

Synthesis and Reactivity of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ - (dppm-) Stabilized Pd-Co and Pd-Pt-Co Clusters. Effect of Platinum versus Palladium on the Neighboring Palladium Center

Pierre Braunstein,* Claude de Méric de Bellefon, and Michel Ries

Received April 7, 1987

The quantitative and regioselective synthesis of the mixed-metal cluster $[\text{PdPtCo}_2(\text{CO})_7(\text{dppm})_2]$ (**1b**) was achieved by the reaction of the bimetallic complex $[\text{PdPtCl}_2(\text{dppm})_2]$ ($\text{dppm} = \mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2$) with $[\text{Co}(\text{CO})_4]^-$. As a result of phosphorus migration from palladium to cobalt, formal insertion of the $\text{Co}(\text{CO})_3$ fragment into a metal-phosphorus bond of the precursor exclusively occurs into the more labile P-Pd bond. The presence of numerous potential reaction centers (e.g., metal(s), metal-metal bonds, and CO and dppm ligands) in these clusters led to an investigation of the site selectivity toward attack by nucleophiles. The lability of the exocyclic $\text{Co}(\text{CO})_4$ fragment was evidenced and compared between **1b** and $[\text{Pd}_2\text{Co}_2(\text{CO})_7(\text{dppm})_2]$ (**1a**). Although a Pd-Co bond is involved, this lability is very sensitive to the neighboring metal center (Pd or Pt). Transmission of electronic effects from one metal center to another was evidenced, and a "platinum effect" was observed in dissociating solvents, where **1a** is partly dissociated but **1b** is completely dissociated into $[\text{PdPtCo}(\text{CO})_3(\text{S})(\text{dppm})_2][\text{Co}(\text{CO})_4]$ (S = solvent). This is a reversible process, as is the equilibrium between **1** and halide anions. Solvent clusters were prepared that possess a labile coordination site on Pd leading to completely regioselective reactions with donor molecules, e.g., phosphines, CO, or C_2Ph_2 . These ligands are labile ($\text{PR}_3 < \text{CO} < \text{C}_2\text{Ph}_2 < \text{MeCN} < \text{THF}$), and reversible CO uptake and substitution experiments showed that the Pd-bound CO in **4b** is less labile than in **4a**, indicating again a "platinum effect" on the reactive Pd center. The tris[bis(diphenylphosphino)methane] cationic cluster $[\text{Pd}_2\text{Co}(\text{CO})_2(\text{dppm})_3]^+$ was isolated, in which all the metal-metal bonds are bridged by dppm ligands. Spectroscopic IR and ^1H , $^{31}\text{P}\{^1\text{H}\}$, and, sometimes, $^{195}\text{Pt}\{^1\text{H}\}$ NMR data are discussed and confirm that in all these reactions the basic $\text{PdMCo}(\text{dppm})_2$ (M = Pd, Pt) framework is maintained, thus showing a certain robustness and that the reactions investigated all take place in the plane of this framework. The " $\text{Co}(\text{CO})_3\text{P}$ " fragment in the triangulo clusters reported in this work behaves as a neutral 3-electron donor organometallic bridging group vs the Pd-Pd or Pt-Pd unit.

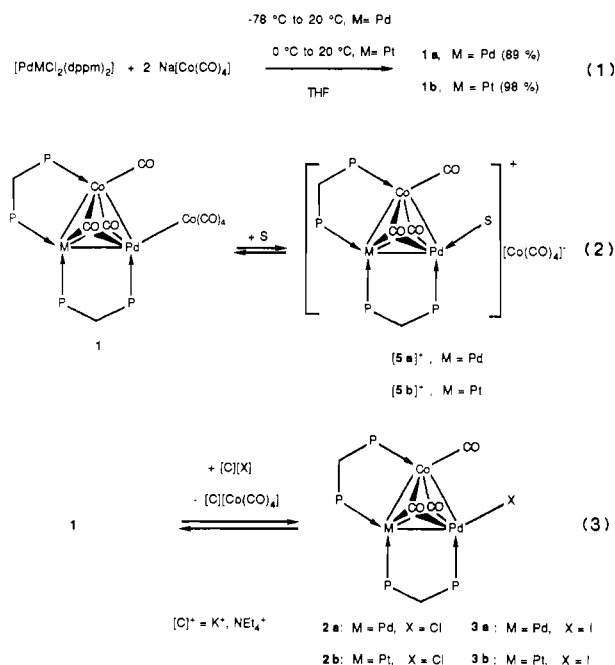
Introduction

As part of our general interest in mixed-metal cluster compounds and more recently in those containing $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ligands,¹ we have described in the preceding paper² the synthesis of tri- and tetranuclear clusters containing palladium and cobalt and two bridging dppm ligands (in the following, $\text{dppm} = \mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2$). The crystal structures of the metalloligated cluster $[\text{Pd}_2\text{Co}_2(\text{CO})_7(\text{dppm})_2]$ (**1a**) (see Scheme I) and of the cationic triangulo cluster $[\text{Pd}_2\text{Co}(\text{CO})_4(\text{dppm})_2][\text{PF}_6]$ (**4a**) (see Scheme III) were determined by X-ray diffraction. One of their most striking features is the almost coplanarity of the metal and phosphorus atoms. In order to investigate the scope of the reaction leading to **1a**, we have also studied the reactivity of the heterobimetallic complex $[\text{PdPtCl}_2(\text{dppm})_2]$ toward carbonylmetalate anions. We thus hoped to shed some light on the consequences of the metal-phosphorus bond lability and to synthesize, in a stepwise manner, heterometallic clusters containing three or four different metal atoms.³ Here we describe new dppm-containing clusters with PdPtCo_2 and PdPtCo cores and compare their properties with those of new or previously described analogous Pd_2Co_2 and Pd_2Co clusters.

Results

Synthesis of the Tetranuclear Cluster $[\text{PdPtCo}_2(\text{CO})_7(\text{dppm})_2]$ (1b**) and Behavior of **1a** and **1b** in Donor Solvents.** The reaction of 2 equiv of $\text{Na}[\text{Co}(\text{CO})_4]$ with the heterobimetallic complex $[\text{PdPtCl}_2(\text{dppm})_2]$ afforded the deep blue-green mixed-metal PdPtCo_2 cluster **1b** in almost quantitative yield (eq 1 in Scheme I). In contrast to the formation of $[\text{Pd}_2\text{Cl}_2(\mu\text{-CO})(\text{dppm})_2]$ during the synthesis of **1a**,² the corresponding A-frame complex $[\text{PdPtCl}_2(\mu\text{-CO})(\text{dppm})_2]$ did not accompany **1b**. This results from the lower reactivity toward CO insertion of the Pd-Pt bond vs the Pd-Pd bond of the $[\text{PdMCl}_2(\text{dppm})_2]$ (M = Pd, Pt) complexes.⁴ On the basis of IR and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR data (Tables I-III) the structure of **1b** appears closely related to that of **1a**. Interestingly, these data and ^{195}Pt NMR spectroscopy

Scheme I



unambiguously indicate that **1b** is not contaminated by the isomer **1c** where Pd and Pt would have exchanged positions, i.e., in which the $\text{Co}(\text{CO})_4$ group is bonded to Pt.

During the synthesis of both **1a** and **1b**, the color of the reaction mixture goes through a deep violet stage at ca. 0°C , corresponding to a labile intermediate that could not be isolated, before turning deep green at room temperature. In order to evaluate the expected different reactivity of $[\text{Co}(\text{CO})_4]^-$ toward the Pd-Cl and Pt-Cl bonds of $[\text{PdPtCl}_2(\text{dppm})_2]$, the latter complex was reacted with only 1 equiv of $\text{Na}[\text{Co}(\text{CO})_4]$. The only product observed was **1b**, ca. 50% of the precursor bimetallic complex being recovered. In particular, no formation of $[\text{PdPtCoCl}(\text{CO})_3(\text{dppm})_2]$ (**2b**) was evidenced in this reaction, although it could be independently synthesized (see below). It is well documented that in mononuclear complexes of the type $[\text{MCl}_2\text{L}_2]$ (M = Pd(II), Pt(II)), the Pd-Cl bond reacts much faster with carbonylmetalates than the Pt-Cl

- Braunstein, P. *Nouv. J. Chim.* **1986**, *10*, 365.
- Braunstein, P.; de Méric de Bellefon, C.; Ries, M.; Fischer, J.; Bouaoud, S.-E.; Grandjean, D. *Inorg. Chem.*, preceding paper in this issue.
- Braunstein, P.; de Méric de Bellefon, C.; Ries, M. *J. Organomet. Chem.* **1984**, *262*, C14.
- Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889.

Table I. Infrared Spectral Data

complex	IR abs max $\nu(\text{CO})$, ^a cm ⁻¹		other IR
	solid state ^b	solution ^c	
Pd ₂ Co ₂ (CO) ₇ (dppm) ₂ (1a)	2009 (vs), 1985 (s), 1924 (vs), 1896 (vs), 1879 (vs)	2010 (vs), 1995 (s), 1938 (vs), 1900 (s, br)	
PdPtCo ₂ (CO) ₇ (dppm) ₂ (1b)	2006 (vs), 1995 (sh), 1918 (vs), 1890 (vs), 1871 (vs)	2015 (vs), 1997 (s), 1927 (vs), 1899 (s, br)	
Pd ₂ CoCl(CO) ₃ (dppm) ₂ (2a)	1992 (s), 1900 (sh), 1854 (m, br)	2000 (s), 1866 (m, br)	
PdPtCoCl(CO) ₃ (dppm) ₂ (2b)	1996 (s), 1862 (m, br)	2009 (s), 1878 (m, br)	
Pd ₂ CoI(CO) ₃ (dppm) ₂ (3a)	1989 (s), 1900 (sh), 1868 (m, br)	2000 (s), 1880 (m, br)	
PdPtCoI(CO) ₃ (dppm) ₂ (3b)	1994 (s), 1910 (sh), 1870 (m, br)	2007 (s), 1872 (m, br)	
[Pd ₂ Co(CO) ₄ (dppm) ₂]PF ₆ (4a)	2072 (s), 2007 (s), 1896 (m, br)	2078 (s), 2013 (s), 1897 (m, br)	d
[PdPtCo(CO) ₄ (dppm) ₂]PF ₆ (4b)	2064 (s), 2004 (s), 1891 (m, br)	2067 (s), 2009 (s), 1898 (m, br) ^e	d
[Pd ₂ Co(CO) ₃ (dppm) ₂ (DMSO)] ⁺ ([5a] ⁺)		1990 (m) ^f	
[Pd ₂ Co(CO) ₃ (dppm) ₂ (CH ₃ CN)] ⁺ ([6a] ⁺)		2000 (s), 1879 (m, br)	
[PdPtCo(CO) ₃ (dppm) ₂ (CH ₃ CN)] ⁺ ([6b] ⁺)		2001 (s), 1883 (m, br)	
[Pd ₂ Co(CO) ₃ (dppm) ₂ (C ₂ Ph ₂)]PF ₆ (7a)	1994 (s), 1873 (m, br) ^g	2006 (s), 1872 (m, br) ^h	d
[Pd ₂ Co(CO) ₃ (dppm) ₂ (PMe ₂ Ph)]PF ₆ (8a)	1986 (s), 1910 (sh), 1868 (m, br)	1991 (s), 1870 (m, br)	d
[PdPtCo(CO) ₃ (dppm) ₂ (PMe ₂ Ph)]PF ₆ (8b)	1989 (s), 1916 (sh), 1867 (m, br)	1995 (s), 1880 (m, br)	d
[PdPtCo(CO) ₃ (dppm) ₂ (PPh ₃)]PF ₆ (9b)	1993 (s), 1870 (m, br)	2004 (s), 1861 (m, br)	d
[PdPtCo(CO) ₃ (dppm) ₂ (AsPh ₃)]PF ₆ (10b)	1995 (s), 1868 (m, br)	2007 (s), 1870 (m, br)	d
[Pd ₂ Co(CO) ₂ (dppm) ₃]PF ₆ (11a)	1845 (m, br)		d

^a Abbreviations: vs = very strong, s = strong, m = medium, sh = shoulder, br = broad. ^b In KBr, except where noted. ^c In THF, except where noted. ^d For PF₆⁻, the $\nu(\text{PF})$ value recorded in KBr is 838 (vs) cm⁻¹. ^e Values recorded in CH₂Cl₂ are 2078 (s), 2014 (s), 1896 (m, br) cm⁻¹. ^f Recorded in DMSO; the lower wavenumber absorption is occulted by the very strong $\nu(\text{CO})$ absorption band of the Co(CO)₄⁻ counteranion (1885 cm⁻¹). ^g Recorded as mineral oil mull. ^h Recorded in CH₂Cl₂.

Table II. ¹H NMR Data^a

complex	P-CH ₂ -P			P-CH ₂ -P			comment
	δ	² J(PH), Hz	⁴ J(PH), Hz	³ J(PtH), Hz	δ	² J(PH), Hz	
Pd ₂ Co ₂ (CO) ₇ (dppm) ₂ (1a)	4.51 (dt)	9.3	3.3		3.97 (t)	9.6	
Pd ₂ CoCl(CO) ₃ (dppm) ₂ (2a)	4.30 (dt)	9.1	2.5		3.98 (t)	9.7	
Pd ₂ CoI(CO) ₃ (dppm) ₂ (3a)	4.54 (dt)	9.0	3.0		4.11 (t)	9.5	
[Pd ₂ Co(CO) ₄ (dppm) ₂]PF ₆ (4a)	4.72 (dt)	9.8	2.0		4.35 (t)	10.2	
[Pd ₂ Co(CO) ₃ (dppm) ₂ (C ₂ Ph ₂)]PF ₆ (7a)	4.36 (t)	9.4			4.18 (t)	10.0	b
[Pd ₂ Co(CO) ₃ (dppm) ₂ (PMe ₂ Ph)]PF ₆ (8a)	4.64 (t)	9.8			4.21 (t)	9.7	c
[Pd ₂ Co(CO) ₂ (dppm) ₃]PF ₆ (11a)	4.55 (m)	9.3			4.02 (t)	6.1	d
PdPtCo(CO) ₃ (dppm) ₂ (1b)	4.89 (dd)	6.6, 10.4		68	4.27 (t)	9.2	37
PdPtCoCl(CO) ₃ (dppm) ₂ (2b)	4.67 (dd)	5.8, 10.6		68	4.27 (t)	9.6	38.5
PdPtCoI(CO) ₃ (dppm) ₂ (3b)	4.86 (dd)	6.0, 10.8		67	4.41 (t)	9.6	39
[PdPtCo(CO) ₄ (dppm) ₂]PF ₆ (4b)	5.11 (t)	10.0		70	4.56 (t)	10.2	36
[PdPtCo(CO) ₃ (dppm) ₂ (PPh ₃)]PF ₆ (9b)	4.88 (t)	8.8		74	4.48 (t)	9.9	38
[PdPtCo(CO) ₃ (dppm) ₂ (AsPh ₃)]PF ₆ (10b)	4.83 (t)	9.5		71	4.50 (t)	10.0	40

^a Run in CDCl₃. Key: t = triplet, dt = doublet of triplet, dd = doublet of doublet, m = multiplet. All compounds exhibit complex multiplet due to phenyl groups of the dppm ligands in the range 7.8–6.85 (40 H) ppm. The integration of the P-CH₂-P resonance corresponds to 2 H, unless otherwise specified. ^b Phenyl resonances (50 H). ^c Resonances owing to the PMe₂Ph ligand: phenyl resonances (45 H); methyl resonances at δ 1.30 (3 H, d, ²J(PH) = 8.0 Hz), 1.31 (3 H, d, ²J(PH) = 8.0 Hz). ^d Phenyl resonances (60 H); methylene resonances at δ 4.02 (4H), 4.55 (2H). ^e Phenyl resonances (55 H).

Table III. ³¹P{¹H} and ¹⁹⁵Pt{¹H} NMR Data^a

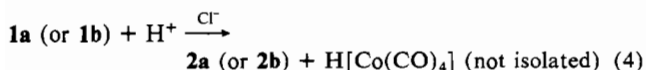
complex	δ (³¹ P{ ¹ H}) ^b				J(PP) , Hz						J(PtP) , Hz			δ (¹⁹⁵ Pt- ¹ H)
	δ_4^c	δ_3	δ_2	δ_1	J(12)	J(13)	J(14)	J(23)	J(24)	J(34)	J(PtP ¹)	J(PtP ²)	J(PtP ³)	
Pd ₂ Co ₂ (CO) ₇ (dppm) ₂ (1a)	28.0	-3.16 (dt)	-10.90 (ddd)	-0.93 (ddd)	119	22	142	55	36	12				
Pd ₂ CoCl(CO) ₃ (dppm) ₂ (2a)	27.8	-8.73 (ddd)	-21.09 (dt)	-5.91 (ddd)	92	13	120	43	38	11				
Pd ₂ CoBr(CO) ₃ (dppm) ₂ (3a)	27.0	-7.86 (ddd)	-19.06 (dt)	-5.54 (ddd)	91	12	127	39	39	10				
Pd ₂ CoI(CO) ₃ (dppm) ₂ (3a)	25.1	-6.63 (dt)	-17.21 (dt)	-4.20 (ddd)	94	14	128	41	41	14				
Pd ₂ Co(SCN)(CO) ₃ -(dppm) ₂	26.6	-6.60 (ddd)	-16.84 (ddd)	-3.39 (ddd)	76	11	119	41	38	<10				
[Pd ₂ Co(CO) ₄ (dppm) ₂]-PF ₆ ^d (4a)	22.4	-7.97 (d)	-13.38 (ddd)	-6.17 (dd)	76	<10	95	46	31	<10				
[Pd ₂ Co(CO) ₃ (dppm) ₂ -(C ₂ Ph ₂)]PF ₆ (7a)	24.6	-6.98 (d)	-17.64 (ddd)	-4.66 (ddd)	92	12	122	47	36	<10				
PdPtCo ₂ (CO) ₇ (dppm) ₂ (1b)	24.2	5.91 (q)	-2.47 (ddd)	-0.89 (ddd)	114	12	128	10.5	31.5	<10	3164	3936	-2509 ^e	
PdPtCoCl(CO) ₃ -(dppm) ₂ ^f (2b)	25.3	1.53 (m)	-7.12	-6.97	83	16	118.5	7	35.5	6	48	3145	3807.5	
PdPtCoI(CO) ₃ (dppm) ₂ (3b)	22.1	3.54 (m)	-5.58 (ddd)	-4.28 (ddd)	88	13.5	119	8	35	<8	3227	3845	-2509 ^e	
[PdPtCo(CO) ₄ -(dppm) ₂]PF ₆ ^d (4b)	19.4	1.55 (t)	-5.21 (ddd)	-7.96 (ddd)	76	11.5	93	13	31	<4	34	3139	3768	
[PdPtCo(CO) ₃ (dppm) ₂ -(AsPh ₃)]PF ₆ (10b)	21.5	3.50 (t)	-5.46 (ddd)	-3.73 (ddd)	84	12	97	13	33	<4	47	3160.5	3821	

^a Run in CH₂Cl₂/CDCl₃ (1:1). Key: d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, t = triplet, dt = doublet of triplet, q = quadruplet. The PF₆⁻ anion exhibits a septuplet at -143.8 ppm (¹J(PF) = 711 Hz). The absolute values are those measured on the spectrum and are at ± 0.5 Hz from those resulting from simulation when needed. ^b For phosphorus assignment see Chart I. ^c Phosphorus on cobalt appears as a broadened multiplet owing to the high quadrupolar moment of the cobalt atom. ^d Recorded under CO atmosphere. ^e Appears as a ddt, but insufficient resolution prevents the determination of ²J(PtP⁴). ^f Recorded at 162 MHz.

bond, isostructural products being however often isolated.⁵ Related features are now observed and discussed below with the dinuclear complexes $[\text{PdMCl}_2(\text{dppm})_2]$ ($M = \text{Pd}(\text{I}), \text{Pt}(\text{I})$).

The relative lability of the exocyclic metal-metal bond in **1** was clearly evidenced by a range of reactions. In donor solvents *S* (e.g., MeCN, DMSO) both **1a** and **1b** dissociate with a change of color from deep green or blue-green to red and liberation of $[\text{Co}(\text{CO})_4]^-$, according to eq 2 (Scheme I). This equilibrium was monitored by IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic methods. Thus, the IR spectra of **1a** and **1b** in DMSO are characterized by the very strong absorption at 1885 cm^{-1} of $[\text{Co}(\text{CO})_4]^-$ and by a medium absorption at 1990 cm^{-1} , assigned to the linear carbonyl of the triangular core of $[\text{5}]^+$. On the other hand, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1a** in DMSO/DMSO-*d*₆ exhibits four multiplets centered at δ 27.2 (quadrupole broadened), -1.6, -4.3, and -15.0, each representing one phosphorus atom. The corresponding resonances for **1b** in DMSO are found at δ 25.3 (quadrupole broadened, 1 P), 4.4 (1 P), and -2.2 to -4.8 (2 P). These values are different from those of **1a** and **1b**, in, e.g., CDCl_3 , where no dissociation occurs (Table III). The heterolytic cleavage of the Pd-Co bond is more extensive in DMSO than in MeCN, and the equilibrium is almost completely shifted to the right in the case of **1b** in DMSO (ca. 0.02 M, 25 °C) whereas under similar conditions, **1a** is dissociated to ca. 75%, as estimated from integration of the respective ^{31}P NMR resonances. Evaporation of solvent *S* or freezing a DMSO solution of **1a** or **1b** (ca. -20 °C) causes reversal of the equilibrium of eq 2 (Scheme I), regenerating **1a** or **1b** quantitatively, as indicated by IR spectroscopy and the characteristic color change. In view of the easy cleavage of the exocyclic Pd-Co bond of these molecules, they were reacted with typical nucleophiles such as halides, carbon monoxide, and phosphines. These reagents were expected to attack at the Pd center, although reactions at Co or, less likely, at M could not be ruled out a priori.

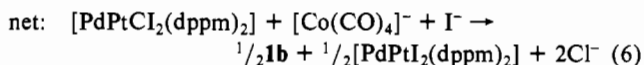
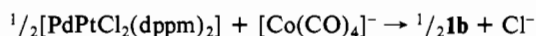
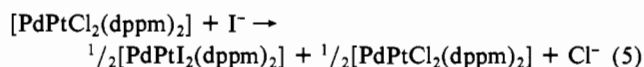
Reactions of 1a and 1b with Cl⁻ and I⁻. These reactions (eq 3, Scheme I) are accompanied by a color change from green or blue-green to red-brown or red for $M = \text{Pd}$ or Pt , respectively. We have previously shown for $M = \text{Pd}$ that the position of the equilibrium can be shifted by varying the solvent and/or the cation associated with the nucleophile.² The equilibrium of eq 3 can be shifted to the left with re-formation of the Pd-Co bond, by adding, e.g., Et₂O or hexane. When $M = \text{Pt}$, the iodo complex **3b** could be prepared almost quantitatively by reaction of **1b** with KI in acetone/H₂O or $[\text{Et}_4\text{N}]\text{I}$ in THF, isolated upon solvent evaporation, and further purified from $[\text{C}][\text{Co}(\text{CO})_4]$. The chloro complex **2b** was formed upon reaction of **1b** with KCl, but the reaction was never complete, unreacted **1b** being always present. In contrast, **1a** completely re-formed upon solvent evaporation, showing an easier back-reaction in eq 3 when $M = \text{Pd}$. We also found that **1b** slowly transformed to **2b** when dissolved in CHCl_3 . Shifting the position of the equilibrium of eq 3 to the right was possible when a protonating agent was used in the presence of chloride ions. Thus, **2a** and **2b** were obtained in good yields by reacting either **1a** with HCl alone or **1b** with HBF₄ in the presence of Cl⁻ (eq 4). No reaction occurred when **1a** was treated with



HBF₄ in THF, consistent with a weaker coordinating ability of $[\text{BF}_4]^-$ vs Cl⁻. This reaction therefore appears to involve substitution of $[\text{Co}(\text{CO})_4]^-$ by Cl⁻ prior to its protonation, the first step being slower. Reaction of **1a** with HI did not allow isolation of **3a**, oxidation products being formed probably via the intermediacy of I₂. A different procedure has been used to isolate **3a**.² Note that **3b** was independently shown to afford mononuclear Pd(II) and Pt(II) complexes upon reaction with I₂ (see Experimental Section).

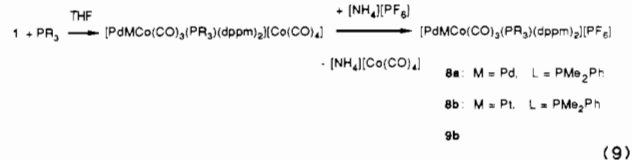
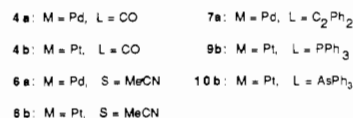
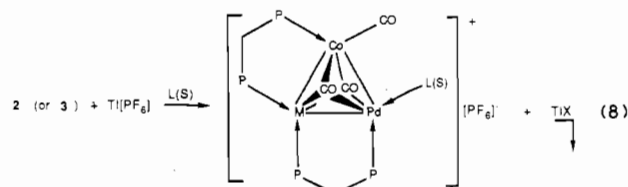
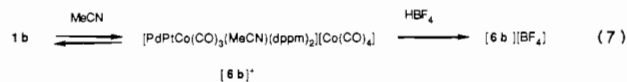
Attempted Direct Synthesis of 3b from [PdPtCl₂(dppm)₂]. Combining the results of eq 1 and eq 3 led us to envisage the possibility of a direct synthesis of **3b** using only 1 equiv each of $\text{Na}[\text{Co}(\text{CO})_4]$ and KI. However, the only products were $[\text{PdPtI}_2(\text{dppm})_2]$ (54% based on Pt) and **1b**, the reaction proceeding according to eq 6 in Scheme II. The isolation of $[\text{PdPtI}_2(\text{dppm})_2]$ results from the fast metathesis reaction (eq 5)⁴ and the reluctance of this complex to react with $[\text{Co}(\text{CO})_4]^-$. Indeed, we have independently verified that the reaction of $[\text{PdPtI}_2(\text{dppm})_2]$ with 2 equiv of $[\text{Co}(\text{CO})_4]^-$ is much slower than the reaction of its chloro analogue.

Scheme II



Synthesis and Reactivity of the Trinuclear Pd₂Co and PdPtCo Cationic Clusters. In order to obtain and possibly isolate as their $[\text{BF}_4]^-$ salts cationic species of type $[\text{5}]^+$ having a labile coordination site on palladium, **1b** was dissolved in MeCN giving $[\mathbf{6b}]^+[\text{Co}(\text{CO})_4]^-$, and then treated with HBF₄ to form $[\mathbf{6b}]^+[\text{BF}_4]^-$ (eq 7 in Scheme III). Cationic species similar to **6b** were obtained by treating the neutral halogeno clusters with a halide abstractor (e.g., $\text{Ti}[\text{PF}_6]$, $\text{Ag}[\text{CF}_3\text{SO}_3]$) in the presence of coordinating solvents *S* or neutral nucleophiles *L* (e.g., CO, C₂H₂, PR₃, or AsPh₃) (eq 8 in Scheme III). Reaction of **2a** with $\text{Ag}[\text{CF}_3\text{SO}_3]$ in THF similarly afforded $[\text{Pd}_2\text{Co}(\text{CO})_3(\text{THF})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$. The cationic clusters **8-10** present very similar $\nu(\text{CO})$ values compared to those of **2** and **3**. Thus, the increased electron density on the cluster due to the basic phosphine is balanced by the cationic charge.

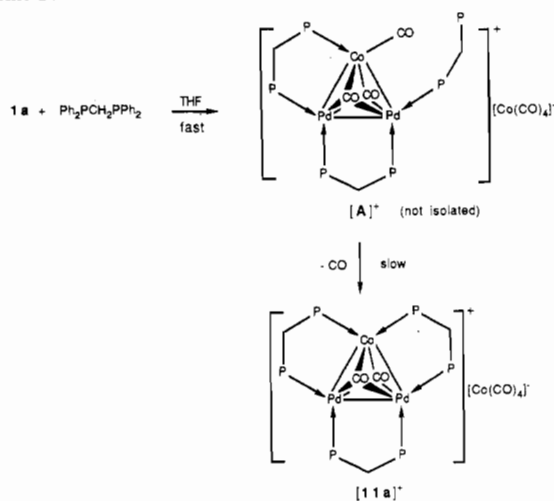
Scheme III



The coordination of the Pd-bound terminal CO in **4a** and **4b** is reversible, as shown by the disappearance of its $\nu(\text{CO})$ frequency (2078 and 2067 cm⁻¹, respectively) when acetone, THF, or MeCN solutions of these clusters are evaporated to dryness in vacuo, and by its reappearance when CO is bubbled into a solution of, e.g., **6a** or **6b**. This CO ligand is more tightly bound in **4b** since it remains coordinated when a CH₂Cl₂ solution of **4b** is evaporated to dryness, whereas it is displaced in **4a**. The alkyne ligand in dark violet **7a** is readily displaced either in the solid-state by Br⁻

(5) (a) Bender, R.; Braunstein, P.; Jud, J.-M.; Dusausoy, Y. *Inorg. Chem.* **1983**, *22*, 3394. (b) Bender, R.; Braunstein, P.; Jud, J.-M.; Dusausoy, Y. *Ibid.* **1984**, *23*, 4489.

Scheme IV



(e.g., when preparing a KBr pellet), affording $[Pd_2CoBr(CO)_3(dppm)_2]^+$ or in solution upon CO bubbling, yielding **4a**. The phosphine-substituted cluster **9b** was also prepared directly from **1b** (eq 9) and is described below. In $[PdPtCo(CO)_3(AsPh_3)(dppm)_2][PF_6]$ (**10b**), the presence of As results in a simplification of the $^{31}P\{^1H\}$ NMR spectrum compared to that of **9b**.

Reactions of Clusters 1a and 1b with Phosphines. Like the donor solvents MeCN and DMSO, monodentate phosphines reacted with **1** via heterolytic cleavage of the exocyclic Pd-Co bond, and the orange-red complexes **8** and **9b** were isolated after metathetical exchange of $[Co(CO)_4]^-$ for $[PF_6]^-$ (eq 9 in Scheme III).

These clusters were identified by IR and 1H NMR spectroscopies (Tables I and II). They exhibit a complex $^{31}P\{^1H\}$ NMR spectrum owing to coupling between five chemically different phosphorus atoms (see below). In the presence of slightly more than 1 equiv of monodentate phosphine, no further reaction, i.e. no CO substitution, could be evidenced. Interestingly however, reaction of 1 molar equiv of dppm with **1a** in THF at room temperature occurred with two successive color changes (green \rightarrow red \rightarrow yellow brown) and resulted in both exocyclic Pd-Co bond cleavage and CO substitution at the remaining Co atom, yielding the brown tris[bis(diphenylphosphino)methane] mixed-metal cluster $[11a][Co(CO)_4]$ (Scheme IV), easily converted into $[11a][PF_6]$ by addition of $[NH_4][PF_6]$. The $^{31}P\{^1H\}$ NMR spectrum of $[11a]^+$ reveals three distinct resonances, each corresponding to two chemically equivalent phosphorus atoms. The IR spectrum of $[11a][PF_6]$ shows a single broad $\nu(CO)$ absorption at 1845 cm^{-1} , which is at lower wavenumbers than that of the triply semibridging CO in **1a** and is in accord with an increased electron density on the metals, owing to the presence of three dppm ligands. This value can be compared to that found in the dicationic triangular cluster $[Pd_3(\mu_3-CO)(\mu-dppm)_3][CF_3CO_2]_2$ (1820 cm^{-1}).⁶ Thus, the two carbonyl ligands in $[11a]^+$ should be considered as triply semibridging, one on each side of the Pd_2Co triangular core, and thus they constitute interesting models of μ_3-CO ligands bound on to a "heterometallic surface". The reaction of **1a** with 1 molar equiv of dppm was followed by IR and $^{31}P\{^1H\}$ variable-temperature NMR spectroscopy. Upon mixing the reagents at 0°C , the bright red color of the solution, which is reminiscent of that of the complexes with PR_3 , can be kept for at least 0.25 h, allowing regular IR monitoring in the $\nu(CO)$ region. It reveals a very strong absorption at 1885 cm^{-1} , typical for $[Co(CO)_4]^-$, and a weaker band at ca. 1995 cm^{-1} . When the temperature is raised to 20°C , a progressive change of the spectrum occurs, and after 0.25 h, the absorption due to $[Co(CO)_4]^-$ is unchanged while that at 1995 cm^{-1} has vanished and a new band at $1848\text{ (w)}\text{ cm}^{-1}$ has appeared. The latter absorption is that of $[11a]^+$ while the

former is assigned to the red intermediate $[A]^+$ (Scheme IV). In parallel, $^{31}P\{^1H\}$ monitoring was started at -78°C . At this temperature, the reaction mixture presented a spectrum consisting of the signals of free dppm ($\delta -21$) (ca. 25% from $^{31}P\{^1H\}$ integration), of **1a**, and of a new species having resonances at $\delta 28.7$ (br d, $J(PP) \approx 107\text{ Hz}$, 1 P), -1.9 (m, 2 P), and -11.0 (m, 3 P), assigned to $[A]^+$. When the temperature was raised to 20°C , the signal of free dppm completely disappeared as well as the signals of **1a**, the only phosphorus-containing species observed being $[A]^+$. The second step of the reaction between **1a** and dppm is more difficult than the first. A dppm-bridged structure of type $[(dppm)_2(OC)_3CoPd_2\{\mu-dppm\}Pd_2Co(CO)_3(dppm)_2]^{2+}$, $[B]^{2+}$, analogous to that found when, e.g., $[Ru_3(CO)_{12}]$ is reacted with 0.5 equiv of dppm,⁷ could be ruled out for the intermediate on the basis of $^{31}P\{^1H\}$ NMR data and the fact that half of the dppm involved should be present as free ligand at this stage, which was not observed. Furthermore, the required $P \rightarrow Pd$ dissociation in $[B]^{2+}$, leading to $[11a]^+$, appears unlikely in view of the stability of the $R_3P \rightarrow Pd$ bond in **8a**.

Preliminary reactivity studies were performed on some of the cationic clusters described above. They were treated with various reagents (e.g., Cl^- , $NaBH_4$, $NaOMe$, $KO-t-Bu$, $NaOCHO$, $MeLi$, or CH_2N_2), which all caused disappearance of the Pd-bound terminal CO. Well-defined new products could not be identified, with the exception of **2b**. Even in the presence of a large excess of CH_2N_2 , no CH_2 insertion into the metal-metal bonds was observed, in contrast to the synthesis of $[Pd_2Cl_2(\mu-CH_2)(dppm)_2]$ from $[Pd_2Cl_2(dppm)_2]$.² Clusters **1a** and **3a** were unreactive toward CH_2N_2 , and Me_3NO in donor solvents induced their decomposition.

Discussion

Whereas the reaction of eq 1 (Scheme I) begins at ca. -20°C for the Pd₂ system, it only starts at ca. $+10^\circ\text{C}$ for the PdPt one, this being consistent with the greater reactivity of Pd complexes compared to their Pt analogues. Furthermore, the greater reactivity observed for the Pt center in $[PdPtCl_2(dppm)_2]$ compared to that in $[PtCl_2(PR_3)_2]$ complexes^{5b} may be attributed either to the influence of the neighboring Pd atom or to the expected greater rate of substitution at a Pt(I) vs a Pt(II) metal center.⁸ An important feature of eq 1 is its regioselectivity, as **1c**, a possible isomer of **1b**, is never observed even though Pt-Co bonds are expected to be more stable than Pd-Co bonds.⁹ Note also that **1b** could not be isomerized to **1c**. The reactions in eq 1 can be visualized as the formal insertion of a $Co(CO)_3$ moiety into a Pd-P bond resulting from a phosphorus migration from palladium to cobalt, the greater lability of Pd-P vs Pt-P bonds accounting for the complete regioselectivity observed. These reactions appear to be under kinetic control, as also evidenced when $[Fe(CO)_4]^{2-}$ is used in place of $[Co(CO)_4]^-$.¹⁰ The first step would involve the well-known substitution reaction of a halide by a carbonyl-metalate anion, leading to a Pd-substituted intermediate $Cl-Pt-Pd-m$ ($m = Co(CO)_4$) $[C]$. This isomer is favored over that with a $m-Pt-Pd-Cl$ linkage because of the greater reactivity of the Pd-Cl vs the Pt-Cl bond. Subsequent formation of an intermediate with a $m-M-Pd-m$ array $[D]$, either by ligand exchange⁴ ($2[C] \rightarrow [D] + [MPdCl_2(dppm)_2]$) or by a second metathesis reaction, would be followed by rapid rearrangement because of the unfavorable steric situation resulting from four PPh₂ groups in a cis position with respect to bulky metal carbonyl fragments. Indeed, systems of the type *trans*- $m-ML_2-m$ ($M = Pd$ or Pt) have not been isolated with bulky ligands L, such as phosphines, which destabilize the system.⁵ This reaction sequence is supported by $^{31}P\{^1H\}$ NMR monitoring of the formation of related $[Pd_2Fe(dppm)_2]$ clusters.¹¹

(6) (a) Manojlović-Muir, L.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. *J. Chem. Soc., Chem. Commun.* **1983**, 1336. (b) Manojlović-Muir, L.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. *J. Chem. Soc., Chem. Commun.* **1985**, 536.

(7) Bruce, M. I.; Matison, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, 247, 321.

(8) Shimura, M.; Espenson, J. H. *Inorg. Chem.* **1984**, 23, 4069.

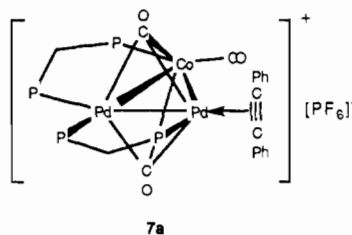
(9) (a) Braunstein, P.; Dehand, J. C. *R. Seances Acad. Sci. Ser. C* **1972**, 274, 175. (b) Braunstein, P.; Dehand, J. *Bull. Soc. Chim. Fr.* **1975**, 1997.

(10) Braunstein, P.; Kervennal, J.; Richert, J.-L. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 768.

The reactivity of the metalloligated clusters **1** is dominated by the lability and easy heterolytic cleavage of the exocyclic Pd–Co bond, even in weakly coordinating solvents (eq 2, Scheme I). Dissociation is more extensive in DMSO than in MeCN and is not observed in THF or Et₂O, in agreement with the decrease of the relative dielectric constant of these solvents in the sequence DMSO > MeCN >> THF.¹⁴ Comparative ³¹P{¹H} NMR studies of the dissociation of **1a** and **1b** in DMSO show that the latter is complete. This observation qualitatively indicates that the Δ*G* value of the equilibrium (eq 2) is greater for the PdPtCo system than for the Pd₂Co system. This could be due to the ability of the platinum center to release electron density through the metal–metal bond to the neighboring electron-deficient palladium center. This is supported by the IR data for **4a** and **4b** (see below). Thus, the vacant coordination site on palladium will be less electron-demanding in cation [**5b**]⁺ than in [**5a**]⁺. At room temperature, species **1a** and [**5a**][Co(CO)₄] are distinct, indicating that no rapid dissociation occurs on the time scale of the NMR experiment. This contrasts with, e.g., the very fast reversible dissociation observed for the Rh–Co bond in the dinuclear complex [(PEt₃)₂(CO)Rh–Co(CO)₄].¹⁵

Halide complexes, e.g., **2** or **3**, were prepared from their tetranuclear precursors. The iodo derivatives were generally easier to make and isolate than their chloro analogues and were found to be more reactive toward carbonylmetalates when M = Pd instead of M = Pt, making more difficult the isolation of **3a** from the reaction of eq 3. Labile, cationic, solvento species, e.g. [**5a**]⁺, could be isolated in the solid state even in the case of S = THF. Other nucleophiles can occupy this coordination site, and the lability of the Pd–L(S) bond was found to increase in the order PR₃ < CO < C₂Ph₂ < MeCN < THF, in accord with the nucleophilic character of these ligands. The Pd–CO bond in **4b** is less labile than that in **4a**, again owing to the greater electron density on the corresponding metal center in **4b**. No further reaction is observed with CO, i.e., no insertion into a metal–metal bond, perhaps because of the rigidity and stability of the triangular metal core. This contrasts with the reactions of the complexes [PdMCl₂(dppm)₂] with CO, which leads to the A-frames [PdMCl₂(μ-CO)(dppm)₂],^{4,16} perhaps via an intermediate with a terminal carbonyl ligand,¹⁷ such as [Pt₂Cl(CO)(dppm)₂]Cl.¹⁸ The Pd₂ or the PdPt analogues of the latter complex have not been reported, although related Pd₂Co and PdPtCo versions are now available with **4a** and **4b**.

Diphenylacetylene in **7a** is bonded to one Pd atom. No interaction with a second metal was evidenced. We can therefore



7a

assume that the alkyne acts as a 2-electron donor, a situation rarely

- (11) Braunstein, P.; de Méric de Bellefont, C.; Fischer, J.; Ries, M. *Organometallics* **1988**, *7*, 332–343.
 (12) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99 and references cited therein.
 (13) (a) Balch, A. L. In *Catalytic Aspects of Metal Phosphine Complexes*; Alyea, E. L., Meek, D. W., Eds.; Advances in Chemistry 196; American Chemical Society: Washington, DC, 1982; p 243. (b) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; p 167 and references cited therein.
 (14) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225.
 (15) (a) Roberts, D. A.; Mercer, W. C.; Zahurak, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 910. (b) Roberts, D. A.; Mercer, W. C.; Geoffroy, G. L.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 1439.
 (16) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.
 (17) Hoffman, D. M.; Hoffman, R. *Inorg. Chem.* **1981**, *20*, 3543.
 (18) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1540.

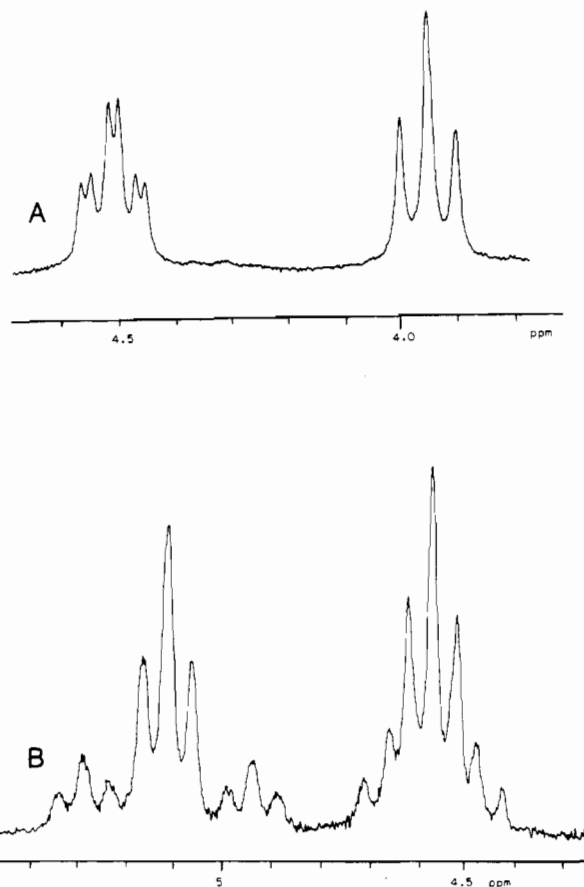


Figure 1. (A) Methylene region of the ¹H NMR spectrum of [Pd₂Co₂(CO)₇(dppm)₂] (**1a**). (B) Methylene region of the ¹H NMR spectrum of [PdPtCo(CO)₄(dppm)₂][PF₆] (**4b**).

encountered in cluster chemistry.¹⁹ This π-coordination is rather weak, as CO or Br[−] readily displaces the coordinated alkyne. With stronger but more bulky nucleophiles (phosphines), the cleavage of the exocyclic Pd–Co bond of **1a** or **1b** is irreversible (eq 9). Even with an excess of monodentate phosphine or upon reaction with a well-known CO abstractor (Me₃NO, in the presence of a coordinating solvent), CO substitution on the endocyclic cobalt atom did not occur. Such a substitution must require more energetic conditions. However, reaction of **1a** with dppm led to intermediate [A]⁺, which undergoes an intramolecular CO substitution reaction leading to [**11a**]⁺ (Scheme IV). Similarly, [Ru₃(CO)₉(dppm)(η¹-dppm)] readily leads to [Ru₃(CO)₈(dppm)₂].²⁰ Cluster [**11a**]⁺ represents a rare example of a tris(diphenylphosphino)methane] heterotrinnuclear cluster, systems that are sometimes difficult to obtain.²¹

The bonding in the tri- and tetranuclear Pd–Pt–Co clusters reported in this work is similar to that presented for their dipalladium analogues.² In both series, the “Co(CO)₃P” fragment behaves as a neutral 3-electron-donor organometallic bridging group vs the Pd–Pd or Pt–Pd unit, respectively. There is a precedent for such a bonding situation in a closo cluster.²²

Spectroscopic Properties. The infrared spectra of the platinum-containing clusters present the same pattern as those of their palladium analogues (Table I).² The difference in the highest ν(CO) value between **4a** (2078 cm^{−1}) and **4b** (2067 cm^{−1}) indicates

- (19) (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169.
 (20) Cartwright, S.; Clucas, J. A.; Dawson, R. H.; Foster, D. F.; Harding, M. M.; Smith, A. K. *J. Organomet. Chem.* **1986**, *302*, 403.
 (21) Evans, D. G.; Howard, J. A. K.; Jeffery, J. C.; Lewis, D. B.; Lewis, G. E.; Grosse-Ophoff, M. J.; Parrott, M. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 1723.
 (22) Bender, R.; Braunstein, P.; Metz, B.; Lemoine, P. *Organometallics* **1984**, *3*, 381.

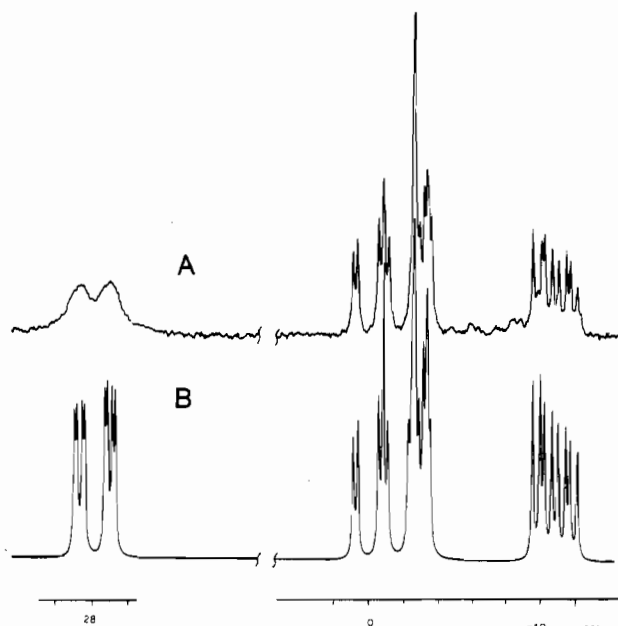


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Pd}_2\text{Co}_2(\text{CO})_7(\text{dppm})_2]$ (**1a**) at 81 MHz: (A) experimental; (B) simulated.

a platinum neighboring effect, which increases slightly the electron density on the palladium center of **4b**.

The ^1H NMR spectral data for these new molecules are presented in Table II. The phenyl regions of these compounds are generally uninformative and are therefore not discussed. Since the dppm ligands bridge two different metal-metal bonds, their methylene groups appear at different chemical shifts (see Figure 1). The high-field multiplet appears as a triplet owing to similar coupling with the two proximate P atoms, with the low-field multiplet appearing as a doublet of doublet or a triplet or as a doublet of triplet owing to additional coupling to a P atom of the second dppm ligand. Both multiplets are shifted downfield from the Pd_2 to the PdPt systems, and this is in agreement with the chemical shifts of the dppm methylene protons in " $\text{Pt}_2(\text{dppm})_2$ " systems²³ generally appearing at lower field compared to those in " $\text{Pd}_2(\text{dppm})_2$ " systems.²⁴ In the PdPtCo clusters, the low-field multiplet always exhibits Pt-H coupling constants of ca. 70 Hz, comparable to that found in $[\text{PdPtCl}_2(\text{dppm})_2]$ (69.8 Hz).⁴ This multiplet is therefore assigned to the methylene protons of the dppm bridging the Pt-Pd bond. This is further supported by the similar low-field value found in **[11a]**⁺ for the dppm bridging the Pd-Pd bond. In both the Pd_2Co and PdPtCo clusters, the chemical shifts increase compared to those of the parent complexes $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$ (4.17 ppm)²⁴ and $[\text{PdPtCl}_2(\text{dppm})_2]$ (4.27 ppm).⁴ Accordingly, the high-field multiplet corresponds to the methylene protons of the dppm bridging the Pd(Pt)-Co bond. When the $^3J(\text{Pt-H})$ values are considered, a general feature emerges for the PdPtCo clusters: this coupling constant is metal-metal-bond sensitive, ranging from 67–74 Hz for a Pd-Pt bond to 36–40 Hz for a Pt-Co bond. The trend from neutral to cationic clusters shows that the chemical shifts of the dppm methylene protons increase. A similar trend is observed in Pt dinuclear complexes, from the neutral $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$ (4.46 ppm)²³ to $[\text{Pt}_2\text{Cl}(\text{CO})(\text{dppm})_2]^+$ (4.65 ppm)¹⁸ and to the dicationic $[\text{Pt}_2(\text{CO})_2(\text{dppm})_2]^{2+}$ (5.80 ppm) complexes.²⁵ Even in neutral clusters, changing the chloride to bromide or iodide (i.e. **2** and **3**) increases the chemical shifts, as also seen in complexes $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$ (X = Cl, Br, I).²⁴ It therefore appears that ^1H NMR spectroscopy of the dppm CH_2 protons is more informative than IR spectroscopy in accounting for ligand substitution on the Pd atom.

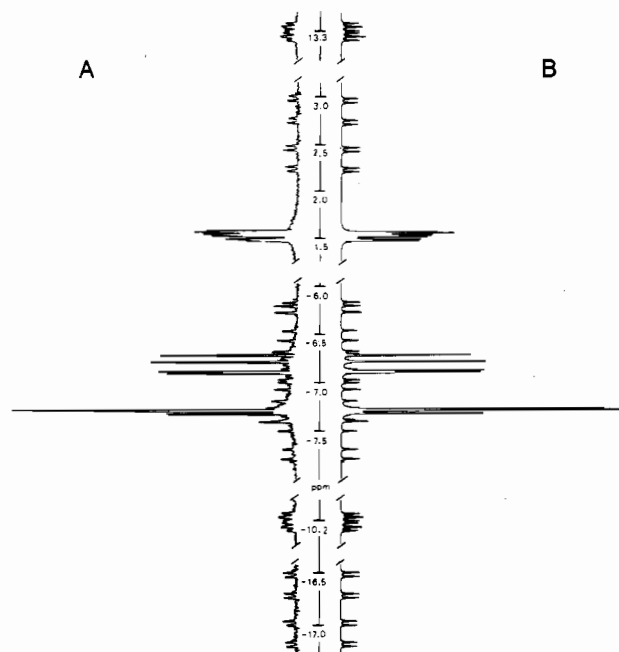
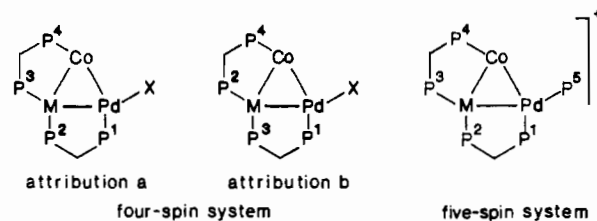


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{PdPtCoCl}(\text{CO})_3(\text{dppm})_2]$ (**2b**) at 162 MHz: (A) experimental; (B) simulated. The resonance of the phosphorus bonded to cobalt is not shown.

Chart I



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are very informative, and data are given in Table III for the clusters containing four phosphorus atoms, which are chemically inequivalent and coupled to each other. Thus, the $^{31}\text{P}\{^1\text{H}\}$ spin system is generally defined by 10 parameters: four chemical shifts and six coupling constants, giving rise to complex spectra (e.g., Figures 2 and 3). $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy is useful in determining the structure of all the synthesized complexes by comparison with those for which the solid-state structure has been established by X-ray diffraction methods (**1a**, **4a**). In contrast to the well-documented dinuclear systems symmetrically bridged by two dppm ligands,^{13b} relatively few higher nuclearity complexes with two nonequivalent dppm ligands have had their ^{31}P NMR spectra fully analyzed.²⁶ Thus an attempt is made here to understand the $^{31}\text{P}\{^1\text{H}\}$ NMR data and relate them to the solid-state structure of the tri- and tetranuclear clusters of Tables III. The accuracy of the NMR analysis has been checked by an iterative computer simulation.²⁷ The calculated values are very close to the experimental ones (ca. 0.5 Hz) (Figures 2 and 3). In general, chemical shifts are in the range found for tertiary phosphines bonded to Co, Pd, and Pt centers.²⁸ All spectra exhibit a quadrupole-broadened signal in the range 19–28 ppm, attributed unambiguously to the Co-bound phosphorus P(4) (see Chart I). In the case of the Pd_2Co systems, the different multiplets cannot be assigned to P(1), P(2), or P(3) on the basis of their chemical shifts only. However, in the PdPtCo systems,

(23) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1977**, 951.

(24) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 1641.

(25) Brown, M. P.; Franklin, S. J.; Puddephatt, R. J.; Thomson, M. A.; Seddon, K. R. *J. Organomet. Chem.* **1979**, *178*, 281.

(26) Grosse, M. C.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1983**, *253*, C50.

(27) PANIC (parameter adjustment in NMR by iteration calculation) is a minicomputer version of the LAOCOON-type programs, provided by Bruker.

(28) Pregosin, P. S.; Kunz, R. W. *NMR, Principles and Progress*; Springer-Verlag: New-York, 1979; Vol. 16.

one of the three multiplets appears weakly coupled to ^{195}Pt , and is assigned to P(1) (Figure 3). Consistent with isomer **1b** but not **1c** (see Results), the two other multiplets present direct coupling $^1J(^{195}\text{Pt}-^{31}\text{P})$, indicative of two platinum-bound phosphorus atoms, P(2) and P(3).²⁹ Nevertheless, these latter cannot be distinguished from each other and either of the assignments, a or b, can be envisaged. Interestingly, in the PdPtCo systems, P(1) and one of the Pt-bound phosphorus atoms (P(2) or P(3)) appears as an AB pattern ($J(\text{AB})/\nu_0\Delta(\delta(\text{A}) - \delta(\text{B}))$) is between 0.3 and 2;³⁰ a particularly complex case is presented in Figure 3). The analysis of such a second-order spectrum is facilitated by the fact that the satellites of the Pt-bound phosphorus are first order (Figure 3).³¹

Among the six $J(\text{P}-\text{P})$ coupling constants, $J[\text{P}(1)-\text{P}(4)]$ and $J[\text{P}(2)-\text{P}(3)]$ can be correlated to the structure of the molecules. The latter constant is very small, consistent with the cis relationship of P(2) and P(3).^{13b} Although $J[\text{P}(1)-\text{P}(4)]$ is a three-bond coupling, its value appears to be large, in agreement with a transoid P(1)-Pd-Co-P(4) arrangement.³² Assignment a for the phosphorus spectrum of the Pd₂Co and the PdPtCo systems is preferred over assignment b on the basis of the value of $J[\text{P}(1)-\text{P}(2)]$, which seems too large for a three-bond "zigzag" coupling but is consistent with the coupling between two P atoms of a dppm ligand bridging a Pd-M (M = Pd, Pt) bond. This value is slightly higher than that found in $[\text{PdPtCl}_2(\text{dppm})_2]$ (59 Hz).⁴ The coupling constant $J[\text{P}(3)-\text{P}(4)]$ should be viewed as the sum of a two-bond coupling constant (through the dppm bridge) and a three bond coupling constant (through the Pt-Co bond): $J[\text{P}(3)-\text{P}(4)] = ^2J[\text{P}(3)-\text{P}(4)] + ^3J[\text{P}(3)-\text{P}(4)]$.³⁵ An opposite sign for the two components could account for the small value of $J[\text{P}(3)-\text{P}(4)]$.³⁶ A definitive assignment needs further studies (e.g., $^1\text{H}\{^{31}\text{P}\}$ NMR experiments) as the analysis of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the clusters containing five P atoms (**8a**, **8b**, and **9b**) reveals a very strong three-bond "zigzag" coupling constant $J[\text{P}(2)-\text{P}(5)]$ (ca. 250 Hz), which is of course absent in, e.g., the AsP_3 analogue **10b**.

Experimental Section

All experimental procedures and physical measurements were performed as described in the preceding paper.² The $^{195}\text{Pt}\{^1\text{H}\}$ spectra were recorded at 42.95 MHz on a FT-Bruker WP 200 SY instrument and were externally referenced to 0.3 M K_2PtCl_4 in D_2O . The $^{31}\text{P}\{^1\text{H}\}$ spectrum of **2b** was recorded at 162 MHz on a FT-Bruker AM 400 instrument and externally referenced to 85% H_3PO_4 in D_2O . The UV spectra were recorded in solution on a Beckman Acta CIII spectrophotometer. The complex $[\text{PdPtCl}_2(\text{dppm})_2]$ was prepared in benzene with a slight modification of the published procedure,⁴ starting from $[\text{PtCl}_2(\text{PhCN})_2]$ instead of $[\text{PtCl}_2(t\text{-BuCN})_2]$. Yields are similar in both cases. The complex $[\text{PdPtI}_2(\text{dppm})_2]$ was prepared as described.⁴ The clusters of Table III not described in this work were reported previously.²

[PdPtCo₂(CO)₇(dppm)₂] (1b). A filtered solution of $\text{Na}[\text{Co}(\text{CO})_4]$ (0.1 M) in THF (40 mL) was added to a cooled (0 °C) and stirred orange suspension of $[\text{PdPtCl}_2(\text{dppm})_2]$ (2.29 g, 2 mmol) in THF (80 mL). The solution turned deep blue-green when raised to ambient temperature. After being stirred for 3 h, the solution was concentrated (to ca. 80 mL) in vacuo and filtered on a class-4 glass frit to remove NaCl.

Addition of pentane (150 mL) gave, after cooling at -20 °C, a quantitative yield of a dark blue-green microcrystalline powder of **1b**, which was washed with water and dried in vacuo (2.70 g, 98% based on Pt) (mp 173 °C). Anal. Calcd for $\text{C}_{57}\text{H}_{44}\text{Co}_2\text{O}_7\text{PdPt}$ ($M_r = 1384.24$): C, 49.46; H, 3.20. Found: C, 49.30; H, 3.17.

Reaction of 1b with NEt_4I . Solid NEt_4I (0.315 g, 1.22 mmol) was added to a solution of **1b** (1.54 g, 1.11 mmol) in THF (100 mL). The color of the reaction mixture turned from green to red. The solvent was removed in vacuo, and the resulting red residue was washed with water (300 mL) and recrystallized from a mixture of CH_2Cl_2 (50 mL) and *n*-hexane (150 mL). The IR spectrum of the resulting microcrystalline red-violet powder showed the characteristic $\nu(\text{CO})$ absorption band of $[\text{Co}(\text{CO})_4]^-$ at 1886 cm^{-1} in THF (1874 cm^{-1} in KBr). This observation prompted us to purify the powder by passage of its CH_2Cl_2 solution through a silica gel chromatography column (7 cm). The first, green fraction eluted with CH_2Cl_2 (80 mL) was identified by IR spectroscopy as **1b**. Further elution with a mixture of CH_2Cl_2 (20 mL) and THF (5 mL) afforded a red fraction, which was identified by IR spectroscopy as **3b** (1.01 g, 68% based on Pt).

Reaction of 1b with KCl. A solution of KCl (0.110 g, tenfold excess) in a mixture of acetone (20 mL) and water (0.5 mL) was added to a suspension of **1b** (0.190 g, 0.137 mmol) in acetone (100 mL). After the mixture was stirred for 1 day, the color had turned from green to brown and an IR spectrum of the solution showed $\nu(\text{CO})$ absorption bands assigned to **1b**, **2b**, and $[\text{Co}(\text{CO})_4]^-$. All attempts to transform **1b** completely into **2b** by, e.g., addition of a large excess of KCl (0.5 g, 6.70 mmol) in H_2O (50 mL) or evaporation under reduced pressure, failed and only afforded a mixture of **1b**, **2b**, and $\text{K}[\text{Co}(\text{CO})_4]$ as a brown solid.

Reaction of 1b with CHCl_3 under Ambient Conditions. Two solutions of **1b** were prepared: the first (A) contained ca. 10 mg in CHCl_3 (5 mL), the second (B) ca. 10 mg in THF (5 mL). After being stirred for 2 days, sample A had turned from green to red-brown and the IR spectrum of an aliquot, recorded in CHCl_3 , showed $\nu(\text{CO})$ absorption bands at 2007 (s), 1950 (sh), and 1875 (m, br) cm^{-1} . Under the same conditions, sample B remained green and its IR spectrum confirmed that no transformation of **1b** had occurred in THF.

Reaction of 1b with HBF_4 . HBF_4 (0.5 mL in 34% aqueous solution) was added to a solution of **1b** (0.14 g, 0.10 mmol) in MeCN (15 mL). The red-brown solution immediately turned orange-red. The IR spectrum of the solution before addition of HBF_4 showed the characteristic intense absorption band of $[\text{Co}(\text{CO})_4]^-$ (1889 cm^{-1}), in agreement with the equilibrium of eq 2. Addition of HBF_4 , followed by evaporation to dryness under reduced pressure and redissolution in THF of the solid residue, afforded a red solution whose IR spectrum in THF showed $\nu(\text{CO})$ absorption bands at 2001 (s) and 1883 (m, br) cm^{-1} , characteristic of the $[\text{PdPtCoS}(\text{CO})_3(\text{dppm})_2]^+ ([5b]^+)$ cation.

Reaction of 1a with HBF_4 . A solution of HBF_4 (34% in water, 2.5 mL) was added to a solution of **1a** (0.58 g, 0.45 mmol) in THF (100 mL). Stirring was maintained for 2 days. The color of the solution turned from green to brown-green. After addition of *n*-hexane, the green solid obtained was removed by filtration and identified as **1a**.

Reaction of 1a with HI. A solution of HI (65% in water, 0.005 mL) was added to a solution of **1a** (0.020 g, 0.015 mmol) in THF (20 mL). The green mixture turned red instantaneously and white vapors were formed. After 0.25 h of stirring, it was evaporated to dryness. The residue was washed with water (which colored deep red (iodine?)) and was dried. The residue thus obtained was poorly soluble. The IR (KBr) spectrum of this solid showed only absorption bands of the dppm ligand.

Reaction of 1a with Diazomethane. CH_2N_2 (ca. 0.5 M in Et_2O , 2 mL) was added to a cooled (-78 °C) solution of **1a** (0.170 g, 0.131 mmol) in Et_2O (100 mL). No color change was observed. The mixture was allowed to rise to ambient temperature, and stirring was maintained overnight. The solution was evaporated to dryness, and the IR spectrum of the solid showed unreacted **1a**.

Reaction of 1a with Me_3NO . Solid Me_3NO (previously dried by heating in vacuo) (0.010 g, 0.133 mmol) was added to a solution of **1a** (0.150 g, 0.116 mmol) in THF (30 mL). The color of the mixture changed slowly from deep green to brown (2 h). The IR (KBr) spectrum of a dried sample of the reaction mixture showed absorption bands at 1989, 1937, and 1857 (br) cm^{-1} . After being stirred for 3 h more, the mixture was evaporated to dryness and the residue dissolved in benzene. *n*-Hexane was added to the filtered solution, affording a brown powder (decomposition products).

$[\text{Pd}_2\text{CoCl}(\text{CO})_3(\text{dppm})_2]$ (2a). HCl (37% in water, 3 mL) was added to a THF (50 mL) solution of **1a** (0.96 g, 0.74 mmol), which was then stirred overnight. The reaction mixture turned from green to red-brown. The solution was filtered to remove some insoluble cobalt chloride. *n*-Hexane was added to the solution, and the resulting solid was collected by filtration, washed with water, and dried in vacuo. Recrystallization in CH_2Cl_2 /*n*-hexane afforded **2a** (0.50 g, 58% based on Pd), contami-

- (29) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.
 (30) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon: Oxford, England, 1967; Vol. 1.
 (31) An ABX spin system becomes first order when $J(\text{AX})$ or $J(\text{BX}) \gg J(\text{AB})$ and ν_X is greatly different from ν_A and ν_B .^{30,37b}
 (32) Such linear arrangements have been mostly studied on "P-Pt-Pt-P" systems. See for example ref 5b, 25, 33, and 34.
 (33) Boag, N. M.; Browning, J.; Crocker, C.; Goggin, P. L.; Goodfellow, R. J.; Murray, M.; Spencer, J. L. *J. Chem. Res., Miniprint* **1978**, 2962; *J. Chem. Res., Synop.* **1978**, 228.
 (34) Messbauer, B.; Meyer, H.; Walther, B.; Heeg, M. J.; Maqsdur Rahman, A. F. M.; Oliver, J. P. *Inorg. Chem.* **1983**, *22*, 272.
 (35) Grossel, M. C.; Batson, J. R.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1986**, *304*, 391.
 (36) Such hypotheses concerning the direct and indirect components of a coupling through different pathways have been postulated for, e.g., " $\text{Pt}_2(\text{dppm})_2$ " systems^{37a} and $[\text{Pt}_3(\text{CO})_3(\text{PR}_3)_3]$ clusters.^{37b}
 (37) (a) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Organomet. Chem.* **1978**, *161*, C46. (b) Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chim. Acta* **1981**, *48*, 153.

nated with a small amount of $[\text{PdCl}_2(\eta^2\text{-dppm})]$ ($^{31}\text{P}\{^1\text{H}\}$ NMR evidence).³⁸ Although this reaction most likely proceeds via formation of $\text{HCo}(\text{CO})_4$, it was not unambiguously identified. When this synthesis was performed by adding NaCl (2.37 g, 41 mmol) in water (40 mL) and aqueous HBF_4 (38 mL, 34%) to an acetone solution (450 mL) of **1a** (5.60 g, 4.32 mmol), **2a** was obtained in 96% yield.

[PdPtCoCl(CO)₃(dppm)₂] (**2b**). An aqueous solution of HBF_4 (5 mL, 34%) was added to a green mixture of **1b** (0.750 g, 0.54 mmol) and KCl (0.500 g, tenfold excess) in THF (50 mL). After being stirred overnight, the solution turned red. The solvents were removed in vacuo. The red residue was extracted with CH_2Cl_2 (40 mL), and the solution was filtered. Addition of *n*-hexane (50 mL) afforded a red powder of **2b** (0.600 g, 89% based on Pt) (mp 214 °C). Anal. Calcd for $\text{C}_{53}\text{H}_{44}\text{ClCoO}_3\text{P}_4\text{PdPt}$ ($M_r = 1248.71$): C, 50.98; H, 3.55. Found: C, 50.42; H, 3.36.

[PdPtCoI(CO)₃(dppm)₂] (**3b**). A solution of KI (1.16 g, 7.0 mmol) in a mixture of acetone (100 mL) and water (0.5 mL) was added to a stirred solution of **1b** (3.16 g, 2.28 mmol) in acetone (100 mL). The dark green solution immediately turned red. After 3 h of stirring, the solvents were evaporated in vacuo. The red solid residue was washed with water to remove $\text{K}[\text{Co}(\text{CO})_4]$ (identified by its IR absorption in THF at 1887 cm^{-1}) and the excess of KI . Extraction with CH_2Cl_2 (70 mL) gave a red solution of **3b**. After addition of *n*-hexane (150 mL), dark red crystals of **3b** were obtained at -20 °C (2.55 g, 96% based on Pt) (mp 215 °C). Anal. Calcd for $\text{C}_{53}\text{H}_{44}\text{CoI}_2\text{O}_3\text{P}_4\text{PdPt}$ ($M_r = 1340.17$): C, 47.50; H, 3.31; Co, 4.40; Pd, 7.94; Pt, 14.56. Found: C, 47.39; H, 3.26; Co, 4.91; Pd, 7.87; Pt, 13.83.

Reaction of 3b with TlPF₆ in MeCN. TlPF_6 (0.060 g, twofold excess) was added to a red solution of **3b** (0.113 g, 0.085 mmol) in MeCN (15 mL). After being stirred overnight, the reaction mixture had become red-orange and a light yellow precipitate of TII was formed. The suspension was filtered through a Celite-padded filter funnel (medium porosity) and dried in vacuo. An IR spectrum in THF of the resulting red residue showed $\nu(\text{CO})$ absorption bands at 2001 (s) and 1883 (m, br) cm^{-1} , characteristic of the cation $[\text{PdPtCoS}(\text{CO})_3(\text{dppm})_2]^+$ (**[5b]⁺**).

Reaction of 3b with Iodine. To a solution of **3b** (0.100 g, 0.075 mmol) in DMSO (2 mL) was added I_2 (0.036 g, 0.142 mmol). This resulted in an immediate color change from deep red to red-orange. A sample of this reaction mixture was transferred via syringe into a NMR tube. For the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: δ -22.6 (s) (dppm), -54.5 (s) ($[\text{Pd}(\eta^2\text{-dppm})(\text{DMSO})_2]_2$), -66.1 (s, $^1J(\text{PtP}) = 2873$ Hz) ($[\text{Pt}(\eta^2\text{-dppm})(\text{DMSO})_2]_2$), having relative integrated intensities of 5%, 40%, and 55%, respectively.

Reaction of 3a with KO-*t*-Bu. A suspension of KO-*t*-Bu (0.004 g, 0.036 mmol) in THF (5 mL) was added to a solution of **3a** (0.030 g, 0.032 mmol) in THF (5 mL). As no reaction was occurring, a second molar equivalent of KO-*t*-Bu was added. The color of the solution turned slowly from red-brown to light red. Upon filtration on a Celite-padded funnel, the solution darkened. It was evaporated to dryness, and the IR spectrum in the $\nu(\text{CO})$ region of the solid residue showed absorption bands at 1953 (s) and 1845 (w, br) cm^{-1} . After further treatment the product decomposed (lack of CO vibrations in the IR spectrum).

Reaction of 3a with Diazomethane. CH_2N_2 (ca. 0.5 M in Et_2O , 0.3 mL) was added to a cooled (0 °C) solution of **3a** (0.165 g, 0.132 mmol) in THF (30 mL). No color change was noticed even after 3 days of stirring at room temperature, and **3a** was recovered unchanged.

Reaction of 3a with Me₃NO. Solid, dried Me_3NO (0.009 g, 0.120 mmol) was added to a solution of **3a** (0.150 g, 0.120 mmol) in MeCN (30 mL). No change in the IR spectrum of the solution had occurred after 1 h of stirring. A slight excess of Me_3NO was then added to the mixture, but no reaction occurred. When the mixture was refluxed overnight, it decomposed (metallic deposit on the flask).

[PdPtCo(CO)₄(dppm)₂][PF₆] (**4b**). The following reactions and manipulations were performed under a CO atmosphere. Carbon monoxide was bubbled for 0.5 h through a red solution of **3b** (1.23 g, 0.89 mmol) in a mixture of acetone (40 mL) and THF (40 mL). A solution of TlPF_6 (0.370 g, 1.06 mmol) in acetone (15 mL) was then added. An immediate color change to orange-red occurred and a yellow precipitate of TII was formed. The solution was filtered through a Celite-padded filter funnel (medium porosity) and its volume reduced to ca. 10 mL. CO was bubbled through again to ensure saturation of the solution, and addition of pentane (10 mL) afforded an orange powder of **4b** (1.21 g, 97% based on Pt). Crystals were obtained from acetone/*n*-hexane at -20 °C (mp 203 °C). Anal. Calcd for $\text{C}_{53}\text{H}_{44}\text{CoF}_6\text{O}_4\text{P}_5\text{PdPt}$ ($M_r = 1386.24$): C, 46.79; H, 3.20. Found: C, 46.40; H, 3.08.

Reaction of 4b with NEt₃Cl. NEt_3Cl (0.053 g, 0.32 mmol) was added under a CO atmosphere to a solution of **4b** (0.224 g, 0.161 mmol) in THF (20 mL). The orange-red solution immediately turned red. IR and

$^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the reaction medium showed only the presence of **2b**. The solvent was removed under vacuum, and the residue was dissolved in a mixture of CH_2Cl_2 (3 mL) and toluene (15 mL). The solution was filtered, and slow diffusion of *n*-hexane at room temperature afforded red translucent crystals of **2b** (0.153 g, 76% based on Pt).

Reaction of 4b with NaBH₄. NaBH_4 (0.0013 g, 0.034 mmol) was added to a solution of **4b** (0.035 g, 0.025 mmol) in acetone (15 mL). The stirred solution turned from orange-red to intense green after 3 h of reaction. Spectroscopic data of the reaction mixture: IR (KBr) $\nu(\text{CO})$ 1962 (s, br), 1837 (s, br) cm^{-1} ; UV (acetone) λ_{max} 618 nm; $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone-*d*₆) δ 26.5 (very br, 1 P), from +3.5 to -10.3 (broad multiplets, 3 P).

Reaction of 4b with NaOMe. NaOMe (0.005 g, 0.092 mmol) was added to a solution of **4b** (0.100 g, 0.072 mmol) in acetone (20 mL). The solution immediately turned from red-orange to yellow-brown and after 0.1 h to olive-green. After 1.5 h of stirring, the solution had become an intense green. The solvent was removed in vacuo and the green residue extracted with a mixture of toluene (40 mL) and acetone (10 mL) and filtered. The resulting solution was evaporated to dryness, affording a green powder of an unidentified compound. Recrystallization in THF/pentane gave a microcrystalline green powder (0.072 g). IR (KBr): $\nu(\text{CO})$ 1997 (s), 1860 (m, br); $\nu(\text{PF})$ 838 (vs) cm^{-1} . UV (acetone): λ_{max} 629 nm. ^1H NMR (acetone-*d*₆): δ 7.7-6.8 (m, 40 H, C_6H_5), 5.02 (m, 2 H, CH_2), 4.88 (m, 2 H, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone/acetone-*d*₆): δ 28 (m, 1 P, P→Co), +4.4 to -10.4 (m, 3 P, 2P→Pt, 1P→Pd, $^1J(\text{PtP}) = 4263$ Hz).

Reaction of 4b with NaOCHO. Solid NaOCHO (0.008 g, 0.12 mmol) was added to an orange-red solution of **4b** (0.095 g, 0.068 mmol) in acetone (20 mL). After being stirred for 0.25 h, the solution turned green, and 1.5 h later its color had changed to an intense green. The solvent was removed under reduced pressure, and the resulting green residue was extracted with a mixture of toluene (40 mL) and acetone (10 mL) and filtered. Addition of pentane (50 mL) to the solution at -20 °C afforded 0.087 g of a green powder. IR (THF): $\nu(\text{CO})$ 1990 (s), 1881 (m, br) cm^{-1} . IR (KBr): $\nu(\text{CO})$ 1996 (s), 1868 (m, br); $\nu(\text{PF})$ 838 (vs) cm^{-1} . UV (acetone): λ_{max} 629 nm. ^1H NMR (acetone-*d*₆): δ 7.7-6.8 (m, 40 H, C_6H_5), 5.04 (m, 2H, CH_2), 4.88 (m, 2 H, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone/acetone-*d*₆): δ 28 (br m, 1 P, P→Co), +4.4 to -10.1 (m, 3 P, 2P→Pt, P→Pd, $^1J(\text{PtP}) = 4262$ Hz), -143.5 (hept, 1 P, PF_6 , $^1J(\text{PF}) = 706$ Hz).

Reaction of 4a with MeLi. MeLi (1.55 M in Et_2O , 0.05 mL) was added by syringe to a cooled solution (-78 °C) of **4a** (0.050 g, 0.038 mmol) in THF (10 mL). The mixture was raised to ambient temperature, and its color changed to orange. The solution was evaporated to dryness and the residue dissolved in toluene (poorly soluble). The resulting solution was filtered and evaporated to dryness, and the IR spectrum of the solid showed weak-intensity $\nu(\text{CO})$ absorption bands (compared to the bands of the ligand) at 1957 and 1832 cm^{-1} and the presence of $[\text{PF}_6]^-$ (838 cm^{-1}). No further purification was attempted.

Reaction of 4a with Diazomethane. CH_2N_2 (ca. 0.5 M in Et_2O , 0.1 mL) was added dropwise to a cooled solution (-78 °C) of **4a** (0.042 g, 0.032 mmol) in THF (25 mL) (previously saturated by CO bubbling). The color of the reaction mixture slowly turned from orange to red. *n*-Hexane was added to the solution, affording a red powdery precipitate, which was collected by filtration. Its IR spectrum (in KBr) showed $\nu(\text{CO})$ absorption bands at 1978 (s) and 1875 (br) cm^{-1} and the presence of $[\text{PF}_6]^-$. Further treatment led to decomposition.

[Pd₂Co(CO)₃(dppm)₂(C₂Ph₂)]PF₆ (**7a**). C_2Ph_2 (0.017 g, 0.095 mmol) was added to a solution of **3a** (0.089 g, 0.071 mmol) in acetone (12 mL). On addition of $\text{Tl}[\text{PF}_6]$ (0.025 g, 0.071 mmol) and stirring, the reaction mixture turned dark violet. Filtration through a Celite-padded filter funnel removed TII, and *n*-hexane was added to the solution, affording the violet solid **7a** (0.078 g, 76% based on Pd) (mp 193 °C dec). Recrystallization from CH_2Cl_2 /*n*-hexane gave solvated **7a**. Anal. Calcd for $\text{7a} \cdot 3.5\text{CH}_2\text{Cl}_2$ ($\text{C}_{70.5}\text{H}_{61}\text{Cl}_7\text{CoF}_6\text{O}_3\text{P}_5\text{Pd}_2$) ($M_r = 1745.03$): C, 48.52; H, 3.52. Found: C, 48.45; H, 3.35.

[Pd₂Co(CO)₃(dppm)₂(PMe₂Ph)]PF₆ (**8a**). PMe_2Ph (0.05 mL, 0.39 mmol) was added dropwise to a solution of **1a** (0.508 g, 0.39 mmol) in THF (50 mL). The solution immediately turned from dark green to intense red and was then stirred with $[\text{NH}_4][\text{PF}_6]$ (0.14 g, twofold excess). After addition of *n*-hexane, the resulting solid was filtered off, washed with water, and dried in vacuo. In order to remove the residual diethyl ether soluble $[\text{NH}_4][\text{Co}(\text{CO})_4]$, the solid was dissolved in THF, the solution was filtered, and Et_2O was added. Further addition of *n*-hexane and cooling of the solution to -20 °C resulted in precipitation of a red powder of **8a**, which was collected by filtration and vacuum-dried (0.410 g, 75% based on Pd) (mp 156-158 °C dec). Anal. Calcd for $\text{C}_{61}\text{H}_{55}\text{CoF}_6\text{O}_3\text{P}_6\text{Pd}_2$ ($M_r = 1407.72$): C, 52.05; H, 3.94. Found: C, 52.34; H, 4.02. $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$): δ 27.3 (1 P, br m, P→Co), -3.80 (2 P, unresolved m), -9.8 to -22.4 (2 P, AB pattern,

$J(\text{AB}) = 281$ Hz, consisting of a ddd, $J(\text{PP}) = 72, 51,$ and 33 Hz, and a dt, $J(\text{PP}) = 49, 49,$ and 23 Hz), -143.8 (1 P, sept, PF_6 , $^1J(\text{PF}) = 711$ Hz).

Reaction of 8a with KO-*t*-Bu. A suspension of KO-*t*-Bu (0.014 g, 0.121 mmol) in THF (10 mL) was added to a solution of **8a** (0.170 g, 0.121 mmol). The color of the mixture turned from red to brown, and the IR spectrum of the solution showed the presence of both starting complex **8a** and a new species with $\nu(\text{CO})$ absorption bands at ca. 1950 and 1850 cm^{-1} . The solution was filtered, and *n*-hexane was added to induce the precipitation of a red solid identified as **8a** (IR and ^1H NMR spectroscopy), which was removed by filtration. Evaporation to dryness of the mother liquor afforded a brown residue with an IR spectrum showing weak $\nu(\text{CO})$ bands at 1958 and $1847\text{ (br cm}^{-1})$ (very similar to the product observed in the reaction of **3a** with KO-*t*-Bu) and no presence of $[\text{PF}_6]^-$ or $[\text{-}t\text{-BuO}]^-$. When the reaction was performed with an excess of KO-*t*-Bu, the resulting product presented the same IR pattern as above, together with the absorption bands of **8a**.

[PdPtCo(CO)₃(dppm)₂(PMe₂Ph)]PF₆ (8b**).** PMe_2Ph (0.05 mL, twofold excess) was added to a solution of **1b** (0.25 g, 0.18 mmol) in THF (50 mL). The green solution immediately turned red. An IR spectrum of the solution indicated the presence of the $[\text{Co}(\text{CO})_4]^-$ anion ($\nu(\text{CO}) = 1887\text{ cm}^{-1}$). A solution of $[\text{NH}_4][\text{PF}_6]$ (0.4 mmol, twofold excess) in THF (5 mL) was added to the reaction mixture, which was then concentrated (to ca. 20 mL) under reduced pressure. Addition of Et_2O (150 mL) afforded a red-brown powder, which was washed with water (20 mL) and dried in vacuo. Recrystallization from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ gave red-orange crystalline flakes of **8b** (0.15 g, 56% based on Pt). Anal. Calcd for $\text{C}_{61}\text{H}_{55}\text{CoF}_6\text{O}_3\text{P}_6\text{PdPt}$ ($M_r = 1496.38$): C, 48.96; H, 3.70. Found: C, 48.80; H, 3.71. $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$): δ 21.5 (1 P, br m, $\text{P}\rightarrow\text{Co}$), +4.5 (1 P, m, $^1J(\text{PtP}) = 3968$ Hz, $\text{P}\rightarrow\text{Pt}$), +0.4 to -7.1 (3 P, m, $J(\text{PP}) = 82, 32, 15,$ and 223 Hz, $^1J(\text{PtP}) = 3042$ Hz).

[PdPtCo(CO)₃(dppm)₂(PPh₃)]PF₆ (9b**).** **Method 1.** Solid **3b** (0.18 g, 0.135 mmol), PPh_3 (0.04 g, 0.15 mmol), and $\text{Ti}[\text{PF}_6]$ (0.08 g, 0.23 mmol) were dissolved in THF (50 mL). After being stirred for 0.5 h at room temperature, the reaction mixture was concentrated under vacuum (to ca. 10 mL) and Et_2O (10 mL) was added. The solution was filtered, and slow diffusion of additional Et_2O (50 mL) afforded a light orange microcrystalline powder of **9b** (0.14 g, 64% based on Pt) (mp 181°C). Anal. Calcd for $\text{C}_{71}\text{H}_{59}\text{CoF}_6\text{O}_3\text{P}_6\text{PdPt}$ ($M_r = 1620.52$): C, 52.62; H, 3.67. Found: C, 52.60; H, 3.68. $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$): δ 22.2 (1 P, br m, $\text{P}\rightarrow\text{Co}$), 14.8 (1 P, m, PPh_3 , $J(\text{PP}) = 229$ Hz), 4.9 (1 P, quart, $\text{P}\rightarrow\text{Pt}$, $^1J(\text{PtP}) = 3910$ Hz, $J(\text{PP}) = 14$ Hz), -2 to -6 (2 P, AB pattern $J(\text{AB}) = 84$ Hz, $\text{P}\rightarrow\text{Pd}$ and $\text{P}\rightarrow\text{Pt}$, $^1J(\text{PtP}) = 3068$ Hz).

Method 2. PPh_3 (0.04 g, 0.15 mmol) was added to a solution of **1b** (0.19 g, 0.14 mmol) in THF (50 mL). The dark-green solution immediately turned red. $[\text{NH}_4][\text{PF}_6]$ (0.05 g, 0.3 mmol) was then added to the reaction mixture. The solution was concentrated under vacuum (to ca. 20 mL) and the product was precipitated with *n*-hexane (100 mL). The red-brown solid was filtered off and extracted with CH_2Cl_2 , leaving an insoluble orange-brown product identified by IR spectroscopy as $[\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2]$.³⁹ Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/n\text{-hexane}$ afforded light red-orange flakes of **9b** (0.125 g, 57% based on Pt).

[PdPtCo(CO)₃(dppm)₂(AsPh₃)]PF₆ (10b**).** This complex was prepared by using the same procedure as for **9b**, by reacting **3b** (0.057 g, 0.042 mmol) in THF (10 mL) with solid AsPh_3 (0.015 g, 0.047 mmol) and $\text{Ti}[\text{PF}_6]$ (0.030 g, 0.084 mmol). Complex **10b** was obtained as an orange-red powder (0.060 g, 86% based on Pt). Anal. Calcd for $\text{C}_{71}\text{H}_{59}\text{AsCoF}_6\text{O}_3\text{P}_6\text{PdPt}$ ($M_r = 1664.41$): C, 51.23; H, 3.57. Found: C, 50.94; H, 3.12.

[Pd₂Co(CO)₂(dppm)₃]PF₆ ([11a]PF₆**).** The ligand dppm (0.030 g, 0.078 mmol) and $[\text{NH}_4][\text{PF}_6]$ (0.020 g, slight excess) were added to a solution of **1a** (0.100 g, 0.072 mmol) in THF (30 mL). Immediately after addition of the diphosphine, the reaction mixture turned from green to red, and after 0.25 h of stirring at room temperature, its color had

turned to yellow-brown. Stirring was continued for 1 h. Monitoring of the reaction by IR spectroscopy showed the disappearance of the $\nu(\text{CO})$ vibrations of **1a** and a new very intense band at $1885\text{ (vs cm}^{-1})$, indicating the presence of $[\text{Co}(\text{CO})_4]^-$. The solvent was removed in vacuo, and the residue was washed with water and dried. Purification was achieved by dissolving the compound in THF, filtering the solution, and precipitating the brown solid with a mixture of $\text{Et}_2\text{O}/n\text{-hexane}$ (3:1), leaving $[\text{NH}_4][\text{Co}(\text{CO})_4]$ in solution. The resulting product was recrystallized from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$, affording brown needles of **[11a]PF₆** (0.080 g, 63% based on Pd) (mp 146°C). Anal. Calcd for $\text{C}_{77}\text{H}_{66}\text{CoF}_6\text{O}_2\text{P}_7\text{Pd}_2$ ($M_r = 1625.95$): C, 56.88; H, 4.09. Found: C, 57.12; H, 3.76. $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$): δ 26.7 (2 P, br m, $\text{P}\rightarrow\text{Co}$), -6.25 (2 P, dd, $\text{P}\rightarrow\text{Pd}$, $J(\text{PP}) = 78$ and 26 Hz), -9.51 (2 P, t, $\text{P}\rightarrow\text{Pd}$, $J(\text{PP}) = 26$ Hz), -143.5 (1 P, hept, PF_6 , $^1J(\text{PF}) = 711$ Hz).

Using the same procedure without the addition of $[\text{NH}_4][\text{PF}_6]$ led to the isolation of cluster **[11a][Co(CO)₄]**, which was recrystallized from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$. Anal. Calcd for **[11a][Co(CO)₄]** $\cdot 0.5\text{CH}_2\text{Cl}_2$ ($\text{C}_{81.5}\text{H}_{67}\text{ClCo}_2\text{O}_6\text{P}_6\text{Pd}_2$) ($M_r = 1694.43$): C, 57.77; H, 3.99. Found: C, 57.54; H, 4.16.

[Pd₂Co(CO)₃(THF)(dppm)₂][CF₃SO₃]. Solid $\text{Ag}[\text{CF}_3\text{SO}_3]$ (0.021 g, 0.080 mmol) was added to a solution of **2a** (0.092 g, 0.080 mmol) in THF (10 mL). After the mixture was stirred overnight, the color was deep red. It was filtered to remove a gray insoluble material (AgCl) and pentane was added to the solution, precipitating a dark red solid (0.090 g, 83% based on Pd). An IR spectrum recorded in KBr showed $\nu(\text{CO})$ absorptions bands at 1990 (s) and $1860\text{ (br cm}^{-1})$ (probably due to $[\text{Pd}_2\text{CoBr}(\text{CO})_3(\text{dppm})_2]$ formed by reaction with Br^- in the solid state) and characteristic bands of the $[\text{CF}_3\text{SO}_3]^-$ anion (1255 (vs), 1150 (m), 1022 (s), 631 (s) cm^{-1}). Anal. Calcd for $\text{C}_{58}\text{H}_{52}\text{CoF}_3\text{O}_7\text{P}_4\text{Pd}_2\text{S}$ ($M_r = 1345.78$): C, 51.76; H, 3.89. Found: C, 51.47; H, 4.07.

Reaction of [PdPtCl₂(dppm)₂] with 1 equiv of Na[Co(CO)₄] in the Presence of KI. A THF solution of $\text{Na}[\text{Co}(\text{CO})_4]$ (0.05 M, 5 mL) was added at 0°C to a mixture of $[\text{PdPtCl}_2(\text{dppm})_2]$ (0.300 g, 0.24 mmol) and KI (0.050 g, 0.3 mmol) in THF (50 mL). After 2 h of reaction at 0°C and 2 h of reaction at room temperature, the pale yellow solution had turned brown-red. Filtration and crystallization in $\text{THF}/\text{Et}_2\text{O}$ afforded a light orange powder of $[\text{PdPtI}_2(\text{dppm})_2]$ (0.19 g, 54% based on Pt), identified by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy by comparison with an authentic sample.⁴ The IR spectrum (in THF, $\nu(\text{CO})$ region) of the green mother liquor revealed exclusively the presence of **1b**.

Reaction of [PdPtI₂(dppm)₂] with Na[Co(CO)₄]. A filtered solution of $\text{Na}[\text{Co}(\text{CO})_4]$ (0.16 M) in THF (1 mL) was added to a cooled (0°C) and stirred orange suspension of $[\text{PdPtI}_2(\text{dppm})_2]$ (0.100 g, 0.075 mmol) in THF (20 mL). After 1 day of stirring at room temperature, the solution was orange-brown and the orange precipitate of the starting material was still present. An IR spectrum of the solution showed only the presence of the $[\text{Co}(\text{CO})_4]^-$ anion ($\nu(\text{CO})$ 1887 (vs), $1854\text{ (m cm}^{-1})$). After 1 week, traces of the orange precipitate were still evident, but the solution was more brown. Changing THF to a noncoordinating NMR solvent (e.g. CDCl_3) afforded a green solution, which was shown by $^{31}\text{P}\{^1\text{H}\}$ NMR to be a mixture of **1b** (80%) and unidentified products. When the NMR solvent was removed in vacuo, the resulting solid was red. Extraction with toluene (30 mL) gave a green solution of **1b**.

Acknowledgment. We are grateful to the CNRS for financial support and for a grant to M.R., and we also thank the Johnson Matthey Technology Center for a generous loan of PdCl_2 .

Registry No. **1a**, 113109-24-3; **1b**, 113109-37-8; **2a**, 113109-26-5; **2b**, 113132-11-9; **3a**, 113109-28-7; **3b**, 113132-12-0; **4a**, 113109-35-6; **4b**, 113132-14-2; **[5a][Co(CO)₄]**, 113132-18-6; **[6a]⁺**, 113109-51-6; **[6b]⁺**, 113109-52-7; **7a**, 113109-39-0; **8a**, 113109-41-4; **8b**, 113109-43-6; **9b**, 113109-45-8; **10b**, 113109-47-0; **[11a]PF₆**, 113109-49-2; **[11a][Co(CO)₄]**, 113109-50-5; $\text{Na}[\text{Co}(\text{CO})_4]$, 14878-28-5; $[\text{PdPtCl}_2(\text{dppm})_2]$, 82307-36-6; HBF_4 , 16872-11-0; $[\text{Pt}(\eta^2\text{-dppm})(\text{DMSO})_2]_2$, 113132-15-3; $[\text{Pd}_2\text{Co}(\text{CO})_3(\text{THF})(\text{dppm})_2][\text{CF}_3\text{SO}_3]$, 113132-16-4; $[\text{PdPtI}_2(\text{dppm})_2]$, 82307-38-8; $[\text{Pd}(\eta^2\text{-dppm})(\text{DMSO})_2]_2$, 113132-19-7; CH_2N_2 , 334-88-3; Pd, 7440-05-3; Co, 7440-48-4; Pt, 7440-06-4.