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Carbonylmetalate-Induced Phosphorus Migration and $Ph_2PCH_2PPh_2$- (dppm-) Assisted Synthesis of Bimetallic Complexes and Clusters of Pd and Pt with Mo, W, Mn, and Co

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The new triangular clusters $[\text{PtCo}_2(\text{CO})_7(\mu\text{-dppm})]$ (**1**), $[\text{PtMo}_2\text{Cp}_2(\text{CO})_5(\mu\text{-dppm})]$ (**2**), and $[\text{PtW}_2\text{Cp}_2(\text{CO})_5(\mu\text{-dppm})]$ (**3**) were obtained from the reactions of $[\text{PtCl}_2(\eta^2\text{-dppm})]$ with 2 equiv of the carbonylmetalates $[\text{Co(CO)}_4]^-$, $[\text{Mo(CO)}_3\text{Cp}]^-$, or $[\text{W(CO)}_3\text{Cp}]^-$, respectively. In the case of $[\text{Mn(CO)}_5]^-$ and depending on the stoichiometry used, the bimetallic $[(\eta^2\text{-dppm})\text{PtCl}\{\text{Mn(CO)}_5\}]$ (**4**) or the trinuclear chain $[(\text{OC})_5\text{Mn}\overline{\text{Pt(CO)(}\mu\text{-dppm)Mn}}(\text{CO})_4]$ (**5**) were obtained instead. Clusters **2** and **3** react reversibly with CO to give respectively the chain complexes $[\text{Cp(OC)}_3\text{Mo}\overline{\text{Pt(CO)(}\mu\text{-dppm)Mo}}(\text{CO})_2\text{Cp}]$ (**6**) and $[\text{Cp(OC)}_3\text{W}\overline{\text{Pt(CO)(}\mu\text{-dppm)W}}(\text{CO})_2\text{Cp}]$ (**7**), analogous to **5**. Cluster **1** undergoes CO substitution by dppm to give $[\text{PtCo}_2(\text{CO})_5(\mu\text{-dppm})_2]$ (**8**) in which the Pt–Co bonds are bridged by dppm ligands. Dppm also reacts with clusters **2**, **3**, and **5** to afford the bimetallic ionic complexes $[(\eta^2\text{-dppm})\overline{\text{Pt(}\mu\text{-dppm)Mo}}(\text{CO})_2\text{Cp}][\text{Mo(CO)}_3\text{Cp}]$ (**9**), $[(\eta^2\text{-dppm})\overline{\text{Pt(}\mu\text{-dppm)W}}(\text{CO})_2\text{Cp}][\text{W(CO)}_3\text{Cp}]$ (**10**), and $[(\eta^2\text{-dppm})\overline{\text{Pt(}\mu\text{-dppm)Mn}}(\text{CO})_4][\text{Mn(CO)}_5]$ (**11**). Alternatively, these complexes as well as the analogous $[(\eta^2\text{-dppm})\overline{\text{Pt(}\mu\text{-dppm)Co}}(\text{CO})_3][\text{Co(CO)}_4]$ (**12**) may be prepared from $[\text{Pt}(\eta^2\text{-dppm})_2]\text{Cl}_2$ and the corresponding carbonylmetalates. The reaction of $[\text{PdCl}_2(\eta^2\text{-dppm})]$ with 2 equiv of the carbonylmetalate $[\text{Co(CO)}_4]^-$ affords at −30 °C the cluster $[\text{PdCo}_2(\text{CO})_7(\mu\text{-dppm})]$ which was not isolated but is analogous to **1**. In solution, this cluster undergoes a redox process leading to the known $[\text{Pd}_2\text{Co}_2(\text{CO})_7(\mu\text{-dppm})_2]$ (**13**) or, alternatively, reacts with dppm to yield the stable complex $[\text{PdCo}_2(\text{CO})_5(\mu\text{-dppm})_2]$ (**14**), analogous to **8**. The latter cluster was also prepared from $[\text{Pd}(\eta^2\text{-dppm})_2][\text{BF}_4]_2$ and 2 equiv of $[\text{Co(CO)}_4]^-$. If chloride ions are added in the latter reaction, $[\text{Cl}\overline{\text{Pd(}\mu\text{-dppm)}_2\text{Co}}(\text{CO})_2]$ (**15**) is formed instead. It reacts in toluene with $[\text{Co(CO)}_4]^-$ to give $[(\text{OC})_4\text{Co}\overline{\text{Pd(}\mu\text{-dppm)}_2\text{Co}}(\text{CO})_2]$ (**16**), which transforms slowly in **14** by loss of CO and formal insertion of a Co(CO)_3 moiety into a Co–P bond. On the basis of these results, the influence of the nature of the d^8 metal (Pd or Pt), of the carbonylmetalates, and of the dppm stoichiometry on the structure of the products is discussed.

Introduction

The synthesis and structural characterization of the first mixed-metal clusters containing the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) ligand from the reactions of $[\text{Cl}\overline{\text{Pd(}\mu\text{-dppm)}_2\text{Pd}}\text{Cl}]$ with carbonylmetalates $[\text{m(CO)}]^-$ showed that the mobility of this ligand, i.e., the lability of the Pd–P bond, could be triggered by the nucleophilic substitution of the Pd–Cl with Pd–transition metal bonds.[1–4] This resulted in the formal insertion of the metal carbonyl fragment into the Pd–P bond. We wondered whether this carbonylmetalate-induced lability of the metal–phosphorus bond could be extended to simple mononuclear complexes, such as $[\text{MCl}_2(\eta^2\text{-dppm})]$ (M = Pd, Pt), which contain a dppm ligand whose change of coordination mode from chelating to bridging would result in a dppm-stabilized bimetallic unit. One could foresee that complexes containing such a five-membered $\overline{\text{M(}\mu\text{-dppm)m}}$ moiety might display a more versatile reactivity than those with two dppm bridges between the metals, of the type $\overline{\text{M(}\mu\text{-dppm)}_2\text{m}}$,[5,6] owing to the more open nature of one side of the molecule.[7]

In the following, we shall report: i) on the reactions of the mono dppm $[\text{MCl}_2(\eta^2\text{-dppm})]$ and the bis dppm $[\text{M}(\eta^2\text{-dppm})_2]\text{Cl}_2$ complexes (M = Pd, Pt) with the carbonylmetalate anions $[\text{Mo(or W)(CO)}_3\text{Cp}]^-$, $[\text{Mn(CO)}_5]^-$ or $[\text{Co(CO)}_4]^-$ which afford heterobimetallic complexes; ii) on the influence of the nature of the d^8 metal in the precursor (Pd vs Pt), of the carbonylmetalate anion, and of the dppm stoichiometry on the nature and structure of the products. A preliminary account on part of the work concerned with the platinum complexes, has been published.[8]

Results

Complexes with Platinum and One dppm Ligand. Reaction of the Pt(II) precursor $[\text{PtCl}_2(\eta^2\text{-dppm})]$ with 2 equiv of the carbonylmetalates $[\text{Co(CO)}_4]^-$, $[\text{Mo(CO)}_3\text{Cp}]^-$ or $[\text{W(CO)}_3\text{Cp}]^-$

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(1) (a) Braunstein, P.; Jud, J.-M.; Dusausoy, Y.; Fischer, Y. *Organometallics* **1983**, *2*, 180. (b) Braunstein, P.; de Méric de Bellefon, C.; Ries, M.; Fischer, J.; Bouaoud, S.-E.; Grandjean, D. *Inorg. Chem.* **1988**, *27*, 1327. (c) Braunstein, P.; de Méric de Bellefon, C.; Ries, M. *Ibid.* **1988**, *27*, 1338.

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(8) Braunstein, P.; Guarino, N.; de Méric de Bellefon, C.; Richert, J.-L. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 88.

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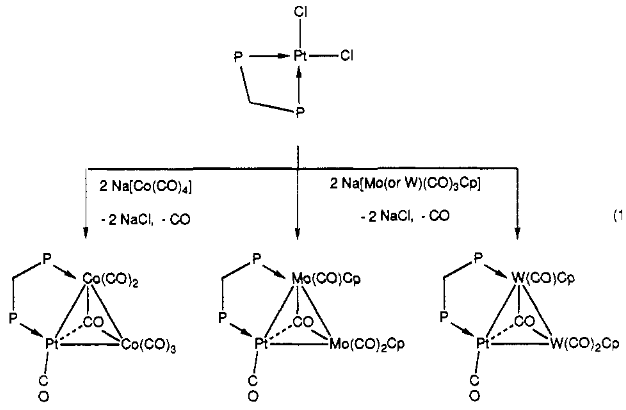
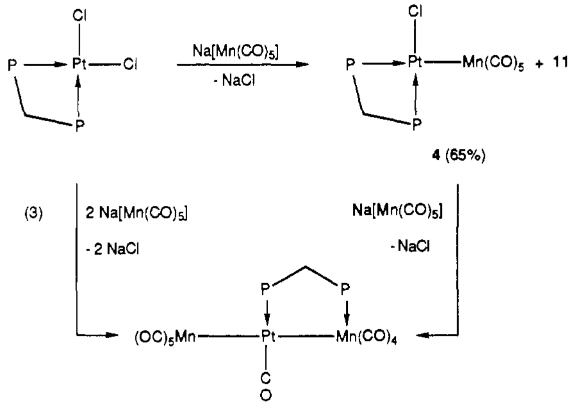
afforded in quantitative spectroscopic yields the new triangular heterometallic clusters [$PtCo_2(CO)_7(\mu$-dppm)] (**1**), [$PtMo_2Cp_2(CO)_5(\mu$-dppm)] (**2**) or [$PtW_2Cp_2(CO)_5(\mu$-dppm)] (**3**), respectively (eq 1). These clusters were characterized by elemental analysis, IR and ^1H, $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopic methods. When the reactions of eq 1 were carried out with only 1 equiv of the carbonylmetalates, the corresponding clusters **1–3** were obtained in ca. 50% yields and 50% of unreacted [$PtCl_2(\eta^2$-dppm)] was recovered. In these clusters, the dppm ligand bridges an heterometallic bond, as evidenced by the values of the phosphorus chemical shifts and the observation of ^1J(Pt–P) couplings.



(1)

1 (80%) **2** (71%) **3** (47%)

The situation is different with the carbonylmanganate anion [$Mn(CO)_5]^-$ since it affords the binuclear complex [(η^2-dppm)$PtCl\{Mn(CO)_5\}$] (**4**) and some [(η^2-dppm)Pt(μ-dppm)$Mn(CO)_4$][$Mn(CO)_5$] (**11**) when reacted with 1 equiv of [$PtCl_2(\eta^2$-dppm)] (eq 2) and the heterotrinuclear chain complex [$(OC)_5MnPt(CO)(\mu$-dppm)$Mn(CO)_4$] (**5**) when reacted with 0.5 equiv of [$PtCl_2(\eta^2$-dppm)] (eq 3).[8] We have verified that compound **4** reacts further with 1 equiv of [$Mn(CO)_5]^-$ to afford **5** and could thus be considered as an intermediate in the reaction of eq 3. It is interesting to note that the chain complex [$Cp(OC)_3MoPt(CO)(\mu$-dppm)$Mo(CO)_2Cp$] (**6**), analogous to **5**, could be prepared by the mild, reversible carbonylation of cluster **2** (eq 4). Thus, bubbling of CO into a blue solution of **2** afforded an orange solution of **6**. This complex formally results from cleavage of the Mo–Mo bond of **2** and addition of CO to a Mo center, this being accompanied by a change in the P→Pt–CO coordination around the platinum center from cis in **2** to trans in **6** (see below). This process is reversible since **2** is quantitatively regenerated when a solution of **6** is exposed to a nitrogen purge or evacuated under vacuum at room temperature. This transformation can also be achieved with a finely divided solid. Cluster **3** undergoes a similar reversible CO uptake, leading to [$Cp(OC)_3WPt(CO)(\mu$-dppm)$W(CO)_2Cp$] (**7**) that was characterized in solution by IR and $^{31}P\{^1H\}$ NMR. In contrast, **1** does not react with CO under ambient conditions. Attempts to remove a CO ligand from the open chain complex **5** e.g., by refluxing a toluene solution, did not result in the formation of a triangular cluster [$PtMn_2(CO)_9(\mu$-dppm)], which would have been similar to clusters **1–3**, but only resulted in partial transformation into the ionic complex **11** (see below, IR and $^{31}P\{^1H\}$ NMR evidence).

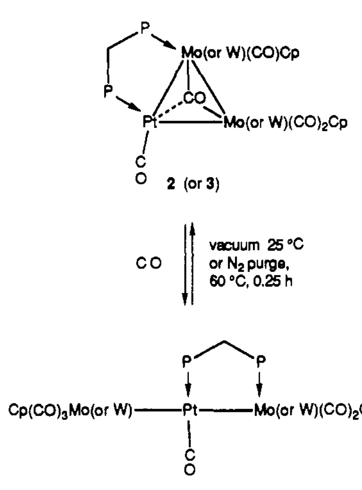


(2)

4 (65%)

(3)

5 (90%)

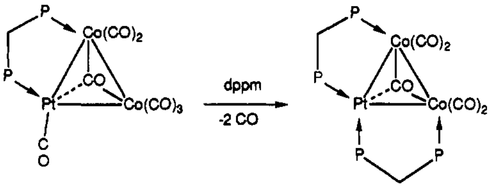


2 (or **3**)

(4)

6 (or **7**)

Complexes with Platinum and Two dppm Ligands. In order to investigate possible pathways for the transformation of complex **5** into **11** and, more generally, to examine the reactivity of complexes **1–3** and **5**, they were reacted with dppm. When 1 equiv of dppm was used, **1** afforded in quantitative spectroscopic ($^{31}P\{^1H\}$ NMR) yield the new trinuclear cluster [$PtCo_2(CO)_5(\mu$-dppm)$_2$] (**8**) in which the dppm ligands each bridge a Pt–Co bond (AA′XX′ spin system in the $^{31}P\{^1H\}$ NMR spectrum, see below) (eq 5).



(5)

1 **8** (63%)

The behavior of complexes **2**, **3**, and **5** toward substitution by dppm is different from that of **1**. Thus, they react with 1 equiv of dppm with cleavage of metal–metal bonds to afford the ionic complexes [(η^2-dppm)Pt(μ-dppm)$Mo(CO)_2Cp$][$Mo(CO)_3Cp$] (**9**), [(η^2-dppm)Pt(μ-dppm)$W(CO)_2Cp$][$W(CO)_3Cp$] (**10**), and [(η^2-dppm)Pt(μ-dppm)$Mn(CO)_4$][$Mn(CO)_5$] (**11**), respectively (eqs 6 and 8 in Scheme I).

Compounds **9–11** were independently prepared in quantitative yields from the reactions of the carbonylmetalates [$Mo(CO)_3Cp]^-$, [$W(CO)_3Cp]^-$ or [$Mn(CO)_5]^-$, respectively, with the bis-chelate complex [$Pt(\eta^2$-dppm)$_2$]Cl_2 (eq 7 in Scheme I) and their structures were established from spectroscopic data and by an X-ray diffraction study of [(η^2-dppm)Pt(μ-dppm)$Mo(CO)_2(\eta$-C_5H_4-$Me)]_2[Mo_2O_7]$[9] and of **10a**.[10a] Interestingly, when the reaction

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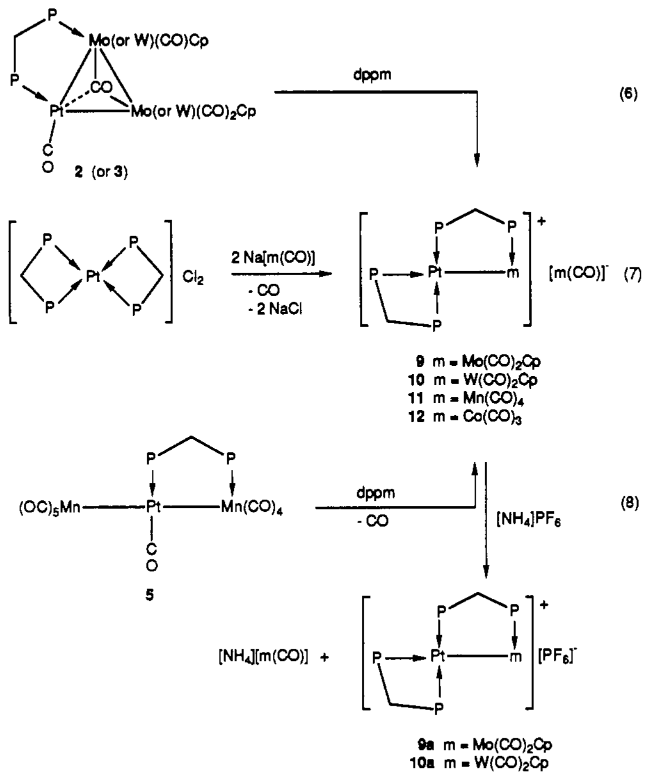
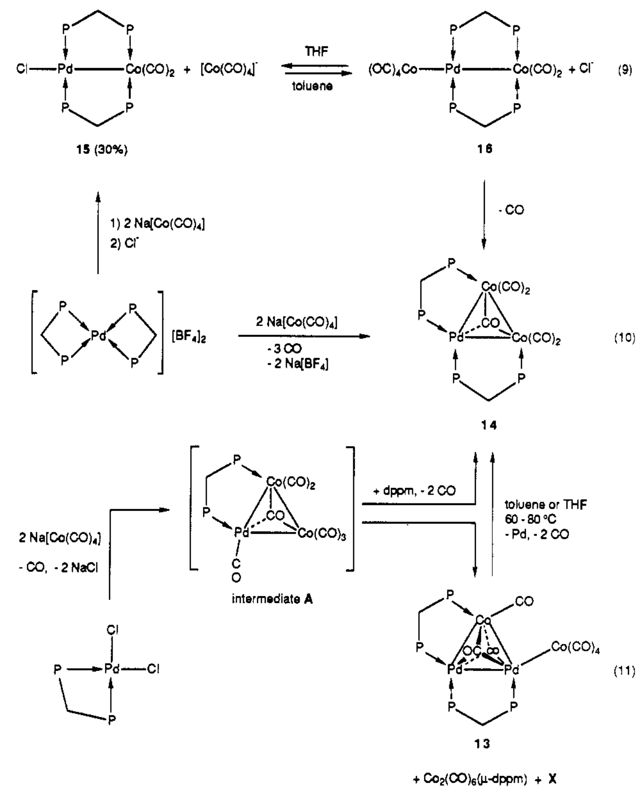
[9] Braunstein, P.; de Méric de Bellefon, C.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1984**, *3*, 1772.

Scheme I



Scheme II

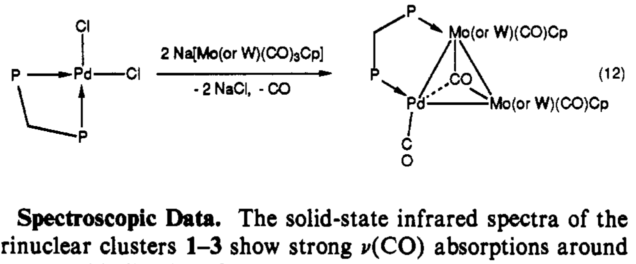


of eq 7 was performed with $[Co(CO)_4]^-$, it did not afford the triangular cluster $[PtCo_2(CO)_5(\mu\text{-dppm})_2]$ (**8**) but led quantitatively to the bimetallic complex $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{Co}}(CO)_3][Co(CO)_4]$ (**12**), analogous to **9–11** (eq 7 in Scheme I).

Complexes with Palladium. The reaction of the bis-dppm complex $[Pd(\eta^2\text{-dppm})_2][BF_4]_2$ with 2 equiv of $[Co(CO)_4]^-$ yielded the trinuclear cluster **14** (eq 10 in Scheme II). A violet intermediate was observed at −30 °C which, if the reaction was carried out in the presence of chloride ions (LiCl), quantitatively led to $[Cl\overline{\text{Pd}(\mu\text{-dppm})_2\text{Co}}(CO)_2]$ (**15**) (Scheme II). When **15** was reacted with 1 equiv of $[Co(CO)_4]^-$ in toluene it afforded a violet trinuclear chain complex $[(OC)_4Co\overline{\text{Pd}(\mu\text{-dppm})_2\text{Co}}(CO)_2]$ (**16**) (eq 9 in Scheme II) which was too labile to be isolated as a pure solid ($^{31}P\{^1H\}$ NMR (toluene/C_6D_6): AA′XX′ spin system δ 26.7 (br, m, P→Co), 7.6 (t, P→Pd, $N = |J(P_AP_X) + J(P_AP_{X'})| = 125$ Hz); IR (toluene) 2045 (w), 2021 (m), 2000 (m), 1955 (s), 1888 (w, br)). Complex **16** regenerates **15** when stirred in THF in the presence of chloride ions, but spontaneously loses CO at room temperature (25 °C, $t_{1/2} \cong 0.5$ h) to form quantitatively **14** (Scheme II).

The reaction of $[PdCl_2(\eta^2\text{-dppm})]$ with 2 equiv of $[Co(CO)_4]^-$ afforded the known, tetranuclear metalloligated cluster $[Pd_2Co_2(CO)_7(\mu\text{-dppm})_2]$ (**13**)[1] and the dicobalt complex $[Co_2(CO)_6(\mu\text{-dppm})]$[11] in an approximate 1:1 molar ratio ($^{31}P\{^1H\}$ NMR), clearly indicating that a redox process and intermolecular ligand transfer have occurred (eq 11 in Scheme II). During this reaction, an untractable deep blue compound X also formed in trace amount. Its spectroscopic $^{31}P\{^1H\}$ NMR and IR data point to a $[PdCo(CO)_2(\mu\text{-dppm})]_n$ formulation but it was not further investigated owing to separation problems.

We observed that the reaction of eq 11 proceeded through a red intermediate A that formed around −30 °C and transformed into the products at room temperature. Its $^{31}P\{^1H\}$ NMR spectrum at −20 °C contains a broad signal at δ 28 ppm and a doublet at δ −13 ppm ($J(PP) = 32$ Hz) and the IR spectrum displays $\nu(CO)$ bands at 2063 (s), 2032 (vs), 1991 (s), 1982 (s) and 1751 (m) cm^{-1}. These compare well with the corresponding data for the platinum cluster $[PtCo_2(CO)_7(\mu\text{-dppm})]$ (**1**) (see above). The spontaneous evolution of intermediate A could be stopped by the addition of 1 equiv of dppm at −20 °C which afforded the known red-brown trinuclear cluster $[PdCo_2(CO)_5(\mu\text{-dppm})_2]$ (**14**)[1b] and $[Cl\overline{\text{Pd}(\mu\text{-dppm})_2\text{Co}}(CO)_2]$ (**15**) in a ca. 3:1 molar ratio ($^{31}P\{^1H\}$ NMR). However, column chromatography of this reaction mixture only yielded **14** (33% based on Pd). On the other hand, the platinum analogue of **14**, $[PtCo_2(CO)_5(\mu\text{-dppm})_2]$ (**8**), was obtained from the reaction of **1** with 1 equiv of dppm (eq 5). On the basis of these spectroscopic and reactivity arguments, we assign the structure shown to intermediate A. It is further supported by our recent isolation of $PdMo_2$ and PdW_2 clusters similar to A from the reactions of $[PdCl_2(\eta^2\text{-dppm})]$ with 2 equiv of $[CpMo(CO)_3]^-$ and $[CpMo(CO)_3]^-$, respectively (eq 12).[10b]



Spectroscopic Data. The solid-state infrared spectra of the trinuclear clusters **1–3** show strong $\nu(CO)$ absorptions around 1750 cm^{-1} indicative of a semi triply bridging carbonyl ligand.[12] This value is similar to those observed for the structurally characterized clusters $[PtCo_2(\mu\text{-}CO)(CO)_7(PPh_3)]$ ($\nu(CO)$ (KBr)

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(10) (a) Braunstein, P.; de Méric de Bellefon, C.; Oswald, B.; Ries, M.; Tiripicchio, A. *Inorg. Chem.*, preceding paper in this issue. (b) Braunstein, P.; Oswald, B.; DeCian, A.; Fischer, J. *J. Chem. Soc., Dalton Trans.* **1991**, 2685.

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(12) (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219.

at 1768 (s), 1775 (sh) cm^{-1})[13] or $[Pd_2MoCpCl(\mu\text{-}CO)_2(\mu\text{-dppm})_2]$ (ν(CO) (KBr) at 1797 (w), 1756 (s)).[3] In cluster **8** this absorption is shifted to 1662 cm^{-1}, a very low frequency, owing to the presence of two dppm ligands which increase the metal to CO back-bonding. The highest frequency absorption band (in THF) of **4** (2056 cm^{-1}) and of **5** (2073 cm^{-1}) is assigned to the linear carbonyls of the $Mn(CO)_5$ fragment,[2] whereas the absorption bands of **5** at 2022 cm^{-1}, of **6** at 2027 cm^{-1} and of **7** at 2023 cm^{-1} correspond to the linear carbonyl ligand bound to the platinum atom.[14] The ν(PtCl) vibration of **4** appears at 287 cm^{-1}, a value similar to that observed for $[PtCl_2(\eta^2\text{-dppm})]$ (305, 292 cm^{-1})[15a] or $[PtCl_2(\eta^2\text{-dppe})]$ (315, 292 cm^{-1}).[15b] The ν(PdCl) vibration of **15** at 262 cm^{-1} is, as expected, very close to that observed for the related isoelectronic complex $[Cl\overline{Pd(\mu\text{-dppm})_2Mn}(CO)_3]$ (264 cm^{-1}).[16b]

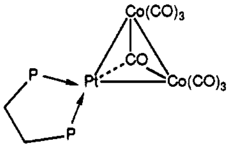
The pattern of the ^{1}H NMR spectrum in the region of the dppm methylene protons is very characteristic as it shows a triplet for **2** and **5**, a doublet of triplets for **3** (ABXY spin system) or a doublet of doublets for **1** with ^2J(PH) and ^3J(PtH) values of ca. 10 Hz and 40 Hz, respectively.[3,17] The quintet observed for the CH_2 protons of **15** is due to virtual coupling with the four phosphorus atoms. This is characteristic of a binuclear unit doubly bridged by trans dppm ligands.[2,16,18]

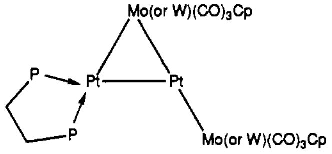
The $^{31}P\{^1H\}$ NMR resonances for **1–3** and **5–7** indicate that the two phosphorus atoms of the dppm ligand are chemically inequivalent and are coupled to each other, giving two doublets with a ^2J(PP) value of ca. 60 Hz, a ^1J(PtP) coupling of ca. 3800 Hz for the phosphorus atom directly bonded to platinum[19] and a ^{2+3}J(PtP) coupling of ca. 100 Hz for the phosphorus atom bonded to the other metal atom. The resonances for compound **4** are typical of a chelating dppm ligand and the phosphorus atom trans to manganese resonates at −36.2 ppm with ^1J(PtP) = 2241 Hz and the phosphorus atom trans to chloride at −47.4 ppm with ^1J(PtP) = 3364 Hz and ^2J(PP) = 60 Hz.[20] This molecule represents an interesting additional example where two phosphino groups of a chelated dppm ligand are chemically inequivalent. For complexes **15** and **16**, the triplets observed in the $^{31}P\{^1H\}$ NMR spectrum may be interpreted as "deceptively simple" examples of AA'XX' spectra with a coupling constant $N = |J(P_AP_X) + J(P_AP_{X'})|$ of 124 and 125 Hz, respectively, characteristic for this type of binuclear complex.[21]

Discussion

In this work, we have shown that readily available mononuclear d^8 complexes of Pd(II) or Pt(II) having chelating dppm ligand(s) are convenient precursors to heterometallic complexes containing a moiety $\overline{M(\mu\text{-dppm})m}$ (M = Pd, Pt; m = $Mo(CO)_2Cp$, $W(CO)_2Cp$, $Mn(CO)_4$, $Co(CO)_3$) upon reaction with the appropriate carbonylmetalate anion. In all mixed-metal complexes reported here the palladium and platinum centers have their usual 16e count and the metal contained in m its 18e count. The driving force for these reactions is to be found in the formation of a stable five-membered ring from a four-membered ring. The lability of the metal–phosphorus bond which accounts for the formation of the products is greater for M = Pd than for M = Pt and parallels that observed previously in the reactions of the dinuclear d^9–d^9 complexes of the type $[Cl\overline{Pd(\mu\text{-dppm})_2Pt}Cl]$ with carbonylmetalate anions.[1b,3,17] In the latter cases, a $\overline{Pd(\mu\text{-dppm})Pt}$ moiety was retained and a new $\overline{Pt(\mu\text{-dppm})m}$ moiety was formed, as a result of a selective formal insertion of the fragment m into the more labile Pd–P bond. It is noteworthy that the hydridocarbonylmetalates $[HCr(CO)_5]^-$ and $[HW(CO)_5]^-$ reacted with $[PtCl_2(\eta^2\text{-dppm})]$ to form $[Pt_2(\mu\text{-}H)(\mu\text{-dppm})_2(H)_2]^+$ in high yield, and although opening of the chelating dppm had also occurred in these cases, no heterometallic complex was isolated.[22]

The $Ptm_2(\mu\text{-dppm})$ clusters **1–3** were formed without occurrence of a redox reaction. Their structures are proposed on the basis of analytical and spectroscopic results and by analogy with those determined by X-ray diffraction for the related clusters $[PtCo_2(\mu\text{-}CO)(CO)_7(PPh_3)]$[13] and $[PtCo_2(\mu\text{-}CO)(CO)_6(\eta^2\text{-dppe})]$ (dppe = $Ph_2PCH_2CH_2PPh_2$).[23a] At this point, it is interesting to remember that when similar reactions were performed between cis-$[PtCl_2(PR_3)_2]$ and e.g. $[Mo(CO)_3Cp]^-$, they resulted in a redox process leading to heterotetranuclear clusters of the type Pt_2m_2 which contain Pt(I) centers.[24] On the other hand, reactions of these carbonylmetalates with cis-$[PtCl_2(\eta^2\text{-dppe})]$ afforded the 46 electron triangulo cluster $[PtCo_2(CO)_7(\eta^2\text{-dppe})]$[23b,c] and the 58 electron metalloligated clusters $[Pt_2Mo_2Cp_2(CO)_6(\eta^2\text{-dppe})]$ or $[Pt_2W_2Cp_2(CO)_6(\eta^2\text{-dppe})]$,[1a] respectively, in which a stable, five-membered ring $Pt(\eta^2\text{-dppe})$ moiety is retained.





The reaction of eq 1 proceeds by consecutive nucleophilic substitution of the chloride ligands, as supported by the isolation of the monosubstituted intermediate in the reaction of eq 2. Migration of the phosphorus atom from platinum to manganese, accompanied with CO migration from manganese to platinum, only occurs after substitution of the second chloride ligand and yields the Mn–Pt–Mn chain complex **5** in high yield (eq 3).

That the dppm ligand remains chelated to Pt in **4** as well as the open structure of **5** is consistent with a CO ligand being more difficult to remove from a $Mn(CO)_5$ than e.g. a $Co(CO)_4$ moiety. Attempts to convert **5** into a cluster analogous to **1–3** failed. With **6** and **7** on the contrary, the equilibrium of eq 4 is easily and rapidly established upon changing the CO partial pressure. Thus, breaking/formation of a Mo–Mo or W–W bond in the systems **2**, **6** and **3**, **7**, respectively, does not require much energy. The presence of a trans-P–Pt–CO arrangement in **5–7** is deduced from the high ν(CO) vibration (ca. 2025 cm^{-1}) in their IR spectra by comparison with those found in the parent clusters **2** and **3** (ca. 1920 cm^{-1}). This is consistent with observations reported for the cis–trans isomers in the series $[PtCl_2(CO)(PR_3)]$.[25]

Reaction of **1** with dppm occurs with retention of the $PtCo_2$ core, affording regioselectively **8** in which each Pt-Co edge is

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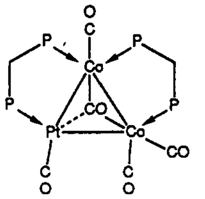
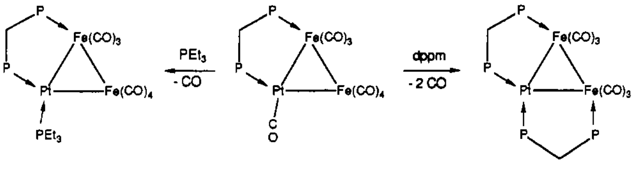
bridged by a dppm ligand (eq 5). In view of the known lability of the Co-bound CO ligands, an isomer of type **B** would have



B

been a conceivable alternative but was not observed. This suggests that the first step of the reaction of eq 5 is the substitution of the Pt-bound carbonyl by dppm, leading to a η^1-dppm intermediate which would transform into **8** by CO substitution at cobalt. This is furthermore supported by the reactions of the related cluster $[PtFe_2(CO)_8(\mu\text{-dppm})]$ with PEt_3 or dppm which afforded $[PtFe_2(CO)_7(PEt_3)(\mu\text{-dppm})]$ and $[PtFe_2(CO)_6(\mu\text{-dppm})_2]$, respectively.[26]



Reaction of **1** with 2 equiv of dppm only resulted in **8**, which was independently shown to be unreactive toward further dppm. Although triangulo clusters containing 3 bridging dppm ligands are known, e.g., $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$,[27] or $[Pd_2Co(\mu\text{-CO})_2(\mu\text{-dppm})_3]^+$,[1c] thus showing that this is sterically possible, we have not observed formation of a third dppm bridge between two m fragments (only between m and Pd or Pt).

In contrast to **1**, reactions of clusters **2** and **3** with dppm resulted in metal–metal bond heterolytic rupture and formation of the known **9** and **10**, respectively (eq 6). For electronic and steric reasons, substitution of a Mo- or W-bound CO is less favorable here than in the cobalt case, resulting in chelation of dppm to Pt. With the open chain complex **5**, rupture of only one metal–metal bond is sufficient to lead to **11** (eq 8). Complexes **9**–**11** have been prepared previously by the reaction of the trinuclear chain complexes trans-[Pt{m(CO)}$_2$(NCPh)$_2$] with 2 equiv of dppm and are readily converted into their PF_6^- salts **9a** and **10a**. An additional access to these complexes consists of the reaction of $[Pt(\eta^2\text{-dppm})_2]^{2+}$ with 2 equiv of the carbonylmetalates (eq 7), which also applies to the Mn and Co analogues **11** and **12**,[10a] respectively. When comparing the reactions of eq 7 and 10, it is noteworthy that **8** was not formed in the former reaction, in contrast to **14** in the latter. When considering the reactions of eqs 6 and 8, it is interesting that the entering dppm ligand is chelated to Pt in the products. These were the first examples of heterometallic complexes containing bridging and chelating dppm ligands to be fully characterized.[9] They have no palladium equivalents (complexes with 2 bridging dppm ligands are formed instead), and this is consistent with the greater Pd–P bond lability which allows the release of the strain associated with a four-membered ring structure.[28]

In the reaction of $[Pd(\eta^2\text{-dppm})_2][BF_4]_2$ with 2 equiv of $Na[Co(CO)_4]$, two Pd–P bonds are broken, with formation of **14**. The formation of the violet intermediate observed at −30 °C is quenched by addition of excess chloride ions to give **15**. This bimetallic complex, analogous to the structurally characterized $[BrPd(\mu\text{-dppm})_2Mn(CO)_4]$,[16] was shown to react with $[Co(CO)_4]^-$ to give the chain complex **16** in which the unsupported Pd–Co bond is sufficiently labile to be cleaved by chloride ions in THF, regenerating **15** (eq 9). Related, facile Pd–Co bond breaking reactions have been reported previously with the metalloligated cluster $[Pd_2Co_2(CO)_7(\mu\text{-dppm})_2]$ (**13**).[1b] The structure and synthetic origin of complex **16** is related to that of the violet trimetallic complex $[(OC)_4CoPd(\mu\text{-dppm})_2Mn(CO)_3]$ which was prepared by the reaction of $[BrPd(\mu\text{-dppm})_2Mn(CO)_3]$ with $[Co(CO)_4]^-$.[10a] Complex **16** spontaneously looses CO to give **14**, the palladium analogue of **8**, by formal intramolecular insertion of the $Co(CO)_3$ fragment, selectively into a Co–P vs a Pd–P bond. Cluster **14** has also been obtained by three other routes: (i) the reaction of $[PdCl_2(\eta^2\text{-dppm})]$ with 2 equiv of $[Co(CO)_4]^-$ followed by the addition of 1 equiv of dppm to intermediate **A** (Scheme II), (ii) the thermal treatment of **13** in toluene at 80 °C (Scheme II),[1b] and (iii) the reaction of the chain complex trans-[Pd{Co(CO)$_4$}$_2$(PhCN)$_2$] with 2 equiv of dppm.[10a]

In the reaction of eq 11, the metal centers undergo an overall disproportionation since the palladium centers in **A** and **13** may formally be considered as Pd(II) and Pd(I), respectively and the cobalt centers in **A** and $[Co_2(CO)_6(\mu\text{-dppm})_2]$ as Co(−I) and Co(0), respectively. Although the reaction intermediates are unknown, one might speculate that in the absence of a further stabilizing dppm ligand, **A** would fragment into $[Co_2(CO)_6(\mu\text{-dppm})]$ and Pd(0) species. The latter could then react with the Pd(II)/dppm mixture present to afford $[ClPd(\mu\text{-dppm})_2PdCl]$, which is known to be an excellent precursor of **13** via its reaction with 2 equiv $[Co(CO)_4]^-$.[1b]

In conclusion, we have described a series of reactions in which dppm-assisted metal–metal bond formation led to di- and trinuclear complexes associating palladium or platinum with other transition metals. The reaction conditions and the structure of the products were found to be very sensitive to the nature of the metals, even within an isoelectronic series. Different synthetic procedures and pathways sometimes lead to the same clusters, which allows a better identification of the parameters responsible for improved selectivity and yields. The generally greater lability of the P–Pd vs P–Pt bond accounts for the fact that four-membered ring structures of the type Pd(η^2-dppm) easily rearrange with formation of metal–metal bonded complexes containing a dppm bridge. The reactions of eq 6 in which the bridging $[Mo(CO)_3Cp]^-$ or $[W(CO)_3Cp]^-$ anions have been displaced by a dppm ligand support their view as 4e donor fragments.[24b,c]

Experimental Section

The experimental techniques and general procedures used in this work have been described previously.[16,24b] The reagents $Ph_2PCH_2PPh_2$ (dppm),[29] $Na[Co(CO)_4]$,[30] $[PtCl_2(\eta^2\text{-dppm})]\cdot C_6H_6$, $[PtCl_2(\eta^2\text{-dppm}]\cdot CH_2Cl_2$,[22] $Na[M(CO)_3Cp]\cdot 2DME$ (M = Mo, W),[31] $Na[Mn(CO)_5]$,[32] [PdCl$_2$-

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(η^2-dppm],[33] and [Pd(η^2-dppm)$_2$][BF$_4$]$_2$[33] were prepared according to published procedures. [Pt(η^2-dppm)$_2$]Cl$_2$[34] was prepared by dropwise addition of a stoichiometric amount of a solution of dppm in CH$_2$Cl$_2$ to a suspension of [PtCl$_2$(PhCN)$_2$]. After 2 h stirring the precipitate was filtered off and recrystallized from CH$_2$Cl$_2$/hexane (97% yield based on Pt). Tl[PF$_6$] (Strem Chemicals), [NH$_4$][PF$_6$] and carbon monoxide (Air Liquide) were used as received without further purification.

Synthesis of [PtCo$_2$(CO)$_7$(μ-dppm)] (1). A filtered solution of Na[Co(CO)$_4$] (0.1 M in THF, 40 mL) was added to a suspension of [PtCl$_2$(η^2-dppm)·C$_6$H$_6$ (1.52 g, 2.0 mmol) in THF (50 mL). The mixture was heated (40 °C) for 3 h after which time its color had changed from light yellow to red-brown and a white precipitate had formed. The solvent was removed in vacuo and the residue was extracted with CH$_2$Cl$_2$ and filtered on a Celite-padded filter funnel. The filtered solution was concentrated to ca. 30 mL and the addition of *n*-hexane (90 mL) afforded a red-brown microcrystalline powder of **1** (1.44 g, 1.6 mmol, 80% based on Pt). Anal. Calcd for C$_{32}$H$_{22}$Co$_2$O$_7$P$_2$Pt (M_r = 893.43): C, 43.02; H, 2.48; Co, 13.19; P, 6.93; Pt, 21.84. Found: C, 42.50; H, 2.56; Co, 11.27; P, 6.57; Pt, 20.64. IR ν(CO) (KBr): 2051 (s), 2016 (s), 1990 (s, br), 1975 (m, sh), 1946 (m), 1745 (s); (THF) 2052 (vs), 2017 (vs), 1955 (s, br), 1988 (s, br), 1886 (w), 1757 (m, br) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.50–6.85 (m, 20 H, C$_6$H$_5$), 4.63 (dd, 2 H, CH$_2$, ^2J(PH) = 10.2, 11.2, ^3J(PtH) = 48 Hz). ^{31}P{^{1}H} NMR (CHCl$_3$/CDCl$_3$): δ 22.0 (br, m, P→Co), −1.5 (d, P→Pt, ^1J(PtP) = 3295 Hz, ^2J(PP) = 26 Hz). ^{195}Pt{^{1}H} NMR (CDCl$_3$): δ −2502 (dd, ^1J(PtP) = 3295 Hz, ^2J(PP) = 47 Hz).

Synthesis of [PtMo$_2$Cp$_2$(CO)$_5$(μ-dppm)] (2). A mixture of Na[Mo(CO)$_3$Cp]·2DME (0.913 g, 2.04 mmol) and [PtCl$_2$(η^2-dppm]·CH$_2$Cl$_2$ (0.760 g, 1.02 mmol) in THF (60 mL) was heated under reflux for 4 h. The color of the mixture slowly turned from light yellow to deep blue. The solvent was evaporated to dryness under reduced pressure, the residue was extracted with toluene (60 mL) and the solution was filtered through a Celite-padded filter funnel. Upon cooling to −30 °C, the blue solution afforded dark blue microcrystals which were washed with *n*-hexane (40 mL) and dried in vacuo, yielding violet microcrystalline **2** (0.752 g, 0.72 mmol, 71% yield based on Pt). Anal. Calcd for C$_{40}$H$_{32}$Mo$_2$O$_5$P$_2$Pt (M_r = 1041.62): C, 46.12; H, 3.10. Found: C, 46.20; H, 3.25. IR ν(CO) (KBr): 1921 (s), 1895 (vs), 1850 (s), 1783 (s), 1760 (s); (THF) 1921 (s), 1901 (vs), 1849 (br, s), 1778 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.50–7.15 (m, 20 H, C$_6$H$_5$), 5.32 (s, 5 H, C$_5$H$_5$), 5.24 (s, 5 H, C$_5$H$_5$), 4.13 (t, 2 H, CH$_2$, ^2J(PH) = 9.5, ^3J(PtH) = 55 Hz). ^{31}P{^{1}H} NMR (CHCl$_3$/CDCl$_3$): δ 46.3 (d, 1P, P→Mo, ^2J(PtP) = 118 Hz, ^2J(PP) = 45 Hz), 27.3 (d, 1P, P→Pt, ^1J(PtP) = 4062 Hz, ^2J(PP) = 45 Hz).

Synthesis of [PtW$_2$Cp$_2$(CO)$_5$(μ-dppm)] (3). A mixture of Na[W(CO)$_3$Cp]·2DME (0.409 g, 0.74 mmol) and [PtCl$_2$(η^2-dppm]·CH$_2$Cl$_2$ (0.273 g, 0.36 mmol) in THF (50 mL) was heated under reflux for 2 h. The color of the mixture slowly turned from light yellow to deep purple. The solvent was evaporated to dryness under reduced pressure, the residue was extracted with a mixture of dichloromethane (20 mL) and *n*-hexane (20 mL) and the solution was filtered through a Celite-padded filter funnel. The solvents were removed in vacuo and the residue was recrystallized in a mixture of THF (15 mL) and diethyl ether (60 mL) at −20 °C to afford purple microcrystalline **3** (0.210 g, 0.17 mmol, 47% yield based on Pt). Anal. Calcd for C$_{40}$H$_{32}$O$_5$P$_2$PtW$_2$ (M_r = 1217.42): C, 39.46; H, 2.65; P, 5.09; Pt, 16.02; W, 30.20. Found: C, 39.46; H, 2.86; P, 5.58; Pt, 15.72; W, 30.19. IR ν(CO): (KBr) 1911 (s), 1887 (vs), 1836 (s), 1775 (sh), 1754 (s); (THF) 1920 (m), 1897 (vs), 1840 (s), 1779 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.50–7.04 (m, 20 H, C$_6$H$_5$), 5.41 (s, 5 H, C$_5$H$_5$), 5.27 (s, 5 H, C$_5$H$_5$), 4.52 (dt, 1 H, CH_AH$_\text{B}$, ^2J(H$_\text{A}$H$_\text{B}$) = 13 Hz, ^2J(PH$_\text{A}$) = 10.5 Hz), 4.26 (dt, 1 H, CH$_\text{A}$$H_\text{B}$, ^2J(H$_\text{A}H_\text{B}$) = 13 Hz, ^2J(PH$_\text{B}$) = 10.9 Hz) (^3J(PtH) not determined owing to insufficient S/N ratio). ^{31}P{^{1}H} NMR (CHCl$_3$/CDCl$_3$): δ 21.6 (d, 1P, P→Pt, ^1J(PtP) = 3936 Hz, ^2J(PP) = 53 Hz), 15.3 (d, 1P, P→W, ^2J(PtP) = 114 Hz, ^2J(PP) = 53 Hz, ^1J(PW) = 327 Hz).

Synthesis of [(η^2-dppm)PtCl{Mn(CO)$_5$}] (4). A solution of Na[Mn(CO)$_5$] (0.1 M in THF, 21 mL, 2.1 mmol) was added dropwise to a cooled (−40 °C) suspension of [PtCl$_2$(η^2-dppm]·CH$_2$Cl$_2$ (1.30 g, 2.0 mmol) in THF (100 mL). The temperature was allowed to reach ambient and the mixture was further stirred for 3 h. The solution was concentrated to ca. 20 mL and filtered, yielding some unreacted [PtCl$_2$(η^2-dppm] (20% yield based on Pt) and NaCl. *n*-Hexane was added to the filtrate and cooling at −20 °C afforded microcrystalline **4** (1.14 g, 1.3 mmol, 65% yield based on Pt) contaminated with [PtCl$_2$(η^2-dppm] (7% by NMR). Attempts to recrystallize **4** always led to a similar mixture and the use of an excess of Na[Mn(CO)$_5$] afforded the heterodinuclear cationic complex $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{M}}\text{n(CO)}_4][\text{Mn(CO)}_5]$ (**11**). Data for **4**: IR ν(CO) (THF): 2056 (vs), 1976 (m, br), 1954 (vs, br), 1933 (vs, br) cm^{-1}; (KBr): 2052 (vs), 1976 (sh), 1952 (vs), 1928 (vs) cm^{-1}. FT-IR ν(PtCl) 287 cm^{-1}. ^{31}P{^{1}H} NMR (THF/C$_6$D$_6$): δ −36.2 (d, 1 P, P→Pt, trans to Mn, ^1J(PtP) = 2241 Hz, ^2J(PP) = 60 Hz), −47.4 (d, 1P, P→Pt, trans to Cl, ^1J(PtP) = 3364 Hz, ^2J(PP) = 60 Hz). Spectroscopic data for **11**: see ref 10a.

Synthesis of $[(\text{OC})_5\text{Mn}\overline{\text{Pt(CO)}(\mu\text{-dppm})\text{M}}\text{n(CO)}_4]$ (5). A solution of Na[Mn(CO)$_5$] (0.1 M in THF, 8.3 mL, 0.83 mmol) was added dropwise to a cooled (0 °C) suspension of [PtCl$_2$(η^2-dppm)]·CH$_2$Cl$_2$ (0.305 g, 0.415 mmol) in THF (50 mL). The mixture was stirred for 2 h and the temperature was raised to ambient. After further stirring (2 h), the color of the solution had turned red-brown. The solvent was removed under reduced pressure, the residue was extracted with toluene (50 mL) and the solution was filtered through a silica gel-padded filter funnel. Addition of *n*-hexane to the toluene solution afforded a red-brown precipitate of **5** (0.36 g, 0.37 mmol, 90% yield based on Pt). Anal. Calcd for C$_{35}$H$_{22}$Mn$_2$O$_{10}$P$_2$Pt (M_r = 969.46): C, 43.36; H, 2.29. Found: C, 43.32; H, 2.24. IR ν(CO) (THF): 2073 (m), 2022 (s), 1996 (w), 1966 (s, br), 1923 (sh) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.53–7.23 (m, 20 H, C$_6$H$_5$), 4.28 (t, 2 H, CH$_2$, ^2J(PH) = 10.3, ^3J(PtH) = 51 Hz). ^{31}P{^{1}H} NMR (THF/C$_6$D$_6$): δ 57.5 (br, m, P→Mn), 19.3 (d, 1P, P→Pt, ^2J(PtP) = 3515 Hz, ^2J(PP) = 79 Hz).

Synthesis of $[\text{Cp(OC)}_3\text{Mo}\overline{\text{Pt(CO)}(\mu\text{-dppm})\text{M}}\text{o(CO)}_2\text{Cp}]$ (6). Upon stirring under an atmosphere of CO, a blue solution of the complex [PtMo$_2$Cp$_2$(CO)$_5$(μ-dppm)] (**2**) (0.250 g, 0.24 mmol) in toluene (25 mL) turned red-orange within 0.10 h. Upon cooling to −30 °C, red-orange microcrystals of **6**·toluene were obtained (0.21 g, 0.18 mmol, 75% based on Pt). Anal. Calcd for **6**·toluene, C$_{48}$H$_{40}$Mo$_2$O$_6$P$_2$Pt (M_r = 1161.75): C, 49.63; H, 3.47; Pt, 16.80. Found: C, 50.66; H, 3.68; Pt, 15.86. IR ν(CO) (KBr): 2024 (s), 1931 (s), 1898 (vs), 1818 (s); (THF) 2027 (m), 1939 (s), 1901 (vs), 1861 (m), 1835 (s) cm^{-1}. ^{31}P{^{1}H} NMR (toluene-d_8, under a CO atmosphere): δ 42.8 (d, 1 P, P→Mo, ^2J(PtP) = 213 Hz, ^2J(PP) = 71 Hz), 6.6 (d, 1 P, P→Pt, ^1J(PtP) = 3445 Hz, ^2J(PP) = 71 Hz).

Synthesis of $[\text{Cp(OC)}_3\text{W}\overline{\text{Pt(CO)}(\mu\text{-dppm})\text{W}}\text{(CO)}_2\text{Cp}]$ (7). This complex was prepared in a manner analogous to **6** in 76% yield. IR ν(CO) (THF): 2023 (m), 1934 (s), 1892 (s), 1853 (m,sh), 1824 (s) cm^{-1}. ^{31}P{^{1}H} NMR (toluene-d_8, under a CO atmosphere): δ 12.6 (d, 1 P, P→W, ^2J(PtP) = 250 Hz, ^2J(PP) = 71 Hz), −0.2 (d, 1 P, P→Pt, ^1J(PtP) = 3227 Hz, ^2J(PP) = 71 Hz).

Synthesis of [PtCo$_2$(CO)$_5$(μ-dppm)$_2$] (8). Upon addition of dppm (0.117 g, 0.3 mmol) to a solution of the complex [PtCo$_2$(CO)$_7$(μ-dppm)] (**1**) (0.268 g, 0.3 mmol) in THF (15 mL) at room temperature, gas evolution was observed, indicating that a reaction was occurring. The solvent was removed in vacuo and the solid was washed with toluene (10 mL) and *n*-hexane (10 mL), affording a red-brown powder of **7** (0.235 g, 63% based on Pt). Anal. Calcd for C$_{55}$H$_{44}$Co$_2$O$_5$P$_4$Pt (M_r = 1221.79): C, 54.07; H, 3.63. Found: C, 53.12; H, 3.66. IR ν(CO) (KBr): 1993 (vs), 1941 (vs), 1913 (sh), 1662 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.48–6.98 (m, 40 H, C$_6$H$_5$), 4.57 (m, br, 4 H, CH$_2$). ^{31}P{^{1}H} NMR (CHCl$_3$/CDCl$_3$): δ 26.0 (br, m, P→Co), 4.8 (d, P→Pt, ^1J(PtP) = 3610 Hz, N[35] = $|J(\text{P}_\text{A}\text{P}_\text{X}) + J(\text{P}_\text{A}\text{P}_{\text{X}'})|$ = 50 Hz).

Synthesis of $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{M}}\text{o(CO)}_2\text{Cp}][\text{PF}_6]$ (9a). 1. Starting from [PtCl$_2$(η^2-dppm]·CH$_2$Cl$_2$. The complex [PtMo$_2$Cp$_2$(CO)$_5$(μ-dppm)] (**2**) was prepared in situ as described above from [PtCl$_2$(η^2-dppm)]·CH$_2$Cl$_2$ (0.367 g, 0.5 mmol) and Na[Mo(CO)$_3$Cp]·2DME (0.447 g, 1 mmol) in THF (15 mL). Solid dppm (0.192 g, 0.5 mmol) was added at 40 °C and immediately the color of the solution changed from deep blue to red and its IR spectrum in the ν(CO) region showed the typical absorptions of the anion [Mo(CO)$_3$Cp]$^-$. After 1 h of stirring, the mixture was evaporated to dryness under reduced pressure. The ^{31}P{^{1}H} NMR (THF/C$_6$H$_6$) of this red residue showed the complete conversion in $[(\eta^2\text{-dppm})\overline{\text{Pt}(\mu\text{-dppm})\text{M}}\text{o(CO)}_2\text{Cp}][\text{Mo(CO)}_3\text{Cp}]$ (**9**). Solid [NH$_4$][PF$_6$]

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(0.098 g, 0.6 mmol) was added to a THF solution of **9** and the mixture was stirred for 1 h. Recrystallization from CH_2Cl_2/hexane yielded a red powder of **9a** (0.54 g, 89% based on Pt). Spectroscopic data for **9a**, see ref 10a.

2. Starting from $[Pt(\eta^2\text{-dppm})_2]Cl_2$. A solution of $Na[Mo(CO)_3Cp]\cdot 2DME$ (0.224 g, 0.5 mmol) in THF (10 mL) was added dropwise to a suspension of $[Pt(\eta^2\text{-dppm})_2]Cl_2$ (0.26 g, 0.25 mmol) in THF (20 mL). A red solution rapidly formed and was filtered after 1 h of stirring and was evaporated to dryness under reduced pressure. The $^{31}P\{^1H\}$ NMR spectrum (THF/C_6H_6) of the red residue showed complete conversion in **9**. Solid $[NH_4][PF_6]$ (0.042 g, 0.26 mmol) was added to a THF solution of **9** and the mixture was stirred for 1 h. Recrystallization from CH_2Cl_2/hexane yielded a red powder of **9a** (0.27 g, 91% based on Pt).

Synthesis of $[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})W(CO)_2Cp][PF_6]$ (10a). This complex was prepared using $Na[W(CO)_3Cp]\cdot 2DME$ and $[Pt(\eta^2\text{-dppm})Cl_2]$ or $[Pt(\eta^2\text{-dppm})_2]Cl_2$ according to either of the two methods described for **9a**. Reaction conditions and yields were similar. Spectroscopic data for **10** and **10a**, see ref 10a.

Synthesis of $[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})Mn(CO)_4][Mn(CO)_5]$ (11). 1. Starting from $[Pt(\eta^2\text{-dppm})_2]Cl_2$. A solution of $Na[Mn(CO)_5]$ (0.1 M in THF, 5.0 mL, 0.50 mmol) was added dropwise to a suspension of $[Pt(\eta^2\text{-dppm})_2]Cl_2$ (0.258 g, 0.25 mmol) in THF (25 mL) at room temperature. The mixture was stirred for 12 h and the color of the solution turned yellow. The solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2 (50 mL) and the solution was filtered through a silica gel-padded filter funnel. Addition of *n*-hexane to the CH_2Cl_2 solution afforded a yellow precipitate of **11** (0.26 g, 79% yield based on Pt). Spectroscopic data of **11**, see ref 10a.

2. Starting from $[(OC)_5MnPt(CO)(\mu\text{-dppm})Mn(CO)_4]$ (5). A solution of dppm (0.096 g, 0.25 mmol) in THF (10 mL) was added dropwise to a solution of **5** (0.242 g, 0.25 mmol) in THF (20 mL). A yellow solution rapidly formed after 1 h of stirring and was evaporated to dryness under reduced pressure. The $^{31}P\{^1H\}$ NMR spectrum (THF/C_6H_6) of the yellow residue showed complete conversion in **11**. Spectroscopic data of **11**, see ref 10a.

Synthesis of $[(\eta^2\text{-dppm})Pt(\mu\text{-dppm})Co(CO)_3][Co(CO)_4]$ (12). A solution of $Na[Co(CO)_4]$ (0.1 M in THF, 5.0 mL, 0.50 mmol) was added dropwise to a suspension of $[Pt(\eta^2\text{-dppm})_2]Cl_2$ (0.258 g, 0.25 mmol) in THF (25 mL) at room temperature. The mixture was stirred for 12 h and the color of the solution turned deep red. The solvent was removed under reduced pressure, the residue was extracted with CH_2Cl_2 (50 mL) and the solution was filtered through a silica gel-padded filter funnel. Addition of *n*-hexane to the CH_2Cl_2 solution afforded a red precipitate of **12** (0.28 g, 89% yield based on Pt). Spectroscopic data of **12**, see ref 10a.

Synthesis of $[PdCo_2(CO)_5(\mu\text{-dppm})_2]$ (14). A solution of $Na[Co(CO)_4]$ (0.1 M in THF, 2.5 mL, 0.25 mmol) was added dropwise to a suspension of $[PdCl_2(\eta^2\text{-dppm})]$ (0.14 g, 0.25 mmol) in THF (20 mL) at −30 °C. The color of the suspension slowly turned from light yellow to red. After this time dppm (0.096 g, 0.25 mmol) was added. The $^{31}P\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$) spectrum of the reaction mixture revealed the presence of **14** and **15** in a ca. 3:1 molar ratio. Chromatographic separation using toluene only yielded **14** (0.062 g, 33% based on Pd). Spectroscopic data for **14**, see ref 1b.

Synthesis of $[ClPd(\mu\text{-dppm})_2Co(CO)_2]$ (15). A filtered solution of $Na[Co(CO)_4]$ (0.1 M in THF, 12 mL) and $[Pd(\eta^2\text{-dppm})_2][BF_4]_2$ (0.96 g, 1 mmol) in THF (25 mL) was stirred for 2 h at −30 °C. The color of the mixture slowly turned from light yellow to brown. After this time LiCl (0.042 g, 1 mmol) was added. The solvent was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane (20 mL) and the solution was filtered through a Celite-padded filter funnel. The solvent was removed in vacuo and the residue was recrystallized from a mixture of THF (15 mL) and *n*-hexane (60 mL) at −20 °C to afford green-brown microcrystalline **15**·THF (0.31 g, 30% yield based on Pd). Anal. Calcd for $C_{52}H_{44}ClCoO_2P_4Pd\cdot THF$ (M_r = 1097.73): C, 61.27; H, 4.77. Found: C, 61.31; H, 4.67. IR ν(CO) (KBr): 1939 (s), 1869 (s) cm^{-1}. FT-IR ν(PdCl) 262 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.65–7.09 (m, 40 H, C_6H_5), 4.04 (q, 4 H, CH_2, $J(PH) = 3.5$ Hz), 3.75 and 1.85 (THF signals). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): δ 26.7 (br, m, P→Co), 9.2 (t, P→Pd, $N = |J(P_AP_X) + J(P_AP_{X'})| = 124$ Hz).

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