"Neutralization" of Palladium Hydroxides, [L₂Pd₂(R)₂(μ-OH)₂], by M−H Acids, [CpM(CO)₃H] (M = W, Mo, Cr)

Vladimir F. Kuznetsov,[†] Corinne Bensimon,[†] Glenn A. Facey,[†]
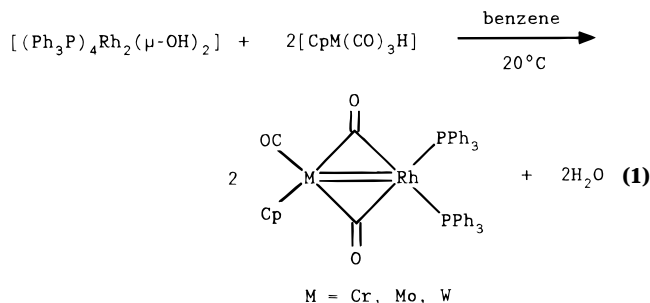Vladimir V. Grushin,[†,‡] and Howard Alper*,[†]

*Departments of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario,
Canada K1N 6N5, and Wilfrid Laurier University, Waterloo, Ontario, Canada N2L 3C5*

Received June 26, 1996[⊗]

The reaction of [L₂Pd₂(Ph)₂(μ-OH)₂] (L = Ph₃P, Cy₃P) with an equimolar amount of [CpM-(CO)₃H] (M = W, Mo, Cr) afforded the organometallic hydroxo clusters [L₂Pd₂(Ph)₂(μ-OH)-(μ-CO)₂(μ₃-CO)MCp] (**1**−**3**) in high yield. These reactions can be regarded as the "neutral-ization" of an acidic transition-metal hydride by a basic transition-metal hydroxide. The structure of the Pd₂Cr cluster **3** was established by a single-crystal X-ray diffraction study. The trinuclear hydroxo clusters are stable in the solid state but slowly decompose in solution, the decomposition path being strongly dependent on the nature of M. Facile and selective decomposition of **1** (M = W) resulted in the formation of [(Ph₃P)₂Pd₂(Ph)₂(μ-OH)₂], biphenyl, and the tetranuclear Pd₂W₂ cluster **4**. Similar tetranuclear clusters **4**−**8** were obtained in high yield when the palladium hydroxo dimers were neutralized with excess [CpM(CO)₃H] or [Cp*W(CO)₃H]. However, these reactions proceed by a different pathway involving Ph/H exchange processes, and resulted in the formation of benzene and [CpM(CO)₃Ph] or [Cp*W-(CO)₃Ph], respectively. Labeling experiments suggested that H atoms of the hydrido and hydroxo ligands underwent an exchange which was faster than the neutralization and the concomitant formation of the metal−metal bond. Infrared and NMR studies show that the structures of the trinuclear hydroxo clusters were more rigid than those of the tetranuclear species. Tetranuclear systems containing three different metals, Pd₂WMo (**9**) and Pd₂WCr (**10**), were prepared and characterized.

Introduction

The Brønsted acidity of some transition-metal hy-drides has been established beyond any doubt and is now well-documented.[1] One of the most exciting ap-plications of acidic transition-metal hydrides is their "neutralization" with hydroxo complexes of transition metals, resulting in metal−metal bond formation. To our knowledge, this approach had not been used for the synthesis of heterobimetallic and polymetallic com-plexes.[2,3] We have recently reported[4] that treatment of the rhodium hydroxo dimer [(Ph₃P)₄Rh₂(μ-OH)₂] with acidic[5] [CpM(CO)₃H] (M = Cr, Mo, W) results in the smooth formation of [CpM(CO)(μ-CO)₂Rh(PPh₃)₂] and water, according to eq 1. In this paper we report the formation of tri- and tetranuclear heterometallic com-

plexes as a result of neutralization of organopalladium binuclear hydroxo complexes by [CpM(CO)₃H].

Synthesis and Characterization of Trinuclear Pd₂M (M = Cr, Mo, W) Hydroxo Complexes 1−3: X-ray Structure of 3

Treatment of the hydroxo-bridged Pd dimers [L₂Pd₂-Ph₂(μ-OH)₂] (L = Ph₃P, Cy₃P)[6,7] with 1 molar equiv of the acidic hydrides [CpM(CO)₃H] (M = W, Mo, Cr) affords the corresponding trinuclear monohydroxo com-plexes by neutralization of one of the two OH ligands (eq 2). These trinuclear complexes were isolated in high yield as yellow (M = W, Mo) or orange (M = Cr) crystalline materials. Not only do complexes **1**−**3** belong to the still very limited group of neutral orga-

† University of Ottawa.
‡ Wilfrid Laurier University.
⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1996.
(1) (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Kristjánsdóttir, S. S.; Norton, J. R. Acidity of Hydrido Transition Metal Complexes in Solution. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991; p 309. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Grushin, V. V. *Acc. Chem. Res.* **1993**, *26*, 279.
(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms,* 2nd ed.; Clarendon Press: Oxford, U.K., 1993.
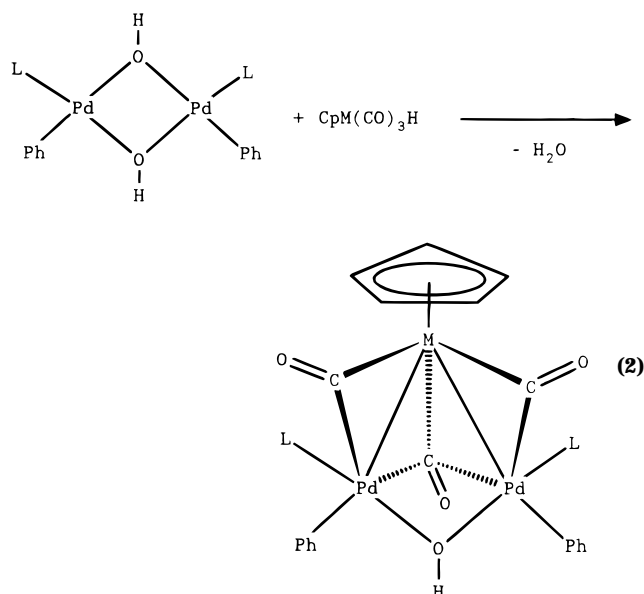(3) (a) The formation of heterobimetallic complexes with concomitant loss of alcohol has been reported in the reactions of [CpW(CO)₃H] with [L₂Re(CO)₃(OMe)][3b] and of [HMn(CO)₅] with [(*i*-PrO)₄Ti].[3c] (b) Simp-son, R. D.; Bergman, R. G. *Organometallic* **1992**, *11*, 3980. (c) Belyi, A. A.; Kuznetsov, V. F.; Blumenfeld, A. L. *Russ. Chem. Bull.* **1993**, *42*, 130 (English translation of *Izv. Acad. Nauk, Ser. Khim.-Moskva*).
(4) Grushin, V. V.; Kuznetsov, V. F.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3927.
(5) For [CpM(CO)₃H] (where M = Cr, Mo, W), p*K*ₐ(MeCN, 25 °C) = 13.3(1), 13.9(1), and 16.1(1), respectively. See: Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(6) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890.
(7) In solution, [(Ph₃P)₂Pd₂Ph₂(μ-OH)₂] and [(Cy₃P)₂Pd₂Ph₂(μ-OH)₂] exist as 4:1 and 6:1 mixtures of *trans* and *cis* isomers, respectively.[6]

(2)

1,   M = W; L = Ph$_3$P

1a, M = W; L = Cy$_3$P

2,   M = Mo; L = Ph$_3$P

3,   M = Cr; L = Ph$_3$P

Table 1. Crystallographic Data for
[(Ph$_3$P)$_2$Pd(μ-OH)(μ-CO)$_2$(μ_3-CO)CrCp]·MeOH

formula	C$_{57}$H$_{46}$CrO$_5$P$_2$Pd$_2$
fw	1137.72
cryst shape	plate
cryst dimens	0.3 × 0.2 × 0.1
cryst syst	monoclinic
lattice params	$a = 32.9701(4)$ Å
	$b = 10.6761(1)$ Å
	$c = 28.9941(2)$ Å
	$\beta = 108.405(1)°$
space group	$C2/c$
Z	8
V	9683.71(16) Å^3
d_{calcd}	1.561 g/cm^3
T, K	123
radiation (λ)	Mo Kα_1 (0.709 30 Å)
μ	1.03 mm^{-1}
R (R_w)^a	6.1% (7.8%)

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

Figure 1. ORTEP drawing of complex **3** with adopted numbering scheme. Hydrogen atoms (except for O–H) are omitted for clarity.

nopalladium hydroxo comnplexes$^{6,8-11}$ but they also represent the first examples of heteropolymetallic species containing a Pd−OH unit. These compounds can be regarded as the simplest soluble models for heterogeneous hydroxopalladium catalysts, e.g. Pearlman's catalyst (palladium hydroxide on carbon),^{12} which possesses interesting catalytic properties in some processes.^{13} Pearlman's catalyst has proven successful even when other Pd/C systems exhibit no catalytic activity. It is also worth noting that soluble hydroxo complexes of Pd are catalytically active in various processes,^{14} including the water-gas shift reaction^{15} and the hydroxycarbonylation of organic halides.^{6,16}
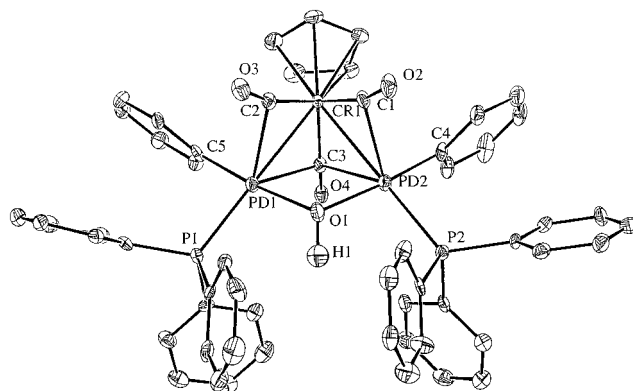
It is remarkable that complexes **1−3** are stable, despite the fact that their palladium centers bear OH, σ-Ph, and CO ligands in the same coordination sphere. To our knowledge, no Pd complexes have been described in the literature containing a set of OH, CO, and σ-aryl (alkyl) ligands situated around one Pd center.^{17} In fact, σ-alkyls (aryls) and especially hydroxo ligands on Pd are prone to migratory insertion reactions with carbonyls

coordinated to the metal.$^{14,18-22}$ The striking stability of **1−3** may be due to their rigidity, which prevents these compounds from adopting the conformations required for migratory insertion. Perhaps more important is that the OH and Ph ligands are coordinated entirely to the Pd centers, whereas the semibridging carbonyls are bound primarily to Cr, Mo, and W (see below). Therefore, migratory insertion in such systems would, in fact, require ligand transfer from one metal to a carbonyl group on another metal, which is unlikely.

Complexes **1−3** were characterized by elemental analysis, IR spectra, and ^{1}H, ^{13}C, and ^{31}P NMR spectra. In addition, the structure of **3** (methanol solvate) was determined by single-crystal X-ray diffraction. Crystallographic data and the structure of **3**·MeOH are presented in Table 1 and Figure 1, respectively. Selected bond distances and bond angles are given in Table 2.

The molecule of **3** contains an open triangular Pd−Cr−Pd fragment. The Pd···Pd separation (3.381(6) Å)

(8) Gilje, J. W.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 895.

(9) (a) López, G.; Ruiz, J.; Garcia, G.; Vicente, C.; Marti, J. M.; Santana, M. D. *J. Organomet. Chem.* **1990**, *393*, C53. (b) Ruiz, J.; Vicente, C.; Marti, J. M.; Cutillas, N.; Garcia, G.; López, G. *J. Organomet. Chem.* **1993**, *460*, 241.

(10) Ruiz, J.; Cutillas, N.; Torregrosa, J.; Garcia, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B.; Harrison, R. M. *J. Chem. Soc., Dalton Trans.* **1994**, 2353.

(11) Grushin, V. V.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3295.

(12) Pearlman, W. M. *Tetrahedron Lett.* **1967**, *17*, 1663.

(13) Fieser, M. *Fieser and Fiesers Reagents for Organic Synthesis*; Wiley: New York, 1992; Vol. 16, p 269.

(14) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(15) Kullberg, M. L.; Kubiak, C. P. *C$_1$ Mol. Chem.* **1984**, *1*, 171.

(16) Grushin, V. V.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4305.

(17) (a) Palladium complexes containing a set of both CO and OH (e.g., [(μ-dmpm)$_2$Pd$_2$(OH)$_2$(μ-CO)]^{15,17b} or both CO and σ-aryl ligands (e.g., *cis*-[PdCl$_2$(CO)(Ar)])^{17c} in the inner coordination sphere are very rare.^{14} (b) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632. (c) Vicente, J.; Arcas, A.; Borrachero, M. V.; Tiripicchio, A.; Camellini, M. T. *Organometallics* **1991**, *10*, 3873.

(18) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vols. 1 and 2.

(19) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980.

(20) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(21) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991.

(22) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [(Ph₃P)₂Pd₂(μ-OH)(μ-OH)₂(μ₃-CO)CrCp]·MeOH

Pd(1)−Cr	2.7523(15)	Pd(1)−C(5)	1.998(9)
Pd(2)−Cr	2.7604(15)	C(2)−O(3)	1.182(10)
Pd(1)−P(1)	2.3035(23)	C(3)−O(4)	1.184(10)
Pd(1)−O(1)	2.125(6)	Cr−C(2)	1.846(9)
Pd(1)−C(3)	2.324(8)	Cr−C(3)	1.889(9)
Pd(1)−C(2)	2.305(9)	Cr−centroid Cp	1.842(5)

C(3)−Pd(1)−O(1)	79.8(3)	Pd(1)−Cr−C(3)	56.5(3)
Pd(1)−O(1)−Pd(2)	105.4(3)	C(2)−Cr−C(1)	79.7(4)
Pd(1)−C(3)−Pd(2)	93.3(3)	C(2)−Cr−C(3)	112.4(4)
Cr−Pd(1)−P(1)	178.93(7)	O(2)−C(1)−Cr	164.1(8)
Cr−Pd(1)−C(5)	92.28(24)	O(2)−C(1)−Pd(2)	113.0(6)
O(1)−Pd(1)−C(5)	174.7(3)	Pd(1)−C(2)−Cr	82.3(3)
P(1)−Pd(1)−O(1)	97.54(17)	O(4)−C(3)−Cr	161.6(7)
P(1)−Pd(1)−C(5)	87.74(25)	O(4)−C(3)−Pd(1)	110.7(6)
Pd(1)−Cr−Pd(2)	75.68(4)	Pd(1)−C(3)−Cr	80.9(3)

Table 3. Bond Distances (Å) and Angles (deg) for the Pd₂M(μ-CO)₂(μ₃-CO) Units in 3 and Relevant Clusters (See Text)

| bond distance/angle	Pd₂Cr[23]	Pd₂Mo[24]	**3**
Pd−C (μ-CO)	2.30(1)	2.304(7)	2.305(9)
	2.34(1)	2.243(6)	
Pd−C (μ₃-CO)	2.34(1)	2.311(8)	2.324(8)
	2.26(1)	2.321(7)	
Cr−C (μ-CO)	1.84(1)	NA[a]	1.846(9)
Cr−C (μ₃-CO)	1.92(1)	NA	1.889(9)
Pd−C−O (μ-CO)	114.7(6)	116.7(5)	113.0(6)
	117.9(6)	116.8(7)	
Pd−C−O (μ₃-CO)	118.1(8)	118.3(5)	110.7(6)
	117.7(6)	119.2(5)	
Cr−C−O (μ-CO)	165.7(7)	NA	164.1(8)
	159.8(7)		
Cr−C−O (μ₃-CO)	156.6(5)	NA	161.6(7)

[a] NA = not applicable.

is much longer than the sum of the two covalent radii (2.98 Å), suggesting that there is no Pd−Pd bond in the complex. The four-membered Pd(1)−O(1)−Pd(2)−C(3) metallacycle is slightly puckered (the torsion angles lie in the range of 9.5−10.8(3)°), and it assumes a dihedral angle of 49.25(22)° with the Pd₂Cr frame. The two phosphines are *syn*, the Pd−P bonds are collinear with the corresponding Pd−Cr bond. The two μ-carbonyls are situated above and the μ₃-carbonyl is located below the CrPd₂ plane in a manner analogous to that found in Braunstein's[23] tetranuclear Pd₂M₂ (M = W, Mo, Cr; see below) and Werner's[24] trinuclear Pd₂Mo clusters. As can be seen from Table 3, the metal−carbonyl cores are structurally similar in [(Et₃P)₂Pd₂Cp₂Cr₂(μ-CO)₄(μ₃-CO)₂],[23] [(*i*-Pr₃P)₂Pd₂Mo(μ-CO)₂(μ₃-CO)Cp₂],[24] and **3**. This indicates similar bonding for the semibridging and semi-triply-bridging μ- and μ₃-carbonyls[25] to the metals in all three complexes. However, from our IR and NMR studies (see below) it is clear that the metal−carbonyl units in **1−3** are remarkably rigid, whereas that in Braunstein's Pd₂Cr₂ cluster was found to be fluxional.[23]

The solid-state IR carbonyl bands for **1−3** are very similar in shape, frequency, and intensity to those of the tetranuclear complexes **4−6**.[23] This is in line with the X-ray structural data, which demonstrate that the [MPd₂(CO)₃] frameworks in **1−6** are similar in structure. However, the carbonyl bands in **1−3** are obviously

(23) Bender, R.; Braunstein, P.; Jud, J.-M.; Dusausoy, Y. *Inorg. Chem.* **1983**, *22*, 3394.
(24) Werner, H.; Thometzek, P.; Krüger, C.; Kraus, H.-J. *Chem. Ber.* **1986**, *119*, 2777.
(25) Colton, R.; McCormic, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

4, M = W
5, M = Mo
6, M = Cr
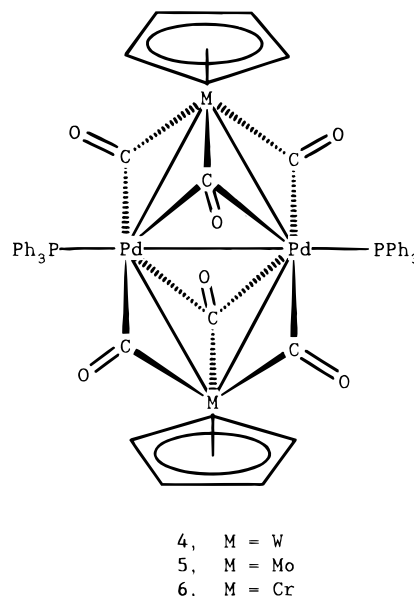
sharper, as compared to the analogous bands in the IR spectra of **4−6**, measured under similar conditions. This observation indicates structural rigidity of the trinuclear clusters, which is supported by the NMR studies described below.

The ¹H NMR spectra of **1−3**, while not informative in the aromatic region, exhibit sharp, well-resolved triplets at −3.7 to −4.0 ppm ($J_{H−P}$ = ca. 2 Hz) due to the OH ligand *trans* to the phosphines. Since the Cp protons occur as sharp singlets in the ¹H NMR spectra (CDCl₃, recorded from −25 to +20 °C), the rotation of the cyclopentadienyl rings across the M−Cp axis in the trinuclear hydroxides must have a low activation barrier.

Narrow singlet resonances at 23.4, 18.5, and 18.0 ppm were observed in the ³¹P NMR spectra of **1**, **2**, and **3**, respectively. The symmetry of complexes **1−3** dictates that the two phosphorus atoms be chemically equivalent. Although these atoms are magnetically nonequivalent, singlet resonances were observed in the ³¹P NMR spectra of **1−3**. This situation makes it impossible to measure $J_{P−P}$ in the ³¹P NMR spectrum. However, in certain instances, this parameter can be measured indirectly *via* the ¹³C NMR spectrum, where ³¹P−³¹P coupling can lead to second-order effects. Such an example is the Pd₂Cr complex **3**, where the ¹³C NMR spectrum has second-order properties in both the carbonyl and aromatic regions.

The carbonyl region of the ¹³C spectrum of **3** consists of two signals in a 2:1 intensity ratio. The downfield signal centered at 244.6 ppm is due to the two chemically equivalent μ-carbonyl groups bridging the Pd and Cr centers. It is a second-order pattern of the AXX′ type. The pattern can be simulated[26] with the following parameters: $\delta_X = \delta_{X'}$, $J_{A−X} = \pm 19$ Hz, $J_{A−X'} = \mp 5$ Hz, and $|J_{X−X'}| = 5$ Hz. The relative signs of the coupling constants between the carbon and each magnetically nonequivalent phosphorus must be different in order to reproduce the experimental spectrum (see Figure 2). The upfield carbonyl resonance centered at 243.2 ppm appears as a first-order triplet ($J_{C−P}$ = 12.3 Hz). The *ortho* and *meta* carbons of the triphenylphosphine

(26) The PC-based program DSYM-PC by S. Goudetsidis and G. Hägele was used for the simulation.
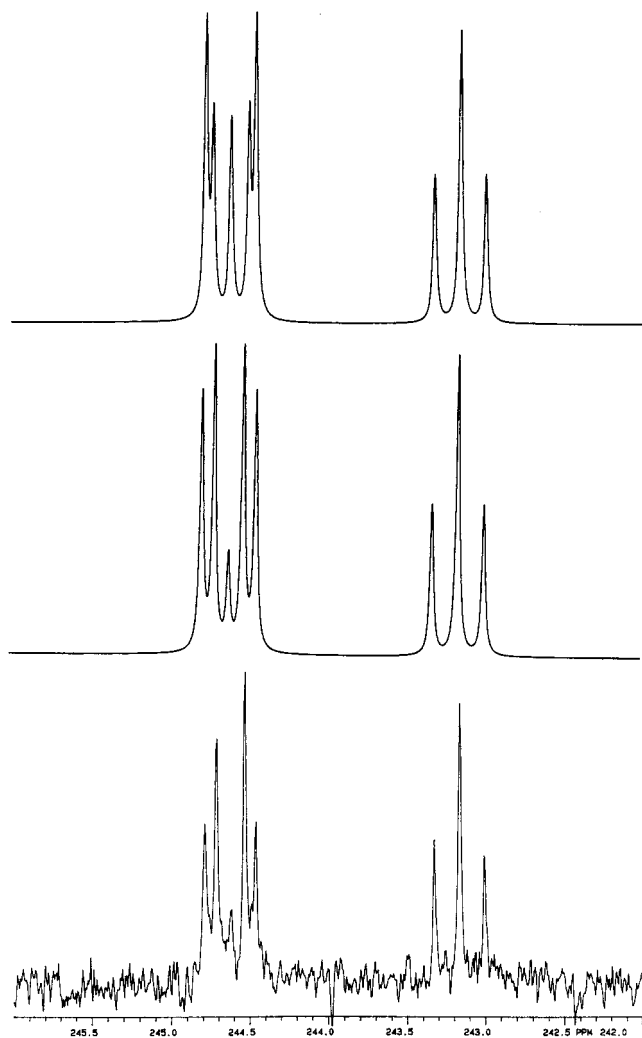
Figure 2. $^{13}C\{^1H\}$ NMR of **3** (carbonyl region): (a, bottom) experimental spectrum of **3** at -20 °C in CDCl$_3$; (b, middle) simulated spectrum with $J_{C-P1} = -19$ Hz, $J_{C-P2} = 5$ Hz, and $J_{P1-P2} = 5$ Hz; (c, top) simulated spectrum with $J_{C-P1} = 19$ Hz, $J_{C-P2} = 5$ Hz, and $J_{P1-P2} = 5$ Hz.

ligands are also second-order patterns, consistent with $|J_{P-P}| = 5$ Hz. The ^{13}C NMR carbonyl regions of complexes **1** and **2** appear to be first order, suggesting that the $^{31}P-^{31}P$ coupling is much weaker in these compounds. The *ortho* and *meta* carbon signals of the PPh$_3$ ligands show only very small second-order effects. From the NMR data it is clear that there is no positional exchange between the carbonyl ligands in **1–3**. In contrast, carbonyls in the closely related tetranuclear clusters **4–6** undergo fast (on the NMR time scale) exchange even at -90 °C.[23] Both the IR (see above) and NMR studies point to the fact that the trinuclear hydroxo clusters **1–3** possess considerably more rigid structures than Braunstein's tetranuclear complexes **4–6**. This remarkable difference in fluxionality may be due to the presence of the Pd–Pd bond in **4–6** and its absence in the trinuclear hydroxo complexes. As carbon monoxide is known to insert into Pd–Pd bonds of some complexes,[15,17b] the coordinated CO ligands in **4–6** may reversibly do so, thus undergoing facile positional exchange. Obviously, such a mechanism is inconceivable for **1–3**, which have no bonding Pd–Pd interaction.

As the hydroxo clusters slowly decompose in solution at room temperature (see below), their ^{13}C NMR spectra were measured at -25 °C in order to slow down the decomposition and obtain a well-resolved pattern in the carbonyl region. It was noticed that, at -25 °C, both *ortho* and *meta* carbons of the σ-phenyls were magnetically nonequivalent within each pair, probably because of the hindered rotation across the Pd–Ph bond. Moreover, the *ortho* carbon resonances were noticeably broadened. At ambient temperature, this nonequivalence vanished for **1–3** but was still observed in the ^{1}H and ^{13}C NMR spectra of the tricyclohexylphosphine complex **1a**, due to the bulkiness of Cy$_3$P.

Decomposition of 1–3 in Solution

In the solid state, complexes **2** and **3** can be stored in air for months. Although the tungsten counterpart **1** is less stable and should be kept under nitrogen in a freezer, it can be handled in air for hours, without any sign of decomposition. In solution, however, the hydroxo clusters decompose even in the absence of air, with their stability decreasing in the order **3** (Cr) > **2** (Mo) > **1** (W). At ambient temperature, the tungsten–palladium hydroxide **1** decomposes completely within ca. 20 h in benzene or toluene, to give exclusively the tetranuclear complex **4**, the original binuclear organopalladium dihydroxide [(Ph$_3$P)$_2$Pd$_2$Ph$_2$(μ-OH)$_2$], and biphenyl, all being formed in quantitative yield. The absence of benzene and bibenzyl among the decomposition products, when the reaction is run in toluene, points to a nonradical mechanism for this process.[27] Perhaps, the decomposition of **1** involves disproportionation, followed by reductive elimination of biphenyl (Scheme 1). Examples of binuclear reductive elimination from Pd complexes have been reported previously.[28] Usually, these processes involve migration of one of the two groups from one metal center to the other, which eventually leads to the reductive elimination from *one* metal. The intermediate shown in Scheme 1 might exhibit similar behavior, provided the carbonyl ligands would serve as a channel for the transfer of the Ph ligands from one Pd to the other via a series of migratory insertion–deinsertion processes. Considering the steric strain and coordinative saturation of the intermediate, the transfer of a phenyl group and the reductive elimination of the Ph$_2$ could be facile enough to prevent an observation of the intermediate by NMR.

The decomposition of **1** is convenient to monitor by ^{31}P NMR spectroscopy, by following the gradual disappearance of the resonance due to **1** (23.4 ppm) and the growth of signals for **4** (21.0 ppm)[23] and [(Ph$_3$P)$_2$Pd$_2$-Ph$_2$(μ-OH)$_2$] (33.9 and 33.2 ppm due to the *trans* and *cis* isomers, respectively).[6,7]

Unlike the smooth and straightforward disproportionation of **1**, the decomposition of the chromium counterpart **3** is much more sluggish, taking days and resulting in complex mixtures of products which were neither isolated nor identified. It is remarkable that neither **6** nor [(Ph$_3$P)$_2$Pd$_2$Ph$_2$(μ-OH)$_2$] emerged from the decomposition of **3** (^{31}P NMR). The Pd$_2$Mo hydroxo cluster **2** decomposed faster than **3** and slower than **1**; the reaction took approximately 2 days at room tem-

(27) (a) According to GC and GC–MS analyses, less than 0.5% of bibenzyl formed when **1** was disproportionated in toluene. (b) Nonhebel, D. C.; Walton, J. C. *Free-Radical Chemistry*; Cambridge University Press: Cambridge, U.K., 1974.
(28) See, for example: Young, S. J.; Kellenberger, B.; Reibenspies, J. H.; Himmel, S. E.; Manning, M.; Anderson, O. P.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 5744.
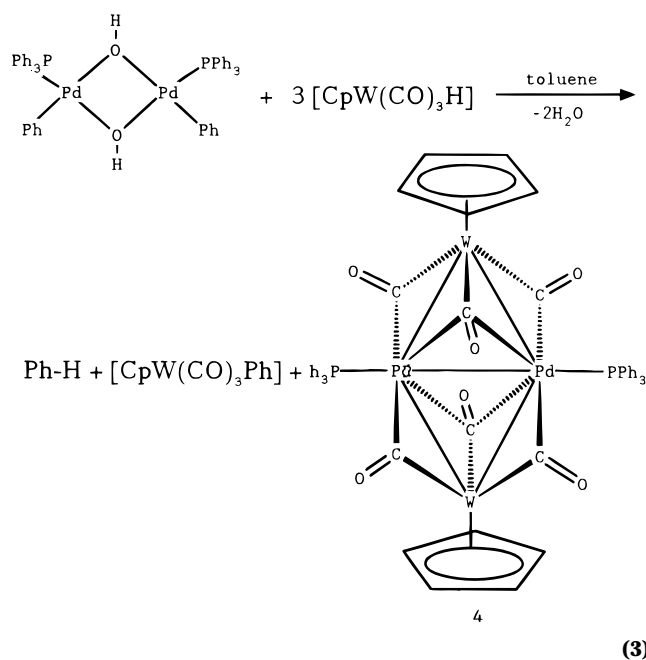
Scheme 1
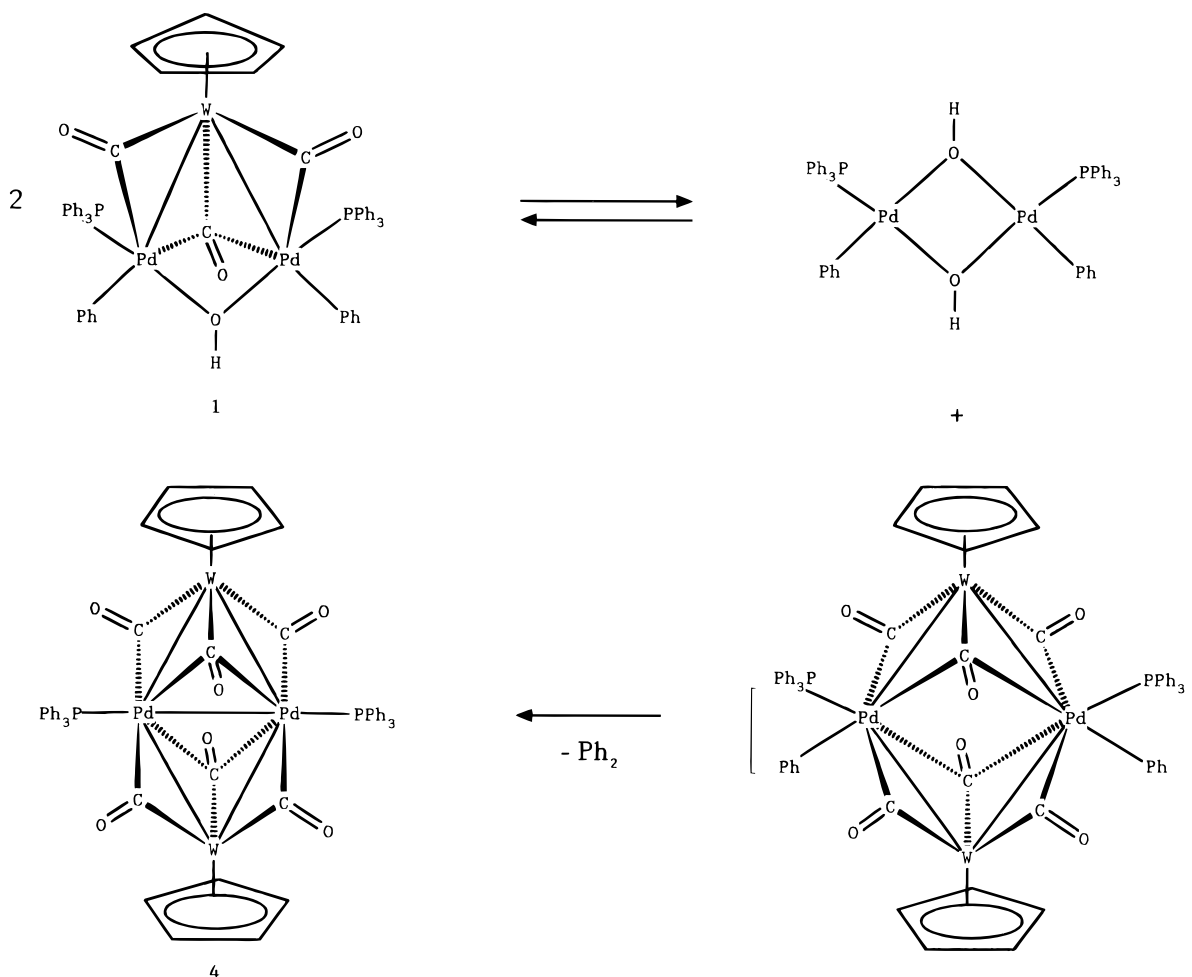
perature. Both **5** and $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]$ (1:1 molar ratio) were formed, among other unidentified products.

Reactions of Organopalladium Hydroxo Dimers with Excess [CpM(CO)₃H]

According to eq 2 and Scheme 1, the tetranuclear Pd_2W_2 cluster **4** can be prepared from $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]$ and 2 molar equiv of $[CpW(CO)_3H]$. However, the 2:1 stoichiometry was observed only if the hydride was added to the hydroxo dimer very slowly. Fast addition of the of the tungsten hydride to **1** or to $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]$, while affording **4** in quantitative yield, did so by a *totally different* reaction pathway. When 3 molar equiv or more of $[CpW(CO)_3H]$ was added, in one portion, to $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]$ in toluene, complex **4** (90% isolated yield), benzene (83% GC yield; see Experimental Section), and $[CpW(CO)_3Ph]$[29] (91% isolated yield) were formed (eq 3), but no biphenyl or bibenzyl was found among the reaction products.

Monitoring reaction 3 by ³¹P NMR spectroscopy revealed the rapid (seconds) formation of **1** upon addition of the W hydride to the Pd dihydroxide, followed by the gradual disappearance of **1** and concomitant formation of **4**. The spontaneous disproportionation of **1** (Scheme 1) was much slower (20 h) than the interac-

tion between **1** and the tungsten hydride (eq 3), which took less than 30 min under similar conditions. Clearly, reaction 3 proceeded through the formation of **1**, which then interacted with 2 equiv more of the hydride to give **4**, benzene, and $[CpW(CO)_3Ph]$ (Scheme 2). Indeed, the addition of 2 equiv of $[CpW(CO)_3H]$ to **1** resulted in the formation of **4**, benzene, and the (σ-phenyl)tungsten
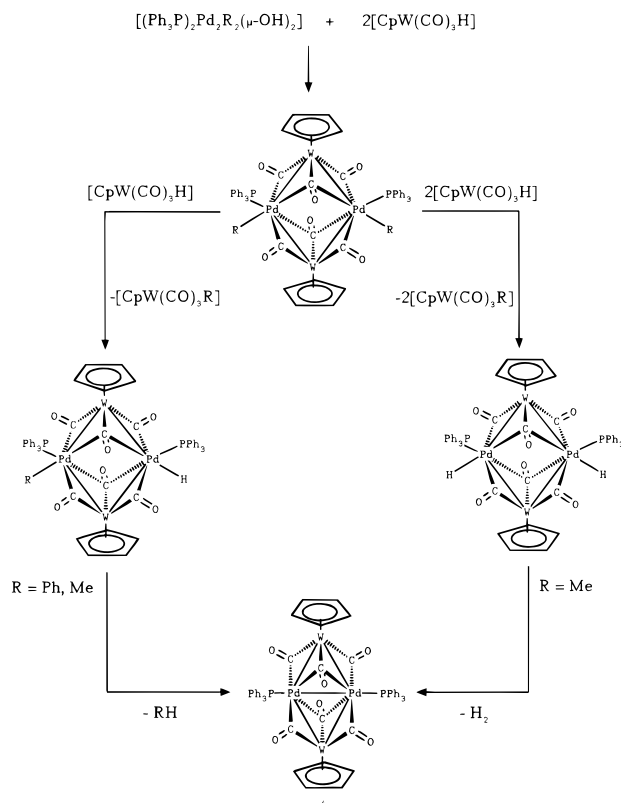
(29) (a) Nesmeyanov, A. N.; Chapovsky, Yu. A.; Lokshin, B. V.; Kisin, A. V.; Makarova, L. G. *Dokl. Akad. Nauk SSSR* **1966**, *171*, 637. (b) Mahmond, K. A.; Rest, A. J.; Alt, H. G.; Eichner, M. E.; Jansen, B. M. *J. Chem. Soc., Dalton Trans.* **1984**, 175.

(3)
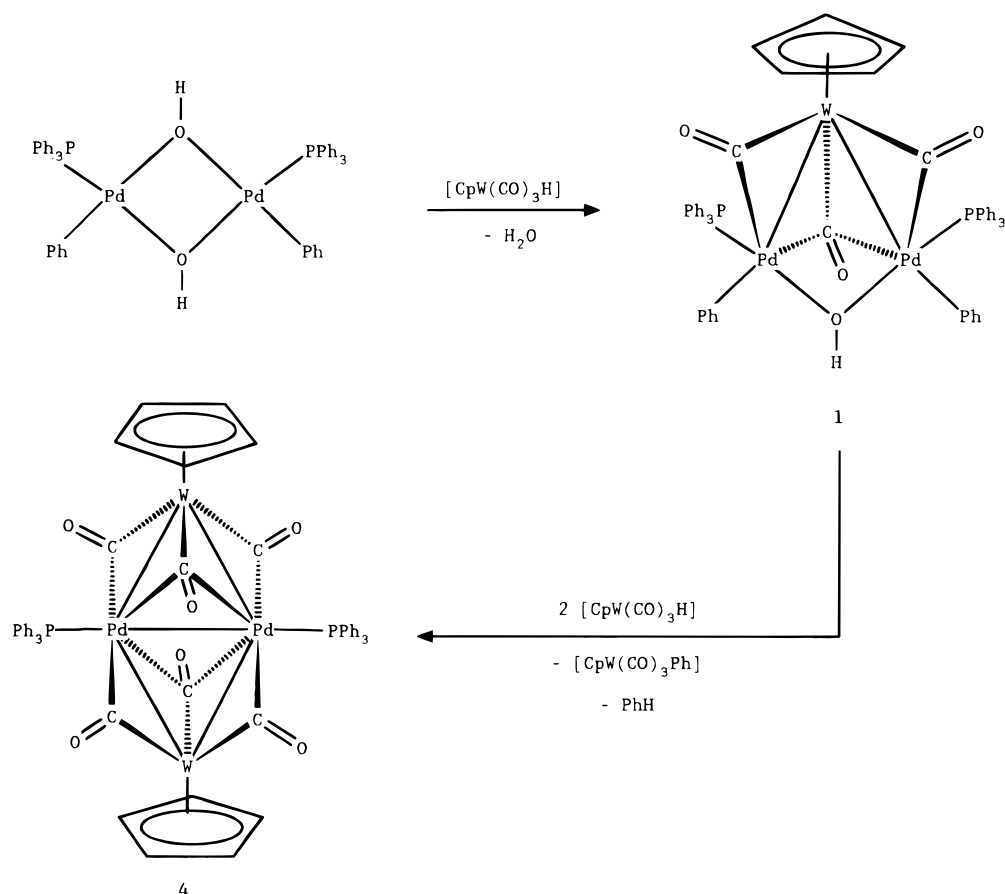
Scheme 2

Scheme 3

derivative, in high yield. It is conceivable that the formation of benzene and the (σ-phenyl)tungsten complex is due to a Ph/H exchange between the W hydride and *one* of the two Pd–Ph centers in an intermediate binuclear species. For instance (Scheme 3), the proposed tetranuclear intermediate (also presented in Scheme 1) may form upon neutralization of both OH ligands in [(Ph$_3$P)$_2$Pd$_2$Ph$_2$(μ-OH)$_2$] with 2 equiv of the hydride. If *one* of the two σ-Ph ligands in this intermediate exchanged for H from the still-present [CpW(CO)$_3$H], binuclear reductive elimination of PhH from the resulting Pd(H)Pd(Ph) species would give benzene and complex **4**. Should both organic ligands be replaced by hydrides, the elimination might result in the formation of H$_2$ due to reductive elimination. Indeed, the formation of both CH$_4$ and H$_2$ was experimentally observed in a similar reaction between [(Ph$_3$P)$_2$Pd$_2$(Me)$_2$-(μ-OH)$_2$] and excess [CpW(CO)$_3$H]. When [(Ph$_3$P)$_2$Pd$_2$-(Me)$_2$(μ-OH)$_2$][11] was treated with an excess of [CpW-(CO)$_3$H], **4** and [CpW(CO)$_3$Me][30] were formed as the only organometallic products in high yield, with both CH$_4$ and H$_2$ (6:1 molar ratio) being found in the gas phase (GC). These results can be rationalized in terms of the mechanism outlined in Scheme 3. The mechanism of the W–H/Pd–R exchange remains unclear; perhaps it involves oxidative addition of the W–H bond to the Pd

center, followed by reductive elimination of the W–R complex.[31] If so, this reaction sequence might involve significant changes in the cluster structures, due to

(30) (a) The resulting [CpW(CO)$_3$Me] was identified by comparison of its ^{1}H and ^{13}C NMR spectra with the literature data.[30b,c] ^{1}H NMR (C$_6$D$_6$): δ 0.6 (s, 3H, Me), 4.4 (s, 5H, Cp). ^{13}C NMR (C$_6$D$_6$): δ −34.2 (s, J_{C-W} = 28.8 Hz, Me), 91.6 (s, Cp). (b) For the ^{1}H NMR spectrum, see: McFarlane, H. C.; McFarlane, W.; Rycroft, D. C. *J. Chem. Soc., Dalton Trans.* **1976**, 1616. (c) For the ^{13}C NMR spectrum, see: Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*, 2nd ed.; VCH: New York, 1992; p 297.

steric requirements for the oxidative addition. Attempted preparation of the σ-methyl analog of **1** failed, apparently because the desired hydroxo complex and the starting hydroxide, $[(Ph_3P)_2Pd_2(Me)_2(\mu\text{-OH})_2]$, exhibited similar reactivity toward the hydride.[32]

Treating $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-OH})_2]$ with 3 equiv of $[CpW(CO)_3D]$ in dry toluene gave benzene, with the ratio of C_6H_6 to C_6H_5D being approximately 1:1 (GC–MS). When $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-OD})_2]$ was used for the reaction with $[CpW(CO)_3D]$, the benzene product contained 90% C_6H_5D. Both experiments demonstrated that, in the course of the reaction, extensive exchange occurred between the hydrido and hydroxo hydrogens of the organometallic reactants. In line with the proposed mechanism (Scheme 2), the hydrido/hydroxo H/D exchange was found to occur noticeably faster than the neutralization reactions. When 1 equiv of $[CpW(CO)_3D]$ (90% D) was added to nondeuterated **1** in toluene-d_8 at -40 °C, neither H/D exchange nor formation of **4** was observed (^{1}H NMR) over 30 min. The hydrido region of the spectrum contained a triplet (-3.7 ppm) due to the μ-OH and the residual resonance of the tungsten hydride (-7.2 ppm). The sample was then quickly warmed and kept at room temperature for ca. 1 min, and the spectrum was again recorded at -40 °C. This brief exposure at room temperature was sufficient for complete scrambling of the D label over the hydrido/hydroxo sites. At the same time, it was clear (from the ^{1}H NMR spectrum) that less than 5% of **1** underwent conversion to **4**. An independent experiment was conducted to show that the H/D exchange between $[CpW(CO)_3D]$ (in benzene or toluene) and H_2O is very slow, taking days at room temperature.[33] Therefore, the above H/D scrambling observed was due to the *direct* hydrido/hydroxo exchange and required no water. The above experiments account for the formation of both C_6H_6 and C_6H_5D in the reaction between $[CpW(CO)_3D]$ and $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-OH})_2]$, according to Schemes 2 and 3.

Complexes **5**, **6**, and $[(Cy_3P)_2Pd_2Cp_2W_2(\mu\text{-CO})_4(\mu_3\text{-CO})_2]$ **(7)** were prepared by neutralization of the hydroxopalladium complexes with the corresponding hydrides using a 1:3 molar ratio (eq 4). Similarly, the

$$[(R_3P)_2Pd_2(Ph)_2(\mu\text{-OH})_2] + 3[CpM(CO)_3H] \rightarrow$$

$$[(R_3P)_2Pd_2M_2Cp_2(CO)_6] \quad (4)$$
$$\textbf{4–8}$$
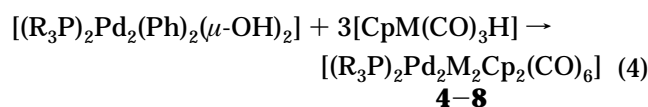
4: R = Ph, M = W

5: R = Ph, M = Mo

6: R = Ph, M = Cr

7: R = Cy, M = W

---

(31) Fukuoka, A.; Sadashima, T.; Endo, I.; Ohashi, N.; Kambara, Y.; Sugiura, T.; Miki, K.; Kasai, N.; Komiya, S. *Organometallics* **1994**, *13*, 4033.

(32) When $[CpW(CO)_3H]$ was gradually added to $[(Ph_3P)_2Pd_2(Me)_2(\mu\text{-OH})_2]$ in benzene (the reaction was monitored by ^{31}P NMR), a singlet was observed at 32 ppm in the spectrum which could be assigned to the σ-methyl analog of **1**. This singlet rapidly disappeared.

(33) (a) In contrast, $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-OH})_2]$ readily exchanges with D_2O within seconds under similar conditions. For instance, adding 1 drop of D_2O to a solution of this Pd hydroxo dimer in CDCl$_3$ (ca. 1 mL in a 5 mm NMR tube) and shaking the mixture for 5 s resulted in complete deuteration of the OH ligands (^{1}H NMR).[33b] (b) Grushin, V. V. Unpublished observations, 1993.

8: R = Ph, M = W, Cp = Cp* = $\eta^5\text{-C}_5\text{Me}_5$

reaction between $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-OH})_2]$ and $[Cp*W(CO)_3H]$ $(Cp* = \eta^5\text{-C}_5\text{Me}_5)$ furnished, as anticipated, $[(Ph_3P)_2Pd_2Cp^*_2W_2(\mu\text{-CO})_4(\mu_3\text{-CO})_2]$ **(8)** along with $[Cp*W(CO)_3Ph]$ in 60% and 72% isolated yields, respectively. The $[CpM(CO)_3Ph]$ byproducts were not isolated in all these cases, but their formation was confirmed by TLC and ^{1}H NMR spectral data.

Spectral (IR, NMR) parameters obtained for complexes **4–6** were identical with those previously reported by Braunstein and co-workers.[23] The new clusters **7** and **8** were characterized by elemental analysis and IR and NMR spectral data (see Experimental Section).
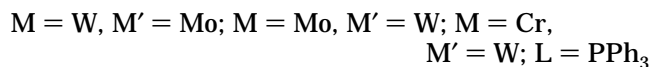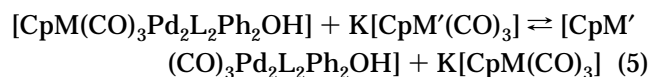
Formation of Tetranuclear Trimetallic Pd$_2$MM′ Clusters

Having established the fact that the reactions between $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-OH})_2]$ and excess $[CpM(CO)_3H]$ occur via the intermediate formation of trinuclear hydroxo clusters **1–3**, we attempted the synthesis of tetranuclear trimetallic Pd$_2$MM′ systems. It is worth noting that such clusters cannot be prepared by Braunstein's method.[23] First, we found that a 1:1 mixture of **4** and **5** in benzene did not exhibit any sign of a W/Mo exchange (weeks at room temperature; ^{31}P NMR control). Nonetheless, when **1** was treated with 2 equiv of $[CpMo(CO)_3H]$, the three clusters **4**, **5**, and the mixed Pd$_2$MoW species **9** were found in the reaction mixture in a ca. 1:10:2 ratio. The reaction between **2** and $[CpW(CO)_3H]$ also resulted in the formation of **4**, **5**, and **9**, although in a ratio of 7:1:10. From this experiment, complex **9** was isolated by column chromatography (55% yield) and characterized by elemental analysis and IR and NMR spectral data. Having been kept in benzene for 24 h, **9** did not disproportionate or decompose, suggesting that the observed scrambling cannot be explained by the instability of the mixed species. We also tried to prepare the Pd$_2$WCr and Pd$_2$MoCr mixed clusters by applying the above techniques. None of the reactions gave the desired complexes selectively; mixtures of all three possible clusters were obtained instead. It is worth mentioning that the reaction between $[L_2Pd_2(\mu\text{-Cl})(\mu\text{-CO})_2(\mu_3\text{-CO})MCp]$ and $[CpM'(CO)_3]^-$ (M, M′ = W, Mo, Cr) also gave mixtures of all possible clusters, which were not isolated.[24]

Clearly, the unexpected M/M′ scrambling observed did not result from exchange between the Pd$_2$M$_2$ and Pd$_2$M′$_2$ units or disproportionation of Pd$_2$MM′ (see above). Neither could it be accounted for by exchange between the already formed Pd$_2$MM′ and the as yet unreacted $[CpM(CO)_3H]$. In fact, although some W/Cr exchange was observed when **6** was mixed with $[CpW(CO)_3H]$ in benzene, the reaction was very sluggish, taking several hours at room temperature before the Pd$_2$WCr **(10)** and Pd$_2$W$_2$ species **(4)** formed in concentrations observable by ^{31}P NMR techniques. The palladium–tungsten–chromium cluster was obtained in this manner and isolated in 34% yield after 70 h of reaction. In contrast, all reactions of **1–3** and various $[CpM(CO)_3H]$ complexes were significantly more facile, reaching completion in less than 30 min. Therefore, the M/M′ scrambling obviously occurred at earlier steps of the reaction.

Unlike $[CpM(CO)_3H]$ (M = W, Mo, Cr), the corresponding potassium salts $K^+[CpM(CO)_3]^-$ readily and

rapidly exchanged with **4**−**6** in 30 min. Trinuclear hydroxo clusters **1**−**3** also underwent exchange with the potassium carbonylates (eq 5), equilibria being reached in less than 30 min at ambient temperature (^{31}P NMR).

$$[CpM(CO)_3Pd_2L_2Ph_2OH] + K[CpM'(CO)_3] \rightleftharpoons [CpM'$$
$$(CO)_3Pd_2L_2Ph_2OH] + K[CpM(CO)_3] \quad (5)$$

M = W, M′ = Mo; M = Mo, M′ = W; M = Cr,
M′ = W; L = PPh₃

Remarkably, two sharp singlets were observed in the carbonyl region of the ^{13}C NMR spectra of **9** and **10**, indicating that the positional exchange of the carbonyl ligands takes place only within each Pd₂M unit, with no CO exchange occurring between the two Pd₂M frameworks. This is probably true for clusters **4**−**8**, which exhibit only one carbonyl ^{13}C NMR resonance due to symmetry.

Conclusions

The above reactions (eqs 2 and 3) represent the first examples of palladium−transition-metal bond formation due to acid−base interaction between a hydroxo Pd species and an acidic metal hydride. Although reactions 2 and (to a certain degree) 3 could be regarded as simple neutralization processes, their mechanisms may be more sophisticated than the simple hydrido and hydroxo ligands coming together to form a molecule of water. At this moment, not enough data have been accrued to draw any conclusions regarding the mechanisms of this unusual neutralization chemistry, which may involve a series of oxidative-addition and reductive-elimination processes. Another aspect which merits emphasis is the "peaceful coexistence" of the OH, σ-phenyl, and carbonyl ligands, all attached to each of the palladium centers in molecules of **1**−**3**. We are unaware of any other palladium complexes bearing CO, OH, and σ-aryl (alkyl) ligands on one metal atom. From this perspective, "polyfunctional" complexes **1**−**3** are of potential interest in inorganic and organometallic synthesis, as well as in the chemistry of catalytic carbonylation of organic substrates in the presence of alkali-metal and homogeneous Pd catalysts.[19−22]

Experimental Section

The following instruments were used: Varian Gemini-200 (^{1}H NMR), Varian XL 300 (^{1}H, ^{13}C, and ^{31}P NMR), Bruker AMX 500 (^{1}H, ^{13}C, and ^{31}P NMR), Hewlett-Packard 5890 Series II-Kratos Concept II H (GC−MS), Bomem MB-100 (FT-IR), and Perkin-Elmer 2400 Series II (combustion microanalysis). All chemicals were purchased from Aldrich, Strem, Organometallics, and MSD Isotopes and used as received. The metal complexes [(Ph₃P)₂Pd₂(Ph)₂(μ-OH)₂],[6] [(Cy₃P)₂Pd₂(Ph)₂(μ-OH)₂],[6,16] [(Ph₃P)₂Pd₂(Me)₂(μ-OH)₂],[11] [CpW(CO)₃H],[29] [CpMo(CO)₃H],[34] Hg[CpCr(CO)₃]₂,[35] and [Cp*W(CO)₃H][36] were prepared as described in the literature.

Synthesis of [(Ph₃P)₂Pd₂(Ph)₂(μ-OH)W(CO)₃Cp] (1). Solid [CpW(CO)₃H] (34 mg; 0.102 mmol) was added to a vigorously stirred solution of [(Ph₃P)₂Pd₂(Ph)₂(μ-OH)₂] (100 mg; 0.108 mmol) in benzene (20 mL). Heptane (20 mL was added to the resulting yellow-brown mixture, and the solution was

(34) Fischer, E. O. *Inorg. Synth.* **1963**, *7*, 136.
(35) Burtlitch, J. M.; Ferrari, A. *Inorg. Chem.* **1970**, *9*, 563.
(36) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 2012.

reduced in volume under vacuum until it became slightly turbid. The clear yellow solution was decanted from the dark solid and evaporated until yellow crystals were formed and the liquid phase became colorless. The crystals were separated, washed with pentane (3 × 10 mL), and dried under vacuum. The yield of analytically and spectroscopically pure **1** was 103 mg (81%). Anal. Calcd for C₅₆H₄₆O₄P₂Pd₂W: C, 54.2; H, 3.7. Found: C, 54.3; H, 3.8. ^{1}H NMR (CDCl₃, 20 °C): δ −3.7 (t, $J_{H–P}$ = 2.1 Hz, 1H, PdOH), 4.4 (s, 5H, C₅H₅), 6.5−7.4 (m, 40H, C₆H₅). ^{31}P NMR (C₆D₆, 20 °C): δ 23.4 (s). ^{13}C NMR (CDCl₃, −25 °C): δ 91.2 (s, C₅H₅), 122.0 (s, *p*-C₆H₅Pd), 126.4 (s, *m*-C₆H₅Pd), 127.0 (s, *m*-C₆H₅Pd), 128.3 (d, $J_{C–P}$ = 10.4 Hz, *m*-C₆H₅P), 129.5 (d, $J_{C–P}$ = 40.0 Hz, q-C₆H₅P), 130.0 (s, *p*-C₆H₅P), 133.8 (d, $J_{C–P}$ = 12.9 Hz, *o*-C₆H₅P), 135.5 (br s, *o*-C₆H₅P), 139.4 (m, q-C₆H₅P), 225.8 (t, $J_{C–P}$ = 14.0 Hz, μ_3-CO), 228.0 (d, $J_{C–P}$ = 15.5 Hz, μ-CO). IR (KBr): ν_{CO} (cm^{-1}) 1861 (vs), 1785 (vs), 1750 (vs).

Synthesis of [(Cy₃P)₂Pd₂(Ph)₂(μ-OH)W(CO)₃Cp] (1a). Solid [CpW(CO)₃H] (38 mg; 0.114 mmol) was added to a vigorously stirred solution of [(Cy₃P)₂Pd₂(Ph)₂(μ-OH)₂] (130 mg; 0.116 mmol) in a mixture of CH₂Cl₂ (15 mL), heptane (15 mL), and toluene (2 mL), at 0 °C. The resulting clear yellow solution was stirred at 0 °C for 10 min, reduced in volume under vacuum to ca. 10 mL, and kept at −78 °C for 3 days. The yellow crystals that precipitated were separated, washed with cold (−78 °C) pentane, and dried under vacuum. The yield of spectroscopically pure [(Cy₃P)₂Pd₂(Ph)₂(μ-OH)W(CO)₃Cp]·C₆H₅-CH₃ was 110 mg (70%). The compound was recrystallized from a 1:1 mixture of toluene−pentane (8 mL) for elemental analysis. Anal. Calcd for C₆₃H₉₀O₄P₂Pd₂W: C, 55.2; H, 6.6. Found: C, 55.5; H, 6.6. ^{1}H NMR (C₆D₆, 20 °C): δ −1.4 (s, 1H, PdOH), 1.0−2.2 (m, 69H, C₆H₁₁ + Me), 4.4 (s, 5H, C₅H₅), 6.8 (t, $J_{H–H}$ = 7.1 Hz, 2H, 4-C₆H₅Pd), 7.0 (m, 4H, 3-C₆H₅Pd), 7.1−7.2 (m, 5H, C₆H₄Me), 7.8 (d, $J_{H–H}$ = 8.0 Hz, 2H, 2-C₆H₅Pd), 8.2 (d, $J_{H–H}$ = 7.7 Hz, 2H, 2-C₆H₅Pd). ^{31}P NMR (CDCl₃, 20 °C): δ 28.1 (s). ^{13}C NMR (CDCl₃, −40 °C): δ 23.4 (s, Me), 26.2 (s, C₆H₁₁), 27.5 (br s, C₆H₁₁), 29.0 (m, C₆H₁₁), 31.2 (br s, C₆H₁₁), 91.3 (s, C₅H₅), 122.0 (s, *p*-C₆H₅Pd), 125.3 (s, *C*₆H₅Me), 125.9 (s, *m*-C₆H₅Pd), 126.7 (s, *m*-C₆H₅Pd), 128.4 (s, *C*₆H₅Me), 129.2 (s, *C*₆H₅Me), 134.7 (s, *o*-C₆H₅Pd), 128.4 (s, *C*₆H₅Me), 129.2 (s, *C*₆H₅Me), 134.7 (s, *o*-C₆H₅Pd), 135.3 (s, *o*-C₆H₅Pd), 137.2 (s, *C*₆H₅Me), 140.1 (s, q-C₆H₅Pd), 226.7 (t, $J_{C–P}$ = 14.0 Hz, μ_3-CO), 230.4 (d, $J_{C–P}$ = 16.5 Hz, μ-CO). IR (KBr): ν_{CO} (cm^{-1}) 1856 (vs), 1783 (vs), 1744 (vs).

Synthesis of [(Ph₃P)₂Pd₂(Ph)₂(μ-OH)Mo(CO)₃Cp] (2). A solution of freshly purified [CpMo(CO)₃H] (33 mg; 0.134 mmol) in heptane (4 mL) was added to a vigorously stirred solution of [(Ph₃P)₂Pd₂(Ph)₂(μ-OH)₂] (128 mg; 0.138 mmol) in benzene (20 mL). Heptane (20 mL) was added, and the clear yellow solution was reduced in volume under vacuum to ca. 20 mL. The yellow crystals were separated, washed with pentane (3 × 10 mL), and dried under vacuum. The yield of analytically and spectroscopically pure **2** was 138 mg (89%). Anal. Calcd for C₅₆H₄₆MoO₄P₂Pd₂: C, 58.3; H, 4.0. Found: C, 58.7; H, 3.9. ^{1}H NMR (CDCl₃, 20 °C): δ −3.8 (t, $J_{H–P}$ = 2.1 Hz, 1H, PdOH), 4.3 (s, 5H, C₅H₅), 6.6−7.4 (m, 40H, C₆H₅). ^{13}P NMR (C₆D₆, 20 °C): δ 18.5 (s). ^{13}C NMR (CDCl₃, −25 °C): δ 102.2 (s, C₅H₅), 121.7 (s, *p*-C₆H₅Pd), 126.2 (s, *m*-C₆H₅Pd), 126.8 (s, *m*-C₆H₅-Pd), 128.0 (second-order m, $J_{C–P}$ = ca. 10.6 Hz, *m*-C₆H₅Pd), 129.4 (d, $J_{C–P}$ = 40.1 Hz, q-C₆H₅P), 130.7 (s, *p*-C₆H₅P), 133.7 (second-order m, $J_{C–P}$ = ca. 13.0 Hz, *o*-C₆H₅P), 134.0 (s, *o*-C₆H₅-Pd), 135.5 (s, *o*-C₆H₅Pd), 139.3 (m, q-C₆H₅Pd), 233.4 (t, $J_{C–P}$ = 17.1 Hz, μ_3-CO), 236.1 (d, $J_{C–P}$ = 20.5 Hz, μ-CO). IR (KBr): ν_{CO} (cm^{-1}) 1867 (vs), 1799 (vs), 1762 (vs).

Synthesis of [(Ph₃P)₂Pd₂(Ph)₂(μ-OH)Cr(CO)₃Cp] (3). A mixture of [CpCr(CO)₃]₂Hg (210 mg; 0.348 mol), THF (5 mL), and a Na/K alloy (1 mL) was stirred for 1 h. The THF solution was filtered and treated with AcOH (1 mL). After it was stirred for 10 min, the mixture was evaporated to dryness, and the residue was washed with water (10 mL). The bright yellow solid ([CpCr(CO)₃H]) was dried under vacuum and dissolved in pentane (5 mL). The solution was filtered, and evaporation

of pentane gave 60 mg (42%) of yellow [CpCr(CO)$_3$H]. The prepared chromium hydride was dissolved in heptane (4.0 mL), and an aliquot of this solution (1.8 mL; 0.133 mmol of [CpCr-(CO)$_3$H]) was added to a vigorously stirred solution of [(Ph$_3$P)$_2$-Pd$_2$(Ph)$_2$(μ-OH)$_2$] (135 mg; 0.146 mmol) in benzene (20 mL). Heptane (20 mL) was added; the mixture was reduced in volume to ca. 20 mL and kept first at room temperature (30 min) and then at −17 °C (1 h). The resulting orange crystals were separated, washed with pentane (3 × 10 mL), and dried under vacuum. The yield of analytically and spectroscopically pure **3** was 133 mg (90%). Anal. Calcd for C$_{56}$H$_{46}$CrO$_4$P$_2$Pd$_2$: C, 60.6; H, 4.2. Found: C, 60.4; H, 4.3. ^{1}H NMR (CDCl$_3$, 20 °C): δ −4.0 (t, J_{H-P} = 2.0 Hz, 1H, PdOH), 3.7 (s, 5H, C$_5$H$_5$), 6.5−7.6 (m, 40H, C$_6$H$_5$). ^{31}P NMR (C$_6$D$_6$, 20 °C): δ 18.0 (s). ^{13}C NMR (CDCl$_3$, −25 °C): δ 89.4 (s, C$_5$H$_5$), 121.8 (s, p-C$_6$H$_5$-Pd), 126.4 (s, m-C$_6$H$_5$Pd), 127.1 (s, m-C$_6$H$_5$Pd), 128.1 (second-order m, J_{C-P} = ca. 10.2 Hz, m-C$_6$H$_5$P), 129.4 (d, J_{C-P} = 41.5 Hz, q-C$_6$H$_5$P), 129.9 (s, p-C$_6$H$_5$), 133.7 (second-order m, J_{C-P} = ca. 12.8 Hz, o-C$_6$H$_5$P), 135.3 (s, o-C$_6$H$_5$Pd), 142.2 (m, q-C$_6$H$_5$-Pd), 243.2 (t, J_{C-P} = 12.3 Hz, μ_3-CO), 244.6 (second-order m, μ-CO; see text). IR (KBr pellet): ν_{CO} (cm^{-1}) 1859 (vs), 1792 (vs), 1760 (vs).

Disproportionation of 1. The gradual disappearance of **1** (benzene or toluene solutions) and concomitant formation of **4** and [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] was monitored by ^{31}P NMR spectroscopy (see text).

(b) Solid [CpW(CO)$_3$H] (16 mg; 0.048 mmol) was added to a stirred mixture of [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] (64 mg; 0.069 mmol) and toluene (4 mL) at −78 °C. The mixture was warmed to room temperature and left overnight. The volatiles were transferred (vacuum) to a small flask and mixed with n-butylbenzene (internal standard, 5 μL). The residue, after distillation, was stirred with hexane (4 mL) containing n-butylbenzene (internal standard, 5 μL), and the pale yellow liquid phase was decanted from the dark blue precipitate of **4**. Analysis of the liquids by GLC indicated that biphenyl was formed in 73% yield.

Preparation of [CpW(CO)$_3$D]. A mixture of [CpW(CO)$_3$H] (173 mg; 0.518 mmol), THF (5 mL), and Na/K alloy (0.2 mL) was stirred for 1 h. The resulting THF solution was filtered, treated with AcOD (0.5 mL), stirred for 10 min, and evaporated to dryness. The residue was washed with D$_2$O (2 mL), dried under vacuum, and dissolved in pentane (4 mL). The pentane solution was filtered through cotton and evaporated to give 130 mg of white crystals of [CpW(CO)$_3$D] (95% D, ^{1}H NMR).

Preparation of [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OD)$_2$]. A mixture of [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] (100 mg; 0.108 mmol), CH$_2$Cl$_2$ (5 mL), and D$_2$O (1 mL) was stirred for 15 min. The organic layer was separated, filtered through cotton, and evaporated to dryness to give 94 mg of white [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OD)$_2$].

Reaction of [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] with Excess [CpW(CO)$_3$H]. (a) Isolation of [Cp(CO)$_3$WPh] and Determination of the Amount of Benzene. A mixture of [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] (41 mg; 0.044 mmol), [CpW(CO)$_3$H] (52 mg; 0.155 mmol), and toluene (2 mL) was stirred for 1 h. The volatiles were vacuum-transferred, n-butylbenzene (internal standard) was added, and the distillate was analyzed by GLC. The amount of benzene formed was 37 mmol (83%). Trace amounts of cyclopentadiene, biphenyl, and bibenzyl were also found (GC−MS). The residue after distillation was extracted with pentane (3 × 1 mL), and the resulting yellow solution was chromatographed on silica (toluene/heptane) to give pure [CpW(CO)$_3$Ph][29] (16.6 mg; 91%). ^{1}H NMR (CDCl$_3$, 20 °C): δ 5.5 (s, 5H, C$_5$H$_5$), 7.0 (m, 3H, 3,4,5-C$_6$H$_5$), 7.7 (m, 2H, 2,6-C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 20 °C): δ 92.4 (s, C$_5$H$_5$), 124.4 (s, q-C$_6$H$_5$), 124.5 (s, p-C$_6$H$_5$), 128.4 (s, m-C$_6$H$_4$), 147.3 (s, o-C$_6$H$_5$), 218.3 (s, J_{W-C} = 158 Hz, CO), 228.2 (s, J_{W-C} = 112 Hz, CO). IR (KBr pellet): ν_{CO} (cm^{-1}) 2017 (m), 1915 (vs), 1896 (vs).

(b) Reaction of [CpW(CO)$_3$D] with [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] and with [(Ph$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OD)$_2$]. These reactions were conducted in absolute toluene, as described above. The

benzene-containing distillates were analyzed by GC−MS. The composition of C$_6$H$_5$D/C$_6$H$_6$ mixtures was calculated from the abundances of isotopic peaks in the electron impact mass spectra, using an ISONETA program.[37]

(c) Synthesis of [(Ph$_3$P)$_2$Pd$_2$Cp$_2$W$_2$(μ-CO)$_4$(μ_3-CO)$_2$] (4). A mixture of [CpW(CO)$_3$H] (240 mg; 0.72 mmol), [(Ph$_3$P)$_2$Pd$_2$-(Ph)$_2$(μ-OH)$_2$] (139 mg; 0.15 mmol), and benzene (10 mL) was stirred for 30 min, treated with MeOH (10 mL), and left overnight. The precipitated dark green crystals of **4**[23] were separated, washed with MeOH (3 × 10 mL), pentane (3 × 10 mL), and dried under vacuum. The yield of the analytically and spectroscopically pure **4** thus obtained was 190 mg (90%). Anal. Calcd for C$_{52}$H$_{40}$O$_6$P$_2$Pd$_2$W$_2$: C, 44.5; H, 2.9. Found: C, 44.3; H, 2.9. ^{1}H NMR (CDCl$_3$, 20 °C): δ 4.7 (s, 10H, C$_5$H$_5$), 7.4 (m, 18H, 3,4,5-C$_6$H$_5$), 7.6 (m, 12H, 2,6-C$_6$H$_5$). ^{31}P NMR (CDCl$_3$, 20 °C): δ 20.7 (s). IR (KBr pellet): ν_{CO} (cm^{-1}) 1916 (m), 1853 (s), 1821 (vs), 1784 (s).

Synthesis of [(Ph$_3$P)$_2$Pd$_2$Cp$_2$Mo$_2$(μ-CO)$_4$(μ_3-CO)$_2$] (5). A mixture of [CpMo(CO)$_3$H] (155 mg; 0.63 mmol), [(Ph$_3$P)$_2$Pd$_2$-(Ph)$_2$(μ-OH)$_2$] (140 mg; 0.15 mmol), and benzene (4 mL) was stirred for 30 min. The resulting deep green solutions were treated with MeOH (8 mL), stirred for 10 min, and filtered. The green solid was thoroughly washed with acetone and pentane and dried under vacuum to give 155 mg (84%) of analytically and spectroscopically pure **5**.[23] Anal. Calcd for C$_{52}$H$_{40}$Mo$_2$O$_6$P$_2$Pd$_2$: C, 50.9; H, 3.3. Found: C, 50.7; H, 3.2. ^{1}H NMR (CDCl$_3$, 20 °C): δ 4.6 (s, 10H, C$_5$H$_5$), 7.4 (m, 18H, 3,4,5-C$_6$H$_5$), 7.6 (m, 12H, 2,6-C$_6$H$_5$). ^{31}P NMR (CDCl$_3$, 20 °C): δ 24.5 (s). IR (KBr): ν_{CO} (cm^{-1}) 1915 (m), 1852 (s), 1829 (vs), 1784 (s).

Synthesis of [(Ph$_3$P)$_2$Pd$_2$Cp$_2$Cr$_2$(μ-CO)$_4$(μ_3-CO)$_2$] (6). Solid [(Ph$_3$P)$_2$Pd(Ph)$_2$(μ-OH)$_2$] (100 mg; 0.108 mmol) was added to a solution of [CpCr(CO)$_3$H] (73 mg; 0.363 mmol) in benzene (3 mL), and the mixture was stirred for 30 min. The resulting solution was reduced in volume to ca. 1 mL, treated with pentane (8 mL), and left overnight. The precipitated solid was separated, washed with MeOH (3 × 6 mL) and pentane (3 × 6 mL), dried, and recrystallized from CH$_2$Cl$_2$/MeOH to give 96 mg (78%) of spectroscopically pure **6**.[23] ^{1}H NMR (CDCl$_3$, 20 °C): δ 4.1 (s, 10H, C$_5$H$_5$), 7.4 (m, 18H, 3,4,5-C$_6$H$_5$), 7.5 (m, 12H, 2,6-C$_6$H$_5$). ^{31}P NMR (CDCl$_3$, 20 °C): δ 26.8 (s). IR (KBr pellet): ν_{CO} (cm^{-1}) 1902 (m), 1847 (vs), 1824 (vs), 1789 (s).

Synthesis of [(Cy$_3$P)$_2$Pd$_2$Cp$_2$W$_2$(μ-CO)$_4$(μ_3--CO)$_2$] (7). A mixture of [(Cy$_3$P)$_2$Pd$_2$(Ph)$_2$(μ-OH)$_2$] (50 mg; 0.052 mmol), [CpW(CO)$_3$H] (80 mg; 0.239 mmol), and benzene (4 mL) was stirred for 30 min, diluted with MeOH (5 mL), and left overnight. The precipitated solid was separated, washed with MeOH (3 × 5 mL) and pentane (2 × 5 mL), and dried under vacuum to give 71 mg (95%) of analytically and spectroscopically pure, dark blue **7**. Anal. Calcd for C$_{52}$H$_{76}$O$_6$P$_2$Pd$_2$W$_2$: C, 43.4; H, 5.3. Found: C, 43.2; H, 5.0. ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 1.2−2.2 (m, 66H, C$_6$H$_{11}$), 5.2 (s, 10H, C$_5$H$_5$). ^{31}P NMR (CH$_2$Cl$_2$, 20 °C): δ 33.8 (s). IR (KBr pellet): ν_{CO} (cm^{-1}) 1895 (m), 1820 (vs), 1795 (vs).

Synthesis of [(Ph$_3$P)$_2$Pd$_2$Cp*$_2$W$_2$(μ-CO)$_4$(μ_3-CO)$_2$] (8). A mixture of [Cp*W(CO)$_3$H] (179 mg; 0.443 mmol), [(Ph$_3$P)$_2$Pd$_2$-(Ph)$_2$(μ-OH)$_2$] (116 mg; 0.125 mmol), and benzene (4 mL) was stirred for 1 h, and the resulting emerald green solution was chromatographed on a silica gel column (toluene/CH$_2$Cl$_2$). The orange-yellow and green fractions were collected, and evaporation of the latter gave 182 mg of **8** (90% purity according to ^{31}P NMR). Crude **8** was dissolved in CH$_2$Cl$_2$ (2 mL), pentane (10 mL) was added, and the mixture was kept at −17 °C overnight, forming long green needles of **8**, which were separated, washed with cold pentane (2 × 5 mL), and dried under vacuum. The yield of **8** was 115 mg (60%). Anal. Calcd for C$_{62}$H$_{60}$O$_6$P$_2$Pd$_2$W$_2$: C, 48.2; H, 3.9. Found: C, 49.0; H, 4.0. ^{1}H NMR (CDCl$_3$, 20 °C): δ 1.4 (s, 30H, CH$_3$), 7.3−7.7 (m, 30H, C$_6$H$_5$). ^{31}P NMR (C$_6$D$_6$, 20 °C): δ 15.1 (s). ^{13}C NMR (CDCl$_3$,

(37) Sukharev, Yu. N.; Nekrasov, Yu. S. *Org. Mass Spectrom.* **1976**, *11*, 1239.

20 °C): δ 9.8 (s, CH$_3$), 100.5 (s, C$_5$), 128.0 (virtual t, J_{C-P} = 4.8 Hz, m-C$_6$H$_5$), 129.2 (s, p-C$_6$H$_5$), 134.3 (virtual t, J_{C-P} = 7.2 Hz, o-C$_6$H$_5$), 135.6 (virtual t, J_{C-P} = 16.1 Hz, q-C$_6$H$_5$), 236.1 (s, CO). IR (KBr): ν_{CO} (cm^{-1}) 1887 (m), 1836 (sh), 1811 (sh), 1795 (vs). The orange-yellow fraction was evaporated and chromatographed on silica (heptane/toluene) to give 43 mg (72%) of spectroscopically pure [Cp*W(CO)$_3$Ph]. The compound was recrystallized from pentane for elemental analysis. Anal. Calcd for C$_{19}$H$_{20}$O$_3$W: C, 47.5; H, 4.2. Found: C, 47.8; H, 3.9. ^{1}H NMR (CDCl$_3$, 20 °C): δ 1.9 (s, 15H, CH$_3$), 7.1 (m, 3H, 3,4,5-C$_6$H$_5$), 7.7 (m, 2H, 2,6-C$_6$H$_5$). ^{13}C NMR (CDCl$_3$, 20 °C): δ 10.6 (s, CH$_3$), 104.5 (s, C$_5$), 124.6 (s, p-C$_6$H$_5$), 128.5 (s, m-C$_6$H$_5$), 136.8 (s, q-C$_6$H$_5$), 145.8 (s, o-C$_6$H$_5$), 222.4 (s, CO), 233.1 (s, CO). IR (KBr): ν_{CO} (cm^{-1}) 1999 (s), 1912 (s), 1892 (vs).

Synthesis of [(Ph$_3$P)$_2$Pd$_2$Cp$_2$MoW(μ-CO)$_4$(μ_3-CO)$_2$] (9). Solid [CpW(CO)$_3$H] (65 mg; 0.195 mmol) was added to a stirred solution of **2** (101 mg; 0.088 mmol) in benzene (20 mL), causing the color to change first to brown and then to green. The mixture was stirred for 1 h, reduced in volume, and chromatographed on a silica column (25 × 250 mm; toluene$-$CH$_2$Cl$_2$). The first pink-brown band was discarded, and the subsequent bright green, green-blue, and violet bands were collected. The green-blue band was evaporated to dryness under vacuum, affording 57 mg (49%) of [(Ph$_3$P)$_2$Pd$_2$Cp$_2$MoW(μ-CO)$_4$(μ_3-CO)$_2$] as a green solid. Anal. Calcd for C$_{52}$H$_{40}$MoO$_6$P$_2$Pd$_2$W: C, 47.5; H, 3.1. Found: C, 47.4; H, 2.9. ^{1}H NMR (CDCl$_3$, 20 °C): δ 4.65 (s, 5H, MoC$_5$H$_5$), 4.7 (s, 5H, WC$_5$H$_5$), 7.4 (m, 18H, 3,4,5-C$_6$H$_5$), 7.6 (m, 12H, 2,6-C$_6$H$_5$). ^{31}P NMR (CH$_2$Cl$_2$, 20 °C): δ 22.9 (s). ^{13}C NMR (CDCl$_3$, 20 °C): δ 87.3 (s, C$_5$H$_5$Mo), 90.9 (s, C$_5$H$_5$W), 128.1 (virtual t, J_{C-P} = 4.5 Hz, m-C$_6$H$_5$), 129.8 (s, p-C$_6$H$_5$), 134.3 (virtual t, J_{C-P} = 7.0 Hz, o-C$_6$H$_5$), 134.4 (virtual t, J_{C-P} = 17.7 Hz, q-C$_6$H$_5$), 228.6 (s, MoCO), 240.3 (s, WCO). IR (KBr): ν_{CO} (cm^{-1}) 1916 (m), 1854 (s), 1825 (vs), 1781 (s). The bright green and violet fractions gave **5** and **4**, respectively (identified by ^{31}P NMR), whose yields were not determined.

Synthesis of [(Ph$_3$P)$_2$Pd$_2$Cp$_2$CrW(μ-CO)$_4$(μ_3-CO)$_2$] (10). A mixture of **6** (105 mg; 0.089 mmol), [CpW(CO)$_3$H] (77 mg; 0.229 mmol), and benzene (15 mL) was stirred at room temperature (the reaction was monitored by ^{31}P NMR spectroscopy). After 70 h, when the solution contained **10** and **4** in a ca. 3:1 ratio and only trace amounts of **6**, the mixture was chromatographed on a silica column (25 × 250 mm; toluene$-$CH$_2$Cl$_2$). The first pink-brown band was discarded, and the following green and violet fractions were collected. The green fraction was evaporated to dryness under vacuum to give 40 mg (34%) of analytically and spectroscopically pure [(Ph$_3$P)$_2$Pd$_2$Cp$_2$CrW(μ-CO)$_4$(μ-CO)$_2$] **(10).** Anal. Calcd for C$_{52}$H$_{40}$CrO$_6$P$_2$Pd$_2$W: C, 49.1; H, 3.2. Found: C, 48.9; H, 2.9. ^{1}H NMR (CDCl$_3$, 20 °C): δ 4.0 (s, 5H, CrC$_5$H$_5$), 4.7 (s, 5H, WC$_5$H$_5$), 7.4

(m, 18H, 3,4,5-C$_6$H$_5$), 7.6 (m, 12H, 2,6-C$_6$H$_5$). ^{31}P NMR (C$_6$H$_6$, 20 °C): δ 24.2 (s). ^{13}C NMR (CDCl$_3$, 20 °C): δ 86.8 (s, C$_5$H$_5$-Cr), 89.8 (s, C$_5$H$_5$W), 128.2 (virtual t, J_{C-P} = 4.8 Hz, m-C$_6$H$_5$), 129.9 (s, p-C$_6$H$_5$), 134.3 (virtual t, J_{C-P} = 7.1 Hz, o-C$_6$H$_5$), 134.3 (virtual t, J_{C-P} = 17.5 Hz, q-C$_6$H$_5$), 227.6 (s, CrCO), 251.9 (s, WCO). IR (KBr pellet): ν_{CO} (cm^{-1}) 1922 (m), 1849 (s), 1822 (s), 1792 (s). Evaporation of the violet fraction gave 10 mg (8%) of **4** (identified by ^{31}P NMR).

Single-Crystal X-ray Diffraction Study of [(Ph$_3$P)$_2$-Pd$_2$(Ph)$_2$(μ-OH)Cr(CO)$_3$Cp]·MeOH (3·MeOH). Well-shaped, transparent orange crystals of the complex were obtained by slow diffusion of pentane into a solution of **3** in dichloromethane containing traces of methanol, over 1 week at $-$17 °C. One of the crystals (ca. 0.3 × 0.2 × 0.1 mm) was mounted on a glass capillary. All measurements were made at $-$150 °C on a Siemens SMART CCD diffractometer with Mo Kα_1 radiation. During the data collection, standards were measured after every 150 reflections. No crystal decay was noticed. A total of 17 590 reflections were collected. The unique set contained 6379 reflections. Using the criterion I > 2.5$\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from the counting statistics, 5328 reflections were used. The data were corrected for Lorentz and polarization effects.[38] No absorption correction was made. The structure was solved by direct methods. All atoms were refined anisotropically, except for hydrogens. The refinement was made on F. The hydrogen atoms were calculated. The final cycle of full-matrix least-squares refinement was based on 5328 observed reflections and 605 variable parameters. Weights based on calculated statistics were used. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.820 and $-$0.720 e/Å^3, respectively. All the calculations were performed using the NRCVAX crystallographic software package.[39]

Supporting Information Available: Listings of crystallographic details, atomic parameters, bond distances and angles, torsion and dihedral angles, and isotropic and anisotropic thermal parameters and ORTEP drawings for **3**·MeOH (27 pages). Ordering information is given on any current masthead page.

OM9605138

(38) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.
(39) Gabe, E. J.; Lee, F. L.; Lepage, Y. *J. Appl. Crystallogr.* **1989**, *22*, 384.