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Synthesis and Coordination Properties with Copper(I) Triflate of 1,1'-Dimethyl-*P*-phenyl-2,2'-bis(ferrocenylmethylene)phosphonothioic Dihydrazide

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Introduction

The synthesis of redox-active macrocycles receptor molecules in which a redox center is in close proximity to a host binding site is actually an increasing field of activity.[1] These macrocycles can electrochemically recognize cationic and anionic guest species;[2] moreover, the binding constant of the macrocycle toward guest species can be modified by oxidation or reduction of the redox-active center of the macrocycle.[1]

Recently, one of us has shown that phosphohydrazides RP(X)(N(CH$_3$)NH$_2$)$_2$ (**1**; X = O, S) are well adapted to build up phosphorus-containing organic macrocycles by condensation with various functionalized aldehydes.[3] It was tempting to extend this study to aldehydes containing redox active centers. To check the feasibility of the synthesis of such types of macrocycles, we have, in a first approach, studied the condensation of **1a** (R = Ph, X = S) with ferrocenecarboxaldehyde. In this paper, we report the high-yield synthesis of the expected 1,1'-dimethyl-*P*-phenyl-2,2'-bis(ferrocenylmethylene)phosphonothioic dihydrazide (**2**) and the study of its complexing properties with copper(I) triflate. From this study a dinuclear copper complex (**3**) has been isolated and fully characterized by an X-ray structure determination.

Results and Discussion

The phenylphosphonothioic dihydrazide PhP(S)(N(CH$_3$)NH$_2$)$_2$ (**1a**) reacts smoothly with 2 equiv of ferrocenecarboxaldehyde (FcCHO) in ethanol at room temperature to give an orange solid, **2**, which has been isolated in a 87% yield after purification. Analytical and NMR data (see Experimental Section) are consistent with the SP(C$_6$H$_5$)(N(CH$_3$)NCHFc)$_2$ formulation for **2**.

To have some insight into the bonding properties of **2**, its reactivity toward copper(I) triflate has been investigated. This metal has been selected as it shows good bonding capability with either tertiary phosphine chalcogenides[4] or imine ligands.[5]

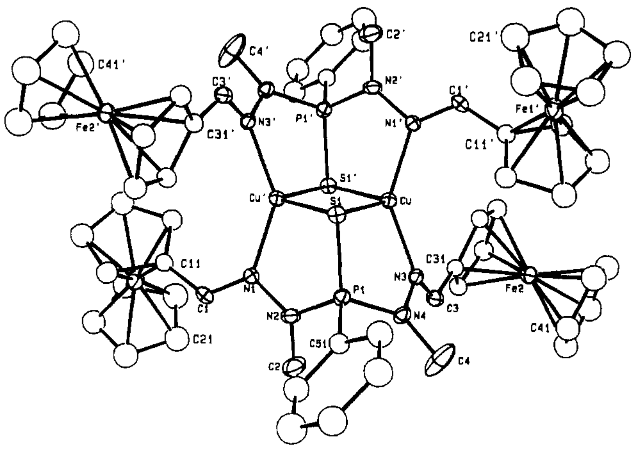

Figure 1. Perspective view of the cationic part of the complex [(C$_6$H$_5$P(S)(N(CH$_3$)N=CHC$_5$H$_4$FeC$_5$H$_5$)$_2$)Cu]$_2$[CF$_3$SO$_3$]$_2$ (**3**). Vibrational ellipsoids are drawn at the 30% probability level.

Table I. Selected Bond Distances (Å) and Bond Angles (deg), with Esd's in Parentheses, for Compound **3**

	Bond Distances		
Cu–S(1)	2.408 (3)	N(2)–C(2)	1.44 (1)
Cu–S(1)'	2.449 (3)	N(3)–N(4)	1.45 (1)
Cu–N(1)'	1.997 (9)	N(3)–C(3)	1.27 (1)
Cu–N(3)	1.997 (9)	C(1)–C(11)	1.44 (1)
S(1)–P(1)	1.979 (4)	C(3)–C(31)	1.45 (1)
P(1)–N(2)	1.654 (7)	Cu–Cu'	2.727 (2)
P(1)–N(4)	1.663 (7)		
P(1)–C(51)	1.77 (1)		
N(1)–N(2)	1.42 (1)		
N(1)–C(1)	1.28 (1)		
	Bond Angles		
S(1)–Cu–S(1)'	111.69 (8)	Cu'–N(1)–N(2)	115.8 (5)
S(1)–Cu–N(1)'	110.1 (2)	Cu'–N(1)–C(1)	128.6 (8)
S(1)–Cu–N(3)	95.8 (3)		
S(1)'–Cu–N(1)'	89.0 (2)	N(2)–N(1)–C(1)	115.7 (9)
S(1)'–Cu–N(3)	107.8 (2)	P(1)–N(2)–N(1)	119.7 (6)
N(1)'–Cu–N(3)	141.5 (3)	P(1)–N(2)–C(2)	121.8 (8)
Cu–S(1)–Cu'	68.31 (8)	N(1)–N(2)–C(2)	117.1 (8)
Cu–S(1)–P(1)	87.6 (1)	Cu–N(3)–N(4)	114.9 (5)
Cu'–S(1)–P(1)	92.9 (1)	Cu–N(3)–C(3)	128.9 (9)
S(1)–P(1)–N(2)	111.2 (4)	N(4)–N(3)–C(3)	115.0 (9)
S(1)–P(1)–N(4)	113.3 (4)	P(1)–N(4)–N(3)	113.0 (7)
S(1)–P(1)–C(51)	112.0 (3)	P(1)–N(4)–C(4)	128.2 (9)
N(2)–P(1)–N(4)	106.9 (4)	N(3)–N(4)–C(4)	118.7 (9)
N(2)–P(1)–C(51)	108.7 (4)	N(4)–P(1)–C(51)	104.4 (5)

In THF, **2** reacts with 1 equiv of Cu(CF$_3$SO$_3$)·0.5C$_6$H$_6$ to give an orange solid **3**, which analyzed as [(**2**)CuCF$_3$SO$_3$]·1.5THF. The ^{31}P NMR spectrum of **3** shows only one signal at 72.4 ppm. Compared to **2** the small shift to higher field observed ($\Delta\delta$ = 5.5 ppm) suggests that the sulfur atom of the PS group is coordinated. ^{1}H NMR data show that the imino part of **2** is complexed, as the N=CH resonance moves from 7.36 to 8.64 ppm. More generally, a deshielding is observed for all the resonances in **3** compared to **2** (see Experimental Section). Four signals are observed for the hydrogen on the substituted cyclopentadienyl rings.

Careful comparison of the infrared spectra of **2** and **3** in the solid state shows a slight decrease (11 cm^{-1}) of the ν_{CN} stretching vibration and the disappearance of the absorption attributed to the $\nu_{P=S}$ at 731 cm^{-1} in **2**. Even though the absorption of the P=S bond in **3** could not be clearly detected, this result implies that this group is certainly coordinated to a copper atom.[4]

The structure of **3** has been established by an X-ray diffraction study. A perspective view of the cationic part of **3** is shown in Figure 1, along with the labeling scheme. Bond lengths and bond angles of interest are gathered in Table I.

Complex **3** consists of a dinuclear copper unit bridged by two ligands **2**. The molecule processes an inversion center, which is the middle of the Cu–Cu' vector. Each ligand is coordinated via the two nitrogen atoms of the imino groups to two different copper atoms (Cu'–N(1) = 1.997 (9) Å; Cu–N(3) = 1.997 (9) Å), and via the sulfur atom that bridges the Cu–Cu' vector (Cu–S(1) =

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2.408 (3) Å; Cu–S(1)′ = 2.449 (3) Å), as was suggested by the IR data. The two copper atoms are at a nonbonding distance (Cu–Cu′ = 2.727 (2) Å).[6] The copper atoms thus display a distorted tetrahedral environment. Of interest is the quite unusual "sofa"-like structure of this complex with the Cu–S(1)′–Cu′–N(3)′–P(1)′–N(2)′–N(1)′ part as the back, the Cu–S(1)–Cu′–S(1)′ part as the seat and the Cu–N(3)–N(4)–P(1)–N(2)–N(1)–Cu′–S(1) moieties as the fore part! Considering the ligand modifications induced by complexation, comparison with the structure of the closely related free ligand $SP(N(CH_3)NCH(C_6H_4\text{-}2\text{-}OH))_3$[7] (**4**) shows that the geometry around phosphorus is not significantly modified (mean internal angle of 106.9° in **3** and 105.4° in **4**). Complexation of the nitrogen of the imino group does not induce significant changes in the CN bond lengths (C(1)–N(1) = 1.28 (1) Å and C(3)–N(3) = 1.27 (1) Å, compared to 1.285 (4) Å in **4**). The most important change concerns, as was expected, the PS bond: a lengthening from 1.921 (1) Å in **4** to 1.979 (4) Å in **3** is observed due to the bridging mode of bonding of the sulfur atom. Indeed, in the case of the related phenyl bis(*N*,*N*′-dimethylhydrazido)thiophosphate–Cd^{II} complex, in which the sulfur atom is terminally bonded to the metal, the P–S bond length is only 1.957 (2) Å.[8] The same phenomenom was also observed for *cyclo*-tris(*μ*-trimethylthiophosphane)tris(chlorocopper(I)), $[(Me_3PS)CuCl]_3$,[6] in which the sulfur atom bridges two copper atoms: the P–S bond lengthening from the free thiophosphane to the complexed phosphine is 0.066 (2) Å.[9]

To summarize, this structure shows that the ligand **2** has good bonding capacities since the imino functions are implicated and the sulfur atom acts as a bridging ligand.

The cyclic voltammogram of compound **2** shows a reversible oxidation peak at +0.34 V vs SCE (at 0.1 V s^{-1} rate, $\Delta E_p = E_{pa} - E_{pc} = 87$ mV, and $I_{pc}/I_{pa} = 1$). This peak is attributable to the oxidation of the ferrocene part of the molecule as, under the same conditions, ferrocene has a reversible oxidation peak at +0.32 V vs SCE. Moreover the closely related $PhP(S)(NMeN{=}CHPh)_2$ ligand is not electroactive in the same area.

Potential-controlled coulometry indicates that two electrons (n_{exp} = 1.91 e) are exchanged during the oxidation. This result shows that the two redox centers are independent, contrary to some other biferrocene molecules in which the bridging ligands allow some degree of interaction between ferrocenyl centers.[10,11] Electrochemical reduction regenerates **2** (n_{exp} = 1.88 e).

In the 0–1600-mV region, moving to anodic potential, the complex **3** shows an oxidation peak at +0.54 V vs SCE which is attributed to the ferrocene part of the molecule; we did not observed a well-defined wave which could be due to the Cu^I → Cu^{II} oxidation step. Nevertheless, if one moves back to cathodic potential, a reduction peak corresponding to the ferrocene part of the molecule is observed at ≈0.49 V vs SCE, and another largest peak is detected at 0.36 V vs SCE. This last peak is attributed to a redissolution of a deposit on the electrodes produced as the scan toward more anodic potential takes place. This is corroborated by limiting the scanning to the 0–650-mV scale: in this case only a quasireversible oxidation peak is observed centered at 0.53 V vs SCE at 0.1 V/s rate (ΔE_p = 39 mV and I_{pc}/I_{pa} = 0.7). (ΔE_p increases to 92 mV by increasing the scan rate to 3V/s). Comparison with compound **2** shows, as expected, that complexation has induced a 0.2-V shift of the oxidation potential of the ferrocene part of the molecule toward a more anodic value.

Table II. Crystallographic Data for the Compound $[[(CpFe(C_5H_4CHNN(Me)))_2P(S)(Ph)]Cu]_2[CF_3SO_3]_2\cdot EtOH$ (**3**·EtOH)

chem formula: $C_{32}H_{34}CuF_3Fe_2O_{3.5}PS_2$
a = 12.381 (3) Å
b = 14.029 (1) Å
c = 12.232 (2) Å
α = 106.24 (1)°
β = 117.66 (1)°
γ = 78.53 (1)°
V = 1800 Å^3
Z = 2
R (on F_o, $F_o^2 > 3\sigma(F_o^2))^b$ = 0.066
R_w (on F_o, $F_o^2 > 3\sigma(F_o^2))^c$ = 0.071

fw = 769.90
space group: C_i^1-$P\bar{1}$
t = 22 °C
$\lambda(\text{Mo K}\alpha_1)$ = 0.7093 Å
ρ_{calcd} = 1.420 g·cm^{-3}
μ = 15.3 cm^{-1}
transm coeff^a = 0.89–0.99

[a] Ψ-scan method. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$, unit weights.

Potential-controlled coulometry at 0.7 V indicates that four electrons (n_{exp} = 4.2 e) are exchanged during the oxidation step, in agreement with the oxidation of the four ferrocene parts of the molecule. In the linear voltammetry, after electrolysis, a new cathodic wave was observed at $E_{1/2}$ = 0.35 V, suggesting a transformation of **3**.

To conclude, 1,1′-dimethyl-*P*-phenyl-2,2′-bis(ferrocenylmethylene)phosphonothioic dihydrazide, first example of a derivative possessing ferrocenyl, hydrazone, and thiophosphanyl moieties, shows a remarkable ability to give a chelated dicopper complex. Extension to other type of complexations is underway.

Experimental Section

All the syntheses have been performed under nitrogen using standard Schlenk tube techniques. ^{1}H and ^{13}C NMR spectra have been done on a Bruker AC200 spectrometer, and the ^{31}P spectra were obtained on a Bruker AC80 instrument ^{1}H and ^{13}C NMR spectra are referenced to external tetramethylsilane. ^{31}P NMR spectra are referenced to external 85% H_3PO_4. IR spectra have been performed on a Perkin-Elmer 983 instrument in KBr pellets. Microanalysis have been obtained from the Centre de Microanalyse du CNRS. $PhP(S)(NMeNH_2)_2$ has been prepared by a published procedure.[12]

Synthesis of $PhP(S)(NMeNCHC_5H_4FeC_5H_5)_2$ (2). A mixture of 2.24 g of $CpFeC_5H_4CHO$ (10.46 mmol) and 1.22 g of $PhP(S)(NMeNH_2)_2$ (5.3 mmol) in 120 mL of ethanol was stirred under nitrogen for 16 h. An orange precipitate slowly appeared. This precipitate was filtered off and washed with 40 mL of ethanol and 60 mL of pentane and then dried under vacuo to give **2** in 87.5% yield. Anal. Calcd for $C_{30}H_{31}N_4SPFe_2$: C, 57.91; H, 4.99; N, 9.01; P, 4.98; S, 5.15; Fe, 17.97. Found: C, 57.67; H, 4.95; N, 9.0; P, 4.95; S, 5.89; Fe, 17.81. ^{1}H NMR ($CDCl_3$); δ; [8.13 (m), 7.48 (m)] (5 H, C_6H_5); 7.36 (s, 1 H, CHN); [4.17 (m), 4.38 (m)] (4 H, C_5H_4); 4.01 (s, 5 H, C_5H_5); 3.16 (d, 3 H, J = 10 Hz, NCH_3). ^{31}P NMR (C_6D_6), δ: 77.9 ppm. ^{13}C NMR ($CDCl_3$) δ: 137.3 (dd, J_{PC} = 13.5 Hz, J_{CH} = 148 Hz, CH=N); [133.6 (dd, J_{PC} = 10.1 Hz, J_{CH} = 161 Hz), 131 (d, J_{PC} = 135 Hz), 131.4 (dd, J_{PC} = 2.5 Hz, J_{CH} = 162 Hz), 127.2 (dd, J_{PC} = 14.5 Hz, J_{CH} = 160 Hz)] (C_6H_5P); [81.3 (s), 67.3 (d, J_{CH} = 176 Hz), 67.3 (d, J_{CH} = 177 Hz), 66.9 (d, J_{CH} = 177 Hz)] (C_5H_5 and C_5H_4); 31.2 (dq, J_{PC} = 9 Hz, J_{CH} = 138 Hz, $N(CH_3)$).

Synthesis of 3. A 0.280-g (0.45 mmol) sample of **2** was dissolved in 20 mL of THF and added to a suspension of 0.113 g (0.45 mmol) of $Cu(CF_3SO_3)\cdot 0.5C_6H_6$ in 10 mL of THF. An orange precipitate rapidly formed. After 3 h of stirring, the precipitate was filtered, washed with 30 mL of Et_2O, and then dried under vacuum. **3** was isolated in 78% yield as a red powder. Anal. Calcd for **3**·1.5THF, $C_{37}H_{43}F_3N_4O_{4.5}S_2PCuFe$: C, 47.11; H, 4.56; N, 5.94. Found: C, 46.71; H, 4.36; N, 5.92. ^{1}H NMR ($CDCl_3$), δ: 8.64 (CH=N); [8.17 (m), 7.73 (m)] (5 H, C_6H_5); [5.14 (m) 4.91 (m), 4.58 (m), 4.54 (m)] (4 H, C_5H_4); 4.20 (s, 5 H, C_5H_5); 3.23 (d, 3 H, J = 11 Hz, NCH_3). ^{31}P NMR ($CDCl_3$), δ: 72.4 ppm.

Electrochemical Studies. Electrochemical studies have been done in 0.1 M dichloromethane solutions of Bu_4NPF_6 containing the sample to be studied at 10^{-3} M concentration for **2** and 5×10^{-4} for **3**, with a homemade potentiostat controlled by an Apple IIe microcomputer.[13] For cyclic voltammetry, the working electrode was a Pt disk (area: 3.14 mm^2), and the auxiliary electrode was a Pt wire. Electrolyses have been performed with a Pt gauze as working electrode. Dichloromethane was purified just before use by passing through an alumina column and degassed by bubbling argon during the experiments.

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Table III. Fractional Atomic Coordinates with Esd's in Parentheses

atom	x/a	y/b	z/c
Cu	0.4828 (1)	0.59922 (8)	0.5466 (1)
Fe(1)	0.3235 (2)	0.1584 (1)	0.0529 (1)
Fe(2)	0.2021 (1)	0.9003 (1)	0.4295 (1)
S(1)	0.6773 (2)	0.5173 (2)	0.5592 (2)
P(1)	0.6370 (2)	0.5572 (2)	0.4007 (2)
N(1)	0.5271 (6)	0.3884 (5)	0.2915 (6)
N(2)	0.5547 (7)	0.4754 (6)	0.2754 (7)
N(3)	0.4584 (7)	0.6798 (5)	0.4246 (7)
N(4)	0.5578 (7)	0.6675 (5)	0.3895 (7)
C(1)	0.5136 (8)	0.3116 (7)	0.2010 (8)
C(2)	0.487 (1)	0.4993 (9)	0.152 (1)
C(3)	0.3615 (9)	0.7264 (7)	0.3581 (9)
C(4)	0.581 (1)	0.748 (1)	0.358 (2)
C(11)	0.4744 (7)	0.2209 (5)	0.1986 (7)
C(12)	0.3919 (7)	0.2093 (5)	0.2438 (7)
C(13)	0.3736 (7)	0.1064 (5)	0.2115 (7)
C(14)	0.4448 (7)	0.0545 (5)	0.1462 (7)
C(15)	0.5070 (7)	0.1252 (5)	0.1383 (7)
C(21)	0.2320 (9)	0.2548 (6)	−0.0665 (9)
C(22)	0.2790 (9)	0.1677 (6)	−0.1285 (9)
C(23)	0.2286 (9)	0.0846 (6)	−0.1299 (9)
C(24)	0.1505 (9)	0.1204 (6)	−0.0688 (9)
C(25)	0.1526 (9)	0.2255 (6)	−0.0296 (9)
C(31)	0.2585 (5)	0.7551 (5)	0.3894 (5)
C(32)	0.2609 (5)	0.7802 (5)	0.5113 (5)
C(33)	0.1405 (5)	0.8152 (5)	0.4977 (5)
C(34)	0.0636 (5)	0.8117 (5)	0.3674 (5)
C(35)	0.1365 (5)	0.7746 (5)	0.3005 (5)
C(41)	0.3160 (8)	0.9825 (7)	0.4214 (9)
C(42)	0.3155 (8)	1.0107 (7)	0.5421 (9)
C(43)	0.1938 (8)	1.0443 (7)	0.5246 (9)
C(44)	0.1189 (8)	1.0368 (7)	0.3932 (9)
C(45)	0.1945 (8)	0.9986 (7)	0.3293 (9)
C(51)	0.7704 (7)	0.5703 (5)	0.3883 (6)
C(52)	0.7905 (7)	0.5179 (5)	0.2834 (6)
C(53)	0.8979 (7)	0.5267 (5)	0.2776 (6)
C(54)	0.9851 (7)	0.5880 (5)	0.3768 (6)
C(55)	0.9650 (7)	0.6404 (5)	0.4817 (6)
C(56)	0.8576 (7)	0.6316 (5)	0.4874 (6)
S(2)	0.2668 (4)	0.7593 (4)	0.0049 (4)
C(5)	0.144 (1)	0.802 (1)	−0.111 (1)
O(1)	0.331 (1)	0.8384 (7)	0.104 (1)
O(2)	0.344 (1)	0.6825 (9)	−0.035 (1)
O(3)	0.201 (2)	0.716 (1)	0.047 (2)
F(1)	0.070 (1)	0.733 (1)	−0.197 (1)
F(2)	0.075 (1)	0.874 (1)	−0.071 (2)
F(3)	0.189 (2)	0.840 (2)	−0.169 (2)
C(s)	0.051 (2)	0.512 (2)	0.060 (2)
O(s)	0.177 (3)	0.516 (2)	0.072 (3)

Crystallographic Studies. Crystals of **3** suitable for X-ray diffraction were obtained at room temperature from a saturated ethanol solution. Data were collected on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range $24° < 2\theta(\text{Mo K}\alpha_1) < 28°$. The space group was determined by careful examination of systematic extinctions in the listing of the measured reflections. Data reductions were carried out using the SDP crystallographic computing package.[14] Table II presents further crystallographic information.

The structure was solved and refined using a combination of the SDP crystallographic computing package[14] and the SHELX-76 package.[15] The position of Fe, S, and P atoms was determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. The compound crystallizes with half a molecule of ethanol per unit cell. The CF_3SO_3 group was found to be highly disordered. No splitting model was successful. We finally constrained the C–F, S–O, F–F, and O–O bond lengths to 1.33, 1.43, 2.16, and 2.33 Å, respectively, and we took the high anisotropic values, since the rest of the structure refined nicely. Atomic scattering factors were taken from the usual tabulations.[16] Anomalous dispersion terms for Fe, S, and P atoms were included in F_c.[17] An empirical absorption correction was applied.[18] The final refinements were conducted using the SHELX-76 program. All non-hydrogen atoms were allowed to vibrate anisotropically, except carbon atoms of the phenyl and cyclopentadienyl rings which were refined as isotropic rigid groups in order to reduce the number of variable parameters (C_6H_5 ring, C–C = 1.395 Å; C_5H_5 and C_5H_4 rings, C–C = 1.420 Å). Hydrogen atoms were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart et al.[19]

Final atomic coordinates for non-hydrogen atoms are given in Table III. Structure amplitudes ($10|F_o|$ vs $10|F_c|$) are available as Table S1.[20] Table S2 lists the anisotropic thermal parameters (×100).[20] Table S3 lists the isotropic thermal parameters (×100).[20]

Acknowledgment. We thank Dr. D. de Montauzon for electrochemical measurements and for fruitful discussions.

Supplementary Material Available: Table S2, giving anisotropic thermal parameters for compound **3**, and Table S3, giving isotropic thermal parameters for compound **3** (2 pages); Table S1, listing structure factor amplitudes (×10) for compound **3** (18 pages). Ordering information is given on any current masthead page.

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Mixed Platinum–Rhodium Carbonyl Clusters. The Isolation of $[Pt_4Rh_{18}(CO)_{35}]^{4-}$, an Example of a Cherry-like Cluster with a Semiexposed Tetraplatinum Core

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Our previous studies of Pt–Rh mixed clusters led to the isolation of several carbonyl anions[2-7] which contain platinum as the minor component of the metal skeleton. Partitioning these species into classes according to the size, we have the small clusters such as $[PtRh_4(CO)_{14}]^{2-}$,[2,3] $[PtRh_4(CO)_{12}]^{2-}$,[2,3] $[PtRh_5(CO)_{15}]^{-}$,[2] and $[PtRh_6(CO)_{16}]^{2-}$,[4] whose structures consist of simple polyhedra where the Pt atom has a metallic connectivity of 3 or 4. With the species of intermediate size, such as $[PtRh_8(CO)_{19}]^{2-}$ [5] and $[Pt_2Rh_9(CO)_{22}]^{3-}$,[6] the tendency of the Pt atom(s) to occupy the

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