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Contribution from the Laboratoire de Chimie de Coordination, associé au CNRS (ERA 670), Université Louis Pasteur,
67070 Strasbourg Cédex, France, and the Laboratoire de Minéralogie-Cristallographie,
associé au CNRS (ERA 162), Université de Nancy 1, 54037 Nancy, France

Syntheses of Tetrametallic Planar, Triangulated Mixed-Metal Palladium Clusters. X-ray Crystal Structures of $Pd_2M_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PEt_3)_2$ with M = Cr, Mo, and W[1]

ROBERT BENDER,[2a] PIERRE BRAUNSTEIN,*[2a] JEAN-MARC JUD,[2a] and YVES DUSAUSOY[2b]

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The first family of heterotetrametallic palladium clusters has been synthesized, characterized, and structurally investigated. They contain two palladium and two group 6 transition-metal atoms. Thus, the clusters $Pd_2M_2Cp_2(CO)_6(PR_3)_2$ (Cp = η^5-C_5H_5), where M = Cr, Mo, W and PR_3 = PMe_3, PEt_3, P-*n*-Bu_3, PMe_2Ph, PPh_3, were prepared by following two different synthetic strategies. In method a, we reacted the sodium carbonylmetalates $Na[M(CO)_3Cp]$ with the $PdCl_2(PR_3)_2$ complexes in THF. The NaCl elimination is accompanied by a redox reaction, ligand exchange, and cluster formation. Thus, the dimers $[M(CO)_3Cp]_2$ and/or derivatives thereof, such as the new complexes $M_2(CO)_5(PEt_3)Cp_2$ (M = Mo, W), were obtained, together with the desired mixed-metal clusters. In method b, 1 equiv of phosphine in THF is reacted with the reactive linear trimetallic complexes $Cp(OC)_3M\text{-}Pd(PhCN)_2\text{-}M(CO)_3Cp$ (formed in situ at −76 °C from $PdCl_2(PhCN)_2$ and 2 equiv of $Na[M(CO)_3Cp]$ (M = Cr, Mo, W)). The dimers are also formed, and the mixed-metal clusters are obtained in generally higher yields (up to 90%) than with method a. Other advantages of method b include its generality and the use of only half the stoichiometric amount in phosphine needed in method a. Mechanisms for these reactions are proposed, involving radical intermediates. An X-ray diffraction study has been performed on the complexes $Pd_2M_2Cp_2(CO)_6(PEt_3)_2$ where M = Cr (**1b**), Mo (**2b**), and W (**3b**). These three clusters are isostructural: monoclinic, space group $P2_1/c\text{-}C^5_{2h}$ with $Z = 2$, a = 10.838 (2), 10.924 (2), 10.919 (1) Å, b = 9.491 (5), 9.474 (2), 9.467 (2) Å, c = 17.476 (4), 17.596 (5), 17.536 (2) Å, β = 115.40 (2), 114.89 (3), 114.91 (1)°, and ρ(calcd) = 1.58, 1.73, 2.06 g cm^{-3}, for **1b**, **2b**, and **3b**, respectively. The structures of **1b**, **2b**, and **3b** were solved by using 2525 reflections with $I > \sigma(I)$, 3179 with $I > 2\sigma(I)$, and 2397 with $I > \sigma(I)$ and refined to conventional R values 0.039, 0.032, and 0.043, respectively. All three structures are characterized by a planar, triangulated parallelogram framework for the metallic core. Such an arrangement has to date only rarely been encountered in clusters. The center of symmetry of these molecules is at the middle of the Pd–Pd′ bond, which has an average length of 2.578 Å and is among the shortest values reported for such a bond. The average Pd–Cr, Pd–Mo, and Pd–W distances in **1b**, **2b**, and **3b** are 2.759, 2.846, and 2.849 Å, respectively. The PEt_3 ligands are coordinated to the Pd atoms with an average Pd′–Pd–P angle of 177.5° and an average Pd–P distance of 2.337 Å. The planes of the η^5-Cp ligands are parallel to each other and form a dihedral angle of ca. 75° with the metallic plane. The carbonyl ligands C(1)O(1) and C(3)O(3) are semibridging the M–Pd′ and M–Pd edges, respectively, whereas C(2)O(2) is semi triply bridging the heterotrimetallic face MPdPd′. By symmetry, an identical situation is found with the carbonyls bridging M′, Pd′, and Pd. The M–CO distances are always shorter than the Pd– or Pd′–CO distances. The bridging situation of the carbonyl ligands can be related to the fact that the M–Pd′ distances are shorter than the corresponding M–Pd distances. In these diamagnetic clusters, the $CpM(CO)_3$ fragments "bridging" the L–Pd–Pd′–L unit present the original structure of a three-legged piano stool with two extra atoms (Pd and Pd′) located within the $M(CO)_3$ cone. We favor a description of the 18-electron $[CpM(CO)_3]^-$ fragments acting as 4-electron donors toward the $L\rightarrow Pd^{I}\text{—}Pd^{I}\leftarrow L$ unit. Spectroscopic (IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR) data indicate that all the "Pd_2M_2" clusters presented here have the same basic structures as **1b**, **2b**, and **3b**. These data are discussed in relation to the structure and bonding modes within the metal–metal and metal–ligand systems.

Introduction

Organometallic cluster chemistry has now become a classical chapter of modern inorganic chemistry.[3a] This is related to the increasing number of cluster complexes that synthetic chemists prepare, to the fascinating properties of these molecules, to their role in homogeneous and heterogeneous catalysis, and to the key position of this area of chemistry at the frontiers of other disciplines.[3b]

Of particular importance are the mixed-metal clusters in which different metals are bonded to each other in a molecular framework. The first molecules ever reported in this class of compounds were the anion $[FeCo_3(CO)_{12}]^-$ and the hydride $[HFeCo_3(CO)_{12}]$.[3c] They have stimulated a considerable interest in the synthesis, structure, and reactivity of mixed-metal clusters.

As part of continuing studies in our laboratory, we have investigated the possibility of preparing mixed-metal clusters containing palladium and another transition metal. This was motivated by the absence of such clusters at the time when we started this study and by their potential interest for catalysis. We therefore investigated the reaction of palladium(II) complexes with group 6 carbonylmetalates, following the scheme we had used to prepare the first complexes containing a palladium–transition-metal bond[4] (eq 1; Cp = η^5-C_5H_5, py = pyridine). Indeed we found that replacing pyridine with

$$\textit{trans}\text{-}PdCl_2(py)_2 + 2Na[Mo(CO)_3Cp] \rightarrow \textit{trans}\text{-}Pd[Mo(CO)_3Cp]_2(py)_2 + 2NaCl \quad (1)$$

PEt_3 in the above starting complexes dramatically alters the course of the reaction, affording a new type of mixed-metal palladium cluster. A preliminary note[5] has been published on one of them, $Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$. We present here the synthesis and characterization of the $Pd_2M_2Cp_2(CO)_6(PR_3)_2$ class of complexes, where M = Cr, Mo, W and PR_3 = PMe_3, PEt_3, P-*n*-Bu_3, PMe_2Ph, PPh_3 (Me = CH_3, Et = C_2H_5, *n*-Bu = C_4H_9, Ph = C_6H_5). These were obtained by two different chemical routes.

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Table I. Quantitative Data for Syntheses by Method a

complexes	amt of $PdCl_2L_2$, g (mmol)	amt of $NaM(CO)_3Cp$, mmol	reacn time, h	eluent toluene/pentane (v/v)	isolated products[a]	mass, g	% total yield[b]
1b	2.20 (4)	8	16	2:1	1b	0.100	6
1e	2.80 (4)	8	20	1:0	1e	0.684	30
2b	2.06 (5)	10	7.5	1:2	$Mo_2(CO)_5(PEt_3)Cp_2$	0.03	0.5
				1:0	2b	1.75	75
2e	2.00 (2.85)	5.7	4	1:2	$[Mo(CO)_3Cp]_2$	0.55	39
				1:0	2e	1.04	60
3b	2.69 (6.5)	14.3	6.5	1:3	$W_2(CO)_5(PEt_3)Cp_2$	0.05	0.9
				1:0	3b	1.90	52
3e[c]	3.16 (4.5)	10	5	3:4	$[W(CO)_3Cp]_2$	0.11	3
				1:0	3e	2.52	80

[a] 1b and 1e have been recrystallized from THF/pentane, 2b from toluene/pentane, and 2e, 3b, and 3e from CH_2Cl_2/pentane. [b] Yields of clusters are based on Pd and the others on Mo or W, respectively. [c] A 1.8-g amount of 3e (57.1%) precipitated from the reaction mixture.

Two different strategies can be envisaged to prepare phosphine-substituted mixed-metal clusters. Method a would consist of the formal addition of the second metal to a phosphine complex of the first one. Method b would involve the addition of the phosphine to a preformed mixed-metal complex. Since these strategies have not yet been systematically compared in terms of feasibility and cluster yields, it is difficult to anticipate reaction mechanisms for them. We present in this paper two synthetic methods corresponding to methods a and b for obtaining phosphine-substituted palladium mixed-metal clusters. The metal and ligand redistributions observed allow us to compare the two methods and their efficiency (cluster yield) under similar conditions. Rational pathways are also suggested for the reaction mechanisms.

Experimental Section

A. Reagents and Physical Measurements. All reactions were performed in Schlenk-type flasks under nitrogen or argon if specified. Solvents were distilled under argon from sodium–benzophenone ketyl prior to use except dichloromethane, which was dried and distilled from P_2O_5. Ethanol was distilled from $Mg(OEt)_2$. Nitrogen (Air Liquide purified grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water.

Column chromatography was performed under nitrogen with use of silica gel (Kieselgel 60, Merck) or celite (545 Prolabo).

Elemental analyses of C, H, and P 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 as KBr pellets, Nujol mulls, or CH_2Cl_2 solutions.

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 90.00, 200.13, or 250.00, 22.63, 50.32, or 62.86, and 36.43 MHz, respectively, on FT Bruker WH-90, Bruker WP 200SY, and Cameca 250 instruments. Proton and carbon chemical shifts are positive downfield relative to external Me_4Si. Positive phosphorus chemical shifts indicate a downfield position relative to H_3PO_4.

B. Syntheses. The phosphine ligands, PEt_3, P-n-Bu_3, PMe_2Ph, and PPh_3, were used as received (Fluka commercial grade) except PMe_3, which was prepared according to the procedure of Markham et al.[6] The palladium complexes $PdCl_2L_2$ were prepared according to the literature methods for L = PhCN, PEt_3, and PPh_3.[7] The sodium carbonylmetalates were initially prepared by Na/Hg reduction[8,9] of the $[M(CO)_3Cp]_2$ dimers.[10] We then developed some modifications of the previously described syntheses[9,11,12] for the obtainment from $M(CO)_6$ and stabilization of these anions as dimethoxyethane (DME) solvates. This has already been reported for M = Cr.[13]

Improved Syntheses of $Na[M(CO)_3Cp]\cdot 2DME$ (M = Cr, Mo, W). (a) M = Cr. To a stirred suspension of $Cr(CO)_6$ (6.404 g, 29.1 mmol; Ventron commercial grade) in DME (120 mL) was added NaCp·DME (5.19 g, 29.1 mmol) prepared according to Wrighton et al.[12] After 24 h of stirring and refluxing, the mixture was allowed to cool to room temperature and $Na[Cr(CO)_3Cp]\cdot 2DME$ was precipitated with pentane (400 mL) at −76 °C. The pale yellow powder was filtered, washed with pentane, and dried, affording $Na[Cr(CO)_3Cp]\cdot 2DME$ (10.10 g, 25 mmol, 86% based on Cr). IR (THF): $\nu(CO)$ = 1898 s, 1794 s, 1744 s cm^{-1}.

(b) M = Mo. The same procedure as for M = Cr was followed, with use of $Mo(CO)_6$ (7.68 g, 29.1 mmol). $Na[Mo(CO)_3Cp]\cdot 2DME$ was isolated as a white solid (11.74 g, 26.19 mmol, 90% based on Mo). IR (DME): $\nu(CO)$ = 1879 s, 1779 s, 1748 s cm^{-1}.

(c) M = W. The same procedure as for M = Cr was followed, with use of $W(CO)_6$ (10.24 g, 29.1 mmol). $Na[W(CO)_3Cp]\cdot 2DME$ was isolated as a white solid (14.04 g, 26.19 mmol, 90% based on W). IR (THF): $\nu(CO)$ = 1895 s, 1792 s, 1742 s cm^{-1}.

Syntheses of the Clusters $Pd_2M_2Cp_2(CO)_6L_2$.

M	L = PMe_3	L = PEt_3	L = P-n-Bu_3	L = PMe_2Ph	L = PPh_3
Cr	1a	1b	1c		1e
Mo	2a	2b	2c		2e
W	3a	3b	3c	3d	3e

Two different synthetic methods have been developed and are discussed in the text. The first, method a, uses the reaction of the sodium carbonylmetalates with the $PdCl_2(PR_3)_2$ complexes, whereas method b concerns the reaction of free PR_3 with the linear trimetallic complexes *trans*-$Pd[M(CO)_3Cp]_2(PhCN)_2$ formed in situ from $PdCl_2(PhCN)_2$ and $Na[M(CO)_3Cp]$.

The syntheses of 1b, 2b, and 3b are described explicitly. The other clusters have been prepared according to similar procedures. Quantitative data for these syntheses are given in Tables I and II. Table III summarizes the characterization of the products.

Infrared and NMR data (where available) are given in Tables XIII and XIV, respectively. The reactions described below were monitored by IR spectroscopy in the $\nu(CO)$ region.

Preparation of $Pd_2Cr_2Cp_2(CO)_6(PEt_3)_2$ (1b). Method a. To a stirred suspension of *trans*-$PdCl_2(PEt_3)_2$ (2.20 g, 4 mmol) in THF (50 mL) was added at room temperature a filtered solution of $Na[Cr(CO)_3Cp]$ (8 mmol) in THF (50 mL) prepared by Na/Hg reduction of $[Cr(CO)_3Cp]_2$ (1.609 g, 4 mmol). After 16 h of stirring the dark green solution was filtered and the solvent was removed under vacuum. The residue was chromatographed on a silica gel column. Elution with toluene/pentane (2:1) gave a dark green solution of **1b** (0.100 g, 0.12 mmol, 6% based on Pd, after recrystallization from THF/pentane). Further elution with a toluene/THF mixture afforded a trace amount of unstable compounds which have not yet been characterized.

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Table II. Quantitative Data for Syntheses by Method b

					$[M(CO)_3Cp]_2$ [b]			cluster[c]		
cluster	amt of $PdCl_2(PhCN)_2$, mmol	amt of $Na[M(CO)_3Cp]$, mmol	amt of L, mmol	total reacn time,[a] h	eluent[d] To/Pn (v/v)	amt, g	% yield	eluent[d] (v/v)	amt, g	% yield
1a	2	4	2	3.25	3:10	0.10	12.5	To/ CH_2Cl_2 1:1	0.575	75
1b	2	4	2	3.25	3:10	0.05	6	To/ THF 10:1	0.766	90
1c	2	4	2	3.25	3:10	0.03	3.8	To/ THF 10:1	0.612	60
1e	2	4	2	4.25	3:10	0.90	11.25	To	0.969	85
2a	1.8	3.6	1.8	3.25	3:10	0.40	45	To	0.619	78
2b	2	4	2	3.25	3:10	0.45	46	To	0.736	78
2c	1.5	3	1.5	3.25	1:1	0.30	41	Pn	0.498	60
2e[e]	1	2	1	3.75		0.20	41		0.549	89
3a	2	4	2	4.45	1:1	0.50	37	To/ CH_2Cl_2 1:1	0.824	80
3b	2	4	2	4.25	1:1	0.45	34	To/ CH_2Cl_2 1:1	0.836	75
3c	2.05	4.1	2.05	4.75	4:10	0.40	29	Pn	0.805	62
3d	2.05	4.1	2.05	4.35	6:10	0.35	25	To	0.920	78
3e[f]	2	4	2	3.35	6:10	0.40	30	To	1.125	80

[a] This includes 0.25 h at −76 °C and the time required to reach room temperature. [b] All chromatographic separations were performed on a Celite column except those leading to **1b** and **1c**, for which silica gel was used. [c] All these clusters have been recrystallized from CH_2Cl_2/pentane, except **1c**, **2c**, and **3c** which were crystallized from pentane at −100 °C. [d] Abbreviations: To = toluene, Pn = pentane, THF = tetrahydrofuran. [e] 2e was precipitated after concentration of the reaction mixture and addition of pentane, filtered, washed with H_2O and EtOH, and dried. The solution afforded $[Mo(CO)_3Cp]_2$. [f] 3e was partly precipitated during the reaction, filtered, washed with H_2O and EtOH, and dried (0.228 g, 16%).

Table III. Characterization of the Clusters $Pd_2M_2Cp_2(CO)_6L_2$

				anal. calcd (found)	
complex	color	mp, °C	formula (mol wt)	% C	% H
1a	green	>160 dec	$C_{22}H_{28}Cr_2O_6P_2Pd_2$ (767.20)	34.44 (34.19)	3.68 (3.59)
1b	dark green	>170 dec	$C_{28}H_{40}Cr_2O_6P_2Pd_2$ (851.36)	39.50 (39.20)	4.73 (4.59)
1c	dark green	140	$C_{40}H_{64}Cr_2O_6P_2Pd_2$ (1019.68)	47.12 (47.01)	6.32 (6.20)
1e	dark green	>170 dec	$C_{52}H_{40}Cr_2O_6P_2Pd_2$ (1139.62)	54.80 (54.50)	3.54 (3.50)
2a	brown-violet	>160 dec	$C_{22}H_{28}Mo_2O_6P_2Pd_2$ (855.09)	30.90 (30.24)	3.30 (3.12)
2b	violet	193–195	$C_{28}H_{40}Mo_2O_6P_2Pd_2$ (939.25)	35.80 (35.87)	4.29 (4.12)
2c	violet	150 dec	$C_{40}H_{64}Mo_2O_6P_2Pd_2$ (1107.58)	43.38 (43.15)	5.82 (5.60)
2e	grey-green	>170 dec	$C_{52}H_{40}Mo_2O_6P_2Pd_2$ (1227.51)	50.88 (51.02)	3.28 (3.05)
3a	violet	176	$C_{22}H_{28}O_6P_2Pd_2W_2$ (1030.91)	25.63 (25.35)	2.73 (2.60)
3b	dark violet	168–170	$C_{28}H_{40}O_6P_2Pd_2W_2$ (1115.07)	30.16 (29.9)	3.61 (3.50)
3c	violet	151–152	$C_{40}H_{64}O_6P_2Pd_2W_2$ (1283.39)	37.43 (37.61)	4.82 (4.87)
3d	violet	159	$C_{32}H_{32}O_6P_2Pd_2W_2$ (1155.05)	33.27 (33.17)	2.79 (2.84)
3e	dark violet	198–200	$C_{52}H_{40}O_6P_2Pd_2W_2$ (1403.33)	44.50 (44.30)	2.87 (2.97)

Method b. To a stirred solution of *trans*-$PdCl_2(PhCN)_2$ (0.767 g, 2 mmol) in THF (50 mL) was added at −76 °C a solution of $Na[Cr(CO)_3Cp]\cdot 2DME$ (1.617 g, 4 mmol) in THF (75 mL). After 0.25 h of stirring, PEt_3 (0.236 g, 2 mmol) in THF (30 mL) was added dropwise at −76 °C. Under constant agitation, the temperature was slowly raised to 20 °C in 3 h. The resulting dark green mixture was evaporated to dryness, and the residue was chromatographed on a silica gel column. Elution with a toluene/pentane mixture (3:10) gave a dilute solution of $[Cr(CO)_3Cp]_2$ (0.050 g, 0.12 mmol, 6% based on Cr after recrystallization from CH_2Cl_2/pentane at −20 °C). Further elution with toluene/THF (10:1) produced a dark green solution of **1b** (0.766 g, 0.90 mmol, 90% based on Pd, after recrystallization from CH_2Cl_2/pentane).

Preparation of $Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$ (2b). Method a. To a stirred suspension of *trans*-$PdCl_2(PEt_3)_2$ (2.06 g, 5 mmol) in THF (50 mL) was added at room temperature a filtered solution of $Na[Mo(CO)_3Cp]$ (10 mmol) in THF (60 mL) prepared by Na/Hg reduction of $[Mo(CO)_3Cp]_2$ (2.15 g, 5 mmol). After 7.5 h of stirring the mixture was filtered and the solvent was removed under vacuum. The residue was chromatographed on a silica gel column. Elution with a toluene/pentane mixture (1:10) gave a yellow compound (0.025 g) which has not yet been characterized (IR (KBr): $\nu(CO)$ = 1932 vs, 1850 vs cm^{-1}). Further elution with toluene/pentane (1:2) produced a red-violet solution of $Mo_2(CO)_5PEt_3Cp_2$ (0.03 g, 0.05 mmol, 0.5%

Table IV. Summary of Crystal Data and Intensity Collection of 1b, 2b, and 3b

	$Pd_2Cr_2Cp_2(CO)_6(PEt_3)_2$ (1b)	$Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$ (2b)	$Pd_2W_2Cp_2(CO)_6(PEt_3)_2$ (3b)
formula	$C_{28}H_{40}Cr_2O_6P_2Pd_2$	$C_{28}H_{40}Mo_2O_6P_2Pd_2$	$C_{28}H_{40}O_6P_2Pd_2W_2$
fw	851.36	939.25	1115.07
cryst syst	monoclinic	monoclinic	monoclinic
a, Å	10.838 (2)	10.924 (2)	10.919 (1)
b, Å	9.491 (5)	9.474 (2)	9.467 (2)
c, Å	17.476 (4)	17.596 (5)	17.536 (2)
β, deg	115.40 (2)	114.89 (3)	114.91 (1)
V, Å^3	1623.86 (10)	1652.05 (8)	1644.07 (9)
Z	2	2	2
density (calcd), g cm^{-3}	1.58	1.73	2.06
cryst dimens, mm	0.2 × 0.1 × 0.1	0.1 × 0.2 × 0.2	0.1 × 0.1 × 0.08
space group	$P2_1/c\text{-}C_{2h}^5$	$P2_1/c\text{-}C_{2h}^5$	$P2_1/c\text{-}C_{2h}^5$
temp, °C	25	25	25
radiation	Mo Kα (from monochromator λ(Mo Kα) = 0.709 30 Å)		
linear coeff, cm^{-1}	14.6	18.8	83.6
scan θ/scan ω	1/1	2/3	2/3
scan width, deg	$1 + 0.35 \tan \theta$	$1 + 0.35 \tan \theta$	$1 + 0.35 \tan \theta$
2θ limits, deg	2-54	2-54	2-54
data collected	3952	3785	3769
unique data used	2525 ($I > \sigma(I)$)	3179 ($I > 2\sigma(I)$)	2397 ($I > \sigma(I)$)
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.039	0.032	0.043
$R_w = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2)^{1/2}$	0.064	0.048	0.086
std error in an observn of unit wt	0.6	0.9	0.7

Table V. Atomic Coordinates ×10^4 for $Pd_2Cr_2Cp_2(CO)_6(PEt_3)_2$ (1b)

atom[a]	x	y	z
Pd	784.7 (5)	5695.6 (6)	4753.7 (3)
Cr	1842 (1)	3342 (1)	5774 (1)
P	2147 (2)	7008 (2)	4280 (1)
O(1)	−372 (6)	1488 (6)	4557 (4)
O(2)	1403 (6)	5940 (6)	6639 (3)
O(3)	2462 (7)	3548 (7)	4272 (4)
C(1)	360 (7)	2323 (8)	5032 (5)
C(2)	1329 (8)	5048 (8)	6158 (4)
C(3)	2119 (8)	3713 (9)	4823 (5)
C(4)	3560 (10)	3427 (12)	7054 (6)
C(5)	2603 (10)	2374 (13)	7047 (6)
C(6)	2521 (10)	1323 (11)	6442 (7)
C(7)	3435 (10)	1742 (11)	6081 (6)
C(8)	4050 (9)	3025 (12)	6459 (6)
C(9)	1791 (9)	8915 (8)	4163 (6)
C(10)	2752 (11)	9806 (10)	3903 (6)
C(11)	2093 (9)	6455 (9)	3252 (5)
C(12)	587 (11)	6406 (14)	2557 (6)
C(13)	3980 (7)	6863 (10)	4978 (5)
C(14)	4311 (10)	7325 (14)	5900 (6)

[a] Atoms are labeled in agreement with Figure 1.

based on Mo, after recrystallization from toluene/pentane) characterized by IR, elemental analysis, and ^1H NMR. IR (KBr): ν(CO) = 1960 vs, 1895 vs, 1875 vs, 1855 vs, 1805 vs cm^{-1}. Anal. Calcd for $C_{21}H_{25}Mo_2O_5P$: C, 43.47; H, 4.34; P, 6.59. Found: C, 43.47; H, 4.30; P, 6.30. ^1H NMR ($CDCl_3$): δ 5.21 (5 H, s, C_5H_5), 4.95 (5 H, d, C_5H_5, ^3J(PH) = 2 Hz), 1.92 (2 H, m, CH_2CH_3), 1.18 (3 H, m, CH_2CH_3). Using toluene as eluent afforded a violet solution of **2b** (1.75 g, 0.186 mmol, 75% based on Pd, after recrystallization from toluene/pentane).

Method b. To a stirred solution of *trans*-$PdCl_2(PhCN)_2$ (0.767 g, 2 mmol) in THF (50 mL) was added at −76 °C a filtered solution of Na[Mo(CO)$_3$Cp] (4 mmol) in THF (75 mL) prepared by Na/Hg reduction of [Mo(CO)$_3$Cp]$_2$ (0.980 g, 2 mmol). After 0.25 h of stirring, PEt_3 (0.236 g, 2 mmol) in THF (35 mL) was added dropwise at −76 °C. Under constant agitation the temperature was slowly raised to reach 20 °C in 3 h. The resulting brown-violet mixture was evaporated to dryness, and the residue was chromatographed on a Celite column. Elution with toluene/pentane (3:10) gave a solution of [Mo(CO)$_3$Cp]$_2$ (0.450 g, 0.9 mmol, 46% based on Mo after recrystallization from toluene/pentane at −20 °C). Further elution with toluene produced a violet solution of **2b** (0.736 g, 0.78 mmol, 78% based on Pd, after recrystallization from CH_2Cl_2/pentane).

Preparation of $Pd_2W_2Cp_2(CO)_6(PEt_3)_2$ (3b). Method a. To a stirred suspension of *trans*-$PdCl_2(PEt_3)_2$ (2.69 g, 6.5 mmol) in THF (75 mL) was added at room temperature a filtered solution of Na[W(CO)$_3$Cp] (14.3 mmol) in THF (75 mL) prepared by Na/Hg reduction of [W(CO)$_3$Cp]$_2$ (4.762 g, 7.15 mmol). After 6.5 h of stirring the mixture was filtered and the solvent was removed under vacuum. The residue was chromatographed on a silica gel column. Elution with toluene/pentane (1:3) gave a red solution of $W_2(CO)_5PEt_3Cp_2$ (0.050 g, 0.07 mmol, 0.9% based on W) characterized by IR, elemental analysis, and ^1H NMR. IR (THF): ν(CO) = 1953 m, 1883 sh, 1872 vs, 1800 m cm^{-1}. Anal. Calcd for $C_{21}H_{25}O_5PW_2$: C, 33.46; H, 3.33; P, 5.55. Found: C, 33.24; H, 3.44; P, 5.28. ^1H NMR ($CDCl_3$): δ 5.297 (5 H, s, C_5H_5), 5.032 (5 H, d, C_5H_5, ^3J(PH) = 1.7 Hz), 1.88 (2 H, m, CH_2CH_3), 1.14 (3 H, m, CH_2CH_3). Further elution with toluene produced a violet solution of **3b** (1.90 g, 1.7 mmol, 52% based on Pd, after recrystallization from CH_2Cl_2/pentane).

Method b. To a stirred solution of *trans*-$PdCl_2(PhCN)_2$ (0.767 g, 2 mmol) in THF (50 mL) was added at −76 °C a THF solution (75 mL) of Na[W(CO)$_3$Cp]·2DME (2.145 g, 4 mmol). After 0.25 h of stirring, PEt_3 (0.236 g, 2 mmol) in Et_2O (30 mL) was added dropwise at −76 °C. Under constant agitation, the temperature was slowly raised to reach 20 °C in 4 h. The resulting red-violet mixture was evaporated to dryness, and the residue was chromatographed on a Celite column. Elution with toluene/pentane (1:1) produced a red solution of [W(CO)$_3$Cp]$_2$ (0.450 g, 0.68 mmol, 34% based on W, after recrystallization from CH_2Cl_2/pentane at −20 °C). Further elution with toluene/CH_2Cl_2 (1:1) gave a violet solution of **3b** (0.836 g, 0.75 mmol, 75% based on Pd, after recrystallization from CH_2Cl_2/pentane).

C. Collection of the X-ray Data and Structure Determination. Single crystals of **1b** were obtained by slow diffusion of pentane into a THF solution of the complex. Single crystals of **2b** and **3b** were grown in a similar manner from toluene/pentane. Cell constants and other pertinent data are presented in Table IV. Intensity data were collected on a four-circle Enraf-Nonius CAD 4 diffractometer. No intensity decay was observed during the data collection periods. The quality of the structure determination is given by R and R_w (Table IV) and the σ values (Tables VIII and IX). Absorption corrections were omitted in view of the low linear absorption coefficient. The structures were solved by Patterson and Fourier methods. Refinements by full-matrix least squares (all non-hydrogen atoms anisotropic) proceeded to the R factor values indicated in Table IV, using the Busing ORX FLS 3 method.[15] Final positional parameters for **1b**, **2b**, and **3b** are given in Tables V–VII. Thermal parameters and observed and calculated structure factor amplitudes of the reflections used in the refinement of all three structures are available as supplementary material.[16]

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Table VI. Atomic Coordinates ×10^4 for $Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$ (**2b**)

atom^a	x	y	z
Pd	779.6 (4)	5680.1 (4)	4743.9 (2)
Mo	1876.0 (5)	3268.5 (5)	5794.1 (3)
P	2108 (1)	6993 (1)	4251 (1)
O(1)	−469 (5)	1450 (5)	4523 (3)
O(2)	1394 (5)	6012 (5)	6638 (3)
O(3)	2512 (6)	3554 (5)	4243 (3)
C(1)	274 (6)	2233 (6)	4995 (4)
C(2)	1328 (6)	5104 (6)	6167 (3)
C(3)	2156 (6)	3673 (6)	4780 (4)
C(4)	3645 (7)	3238 (8)	7139 (4)
C(5)	2717 (7)	2172 (10)	7115 (4)
C(6)	2707 (8)	1148 (7)	6504 (5)
C(7)	3609 (7)	1620 (8)	6176 (5)
C(8)	4177 (7)	2896 (9)	6562 (5)
C(9)	1806 (6)	8915 (6)	4169 (4)
C(10)	2733 (8)	9791 (7)	3897 (5)
C(11)	1988 (7)	6475 (7)	3215 (4)
C(12)	499 (8)	6457 (10)	2548 (4)
C(13)	3927 (6)	6826 (7)	4907 (4)
C(14)	4310 (7)	7238 (10)	5822 (4)

^{a} Atoms are labeled in agreement with Figure 1.

Table VII. Atomic Coordinates ×10^4 for $Pd_2W_2Cp_2(CO)_6(PEt_3)_2$ (**3b**)

atom^a	x	y	z
Pd	772 (1)	5674 (1)	4738 (1)
W	1877.4 (6)	3254 (1)	5788.8 (4)
P	2101 (4)	6988 (4)	4245 (3)
O(1)	−496 (12)	1448 (13)	4512 (8)
O(2)	1442 (13)	6001 (13)	6648 (7)
O(3)	2518 (15)	3564 (14)	4224 (9)
C(1)	294 (16)	2242 (18)	4985 (10)
C(2)	1385 (17)	5111 (20)	6197 (11)
C(3)	2175 (17)	3649 (19)	4772 (12)
C(4)	3618 (20)	3235 (23)	7145 (13)
C(5)	2700 (21)	2180 (28)	7125 (13)
C(6)	2661 (22)	1046 (22)	6514 (14)
C(7)	3623 (19)	1601 (25)	6189 (14)
C(8)	4174 (19)	2922 (23)	6591 (13)
C(9)	1784 (18)	8905 (17)	4161 (13)
C(10)	2723 (21)	9824 (21)	3888 (14)
C(11)	1989 (18)	6474 (19)	3202 (11)
C(12)	496 (21)	6445 (29)	2531 (11)
C(13)	3911 (15)	6848 (20)	4902 (12)
C(14)	4316 (19)	7252 (27)	5841 (12)

^{a} Atoms are labeled in agreement with Figure 1.

Results and Discussion

Crystal Structures. Thermal parameters and observed and calculated structure factors of $Pd_2M_2Cp_2(CO)_6(PEt_3)_2$ (M = Cr (**1b**), Mo (**2b**), W (**3b**)) are given in Tables XV–XVIII of the supplementary material. Selected bond distances and angles for the three clusters are given in Tables VIII and IX, respectively. The labeling scheme used in the description of these molecules on the ORTEP plot is given in Figure 1.

The three clusters **1b**, **2b**, and **3b** are isostructural, and Figure 1 represents their molecular structure for M = Cr, Mo, W. The four metal atoms are coplanar and form a triangulated parallelogram with the center of symmetry at the middle of the Pd–Pd′ bond. The two PEt_3 ligands, each one bonded to a Pd atom, are collinear with the Pd–Pd′ bond. Each Cp ligand is η^5 bonded to a M atom whereas the CO ligands of each $M(CO)_3$ tripod occupy asymmetric bridging positions, with C(1)O(1) and C(3)O(3) between M and Pd′ or Pd, respectively, and C(2)O(2) between M, Pd, and Pd′.

Table VIII. Bond Lengths (Å) in Crystalline $Pd_2M_2Cp_2(CO)_6(PEt_3)_2$ Complexes (M = Cr, Mo, W)^a

	compd		
bond^b	M = Cr (**1b**)	M = Mo (**2b**)	M = W (**3b**)
Pd–Pd′	2.578 (1)	2.582 (1)	2.573 (3)
Pd′–M	2.741 (1)	2.827 (1)	2.829 (1)
Pd–M	2.777 (1)	2.864 (1)	2.868 (1)
Pd–P	2.339 (2)	2.338 (2)	2.335 (5)
Pd–C(1)	2.30 (1)	3.37 (1)	3.35 (2)
Pd–C(2)	2.34 (1)	2.38 (1)	2.41 (2)
Pd–C(3)	2.34 (1)	2.41 (1)	2.44 (2)
Pd′–C(1)	2.37 (1)	2.42 (1)	2.44 (2)
Pd′–C(2)	2.26 (1)	2.31 (1)	2.35 (2)
Pd′–C(3)	3.57 (1)	3.69 (1)	3.72 (2)
M–C(1)	1.84 (1)	1.98 (1)	1.96 (1)
M–C(2)	1.92 (1)	2.04 (1)	2.05 (2)
M–C(3)	1.84 (1)	1.97 (1)	1.98 (2)
C(1)–O(1)	1.17 (1)	1.15 (1)	1.18 (2)
C(2)–O(2)	1.17 (1)	1.17 (1)	1.14 (2)
C(3)–O(3)	1.18 (1)	1.16 (1)	1.17 (3)
M–C(4)	2.21 (1)	2.34 (1)	2.34 (2)
M–C(5)	2.21 (1)	2.34 (1)	2.36 (2)
M–C(6)	2.20 (1)	2.34 (1)	2.33 (2)
M–C(7)	2.18 (1)	2.32 (1)	2.33 (2)
M–C(8)	2.18 (1)	2.32 (1)	2.32 (2)
M-centroid Cp	1.84 (1)	2.00 (1)	2.00 (1)
C(4)–C(5)	1.41 (2)	1.43 (1)	1.40 (3)
C(5)–C(6)	1.43 (2)	1.43 (1)	1.44 (3)
C(6)–C(7)	1.44 (2)	1.42 (1)	1.45 (4)
C(7)–C(8)	1.41 (1)	1.40 (1)	1.44 (3)
C(8)–C(4)	1.41 (2)	1.41 (1)	1.38 (3)
P–C(9)	1.84 (1)	1.84 (1)	1.84 (2)
P–C(11)	1.85 (1)	1.84 (1)	1.85 (2)
P–C(13)	1.83 (1)	1.84 (1)	1.83 (2)
C(9)–C(10)	1.55 (2)	1.53 (1)	1.56 (3)
C(11)–C(12)	1.56 (1)	1.55 (1)	1.56 (2)
C(13)–C(14)	1.55 (1)	1.54 (1)	1.56 (3)

^{a} Figures in parentheses are the estimated standard deviations in the last significant digits. ^{b} Atoms are labeled in agreement with Figure 1.

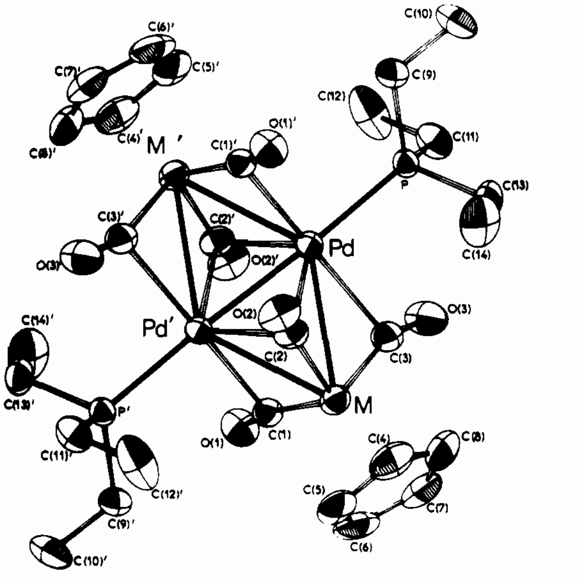

Figure 1. ORTEP diagram of the molecular structure of the $Pd_2M_2Cp_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PEt_3)_2$ clusters (M = Mo, **2b**) illustrating the numbering scheme. Thermal ellipsoids enclose 50% of the electron density. The ORTEP diagram is identical when M = Cr (**1b**) or M = W (**3b**).

In general, for the three structures, the bond lengths and angles not involving the metal atom M are not significantly different (within 3σ) (Tables VIII and IX) and will therefore often be quoted as average values in the following.

The Metallic Core. A planar triangulated tetrametallic framework of metal atoms has until now only been rarely encountered in cluster chemistry. At the time of our prelim-

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(16) See paragraph at the end of the paper regarding supplementary material.

Table IX. Bond Angles (deg) in Crystalline $Pd_2M_2Cp_2(CO)_6(PEt_3)_2$ Complexes (M = Cr, Mo, W)[a]

	compd		
angle[b]	M = Cr (1b)	M = Mo (2b)	M = W (3b)
Pd-Pd'-M	62.85 (3)	63.77 (2)	63.93 (4)
M-Pd-M'	124.30 (3)	126.04 (2)	126.29 (5)
Pd'-Pd-M	61.45 (3)	62.28 (2)	62.36 (5)
Pd'-Pd-P	178.06 (5)	177.20 (4)	177.26 (4)
C(1)-M-C(2)	113.2 (4)	111.1 (2)	112.8 (7)
C(1)-M-C(3)	84.2 (4)	83.2 (3)	82.8 (7)
C(2)-M-C(3)	109.7 (4)	107.9 (3)	108.6 (8)
Pd'-C(1)-M	80.2 (3)	79.1 (2)	79.2 (6)
Pd'-C(1)-O(1)	114.7 (6)	114.4 (4)	113 (1)
M-C(1)-O(1)	165.7 (7)	166.4 (6)	168 (1)
Pd-C(2)-Pd'	68.0 (2)	66.7 (1)	65.3 (4)
Pd-C(2)-M	80.5 (3)	80.3 (2)	79.4 (7)
Pd'-C(2)-M	81.3 (3)	80.9 (2)	79.5 (6)
Pd-C(2)-O(2)	118.1 (8)	119.0 (4)	119 (1)
Pd'-C(2)-O(2)	117.7 (6)	118.3 (5)	118 (1)
M-C(2)-O(2)	156.6 (5)	156.2 (4)	158 (1)
Pd-C(3)-M	82.1 (4)	80.9 (3)	80.2 (6)
Pd-C(3)-O(3)	117.9 (6)	118.3 (4)	117 (1)
M-C(3)-O(3)	159.8 (7)	160.7 (5)	163 (1)
C(4)-M-C(5)	38.0 (4)	35.2 (3)	34.8 (8)
C(5)-M-C(6)	37.8 (4)	35.6 (3)	35.7 (9)
C(6)-M-C(7)	38.4 (5)	34.4 (3)	36.4 (9)
C(7)-M-C(8)	37.6 (4)	34.9 (3)	35.9 (7)
C(8)-M-C(4)	37.4 (4)	35.1 (3)	34.4 (9)
C(4)-C(5)-C(6)	108 (1)	107 (1)	107 (2)
C(5)-C(6)-C(7)	107 (1)	108 (1)	107 (2)
C(6)-C(7)-C(8)	108 (1)	108 (1)	107 (2)
C(7)-C(8)-C(4)	109 (1)	109 (1)	108 (2)
C(8)-C(4)-C(5)	107.8 (9)	108.5 (7)	111 (2)
Pd-P-C(9)	115.4 (4)	115.8 (3)	115.4 (7)
Pd-P-C(11)	115.7 (3)	115.4 (2)	115.7 (6)
Pd-P-C(13)	113.2 (3)	113.5 (3)	113.8 (7)
C(9)-P-C(11)	104.7 (4)	104.5 (3)	104.3 (9)
C(9)-P-C(13)	105.2 (4)	104.2 (3)	103.8 (8)
C(11)-P-C(13)	101.2 (4)	101.8 (3)	102.0 (9)
P-C(9)-C(10)	115.6 (7)	116.0 (5)	116 (1)
P-C(11)-C(12)	110.3 (7)	111.2 (6)	111 (1)
P-C(13)-C(14)	111.4 (7)	112.2 (5)	113 (1)

[a] Figures in parentheses are the estimated standard deviations in the last significant digits. [b] Atoms are labeled in agreement with Figure 1.

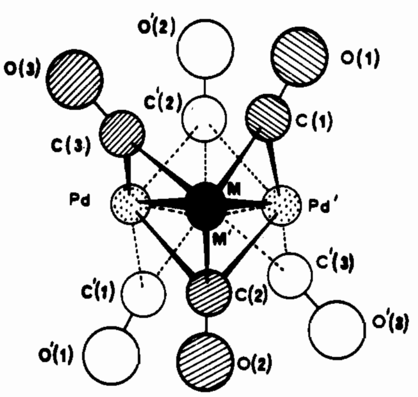

Figure 2. View of the orientation of the $M(CO)_3$ tripods in $Pd_2M_2Cp_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PEt_3)_2$. The Cp and the PEt_3 ligands have been omitted for clarity. Dotted lines are in the rear of the projection, and solid lines are in the front of the projection.

inary communication on $Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$,[5] only two other examples were known: $[Re_4(CO)_{16}]^{2-}$ [17] and $HOs_3Re(CO)_{15}$.[18] Four more members of this class of complexes have been reported since: $Pt_2Mo_2Cp_2(CO)_6(PEt_3)_2$,[19] $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$,[20a] $Re_3(\mu\text{-}H)(\mu\text{-}SnMe_2)(CO)_{12}$,[20b] and $WOs_3Cp(CO)_{11}[C(O)CH_2C_6H_4Me]$.[21] Such a planar arrangement for an heterometallic core is relevant to the question of the relationship between structure and reactivity of the surface of heterogeneous metallic catalysts.[22] Indeed, triply or semitriply bridging ligands are found in some of these molecules, like an acyl group in the WOs_3 cluster[21] and carbonyl ligands in the Pd_2M_2 and Pt_2M_2[19] clusters. This is particularly important and interesting in the case of mixed-metal clusters where preferential or selective interactions within the metal–ligand system can be structurally investigated. We shall come back to this point later in the discussion of the metal–carbonyl interactions in our clusters.

The average Pd–Pd' distance in **1b**, **2b**, and **3b** is 2.578 Å. As seen from Table XI, this is among the shortest values ever reported for a palladium–palladium bond in either a molecular complex or in the bulk metal. This is consistent with the description of the palladium atoms as Pd(I) centers (see later) in our clusters.

For the three structures, the heterometallic distances M–Pd' are significantly shorter than the corresponding M–Pd ones. This can be related to the bridging situation of the carbonyl ligands (see below). The Pd–Cr, Pd–Mo, and Pd–W distances in **1b**, **2b**, and **3b** (Table VIII) are all much shorter than the sum of the corresponding covalent radii:[24,49] 3.015, 2.992, and

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Table XI. Selected Pd–Pd Bond Distances[a]

complex	Pd oxidn state	Pd–Pd, Å	bridging ligand	ref
metallic Pd	0	2.751		23
2 (covalent radius)	0	2.98		24
$(\pi\text{-}C_3H_5)_2Pd_2(\mu\text{-}OAc)_2$		2.94	2 OAc	25
$[PdAl_2Cl_7C_6H_6]_2$	1	2.57 (1)	2 $\pi\text{-}C_6H_6$	26
$[PdAlCl_4C_6H_6]_2$	1	2.57 (1)	2 $\pi\text{-}C_6H_6$	27
$[PdS_4C_4H_4]_2$	1	2.79		28
$(\mu\text{-}C_3H_5)Pd_2(PPh_3)_2I\cdot C_6H_6$	1	2.686 (7)	C_3H_5, I	29
$(\mu\text{-}PhC{\equiv}CPh)(\pi\text{-}C_5Ph_5)_2Pd_2$	1	2.639 (1)	$PhC{\equiv}CPh$	30
$[Pd_2(CH_3NC)_6][PF_6]_2$	1	2.5310 (9)		32
$(\mu\text{-}(\eta^3\text{-}C_5H_5))(\mu\text{-}Br)Pd_2[P(i\text{-}Pr)_3]_2$	1	2.609	$\eta^3\text{-}C_5H_5$, Br	33
$Pd_2Br_2(\mu\text{-}dppm)_2$	1	2.699 (5)	2 dppm	35
$(\mu\text{-}(\eta\text{-}C_5H_5))(\mu\text{-}(\eta\text{-}C_4H_7))Pd_2[P(C_6H_5)_3]_2$	1	2.679	$\eta\text{-}C_5H_5$, $\eta\text{-}C_4H_7$	37
$(\mu\text{-}(\eta\text{-}C_5H_5))(\mu\text{-}(\eta\text{-}C_4H_7))Pd_2[P(OC_6H_4\text{-}o\text{-}CH_3)_3]_2$	1	2.689 (1)	$\eta\text{-}C_5H_5$, $\eta\text{-}C_4H_7$	37
$[N\text{-}n\text{-}Bu_4]_2[Pd_2Cl_4(\mu\text{-}CO)_2]$	1	2.697 (5)	2 CO	41
$Pd_3(SO_2)_2(t\text{-}BuNC)_5\cdot 2C_6H_6$	0	2.734 (4)	SO_2	31
		2.760 (3)		
		2.734 (4)	SO_2	
$[(CH_3NC)_6((C_6H_5)_3P)_2Pd_3][PF_6]_2$	$^2/_3$ (av)	2.5921 (5)		34
$[Pd_3Cl(PPh_2)_2(PEt_3)_3][PF_4]$	$^4/_3$ (av)	2.93	PPh_2	36
		2.93	PPh_2	
		2.89	Cl	
$[Pd_4(CO)_4(OAc)_4]\cdot 2AcOH$	1	2.663 (1)	2 CO	38
		2.909	2 OAc	
$Pd_4[P(C_6H_5)_2(CH_3)]_4(CO)_5$	0	2.750 (av)	CO	39
$Pd_{10}(CO)_{12}(P\text{-}n\text{-}Bu_3)_6$	0	2.700–2.850	CO	40
$Pd_2Cr_2Cp_2(CO)_6(PEt_3)_2$	1	2.578 (1)	CO	this work
$Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$	1	2.582 (1)	CO	5, this work
$Pd_2W_2Cp_2(CO)_6(PEt_3)_2$	1	2.573 (3)	CO	this work
$Pd_2Mn_2(CO)_9(dppm)_2\cdot C_6H_5Cl$	1	2.681 (1)	dppm	43a
$Pd_2Co_2(CO)_7(dppm)_2$	1	2.586 (1)	dppm	43b
$[N(CH_3)_3CH_2Ph]_3[Fe_6Pd_6(CO)_{24}H]\cdot 2CH_3CN$		2.810		42
		2.948		

[a] Absence of standard deviations occurs only when those values are omitted in the original reference.

Table XII. Pd–M Bond Distances[a]

complex	Pd–M, Å	bridging ligand	ref
Pd–Cr			
$Pd_2Cr_2Cp_2(CO)_6(PEt_3)_2$	2.741 (1), 2.777 (1)	CO	this work
Pd–Mo			
$[(PdNMe_2CH_2C_6H_4)_2(\mu\text{-}(Mo(CO)_3(\eta\text{-}C_5H_5))(\mu\text{-}Cl)]$	2.832 (1), 2.788 (1)	CO	44
$(8\text{-}mq)PdP(PhMe_2)Mo(CO)_3Cp$	3.059 (1)	CO	45
$Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$	2.827 (1), 2.864 (1)	CO	5, this work
Pd–W			
$Pd_2W_2Cp_2(CO)_6(PEt_3)_2$	2.829 (1), 2.868 (1)	CO	this work
Pd–Mn			
$Pd_2Mn_2(\mu\text{-}CO)_2(CO)_7(Ph_2PCH_2PPh_2)_2\cdot C_6H_5Cl$	2.580 (2)	dppm	43a
	2.698 (1)	CO	
	2.821 (2)	...	
Pd–Fe			
$[FePd(\mu\text{-}Cl)(\mu\text{-}PPh_2)(CO)_4]_2$	2.59 ± 0.01	PPh_2	46
$[N(CH_3)_3CH_2Ph]_2[Fe_4Pd(CO)_{16}]$	2.599	CO	42
$[N(CH_3)_3CH_2Ph]_3[Fe_6Pd_6H(CO)_{24}]\cdot 2CH_3CN$	2.698, 2.609	CO	42
Pd–Ru			
$PdRu(Ph_2Ppy)_2(CO)_2Cl_2$	2.660 (1)	Ph_2Ppy	95
Pd–Co			
$(CoPd(CO)_4(py))[N(NHPh)C(CH_3)C_6H_4]$	2.604 (1)	CO	47
$[(PdNMe_2CH_2C_6H_4)_2(\mu\text{-}(Co(CO)_4)(\mu\text{-}Cl)]$	2.597 (1), 2.595 (1)	CO	44
$Pd_2Co_2(CO)_7(Ph_2PCH_2PPh_2)_2$	2.511 (1)	dppm	43b
	2.613 (1)	CO	
	2.729 (1)	...	
Pd–Rh			
$RhPd(Ph_2Ppy)_2(CO)Cl_3$	2.594 (1)	Ph_2Ppy	48

[a] Absence of standard deviations occurs only when these values were omitted in the original reference.

2.986 Å, respectively. This is connected (either as a cause or as a consequence) with the "flattening" of the $M(CO)_3$ tripod. This point is discussed next.

As seen from Table XII, the number of structurally characterized palladium–transition-metal bonds is still very limited. Whereas the first complexes containing palladium to transi-

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(49) Covalent radii for Cr, Mo, W are taken as half of the metal–metal bond lengths within $[M(CO)_3Cp]_2$ (Cr,[51] 1.640 Å; Mo,[52] 1.617 Å; W,[52] 1.611 Å).

tion-metal bonds were prepared in the early 1970s,[4] the first crystal structure for such a complex only appeared in 1977.[47] Complex **2b** was the first mixed-metal palladium cluster[5] and also provided the first Pd–Mo distances. Two more Pd–Mo distances have since been reported,[44,45] whereas **1b** and **3b** are still the only examples where Pd–Cr and Pd–W bond lengths have been determined. The Pd–M distances in these clusters cannot therefore be compared with those in related molecules.

Metal–Ligand Systems. The phosphine ligands are linearly coordinated to the palladium atoms with an average Pd′–Pd–P angle of 177.5° (Figure 1). The average Pd–P distance of 2.338 Å is normal and compares well with that found in $[Pd_3Cl(PPh_2)_2(PEt_3)_3][BF_4]$.[36] The conformation of the ethyl groups is similar in the three structures, with two C_2H_5 chains of each phosphine bending toward the core of the cluster and the third one in the opposite direction (Figure 1).

The planes of η^5-cyclopentadienyl ligands form angles of 75° (M = Cr), 75° (M = Mo), and 74° (M = W) with the plane of the four metals. They are parallel to the planes of the three carbonyl carbon atoms and of the three oxygen atoms, which is typical for the "piano-stool" $CpM(CO)_3$ fragments[50] (Table X[16]). The distances between M and the Cp carbon atoms (Table VIII) are similar to those found in the $[M(CO)_3Cp]_2$ dimers (M = Cr,[51] Mo,[52] W[52]) or in the $[Mo(CO)_3Cp]^-$ anion.[53]

The description of the bonding modes of the carbonyl ligands is less straightforward. Since these structures are centrosymmetric, we shall only discuss the situation in the MPdPd′ triangle. The staggered conformation of the two $M(CO)_3$ tripods is clearly seen in Figure 2. The carbonyls C(1)O(1) and C(3)O(3) asymmetrically span the M–Pd′ and M–Pd bonds, respectively, in a very similar manner (if the Pd–C(1) and Pd–C(3) distances and the M–C(1)–O(1) and M–C(3)–O(3) angles are used as criteria) (Tables VIII and IX). For each molecule, the M–C(1) and M–C(3) distances are equivalent, with an average value of 1.84 Å for M = Cr, 1.98 Å for M = Mo, and 1.97 Å for M = W, with the smallest value for the metal of smallest covalent radius.[49] The M–C(2) distances are significantly longer: 1.92 (1), 2.04 (1), and 2.05 (1) Å, respectively; this is consistent with a C(2)O(2) ligand interacting with both Pd atoms, being always closer to Pd′ than to Pd. As expected, these M–C(2) distances are also longer than those observed for the terminal M–CO ligands in $[M(CO)_3Cp]_2$, 1.86 Å (M = Cr)[51] and 1.98 Å (M = Mo, W),[52] or in $CpM(CO)_3X$ molecules[50] (X = Cl, C_2H_5, HgCl, $AuPPh_3$, ...). The Cr–C(1) and Cr–C(3) distances are not significantly different from those between Cr and the asymmetrically bridging CO's in $Cp(OC)NiCr(CO)_3Cp$[54] (Cr–C = 1.88 (1) Å). Interestingly, the Mo–C(2) distances are slightly longer than in $Cp_2NbMo(CO)_3Cp$, where both a π-bonded (Mo–C = 1.94 (1) Å) and an asymmetric (Mo–C = 2.02 (1) Å) CO ligand are found.[55]

Further comparisons between the structural parameters of the CO ligands in our systems (particularly C(2)O(2)) with literature data are precluded by the fact that $CpM(CO)_3$ fragments are usually not found in clusters. Indeed, CO elimination generally occurs and leads to the more unsaturated $CpM(CO)_2$ units.[56–58]

The Pd′–C(1), Pd–C(2), and Pd–C(3) bond lengths are equivalent in each molecule (within 3σ), with an average length of 2.35 Å for M = Cr, 2.41 Å for M = Mo, and 2.43 Å for M = W. In each case, Pd′–C(2) is the shortest palladium–carbonyl distance: 2.26 (1), 2.31 (1), and 2.35 (1) Å, respectively. As mentioned above, this increased bonding contribution leads to a M–Pd′ metal–metal bond shorter than the M–Pd one. The palladium–carbonyl distances increase on going from Cr to Mo to W, as expected from the increase in the metal covalent radii,[49] allowing the $Cr(CO)_3$ tripod a closer proximity to the Pd–Pd′ vector.

All the palladium–carbon (CO) distances in **1b**, **2b**, and **3b** are much longer than those found, for example, in the Pd(I) complexes $[Pd(dam)Cl]_2(\mu\text{-}CO)$[59] or $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$,[41] where the symmetrically bridging CO ligands are at average Pd–C distances of 1.90 and 1.994 Å, respectively. This clearly is in favor of weaker palladium–carbonyl interactions in our complexes, compared to those involving classical μ-CO ligands.

Considering now the M–C–O angles, one finds that the M–C(2)–O(2) angle (average 157°) is always smaller than M–C(1)–O(1) and M–C(3)–O(3) (average 167 and 161°, respectively) (Table IX), all being in the range displayed by semibridging carbonyls.[60,61] .

Both the metal–carbonyl distances and metal–carbon–oxygen angles therefore lead to the description of C(1)O(1) and C(3)O(3) as semibridging and C(2)O(2) as semi triply bridging ligands. This also meets the criteria used by Colton and McCormick for differentiating between asymmetrical μ_2 and semi-bridging μ_2 carbonyls: "if the difference in the metal–carbon bond lengths is less than 0.3 Å and the difference in the metal–C–O angles is less than 20°, we refer to the bridging carbonyl group as asymmetric".[61]

In the three structures, the C(1)–M–C(3) angle (average 83.4°) is smaller than C(1)–M–C(2) and C(2)–M–C(3) (112.4 and 108.7°, respectively) (Table IX). These values also indicate a flattening of the $M(CO)_3$ tripod in our complexes when compared with that of $CpMo(CO)_3^-$, for example. Thus, in the latter case, the average C–Mo–C angle is only 88.2°.[53] As expected, the C–M–C angles between two cis carbonyls in *four*-legged piano-stool molecules $CpM(CO)_3X$ are smaller, ranging usually between 77 and 81°.[50–52]

Clearly, the unusual bonding mode observed in our clusters for two $CpM(CO)_3$ fragments "bridging" the L–Pd–Pd′–L unit results in very specific geometrical modifications. In contrast to all $CpM(CO)_3X$ molecules (X = H, halide, organic group, other metallic fragment, ...[50–52,64]) for which a four-legged piano-stool structure about M is observed, **1b**, **2b**, and **3b** present a *three*-legged piano-stool structure with two extra atoms (here Pd) located *within* the $M(CO)_3$ cone (Figure 2).

Noteworthy is that in all three structures presented in this paper, the M–CO distances are shorter than the Pd– or Pd′–CO distances. This constitutes a parallel with the known high affinity of group 6 metals for CO.

We can therefore say that the C(2)O(2) ligand capping the heterotrimetallic Pd_2M face is able to discriminate between the metals and prefers to bind more strongly to the group 6 metal. Though this effect also depends upon the other ligands present in the coordination sphere of the metals, such obser-

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vations are interesting in the context of mixed-metal cluster faces as structural models for selective interactions between ligands and heterogeneous bimetallic catalysts.

Syntheses. Two different routes have been followed for the preparation of these $Pd_2M_2Cp_2(CO)_6L_2$ clusters. The first, method a, involves the reaction of the carbonylmetalates $Na^+[M(CO)_3Cp]^-$ with *trans*-$PdCl_2L_2$ complexes in THF, according to eq 2.

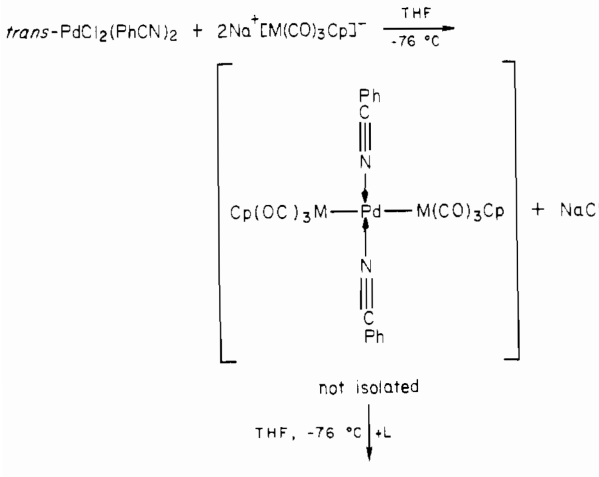
method a

$$\textit{trans}\text{-}PdCl_2L_2 + 2Na^+[M(CO)_3Cp]^- \xrightarrow{THF} Pd_2M_2Cp_2(CO)_6L_2 + [M(CO)_3Cp]_2 + Cp(OC)_3M\text{-}M(CO)_2LCp + NaCl + ... \quad (2)$$

$$L = PEt_3, PPh_3;\ M = Cr, Mo, W$$

The second synthetic method, method b, concerns the reaction of PR_3 with linear heterotrimetallic complexes prepared in situ, according to eq 3 and 4.

method b



(3)

(4)

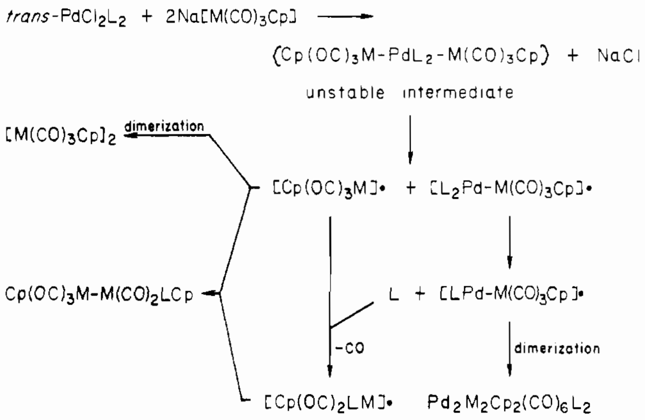
$L = PMe_3, PEt_3, P\text{-}n\text{-}Bu_3, PMe_2Ph, PPh_3; M = Cr, Mo, W$

In order to allow a better comparison between them, these two different methods have been applied to the synthesis of the same clusters in the cases where $L = PEt_3$, PPh_3. Let us first consider and discuss method a.

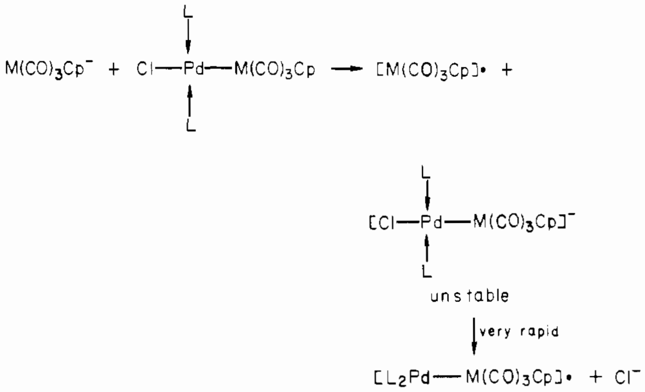
Synthetic Method a. This method results from our continuing interest in the reactivity of carbonylmetalates with palladium or platinum complexes (see previous paper in this series noted in ref 1). This reaction type has been shown to lead to the synthesis of homo- or heteropolymetallic complexes whose composition and structure depend strongly on the nature both of the transition metals and of the neutral ligands bonded to the d^8 center. Replacing py by PR_3 in reaction 1 dramatically changes the nature of the products, since the heterotetrametallic clusters $Pd_2Mo_2Cp_2(CO)_6(PR_3)_2$ are now produced, instead of the trimetallic complexes.[5] Analogous observations have also been made in the case where platinum replaces palladium,[19] and this will be discussed in a subsequent paper.[62] Explanations for this unexpected reaction course can be related to the increased lability of tertiary phosphines compared with that of pyridine when coordinated to palladium.

Reactions 1 and 3 are very rapid at low temperature (−76 °C), and one can reasonably assume that in both reactions the first step is the replacement of one chloride by the carbonylmetalate anion. This is supported by the isolation of the bimetallic complex $ClPt(py)_2Mo(CO)_3Cp$,[4a] made possible by slower reaction rates with platinum than with palladium.

Scheme I



Scheme II



Whereas the second step of reaction 1 is clearly the replacement of the second chloride by another carbonylmetalate anion, it is more speculative in the case of reaction 2. We can envisage two possibilities:

(i) The second step for reaction 2 is similar to that of reaction 1, but the $M\text{-}Pd(PR_3)_2\text{-}M$ intermediate is highly unstable because of the steric hindrance about the palladium atom. Thus, the only trimetallic linear complexes isolated so far with a d^8 metal in the middle of the chain have involved "flat or linear ligands" such as pyridine or substituted pyridines,[4] organonitriles,[62] isocyanides,[63] carbene,[64] or CO,[65] all ligands of small steric bulk. No such examples are well established with bulky ligands.

The unstable $Cp(CO)_3M\text{-}Pd(PR_3)_2\text{-}M(CO)_3Cp$ intermediate could then collapse into two radicals: $[Cp(CO)_3M\text{-}Pd(PR_3)_2]\cdot$ and $[M(CO)_3Cp]\cdot$. The former would further easily lose one PR_3 ligand (radicals are known to be labile) and "dimerize" into the $Pd_2M_2Cp_2(CO)_6(PR_3)_2$ cluster whereas $[M(CO)_3Cp]\cdot$ could either dimerize (giving the observed $[M(CO)_3Cp]_2$) or react with the PR_3 ligand liberated from the bimetallic radical to afford the radical $[Mo(CO)_2(PR_3)Cp]\cdot$. The latter, by reacting with $[M(CO)_3Cp]\cdot$, would lead to the observed $Cp(OC)_3Mo\text{-}Mo(CO)_2(PR_3)Cp$. (We cannot exclude, but consider less likely, a direct reaction between the coordinated L and $[Mo(CO)_3Cp]\cdot$, to form $[Mo(CO)_2LCp]\cdot$). This is summarized in Scheme I.

It is clear that the lifetime and the reactivity of the above-mentioned radicals will depend upon the nature of the metal M and the ligand L. The fact that in some reactions

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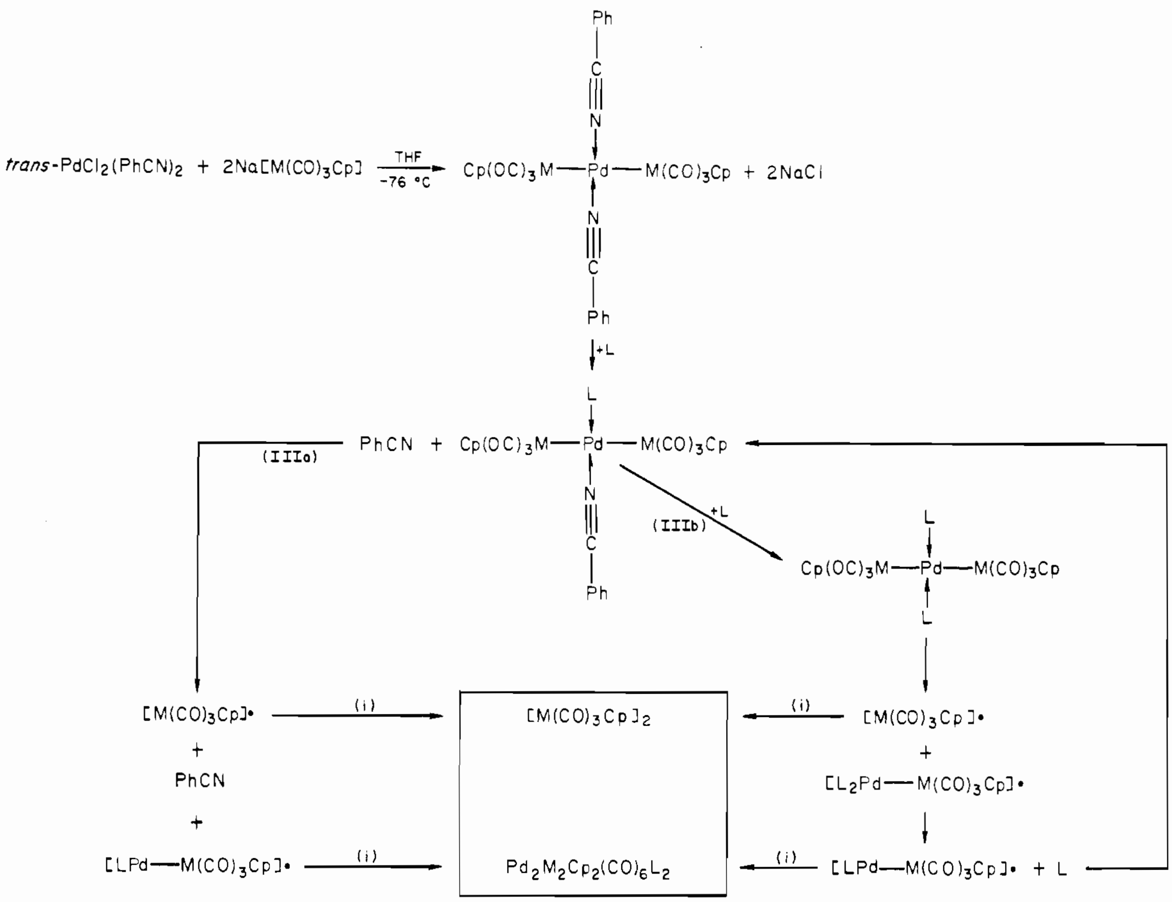
Scheme III[a]



[a] (i) = dimerization.

(see Experimental Section) the dimers $[M(CO)_3Cp]_2$ or in other reactions their monosubstituted derivatives $M_2(CO)_5LCp_2$ were not isolated after chromatography is therefore not too surprising. Furthermore, some decomposition always occurs on a chromatography column, precluding an exact knowledge of the composition of the mixture at the end of the reaction.

(ii) The second step in reaction 2 is an electron transfer from $M(CO)_3Cp^-$ to the intermediate $ClPdL_2M(CO)_3Cp$, and one could envisage the sequence given in Scheme II.

The first unstable intermediate sterically less crowded than *trans*-$Pd[M(CO)_3Cp]_2L_2$ could readily lose a chloride anion (good leaving group) and generate the same bimetallic radical as invoked in Scheme I. The next steps would then be analogous to those described above.

The radical reaction mechanism suggested here is indirectly supported by recent observations on related platinum complexes. Thus, heterobimetallic radicals can be generated by electrochemical reduction of trimetallic complexes.[66] In one case, the $[(PPh_3)Pt-Co(CO)_4]\cdot$ radical dimerizes into the heterotetrametallic $Pt_2Co_2(CO)_8(PPh_3)_2$ cluster.[67]

Finally, another argument for the possible intermediacy of $[M(CO)_3Cp]\cdot$ radicals is the formation of the substituted dimers $M_2(CO)_5(PR_3)Cp_2$ under conditions (low temperature, no $h\nu$ activation) where the direct substitution reaction

$$Cp(OC)_3M-M(CO)_3Cp + L \rightarrow Cp(OC)_3M-M(CO)_2LCp + CO \quad (5)$$

cannot occur.[14,68] Moreover, it has been shown that if $[M(CO)_3Cp]\cdot$ radicals are generated from their dimers, they will readily lead to substitution products in the presence of L.[69]

To the best of our knowledge, the $M_2(CO)_5(PEt_3)Cp_2$ (M = Mo, W) complexes observed in method a have not been reported previously. Their spectroscopic data are given in the Experimental Section and are analogous to those reported for other $Mo_2(CO)_5LCp_2$ complexes[14] (L = PPh_3, $P(cyclohexyl)_3$).

Synthetic Method b. Previous studies on the synthesis and reactivity of the linear heterotrimetallic $M-Pt(ligand)_2-M$[4,63] complexes have shown that tertiary phosphines attack the Pt center with rupture of the Pt–M bonds[70] and that, in contrast to the behavior of e.g. $Hg[Co(CO)_4]_2$,[71-73] no CO substitution at M is observed.

We considered the possibility of preparing linear $M-Pd(PhCN)_2-M$ and $M-Pt(PhCN)_2-M$ complexes in which the lability of the benzonitrile ligand could in principle allow its displacement by better nucleophiles such as tertiary phosphines without metal–metal bond breaking. It was then open to speculation whether the simple substitution products M–Pt(or Pd)$(PR_3)_2$–M could be isolated. Thus, in a subsequent paper,[62] we shall describe the synthesis of the *trans*-$Pt[M(CO)_3Cp]_2(PhCN)_2$ complexes (M = Cr, Mo, W) and their reaction with phosphines affording the $Pt_2M_2Cp_2(CO)_6L_2$ clusters. The linear $Cp(OC)_3M-Pd(PhCN)_2-M(CO)_3Cp$ complexes were formed at -76 °C from $PdCl_2(PhCN)_2$ and $NaM(CO)_3Cp$. Immediate reaction occurs, and the color of the solution changes from light yellow to deep violet. The

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thermal lability of the products did not allow their isolation and full characterization. Nevertheless, we are confident about their formulation, since this reaction is very similar to (1), which affords *trans*-$Pd[Mo(CO)_3Cp]_2(py)_2$ as isolated and characterized deep violet microcrystals.[4a]

The linear $Pd[M(CO)_3Cp]_2(PhCN)_2$ complexes were reacted in situ at −76 °C with 1 equiv of PR_3. The reaction mixture was slowly brought to room temperature. Details of the workup are given in the Experimental Section. The products formed and isolated after purification are the cluster $Pd_2M_2Cp_2(CO)_6L_2$ and $[M(CO)_3Cp]_2$. We suggest Scheme III to explain this.

The radical pathway discussed above for method a holds, we believe, for method b. Here, the origin of the unstable intermediate $LPd–M(CO)_3Cp\cdot$ could be explained by both routes IIIa and IIIb. We favor route IIIb because the trimetallic intermediate $Pd[M(CO)_3Cp]_2L_2$ is sterically more crowded than $Pd[M(CO)_3Cp]_2(PhCN)L$ (route IIIa) and therefore more susceptible to collapse into the desired fragments. It is also more electron rich.

This route suggests that L rapidly displaces both benzonitrile ligands although the global L/Pd stoichiometry employed is one to one. But, as soon as the first bimetallic radicals are generated as in Scheme I, they will release one phosphine ligand, which can then substitute another PhCN ligand. The overall stoichiometry is therefore respected. In contrast to method a, $M_2(CO)_5(L)Cp_2$ products are not found here, probably because of a stronger affinity of L for the $Pd[M(CO)_3Cp]_2(PhCN)_2$ complex than for the $[M(CO)_3Cp]\cdot$ radical.

This method provides an elegant route to substituted heterotetrametallic clusters from heterotrimetallic precursors.

A comparison between methods a and b indicates that the latter usually affords better yields of cluster. The most striking difference is observed with **1b**, where the yield is improved from 6 to 90% (see Experimental Section). Other advantages of method b are the use of the readily available precursor $PdCl_2(PhCN)_2$ and the economy in ligand realized, since in the first method, one L per Pd is "lost" (not found in the final cluster). This point is of particular importance when expensive or sophisticated ligands are used, which could be desired, for example, for functionalizing such clusters or anchoring them on supports.

Spectroscopic Characterization. The infrared spectral data in the $\nu(CO)$ region are given for all clusters in Table XIII. Three main absorptions are usually found in the solid state, the most intense features being generally located around 1840 and 1760 cm^{-1}. The latter is clearly assigned to the $\nu(CO)$ vibration of the semi triply bridging C(2)O(2) ligand, whereas the absorptions at higher wavenumbers are assigned to the semibridging C(1)O(1) and C(3)O(3) ligands. Only two main IR absorptions are found for CH_2Cl_2 solutions. An increase in the basicity of the phosphine L (from PPh_3 to PMe_3 for example) generally causes a shift of the $\nu(CO)$ frequencies toward lower wavenumbers. This is easily related to an increase of the π back-donation from the palladium centers toward the carbonyl ligands.

The ^1H, ^{31}P, and $^{13}C\{^1H\}$ NMR data are collected in Table XIV. In the ^1H NMR spectra of all the clusters, the η^5-C_5H_5 protons are equivalent and appear as a singlet. The PMe_3 protons of **1a**, **2a**, and **3a** give rise to a triplet because of the "virtual coupling" occurring along the linear $R_3P–Pd–Pd–PR_3$ arrangement.[74] Similarly, the CH_3 protons of PEt_3 give rise to a typical quintet[75] for **1b**, **2b**, and **3b**, with $^3J(HH) = {}^1/_2|^3J(PH) + {}^6J(PH)| \simeq 7.5$ Hz. The CH_2 protons give rise to a complex multiplet, as do those of P-*n*-Bu_3 in **1c**, **2c**, **3c** (see Table XIV).

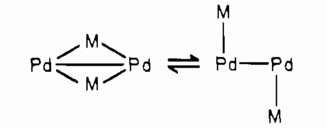
For all complexes, the ^{31}P NMR spectra (Table XIV) confirm the equivalence found in the solid state for the phosphine ligands. The chemical shifts measured for **1a**, **2a**, **3a** are slightly upfield of the ^{31}P resonance of *trans*-$PdCl_2(PMe_3)_2$ (−12.1 ppm[76]), whereas a downfield shift is observed for **1b**, **2b**, **3b** and **1c**, **2c**, **3c** compared to the resonances for *trans*-$PdCl_2(PEt_3)_2$ (17.8 ppm[77]) and *trans*-$PdCl_2$(P-*n*-$Bu_3)_2$ (10.0 ppm[78]), respectively. In two instances, **3b** and **3c**, the $^{31}P–^{183}W$ coupling has been observed and found equal to 12 Hz. It must be emphasized that this coupling constant represents the algebraic sum of the direct and through-bridge contributions.

In the $^{13}C\{^1H\}$ NMR spectra (Table XIV), the cyclopentadienyl carbons give rise to the expected singlet between 88 and 91 ppm for M = Cr, Mo, W. These values are in the range observed for mono-[79–81] or bimetallic[82,83] complexes containing the $M(CO)_3Cp$ moiety.

The carbon atoms of the PMe_3 ligands in **1a** show a "virtual triplet" ($|^1J(PC) + {}^4J(PC)| = 20$ Hz) as expected from the ^1H NMR results. Similarly, a "virtual triplet" is observed for the α-carbons of PEt_3 in **2b** and **3b** whereas a singlet is found for their β-carbons. The α- and γ-carbons of P-*n*-Bu_3 give a "virtual triplet" in **1c** and **3c** and a multiplet and a singlet, respectively, for **2c**. The δ carbons of P-*n*-Bu_3 always give a singlet. Details of the assignments and coupling constants are given in Table XIV.

The carbonyl ligands when detected in the ^{13}C spectra always give rise to a singlet (see Table XIV) between 192 and 242 ppm, depending on the nature of M and L. The singlet was still observed from −90 to +30 °C for **2c** and **3c**, indicating equivalence of the three carbonyls on the NMR time scale (they are differentiated on the IR time scale). This can be visualized as a rapid rotation of the $M(CO)_3Cp$ fragment about its symmetry axis.

A similar behavior has been found for the related $Pt_2M_2Cp_2(CO)_6(PR_3)_2$ clusters, in some of which the ^1H NMR spectra of the Cp ligands exhibit satellites due to coupling with two equivalent Pt atoms. However, this does not rule out the possibility of a rapid equilibrium such as



where the carbonyls should exchange easily in the open structure.[84] The CO chemical shifts for **1c** and **1e** are at high field to that reported for $[Cr(CO)_3Cp]^-$ (246.7 ppm[85]). Conversely, the δ(CO) shifts for **2b** and **2c** are downfield of $[Mo(CO)_3Cp]_2$ (218.6 ppm[80]), as are the shifts for **3b** and **3c** compared to that for $[W(CO)_3Cp]$ (223.9 ppm[83]). This indicates that the $M(CO)_3Cp$ groups have an anionic character in the clusters, intermediate between that in the free anions (1−) and in the dimers (0).[86]

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Table XIII. Infrared Spectral Data

complex	IR abs max ν(CO),[a] cm^{-1}		
	KBr[b]	Nujol	CH$_2$Cl$_2$
$Pd_2Cr_2Cp_2(CO)_6(PMe_3)_2$ (1a)	1835 s, 1783 m, sh, 1767 s	1834 s, 1781 m, sh, 1766 s	1836 s, 1789 ms
$Pd_2Mo_2Cp_2(CO)_6(PMe_3)_2$ (2a)	1835 s, 1789 m, sh, 1758 s	1834 s, 1790 m, 1756 s	
$Pd_2W_2Cp_2(CO)_6(PMe_3)_2$ (3a)	1828 s, 1782 m, 1751 s	1829 s, 1784 m, 1755 s	1831 s, 1767 m, br
$Pd_2Cr_2Cp_2(CO)_6(PEt_3)_2$ (1b)	1837 s, 1785 sh, 1773 s	1837 s, 1792 m, 1775 s	1836 s, 1788 s, br
$Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$ (2b)	1837 s, 1792 m, 1768 s	1836 s, 1797 m, 1768 s	1885 w, 1838 s, 1775 m, br
$Pd_2W_2Cp_2(CO)_6(PEt_3)_2$ (3b)	1833 s, 1801 sh, 1789 m, 1760 s	1835 s, 1804 sh, 1788 m, 1763 s	1880 w, 1833 s, 1775 s, br
$Pd_2Cr_2Cp_2(CO)_6(P\text{-}n\text{-}Bu_3)_2$ (1c)	1934 w, 1845 s, 1798 m, sh, 1782 s	1937 w, 1842 s, 1799 m, sh, 1780 s	1957 w, 1890 w, 1840 s, 1770 ms, br
$Pd_2Mo_2Cp_2(CO)_6(P\text{-}n\text{-}Bu_3)_2$ (2c)	1954 w, 1841 s, 1819 m, sh, 1764 s	1957 vw, 1845 s, 1818 m, sh, 1765 s	
$Pd_2W_2Cp_2(CO)_6(P\text{-}n\text{-}Bu_3)_2$ (3c)	1948 vw, 1839 s, 1812 m, sh, 1755 s	1957 vw, 1838 s, 1823 sh, 1755 s	1954 w, 1832 s, 1765 ms, br
$Pd_2W_2Cp_2(CO)_6(PMe_2Ph)_2$ (3d)	1946 w, 1835 m, sh, 1818 s, 1723 s	1835 m, sh, 1816 s, 1723 s	1955 s, 1906 m, 1835 s, 1770 m, br
$Pd_2Cr_2Cp_2(CO)_6(PPh_3)_2$ (1e)	1939 w, 1901 vw, 1848 s, 1809 ms, 1789 ms		1903 m, 1852 s, 1822 s
$Pd_2Mo_2Cp_2(CO)_6(PPh_3)_2$ (2e)	1914 m, 1840 vs, br, 1784 s	1916 mw, 1857 m, sh, 1837 sh, 1827 s, 1780 s	
$Pd_2W_2Cp_2(CO)_6(PPh_3)_2$ (3e)	1953 sh, 1917 mw, 1851 s, 1830 sh, 1820 s, 1775 s		1953 m, 1905 m, 1848 s, 1818 sh, 1777 m

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad. [b] The relative intensities in the solid-state spectrum of a cluster are sometimes influenced by the solvents used to crystallize it. It has been verified that this corresponds to a solid-state effect since the corresponding solution spectra are always identical.

Table XIV. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR Spectral Data[a-c]

complex	$\delta(^1H)$	$\delta(^{31}P\{^1H\})$	$\delta(^{13}C\{^1H\})$
$Pd_2Cr_2Cp_2(CO)_6(PMe_3)_2$ (1a)	*4.68 (s, 10 H, C_5H_5), 1.42 (t, 18 H, CH_3, $\lvert {}^2J(PH) + {}^5J(PH)\rvert = 7.8$)	*−14.0 (s)	*88.2 (s, C_5H_5), 16.5 (t, CH_3, $\lvert {}^1J(PC) + {}^4J(PC)\rvert = 20$)
$Pd_2Mo_2Cp_2(CO)_6(PMe_3)_2$ (2a)	**5.23 (s, 10 H, C_5H_5), 1.38 (t, 18 H, CH_3, $\lvert {}^2J(PH) + {}^5J(PH)\rvert = 8.4$)	*−15.1 (s)	*c*
$Pd_2W_2Cp_2(CO)_6(PMe_3)_2$ (3a)	*5.34 (s, 10 H, C_5H_5), 1.32 (t, 18 H, CH_3, $\lvert {}^2J(PH) + {}^5J(PH)\rvert = 8.2$)	*−19.6 (s)	*c*
$Pd_2Cr_2Cp_2(CO)_6(PEt_3)_2$ (1b)	**4.65 (s, C_5H_5), 1.01 (qt, $CH_2C\mathit{H}_3$, $^3J(HH) = 7.5$, $\lvert {}^3J(PH) + {}^6J(PH)\rvert = 15$), 1.22 (m, $C\mathit{H}_2CH_3$)	*21.6 (s)	*c*
$Pd_2Mo_2Cp_2(CO)_6(PEt_3)_2$ (2b)	**5.24 (s, C_5H_5), 1.02 (qt, $CH_2C\mathit{H}_3$, $^3J(HH) = 7.5$, $\lvert {}^3J(PH) + {}^6J(PH)\rvert = 15$), 1.74 (m, $C\mathit{H}_2CH_3$)	*22.9 (s)	**241.3 (s, CO), 90.4 (s, C_5H_5), 17.2 (t, $\mathit{C}H_2CH_3$, $\lvert {}^1J(PC) + {}^4J(PC)\rvert = 20$), 8.3 (s, $CH_2\mathit{C}H_3$)
$Pd_2W_2Cp_2(CO)_6(PEt_3)_2$ (3b)	**5.77 (s, C_5H_5), 1.18 (qt, $CH_2C\mathit{H}_3$, $^3J(HH) = 8$, $\lvert {}^3J(PH) + {}^6J(PH)\rvert = 16$), 1.87 (m, $C\mathit{H}_2CH_3$)	**30.8 (s) $J(PW) = 12$	**234.5 (s, CO), 88.4 (s, C_5H_5), 17.2 (t, $\mathit{C}H_2CH_3$, $\lvert {}^1J(PC) + {}^4J(PC)\rvert = 20$), 8.2 (s, $CH_2\mathit{C}H_3$)
$Pd_2Cr_2Cp_2(CO)_6(P\text{-}n\text{-}Bu_3)_2$ (1c)	**4.59 (s, C_5H_5), 0.80–1.71 (m, *n*-Bu)	*15.7 (s)	*192.9 (s, CO), 88.9 (s, C_5H_5), 24.7 (t, $\mathit{C}H_2CH_2CH_2CH_3$), 24.4 (t, $CH_2CH_2\mathit{C}H_2CH_3$), 26.4 (s, $CH_2\mathit{C}H_2CH_2CH_3$), 13.8 (s, $CH_2CH_2CH_2\mathit{C}H_3$)
$Pd_2Mo_2Cp_2(CO)_6(P\text{-}n\text{-}Bu_3)_2$ (2c)	*5.22 (s, C_5H_5), 0.84–1.73 (m, *n*-Bu)	*15.1 (s)	*241.6 (s, CO), 90.5 (s, C_5H_5), 26.5 (m, $\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2\mathit{C}H_3$), 13.7 (s, $CH_2CH_2CH_2\mathit{C}H_3$)
$Pd_2W_2Cp_2(CO)_6(P\text{-}n\text{-}Bu_3)_2$ (3c)	*5.31 (s, C_5H_5), 0.80–1.63 (m, *n*-Bu)	*10.7 (s, $J(PW) = 12$)	*230.0 (s, CO), 88.8 (s, C_5H_5), 25.1 (t, $\mathit{C}H_2CH_2CH_2CH_3$, $\lvert {}^1J(PC) + {}^4J(PC)\rvert = 18$), 26.5 (t, $CH_2\mathit{C}H_2CH_2CH_3$, $\lvert {}^2J(PC) + {}^5J(PC)\rvert = 2$), 24.7 (t, $CH_2CH_2\mathit{C}H_2CH_3$, $\lvert {}^3J(PC) + {}^6J(PC)\rvert = 14$), 13.8 (s, $CH_2CH_2CH_2\mathit{C}H_3$)
$Pd_2Cr_2Cp_2(CO)_6(PPh_3)_2$ (1e)	*4.21 (s, 10 H, C_5H_5), 7.6–7.4 (m, 30 H, C_6H_5)	*28.3 (s)	*209.2 (s, CO), 89.6 (s, C_5H_5), 128.3–134.4 (m, C_6H_5)
$Pd_2Mo_2Cp_2(CO)_6(PPh_3)_2$ (2e)	*4.71 (s, C_5H_5), 7.6–7.4 (m, C_6H_5)	**24.5 (s)	*b*
$Pd_2W_2Cp_2(CO)_6(PPh_3)_2$ (3e)	**4.83 (s, C_5H_5), 7.8–7.3 (m, C_6H_5)	**20.5 (s)	*b*

[a] Measured in CD_2Cl_2 (*) or in $CDCl_3$ (**) at room temperature. Coupling constants are in Hz (see part A of the Experimental Section). [b] NMR spectra not measured due to insufficient solubility. [c] NMR spectra not measured due to instability. [d] Abbreviations: s, singlet; t, virtual triplet; qt, quintuplet; m, multiplet.

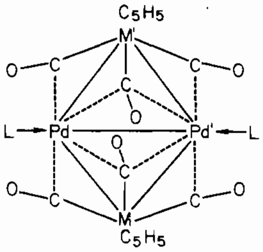
Bonding Description. The clusters described in this work have a total number of 58 valence electrons. Considering two 18-electron group 6 metals M and two 16-electron palladium atoms (Pd and Pt atoms in clusters are mostly found with 16 rather than 18 electrons), this accounts for five metal–metal bonds in these clusters and is consistent with their diamagnetism observed between 298 and 4 K (Foner magnetometer). We prefer this description to that suggested earlier.[5]

In a formal manner, one could consider these molecules as constituted of d^9 Pd^I and d^6 M^0 centers, two 18-electron $[M(CO)_3Cp]^-$ fragments interacting with the 22-electron $[Pd_2L_2]^{2+}$ unit. Many complexes are now known where two d^9 Pd^I centers are bonded to each other.[87] This description is chemically supported by the reaction balance observed in their synthesis according to method b (in method a, the experimental reaction balance is more difficult to achieve). Thus, the linear $Cp(OC)_3M–Pd(PhCN)_2–M(CO)_3Cp$ complexes can be considered as Pd(II) complexes, by analogy with $Pd[Mo(CO)_3Cp]_2(py)_2$.[4a,d] Their reaction with phosphines L induces a homolytic cleavage of one Pd–M bond during which formal reduction from Pd^{II} to Pd^I occurs. The concommitant one-electron oxidation of a $[M(CO)_3Cp]^-$ fragment leads to the formation of ca. 1 mol of $[M(CO)_3Cp]_2$/mol of cluster, which is indeed found, except for M = Cr because of its instability (see Experimental Section).

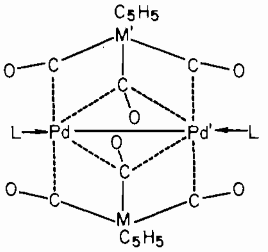
Furthermore, the IR data of the clusters in the ν(CO) region indicate that the $M(CO)_3Cp$ fragment is very electron rich. The two $[M(CO)_3Cp]^-$ fragments must each contribute 4 electrons to the $L \rightarrow Pd^I—Pd^I \leftarrow L$ unit in order to reach a 16-electron configuration on each palladium. This can be achieved by the overlap of two donor orbitals of symmetry a_1 and b_2 with the corresponding acceptor orbitals of the Pd_2 moiety.[88] This is analogous to the situation in the

molecules (X = allyl,[89] halide[29,90]) in which each anionic bridging group acts as a 4-electron donor toward the $L \rightarrow Pd^I—Pd^I \leftarrow L$ unit. Recently, a related example of a "bridging" $Mo(CO)_3Cp$ moiety has been found in our laboratory[44] and elsewhere.[94]

Depending on the extent of direct metal–metal bonding and "through-bridge" interactions, the bonding descriptions A or B could be considered.



A



B

In the latter, the short Pd–M distances would then result from strong "through-bridge" interactions, as in $[Fe(CO)_2Cp]_2$, for example.[91] It is interesting to note the analogy between this bonding description B and the structure of the W_3O_{13} "caps" in α-$P_2W_{18}O_{62}{}^{6-}$ where one triply bridging and two doubly bridging oxygen atoms connect the tungsten atoms.[92]

At this point, we are inclined toward a bonding description involving a certain degree of metal–metal bonding between the Pd(I) and group 6 metal centers (model A). Clearly, a detailed molecular orbital treatment of such molecules would be highly desirable.

Conclusion

We have described in this paper two different synthetic strategies leading to the first Pd–Cr, Pd–Mo, and Pd–W mixed-metal clusters, of general formula $Pd_2M_2Cp_2(CO)_6(PR_3)_2$. Synthetic method a involves the reaction of the sodium carbonylmetalates $Na[M(CO)_3Cp]$ with the $PdCl_2(PR_3)_2$ complexes. In Method b, 1 equiv of PR_3 was reacted with the reactive linear trimetallic complexes $Cp(OC)_3M–Pd(PhCN)_2–M(CO)_3Cp$ (formed in situ at −76 °C from $PdCl_2(PhCN)_2$ and 2 equiv of $Na[M(CO)_3Cp]$). Mechanisms involving radical intermediates are proposed for both methods. They involve the generation of reactive unsaturated fragments which combine with each other in order to form the thermodynamically stable compounds. In general, method b presents significant advantages over method a, namely, (1) higher cluster yield (up to 90%), (2) a readily available stable palladium precursor, and (3) generality and economy of introduction of a phosphine ligand into a cluster molecule.

Method b represents an original way to prepare heterotetrametallic clusters from heterotrimetallic precursors. The interest in developing high-yield and, if possible, rational syntheses for mixed-metal clusters is mainly motivated by the need for such molecules in order to prepare new homogeneous and/or heterogeneous catalysts. After developing these high-yield syntheses, we demonstrated that $Pd_2Mo_2Cp_2(CO)_6(PPh_3)_2$ could be used to prepare a mixed-metal cluster derived catalyst for the carbonylation of aromatic nitro derivatives.[93]

The X-ray structure determination of the three isostructural clusters $Pd_2M_2Cp_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PEt_3)_2$ (M = Cr, Mo, W) has revealed a rarely found planar, triangulated parallelogram framework for the metallic core. The clusters possess a center of symmetry at the middle of the Pd–Pd′ bond. This bond has a very short length of 2.578 Å (average value). The first determined Pd–Cr and Pd–W bond lengths have average values of 2.759 and 2.849 Å, respectively, the latter being close to the average value of 2.846 Å found for the Pd–Mo bonds in **2b**. The bonding modes of the carbonyl ligands, semibridging for C(1)O(1) and C(3)O(3) and semi triply bridging for C(2)O(2), were deduced from their structural parameters and are consistent with their ν(CO) stretching frequencies. The interactions between ligands and a planar arrangement of different metal atoms are particularly germane to the relevance of clusters to the structure and reactivity of the surface of heterogeneous metallic catalysts.[22]

Comparisons between the structural and spectroscopic data for this family of 58-electron clusters were made and allowed the description of the 18-electron $[M(CO)_3Cp]^-$ fragments as *three*-legged piano stools acting as 4-electron donors when bridging the $L \rightarrow Pd^I—Pd^I \leftarrow L$ moiety in such a way that the two Pd atoms are located *within* the $M(CO)_3$ cone. Such a bonding mode is highly unusual and may now be anticipated to occur in other clusters.

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Registry No. **1a**, 87114-37-2; **1b**, 87114-38-3; **1c**, 87114-39-4; **1e**, 86403-93-2; **2a**, 87114-40-7; **2b**, 87114-41-8; **2c**, 87114-42-9; **2e**, 58640-56-5; **3a**, 87114-43-0; **3b**, 87114-44-1; **3c**, 87114-45-2; **3d**, 87114-46-3; **3e**, 86403-94-3; $Mo_2(CO)_5(PEt_3)Cp_2$, 87114-47-4; $[Mo(CO)_3Cp]_2$, 12091-64-4; $W_2(CO)_5(PEt_3)Cp_2$, 87114-48-5; $[W(CO)_3Cp]_2$, 12091-65-5; $Na[Cr(CO)_3Cp]$, 12203-12-2; $Na[Mo(CO)_3Cp]$, 12107-35-6; $Na[W(CO)_3Cp]$, 12107-36-7; *trans*-$PdCl_2(PEt_3)_2$, 15642-19-0; *trans*-$PdCl_2(PPh_3)_2$, 28966-81-6; *trans*-$PdCl_2(PhCN)_2$, 15617-18-2.

Supplementary Material Available: Selected least-squares planes (Table X), anisotropic thermal parameters for **1b**, **2b**, and **3b** (Tables XV–XVII), and observed and calculated structure factors (Table XVIII) (62 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Baker Laboratory, Cornell University, Ithaca, New York 14853

Reactions of Transition-Metal Carbonyl Anions with Group 2B Metal Acceptors and the Crystal Structure of Tetra-*n*-butylammonium Tris(dicarbonyl(η^5-cyclopentadienyl)iron)zincate

ROBERT B. PETERSEN, JOSEPH M. RAGOSTA, GEORGE E. WHITWELL II, and JAMES M. BURLITCH*

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Complexes of the type $M'(ML_n)_3^-$ were prepared from the reaction of bis(transition-metal carbonyl)–group 2B metal acceptors, $M'(ML_n)_2$, where M′ is Zn, Cd, or Hg, with metal carbonyl anions, $ML_n^- = FeCp(CO)_2$, $WCp(CO)_3$, $CrCp(CO)_3$, and $Co(CO)_4$ (Cp = η^5-C_5H_5), in dichloromethane or tetrahydrofuran. Among the crystalline complexes isolated was $(n\text{-}Bu)_4N^+Zn[FeCp(CO)_2]_3^-$, which was characterized by single-crystal X-ray structure analysis. This compound crystallizes in space group $P2_1/c$ with $Z = 4$ and monoclinic unit cell dimensions $a = 9.8192$ (3) Å, $b = 21.813$ (7) Å, $c = 18.650$ (5) Å, and $\beta = 106.93$ (2)°. This is the first tetrametal trigonal-planar zinc complex and has an average Zn–Fe distance of 2.541 Å. A partially refined X-ray structure of $Me_4N^+Hg[Co(CO)_4]_3^-$ revealed trigonal-planar coordination about mercury. By analysis of infrared spectroscopic data, approximate formation constants were determined for the complexes. For all complexes studied, the magnitudes of these constants were in the order Cd > Zn > Hg. The relative magnitudes of the formation constants were found to depend on M′, ML_n, and solvent in a systematic way. Increasing the basicity of ML_n in $M'(ML_n)_2$ decreases the magnitude of the complex formation for a given anion. Complex formation is decreased in solvents with high donor numbers. Evidence was also obtained for the equilibrium nature of complex formation.

Introduction

Although there has been a great deal of study of the Lewis acidity of the group 2B metals, very little is known about the structure of the acid–base complexes they form. The best studied complex, $Hg[Co(CO)_4]_3^-$, was first postulated to be a radical anion, $Hg[Co(CO)_4]_2\cdot^-$,[1] and later correctly identified as a tetrametallic cluster by several groups.[2-4] By analysis of infrared (IR) spectra and by derivative formation, the compound was identified as an adduct between the Lewis acid $Hg[Co(CO)_4]_2$ and the base $Co(CO)_4^-$, but the structure remained unknown.

Prior to this work there were no definitive structural studies of three-coordinate zinc or cadmium. Recently Boersma and co-workers described the structure of an internally coordinated organozinc–transition metal compound, $(CH_3)_2N(CH_2)_3ZnW(\eta^5\text{-}C_5H_5)(CO)_3$, which contains a nearly planar sphere including carbon, nitrogen, and tungsten.[5] Only one structure of a complex containing a transition metal coordinated to three-coordinate mercury has been described, viz. $[Ru(Cp)_2HgCl_2]RuCp_2(HgCl_2)_2$,[6] which contains one trigonal, one tetrahedral, and one octahedral mercury. The five-coordinate complex $[CoCp(CO)_2]HgCl_2$ is trigonal bipyramidal, with very long intermolecular axial Hg–Cl interactions, so it is assigned a primary coordination number of 3.[7]

Although structural studies of complexes formed from group 2B Lewis acids and transition-metal Lewis bases are scarce, there have been several studies of these complexes. In addition to those already mentioned, the following complexes have been described: $[Mo(mes)(CO)_3]HgCl_2$,[8] $Fe(CO)_3L_2HgCl_2$,[7] $Fe(CO)_5HgCl_2$,[9] and $Hg[FeCp(CO)_2]_2Bu^-$.[10] The complex $Hg[FeCp(CO)_2]_3^-$ has been formed from the electrochemical reduction of $Hg[FeCp(CO)_2]_2$ at a dropping-mercury electrode and by the reaction of $Hg[FeCp(CO)_2]_2$ with $FeCp(CO)_2^-$.[11] The formation of a complex from $Hg[Co(CO)_4]_2$ and X^- (X = Cl, Br)[3,12] has also been observed. The only reported adducts containing cadmium are $Cd[MoCp(CO)_3]_2I^-$, $Cd[MoCp(CO)_3]I_2^-$,[13] and $CdCo(CO)_4Br_2^-$.[14] No adducts with metal bases have been reported for zinc besides those in our preliminary report of this work.[11b]

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