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Phosphido-Bridged, Heterodi-, Heterotri-, and Heterotetranuclear Complexes of Palladium and Platinum with Transition Metals. Crystal Structure of $[\{(OC)_4\overline{Mn(\mu\text{-}PPh_2)\}_2Pt}(PPh_3)]$ (*Mn–Mn*, 2 *Mn–Pt*)

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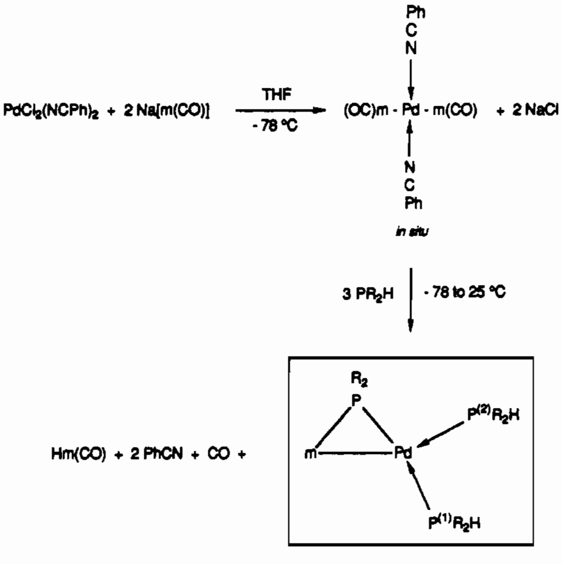
Two methodologies have been used for the synthesis of phosphido-bridged heterometallic complexes of palladium or platinum with transition metals. First, trinuclear mixed-metal chain complexes *trans*-$[Pd\{m(CO)\}_2(NCPh)_2]$ (m = $Cr(CO)_2Cp$, $Mo(CO)_2Cp$, $W(CO)_2Cp$, $Mn(CO)_4$) were reacted with 3 equiv of secondary phosphines PR_2H (R = Ph, Cy), affording the dinuclear complexes $\overline{m(\mu\text{-}PR_2)Pd}(PR_2H)_2$ (**1–6**). When the complexes *trans*-$[Pt\{m(CO)\}_2(NCPh)_2]$ were reacted with 2 equiv of PCy_2H, dinuclear complexes of the type $\overline{m(\mu\text{-}PCy_2)Pt}(CO)(PCy_2H)$ were obtained. We have generally observed that oxidative addition of the P–H bond of PR_2H coordinated to Pt across a metal–metal bond is easier when R = Ph than R = Cy. The second method used involved the in situ reaction of a metallophosphine R_2P–m(CO) with a Pt(0) complex. The terminal phosphine ligand which is trans with respect to the μ-PR_2 bridging ligand appears to be preferentially replaced by an incoming CO ligand. The new complex $[\{(CO)_4\overline{Mn(\mu\text{-}PPh_2)\}_2Pt}(PPh_3)]$ (**19a**) was best prepared and isolated by substitution of the ethylene ligands of $[Pt(C_2H_4)_2(PPh_3)]$ by "Ph_2P–$Mn(CO)_4$" fragments, generated from Ph_2P–$Mn(CO)_5$. Crystals of **19a**·C_7H_8 are triclinic, space group $P\bar{1}$, with Z = 2 in a unit cell of dimensions a = 13.275 (5) Å, b = 17.718 (6) Å, c = 11.970 (3) Å, α = 94.61 (2)°, β = 107.89 (2)°, and γ = 97.74 (2)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 6612 observed reflections to R = 0.0401 and R_w = 0.0531. Although **19a** is closely related to its carbonyl analogue $[\{(CO)_4\overline{Mn(\mu\text{-}PPh_2)\}_2Pt}(CO)]$, which has a bent-chain structure, it displays a weak Mn–Mn bonding interaction, thus resulting in a closed rather than an open structure. The triangular metal framework has Pt–Mn distances of 3.082 (1) and 2.987 (1) Å and an Mn–Mn edge of 3.245 (2) Å. Two phosphido ligands almost symmetrically bridge the Pt–Mn edges, four terminal carbonyl groups are bonded to each Mn atom, and a PPh_3 ligand completes the coordination around the Pt atom. The 3c–4e bonding in **19a** has been analyzed by extended Hückel calculations and compared with that in $[\{(CO)_4\overline{Mn(\mu\text{-}PPh_2)\}_2Pt}(CO)]$. Heterotetranuclear, bent-chain complexes W–Pt–Pt–W (**21**) and Mn–Pt–Pt–Mn (**22**) have been prepared by the reaction of $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$ with $Na[W(CO)_3Cp]$ or $Na[Mn(CO)_5]$, respectively.

The chemistry of heterometallic complexes stabilized by bridging phosphido groups (μ-PR_2) continues to attract considerable interest since the first report of such complexes.[1] It is expected that the nature of the metals and of the substituents R at phosphorus will critically influence the chemistry of these complexes. Whether closed (i.e. with significant bonding interaction between the metals) or open M–(μ-PR_2)–M′ bridge bonds are formed depends on the electronic requirements of the metal–ligand fragments involved.[2]

We have recently described synthetic routes to complexes containing electron-rich $\overline{M\text{–}(\mu\text{-}PR_2)\text{–}M'}$ units (M = Pd, Pt; M′ = Cr, Mo, W, Mn; R = Ph, Cy). They involved the reactions of trinuclear mixed-metal chain complexes of the type *trans*-[M{m(CO)}$_2$(NCPh)$_2$] (M = Pd, Pt; m = $Cr(CO)_2Cp$, $Mo(CO)_2Cp$, $W(CO)_2Cp$, $Mn(CO)_4$) with secondary phosphines PR_2H (R = Ph, Cy)[3-5] or between the metallophosphine Ph_2P–$W(CO)_3Cp$ and platinum(0) complexes.[6] Herein, we report full details on these reactions and describe their extension to the preparation of new heterometallic complexes. Reactivity studies are presented, and we report the X-ray crystal structure of the new 48e cluster $[\{(OC)_4\overline{Mn(\mu\text{-}PPh_2)\}_2Pt}(PPh_3)]$ (**19a**), which is characterized by an expanded triangular metal skeleton.

Results

Synthesis and Characterization of the Complexes. The heterobinuclear complexes **1–6** were prepared by the sequence of reactions outlined in eq 1. First, nucleophilic displacement of the chloride ligands of $PdCl_2(NCPh)_2$ by the carbonylmetalates leads to the thermally labile *trans*-[Pd{m(CO)}$_2$(NCPh)$_2$] chain complexes that are kept in solution at ca. −78 °C and not isolated.[7] In situ addition of the secondary phosphine results in oxidative



(1)

1a m = $Cr(CO)_2Cp$; R = Cy
2a m = $Mo(CO)_2Cp$; R = Cy
2b m = $Mo(CO)_2Cp$; R = Ph
3a m = $W(CO)_2Cp$; R = Cy
3b m = $W(CO)_2Cp$; R = Ph
4a m = $Mn(CO)_4$; R = Cy
4b m = $Mn(CO)_4$; R = Ph
5a m = Fe(CO)Cp; R = Cy
6a m = $Co(CO)_3$; R = Cy

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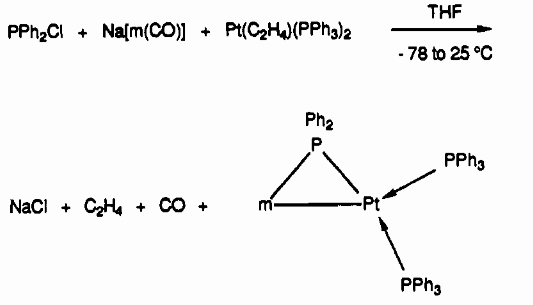
addition of the P–H bond across a heterometallic bond and formation of the dinuclear complexes **1–6**. For the synthesis of the Fe–Pd complex **5a**, the phosphine ligand was added prior to $Fe(CO)_2Cp^-$ in order to ensure rapid consumption of the very labile Fe–Pd–Fe intermediate. It was generally observed that the reactivity of PPh_2H is greater than that of PCy_2H.[4] The reactions require 3 molar equivalents of PR_2H for completion, and **1–6** were the only phosphido-bridged complexes observed. Preparation of $[(OC)_3\overline{Co(\mu\text{-}PPh_2)Pd}(PPh_2H)_2]$ by this method failed, owing to decomposition. Attempts to form this complex between −78 °C and room temperature by the reaction of W–Pd **3a** with $Ph_2P\text{–}Co(CO)_4$[8] led instead to Co–Pd **6a**, showing that, somewhat surprisingly, metal exchange is preferred here over replacement of the whole metallophosphine moiety.

Experimental details and spectroscopic data for all complexes are given in the Experimental Section. As with other phosphido-bridged complexes, the $^{31}P\{^1H\}$ NMR data are very informative. Each complex shows a downfield resonance (doublet of doublets), due to the bridging PR_2 ligand, and two other resonances (doublet of doublets and pseudo triplet), due to the chemically inequivalent terminal PR_2H ligands. The large downfield shifts of the bridging ligand by ca. 175–210 ppm for μ-PPh_2 and ca. 220–290 ppm for μ-PCy_2 are indicative of metal–metal bonding.[9] This was confirmed by the X-ray crystal structure determination of **2a** (Mo–Pd = 2.916 (2) Å) and **4a** (Mn–Pd = 2.689 (2) Å).[5]

The m–Pt complexes **7–9** were prepared in 60–70% yields by using a different method which consisted in the reaction of the metallophosphines $Ph_2P\text{–}m(CO)$,[8,10] generated in situ from Ph_2PCl and Na[m(CO)], with the Pt(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ (eq 2). Analytical and spectroscopic data (see Experimental Section)

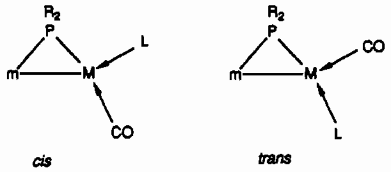


(2)

7 m = W(CO)$_2$Cp
8 m = Mn(CO)$_4$
9 m = Co(CO)3

are again consistent with the structures drawn. In particular, the downfield position of the μ-PPh_2 resonance for **7–9**, in the range ca. 150–200 ppm with $^1J[(\mu\text{-}P)Pt]$ coupling constants between ca. 2400 and 2800 Hz, implies the presence of a metal–metal bond.[9] Displacement of the metalloligand $Cy_2P\text{–}m$ from **1a–3a** by ethylene (1 atm, 25 °C, CH_2Cl_2) proved impossible (IR and $^{31}P\{^1H\}$ NMR).

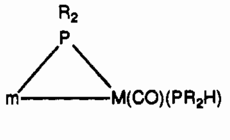
Table I. Percentage of the Cis and Trans Isomers of **10–14** and Related Complexes at Equilibrium, As Determined by $^{31}P\{^1H\}$ NMR Spectroscopy



M	L	R	m	no.	cis, %	trans, %
Pd	PCy_2H	Cy	$Cr(CO)_2Cp$	**10**	78	22
			$Mo(CO)_2Cp$	**11**	86	14
			$W(CO)_2Cp$	**12**	84	16
			$Co(CO)_3$	**13**	100	
Pt	PCy_2H	Cy	$Mo(CO)_2Cp$		67	33[a]
			$W(CO)_2Cp$		67	33[a]
Pt	PPh_3	Ph	$W(CO)_2Cp$	**14**	100	

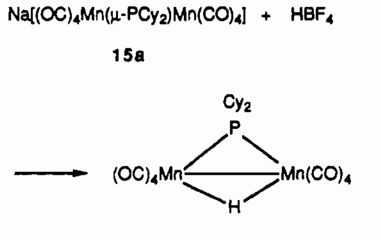
[a] Reference 3.

The m–Pd complexes **10–12** and W–Pt **14** were formed and identified by $^{31}P\{^1H\}$ NMR spectroscopy in CO-saturated CH_2Cl_2/C_6D_6 solutions of the corresponding bis(phosphino) complexes **1a–3a** and **7**, respectively (see Discussion). However, mainly the bis(phosphine) complexes were isolated by precipitation from these solutions. Although the Co–Pd complex **6a** did not react with CO under these conditions, **13** was obtained as a byproduct in the preparation of **6a** (eq 1). Complexes **10–12** were formed as an equilibrium mixture of cis and trans isomers with respect to the μ-PCy_2 ligand,[5] whereas only the cis isomers of **13** and **14** were observed. The stereoselectivity of the reactions and the cis/trans ratios of the products (Table I) were deduced from $^{31}P\{^1H\}$ NMR spectroscopy. The difference in relative stability of the cis and trans isomers of **10–13** clearly illustrates the changes in electronic properties of the trans $Cy_2P\text{–}m$ fragment when m varies. From the $^{31}P\{^1H\}$ NMR data at different temperatures, the values of $\Delta H° = 7.1 \pm 0.4$ kJ·mol^{-1} and $\Delta S° = 10.5 \pm 1$ J·mol^{-1}·K^{-1} were calculated for the cis-**12**/trans-**12** equilibrium.



10 M = Pd; m = Cr(CO)$_2$Cp; R = Cy
11 M = Pd; m = Mo(CO)$_2$Cp; R = Cy
12 M = Pd; m = W(CO)$_2$Cp; R = Cy
13 M = Pd; m = Co(CO)$_3$; R = Cy
14 M = Pt; m = W(CO)$_2$Cp; R = Ph

When the reaction leading to the Mn–Pd complex **4a** was performed with a Pd/Mn/PCy_2H ratio of 1:4:3 instead of 1:2:3, the dimanganese complex $Na[Mn_2(\mu\text{-}PCy_2)(CO)_8]$ (**15a**) was isolated as the major product. However, it proved too unstable to characterize fully, and it was converted to the tetrabutylammonium salt $(n\text{-}Bu_4N)[Mn_2(\mu\text{-}PCy_2)(CO)_8]$ (**15b**) or to the neutral, hydrido complex $[Mn_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8]$ (**16**)[11] (eq 3). Since **15a** was not observed in the reaction between Na-



(3)

16

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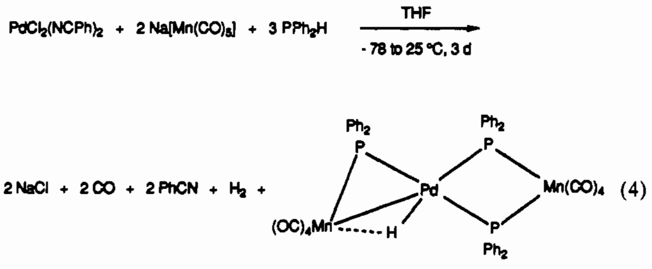
$[Mn(CO)_5]$, $Mn_2(CO)_{10}$ and PCy_2H in THF at room temperature and was formed only in trace amounts in the reaction between Mn–Pd **4a**, $Na[Mn(CO)_5]$, and PCy_2H in THF (room temperature, 4 days), its formation appears to involve a Pd-containing intermediate which would then undergo Mn for Pd metal exchange.

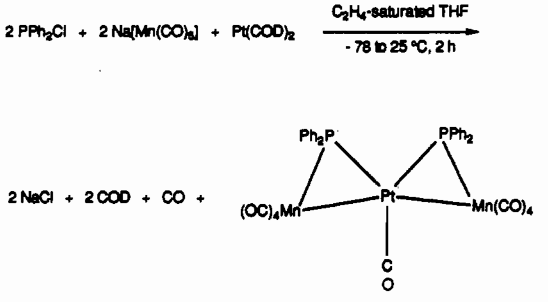
When the synthesis of Mn–Pd **4b** was carried out under the same conditions but with a reaction time of 3 days, the new complex $[(OC)_4Mn(\mu\text{-H})(\mu\text{-PPh}_2)Pd(\mu\text{-PPh}_2)_2Mn(CO)_4]$ (**17**) was formed in addition and isolated in ca. 18% yield (this complex is not detected after short reaction times) (eq 4). Particularly characteristic are its $^{31}P\{^1H\}$ NMR resonances at δ 140 (dd, $^2J(PP)$ = 272 and 26 Hz) for the μ-PPh_2 group bridging the Mn–Pd bond and at δ −81 and −101 (complex multiplets) for the phosphido bridges not spanning a metal–metal bond.[9] The ^1H NMR resonance at δ −11.0 (ddd) is consistent with a hydride bridging a Mn–Pd bond (this resonance was observed at δ −11.1 with ^1J(Pt–H) = 526 Hz in Mn_2Pt **20**, the Pt analogue of **17**).[12,13]



(4)

17

The platinum analogue of **17** has been previously obtained by the reaction of $Pt(PPh_2Cl)_2Cl_2$ with $Na[Mn(CO)_5]$.[13] This reaction also yielded $[(OC)_4Mn(\mu\text{-PPh}_2)Pt(CO)(\mu\text{-PPh}_2)Mn(CO)_4]$ (**18**), which has now been prepared in 89% yield by the reaction of eq 5. The formation of **18** nicely extends to the metallophosphine $Ph_2P\text{–}Mn(CO)_5$[10c] the procedure previously described for $Ph_2P\text{–}W(CO)_3Cp$, which afforded the related bent-chain complex $[Cp(OC)_2W(\mu\text{-PPh}_2)Pt(CO)(\mu\text{-PPh}_2)W(CO)_2Cp]$.[6]



(5)

18

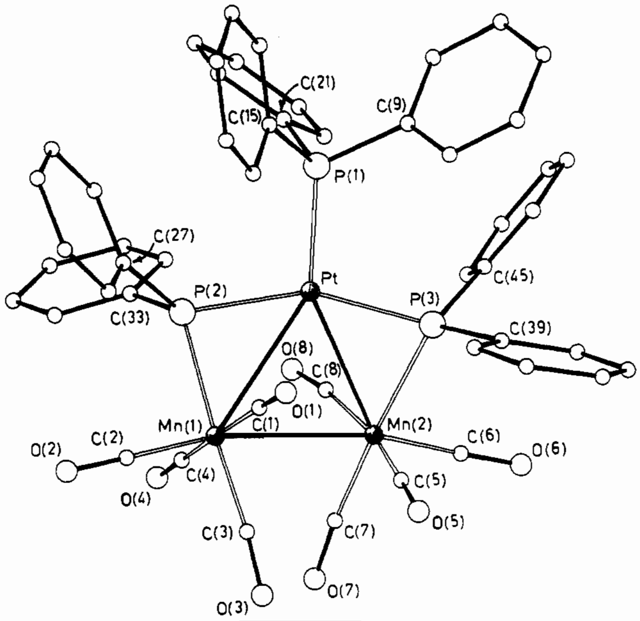
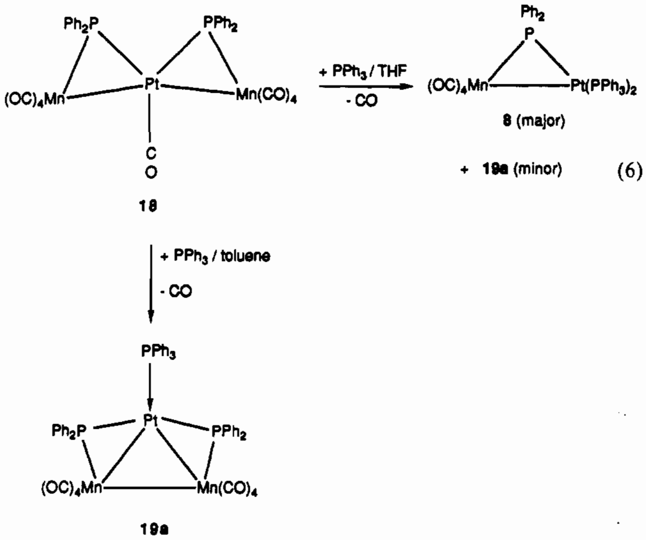
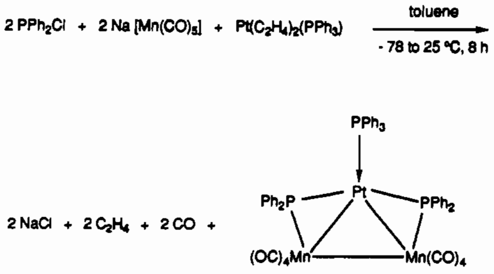


Figure 1. View of $[\{(OC)_4Mn(\mu\text{-PPh}_2)\}_2Pt(PPh_3)]$ in **19a**·C_7H_8 together with the atom-numbering scheme.



(6)



(7)

19a

The R_2P–m fragment, isolobal with ethylene,[13,14] coordinates to platinum in a manner reminiscent of that in $PtL(olefin)_2$ complexes. In similarity with the reaction of $[Cp(OC)_2W(\mu\text{-PPh}_2)Pt(CO)(\mu\text{-PPh}_2)W(CO)_2Cp]$ with PPh_3 which afforded the heterodinuclear complex W–Pt **7** via decoordination of the "ethylene-like" fragment $R_2P\text{–}W(CO)_2Cp$[15] and substitution of the Pt-bound CO,[6] the reaction of Mn_2Pt **18** with 1 equiv of PPh_3 in THF produced mainly Mn–Pt **8** (eq 6). A byproduct of this reaction is $[\{(CO)_4Mn(\mu\text{-PPh}_2)\}_2Pt(PPh_3)]$ (**19a**), which becomes the major product when the reaction is performed in *toluene* (see Experimental Section). However, this new complex is best prepared and isolated (53% yield) by the reaction of eq 7. This latter reaction formally involves substitution of the ethylene ligands of $[Pt(C_2H_4)_2(PPh_3)]$ by "$Ph_2P\text{–}Mn(CO)_4$" fragments generated from $Ph_2P\text{–}Mn(CO)_5$.[10c] Although **19a** only differs from **18** by the nature of the 2e donor ligand bound to Pt, the structures of these complexes are dramatically different, since **19a** was shown by X-ray diffraction to display a Mn–Mn bonding interaction,

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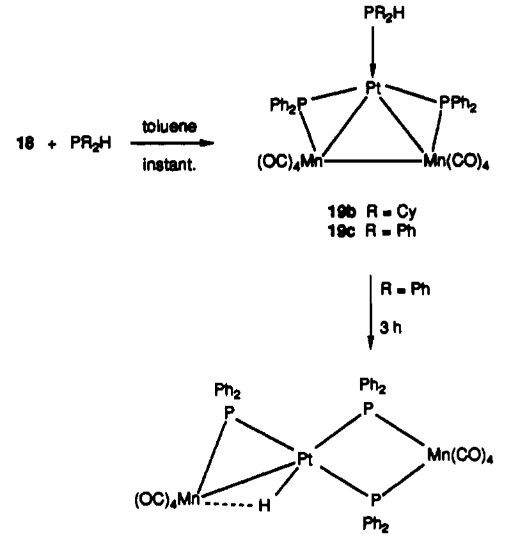
thus resulting in a closed rather than an open structure (see below). The cobalt derivatives [{(OC)$_3$Co(μ-PPh$_2$)}$_2$Pt(CO)] and [{(OC)$_3$Co(μ-PPh$_2$)}$_2$Pt(PPh$_3$)], respectively, analogous to **18** or **19a**, could not be isolated by using these methods. Instead, precipitation of Pt(0) was observed.

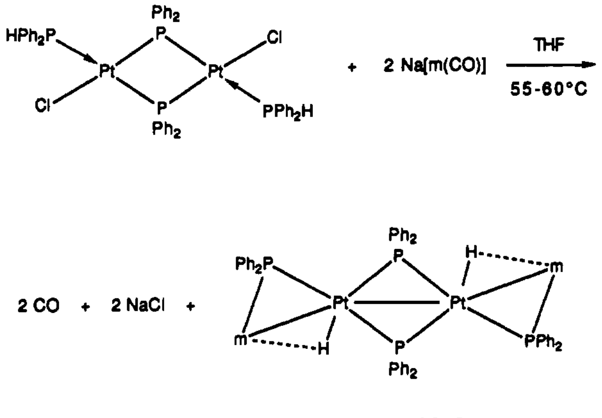
In contrast to the fragmentation observed with PPh$_3$ (eq 6), Mn$_2$Pt **18** instantaneously reacted with PR$_2$H (R = Cy, Ph) in toluene to produce **19b** and **19c**, respectively, which were characterized spectroscopically (see Experimental Section). It thus appears that the reactivity of **18** largely depends upon the steric properties of the entering phosphine. Monitoring of the reaction by ^{31}P{^{1}H} NMR spectroscopy showed no change of the typical resonances of **19b** in toluene after 12 h, whereas **19c** transformed after 3 h (see Experimental Section) to produce [(OC)$_4$Mn(μ-H)(μ-PPh$_2$)Pt(μ-PPh$_2$)$_2$Mn(CO)$_4$] (**20**),[13] the known platinum analogue of **17** (eq 8).



(8)

20

We also prepared the tetranuclear, bent-chain complexes W–Pt–Pt–W (**21**) and Mn–Pt–Pt–Mn (**22**) (eq 9) by the method

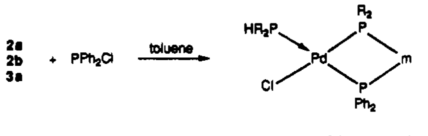


(9)

21 m = W(CO)$_2$Cp
22 m = Mn(CO)$_4$

recently used when m = Mo(CO)$_2$Cp.[4] Complex **22**, now isolated in 56% yield, has previously been obtained in lower yield from the reaction of Pt(PPh$_2$Cl)$_2$Cl$_2$ with Na[Mn(CO)$_5$] and fully characterized by X-ray diffraction.[13] On the basis of the spectroscopic similarities between **21** and its structurally characterized Mo$_2$Pt$_2$ analogue,[4] we assume a similar structure for these tetranuclear chain complexes, which appear to display various conformations in solution.[4] In particular, the ^{1}H NMR spectrum of the major conformer of **21** contains a multiplet resonance at δ −8.87 with ^1J(HPt) = 505 Hz (cf. δ −8.70 with ^1J(HPt) = 540 Hz in [Cp(OC)$_2$Mo(μ-H)(μ-PPh$_2$)Pt(μ-PPh$_2$)]$_2$), consistent with a (semi) bridging hydride ligand.[12,16] Its ^{31}P{^{1}H} NMR spectrum contains a set of resonances at low field, centered around δ 112, attributed to a μ-PPh$_2$ unit bridging a W–Pt bond, and a second set at δ −139, assigned to a μ-PPh$_2$ unit connecting two nonbonded Pt atoms (cf. the corresponding multiplets at δ 152 and −123 in [Cp(OC)$_2$Mo(μ-H)(μ-PPh$_2$)Pt(μ-PPh$_2$)]$_2$).

The reactions of **2a**, **2b**, and **3a** which afforded complexes **23a**, **23b**, and **24a**, respectively (eq 10), occurred by substitution of



(10)

23a m = Mo(CO)$_2$Cp; R = Cy
23b m = Mo(CO)$_2$Cp; R = Ph
24a m = W(CO)$_2$Cp; R = Cy

PR$_2$H and oxidative addition of PPh$_2$Cl across the m–Pd bond. However, these products could not be isolated analytically pure, owing to contamination with [m(μ-PR$_2$)(μ-H)PdCl(PR$_2$H)],[17] which resulted from the reaction of **2a**–**3a** with some HCl present in PPh$_2$Cl.

Description of the Crystal Structure of [{(OC)$_4$Mn(μ-PPh$_2$)}$_2$Pt(PPh$_3$)]·C$_7$H$_8$ (19a·C$_7$H$_8$). Heterotrinuclear clusters [{(OC)$_4$Mn(μ-PPh$_2$)}$_2$Pt(PPh$_3$)] and toluene molecules of solvation, separated by normal van der Waals contacts, are present in the crystals. A view of the structure is shown in Figure 1 together with the atom-numbering scheme. Selected bond distances and angles are given in Table II. The metals adopt a triangular arrangement, at variance with the previously known linear or bent Mn$_2$Pt chains.[18] This triangle is characterized by Mn–Pt edges of 3.082 (1) and 2.987 (1) Å and a Mn–Mn edge of 3.245 (2) Å. Two phosphido ligands bridge the Pt–Mn bonds almost symmetrically, four terminal carbonyl groups are bonded to each Mn atom, and a PPh$_3$ ligand completes the coordination of the Pt atom. If the Mn–Pt bonds are ignored, the coordination geometry around Mn is pseudooctahedral and that of Pt is trigonal planar. The bridging P(2) and P(3) atoms lie on opposite sides with respect to the metal triangle and form dihedral angles of 36.2 (1) and 27.3 (1)° with it, whereas P(1) is practically coplanar, deviating only by 0.063 (2) Å. The Mn–Pt distances are much longer than those reported for complexes containing a Mn–Pt metal–metal bond[18] (in the range 2.602–2.847 Å, from the Cambridge Crystallographic Data Centre). In particular, the Mn–Pt distances found in the Mn(μ-PPh$_2$)Pt moieties constituting clusters **18**, **20**, and [Mn$_2$Pt$_2$(μ-PPh$_2$)$_4$(CO)$_8$] were found in the range 2.710 (2)–2.847 (2) Å.[13] The Mn–Mn distance is much longer than for an unsupported metal–metal single bond, e.g. in [Mn$_2$(CO)$_{10}$] (2.895 (1) Å),[19] or in [Mn$_2$(μ-H)(μ-PPh$_2$)(CO)$_8$] (2.937 (5) Å), where a symmetric, bent, three-center, two-electron bond between Mn–H–Mn was suggested.[11c]

From a chemical point of view, the 48e complexes **18** and **19a** only differ by the nature of the 2 electron donor ligand bound to Pt, CO vs PPh$_3$. Steric hindrance prevents the PPh$_3$ ligand from occupying the position of the Pt-bound carbonyl in **18**. This in turn induces a closing of the Mn–Pt–Mn angle, from 159.6 (1)° in **18**[13a] to 64.61 (4)° in **19a**. The two Mn–Pt distances are also significantly different in these clusters: 2.741 (1) and 2.747 (1) Å in **18** and 2.987 (1) and 3.082 (1) Å in **19a**. In order to delineate better the electronic and steric reasons for these dramatic structural

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(16) (a) Powell, J.; Sawyer, J. F.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1312. (b) Powell, J.; Sawyer, J. F.; Gregg, M. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1149.

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(18) (a) Bars, O.; Braunstein, P.; Jud, J.-M. *Nouv. J. Chim.* **1984**, *8*, 771 and references cited. (b) Powell, J.; Sawyer, J. F.; Shiralian, M. *Organometallics* **1989**, *8*, 577. (c) Kunz, E.; Muller, J.; Schubert, U. *J. Organomet. Chem.* **1987**, *320*, C11.

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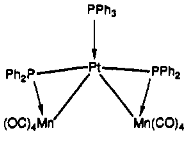
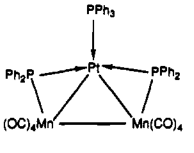
Table II. Selected Bond Distances (Å) and Angles (deg) for **19a**·C_7H_8

Pt–Mn(1)	3.082 (1)	Pt–Mn(2)	2.987 (1)
Mn(1)–Mn(2)	3.245 (2)	Pt–P(2)	2.299 (2)
Pt–P(1)	2.248 (2)	Pt–P(3)	2.283 (2)
Mn(1)–P(2)	2.290 (2)	Mn(2)–P(3)	2.310 (2)
Mn(1)–C(1)	1.844 (8)	Mn(2)–C(5)	1.835 (8)
Mn(1)–C(2)	1.799 (9)	Mn(2)–C(6)	1.781 (9)
Mn(1)–C(3)	1.835 (8)	Mn(2)–C(7)	1.828 (8)
Mn(1)–C(4)	1.843 (9)	Mn(2)–C(8)	1.853 (9)
P(1)–C(9)	1.820 (7)	C(1)–O(1)	1.15 (1)
P(1)–C(15)	1.824 (8)	C(2)–O(2)	1.14 (1)
P(1)–C(21)	1.818 (8)	C(3)–O(3)	1.13 (1)
P(2)–C(27)	1.823 (7)	C(4)–O(4)	1.15 (1)
P(2)–C(33)	1.824 (7)	C(5)–O(5)	1.15 (1)
P(3)–C(39)	1.834 (8)	C(6)–O(6)	1.16 (1)
P(3)–C(45)	1.839 (7)	C(7)–O(7)	1.14 (1)
		C(8)–O(8)	1.15 (1)
Mn(1)–Pt–Mn(2)	64.61 (4)	P(2)–Pt–P(3)	154.33 (8)
P(1)–Pt–P(2)	101.64 (8)	Pt–Mn(1)–Mn(2)	56.28 (4)
P(1)–Pt–P(3)	103.29 (9)	Pt–Mn(2)–Mn(1)	59.11 (4)
P(2)–Mn(1)–Mn(2)	97.25 (8)	P(3)–Mn(2)–Mn(1)	103.84 (7)
P(2)–Mn(1)–C(1)	89.9 (2)	P(3)–Mn(2)–C(5)	88.8 (3)
P(2)–Mn(1)–C(2)	91.5 (3)	P(3)–Mn(2)–C(6)	84.3 (3)
P(2)–Mn(1)–C(4)	88.4 (3)	P(3)–Mn(2)–C(8)	95.5 (3)
C(1)–Mn(1)–C(2)	96.2 (4)	C(5)–Mn(2)–C(6)	93.5 (4)
C(1)–Mn(1)–C(3)	89.0 (4)	C(5)–Mn(2)–C(7)	91.2 (4)
C(2)–Mn(1)–C(3)	91.6 (4)	C(6)–Mn(2)–C(7)	91.7 (4)
C(2)–Mn(1)–C(4)	90.5 (4)	C(6)–Mn(2)–C(8)	99.5 (4)
C(3)–Mn(1)–C(4)	92.3 (4)	C(7)–Mn(2)–C(8)	85.5 (4)
C(1)–Mn(1)–Mn(2)	93.6 (3)	C(5)–Mn(2)–Mn(1)	78.0 (2)
C(3)–Mn(1)–Mn(2)	79.8 (3)	C(7)–Mn(2)–Mn(1)	80.1 (3)
C(4)–Mn(1)–Mn(2)	80.0 (3)	C(8)–Mn(2)–Mn(1)	88.7 (3)
Mn(1)–P(2)–Pt	84.4 (1)	Mn(2)–P(3)–Pt	81.1 (1)
Pt–P(2)–C(27)	120.8 (2)	Pt–P(3)–C(39)	122.5 (2)
Pt–P(2)–C(33)	116.6 (2)	Pt–P(3)–C(45)	116.9 (2)
Mn(1)–P(2)–C(27)	118.7 (2)	Mn(2)–P(3)–C(39)	113.6 (2)
Mn(1)–P(2)–C(33)	116.7 (2)	Mn(2)–P(3)–C(45)	118.8 (3)
C(27)–P(2)–C(33)	100.8 (3)	C(39)–P(3)–C(45)	103.8 (4)

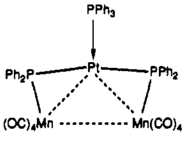
changes, extended Hückel calculations have been performed that are detailed below. Two limiting bonding descriptions for **19a** are depicted in A and B. They involve a 16e Pt center and two



(A)



(B)



(C)

2e–2c Mn–Pt bonds or a 18e Pt center and three 2e–3c metal–metal bonds, respectively. For geometric and electronic reasons, we favor the bonding description shown in C, which involves a 16e Pt and three 4e–3c metal–metal bonds. Such a bonding is reminiscent of that encountered in the 44e cluster $[Pt_3(\mu\text{-}PPh_2)_3Ph(PPh_3)_2]$, which has 4 metal–metal bonding electrons and for which energetically comparable solid-state structures are known, with either "two short and one very long" or three "medium" metal–metal distances, as a result of metal core isomerism.[20]

Extended Hückel Calculations. These calculations[21,22] have been carried out on the $[\{(CO)_4Mn(\mu\text{-}PH_2)\}_2PtL]$ systems (L = PH_3, CO) in both geometries I and II. I, which we will call trans

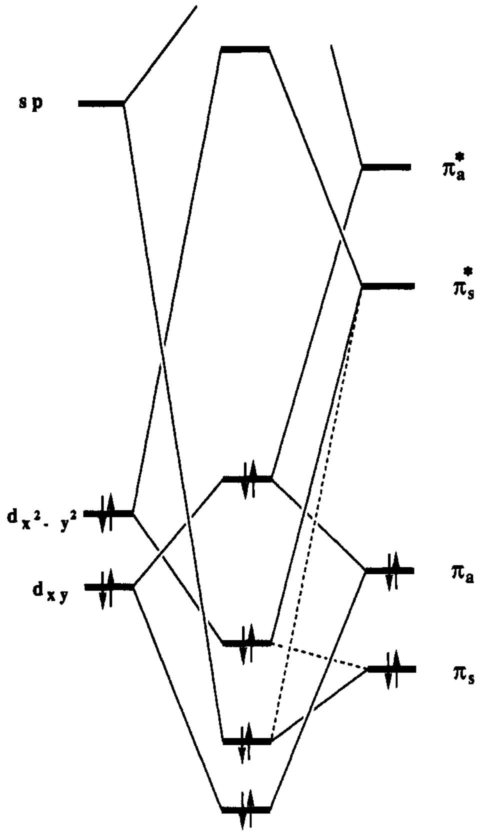
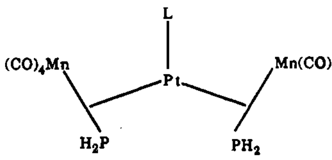
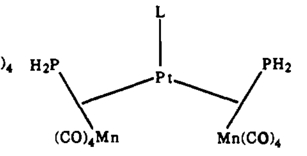


Figure 2. Partial interaction diagram illustrating the interactions shown in IVa–VIa for L = PH_3.

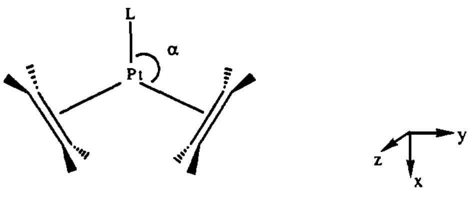


I



II

according to the respective arrangement of the Mn–Pt–Mn unit, stands as a model for **18** (when L = CO). Its cis counterpart II is representative of **19a** when L = PH_3. Note that the schematic drawings I and II stress on purpose their isolobal analogy[13,14] with the $Pt(C_2H_4)_2L$ (L = PH_3, CO) system III, the valence orbitals



III

of which will be analyzed first. These orbitals are much like the known valence orbitals of the $Ni(C_2H_4)_2L$ analogue.[25] They can be derived from the interactions of the π and π^* orbitals of the two ethylene ligands with the appropriate s, p, and d orbitals of the platinum atom. These interactions are shown in IVa–VIa for L = PH_3 and materialized on the partial interaction diagram of Figure 2. We denote π_s and π^*_s the in-phase combinations of the π and π^* orbitals of the two C_2H_4 ligands. Similarly, π_a and π^*_a refer to the corresponding out-of-phase combinations. In IVa

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(21) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 3179; *Ibid.* **1962**, *37*, 2872.

(22) *Computational details*: The parameters used in the extended Hückel calculations for Pt and Mn were taken from ref 23. The modified Wolfsberg-Helmolz formula[24] was used throughout this work. The geometries were taken from the experimental ones (see ref 13 and this work).

(23) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

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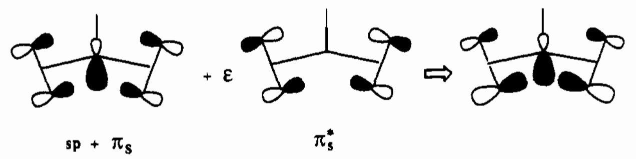
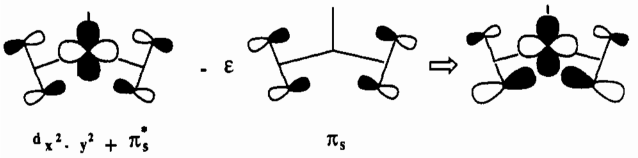
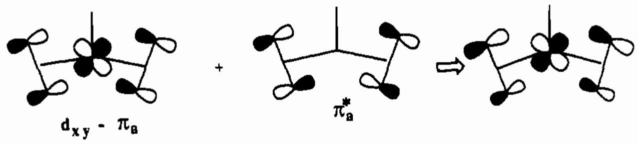


IVa



Va

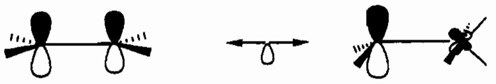


VIa

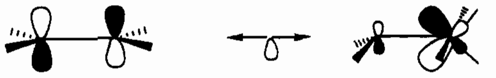
the sp platinum hybrid *stabilizes* the π_s and—but to a lesser extent—π^*_s combinations. Va is also a 2-electron *stabilizing* interaction between π^*_s and $d_{x^2-y^2}$, somewhat destabilized by a small repulsive interaction with the doubly occupied π_s combination. VIa is a 4-electron *destabilizing* interaction between d_{xy} and π_a, but the destabilization is weakened by the mixing with the empty π^*_a combination. Two special features deserve a comment: First, the 2-electron interaction IVa, which was not important in the nickel system, now becomes highly involved in the bonding pattern. Next, the weights of the mixing of π_s, π^*_s, π_a, and π^*_a with sp, $d_{x^2-y^2}$, and d_{xy} will depend on the value of the α angle (see III for the definition of α). For instance, when α is decreased from 120 to 90°, the mixings between sp and π_s in IVa, between $d_{x^2-y^2}$ and π^*_s in Va, and between d_{xy} and π_a in VIa become less important. On the other hand, the respective contribution of π^*_s, π_s, and π^*_a increases. VIa is therefore less destabilizing, but this does not compensate the decrease of the stabilizing interactions in IVa and Va and the whole system is destabilized. For angles greater than 120°, the repulsion between the two ethylene ligands leads also to an overall destabilization, so that an optimum value for α is found around 115–120°.

A first result obtained from the EH calculations on the bis(ethylene) carbonyl and phosphine complexes is that the carbonyl system is intrinsically more stable than the phosphine system by about 0.52 eV (50.1 kJ·mol^{-1}).[26] This is essentially traced to the changes which are undergone in our model system by d_{xy} and $d_{x^2-y^2}$: When CO is substituted by PH_3, the π back-donation process leads to a delocalization of the d_{xy} orbital onto the π^*_{CO} orbital. The overlap of d_{xy} with π_a therefore decreases (from 0.052 to 0.038), and the corresponding destabilizing interaction with π_a (see VIa) is weakened[27] (the destabilization achieved in VIa is decreased by 0.18 eV). In addition the $d_{x^2-y^2}$ orbital is destabilized more in the carbonyl complex.[28] As a result, its capacity to interact in a bonding way with π^*_s (see Va and Figure 2) is increased (the stabilization achieved in Va is increased by 0.16 eV).

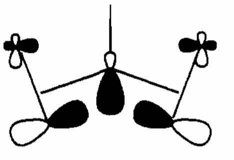
Similar interactions in IVa–VIa are found when the ethylene ligands are replaced by two $[(CO)_4Mn{-}PH_2]$ entities. But the strong polarization of the π and π^* orbitals of $[(CO)_4Mn{-}PH_2]$ (which is due to the electronegativity difference between $Mn(CO)_4$ and PH_2) now orients the stereochemistry of the trimetallic system. As shown in VII, the π orbital is localized on the more electronegative PH_2 group, whereas its π^* counterpart (see VIII) is highly metallic in character. The interactions sketched in IVa–VIa for $Pt(C_2H_4)_2L$ therefore become IVb–VIb for the trans isomer I and IVc–VIc for the cis isomer II. It is first clear that the 2-electron stabilizing interaction between the sp hybrid and π_s is much greater in IVb than in IVc. Vb is also a stronger stabilizing interaction than Vc. On the other hand, VIb is somewhat more destabilizing than VIc but the two first interactions prevail and the overall preference is for the trans isomer I. Note here that for the cis isomer II, Vc and VIc have no appreciable component on the phosphido group. This arises from the localization of the π orbital of $[(CO)_4Mn{-}PH_2]$: Thus, in Vc the mixing of π_s into $d_{x^2-y^2} + \pi^*_s$ is much stronger than in Va and this leads to the disappearance of the phosphido component. Moreover the bending back of the equatorial CO ligands in the $Mn(CO)_4$ group increases the overlap of π^*_s (which is localized mainly on the Mn atom) with $d_{x^2-y^2}$. In VIc, the major component of π_a would point toward the nodal plane of d_{xy}.[29] It has almost no interaction with this orbital, and VIc is therefore essentially a $d_{xy} + \pi^*_a$ combination.



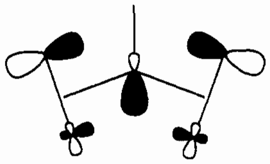
VII



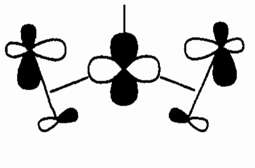
VIII



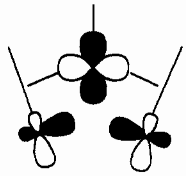
IVb



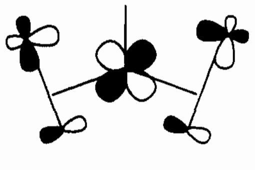
IVc



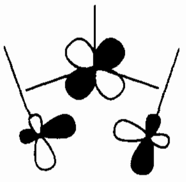
Vb



Vc



VIb



VIc

Having established the intrinsic preference for the trans geometry, one may therefore wonder about the reasons behind the observed cis geometry when L is a phosphine ligand. We trace this preference to the steric repulsion which would arise, in the trans geometry, between the phosphine ligand on the Pt atom and two in-plane carbonyl ligands (one on each Mn atom): the calculated repulsion between two carbonyls and one phosphine with a geometry corresponding to the trans geometry amounts

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(26) This value is obtained as the difference between the interaction energies of LPt (L = PH_3, CO) with two ethylenes to give $Pt(C_2H_4)_2L$.

(27) The interaction of d_{xy} with π^*_{CO} of course stabilizes d_{xy}, which should then interact more with π_a, but the overlap factor (which is proportional to the square of the overlap) is the dominant factor.

(28) With the EH parameters used here, the CO ligand is found to be a better σ donor than the PH_3 model ligand (the corresponding lone-pair energies are −13.37 and −14.34 eV). One should be aware however that the experimental proton affinities in the gas phase show that, as expected, PH_3 is more basic than CO (the proton affinities are 197 and 145 kcal/mol, respectively. PPh_3 is found even more basic, its proton affinity amounting to about 230 kcal/mol).

(29) This is perhaps not apparent from the *schematic* drawing of VIc but can be easily seen in Figure 1 from the disposition of the $[(CO)_4Mn{-}PH_2]$ unit around the Pt atom.

to 2.02 eV (195 kJ·mol^{-1}). The trimetallic system therefore adopts the cis geometry II. As said before, this geometry is characterized by the Vc interaction. Vc is nothing else than a 3-center–4-electron interaction between the three metal atoms. It is this interaction which accounts for the lengthening of the Pt–Mn bond in II with respect to I.

Discussion

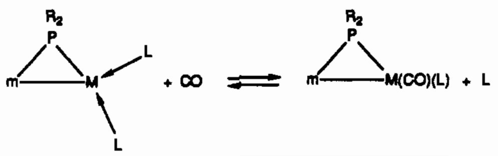
The synthesis of phosphido-bridged heterometallic complexes of palladium or platinum with transition metals has been achieved by using two different approaches. In the first case (eq 1), the trinuclear mixed-metal chain complexes *trans*-[Pd{m(CO)}$_2$(NCPh)$_2$] (m = Cr(CO)$_2$Cp, Mo(CO)$_2$Cp, W(CO)$_2$Cp, Mn(CO)$_4$) were reacted with 3 equiv of secondary phosphines PR$_2$H (R = Ph, Cy), and this afforded the complexes m(μ-PR$_2$)Pd(PR$_2$H)$_2$ (**1**–**6**) (in the case where m = W(CO)$_2$Cp, we observed that 2 equiv of PCy$_2$H mostly afforded **3a** and small amounts of **12**). The reaction of the corresponding platinum complexes *trans*-[Pt{m(CO)}$_2$(NCPh)$_2$] (m = Mo(CO)$_2$Cp, W(CO)$_2$Cp) with 1 or 2 equiv of PPh$_2$H has previously yielded trinuclear [m(μ-PPh$_2$)Pt(CO)(μ-PPh$_2$)m] (related to **18**) and tetranuclear heterometallic complexes [m(μ-PPh$_2$)Pt(μ-PPh$_2$)]$_2$ and [m(μ-PPh$_2$)Pt(H)(μ-PPh$_2$)]$_2$ (related to **21**).[4] When the chain complexes *trans*-[Pt{m(CO)}$_2$(NCPh)$_2$] were reacted with 2 equiv of PCy$_2$H, they afforded inter alia dinuclear complexes of the type m(μ-PCy$_2$)Pt(CO)(PCy$_2$H).[3] We have generally observed that oxidative addition of the P–H bond of PR$_2$H coordinated to Pt is much easier when R = Ph than R = Cy. This is particularly notable in the transformation shown in eq 8, which does not take place with R = Cy in place of Ph. No further phosphido bridge was formed when a toluene solution of Pd–W **3a** was refluxed overnight (IR and ^{31}P{^{1}H} NMR), consistent with the stability of the terminal P–H bond but ruling out the thermal synthesis of tri- or tetranuclear derivatives (e.g. a Pd analogue of **21**). It has been noted before that PPh$_2$H is more reactive than PCy$_2$H when coordinated to a W(CO)$_5$ fragment.[30]

The second approach used to generate phosphido-bridged heterometallic complexes involves the reaction of a metallophosphine R$_2$P–m(CO), prepared in situ, with a Pt(0) complex (eqs 2 and 5). The dinuclear complexes **7**–**9** are analogous to the palladium compounds **1**–**6**. In both cases, the terminal phosphine ligand which is trans with respect to the μ-PR$_2$ bridging ligand appears to be preferentially replaced by an incoming CO ligand. This substitution reaction often leads to a thermodynamic mixture of isomers, in which that with a *cis*-P–M–(μ-PR$_2$) arrangement is always the major one or even the only isomer in the case of Co–Pd **13** and W–Pt **14**. Complex **14** has also been previously reported as the cis isomer with respect to the P–Pt–(μ-P) arrangement.[16a] It is interesting that the related complex Cp(OC)$_2$W(μ-PCy$_2$)Pt(CO)(PCy$_2$H) exists as a mixture of cis (major) and trans (minor) isomers.[3]

Some reactions reported here may be viewed as exchanges of apical fragments in the M(μ-PR$_2$)m triangles. Thus, in the reaction of W–Pd **3a** with Ph$_2$P–Co(CO)$_4$, which leads to Co–Pd **6a**, W(CO)$_2$Cp is replaced by Co(CO)$_3$, and in the preparation of Mn$_2$ **15a** from Mn–Pd **4a** and [Mn(CO)$_5$]$^-$, a PtL$_2$ moiety is replaced by Mn(CO)$_4$$^-$.

Formation of Mn$_2$Pd **17** by the reaction of eq 4 is most likely to proceed by an oxidative-addition reaction of the HMn(CO)$_5$ present (eq 1) to Mn–Pd **4b**. That this reaction was not observed with the μ-PCy$_2$ derivative **4a** is in agreement with PPh$_2$H being more reactive than PCy$_2$H. Furthermore, it only took place for m = Mn(CO)$_4$ (no equivalent of **17** has been observed with other m moieties), illustrating how changing a metal (here in m) in a bimetallic complex of type **1**–**6** can influence the reactivity at the adjacent metal center (here Pd).

Table III. Data for Substitution of a Phosphine by CO in CO-Saturated CH$_2$Cl$_2$/C$_6$D$_6$ Solutions of Complexes 1–7, As Determined by ^{31}P{^{1}H} NMR Spectroscopy



				situation at equilibrium, %				
M	L	R	m	[m(μ-PR$_2$)ML$_2$]			[m(μ-PR$_2$)ML(CO)]	
Pd	PCy$_2$H	Cy	Cr(CO)$_2$Cp	**1a**	59	slow on NMR scale time $\rightleftharpoons$	**10**	41
			Mo(CO)$_2$Cp	**2a**	51	slow on NMR scale time $\rightleftharpoons$	**11**	49
			W(CO)$_2$Cp	**3a**	37	slow on NMR scale time $\rightleftharpoons$	**12**	63
			Mn(CO)$_4$	**4a**	100			
			Co(CO)$_3$	**6a**	100	1 night $\longleftarrow$	**13**	
	PPh$_2$H	Ph	Mo(CO)$_2$Cp	**2b**	100		not observed	
			W(CO)$_2$Cp	**3b**	100		not observed	
			Mn(CO)$_4$	**4b**	100	NMR scale time $\leftrightharpoons$		
Pt	PCy$_2$H	Cy	W(CO)$_2$Cp			slow on NMR scale time $\rightleftharpoons$		100 (ref. 3)
	PPh$_3$	Ph	W(CO)$_2$Cp	**7**		slow on NMR scale time $\rightleftharpoons$	**14**	100

It is noteworthy that the designed synthesis of trinuclear, phosphido-bridged mixed-metal chain complexes such as Mn$_2$Pt **18** is not always straightforward. Thus, for example, previous attempts to prepare molecules containing the moiety Fe(μ-PPh$_2$)Rh(μ-PPh$_2$)Fe[31] or Fe(μ-PMe$_2$)Ni(μ-PMe$_2$)Fe[32] led instead to different molecules. However, the use of carbyne bridges has proven very successful for the stabilization of heterotrinuclear chain complexes.[33]

When the electron-counting convention of assigning zero oxidation states to all atoms is adopted, the μ-PR$_2$ ligands are net 3-electron donors and the metal centers in m and M = Pd and Pt achieve 18e and 16e configurations, respectively, in all the complexes reported here.

Phosphine and Carbonyl Exchange in the Platinum Coordination Sphere. The m–Pd complexes **1a**–**3a** and W–Pt **7** rapidly established equilibrium with **10**–**12** and **14**, respectively, when dissolved in CO-saturated CH$_2$Cl$_2$/C$_6$D$_6$ solutions (^{31}P{^{1}H} NMR monitoring) (Table III). In contrast, formation of carbonyl complexes was not observed for Mn–Pd **4a**, Co–Pd **6a**, and **2b**–**4b**. In the case of Co–Pd **6a**, a high activation energy barrier toward substitution may account for this behavior, consistent with the carbonyl complex **13** (obtained as a byproduct in the synthesis of **6a**) requiring ca. 10 h to be converted to **6a** upon addition of phosphine. For **4a** and **2b**–**4b**, the instability of the carbonyl complex with respect to the phosphine complex is a more plausible reason, as confirmed in the case of Mn–Pd **4b**. Thus, in the presence of CO, the phosphine ligands of **4b** undergo rapid exchange, as indicated in the ^{31}P{^{1}H} NMR spectrum in toluene-d_8

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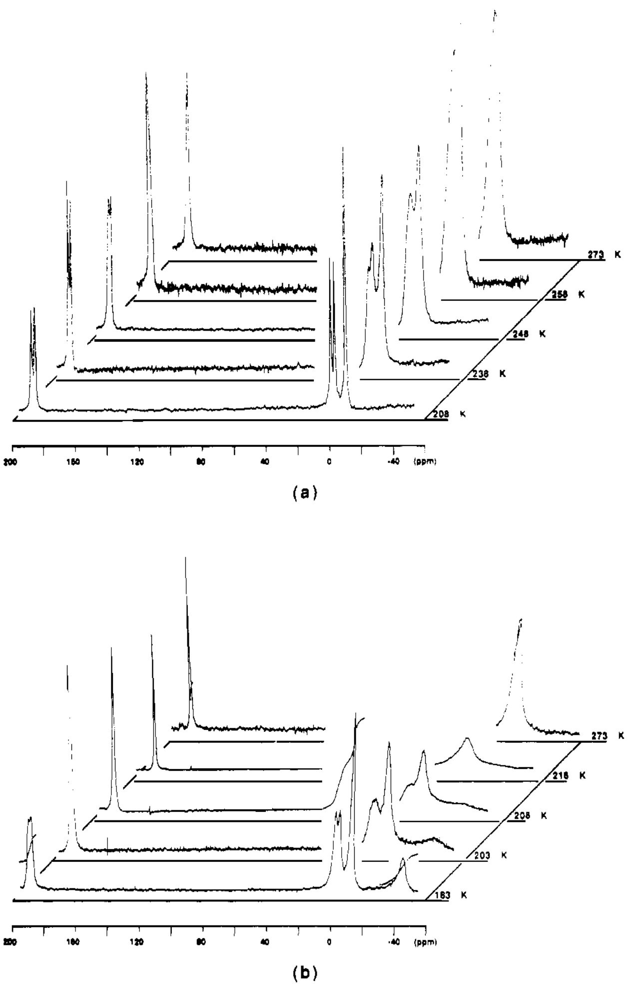


(a)

(b)

Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[(OC)_4\overline{Mn(\mu\text{-}PPh_2)Pd}(PPh_2H)_2]$ (**4b**) in toluene-d_8 solutions in the presence of (a) CO or (b) free PPh_2H.

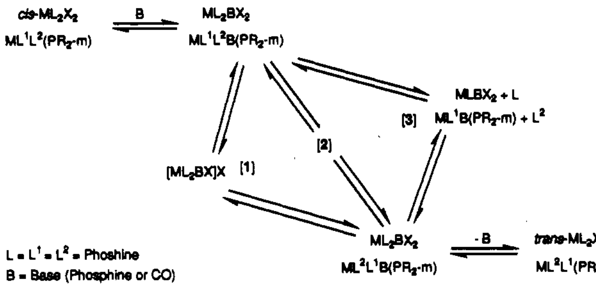
by the coalescence of their signals at ca. −15 °C and the replacement of the doublet of doublets for the μ-PPh_2 by a singlet (Figure 3a). Below this temperature, only the signals of Mn–Pd **4b** were observed, suggesting that the carbonyl complex is only an unstable intermediate in the phosphine exchange process. Table III summarizes the kinetic and thermodynamic influences of the R_2P–m fragment on the platinum or palladium coordination sphere. The M–CO bond appears more stable for platinum than for palladium, for Cr, Mo, or W than for Mn, and for R = cyclohexyl more than for phenyl complexes.

In order to better understand the labilization of the Pt–L bonds in Mn–Pd **4b**, we monitored by $^{31}P\{^1H\}$ NMR spectroscopy the behavior of toluene-d_8 solutions of this compound in the presence of variable concentrations of free phosphine at variable temperatures. As in the case of CO, rapid exchange between free and coordinated phosphines was observed. At higher temperatures (Figure 3b), only one signal for the μ-PR_2 and another for the PPh_2H ligands were observed. At low temperatures, the spectrum contained two independent sets of signals, corresponding to **4b** and free phosphine, respectively. The coalescence temperature (Table IV) decreases when the phosphine concentration increases, clearly indicating that the exchange rate increases and that the substitution mechanism is of the associative type.

This equivalencing phenomenon of the phosphine ligands is related to the cis–trans isomerization of L_2PtX_2 complexes catalyzed by free ligand.[34] The proposed associative mechanism proceeds through pentacoordinate transition states. Three pathways have been proposed as illustrated in eq 11, where the parallel with our system is shown for the more related pathways 2 and 3. The coalescence of the signals for free and coordinated phosphines indicates that pathway 3, which implies exchange between these ligands, has a rate constant of the same order as the overall exchange process. In turn, for the concentrations studied, the overall rate constant is on the order of the ^{31}P NMR time scale.

Table IV. Coalescence Temperatures for the PPh_2H and μ-PPh_2 Signals in the $^{31}P\{^1H\}$ NMR Spectra of 5×10^{-2} mol·L^{-1} Solutions of **4b** in the Presence of Variable Concentrations of Free Phosphine

concn of PPh_2H, 10^{-3} mol·L^{-1}	coalescence temp, K		concn of PPh_2H, 10^{-3} mol·L^{-1}	coalescence temp, K	
	PPh_2H	μ-PPh_2		PPh_2H	μ-PPh_2
2	>310	283	57	216	198
23	243	218	215	212	<190



(11)

Experimental Section

A. Reagents and General Techniques. All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were dried and distilled under nitrogen: diethyl ether and tetrahydrofuran from sodium benzophenone ketyl; toluene, pentane, and hexane from sodium; dichloromethane over P_2O_5; acetone over $CaCl_2$. 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 20) and used without further purification. Unless otherwise stated, reagents were obtained from commercial sources and used as received. Elemental analyses (C, H, and N) were performed by the Service Central de Microanalyses du CNRS. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer, and the data are given in cm^{-1}. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 200.13, 50.32, and 81.02 MHz, respectively, on a FT-Bruker WP 200 SY instrument. Chemical shifts, in ppm, are positive downfield relative to external Me_4Si for ^1H and ^{13}C and to external 85% H_3PO_4 in H_2O for ^{31}P NMR spectra; coupling constants are in Hz. The ^1H NMR signals of the Cy and Ph groups are not given.

B. Syntheses. $[PdCl_2(NCPh)_2]$,[35] $[PdCl(\mu\text{-}PPh_2)(PPh_2H)]_2$,[36] $[Pt(COD)_2]$, $[Pt(C_2H_4)_2(PPh_3)]$,[37] $[Pt(C_2H_4)(PPh_3)_2]$,[38] $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$,[39] $Na[Cr(CO)_3Cp]\cdot 2DME$, $Na[Mo(CO)_3Cp]\cdot 2DME$, and $Na[W(CO)_3Cp]\cdot 2DME$[7,40] were prepared according to literature methods. Solutions of $Na[Fe(CO)_2Cp]$,[41] $Na[Co(CO)_4]$,[42] and $Na[Mn(CO)_5]$[43] were prepared by Na/Hg reduction of THF solutions of $[Fe_2(CO)_4Cp_2]$, $[Co_2(CO)_8]$, and $[Mn_2(CO)_{10}]$, respectively. The synthesis and spectroscopic data for **7** have been reported elsewhere.[6]

$[Cp(OC)_2\overline{Cr(\mu\text{-}PCy_2)Pd}(PCy_2H)_2]$ (1a). The procedure is similar to that detailed below for **3a**. Addition of $Na[Cr(CO)_3Cp]\cdot 2DME$ (3.600 g, 8.90 mmol) in THF (60 mL) to $[PdCl_2(NCPh)_2]$ (1.707 g, 4.45 mmol) at −78 °C produced a green solution that became orange after addition

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of PCy$_2$H (2.93 mL, 13.35 mmol) and having reached room temperature. The product (2.58 g, 66.8%) is a red solid, which is sparingly soluble in hexane, acetone, or methanol and should be stored under an inert atmosphere (mp 195 °C dec). Anal. Calcd for $C_{43}H_{73}CrO_2P_3Pd$ (M_r = 873.38): C, 59.13; H, 8.42. Found: C, 59.42; H, 8.35. IR (KBr): ν(CO) 1870 vs, 1802 vs. IR (CH$_2$Cl$_2$): ν(CO) 1861 vs, 1786 vs. ^{1}H NMR (C$_6$D$_6$): δ 4.97 (s, 5 H, Cp), 4.37 (dm, 2 H, PCy$_2$*H*). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 285.9 (dd, 1 P, μ-PCy$_2$, ^2J(PP) = 121 and 39), 9.7 (d, 1 P, PCy$_2$H trans to PCy$_2$, J(PP) = 121, from ^{31}P NMR, ^1J(PH) = 291), 7.0 (d, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(PP) = 39, from ^{31}P NMR, ^1J(PH) = 273).

[Cp(OC)$_2\overline{\mathrm{Mo}(\mu\text{-}\mathrm{PCy_2})\mathrm{P}}$d(PCy$_2$H)$_2$] (2a). The same method as for **3a** was employed, using [PdCl$_2$(NCPh)$_2$] (2.461 g, 6.42 mmol), Na[Mo(CO)$_3$Cp]·2DME (5.756 g, 12.83 mmol), and PCy$_2$H (4.22 mL, 19.25 mmol). The orange product (3.20 g, 54%) is sparingly soluble in hexane, acetone, or methanol and should be kept under an inert atmosphere (mp 158 °C dec). Anal. Calcd for $C_{43}H_{73}MoO_2P_3Pd$ (M_r = 917.32): C, 56.30; H, 8.02. Found: C, 56.20; H, 8.15. IR (KBr): ν(CO) 1882 vs, 1806 vs; ν(PH) 2292 w. IR (CH$_2$Cl$_2$): ν(CO) 1878 vs, 1790 vs. ^{1}H NMR (C$_6$D$_6$): δ 5.42 (s, 5 H, Cp), 4.3 (dm, 2 H, PCy$_2$*H*). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 261.6 (dd, 1 P, PCy$_2$, ^2J(PP) = 153 and 23), 10.8 (dd, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(PP) = 153 and 17, from ^{31}P NMR, ^1J(PH) = 292), 0.7 (pseudo t, 1 P, PCy$_2$H cis to PCy$_2$, from ^{31}P NMR, ^1J(PH) = 290).

[Cp(OC)$_2\overline{\mathrm{Mo}(\mu\text{-}\mathrm{PPh_2})\mathrm{P}}$d(PPh$_2$H)$_2$] (2b). [PdCl$_2$(NCPh)$_2$] (1.500 g, 3.90 mmol), Na[Mo(CO)$_3$Cp]·2DME (3.500 g, 7.80 mmol), and PPh$_2$H (2.04 mL, 11.7 mmol) were reacted in THF as for **3a**. After solvent evaporation, the residue was washed with 30 mL of hexane and chromatographed over a 25 × 2.5 cm column of Florisil 60–100 mesh. After elution with hexane and with 20:80 and 40:60 dichloromethane/hexane (yielding mostly [CpMo(CO)$_2$]$_2$), the THF fraction was collected and evaporated to dryness and the solid washed with 30 mL of hexane and dried in vacuo. A red microcrystalline solid was obtained (2.10 g, 61.2%), which is insoluble in hexane but soluble in acetone, toluene, or dichloromethane (mp 236 °C dec). Anal. Calcd for $C_{43}H_{37}MoO_2P_3Pd$ (M_r = 881.03): C, 58.62; H, 4.23. Found: C, 58.48; H, 4.33. IR (KBr): ν(CO) 1884 vs, 1802 vs. IR (CH$_2$Cl$_2$): ν(CO) 1890 vs, 1806 vs. ^{1}H NMR (C$_6$D$_6$): δ 6.8 (dm, 1 H, PPh$_2$*H*), 6.2 (dm, 1 H, PPh$_2$*H*), 4.84 (s, 5 H, Cp). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 209.7 (dd, 1 P, μ-PPh$_2$, ^2J(PP) = 162 and 27), −2.0 (dd, 1 P, PPh$_2$H trans to PPh$_2$, ^2J(PP) = 162 and 18, from ^{31}P NMR, ^1J(PH) = 329), −14.0 (dd, 1 P, PPh$_2$H cis to PPh$_2$, ^2J(PP) = 27 and 18, from ^{31}P NMR, ^1J(PH) = 323).

[Cp(OC)$_2\overline{\mathrm{W}(\mu\text{-}\mathrm{PCy_2})\mathrm{P}}$d(PCy$_2$H)$_2$] (3a). To [PdCl$_2$(NCPh)$_2$] (2.044 g, 5.33 mmol) dissolved in THF (100 mL) was added dropwise (45 min) at −78 °C a solution of Na[W(CO)$_3$Cp]·2DME (5.720 g, 10.67 mmol) in THF (120 mL). The violet solution was stirred for 15 min, and PCy$_2$H (3.50 mL, 15.9 mmol) was added dropwise. CO evolution was observed, and the dark yellow-orange solution was allowed to reach room temperature (3 h), stirred overnight, and evaporated to dryness. The residue was dried for 3 h and extracted with ca. 6 × 70 mL of toluene and filtered through a 50 × 25 mm Celite column. Upon addition of 40–50 mL of acetone, the oil obtained after solvent evaporation crystallized overnight at −20 °C. After filtration, the yellow, air-stable product was washed with 3 × 10 mL of acetone and dried in vacuo (4.20 g, 78.4%). It is sparingly soluble in hexane, acetone, or methanol (mp 195 °C dec). Anal. Calcd for $C_{43}H_{73}O_2P_3PdW$ (M_r = 1005.23): C, 51.37; H, 7.31. Found: C, 51.54; H, 7.17. IR (KBr): ν(CO) 1878 vs, 1803 vs; ν(PH) 2288 w. IR (CH$_2$Cl$_2$): ν(CO) 1871 vs, 1788 vs. ^{1}H NMR (C$_6$D$_6$): δ 5.39 (s, 5 H, Cp), 4.3 (dm, 2 H, PCy$_2$*H*). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 221.4 (dd with W satellites, 1 P, μ-PCy$_2$, ^2J(PP) = 158 and 27, ^1J(PW) = 366), 6.75 (dd, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(PP) = 158 and 13, from ^{31}P NMR, ^1J(PH) = 296), −11.9 (pseudo t, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(PP) $\approx$ 27 and 13, from ^{31}P NMR, ^1J(PH) = 278).

[Cp(OC)$_2\overline{\mathrm{W}(\mu\text{-}\mathrm{PPh_2})\mathrm{P}}$d(PPh$_2$H)$_2$] (3b). The same procedure as for **3a** was employed using [PdCl$_2$(NCPh)$_2$] (0.383 g, 1.0 mmol), Na[W(CO)$_3$Cp]·2DME (1.072 g, 2.0 mmol), and PPh$_2$H (0.52 mL, 3.0 mmol). A red solid (0.510 g, 52.3%) was obtained, which is insoluble in hexane but soluble in acetone, toluene, or dichloromethane and should be stored under an inert atmosphere (mp 168 °C dec). Anal. Calcd for $C_{43}H_{37}O_2P_3PdW$ (M_r = 968.94): C, 53.31; H, 3.85. Found: C, 52.83; H, 3.84. IR (KBr): ν(CO) 1896 vs, 1816 vs. IR (CH$_2$Cl$_2$): ν(CO) 1884 vs, 1799 vs. ^{1}H NMR (C$_6$D$_6$): δ 6.8 (dm, 1 H, PPh$_2$*H*), 6.3 (dm, 1 H, PPh$_2$*H*), 4.83 (s, 5 H, Cp). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 174.5 (dd with W satellites, 1 P, μ-PPh$_2$, ^2J(PP) = 165 and 29, ^1J(PW) = 410), −5.4 (dd, 1 P, PPh$_2$H trans to PPh$_2$, ^2J(PP) = 165 and 16, from ^{31}P NMR, ^1J(PH) = 331), −26.0 (pseudo t, 1 P, PPh$_2$H cis to PPh$_2$, ^2J(PP) $\approx$ 29 and 16, from ^{31}P NMR, ^1J(PH) = 323).

[(OC)$_4\overline{\mathrm{Mn}(\mu\text{-}\mathrm{PCy_2})\mathrm{P}}$d(PCy$_2$H)$_2$] (4a). [PdCl$_2$(NCPh)$_2$] (0.600 g, 1.56 mmol), Na[Mn(CO)$_5$] (31.2 mL of a 0.1 M THF solution), and PCy$_2$H (1.03 mL, 4.68 mmol) were reacted in THF as for **3a**. The solution was evaporated to dryness, and a yellow solid was obtained after elimination of volatile HMn(CO)$_5$. This solid was dissolved in 25 mL of CH$_2$Cl$_2$, the solution was filtered over Celite and concentrated to 2 mL, and the product was crystallized with 15 mL of acetone, washed with 2 × 5 mL of acetone and 3 × 20 mL of hexane, and dried in vacuo. The yellow product (1.120 g, 82.5%) obtained is sparingly soluble in hexane, acetone, and methanol and should be stored under nitrogen (mp 163 °C). Anal. Calcd for $C_{40}H_{68}MnO_4P_3Pd$ (M_r = 867.24): C, 55.40; H, 7.90. Found: C, 55.42; H, 7.75. IR (KBr): ν(CO) 1993 m, 1902 vs br; ν(PH) 2270 w, 2290 w. IR (CH$_2$Cl$_2$): ν(CO) 1996 m, 1904 vs, 1888 sh. ^{1}H NMR (C$_6$D$_6$): δ 4.50 (dm, 1 H, PCy$_2$*H*), 4.30 (dm, 1 H, PCy$_2$*H*). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 228.3 (d br, 1 P, μ-PCy$_2$, ^2J(PP) = 194), 14.3 (dd, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(PP) = 194 and 30, from ^{31}P, ^1J(PH) = 292), 3.8 (pseudo t, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(PP) $\approx$ 30 and 20, from ^{31}P, ^1J(PH) = 290).

[(OC)$_4\overline{\mathrm{Mn}(\mu\text{-}\mathrm{PPh_2})\mathrm{P}}$d(PPh$_2$H)$_2$] (4b). [PdCl$_2$(NCPh)$_2$] (0.766 g, 2.00 mmol), Na[Mn(CO)$_5$] (40 mL of a 0.1 M THF solution) and PPh$_2$H (1.04 mL, 6.0 mmol) were reacted in THF as for **3a**, but the residue obtained after THF evaporation was crystallized from 30 mL of cold methanol. The solid was chromatographed over a 25 × 2.5 cm column of Florisil 60–100 mesh. The orange-red CH$_2$Cl$_2$/hexane (20:80) fraction was evaporated to dryness and the solid washed with hexane and dried in vacuo. A yellow-orange microcrystalline product was obtained (0.880 g, 53.0%). It is insoluble in hexane and soluble in acetone, toluene, or dichloromethane (mp 117 °C). Anal. Calcd for $C_{40}H_{32}MnO_4P_3Pd$ (M_r = 830.96): C, 57.81; H, 3.88. Found: C, 57.69; H, 3.94. IR (KBr): ν(CO) 2012 m, 1936 m, 1925 vs, 1903 vs. IR (CH$_2$Cl$_2$): ν(CO) 2016 m, 1929 vs br, 1905 vs. ^{1}H NMR (C$_6$D$_6$): δ 6.2 (dm, 1 H, PPh$_2$*H*), 7.2 (dm, 1 H, PPh$_2$*H*). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 184.0 (d br, 1 P, μ-PPh$_2$, ^2J(PP) = 201), −4.7 (dd, 1 P, PPh$_2$H trans to PPh$_2$, ^2J(PP) = 201 and 25, from ^{31}P, ^1J(PH) = 337), −12.1 (pseudo t, 1 P, PPh$_2$H cis to PPh$_2$, ^2J(PP) $\approx$ 36 and 25, from ^{31}P, ^1J(PH) = 324).

[Cp(OC)$\overline{\mathrm{Fe}(\mu\text{-}\mathrm{PCy_2})\mathrm{P}}$d(PCy$_2$H)$_2$] (5a). To [PdCl$_2$(NCPh)$_2$] (0.383 g, 1.00 mmol) dissolved in THF (50 mL) was added dropwise PCy$_2$H (0.66 mL, 3.0 mmol); the solution was cooled at −78 °C, and then a 0.1 M THF solution of Na[Fe(CO)$_2$Cp] (20 mL) was added dropwise. The reaction was performed as for **3a**, but the product could not be isolated analytically pure (contamination with [CpFe(CO)$_2$]$_2$). IR (KBr): ν(CO) 1853 m; ν(PH) 2230 w. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 219.2 (dd, 1 P, μ-PCy$_2$, ^2J(PP) = 181 and 58), 12.2 (dd, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(PP) = 58 and 18, from ^{31}P NMR, ^1J(PH) = 285), −9.1 (dd, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(PP) = 181 and 18, from ^{31}P NMR, ^1J(PH) = 279).

[(OC)$_3\overline{\mathrm{Co}(\mu\text{-}\mathrm{PCy_2})\mathrm{P}}$d(PCy$_2$H)$_2$] (6a). At −78 °C, a 0.1 M THF solution of Na[Co(CO)$_4$] (75 mL) was added dropwise (45 min) to [PdCl$_2$(NCPh)$_2$] (1.438 g, 3.75 mmol) dissolved in THF (30 mL). The violet solution was stirred for 0.4 h, and PCy$_2$H (2.47 mL, 11.2 mmol) in THF (15 mL) was added dropwise. CO evolution was observed. A brown solution was obtained that was brought to room temperature (3 h), stirred overnight and evaporated to dryness. The residue was extracted with ca. 80 mL of toluene and filtered through a 5 × 2.5 cm column of Celite. After solvent evaporation, the residue was crystallized with 20 mL of acetone. Using chromatography (10:90 CH$_2$Cl$_2$/hexane) over a 40 × 3 cm column of Kiesegel resin, two fractions were separated: the green one contained **13** (see below) and evaporation of the yellow fraction afforded a yellow complex (1.200 g, 37.9%), sparingly soluble in hexane and diethyl ether and soluble in toluene and CH$_2$Cl$_2$ (mp 168 °C). Anal. Calcd for $C_{39}H_{68}CoO_3P_3Pd$ (M_r = 843.23): C, 55.55; H, 8.13. Found: C, 55.47; H, 8.19. IR (KBr): ν(CO) 1977 s, 1901 vs; ν(PH) 2300 w. IR (CH$_2$Cl$_2$): ν(CO) 1977 s, 1903 vs. ^{1}H NMR (C$_6$D$_6$): δ 4.26 (dm, 1 H, PCy$_2$*H*), 4.10 (dm, 1 H, PCy$_2$*H*). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 287.1 (d br, 1 P, μ-PCy$_2$, ^2J(PP) = 168), 11.5 (dd, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(PP) = 168 and 38, from ^{31}P, ^1J(PH) = 296), 5.2 (dd, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(PP) = 38 and 10, from ^{31}P, ^1J(PH) = 301).

[(OC)$_4\overline{\mathrm{Mn}(\mu\text{-}\mathrm{PPh_2})\mathrm{P}}$t(PPh$_3$)$_2$] (8). PPh$_2$Cl (0.045 mL, 0.25 mmol) was added at −78 °C to a 0.1 M THF solution of Na[Mn(CO)$_5$] (2.5 mL). Solid [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] (0.187 g, 0.250 mmol) was added under stirring to this yellow solution. The solution was allowed to reach room temperature and evaporated to dryness, and the residue was extracted with toluene. The solvent was evaporated under reduced pressure, and the residue was crystallized from acetone (5 mL)/hexane (5 mL) and then dried in vacuo to afford the product as a yellow solid (0.180 g, 67%). Anal. Calcd for $C_{52}H_{40}MnO_4P_3Pt$ (M_r = 1071.85): C, 58.27; H, 3.76. Found: C, 58.23; H, 3.98. IR (KBr): ν(CO) 2060 w, 2018 s, 1995 w, 1980 w, 1950 s, 1939 sh, 1929 s, 1905 s. IR (CH$_2$Cl$_2$): ν(CO) 2063 w, 2014 s, 1987 w, 1979 w, 1925 s, 1901 s. ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 165.6 (d br with Pt satellites, 1 P, μ-PPh_2, ^2J(PP) = 236, ^1J(PPt) = 2471), 31.1 (d with Pt satellites, 1 P, PPh_3 trans to PPh_2, ^2J(PP) = 236, ^1J(PPt) = 3198), 30.3 (d with Pt satellites, 1 P, PPh_3 cis to PPh_2, ^2J(PP) = 21, ^1J(PPt) = 3262).

[(OC)$_3$Co(μ-PPh$_2$)Pt(PPh$_3$)$_2$] (9). A 0.1 M THF solution of Na[Co(CO)$_4$] (2.5 mL), PPh_2Cl (0.045 mL, 0.25 mmol), and [Pt(C_2H_4)(PPh_3)$_2$] (0.187 g, 0.250 mmol) was mixed at −78 °C as for **8**. The red solution was stirred overnight and evaporated to dryness and the residue washed with hexane and recrystallized from toluene/hexane. The red product (0.153 g, 57%) is soluble in toluene and CH_2Cl_2 but sparingly soluble in acetone or hexane. Anal. Calcd for $C_{51}H_{40}CoO_3P_3Pt$ (M_r = 1047.83): C, 58.46; H, 3.85. Found: C, 58.75; H, 3.84. IR (KBr): ν(CO) 1990 s, 1936 s, 1930 s, 1915 s, 1902 s. IR (CH_2Cl_2): ν(CO) 1992 s, 1925 s, br, 1915 s, br. ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 199.9 (d br with Pt satellites, 1 P, PPh_2, ^2J(PP) = 222, ^1J(PPt) = 2827), 30.3 (d with Pt satellites, 1 P, PPh_3 trans to PPh_2, ^2J(PP) = 222, ^1J(PPt) = 3170), 23.8 (d with Pt satellites, 1 P, PPh_3 cis to PPh_2, ^2J(PP) = 19, ^1J(PPt) = 3719).

Reactions of 1–7 with CO. Solutions 5 × 10^{-2} M in compounds **1**–**4** and **6a** in CH_2Cl_2/C_6D_6 (1:1) were prepared in 10-mm NMR tubes. CO was slowly bubbled into the solution for 10 min and the tube sealed. For compounds **1a**, **2a**, and **3a**, the solution contained (^{31}P{^{1}H} NMR) an equilibrium mixture of these compounds, the cis and trans CO substituted **10**–**12**, respectively, and free PCy_2H (Tables I and III). Bubbling N_2 into the solution resulted in immediate CO elimination and quantitative regeneration of **1a**–**3a**.

[Cp(OC)$_2$Cr(μ-PCy$_2$)Pd(CO)(PCy$_2$H)] (10). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ (cis, 77%) 294.0 (s, 1 P, μ-PCy_2), 2.4 (s, 1 P, PCy_2H); δ (trans, 23%) 307.2 (d, 1 P, μ-PCy_2, ^2J(PP) = 105), 10.0 (d, 1 P, PCy_2H, ^2J(PP) = 105).

[Cp(OC)$_2$Mo(μ-PCy$_2$)Pd(CO)(PCy$_2$H)] (11). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ (cis, 85%) 267.4 (d, 1 P, μ-PCy_2, ^2J(PP) = 24), −1.7 (d, 1 P, PCy_2H, ^2J(PP) = 24); δ (trans, 15%) 282.0 (d, 1 P, μ-PCy_2, ^2J(PP) = 119), 11.7 (d, 1 P, PCy_2H, ^2J(PP) = 119).

[Cp(OC)$_2$W(μ-PCy$_2$)Pd(CO)(PCy$_2$H)] (12). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ (cis, 84%) 226.7 (d with W satellites, 1 P, μ-PCy_2, ^2J(PP) = 26, J(PW) = 180), −11.8 (d, 1 P, PCy_2H, ^2J(PP) = 26); δ (trans, 16%) 239.1 (d, 1 P, μ-PCy_2, ^2J(PP) = 117), 8.1 (d, 1 P, PCy_2H, ^2J(PP) = 117). The ^{31}P{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2) spectrum of **12** was recorded at different temperatures (from −85 to 20 °C with 15 °C intervals). From integration of the signals for the cis and trans isomers, the equilibrium constant (K) at each temperature was estimated. Least-squares methods were used for fitting the data of the linear function: $\ln K = -(\Delta H^\circ/R)T^{-1} + \Delta S^\circ/R$. For the cis-**12**/trans-**12** equilibrium the values $\Delta H^\circ = 7.1 \pm 0.4$ kJ·mol^{-1} and $\Delta S^\circ = 10.5 \pm 1$ J·mol^{-1}·K^{-1} were calculated.

For compounds **2b**, **3b**, and **4a** no substitution reaction with CO was observed. For **4b**, no substitution was observed (^{31}P{^{1}H} NMR spectrum at −70 °C) but at 25 °C both phosphine ligands became equivalent and no coupling was observed with the μ-PPh_2 phosphorus atom. The coalescence temperature was found between −20 and −10 °C.

For compound **6a** no substitution was observed, but compound **13** has been obtained by other methods. The reaction of **13** with PCy_2H was monitored by ^{31}P{^{1}H} NMR spectroscopy. Complete transformation in **6a** required 1 night of reaction time.

[(OC)$_3$Co(μ-PCy$_2$)Pd(CO)(PCy$_2$H)] (13). The green chromatographic fraction collected in the preparation of **6a** afforded a green solid (1.30 g, 51.5%), sparingly soluble in acetone and soluble in dichloromethane and toluene (mp 193 °C dec). Anal. Calcd for $C_{28}H_{45}CoO_4P_2Pd$ (M_r = 672.95): C, 49.97; H, 6.74. Found: C, 49.86; H, 6.90. IR (KBr): ν(CO) 1970 s, 1910 vs. IR (CH_2Cl_2): ν(CO) 1971 s, 1907 vs. ^{1}H NMR (C_6D_6): δ 4.14 (dm, 1 H, PCy_2*H*). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 280.1 (s br, 1 P, μ-PCy_2), 5.8 (s, 1 P, PCy_2H, from ^{31}P, ^1J(PH) = 311).

For compound **7**, complete transformation in [Cp(OC)$_2$W(μ-PPh$_2$)Pt(CO)(PPh$_3$)] (**14**) occurred by substitution of one phosphine ligand by a CO group, as shown by ^{31}P{^{1}H} NMR monitoring. Compound **7** can be regenerated by evaporation to dryness, addition of CH_2Cl_2, and stirring (1 h). Compound **14** has been identified by comparison of its IR and ^{1}H and ^{31}P{^{1}H} NMR spectra with the literature data.[16a]

Na[(OC)$_4$Mn(μ-PCy$_2$)Mn(CO)$_4$] (15a). This was the major product when the preparation of **4a** was carried out using [PdCl$_2$(NCPh)$_2$] (1.151 g, 3.00 mmol), a 0.1 M THF solution of Na[Mn(CO)$_5$] (120 mL), and PCy_2H (1.97 mL, 9.00 mmol) in THF. The residue was extracted with acetone, the solution evaporated, and the residue washed with small amounts of dichloromethane and dried in vacuo. The lemon yellow product (1.57 g, 47.2% based on Mn) is sparingly soluble in dichloromethane and decomposes immediately in air. The spectroscopic data are similar to those for **15b**. Interestingly, only traces (ca. 0.5% based on P) of **15a** were observed by ^{31}P NMR spectroscopy in the reaction (4 days) of **4a**, Na[Mn(CO)$_5$], and PCy_2H in THF at room temperature. Formation of **15a** was not observed in the reaction of Na[Mn(CO)$_5$] and [Mn$_2$(CO)$_{10}$] with PCy_2H in THF at room temperature (5 days).

[NBu$_4$][(OC)$_4$Mn(μ-PCy$_2$)Mn(CO)$_4$] (15b). Addition of the stoichiometric amount of [NBu$_4$]Br to **15a** in acetone led to cation exchange. NaBr was removed by filtration, and the solution was evaporated to dryness. The yellow solid obtained is very stable in air (mp 228 °C dec). Anal. Calcd for $C_{36}H_{58}Mn_2NO_8P$ (M_r = 773.72): C, 55.88; H, 7.55; N, 1.81. Found: C, 56.12; H, 7.61; N, 1.75. IR (KBr): ν(CO) 2020 s, 1956 vs, 1910 vs, 1898 vs, 1866 sh. IR (CH_2Cl_2): ν(CO) 2027 s, 1960 vs, 1923 vs, 1903 sh, 1882 vs, 1860 vs. ^{13}C{^{1}H} NMR (THF/CD_2Cl_2): δ 228.4 (s br, CO). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 208.5 (s br, μ-PCy_2).

[(OC)$_4$Mn(μ-PCy$_2$)(μ-H)Mn(CO)$_4$] (16). To a solution of **15a** (0.103 g, 0.133 mmol) in dichloromethane (20 mL) was added 0.14 mmol of HBF_4 in diethyl ether. The colorless solution was evaporated to dryness and the residue extracted with 15 mL of hexane. A light yellow solid (46 mg, 65%) was obtained from the hexane solution (mp 186 °C). Anal. Calcd for $C_{20}H_{23}Mn_2O_8P$ (M_r = 532.25): C, 45.13 H, 4.36. Found: C, 46.03; H, 5.00. IR (KBr): ν(CO) 2083 m, 2051 s, 1990 vs br, 1940 vs br. IR (CH_2Cl_2): ν(CO) 2081 m, 2050 s, 1992 vs br, 1959 vs br. ^{1}H NMR (C_6D_6): δ −16.65 (d br, 1 H, μ-H, ^1J(HP) = 30). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 184.5 (s br, 1 P, μ-PCy_2).

[(OC)$_4$Mn(μ-PPh$_2$)(μ-H)Pd(μ-PPh$_2$)$_2$Mn(CO)$_4$] (17). The procedure described for **4b** was followed, the reaction mixture being stirred for 3 days and then evaporated to dryness. Purification was performed by column chromatography, and from the 20:80 dichloromethane/hexane fraction, an orange-yellow solid (0.366 g, 18.4%) was isolated and characterized as **17**. Anal. Calcd for $C_{44}H_{31}Mn_2O_8P_3Pd$ (M_r = 996.93): C, 53.01; H, 3.13. Found: C, 52.92; H, 3.04. IR (CH_2Cl_2): ν(CO) 2058 s, 1987 vs, 1955 vs. ^{1}H NMR (C_6D_6): δ −11.0 (ddd br, 1 H, μ-H, ^2J(HP) = 64.3, 26.0, and 13.8). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 140.0 (dd, 1 P, μ-PPh_2 spanning the Pd–Mn bond, ^2J(PP) = 272 and 26), −81 (complex m, 1 P, μ-PPh_2), −101 (complex m, 1 P, μ-PPh_2).

[(OC)$_4$Mn(μ-PPh$_2$)Pt(CO)(μ-PPh$_2$)Mn(CO)$_4$] (18). At −60 °C, 20 mL of THF was saturated with ethylene, and then Pt(COD)$_2$ (0.200 g, 0.486 mmol) was dissolved. At −70 °C, PPh_2Cl (9.72 mL of a 0.1 M solution in THF) and Na[Mn(CO)$_5$] (9.72 mL of a 0.1 M solution in THF) were first mixed and then added under an ethylene atmosphere to the solution of [Pt(COD)$_2$]. The temperature was slowly (2 h) raised to room temperature. The initially yellow solution became red and was evaporated to dryness in vacuo. The residue was extracted with hexane, and the solution was filtered through a Celite-padded glass frit (5.0 × 2.5 cm) and evaporated to dryness. The orange solid product (0.400 g, 89%) was dried in vacuo. It is soluble in all common solvents. Anal. Calcd for $C_{33}H_{20}Mn_2O_9P_2Pt$ (M_r = 927.43): C, 42.74; H, 2.17. Found: C, 43.00; H, 2.50. IR (KBr): ν(CO) 2062 s, 2040 s, 1988 vs, 1965 vs, 1942 vs. IR (CH_2Cl_2): ν(CO) 2072 s, 2047 s, 2006 sh, 1984 vs, 1944 s. ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 161.9 (s with satellites of Pt, ^1J(PPt) = 2266).

[{(OC)$_4$Mn(μ-PPh$_2$)}$_2$Pt(PPh$_3$)]·C$_7$H$_8$ (19a). PPh_2Cl (12.4 mL of a 0.1 M solution in toluene) was added at −78 °C to a suspension of Na[Mn(CO)$_5$] (0.270 g, 1.238 mmol) in toluene (20 mL). Solid [Pt(C_2H_4)$_2$(PPh_3)] (0.180 g, 0.619 mmol) was then added in small portions to the stirred solution. The reaction mixture was allowed to reach room temperature while stirring was continued overnight. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy. Initially, the carbonyl derivative **18** was obtained, but the Pt-bound CO was slowly substituted by the phosphine ligand (see below). When complete transformation was achieved (≈8 h), the solution was concentrated to 4–5 mL and hexane (35 mL) was added. A red solid (0.380 g, 49%) characterized as **19a** solvated by a molecule of toluene was obtained (mp 130 °C dec). It is soluble in all common solvents except hexane and decomposes slowly in air. If this reaction is carried out in THF in place of toluene, important amounts of the dinuclear complex **8** are obtained beside **19a** (see below). Anal. Calcd for $C_{50}H_{35}Mn_2O_8P_3Pt \cdot C_7H_8$ (M_r = 1253.85): C, 54.60; H, 3.46. Found: C, 54.20; H, 3.48. IR (KBr): ν(CO) 2042 m, 2000 m, 1969 s, 1932 s, 1912 s. IR (CH_2Cl_2): ν(CO) 2051 m, 2005 m, 1978 s, 1945 s, 1919 s. ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 110.0 (d with Pt satellites, 2 P, μ-PPh_2, ^2J(PP) = 7, ^1J(PPt) = 2204), 34.8 (t with satellites of Pt, 1 P, PPh_3, ^2J(PP) = 7, ^1J(PPt) = 4662).

Reaction of 18 with Phosphines. The CO coordinated to platinum in **18** is readily displaced by phosphine ligands. The reaction of **18** (0.084 g, 0.091 mmol) with PPh_3 (0.024 g, 0.091 mmol) produced the following: (a) in toluene, only substitution of the CO group by the phosphine ligand,

Table V. Crystallographic Data for $[\{(OC)_4Mn(\mu\text{-}PPh_2)\}_2Pt(PPh_3)]\cdot C_7H_8$ (**19a**·C_7H_8)

formula	$C_{50}H_{35}Mn_2O_8P_3Pt\cdot C_7H_8$
fw	1253.85
cryst system	triclinic
space group	$P\bar{1}$
radiation	graphite-monochr Mo Kα (0.71073)
a, Å	13.275 (5)
b, Å	17.718 (6)
c, Å	11.970 (3)
α, deg	94.61 (2)
β, deg	107.89 (2)
γ, deg	97.74 (2)
V, Å^3	2633 (2)
Z	2
D_{calcd}, g cm^{-3}	1.582
F(000)	1244
μ(Mo Kα), cm^{-1}	32.73
R^a	0.0401
$R_w{}^a$	0.0531

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

leading to complex **19a**; (b) in THF, partial substitution of a "$Ph_2P-Mn(CO)_4$" fragment, leading to a mixture of **8** (major, if 2 equiv of phosphine are added) and **19a** (minor). The phosphine complex **19a** did not react under 1 atm of CO to regenerate **18**. The kinetics of this irreversible reaction was studied. A 1-mL volume of a 10^{-4} M solution of PPh_3 was mixed with 1 mL of a 10^{-4} M solution of **18** in toluene-d_8, and the variations in phosphine and **19a** concentrations were monitored by $^{31}P\{^1H\}$ NMR spectroscopy. At 20 °C, the estimated rate constant for a second-order process was $k = 1.5 \times 10^{-3}$ L·mol^{-1}·s^{-1}.

The reaction of **18** (0.120 g, 0.129 mmol) with PCy_2H (1.29 mL of a 0.1 M solution in toluene) was instantaneous. The red product $[\{(OC)_4Mn(\mu\text{-}PPh_2)\}_2Pt(PCy_2H)]$ (**19b**) was only characterized by spectroscopy. $^{31}P\{^1H\}$ NMR (C_7H_8/C_6D_6): δ 114.9 (s with Pt satellites, 2 P, μ-PPh_2, ^1J(PPt) = 2029), 25.3 (s with Pt satellites, 1 P, PCy_2H, ^1J(PPt) = 2890, from ^{31}P NMR, ^1J(PH) = 305). No evolution of the $^{31}P\{^1H\}$ NMR spectrum was observed after 12 h.

The reaction of **18** (0.365 g, 0.395 mmol) with PPh_2H (3.95 mL of a 0.1 M solution in toluene) was instantaneous in toluene. The red product $[\{(OC)_4Mn(\mu\text{-}PPh_2)\}_2Pt(PPh_2H)]$ (**19c**) was only characterized by spectroscopy. It transforms in toluene (3 h) to produce yellow **20**. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 113.4 (s with Pt satellites, 2 P, μ-PPh_2, ^1J(PPt) = 2031), 12.8 (s with Pt satellites, 1 P, PPh_2H, ^1J(PPt) = 4348).

$[(OC)_4Mn(\mu\text{-}H)(\mu\text{-}PPh_2)Pt(\mu\text{-}PPh_2)_2Mn(CO)_4]$ (20). The dark red solution obtained during the synthesis of **19c** from the reaction of **18** with PPh_2H (see above) became light yellow after being stirred for 3 h. The solution was evaporated to dryness, and the yellow solid (0.305 g, 71.1%) was washed with hexane and dried in vacuo (mp >200 °C). Anal. Calcd for $C_{44}H_{31}Mn_2O_8P_3Pt$ (M_r = 1085.62): C, 48.68; H, 2.87. Found: C, 48.52; H, 2.72. IR (KBr): ν(CO) 2060 s, 1990 vs, 1978 vs, 1954 vs. IR (CH_2Cl_2): ν(CO) 2070 m, 2058 m, 1985 vs, 1954 vs. ^1H NMR (C_6D_6): δ −10.75 (ddd, br with Pt satellites, 1 H, μ-H, ^2J(HP) = 55.6, 18.1, and 6.5, ^1J(HPt) = 526). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 124.2 (d, br with Pt satellites, 1 P, μ-PPh_2 spanning Pt–Mn bond, ^2J(PP) = 240, ^1J(PPt) = 1743), ca. −83 (complex m with Pt satellites, 1 P, μ-PPh_2, ^1J(PPt) = 2352), ca. −102 (complex m with Pt satellites, 1 P, μ-PPh_2, ^1J(PPt) = 1698).

The kinetics of the P–H addition reaction was studied by $^{31}P\{^1H\}$ NMR monitoring of the concentration decrease of a 3.6×10^{-5} M solution of **19c** in toluene-d_8. At 20 °C, the estimated rate constant for the first-order process was $k = 1.3 \times 10^{-3}$ s^{-1}.

$[Cp(OC)_2W(\mu\text{-}H)(\mu\text{-}PPh_2)Pt(\mu\text{-}PPh_2)]_2$ (21). $Na[W(CO)_3Cp]\cdot 2DME$ (0.565 g, 1.05 mmol) was added to a stirred suspension of $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$ (0.634 g, 0.527 mmol) in THF (70 mL). The temperature was raised to reach 55–60 °C. After 1 h, the white solid has turned yellow, and after 5 h, the solid has completely dissolved. Stirring was continued overnight, and the orange solution was filtered and evaporated under reduced pressure. The solid residue was extracted with toluene, and the solution was filtered and evaporated in vacuo. The residue was chromatographed on a silica gel column (3 × 24 cm; Kieselgel Merck 60; 70–230 mesh). The column was eluted with CH_2Cl_2/hexane (1:4 and 2:3). The latter fraction was evaporated to dryness. Yellow solid **21** was obtained, recrystallized from acetone/hexane, and isolated as a mixture of isomers (0.560 g, 61.0%). It is sparingly soluble in acetone and insoluble in hexane. Anal. Calcd for $C_{62}H_{52}O_4P_4Pt_2W_2$ (M_r = 1742.89): C, 42.72; H, 3.01. Found: C, 42.71; H, 3.40. IR (KBr): ν(CO) 1938 s, 1861 s. IR (CH_2Cl_2): ν(CO) 1934 s, 1855 s. ^1H NMR (C_6D_6): δ [only for major isomer, the other having similar chemical shifts] 4.36 (s, 10 H, C_5H_5), −8.87 (ddd with Pt satellites, 2 H, μ-H, ^2J(HP) = 54, 18, and 8, ^1J(HPt) = 505). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6):

Table VI. Fractional Atomic Coordinates (×10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of **19a**·C_7H_8

	x/*a*	*y*/*b*	*z*/*c*
Pt	1355 (1)	2708 (1)	1256 (1)
Mn(1)	−690 (1)	1726 (1)	−517 (1)
Mn(2)	928 (1)	2971 (1)	−1270 (1)
P(1)	2354 (1)	3005 (1)	3174 (1)
P(2)	−313 (1)	2283 (1)	1391 (2)
P(3)	2517 (2)	3123 (1)	284 (2)
O(1)	933 (4)	699 (3)	279 (6)
O(2)	−2537 (5)	668 (4)	−373 (7)
O(3)	−1140 (5)	1014 (4)	−2978 (5)
O(4)	−2165 (5)	2853 (4)	−1326 (6)
O(5)	1399 (5)	1491 (3)	−2198 (5)
O(6)	2257 (6)	3883 (4)	−2408 (5)
O(7)	−975 (6)	2889 (4)	−3397 (5)
O(8)	−31 (6)	4221 (3)	−349 (6)
C(1)	328 (6)	1108 (4)	−2 (6)
C(2)	−1806 (6)	1069 (5)	−412 (7)
C(3)	−920 (7)	1306 (5)	−2045 (7)
C(4)	−1572 (7)	2437 (5)	−1008 (7)
C(5)	1230 (6)	2058 (4)	−1814 (7)
C(6)	1717 (7)	3528 (4)	−1972 (7)
C(7)	−275 (7)	2886 (5)	−2559 (7)
C(8)	381 (7)	3746 (4)	−633 (7)
C(9)	3808 (5)	3214 (4)	3555 (6)
C(10)	4285 (6)	2664 (4)	3109 (7)
C(11)	5395 (7)	2748 (5)	3446 (8)
C(12)	6022 (8)	3374 (6)	4213 (8)
C(13)	5555 (8)	3906 (6)	4657 (9)
C(14)	4441 (7)	3843 (5)	4336 (7)
C(15)	2322 (5)	2274 (4)	4158 (6)
C(16)	2015 (6)	1516 (4)	3672 (7)
C(17)	2121 (7)	933 (5)	4398 (8)
C(18)	2555 (7)	1125 (6)	5604 (8)
C(19)	2883 (7)	1880 (5)	6105 (9)
C(20)	2772 (6)	2467 (5)	5372 (7)
C(21)	2000 (5)	3872 (4)	3764 (6)
C(22)	1514 (6)	3908 (5)	4645 (7)
C(23)	1232 (7)	4605 (5)	4980 (8)
C(24)	1382 (7)	5233 (5)	4422 (8)
C(25)	1831 (6)	5208 (5)	3559 (7)
C(26)	2148 (6)	4520 (4)	3219 (6)
C(27)	−466 (5)	1673 (4)	2503 (6)
C(28)	−607 (5)	880 (4)	2327 (6)
C(29)	−679 (6)	436 (5)	3223 (7)
C(30)	−588 (7)	791 (5)	4323 (8)
C(31)	−452 (7)	1593 (5)	4530 (8)
C(32)	−379 (6)	2031 (4)	3644 (6)
C(33)	−1092 (5)	3020 (4)	1622 (6)
C(34)	−2160 (6)	2799 (5)	1554 (7)
C(35)	−2765 (7)	3364 (5)	1736 (7)
C(36)	−2312 (7)	4120 (5)	1963 (8)
C(37)	−1260 (6)	4337 (5)	2021 (7)
C(38)	−647 (6)	3787 (4)	1846 (6)
C(39)	3484 (5)	2548 (4)	3 (6)
C(40)	3364 (6)	1771 (4)	175 (7)
C(41)	4020 (7)	1314 (6)	−128 (8)
C(42)	4814 (8)	1630 (6)	−573 (9)
C(43)	4911 (8)	2383 (6)	−747 (8)
C(44)	4262 (6)	2844 (5)	−461 (7)
C(45)	3309 (6)	4092 (4)	807 (6)
C(46)	4363 (7)	4196 (5)	1546 (7)
C(47)	4930 (8)	4931 (5)	2044 (8)
C(48)	4434 (8)	5544 (6)	1792 (8)
C(49)	3399 (7)	5473 (6)	1037 (8)
C(50)	2843 (7)	4735 (5)	549 (8)
C(51)	5840 (11)	1113 (7)	4817 (11)
C(52)	6688 (11)	1145 (7)	4381 (12)
C(53)	6565 (14)	824 (10)	3243 (16)
C(54)	5623 (14)	473 (10)	2524 (16)
C(55)	4742 (14)	466 (10)	2908 (15)
C(56)	4802 (12)	794 (8)	4079 (14)
C(57)	5993 (13)	1504 (11)	6047 (15)

δ 112.3 (AA′ part of an AA′XX′ spin system with Pt satellites, 2 P, μ-PPh_2 spanning Pt–W bond, $^2J(PP)$ = 188, $^1J(PPt)$ = 1642), −139.5 (XX′ part of an AA′XX′ spin system with Pt satellites, 2 P, μ-PPh_2, $^1J(PPt)$ = 2255).

$[(OC)_4\overline{Mn(\mu\text{-}H)(\mu\text{-}PPh_2)Pt}(\mu\text{-}PPh_2)]_2$ (22). A 0.1 M solution of $Na[Mn(CO)_5]$ (6.64 mL, 0.664 mmol) in THF was added to a stirred suspension of $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$ (0.400 g, 0.332 mmol) in THF (100 mL). The reaction occurred as described for **21**. From the THF solution, a yellow solid was obtained as a mixture of isomers after recrystallization from acetone/hexane (0.270 g, 55.4%). Anal. Calcd for $C_{56}H_{42}Mn_2O_8P_4Pt_2$ (M_r = 1466.91): C, 45.85; H, 2.88. Found: C, 45.82; H, 3.08. IR (KBr): ν(CO) 2060 m, 1978 s, 1947 s. IR (CH_2Cl_2): ν(CO) 2067 m, 1984 s, 1949 s. ^1H NMR (C_6D_6): δ [only for major isomer, the other having similar chemical shifts] ca. −10.2 (br signals with Pt satellites, 2 H, μ-H, $^1J(HPt) \approx 530$). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 125.0 (AA′ part of an AA′XX′ spin system with Pt satellites, 2 P, μ-PPh_2 spanning Pt–Mn bond, $^2J(PP)$ = 205, $^1J(PPt)$ = 1642), −123.9 (XX′ part of an AA′XX′ spin system with Pt satellites, 2 P, μ-PPh_2).

Reactions of 1a–3a with PPh_2Cl. The W–Pd complex **3a** (0.227 g, 0.226 mmol) in toluene (20 mL) reacted immediately with PPh_2Cl (0.41 mL of a 1:10 solution in toluene, 0.23 mmol). The yellow solution contained (^{31}P NMR) a species that we propose to formulate as **24a**, contaminated with large amounts of the hydride **18a**. Similar species **23a** and **23b** were observed from the Mo–Pd derivatives **2a** and **2b**, respectively. However, the reaction of PPh_2Cl with the Cr–Pd complex **1a** led to decomposition.

$[Cp(OC)_2\overline{Mo(\mu\text{-}PCy_2)(\mu\text{-}PPh_2)Pd}Cl(PCy_2H)]$ (23a). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 16.0 (dd, 1 P, PCy_2H, $^2J(PP)$ = 340 and 39, from ^{31}P NMR, $^1J(PH)$ = 338), −140.7 (dd, 1 P, μ-P cis to PCy_2H, $^2J(PP)$ = 336 and 39), −173.4 (pseudo t, 1 P, μ-P trans to PCy_2H, $^2J(PP)$ = 340 and 336).

$[Cp(OC)_2\overline{Mo(\mu\text{-}PPh_2)_2Pd}Cl(PPh_2H)]$ (23b). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ −1.3 (dd, 1 P, PPh_2H, $^2J(PP)$ = 386 and 29, from ^{31}P NMR, $^1J(PH)$ = 338), −138.7 (dd, 1 P, μ-PPh_2 cis to PPh_2H, $^2J(PP)$ = 336 and 29), −168.4 (dd, 1 P, μ-PPh_2 trans to PPh_2H, $^2J(PP)$ = 386 and 336).

$[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}PPh_2)PdCl(PCy_2H)]$ (24a). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 16.8 (dd, 1 P, PCy_2H, $^2J(PP)$ = 340 and 34, from ^{31}P NMR, $^1J(PH)$ = 328), −187.3 (dd with W satellites, 1 P, μ-P cis to PCy_2H, $^2J(PP)$ = 307 and 34, $^1J(PW)$ = 135), −215.2 (dd with W satellites, 1 P, μ-P trans to PCy_2H, $^2J(PP)$ = 340 and 307, $^1J(PW)$ = 153).

Reaction of 3a with $[Ph_2PCo(CO)_4]$. At −78 °C, 0.25 mL (0.25 mmol) of a 1 M solution of PPh_2Cl in THF was added to 2.5 mL of a 0.1 M of $Na[Co(CO)_4]$ in THF. Complex **3a** (0.250 g, 0.249 mmol) was added to this orange solution, and the mixture was allowed to reach room temperature (1 h). The solution was shown by ^{31}P NMR spectroscopy to contain mainly **6a**.

Reaction of 2b with $[Pt(C_2H_4)(PPh_3)_2]$. The reaction using 0.148 mmol was carried out in dichloromethane. The solution was stirred for 1 day. ^{31}P NMR spectroscopy showed that only phosphine exchange had occurred, $[Cp(OC)_2\overline{Mo(\mu\text{-}PPh_2)Pd}(PPh_3)_2]$ being the major product. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 210.3 (dd, 1 P, μ-PPh_2, $^2J(PP)$ = 159 and 26), 24.3 (dd, 1 P, PPh_2H trans to PPh_2, $^2J(PP)$ = 159 and 23), 14.3 (pseudo t, 1 P, PPh_2H cis to PPh_2).

Reaction of $[PdCl(\mu\text{-}PPh_2)(PPh_2H)]_2$ with $Na[W(CO)_3Cp]\cdot 2DME$ or $Na[Mn(CO)_5]$. $Na[W(CO)_3Cp]\cdot 2DME$ (0.403 g, 0.75 mmol) was added at −78 °C to a stirred suspension of $[PdCl(\mu\text{-}PPh_2)(PPh_2H)]_2$ (0.386 g, 0.375 mmol) in THF (70 mL). The temperature was raised to 25 °C. After being stirred for 2 h at room temperature, a red brown solution was obtained. It did not contain (^{31}P NMR) any upfield signal assignable to a μ-PPh_2 group across a non Pd–Pd bond. **3b** was identified as one of the major products. Similar results were obtained in the reaction with $Na[Mn(CO)_5]$, and formation of **17** was also observed.

NMR Interpretation. The second-order NMR spectra were interpreted with the help of the LAOCOON3 program (IBM PC) and the PANIC program (Bruker Aspect 2000 computer).

X-ray Crystal Structure Determination of $[[(OC)_4\overline{Mn(\mu\text{-}PPh_2)]_2Pt}(PPh_3)]\cdot C_7H_8$ ($19a\cdot C_7H_8$). A crystal of **19a**$\cdot C_7H_8$ suitable for single-crystal X-ray diffraction was grown from toluene/hexane. Crystallographic data are summarized in Table V, and the final atomic coordinates for the non-hydrogen atoms are given in Table VI. Unit cell parameters were determined from the θ values of 29 carefully centered reflections, having $11.0 < \theta < 17.5°$. All reflections with θ in the range 3–25° were measured; of 9316 independent reflections, 6612, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[44] Intensities were corrected for Lorentz and polarization effects; a semiempirical absorption correction was applied (maximum and minimum values for the transmission factors were 1.277 and 1.000).[45] 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 and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms excepting the carbon atoms of the phenyl groups. The final ΔF map revealed the presence of a toluene molecule of solvation, which was refined isotropically. All hydrogen atoms were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 397 variables. After the last cycle, no parameter shifted by more than 0.9 esd. The largest remaining peak (close to the Pt atom) in the final difference map was equivalent to about 1.5 e/Å^3. In the final cycles of refinement a weighting scheme, $w = K/[\sigma^2(F_o) + gF_o^2]$, was used; at convergence the K and g values were 0.647 and 0.0122, respectively. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 46.

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, Italy) and on the Gould Powernode 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR (Parma, Italy) using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[47]

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Registry No. **1a**, 125778-34-9; **2a**, 125778-35-0; **2b**, 125778-36-1; **3a**, 125778-37-2; **3b**, 125778-38-3; **4a**, 125797-80-0; **4b**, 137966-58-6; **5a**, 137916-17-7; **6a**, 137916-18-8; **7**, 125046-18-6; **8**, 137916-09-7; **9**, 137916-10-0; *cis*-**10**, 125827-63-6; *trans*-**10**, 125778-24-7; *cis*-**11**, 125827-64-7; *trans*-**11**, 125778-25-8; *cis*-**12**, 125874-52-4; *trans*-**12**, 125778-26-9; *cis*-**13**, 137966-59-7; *cis*-**14**, 101307-75-9; **15a**, 138008-52-3; **15b**, 138008-51-2; **16**, 137966-60-0; **17**, 137966-63-3; **18**, 71597-15-4; **19a**$\cdot C_7H_8$, 137966-62-2; **19b**, 138008-53-4; **19c**, 137966-64-4; **20**, 137966-65-5; **21**, 137966-66-6; **22**, 137966-67-7; **23a**, 137966-68-8; **23b**, 137966-69-9; **24a**, 137966-70-2; I (L = PH_3), 137966-71-3; I (L = CO), 137966-72-4; III (L = PH_3), 113509-18-5; III (L = CO), 137966-73-5; III (L = PPh_3), 60038-75-7; $PdCl_2(NCPh)_2$, 14220-64-5; $Na[Cr(CO)_3Cp]$, 12203-12-2; $Na[Mo(CO)_3Cp]$, 12107-35-6; $Na[W(CO)_3Cp]$, 12107-36-7; $Na[Mn(CO)_5]$, 13859-41-1; $Na[Fe(CO)_2Cp]$, 12152-20-4; $Na[Co(CO)_4]$, 14878-28-5; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; $Pt(COD)_2$, 12130-66-4; $[PtCl(\mu\text{-}PPh_2)(PPh_2H)]_2$, 80374-72-7; $[Cp(OC)_2Mo(\mu\text{-}PPh_2)Pd(PPh_3)_2]$, 138008-54-5; Mn, 7439-96-5; Pt, 7440-06-4; Pd, 7440-05-3; Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7; Fe, 7439-89-6; Co, 7440-48-4.

Supplementary Material Available: Tables of crystallographic data, hydrogen atom coordinates and thermal parameters, and anisotropic and isotropic thermal parameters for the non-hydrogen atoms (4 pages); listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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