©*Proc. Indian natn. Sci. Acad.*, **52**, A, No. 4, 1986, pp. 744-748
Printed in India.

# NEW DEVELOPMENTS IN THE CHEMISTRY OF BIMETALLIC SYSTEMS*

BERNARD L SHAW

*School of Chemistry, University of Leeds, Leeds, LS2 9JT, U.K.*

(*Received 7 March 1986*)

New methods of synthesizing heterobimetallic systems containing bridging $Ph_2PCH_2PPh_2$ (dppm) are described i.e. complexes containing the moiety $M^1(\mu\text{-dppm})_2M^2$. Four general methods of synthesis have been devised (1) REDOX, (2) Using monodentate dppm complexes, (3) Ring-opening reactions and (4) Transmetallation, enabling many hetero- and homo-bimetallic systems containing $M^1(\mu\text{-dppm})_2M^2$ moieties to be synthesized. $M^1$ and $M^2$ can be drawn from Cr, Mo, W, Mn, Re, Os, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Cd or Hg: associated ligands include $C\equiv CR$, $C\equiv N$, $C\equiv NR$, halides, alkyl, aryl, H, Co, $RC\equiv CR$. Many of the complexes are fluxional and *trans*-, *cis*- and other stereochemistries are exhibited by the metals. Various reactions of these complexes are described.

**Key Words : Heterobimetallic Systems; *Bis*(diphenylphosphino) Methane Bridging**

## INTRODUCTION

TERTIARY phosphine ligands are very important in present day organometallic and transition metal hydride chemistry. They are increasingly used in organic synthesis and some industrial processes use $M\text{-}PR_3$ or $M\text{-}P(OR)_3$ systems as catalysts. In the application of metal-$PR_3$ complexes to organic synthesis and catalysis, generally only one metal centre is involved, but clearly if two metal-tertiary phosphine centres could be held in a *flexible* manner in close proximity, then new chemistry should be generated. The ligand $Ph_2PCH_2PPh_2$(dppm) has the ability to bridge two metals in this way. In addition to forming 4-membered ring chelates it can form 'face to face' complexes such as *trans*, *trans*-[(OC) $ClRh(\mu\text{-dppm})_2$ RhCl(CO)] with an 8-membered ring: 'A-frames' such as [$ClPt(\mu\text{-CO})$ $(\mu\text{-dppm})_2$ PtCl] in which the bridging carbonyl group has an unusually low value for $\nu(C=O)$ (1638cm$^{-1}$): metal-metal multiple bonded species, e.g. $(Cl_2Mo(\mu\text{-dppm})_2\text{-}MoCl_2$ ($Mo\equiv Mo$): complexes such *cis*, *cis*-$Me_2Pt$ $(\mu\text{-dppm})_2$ Pt $Me_2$] with platinum-platinum separation >4Å, and many other types.

Until we published our work[1] in 1982, all the examples were homobimetallic, i.e. two rhodiums, two palladiums etc. there being no examples with two different metals. However, devising highly specific and convenient routes to such heterobimetallic compounds with metals in $d^{10}$-$d^6$ configurations drawn from Cr, Mo, W, Mn, Re, Os, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Cd or Hg has been successfully achieved.

*Presented at the INSA Golden Jubilee Symposiam on *Recent Trends in Inorganic Chemistry* held in Calcutta in December 1985.

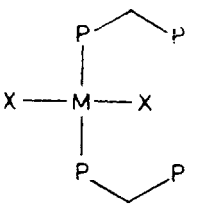
We have devised four general methods of synthesis of heterobimetallic systems—(1) REDOX, (2) Syntheses with monodentate dppm complexes, (3) Ring-opening or ring-expansion reactions and (4) Transmetallation.

## REDOX

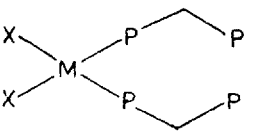
In this method,[1,2] we used a labile Pd(O) complex, *viz.* $Pd(PPh_3)_4$, + dppm and added a labile Pt(O) complex, $[PtCl_2(NCBu^t)_2]$. This gave $[ClPt(\mu\text{-dppm})_2PdCl]$, 90–95 per cent yields, free from the corresponding $Pt_2$ and $Pd_2$ complexes. This complex reacted with molecules such as CO, $SO_2$, $CS_2$ or MeOOCC≡CCOOMe to give 'A-frames'. These and other complexes we have prepared, give characteristic $^{31}P\{^1H\}$nmr spectra consisting of *AA'XX'* patterns with satellites due to coupling to platinum-195 and reactions can be followed in solution by nmr spectroscopy.

## SYNTHESES WITH MONODENTATE dppm COMPLEXES

The REDOX method was limited in its application but, clearly, if one could bond two dppms, each through one *P* and leave the other *P* uncoordinated, as in (I) and (II), then one should be able to effect systematic syntheses




trans (I)




cis (II)

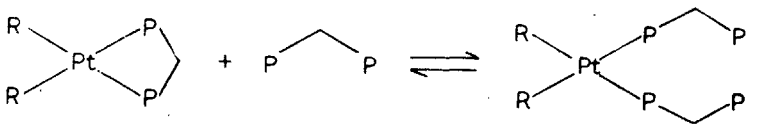
of heterobimetallics using the two, uncoordinated *P* atoms. In order that compounds of type (I) or (II) could be isolable, e.g. with *M* = Pt or Pd, then the ligands '*X*' must be strongly bonded to *M* and should not be displaced as anions. It was assumed that ligands '*X*' suitable for the *trans*-configuration (I) would be C≡C*R*, CN or C≡N*R*, and that for the *cis*-configuration (III) *X* = alkyl (or possibly aryl) might be suitable.

We found that treatment of $[PtCl_2$ (dppm-*P*, *P'*)] with LiC≡CR gave the 8-membered ring complex *trans*, *trans*-$[(RC{\equiv}C)_2\ Pt(\mu\text{-dppm})_2\ Pt(C{\equiv}CR)_2$ which with dppm gave the required *trans*-$[(RC{\equiv}C)_2\ Pt(dppm\text{-}P)_2]$ of type (I).[3] We have used such compounds to make heterobimetallic compound with Mo, W, Rh, Ir, Pt, Cu, Ag, Au, Hg etc. For example, *trans*-$[PhC{\equiv}C)_2$ dppm-*P*)$_2$] reacts with *trans*-$[Ir\ Cl\ (CO)\ PPh_3)_2]$ to give *trans*, *trans*-$[(PhC{\equiv}C)_2\ Pt(\mu\text{-dppm})_2\ IrCl(CO)]$, which with $NaBPh_4$ give the orange-red cation *trans*, *trans*-$[(PhC{\equiv}C)\ Pt(\mu\text{-}C{\equiv}CPh)(\mu\text{-dppm})_2\ Ir\ (CO)]^+$. This cation reacts with $H_2$, CO, $CH_2{=}CHCH{=}CH_2$, $CH_2{=}CMeCH{=}CH_2$) etc. without the $Pt(\mu\text{-dppm})_2Ir$ framework breaking down. Sometimes in our complexes a bridging acetylide group is endways ($\sigma^-$) bonded to one metal

and sideways ($\pi^-$) (bonded to the second metal, as in [(PhC≡C) Pt($\sigma$, $\pi$-C≡CPh) ($\mu$-dppm)$_2$ Rh(CO)]$^+$ whereas in other cases it is $\eta^1$–, i.e. 3-centre bonded, as in [(MeC≡C) Pt($\eta^1$–C≡CMe) ($\mu$-dppm)$_2$ W(CO)$_3$]. Many of these complexes are fluxional.[4,5]

*trans*-[(PhC≡C)$_2$ Pt(dppm-*P*)$_2$] reacts with *trans*-[PtHCl(PPH$_3$)$_2$] to give [PhC≡CPt($\mu$–H) ($\mu$-dppm)$_2$ Pt(C≡CPh]$^+$ which is deprotonated by bases to give the diplatinum(I) complex [(PhC≡C) Pt($\mu$-dppm)$_2$ Pt(C≡CPh)].[6]

The example discussed above involve a *trans*-configuration of two *P*-donor atoms of dppms around at least one of the metals (Pt. Rh, Ir, Mo, Mn etc.). Bimetallic complexes with dppms arranged in a *cis*-configuration are much less common. In order to effect their synthesis, the equilibria set up has been studied by treating the dialkyl- or diaryl-platinum complexes *cis*-[R$_2$Pt(dppm–*P*, *P'*)] (III) with



(III) (IV)

dppm, *viz*. The largest equilibrium constant (K) was found for [CH$_2$CH$_2$CH$_2$CH$_2$Pt (dppm-*P*,*P'*)],[7] others for *R* = Me, Ph, *p*-tolyl, C$_6$F$_5$, 1-naphthyl or *o*-tolyl were sufficiently large for us to be able to drive the above equilibrium to the right hand side and isolate[8] complexes of type (IV). With *R* = Et, CH$_2$Ph or CH$_2$CMe$_3$, however, *K*-values were small. In several instances we were able to convert complexes of type bimetallic systems, e.g. with Ag, Au, Rh, Pd or Pt as the second metal.[9] With *R* = 1-naphthyl or *o*-tolyl there is restricted rotation around the platinum-aryl bond and *syn*- and *anti*-isomers were formed e.g. treatment of [(*o*-tolyl)$_2$ Pt(dppm-*P*)$_2$] with [Pt Me$_2$ (1,5-cyclo-octadiene] gave [(*o*-tolyl)$_2$ Pt($\mu$-dppm)$_2$ PtMe$_2$] *syn*- and *anti*-isomers, of which the crystal structure of the *syn*-isomer has been determined.[9]

## Ring-opening or Ring-expansion Reactions

This has proved to be the most generally useful of the synthetic methods. Initially it was found that the salt [Pt (dppm-*P*,*P'*)$_2$]Cl$_2$, when treated with an equilibrium amount of [Hg(C≡CR)$_2$], or with [Hg(OAc)$_2$] + *R*C≡CH, gave [*R*C≡C)$_2$ Pt($\mu$–dppm)$_2$HgCl$_2$] in essentially quantitative yield. Similar reactions occur with CuC≡CPh, with AgOAC + *R*C≡CH, or with (AuC≡CPh)$_x$[10]. Ring opening also occurs with Pd-dppm or Ni-dppm complexes, e.g. [NiCl$_2$ (dppm)$_2$] reacts with Hg(C≡CPh)$_2$ to give [(PhC≡C)$_2$ Ni($\mu$-dppm)$_2^-$ HgCl$_2$].

We also found that the 4-membered dppm chelate rings would open when the 5-coordinate complexes [*M*(CO) (dppm-*P*,*P'*)$_2$] were treated with labile complexes of a second metal e.g. [Rh (CO) (dppm-*P*,*P'*)$_2$] reacts with [Ag$_4$Cl$_4$ (PPh$_3$)$_4$] to

give an essentially quantitative yield of [Cl(OC) Rh–($\mu$–dppm)$_2$ AgCl][11] and [Ir(CO)-(dppm-*P*,*P*′)$_2$] reacts with CuC≡CPh to give the deep red crystalline complex. [(PhC≡C) (OC)Ir ($\mu$–dppm)$_2$ CuCl] (crystal structure) or with ClAg(CN*R*) to give [(*R*NC) (OC) Ir($\mu$–dppm)$_2$ AgCl].[12]

Remarkably, the octahedral, $d^6$–complex *trans*-[OsCl$_2$(dppm-*P*,*P*′)$_2$] reacts rapidly with [Rh$_2$Cl$_2$(CO)$_4$] to give an essentially quantitative yield of [Cl$_2$Os ($\mu$–CO)$_2$($\mu$–dppm)$_2$RhCl) (crystal structure).[13]

We also find that many complexes containing the moiety *M*(dppm-*P*,*P*′)-(dppm-*P*) undergo ring-opening reactions to give heterobimetallic complexes, e.g. compounds of the types *mer*-[*M* (CO)$_3$ (dppm-*P*,*P*′) (dppm-*P*)], *M* = Cr, Mo or W (and sometimes the *fac*-isomers also) react with labile complexes of Rh, Ir, Pd, Pt, Cu or Ag in this way.[14] For example *mer*-[W(CO)$_3$ (dppm-*P*,*P*′) (dppm-*P*) reacts with CuCl to give [(OC)$_2$ W($\mu$–CO) ($\mu$–Cl) ($\mu$–dppm)$_2$ Cu] (crystal structure) or it reacts with [PtHCl(PPh$_3$)$_2$] to give [(OC)$_3$ W($\mu$–dppm)$_2$ PtHCl].[15] We have also carried out many similar ring reactions of manganese complexes of type [Mn*X*(CO)$_2$ (dppm-*P*,*P*′) (dppm-*P*) with Pt, Rh or Ir complexes and similar chemistry with rhenium complexes.[15,16]

## Transmetallation

In this method, a metal with $d^{10}$-electron configuration is displaced from a heterobimetallic complex by a $d^8$ or or $d^6$ metal. An example is the displacement of mercury (as HgCl$_2$) from [*R*C≡C)$_2$ Pt($\mu$–dppm)$_2$ HgCl] on treatment with [Rh$_2$Cl$_2$(CO)$_4$]: the product [(*R*C≡C) Pt($\mu$–C≡C*R*) ($\mu$–dppm)$_2$ Rh(CO)]Cl is formed in essentially quantitative yield.[17] Similarly, treatment of [(*R*C≡C)$_2$ Pt($\mu$–dppm)$_2$ AgCl] with [(MeCN)$_3$ W(CO)$_3$] or with [(cycloheptatriene)-Me(CO)$_3$] give [(*R*C ~ C) Pt ($\mu$–C≡C*R*) ($\mu$–dppm)$_2$ M(CO)$_3$] (*M* = Mo or W) in high yield.[15,17]

As combination of a ring opening reaction and a transmetallic reaction is often the best method for the synthesis of a heterobimetallic complex.

## References


1. P G Pringle and B L Shaw *J chem Soc chem Commun* (1982) 81
2. P G Pringle and B L Shaw *J chem Soc Dalton Trans* (1983) 889
3. P G Pringle and B L Shaw *J chem Soc chem Commun* (1982) 581
4. D M McEwan P G Pringale and B L Shaw *J chem Soc chem Commun* (1982) 859
5. A T Hutton C R Langrick D M McEwan P G Pringle and B L Shaw *J chem Soc Dalton Trans* (1985) 2121
6. C R Langrick P G Pringle and B L Shaw *J chem Soc Dalton Trans* (1985) 1015
7. P G Pringle and B L Shaw *J chem Soc Dalton Trans* (1984) 849
8. F S M Hassan D M McEwan P G Pringle and B L Shaw *J chem Soc Dalton Trans* (1985) 1501
9. A T Hutton P G Pringle and B L Shaw *J chem Soc Dalton Trans* (1985) 1677
10. D M McEwan P G Pringle and B L Shaw *J chem Soc chem Commun* (1982) 1240
11. A T Hutton P G Pringle and B L Shaw *Organometallics* **2** (1983) 1889

12. C R Langrick P G Pringle and B L Shaw *J chem Soc Dalton Trans* (1984) 1233
13. J A Iggo D P Markham B L Shaw and M Thornton-Pett *J chem Soc chem Commun* (1985) 432
14. A Blagg A T Hutton B L Shaw and M Thornton-Pett *Inorg Chim Acta* **100** (1985) L33
15. B L Shaw *Unpublished results*
16. S W Carr B L Shaw and M Thornton-Pett *J chem Soc Dalton Trans* (1985) 2131
17. G R Cooper A T Hutton D M McEwan P G Pringle and B L Shaw *Inorg Chim Acta* **76** (1983) L267