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Electrophilic Additions to Phosphido-Bridged Palladium- and Platinum-Transition-Metal Bonds. Synthesis and Crystal Structure of the Heterotetranuclear Cluster $[\{Cp(OC)_2W(\mu\text{-}CO)(\mu\text{-}PPh_2)\}\{Cp(OC)_2W(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)\}Pt][PF_6]\cdot 2THF$ (*Au–Pt*, *Au–W*, 2 *W–Pt*) (THF = Tetrahydrofuran)

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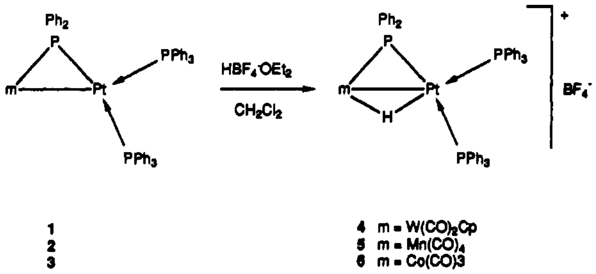
The reactions of a series of phosphido-bridged heterodinuclear complexes with HBF_4 in CH_2Cl_2 afforded the corresponding hydrido-bridged complexes $[m(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2][BF_4]$ (**4**, m = $W(CO)_2Cp$; **5**, m = $Mn(CO)_4$; **6**, m = $Co(CO)_3$) and $[m(\mu\text{-}PR_2)(\mu\text{-}H)Pd(PR_2H)_2][BF_4]$ (**13a**, m = $Cr(CO)_2Cp$, R = Cy; **14a**, m = $Mo(CO)_2Cp$, R = Cy; **14b**, m = $Mo(CO)_2Cp$, R = Ph; **15a**, m = $W(CO)_2Cp$, R = Cy; **15b**, m = $W(CO)_2Cp$, R = Ph; **16a**, m = $Mn(CO)_4$, R = Cy; **16b**, m = $Mn(CO)_4$, R = Ph; **17a**, m = Fe(CO)Cp, R = Cy; **18a**, m = $Co(CO)_3$, R = Cy). However, reactions of $[m(\mu\text{-}PCy_2)Pd(PCy_2H)_2]$ (**7a**, m = $Cr(CO)_2Cp$; **8a**, m = $Mo(CO)_2Cp$; **9a**, m = $W(CO)_2Cp$) with HCl in acetone yielded the corresponding chloro complexes $[m(\mu\text{-}PCy_2)(\mu\text{-}H)PdCl(PCy_2H)]$ (**19a–21a**). It was shown that coordination of the chloride occurs on the labile protonated intermediate. Addition of CuCl to **8b** yielded $[Cp(OC)_2Mo(CuCl)(\mu\text{-}PPh_2)Pd(PPh_2H)_2]$ (**22**) for which isomers were characterized: **22A** in which the CuCl group is terminally bound to Mo and **22B** in which this group bridges the Mo–Pd bond. In solution, the latter is in equilibrium with yet another isomer, $[Cp(OC)_2Mo\{\mu\text{-}Cu(PPh_2H)\}(\mu\text{-}PPh_2)PdCl(PPh_2H)]$ (**23**), which results from a 1,2-mutual exchange between the ligands Cl and PPh_2H. The basicity of the phosphido-bridged W–Pt bonds of the trinuclear, bent-chain complex $[\{Cp(OC)_2W(\mu\text{-}PPh_2)\}_2Pt(CO)]$ (**24**) was investigated in reactions with HBF_4, HCl, or $[AuPPh_3]^+$, which afforded the hydrido complexes **25** and **26** and the heterotetranuclear cluster $[\{Cp(OC)_2W(\mu\text{-}CO)(\mu\text{-}PPh_2)\}\{Cp(OC)_2W(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)\}Pt][PF_6]$ (**27**), respectively. The solid-state structure of the tetrahydrofuran solvate of **27** has been determined by a single-crystal X-ray analysis. It crystallizes in the monoclinic space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 30.867$ (8) Å, $b = 18.855$ (4), $c = 11.168$ (3) Å, and $\beta = 90.46$ (1)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 4195 observed reflections to R and R_w values of 0.0684 and 0.0877, respectively. The structure of the cationic part of **27** shows an almost linear W(1)–Pt–W(2) chain [W(1)–Pt–W(2) angle = 170.9 (1)°], with both the W(1)–Pt and W(2)–Pt bonds being doubly bridged. The $\mu\text{-}PPh_2$ ligands, each bridging a W–Pt bond, are in a quasi trans disposition with respect to the Pt atom [P(1)–Pt–P(2) = 177.7 (3)°]. In addition, the W–Pt bonds are bridged respectively by a $AuPPh_3$ fragment [Au–W(1) = 2.738 (2) and Au–Pt = 2.858 (3) Å] and by a carbonyl ligand, which are also in a quasi trans disposition with respect to the Pt atom [Au–Pt–C(5) = 170.5 (8)°].

Introduction

The elucidation of the factors governing the selectivity of a chemical reaction occurring at a heterometallic complex remains a topic of high current interest.[1,2] Metal–metal-bonded molecules containing an electron-rich moiety $M\text{–}(\mu\text{-}PR_2)\text{–}M'$ are particularly suitable for studying the site selectivity of reactions with electrophilic reagents. Thus, reactions may occur at M or M′, at the metal–metal bond, or at a metal–phosphorus bond.[3] We wish to report here on reactions of electrophilic reagents (H^+, CuCl, $(AuPPh_3)^+$) with a series of dimetallic complexes described recently[4,5] which contain an electron-rich $M\text{–}(\mu\text{-}PR_2)\text{–}m$ moiety (M = Pd, Pt; m = Cr(or Mo, W)$(CO)_2Cp$, $Mn(CO)_4$, Fe(CO)Cp, $Co(CO)_3$). We have also studied the reactions of the trinuclear, bent-chain complex $[\{Cp(OC)_2W(\mu\text{-}PPh_2)\}_2Pt(CO)]$ (**24**) with acids and $(AuPPh_3)^+$ and describe the X-ray crystal structure of the resulting heterotrimetallic, tetranuclear W_2AuPt complex $[\{Cp(OC)_2W(\mu\text{-}CO)(\mu\text{-}PPh_2)\}\{Cp(OC)_2W(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)\}Pt][PF_6]$ (**27**).

Results

Synthesis and Characterization of the Complexes. Preparative details and spectroscopic data for all complexes are given in the Experimental Section. The heterobimetallic m–Pt complexes **1–3**[4,5] were reacted in CH_2Cl_2 with diethyl ether solutions of HBF_4 and afforded the cationic complexes **4–6**, respectively (eq 1), as



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[†] Université Louis Pasteur.

[‡] Università di Parma.

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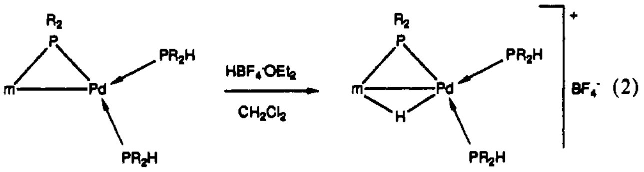
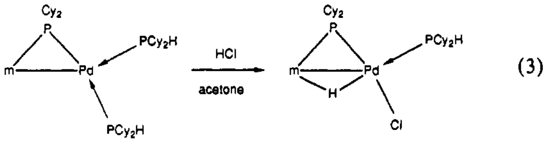
a result of electrophilic attack of the proton at the metal–metal bond. A similar reactivity has been observed for the m–Pd complexes **7–12**, reported earlier,[5] and has led to the cationic compounds **13–18**, respectively (eq 2). The cationic complexes m–Pt **4–6** and m–Pd **13–18** present a $^{31}P\{^1H\}$ NMR spectrum similar to that of their corresponding, neutral precursors. Each complex shows a downfield resonance (doublet of doublets or broad doublet when m contains a quadrupolar nucleus), due to the bridging PR_2 ligand, and two other resonances (two doublets of doublets, one of them appearing sometimes as a pseudotriplet or a doublet), due to the phosphine ligands. The large downfield shifts of ca. 148–229 ppm for the μ-PPh_2 ligand and ca. 228–311 ppm for the μ-PCy_2 bridges are indicative of a metal–metal bond.[6] Each complex shows in the ^1H NMR spectrum an upfield resonance (doublet of doublets of doublets, broadened when m contains a quadrupolar nucleus) in the range of −13 to −8 ppm, due to the hydride ligand. The bridging nature of the latter is confirmed for the W–Pt complex **4** by the values of the ^1J(HPt) and ^1J(HW) coupling constants of 480 and 41 Hz, respectively,[2,7,8] with ^2J(HP) coupling constants of 74, 20, and 18 Hz. That similar values are observed for ^1J(HPt) in Mn–Pt **5** and Co–Pt **6**, for ^1J(HW) in W–Pd **15a,b**, and for ^2J(HP) in all the dinuclear complexes is in agreement with the hydride always occupying a bridging position.



7a
8a
8b
9a
9b
10a
10b
11a
12a

13a m = $Cr(CO)_2Cp$; R = Cy
14a m = $Mo(CO)_2Cp$; R = Cy
14b m = $Mo(CO)_2Cp$; R = Ph
15a m = $W(CO)_2Cp$; R = Cy
15b m = $W(CO)_2Cp$; R = Ph
16a m = $Mn(CO)_4$; R = Cy
16b m = $Mn(CO)_4$; R = Ph
17a m = $Fe(CO)Cp$; R = Cy
18a m = $Co(CO)_3$; R = Cy

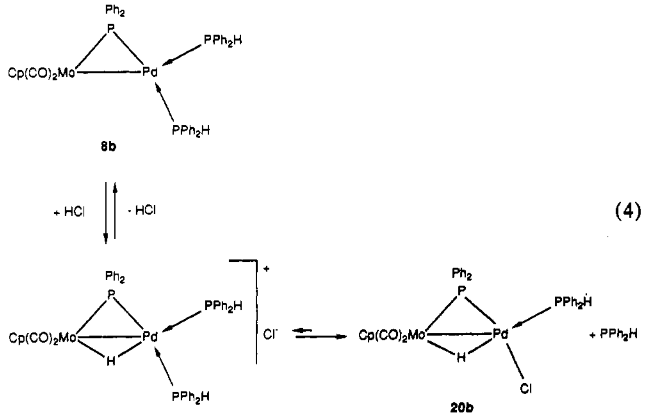
The reaction of the palladium complexes **7a–12a** with HCl has been also studied. In the case of **7a–9a** (eq 3), the reaction product **19a–21a** results from electrophilic attack of the proton at the Pd–m bond and nucleophilic displacement of the phosphine trans with respect to the phosphido bridge by the chloride anion. When a similar reaction was carried out with Mn–Pd **10a** or Co–Pd **12a**, we observed the disappearance in the $^{31}P\{^1H\}$ NMR spectrum of the downfield resonance due to the PCy_2 bridge. Addition of soluble halide salts to a solution of Mo–Pd **8a** did not result in phosphine substitution, indicating that this step only occurs with cationic compounds and therefore follows the protonation step.[9] The $^{31}P\{^1H\}$ NMR spectrum of **19a–21a** contains a downfield resonance (singlet), due to the bridging PR_2 ligand, whose chemical shift ranges from ca. 225 to 295 ppm, again consistent with the presence of a metal–metal bond.[6] The absence of ^2J(PP) coupling is in agreement with the cis structure proposed for **19a–21a**. The ^1H NMR upfield resonance (doublet of doublets), due to the hydride, is found in the region −11 to −9 ppm. The corresponding ^1J(HW) coupling constant of 50 Hz in **21a** and the ^2J(HP) values of 67–73 and 30–46 Hz confirm the bridging nature of the hydride ligand in **19a–21a**.



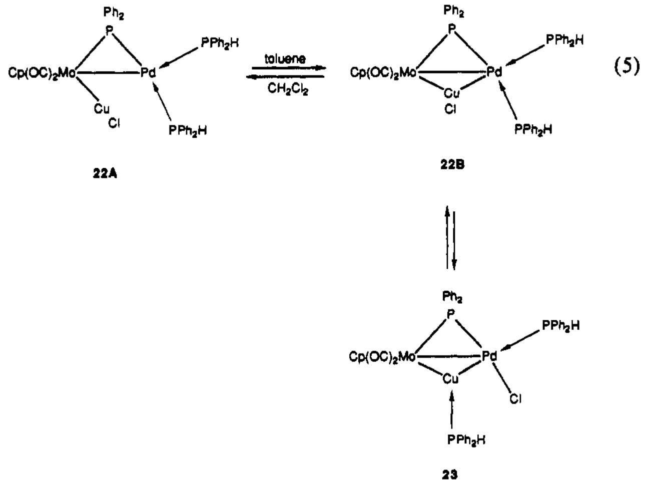
7a
8a
9a

19a m = $Cr(CO)_2Cp$
20a m = $Mo(CO)_2Cp$
21a m = $W(CO)_2Cp$

The reaction of the Mo–Pd complex **8b** with HCl in toluene or CH_2Cl_2 (eq 4) affords a solution whose spectrum in the ν(CO) region corresponds to that of compound **20b**. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture in toluene shows a downfield singlet at 226 ppm and a singlet at ca. 0 ppm, as anticipated for such a structure. However, the two resonances integrate in a 1:2 ratio in place of 1:1 and no resonance corresponding to uncoordinated phosphine is observed. Upon a decrease of the temperature, a more complicated spectrum appears. All attempts to isolate **20b** only led to the recovery of its precursor **8b**. Variable-temperature ^1H NMR studies showed that, at low temperature (−60 °C), **20b** is the only species present and its hydride resonates at −8.7 ppm as a doublet of doublets [^2J(HP) = 72 and 22 Hz]. When the temperature is raised to ambient, the ^2J[HP(trans to μ-P)] coupling of 72 Hz disappears owing to rapid exchange involving the trans PPh_2H ligand. The coalescence temperature was found to be ca. −40 °C. The equilibria shown in eq 4 would account for these observations.



The trimetallic complex $[\mathrm{Cp(OC)_2}\overline{\mathrm{Mo(CuCl)(\mu\text{-}PPh_2)Pd}}\mathrm{(PPh_2H)_2}]$ (**22**) was obtained from the reaction of **8b** with CuCl as two isomers depending on the solvent used: the yellow isomer **22A** was isolated from CH_2Cl_2 or acetone, and the red isomer **22B**, from toluene (eq 5). Each isomer (see Experimental Section) presents a $^{31}P\{^1H\}$ NMR spectrum similar to that of the Mo–Pd complexes **8b** and **14b**, with a downfield resonance due to the bridging PPh_2 and two other resonances (doublet of doublets and pseudo triplet) due to the PPh_2H ligands. Broadening of ^{31}P resonances due to coupling with the quadrupoles of ^{63}Cu and ^{65}Cu was observed and used as diagnostic for assigning the likely



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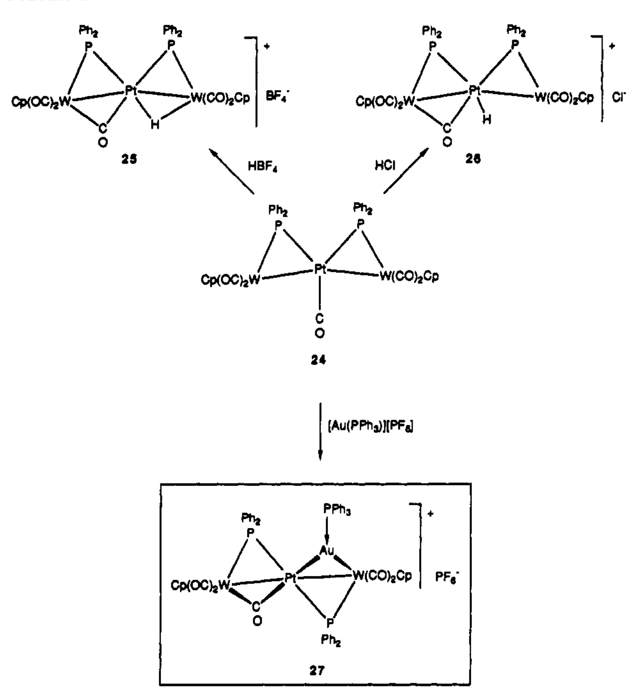
Scheme I



structure of each isomer: all the ^{31}P resonances are broad in isomer **22B**, indicating stronger P–Cu interactions than in **22A** where only the μ-PPh_2 resonance is slightly broadened. Furthermore, we observed that, in solution, **22B** is in equilibrium with yet another isomer **23**, which we suggest results from a 1,2-mutual exchange between the ligands Cl and PPh_2H. This complex could not be isolated pure, and its formulation is based on spectroscopic data; e.g., the phosphine ligand coordinated to copper now appears in the ^{31}P NMR spectrum as a broad singlet at −34.6 ppm.

The reaction between the trinuclear, bent-chain complex $[\{Cp(OC)_2W(\mu\text{-}PPh_2)\}_2Pt(CO)]$ (**24**)[4] and HBF_4 in CH_2Cl_2 afforded **25** as a result of electrophilic attack of H^+ at a Pt–W bond (Scheme I). However, reaction with HCl in CH_2Cl_2 led to **26**, which contains a terminal, Pt-bound hydrido ligand. The structure of the isomeric cations of **25** and **26** is proposed on the basis of their spectroscopic and analytical data (see Discussion) and by analogy with that determined for the related gold adduct $[\{Cp(OC)_2W(\mu\text{-}CO)(\mu\text{-}PPh_2)\}\{Cp(OC)_2W(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)\}Pt][PF_6]$ (**27**) (see below).

When we used electrophilic metal complexes as reagents, we found that $[AuPPh_3]^+$ reacted with W_2Pt **24**, in contrast to $[AuCl(PPh_3)]$ or $[Cu(MeCN)_4][BF_4]$. The structure of the product AuW_2Pt **27** has been established by an X-ray diffraction study (see below). Addition of the $AuPPh_3$ fragment to a W–Pt bond has occurred but resulted in notable structural changes when compared to the precursor **24**. The two μ-PPh_2 groups are now trans to one another, and the CO originally bonded to platinum now bridges a Pt–W bond and is trans to the $AuPPh_3$ fragment, which bridges the other W–Pt bond. The spectroscopic data for **27** are very similar to those for **25**: the $^{31}P\{^1H\}$ NMR spectrum contains two μ-PPh_2 resonances at 85 (dd) and 16 ppm (d), with a $^2J(PP)$ coupling of 200 Hz, corresponding to a trans situation for the phosphorus atoms. The downfield resonance at 85 ppm displays coupling with the PPh_3 ligand coordinated to the Au atom [$^2J(PP)$ = 20 Hz] and is therefore assigned to the μ-PPh_2 spanning the same W–Pt bond as the $AuPPh_3$ group. By comparison with the value of 144.8 ppm found in W_2Pt **24**, this resonance is shifted upfield by ca. 60 ppm in AuW_2Pt **27**, a trend comparable to that observed e.g. on going from $[Cp(OC)_2W(\mu\text{-}PCy_2)Pt(CO)(PCy_2H)]$ (δ 196.6) to its $[AuPPh_3]^+$ adduct $[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}AuPPh_3)Pt(CO)(PCy_2H)][PF_6]$ (δ 158.9).[10]

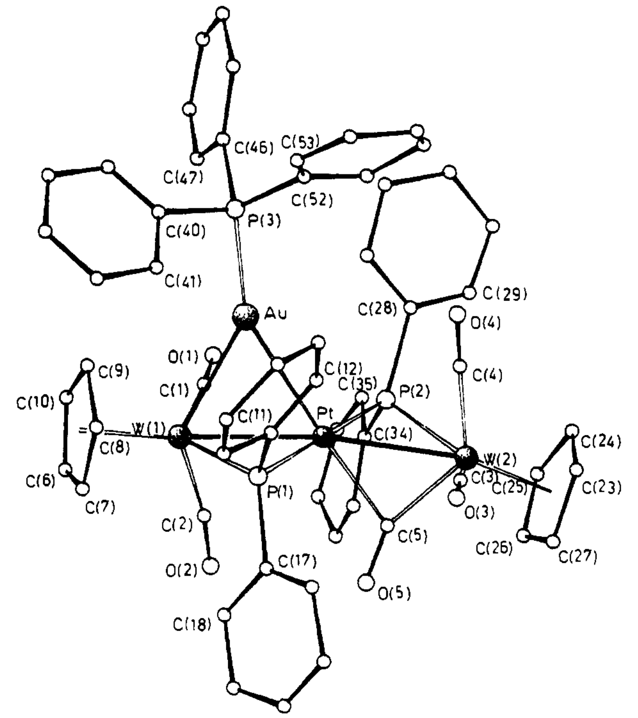


Figure 1. Perspective view of the structure of the cation $[\{Cp(OC)_2W(\mu\text{-}CO)(\mu\text{-}PPh_2)\}\{Cp(OC)_2W(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)\}Pt]^+$ in complex **27**·2THF, with the atom-numbering scheme.

Description of the Crystal Structure of $[\{Cp(OC)_2W(\mu\text{-}CO)(\mu\text{-}PPh_2)\}\{Cp(OC)_2W(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)\}Pt][PF_6]$·2THF (27·2THF). In the crystals heterotrimetallic, tetranuclear $[\{Cp(OC)_2W(\mu\text{-}CO)(\mu\text{-}PPh_2)\}\{Cp(OC)_2W(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)\}Pt]^+$ cations, PF_6^- anions, and tetrahydrofuran molecules of solvation, separated by normal contacts, are present. A view of the cationic cluster is shown in Figure 1 together with the atom-numbering scheme. Selected bond distances and angles are given in Table I. In the almost linear W(1)–Pt–W(2) chain [W(1)–Pt–W(2) angle = 170.9 (1)°], both W(1)–Pt and W(2)–Pt bonds are doubly bridged. Each W–Pt bond is bridged by a μ-PPh_2 ligand in a quasi trans disposition, the P(1)–Pt–P(2) angle being 177.7 (3)°. The two phosphido bridges are asymmetric [W(1)–P(1) = 2.400 (9) and Pt–P(1) = 2.281 (9) Å; W(2)–P(2) = 2.485 (9) and Pt–P(2) = 2.300 (10) Å], and the dihedral angle between the triangles W(1)–P(1)–Pt and W(2)–P(2)–Pt is only of 9.9 (2)°. The W(1), P(1), W(2), and P(2) atoms form approximately a parallelogram, the deviations from the mean plane passing through them being of 0.013 (2), −0.170 (9), 0.012 (2), and −0.179 (9) Å, respectively. The Pt atom is out of this plane by −0.210 (2) Å. The W(1)–Pt and W(2)–Pt bonds are also asymmetrically bridged by a $AuPPh_3$ fragment [Au–W(1) = 2.738 (2) and Au–Pt = 2.858 (3) Å] and by a carbonyl ligand, respectively, which are also in a quasi trans disposition with respect to the Pt atom [Au–Pt–C(5) = 170.5 (8)°]. The Au–W(1)–Pt and C(5)–W(2)–Pt planes form a dihedral angle of 166.5 (8)°. The dihedral angle between the two bridges on the W(2)–Pt bond is 66.0 (8)°, whereas the two bridges on the W(1)–Pt bond are almost perpendicular to each other [dihedral angle 83.3 (2)°]. The metal–metal distances (Table I) fall within the range observed in other complexes containing Pt–W [2.602 (1)–2.902 (1) Å], Au–W [2.698 (3)–2.952 (1) Å], and Au–Pt bonds [2.575 (3)–3.034 (1) Å] (from refs 10–12 and from the Cambridge

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Table I. Important Interatomic Distances (Å) and Angles (deg) for **27**[a]

W(1)–Pt	2.789 (2)	W(2)–C(3)	1.95 (5)
W(2)–Pt	2.831 (2)	W(2)–C(4)	1.97 (3)
W(1)–Au	2.738 (2)	W(2)–C(5)	2.04 (3)
Pt–Au	2.858 (3)	Pt–C(5)	2.12 (3)
W(1)–P(1)	2.400 (9)	W(1)–CE(1)	2.00 (4)
Pt–P(1)	2.281 (9)	W(2)–CE(2)	1.98 (4)
W(2)–P(2)	2.485 (9)	C(1)–O(1)	1.18 (4)
Pt–P(2)	2.300 (10)	C(2)–O(2)	1.19 (4)
Au–P(3)	2.289 (9)	C(3)–O(3)	1.20 (6)
W(1)–C(1)	1.98 (4)	C(4)–O(4)	1.11 (4)
W(1)–C(2)	1.93 (3)	C(5)–O(5)	1.17 (4)
W(1)–Pt–W(2)	170.9 (1)	C(3)–W(2)–C(4)	78.9 (17)
W(1)–Pt–Au	58.0 (1)	C(4)–W(2)–P(2)	79.0 (10)
Au–Pt–P(1)	77.3 (2)	P(2)–W(2)–C(5)	79.3 (9)
Au–Pt–P(2)	103.3 (2)	C(5)–W(2)–C(3)	77.1 (16)
P(1)–Pt–P(2)	177.7 (3)	CE(2)–W(2)–C(3)	113.5 (17)
P(1)–Pt–C(5)	97.6 (8)	CE(2)–W(2)–C(4)	122.0 (15)
P(2)–Pt–C(5)	82.1 (9)	CE(2)–W(2)–C(5)	116.1 (13)
W(1)–Au–Pt	59.7 (1)	CE(2)–W(2)–P(2)	114.6 (11)
W(1)–Au–P(3)	146.5 (2)	W(1)–P(1)–Pt	73.1 (3)
Pt–Au–P(3)	152.6 (2)	W(2)–P(2)–Pt	72.4 (3)
C(1)–W(1)–C(2)	82.9 (14)	W(1)–C(1)–O(1)	175 (3)
C(2)–W(1)–P(1)	88.8 (10)	W(1)–C(2)–O(2)	169 (3)
P(1)–W(1)–Au	77.9 (2)	W(2)–C(3)–O(3)	176 (4)
Au–W(1)–C(1)	71.2 (10)	W(2)–C(4)–O(4)	176 (3)
CE(1)–W(1)–C(1)	113.7 (16)	W(2)–C(5)–O(5)	150 (2)
CE(1)–W(1)–C(2)	115.7 (16)	Pt–C(5)–O(5)	124 (2)
CE(1)–W(1)–P(1)	117.0 (13)	Pt–C(5)–W(2)	86 (1)
CE(1)–W(1)–Au	109.8 (12)		

[a] CE(1) and CE(2) are the centroids of the C(6)···C(10) and C(23)···C(27) cyclopentadienyl rings, respectively.

Crystallographic Data Centre).

The structure of the $Cp(OC)_2W(\mu\text{-}AuPPh_3)(\mu\text{-}PPh_2)Pt$ moiety of **27** may be compared with that of $[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}AuPPh_3)Pt(CO)(PCy_2H)][PF_6]$ (**28**),[10] where the same two bridges support the W–Pt bond [of length 2.827 (2) Å], and are again almost perpendicular to one another [dihedral angle of 83.9 (1)°]. The W–P and Pt–P distances in the μ-PCy$_2$ bridge of **28**, 2.433 (5) and 2.303 (7) Å, respectively, are only slightly longer than in the μ-PPh$_2$ bridge of **27**, whereas the W–P–Pt angle remains practically unchanged [73.2 (2)° in **28**]. The Pt–Au and W–Au distances with the μ-AuPPh$_3$ bridge in **28** [2.763 (2) and 2.827 (2) Å] are also closely comparable to those found in **27**, even though the W–Au–P and Pt–Au–P angles [168.8 (2) and 128.6 (2)° in **28** and 146.5 (2) and 152.6 (2) in **27**, respectively] are in favor of a AuPPh$_3$ fragment being preferentially bound to the W atom and therefore in a semibridging situation in **28**. These results could indicate a greater Pt–Au interaction in **27** than in **28**, consistent with the observed $^2J[P(3)\text{–}Pt]$ coupling constant of 300 Hz for **27** and of 205 Hz for **28**.[10] However, it should be noted that the difference in character of the μ-AuPPh$_3$ bridge is more reflected by the values of the W–Au–P and Pt–Au–P angles than by those of the Au–Pt and Au–W distances, which are very similar in both complexes.

Concerning the bridging carbonyl in **27**, the W(2)–C(5) distance of 2.04 (3) Å is slightly longer than the other W–CO(terminal) distances [in the range 1.93 (3)–1.98 (4) Å], while the Pt–C(5) distance of 2.12 (3) Å is clearly longer than Pt–CO(terminal) distances [for example it is of 1.86 (2) Å in **28** and of 1.88 (1) Å in the Mo analogue of **24**[13]]. Also the O(5)–C(5)–W(2) and O(5)–C(5)–Pt angles of 150 (2) and 124 (2)° confirm the preferential bonding of the μ-CO group to the W atom.

The coordination geometry around both W atoms can be described as being of the four-legged piano stool type, as found in CpML$_4$ complexes, with two legs occupied by two terminal CO in a cis disposition, one by the P atom of the bridging phosphido ligand, and the other by the gold atom of the μ-AuPPh$_3$ group for W(1) or the carbon atom C(5) of μ-CO for W(2). The angles between the legs range from 71.1 (10) to 88.8 (10)° for W(1) and from 77.1 (16) to 79.3 (9)° for W(2), while the angles between the W–CE vector (CE is the centroid of the cyclopentadienyl ring) and the legs are in the range 109.8 (12)–117.0 (13)° for W(1) and 113.5 (17)–122.0 (15)° for W(2). A fifth leg opposite to each cyclopentadienyl ring is occupied by the platinum that connects the W moieties in a transoid manner.[10]

If the Pt–W bonds are ignored, the Pt atom displays a square-planar coordination involving the Au atom, the P(1) and P(2) atoms of the phosphido ligands, and the C(5) atom from the bridging carbonyl, these atoms deviating by –0.001 (2), 0.041 (9), 0.045 (10), and –0.30 (3) Å, respectively, from the mean plane passing through them, and the Pt atom is out of this plane by –0.002 (2) Å. The structural results are consistent with the presence of 18e W centers and a 16e Pt center, with the interactions in the W(1)–Au–Pt triangle resulting from two-electron, three-center (2e–3c) bonding.

Discussion

It is interesting that bimetallic complexes containing a terminal PPh$_2$H ligand could be isolated in the case of palladium (**8b**, **9b**, and **10b**) whereas when this ligand is coordinated to platinum in the corresponding m–Pt complexes, they proved too reactive to be isolated and formation of μ-PPh$_2$ bridges occurred.[13]

Reactions of dinuclear complexes with H$^+$ provide interesting probes of whether electrophilic addition occurs via charge or orbital control. The latter is often encountered,[14] and in general, electrophiles may interact with a dinuclear complex by adding to one metal center in a terminal manner or by bridging the metal–metal bond.[2c,9] Small energy differences are often sufficient to observe the corresponding isomerizations. The heterobimetallic complexes m–Pt **1–3** and m–Pd **7–12** present two main reactivity patterns. The first consists in the nucleophilic substitution of a phosphine ligand and has been observed in some cases (e.g. with CO).[5,10] A second kind of reactivity, also noted previously,[9,10] consists in the electrophilic attack to the metal–metal bond, as illustrated by the synthesis of the cationic complexes m–Pt **4–6** and m–Pd **13–18**. In this work, bridging situations were mostly encountered. As expected, protonation of the metal–metal bond of **1–3** results in a significant decrease (ca. 600–800 Hz) of the $^1J[(\mu\text{-}P)\text{–}Pt]$ coupling. With complexes m–Pt **1–3** and m–Pd **7a–12a**, it causes an increase of the $^1J(PH)$ values, particularly notable for the phosphine which is cis to the bridging phosphido group, whereas the $^2J[(P\text{–}(\mu\text{-}P)]$ value decreases for the cis but increases for the trans phosphine ligand. Also, ^{31}P NMR chemical shifts for the trans phosphine are generally larger than for the cis, but the reverse is true for their protonated derivatives m–Pt **4–6** and m–Pd **13a–18a**. This difference on protonation of the metal–metal bond may be traced back to the electronic factors that favor the cis isomer when a mixture of cis + trans $[Cp(OC)_2W(\mu\text{-}PCy_2)Pt(CO)(PCy_2H)]$ is protonated.[9] Rapid H/D exchange was observed between the bridging H of Mo–Pd **14a** and CH$_3$OD, but no exchange with the P–H bonds was evidenced after 1 week.

Reaction of m–Pd **7–9** with HCl occurred with combination of protonation and nucleophilic substitution, resulting in the formation of the neutral complexes **19a–21a**, respectively. Their chloride ligand occupies preferentially the position trans to the μ-PCy$_2$ bridge with respect to palladium. Since the most stable isomer of complexes $[Cp(OC)_2W(\mu\text{-}PCy_2)(\mu\text{-}H)Pt(CO)(PCy_2H)][BF_4]$ is that where the Pt-bound CO ligand is cis to the μ-PCy$_2$ bridge,[9] it would appear that in such systems the μ-H ligand favors the better π-acceptor/σ-donor ligand trans to it.[15] (In the neutral precursor $[Cp(OC)_2W(\mu\text{-}PCy_2)Pt(CO)(PCy_2H)]$ the major isomer has CO trans to the μ-PCy$_2$ bridge.[10]) Inter-

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(15) MO calculations are in progress to analyze these factors.

estingly, it has recently been suggested that in complexes of the type $[(OC)_4Mn(\mu\text{-}SiR_2)(\mu\text{-}H)Pt(PPh_3)_2]$, CO substitutes the PPh_3 ligand trans to the silylene bridge.[2d] No reaction was observed between W–Pd **9a** and MeI or $[(CH_3)_3O]BF_4$.

The isomeric W_2Pt complexes **25** and **26** show in the ^{1}H NMR hydride region a doublet of doublets respectively at –6.79 and –15.68 ppm, with Pt satellites (^1J(HPt) = 584 and 681 Hz, respectively) and, in the case of **25**, also W satellites, with ^1J(HW) = 46 Hz, a value similar to those found in the $W(\mu\text{-}H)(\mu\text{-}PR_2)M$ complexes **4** (M = Pt) and **15** and **21a** (M = Pd). Therefore, we suggest that the position of the hydride ligand is bridging in **25** and terminal in **26**. Both complexes show in the ^{1}H NMR spectrum two different resonances for the Cp groups and in the ^{31}P{^{1}H} NMR spectrum two different μ-PPh_2 groups, in agreement with their having a rigid structure on the NMR time scale. However, the solid-state structure of **25** may be different from that proposed on the basis of spectroscopic data for the solution. In fact, the ν(CO) absorptions (2026, 1942, and 1861 cm^{-1}) in KBr for **25** are significantly different from those found in CH_2Cl_2 (2046, 1962, and 1890 cm^{-1}) but very close to those found for **26** in KBr (2028, 1944, and 1863 cm^{-1}).

Reactivity studies were extended to electrophilic metal reagents such as $[AuPPh_3]^+$ or CuCl. With the former reagent, no reaction was observed with W–Pd **15a**, in contrast to W_2Pt **24**, which yielded the tetranuclear complex AuW_2Pt **27**. With CuCl, complex Mo–Pd **8b** formed an adduct whose structure was found to be solvent dependent (eq 5). Again, only small energy differences must be involved when a change is made from a terminal to a bridging position for the electrophile. The complex W–Pd **15a** adds CuCl, and not $[AuPPh_3]^+$, but the reaction product, analogous to Cu–Mo–Pd **23** (by ^{31}P{^{1}H} NMR), could not be isolated pure. The crystal structure of AuW_2Pt **27** showed that a major structural rearrangement concerning the phosphido bridges had occurred upon addition of the $AuPPh_3$ fragment. The ^{31}P{^{1}H} NMR resonances at 142.7, 128.3, and 85.5 ppm for **25**, **26**, and **27**, respectively, correspond to the μ-PPh_2 group least perturbed by the addition of the electrophile and compare with the value of 144.8 ppm found in the precursor complex W_2Pt **24**. The upfield resonance at ca. 25 ppm is tentatively assigned to the μ-PPh_2 spanning the same W–Pt bond as the CO group (^2J(PH) = 45 Hz for **25** and ca. 10 Hz for **26**), in agreement with the corresponding value of 16.1 ppm found in **27**. However, it would also be compatible with a neutral formulation with no Pt–W bond and a terminal W–Cl bond. Interestingly, no reaction was observed between $[(OC)_4Mn(\mu\text{-}PPh_2)Pt(CO)(\mu\text{-}PPh_2)Mn(CO)_4]$,[16] the Mn analogue of W_2Pt **24**, and HBF_4. Preliminary experiments between Mn–Pd **10a** and $HgCl_2$ have led to an adduct formulated as $[(OC_4)Mn(\mu\text{-}PCy_2)(\mu\text{-}HgCl)PdCl(PCy_2H)]$, which undergoes ligand disproportionation[17] with formation of $HgCl_2$ and $[\{(OC_4)Mn(\mu\text{-}PCy_2)PdCl(PCy_2H)\}_2(\mu_4\text{-}Hg)]$.

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; CH_2Cl_2 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. Unless otherwise stated, reagents were obtained from commercial sources and used as received. Elemental analyses (C and H) 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. IR data are given in cm^{-1}. The ^{1}H and ^{31}P NMR spectra were recorded at 200.13 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 ^{1}H and to external 85% H_3PO_4 in H_2O for ^{31}P NMR spectra; coupling constants are in Hz. The ^{1}H NMR resonances of Cy and Ph groups are not given. The second-order NMR spectra were interpreted with the help of the PANIC program running on a Bruker Aspect 2000 computer.

B. Syntheses. The complexes **1–3** and **7–12** were prepared according to methods reported previously.[4,5]

$[Cp(OC)_2W(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2][BF_4]$ (4). At –78 °C, a diethyl ether solution of HBF_4 (0.25 mmol) in CH_2Cl_2 (10 mL) was slowly added to **1** (0.300 g, 0.248 mmol) dissolved in CH_2Cl_2 (10 mL). The yellow solution was allowed to reach room temperature and evaporated to dryness. A yellow solid (0.196 g, 60.9%) is obtained after washing with hexane. It is soluble in CH_2Cl_2 and acetone and insoluble in hexane and can be recrystallized from diethyl ether. Anal. Calcd for $C_{55}H_{46}BF_4O_2P_3PtW$ (M_r = 1297.64): C, 50.90; H, 3.57. Found: C, 50.14; H, 3.72. IR (KBr): ν(CO) 1950 s, 1872 s. IR (CH_2Cl_2): ν(CO) 1964 s, 1890 s. ^{1}H NMR (CD_2Cl_2): δ 4.54 (s, 5 H, C_5H_5), –9.43 (ddd with Pt and W satellites, 1 H, μ-H, ^2J(HP) = 74.3, 20.2, and 18.1, ^1J(HPt) = 479.8, ^1J(HW) = 41.2). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 148.5 (dd with Pt and W satellites, 1 P, μ-PPh_2, ^2J(PP) = 218 and 10, ^1J(PPt) = 1785, ^1J(PW) = 208), 13.6 (A part of an ABX spin system with Pt satellites, 1 P, PPh_3 cis to PPh_2, ^2J(AB) = 23, ^2J(AX) = 218, ^1J(PPt) = 3931), 11.8 (B part of an ABX spin system with Pt satellites, 1 P, PPh_3 trans to PPh_2, ^2J(AB) = 23, ^2J(BX) = 218, ^1J(PPt) = 2479).

$[(OC)_4Mn(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2][BF_4]$ (5). Starting from 0.342 mmol of **2**, we followed a method of preparation similar to that of **4**. The light yellow product (0.286 g, 72.1%) is insoluble in toluene and soluble in CH_2Cl_2 and acetone. Anal. Calcd for $C_{52}H_{41}BF_4MnO_4P_3Pt$ (M_r = 1159.66): C, 53.85; H, 3.56. Found: C, 53.43; H, 3.72. IR (KBr): ν(CO) 2080 m, 2041 w, 1990 s, br, 1910 s. IR (CH_2Cl_2): ν(CO) 2083 m, 2050 w, 2015 m, 1996 s, 1984 sh, 1953 m, 1914 w. ^{1}H NMR (CD_2Cl_2): δ –11.94 (br d of pseudo t with Pt satellites, 1 H, μ-H, ^2J(HP) = 77.0 and ≈21, ^1J(HPt) = 494.3). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 157.6 (d br with Pt satellites, 1 P, μ-PPh_2, ^2J(PP) = 232, ^1J(PPt) = 1863), 23.0 (pseudo t with Pt satellites, 1 P, PPh_3 cis to PPh_2, ^2J(PP) ≈ 20, ^1J(PPt) = 3736, from ^{31}P NMR, ^2J(PH) = 75), 12.5 (dd with Pt satellites, 1 P, PPh_3 trans PPh_2, ^2J(PP) = 232 and 20, ^1J(PPt) = 2395).

$[(OC)_3Co(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2][BF_4]$ (6). Starting from 0.300 mmol of **3**, we followed a method of preparation similar to that of **4**. The orange-yellow product (0.266 g, 78%) is insoluble in toluene and soluble in CH_2Cl_2 or acetone. Anal. Calcd for $C_{51}H_{41}BCoF_4O_3P_3Pt$ (M_r = 1135.64): C, 53.94; H, 4.22. Found: C, 53.41 H, 3.97. IR (KBr): ν(CO) 2060 s, 1987 vs, br. IR (CH_2Cl_2): ν(CO) 2072 s, 2020 vs, 2000 vs. ^{1}H NMR (CD_2Cl_2): δ –9.16 (ddd br with Pt satellites, 1 H, μ-H, ^2J(HP) = 74.6, 26.8, and 14.2, ^1J(HPt) = 476.1). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 200.8 (d br with Pt satellites, 1 P, μ-PPh_2, ^2J(PP) = 264, ^1J(PPt) = 2085), 19.5 (pseudo t with Pt satellites, 1 P, PPh_3 cis to PPh_2, ^2J(PP) = 20, ^1J(PPt) = 3732), 13.5 (dd with Pt satellites, 1 P, PPh_3 trans to PPh_2, ^2J(PP) = 264 and 20, ^1J(PPt) = 2530).

$[Cp(OC)_2Cr(\mu\text{-}PCy_2)(\mu\text{-}H)Pd(PCy_2H)_2][BF_4]$ (13a). Following the method detailed below for **15a**, but starting from **7a** (0.333 mmol), we obtained 0.266 g (83.2%) of an orange solid. Anal. Calcd for $C_{43}H_{74}BCrF_4O_2P_3Pd$ (M_r = 961.19): C, 53.75; H, 7.76. Found: C, 53.63; H, 7.59. IR (KBr): ν(CO) 1939 vs, 1880 vs; ν(PH) 2310 w. IR (CH_2Cl_2): ν(CO) 1957 vs, 1899 vs. ^{1}H NMR (CD_2Cl_2): δ 4.86 (s, 5 H, Cp), 4.4 (dm, 2 H, PCy_2*H*), –11.46 (ddd, 1 H, μ-H, ^2J(HP) = 75.6, 35.6, and 10.2). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 297.3 (d, 1 P, μ-PCy_2, ^2J(PP) = 175), 11.5 (d, 1 P, PCy_2H cis to PCy_2, ^2J(PP) = 46, from ^{31}P NMR, ^1J(PH) = 334, ^2J(PH) = 75), 2.65 (dd, 1 P, PCy_2H trans to PCy_2, ^2J(PP) = 174 and 46, from ^{31}P NMR, ^1J(PH) = 314).

$[Cp(OC)_2Mo(\mu\text{-}PCy_2)(\mu\text{-}H)Pd(PCy_2H)_2][BF_4]$ (14a). Following the method described below for **15a**, but starting from **8a** (0.184 mmol), we obtained 0.144 g (77.9%) of a yellow solid. Anal. Calcd for $C_{43}H_{74}BF_4MoO_2P_3Pd$ (M_r = 1005.13): C, 51.38, H, 7.42. Found: C, 51.35; H, 7.55. IR (KBr): ν(CO) 1945 vs, 1872 vs. IR (CH_2Cl_2): ν(CO) 1967 vs, 1897 vs. ^{1}H NMR (CD_2Cl_2): δ 5.36 (s, 5 H, Cp), 4.4 (dm, 2 H, PCy_2*H*), –10.47 (ddd, 1 H, μ-H, ^2J(HP) = 76.1, 22.3, and 13.1). ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 269.2 (d, 1 P, μ-PCy_2, ^2J(PP) = 185), 9.7 (d, 1 P, PCy_2H cis to PCy_2, ^2J(PP) = 46, from ^{31}P NMR, ^1J(PH) = 337, ^2J(PH) = 72), 2.2 (dd, 1 P, PCy_2H trans to PCy_2, ^2J(PP) = 185 and 46, from ^{31}P NMR, ^1J(PH) = 319).

Dissolution of **14a** in CD_3OD and evaporation to dryness led to isolation of the deuteride complex $[Cp(OC)_2Mo(\mu\text{-}PCy_2)(\mu\text{-}D)Pd(PCy_2H)_2][BF_4]$. No H/D exchange involving the P–H protons was observed (^{31}P NMR) in CH_2Cl_2/C_6D_6 after 1 week at room temperature. ^{31}P{^{1}H} NMR (CH_2Cl_2/C_6D_6): δ 269.2 (d br, 1 P, μ-PCy_2, J(PP) = 185), 9.5 (d of 1:1:1 triplet, 1 P, PCy_2H cis to PCy_2, ^2J(PP) = 46, ^2J(PD)

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= 7), 2.2 (dd of 1:1:1 triplet, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(PP) = 185 and 46, ^2J(PD ≈ 4).

[Cp(OC)$_2$Mo(μ-PPh$_2$)(μ-H)Pd(PPh$_2$H)$_2$][BF$_4$] (14b). Starting from **8b**, we obtained similarly to **15a** a product that was only identified spectroscopically. IR (KBr): ν(CO) 1967 vs, 1888 vs. IR (CH$_2$Cl$_2$): ν(CO) 1972 vs, 1906 vs. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.66 (s, 5 H, Cp), −8.95 (ddd, 1 H, μ-H, ^2J(HP) = 79.2, 22.4, and 13.6). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 229.5 (d, 1 P, μ-PPh$_2$, ^2J(PP) = 200), −0.4 (dd, 1 P, PPh$_2$H trans to PPh$_2$, ^2J(PP) = 200 and 49, from ^{31}P NMR, ^1J(PH) = 385, ^2J(PH) = 74), −5.6 (d, 1 P, PPh$_2$H cis to PPh$_2$, ^2J(PP) = 49, from ^{31}P NMR, ^1J(PH) = 359).

[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pd(PCy$_2$H)$_2$][BF$_4$] (15a). At −78 °C, a diethyl ether solution of HBF$_4$ (0.25 mmol) in dichloromethane (10 mL) was slowly added to **9a** (0.250 g, 0.249 mmol) dissolved in dichloromethane (20 mL). The yellow solution was allowed to reach room temperature and evaporated. The resulting yellow oil was washed with hexane until a solid was obtained (0.234 g, 86.0%). This yellow product is soluble in dichloromethane and acetone and insoluble in hexane, and it can be recrystallized from diethyl ether. Anal. Calcd for C$_{43}$H$_{74}$BF$_4$O$_2$P$_3$PdW (M_r = 1093.04): C, 47.25; H, 6.82. Found: C, 46.81; H, 6.73. IR (KBr): ν(CO) 1948 vs, 1873 vs; ν(PH) 2305 w. IR (CH$_2$Cl$_2$): ν(CO) 1960 vs, 1887 vs. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.46 (s, 5 H, Cp), 4.45 (dm, 1 H, PCy$_2$*H*), 4.33 (dm, 1 H, PCy$_2$*H*), −10.28 (ddd with W satellites, 1 H, μ-H, ^2J(HP) = 68.7, 22.4 and 12.8, ^1J(HW) = 23.8). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 228.1 (dd with Pt satellites, 1 P, μ-PCy$_2$, ^2J(PP) = 174 and 14, ^1J(PW) = 267), 5.6 (dd, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(PP) = 49 and 14, from ^{31}P NMR, ^1J(PH) = 315), 3.1 (dd, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(PP) = 174 and 49, from ^{31}P NMR, ^1J(PH) = 309).

[Cp(OC)$_2$W(μ-PPh$_2$)(μ-H)Pd(PPh$_2$H)$_2$][BF$_4$] (15b). Starting from **9b** (0.243 mmol), we followed the method described for **15a**. We obtained a yellow product insoluble in hexane (0.124 g, 48.3%). Anal. Calcd for C$_{43}$H$_{38}$BF$_4$O$_2$P$_3$PdW (M_r = 1056.76): C, 48.87; H, 3.62. Found: C, 48.62; H, 3.81. IR (KBr): ν(CO) 1949 vs, 1875 vs. IR (CH$_2$Cl$_2$): ν(CO) 1970 vs, 1901 vs. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.77 (s, 5 H, Cp), 6.27 (dm, 1 H, PPh$_2$*H*), 6.12 (dm, 1 H, PPh$_2$*H*), −8.61 (ddd with W satellites, 1 H, μ-H, ^2J(HP) = 69.8, 22.5, and 13.0, ^1J(HW) = 44.1). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 193.5 (dd, 1 P, PPh$_2$, ^2J(PP) = 197 and 14, ^1J(PW) = 237), −3.8 (A part of an ABX spin system, 1 P, PPh$_2$H cis to PPh$_2$, ^2J(AB) = 47, ^2J(AX) = 14, from ^{31}P NMR, ^1J(PH) = 373), −4.9 (B part of an ABX spin system, 1 P, PPh$_2$H trans to PPh$_2$, ^2J(AB) = 47, ^2J(BX) = 197, from ^{31}P NMR, ^1J(PH) = 360).

[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)Pd(PCy$_2$H)$_2$][BPh$_4$] (15c). Addition of a stoichiometric amount of Na[BPh$_4$] to a solution of **15a** in THF, filtration of the precipitated Na[BF$_4$], and recrystallization from CH$_2$Cl$_2$/hexane afforded the product. Anal. Calcd for C$_{67}$H$_{93}$BO$_2$P$_3$PdW (M_r = 1325.48): C, 60.71; H, 7.14. Found: C, 60.62; H, 7.11. IR and ^{1}H and ^{31}P NMR data are similar to those for **15a**.

[(OC)$_4$Mn(μ-PCy$_2$)(μ-H)Pd(PCy$_2$H)$_2$][BF$_4$] (16a). Starting from **10a** (0.120 mmol), we followed the method described for **15a**. We obtained a light yellow-white product, insoluble in hexane (0.092 g, 80%). Anal. Calcd for C$_{40}$H$_{69}$BF$_4$MnO$_4$P$_3$Pd (M_r = 955.06): C, 50.30; H, 7.28. Found: C, 50.50; H, 7.26. IR (KBr): ν(CO) 2060 m, 1972 s br. IR (CH$_2$Cl$_2$): ν(CO) 2075 m, 1986 s. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.83 (dm, 1 H, PCy$_2$*H* trans to PCy$_2$, ^1J(HP) = 332), 4.35 (dm, 1 H, PCy$_2$*H* cis to PCy$_2$, ^1J(HP) = 355), −12.45 (ddd br, 1 H, μ-H, ^2J(HP) = 75.5, 19.1, and 17.2). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 240.1 (d br, 1 P, μ-PCy$_2$, ^2J(PP) = 206), 7.3 (dd, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(PP) = 42 and 11, from ^{31}P NMR, ^1J(PH) = 348, ^2J(PH) = 67), 3.1 (dd, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(PP) = 206 and 11, from ^{31}P NMR, ^1J(PH) = 338).

[(OC)$_4$Mn(μ-PPh$_2$)(μ-H)Pd(PPh$_2$H)$_2$][BF$_4$] (16b). Starting from **10b**, we obtained similarly a yellow solid. Anal. Calcd for C$_{40}$H$_{33}$BF$_4$MnO$_4$P$_3$Pd (M_r = 918.77): C, 52.29, H, 3.62. Found: C, 52.66; H, 3.89. IR (Nujol/polyethylene): ν(CO) 2079 m, 2010 sh, 1975 vs br. IR (CH$_2$Cl$_2$): ν(CO) 2082 m, 2015 m, 1995 s. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.60 (dm, 1 H, PPh$_2$*H* cis to PCy$_2$, ^1J(HP) = 383), 5.93 (dm, 1 H, PPh$_2$*H* trans to PCy$_2$, ^1J(HP) = 364), −11.6 (ddd br, 1 H, μ-H, ^2J(HP) = 82.0, 21.4, and 14.2). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 196.4 (d br, 1 P, PPh$_2$, ^2J(PP) = 213), 0.6 (d, 1 P, PPh$_2$H cis to PCy$_2$, ^2J(PP) = 47, from ^{31}P NMR, ^1J(PH) = 392), −5.0 (dd, 1 P, PPh$_2$H trans to PPh$_2$, ^2J(PP) = 213 and 47, from ^{31}P NMR, ^1J(PH) = 367).

[Cp(OC)Fe(μ-PCy$_2$)(μ-H)Pd(PCy$_2$H)$_2$][BF$_4$] (17a). Spectroscopically pure **17a** was isolated from the reaction of **11a** with HBF$_4$ in diethyl ether (see **15a**) by using chromatography on a 18 × 4.0 cm column of florisil (60–100 mesh). The product was extracted with THF. IR (KBr): ν(CO) 1934 m. IR (CH$_2$Cl$_2$): ν(CO) 1948 vs. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.86 (s, 5 H, Cp), 4.5 (dm, 2 H, PCy$_2$*H*), −11.65 (ddd, 1 H, μ-H, ^2J(HP) = 72, 27, and 24). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 263.45 (dd, 1 P, μ-PCy$_2$, ^2J(PP) = 212 and 33), 6.8 (A part of an ABX spin system, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(AX) = 33, ^2J(AB) = 50), 5.7 (B part of an ABX spin system, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(BX) = 212, ^2J(AB) = 50).

[(OC)$_3$Co(μ-PCy$_2$)(μ-H)Pd(PCy$_2$H)$_2$][BF$_4$] (18a). Starting from **12a** (0.376 mmol), we obtained (see preparation of **15a**) a yellow product (0.250 g, 71.4%). Anal. Calcd for C$_{39}$H$_{69}$BCoF$_4$O$_3$P$_3$Pd (M_r = 931.04): C, 50.31; H, 7.47. Found: C, 50.63; H, 7.49. IR (Nujol/polyethylene): ν(CO) 2061 s, 1983 vs. IR (CH$_2$Cl$_2$): ν(CO) 2063 s, 2003 vs. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.71 (dm, 1 H, PCy$_2$*H*, ^1J(HP) = 352), 4.37 (dm, 1 H, PCy$_2$*H*, ^1J(HP) = 331), −13.34 (ddd br, 1 H, μ-H, ^2J(HP) = 69.0, 22.4, and 9.5). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 310.6 (d br, 1 P, μ-PCy$_2$, ^2J(PP) = 234), 6.6 (A part of an ABX spin system, 1 P, PCy$_2$H trans to PCy$_2$, ^2J(AX) = 234, ^2J(AB) = 42, from ^{31}P NMR, ^1J(PH) = 319), 5.2 (B part of an ABX spin system, 1 P, PCy$_2$H cis to PCy$_2$, ^2J(AB) = 42, from ^{31}P NMR, ^1J(PH) = 331).

[Cp(OC)$_2$Cr(μ-PCy$_2$)(μ-H)PdCl(PCy$_2$H)] (19a). Starting from **7a** (0.401 mmol), we obtained (see preparation of **21**) an orange product (0.120 g, 42.1%) (mp 102 °C dec) which is soluble in all common solvents. It decomposes rapidly when exposed to air. Anal. Calcd for C$_{31}$H$_{51}$ClCrO$_2$P$_2$Pd (M_r = 711.55): C, 52.32; H, 7.22. Found: C, 52.20; H, 7.46. IR (KBr): ν(CO) 1940 vs, 1870 vs; ν(PH) 2300 w. IR (CH$_2$Cl$_2$): ν(CO) 1942 vs, 1878 vs. ^{1}H NMR (C$_6$D$_6$): δ 4.76 (s, 5 H, Cp), 3.96 (dm, 2 H, PCy$_2$*H*), −10.48 (dd, 1 H, μ-H, ^2J(HP) = 69.2 and 46.2). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 294.2 (s, 1 P, μ-PCy$_2$, from ^{31}P NMR, ^2J(PH) = 39), 14.95 (s, 1 P, PCy$_2$H, from ^{31}P NMR, ^1J(PH) = 317, ^2J(PH) = 65).

[Cp(OC)$_2$Mo(μ-PCy$_2$)(μ-H)PdCl(PCy$_2$H)] (20a). Starting from **8a** (0.320 mmol), we obtained (see preparation of **21a**) a yellow product (0.060 g, 25%) (mp 104 °C dec) which is soluble in all common solvents. Anal. Calcd for C$_{31}$H$_{51}$ClMoO$_2$P$_2$Pd (M_r = 755.49): C, 49.28; H, 6.80. Found: C, 49.50; H, 6.93. IR (KBr): ν(CO) 1950 vs, 1870 vs; ν(PH) 2310 w. IR (CH$_2$Cl$_2$): ν(CO) 1952 vs, 1877 vs. ^{1}H NMR (C$_6$D$_6$): δ 5.14 (s, 5 H, Cp), 3.90 (dm, 1 H, PCy$_2$*H*, ^1J(HP) = 318), −9.60 (dd, 1 H, μ-H, ^2J(HP) = 72.8 and 30.5). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 265.2 (s, 1 P, μ-PCy$_2$), 14.05 (s, 1 P, PCy$_2$H, from ^{31}P NMR, ^1J(PH) = 320, ^2J(PH) = 71).

Reaction of 8b with HCl. When the procedure described for **21a** was used by starting from **8b**, only the latter was recovered. The solution contains a hydrido complex (^{1}H NMR, IR) in which the phosphine trans to μ-P undergoes rapid exchange, similar to that observed for **10b** with CO and free PPh$_2$H,[5] that makes the phosphine ligands become equivalent on the NMR time scale at room temperature. Elimination of HCl by evaporation of the solution to dryness or washing with water regenerates **8b**. IR (CH$_2$Cl$_2$): ν(CO) 1966 vs, 1892 vs. ^{1}H NMR (C$_7$D$_8$, 25 °C): δ 4.59 (s br, 5 H, Cp), −8.72 (d br, 1 H, μ-H, J(HP) = 24.5). ^{1}H NMR (C$_7$D$_8$, −60 °C): δ 4.69 (s, br, 5 H, Cp), −8.70 (dd br, 1 H, μ-H, ^2J(HP) = 72 and 22). ^{31}P{^{1}H} NMR (C$_7$H$_8$/C$_7$D$_8$): δ 225.7 (s, 1 P, μ-PPh$_2$), 0.48 (s, 2 P, PPh$_2$H, from ^{31}P NMR, ^1J(PH) = 332).

[Cp(OC)$_2$W(μ-PCy$_2$)(μ-H)PdCl(PCy$_2$H)] (21a). At −78 °C, 5 mL of a saturated solution of HCl in acetone was slowly added to **9a** (0.406 g, 0.404 mmol) dissolved in acetone (20 mL). The light yellow solution was allowed to reach room temperature and evaporated to dryness. The resulting yellow oil was extracted with hexane, and from the solution, an orange-yellow solid was obtained (0.162 g, 47.5%) which is soluble in all common solvents (mp 115 °C dec). Anal. Calcd for C$_{31}$H$_{51}$ClO$_2$P$_2$PdW (M_r = 843.40): C, 44.14; H, 6.09. Found: C, 44.42; H, 6.14. IR (KBr): ν(CO) 1943 vs, 1868 vs; ν(PH) 2300 w. IR (CH$_2$Cl$_2$): ν(CO) 1945 vs, 1870 vs. ^{1}H NMR (C$_6$D$_6$): δ 5.16 (s, 5 H, Cp), 3.93 (dm, 1 H, PCy$_2$*H*, ^1J(HP) = 312.3), −9.44 (dd with W satellites, 1 H, μ-H, ^2J(HP) = 66.9 and 30.6, ^1J(HW) = 50.0). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/C$_6$D$_6$): δ 225.6 (s with W satellites, 1 P, μ-PCy$_2$, ^1J(PW) = 212), 13.7 (s, 1 P, PCy$_2$H, from ^{31}P NMR, ^1J(PH) = 314, ^2J(PH) = 65).

[Cp(OC)$_2$Mo(CuCl)(μ-PPh$_2$)Pd(PPh$_2$H)$_2$] (22). *The reaction of* **8b** (0.396 g, 0.450 mmol) with CuCl (0.050 g, 0.500 mmol) was carried out in 25 mL of CH$_2$Cl$_2$. The red solution was stirred for 2 h, after which time CuCl had dissolved and the solution became dark yellow. The solution was filtered through Celite and evaporated to dryness. Two isomers were identified, depending on the solvent used.

Isomer **22A** was obtained as a yellow solid by recrystallization of the residue from acetone. Anal. Calcd for C$_{43}$H$_{37}$ClCuMoO$_2$P$_3$Pd (M_r = 980.03): C, 52.70; H, 3.81. Found: C, 52.49; H, 3.96. IR (KBr): ν(CO) 1880 s, 1801 s. IR (CH$_2$Cl$_2$): ν(CO) 1882 s, 1805 s. IR (acetone): ν(CO) 1890 s, 1808 s. ^{1}H NMR (CD$_2$Cl$_2$): δ 4.55 (s, 5 H, Cp), 6.5 (dm, 2 H, PPh$_2$*H*). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): δ 198.9 (v br, 1 P, μ-PPh$_2$), 0.63 (dd, 1 P, PPh$_2$H trans to PPh$_2$, ^2J(PP) = 182 and 31, from ^{31}P NMR, ^1J(PH) = 342), −10.7 (pseudo t, 1 P, PPh$_2$H cis to PPh$_2$,

Table II. Summary of Crystal Data and Data Collection for **27**·2THF

formula: $C_{57}H_{45}AuF_6O_5P_4PtW_2\cdot 2C_4H_8O$	fw: 1951.84
a = 30.867 (8) Å	space group: monoclinic $P2_1/a$
b = 18.855 (4) Å	T = 25 °C
c = 11.168 (3) Å	λ = 0.71073 Å
β = 90.46 (1) deg	ρ_{calcd} = 1.995 g/cm^3
V = 6500 (3) Å^3	μ(Mo Kα) = 81.84 cm^{-1}
Z = 4	$R(F_o)$ = 0.0684[a]
	$R_w(F_o)$ = 0.0877[a]

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

from ^{31}P NMR, ^1J(PH) = 342). ^{31}P{^{1}H} NMR (acetone/acetone-d_8): δ 206.7 (v br, 1 P, μ-PPh$_2$), 3.7 (dd, 1 P, PPh$_2$H trans to PPh$_2$, ^2J(PP) = 176 and 25), −6.4 (pseudo t, 1 P, PPh$_2$H cis to PPh$_2$, ^2J(PP) ≈ 25).

Isomer **22A** transformed in isomer **22B** upon standing in toluene. The initial yellow solution became red after a few minutes. Isomer **22B** could be obtained as a red solid by concentration of the toluene solution. It crystallizes with half a molecule of solvent (mp 98 °C). Anal. Calcd for $C_{43}H_{37}ClCuMoO_2P_3Pd\cdot{}^1/_2C_7H_8$ (M_r = 1026.10): C, 54.43; H, 4.03. Found: C, 54.29; H, 4.07. IR (KBr): ν(CO) 1884 s, 1825 s, 1790 s. Isomer **22B** is rapidly converted back to isomer **22a** when dissolved in CH$_2$Cl$_2$ (^{31}P{^{1}H} NMR evidence). Furthermore, we observed in toluene an equilibrium between **22B** (≈60%) and a species formulated as [Cp(OC)$_2$Mo{μ-Cu(PPh$_2$H)}(μ-PPh$_2$)PdCl] (**23**) (≈40%) on the basis of its spectroscopic data. IR (C$_7$H$_8$): ν(CO) 1900 vs, 1802 vs (for **22**) and 1939 s, 1860 s (for **23**). ^{1}H NMR (C$_6$D$_6$): δ 4.56 (v br, 5 H, Cp). ^{31}P{^{1}H} NMR (C$_7$H$_8$/C$_6$D$_6$): δ 200–225 (v br, 1 P, μ-PPh$_2$ of **22** and **23**), 7.4 (d br, 1 P, PPh$_2$H of **23**, ^2J(PP) = 69), −1.7 (d br, 1 P, PPh$_2$H trans to PPh$_2$ of **22**, ^2J(PP) = 186), −11.5 (s br, 1 P, PPh$_2$H cis to PPh$_2$ of **22**), −34.6 (s br, PPh$_2$H bound to Cu of **23**).

Reaction of 15a with CuCl. The reaction of **15a** (0.400 mmol) with CuCl (0.400 mmol) was carried out in 25 mL of CH$_2$Cl$_2$. The solution contained a complex formulated as [Cp(OC)$_2$W(μ-PCy$_2$){μ-Cu(PCy$_2$H)}PdCl(PCy$_2$H)] (spectroscopic evidence). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): δ 197.0 (v br, 1 P, μ-PCy$_2$), 0.71 (d br, 1 P, PCy$_2$H, ^2J(PP) = 72), −15.3 (s br, PCy$_2$H bound to Cu).

[{Cp(OC)$_2$W(μ-PPh$_2$)}$_2$Pt(CO)]·C$_7$H$_8$ (24). To a solution of Na[W(CO)$_3$Cp]·2DME (0.500 g, 0.932 mmol) in THF (20 mL) was added at −78 °C PPh$_2$Cl (0.932 mmol) in THF (50 mL), and after the mixture was stirred for 0.25 h, [Pt(C$_2$H$_4$)$_2$(PPh$_3$)] (0.239 g, 0.466 mmol) was added. The mixture was allowed to reach room temperature (1 h), and the resulting red solution was evaporated to dryness. The residue was extracted with 2 × 15 mL of toluene. After concentration of the solution to 2–3 mL and addition of 40 mL of hexane, 0.470 g (78%) of the orange-red product was precipitated. The solid was dried in vacuo and characterized as **24** solvated by one molecule of toluene (mp >260 °C). Analytical and spectroscopic details have been reported elsewhere.[4]

[{Cp(OC)$_2$W(μ-PPh$_2$)}{Cp(OC)$_2$W(μ-H)(μ-PPh$_2$)}Pt(CO)][BF$_4$] (25). A diethyl ether solution of HBF$_4$ (0.045 mmol) was added at −78 °C to a solution of **24** (0.054 g, 0.045 mmol) in CH$_2$Cl$_2$ (20 mL). The mixture was allowed to reach room temperature (1 h), and the resulting solution was evaporated to dryness. The residue was dissolved in acetone (2 mL), and diethyl ether (25 mL) was slowly added to the stirred solution. The orange precipitate (0.047 g, 81%) was filtered out and dried in vacuo (mp 150 °C dec). The product is insoluble in diethyl ether and hexane. Anal. Calcd for $C_{39}H_{31}BF_4O_5P_2PtW_2$ (M_r = 1291.22): C, 36.27; H, 2.42. Found: C, 37.1; H, 2.81. IR (KBr): ν(CO) 2026 m,

Table III. Fractional Atomic Coordinates (×10^4) with Esd's in Parentheses

atom	x/a	y/b	z/c
Au	−1224 (1)	3174 (1)	397 (1)
Pt	−781 (1)	1847 (1)	581 (1)
W(1)	−938 (1)	2501 (1)	−1620 (1)
W(2)	−538 (1)	1033 (1)	2608 (1)
P(1)	−1349 (3)	1585 (4)	−661 (8)
P(2)	−190 (3)	2110 (4)	1767 (9)
P(3)	−1640 (3)	4069 (4)	1160 (8)
P(4)	−1249 (4)	8257 (7)	4216 (12)
O(1)	−157 (8)	3397 (13)	−572 (27)
O(2)	−220 (9)	1423 (14)	−2295 (37)
O(3)	−1458 (10)	348 (15)	2268 (30)
O(4)	−1126 (10)	2185 (14)	3670 (29)
O(5)	−479 (6)	401 (10)	50 (20)
F(1)	−1417 (25)	9016 (42)	4696 (67)
F(2)	−1143 (22)	8683 (31)	2978 (61)
F(3)	−1543 (25)	7850 (38)	3225 (68)
F(4)	−1019 (22)	7614 (36)	3984 (61)
F(5)	−875 (22)	8490 (34)	5064 (59)
F(6)	−1585 (27)	8048 (43)	5147 (79)
C(1)	−452 (12)	3052 (17)	−915 (33)
C(2)	−488 (11)	1815 (17)	−1920 (30)
C(3)	−1113 (16)	630 (24)	2379 (42)
C(4)	−903 (11)	1784 (17)	3293 (32)
C(5)	−551 (10)	798 (15)	828 (29)
C(6)	−862 (14)	2803 (21)	−3663 (39)
C(7)	−1277 (14)	2375 (21)	−3463 (38)
C(8)	−1543 (16)	2747 (22)	−2750 (42)
C(9)	−1365 (15)	3419 (24)	−2407 (43)
C(10)	−964 (16)	3413 (25)	−3065 (43)
C(11)	−1898 (10)	1710 (14)	−42 (27)
C(12)	−1967 (12)	1961 (17)	1081 (33)
C(13)	−2358 (13)	2112 (19)	1466 (39)
C(14)	−2700 (16)	2034 (22)	803 (42)
C(15)	−2663 (15)	1760 (22)	−448 (42)
C(16)	−2238 (13)	1619 (18)	−836 (37)
C(17)	−1418 (12)	657 (17)	−1265 (33)
C(18)	−1203 (13)	508 (20)	−2277 (36)
C(19)	−1211 (13)	−198 (20)	−2684 (39)
C(20)	−1430 (13)	−688 (22)	−2050 (38)
C(21)	−1645 (14)	−560 (22)	−1072 (40)
C(22)	−1601 (11)	187 (17)	−672 (33)
C(23)	−469 (13)	309 (18)	4191 (36)
C(24)	−175 (13)	885 (20)	4380 (37)
C(25)	160 (10)	812 (15)	3473 (28)
C(26)	57 (12)	261 (18)	2781 (34)
C(27)	−330 (12)	−76 (18)	3267 (33)
C(28)	−181 (11)	2843 (17)	2892 (31)
C(29)	61 (13)	2796 (19)	3812 (35)
C(30)	126 (16)	3311 (23)	4724 (44)
C(31)	−141 (16)	3884 (25)	4557 (46)
C(32)	−397 (17)	3993 (26)	3513 (46)
C(33)	−403 (11)	3460 (16)	2662 (32)
C(34)	343 (11)	2075 (17)	1034 (33)
C(35)	642 (14)	2548 (22)	1307 (40)
C(36)	1005 (18)	2549 (29)	488 (49)
C(37)	1099 (12)	2052 (18)	−283 (35)
C(38)	816 (15)	1503 (25)	−258 (44)
C(39)	444 (18)	1538 (27)	349 (47)
C(40)	−2043 (10)	4269 (15)	27 (28)
C(41)	−2256 (11)	3697 (16)	−432 (29)
C(42)	−2610 (15)	3750 (22)	−1415 (42)
C(43)	−2633 (15)	4449 (22)	−1789 (41)
C(44)	−2429 (13)	5002 (21)	−1364 (38)
C(45)	−2122 (12)	4897 (18)	−407 (33)
C(46)	−1349 (12)	4901 (17)	1477 (34)
C(47)	−957 (18)	5016 (27)	893 (50)
C(48)	−712 (25)	5619 (32)	1104 (61)
C(49)	−906 (16)	6102 (26)	1920 (44)
C(50)	−1329 (18)	6063 (28)	2439 (50)
C(51)	−1510 (15)	5432 (22)	2182 (41)
C(52)	−1915 (10)	3941 (15)	2536 (28)
C(53)	−2353 (15)	3921 (22)	2641 (45)
C(54)	−2595 (16)	3809 (21)	3651 (42)
C(55)	−2359 (13)	3618 (19)	4649 (37)
C(56)	−1944 (21)	3626 (28)	4572 (60)
C(57)	−1704 (16)	3696 (23)	3465 (44)
C(58)	−3699 (34)	903 (54)	2609 (98)
C(59)	−3922 (41)	345 (65)	2300 (111)
C(60)	−4176 (31)	152 (43)	3571 (96)
C(61)	−3929 (39)	226 (53)	4460 (100)
C(62)	−3579 (51)	566 (80)	3796 (150)
C(63)	2578 (36)	3273 (51)	5853 (103)
C(64)	2960 (28)	3614 (89)	5247 (147)
C(65)	2814 (62)	4364 (86)	4934 (149)
C(66)	2456 (73)	4544 (52)	5803 (202)
C(67)	2270 (38)	3854 (87)	6222 (153)
C(68)	2464 (44)	3439 (71)	4509 (110)
C(69)	2845 (51)	3830 (88)	4005 (93)
C(70)	3099 (33)	4117 (62)	5115 (125)
C(71)	2901 (42)	3833 (68)	6280 (91)

1942 s, 1861 s. IR (CH_2Cl_2): ν(CO) 2046 m, 1963 vs, 1890 s. ^{1}H NMR (CD_2Cl_2): δ 5.94 (s, 5 H, Cp), 5.07 (s, 5 H, Cp), −6.79 (dd with Pt and W satellites, 1 H, μ-H, ^2J(HP) = 45.8 and 19.8, ^1J(HPt) = 583.8, ^1J(HW) = 45.8). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 142.7 (s with Pt and W satellites, 1 P, μ-PPh_2 opposite to μ-H, ^1J(PPt) = 2980, ^1J(PW) = 222), 25.1 (s with Pt and W satellites, 1 P, μ-PPh_2 opposite to μ-CO, ^1J(PPt) = 3019, ^1J(PW) = 136, from ^{31}P NMR, ^2J(PH) = 45).

[{Cp(OC)$_2$W(μ-PPh$_2$)}$_2$Pt(H)(CO)][Cl] (26). HCl was slowly bubbled through a solution of **24** (0.075 g, 0.064 mmol) in CH_2Cl_2 (20 mL) until the red solution became orange. After solvent evaporation, the residue was dissolved in diethyl ether and the solution filtered and evaporated to dryness. The orange product **26** precipitated and was dried in vacuo. Anal. Calcd for $C_{39}H_{31}ClO_5P_2PtW_2$ (M_r = 1239.87): C, 37.78; H, 2.52. Found: C, 38.60; H, 2.87. IR (KBr): ν(CO) 2026 m, 1945 s, 1860 s. IR (CH_2Cl_2): ν(CO) 2028 m, 1944 vs, 1863 s. ^{1}H NMR (CD_2Cl_2): δ 5.83 (s, 5 H, Cp), 4.61 (s, 5 H, Cp), −15.68 (dd with Pt satellites, 1 H, H, ^2J(HP) = 15.7 and 8.0, ^1J(HPt) = 681.2). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 128.3 (s with Pt and W satellites, 1 P, μ-PPh_2 opposite to H, ^1J(PPt) = 2868, ^1J(PW) = 207), 24.2 (s with Pt and W satellites, 1 P, μ-PPh_2 opposite to μ-CO, ^1J(PPt) = 4345, ^1J(PW) = 272).

[{Cp(OC)$_2$W(μ-CO)(μ-PPh$_2$)}{Cp(OC)$_2$W(μ-AuPPh$_3$)(μ-PPh$_2$)}Pt]-[PF$_6$] (27). Solid $TlPF_6$ (0.045 g, 0.128 mmol) was added to a stirred THF solution (10 mL) of AuCl(PPh_3) (0.064 g, 0.128 mmol). Then, **24** (0.154 g, 0.128 mmol) in THF (10 mL) was added. The red solution was evaporated to dryness in vacuo. The residue was extracted with 20 mL of CH_2Cl_2, and the solution was separated from the precipitated TlCl by filtration through a Celite-padded glass frit (4.0 × 2.5 cm). Concentration to 2 mL and addition of 10 mL of diethyl ether precipitated a red solid (0.150 g, 64.8%), which can be recrystallized from CH_2Cl_2/diethyl ether. Anal. Calcd for $C_{57}H_{45}AuF_6O_5P_4PtW_2$ (M_r = 1807.63): C, 37.87; H, 2.50. Found: C, 38.58; H, 2.56. IR (KBr): ν(CO) 2020 m, 1945 vs, 1895 vs. IR (CH_2Cl_2): ν(CO) 2023 m, 1971 sh, 1949 vs, 1898 vs. ^{1}H NMR (CD_2Cl_2): δ 5.40 (s, 5 H, Cp), 5.29 (d, 5 H, Cp, ^3J(HP) = 0.7). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 85.5 (dd with Pt and W satellites, μ-PPh_2 opposite to Au, ^2J(PP) = 200, ^3J(PP) = 20, ^1J(PPt) = 1939, ^1J(PW) = 142), 55.3 (d with Pt satellites, PPh_3, ^3J(PP) = 20, ^2J(PPt) = 300), 16.1 (d with Pt and W satellites, μ-PPh_2 opposite to μ-CO, ^2J(PP) = 200, ^1J(PPt) = 2149, ^1J(PW) = 131), −143.5 (sept, PF_6).

Reactions of 10a with HgCl$_2$. In a preliminary experiment, solid $HgCl_2$ (0.200 mmol) was added to a stirred solution (20 mL) of **10a** (0.200 mmol) in CH_2Cl_2 (20 mL). A yellow solution was obtained that contained a complex formulated as *cis*-[(OC)$_4$Mn(μ-PCy$_2$)(μ-HgCl)-PdCl(PCy$_2$H)] (spectroscopic evidence). This solution evolved with precipitation of $HgCl_2$ and likely formation of the "bow-tie" complex [{(OC)$_4$Mn(μ-PCy$_2$)PdCl(PCy$_2$H)}$_2$(μ_4-Hg)]. Spectroscopic data for *cis*-[(OC)$_4$Mn(μ-PCy$_2$)(μ-HgCl)PdCl(PCy$_2$H)] are as follows. IR (CH_2Cl_2): ν(CO) 2052 m, 1988 sh, 1971 vs. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 255.4 (s with Hg satellites, μ-PCy_2, ^2J(PHg) = 154), 21.6 (s with Hg satellites, PCy_2H, ^2J(PHg) = 1298, from ^{31}P NMR, ^1J(PH) = 329). Spectroscopic data for [{(OC)$_4$Mn(μ-PCy$_2$)PdCl(PCy$_2$H)}$_2$(μ_4-Hg)]: IR (CH_2Cl_2) ν(CO): 2052 m, 2037 m, 1992 s, 1957 vs. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 246.9 (s with Hg satellites, μ-PCy_2, ^2J(PHg) = 146), 25.9 (s with Hg satellites, PCy_2H, ^2J(PHg) = 754, from ^{31}P NMR: ^1J(PH) = 319).

C. X-ray Crystal Structure Determination of [{Cp(OC)$_2$-W(μ-CO)(μ-PPh$_2$)}{Cp(OC)$_2$W(μ-AuPPh$_3$)(μ-PPh$_2$)}Pt][PF$_6$]·2THF (27·2THF). Crystals of **27**·2THF for X-ray diffraction were grown from a THF/Et_2O solution. They were of rather poor quality, probably because of the presence of THF molecules of solvation (see below). A single crystal suitable for X-ray analysis was selected for data collection. The crystallographic data are summarized in Table II. Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having 12.3 < θ < 19.4°. All reflections with θ in the range 3–26° were measured; of 12 877 independent reflections, 4195, having $I \geq 3\sigma(I)$, were considered observed and used in the analysis. Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[18] Intensities were corrected for Lorentz and polarization effects; a semiempirical absorption correction was applied (maximum and minimum values for the transmission factors were 1.438 and 0.756).[19] 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 the Au, Pt, W, P, and O atoms only. The final ΔF map revealed the presence of two tetrahydrofuran molecules of solvation, one of which was found disordered and distributed in two positions having an atom in common. All atoms of the solvent were considered as carbons and refined isotropically with constrained distances. All hydrogen atoms, excepting those of the tetrahydrofuran molecules, were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms with fixed thermal parameter. The final cycles of refinement were carried out on the basis of 426 variables. After the last cycle, no parameter (excepting those of the molecules of solvation) shifted by more than 1.0 esd. The largest remaining peak (close to the Au atom) in the final difference map was equivalent to about 2.1 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 0.637 and 0.0313, respectively. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 20. 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.[21] The final atomic coordinates for the non-hydrogen atoms are given in Table III. The atomic coordinates of the hydrogen atoms are given in Table S-II, the anisotropic thermal parameters in Table S-III, and the isotropic thermal parameters in Table S-IV.

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Supplementary Material Available: For **27**·2THF, crystallographic data (Table S-I), hydrogen atom coordinates (Table S-II), and anisotropic and isotropic thermal parameters for the non-hydrogen atoms (Tables S-III and S-IV) (3 pages); a listing of observed and calculated structure factors (Table S-V) (25 pages). Ordering information is given on any current masthead page.

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