Organometallics 1984, *3*, 381–384 381

Unusual Four-Electron Donor Bridging $[Co(CO)_3PPh_3]^-$ Fragment in the Triangulo Cluster $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$: Synthesis, Structure, and Electrochemistry

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From $Co_2Pt_2(CO)_8(PPh_3)_2$, the cluster $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$, 1, has been synthesized and characterized by a complete single-crystal X-ray diffraction study. It crystallizes in the space group $P\bar{1}$ with $a = 14.807$ (8) Å, $b = 15.051$ (8) Å, $c = 14.047$ (8) Å, $\alpha = 93.14$ (5)°, $\beta = 108.75$ (4)°, $\gamma = 94.55$ (5)°, $V = 2944$ Å^3, and $Z = 2$. The structure was refined by using the 4717 reflections with $I \geq 3\sigma(I)$ to $R = 0.058$ and $R_w = 0.070$. The metal atoms of 1 form a closed triangular $CoPt_2$ arrangement. The Pt(1)–Co and Pt(2)–Co distances of 2.540 (2) and 2.574 (2) Å, respectively, are bridged by an asymmetric carbonyl. The Pt(1)–Pt(2) bond of 2.664 (1) Å is bridged by a μ-PPh_2 ligand. Each metal atom is coordinated by a PPh_3 ligand. A terminal carbonyl, C(10)–O(10), and two asymmetric bridging CO's are further bonded to the Co atom. The $CoPt_2(\mu\text{-}P(2))$ core is planar, and this arrangement is compared with that of related molecules. In addition, the three metal atoms and the four P atoms define a mean plane (maximum deviation P(3) = –0.19 (1) Å) which makes a dihedral angle of 98.4° with the CoP(1)P(2)C(10) plane. The unique bonding mode of the bridging μ-$Co(CO)_3PPh_3$ fragment supports the description of 1 as being constituted of two Pt(I) centers bridged by two monoanionic groups, $[\mu\text{-}Co(CO)_3PPh_3]^-$ and $[\mu\text{-}PPh_2]^-$, acting as four-electron donors. The electrochemistry of 1 has been investigated, and the results are in agreement with a strengthening effect of the μ-PPh_2 group.

There is much current interest in the synthesis of phosphido-bridged mixed-metal clusters because the μ-PR_2 ligands are expected to stabilize the metallic core and retard fragmentation under reaction conditions.[1] This is particularly relevant to the use of clusters as homogeneous catalysts.[2] Different methods have been developed for the synthesis of such clusters,[3] and it is well-known that thermolysis of transition-metal phosphine complexes may afford polynuclear compounds containing one or more phosphido bridges.[4] This unforeseeable route has not yet been systematically exploited.

We have now found that heating the butterfly $Co_2Pt_2(CO)_8(PPh_3)_2$ cluster[5] in the solid state affords the new phosphido-bridged cluster $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$, 1. Since spectroscopic data were insufficient to fully define the nature of this complex, a single-crystal X-ray diffraction study was undertaken, the results of which are described herein. Remarkably, the latter has revealed an unprecedented bonding mode for the $[\mu\text{-}Co(CO)_3PPh_3]$ fragment.

Experimental Section

Solvents were dried by standard methods, and all manipulations were conducted under a prepurified nitrogen or argon atmosphere by using standard Schlenk tube procedures. Elemental analyses of C, H, and P were performed by the Service Central de Microanalyses du C.N.R.S. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer as KBr pellets. Electrochemical measurements were performed under conditions similar to those described in previous works.[6] The cluster $Co_2Pt_2(CO)_8(PPh_3)_2$ was prepared according to the literature.[5]

Preparation of $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$, 1. Solid $Co_2Pt_2(CO)_8(PPh_3)_2$ (1.23 g, 1.00 mmol) was heated under N_2 at 145 °C for 20 h. Extraction of the solid residue with toluene, solvent removal, and recrystallization from toluene/pentane afforded green, air-stable crystals of 1 (0.270 g, 0.18 mmol, 18% yield): IR (KBr) ν(CO) 2005 (w), 1958 (s), 1951 (s), 1814 (s), 1800 (s), 1760 (vs) cm^{-1}; (CH_2Cl_2) 2008 (w), 1953 (s), 1800 (s), 1757 (vs) cm^{-1}. Anal. Calcd for $C_{69}H_{55}CoO_3P_4Pt_2$ (M = 1505.21): C, 55.02; H, 3.68; P, 8.23. Found: C, 55.61; H, 4.03; P, 8.07.

Crystallographic Analyses. Single crystals of 1 were obtained from toluene/pentane by slow diffusion at –20 °C. A suitable prism of dimensions 0.10 × 0.12 × 0.28 mm was sealed in a Lindemann glass capillary. A preliminary diffractometer search revealed triclinic symmetry. Diffraction data were collected at 293 K on a Picker FACS-1 diffractometer equipped with graphite-monochromated Mo Kα radiation. Twelve accurately centered reflections in the range $16 < 2\theta < 35°$ were used for determination and least-squares refinement of the unit cell parameters. The step-scan method was used to record the intensities for a unique set of reflections, where $7 \leq 2\theta \leq 55°$. The step was 0.05° in 2θ, and the measuring time was 2 s/step. Only the reflections expected to be sufficiently strong were measured. The reflections for which $\sigma^2(I)/I$ was smaller than a given threshold were stored in the memory of the PDP 8A computer, which monitors the diffraction measurements. The step-scan data were converted to intensities with their standard deviations with the

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Table I. Summary of Crystallographic Parameters for $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$, 1

(A) Crystal Parameters

formula	$C_{69}H_{55}CoO_3P_4Pt_2$	a, Å	14.807 (8)
fw	1505.21	b, Å	15.051 (8)
space group	$P\bar{1}$	c, Å	14.047 (8)
V, Å^3	2944.4	α, deg	93.14 (5)
Z	2	β, deg	108.75 (4)
D(calcd), g/cm^3	1.69	γ, deg	94.55 (5)
D(measd), g/cm^3	1.67(1) (flotation in aqueous ZnI_2)		

(B) Measurements of Intensity Data and Treatment

data collectn instrument	Picker FACS 1
radiatn	Mo Kα (λ = 0.7093 Å)
scan step	2 s count every 0.05°
scan range, deg	dissymmetric 0.95 + $\alpha_1\alpha_2$ separation + 0.85
data collection range	$+h, \pm k, \pm l$; $7 < 2\theta < 55°$
unique data ($I > 3\sigma(I)$)	4717
parameters refined	712
crystal size, mm	0.10 × 0.12 × 0.28
μ(Mo Kα), cm^{-1}	52.2
p factor	0.04
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.058
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o\rvert^2]^{1/2}$	0.070
esd of unit weight	2.6

Lehmann–Larsen algorithm.[7] A total of 6070 reflections were collected, of which 4717 had $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization factors, and absorption corrections were applied. Three standard reflections, measured after every 200 reflections, showed a steady decrease of intensity during the course of data collection. A linear decay correction was applied. All computations were done with the Enraf-Nonius structure determination package.[8] The structure was successfully solved in the $P\bar{1}$ space group. The position of the two platinum atoms was determined from the three-dimensional Patterson map. The rest of the structure was revealed by alternate calculations of Fourier, difference Fourier maps, and cycles of refinement (full-matrix least squares). All non-hydrogen atoms were located and refined anisotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o)^2/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (pF_o^2)^2]^{1/2}/Lp$. The position of the phenyl hydrogen atoms were calculated by using an assumed C–H bond length of 0.95 Å. Their contributions were included in the structure factor calculations but were not refined. The final residuals $R = 0.058$ and $R_w = 0.070$. Several peaks in the final difference Fourier synthesis were between 1.00 and 2.02 e/Å^3, all ghosts of the platinum atoms. Crystallographic data and data collection parameters for the structure are listed in Table I.

Results and Discussion

The new phosphido-bridged heterotrimetallic cluster $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$, 1, has been isolated after thermal treatment of solid $Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$, 2. Infrared data in the ν(CO) region indicated the presence of terminal and bridging carbonyl ligands (see Experimental Section). The molecular structure of 1 was determined by a single-crystal X-ray diffraction study.

The structure (Figure 1) consists of a triangular arrangement of metal atoms. Selected bond lengths and angles are listed in Table II and least-squares planes in Table III.[9] The Pt(1)–Pt(2) bond is bridged by the μ-PPh$_2$ group, the phosphorus atom P(2) of which is in the plane of the metals. The metal–metal distances are in the range found for other PPh$_2$-bridged Pt–Pt bonds[10] and for Pt–Co bonds in clusters.[5,11,12] The phosphorus atoms of the PPh$_3$ ligands terminally bonded to each metal deviate from the metallic plane by a maximum of 0.35 Å [P(1)]. The carbon atoms C(20) and C(30) are 1.87 (1) and 1.82 (1) Å from the cobalt atom and 2.104 (14) and 2.134 (14) Å from Pt(2) and Pt(1), respectively. With Co–C(20)–O(20) and Co–C(30)–O(30) angles of 147 (1) and 146 (1)°, respectively, the corresponding carbonyls can be referred to as asymmetric bridges.[13] The carbonyl C(10)–O(10) is linear and defines with C(20)–O(20) and C(30)–O(30) and with P(1) a trigonal-pyramidal environment about the cobalt atom. The latter lies at 0.195 Å above the C(10)–C(20)–C(30) plane. The atoms Co, P(1), C(10), O(10), and P(2) are in the same plane, and it intersects Pt(1)–Pt(2) in its middle and forms an angle of 99.4° with the metallic plane.

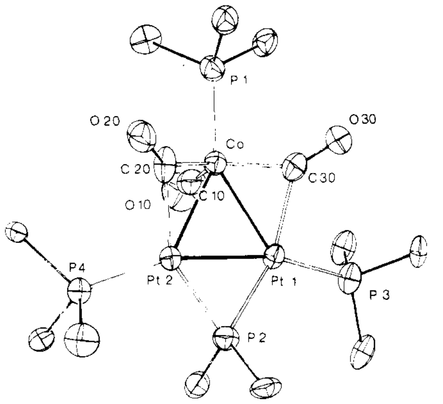
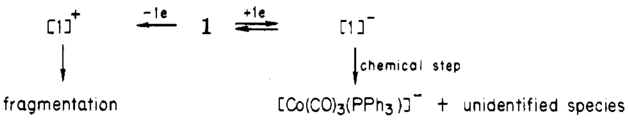


Figure 1. Molecular structure of $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$ (1). Phenyl groups on the phosphorus atoms are normal and have been omitted for clarity.

Scheme I



A unique structural feature of this 44-electron cluster is the bonding mode of the bridging μ-Co(CO)$_3$PPh$_3$ fragment. It can be described in two different but formally equivalent ways.

(i) The neutral μ-Co(CO)$_3$PPh$_3$ group could be considered, like the μ-PPh$_2$ group, as a three-electron donor toward the neutral P→Pt–Pt←P unit.

(ii) Cluster 1 can be envisaged as being constituted of two Pt(I) centers bridged by two monoanionic groups, $[\mu\text{-}Co(CO)_3PPh_3]^-$ and $(\mu\text{-}PPh_2)^-$, acting as four-electron donors. The value of the Pt–Pt distance in 1 falls very well in the range found for Pt(I)–Pt(I) systems,[14] supporting this formal description.

This constitutes a striking analogy with the known complex $Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2$[10a] in which a PPh$_2$ replaces the Co(CO)$_3$PPh$_3$ fragment of 1 and with the planar, triangulated $Pt_2m_2Cp_2(CO)_6(PR_3)_2$ (m = Cr, Mo, W) clus-

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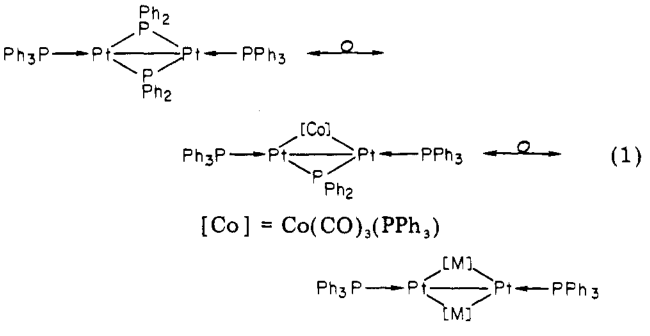
Table II. Selected Interatomic Distances (Å) and Angles (deg) in $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$ (1)

Bond Distances			
Pt(1)-Pt(2)	2.664 (1)	Co-P(1)	2.163 (4)
Pt(1)-Co	2.540 (2)	Co-C(10)	1.80 (2)
Pt(1)-P(2)	2.258 (3)	Co-C(20)	1.87 (1)
Pt(1)-P(3)	2.245 (3)	Co-C(30)	1.82 (1)
Pt(1)-C(30)	2.134 (14)	C(10)-O(10)	1.16 (2)
Pt(2)-Co	2.574 (2)	C(20)-O(20)	1.15 (1)
Pt(2)-P(2)	2.252 (4)	C(30)-O(30)	1.18 (1)
Pt(2)-P(4)	2.265 (3)	P-C(phenyl)(av)	1.83 (1)
Pt(2)-C(20)	2.101 (14)	C-C(phenyl)(av)	1.37 (2)
Bond Angles			
At the Pt Atoms			
Pt(2)-Pt(1)-Co	59.23 (4)	Pt(1)-Pt(2)-Co	57.98 (4)
Pt(2)-Pt(1)-P(2)	53.69 (9)	Pt(1)-Pt(2)-P(2)	53.90 (8)
Pt(2)-Pt(1)-P(3)	165.57 (1)	Pt(1)-Pt(2)-P(4)	162.98 (9)
Pt(2)-Pt(1)-C(30)	95.6 (4)	Pt(1)-Pt(2)-C(20)	98.4 (3)
Co-Pt(1)-P(2)	112.6 (1)	Co-Pt(2)-P(2)	111.54 (9)
Co-Pt(1)-P(3)	133.9 (1)	Co-Pt(2)-P(4)	138.3 (1)
Co-Pt(1)-C(30)	44.9 (4)	Co-Pt(2)-C(20)	45.9 (3)
P(2)-Pt(1)-P(3)	112.3 (1)	P(2)-Pt(2)-P(4)	109.2 (1)
P(2)-Pt(1)-C(30)	144.2 (4)	P(2)-Pt(2)-C(20)	149.0 (3)
P(3)-Pt(1)-C(30)	98.9 (4)	P(4)-Pt(2)-C(20)	98.4 (3)
At the Co Atom			
Pt(1)-Co-Pt(2)	62.79 (4)	Pt(2)-Co-P(1)	146.3 (1)
Pt(1)-Co-P(1)	148.5 (1)	Pt(2)-Co-C(10)	93.5 (4)
Pt(1)-Co-C(10)	85.2 (5)	Pt(2)-Co-C(20)	53.6 (4)
Pt(1)-Co-C(20)	109.6 (4)	Pt(2)-Co-C(30)	107.5 (4)
Pt(1)-Co-C(30)	55.7 (4)	C(10)-Co-C(20)	123.0 (6)
P(1)-Co-C(10)	100.1 (5)	C(10)-Co-C(30)	114.5 (7)
P(1)-Co-C(20)	93.5 (4)	C(20)-Co-C(30)	119.1 (6)
P(1)-Co-C(30)	94.7 (5)		
Within the Ligands			
Co-C(10)-O(10)	175 (1)	Co-C(30)-Pt(1)	79.4 (5)
Co-C(20)-O(20)	147 (1)	Pt(1)-C(30)-O(30)	134 (1)
Co-C(20)-Pt(2)	80.5 (5)	Pt(2)-C(20)-O(20)	132.4 (9)
Co-C(30)-O(30)	146 (1)		

ters[14] in which two $m(CO)_3Cp$ groups replace the PPh_2 and the $Co(CO)_3PPh_3$ fragments of 1. The resulting isolobal analogy[15] between these complexes is described in eq 1.



[Co] = $Co(CO)_3(PPh_3)$

[M] = $m(CO)_3Cp$ (m = Cr, Mo, W)

A general study of the planar, triangulated $Pd_2m_2Cp_2(CO)_6(PR_3)_2$ clusters[16] has also suggested to consider the $[m(CO)_3Cp]^-$ fragments as four-electron donor anions. 1 represents hence a further example where this concept can be applied, involving now a cobalt carbonyl fragment in a closo structure. Such a bonding mode for these otherwise two-electron donor anions[17] remains exceptional[18] but can now be anticipated to occur in other polymetallic systems.

The strengthening effect of the μ-PPh_2 ligand is evidenced both by the relatively short Pt–Pt distance and by the electrochemical behavior of 1.

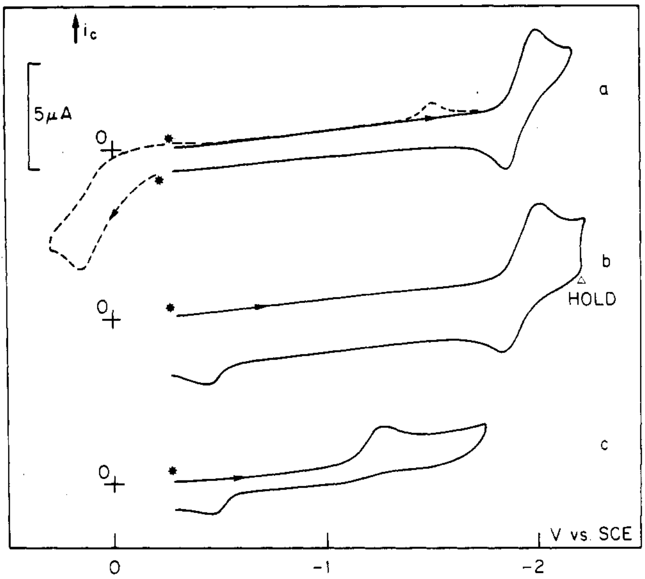


Figure 2. Cyclic voltammetry of 1 (curves a and b) compared with $Co_2(CO)_6(PPh_3)_2$ (curve c) (ca. 4 × 10^{-4} M in THF + 0.1 M $[(C_6H_{13})_4N]ClO_4$; Pt electrode (3.14 mm^2), potential scan rate 0.4 V s^{-1}). An asterisk denotes the start of the scan.

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[17] In its "classical" complexes, it is equally acceptable to treat the $Co(CO)_4$ group as neutral, one-electron donor or as negative, two-electron donor. By analogy, in this work, the $Co(CO)_3PPh_3$ group can be envisaged as neutral, three-electron donor or as negative, four-electron donor. Obviously, this is a formal electron-counting procedure that does not anticipate what is the actual charge distribution in the molecule.

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Table III. **Selected Least-Squares Planes for 1**

plane no.	atoms	dist from plane, Å	plane no.	atoms	dist from plane, Å
1	Pt(1)		4	Co	−0.001 (2)
	Pt(2)			P(1)	0.001 (5)
	Co			P(2)	0.001 (5)
	P(1)[a]	0.350 (5)		C(10)	0.043 (21)
	P(2)[a]	−0.232 (5)		O(10)	−0.017 (18)
	P(3)[a]	−0.224 (5)			
	P(4)[a]	−0.171 (5)			
2	Pt(1)	0.004 (1)	5	C(10)	
	Pt(2)	0.004 (1)		C(20)	
	Co	−0.036 (2)		C(30)	
	P(2)	−0.195 (5)		Co[a]	0.195 (2)
				O(10)[a]	−0.087 (18)
3	Pt(1)	0.009 (1)		O(20)[a]	0.493 (14)
	Pt(2)	0.007 (1)		O(30)[a]	0.533 (15)
	Co	−0.102 (2)			
	P(1)	0.142 (5)			
	P(2)	−0.133 (5)			
	P(3)	−0.187 (5)			
	P(4)	−0.134 (5)			

Dihedral Angles between the Planes

plane	angle, deg	plane	angle, deg
1-2	1.0	1-5	84.5
1-3	2.9	3-4	99.5
1-4	99.4		

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	−0.4050	0.0083	−0.9143	−6.8038
2	−0.4183	−0.0026	−0.9083	−6.9351
3	−0.4418	−0.0210	−0.8969	−7.1603
4	0.6159	−0.7812	−0.1017	3.4284
5	0.6902	0.5996	−0.4050	8.3676

[a] This atom was not used in defining the plane.

Electrochemical studies of 1 have been carried out under argon in THF solutions containing 0.1 M $[(C_6H_{13})_4N]ClO_4$ on a platinum electrode. Cluster 1 undergoes a well-defined one-electron reduction [$E_{1/2}$ = −2 V vs. saturated calomel electrode (SCE)]. The peak current ratio i_{pa}/i_{pc} from cyclic voltammetry experiments remains close to unity ($0.1 < \text{scan rate } v < 1$ V s^{-1}). The current function (proportional to $i_{pc}/v^{1/2}$) is also constant with scan rate. These results indicate that the reduction product is stable during the time of the sweep and that the reduction is electrochemically reversible (Figure 2a). When the potential sweep is interrupted at −2.3 V vs. SCE (Figure 2b), the ratio i_{pa}/i_{pc} decreases and a new anodic peak appears at −0.45 V on the reverse scan. This peak has been assigned to the oxidation of the anion $[Co(CO)_3(PPh_3)]^-$ on the basis of a separate experiment in which the bimetallic $Co_2(CO)_6(PPh_3)_2$ was studied under the same experimental conditions. The latter was reduced into $[Co(CO)_3(PPh_3)]^-$ at $E_{1/2}$ = −1.25 V vs SCE and on the reverse scan, oxidation of the anion occurred at $E_{1/2}$ = −0.45 V vs. SCE (Figure 2c), in agreement with literature data.[19]

Oxidation of 1 occurs at $E_{1/2}$ = 0 V vs. SCE in a first irreversible one-electron step (Figure 2a), associated in the reverse scan with a new cathodic peak at −1.5 V vs. SCE which corresponds to the reduction of an unidentified cluster fragment. Scheme I accounts for the observed results.

Noteworthy is the comparison of these results with those obtained[6] with two other triangulo platinum–cobalt clusters of different but related cores: $Co_2Pt(\mu\text{-}CO)(CO)_7(PPh_3)$ and $Co_2Pt(\mu\text{-}CO)(CO)_6(Ph_2PCH_2CH_2PPh_2)$. (i) Cluster 1 is easier to oxidize and more difficult to reduce than these "Co_2Pt" clusters: this seems related to the greater number of phosphorus donors in 1. (ii) The enhanced stability of $[1]^-$ vs. the $[\text{"}Co_2Pt\text{"}]^-$ anions appears to be a consequence of the stabilizing μ-PPh_2 bridge as evidenced in other systems.[20] This point is under further study.

Acknowledgment. We are grateful to Dr A. Mitschler for assistance in collecting the X-ray data.

Registry No. 1, 88015-40-1; 2, 56591-77-6; Pt, 7440-06-4; Co, 7440-48-4.

Supplementary Material Available: Figure 3, the molecular structure of 1 with the numbering scheme of all atoms, and tables of positional and thermal parameters and their estimated standard deviations, observed and calculated structure factor amplitudes, bond lengths and angles, and weighted least-squares planes (38 pages). Ordering information is given on any current masthead page.

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