Ring Opening Reactions of [M(CO)$_3$(η^1-Ph$_2$PCH$_2$PPh$_2$)(η^2-Ph$_2$PCH$_2$PPh$_2$)] M = Cr, Mo, or W with Rh or Ir Complexes to give Bimetallic Systems: Synthesis of [(OC)$_3$Mo(μ-Ph$_2$PNHPPh$_2$)$_2$RhCl(CO)]

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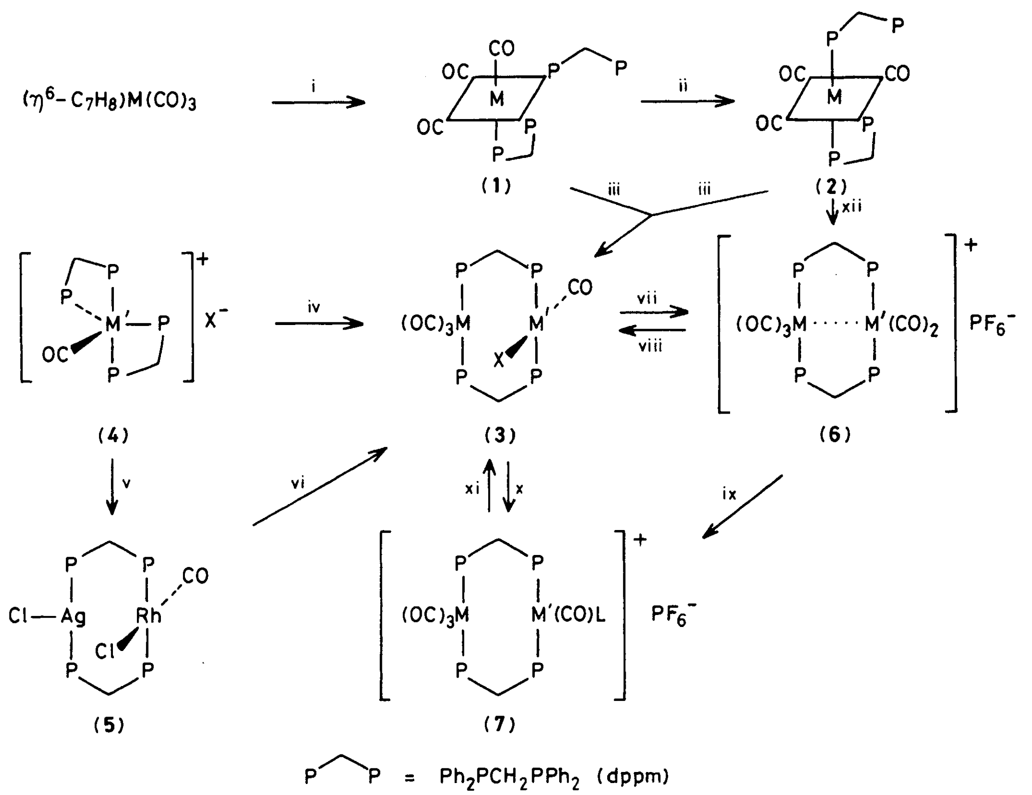
Complexes of the type [(OC)$_3$M(μ-Ph$_2$PCH$_2$PPh$_2$)$_2$M'X(CO)] or [(OC)$_3$M(μ-Ph$_2$PCH$_2$PPh$_2$)$_2$M'(CO)$_2$]$^+$PF$_6^-$ have been made either as described in the title or by a ring opening reaction of [M'(CO)(η^2-Ph$_2$PCH$_2$PPh$_2$)$_2$]Cl (M' = Rh or Ir) with a labile Cr, Mo, or W carbonyl derivative: the first bimetallic complex of Ph$_2$PNHPPh$_2$ is described.

We have shown that ring opening of the 4-membered rings in some η^2-Ph$_2$PCH$_2$PPh$_2$ (dppm) complexes of metals with d^8-electron configuration is an excellent method of producing bimetallic systems containing M(μ-dppm)$_2$M' moieties; M = Pt^{II}, Pd^{II}, Ir^{I}, or Rh^{I}; M' = variety of metals.[1—3] One would expect that similar reactions of η^2-dppm complexes of metals with d^6-electron configuration would be much less likely to occur since such complexes would often be octahedrally co-ordinated and inert. In agreement with this we find that *cis*-[Mo(CO)$_2$(η^2-dppm)$_2$],[4] when treated with a second metal is inert towards ring opening. However, we reasoned that the known complexes *fac*- or *mer*-[Mo(CO)$_3$(η^2-dppm)(η^1-dppm)],[5] should co-ordinate to a second metal *via* the free phosphorus atom and that subsequent opening of the 4-membered chelate ring (η^2-dppmMo) might be possible by an intramolecular process. This appears to be the case since we find that (**1**) or (**2**), M = Mo, react smoothly with [Rh$_2$Cl$_2$(CO)$_4$] in CH$_2$Cl$_2$ solution at 20 °C to give the same product, [(OC)$_3$Mo(μ-dppm)$_2$RhCl(CO)] [(**3**), M = Mo, M' = Rh], as orange microcrystals in >90% isolated yields. The reaction as followed by ^{31}P{^{1}H} n.m.r. spectroscopy was complete in less than 5 minutes. The product gave an AA'MM'X pattern of a type indicative of a *trans,trans*-[Mo(μ-Ph$_2$PCH$_2$PPh$_2$)$_2$Rh] moiety: δ P$_A$ 36.9, δ P$_B$ 24.3 p.p.m., ^1J(RhP$_B$) = 118, $|^2J$(P$_A$P$_B$) + ^4J(P$_A$P$_{B'}$)$|$ = 73 Hz (in CDCl$_3$). The complex was characterized by elemental analysis (C, H, Cl) and i.r. spectroscopy [ν(CO) 1806, 1842, 1959, and 1984 cm^{-1} (KBr disc)]. We could not observe a band attributable to ν(Rh–Cl) (Nujol mull) but commonly find in bimetallic–dppm chemistry that bands due to metal–halogen stretching vibrations are not observed, presumably because of lack of intensity. We have also prepared (**1**), M = W, and (**2**), M = Cr, W, in a similar manner to those reported for the Mo complexes *viz.* treatment of [M(CO)$_3$(η^6-cycloheptatriene)] with dppm (Scheme 1).

Treatment of (**1**), M = W or (**2**), M = Cr or W, with [Rh$_2$Cl$_2$(CO)$_4$] gives [(OC)$_3$M(μ-dppm)$_2$RhCl(CO)] [(**3**)] in 60—70% yields. We also find that treatment of (**1**) or (**2**), M = Mo, with [IrCl(CO)$_2$(*p*-toluidine)] gave [(OC)$_3$Mo(μ-dppm)$_2$IrCl(CO)] [(**3**)] (41% isolated yield) but this complex slowly decomposed in solution to give the known [Ir(CO)(η^2-dppm)$_2$]$^+$ and other, unidentified, products (^{31}P{^{1}H} n.m.r. evidence). The corresponding Cr–Ir complex was observed to form in solution but the W–Ir complex was not formed by this method {much [Ir(CO)(η^2-dppm)$_2$]$^+$ formed}.

We have also found that some of the bimetallic complexes of type (**3**) could be prepared from [M(CO)(η^2-dppm)$_2$]X (M = Rh or Ir; X = Cl, Br, or I). Thus treatment of the Ir salt



Scheme 1. i, dppm in CH_2Cl_2 at 20 °C; ii, 80 °C, C_6H_6, 16 h; iii, $[Rh_2Cl_2(CO)_4]$ or $[IrCl(CO)_2$(*p*-toluidine)]; iv, $[Mo(CO)_3$(cycloheptatriene)], M′ = Ir, X = Cl, Br, or I; v, $Ag_4Cl_4(PPh_3)_4$, M′ = Rh, X = Cl; vi, $[Mo(CO)_3$(cycloheptatriene)], M′ = Rh, X = Cl; vii, CO, PF_6^-; viii, $Bu^n{}_4NX$, X = Cl or Br; ix, MeCN or PhCN = L; x, Bu^tNC = L; xi, $Bu^n{}_4NCl$ for L = MeCN or PhCN; xii, $[Rh_2Cl_2(CO)_4]$ or $[IrCl(CO)_2$(*p*-toluidine)] + NH_4PF_6 + CO.

(**4**), X = Cl, with $[Mo(CO)_3(\eta^6$-cycloheptatriene)] gave $[(OC)_3Mo(\mu\text{-dppm})_2IrCl(CO)]$ (51% yield), identical to that described above: similarly for the corresponding bromo- and iodo-complexes (**3**), X = Br or I, M = Mo, M′ = Ir. The W–Ir complex of type (**3**), X = Cl, was formed similarly ($^{31}P\{^1H\}$ n.m.r. evidence) but not isolated pure. Treatment of $[Rh(CO)(\eta^2\text{-dppm})_2]Cl$ with $[Mo(CO)_3(\eta^6$-cycloheptatriene)] gave none of the hoped for Mo–Rh complex but treatment of the readily prepared Rh–Ag complex (**5**)[3] with $[Mo(CO)_3(\eta^6$-cycloheptatriene)] gave, by transmetallation, the required complex $[(OC)_3Mo(\mu\text{-dppm})_2RhCl(CO)]$ of type (**3**) in 71% isolated yield and identical to that prepared by the alternative route (see above).

The neutral species of type (**3**) react rapidly with CO to give very dark coloured cationic species $[(OC)_3M(\mu\text{-dppm})_2M'(CO)_2]^+$ (**6**), isolated and characterized as their PF_6^- salts for Rh (Cr, Mo, or W) and Ir (Mo or W). These cationic species are more stable in solution than the neutral species of type (**3**), *e.g.* they are stable for days in CH_2Cl_2 (n.m.r. evidence) whereas the neutral species of type (**3**) tend to decompose slowly in solution. I.r. evidence suggests the absence of bridging carbonyls, *e.g.* for $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ ν(CO) = 1837, 1856, 1986, 2005, and 2028 cm^{-1} (Nujol mull) but the intense dark colour suggests some metal ··· metal interaction as depicted in (**6**). These cationic species are readily prepared in one step from (**1**) or (**2**), M = Cr, Mo, or W, by the method shown in Scheme 1. The cations react rapidly with nucleophiles, *e.g.* treatment of (**6**), M = Cr, Mo, or W, M′ = Rh or Ir, with $Bu^n{}_4NCl$ rapidly gives the neutral species (**3**), X = Cl. These salts of type (**6**) react rapidly with other nucleophiles, *e.g.* MeCN or PhCN to give dark coloured salts (**7**), M = Mo, M′ = Ir, L = RCN, and preliminary $^{31}P\{^1H\}$ n.m.r. results show that they react with N_3^-, LiMe, $LiEt_3BH$, to give new heterobimetallic complexes, which we are investigating. Preliminary (n.m.r.) studies also suggest that complexes of type (**3**) undergo oxidative addition reactions with MeI or HCl. Complexes of type (**3**), M = Cr, Mo, or W, M′ = Rh, react with Bu^tNC to give salts of type (**7**).

Although many bimetallic complexes of $Ph_2PCH_2PPh_2$ have been prepared no such complexes of the isoelectronic aminodiphosphine, $Ph_2PNHPPh_2$ (dppa)[6] have been described. We find that $[Mo(CO)_3$(cycloheptatriene)] reacts with dppa (in CH_2Cl_2, 20 °C, 2 h) to give *fac*-$[Mo(CO)_3(\eta^2\text{-dppa})(\eta^1\text{-dppa})]$ (58% yield) which on heating in benzene (80 °C, 2 h) was converted into the corresponding *mer*-isomer (61% yield). Each of these complexes, when treated with $[Rh_2Cl_2(CO)_4]$ in benzene, gave $[(OC)_3Mo(\mu\text{-}Ph_2PNHPPh_2)_2RhCl(CO)]$ in *ca.* 70% yields. This complex has been characterized by elemental analysis and by i.r. and $^{31}P\{^1H\}$ n.m.r. spectroscopy.

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References

1 D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 1240.

2 C. R. Langrick, D. M. McEwan, P. G. Pringle, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1983, 2509.

3 A. T. Hutton, P. G. Pringle, and B. L. Shaw, *Organometallics*, 1983, **2**, 1889.

4 A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, 1975, **14**, 275.

5 E. E. Issacs and W. A. G. Graham, *Inorg. Chem.*, 1975, **14**, 2560.

6 H. Nöth and L. Meinel, *Z. Anorg. Allg. Chem.*, 1967, **349**, 25.