1,3-dipolar M$^+$–O–O$^-$ (end-on) complexes in their activated form. They are believed to be involved in the reaction of metal dioxygen complexes with both nucleophilic and electrophilic substrates.[18] In Co and Fe porphyrin complexes the end-on dioxygen complexes are more stable than the side-on form.[19] Starting from **2a** or **2b**, two isomers of end-on dioxygen intermediates are possible, depending on which Rh–O bond is cleaved. On the basis of the structures of peroxycarbonato complexes **3a** and **3b**, we believe that the Rh–O bond trans to one of the Rh–S bonds opens and the Rh–O trans to the phosphine remains intact. This is in accord with the discussion based on MO calculations (vide supra) that phosphines can push filled metal d orbitals more effectively than the dithiocarbamate ligand can, enhancing back-donation from the metal to the ligand trans to phosphine.

We believe that the next step is attachment of the equatorial phosphine to the axial oxygen atom. The phosphine oxide thus formed will weakly coordinate to the metal and blocks the axial position,[20] forcing the carbonato ligand to chelate at the equatorial site trans to the dtc ligand. Successive displacement of the phosphine oxide by free PPh$_3$ will complete the formation of **5**. In agreement with this scheme, the peroxycarbonato complex with the dppe ligand, **3b**, was found to be much more stable than **3a**, since its solution did not show any change in 4 h, while isolation of pure **3a** was often difficult due to its spontaneous transformation to **5**. If the isomeric peroxycarbonato complex **3a′** was formed by the reaction of **2a** with CO$_2$, it should have given carbonato complex **6** directly. In reality, complex **6** was detected only when the kinetically formed carbonato complex **5** was isomerized by heating.

Supplementary Material Available: Listings of hydrogen atom parameters and temperature factors (2 pages); a table of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

---

(18) (a) Broadhurst, M. J.; Brown, J. M.; John, R. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 47. (b) Ugo, R.; Zanderighi, J. M.; Fusi, A.; Carreri, D. *J. Am. Chem. Soc.* **1980**, *102*, 3745 and references therein.

(19) (a) Rodley, G. A.; Robinson, W. T. *Nature* **1972**, *235*, 438. (b) Collman, J. P.; Halpert, T. R.; Suslick, K. S. *Metal Ion Activation of Dioxygen*; John Wiley & Sons: New York, 1980.

(20) A binuclear iron–μ-dioxygen complex with triphenylphosphine oxide ligands has recently been reported: Sawyer, D. T.; McDowell, M. S.; Spencer, L.; Tsang, K. S. *Inorg. Chem.* **1989**, *28*, 1166.

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Cluster Synthesis. 28. New Platinum–Cobalt Carbonyl Cluster Complexes and Products Obtained from Their Reactions with Alkynes

Richard D. Adams,* Gong Chen, Wengan Wu, and Jianguo Yin

Received March 27, 1990

The reaction of Pt(COD)$_2$, COD = 1,5-cyclooctadiene, with Co$_2$(CO)$_8$ in cyclohexane solvent at 25 °C has yielded the new compounds PtCo$_2$(CO)$_7$(COD) (**1**, 3%) and Pt$_2$Co$_2$(CO)$_8$(COD) (**2**, 31%) and the known compound Co$_4$(CO)$_{12}$ (**3**, 14%). Compounds **1** and **2** were characterized by single-crystal X-ray diffraction analyses. Compound **1** contains a triangular cluster of one platinum and two cobalt atoms with a carbonyl ligand bridging the Co–Co bond. Compound **2** consists of a tetrahedral cluster of two platinum atoms and two cobalt atoms. The Pt–Pt bond is weak, 2.9546 (6) Å. Compound **2** reacts with EtC$_2$Et to yield the new complex Pt$_2$Co$_2$(CO)$_8$(μ_3-EtC$_2$Et)$_2$ (**4**, 8%), and it reacts with PhC$_2$Ph to yield the new complex Pt$_3$Co$_2$(CO)$_6$(COD)$_2$(μ_3-PhC$_2$Ph)$_2$ (**5**, 22%). Compounds **4** and **5** were characterized crystallographically. Compound **4** contains a butterfly cluster of two cobalt and two platinum atoms. The two platinum atoms occupy the hinge positions and are joined by a short Pt–Pt bond, 2.4945 (7) Å. Triply bridging EtC$_2$Et ligands bridge the two Pt$_2$Co triangles. Compound **5** contains a bow-tie cluster of three platinum and two cobalt atoms with a platinum atom in the center. Triply bridging PhC$_2$Ph ligands bridge the two Pt$_2$Co triangular groupings. Crystallographic parameters for **1**: space group *Pbca*, a = 15.076 (3) Å, b = 16.298 (3) Å, c = 14.547 (5) Å, Z = 8, R = 0.033, and R_w = 0.033 for 2149 reflections. For **2**: space group $P2_1/n$, a = 8.835 (2) Å, b = 14.573 (2) Å, c = 15.377 (2) Å, β = 100.69 (1)°, Z = 4, R = 0.024, and R_w = 0.027 for 2140 reflections. For **4**: space group $P2_1/n$, a = 9.430 (2) Å, b = 14.915 (4) Å, c = 17.931 (3) Å, β = 99.11 (2)°, Z = 4, R = 0.022, and R_w = 0.023 for 2236 reflections. For **5**: space group $C2/c$, a = 34.905 (8) Å, b = 15.106 (4) Å, c = 19.028 (3) Å, β = 102.39 (2)°, Z = 8, R = 0.064, and R_w = 0.076 for 3760 reflections.

Introduction

Although platinum has many useful properties, its ability to promote a variety of chemical reactions catalytically is probably its most important.[1,2] Supported bimetallic clusters containing platinum are used commercially in the petroleum reforming process.[2] Because of this, there has been a great interest in the synthesis of heteronuclear cluster complexes containing platinum[3] and in their ability to produce catalysis.[4] Stone has shown that the "ligand-free" platinum complexes are excellent reagents for the preparation of heteronuclear cluster complexes containing platinum.[5]

To date, there are only a few examples of cluster complexes that contain both cobalt and platinum,[6-11] but some of these have

---

(1) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Kummer, J. T. *J. Phys. Chem.* **1986**, *90*, 4747. (c) Rylander, P. N. *Catalytic Hydrogenation Over Platinum Metals*; Academic Press: New York, 1967. (d) Zimmer, H.; Dobrovolszky, M.; Tétényi, P.; Paál, Z. *J. Phys. Chem.* **1986**, *90*, 4758 and references therein.

(2) (a) Sinfelt, J. H. *Bimetallic Catalysts*; Wiley: New York, 1983. (b) Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15.

(3) (a) Farrugia, L. J. *Adv. Organomet. Chem.*, in press. (b) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, England, 1982; Chapter 40.

(4) Braunstein, P.; Rose, J. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1989; Vol. 3, pp 3–138.

(5) (a) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318. (b) Stone, F. G. A. *Inorg. Chim. Acta* **1981**, *50*, 33.

(6) Braunstein, P.; Dehand, J.; Nennig, J. F. *J. Organomet. Chem.* **1975**, *92*, 117.

(7) Bender, R.; Braunstein, P. *Nouv. J. Chim.* **1981**, *5*, 81.

(8) Barbier, J. P.; Braunstein, P.; Fischer, J.; Ricard, L. *Inorg. Chim. Acta* **1978**, *31*, L361.

(9) Bender, R.; Braunstein, P.; Metz, B.; Lemoine, P. *Organometallics* **1984**, *3*, 381.

(10) (a) Braunstein, P.; de Meric de Bellefon, C.; Reis, M. *Inorg. Chem.* **1988**, *27*, 1338. (b) Braunstein, P.; Dehand, J. *Bull. Soc. Chim. Fr.* **1975**, 1997.

0020-1669/90/1329-4208$02.50/0 © 1990 American Chemical Society

Table I. Crystal Data for the Structures of **1**, **2**, **4**, and **5**

	1	**2**	**4**	**5**
formula	$PtCo_2O_7C_{15}H_{12}$	$Pt_2Co_2O_8C_{16}H_{12}$	$Pt_2Co_2O_8C_{20}H_{20}$	$Pt_3Co_2O_6C_{50}H_{44}$
fw	617.21	840.31	896.42	1444.03
a, Å	15.076 (3)	8.835 (2)	9.430 (2)	34.905 (8)
b, Å	16.298 (3)	14.573 (2)	14.915 (4)	15.106 (4)
c, Å	14.547 (5)	15.377 (2)	17.931 (3)	19.028 (3)
β, deg		100.69 (1)	99.11 (2)	102.39 (2)
V, Å^3	3575 (2)	1945.4 (6)	2490 (1)	9799 (4)
space group	*Pbca* (No. 61)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
Z value	8	4	4	8
ρ_{calc}, g/cm^3	2.29	2.87	2.39	1.96
$\mu_{Mo\ K\alpha}$, cm^{-1}	97.55	162.03	126.66	93.32
T, °C	23	23	23	23
R, $R_w(F_o)$	0.033, 0.033	0.024, 0.027	0.022, 0.023	0.064, 0.076

been reported to exhibit significant catalytic activity toward the hydrogenation of terminal alkynes.[12] In recent studies, we discovered the facile formation of new heteronuclear cluster complexes containing platinum from the reactions of $Pt(COD)_2$, COD = 1,5-cyclooctadiene, with $Fe(CO)_5$[13] and $Ru(CO)_5$.[14] We have now investigated the reaction of $Pt(COD)_2$ with $Co_2(CO)_8$ and have obtained the new cobalt–platinum complexes $PtCo_2(CO)_7(COD)$ (**1**) and $Pt_2Co_2(CO)_8(COD)$ (**2**). Compound **2** was found to react with EtC≡CEt and PhC≡CPh to yield the new complexes $Pt_2Co_2(CO)_8(\mu_3\text{-EtC≡CEt})_2$ (**4**) and $Pt_3Co_2(CO)_6(COD)_2(\mu_3\text{-PhC≡CPh})_2$ (**5**), respectively. The results of this study are reported here.

Experimental Section

General Procedures. All reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were dried over molecular sieves and were deoxygenated by purging with nitrogen prior to use. $Co_2(CO)_8$ was purchased from Strem Chemicals. $Pt(COD)_2$ was prepared by the reported procedure.[15] TLC separations were performed in air on plates (0.25-mm silica gel 60 F_{245}). IR spectra were recorded on a Nicolet 5-DXB FT-IR spectrometer. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer. Elemental analyses were performed by Desert Analytics, Tuscon, AZ.

Reaction of $Co_2(CO)_8$ with $Pt(COD)_2$. A 60-mg (0.17-mmol) amount of $Co_2(CO)_8$ and 41 mg (0.10 mmol) of $Pt(COD)_2$ were dissolved in 30 mL of cyclohexane, and the mixture was stirred at 25 °C for 7 h. The solution turned to a dark brown. The solvent was removed under vacuum. The residue was then dissolved in a minimum amount of CH_2Cl_2, and the components were separated by TLC with a CH_2Cl_2/hexane (1:4) solvent mixture. This yielded in order of elution 4.5 mg of dark brown $Co_4(CO)_{12}$[16] (**3**, 14%), 13.1 mg of dark red $Pt_2Co_2(CO)_8(COD)$ (**2**, 31%), and 1.8 mg of red brown $PtCo_2(CO)_7(COD)$ (**1**, 3%). IR (ν(CO) in hexane; cm^{-1}): **1**, 2073 s, 2042 vs, 2037 vs, 2013 m, 2006 m, 1885 vw, 1854 m, 1828 w; **2**, 2071 s, 2031 vs, 2009 m, 1993 s, 1795 m. ^1H NMR (δ in $CDCl_3$ at 25 °C): **1**, 5.30 (t, 2 H, J_{Pt-H} = 33.0 Hz), 4.81 (t, 2 H, J_{Pt-H} = 33.0 Hz), 1.6–2.2 (m, 8 H); **2**, 5.42 (t, 4 H, J_{Pt-H} = 36.4 Hz), 2.22 (m, 4 H), 2.03 (m, 4 H). Anal. Calcd (found) for **2**: C, 22.87 (22.60); H, 1.44 (1.24).

Reaction of 1 with $Pt(COD)_2$. A 12.0-mg (0.03-mmol) amount of $Pt(COD)_2$ was added to a solution of 12.0 mg (0.02 mmol) of **1** in 10 mL of hexane at 25 °C. The mixture was then stirred for 40 min. The solvent was evaporated under vacuum, and the residue was chromatographed as described above to give 4.1 mg of $Pt_2Co_2(CO)_8(COD)$ (**2**, 24%).

Reaction of 2 with EtC≡CEt. Preparation of $Pt_2Co_2(CO)_8(\mu_3\text{-}EtC_2Et)_2$ (4). A 14-mg (0.017-mmol) amount of **2** was dissolved in 15 mL of hexane, 10 μL of EtC_2Et was added, and the solution was gently refluxed for 0.5 h. The solvent was evaporated in vacuo, and the residue was chromatographed by TLC with a hexane/CH_2Cl_2 (3:1) solvent mixture. This yielded 1.2 mg of blue $Pt_2Co_2(CO)_8(\mu_3\text{-}EtC_2Et)_2$ (**4**, 8%). IR (ν(CO) in hexane; cm^{-1}) for **4**: 2072 w, 2037 s, 2029 s, 1987 w, 1983 vw, sh. ^1H NMR (δ in $CDCl_3$): 2.93 (m, 4 H, J_{H-H} = 15 Hz), 2.65 (m, 4 H, J_{H-H} = 15 Hz), 1.12 (t, 12 H). Anal. Calcd (Found): C, 26.80 (27.80); H, 2.25 (2.16).

Reaction of 2 with PhC≡CPh. Preparation of $Pt_3Co_2(CO)_6(COD)_2(\mu_3\text{-}PhC_2Ph)_2$ (5). A 15.0-mg (0.018-mmol) amount of **2** and 7.5 mg (0.042 mmol) of diphenylacetylene were dissolved in 20 mL of toluene. The solution was heated to reflux for 15 min. After cooling, the solvent was evaporated under vacuum, and the residue was chromatographed by TLC with a hexane/CH_2Cl_2 (4:1) solvent mixture. This yielded 1.5 mg of brown $Co_2(CO)_6(PhC_2Ph)$[17] and 4.0 mg of brown $Pt_3Co_2(CO)_6(COD)_2(PhC_2Ph)_2$ (**5**, 22%). IR (ν(CO) in hexane; cm^{-1}) for **5**: 2015 m, sh, 2011 m, sh, 2004 s, 1957 m. ^1H NMR (δ in $CDCl_3$): 6.9–7.5 (m, 20 H), 5.54 (br, 2 H), 5.28 (br, 2 H), 4.11 (br, 2 H), 3.86 (br, 2 H), 1.4–2.4 (m, 16 H). Anal. Calcd (found): C, 41.59 (42.27); H 3.07 (2.97).

Crystallographic Analyses

Crystals of **1**, **2**, and **4** were grown in hexane/CH_2Cl_2 solutions by cooling to −20 °C. Crystals of **3** were grown from a solution in a CH_2Cl_2/hexane solvent mixture by slow evaporation of solvent at 20 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the diffractometer automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were obtained from the standard sources.[18a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[18b] Full-matrix least-squares refinements minimized the function $\sum_{hkl}\omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02F_o^2)^2]^{1/2}/Lp$.

Compound **1** crystallized in the orthorhombic crystal system. The space group *Pbca* was identified uniquely on the basis of the systematic absences in the diffraction data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated, and their scattering contributions were added to the structure factor calculations, but they were not refined.

Compounds **2** and **4** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established for both structures on the basis of the systematic absences observed in the data. The positions of the metal atoms for both structures were determined by direct methods (MITHRIL). All other atom positions were obtained from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. For **2** the hydrogen atom positions were calculated and were included in the structure factor calculations, but they were not refined. For **4** the hydrogen atom positions were located in a difference Fourier synthesis. For this structure the positions of the hydrogen atoms were successfully refined, while their thermal parameters were held constant.

---

(11) Jeffrey, J. C.; Parrott, M. J.; Stone, F. G. A. *J. Organomet. Chem.* **1990**, *382*, 225.

(12) Fusi, A.; Ugo, R.; Psaro, R.; Braunstein, P.; Dehand, J. *Phil. Trans. R. Soc. London A* **1982**, *308*, 125.

(13) Adams, R. D.; Chen, G.; Wang, J. G. *Polyhedron* **1989**, *8*, 2521.

(14) Adams, R. D.; Chen, G.; Wang, J. G.; Wu, W. *Organometallics* **1990**, *9*, 1339.

(15) (a) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271. (b) Spencer, J. L. *Inorg. Synth.* **1979**, *19*, 213.

(16) (a) Carré, F. H.; Cotton, F. A.; Frenz, B. A. *Inorg. Chem.* **1976**, *15*, 380. (b) Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384.

(17) Sternberg, H. W.; Greenfield, H.; Friedel, R. A.; Wotiz, J.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1954**, *76*, 1457.

(18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

Table II. Positional Parameters and *B*(eq) for $PtCo_2(CO)_7(C_8H_{12})$ (**1**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt	0.84979 (02)	0.139401 (18)	0.10949 (02)	3.32 (2)
Co(1)	0.68689 (08)	0.11441 (07)	0.08553 (09)	3.81 (6)
Co(2)	0.76843 (08)	0.03935 (06)	0.21055 (09)	3.77 (6)
O(11)	0.6945 (06)	0.1440 (05)	-0.1109 (06)	7.3 (5)
O(12)	0.7602 (05)	-0.0444 (04)	0.0335 (06)	7.1 (4)
O(13)	0.5051 (05)	0.0513 (05)	0.1025 (07)	8.7 (6)
O(14)	0.6790 (05)	0.2744 (04)	0.1782 (06)	8.0 (5)
O(21)	0.6310 (05)	-0.0595 (05)	0.2971 (07)	8.3 (5)
O(22)	0.7777 (07)	0.1730 (05)	0.3467 (06)	8.7 (6)
O(23)	0.9243 (05)	-0.0630 (04)	0.2359 (06)	6.9 (5)
C(1)	0.9936 (10)	0.1724 (10)	-0.0328 (11)	9 (1)
C(2)	0.9014 (08)	0.1983 (07)	-0.0166 (08)	5.7 (6)
C(3)	0.8793 (07)	0.2593 (07)	0.0427 (09)	6.0 (6)
C(4)	0.9403 (11)	0.3050 (07)	0.1037 (10)	9.3 (9)
C(5)	0.9795 (09)	0.2652 (07)	0.1809 (11)	8.6 (9)
C(6)	0.9656 (07)	0.2652 (07)	0.1891 (09)	6.3 (6)
C(7)	0.9926 (06)	0.1181 (06)	0.1298 (10)	5.9 (6)
C(8)	1.0421 (09)	0.1358 (09)	0.0408 (14)	10 (1)
C(11)	0.6925 (06)	0.1328 (06)	-0.0336 (08)	4.9 (5)
C(12)	0.7487 (06)	0.0102 (06)	0.0852 (07)	4.8 (5)
C(13)	0.5751 (07)	0.0761 (07)	0.0964 (07)	5.6 (6)
C(14)	0.6832 (07)	0.2122 (06)	0.1442 (08)	5.3 (5)
C(21)	0.6845 (07)	-0.0215 (06)	0.2628 (08)	5.5 (6)
C(22)	0.7730 (07)	0.1229 (06)	0.2936 (08)	5.5 (6)
C(23)	0.8634 (07)	-0.0238 (05)	0.2269 (07)	4.8 (5)

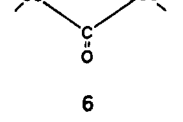
Table III. Intramolecular Distances (Å) for **1**

Pt-C(6)	2.18 (1)	Co(2)-C(23)	1.78 (1)
Pt-C(7)	2.20 (1)	Co(2)-C(22)	1.82 (1)
Pt-C(2)	2.21 (1)	Co(2)-C(12)	1.91 (1)
Pt-C(3)	2.23 (1)	C(1)-C(8)	1.43 (2)
Pt-Co(1)	2.514 (1)	C(1)-C(2)	1.47 (2)
Pt-Co(2)	2.515 (1)	C(2)-C(3)	1.36 (2)
Co(1)-C(11)	1.76 (1)	C(3)-C(4)	1.48 (2)
Co(1)-C(13)	1.80 (1)	C(4)-C(5)	1.42 (2)
Co(1)-C(14)	1.81 (1)	C(5)-C(6)	1.47 (1)
Co(1)-C(12)	1.94 (1)	C(6)-C(7)	1.34 (2)
Co(1)-Co(2)	2.513 (2)	C(7)-C(8)	1.52 (2)
Co(2)-C(21)	1.78 (1)	O-C(av)	1.14 (1)

Compound **5** crystallized in the monoclinic crystal system. The systematic absences in the data were consistent with either of the space groups *C*2/*c* or *Cc*. The centrosymmetrical space *C*2/*c* was assumed with $Z = 8$, having one independent molecular unit in the asymmetric crystal unit. This selection was supported by the successful solution and refinement of the structure and by our inability to obtain a better quality structure in the lower symmetry space group. The structure was solved by direct methods (MITHRIL). The hydrogen atom positions on the phenyl rings were calculated and their scattering was added to the structure factor calculations, but their positions were not refined.

Results

From the reaction of $Pt(COD)_2$ with $Co_2(CO)_8$ two new platinum-cobalt carbonyl cluster complexes $PtCo_2(CO)_7(COD)$ (**1**, 3%) and $Pt_2Co_2(CO)_8(COD)$ (**2**, 31%) and the known compound $Co_4(CO)_{12}$[16] (**3**, 14%) were obtained. Compound **2** was obtained independently in 24% yield from a reaction of **1** with $Pt(COD)_2$. This latter reaction may account in part for the low yield of **1** in the original reaction. Compounds **1** and **2** have been characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **1** is shown in Figure 1. Final positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The molecule consists of a triangular cluster containing two cobalt and one platinum atom and is very similar to the related compound $PtCo_2(CO)_8(PPh_3)$ (**6**) that was obtained by Bender et al. from the reaction of $Pt_5(CO)_6(PPh_3)_4$ with $Co_2(CO)_8$.[7] The metal-metal bond distances in **1**, Co–Co = 2.513 (2) Å, Co(1)–Pt = 2.514 (1) Å, and Co(2)–Pt = 2.515 (1) Å, are very similar to those in **6**. However, it does seem to be a little surprising that the Co–Pt bond distances in these compounds are not significantly longer than the Co–Co bond distance. The Co–Co bond distance in $Co_2(CO)_8$ is 2.52 Å.[19] The platinum atom in **1** contains a COD ligand that exhibits no unusual structural features. There is a bridging CO ligand across the Co–Co bond. The formation of **1** can be viewed as the replacement of one of the bridging CO ligands in $Co_2(CO)_8$ with a bridging Pt(COD) group, although the mechanism of this process has not been established.



6

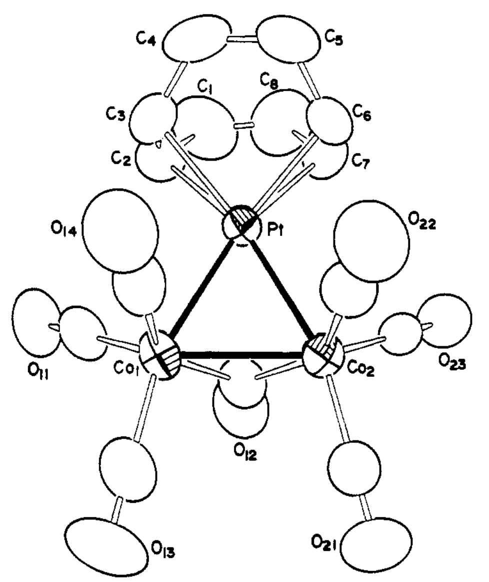


Figure 1. ORTEP drawing of $PtCo_2(CO)_7(COD)$ (**1**), showing 50% probability thermal ellipsoids.

Table IV. Intramolecular Bond Angles (deg) for **1**

C(6)-Pt-Co(1)	154.3 (4)	C(12)-Co(1)-Co(2)	48.7 (3)
C(6)-Pt-Co(2)	104.9 (3)	C(12)-Co(1)-Pt	70.9 (3)
C(7)-Pt-Co(1)	161.6 (3)	Co(2)-Co(1)-Pt	60.04 (4)
C(7)-Pt-Co(2)	107.2 (3)	C(21)-Co(2)-Co(1)	103.5 (3)
C(2)-Pt-Co(1)	107.4 (3)	C(21)-Co(2)-Pt	163.4 (3)
C(2)-Pt-Co(2)	159.7 (3)	C(23)-Co(2)-Co(1)	140.5 (4)
C(3)-Pt-Co(1)	106.1 (3)	C(23)-Co(2)-Pt	93.5 (3)
C(3)-Pt-Co(2)	157.1 (3)	C(22)-Co(2)-Co(1)	97.7 (3)
Co(1)-Pt-Co(2)	59.96 (4)	C(22)-Co(2)-Pt	83.4 (3)
C(11)-Co(1)-Co(2)	140.5 (3)	C(12)-Co(2)-Co(1)	49.7 (3)
C(11)-Co(1)-Pt	93.6 (3)	C(12)-Co(2)-Pt	71.3 (3)
C(13)-Co(1)-Co(2)	103.0 (4)	Co(1)-Co(2)-Pt	60.00 (4)
C(13)-Co(1)-Pt	163.1 (4)	O(12)-C(12)-Co(2)	140.8 (8)
C(14)-Co(1)-Co(2)	95.9 (3)	O(12)-C(12)-Co(1)	137.3 (9)
C(14)-Co(1)-Pt	79.8 (3)	O-C(av)-Co	178 (1)

An ORTEP drawing of the molecular structure of **2** is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. The molecule consists of a cluster of two platinum and two cobalt atoms in the form of a closed tetrahedron. The Pt–Pt distance is fairly long, 2.9546 (6) Å, indicating that there is only a weak bonding interaction between these atoms. The four Pt–Co distances are similar to those in **1**, but it is a little surprising that the Pt–Co bonds that contain bridging carbonyl ligands, Pt(2)–Co(1) = 2.551 (1) Å and Pt(2)–Co(2) = 2.556 (1) Å, are slightly longer than the Pt–Co bond distances that do not contain bridging carbonyl ligands, Pt(1)–Co(1) = 2.514 (1) Å and Pt(1)–Co(2) = 2.538 (1) Å. The Co(1)–Co(2) distance of 2.530

---

[19] Sumner, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

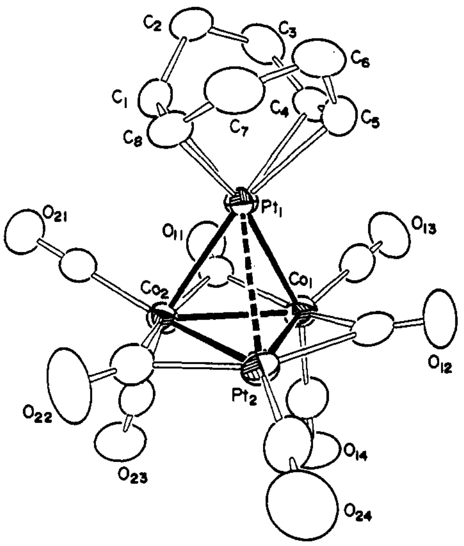
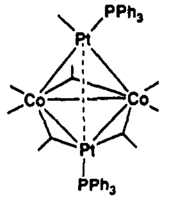


Figure 2. ORTEP drawing of $Pt_2Co_2(CO)_8(COD)_2$ (**2**), showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and B(eq) for $Pt_2Co_2(CO)_8(C_8H_{12})$ (**2**)

atom	x	y	z	B(eq), Å^2
Pt(1)	0.23774 (04)	0.30762 (02)	0.37391 (02)	2.32 (2)
Pt(2)	0.16916 (04)	0.31508 (02)	0.55467 (02)	2.62 (2)
Co(1)	0.23097 (14)	0.17131 (08)	0.47332 (08)	2.57 (5)
Co(2)	−0.01452 (13)	0.25908 (08)	0.41654 (07)	2.40 (5)
O(11)	0.0626 (08)	0.1185 (05)	0.2967 (05)	4.5 (3)
O(12)	0.4986 (08)	0.2437 (05)	0.5980 (05)	5.0 (4)
O(13)	0.4515 (08)	0.0533 (05)	0.4086 (05)	5.3 (4)
O(14)	0.1105 (10)	0.0404 (06)	0.5901 (05)	5.9 (4)
O(21)	−0.1981 (08)	0.3414 (06)	0.2593 (05)	5.4 (4)
O(22)	−0.1250 (09)	0.4233 (06)	0.4961 (06)	6.5 (4)
O(23)	−0.2536 (10)	0.1460 (06)	0.4723 (05)	6.0 (4)
O(24)	0.2042 (10)	0.4211 (07)	0.7246 (06)	7.2 (5)
C(1)	0.1821 (10)	0.4042 (06)	0.2572 (06)	2.8 (4)
C(2)	0.2922 (11)	0.3899 (07)	0.1946 (06)	3.2 (4)
C(3)	0.3920 (11)	0.3023 (08)	0.2141 (07)	4.1 (5)
C(4)	0.4377 (11)	0.2817 (07)	0.3092 (07)	3.6 (5)
C(5)	0.4848 (11)	0.3444 (08)	0.3761 (07)	4.0 (5)
C(6)	0.5020 (12)	0.4451 (08)	0.3641 (06)	4.2 (5)
C(7)	0.3580 (13)	0.5007 (07)	0.3721 (06)	4.0 (5)
C(8)	0.2120 (11)	0.4543 (06)	0.3349 (06)	3.2 (4)
C(11)	0.0827 (11)	0.1624 (07)	0.3601 (06)	3.1 (4)
C(12)	0.3717 (12)	0.2401 (06)	0.5633 (06)	3.3 (4)
C(13)	0.3681 (12)	0.1011 (07)	0.4351 (06)	3.4 (4)
C(14)	0.1556 (13)	0.0914 (07)	0.5444 (07)	4.3 (5)
C(21)	−0.1263 (11)	0.3094 (07)	0.3205 (06)	3.1 (4)
C(22)	−0.0373 (11)	0.3655 (07)	0.4902 (06)	3.4 (4)
C(23)	−0.1599 (12)	0.1897 (07)	0.4533 (06)	3.6 (5)
C(24)	0.1987 (12)	0.3827 (07)	0.6597 (07)	4.0 (5)

(2) Å is similar to that in **1** and **5**. Compound **2** is structurally very similar to the compound $Pt_2Co_2(CO)_8(PPh_3)_2$ (**7**) that was



7

prepared by Braunstein.[6] There is a COD ligand coordinated to Pt(1) and three symmetrical bridging carbonyl ligands across each metal–metal bond of the Co(1), Co(2), Pt(2) trimetal grouping. The latter feature is similar to that found in **3**.[16]

The only characterizable product that was formed in the reaction of **2** with 3-hexyne is $Pt_2Co_2(CO)_8(\mu_3\text{-EtC}{\equiv}\text{CEt})_2$ (**4**, 8%). The compound was characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **4** is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected inter-

Table VI. Intramolecular Distances (Å) for **2**

Pt(1)–C(4)	2.214 (9)	Co(1)–C(11)	1.98 (1)
Pt(1)–C(8)	2.220 (9)	Co(1)–Co(2)	2.530 (2)
Pt(1)–C(5)	2.24 (1)	Co(2)–C(21)	1.78 (1)
Pt(1)–C(1)	2.262 (9)	Co(2)–C(23)	1.81 (1)
Pt(1)–Co(1)	2.514 (1)	Co(2)–C(11)	1.94 (1)
Pt(1)–Co(2)	2.538 (1)	Co(2)–C(22)	1.95 (1)
Pt(1)–Pt(2)	2.9546 (6)	C(1)–C(8)	1.38 (1)
Pt(2)–C(24)	1.87 (1)	C(1)–C(2)	1.50 (1)
Pt(2)–C(22)	2.04 (1)	C(2)–C(3)	1.55 (1)
Pt(2)–C(12)	2.08 (1)	C(3)–C(4)	1.47 (1)
Pt(2)–Co(1)	2.551 (1)	C(4)–C(5)	1.38 (1)
Pt(2)–Co(2)	2.556 (1)	C(5)–C(6)	1.49 (1)
Co(1)–C(13)	1.77 (1)	C(6)–C(7)	1.53 (0)
Co(1)–C(14)	1.81 (1)	C(7)–C(8)	1.47 (1)
Co(1)–C(12)	1.96 (1)	O–C(av)	1.15 (1)

Table VII. Intramolecular Bond Angles (deg) for **2**

C(4)–Pt(1)–Co(1)	104.4 (2)	C(11)–Co(1)–Co(2)	49.0 (3)
C(4)–Pt(1)–Co(2)	151.7 (3)	C(11)–Co(1)–Pt(2)	108.6 (3)
C(4)–Pt(1)–Pt(2)	138.5 (3)	Pt(1)–Co(1)–Co(2)	60.41 (4)
C(8)–Pt(1)–Co(1)	155.8 (2)	Pt(1)–Co(1)–Pt(2)	71.37 (3)
C(8)–Pt(1)–Co(2)	106.7 (2)	Co(2)–Co(1)–Pt(2)	60.41 (4)
C(8)–Pt(1)–Pt(2)	101.0 (2)	C(21)–Co(2)–Co(1)	143.6 (3)
C(5)–Pt(1)–Co(1)	108.2 (3)	C(21)–Co(2)–Pt(1)	92.9 (3)
C(5)–Pt(1)–Co(2)	164.2 (3)	C(21)–Co(2)–Pt(2)	136.8 (3)
C(5)–Pt(1)–Pt(2)	110.2 (3)	C(23)–Co(2)–Co(1)	102.9 (3)
C(1)–Pt(1)–Co(1)	161.4 (2)	C(23)–Co(2)–Pt(1)	161.2 (3)
C(1)–Pt(1)–Co(2)	107.8 (2)	C(23)–Co(2)–Pt(2)	107.3 (3)
C(1)–Pt(1)–Pt(2)	132.2 (2)	C(11)–Co(2)–Co(1)	50.5 (3)
Co(1)–Pt(1)–Co(2)	60.10 (4)	C(11)–Co(2)–Pt(1)	66.6 (3)
Co(1)–Pt(1)–Pt(2)	54.89 (3)	C(11)–Co(2)–Pt(2)	109.8 (3)
Co(2)–Pt(1)–Pt(2)	54.84 (3)	C(22)–Co(2)–Co(1)	112.0 (3)
C(24)–Pt(2)–Co(1)	148.1 (3)	C(22)–Co(2)–Pt(1)	96.8 (3)
C(24)–Pt(2)–Co(2)	148.4 (3)	C(22)–Co(2)–Pt(2)	51.8 (2)
C(24)–Pt(2)–Pt(1)	144.3 (3)	Co(1)–Co(2)–Pt(1)	59.49 (4)
C(22)–Pt(2)–Co(1)	108.1 (3)	Co(1)–Co(2)–Pt(2)	60.20 (4)
C(22)–Pt(2)–Co(2)	48.7 (3)	Pt(1)–Co(2)–Pt(2)	70.91 (3)
C(22)–Pt(2)–Pt(1)	83.0 (3)	C(8)–C(1)–C(2)	125.7 (8)
C(12)–Pt(2)–Co(1)	48.7 (3)	C(1)–C(2)–C(3)	113.7 (8)
C(12)–Pt(2)–Co(2)	107.0 (3)	C(4)–C(3)–C(2)	113.6 (8)
C(12)–Pt(2)–Pt(1)	73.5 (3)	C(5)–C(4)–C(3)	126 (1)
Co(1)–Pt(2)–Co(2)	59.39 (4)	C(5)–C(4)–Pt(1)	73.0 (6)
Co(1)–Pt(2)–Co(2)	59.39 (4)	C(4)–C(5)–C(6)	125.6 (9)
Co(1)–Pt(2)–Pt(1)	53.74 (3)	C(5)–C(6)–C(7)	113.9 (8)
Co(2)–Pt(2)–Pt(1)	54.25 (3)	C(8)–C(7)–C(6)	113.9 (8)
C(13)–Co(1)–Pt(1)	99.2 (3)	C(1)–C(8)–C(7)	126.2 (8)
C(13)–Co(1)–Co(2)	140.8 (3)	O(11)–C(11)–Co(2)	140.5 (8)
C(13)–Co(1)–Pt(2)	149.4 (3)	O(11)–C(11)–Co(1)	139.0 (8)
C(14)–Co(1)–Pt(1)	158.5 (3)	O(12)–C(12)–Co(1)	142.0 (8)
C(14)–Co(1)–Co(2)	98.4 (3)	O(12)–C(12)–Pt(2)	139.4 (8)
C(14)–Co(1)–Pt(2)	95.5 (3)	O(22)–C(12)–Pt(2)	139.4 (8)
C(12)–Co(1)–Pt(1)	86.6 (3)	O(22)–C(22)–Co(2)	139.8 (8)
C(12)–Co(1)–Co(2)	112.1 (3)	O(22)–C(22)–Pt(2)	140.6 (8)
C(12)–Co(1)–Pt(2)	53.0 (3)	Co(2)–C(22)–Pt(2)	79.5 (4)
C(11)–Co(1)–Pt(1)	66.7 (3)	O–C(av)–M	178.0 (3)

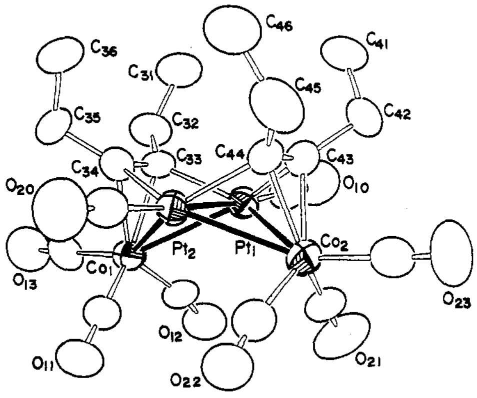


Figure 3. ORTEP drawing of $Pt_2Co_2(CO)_6(\mu_3\text{-PhC}_2\text{Ph})_2$ (**4**).

Table VIII. Positional Parameters and *B*(eq) for $Pt_2Co_2(CO)_8(EtC_2Et)_2$ (**4**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.73885 (04)	0.28919 (03)	0.370929 (19)	3.48 (2)
Pt(2)	0.50524 (04)	0.21112 (03)	0.330946 (19)	3.31 (2)
Co(1)	0.64125 (14)	0.27786 (09)	0.22274 (07)	3.85 (6)
Co(2)	0.70383 (15)	0.12454 (09)	0.42673 (07)	4.23 (6)
O(10)	1.0061 (09)	0.3998 (07)	0.4307 (06)	8.7 (5)
O(11)	0.5361 (09)	0.1037 (06)	0.1616 (04)	6.6 (4)
O(12)	0.9510 (08)	0.2570 (06)	0.2276 (05)	7.1 (5)
O(13)	0.5869 (10)	0.3862 (06)	0.0856 (04)	7.9 (5)
O(20)	0.2129 (08)	0.1226 (06)	0.2815 (05)	7.3 (5)
O(21)	0.9997 (10)	0.1192 (07)	0.3942 (06)	9.2 (6)
O(22)	0.5702 (10)	−0.0213 (06)	0.3308 (05)	7.6 (5)
O(23)	0.7437 (11)	0.0245 (06)	0.5683 (05)	8.8 (5)
C(10)	0.9091 (12)	0.3579 (09)	0.4063 (06)	5.6 (6)
C(11)	0.5715 (11)	0.1700 (08)	0.1907 (06)	4.8 (5)
C(12)	0.8310 (12)	0.2659 (07)	0.2320 (06)	4.9 (5)
C(13)	0.6062 (11)	0.3419 (08)	0.1387 (06)	5.2 (6)
C(20)	0.3193 (11)	0.1547 (07)	0.3015 (06)	4.2 (5)
C(21)	0.8852 (14)	0.1272 (08)	0.4048 (06)	5.9 (6)
C(22)	0.6175 (13)	0.0389 (09)	0.3646 (06)	5.4 (6)
C(23)	0.7342 (13)	0.0631 (07)	0.5134 (06)	5.5 (6)
C(31)	0.6234 (15)	0.5282 (09)	0.3601 (08)	5.8 (7)
C(32)	0.6442 (13)	0.4743 (07)	0.2926 (06)	4.9 (5)
C(33)	0.6142 (10)	0.3764 (07)	0.2990 (05)	3.8 (4)
C(34)	0.4855 (10)	0.3347 (07)	0.2769 (05)	3.9 (5)
C(35)	0.3433 (12)	0.3738 (09)	0.2424 (06)	4.9 (5)
C(36)	0.2498 (15)	0.4009 (10)	0.2993 (08)	6.4 (7)
C(41)	0.6984 (17)	0.3821 (11)	0.5579 (08)	7.2 (8)
C(42)	0.7346 (14)	0.2833 (09)	0.5462 (05)	5.8 (6)
C(43)	0.6700 (11)	0.2482 (07)	0.4688 (05)	4.2 (5)
C(44)	0.5396 (10)	0.2076 (07)	0.4476 (05)	4.0 (4)
C(45)	0.4217 (16)	0.1882 (09)	0.4935 (07)	6.4 (7)
C(46)	0.3153 (15)	0.2650 (10)	0.4907 (08)	6.7 (8)

Table IX. Intramolecular Distances (Å) for **4**

Pt(1)–C(10)	1.93 (1)	Co(1)–C(11)	1.80 (1)
Pt(1)–C(43)	2.06 (1)	Co(1)–C(33)	2.05 (1)
Pt(1)–C(33)	2.06 (1)	Co(1)–C(34)	2.07 (1)
Pt(1)–Pt(2)	2.4945 (7)	Co(2)–C(23)	1.79 (1)
Pt(1)–Co(1)	2.676 (1)	Co(2)–C(22)	1.80 (1)
Pt(1)–Co(2)	2.692 (2)	Co(2)–C(21)	1.82 (1)
Pt(2)–C(20)	1.94 (1)	Co(2)–C(43)	2.04 (1)
Pt(2)–C(44)	2.066 (9)	Co(2)–C(44)	2.06 (1)
Pt(2)–C(34)	2.08 (1)	C(33)–C(34)	1.37 (1)
Pt(2)–Co(2)	2.666 (1)	C(43)–C(44)	1.37 (1)
Pt(2)–Co(1)	2.681 (1)	O–C(av)	1.14 (1)
Co(1)–C(13)	1.77 (1)	C–C(av)	1.51 (2)
Co(1)–C(12)	1.78 (1)		

Table X. Intramolecular Boond Angles (deg) for **4**

C(10)–Pt(1)–Pt(2)	174.5 (3)	C(13)–Co(1)–Pt(1)	143.1 (4)
C(10)–Pt(1)–Co(1)	119.9 (3)	C(13)–Co(1)–Pt(2)	140.4 (3)
C(10)–Pt(1)–Co(2)	120.5 (4)	C(12)–Co(1)–Pt(1)	74.4 (3)
C(43)–Pt(1)–C(33)	119.7 (4)	C(12)–Co(1)–Pt(2)	119.0 (3)
C(43)–Pt(1)–Pt(2)	73.9 (3)	C(11)–Co(1)–Pt(1)	115.1 (3)
C(43)–Pt(1)–Co(1)	136.3 (3)	C(11)–Co(1)–Pt(2)	72.9 (4)
C(43)–Pt(1)–Co(2)	48.5 (3)	C(33)–Co(1)–Pt(1)	49.6 (3)
C(33)–Pt(1)–Pt(2)	74.0 (3)	C(33)–Co(1)–Pt(2)	70.1 (3)
C(33)–Pt(1)–Co(1)	49.2 (3)	C(34)–Co(1)–Pt(1)	70.5 (3)
C(33)–Pt(1)–Co(2)	135.8 (3)	C(34)–Co(1)–Pt(2)	49.8 (3)
Pt(2)–Pt(1)–Co(1)	62.35 (3)	Pt(1)–Co(1)–Pt(2)	55.50 (3)
Pt(2)–Pt(1)–Co(2)	61.72 (3)	C(23)–Co(2)–Pt(2)	143.9 (4)
Co(1)–Pt(1)–Co(2)	105.56 (4)	C(23)–Co(2)–Pt(1)	141.1 (3)
C(20)–Pt(2)–Pt(1)	177.5 (3)	C(22)–Co(2)–Pt(2)	75.1 (4)
C(20)–Pt(2)–Co(2)	118.5 (3)	C(22)–Co(2)–Pt(1)	119.1 (4)
C(20)–Pt(2)–Co(1)	118.7 (3)	C(21)–Co(2)–Pt(2)	116.1 (4)
C(44)–Pt(2)–C(34)	118.9 (4)	C(21)–Co(2)–Pt(1)	74.0 (4)
C(44)–Pt(2)–Pt(1)	74.4 (3)	C(43)–Co(2)–Pt(2)	70.4 (3)
C(44)–Pt(2)–Co(2)	49.7 (3)	C(43)–Co(2)–Pt(1)	49.2 (3)
C(44)–Pt(2)–Co(1)	136.5 (3)	C(44)–Co(2)–Pt(2)	49.8 (2)
C(34)–Pt(2)–Pt(1)	74.3 (3)	C(44)–Co(2)–Pt(1)	70.1 (3)
C(34)–Pt(2)–Co(2)	137.1 (3)	Pt(2)–Co(2)–Pt(1)	55.50 (3)
C(34)–Pt(2)–Co(1)	49.5 (3)	C(34)–C(33)–C(32)	126 (1)
Pt(1)–Pt(2)–Co(2)	62.78 (4)	C(33)–C(34)–C(35)	130 (1)
Pt(1)–Pt(2)–Co(1)	62.15 (3)	C(44)–C(43)–C(42)	128 (1)
Co(2)–Pt(2)–Co(1)	106.16 (4)	C(43)–C(44)–C(45)	130 (1)
O–C(av)–M	174 (1)		

Table XI. Positional Parameters and *B*(eq) for $Pt_3Co_2(CO)_6(COD)_2(PhC_2Ph)_2$ (**5**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.69798 (03)	0.05394 (08)	0.05707 (06)	4.44 (5)
Pt(2)	0.63227 (03)	0.17922 (07)	0.08697 (06)	3.90 (5)
Pt(3)	0.57154 (04)	0.30351 (15)	0.12186 (07)	9.5 (1)
Co(1)	0.64274 (12)	0.3440 (02)	0.1175 (02)	5.1 (2)
Co(2)	0.62683 (10)	0.0585 (03)	−0.01180 (18)	4.5 (2)
O(1)	0.6605 (06)	0.3024 (14)	−0.0191 (11)	7.4 (5)
O(2)	0.5965 (10)	0.497 (02)	0.0547 (17)	14 (1)
O(3)	0.7132 (10)	0.442 (02)	0.1622 (16)	13 (1)
O(4)	0.5885 (07)	−0.0799 (16)	−0.1120 (12)	8.7 (6)
O(5)	0.5743 (08)	0.1933 (17)	−0.0727 (13)	9.7 (7)
O(6)	0.6780 (06)	0.1191 (13)	−0.1016 (11)	6.9 (5)
C(1)	0.6514 (09)	0.2934 (20)	0.0387 (16)	5.8 (7)
C(2)	0.6119 (14)	0.434 (03)	0.080 (02)	11 (1)
C(3)	0.6853 (14)	0.397 (03)	0.143 (02)	10 (1)
C(4)	0.6038 (10)	−0.028 (02)	−0.0714 (17)	6.4 (8)
C(5)	0.5982 (11)	0.148 (02)	−0.0376 (19)	8 (1)
C(6)	0.6661 (09)	0.0907 (19)	−0.0527 (15)	5.4 (7)
C(11)	0.7529 (09)	0.0853 (19)	0.0112 (15)	5.5 (7)
C(12)	0.7882 (09)	0.026 (02)	0.0438 (15)	6.2 (7)
C(13)	0.7743 (09)	−0.058 (02)	0.800 (15)	6.2 (7)
C(14)	0.7420 (08)	−0.0395 (19)	0.1200 (14)	5.2 (6)
C(15)	0.7382 (08)	0.0331 (19)	0.1636 (14)	5.3 (7)
C(16)	0.7680 (10)	0.110 (02)	0.1803 (16)	6.8 (8)
C(17)	0.7589 (10)	0.190 (02)	0.1249 (17)	7.4 (8)
C(18)	0.7414 (09)	0.160 (02)	0.0473 (16)	6.3 (7)
C(21)	0.5220 (12)	0.316 (03)	0.022 (02)	10 (1)
C(22)	0.5189 (18)	0.226 (04)	0.031 (03)	15 (2)
C(23)	0.4924 (16)	0.192 (04)	0.072 (03)	14 (2)
C(24)	0.4950 (16)	0.208 (03)	0.142 (03)	13 (1)
C(25)	0.5307 (10)	0.261 (02)	0.1802 (16)	6.0 (7)
C(26)	0.5302 (10)	0.345 (02)	0.1814 (16)	6.4 (8)
C(27)	0.5079 (20)	0.407 (05)	0.057 (03)	18 (2)
C(28)	0.4979 (16)	0.410 (03)	0.119 (03)	14 (2)
C(30)	0.6494 (08)	−0.0092 (18)	0.0829 (13)	4.3 (6)
C(31)	0.6533 (08)	−0.1106 (18)	0.0990 (15)	4.9 (6)

atomic distances and angles are listed in Tables IX and X. The molecule consists of a "butterfly" tetrahedral cluster of two platinum and two cobalt atoms. The platinum atoms occupy the "hinge" positions, and on the basis of the short Pt–Pt distance, 2.4945 (7) Å, it can be assumed that there is a strong bond between them. The four Pt–Co distances, 2.666 (1)–2.692 (1) Å, are significantly longer than those in **1**, **2**, **6**, and **7**, and the Co–Co distance of 4.275 (1) Å is clearly a nonbonding interaction. The dihedral angle between the two Pt_2Co groupings is 128.7°. Both Pt_2Co triangular groupings contains a triply bridging EtC_2Et ligand that contains the usual μ_3-|| bonding mode[20] with the CC vectors parallel to the Pt–Pt vector. The metrical parameters of the bridging alkyne ligands are not unusual. Each platinum atom contains one linear terminal carbonyl ligand. The cobalt atoms each have three linear terminal carbonyl ligands. The molecule has C_{2v} symmetry (not crystallographically imposed); thus, the alkyne ligands are equivalent. However, the protons on the CH_2 groups are inequivalent. These appear as complex multiplets due to coupling to each other, to the methyl groups, and long-range coupling to the platinum nuclei. However, when suitably decoupled, they appear as an AB quartet at 2.93 and 2.65 ppm, J_{H-H} = 15 Hz.

The reaction of **2** with $PhC\equiv CPh$ yielded the new compound $Pt_3Co_2(CO)_6(COD)_2(\mu_3\text{-}PhC\equiv CPh)_2$ (**5**, 22%) and a small amount of the known compound $Co_2(CO)_6(\mu\text{-}PhC_2Ph)$.[17] Compound **5** was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **5** is shown in Figure 4. Final atomic positional parameters are listed in Table XI. Selected interatomic distances

---

(20) (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Radiochem.* **1985**, *29*, 169. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, 203.

Scheme I

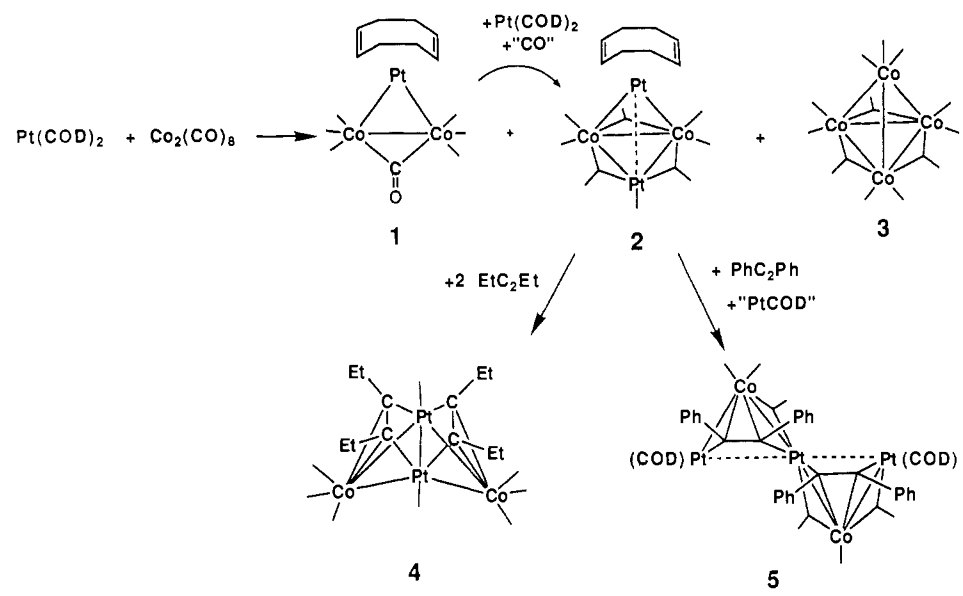


Table XII. Intramolecular Distances (Å) for **5**

Pt(1)–C(30)	2.10 (3)	Co(1)–C(3)	1.67 (5)
Pt(1)–C(6)	2.22 (3)	Co(1)–C(1)	1.77 (3)
Pt(1)–C(15)	2.23 (3)	Co(1)–C(2)	1.78 (5)
Pt(1)–C(14)	2.23 (3)	Co(1)–C(60)	2.11 (3)
Pt(1)–C(18)	2.25 (3)	Co(1)–C(50)	2.15 (2)
Pt(1)–C(11)	2.32 (3)	Co(2)–C(5)	1.69 (4)
Pt(1)–Co(2)	2.548 (4)	Co(2)–C(6)	1.78 (3)
Pt(1)–Pt(2)	3.119 (2)	Co(2)–C(4)	1.81 (3)
Pt(2)–C(40)	2.01 (2)	Co(2)–C(30)	2.07 (3)
Pt(2)–C(50)	2.06 (2)	Co(2)–C(40)	2.14 (2)
Pt(2)–C(1)	2.13 (3)	C(11)–C(18)	1.43 (4)
Pt(2)–C(5)	2.46 (4)	C(14)–C(15)	1.40 (3)
Pt(2)–Co(1)	2.564 (4)	C(21)–C(22)	1.38 (6)
Pt(2)–Co(2)	2.597 (4)	C(25)–C(26)	1.28 (4)
Pt(2)–Pt(3)	3.011 (2)	C(30)–C(40)	1.39 (3)
Pt(3)–C(60)	2.01 (3)	C(30)–C(31)	1.56 (3)
Pt(3)–C(25)	2.09 (3)	C(40)–C(41)	1.50 (3)
Pt(3)–C(26)	2.11 (3)	C(50)–C(60)	1.35 (3)
Pt(3)–C(21)	2.28 (4)	C(50)–C(51)	1.48 (3)
Pt(3)–C(22)	2.52 (6)	C(60)–C(61)	1.53 (3)
Pt(3)–Co(1)	2.578 (4)	O–C(av)	1.17 (5)

Table XIII. Intramolecular Bond Angles (deg) for **5**

Pt(2)–Pt(1)–Co(2)	53.4 (1)	Co(1)–Pt(3)–C(60)	52.9 (7)
Pt(2)–Pt(1)–C(6)	77.3 (7)	Pt(2)–Co(1)–Pt(3)	71.7 (1)
Pt(2)–Pt(1)–C(11)	130.1 (7)	Pt(2)–Co(1)–C(1)	55 (1)
Pt(2)–Pt(1)–C(14)	137.2 (7)	Pt(2)–Co(1)–C(2)	127 (1)
Pt(2)–Pt(1)–C(15)	105.3 (7)	Pt(2)–Co(1)–C(3)	128 (1)
Pt(2)–Pt(1)–C(18)	96.7 (8)	Pt(2)–Co(1)–C(50)	50.9 (6)
Pt(2)–Pt(1)–C(30)	64.5 (7)	Pt(2)–Co(1)–C(60)	76.4 (7)
Co(2)–Pt(1)–C(6)	43.3 (8)	Pt(3)–Co(1)–C(1)	105 (1)
Co(2)–Pt(1)–C(11)	126.4 (7)	Pt(3)–Co(1)–C(2)	72 (1)
Co(2)–Pt(1)–C(14)	140.7 (7)	Pt(3)–Co(1)–C(3)	155 (1)
Co(2)–Pt(1)–C(15)	145.7 (7)	Pt(3)–Co(1)–C(50)	72.7 (7)
Co(2)–Pt(1)–C(18)	122.6 (8)	Pt(3)–Co(1)–C(60)	49.6 (7)
Co(2)–Pt(1)–C(30)	51.9 (7)	Pt(1)–Co(2)–Pt(2)	74.6 (1)
Pt(1)–Pt(2)–Pt(3)	177.31 (5)	Pt(1)–Co(2)–C(4)	124 (1)
Pt(1)–Pt(2)–Co(1)	123.8 (1)	Pt(1)–Co(2)–C(5)	129 (1)
Pt(1)–Pt(2)–Co(2)	51.98 (9)	Pt(1)–Co(2)–C(6)	58 (1)
Pt(1)–Pt(2)–C(1)	95.9 (8)	Pt(1)–Co(2)–C(30)	52.7 (7)
Pt(1)–Pt(2)–C(5)	86 (1)	Pt(1)–Co(2)–C(40)	77.0 (6)
Pt(1)–Pt(2)–C(40)	65.7 (7)	Pt(2)–Co(2)–C(4)	157 (1)
Pt(1)–Pt(2)–C(50)	113.0 (7)	Pt(2)–Co(2)–C(5)	66 (1)
Pt(3)–Pt(2)–Co(1)	54.4 (1)	Pt(2)–Co(2)–C(6)	100 (1)
Pt(3)–Pt(2)–Co(2)	130.7 (1)	Pt(2)–Co(2)–C(30)	76.2 (7)
Pt(3)–Pt(2)–C(1)	83.7 (8)	Pt(2)–Co(2)–C(40)	49.2 (6)
Pt(3)–Pt(2)–C(5)	97 (1)	Pt(2)–C(1)–O(1)	130 (2)
Pt(3)–Pt(2)–C(40)	115.4 (7)	Co(1)–C(1)–O(1)	148 (3)
Pt(3)–Pt(2)–C(50)	64.4 (7)	Pt(2)–C(5)–O(5)	125 (3)
Co(1)–Pt(2)–Co(2)	146.2 (1)	Co(2)–C(5)–O(5)	160 (3)
Co(1)–Pt(2)–C(1)	43.0 (8)	Pt(1)–C(6)–O(6)	130 (2)
Co(1)–Pt(2)–C(5)	115.0 (9)	Co(2)–C(6)–O(6)	151 (3)
Co(1)–Pt(2)–C(40)	160.2 (6)	Pt(1)–C(30)–C(31)	117 (2)
Co(1)–Pt(2)–C(50)	54.0 (7)	Co(2)–C(30)–C(31)	131 (2)
Co(2)–Pt(2)–C(1)	103.8 (8)	C(31)–C(30)–C(40)	128 (2)
Co(2)–Pt(2)–C(5)	39 (1)	Pt(2)–C(40)–C(41)	123 (2)
Co(2)–Pt(2)–C(40)	53.6 (6)	Co(2)–C(40)–C(30)	68 (1)
Co(2)–Pt(2)–C(50)	157.7 (7)	Co(2)–C(40)–C(41)	124 (2)
C(40)–Pt(2)–C(50)	107 (1)	C(30)–C(40)–C(41)	121 (2)
Pt(2)–Pt(3)–Co(1)	54.0 (1)	Pt(2)–C(50)–C(51)	124 (2)
Pt(2)–Pt(3)–C(21)	108 (1)	Pt(2)–C(50)–C(60)	115 (2)
Pt(2)–Pt(3)–C(25)	121.1 (9)	Co(1)–C(50)–C(51)	129 (2)
Pt(2)–Pt(3)–C(26)	153.9 (9)	C(51)–C(50)–C(60)	121 (2)
Pt(2)–Pt(3)–C(60)	67.4 (8)	Pt(3)–C(60)–C(61)	119 (2)
Co(1)–Pt(3)–C(21)	121 (1)	Co(1)–C(60)–C(61)	130 (2)
Co(1)–Pt(3)–C(25)	149.7 (9)	C(50)–C(60)–C(61)	127 (2)
Co(1)–Pt(3)–C(26)	136.1 (9)	O–C(av)–Co	173 (4)

and angles are listed in Tables XII and XIII. The molecule consists of a "bow-tie" cluster containing three platinum and two cobalt atoms (i.e. two Pt_2Co triangular groupings have one atom, Pt(2), in common). The Pt–Co distances are slightly longer than those in **1**, **2**, **6**, and **7** but are slightly shorter than those in **3**. The Pt–Pt distances are quite long, Pt(1)–Pt(2) = 3.119 (2) Å and Pt(2)–Pt(3) = 3.011 (2) Å. Although the bonds appear to be significantly different in length, the large thermal parameter that was produced for Pt(3) and the carbon atoms of the COD ligand attached to Pt(3) suggest the presence of a significant but unresolvable disorder. Thus, we feel that the metrical parameters associated with atom Pt(3) may have considerable error associated with them. The dihedral angle between the two Pt_2Co triangular groupings is 43.1°. The Pt(1)–Pt(2)–Pt(3) angle is nearly linear, 177.31 (5)°. There is a triply bridging μ_3-|| PhC_2Ph ligand on each Pt_2Co group, and these ligands have normal dimensions.[20] There is a COD ligand on atoms Pt(1) and Pt(3). Cobalt atom Co(1) has two linear terminal carbonyl ligands and one that forms a strong semibridge to the central platinum atom, Pt(2). Cobalt atom Co(2) has one terminal carbonyl ligand and one strong semibridging carbonyl ligand to each of the platinum atoms to which it is attached.

Discussion

The results of this investigation are summarized in Scheme I. The new platinum–cobalt cluster complexes **1** and **2** have been obtained from the reaction of $Pt(COD)_2$ with $Co_2(CO)_8$. Compound **1** can be transformed to **2** by reaction with additional $Pt(COD)_2$. This reaction requires the addition of 1 equiv of CO although this was not supplied directly. Interestingly, the addition of CO from an external source was found to be detrimental to the formation of **2**. Lemoine et al. have reported that the diplatinum complex **7** is obtained from **6** when **6** is reduced elec-

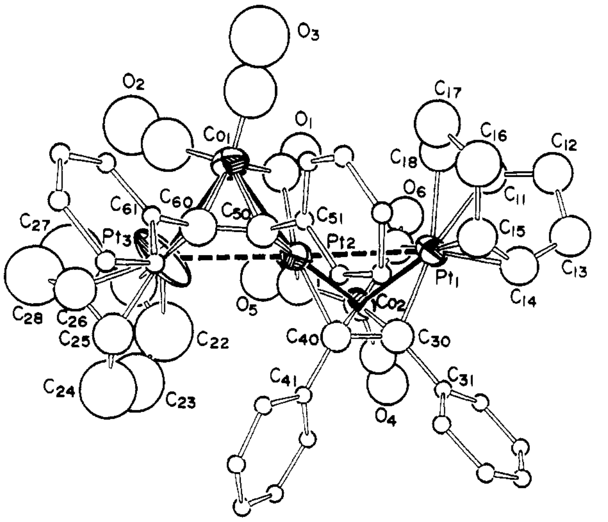
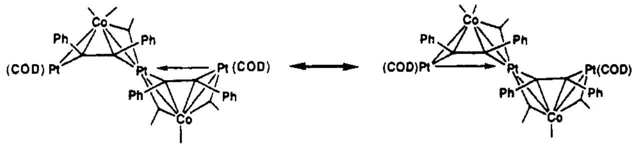


Figure 4. ORTEP drawing of $Pt_3Co_2(CO)_6(COD)_2(\mu_3\text{-}PhC_2Ph)_2$ (**5**), showing 40% probability thermal ellipsoids.

trochemically.[21] Compound **2** contains a total of 58 valence electrons, which is 2 less than the electron-precise value of 60 typically found for tetrahedral M_4 cluster complexes. This lower count has been observed in other platinum-containing M_4 cluster complexes[22,23] and is probably due to the tendency of platinum to form stable complexes with 16-electron configurations.[24] Other 58-electron cluster complexes containing two platinum atoms that have been characterized have also been found to contain long Pt-Pt distances.[6,23] Fusi et al. have reported that compound **6** exhibits a significant ability to catalyze the hydrogenation of terminal alkynes, but no complexes that might shed light upon the mechanism of the process were characterized.[12] We have not yet investigated the ability of **2** to produce catalytic hydrogenation of alkynes; however, since **2** contains a COD ligand that should be easily displaced, we have investigated the reaction of **2** with internal alkynes in the hopes of preparing and characterizing some platinum-cobalt cluster complexes containing alkyne ligands.

The reaction of **2** with EtC_2Et yielded the new bis(alkyne) complex **4**, while the reaction of **2** with PhC_2Ph yielded the bis(alkyne)triplatinumdicobalt complex **5**. Compound **4** contains 62 valence electrons and is electron precise (i.e. all metal atoms obey the effective atomic number rule). However, compound **5** contains a total of 76 valence electrons, which is 2 less than the value of 78 that is expected for an electron-precise bow-tie cluster. As with **2**, the deficiency is probably related to the tendency of platinum to form stable structures with 16 electrons. By using this idea, we propose that the structure of **5** can be represented as an average of the two resonance structures **5a** and **5b**, in which both the external platinum atoms formally have a 16-electron configuration and one of these then has no formal bond to the central atom Pt(2), which has 18 electrons. This idea would also explain the long Pt-Pt bond lengths found in **5**. The presence of three platinum atoms in **5** implies that **2** is undergoing fragmentation processes during its reaction with PhC_2Ph. Fragmentation processes could limit the potential to develop these compounds as catalysts.[12]



5a **5b**

Acknowledgment. This research was supported by the National Science Foundation under Grant CHE-8919786.

Supplementary Material Available: For **1**, **2**, **4**, and **5**, tables of crystallographic data, hydrogen atom coordinates, and anisotropic thermal parameters and, for **5**, a table of coordinates of the carbon atoms of the phenyl rings (9 pages); tables of calculated and observed structure factors for all four structural analyses (72 pages). Ordering information is given on any current masthead page.

---

(21) Lemoine, P.; Giraudeau, A.; Gross, M.; Bender, R.; Braunstein, P. *J. Chem. Soc., Dalton Trans.* **1981**, 2059.

(22) Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 155.

(23) (a) Farrugia, L. J.; Howard, J. A. K.; Mitraprachachon, P.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 260. (b) Bhaduri, S.; Sharma, K. R.; Clegg, W.; Sheldrick, G. M.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1984**, 2851.

(24) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *240*, 321.

Contribution from the Departments of Chemistry, The University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27599-3290, and North Carolina State University, Raleigh, North Carolina 27695

Structure and Magnetic Properties of Bis(*N*,*N*-diisopropyldithiocarbamato)copper(II)

William E. Hatfield,* Phirtu Singh, and Francoise Nepveu

Received February 14, 1990

The complex bis(*N*,*N*-diisopropyldithiocarbamato)copper(II), $C_{14}H_{28}CuN_2S_4$, crystallizes in the space group $P\bar{1}$ of the triclinic system with $Z = 2$. The unit cell has parameters $a = 11.559$ (3) Å, $b = 11.692$ (3) Å, $c = 7.629$ (2), Å, $\alpha = 96.35$ (2)°, $\beta = 96.35$ (2)°, and $\gamma = 88.78$ (2)°. The final weighted R factor is 0.048 based on 1625 [intensity $\geq 2.5\sigma(I)$] measured reflections. The two independent half-molecules in the unit cell are square planar with exactly planar CuS_4 units and nearly planar $>NCS_2$ moieties. The average of the four independent copper-sulfur distances is 2.283 Å, and the average of the four carbon-sulfur distances is 1.716 Å. The latter distance is indicative of considerable double-bond character. The shortest copper-copper intermolecular distance is 7.629 Å, and the shortest copper-sulfur intermolecular distance is 6.041 Å. There are significant intermolecular antiferromagnetic interactions transmitted over these long distances, as reflected by the reduction of the magnetic moment from about 1.8 μ_B near 20 K to 1.5 μ_B at 1.76 K. This observation provides additional documentation that sulfur bridges provide effective superexchange pathways for magnetic interactions between paramagnetic centers.

Introduction

Exchange interactions between paramagnetic centers may occur over relatively long distances. These magnetic interactions may readily be seen if they are antiferromagnetic, since magnetic moments of substances that exhibit these interactions decrease markedly from single-ion magnetic moments. Long-range interactions have been found frequently when the metal ions are bridged by sulfur ligands.[1-4] In our program devoted to the

---

(1) Hatfield, W. E. *Inorg. Chem.* **1983**, *22*, 833.