Synthesis and Reactivity of Bis(diphenylphosphino)methane-(dppm)-bridged Pd–Mo and Pd–W Complexes. Crystal Structure of [Pd(μ-CO)(μ-dppm)$_2$Mo(cp)(CO)][PF$_6$] (cp = η^5-C$_5$H$_5$) *

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Reactions of [PdCl$_2$(dppm-*PP'*)] (dppm = Ph$_2$PCH$_2$PPh$_2$) with Na[M'(CO)]·2dme [M' = Mo(cp)(CO)$_2$ or W(cp)(CO)$_2$; cp = η^5-C$_5$H$_5$, dme = 1,2-dimethoxyethane] gave trinuclear clusters of type [PdM$_2$(cp)$_2$(CO)$_5$(μ-dppm)] (M = Mo, **1**; or W, **2**). Treatment of **1** or **2** with 1 equivalent of dppm resulted in heterolytic metal–metal bond cleavage and afforded dinuclear cationic complexes [Pd(μ-CO)(μ-dppm)$_2$M(cp)(CO)][M(cp)(CO)$_3$] (M = Mo, **3a**; or W, **4a**). The structure of the benzene solvate the PF$_6^-$ salt of **3**, *i.e.* **3b**, was established by a single-crystal X-ray analysis: space group *P*2/*c*, *a* = 23.923(6), *b* = 11.040(3), *c* = 24.012(6) Å, β = 90.79(2)°, *R* = 0.053 for 7361 reflections. The (cp)MoP(1)P(3)(CO)$_2$ fragment is square pyramidal, with the cp at the apex, and the co-ordination at Mo may be viewed as of the 3:4:1 type when including the bonding to Pd [Pd–Mo] 2.799(1) Å]. The unusual geometry around Pd is trigonal planar when considering its bonds to P(2), P(4) and Mo. The bridging carbonyl C(56)O(1) completes its co-ordination sphere. Complexes **3b** and **4b** were also prepared from [Pd(dppm-*PP'*$_2$)$_2$][BF$_4$]$_2$ and 2 equivalents of Na[M'(CO)]·2dme [M' = Mo(cp)(CO)$_2$ or W(cp)(CO)$_2$]. Their characteristic ^{31}P-{^{1}H} NMR spectra are respectively of the AA'XX' and AA'BB' types. Reactivity studies were performed and the new bimetallic complex [(OC)$_2$(cp)Mo(μ-dppm)PtCl(PPh$_3$)] **8** is also described.

We have previously shown that the square-planar complexes [MCl$_2$(dppm-*PP'*)] (M = Pd or Pt, dppm = Ph$_2$PCH$_2$PPh$_2$) ring-open when treated with carbonylmetalates [M'(CO)]$^-$ [M' = Mo(or W)(cp)(CO)$_2$ (cp = η^5-C$_5$H$_5$), Mn(CO)$_4$, or Co(CO)$_3$] to give heterometallic, metal–metal bonded complexes containing respectively Pt(μ-dppm)M' or Pd(μ-dppm)M' moieties.[1] We have also observed that heterodinuclear complexes and mixed-metal clusters containing such moieties can be conveniently prepared by the reactions of dppm with the labile trinuclear chain complexes *trans*-[Pd(or Pt){M'(CO)}$_2$(PhCN)$_2$].[2] This allows a comparison to be made of the respective advantages (yields, selectivity) of each method. In this paper we describe an extension of this type of chemistry to the synthesis of trinuclear mixed-metal clusters containing a PdM$_2$ (M = Mo or W) core stabilized with a bridging dppm ligand, as well as unusual cationic, heterodinuclear complexes PdM (M = Mo or W) containing two bridging dppm ligands, characterized by X-ray diffraction in the case of M = Mo. The synthesis of a new Pt(μ-dppm)Mo complex is also described.

Previous syntheses of dppm-stabilized heterobinuclear complexes containing molybdenum have usually involved (*i*) ring-opening reactions of *fac*- or *mer*-[Mo(CO)$_3$(dppm-*PP'*)(dppm-*P*)] with labile metal complexes which afforded neutral, heterobinuclear complexes containing a *trans-trans* Mo(μ-dppm)$_2$M moiety (M = Rh,[3a,b] Ir,[3a,b] Cu,[3c,4a] Ag,[3c,4a] Au,[3c,4a] Hg,[4a] Fe[3d] or Pt[3e]), (*ii*) reaction of *trans*-[Pd(C≡CPh)$_2$(dppm-*P*)$_2$] with [Mo(CO)$_3$(C$_7$H$_8$)] which yielded [(PhC≡C)Pd{μ-(C≡CPh)}(μ-dppm)$_2$Mo(CO)$_3$],[5a,b] or (*iii*) reaction of [RuH$_2$(dppm-*PP'*)$_2$] with [Mo(CO)$_6$] which yielded [(OC)$_2$Ru(μ-dppm)$_2$(μ-CO)Mo(CO)$_3$].[5c]

Results and Discussion

The reactions are outlined in Scheme 1. Treatment of [PdCl$_2$(dppm-*PP'*)], in tetrahydrofuran, with 2 equivalents of Na[M(cp)(CO)$_3$]·2dme (M = Mo or W; dme = 1,2-dimethoxyethane) gave the green clusters [PdM$_2$(cp)$_2$(CO)$_5$(μ-dppm)] (M = Mo, **1**; or W, **2**) in *ca.* 40% yield [equation (1)]. The new compounds were characterized by elemental analysis and IR and ^{31}P-{^{1}H} NMR spectroscopic methods. The ^{31}P-{^{1}H} NMR spectra of **1** and **2** were similar and consisted of two resonances: a low-field doublet (at δ *ca.* 50), assigned to the phosphorus atom bonded to molybdenum or tungsten, and a doublet at higher field, assigned to the phosphorus atom bonded to palladium. The IR spectra in the carbonyl region were very similar and showed bands at *ca.* 1950 and 1910 cm^{-1} assigned to terminal carbonyls and absorptions in the range 1780–1750 cm^{-1} indicative of bridging carbonyl ligands. Similar low-energy absorptions were found for *e.g.* [M$_2$Mo$_2$(cp)$_2$(CO)$_6$(PEt$_3$)$_2$] [M = Pd or Pt, shown in equation (6), Scheme 2][6] and [Pd$_2$MoCl(cp)(CO)$_3$(μ-dppm)$_2$],[7] where triply and doubly semi-bridging carbonyls were identified by X-ray diffraction, or the platinum analogue of **1**, [PtMo$_2$(cp)$_2$(CO)$_5$(μ-dppm)].[1d] We assign a *triangulo* structure to the 46-electron clusters **1** and **2** consistent with a 16-electron palladium and 18-electron

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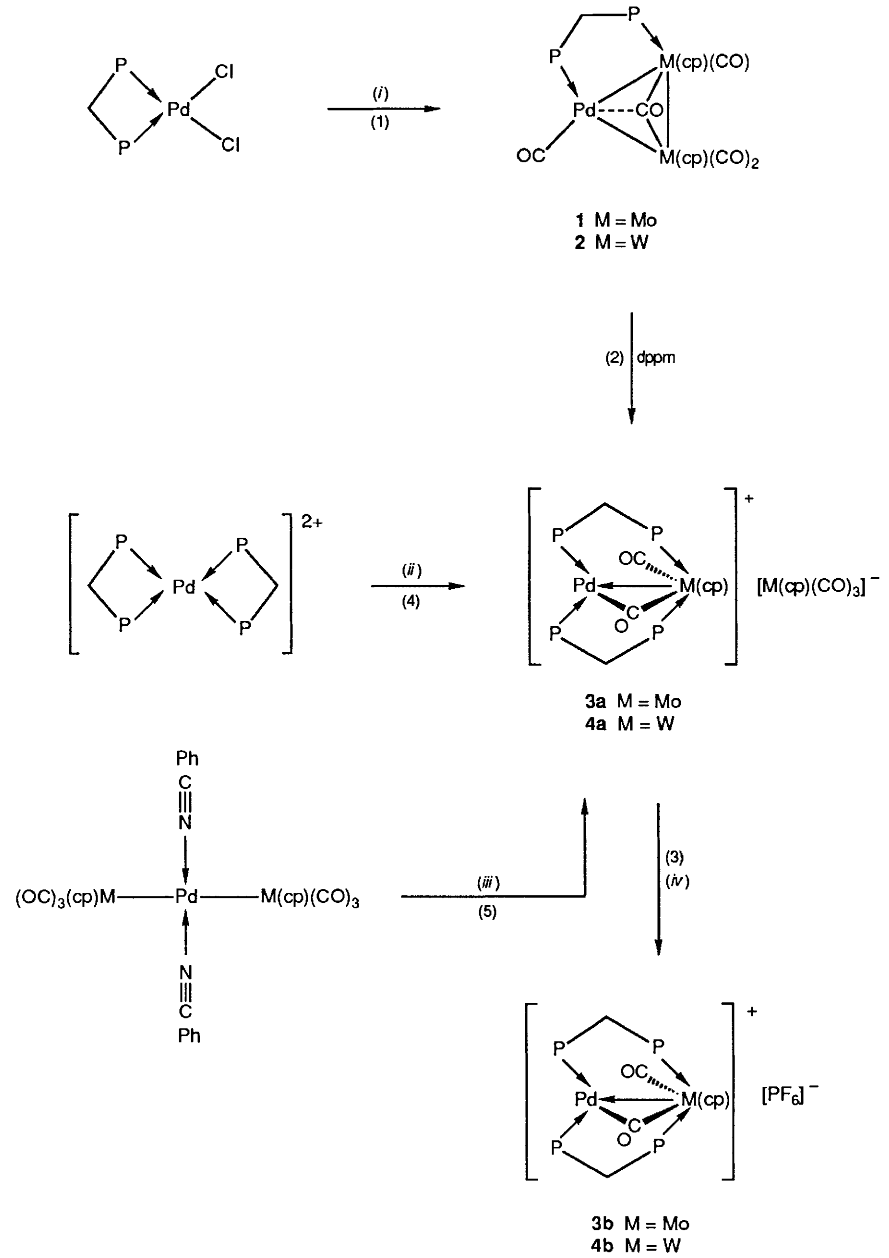
* Bis[μ-bis(diphenylphosphino)methane-1:2κ^2*P*:*P'*]-μ-carbonyl-carbonyl-1κ*C*-1(η^5)-cyclopentadienylmolybdenumpalladium (*Mo*-*Pd*) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



Scheme 1 (*i*) 2 Na[M(cp)(CO)$_3$] (M = Mo or W), thf, −2 NaCl, −2 CO; (*ii*) 2 Na[M(cp)(CO)$_3$] (M = Mo or W), thf, −2Na$^+$, −CO; (*iii*) 2 dppm, thf, −CO, −2 PhCN; (*iv*) [NH$_4$][PF$_6$], thf, −[NH$_4$][M(cp)(CO)$_3$]

molybdenum and tungsten centres, with the phosphorus atoms approximately in the plane of the metal triangle and the M(CO)$_3$(cp) fragment interacting with the Pd–M unit in a similar manner to its bonding to the Pd–Pd unit in [Pd$_2$Mo$_2$(cp)$_2$(CO)$_6$(PEt$_3$)$_2$] (tripod-like arrangement of the carbonyls).[6] Bubbling of CO through solutions of compounds **1** or **2** only resulted in decomposition, in contrast to the reversible CO addition/elimination process observed with their platinum analogue, which occurred *via* reversible rupture of the M–M bond.[1b,d] These observations are consistent with the greater lability generally associated with palladium *vs.* platinum. Treatment of **1** or **2** with 1 equivalent of dppm quantitatively gave the cationic bimetallic complexes $\overline{\mathrm{Pd}(\mu\text{-CO})(\mu\text{-dppm})_2\mathrm{M}}(\mathrm{cp})(\mathrm{CO})]$-[M(cp)(CO)$_3$] (M = Mo, **3a**; or W, **4a**) [equation (2)]. The IR spectrum of the reaction mixture in the ν(CO) region showed the typical absorptions of the anions [M(cp)(CO)$_3$]$^-$ (M = Mo or W). The latter could be exchanged for [PF$_6$]$^-$ [equation (3)]. The molecular structure of **3b** has been determined by X-ray diffraction (see below). The IR spectra of **3b** and **4b** showed a low-frequency ν(CO) absorption at *ca.* 1800 cm^{-1}, indicative of a semi-bridging carbonyl group. The ^{1}H NMR spectrum of **3b** showed a complex multiplet for the PCH$_2$P protons and a triplet with ^3J(PH) = 2.65 Hz for the cyclopentadienyl protons {*cf.* 2.4 Hz for [Mo(cp)(Ph$_2$PCH$_2$CH$_2$PPh$_2$-*PP′*)(C$_2$Me$_2$)]$^+$}.[8] The ^{31}P-{^{1}H} NMR spectra of **3b** (AA′XX′ spin system, Fig. 1) and of **4b** (AA′BB′ spin system with additional satellites on the W-bound P resonances due to molecules containing ^{183}W, Fig. 2) were very characteristic, with patterns consistent with a pseudo-'*trans,trans*-M(μ-dppm)$_2$Pd' (M = Mo or W) moiety.[3c,4d] The *J*(PP) coupling constants given in the Experimental section were obtained by computer simulation. Although the synthesis of these complexes occurred with high spectroscopic yields, salts of **4**$^+$ could not be isolated pure owing to slow decomposition upon recrystallization or chromatography.

The bimetallic cations **3**$^+$ or **4**$^+$ also resulted from the reaction between [Pd(dppm-*PP′*)$_2$][BF$_4$]$_2$ and 2 equivalents of Na[M′(CO)]·2dme [M′ = Mo(cp)(CO)$_2$ or W(cp)(CO)$_2$]

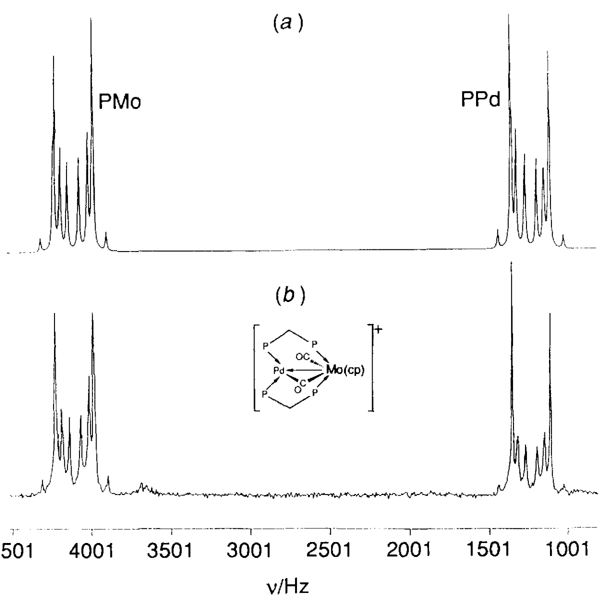


Fig. 1 $^{31}P-\{^1H\}$ NMR spectra of $[Pd(\mu-CO)(\mu-dppm)_2Mo(cp)(CO)][PF_6]$ **3b**: (*a*) simulated and (*b*) experimental at 293 K in thf–C_6D_6

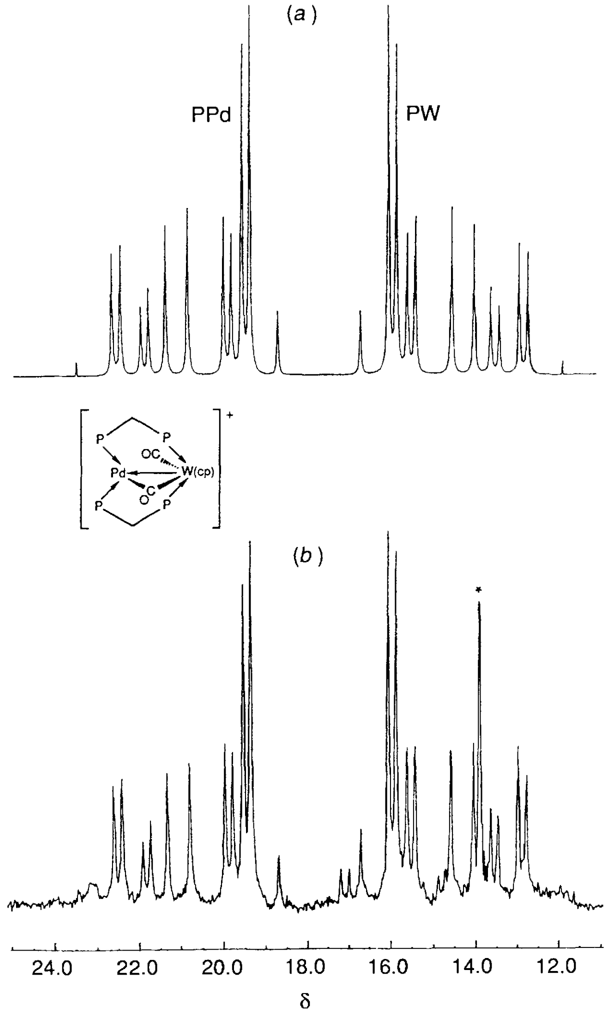


Fig. 2 $^{31}P-\{^1H\}$ NMR spectra of $[Pd(\mu-CO)(\mu-dppm)_2W(cp)(CO)][PF_6]$ **4b**: (*a*) simulated and (*b*) experimental at 293 K in thf–C_6D_6. The asterisk denotes an impurity

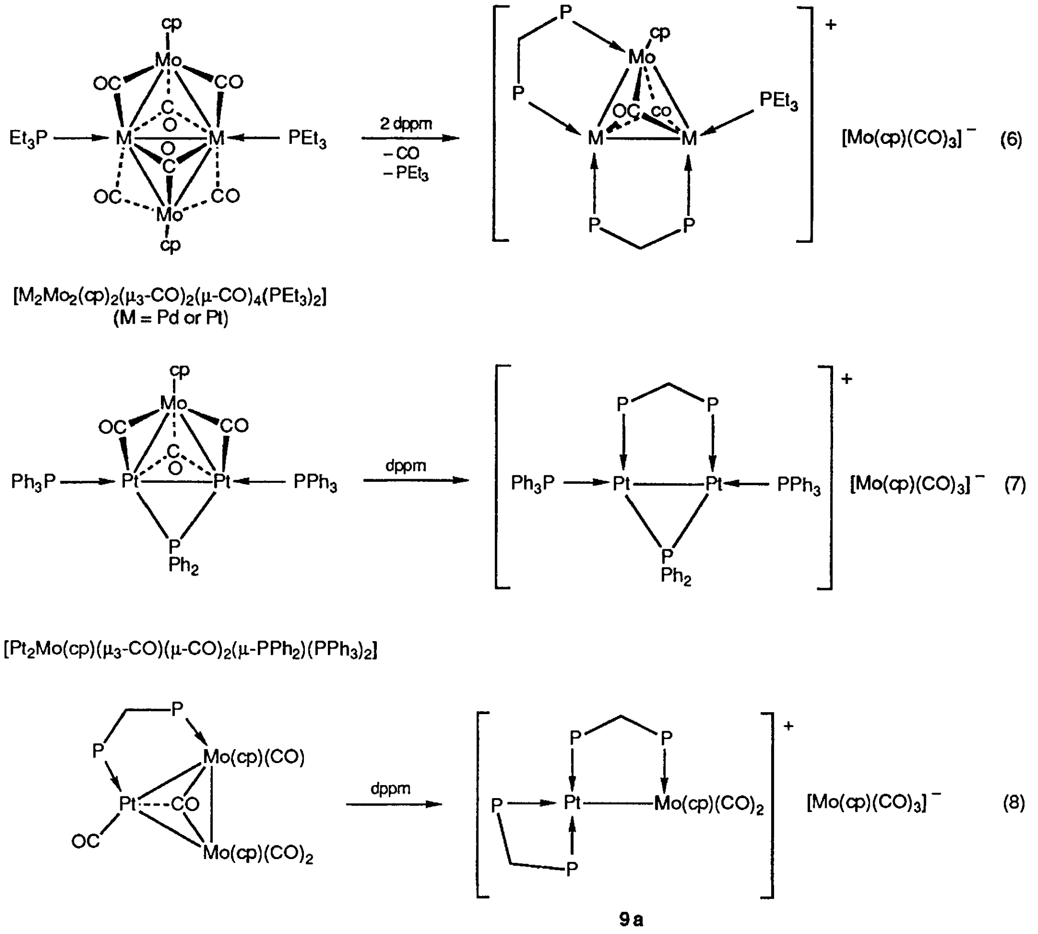
(*ca.* 63% yield) [equation (4)]. Starting from $[Pt(dppm\text{-}PP')_2]^{2+}$, we have previously obtained complexes of the type $[M'(\mu-dppm)Pt(dppm\text{-}PP')][M'(CO)]$, which contain both a chelating and bridging dppm, instead of two bridging dppm ligands.[1d] Finally, compounds **3a** or **4a** were also obtained recently by the reactions of the deep blue chain complexes *trans*-$[Pd\{M'(CO)\}_2(PhCN)_2]$ [M' = $Mo(cp)(CO)_2$ or $W(cp)(CO)_2$] with 2 equivalents of dppm in tetrahydrofuran [equation (5)].[2d] It is interesting that the corresponding platinum chain complex *trans*-$[Pt\{M'(CO)\}_2(PhCN)_2]$ reacted with 2 equivalents of dppm to yield $[M'(\mu-dppm)Pt(dppm\text{-}PP')][M'(CO)]$, of type **9a** [shown in equation (8), Scheme 2].[2d] Other *trans*-$[Pd\{M'(CO)\}_2(PhCN)_2]$ complexes [M' = $Mn(CO)_4$ or $Co(CO)_3$] have also been found to react with dppm with formation, respectively, of the mixed-metal complexes $[ClPd(\mu-dppm)_2Mn(CO)_3]$[2b] and $[PdCo_2(CO)_5(\mu-dppm)_2]$.[2d,9a]

It is noteworthy that in the reactions (2) dppm displaces the anion $[M(cp)(CO)_3]^-$ (M = Mo or W) from compound **1** or **2**. Related observations have been made recently with other palladium- or platinum-molybdenum clusters (Scheme 2). Thus, $[Pd_2Mo_2(cp)_2(CO)_6(PEt_3)_2]$ reacted with 2 equivalents of dppm and yielded quantitatively $[Pd_2Mo(cp)(CO)_2(\mu-dppm)_2(PEt_3)][Mo(cp)(CO)_3]$ [equation (6)],[10a] while $[Pt_2\{\mu-Mo(cp)(CO)_3\}(\mu-PPh_2)(PPh_3)_2]$ reacted with 1 equivalent of dppm and yielded $[Pt_2(\mu-dppm)(\mu-PPh_2)(PPh_3)_2][Mo(cp)(CO)_3]$ (equation (7)],[10] and $[PtMo_2(cp)_2(CO)_5(\mu-dppm)]$ reacted with 1 equivalent of dppm and afforded quantitatively $[(OC)_2(cp)Mo(\mu-dppm)Pt(dppm\text{-}PP')][Mo(cp)(CO)_3]$, **9a**[1d] [equation (8)]. In the latter complex, whose cation has an overall molecular formula similar to that of the Pd–Mo cation $\mathbf{3}^+$, the newly introduced dppm ligand chelates the platinum atom, instead of bridging the Pt–Mo bond, as observed for the Pd–Mo bond of $\mathbf{3}^+$. This is again consistent with the greater lability of the Pd–P bond[7,9] which facilitates access to stable, five-membered rings of the type $Pd(\mu-dppm)M'$.

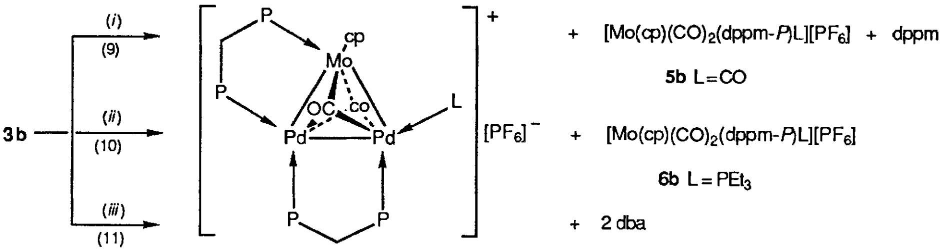
Reactivity Studies.—Reaction of complex **3b** with CO at room temperature led to (partial) fragmentation and formation of the cationic cluster $[Pd_2Mo(cp)(CO)_3(\mu-dppm)_2][PF_6]$,[7] free dppm, and $[Mo(cp)(CO)_3(dppm\text{-}P)][PF_6]$ **5b** [equation (9) in Scheme 3]. The $^{31}P-\{^1H\}$ NMR spectrum of the cation of **5b** consisted of two resonances: a low-field doublet (at δ *ca.* 50), assigned to the phosphorus atom bonded to molybdenum and a doublet at higher field assigned to the unco-ordinated phosphorus atom. Reduction of **3b** with $Na[BH_4]$ yielded $[Pd_2(dppm)_3]$[11] as the only phosphorus-containing product ($^{31}P-\{^1H\}$ NMR evidence). This stands in interesting contrast with the corresponding reaction of $[(OC)_2(cp)Mo(\mu-dppm)Pt(dppm\text{-}PP')]^+$ $\mathbf{9}^+$ with $Na[BH_4]$ which afforded the bimetallic hydrido complex $[(OC)_2(cp)Mo(\mu-dppm)PtH(dppm\text{-}P)]$.[2c] The reaction of **3b** with $[Pd(dba)_2]$ (dba = dibenzylideneacetone) quantitatively yielded the cationic cluster $[Pd_2Mo(cp)(CO)_2(\mu-dppm)_2(thf)][PF_6]$ (thf = tetrahydrofuran),[7] as a result of palladium insertion in one of the phosphorus–molybdenum bonds [equation (11)].

In contrast, no reaction occurred with $[Pt(dba)_2]$. An analogue of cation $\mathbf{5}^+$, namely $[Mo(cp)(CO)_2(dppm\text{-}P)(PEt_3)]^+$ $\mathbf{6}^+$, was obtained as the major product in the reaction of **3b** with PEt_3 [equation (10)], which also yielded traces of $[Pd_2Mo(cp)(CO)_2(\mu-dppm)_2(PEt_3)]^+$.[10] The $^{31}P-\{^1H\}$ NMR spectrum of $\mathbf{6}^+$ consisted of three resonances: a low-field doublet of doublets at δ 51.1 and a doublet at δ 40.2 assigned to the phosphorus atoms bonded to molybdenum and a higher-field doublet at δ −24.9, typical of the unco-ordinated phosphorus atom of a dppm-*P* ligand.

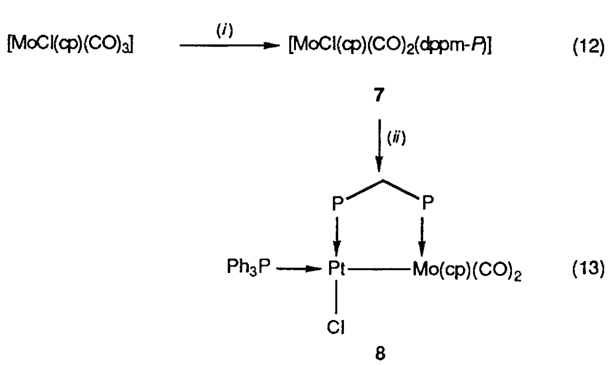
For comparison we also examined the reaction of $[MoCl(cp)(CO)_3]$ with dppm, in toluene at 80 °C, which afforded high yields of $[MoCl(cp)(CO)_2(dppm\text{-}P)]$ **7** [equation (12), Scheme 4], whose IR spectrum in the ν(CO) region [1960s and 1871m(br) cm^{-1}] is similar to that of $[MoCl(cp)(CO)_2(PPh_3)]$.[12] When solid $[Pt(C_2H_4)(PPh_3)_2]$ was added to a red



Scheme 2



Scheme 3 (*i*) CO, L = CO; (*ii*) PEt_3, L = PEt_3; (*iii*) $[Pd(dba)_2]$, L = thf



Scheme 4 (*i*) dppm, −CO; (*ii*) $[Pt(C_2H_4)(PPh_3)_2]$, $-C_2H_4$, $-PPh_3$

solution of 7 in toluene $[(OC)_2(cp)Mo(\mu\text{-dppm})PtCl(PPh_3)]$ **8** was obtained [equation (13)]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **8** consisted of three resonances: a low field doublet of doublets at δ 64 with platinum satellites [^2J(PtP) = 202 Hz], assigned to a dppm phosphorus atom bonded to molybdenum, and two doublets of doublets at δ 44.2 with platinum satellites [^1J(PtP) = 4370] and at 31.5 [^1J(PtP) = 2285 Hz] , assigned respectively to PPh_3 and a dppm phosphorus atom bonded to platinum. The low value of the coupling constant between the Pt-bound phosphorus atoms [^2J(PP) = 44.2. Hz] is characteristic of a *cis* arrangement.[2c] The ν(Pt–Cl) vibration of **8** is observed at 272 cm^{-1}, comparable to the value found for $[(OC)_5MnPtCl(dppm\text{-}PP')]$ (287 cm^{-1}).[1d]

Description of the Structure of $[Pd(\mu\text{-CO})(\mu\text{-dppm})_2Mo(cp)(CO)][PF_6]\cdot 2C_6H_6$ **3b**·$2C_6H_6$.—This complex crystallizes with two molecules of benzene and two half anions $[PF_6]^-$ in the unit cell. There are no short contacts between the cation and the $[PF_6]^-$ anions or C_6H_6 molecules. Selected bond distances and angles are given in Table 1. The labelling scheme used and the ORTEP plot is shown in Fig. 3. The molybdenum atom is co-ordinated by a cyclopentadienyl ligand at a distance of 1.889(5) Å, a phosphorus atom of each of the dppm ligands, with a P(1)–Mo–P(3) internal angle of 151.68(4)°, two carbonyl ligands with a C(56)–Mo–C(57) angle of 90.5(2)° and the palladium atom. The metal–metal distance of 2.799(1) Å is comparable with those found in other complexes containing a

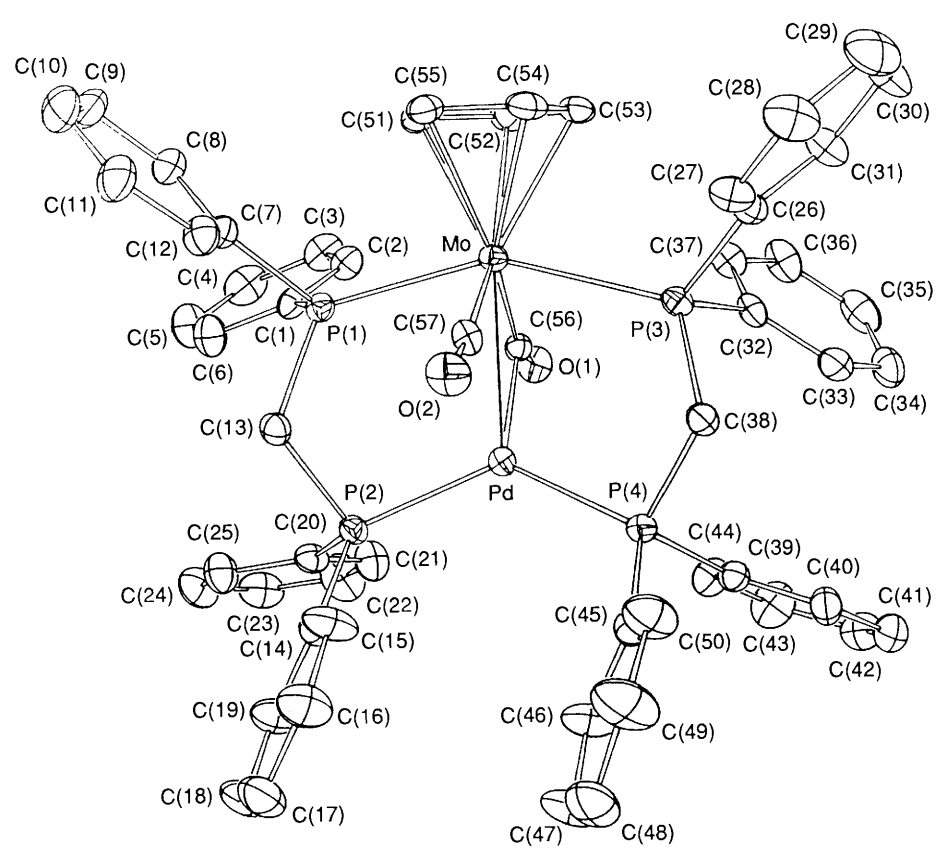


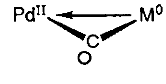
Fig. 3 An ORTEP plot of the bimetallic cation of $[\overline{Pd(\mu\text{-CO})(\mu\text{-dppm})_2Mo}(cp)(CO)][PF_6]$ **3b** showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted

Table 1 Selected bond distances (Å) and angles (°) for complex **3b**

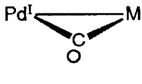
Pd–Mo	2.799(1)	P(3)–C(38)	1.831(5)
P(1)–Mo	2.579(1)	P(4)–Pd	2.308(1)
P(1)–C(1)	1.844(5)	P(4)–C(38)	1.826(6)
P(1)–C(7)	1.827(5)	P(4)–C(39)	1.820(5)
P(1)–C(13)	1.843(5)	P(4)–C(45)	1.826(5)
P(2)–Pd	2.313(1)	Mo–C(56)	2.084(5)
P(2)–C(13)	1.834(5)	C(56)–O(1)	1.171(5)
P(2)–C(14)	1.820(5)	C(56)–Pd	2.046(4)
P(2)–C(20)	1.836(5)	Mo–C(57)	1.979(5)
P(3)–Mo	2.590(1)	C(57)–O(2)	1.137(6)
P(3)–C(26)	1.832(5)	C(57)–Pd	2.626(5)
P(3)–C(32)	1.817(5)		
Mo–P(1)–C(1)	117.4(2)	Mo–P(3)–C(26)	114.9(2)
Mo–P(1)–C(7)	114.1(2)	Mo–P(3)–C(32)	117.4(2)
Mo–P(1)–C(13)	117.6(2)	Mo–P(3)–C(38)	115.9(2)
C(1)–P(1)–C(7)	102.6(2)	C(26)–P(3)–C(32)	101.9(2)
C(1)–P(1)–C(13)	104.9(2)	C(26)–P(3)–C(38)	99.2(2)
C(7)–P(1)–C(13)	97.5(2)	C(32)–P(3)–C(38)	105.1(2)
Pd–P(2)–C(13)	100.2(2)	Pd–P(4)–C(38)	102.7(2)
Mo–C(56)–Pd	85.3(2)	Pd–P(2)–C(13)	100.2(2)
Mo–C(57)–Pd	73.3(2)	Pd–P(3)–C(38)	115.9(2)
Mo–C(56)–O(1)	156.7(5)	Pd–C(56)–O(1)	117.9(4)
Mo–C(57)–O(2)	166.3(5)	Pd–C(57)–O(2)	116.3(5)

Mo–Pd bond.[6a,7,13] The (cp)MP$_2$(CO)$_2$ fragment is square pyramidal, with the cp at the apex, a situation typical of the (cp)ML$_4$ piano-stool type complexes, and the co-ordination at Mo may be viewed as of the 3:4:1 type,[14,15] The palladium atom is further ligated by the other two phosphorus atoms, with an external P(2)–Pd–P(4) angle of 127.79(5)° and the bridging carbonyl ligand C(56)–O(1) with a Pd–C(56) distance of 2.046(4) Å, slightly longer than in the symmetrical complex $[Pd_2(\mu\text{-CO})(\mu\text{-Ph}_2AsCH_2AsPh_2)_2]$ [1.84(5) and 1.95(6) Å].[16] Although the Pd–C(57) separation is much longer [2.626(5) Å], it is similar to those found in *e.g.* $[Pd_2MoCl(cp)(\mu_3\text{-CO})_2(\mu\text{-dppm})_2]$[7] or $[Pd_2Co_2(\mu_3\text{-CO})_2(CO)_5(\mu\text{-dppm})_2]$[2a,17] which contain semi-triply bridging carbonyl ligands. The geometrical parameters within the dppm ligands are unexceptional. The distorted co-ordination about the Pd atom is probably related to the geometrical constraints imposed by the Mo atom on the dppm ligands. The size of the 'pocket' delimited by the almost parallel phenyl rings C(14)–C(19) and C(45)–C(50) (which form a dihedral angle of 7.6°) is too small to allow further co-ordination of a ligand to Pd. This accounts for the observation that this bimetallic cation does not react with *e.g.* Cl$^-$ to form a Pd–Cl bond.

Bonding Description.—The bonding in the 32e cations **3**$^+$ or **4**$^+$ may be viewed as involving a donor–acceptor M→Pd bond resulting in 18-electron metal(0) and 16-electron palladium(II) centres, bridged by a μ-CO ligand, as in **A**. The alternative and formal description **B** involves covalent bonding between palladium(I) and metal(I) centres, but appears less appropriate since all the reactions leading to these complexes occur without any significant redox process. Thus, palladium is



A



B

in an oxidation state +II in all the precursor complexes, and molybdenum or tungsten is in an oxidation state of zero. Redox processes would have been accompanied by the corresponding formation of the dimers $[\{Mo(or\ W)(cp)(CO)_3\}_2]$,[6] which were not observed in significant quantities. Furthermore, the displacement reaction of $[Mo(or\ W)(cp)(CO)_3]^-$ from **1** or **2** by dppm is consistent with these metal centres retaining their oxidation state zero in these complexes. This would also be

Table 2 Positional parameters and their estimated standard deviations

Atom	*x*	*y*	*z*
Pd	0.769 99(2)	0.110 60(4)	0.420 79(2)
Mo	0.714 25(2)	0.204 31(4)	0.327 02(2)
P(1)	0.665 37(6)	0.307 1(1)	0.409 60(7)
P(2)	0.745 55(7)	0.210 0(2)	0.501 64(7)
C(1)	0.601 6(3)	0.234 3(6)	0.436 1(3)
C(2)	0.575 7(3)	0.144 6(6)	0.408 0(3)
C(3)	0.524 6(3)	0.097 9(7)	0.423 9(4)
C(4)	0.501 4(3)	0.143 5(8)	0.472 2(4)
C(5)	0.527 3(3)	0.232 5(8)	0.501 8(4)
C(6)	0.577 1(3)	0.278 6(8)	0.483 8(4)
C(7)	0.642 0(3)	0.461 6(6)	0.395 3(3)
C(8)	0.586 0(3)	0.493 3(6)	0.389 0(3)
C(9)	0.570 9(3)	0.612 7(7)	0.379 5(4)
C(10)	0.611 0(5)	0.699 5(7)	0.373 5(4)
C(11)	0.668 7(4)	0.670 3(7)	0.379 6(4)
C(12)	0.682 8(3)	0.551 0(6)	0.387 9(3)
C(13)	0.708 1(3)	0.340 5(6)	0.472 2(3)
C(14)	0.800 7(3)	0.285 7(6)	0.541 4(3)
C(15)	0.839 4(3)	0.354 0(9)	0.513 1(3)
C(16)	0.883 7(4)	0.410 9(9)	0.538 9(4)
C(17)	0.890 8(4)	0.400 4(9)	0.594 5(4)
C(18)	0.853 6(4)	0.337(1)	0.624 1(3)
C(19)	0.808 8(3)	0.277 7(8)	0.597 7(3)
C(20)	0.697 8(3)	0.143 4(6)	0.552 4(3)
C(21)	0.687 3(3)	0.023 3(7)	0.548 6(3)
C(22)	0.650 1(4)	−0.027 7(9)	0.585 3(4)
C(23)	0.624 1(3)	0.037 9(9)	0.623 5(4)
C(24)	0.633 5(4)	0.158(1)	0.627 4(4)
C(25)	0.671 5(3)	0.212 4(7)	0.591 9(3)
P(3)	0.793 01(6)	0.071 8(1)	0.286 07(7)
P(4)	0.857 08(6)	0.039 9(2)	0.396 44(7)
C(26)	0.815 4(3)	0.115 8(6)	0.216 3(3)
C(27)	0.844 3(3)	0.224 2(7)	0.208 4(3)
C(28)	0.862 1(3)	0.258 7(8)	0.157 6(4)
C(29)	0.850 5(4)	0.186(1)	0.110 9(4)
C(30)	0.822 6(4)	0.078(1)	0.117 5(3)
C(31)	0.805 0(3)	0.043 6(7)	0.169 3(3)
C(32)	0.778 8(3)	−0.088 7(6)	0.277 0(3)
C(33)	0.821 7(3)	−0.172 2(7)	0.275 0(3)
C(34)	0.811 5(4)	−0.294 5(7)	0.266 2(3)
C(35)	0.755 8(5)	−0.331 6(7)	0.255 1(4)
C(36)	0.712 5(3)	−0.250 3(7)	0.256 4(4)
C(37)	0.724 1(3)	−0.129 3(6)	0.268 3(3)
C(38)	0.860 6(2)	0.078 8(6)	0.322 6(3)
C(39)	0.872 7(3)	−0.121 2(6)	0.401 0(3)
C(40)	0.920 7(3)	−0.170 8(7)	0.379 7(3)
C(41)	0.929 2(4)	−0.294 4(7)	0.380 0(4)
C(42)	0.890 0(4)	−0.369 8(7)	0.402 6(4)
C(43)	0.842 3(4)	−0.319 5(8)	0.425 0(5)
C(44)	0.832 6(3)	−0.198 3(7)	0.424 0(4)
C(45)	0.919 1(3)	0.111 6(6)	0.427 1(3)
C(46)	0.927 5(4)	0.095 1(9)	0.483 8(4)
C(47)	0.972 3(4)	0.149(1)	0.511 2(4)
C(48)	1.006 1(4)	0.224(1)	0.483 5(4)
C(49)	0.995 4(4)	0.253(1)	0.429 3(4)
C(50)	0.952 7(3)	0.190 2(9)	0.400 4(4)
C(51)	0.629 2(3)	0.276 6(6)	0.291 0(3)
C(52)	0.637 6(3)	0.165 2(7)	0.265 3(3)
C(53)	0.686 2(3)	0.170 3(7)	0.234 2(3)
C(54)	0.709 3(3)	0.288 8(7)	0.240 5(3)
C(55)	0.673 9(3)	0.354 7(6)	0.274 6(3)
O(1)	0.680 8(2)	−0.039 4(4)	0.389 9(2)
C(56)	0.701 7(2)	0.051 5(5)	0.376 3(2)
O(2)	0.813 6(2)	0.366 1(4)	0.365 7(2)
C(57)	0.778 5(3)	0.300 0(6)	0.355 3(3)
P(5)	0.500	0.134 1(4)	0.750
F(1)	0.509(1)	0.062(2)	0.704(1)
F(2)	0.559(1)	0.138(2)	0.756(1)
F(3)	0.520(1)	0.250(2)	0.718(1)
P(6)	0.000	0.444 6(3)	0.250
F(4)	0.043 9(4)	0.354 6(8)	0.242 1(7)
F(5)	0.046 4(4)	0.463 3(8)	0.745 2(6)
F(6)	0.015 5(6)	0.451(2)	0.308 6(4)
C(58)	0.301 0(8)	0.445(1)	0.391 8(6)
C(59)	0.352 5(9)	0.460(1)	0.390(1)
C(60)	0.384 7(8)	0.414(1)	0.430 4(8)
C(61)	0.357 1(8)	0.355(1)	0.470 5(6)
C(62)	0.297 8(9)	0.333(2)	0.467 6(9)
C(63)	0.266 9(8)	0.370(2)	0.426(1)
C(64)	0.018 7(5)	−0.047 1(8)	0.769 3(7)
C(65)	0.039 8(4)	0.063(1)	0.791 4(5)
C(66)	0.019 4(4)	0.169 2(8)	0.767 5(5)
C(67)	0.489 1(5)	0.256(1)	0.279 2(5)
C(68)	0.475 1(7)	0.347(2)	0.305 9(8)
C(69)	0.486 4(9)	0.459(1)	0.279 5(8)

consistent with the formally platinum(II) centre of [PtMo$_2$(cp)$_2$(CO)$_5$(μ-dppm)] retaining its oxidation state in the reaction product with dppm, namely [(OC)$_2$(cp)$_2$Mo(μ-dppm)Pt(dppm-*PP′*)]$^+$.[1d] A similar Mo^0→Pd^{II} donor-acceptor bond has been described recently in [(OC)$_4$Mo{μ-P(C$_6$H$_{11}$)$_2$}$_2$Pd(PPh$_3$)] [Mo–Pd 2.760(1) Å].[18] It is interesting that a number of heterodinuclear complexes containing a donor–acceptor metal–metal bond have recently been stabilized by use of the dppm ligand.[19]

Experimental

All reactions were carried out under an atmosphere of dry nitrogen, in Schlenk-type flasks. Solvents were purified by standard methods. Column chromatography was performed under nitrogen with use of silica gel (Kieselgel 60, Merck). Infrared spectra were recorded either as KBr pellets or in solutions on a Perkin-Elmer 398 spectrophotometer, NMR spectra on a FT-Bruker WP 200 SY instrument at 200.13 (^{1}H) or 81.02 MHz (^{31}P-{^{1}H}) using solvent resonances as internal standards. Proton chemical shifts were positive downfield relative to external SiMe$_4$, ^{31}P chemical shifts were externally referenced to 85% H$_3$PO$_4$ in water with downfield chemical shifts reported as positive. Elemental analyses were performed by the Service Central de Microanalyses du CNRS. The ligand Ph$_2$PCH$_2$PPh$_2$(dppm)[20] and the complexes [PdCl$_2$(dppm-*PP′*)],[11] [Pd(dppm-*PP′*)$_2$][BF$_4$]$_2$,[11] [Pd(dba)$_2$],[21a] [Pt(dba)$_2$],[21b] [Pt(C$_2$H$_4$)(PPh$_3$)$_2$],[22] Na[M(cp)(CO)$_3$]·2dme (M = Mo or W)[23] and [MoCl(cp)(CO)$_3$][24] were prepared by literature methods.

Preparations.—[PdMo$_2$(cp)$_2$(CO)$_5$(μ-dppm)] **1**. The procedure detailed for the synthesis of complex **2** was used, starting from [PdCl$_2$(dppm-*PP′*)] (0.280 g, 0.5 mmol) and Na[Mo(cp)(CO)$_3$]·2dme (0.447 g, 1 mmol). It afforded **1** which precipitated as a green powder after addition of hexane to the toluene solution (0.25 g, 42% based on Pd) [Found: C, 50.20; H, 3.60. C$_{40}$H$_{32}$Mo$_2$O$_5$P$_2$Pd (*M* = 952.88) requires C, 50.40; H, 3.85%]. IR (toluene): ν(CO) 1952s, 1910vs, 1812m(br), 1778m and 1750m cm^{-1}. ^{31}P-{^{1}H} NMR (D$_2$O–toluene): δ 61.4 [d, *J*(PP) = 151, PMo], and 3.5 [d, *J*(PP) = 151 Hz, PPd]. When only 1 equivalent of Na[Mo(cp)(CO)$_3$]·2dme was used complex **1** was obtained in lower yield (0.105 g, 22% yield based on Pd), and *ca.* 40% unreacted [PdCl$_2$(dppm-*PP′*)] was recovered.

[PdW$_2$(cp)$_2$(CO)$_5$(μ-dppm)] **2**. A solution of Na[W(cp)(CO)$_3$]·2dme (0.535 g, 1 mmol) in thf (10 cm^3) was added dropwise to a solution of [PdCl$_2$(dppm-*PP′*)] (0.280 g, 0.5 mmol) in thf (20 cm^3) at −10 °C. The solution slowly turned green and after 2 h at −10 °C the reaction temperature was progressively raised to 0 °C by replacing the acetone–solid CO$_2$ bath with ice. The temperature was then raised to 20 °C and the colour changed from green to deep green. The solvent was removed under reduced pressure. Extraction of the solid residue with toluene (60 cm^3), filtration of the extract through a Celite-padded filter funnel, concentration to *ca.* 5 cm^3, and addition of hexane (50 cm^3) yielded at −30 °C a green powder of complex **2** (0.32 g, 57% based on Pd) [Found: C, 42.65; H, 3.00. $C_{40}H_{32}O_5P_2PdW_2$ (*M* = 1128.7) requires C, 42.55; H, 2.85%)]. IR (toluene): ν(CO) 1945s, 1905vs, 1803m, 1785m(br) and 1747mw cm^{-1}. ^{31}P-{^{1}H} NMR (D_2O–toluene): δ 19.4 [d, *J*(PP) = 138, PW] and 1.5 [d, *J*(PP) = 138 Hz, PPd].

[Pd(μ-CO)(μ-dppm)$_2$Mo(cp)(CO)][PF$_6$] **3b**. *Starting from* [PdCl$_2$(dppm-*PP′*)]. To a green thf solution (30 cm^3) of [PdMo$_2$(cp)$_2$(CO)$_5$(μ-dppm)], prepared as indicated above from [PdCl$_2$(dppm-*PP′*)] (0.280 g, 0.5 mmol) and Na[Mo(cp)(CO)$_3$]·2dme (0.447 g, 1 mmol), was added solid dppm (0.19 g, 0.5 mmol). The colour of the solution turned red. Solid [NH$_4$][PF$_6$] (0.328 g, 2 mmol) was added, and the mixture was brought to ambient temperature. The solvent was removed under reduced pressure and the residue chromatographed on a silica gel column. Elution with toluene afforded red [{Mo(cp)(CO)$_3$}$_2$] (0.110 g). Further elution with toluene–thf (3:1) afforded an orange band of [Pd(μ-CO)(μ-dppm)$_2$Mo(cp)(CO)][PF$_6$] **3b**. This toluene–thf mixture was evaporated to dryness under reduced pressure. The orange oil was dissolved in thf (5 cm^3) and slow diffusion of benzene yielded orange crystals of **3b** (0.42 g, 68% yield based on Pd) [Found: C, 55.50; H, 3.80; F, 8.30; Mo, 7.50; P, 12.40; Pd, 8.20. $C_{57}H_{49}F_6MoO_2P_5Pd$ (*M* = 1237.23) requires C, 55.35; H, 4.00; F, 9.20; Mo, 7.75; P, 12.50; Pd, 8.60%]. IR: ν(CO) (Nujol) 1864s and 1808s; (thf): 1874m(br) and 1804s(br) cm^{-1}. NMR ^{1}H[(CD$_3$)$_2$CO], δ 7.10–7.55 (m, 40 H, C_6H_5), 4.83 [t, 5 H, C_5H_5, ^3J(PH) = 2.65 Hz] and 3.93 (m, 4 H, CH$_2$); ^{31}P-^{1}H} (thf–C_6D_6), AA′XX′ spin system, $K = |J(P_AP_{A'}) + J(P_XP_{X'})| = 128.5$, $L = |J(P_AP_X) - J(P_AP_{X'})| = 174.5$, $M = |J(P_AP_{A'}) - J(P_XP_{X'})| = 8$, $N = |J(P_AP_X) + J(P_AP_{X'})| = 243.5$, Hz; values obtained using the PANIC computer simulation program, δP$_A$ (PPd) = 15.3, δP$_X$ (PMo) = 50.6, $J(P_AP_{A'}) = 86$, $J(P_AP_X) = J(P_{A'}P_{X'}) = 209$, $J(P_AP_{X'}) = J(P_{A'}P_X) = 34.5$, $J(P_XP_{X'}) = 94$; δ −142.7 [spt, ^1J(PF) = 710 Hz, PF$_6$].

Starting from [Pd(dppm-*PP′*)$_2$][BF$_4$]$_2$. A mixture of [Pd(dppm-*PP′*)$_2$][BF$_4$]$_2$ (1.05 g, 1 mmol) and Na[Mo(cp)(CO)$_3$] (0.89 g, 2 mmol) was allowed to react at room temperature in thf (20 cm^3) for 3 h. The red solution was then evaporated to dryness under reduced pressure. Solid [NH$_4$][PF$_6$] (0.67 g, 4 mmol) was added and the mixture was stirred for 12 h. Complex **3b** (1.55 g, 63% yield based on Pd) was obtained after purification, as described above.

[Pd(μ-CO)(μ-dppm)$_2$W(cp)(CO)][PF$_6$] **4b**. *Starting from* [PdCl$_2$(dppm-*PP′*)]. To a green thf solution (20 cm^3) of [PdW$_2$(cp)$_2$(CO)$_5$(μ-dppm)] (0.56 g, 0.50 mmol) at 0 °C, was added solid dppm (0.19 g, 0.50 mmol). The colour of the solution turned red. Solid [NH$_4$][PF$_6$] (0.328 g, 2 mmol) was added, and the mixture was raised to ambient temperature. The ^{31}P-{^{1}H} NMR spectrum showed the typical AA′BB′ pattern of **4b**, see below.

Starting from [Pd(dppm-*PP′*)$_2$][BF$_4$]$_2$. A mixture of [Pd(dppm-*PP′*)$_2$][BF$_4$]$_2$ (1.05 g, 1.00 mmol) and Na[W(cp)(CO)$_3$] (1.07 g, 2.00 mmol) was allowed to react at room temperature in thf (20 cm^3) for 3 h. Solid [NH$_4$][PF$_6$] (0.67 g, 4 mmol) was then added and the mixture was stirred for 1 h. The ^{31}P-{^{1}H} NMR spectrum showed the typical AA′BB′ pattern of complex **4b**. It was not possible to obtain pure **4b**, despite several attempts by recrystallization or chromatography, owing to slow transformation to [Pd$_2$W(cp)(CO)$_2$(μ-dppm)$_2$(thf)][PF$_6$].[7] Spectroscopic data for **4b**: IR (KBr) ν(CO) 1880s and 1800s cm^{-1}; ^{31}P-{^{1}H} NMR (thf–C_6D_6), AA′BB′ spin system, $K = |J(P_AP_{A'}) + J(P_BP_{B'})| = 170$, $L = |J(P_AP_B) - J(P_AP_{B'})| = 158$, $M = |J(P_AP_{A'}) - J(P_BP_{B'})| = 16$, $N = |J(P_AP_B) + J(P_AP_{B'})| = 250$, Hz; values obtained using the PANIC computer simulation program δP$_A$ (PPd) = 20.7, δP$_B$ (PW) = 14.7, $J(P_AP_{A'}) = 77$, $J(P_AP_B) = J(P_{A'}P_{B'}) = 204$, $J(P_AP_{B'}) = J(P_{A'}P_B) = 46$, $J(P_BP_{B'}) = 93$; δP −142.5 [spt, ^1J(PF) = 705 Hz, PF$_6$]; from the ^{183}W satellites in the P$_B$ resonances, ^1J(^{183}W–P) = 115 Hz.

Reactions of Complex **3b**.—*With* Na[BH$_4$]. A mixture of Na[BH$_4$] (0.005 g, 0.122 mmol) and complex **3b** (0.150 g, 0.061 mmol) in ethanol (25 cm^3) were allowed to react at room temperature for 5 h. A yellow precipitate formed which was filtered off and washed with EtOH and hexane. The IR spectrum showed no ν(CO) band. The ^{31}P-{^{1}H} NMR spectrum (thf–C_6D_6) showed a singlet at δ 14.1(s) corresponding to [Pd$_2$(dppm)$_3$].[11]

With PEt$_3$. A solution of PEt$_3$ (0.022 cm^3, 0.162 mmol) in hexane was added to a thf (20 cm^3) solution of complex **3b** (0.200 g, 0.081 mmol). The mixture was allowed to react at room temperature for 0.5 h. The red solution was evaporated to dryness and the residue was investigated by IR and ^{31}P-{^{1}H} NMR spectroscopy. IR (thf): ν(CO) 1965vs, 1920w, 1880vs and 1806w(br) cm^{-1}. The ^{31}P-{^{1}H} NMR spectrum (thf–C_6D_6) showed the presence of a complex mixture with resonances assigned to [Mo(cp)(CO)$_2$(dppm-*P*)(PEt$_3$)][PF$_6$] **6b**, at δ 51.1 [dd, 1 P, ^2J(PP) = 68 and 19, PCH$_2$*P*Mo), 40.2 [d, 1 P, ^2J(PP) = 19, Et$_3$PM −24.9 [d, 1 P, ^2J(PP) = 67, Mo-PCH$_2$*P*] and −142.5 [spt, 1 P, ^1J(PF) = 879 Hz, PF$_6$], [Pd$_2$Mo(cp)(CO)$_2$(μ-dppm)$_2$(PEt$_3$)][PF$_6$][10] (present in small amounts), and at δ 5.42 (unassigned).

With [Pt(dba)$_2$]. Solid [Pt(dba)$_2$] (0.075 g, 0.122 mmol) was introduced in a thf (10 cm^3) solution of complex **3b** (0.150 g, 0.061 mmol). The violet solution was stirred at room temperature for 5 h. After this time an IR spectrum in the ν(CO) region showed no new bands. The ^{31}P-{^{1}H} NMR spectrum (thf–C_6D_6) revealed only the presence of **3b**.

With [Pd(dba)$_2$]. Solid [Pd(dba)$_2$] (0.041 g, 0.070 mmol) was introduced in a thf (10 cm^3) solution of complex **3b** (0.150 g, 0.061 mmol) and the deep violet solution was stirred at room temperature for 5 h. The ^{31}P-{^{1}H} NMR spectrum (thf–C_6D_6) of this solution revealed only the presence of [Pd$_2$Mo(cp)(CO)$_2$(μ-dppm)$_2$(thf)][PF$_6$].[7]

With CO. Carbon monoxide was bubbled at room temperature through a solution of complex **3b** (0.200 g, 0.081 mmol) in thf (10 cm^3) and the reaction was monitored by ^{31}P-{^{1}H} NMR spectroscopy after 0.5 and 1 h, showing that a slow reaction occurred. The red-brown solution was evaporated to dryness and the ^{31}P-{^{1}H} NMR spectrum (thf–C_6D_6) of the red-brown residue showed the typical resonances of [Pd$_2$Mo(cp)(CO)$_3$(μ-dppm)$_2$][PF$_6$][7] and two doublets at δ 50.79 and −24.55 with ^2J(PP) = 58 Hz, which we assign to [Mo(cp)(CO)$_3$(dppm-*P*)][PF$_6$] **5b**.

With LiCl. Whereas no reaction was observed in thf (24 h, room temperature), a mixture of complex **3b** (0.150 g, 0.061 mmol) and solid LiCl (0.0052 g, 0.122 mmol) in CH$_2$Cl$_2$ (10 cm^3) turned green after stirring at room temperature for 24 h. Evaporation to dryness and extraction with toluene–CH$_2$Cl$_2$ (2:1) yielded a solution which deposited at −30 °C dark green crystals of [Pd$_2$MoCl(cp)(CO)$_2$(μ-dppm)$_2$] (12% yield based on Pd) identified by ^{31}P-{^{1}H} NMR spectroscopy.[7] This *triangulo* cluster also formed upon recrystallization of **3b** from CH$_2$Cl$_2$–hexane.

Reaction of [MoCl(cp)(CO)$_3$] *with dppm*.—A mixture containing [MoCl(cp)(CO)$_3$] (0.300 g, 1.07 mmol) and dppm (0.412 g, 1.07 mmol) in toluene (15 cm^3) was heated at 80 °C for 4 h. Monitoring of the reaction by IR spectroscopy showed the disappearance of the ν(CO) vibrations of [MoCl(cp)(CO)$_3$] and new bands at 1960s and 1871m(br) cm^{-1} assigned to [MoCl(cp)(CO)$_2$(dppm-*P*)] **7**. The ^{31}P-{^{1}H} NMR spectrum (thf–C_6D_6) of this red solution showed two doublets at δ 42.4 and −24.7 with ^2J(PP) = 71 Hz for **7**, and a singlet at δ 8.3 (unassigned).

Synthesis of [(OC)$_2$(cp)Mo(μ-dppm)PtCl(PPh$_3$)] **8**.—A toluene solution (20 cm^3) containing [MoCl(cp)(CO)$_3$] (0.400 g, 1.43 mmol) and dppm (0.55 g, 1.43 mmol) was stirred at 80 °C for 4 h then cooled to room temperature. Solid [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (0.747 g, 1 mmol) was added and the red solution was stirred for 1 h at room temperature. After this time the solution was filtered through a Celite-padded filter funnel, concentrated to *ca.* 5 cm^3 and hexane was added to precipitate a red solid that was collected by filtration. Recrystallization from toluene–hexane afforded a red-brown powder of complex **8** (0.41 g, 38% based on Pt). NMR: ^{1}H (C$_6$D$_6$), 7.73–6.99 δ (m, 35 H, C$_6$H$_5$), 4.97 (s, 5 H, C$_5$H$_5$) and 3.18 (m, 2 H, CH$_2$); ^{31}P-{^{1}H} (thf–C$_6$H$_6$), δ 64.0 [dd, 1 P, PMo, J(PP) = 190, 6, ^2J(PtP) = 202], 44.2 [dd, 1 P, Ph$_3$PPt, J(PP) = 44, 6, ^1J(PtP) = 4370] and 31.53 [dd, 1 P, PPt, J(PP) = 190, 44, ^1J(PtP) = 2285 Hz]. IR (Nujol): ν(CO) 1785s and 1722s; ν(PtCl) 272 cm^{-1}.

Crystal-structure Analysis of Complex **3b**.—*Crystal data.* C$_{69}$H$_{61}$F$_6$MoO$_2$P$_5$Pd, M = 1393.45, monoclinic, space group $P2/c$, a = 23.923(6), b = 11.040(3), c = 24.012(6) Å, β = 90.79(2)°, U = 6341.4 Å^3, D_c = 1.459 g cm^{-3}, Z = 4, Mo-Kα radiation, λ = 0.7093 Å, μ = 6.567 cm^{-1}, F(000) = 2832, T = 293 K.

Data collection and processing. Suitable single crystals of complex **3b** were obtained by slow diffusion of benzene into a thf solution at room temperature. A single crystal of dimensions 0.23 × 0.32 × 0.37 mm was cut and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using an Enraf-Nonius CAD4-F automated diffractometer showed that the crystals belong to the monoclinic system. The resulting data set was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package was used.[25] 12 055 Reflections measured, 7361 with $I > 3\sigma(I)$ observed, three standard reflections measured every hour during the entire data collection period showed no significant alteration. The raw data were converted into intensities and corrected for Lorentz and polarization factors. The structure was solved using the heavy-atom method. The [PF$_6$]$^-$ group is split into two half moieties each on a two-fold axis. In the unit cell there are six non-bonded benzene molecules, four in general position and two on a mirror plane. After refinement of the heavy atoms, a Fourier difference map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure-factor calculations by their computed coordinates (C–H 0.95 Å) and isotropic thermal parameters such as B(H) = 1.3 B_{equiv}(C) Å^2 but not refined. At this stage empirical absorption corrections were applied using the method of Walker and Stuart.[26] Full least-squares refinements; weighting scheme employed: $\sigma^2(F^2) = \sigma^2$ counts + $(0.08\,I)^2$. A final difference map revealed no significant maxima. The scattering-factor and anomalous-dispersion coefficients were taken from ref. 27*a* and *b*. Refinement converged at R 0.053 and R' 0.080. Selected bond distances and angles are given in Table 1, atomic coordinates in Table 2, and a view of the molecule is shown in Fig. 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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