plane is formed by three histidine nitrogens and the anion;[29] Rotilio had suggested that one histidine goes in an apical position upon anion binding;[30] we had suggested that one histidine could be removed from coordination upon anion binding to the enzyme in

order to account for the electronic and ^{1}H NMR spectra of the derivatives.[9,13,15]

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An Unusual Mixed-Metal Cluster: Synthesis and Molecular Structure of FePt5(CO)9(PEt3)4

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The reaction of Na2[Fe(CO)4] with *cis*-PtCl2L2 (L = PEt3, PPh3, P(p-Tol)3, PMe2Ph) in THF yields cluster complexes of nuclearities 3, 5, and 6, and the new hexanuclear heterometallic cluster FePt5(μ-CO)4(CO)5(PEt3)4 (**1**) has been shown by X-ray analysis to possess an unprecedented geometry. The structure of **1** may be regarded as a Pt4 tetrahedron sharing an edge with a FePt3 lozenge in such a way that the metal core is unusually open (noncompact) for a six-atom cluster. The electron count in this 84-electron cluster is discussed. The structure of **1** shows the topological preference of the iron fragment to bridge a Pt–Pt bond and confirms that deltahedra are energetically the most stable structures, since they possess the greatest connectivities for a fixed number of vertices. Cluster **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.421 (2) Å, b = 23.653 (3) Å, c = 18.877 (3) Å, β = 95.16 (2)°, and Z = 4. The final conventional agreement factors were $R(F_o)$ = 0.058 and $R_w(F_o)$ = 0.062.

Questions of current interest in the rapidly expanding field of molecular cluster chemistry include the identification of optimum geometries of transition-metal clusters and the toposelective design of mixed-metal clusters.[1] It has been recently emphasized that the important bonding effects of the valence d electrons in transition-metal clusters account for the polyhedral structures of the latter being relatively compact, in comparison with the boranes.[2] Here we present a new bimetallic Fe–Pt mixed-metal carbonyl cluster, FePt5(μ-CO)4(CO)5(PEt3)4 (**1**), which has an unprecedented and unusually open structure for a six-atom cluster.

Results

In the course of our studies on the synthesis and catalytic applications of Fe–Pd and Fe–Pt carbonyl clusters,[3] we investigated the reaction of Na2[Fe(CO)4] with *cis*-PtCl2(PEt3)2 in tetrahydrofuran (THF). Separation of the reaction products by column chromatography afforded among others Pt5(μ-CO)5(CO)(PEt3)4[4] and FePt5(μ-CO)4(CO)5(PEt3)4 (**1**) (eq 1, Scheme I). The new cluster **1** was characterized by IR spectroscopy, which indicated the presence of terminal and bridging carbonyl ligands, by ^{31}P{^{1}H} NMR spectroscopy, which established that the PEt3 ligands were all bound to Pt atoms (^1J(PtP) values ranging from 4904 to 3800 Hz), and by fast atom bombardment (FAB) mass spectroscopy, which gave the parent ion and the expected fragmentation patterns (Experimental Section). Brown-red crystals of **1** suitable for X-ray analysis were obtained by slow diffusion of hexane into a chlorobenzene solution at −20 °C. A perspective view of the cluster is presented in Figure 1. A summary of crystal data, intensity collection and structural refinement is given in Table I; selected bond distances and angles are given in Table II, and atom coordinates and isotropic thermal parameters, in Tables III and SII (supplementary material).[16] The metal core geometry may be regarded as a Pt4 tetrahedron sharing its Pt(1)–Pt(5) edge with a FePt3 lozenge. The latter is created by the triangles FePt(3)Pt(5) and Pt(1)Pt(3)Pt(5), which make a dihedral angle of 2.1° with

Scheme I
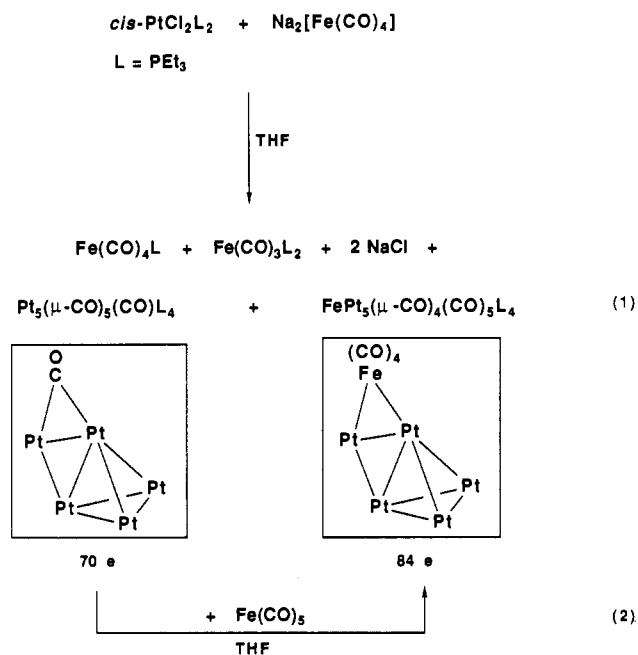
Table I. Crystallographic Data for FePt5(CO)9(PEt3)4

formula: $C_{33}H_{60}FeO_9P_4Pt_5$	fw: 1755.5
a = 11.421 (2) Å	space group: monoclinic $P2_1/n$
b = 23.653 (3) Å	T = 25 °C
c = 18.877 (3) Å	λ = 0.710 73 Å
α = 90.00°	ρ_{calcd} = 2.29 g/cm^3
β = 95.16 (2)°	μ = 148 cm^{-1}
γ = 90.00°	$R(F_o)$ = 0.058
V = 5079.0 (6) Å^3	$R_w(F_o)$ = 0.062
Z = 4	

each other. This lozenge is oriented in such a way that its mean plane is nearly orthogonal to the Pt(1)Pt(2)Pt(4) plane (dihedral

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Table II. Selected Bond Distances (Å) and Angles (deg)[a]

Selected Interatomic Distances			
Fe–Pt(3)	2.603 (4)	C(5)–Pt(1)	1.99 (3)
Fe–Pt(5)	2.570 (4)	C(5)–Pt(3)	1.93 (3)
Pt(3)–Pt(5)	2.709 (2)	C(6)–Pt(5)	1.76 (4)
Pt(3)–Pt(1)	2.727 (2)	C(7)–Pt(2)	2.03 (3)
Pt(1)–Pt(5)	2.722 (2)	C(7)–Pt(4)	1.98 (3)
Pt(1)–Pt(2)	2.767 (2)	C(8)–Pt(1)	2.22 (3)
Pt(1)–Pt(4)	2.762 (2)	C(8)–Pt(4)	1.95 (3)
Pt(2)–Pt(4)	2.666 (1)	C(9)–Pt(2)	1.94 (3)
Pt(4)–Pt(5)	2.869 (2)	C(9)–Pt(1)	2.29 (3)
Pt(2)–Pt(5)	2.895 (1)	C(5)–O(5)	1.25 (4)
Pt(1)–P(1)	2.322 (9)	C(6)–O(6)	1.18 (5)
Pt(2)–P(2)	2.258 (7)	C(7)–O(7)	1.24 (4)
Pt(3)–P(3)	2.271 (9)	C(8)–O(8)	1.20 (4)
Pt(4)–P(4)	2.236 (8)	C(9)–O(9)	1.15 (4)
Fe–C(1)	1.74 (4)	C(1)–O(1)	1.13 (4)
Fe–C(2)	1.72 (3)	C(2)–O(2)	1.19 (4)
Fe–C(3)	1.80 (3)	C(3)–O(3)	1.18 (4)
Fe–C(4)	1.73 (3)	C(4)–O(4)	1.16 (4)

| Bond Angles			
Pt(4)–Pt(1)–Pt(3)	118.60 (5)	Pt(1)–C(5)–O(5)	135 (3)
Pt(2)–Pt(1)–Pt(3)	110.37 (5)	Pt(3)–C(5)–O(5)	136 (3)
Pt(2)–Pt(1)–Pt(4)	57.67 (4)	Pt(2)–C(7)–Pt(4)	83 (1)
Pt(2)–Pt(1)–Pt(5)	63.65 (4)	Pt(2)–C(7)–O(7)	135 (2)
Pt(4)–Pt(1)–Pt(5)	63.08 (4)	Pt(4)–C(7)–O(7)	141 (2)
Pt(1)–Pt(2)–Pt(4)	61.07 (4)	Pt(1)–C(8)–Pt(4)	83 (1)
Pt(1)–Pt(2)–Pt(5)	57.43 (4)	Pt(1)–C(8)–O(8)	129 (2)
Pt(4)–Pt(2)–Pt(5)	61.95 (4)	Pt(4)–C(8)–O(8)	148 (2)
Pt(1)–Pt(3)–Pt(5)	60.09 (4)	Pt(1)–C(9)–Pt(2)	81 (1)
Pt(1)–Pt(3)–Fe	117.9 (1)	Pt(1)–C(9)–O(9)	126 (2)
Pt(5)–Pt(3)–Fe	57.8 (1)	Pt(2)–C(9)–O(9)	152 (3)
Pt(1)–Pt(4)–Pt(2)	61.27 (4)	Fe–Pt(5)–C(6)	97 (1)
Pt(1)–Pt(4)–Pt(5)	57.79 (4)	Pt(3)–Pt(5)–C(6)	156 (1)
Pt(2)–Pt(4)–Pt(5)	62.94 (4)	Pt(1)–Pt(5)–C(6)	144 (1)
Pt(1)–Pt(5)–Pt(2)	58.92 (4)	Pt(4)–Pt(5)–C(6)	86 (1)
Pt(1)–Pt(5)–Pt(3)	60.28 (4)	Pt(2)–Pt(5)–C(6)	94 (1)
Pt(1)–Pt(5)–Pt(4)	59.13 (4)	Pt(3)–Pt(1)–P(1)	140.6 (2)
Pt(1)–Pt(5)–Fe	119.2 (1)	Pt(5)–Pt(1)–P(1)	159.8 (2)
Pt(2)–Pt(5)–Pt(3)	107.15 (5)	Pt(2)–Pt(1)–P(1)	100.1 (2)
Pt(2)–Pt(5)–Fe	145.4 (1)	Pt(4)–Pt(1)–P(1)	98.5 (2)
Pt(3)–Fe–Pt(5)	63.2 (1)	Pt(5)–Pt(2)–P(2)	135.3 (2)
C(1)–Fe–C(2)	101 (2)	Pt(1)–Pt(2)–P(2)	146.8 (2)
C(1)–Fe–C(3)	140 (2)	Pt(4)–Pt(2)–P(2)	149.4 (2)
C(1)–Fe–C(4)	107 (2)	Fe–Pt(3)–P(3)	105.7 (3)
C(2)–Fe–C(3)	102 (2)	Pt(1)–Pt(3)–P(3)	136.1 (3)
C(2)–Fe–C(4)	90 (2)	Pt(5)–Pt(3)–P(3)	162.5 (3)
C(3)–Fe–C(4)	105 (2)	Pt(1)–Pt(4)–P(4)	144.7 (2)
Fe–C(1)–O(1)	172 (3)	Pt(2)–Pt(4)–P(4)	146.2 (2)
Fe–C(2)–O(2)	176 (3)	Pt(5)–Pt(4)–P(4)	141.5 (2)
Fe–C(3)–O(3)	171 (3)	C(8)–Pt(1)–C(9)	144 (1)
Fe–C(4)–O(4)	174 (3)	C(9)–Pt(2)–C(7)	163 (1)
Pt(5)–C(6)–O(6)	177 (3)	C(7)–Pt(4)–C(8)	162 (1)
Pt(1)–C(5)–Pt(3)	88 (1)	C(8)–Pt(1)–C(5)	99 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

angle 93.3°) and that platinum atoms Pt(2) and Pt(4) are situated −1.649 and 0.985 Å on either side of this plane.

The carbonyl ligands bridging the edges of the Pt(1)Pt(2)Pt(4) triangle are almost in the plane of these metal atoms. A fourth
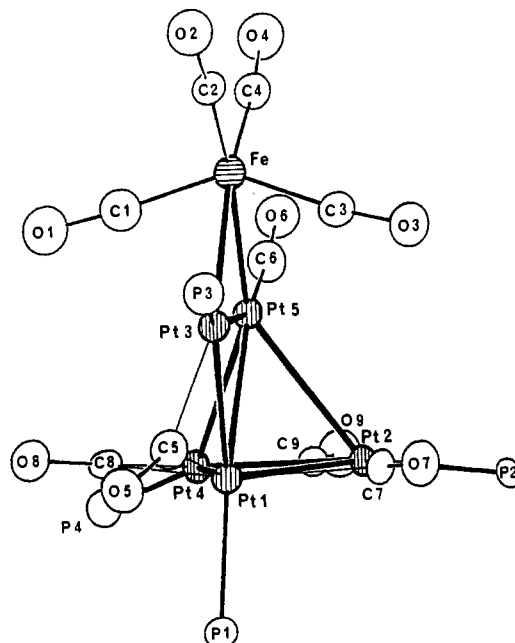
Figure 1. Crystal structure of $FePt_5(\mu\text{-}CO)_4(CO)_5(PEt_3)_4$ (**1**). The ethyl groups have been omitted for clarity.
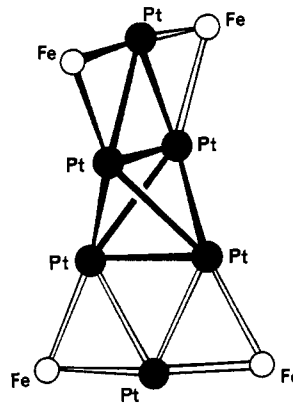
Figure 2. Perspective drawing showing the relationship between the structure of **1** (thick lines) and that of $[Fe_4Pt_6(CO)_{22}]^{2-}$ (from ref 6).

bridging CO spans the Pt(1)–Pt(3) edge, while Pt(5), which is bonded to five metal atoms, bears a terminal CO ligand. The Fe-bound carbonyl ligands are almost linear (angles Fe–C–O > 171°) although the distances between C(1) and Pt(3) or Pt(5) (2.66 (3), 2.68 (3) Å) and C(3) and Pt(3) or Pt(5) (2.59 (3), 2.78 (3) Å) are consistent with weak semibridging interactions. The Pt–Pt distances in **1** (2.666 (1)–2.895 (1) Å) are in the range found in the structurally related platinum cluster $Pt_5(CO)_6(PPh_3)_4$ (**2**) (2.669 (1)–2.919 (1) Å).[4] The Fe–Pt distances are comparable to those found in other Fe–Pt carbonyl clusters.[5-7]

Discussion

Cluster **1** is an 84-electron system, and its structure could not be predicted by conventional skeletal-electron-counting procedures[8] nor by the topological-electron-counting scheme.[9] However, it

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Table III. Final Positional ($\times 10^4$) and Isotropic Equivalent Displacement Parameters (Å^2) with Estimated Standard Deviations in Parentheses for FePt$_5$(CO)$_9$(PEt$_3$)$_4$

atom	x/a	y/b	z/c	B_{eq},^{a} Å^2
Pt(1)	9916 (1)	2128 (1)	675 (1)	2.61 (3)
Pt(2)	10120 (1)	3059 (1)	1563 (1)	2.43 (3)
Pt(3)	8467 (1)	1341 (1)	1190 (1)	2.82 (3)
Pt(4)	8992 (1)	3170 (1)	272 (1)	2.66 (3)
Pt(5)	7930 (1)	2454 (1)	1260 (1)	2.57 (3)
Fe	6556 (3)	1695 (2)	1700 (2)	2.95 (11)
P(1)	11676 (7)	2192 (4)	154 (5)	3.76 (20)
P(2)	11066 (6)	3461 (3)	2538 (4)	2.88 (18)
P(3)	8535 (9)	395 (4)	1396 (5)	4.86 (22)
P(4)	8533 (7)	3747 (4)	−649 (4)	3.77 (20)
C(1)	6302 (28)	1694 (15)	778 (19)	4.98 (33)
O(1)	6022 (23)	1665 (12)	187 (15)	7.46 (33)
C(2)	5784 (27)	1105 (14)	1922 (17)	4.37 (33)
O(2)	5203 (22)	701 (12)	2037 (14)	6.75 (33)
C(3)	7768 (27)	1701 (14)	2380 (18)	4.67 (33)
O(3)	8456 (22)	1684 (12)	2883 (14)	6.86 (32)
C(4)	5502 (27)	2123 (15)	2025 (18)	4.86 (33)
O(4)	4774 (23)	2428 (12)	2189 (15)	7.24 (33)
C(5)	9666 (26)	1303 (13)	532 (18)	4.28 (33)
O(5)	9997 (22)	947 (11)	105 (13)	6.13 (32)
C(6)	7052 (30)	3041 (16)	1433 (19)	5.36 (33)
O(6)	6489 (22)	3435 (12)	1575 (15)	7.17 (32)
C(7)	9408 (23)	3735 (11)	1024 (14)	2.89 (32)
O(7)	9211 (21)	4234 (11)	1177 (13)	6.27 (32)
C(8)	8707 (22)	2452 (12)	−222 (15)	3.21 (32)
O(8)	8290 (19)	2208 (12)	−740 (12)	5.36 (31)
C(9)	10698 (24)	2309 (13)	1810 (16)	3.59 (32)
O(9)	11154 (21)	1988 (9)	2198 (12)	5.51 (31)
C(10)	9968 (35)	105 (19)	1469 (24)	7.93 (34)
C(11)	10734 (39)	483 (22)	2160 (27)	9.62 (34)
C(12)	7944 (31)	136 (17)	2138 (21)	6.43 (34)
C(13)	8007 (37)	−509 (21)	2411 (25)	8.49 (34)
C(14)	7818 (43)	−26 (23)	606 (29)	10.06 (34)
C(15)	6695 (42)	37 (23)	447 (29)	10.11 (34)
C(16)	12611 (27)	1531 (15)	260 (19)	4.99 (33)
C(17)	12867 (31)	1358 (18)	965 (22)	6.66 (34)
C(18)	12605 (33)	2739 (18)	526 (22)	6.80 (34)
C(19)	13772 (36)	2837 (21)	220 (25)	8.34 (34)
C(20)	11462 (28)	2352 (15)	−795 (19)	5.22 (33)
C(21)	11042 (34)	1829 (18)	−1283 (22)	7.26 (34)
C(22)	12702 (24)	3419 (13)	2625 (16)	3.72 (32)
C(23)	13271 (30)	3754 (17)	2068 (20)	6.01 (34)
C(24)	10795 (28)	4228 (15)	2694 (18)	5.06 (33)
C(25)	11270 (34)	4436 (19)	3449 (23)	7.52 (34)
C(26)	10710 (27)	3078 (13)	3346 (16)	4.13 (33)
C(27)	9408 (38)	3104 (21)	3384 (25)	8.59 (34)
C(28)	8309 (32)	4485 (16)	−415 (20)	6.20 (34)
C(29)	7967 (46)	4947 (26)	−1089 (32)	12.23 (35)
C(30)	7191 (32)	3548 (18)	−1221 (21)	6.82 (34)
C(31)	6122 (32)	3445 (18)	−785 (22)	6.88 (34)
C(32)	9656 (38)	3774 (21)	−1315 (24)	8.44 (34)
C(33)	10775 (32)	3984 (18)	−1012 (20)	6.55 (34)

^{a} B values for anisotropically refined atoms given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha]$.

can be rationalized by the condensed polyhedral approach.[10] Thus, cluster **1** may be constructed in two steps by condensing first a Pt$_4$ tetrahedron with an edge-sharing Pt$_3$ triangle (56 + 44 − 30 = 70 electrons, i.e. the correct electron count of **2**) and second the resulting Pt$_5$ cluster with an edge-sharing FePt$_2$ triangle (70 + 44 − 30 = 84 electrons). Alternatively, **1** may be structurally derived from **2** by replacing the carbonyl ligand bridging the edge Pt(3)−Pt(5) with the Fe(CO)$_4$ group, a bulky analogue of CO (70 − 2 + 16 = 84 electrons). This view led to the preparation of **1** from Pt$_5$(CO)$_6$(PEt$_3$)$_4$ and Fe(CO)$_5$ (eq 2, Scheme I).[7b]

It is remarkable that the core geometry of **1** constitutes a substructure of the [Fe$_4$Pt$_6$(CO)$_{22}$]$^{2-}$ cluster, which was thought to derive from the condensation of two hypothetical trapezoidal

[Fe$_2$Pt$_3$(CO)$_{11}$]$^-$ units (Figure 2).[6] Cluster **1** may also be viewed as resulting from face capping by Pt(2) of a Pt$_3$ triangle of the distorted trapezoidal FePt(1)Pt(3)Pt(4)Pt(5) unit. Obviously, steric factors (e.g. phosphine vs carbonyl or hydride ligands) largely control cluster growth. In these Fe−Pt clusters as in the raftlike [Fe$_3$Pt$_3$(CO)$_{15}$]$^-$ anion,[6] the platinum atoms occupy positions that optimize the energetically more favorable Pt−Pt interactions. These structures show the topological preference of the iron fragment to bridge a Pt−Pt bond. They also confirm the idea that deltahedra are energetically the most stable structures, since they possess the greatest connectivities for a fixed number of vertices.[2]

The characterization of **1** shows that structures less compact than anticipated may be stabilized and provides useful information about cluster expansion processes.

Experimental Section

All experimental procedures and physical measurements were performed as described previously.[3,4] Fast atom bombardment (FAB) mass spectra were obtained at McMaster University on a VG analytical ZAB-SE spectrometer with use of 3-nitrobenzyl alcohol as the sample matrix and Xe as the bombarding gas.

A mixture of Na$_2$[Fe(CO)$_4$] (1.38 g, 6.45 mmol) and cis-PtCl$_2$(PEt$_3$)$_2$ (3.00 g, 5.98 mmol) in THF (150 mL) was stirred for 1 h at ambient temperature. The red solution was evaporated to dryness under reduced pressure, and the resulting solid residue was column-chromatographed over silica gel (Kieselgel 60, Merck). Elution with toluene afforded successively Fe(CO)$_4$(PEt$_3$), Fe(CO)$_3$(PEt$_3$)$_2$, the triangular clusters Fe$_2$Pt(CO)$_9$(PEt$_3$)[11] and Fe$_2$Pt(CO)$_8$(PEt$_3$)$_2$,[7] and red Pt$_5$(CO)$_6$(PEt$_3$)$_4$.[4] Further elution with THF gave a red-brown solution, which was evaporated to dryness in vacuo, and the solid was recrystallized by slow diffusion of hexane into a chlorobenzene solution, affording crystalline **1** (0.20 g, 9.5% based on Pt). Anal. Calcd for C$_{33}$H$_6$FeO$_9$P$_4$Pt$_5$ (M_r = 1755.98): C, 22.57; H, 3.44. Found: C, 22.19; H, 3.87. IR (KBr): ν(CO) 2007 (vs), 1972 (s), 1916 (s), 1885 (s), 1854 (m), 1786 (s), 1757 (s) cm^{-1}. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$): δ 54.7 (1 P, P(1), m, ^1J(PtP) = 3800 Hz, ^2J(Pt(3)P) = 531, ^2J(Pt(5)P) = 378 Hz, ^3J(Pt(3)P) = ^3J(Pt(4)P) = 128 Hz, ^3J(P(3)P) = 36 Hz, ^4J(PP) = 3.4 Hz), 44.5 (1 P, P(3), m, ^1J(PtP) = 3970 (Hz, ^1J(Pt(1)P) = 486 Hz, ^2J(PtP) = 57 Hz, ^3J(P(1)P) = 36 Hz, ^3J(Pt(2)P) = 0 Hz), 38.9 (2 P, P(2) and P(4), m, ^1J(PtP) = 4904 Hz, ^2J(Pt(1)P) = 296 Hz, ^2J(Pt(2)P) = 331 Hz, ^2J(Pt(5)P) = 149 Hz, ^3J(Pt(3)P) = 24 Hz, ^3J(PP) = 33 Hz, ^{3+4}J(P(1)P) = 3 Hz). These values and assignments result from spectral simulations (PANIC, Bruker) to be detailed elsewhere.

The same procedure was applied to the synthesis of other FePt$_5$(CO)$_9$L$_4$ clusters. (a) L = PPh$_3$: elution with toluene; yield 11%; IR (KBr) 2020 (vs), 1985 (vs), 1930 (m), 1895 (m), 1790 (vs) cm^{-1}. (b) L = P(p-Tol)$_3$: elution with toluene/pentane (3:2); yield 3%; IR (KBr) 2017 (vs), 1985 (vs), 1925 (m), 1880 (m), 1805 (s), 1770 (m) cm^{-1}; further elution with THF affording a deep red compound not yet identified; IR (KBr) 2030 (m), 1990 (m), 1958 (vs), 1926 (m), 1907 (m), 1880 (w), 1751 (m) cm^{-1}. (c) L = PMe$_2$Ph: only traces detected in the toluene fraction containing the Pt$_5$(CO)$_6$L$_4$ cluster.

Crystallographic Study. Two crystals of approximately the same dimensions were used for X-ray analysis because of the progressive decrease of three reference reflections in spite of all precautions. The experimental conditions are given in Tables I and SI (supplementary material).[16] Unit cell parameters were determined from 25 reflections having 2 < 2θ < 15°. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied with use of DIFABS.[12] Data reduction was made by an SDP package with a decay correction.[13] The positions of the platinum atoms were deduced from the Patterson map, and subsequent sets of Fourier and difference Fourier synthesis revealed the entire structure.[14] The hydrogen atoms of the PCH$_2$ groups were introduced in the structure factor calculations as fixed contributors to the scattering at a distance of 0.95 Å from the bonded carbon atoms and were assigned isotropic thermal parameters of B = 5.0 Å^2. Full least-squares refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged to the R values given in Table I. Atomic scattering factors and anomalous dispersion corrections were taken from standard sources.[14,15]

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(13) "SDP Structure Determination Package"; Enraf-Nonius: Delft, The Netherlands, 1977.

(14) Sheldrick, G. M. "Programs for Crystal Structure Determination"; University of Göttingen: Göttingen, West Germany, 1976.

(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Atomic coordinates with estimated standard deviations and hydrogen atom coordinates (Table SII), anisotropic thermal parameters for all non-hydrogen atoms (Table SIII), a complete list of bond distances and angles (Table SIV), selected least-squares planes (Table SV), and a listing of the observed and calculated structure factor amplitudes used in the refinement (Table SVI) are available as supplementary material.[16]

Registry No. 1, 120711-63-9; Pt(μ-CO)₅(CO)(PEt₃)₄, 68875-49-0; Na₂[Fe(CO)₄], 14878-31-0; *cis*-PtCl₂(PEt₃)₂, 15692-07-6; Fe(CO)₄-(PEt₃), 15078-01-0; Fe(CO)₃(PEt₃)₂, 18533-29-4; Fe₂Pt(CO)₉(PEt₃), 120711-65-1; Fe₂Pt(CO)₈(PEt₃)₂, 120711-64-0.

Supplementary Material Available: Figure SI, showing a perspective view of FePt₅(CO)₉(PEt₃)₄ **(1)** with the complete numbering scheme, Tables SI–SV, listing crystal data and data collection parameters, fractional coordinates and hydrogen atom positions, anisotropic thermal parameters, complete bond distances and angles, and selected least-squares planes (17 pages); Table SVI, listing observed and calculated structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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

Synthesis and Characterization of [Pt₂(μ-S)(μ-dppm)(η¹-dppm)₂] (dppm = Ph₂PCH₂PPh₂) and Its Use in Formation of Tetranuclear Platinum Complexes with μ₄-S Ligands

Nasim Hadj-Bagheri and Richard J. Puddephatt*

The reaction of [Pt₂(μ-dppm)₃] with COS gave a new diplatinum(I) complex [Pt₂(μ-S)(μ-dppm)(η¹-dppm)₂] **(1)**, where dppm = Ph₂PCH₂PPh₂. Complex **1** was also prepared by reaction of [Pt₂Cl₂(μ-dppm)₂] with dppm and sodium sulfide or by reaction of [Pt₂(μ-dppm)₃] with sulfur, but lower yields were obtained by these methods. Complex **1** reacted slowly with air, by oxidation of the free phosphorus atoms, to give [Pt₂(μ-S)(μ-dppm)(Ph₂PCH₂P(O)Ph₂)₂] and with [Pt₂Me₄(μ-SMe₂)₂] or [PtPh₂(SMe₂)₂] to give [Pt₄(μ₄-S)R₄(μ-dppm)₃], where R = Me or Ph, respectively. In the latter reaction, complex **1** acts as an 8-electron bis(bidentate) ligand, using the free phosphorus atoms of the η¹-dppm ligands and both lone pairs of the Pt₂(μ-S) group of **1** as donors, and the products are the first platinum complexes with the μ₄-S ligand. These complexes were characterized by multinuclear NMR spectroscopy.

Introduction

In 1967 Baird and Wilkinson reported the reaction of [Pt-(PPh₃)₃] with carbonyl sulfide, COS, to form the carbonyl sulfide complex [Pt(PPh₃)₂(COS)], which was converted to a binuclear species, characterized soon afterwards as the diplatinum(I) complex [Pt₂(μ-S)(CO)(PPh₃)₃] having a Pt–Pt bond.[1,2] In 1981, Balch and co-workers analyzed the complex ³¹P{¹H} NMR spectrum of this binuclear complex and studied its reactivity. It was shown that the Pt₂S core in this binuclear Pt(I) complex is unreactive toward insertion of small molecules such as carbon monoxide, isocyanides, and acetylenes, but substitution reactions were observed to proceed readily at the positions trans to the sulfur bridge. In this way, a Ph₂PCH₂PPh₂, dppm, derivative was prepared (eq 1).[3]

(1)
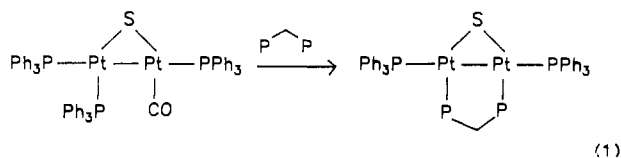
Several related complexes have been prepared, and it is clear that the μ₂-S group is effective in stabilizing the Pt(I) oxidation state.[1-11] This paper reports details of the synthesis and char-

acterization of a new useful derivative [Pt₂(μ-S)(μ-dppm)(η¹-dppm)₂] **(1)**. A preliminary account of parts of this work has been published.[12]

Results and Discussion

Synthesis of [Pt₂(μ-S)(μ-dppm)(η¹-dppm)₂] (1). When carbonyl sulfide was bubbled through a deep red solution of [Pt₂(μ-dppm)₃] **(2)** in toluene at −50 °C, a reaction occurred (eq 2) as indicated

(2)
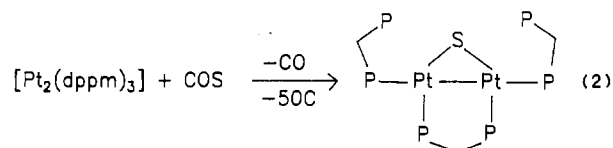
by the color change of the solution to light orange and then yellow as the solution was allowed to warm to room temperature. Complex **1** was isolated as a stable yellow microcrystalline solid in good yield, and though this was usually unnecessary, it could

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