Scheme I

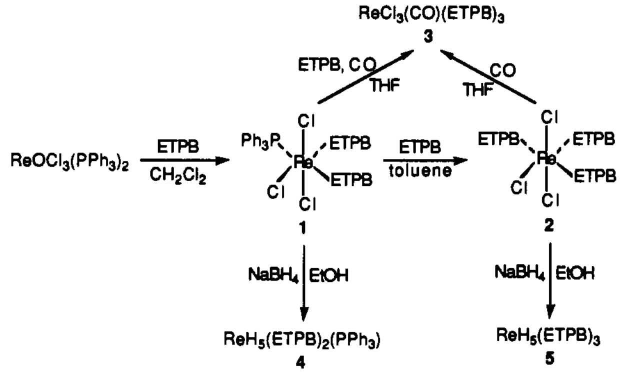

Table I. Variable-Temperature ^{1}H NMR T_1 Measurements on the Hydride Resonances of $\mathrm{ReH_5(ETPB)_2(PPh_3)}$ (**4**) and $\mathrm{ReH_5(ETPB)_3}$ (**5**) in $\mathrm{CD_2Cl_2}$ at 250 MHz

4		5	
temp, K	T_1, ms	temp, K	T_1, ms
213	87	180	140
217	81	190	100
223	78	194	92
228	77	200	84
233	78	207	86
243	86	210	94
250	93	215	96
256	102	220	105
263	113	227	122

2. This method might also be used to prepare other transition-metal polyhydride complexes supported by ETPB. The variable-temperature ^{1}H NMR spectra and T_1 data for **4** and **5** are consistent with classical structures containing no η^2-$\mathrm{H_2}$ ligands.

Experimental Section

General Procedures. All manipulations were performed under a dry $\mathrm{N_2}$ atmosphere by standard Schlenk-tube techniques. Diethyl ether, hexane, toluene, and tetrahydrofuran were distilled from $\mathrm{Na/Ph_2CO}$; dichloromethane was distilled from $\mathrm{CaH_2}$. All solvents were stored under $\mathrm{N_2}$ over 4-Å molecular sieves. $\mathrm{ReOCl_3(PPh_3)_2}$ was prepared according to the literature method.[6a]

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WM 250 or WM 500 spectrometer; ^{1}H and ^{13}C chemical shifts were measured with the residual solvent resonance as reference; ^{31}P chemical shifts were measured with external 85% $\mathrm{H_3PO_4}$ as reference. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. ^{1}H NMR T_1 measurements were carried out by the inversion-recovery method using a standard $180°-\tau-90°$ pulse sequence.

***mer*-*cis*-Trichlorobis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)(triphenylphosphine)rhenium(III) (1).** A mixture of $\mathrm{ReOCl_3(PPh_3)_2}$ (2.80 g, 3.36 mmol) and ETPB (1.63 g, 10.08 mmol) was stirred in $\mathrm{CH_2Cl_2}$ (40 mL) at room temperature for 24 h. The resulting orange solution was filtered through Celite to remove a small amount of an insoluble white solid, and the filtrate was concentrated to 5 mL in vacuo. Addition of $\mathrm{Et_2O}$ (60 mL) resulted in the precipitation of a yellow solid, which was filtered off, washed with $\mathrm{Et_2O}$ (4 × 10 mL), and dried in vacuo. Yield: 2.48 g, 84%. Anal. Calcd for $\mathrm{C_{30}H_{37}Cl_3O_6P_3Re}$: C, 40.99; H, 4.24. Found: C, 41.16; H, 4.29. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 14.50 (d, J = 7.3 Hz, 6 H, ortho H of Ph), 11.38 (s, 6 H, $\mathrm{OCH_2}$), 10.63 (s, 6 H, $\mathrm{OCH_2}$), 8.78 (t, J = 7.3 Hz, 6 H, meta H of Ph), 8.12 (t, J = 7.3 Hz, 3 H, para H of Ph), 4.19 (q, J = 7.8 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.78 (q, J = 7.8 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.08 (t, J = 7.8 Hz, 3 H, $\mathrm{CH_2C}H_3$), 2.73 (t, J = 7.8 Hz, 3 H, $\mathrm{CH_2C}H_3$).

***mer*-Trichlorotris(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhenium(III) (2).** *mer-cis*-$\mathrm{ReCl_3(ETPB)_2(PPh_3)}$ (**1**) (2.00 g, 2.27 mmol) was suspended in a solution of ETPB (0.405 g, 2.50 mmol) in toluene (75 mL), and the mixture was refluxed for 2.5 h. The solvent was removed and the residue extracted with $\mathrm{CH_2Cl_2}$ (4 × 10 mL). A small amount of insoluble impurity was filtered off, and the filtrate was concentrated to ca. 5 mL. Addition of $\mathrm{Et_2O}$ (60 mL) resulted in the precipitation of a greenish yellow solid, which was filtered off, washed with $\mathrm{Et_2O}$ (4 × 10 mL), and dried in vacuo. Yield: 1.40 g, 78%. Anal. Calcd for $\mathrm{C_{18}H_{33}Cl_3O_9P_3Re}$: C, 27.76; H, 4.27. Found: C, 28.01; H, 4.34. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 11.27 (s, 12 H, $\mathrm{OCH_2}$), 10.62 (s, 6 H, $\mathrm{OCH_2}$), 4.31 (q, J = 7.5 Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.70 (q, J = 7.5 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.11 (t, J = 7.5 Hz, 6 H, $\mathrm{CH_2C}H_3$), 2.71 (t, J = 7.5 Hz, 3 H, $\mathrm{CH_2C}H_3$).

***mer*-Trichlorocarbonyltris(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhenium(III) (3). Method 1.** A stream of CO was bubbled for 1 h through a boiling suspension of *mer*-$\mathrm{ReCl_3(ETPB)_3}$ (**2**) (0.40 g, 0.51 mmol) in THF (40 mL). The solvent volume was reduced to ca. 3 mL in vacuo and $\mathrm{Et_2O}$ (40 mL) added. The resulting cream-colored solid was filtered off, washed with $\mathrm{Et_2O}$ (4 × 10 mL), and dried in vacuo. Yield: 0.34 g, 81%. Anal. Calcd for $\mathrm{C_{19}H_{33}Cl_3O_{10}P_3Re}$: C, 28.28; H, 4.12. Found: C, 28.43; H, 4.17. IR (Nujol): ν_{CO} 1952 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 4.40 (br s, 18 H, $\mathrm{OCH_2}$), 1.26 (q, J = 7.6 Hz, 6 H, $\mathrm{C}H_2\mathrm{CH_3}$), 0.83 (t, J = 7.6 Hz, 9 H, $\mathrm{CH_2C}H_3$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 81.4. Off-resonance ^{1}H-decoupled ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 220.0 (q, $^2J_{\mathrm{PC}}$ = 51.3 Hz, 1 C, CO), 76.1 (t, 9 C, $\mathrm{OCH_2}$), 35.2 (c, 3 C, $\mathrm{OCH_2}C$), 22.8 (t, 3 C, $C\mathrm{H_2CH_3}$), 6.4 (q, 3 C, $\mathrm{CH_2}C\mathrm{H_3}$).

Method 2. A stream of CO was bubbled for 1.5 h through a boiling suspension of *mer-cis*-$\mathrm{ReCl_3(ETPB)_2(PPh_3)}$ (**1**) (0.40 g, 0.46 mmol) and ETPB (0.089 g, 0.55 mmol) in THF (40 mL). The solvent was evaporated to ca. 3 mL and $\mathrm{Et_2O}$ (40 mL) added. The resulting cream-colored solid was filtered off, washed with $\mathrm{Et_2O}$ (4 × 10 mL), and dried in vacuo. Yield: 0.31 g, 85%.

Pentahydridobis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)(triphenylphosphine)rhenium(V) (4). A suspension of *mer-cis*-$\mathrm{ReCl_3(ETPB)_2(PPh_3)}$ (**1**) (0.40 g, 0.46 mmol) and $\mathrm{NaBH_4}$ (0.35 g, 9.2 mmol) in EtOH (25 mL) was heated at reflux for 20 min. After removal of the solvent in vacuo, the residue was extracted with $\mathrm{CH_2Cl_2}$ (4 × 10 mL), and the extract was filtered through Celite. The yellow filtrate was concentrated to ca. 2 mL in vacuo. Addition of hexane (40 mL) resulted in the precipitation of an off-white solid, which was filtered off, washed with hexane (4 × 10 mL), and dried in vacuo. Yield: 0.23 g, 65%. Anal. Calcd for $\mathrm{C_{30}H_{42}O_6P_3Re}$: C, 46.32; H, 5.44. Found: C, 46.18; H, 5.39. IR (Nujol): $\nu_{\mathrm{Re-H}}$ 1988, 1946, 1891 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 7.3–7.6 (c, 15 H, Ph), 3.99 (virtual t, $^3J_{\mathrm{PH}}$ = 4.4 Hz, 12 H, $\mathrm{OCH_2}$), 1.07 (q, J = 7.5 Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_3}$), 0.73 (t, J = 7.5 Hz, 6 H, $\mathrm{CH_2C}H_3$), −6.93 (q, $^2J_{\mathrm{PH}}$ = 16.4 Hz, 5 H, Re–H). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 116.7 (d, $^2J_{\mathrm{PP}}$ = 56.0 Hz, 2 P, ETPB), 31.0 (t, $^2J_{\mathrm{PP}}$ = 56.0 Hz, 1 P, $\mathrm{PPh_3}$). Off-resonance ^{1}H-decoupled ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 139.8 (d, $^1J_{\mathrm{PC}}$ = 48.1 Hz, 3 C, C1 of $\mathrm{PPh_3}$), 134.3 (dd, $^2J_{\mathrm{PC}}$ = 11.1 Hz, 6 C, C2 of $\mathrm{PPh_3}$), 129.4 (s, 3 C, C4 of $\mathrm{PPh_3}$), 127.6 (d, $^3J_{\mathrm{PC}}$ = 11.1 Hz, 6 C, C3 of $\mathrm{PPh_3}$), 74.1 (t, 6 C, $\mathrm{OCH_2}$), 34.2 (c, 2 C, $\mathrm{OCH_2C}$), 24.2 (t, 2 C, $C\mathrm{H_2CH_3}$), 7.1 (q, 2 C, $\mathrm{CH_2}C\mathrm{H_3}$).

Pentahydridotris(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhenium(V) (5). A suspension of *mer*-$\mathrm{ReCl_3(ETPB)_3}$ (**1**) (0.40 g, 0.51 mmol) and $\mathrm{NaBH_4}$ (0.39 g, 10.3 mmol) in EtOH (25 mL) was heated at reflux for 20 min. After removal of the solvent in vacuo, the residue was extracted with benzene (4 × 15 mL), and the extract was filtered through Celite. The pale yellow filtrate was concentrated to ca. 1 mL in vacuo. Addition of $\mathrm{Et_2O}$ (40 mL) resulted in the precipitation of a white solid, which was filtered off, washed with $\mathrm{Et_2O}$ (4 × 10 mL), and dried in vacuo. Yield: 0.12 g, 35%. Anal. Calcd for $\mathrm{C_{18}H_{38}O_9P_3Re}$: C, 31.91; H, 5.65. Found: C, 32.04; H, 5.72. IR (Nujol): $\nu_{\mathrm{Re-H}}$ 1960, 1927, 1885 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 298 K): 4.13 (s, 18 H, $\mathrm{OCH_2}$), 1.14 (q, J = 7.6 Hz, 6 H, $\mathrm{C}H_2\mathrm{CH_3}$), 0.77 (t, J = 7.6 Hz, 9 H, $\mathrm{CH_2C}H_3$), −7.94 (q, $^2J_{\mathrm{PH}}$ = 16.3 Hz, 5 H, Re–H). Selectively hydride-coupled ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 298 K): δ 116.3 (sextet, $^2J_{\mathrm{PH}}$ = 15.6 Hz). Off-resonance ^{1}H-decoupled ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 298 K): 74.3 (t, 9 C, $\mathrm{OCH_2}$), 34.2 (virtual q, $^3J_{\mathrm{PC}}$ = 11.1 Hz, 3 C, $\mathrm{OCH_2}C$), 24.2 (t, 3 C, $C\mathrm{H_2CH_3}$), 7.1 (q, 3 C, $\mathrm{CH_2}C\mathrm{H_3}$).

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Structural and Spectroscopic Properties of the $[\mathrm{FeCl_2(Cat)}]_2^{2-}$ Anion

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Much of the bioinorganic chemistry of catechols has concerned complexes of iron. Tris(catecholato)iron(III) complexes are

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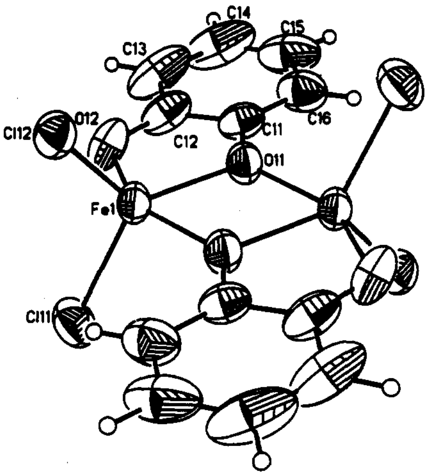

Figure 1. View showing the centrosymmetric $[Fe_2Cl_4(Cat)_2]^{2-}$ anion containing Fe1.

formed by the siderophore enterobactin.[2] Catechol oxidation carried out by the intra- and extradiol dioxygenase enzymes proceeds through an intermediate Fe(III) complex that contains a single chelated catecholate ligand.[3] DOPA-containing proteins including the marine adhesive proteins[4] and ferreascidin[5] have been found to sequester Fe(III) ions by chelation through DOPA catecholate functionalities. Much of the characterization of biological iron(III) catecholate complexes has relied upon spectroscopic data obtained on well-characterized synthetic complexes. Structural studies have been carried out on complexes containing one, two, or three catecholate ligands per iron. The bis(catecholato)iron(III) complexes have been found to have either simple monomeric structures[6,7] or a dimeric structure with catecholate ligands bridging adjacent metals through the electron pairs on one oxygen atom.[8] Complexes containing a single catecholate ligand have been characterized structurally for Fe(NTA)(DBCat)$^{2-}$ and Fe(BPG)(DBCat), where simple chelation was found to occur,[9] and Fe(SALEN)(HDBCat), where the catecholate is singly protonated and coordinated through only the deprotonated oxygen atom.[10]

Recent studies in our laboratory on the coordination of unsubstituted catechol with Fe(III) produced a species of stoichiometry $Fe(Cat)Cl_2^-$ isolated as the PPh_4^+ salt. Herein we describe the structural and spectroscopic properties of this complex.

Experimental Results

Structural characterization of the $Fe(Cat)Cl_2^-$ anion has shown that it is dimeric with the geometry shown in Figure 1. Two independent $[Fe_2(Cat)_2Cl_4]^{2-}$ dianions are located about inversion centers in the unit cell. The dianion containing Fe1, shown in Figure 1, is ordered; the other, containing Fe2, is disordered. Two sets of atoms for complex units approximately related by 2-fold rotation about the Fe2–Fe2′ vector were located. Occupancies are approximately 0.27 and 0.73 for the two sets of superimposed anion orientations. This disorder has limited the precision of the structure determination, but the features of $[Fe_2(Cat)_2Cl_4]^{2-}$ are clearly resolved for the anion containing Fe1. The Fe(III) cations are five-coordinate with distorted trigonal-bipyramidal geometries.

Table I. Selected Bond Distances and Angles for the $[Fe_2Cl_4(Cat)_2]^{2-}$ Anion Containing Fe1

	Distances (Å)		
Fe1–Cl11	2.266 (2)	Fe1–O12	1.919 (3)
Fe1–Cl12	2.259 (2)	O11–C11	1.354 (5)
Fe1–O11	2.029 (3)	O12–C12	1.328 (7)
Fe1–O11′	2.010 (3)	C11–C12	1.400 (7)
Fe1- -Fe1′	3.299 (1)	O11- -O11′	2.329 (6)
	Angles (deg)		
Cl11–Fe1–Cl12	109.8 (1)	O12–Fe1–Cl12	101.9 (1)
Cl11–Fe1–O11	128.0 (1)	O12–Fe1–O11′	149.3 (1)
Cl12–Fe1–O11	121.4 (1)	O11–Fe1–O11′	70.4 (1)
O11–Fe1–O12	79.1 (1)	O11′–Fe1–Cl11	96.3 (1)
Cl11–Fe1–O12	99.6 (1)	O11′–Fe1–Cl12	97.1 (1)
Fe1–O11–Fe1′	109.6 (1)		

Selected bond distances and angles are given in Table I. Chlorine atoms Cl1 and Cl2 in Figure 1 are located in the trigonal plane with bridging oxygen O11 also defining this plane. The axial O12–Fe1–O11′ bond angle is contracted to a value of 149.3 (1)° by the chelation constraints of the Cat ligands and by the repulsive separation of the iron atoms in the anion. Bond lengths involving the iron appear normal, and the ligand C–O lengths are typical of values found for catecholates. The imposed inversion symmetry requires that the $Fe_2(Cat)_2$ unit be rigorously planar. Within this plane the Fe1–O11 length of the chelate ring is found to be slightly longer than the Fe–O11′ length of the bridge.

The electronic spectrum of the dianion in the visible consists of a single broad transition at 584 nm (ϵ 4500 M^{-1} cm^{-1}). Electrochemically, the complex undergoes one irreversible reduction at the iron at −1.86 V (vs Fc/Fc^+) and two irreversible oxidations at −0.56 and 0.03 V corresponding to oxidations of the catecholate ligands.

Discussion

The structural features of the simple $Fe(Cat)Cl_2^-$ anion reveal that it exists as the five-coordinate $[Fe_2(Cat)_2Cl_4]^{2-}$ dimer shown in Figure 1. Bridging catecholate ligands have appeared previously in the structure of $[(CH_3COO)(Fe(Cat)_2)_2]^{3-}$ and for catecholate ligands of $Fe_4(DBSQ)_4(DBCat)_4$,[11] but this is the first such example found for an iron complex containing a single catecholate ligand per iron. The trigonal-bipyramidal geometry about the metal is similar to the $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$ anion,[12] although the axial bond angle is more contracted by the chelated Cat ligands. The low-energy charge-transfer band at 584 nm that is responsible for the dark blue color of the complex is not observed for the ethoxide-bridged dimer, and it is likely a LMCT transition associated with the catecholate ligands. Bands of this energy and intensity seem to appear commonly for bis(catecholato)iron(III) species,[7,8,13] but complexes containing a single chelated catecholate ligand characteristically show two transitions on the higher and lower energy sides of the 550–600-nm region.[9]

The Fe1- -Fe1′ contact of 3.299 (1) Å is not unusual for binuclear complexes of iron(III), but the O11- -O11′ separation of 2.329 (6) Å is somewhat surprising. This value is approximately 0.87 Å longer than twice the covalent radius of oxygen but 0.20 Å shorter than twice the ionic radius. The O- -O interaction across the planar Fe_2O_2 parallelogram appears to be nonbonding, and the short separation results from the strong repuslive interaction between iron centers. A similar O- -O contact appears to exist for the bridging alkoxide oxygen atoms of $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$.

Experimental Section

Preparation of $(PPh_4)_2[Fe_2Cl_4(Cat)_2]$. Anhydrous $FeCl_3$ (0.34 g, 2.1 mmol) and catechol (0.46 g, 4.2 mmol) were dissolved in 50 mL of methanol to give a dark green solution. Ethylamine (0.82 g) dissolved in 30 mL of methanol was slowly added to the solution. The color of the solution turned to a dark blue-purple. PPh_4Br (0.88 g, 2.1 mmol) dissolved in 20 mL of methanol was then added, and the volume of the

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(1) Visiting Scholar from Wuhan University, People's Rupublic of China.
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Table II. Crystallographic Data for $(PPh_4)_2[Fe_2Cl_4(Cat)_2]\cdot(CH_3)_2CO$

mol wt	1206.5	Z	2
cryst system	triclinic	D_{calcd}, g cm^{-3}	1.276
space group	$P\bar{1}$	D_{exptl}, g cm^{-3}	1.25
a, Å	11.490 (2)	μ, cm^{-1}	7.27
b, Å	12.676 (3)	T_{max}, T_{min}	0.837, 0.736
c, Å	22.087 (4)	radiation (λ, Å)	Mo Kα (0.71073)
α, deg	88.32 (3)	temp, K	296–298
β, deg	77.55 (3)	R, R_w	0.055, 0.072
γ, deg	88.7 (3)	GOF	1.30
V, Å^3	3139 (1)		

Table III. Atomic Coordinates ($\times10^4$) for the $[Fe_2Cl_4(Cat)_2]^{2-}$ Anion Containing Fe1

atom	x/a	y/b	z/b
Fe1	4165 (1)	1063 (1)	-59 (1)
Cl11	5029 (1)	2638 (1)	-26 (1)
Cl12	3290 (1)	1051 (1)	-882 (1)
O11	4334 (3)	-269 (2)	450 (1)
O12	2815 (3)	1224 (3)	618 (2)
C11	3486 (4)	-372 (4)	977 (2)
C12	2656 (4)	471 (5)	1057 (2)
C13	1724 (5)	451 (7)	1588 (3)
C14	1659 (6)	-361 (8)	2022 (3)
C15	2498 (7)	-1167 (6)	1934 (3)
C16	3415 (5)	-1183 (5)	1411 (3)

solution was reduced to approximately 25 mL and cooled to 0 °C. The dark blue precipitate was separated from the solution by filtration and recrystallized from acetone. Crystals of $(PPh_4)_2[Fe_2Cl_4(Cat)_2]$ obtained by this procedure as acetone solvates were suitable for crystallographic analysis.

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Cyclic voltammograms were obtained with a Cypress CYSY-1 computer-controlled electroanalysis system in CH_2Cl_2 solutions. A Ag/Ag$^+$ reference electrode was used, $(NBu_4)(PF_6)$ was used as the supporting electrolyte, and the Fc/Fc$^+$ couple was used as an internal standard.

Structure Determination of $(PPh_4)_2[Fe_2Cl_4(Cat)_2]\cdot(CH_3)_2CO$. Crystals of $(PPh_4)_2[Fe_2Cl_4(Cat)_2]$ were obtained by slow evaporation of an acetone solution of the complex as large dark blue parallelopipeds. Axial photographs indicated only triclinic symmetry, and the centered settings of 25 reflections in the 2θ range between 21 and 32° gave the unit cell dimensions listed in Table II. Data were collected by θ–2θ scans within the angular range 3.0–50.0°. The locations of the iron, chlorine, and phosphorus atoms and the phenyl rings of the two independent PPh_4^+ cations were determined by direct methods. A structure factor calculation carried out with these atoms revealed the positions of the atom of the catecholate ligand bonded to Fe1 and the two half-acetone solvate molecules. Refinement of the structure with all atoms except hydrogens and the catecholate ligand of Fe2 was carried out. Thermal parameters of Fe2 and the chlorine atoms bonded to Fe2, Cl21, and Cl22 were unusually large, and the pattern of peaks on a difference Fourier map revealed the disordered catecholate ligand. Two sets of catecholate atoms with occupancies of 0.27 and 0.73 were found to be approximately coplanar, indicating 2-fold disorder about an axis containing Fe2, the inversion center at $[^1/_2, ^1/_2, ^1/_2]$, and Fe2′ generated by the inversion center. Two fractional anions were constructed from the atom parameters of the ordered anion containing Fe1 and located about the inversion center at $[^1/_2, 0, 0]$. These atoms were included in the refinement with the catecholate phenyl ring of the fractional anion with occupancy 0.27 constrained with C–C lengths of 1.392 Å. Final cycles of refinement gave discrepancy indices of $R = 0.055$ and $R_w = 0.072$. Final positional and derived isotropic thermal parameters for the anion containing Fe1 are given in Table III. Tables containing full listings of atom positions, anisotropic thermal parameters, and hydrogen atom locations are available as supplementary material.

Acknowledgment. This research was supported by the National Science Foundation under grant CHE 88-09923.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, hydrogen atom locations, and bond distances and angles for $(PPh_4)_2[Fe_2Cl_4(Cat)_2]\cdot(CH_3)_2CO$ (16 pages); a table of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

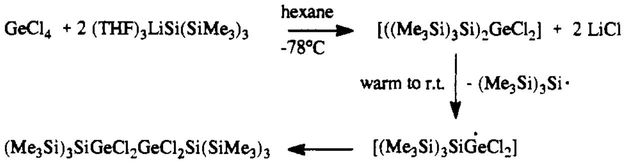
Additions and Corrections

1991, Volume 30

S. P. Mallela and R. A. Geanangel*: Preparation and Structural Characterization of New Derivatives of Digermane Bearing Tris(trimethylsilyl)silyl Substituents.

Page 1480. In the last sentence of the abstract, the formula should be $[(Me_3Si)_3SiGeR_2]_2$.

Page 1481. Scheme I should appear as follows:



$$\begin{tikzcd}
GeCl_4 + 2\,(THF)_3LiSi(SiMe_3)_3 \arrow[r, "hexane", "-78°C"'] & {[((Me_3Si)_3Si)_2GeCl_2] + 2\,LiCl} \arrow[d, "warm to r.t."', "- (Me_3Si)_3Si\cdot"] \\
(Me_3Si)_3SiGeCl_2GeCl_2Si(SiMe_3)_3 & {[(Me_3Si)_3Si\dot{Ge}Cl_2]} \arrow[l]
\end{tikzcd}$$

—R. A. Geanangel