroscopy (Scheme 14).

At 225 K a 1:1 adduct with a linear arrangement of the  $\text{Rh}-\text{Rh}-\text{P}$  atoms is formed when the ratio is 1:1, and the linear  $\text{Rh}-\text{Rh}-\text{P}$  can convert irreversibly to



Scheme 13.





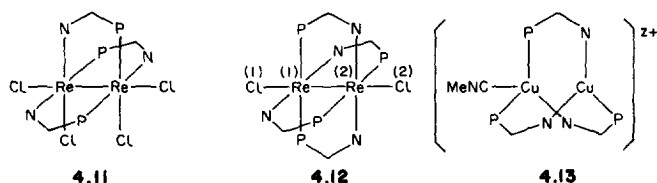
Scheme 14.

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<sub>2</sub>Ppy is added, the <sup>31</sup>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<sub>2</sub>Ppy 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

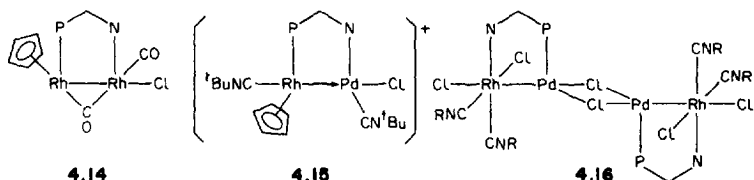
In the binuclear complexes containing Ph<sub>2</sub>Ppy bridging ligands, the number of Ph<sub>2</sub>Ppy bridging ligands can change from one to four. Commonly, the number of Ph<sub>2</sub>Ppy ligands is two, while complexes containing three or four Ph<sub>2</sub>Ppy bridging ligands are rare. Cotton and co-workers have synthesized two novel complexes, **4.11** and **4.12**, in which the Re<sub>2</sub><sup>4+</sup> unit is bridged by three or four Ph<sub>2</sub>Ppy ligands [2,53]. A copper binuclear complex with three bridging Ph<sub>2</sub>Ppy 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<sub>2</sub>Ppy ligands. For example, in **4.12** the two Re—Cl bond lengths differ in spite of the similar



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<sub>2</sub>Ppy 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].



The complexes with two Ph<sub>2</sub>Ppy 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<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub> [12,60], RhPd(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(CO)Cl<sub>3</sub>, [4,13], [Mo<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(NCS)<sub>4</sub>](THF)<sub>2</sub> [57] etc. In all these complexes, the rigidity of the short-bite Ph<sub>2</sub>Ppy 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 torsional angle larger than 10°.

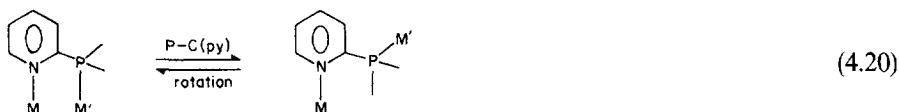
The trans,trans-HH orientation is thermodynamically unstable and can transfer to HT configuration on heating, as for example in PtPd(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub> [15].

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<sub>2</sub>Cl<sub>4</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(PEt<sub>3</sub>) possesses the cis,cis-HT configuration [53].

Binuclear complexes with other bridging ligands usually have trans,trans-HT arrangements. Examples include Rh<sub>2</sub>(μ-CO)(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>, which has a single atom bridge [4,23]; Rh<sub>2</sub>(μ-RC=CR)(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub> (R = CH<sub>3</sub>CO<sub>2</sub>), which has a biatom bridge [61]; and Rh<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-NO<sub>3</sub>)(CO)Cl<sub>3</sub>, 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)).



Lengthening of the M–M' distance by rotation about the P–C(py) bond is, however, limited by the presence of the second Ph<sub>2</sub>Ppy ligand. This leads to a skewing about the M–M' axis of the rigid Ph<sub>2</sub>Ppy 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'(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-CO)(CO)<sub>2</sub>Cl<sub>2</sub> (M = Pt, Pd; M' = Mo, W), the two bridging Ph<sub>2</sub>Ppy 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(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(CO)Cl<sub>3</sub> [13], PdRh(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(CO)Cl<sub>3</sub> [1,4,13] and RuPd(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub> [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].

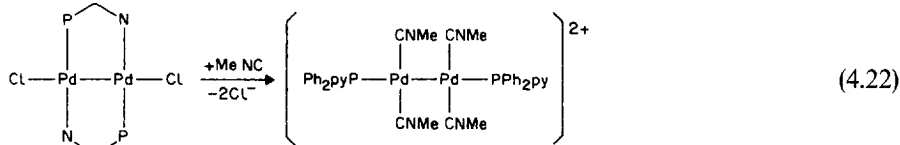
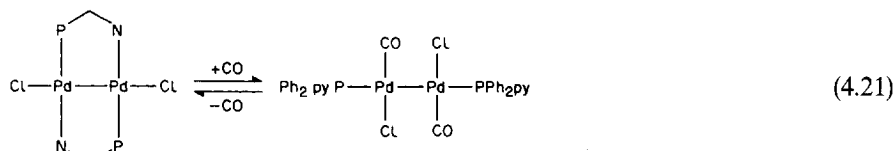
The cobalt binuclear complexes also possess novel structures. For example, both Co<sup>0</sup>Co<sup>I</sup> (μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-CO)(CO)Cl [25,50] and [Co<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-NO)(NO)<sub>2</sub>]-BPh<sub>4</sub> have W-frame structures in which the two bridging Ph<sub>2</sub>Ppy ligands are all in a HH arrangement [22]; and in the complex Co<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-CO)<sub>2</sub>Cl<sub>3</sub>, 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<sub>2</sub>Ppy ligands assume the HT arrangement and are cis to one another on every metal atom; for example, Os<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-O<sub>2</sub>CCH<sub>3</sub>)Cl<sub>4</sub> [51,52], [Re<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-O<sub>2</sub>CCH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> [55], Rh<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> [52], Rh<sub>2</sub>(form)<sub>2</sub>-(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> [59], etc. However, in Mo<sub>2</sub>(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-O<sub>2</sub>CR)<sub>2</sub>Cl<sub>2</sub> the two N–Mo–P units are nearly linear (165.7°).

### 4.2.3. Reaction

There have been many studies on the reactions of  $\text{Ph}_2\text{Ppy}$ -bridged binuclear complexes with a  $\text{M}-\text{M}$  bond, some of which are very novel. However, attempts to insert small molecules such as CO, alkyne, cyanide or isocyanide into the  $\text{M}-\text{M}$  bond have proved unsuccessful.

**4.2.3.1. Ring opening.** The  $\text{M}-\text{M}$  bond is unreactive in  $\text{Ph}_2\text{Ppy}$ -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  $\text{Ph}_2\text{Ppy}$  ligand. This ligand lacks the articulation available to  $\text{dppm}$  which allows the  $\text{M}-\text{M}$  distance in its bridged complexes to vary from 2.2 to 3.5 Å.  $\text{Ph}_2\text{Ppy}$ , because of the planar nature of the pyridine ring and the short  $\text{N}-\text{C}$  distance, does not appear able to span the long end of  $\text{M}-\text{M}$  separations spanned by  $\text{dppm}$ . Consequently the  $\text{M}-\text{M}$  bond is not able to open up to form an A-frame structure (Eqs. (4.21)–(4.22)) [12]

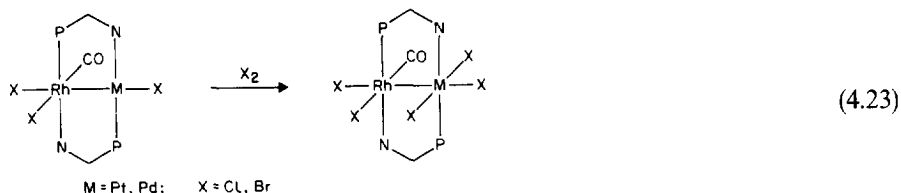


**4.2.3.2. Ligand exchange.** The bridging and terminal ligands in  $\text{Ph}_2\text{Ppy}$ -bridged complexes with a  $\text{M}-\text{M}$  bond can be displaced by other ligands.

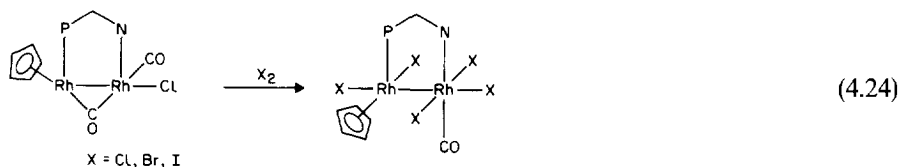
It has been reported that the bridged  $\text{Ph}_2\text{Ppy}$  ligand can be successively displaced by diphosphine ligands  $\text{dpmMe}$  and  $\text{dppm}$  to give  $\text{Pd}_2\text{Cl}_2(\text{dpmMe})_2$  and  $\text{Pd}_2\text{Cl}_2(\text{dpmMe})(\text{dppm})$  [64]. The bridging carbonyl ligands in both  $\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-CO})\text{Cl}_2$  [8,18] and  $(\eta^5\text{-Cp})\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})(\mu\text{-CO})(\text{CO})\text{Cl}$  [61] can be displaced by  $\text{SO}_2$  or alkynes with an electron-withdrawing group, such as  $\text{COOR}$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ ) or  $\text{CF}_3$ . Moreover, replacement of the terminal carbonyl by  $\text{RNC}$  can also occur on the complex  $\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})_2(\text{CO})_2\text{Cl}_4$  [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  $\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-RC}=\text{CR}')\text{Cl}_2$  ( $\text{R} = \text{R}' = \text{CO}_2\text{CH}_3$  or  $\text{R} = \text{CO}_2\text{CH}_3, \text{R}' = \text{H}$ ) leads to the formation of  $\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-RC}=\text{CR}')(\text{CO})_2\text{Cl}_2$  [8,18], while the reactions of CO or  $\text{SO}_2$  with  $(\eta^5\text{-Cp})\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})(\mu\text{-RC}=\text{CR}')(\text{CO})\text{Cl}$  ( $\text{R} = \text{R}' = \text{CO}_2\text{CH}_3$  or  $\text{CO}_2\text{C}_2\text{H}_5$ ) give the corresponding additive products  $(\eta^5\text{-Cp})\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})(\mu\text{-RC}=\text{CR}')(\text{CO})(\text{L})\text{Cl}$  ( $\text{L} = \text{CO}$  or  $\text{SO}_2$ ) [61].

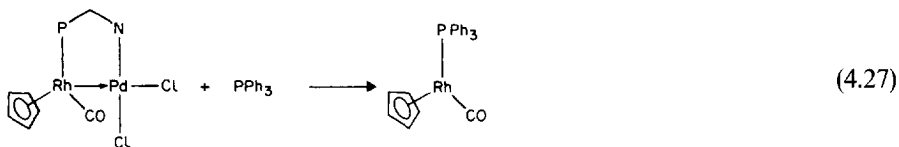
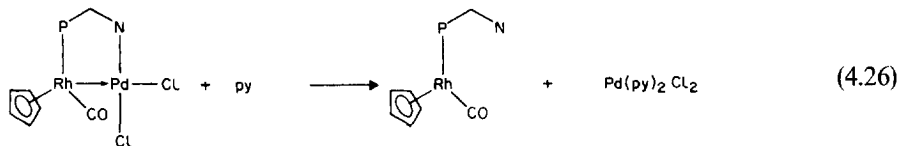
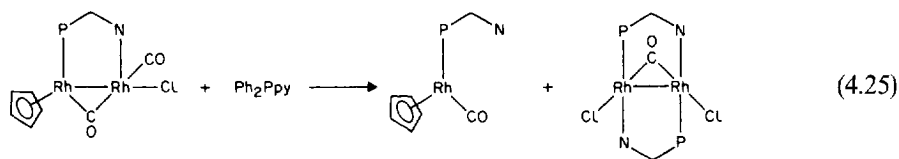
4.2.3.4. *Oxidative addition.* Halogens can oxidatively add to the unsaturated metal center, and the M—M bond is retained (Eq. (4.23)) [1,66].



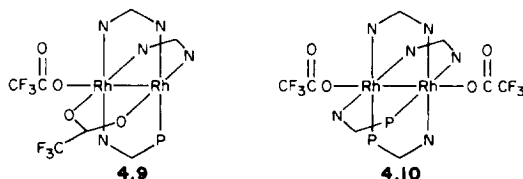
Faraone and co-workers have observed that  $(\eta^5\text{-Cp})\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})(\mu\text{-CO})(\text{CO})\text{Cl}$  has a 16-electron Rh(I) and an 18-electron Rh(I) center, which are very different in basicity and coordination number; but oxidative addition to one of the metals 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].



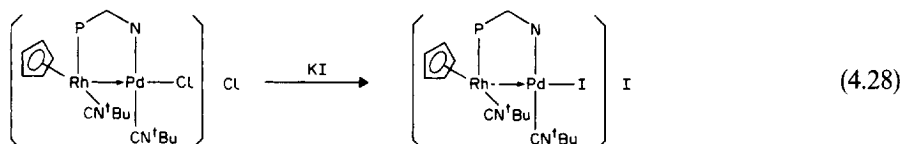
4.2.3.5. *Decomposition.* In the presence of basic species such as  $\text{Ph}_2\text{Ppy}$ , py and  $\text{PPh}_3$ , binuclear complexes with one  $\text{Ph}_2\text{Ppy}$  bridge can decompose to give mononuclear complexes (Eqs. (4.25)–(4.27)) [3,67].



**4.2.3.6. Displacement reaction.** In the presence of some inorganic salts, poorly coordinated ligands can be displaced from  $\text{Ph}_2\text{Ppy}$ -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  $\text{X}^-$  ligands ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) [59].



An analogous reaction occurs for the  $\text{RhPd}$  complexes containing one bridged  $\text{Ph}_2\text{Ppy}$  ligand (Eq. (28)) [3].

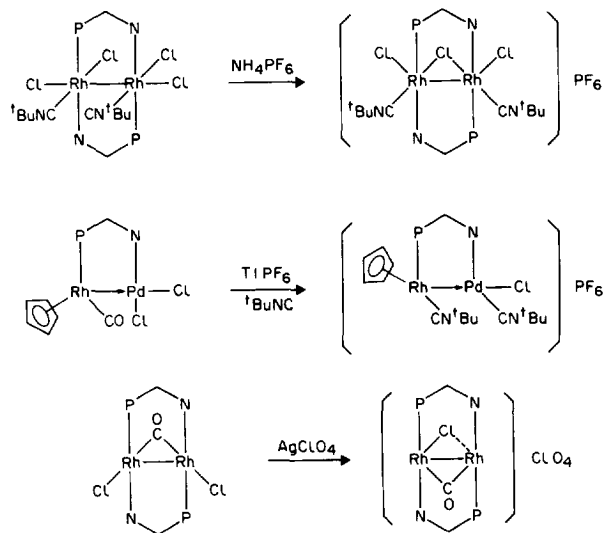


**4.2.3.7. Ionization.** In the presence of halide abstractors, terminal ligands such as  $\text{Cl}^-$  and  $\text{CO}_2\text{CF}_3^-$  are easily drawn from the coordinative plane of the metal center, and various ionic species are formed. A number of examples are shown in Schemes 15 [3,18,65] and 16 [59].

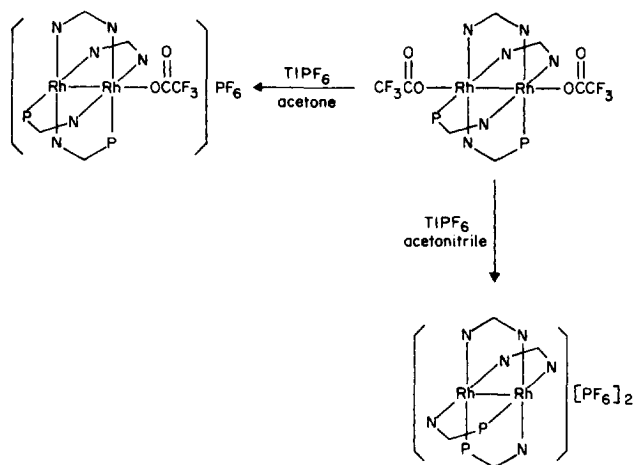
**4.2.3.8. Electrochemical oxidation.** Woods and co-workers have studied the electrochemical reaction of  $\text{Rh}_2(\mu\text{-CO})(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_2$  (Scheme 17) [65,68].

Though  $\text{Cl}^-$  is generally considered to be a better coordinating ligand for transition metals than  $\text{NO}_3^-$ , the binuclear  $\text{Rh}(\text{I})$  species adds a  $\text{Cl}^-$  and a  $\text{NO}_3^-$  instead of two  $\text{Cl}^-$  ions. Even in the absence of an external source of  $\text{Cl}^-$ , oxidation of  $\text{Rh}_2(\mu\text{-CO})(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_2$  in  $\text{CH}_2\text{Cl}_2/\text{TBAN}$  still affords the same product. It is possible that the addition of the bridging  $\text{NO}_3^-$ , instead of a bridging  $\text{Cl}^-$  for instance, may result from the ability of the bridging nitrate to accommodate the twist angle imposed by the  $\text{Ph}_2\text{Ppy}$  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  $\text{Pd}_2(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_2$  lacks the reactivity associated with the  $\text{Pd-Pd}$  bond, and the insertion of small molecules such as  $\text{CO}$ ,  $\text{SO}_2$  and  $\text{RNC}$  hasn't been explored [12]. However,  $\text{Pd}_2(\mu\text{-Ph}_2\text{Ppy})_2\text{Cl}_2$  can readily react with alkynes activated by an electron-withdrawing group, such as  $\text{RC}\equiv\text{CR}$  ( $\text{R} = \text{CH}_3\text{CO}_2$ ), to form the product **4.23**, in which the acetylene appears to be bound as a dimetallated olefin [18]. The reaction of  $\text{Pt}_2(\mu\text{-Ph}_2\text{Ppy})_2\text{Br}_2$  with  $[\text{IrBr}_2(\text{CO})_2]^- [\text{Bu}_4\text{N}]^+$  yields the  $\text{PtIr}$  complex **4.24** [18].



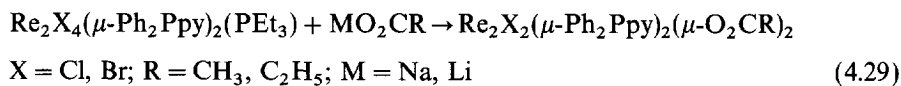
Scheme 15.

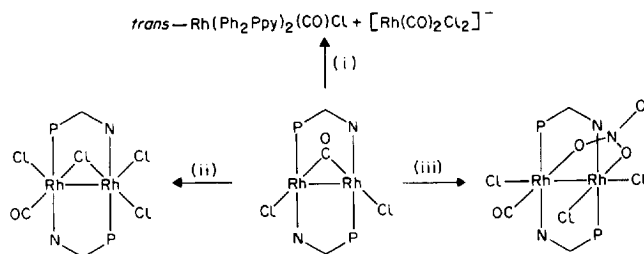


Scheme 16.

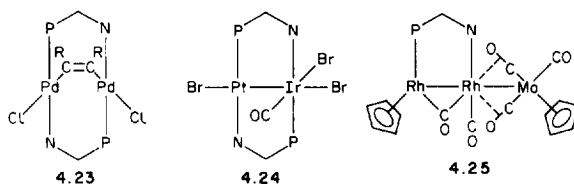
Addition of the sodium salt of the carbonyl metallate anions  $[\text{Mo}(\eta^5\text{-Cp})(\text{CO})_3]^-$  to  $(\eta^5\text{-Cp})\text{Rh}(\mu\text{-CO})(\mu\text{-Ph}_2\text{Ppy})\text{Rh}(\text{CO})\text{Cl}$  gives the near-linear trinuclear complex **4.25**, in which the terminal chloride is replaced by the anion [67].

Walton et al. have found that the  $\text{Re}_2(\text{Ph}_2\text{Ppy})_2$  fragment remains in the reactions of  $\text{Re}_2\text{X}_4(\mu\text{-Ph}_2\text{Ppy})_2(\text{PET}_3)$  with the carboxylate (Eq. (4.29)) [55].





Scheme 17. (i) TBAC, CO; (ii) TBAH/TBAC, or an excess  $\text{Cl}_2$ ; (iii) excess TBAC, TBAN/ $\text{CH}_2\text{Cl}_2$ , ox.



In these complexes,  $\text{Re}_2\text{Cl}_2(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-O}_2\text{CR})_2$  can be very easily oxidized by  $[(\eta^5\text{-Cp})_2\text{Fe}]\text{PF}_6$  to give  $[\text{Re}_2\text{Cl}_2(\mu\text{-Ph}_2\text{Ppy})_2(\mu\text{-O}_2\text{CR})_2]\text{PF}_6$  [55].

## 5. Cluster complexes with $\text{Ph}_2\text{Ppy}$

Cluster complexes are able to react with  $\text{Ph}_2\text{Ppy}$  to give some novel products. A number of reactions involving  $\text{Ru}_3$  cluster complexes have been reported by Lukan and co-workers (Scheme 18) [30,69,70].

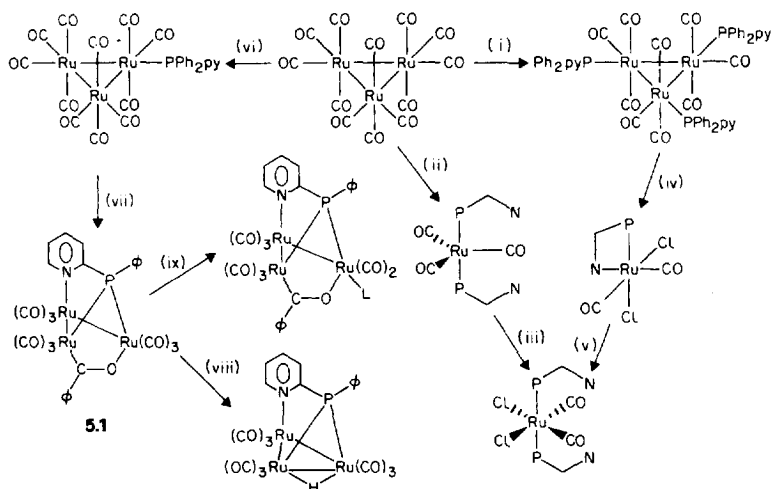
Using either sodium benzophenone ketyl or  $[\text{PPN}]\text{CN}$  can lead to the monosubstituted complex  $\text{Ru}_3(\text{CO})_{11}(\text{Ph}_2\text{Ppy})$ , selectively and quantitatively. The catalysts selectively promote the coordination of the phosphorus atom.

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

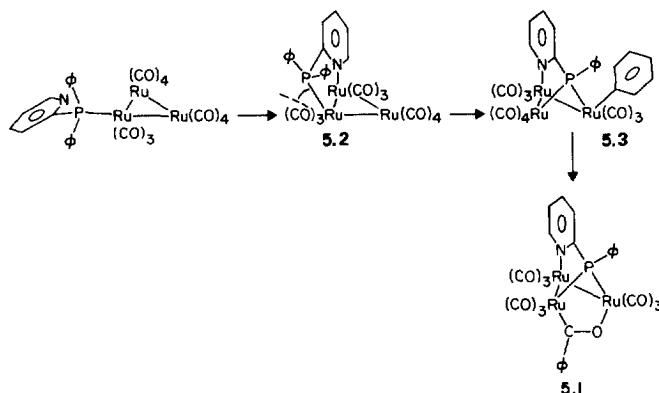
In trimetal clusters, nitrogen ligands have shown a general tendency to coordinate at axial sites [71–73]. If this were to happen **5.2**, it would force the phosphorus atom into an axial position, known to be highly favorable for direct P–C bond cleavage at two metal centers. The oxidative cleavage of a P–C bond in  $\text{Ph}_2\text{Ppy}$  provides an organic fragment  $\text{P}(\text{C}_6\text{H}_5)(\text{C}_5\text{H}_4\text{N})$ , which caps one face of the metal triangle through the bridging phosphido group, and spans the opening of the  $\text{Ru}(2)\text{—Ru}(3)$  edge to form **5.3** with a  $\sigma$ -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  $\text{C}(\text{O})\text{C}_6\text{H}_5$ .

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





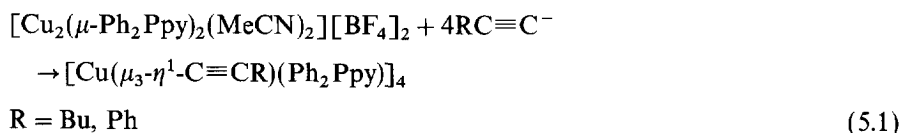
Scheme 18. (i)  $3\text{Ph}_2\text{Ppy}$ ,  $\Delta$ ; (ii)  $6\text{Ph}_2\text{Ppy}$ ,  $h\nu$ ; (iii)  $\text{Cl}_2$ ; (iv)  $\text{Cl}_2$ ; (v)  $\text{Ph}_2\text{Ppy}$ ; (vi)  $[\text{PPN}]\text{CN}$  or sodium benzophenone ketyl; (vii)  $-\text{CO}$  ( $40^\circ\text{C}$ ); (viii)  $\text{H}_2$  ( $80^\circ\text{C}$ ); (ix)  $\text{L}$  ( $25^\circ\text{C}$ ) ( $\text{L} = \text{PPh}_3, \text{Ph}_2\text{PH}, \text{C}_6\text{H}_5\text{PH}$ ).



Scheme 19.

molecular hydrogen is bubbled through, the  $\mu$ -acyl group is removed to give the monohydrido species  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-P}(\text{C}_6\text{H}_5)(\text{C}_5\text{H}_4\text{N}))(\text{CO})_9$  [69,70].

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

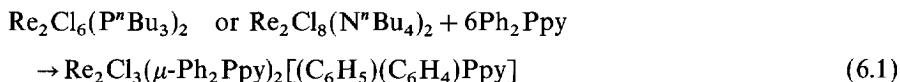


In the clusters, the bonding in the electron deficient “ $\text{Cu}_3\text{C}\equiv\text{CR}$ ” moiety can be described as typical of a four-center two-electron system. Otherwise, in the

“Cu<sub>3</sub>C≡CR” moiety there is a typical triple bond, and the metal–acetylide bonding can be considered to be of a pure  $\sigma$ -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<sub>3</sub>Ppy

Cotton and co-workers have isolated a novel complex containing a tridentate bridging ligand Ph<sub>2</sub>Ppy (Eq. (6.1)) [2,53].



The derivative of the triply-bonded Re<sub>2</sub><sup>4+</sup> 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<sub>2</sub>L<sub>8</sub> 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<sub>2</sub><sup>4+</sup> 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<sub>2</sub>Ppy 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<sub>2</sub>Ppy 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 <sub>2</sub> Ppy) <sub>2</sub> (CO) <sub>6</sub>	88.5	81.3	18.7
FeNi(Ph <sub>2</sub> Ppy) <sub>2</sub> (CO) <sub>3</sub> (NCS) <sub>2</sub>	95.2	52.3	47.7
FeRh(Ph <sub>2</sub> Ppy) <sub>2</sub> (CO) <sub>4</sub> Cl ( <b>7.1</b> )	92.4	48.0	52.0
FeCu(Ph <sub>2</sub> Ppy) <sub>2</sub> (CO) <sub>3</sub> Cl	91.4	76.0	24.0
FeHg(Ph <sub>2</sub> Ppy) <sub>2</sub> (CO) <sub>3</sub> (SCN) <sub>2</sub>	94.4	73.2	26.8
Rh(Ph <sub>3</sub> P) <sub>3</sub> Cl <sup>a</sup>	96.5	52.4	47.6

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

<sup>a</sup> 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<sub>3</sub>P)<sub>3</sub>Cl at different reaction temperatures (Table 5) shows that **7.1** is distinctly superior to Rh(Ph<sub>3</sub>P)<sub>3</sub>Cl at 200 °C for conversion of ethanol (99.5%) and selectivity to propionate (98.6%), although Rh(Ph<sub>3</sub>P)<sub>3</sub>Cl 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<sub>3</sub>P)<sub>3</sub>Cl 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 <sub>3</sub> P) <sub>3</sub> Cl	46.9	61.6	38.4
	FeRh(Ph <sub>2</sub> Ppy) <sub>2</sub> (CO) <sub>4</sub> Cl ( <b>7.1</b> )	38.9	66.1	33.9
180	Rh(Ph <sub>3</sub> P) <sub>3</sub> Cl	90.5	52.4	47.2
	FeRh(Ph <sub>2</sub> Ppy) <sub>2</sub> (CO) <sub>4</sub> Cl ( <b>7.1</b> )	92.4	48.0	52.0
200	Rh(Ph <sub>3</sub> P) <sub>3</sub> Cl	96.4	32.3	67.7
	FeRh(Ph <sub>2</sub> Ppy) <sub>2</sub> (CO) <sub>4</sub> Cl ( <b>7.1</b> )	99.5	1.4	98.6



Table 6

Comparison with CDT<sup>a</sup>, selective hydrogenation

Catalyst	Reaction conditions			Results		
	Amount of catalyst (g)	Temperature (°C)	Pressure of H <sub>2</sub> (MPa)	Conversion CDT (%)	Selectivity (%)	
					CDE <sup>b</sup>	CDA <sup>c</sup>
Homogeneous	0.035	170	20	92.5	93.2	6.8
Heterogeneous	1 <sup>d</sup>	110	20	89.4 <sup>e</sup>	84.2	15.8

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

The Ph<sub>2</sub>Ppy 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(μ-CO)-(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub> heterogeneous catalyst from the cross-linking of 2-(diphenylphosphino)pyridine-4-methenyl polystyrene resin, and have compared this with the corresponding homogeneous catalyst PdMo(μ-Ph<sub>2</sub>Ppy)<sub>2</sub>(μ-CO)(CO)<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>Ppy chemistry, in terms of synthesis, structure and reactivity. Many novel complexes have been obtained from the bridging ligand Ph<sub>2</sub>Ppy. In particular, the utilization of Ph<sub>2</sub>Ppy

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

As the rigidity of the  $\text{Ph}_2\text{Ppy}$  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*- $\text{Fe}(\text{Ph}_2\text{Ppy})_2(\text{CO})_3$  can act as a neutral organometallic tridentate ligand to yield, easily, a binuclear complex with a  $\text{Fe}—\text{M}$  bond. Similarly, another ligand, *trans*- $\text{M}(\text{O})\text{L}_n(\text{P}^-\text{X})_2$  ( $\text{L} = \text{CO}$  or  $\text{CNR}$ ,  $\text{M} = \text{Fe}$ ,  $\text{Os}$ ,  $\text{Cr}$ ,  $\text{Mo}$ ,  $\text{W}$ ;  $\text{X} = \text{O}$ ,  $\text{S}$ ,  $\text{N}$ ,  $\text{P}$ ,  $\text{As}$ ), 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  $\text{Ph}_2\text{Ppy}$  ligand [2,53]. It is to be expected that interesting reactions will be found to occur on the bridging ligands.

The  $\text{Ph}_2\text{Ppy}$  bridging binuclear complexes display catalytic activity when used as homogeneous or heterogeneous catalysts [47,78,79]. In particular, the  $\text{Ph}_2\text{Ppy}$  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  $\text{Ph}_2\text{Ppy}$  chemistry.

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