1638 *Inorg. Chem.* **1993**, *32*, 1638–1648

dppm-Assisted Synthesis and Reactivity of Bimetallic M–Mo, M–W, M–Co, and M–Mn (M = Pt, Pd) Complexes. Crystal Structure of $[(\eta^2\text{-dppm})\text{Pt}(\mu\text{-dppm})\text{W(CO)}_2\text{Cp}][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$)

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Heterometallic carbonyl complexes and clusters were prepared by reaction of dppm (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) with linear trinuclear chain complexes *trans*-[Pt(or Pd){m(CO)}$_2$(NCPh)$_2$] (m(CO) = Mo(CO)$_3$Cp, W(CO)$_3$Cp, Mn(CO)$_5$, Co(CO)$_4$). The reaction of *trans*-[Pd{m(CO)}$_2$(NCPh)$_2$] with dppm afforded products having very different structures depending on the nature of the metal carbonyl fragment m(CO), as exemplified by the synthesis of the cationic bimetallic complexes [Pd(μ-dppm)$_2$m]$^+$ (m = Mo(CO)$_2$Cp, **1**$^+$; m = W(CO)$_2$Cp, **2**$^+$), the neutral bimetallic [ClPd(μ-dppm)$_2$Mn(CO)$_3$] (**3a**), and the trinuclear cluster [PdCo$_2$(CO)$_5$(μ-dppm)$_2$] (**6**). In contrast, the reaction of the Pt precursor *trans*-[Pt{m(CO)}$_2$(NCPh)$_2$] with dppm is much more selective, giving only bimetallic ionic complexes [(η^2-dppm)Pt(μ-dppm)m][m(CO)] (m = Mo(CO)$_2$Cp, **7a**; m = W(CO)$_2$Cp, **8a**; m = Mn(CO)$_4$, **9**; m = Co(CO)$_3$, **10**). Exchange of the anions in **7a** and **8a** with PF$_6^-$ afforded [(η^2-dppm)Pt(μ-dppm)Mo(CO)$_2$Cp][PF$_6$] (**7b**) and [(η^2-dppm)Pt(μ-dppm)W(CO)$_2$Cp][PF$_6$] (**8b**), respectively, which are more soluble. The solid-state structure of the dichloromethane solvate of **8b** has been determined by a single-crystal X-ray analysis. It crystallizes in the triclinic space group *P*1 with *Z* = 1 in a unit cell of dimensions *a* = 11.257(7) Å, *b* = 12.691(6) Å, *c* = 11.055(6) Å, α = 112.20(3)°, β = 101.68(3)°, and γ = 76.71(4)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 5157 observed reflections to *R* and R_w values of 0.0372 and 0.0494, respectively. In the structure of the chiral cation of **8b**, a dppm chelates the Pt atom and the other bridges the W and Pt metals, which are linked by a rather long metal–metal bond [2.902(2) Å]. Compounds **7b** and **8b** react with NaBH$_4$ to give the hydrido complexes [(η^1-dppm)(H)Pt(μ-dppm)m] (m = Mo(CO)$_2$Cp, **11**; m = W(CO)$_2$Cp, **12**) in which the hydride ligand occupies a position trans to phosphorus. The situation is different for [(η^1-dppm)(H)Pt(μ-dppm)Co(CO)$_3$] (**13**), obtained from **10**, in which the hydride ligand is cis to the Pt-bound phosphorus atoms. The structures of all these complexes are consistent with the IR and ^{1}H, ^{31}P, and ^{195}Pt spectroscopic data.

Introduction

We have recently reported the synthesis, structures and catalytic[1] applications of a series of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) stabilized tri- and tetranuclear mixed-metal clusters containing platinum and/or palladium and another transition metal such as Mo,[2a,i] W,[2a,i] Mn,[2b,c,i] Fe,[2c,d,i] and Co.[2e–i] They were conveniently prepared by the reactions of the dinuclear complexes [ClPd(μ-dppm)$_2$MCl] (M = Pd, Pt) with the corresponding carbonylmetalates [m(CO)]$^-$ (m = Mo(CO)$_2$Cp, W(CO)$_2$Cp, Mn(CO)$_4$, Fe(CO)$_2$NO, Co(CO)$_3$). Other bi- and trinuclear mixed-metal complexes were obtained from the reactions of [M(η^2-dppm)Cl$_2$] with [m(CO)]$^-$.[3] We have also investigated reactions of dppm with the trinuclear chain complexes *trans*-[Pt(or Pd){m(CO)}$_2$(NCPh)$_2$],[2e,4] as an extension of reactivity studies of the latter with monodentate phosphines.[5,6] Whereas some clusters may be obtained by either of these two routes, we observed that new heterodinuclear, cationic complexes could be obtained only

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[†] Université Louis Pasteur.

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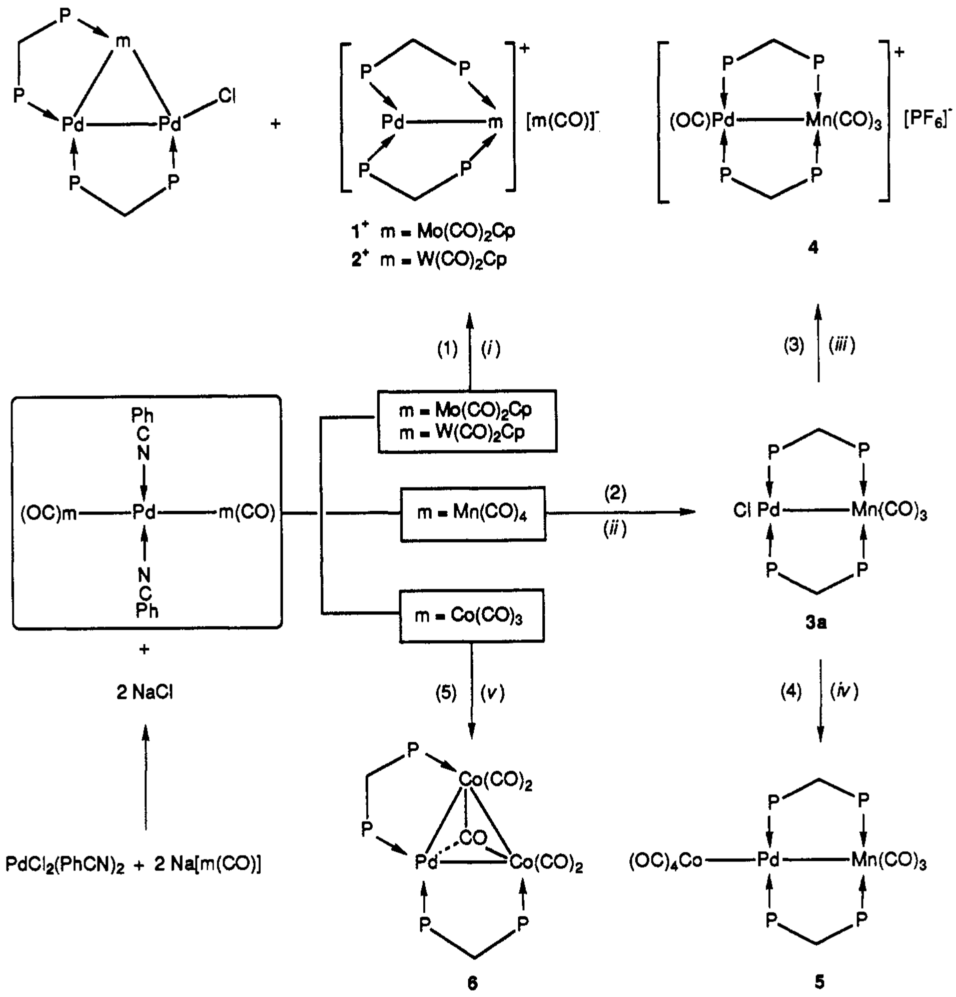
Scheme I



(*i*) + 2 dppm, - CO, - 2 PhCN; (*ii*) + 2 dppm, formation of $Mn_2(CO)_{10}$, $Mn_2(CO)_8(\mu\text{-dppm})$ and *fac*-$[MnCl(CO)_3(\eta^2\text{-dppm})$; (*iii*) + $Tl[PF_6]$, + CO, - TlCl; (*iv*) + $Na[Co(CO)_4]$, - NaCl; (*v*) + 2 dppm, - 3 CO, - 2 PhCN.

by the latter method.[4] These results are reported here, together with the crystal structure of $[(\eta^2\text{-dppm})\overline{Pt(\mu\text{-dppm})W}(CO)_2Cp][PF_6]$ (**8b**) and reactivity studies leading to the synthesis of heterobimetallic hydrido complexes.

Results

Reactions of *trans*-$[Pd\{m(CO)\}_2(NCPh)_2]$ (m = $Mo(CO)_2Cp$, $W(CO)_2Cp$, $Mn(CO)_4$, $Co(CO)_3$) with dppm. The reactions were monitored by IR spectroscopy in the ν(CO) region and are summarized in Scheme I. The violet trinuclear chain complexes *trans*-$[Pd\{m(CO)\}_2(NCPh)_2]$ (m = $Mo(CO)_2Cp$, $W(CO)_2Cp$) were prepared in situ by the reaction of $[PdCl_2(NCPh)_2]$ with 2 equiv Na[m(CO)] in THF at −80 °C.[6a] Their solutions thus always contained chloride ions, which explains the occasional isolation of chloro derivatives in reactions described below. These complexes reacted instantly with 2 equiv of dppm in THF and afforded the dinuclear cations $[\overline{Pd(\mu\text{-dppm})_2m}]^+$ (1^+ or 2^+) (Scheme I, eq 1) and the green cluster $[Pd_2mCl(\mu\text{-dppm})_2]$, whose crystal structure has been determined previously for m = $Mo(CO)_2Cp$.[2a] The characteristic absorptions of $[Mo(CO)_3Cp]^-$ were detected when dppm was introduced. The dinuclear cation 1^+ was characterized by $^{31}P\{^1H\}$ NMR spectroscopy, and its structure was established by an X-ray diffraction study of its $[PF_6]^-$ salt.[7] When the reaction of eq 1 was carried out with only 1 equiv of dppm, 1^+ or 2^+ was isolated in low yield. Complex 2^+ is less stable than 1^+ and could not be chromatographed; it was therefore only characterized in solution. Further details on these compounds are given elsewhere.[7]

The violet linear chain complex *trans*-$[Pd\{Mn(CO)_5\}_2(NCPh)_2]$, prepared in situ by the reaction of $[PdCl_2(NCPh)_2]$ with 2 equiv of $Na[Mn(CO)_5]$, reacted instantly at −80 °C with 2 equiv of dppm in THF (Scheme I, eq 2). It afforded the neutral bimetallic complex $[Cl\overline{Pd(\mu\text{-dppm})_2Mn}(CO)_3]$ (**3a**) in ca. 25% yield, whose characteristic $^{31}P\{^1H\}$ (AA′XX′ pattern) and ^1H NMR data have been reported,[2b,c,8] and $[Mn_2(CO)_{10}]$, $[Mn_2(CO)_8(\mu\text{-dppm})]$[9] and *fac*-$[MnCl(CO)_3(\eta^2\text{-dppm})]$[10] in low yield. When a Pd/dppm ratio of 1:1 or 2:1 was used, formation of **3a** was disfavored or suppressed. The halide ligand in **3a** or in its bromo analogue $[Br\overline{Pd(\mu\text{-dppm})_2Mn}(CO)_3]$ (**3b**) may be substituted

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[6] (a) Bender, R.; Braunstein, P.; Jud, J.-M.; Dusausoy, Y. *Inorg. Chem.* **1983**, *22*, 3394; (b) *Ibid.* **1984**, *23*, 4489; (c) Braunstein, P.; de Méric de Bellefon, C.; Bouaoud, S.-E.; Grandjean, D.; Halet, J.-F.; Saillard, J.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 5282.

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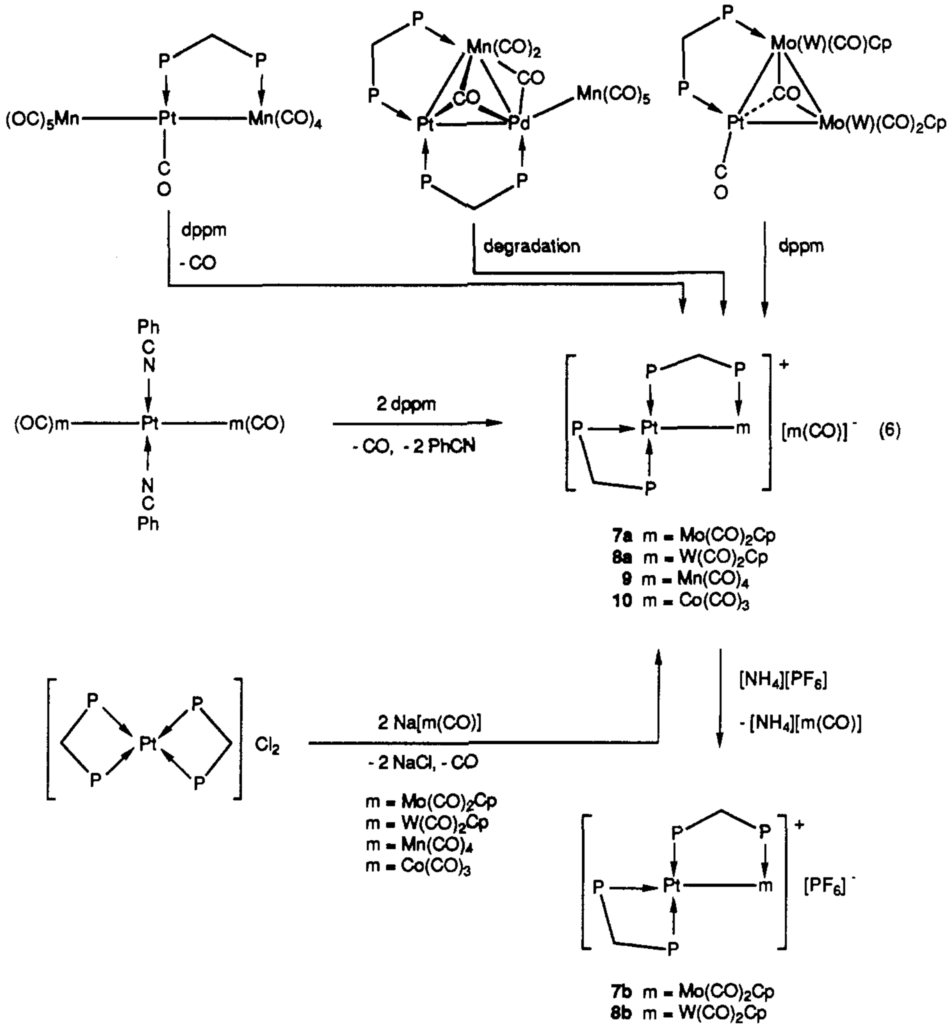
Scheme II



by a carbonyl ligand in the presence of Tl[PF$_6$] as a halide abstractor, to afford the new binuclear complex [(OC)Pd(μ-dppm)$_2$Mn(CO)$_3$][PF$_6$] (**4**) in which a carbonyl ligand is terminally bonded to the palladium center (Scheme I, eq 3). The bimetallic complexes **3a** or **3b** were reacted with [Co(CO)$_4$]$^-$ in Et$_2$O to produce the violet, linear trimetallic complex [(OC)$_4$CoPd(μ-dppm)$_2$Mn(CO)$_3$] (**5**) (Scheme I, eq 4), but no reaction occurred with other carbonylmetalates such as [Mo(CO)$_3$Cp]$^-$, probably owing to steric reasons.[2c,i]

The violet trinuclear chain complex *trans*-[Pd{Co(CO)$_4$}$_2$(NCPh)$_2$] prepared in situ by the reaction of [PdCl$_2$(NCPh)$_2$] with 2 equiv of Na[Co(CO)$_4$], reacted immediately at −80 °C with 2 equiv of dppm in THF, to give the red brown neutral trinuclear cluster [PdCo$_2$(CO)$_5$(μ-dppm)$_2$] (**6**)[3] in 35% yield (Scheme I, eq 5). Its IR spectrum contains strong carbonyl absorptions at 1984 (vs), 1943 (vs), 1928 (vs), 1895 (m) and 1709 (s) cm^{-1}, the latter being consistent with a semitriply bridging carbonyl ligand in **6**, as observed in its platinum analog [PtCo$_2$(CO)$_5$(μ-dppm)$_2$].[3]

Reactions of *trans*-[Pt{m(CO)}$_2$(NCPh)$_2$] (m = Mo(CO)$_2$Cp, W(CO)$_2$Cp, Mn(CO)$_4$, Co(CO)$_3$) with dppm. The reactions are summarized in Scheme II. The red, air-stable linear chain complexes *trans*-[Pt{m(CO)}$_2$(NCPh)$_2$] (m = Mo(CO)$_2$Cp, W(CO)$_2$Cp, Mn(CO)$_4$, Co(CO)$_3$) reacted immediately with 2 equiv of dppm in THF at room temperature to yield quantitatively bimetallic cations having a carbonylmetalate as counterion [(η^2-dppm)Pt(μ-dppm)m][m(CO)] (**7a**, **8a**, **9** and **10**, respectively) (Scheme II, eq 6).

Interestingly, these products are structurally closely related, irrespective of the carbonylmetalate used. Their ^{31}P{^{1}H} NMR spectra are very characteristic (see below) and the IR of the reaction mixtures showed the typical absorptions of the anions. The anion in **7a** or **8a** may be easily replaced by [PF$_6$]$^-$, giving **7b** or **8b** respectively (Scheme II). The X-ray structure of **8b** has been determined (see below). Complex **7a** could be oxidized by bubbling air into its acetone solution at room temperature, giving quantitatively [(η^2-dppm)Pt(μ-dppm)Mo(CO)$_2$Cp]$_2$[Mo$_2$O$_7$] (**7c**).[4] The oxo vibrations ν(Mo=O) are observed in its IR spectrum at 883 (vs) and 783 (vs) cm^{-1} and compare with those found in [*n*-Bu$_4$N]$_2$[Mo$_2$O$_7$].[11] Complex **8a** is also oxidized by air with formation of complex oxo counterion(s), including [W$_6$O$_{19}$]$^{2-}$,[12] but no reaction with air was detected for complexes **9** and **10**.

Synthesis of Heterobimetallic Hydrido Complexes. Complexes **7b**, **8b** and **10** reacted with NaBH$_4$ in ethanol with formation of the heterobimetallic hydrido complexes **11**–**13**, respectively, which contain a bridging and a monodentate dppm ligand (eq 7). These complexes were identified by ^{1}H and ^{31}P{^{1}H} NMR at low temperature and by IR spectroscopy.[4] The ^{1}H and ^{31}P{^{1}H} NMR spectra indicated that the hydride ligand occupies a position cis to the metal–metal bond in **11** and **12**, but cis to the Pt-bound P atoms in **13** (see below). These hydrido complexes may be used as precursors for further mixed-metal cluster synthesis, as

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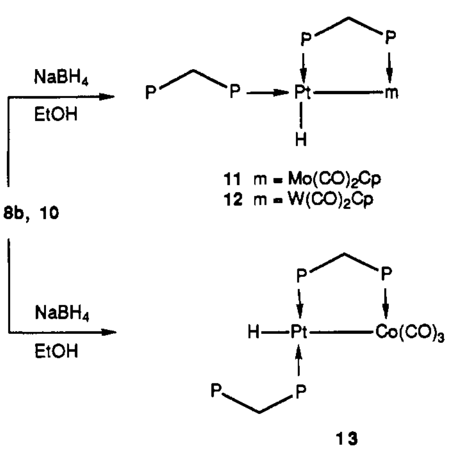
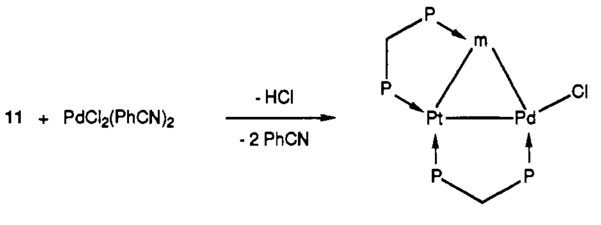


11 m = Mo(CO)$_2$Cp
12 m = W(CO)$_2$Cp

13

(7)

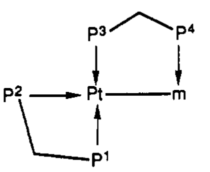
examplified by the reaction of **11** with the labile palladium complex [PdCl$_2$(NCPh)$_2$] which afforded the triangulo heterotrinuclear cluster [PtPdmCl(μ-dppm)$_2$] (**14**, m = Mo(CO)$_2$Cp) (eq 8).[2a]



(8)

14

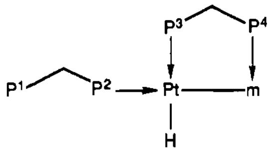
Spectroscopic Characterization. The ^{1}H NMR spectra of complexes **7–10** are unexceptional but their ^{31}P{^{1}H} NMR spectra are more informative (Table I). They have a similar pattern corresponding to four chemically inequivalent phosphorus nuclei that are coupled to each other.



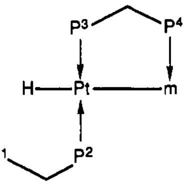
A complete analysis and spectral simulation was performed for complex **7b** (see Figure 1), using the PANIC program (Bruker). It is easy to identify the phosphorus atom bonded to Mo in **7b,c** (δ ca. 52), or to W in **8a,b** (δ ca. 18) which shows a ^{2+3}J(PtP^4) coupling of ca. 160 Hz, in agreement with such a structure.[13] The resonance of the phosphorus atom bound to Mn in **9** (δ 62.5) or Co in **10** (δ 36.1) is quadrupole broadened and the determination of ^{2+3}J(PtP^4) was not possible. Some general comments can be made: (i) The Pt-bound phosphorus atoms show resonances in the range δ –26 to –34 for P^1, δ –5 to –29 for P^2, δ 1 to 29 for P^3 and exhibit expectedly strong ^1J(PtP) coupling constants with ^{195}Pt (1500-3100 Hz). (ii) J(P^{1}P^3) is always large (ca. 400 Hz) typical for a trans coupling. (iii) J(P^{1}P^4) and J(P^{2}P^4) are always smaller than ^2J(P^{1}P^2) and ^{2+3}J(P^{3}P^4). (iv) The small value of J(P^{2}P^3) is consistent with the P^2 and P^3 nuclei being cis to each other.

The ^{1}H NMR spectra of **11–13** have a very characteristic pattern for the hydrido ligands (Figure 2). It is similar for **11** and **12**: a doublet of triplets with the large splitting corresponding to coupling with a trans phosphorus atom (^2J(PH) = 185 Hz for **11** and 188 Hz for **12**). The triplet splitting (J(PH) = 17 Hz) results from accidentally equal coupling with two P nuclei (see below).[14] In contrast, no large coupling is observed in the doublet of doublet of doublet pattern (J(PH) = 14.2, 8 and 4 Hz) for **13**, indicating for the hydride a position cis with respect to the phosphorus nuclei.[15] The hydride resonances in **11–13** show ^{195}Pt satellites with ^1J(PtH) couplings consistent with a terminal position of the hydride ligand. The ^1J(PtH) values in **11** and **12** (861 and 891 Hz, respectively) are comparable to those found in structurally related complexes, e.g. *cis*-[HPt{Mo(CO)$_3$Cp}(PPh$_3$)$_2$].[14a] The ^1J(PtH) value of 1266 Hz in **13** is similar to that observed in [HPt(μ-dppm)$_2$Mn(CO)$_3$] (1145 Hz)[14b] which also contains a terminal hydride ligand.

The ^{31}P{^{1}H} NMR data for **11–13** are given in Table II. The four phosphorus nuclei should be chemically inequivalent and coupled to each other in a static structure. This is indeed the case at 203 K whereas at 363 K a dynamic intramolecular process occurs which rapidly exchanges "end over end" P^2 and P^1 (estimated T$_c$ 333 K and ΔG^* = 13.5 kcal/mol for **11**).[16a,b] In the static regime, the spectra of **11** and **12** exhibit four well-resolved and separated doublets or doublets of doublets that can be analyzed by using the first order approximation. The signal of the Mo- or W-bound P^4 is found at 56.2 and 24.1 ppm, respectively. The two phosphorus atoms bonded to platinum have resonances in the range 25 to 1 ppm for **11** and 25 to 2 ppm for **12**, with strong coupling to ^{195}Pt (2924 and 2852 Hz, for P^2–Pt; 2161 and 2183 Hz for P^3–Pt). Values of ^1J(PtP^2) are almost the same for the three bimetallic hydrides but ^1J(PtP^3) in **13** is greater than in **11** or **12**. No coupling was observed between P^2 and P^3, as a result of their mutual cis position.[13b,17] The assignment of P^1 in **11** or **12** is based on the characteristic chemical shift for an uncoordinated phosphorus atom of a dppm ligand.[16] In the ^{31}P{^{1}H} NMR spectrum of **13**, the four phosphorus nuclei should show chemical inequivalence and coupling to each other. The chemical shift of the resonance due to P^4 is found around 45 ppm and is quadrupole broadened, typical for a phosphorus bound to cobalt. The signals of the platinum-bound phosphorus nuclei P^2 and P^3 are found at δ 26.9 and δ 35.8, respectively, and exhibit strong coupling to ^{195}Pt (ca. 2900 Hz), which confirms that these nuclei are directly bonded to platinum. The value of 425 Hz found for the coupling constant between P^2 and P^3 indicates that these two nuclei are in a trans arrangement and is similar to that found between the trans P^1 and P^3 nuclei in [(η^2-dppm)Pt(μ-dppm)m]$^+$. Phosphorus P^1 resonates at δ –24.5, again typical for an uncoordinated P atom of a monodentate dppm ligand.



11 m = Mo(CO)$_2$Cp
12 m = W(CO)$_2$Cp



13 m = Co(CO)$_3$

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Table I. $^{31}P\{^1H\}$ NMR[a] Data for Complexes **7–10**

	$\delta(^{31}P)$ (ppm)[b]				J(PP) (Hz)						J(PtP) (Hz)			
compd	P^1	P^2	P^3	P^4	P^1P^2	P^1P^3	P^1P^4	P^2P^3	P^2P^4	P^3P^4	PtP^1	PtP^2	PtP^3	PtP^4
7b[c]	–26.09	–9.98	3.73	51.50	51.3	436.6	26.6	24	25.9	62.9	2487	1556	3048	147
7c	–26.5	–4.7	4.8	51.7	49	425	30	22	25	62	2505	1495	3051	
8a	–32.9	–19.8	2.0	18.3	50	443	28	23	30	65	2496	1502	3080	160
8b[d]	–30.7	–17.8	1.3	17.9	48	444	27.5	22	31	68	2488	1489	3057	157
9	–25.9	–17.3	18.7	62.5[e]	58	414	8	*f*	*f*	85	2385	1721	2897	*e*
10	–33.8	–28.9	28.7	36.1[e]	75	434	34	*f*	*f*	109	2145	2282	2668	*e*

[a] Recorded in $CDCl_3$/THF unless otherwise started (δ in ppm; coupling constants in Hz). [b] Phosphorus assignment; see text for details. [c] Calculated values resulting from simulation using the PANIC program (Bruker). [d] PF_6 $\delta(P) = -143$ (hept, $J(PF) = 714$ Hz). [e] Not resolved, quadrupole broadened. [f] Not determined, <5 Hz.

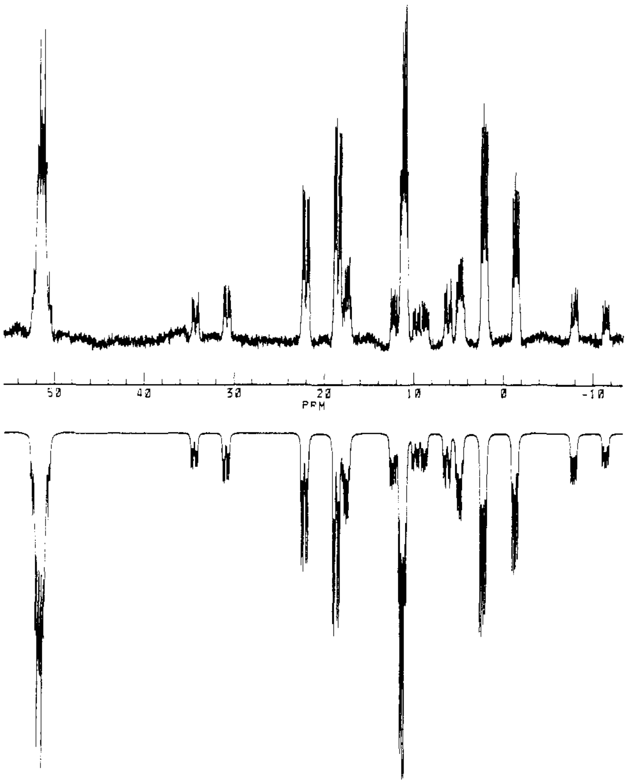

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of the cation $[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})W(CO)_2Cp]^+$ in complex **7b**: Top, experimental; bottom, simulated spectrum.

Description of the Structure of $[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})W(CO)_2Cp][PF_6]\cdot CH_2Cl_2$ (8b). The crystal structure of complex **8b** consists of heterobimetallic $[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})W(CO)_2Cp]^+$ cations, of PF_6^- anions and of CH_2Cl_2 molecules of solvation, separated by normal contacts. The structure of the chiral cation is depicted in Figure 3 together with the atom numbering scheme. The reasons for the occurrence of only one enantiomer in the crystal are not clear. Selected bond distances and angles in **8b** are given in Table III. The two dppm molecules act as ligands in a different way, the former chelates the Pt atom [Pt–P(1) = 2.324(4) and Pt–P(2) 2.309(4) Å], the latter bridges the W and Pt atoms [Pt–P(3) = 2.288(4) and W–P(4) = 2.382(3) Å], which are involved in a rather long metal–metal bond [2.902(2) Å]. The square planar coordination around the Pt atom is distorted, especially because of the narrow bite angle of the dppm chelating ligand [P(1)–Pt–P(2) = 71.1(2)°]. The W, P(1), P(2) and P(3) atoms deviate from the mean plane passing through them by –0.010(2), 0.048(3), –0.051(3) and 0.039(3) Å, respectively, with the Pt atom out of the plane by 0.165(2) Å. The W atom is further bound to a cyclopentadienyl ligand in a η^5-fashion [W–CE = 2.03(2) Å, where CE is the centroid of the ring] and to two carbonyl groups, one of which may be considered as slightly semibridging [W–C(1) = 1.95(1), Pt–C(1) = 2.61(2) Å and W–C(1)–O(1) = 172(1)°]. The coordination geometry around the W atom can be described as being of the four-legged piano stool type with two legs occupied by two CO groups in cis position, one by the P atom from the bridging dppm ligand and the other by the Pt atom. The angles between the legs range from 61.6(5) to 79.6(6)°, while the angles between the W–CE vector and the legs are in the range 115.7(5)–130.5(5)°.

The value of the Pt–W bond in **8b** falls within the upper range found in complexes containing Pt–W bonds [2.602(1)–2.902(1) Å, from Cambridge Crystallographic Data Centre]. A practically identical value, 2.902(1) Å, has been reported for the Pt–W bond in the bimetallic complex $[PtW(\mu\text{-H})(\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_7EtMe_2)(CO)_3(PEt_3)_2]$,[18] while a shorter value, 2.818(3) Å, has been found in the bimetallic complex $[Pt(\mu\text{-dppm})\{\mu\text{-}C(OMe)C_6H_4\text{-}Me\text{-}4\}W(CO)_5]$ which contains a bridging dppm ligand.[13b]

The structure of the cation of **8b** is very similar to that of its Mo analog in $[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})Mo(CO)_2(\eta\text{-}C_5H_4Me)]_2[Mo_2O_7]\cdot CH_2Cl_2$, in which the Mo–Pt separation is 2.912(4) Å and the semibridging carbonyl shows a Pt–C distance of 2.51(2) Å and a W–C–O angle of 169(2)°.[4]

Discussion

Reactions of trinuclear chain complexes of the type *trans*-$[(OC)m\text{–}M(NCPh)_2\text{–}m(CO)]$ (M = Pd, Pt; m = $Mo(CO)_2Cp$, $W(CO)_2Cp$, $Mn(CO)_4$, $Co(CO)_3$) with monodentate phosphine ligands have already proven valuable for the synthesis of heterometallic complexes. Thus, reactions with secondary phosphines HPR_2 (R = Ph, c-C_6H_{11}) afforded heterodinuclear, phosphido-bridged complexes, e.g. $[Cp(OC)_2Mo(\mu\text{-}PR_2)M(PR_2H)_2]$ (M = Pd, Pt)[5] as the result of P–H oxidative addition across the metal–metal bond, whereas tertiary phosphines PR_3 (R = Me, Et, *n*-Bu, Ph) led to heterotetranuclear, triangulated or tetrahedral clusters, e.g. $[M_2Mo_2Cp_2(CO)_6(PR_3)_2]$ (M = Pd, Pt), most likely via radical intermediates generated by homolytic cleavage of a M–m(CO) metal-metal bond of the precursor chain complex.[6]

We were interested in extending these reactivity studies to the diphosphine ligand dppm. The nature of the products was found to be a function of m, and also of M, as summarized in Schemes I and II. Whereas only complexes with bridging dppm ligands were isolated when M = Pd, bimetallic complexes containing a bridging and a chelating dppm ligand were observed with M = Pt (complexes **7–10**). This is ascribed to the greater lability of the Pd–P bond which facilitates access to stable, five-membered ring systems of the type $[M(\mu\text{-dppm})m]$.[2a,b,c,4,19,20] Some of the products observed in the course of this work could be obtained by alternative routes. Thus, cations $\mathbf{1}^+$ or $\mathbf{2}^+$ may be prepared

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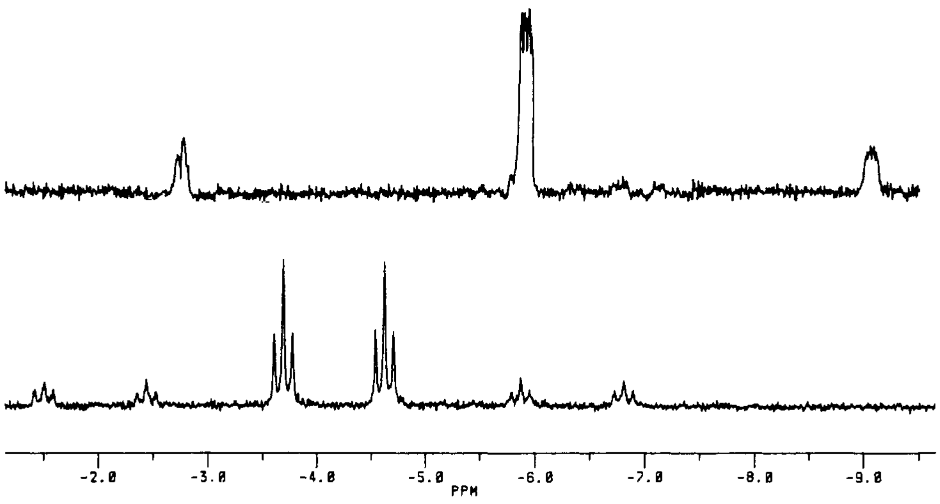

Figure 2. ^{1}H NMR spectra in the hydride region at 233 K of (a) [(η^1-dppm)(H)Pt(μ-dppm)Mo(CO)$_2$(η-C_5H_5)] (**11**) in $CDCl_3$ and (b) [(η^1-dppm)(H)Pt(μ-dppm)Co(CO)$_3$] (**13**) in acetone-d_6.

Table II. ^{31}P{^{1}H} NMR Data for the Hydrido Complexes **11–13**

	δ(ppm)[a]				*J*(PP)				*J*(PtP)			
compd	P^1	P^2	P^3	P^4	P^{1}P^2	P^{2}P^3	P^{2}P^4	P^{3}P^4	PtP^1	PtP^2	PtP^3	PtP^4
11[b]	–29.2 (d)	25.4 (dd)	1.2 (d)	56.2 (dd)	63	*c*	18	96.5	62	2924	2161	149
12[d]	–29.5 (d)	25.3 (dd)	2.5 (d)	24.1 (dd)	58	*c*	22	95	58	2852	2183	155
13[d]	–24.5 (dd)	26.9 (ddd)	35.8 (ddd)	44.6 (m, br)[e]	83.3	425	36.3	108	109	2927	2829	*e*

[a] Phosphorus assignment; see text for details (δ in ppm; coupling constants in Hz). [b] Recorded at 203 K in $CDCl_3$/THF. [c] Not observed, <5 Hz. [d] Recorded at 203 K in acetone-d_6. [e] Not resolved, quadrupole broadened.

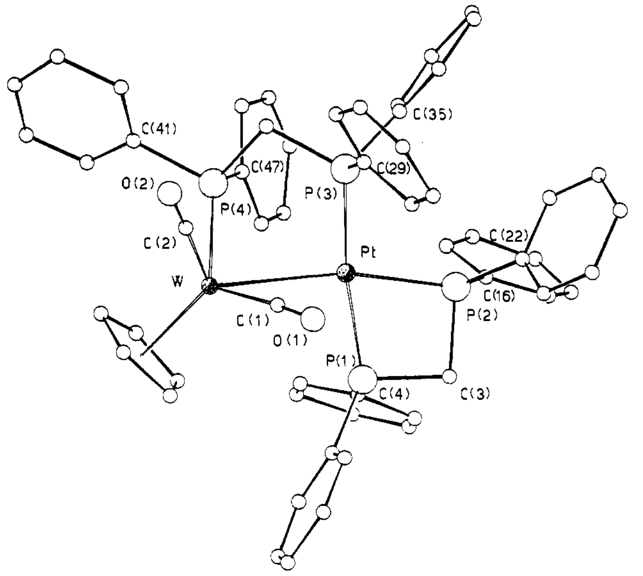

Figure 3. PLUTO view of the molecular structure of the cation [(η^2-dppm)Pt(μ-dppm)W(CO)$_2$Cp]$^+$ in complex **8b**·CH_2Cl_2 with the atomic numbering scheme.

in better yields (ca. 65%) by the reaction of Na[m(CO)]·2DME (m = Mo(CO)$_2$Cp, W(CO)$_2$Cp) with [Pd(η^2-dppm)$_2$]$^{2+}$,[3] or by the reaction of 1 equiv of dppm with [PdMo$_2$(or W$_2$)Cp$_2$(CO)$_5$(μ-dppm)].[7] Complex **3a** was obtained in the reaction of [ClPd(μ-dppm)$_2$PdCl] with 2 equiv of [Mn(CO)$_5$]$^-$,[2b] but is best prepared by the reaction of a Pd(0) complex with [Mn(CO)$_5$Br] in the presence of dppm (ca. 85–90%).[8] Cluster **6** has also been recently synthesized by thermal degradation of [Pd$_2$Co$_2$(CO)$_6$(μ-dppm)$_2$],[2h] by the reaction of [PdCl$_2$(η^2-dppm)] with [Co(CO)$_4$]$^-$ and dppm in THF, or by the reaction of [Pd(η^2-dppm)$_2$]$^{2+}$ with 2 equiv of [Co(CO)$_4$]$^-$ in THF.[3] It is generally observed that when M = Pd, the nature of the products is largely function of the metal carbonyl fragment m.

Complexes **7–10** have also been synthesized in comparable yields (ca. 95%) by the reactions of [Pt(η^2-dppm)$_2$]$^{2+}$ with 2 equiv of the corresponding carbonylmetalates in THF at room temperature (Scheme II).[3] Complexes **7a** and **8a** also result from displacement of the metalloligand [m(CO)]$^-$ from [PtMo$_2$(or W$_2$)(CO)$_5$(μ-dppm)] by 1 equiv of dppm in THF at room temperature, and **9** is also formed by the reaction of dppm with [(OC)$_5$MnPt(CO)(μ-dppm)Mn(CO)$_4$], as a result of nucleophilic displacement of [Mn(CO)$_5$]$^-$,[3] or by thermal degradation of [PtPdMn$_2$(CO)$_9$(μ-dppm)$_2$] which occurs with selective extrusion of the Pd atom.[2c] It is noteworthy that reaction of dppm with [PtCo$_2$(CO)$_7$(μ-dppm)] does not produce **10** by displacement of the metalloligand but instead results in CO substitution to yield the triangular cluster [PtCo$_2$(CO)$_5$(μ-dppm)$_2$].[3] Considering that formation of neutral dimers, e.g. [Mo(CO)$_3$Cp]$_2$, which is usually associated with radical intermediates,[6] was never observed in these reactions, and that the use of only 1 equiv of dppm per mole of *trans*-[(OC)m–Pt(NCPh)$_2$–m(CO)] afforded the same products but with 50% of the precursor being recovered, we suggest the following steps in the reactions of *trans*-[(OC)m–M(NCPh)$_2$–m(CO)] with dppm (Scheme III): (i) substitution of the labile benzonitrile ligands each by a dppm ligand, leading to intermediate (I), (ii) formation of a dppm bridge with CO elimination, resulting in intermediate (II) which could either lose CO to give a (μ-dppm)$_2$ system (III), similar to **5**, or rearrange via heterolytic metal-metal bond cleavage and chelation of the dangling dppm to give (V), (iii) alternatively, the pendant P atom of intermediate (II) could coordinate to m with breaking of the unsupported M–m bond, leading to a complex of type (VIII), which could also be formed from (V) by P migration from M to m, the latter pathway being not available with M = Pt. An alternative access to (V) consists of a chelation of a dangling dppm in (I), leading to (IV), followed by CO loss. This would be consistent with the facile equilibrium observed between bridging and dangling dppm ligands

Table III. Selected Interatomic Distances (Å) and Angles (deg) for the Complex $[Cp(CO)_2W(\mu\text{-dppm})Pt(\eta^2\text{-dppm})][PF_6]\cdot CH_2Cl_2$ ($\mathbf{8b}\cdot CH_2Cl_2$)[a]

	Bond Distances		
Pt–W	2.902(2)	P(4)–C(28)	1.83(1)
Pt–P(1)	2.324(4)	P(4)–C(41)	1.86(2)
Pt–P(2)	2.309(4)	P(4)–C(47)	1.83(2)
Pt–P(3)	2.288(4)	P(5)–F(1)	1.53(2)
W–P(4)	2.382(3)	P(5)–F(2)	1.54(2)
W–C(1)	1.95(1)	P(5)–F(3)	1.54(2)
W–C(2)	1.90(2)	P(5)–F(4)	1.61(2)
W–CE	2.03(2)	P(5)–F(5)	1.50(3)
P(1)–C(3)	1.83(1)	P(5)–F(6)	1.57(2)
P(1)–C(4)	1.79(1)	O(1)–C(1)	1.18(1)
P(1)–C(10)	1.84(1)	O(2)–C(2)	1.17(2)
P(2)–C(3)	1.85(1)	C(53)–C(54)	1.47(3)
P(2)–C(16)	1.81(2)	C(53)–C(57)	1.41(3)
P(2)–C(22)	1.80(1)	C(54)–C(55)	1.34(2)
P(3)–C(28)	1.85(1)	C(55)–C(56)	1.43(3)
P(3)–C(29)	1.80(1)	C(56)–C(57)	1.39(2)
P(3)–C(35)	1.79(2)		
	Bond Angles		
P(2)–Pt–P(3)	101.4(2)	Pt–P(1)–C(10)	126.4(5)
P(1)–Pt–P(3)	170.8(2)	Pt–P(1)–C(4)	116.4(5)
P(1)–Pt–P(2)	71.1(2)	Pt–P(1)–C(3)	92.6(4)
W–Pt–P(3)	88.5(2)	Pt–P(2)–C(22)	126.0(5)
W–Pt–P(2)	166.3(1)	Pt–P(2)–C(16)	119.3(5)
W–Pt–P(1)	98.0(1)	Pt–P(2)–C(3)	92.5(4)
Pt–W–C(2)	113.2(5)	Pt–P(3)–C(35)	116.4(5)
Pt–W–C(1)	61.6(5)	Pt–P(3)–C(29)	115.2(4)
Pt–W–P(4)	76.5(1)	Pt–P(3)–C(28)	113.8(5)
Pt–W–CE	130.5(5)	W–P(4)–C(47)	124.1(5)
C(1)–W–CE	120.1(5)	W–P(4)–C(41)	114.4(5)
C(2)–W–CE	115.7(5)	W–P(4)–C(28)	110.0(5)
P(4)–W–CE	121.5(5)	W–C(1)–O(1)	172(1)
C(1)–W–C(2)	79.6(6)	W–C(2)–O(2)	178(1)
P(4)–W–C(2)	77.9(4)	P(1)–C(3)–P(2)	94.3(6)
P(4)–W–C(1)	118.3(5)	P(3)–C(28)–P(4)	106.0(7)

[a] Estimated standard deviations are given in parentheses. CE is the centroid of the C(53)···C(57) ring.

in mononuclear Pt complexes.[21a] Triangular cluster **6** could result from formal insertion of a cobalt carbonyl fragment into the Co–P bond of an intermediate of type (III). A trinuclear intermediate having a structure of type (VI), similar to that of a known Ni_2Pd complex,[21b] could easily rearrange with CO loss and metal–metal bond formation to give (VII). The relative stabilities of the intermediates would obviously strongly depend on the nature of M and m, accounting for the diversity of structures observed.

Interestingly, we never observed ring opening of the dppm chelate in the cations $[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})m]^+$ of **7–10** to yield $[(OC)Pt(\mu\text{-dppm})_2Mo(\text{or }W)(CO)Cp]^+$, $[(OC)Pt(\mu\text{-dppm})_2Mn(CO)_3]^+$ (the Pt analogue of **4**) or $[(OC)Pt(\mu\text{-dppm})_2Co(CO)_2]^+$, respectively, that would also involve CO migration from Mo, W, Mn or Co to Pt. This differs from results obtained with other $(\eta^2\text{-dppm})$Pt–metal complexes.[13a,19]

However, opening of the dppm chelate in **7b**, **8b** or **10** was achieved by reaction with $[BH_4]^-$, resulting in the bimetallic hydrido complexes **11–13**. Their dynamic behavior exchanging "end over end" P^2 and P^1 contrasts with the static situation encountered with $[(\eta^1\text{-dppm})Pt\{\mu\text{-}C(OMe)Me\}(\mu\text{-dppm})W(CO)_4]$.[13a] The difference in the stereochemistry at Pt between **11**, **12** and **13** might be steric in origin since the smaller $Co(CO)_3$ group could better tolerate an adjacent $Pt\text{–}PPh_2CH_2$ fragment, cis to the metal–metal bond, than could Mo(or W)$(CO)_2Cp$. Substitution of a carbonyl ligand on Mo, W or Co in **11**, **12** or **13** by the uncoordinated phosphorus of the dangling dppm leading to complexes analogous to $[HPt(\mu\text{-dppm})_2Mn(CO)_3]$[14b] was never observed, even in the presence of Me_3NO. However, the potential use of such complexes for further cluster synthesis is shown by the reaction of eq 8 where the newly created Pd–Pt bond is supported by the former dangling dppm ligand.

Experimental Section

Reagents and General Techniques. All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were dried and distilled under nitrogen: tetrahydrofuran and diethyl ether over sodium benzophenone ketyl; *n*-hexane, pentane, benzene and toluene over sodium; dichloromethane and acetonitrile over P_2O_5; and acetone over $CaCl_2$. Water was degassed under reflux and saturated with nitrogen. Nitrogen (Air Liquide R-grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. CO was purchased from Air Liquide (N_2O) and used without further purification. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[Co_2(CO)_8]$ (Ventron) was purified by extraction with *n*-hexane prior to use. Celite (545, Prolabo) was degassed and stored under nitrogen. Elemental analyses were performed by the Service Central de Microanalyses du C.N.R.S. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 200.13, 50.32 and 81.02 MHz, respectively, on a FT-Bruker WP 200 SY instrument. Proton and carbon chemical shifts are positive downfield relative to external Me_4Si. ^{31}P and ^{195}Pt NMR spectra were externally referenced to 85% H_3PO_4 in H_2O and K_2PtCl_4 in D_2O, respectively, with downfield chemical shifts reported as positive. All NMR solvents were freeze–pump–thaw degassed before spectra were recorded. The ligand $Ph_2PCH_2PPh_2$ (dppm)[22] and the complexes *trans*-[Pt(or Pd)$\{m(CO)\}_2(NCPh)_2$] (m = $Mo(CO)_2Cp$, $W(CO)_2Cp$, $Mn(CO)_4$, $Co(CO)_3$)[6] were prepared according to literature methods.

Reaction of *trans*-[Pd{Mo(CO)₃Cp}₂(NCPh)₂] with dppm. Synthesis of [Pd(μ-dppm)₂(μ-CO)Mo(CO)Cp][PF₆] (1[PF₆]). A solution of $Na[Mo(CO)_3Cp]\cdot 2\,DME$ (1.79 g, 4 mmol) in THF (15 mL) was added dropwise to a suspension of $[PdCl_2(NCPh)_2]$ (0.767 g, 2 mmol) at –80 °C in THF (30 mL). Immediately a dark violet color appeared and the mixture was stirred at –80 °C for 3 h. After this time a solution of dppm (0.770 g, 2 mmol) in THF (10 mL) was slowly added (10 min). The color turned red and the reaction temperature was progressively raised to 0 °C by replacing the acetone–dry-ice cooling bath with ice. Solid $[NH_4][PF_6]$ (0.489 g, 3 mmol) was added at 0 °C, and the mixture was further stirred and raised to ambient temperature. The solvent was evaporated to dryness under reduced pressure and the residue was chromatographed on a silica gel column. Elution with toluene gave a red band of $[Mo(CO)_3Cp]_2$, elution with toluene/THF (5:1) gave a green band of $[Pd_2MoCpCl(CO)_2(\mu\text{-dppm})_2]$ (0.173 g, 7% based on Pd). Further elution with toluene/THF (3:1) gave an orange band which afforded after evaporation an orange oil which was dissolved in THF. Slow diffusion of benzene into the solution afforded orange crystals of $[Pd(\mu\text{-dppm})_2(\mu\text{-CO})Mo(CO)Cp][PF_6]$ ($\mathbf{1}[PF_6]$) (0.915 g, 37% yield based on Pd). The data for $\mathbf{1}[PF_6]$ were as described in ref 7.

Reaction of *trans*-[Pd{W(CO)₃Cp}₂(NCPh)₂] with dppm. Synthesis of [Pd(μ-dppm)₂(μ-CO)W(CO)Cp][PF₆] (2[PF₆]). The same procedure as described for $\mathbf{1}[PF_6]$ was used, starting from $Na[W(CO)_3Cp]\cdot 2DME$ (1.07 g, 2 mmol) in THF (15 mL) and $[PdCl_2(NCPh)_2]$ (0.38 g, 1 mmol) in THF (30 mL). After stirring for 3 h at –80 °C, a solution of dppm (0.38 g, 2 mmol) in THF (10 mL) was slowly added (10 min) and solid $[NH_4][PF_6]$ (0.25 g, 1.5 mmol) was added at 0 °C. The color turned red and the reaction temperature was progressively raised to room temperature. It was not possible to isolate analytically pure $\mathbf{2}[PF_6]$, either by several recrystallizations or by column chromatography. For the data of $\mathbf{2}[PF_6]$, see ref 7.

Reaction of *trans*-[Pd{Mn(CO)₅}₂(NCPh)₂] with dppm. Synthesis of [ClPd(μ-dppm)₂Mn(CO)₃] (3a). A filtered solution of $Na[Mn(CO)_5]$ in THF (0.20 M, 100 mL) was added to a cooled (–78 °C) and stirred solution of $[PdCl_2(NCPh)_2]$ (3.83 g, 10.0 mmol) in THF (100 mL). The color of the mixture immediately turned deep purple which indicated the

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[21] (a) Usón, R.; Forniés, J.; Espinet, P.; Navarro, R.; Fortuño, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2077. (b) Ni, J.; Fanwick, P. E.; Kubiak, C. P. *Inorg. Chem.* **1988**, *27*, 2017.

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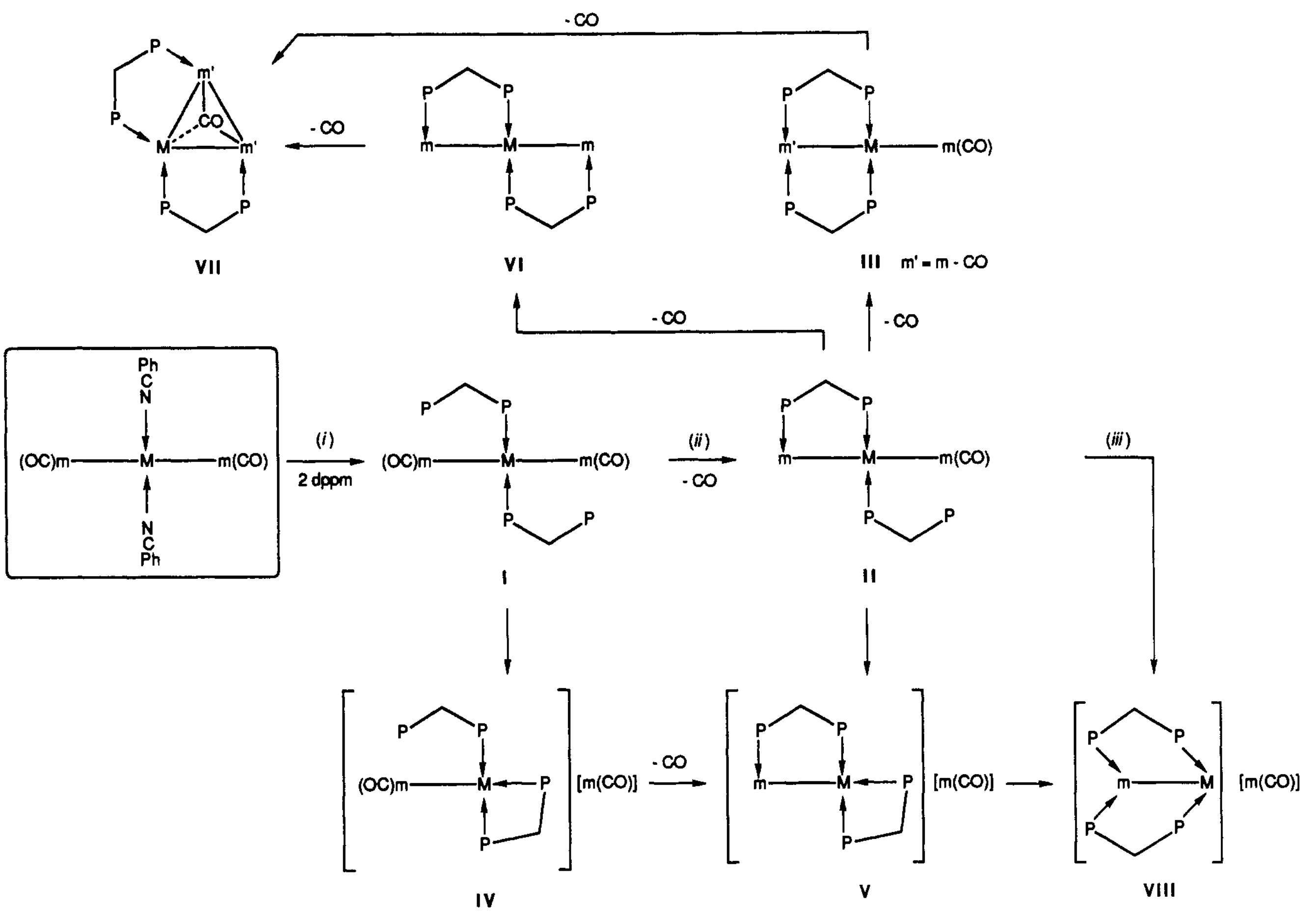
Scheme III



formation of *trans*-[Pd{Mn(CO)$_5$}$_2$(NCPh)$_2$]. After 0.25 h, solid dppm (7.68 g, 20.0 mmol) was added. The temperature was raised to ambient and the solution was further stirred for 6 h during which time the color changed from purple to yellow and then to brown. The reaction mixture was filtered on a class 4 glass frit to remove insoluble material (0.30 g), containing NaCl. The solution was impregnated on silica gel (50 mL), evaporated to dryness and the residue was chromatographed on a silica gel column. Elution with pentane gave first a pale yellow solution of [Mn$_2$(CO)$_{10}$] (1.15 g, 30% based on Mn, characterized by IR spectroscopy), then an oily solution of PhCN (ν(CN) = 2231 cm^{-1}). Elution with a mixture of pentane (67%) and toluene (33%) afforded a yellow solution of [Mn$_2$(CO)$_8$(μ-dppm)] (0.10 g, 1.4% based on Mn, characterized by IR spectroscopy). Elution with a mixture of toluene/THF (95:5) gave first a yellow-brown solution of *fac*-[MnCl(CO)$_3$(η^2-dppm)]. A deep red solution followed, which contained a mixture of *fac*-[MnCl(CO)$_3$(η^2-dppm)] and [ClPd(μ-dppm)$_2$Mn(CO)$_3$] (**3a**) which were separated by recrystallization from a mixture of THF/*n*-hexane. Further elution with THF afforded a small amount of *fac*-[MnCl(CO)$_3$(η^2-dppm)] and some brown material remained on top of the column and could not be eluted with THF or CH$_2$Cl$_2$.

fac-[MnCl(CO)$_3$(η^2-dppm)] (0.92 g, 8% based on Mn after recrystallization from CH$_2$Cl$_2$/*n*-hexane); mp 174–176 °C; IR (KBr) ν(CO) 2016 (s), 1942 (s), 1913 (s) cm^{-1}; IR (CH$_2$Cl$_2$) ν(CO) 2027 (vs), 1954 (s), 1917 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.65–7.31 (20 H, m, Ph), 4.69 (1 H, dt, ^2J(H$_A$H$_B$) = 9 Hz, ^2J(PH) = 8 Hz, PCH$_A$), 4.52 (1 H, dt, ^2J(H$_A$H$_B$) = 9 Hz, ^2J(PH) = 8 Hz, PCH$_B$).

[ClPd(μ-dppm)$_2$Mn(CO)$_3$] (**3a**) (2.62 g, 25% based on Pd after recrystallization from CH$_2$Cl$_2$/*n*-hexane); mp 216 °C dec; IR (KBr): ν(CO) 1917 (m), 1850 (s), 1815 (m); IR (THF) ν(CO) 1930 (m), 1864 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.79–7.20 (40 H, m, Ph), 3.86 (4 H, quint., $|^2J$(PH) + ^4J(PH)$|$ = 5 Hz, CH$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 77.0 (2 P, t, P→Mn), 23.7 (2 P, t, P→Pd), AA'XX' pattern with N = $|J$(P$_A$P$_X$) + J(P$_A$P$_{X'}$)$|$ = 118 Hz. Other spectroscopic data have been reported previously.[8]

Remarks. When the products were separated by successive recrystallizations instead of column chromatography, a brown material, slightly soluble in THF (or CH$_2$Cl$_2$), was isolated in addition to the above-mentioned products. This product had the same spectroscopic data as a compound formed by thermal transformation of [Pd$_2$Mn$_2$(CO)$_9$(μ-dppm)$_2$] and called **X**.[2c]

Reaction of [BrPd(μ-dppm)$_2$Mn(CO)$_3$] (3b) with Tl[PF$_6$] in the Presence of CO. Solid Tl[PF$_6$] (0.041 g, 0.12 mmol) was added to a solution of [BrPd(μ-dppm)$_2$Mn(CO)$_3$] (0.127 g, 0.12 mmol) in acetone (25 mL) and CO was bubbled through the solution. A yellow precipitate of TlBr formed immediately, and the color of the mixture turned from red to orange. The suspension was filtered on a Celite-padded filter funnel and *n*-hexane was added. [(OC)Pd(μ-dppm)$_2$Mn(CO)$_3$][PF$_6$] (**4**) was collected by filtration (0.097 g, 70% based on Pd) and recrystallized from CH$_2$Cl$_2$/*n*-hexane. IR (KBr): ν(CO) 2009 (m), 1928 (vs), 1865 (s); ν(PF) 840 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.66–6.87 (40 H, m, Ph), 3.45 (poorly resolved m, CH$_2$); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 75.02 (2 P, m, P→Mn), 20.57 (2 P, m, P→Pd), AA'XX' spin system pattern, with N = 93 Hz.

Attempted Reactions of 1 with [Cr(CO)$_3$Cp]$^-$ or [W(CO)$_3$Cp]$^-$. A solution of Na[Cr(CO)$_3$Cp]·2DME (0.120 g, 0.30 mmol) in THF (20 mL) was added to a cooled (0 °C) solution of **3a** (0.200 g, 0.19 mmol) in THF (20 mL). The temperature was raised to ambient and the mixture was stirred overnight. The IR spectrum of the solution showed only the ν(CO) bands of the precursor. The mixture was then heated (50 °C) for 2 h but no reaction occurred. Similar observations were made when **3a** was reacted with 1 equiv of Na[W(CO)$_3$Cp]·2DME. However, when the latter reaction was carried out in toluene instead of THF, the solution turned from red to green. The reaction mixture was then filtered to remove unreacted **3a**. Hexane was added to the resulting solution but only **3a** precipitated.

Reaction of [BrPd(μ-dppm)$_2$Mn(CO)$_3$] (3b) with [Co(CO)$_4$]$^-$: Synthesis of [(OC)$_4$CoPd(μ-dppm)$_2$Mn(CO)$_3$] (5). A solution of Na[Co(CO)$_4$] in THF (0.16 M, 2 mL) was added to a suspension of **3b** (0.350 g, 0.32 mmol) in Et$_2$O (100 mL). After 0.25 h of stirring at room temperature, the color of the reaction mixture had turned from red to deep purple.

Table IV. Crystallographic Data and Refinement Details for $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{W}}(\text{CO})_2\text{Cp}][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ (**8b**$\cdot$$\text{CH}_2\text{Cl}_2$)

mol formula	$\text{C}_{57}\text{H}_{49}\text{F}_6\text{O}_2\text{P}_5\text{PtW}\cdot\text{CH}_2\text{Cl}_2$
mol wt	1498.75
cryst system	triclinic
space group	$P1$
radiatn (λ, Å)	Nb-filtered Mo $K\alpha$ (0.710 69)
a, Å	11.257 (7)
b, Å	12.691 (6)
c, Å	11.055 (6)
α, deg	112.20 (3)
β, deg	101.68 (3)
γ, deg	76.71 (4)
V, Å^3	1411 (1)
Z	1
T, K	298
D_{calcd}, g cm^{-3}	1.763
$F(000)$	730
cryst dimens, mm	0.23 × 0.23 × 0.32
μ(Cu $K\alpha$), cm^{-1}	48.77
2θ range, deg	6–54
reflecns measd	$\pm h,\pm k,l$
unique tot. data	5870
unique obsd data	5157 $[I > 2\sigma(I)]$
R^a	0.0372
$R_w{}^a$	0.0494

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

After further stirring for 6 h, the solution was filtered to remove NaBr. *n*-Hexane (100 mL) was added, and **5** precipitated at –20 °C as a dark purple powder. Keeping the solution at –20 °C afforded a second crop of **5** (total 0.347 g, 0.294 mmol, 92% based on Pd) (mp 162 °C dec). Anal. Calcd for $\text{C}_{57}\text{H}_{44}\text{CoMnO}_7\text{P}_4\text{Pd}$ (M_r = 1185.14): C, 57.77; H, 3.74; Co, 4.97; Mn, 4.64; P, 10.45; Pd, 8.98. Found: C, 56.91; H, 3.81; Co, 4.28; Mn, 4.01; P, 9.40; Pd, 7.67. IR (KBr) ν(CO): 2013 (s), 1934 (s), 1888 (s), 1864 (s); IR (THF) ν(CO): 2014 (s), 1948 (s), 1939 (s), 1896 (m), 1871 (m) cm^{-1}. ^{1}H NMR (toluene-d_8): δ 7.98–7.12 (40 H, m, Ph), 4.35 (4 H, broad m, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene-d_8/toluene): δ 70.1 (2 P, P→Mn), 19.6 (2 P, P→Pd), AA′XX′ spin system pattern with N = 97 Hz.

Reaction of *trans*-$[\text{Pd}\{\text{Co(CO)}_4\}_2(\text{NCPh})_2]$ with dppm: Synthesis of $[\text{PdCo}_2(\text{CO})_5(\mu\text{-dppm})_2]$ (6). A filtered solution of $\text{Na[Co(CO)}_4]$ in THF (0.16 M, 15 mL) was added to a cooled (–78 °C) and stirred solution of $[\text{PdCl}_2(\text{NCPh})_2]$ (0.46 g, 1.20 mmol) in THF (20 mL). The solution instantly turned from yellow to dark purple which indicated the formation of *trans*-$[\text{Pd}\{\text{Co(CO)}_4\}_2(\text{NCPh})_2]$. After stirring for 0.25 h, solid dppm (0.92 g, 2.40 mmol) was added. The temperature was raised from –78 °C to ambient and the color of the solution changed to orange-brown. Stirring was maintained for 8 h. The IR spectrum of the solution exhibited the ν(CO) bands of **6**, a strong band at 1885 cm^{-1}, attributed to $[\text{Co(CO)}_4]^-$ and bands at 2043 (m), 2000 (s), 1825 (w) and 1798 (w) cm^{-1}, attributed to $[\text{Co}_2(\text{CO})_6(\mu\text{-dppm})]$.[24] The reaction mixture was filtered to remove insoluble material (NaCl) and *n*-hexane (75 mL) was added to induce the precipitation of a brown powder. The IR spectrum of the solid contained the bands of **6** and $[\text{Co(CO)}_4]^-$, but those due to $[\text{Co}_2(\text{CO})_6(\mu\text{-dppm})]$ disappeared after crystallization. Further purification was achieved by chromatography (silica gel column impregnated with *n*-hexane). Elution with a mixture THF/*n*-hexane (1:1) afforded a brown red solution of pure **6**. Further elution gave a mixture of **6** and traces of $[\text{PdCl}_2(\eta^2\text{-dppm})]$ (characterized by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, δ –53.7).[23] **6** was recrystallized from THF/*n*-hexane and collected as red brown microcrystals (0.48 g, 35% based on Pd) (mp 198–200 °C dec). Anal. Calcd for $\text{C}_{55}\text{H}_{44}\text{Co}_2\text{O}_5\text{P}_4\text{Pd}$ (M_r = 1133.12): C, 58.30; H, 3.91; Co, 10.40; P, 10.93; Pd, 9.39. Found: C, 56.93; H, 4.02; Co, 9.28; P, 9.92; Pd, 8.11. IR (KBr) ν(CO) 1984 (vs), 1943 (vs), 1928 (vs), 1895 (m), 1709 (s) cm^{-1}. ^{1}H NMR (toluene-d_8): δ 7.32–6.89 (40 H, m, Ph), 4.28 (4 H, unresolved m, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene-d_8/THF): δ 28.2 (2 P, quadrupole broadened signal, P→Co), –13.2 (2 P, d, P→Pd), AA′XX′ spin system with N = 34 Hz.

Reactions of *trans*-$[\text{Pt}\{\text{m(CO)}\}_2(\text{NCPh})_2]$ with dppm. Synthesis of complexes of type $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{m}}][\text{m(CO)}]$ (m = $\text{Mo(CO)}_2\text{Cp}$, **7a**; m = $\text{W(CO)}_2\text{Cp}$, **8a**; m = Mn(CO)_4, **9**; m = Co(CO)_3, **10**).

Complex 7a. A mixture of dppm (1.87 g, 4.86 mmol) and *trans*-$[\text{Pt}\{\text{Mo(CO)}_3\text{Cp}\}_2(\text{NCPh})_2]$ (1.90 g, 2.13 mmol) in THF (100 mL) was allowed to react for 2 h at room temperature after which time the volume was reduced to ca. 40 mL under reduced pressure. Slow addition of diethyl ether (300 mL) afforded **7a** as an orange powder (2.85 g, 94% based on Pt). IR (THF): ν(CO) 1897 (s), 1881 (m), 1808 (sh, m), 1780 (vs, br) cm^{-1}.

Complex 8a. Similarly, the reaction of dppm (0.79 g, 2.05 mmol) with *trans*-$[\text{Pt}\{\text{W(CO)}_3\text{Cp}\}_2(\text{NCPh})_2]$ (1.04 g, 0.97 mmol) in THF (75 mL) yielded an orange powder of **8a** (1.28 g, 0.80 mmol, 82% based on Pt). Orange-red microcrystals of the solvated compound **8a**$\cdot\text{CH}_2\text{Cl}_2$ were obtained by slow diffusion of diethyl ether through a CH_2Cl_2 solution. Anal. Calcd for **8a**$\cdot\text{CH}_2\text{Cl}_2$ ($\text{C}_{66}\text{H}_{56}\text{Cl}_2\text{O}_5\text{P}_4\text{PtW}_2$) ($M_r$ = 1686.76): C, 46.99; H, 3.34. Found: C, 46.73; H, 3.29. IR (THF): ν(CO) 1891 (s), 1876 (sh), 1810 (sh), 1777 (vs) cm^{-1}. ^{1}H NMR (CDCl_3): δ 7.90–6.35 (40 H, m, C_6H_5), 5.28 (s, CH_2Cl_2), 5.13 (5 H, s, C_5H_5), 4.92 (2 H, m br, CH_2), 4.69 (5 H, s, C_5H_5), 4.47 (2 H, m br, CH_2).

Complex 9. Similarly, the reaction of dppm (0.16 g, 0.38 mmol) with *trans*-$[\text{Pt}\{\text{Mn(CO)}_5\}_2(\text{NCPh})_2]$ (0.15 g, 0.19 mmol) in THF (20 mL) yielded a dark yellow powder of **9** (0.211 g, 0.16 mmol, 84% based on Pt). Anal. Calcd for $\text{C}_{59}\text{H}_{44}\text{Mn}_2\text{O}_9\text{P}_4\text{Pt}$ (M_r = 1325.86): C, 53.45; H, 3.34; Mn, 8.29; P, 9.34; Pt, 14.71. Found: C, 53.73; H, 3.42; Mn, 6.16; P, 9.42; Pt, 12.91. IR (THF): ν(CO) 2005 (s), 1921 (m, br), 1894 (vs), 1859 (vs) cm^{-1}. ^{1}H NMR (CDCl_3): δ 7.90–6.90 (40 H, m, C_6H_5), 5.28 (2 H, m br, CH_2), 4.08 (2 H, m, br, CH_2).

Complex 10. Similarly, the reaction of dppm (0.124 g, 0.32 mmol) with *trans*-$[\text{Pt}\{\text{Co(CO)}_4\}_2(\text{NCPh})_2]$ (0.120 g, 0.161 mmol) in THF (20 mL) yielded an orange powder of **10** (0.166 g, 0.13 mmol, 79% based on Pt). Anal. Calcd for $\text{C}_{57}\text{H}_{44}\text{Co}_2\text{O}_7\text{P}_4\text{Pt}$ (M_r = 1277.85): C, 53.58; H, 3.47. Found: C, 53.83; H, 3.58. IR (THF): ν(CO) 1998 (m), 1934 (w, br), 1885 (vs) cm^{-1}. ^{1}H NMR (CDCl_3): δ 7.92–6.95 (40 H, m, C_6H_5), 4.75 (2 H, m, br, CH_2), 3.54 (2 H, m br, CH_2).

Synthesis of $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{Mo}}(\text{CO})_2\text{Cp}][\text{PF}_6]$ (7b). Upon addition of a solution of $[\text{NH}_4][\text{PF}_6]$ (0.52 g, 3.20 mmol) in acetone (10 mL) to a suspension of **7a** (2.13 g, 0.80 mmol) in acetone (30 mL), a clear red solution formed. The solvent was removed under vacuum and the resulting red-brown residue was extracted with CH_2Cl_2 (30 mL). The solution was filtered through a Celite-padded filter funnel and added dropwise to a flask containing vigourously stirred diethyl ether (50 mL). This afforded a red microcrystalline powder of **7b**$\cdot2\text{CH}_2\text{Cl}_2$ (2.09 g, 1.40 mmol, 88% based on Pt). Anal. Calcd for **7b**$\cdot2\text{CH}_2\text{Cl}_2$ ($\text{C}_{59}\text{H}_{53}\text{Cl}_4\text{F}_6\text{MoO}_2\text{P}_5\text{Pt}$) ($M_r$ = 1495.79): C, 47.38; H, 3.57. Found: C, 47.65; H, 3.77. IR (KBr): ν(CO) 1866 (s), 1802 (s); ν(PF) 838 (s) cm^{-1}. ^{1}H NMR (CDCl_3): δ 7.7–6.7 (40 H, m, C_6H_5), 5.28 (s, CH_2Cl_2), 4.61 (5 H, s, C_5H_5), 4.87–4.34 (4 H, m br, CH_2).

Synthesis of $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{W}}(\text{CO})_2\text{Cp}][\text{PF}_6]$ (8b). The procedure used was similar to that described for **7b**, starting from **8a** (1.14 g, 0.71 mmol) and $[\text{NH}_4][\text{PF}_6]$ (0.23 g, 1.41 mmol). Complex **8b**$\cdot\text{CH}_2\text{Cl}_2$ was obtained as an orange powder (0.91 g, 0.60 mmol, 85% based on Pt). Slow diffusion of diethyl ether (20 mL) through a CH_2Cl_2 solution of **8b** at –20 °C afforded red crystals suitable for an X-ray diffraction analysis. Anal. Calcd for **8b**$\cdot\text{CH}_2\text{Cl}_2$ ($\text{C}_{58}\text{H}_{51}\text{Cl}_2\text{F}_6\text{O}_2\text{P}_5\text{PtW}$) ($M_r$ = 1498.74): C, 46.48; H, 3.43; P, 10.33; Pt, 13.02. Found: C, 46.85; H, 3.29; P, 9.91; Pt, 12.96. IR (KBr): ν(CO) 1867 (s), 1797 (s); ν(PF) 838 (s) cm^{-1}. ^{1}H NMR (CDCl_3): δ 7.7–6.7 (m, 40 H, C_6H_5), 5.28 (s, 2 H, CH_2Cl_2), 4.88 (m, 2 H, CH_2), 4.70 (s, 5 H, C_5H_5), 4.61 (m, 2 H, CH_2). $^{195}\text{Pt}\ \{^1\text{H}\}$ NMR (CD_2Cl_2): δ –2043.

Synthesis of $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{Mo}}(\text{CO})_2\text{Cp}]_2[\text{Mo}_2\text{O}_7]$ (7c). A solution of **7a** in THF (100 mL) was prepared from dppm (1.87 g, 4.86 mmol) and *trans*-$[\text{Pt}\{\text{Mo(CO)}_3\text{Cp}\}_2(\text{NCPh})_2]$ (1.90 g, 2.13 mmol) as described above. The solvent was evaporated and replaced by acetone (50 mL) and air was bubbled through the solution for 4 h. Diethyl ether was then added to precipitate an orange powder of **7c** (2.72 g, 2.04 mmol, 96% based on Pt). Anal. Calcd for $\text{C}_{114}\text{H}_{98}\text{Mo}_4\text{O}_{11}\text{P}_8\text{Pt}_2$ (M_r = 2665.7): C, 51.36; H, 3.70. Found: C, 51.30; H, 3.79. IR (KBr): ν(CO) 1867 (vs), 1802 (s, br); ν(MoO) 883 (vs), 783 (s) cm^{-1}. ^{1}H NMR (CDCl_3): δ 7.6–6.5 (40 H, m, C_6H_5), 4.81 (2 H, m br, CH_2), 4.61 (5 H, s, C_5H_5), 4.38 (2 H, m br, CH_2).

Synthesis of the Hydrido Complexes $[(\eta^1\text{-dppm})(\text{H})\overline{\text{Pt}(\mu\text{-dppm})\text{m}}]$ (11, m = $\text{Mo(CO)}_2\text{Cp}$; 12, m = $\text{W(CO)}_2\text{Cp}$; 13, m = Co(CO)_3). The preparation of complex **11** is given below and the same method was used for **12** and **13**. A white powder of $\text{Na[BH}_4]$ (0.10 g, 2.60 mmol) was added to a red suspension of **7b**$\cdot2\text{CH}_2\text{Cl}_2$ (0.97 g, 0.65 mmol) in ethanol (100 mL). After stirring for 7 h at room temperature, the color of the

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Table V. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of **8b**·CH_2Cl_2

atom	*x/a*	*y/b*	*z/c*	*U*	atom	*x/a*	*y/b*	*z/c*	*U*
Pt	5000	5000	5000	260(2)^a	C(23)	4791(15)	8753(14)	7082(16)	544(37)
W	5046(1)	2918(1)	5530(1)	299(3)^a	C(24)	4135(22)	9823(20)	7747(23)	793(55)
P(1)	7106(3)	5012(3)	5402(3)	316(11)^a	C(25)	3127(20)	10263(18)	6956(21)	766(52)
P(2)	5342(3)	6721(3)	4987(3)	327(11)^a	C(26)	2831(18)	9640(17)	5632(20)	728(49)
P(3)	2897(3)	5296(3)	4800(3)	311(11)^a	C(27)	3498(15)	8577(14)	5038(16)	541(37)
P(4)	3546(3)	2769(3)	3640(3)	369(11)^a	C(29)	2242(11)	6079(10)	6318(12)	331(24)
P(5)	7614(4)	−614(4)	321(5)	622(19)^a	C(30)	2813(17)	6989(16)	7258(18)	640(43)
O(1)	4938(11)	5196(9)	7974(8)	580(42)^a	C(31)	2267(17)	7700(16)	8375(18)	620(42)
O(2)	2728(13)	2921(12)	6595(14)	804(71)^a	C(32)	1179(18)	7433(17)	8551(19)	677(46)
C(1)	4965(12)	4386(12)	6998(14)	432(60)^a	C(33)	616(17)	6643(16)	7723(18)	642(43)
C(2)	3598(12)	2931(12)	6171(13)	398(54)^a	C(34)	1152(15)	5877(14)	6555(17)	590(40)
C(3)	6886(10)	6585(10)	5943(13)	352(46)^a	C(35)	2088(12)	6053(11)	3725(13)	369(27)
C(28)	2237(12)	3950(10)	4048(15)	440(53)^a	C(36)	1098(14)	6936(13)	4044(15)	497(33)
F(1)	7696(17)	−1520(16)	−1060(18)	1443(57)	C(37)	388(23)	7409(21)	3128(24)	678(66)
F(2)	7001(18)	186(17)	−466(19)	1419(63)	C(38)	700(19)	7015(17)	1853(20)	724(49)
F(3)	6306(18)	−752(17)	379(19)	1413(64)	C(39)	1701(17)	6104(16)	1525(18)	647(43)
F(4)	7480(20)	538(18)	1612(22)	1565(70)	C(40)	2403(14)	5665(13)	2448(15)	496(33)
F(5)	8106(21)	−1369(19)	1141(23)	1743(76)	C(41)	2846(14)	1441(13)	3017(15)	476(32)
F(6)	8967(16)	−465(15)	353(17)	1261(51)	C(42)	1640(20)	1500(19)	3253(21)	768(53)
C(4)	7907(12)	4452(11)	3989(13)	378(27)	C(43)	1115(23)	456(22)	2833(25)	983(68)
C(5)	8530(14)	5189(13)	3681(15)	499(33)	C(44)	1936(26)	−550(24)	2122(28)	992(75)
C(6)	9085(16)	4732(15)	2566(17)	566(38)	C(45)	3092(25)	−618(23)	1855(26)	966(72)
C(7)	9084(16)	3611(15)	1735(17)	574(38)	C(46)	3523(21)	402(19)	2311(22)	807(55)
C(8)	8543(17)	2880(15)	2056(18)	605(41)	C(47)	3844(12)	2804(11)	2092(13)	390(28)
C(9)	7946(14)	3309(13)	3145(15)	479(33)	C(48)	4999(13)	2880(13)	1918(15)	498(33)
C(10)	8186(11)	4653(10)	6734(12)	333(25)	C(49)	5185(17)	2923(15)	754(18)	640(43)
C(11)	9278(14)	3881(12)	6534(15)	468(32)	C(50)	4148(19)	2948(18)	−271(21)	774(53)
C(12)	10059(14)	3667(13)	7562(15)	516(34)	C(51)	3094(19)	2811(18)	−184(21)	748(51)
C(13)	9772(18)	4166(17)	8776(20)	686(46)	C(52)	2833(16)	2718(15)	1048(17)	602(40)
C(14)	8630(17)	5002(16)	9054(18)	647(44)	C(53)	6972(14)	2206(13)	6568(15)	487(34)
C(15)	7859(14)	5224(13)	7998(15)	510(34)	C(54)	7132(15)	1965(15)	5200(16)	554(36)
C(16)	5664(12)	6788(11)	3478(13)	397(28)	C(55)	6375(15)	1234(14)	4428(17)	568(38)
C(17)	6079(16)	7740(14)	3481(17)	570(38)	C(56)	5693(15)	974(13)	5214(16)	518(35)
C(18)	6383(21)	7797(19)	2411(23)	792(55)	C(57)	6057(15)	1594(14)	6528(16)	535(36)
C(19)	6089(20)	6957(18)	1192(21)	743(49)	C(58)	−782(38)	−26(34)	7797(39)	1504(124)
C(20)	5609(21)	6017(19)	1182(22)	825(57)	Cl(1)	−1228(13)	−808(13)	6064(15)	2142(49)
C(21)	5407(15)	5899(14)	2299(16)	549(37)	Cl(2)	−98(15)	983(14)	8184(17)	2424(60)
C(22)	4507(12)	8136(11)	5785(13)	397(28)					

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

precipitate had turned yellow. The solid was filtered, washed with *n*-hexane and dried in vacuo. This yielded a yellow powder of **11** (0.78 g, 0.66 mmol, 96% based on Pt). Anal. Calcd for $C_{57}H_{50}MoO_2P_4Pt\cdot{}^1/_2C_6H_6$ (M_r = 1221.00): C, 59.02; H, 4.37. Found: C, 58.76; H, 4.25. IR (KBr): ν(PtH) 2066 (w); ν(CO) 1842 (s), 1768 (s); IR (toluene) 1848 (s), 1781 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.62–6.33 (40 H, m, C_6H_5), 5.09 (5 H, s, C_5H_5), 5.00 (2 H, m br, CH_2), 4.20 (2 H, m br, CH_2), –4.94 (1 H, m br, Pt-H); ^{1}H NMR (acetone-d_6, 233 K): δ –4.94 (1 H, dt, Pt-H, ^1J(PtH) = 861 Hz, ^2J(PH) = 185 and 17 Hz). $^{31}P\{^1H\}$ NMR data, see Table II.

Complex 12. The reaction of Na[BH_4] (0.10 g, 2.60 mmol) with **8b**·CH_2Cl_2 (0.75 g, 0.5 mmol) in ethanol (100 mL) yielded a yellow powder of **12** (0.60 g, 0.47 mmol, 95% based on Pt). Anal. Calcd for $C_{57}H_{50}O_2P_4PtW$ (M_r = 1269.85): C, 53.91; H, 3.97. Found: C, 54.04; H, 3.88. IR (KBr): ν(PtH) 2056 (vw); ν(CO) 1839 (vs), 1768 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.54–6.17 (40 H, m, C_6H_5), 5.09 (5 H, s, C_5H_5), 4.92 (2 H, m br, CH_2), 4.17 (2 H, m br, CH_2), –4.82 (1 H, m br, Pt-H); ^{1}H NMR (acetone-d_6, 233 K): δ –4.82 (1 H, dt, Pt-H, ^1J(PtH) = 891 Hz, ^2J(PH) = 188 and 17 Hz). $^{31}P\{^1H\}$ NMR data, see Table II.

Complex 13. The reaction of Na[BH_4] (0.10 g, 2.60 mmol) with **10** (0.90 g, 0.70 mmol) in ethanol (100 mL) yielded an orange powder of **13** (0.39 g, 3.64 mmol, 52% based on Pt). Anal. Calcd for $C_{53}H_{45}CoO_3P_4Pt$ (M_r = 1079.87): C, 57.46; H, 4.09. Found: C, 57.33; H, 4.04. IR (KBr): ν(PtH) 2072 (w); ν(CO) 1956 (s), 1877 (s, br), 1833 (s) cm^{-1}. ^{1}H NMR (acetone-d_6, 230 K): δ 7.80–7.06 (40 H, m, C_6H_5), 3.79 (4 H, m, br, CH_2), –6.00 (1 H, ddd, Pt–H, ^1J(PtH) = 1266 Hz, ^2J(PH) = 14.2, 8 and 4 Hz). $^{31}P\{^1H\}$ NMR data see Table II.

Reaction of 9 with $NaBH_4$. The reaction of Na[BH_4] (0.10 g, 2.60 mmol) with **9** (0.90 g, 0.75 mmol) in ethanol (100 mL) at room temperature yielded a red product. No hydride was detected by ^{1}H NMR (acetone-d_6, 230 K): δ 7.54–7.03 (20 H, m, C_6H_5), 3.42 (2 H, m, br, CH_2).

Reaction of 11 with Me_3NO. A CH_2Cl_2 solution (5 mL) of Me_3NO (0.0375 g, 0.5 mmol) was added dropwise to a stirred THF solution (10 mL) of **11** (0.61 g, 0.5 mmol). After 24 h the IR spectrum in the ν(CO) region showed only the presence of **11**.

Synthesis of [PtPdMoCpCl$(CO)_2(\mu$-dppm$)_2$] (14). A solution of [$PdCl_2(NCPh)_2$] (0.19 g, 0.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of **11** (0.61 g, 0.5 mmol) in THF (20 mL). After stirring for 5 h, the solution was filtered and the brown residue was extracted with CH_2Cl_2. The $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum of this extract showed a mixture of 3 products: [$PtCl_2(\eta^2$-dppm)][25] (22%), [$PdCl_2(\eta^2$-dppm)][23] (3%) and **14** (75%, spectroscopic yields). The data for **14** were in agreement with the literature values.[2a]

X-ray Data Collection, Structure Determination, and Refinement for $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{W}}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]\cdot\text{CH}_2\text{Cl}_2$ (8b·CH_2Cl_2). The crystallographic data are summarized in Table IV. Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having $10.3 < \theta < 14.6°$. Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the niobium-filtered Mo K_α radiation and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of 3–12° min^{-1} and a scan width from $(\theta - 0.65)°$ to $(\theta + 0.65 + 0.346 \tan \theta)°$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed following Lehmann and Larsen.[26] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.086 and 0.941).[27] Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic thermal parameters and

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then with anisotropic thermal parameters for all non-hydrogen atoms, excepting for the fluorine atoms, the carbon atoms of the phenyl and cyclopentadienyl rings and the atoms of the dichloromethane molecule of solvation. In an independent final cycle of refinement the coordinates $-x$, $-y$, $-z$ were used for the non hydrogen atoms to test the chirality of the cationic complex. No improvement in the R value was obtained [$R(x,y,z) = 0.0380$; $R(-x,-y,-z) = 0.0391$]. The former model was selected and the reported data refer to this model. All hydrogen atoms were placed at their geometrically calculated positions and introduced in the final structure factor calculation, with fixed isotropic thermal parameters ($U = 0.08$ Å^2). The final cycles of refinement were carried out on the basis of 363 variables; after the last cycles, no parameters shifted by more than 0.95 esd. The largest remaining peak (close to the Pt atom) in the final difference map was equivalent to about 0.88 e/Å^3. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_0) + gF_0^2]^{-1}$ was used; at convergence the K and g values were 0.626 and 0.0023 respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 28. All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the Gould Powernode 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del C.N.R., Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[29] The final atomic coordinates for the non-hydrogen atoms are given in Table V.

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Supplementary Material Available: Tables of calculated hydrogen atom coordinates (Tables S-I), thermal parameters for the non-hydrogen atoms (Table S-II), and complete bond distances and angles (Table S-III) (5 pages). Ordering information is given on any current masthead page.

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