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Manganese(II) and Iron(II) Derivatives of Tris-{(diphenylphosphino)dimethylsilyl}methane: Synthesis and Properties

Sushil K. Gupta and Anoop Kelkar

School of Studies in Chemistry, Jiwaji University, Gwalior-474 011, India

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ABSTRACT: *Treatment of anhydrous MCl_2 (M = Mn, Fe) with $(Ph_2PMe_2Si)_3CH$ in toluene at elevated temperature resulted in the isolation of colorless ($MnCl_2\{(Ph_2PMe_2Si)_3CH\}$) (**1**) and light yellow ($FeCl_2\{(Ph_2PMe_2Si)_3CH\}$) (**2**) in high yield. These paramagnetic complexes have been characterized by elemental analyses, magnetic moment, conductivity measurements, TGA, cyclic voltammetry, mass spectrometry, with IR, electronic, ESR and Mössbauer spectroscopy. The data suggest that complexes **1** and **2** have trigonal bipyramidal geometry around the metal atom with tridentate coordination of the ligand. The thermal stability of the Fe(II) complex **2** is greater than that of the Mn(II) compound **1**. Electrochemical studies of complex **1** and **2** using cyclic voltammetry indicate a quasi-reversible reduction ($E_{1/2}$ = ca. −1.08 V (**1**)) and an irreversible cathodic reduction (E_{pc}, ca. −1.55 V (**2**)) to Mn(0) and to Fe(0), respectively.*

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INTRODUCTION

In recent years, we have witnessed an increasing interest in the chemistry of bulky silyl-substituted ligands containing donor groups [1–3]. Numerous derivatives are made of s, p, and f block elements, but a few compounds of transition metals are known as yet. Very recently binuclear compounds of Mn and Co, viz. $[Mn(\mu\text{-Cl})\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$, $[Mn(THF)(\mu\text{-Cl})\{C(SiMe_3)_2(SiMe_2OMe)\}]_2$, $[Co(\mu\text{-Br})\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ [4] have been reported. The bidentate ligand $C(SiMe_3)_2(SiMe_2C_6H_5N\text{-}2)$ has also been shown to form a monomeric chromium, manganese, cobalt, nickel, and palladium derivatives [5,6]. King et al. have reported [7,8] the synthesis of the compounds $[M(CO)_4L]$ and $[M(CO)_3L]$ (where M = Cr, Mo; L=bis(2-diphenylphosphinoethyl)phenylphosphine), in which the ligand L is bidentate and tridentate, respectively. The compounds $[Co(OAc)L][BPh_4]$ and $[Fe(CH_3CN)_2L][BF_4]_2$, (where $L = HC(CH_2PPh_2)_3$) have been structurally characterized [9], and the ligand L has been shown to be tridentate. We have previously reported [10,11] the synthesis of tris{(diphenylphosphino)dimethylsilyl}methane, $[HC(PPh_2Me_2Si)_3]$, and its reaction with $M(CO)_6$ (where M = Cr, Mo, and W) to give $[M(CO)_3\{(Ph_2PMe_2Si)_3CH\}]$ (where M = Cr and W) [12] and *cis*-$[Mo(CO)_4\{(Ph_2PMe_2Si)_3CH\}]$ [10]. The tripodal ligand is bidentate toward molybdenum and tridentate toward chromium and tungsten. In the present study, we describe the ligating behavior of the tripodal ligand, $HC(SiMe_2PPh_2)_3$ toward manganese(II) and iron(II).

Dedicated to Professor Colin Eaborn, FRS, who passed away on 22 February 2004, aged 81.

Correspondence to: Sushil K. Gupta; e-mail: drskgchem@dataone.in and skggwr@hotmail.com.

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EXPERIMENTAL

All reactions were conducted under an argon atmosphere by the use of standard Schlenk techniques on a double manifold vacuum line. Solvents were purified by distillation from an appropriate drying agent (toluene and THF from potassium, hexane from Na/K alloy). $MnCl_2$ and $FeCl_2$ were obtained from Aldrich. The ligand was synthesized as reported earlier [10].

Physical Measurements

Melting points were recorded in capillary tubes and are uncorrected. Elemental analyses were performed with Carlo-Erba model DP 200 and ICP-AES instruments. The magnetic moment was measured on EG & G PARC model 155 vibrating sample magnetometer at room temperature. Thermogravimetric analysis was carried out on a DuPont TGA 2950 analyzer in the synthetic air atmosphere with a heating rate of 10°C/min. The molar conductance in 10^{-3} mol dm^{-3} DMF solution was measured using a Global DCM-900 digital conductivity meter. The far IR spectra were recorded in the range 500–50 cm^{-1} on a Perkin-Elmer 1700 X FT far IR spectrometer in the solid state by using polyethylene disks. The EI mass spectra were recorded by using a VG Autospec spectrometer at 70 eV: m/z values are given for ^{1}H, ^{12}C, ^{28}Si, ^{35}Cl, ^{55}Mn, and ^{56}Fe. The electronic spectra in 10^{-4} mol dm^{-3} DMF solution were obtained using a Shimadzu UV-160A recording spectrophotometer. The ESR spectra of polycrystalline samples were obtained on a Bruker ESR spectrometer operating in the X-band region at RT and 120 K. The system used for recording Mössbauer spectrum was a Wissel Mössbauer spectroscopy system, Germany, consisting of a Mössbauer drive unit model 360, a digital function generator model DFG 500, a preamplifier PEA 6A, NIM BIN 7022–7033 and a data acquisition card CMCA 500/550, a 50-mC Co^{57} source in rhodium matrix, and a proportional counter. The Mössbauer spectrum of the sample was recorded in the transmission mode. The isomer shift is reported with respect to the r.t. iron(0) transmission spectrum. Cyclic voltammograms were run in a nitrogen atmosphere in 10^{-4} M DMF solution on an EG & G Versastat II system using platinum/glassy carbon as a working electrode, a Pt wire as an auxiliary electrode, and a SCE as the reference electrode. Tetraethylammonium perchlorate (TEAP) (0.1 M solution in DMF) was used as the supporting electrolyte. Scan speed of 50–500 mV s^{-1} was employed. The electrode performance was monitored by observing the ferrocenium/ferrocene (Fc^+/Fc) couple in the same solvent system. Constant-potential electrolyses were carried out in the DMF solution on the same equipment.

*Synthesis of [$MnCl_2\{Ph_2PMe_2Si)_3CH\}$] (**1**)*

A suspension of anhydrous $MnCl_2$ (0.080 g, 0.64 mmol) and $(Ph_2PMe_2Si)_3CH$ (0.48 g, 0.64 mmol) in toluene (70 cm^3) was slowly heated to reflux, then maintained at reflux for 62 h. The solution was allowed to cool to room temperature to give a white solid which was collected by filtration, washed with petroleum ether, and dried in vacuo. Yield: 0.38 g (70%), mp 248°C (dec.). Anal. Found (%): C, 58.6; H, 5.4; Cl, 8.7; P, 9.8. Calcd for $C_{43}H_{49}Cl_2P_3Si_3Mn$: C, 59.4; H, 5.6; Cl, 8.2; P,10.7. μ_{eff} (BM) at RT: 1.68. Λ_M (10^{-3} M, DMF, 298 K): 35 $S\,cm^2\,mol^{-1}$. I.R. (polyethylene, ν (cm^{-1})): 326, 316 [ν (Mn − Cl], 237[ν (Mn − P]. ESR (polycrystalline, R.T./120 K): g 2.01. CV data: $E_{pc} = -1.31$ V; $E_{pa} = -0.86$ V; $E_{pa} = 0.18$ V.

*Synthesis of [$FeCl_2\{ Ph_2PMe_2Si)_3CH\}$] (**2**)*

To a suspension of anhydrous $FeCl_2$ (0.09 g, 0.73 mmol) in toluene (75 cm^3) was added a solution of $(Ph_2PMe_2Si)_3CH$ (0.54 g, 0.73 mmol), and the mixture was slowly heated to reflux for 30 h. After cooling, a pale yellow precipitate was obtained, filtered, and washed with light petroleum (40–60°C) and dried in vacuo. Yield: 0.30 g (75%), mp 240°C (dec.). Anal. Found (%): C, 58.5; H, 5.3; Cl, 8.7; P, 10.1. Calcd for $C_{43}H_{49}Cl_2P_3Si_3Fe$: C, 59.4; H, 5.6; Cl, 8.2; P,10.7. μ_{eff} (BM) at R.T.: 2.02. Λ_M (10^{-3} M, DMF, 298 K): 30 $S\,cm^2\,mol^{-1}$. I.R. (polyethylene, ν (cm^{-1})): 321, 308 [ν (Fe – Cl], 237 [ν (Fe – P)]. Mössbauer (δ, mm s^{-1}, R.T.): 0.48. CV data: $E_{pc} = -1.55$ V; $E_{pa} = 0.16$ V.

RESULTS AND DISCUSSION

Synthesis and Properties

The ligating behavior of tris {(diphenylphosphino)-dimethylsilyl}methane, $(Ph_2PMe_2Si)_3CH$, a tripodal phosphine ligand toward groups 7 and 8 metal halides has been examined. A colorless manganese complex and a light yellow iron compound, which is deduced from the analytical data and from the spectroscopic results having the composition [$MCl_2\{(Ph_2PMe_2Si)_3CH\}$] (where M = Mn (**1**); Fe (**2**)), have been obtained in good yield. Complexes **1** and **2** behave as nonelectrolytes in DMF, suggesting that the chlorine atoms are part of the coordination sphere.

Mass Spectra

The EI mass spectrum of **1** showed the expected molecular ion peak at *m/z* 867 (4%). The peaks at *m/z* 851 (75%), 832 (4%), and 795 (4%) are assigned for the fragments [M^+–H–CH_3], [M^+–Cl] and [M^+–2Cl–2H], respectively, from the molecular ion (M^+). Other important fragments which could be identified are (*m/z*) 777 [M^+–CH_4–$SiMe_3H$, 12%],701 [M^+–CH_3–$SiMe_3H$–Ph, 6%], 551 [M^+–CH_4–2$SiMe_3$–2Ph, 12%], 479 [M^+–CH_3–3$SiMe_3$–2Ph, 14%], 201 [($HPPh_2Me^+$), 100%], 125 [$(MnCl_2)^+$, 20%], 90 [$(MnCl)^+$, 90%], 77 [$(Ph)^+$, 96%].

The EI mass spectrum of complex **2** did not give the molecular ion peak at *m/z* 868, but it showed a peak at *m*/z 833 (70%) due to loss of one Cl atom from the molecular ion (M^+). Other important fragments which could be identified are (*m/z*) 798 [M^+–2Cl, 28%], 768 [M^+–2Cl–2Me, 1%], 691 [M^+–2Cl–2Me–Ph, 1%], 614 [M^+–2Cl–2Me–2Ph, 1%], 584 [M^+–2Cl–4Me–2Ph, 1%], 245 [$(FeCSi_3P_3)^+$, 2%], 214 [$(FeCSi_3P_2)^+$, 7%], 183 [$(FeCSi_3P)^+$, 7%], 152 [$(FeCSi_3)^+$, 7%], 126 [$(FeCl_2)^+$, 41%], and 91 [$(FeCl)^+$, 100%]. The calculated and observed isotopic patterns for $C_{43}H_{49}Cl_2P_3Si_3Fe$, [$M^+$–Cl], are in good agreement.

Thermal Study

The TGA of complex **1** revealed that the weight loss was 3.8% in the temperature range 30–157°C (calculated for loss of Cl, 4.0%) and represents one atom of chlorine. The high temperature necessary for chlorine loss indicates that chlorine is coordinated to Mn(II). From 157 to 315°C, a mass loss of 24.7%, compared with the theoretical value of 25.4% is attributed to the loss of chlorodiphenylphosphine, PPh_2Cl. The loss of dimethylsiloxane, Me_2SiO, with chlorodiphenylphosphine (observed 33.3%, calculated 33.9%) is observed at 425°C. At 515°C, a mass loss of 60.4% with the theoretical value of 59.7% is attributed to the combined loss of two molecules each of dimethylsiloxane and diphenylphosphine. The total mass loss up to 721°C is found to be 68.8% which shows the formation of $MnSiO_3$ (observed residual mass 31.2%, theoretical 30.2%).

The complex **2** registers a mass loss of 9.5% at 179°C compared with the theoretical value of 8.4% which corresponds to the loss of two molecules of HCl. The high temperature necessary for chlorine loss simply indicates that chlorine is coordinated to iron(II). From 179 to 329°C, a mass loss of 17.1% (theoretical 17.0%) is attributed to the loss of two molecules of dimethylsiloxane, Me_2SiO. At 447°C, a mass loss of 26.4% (theoretical 25.4%) is due to PPh_2Cl. The total mass loss up to 495°C is found to be 54.4%. The residual mass 45.6% corresponds to the formation of $FeSiO_3$ and SiO_2 (calculated 44.2%). The higher residual mass indicates that the iron complex is thermally more stable as compared to the manganese complex. From the results of TGA investigations, it is clear that the weight loss due to the decomposition of the complex by heat occurs in the following sequence: (i) Cl/HCl, (ii) Me_2SiO, (iii) PPh_2/PPh_2Cl, and the remaining material after decomposition is metal silicates and silica.

IR Spectra

The IR spectra of complexes **1** and **2** in the fingerprint region (1200–700 cm^{-1}) are similar to that for the free ligand which confirms the presence of the ligand. The far IR spectra of **1** and **2** recorded using polyethylene disk in the 50–500 cm^{-1} region showed two ν (M – Cl) bands in the region of 308–326 cm^{-1} and one ν (M – P) band at 237 cm^{-1}. The observed ν (M – Cl) values are characteristic of terminal chlorines in a cis configuration [13]. The appearance of single ν (M – P) indicates the presence of equatorial phosphines in a tridentate coordination to the metal.

ESR Spectra

The ESR spectrum of complex **1** was recorded in the solid state both at room temperature and at 120 K. In both cases, a single ESR line is observed (Fig. 1). The spectra revealed the presence of a strong signal in the $g = 2.0$ region. No other signal is observed in the 5000-G scan spectra, as would have been expected for noncubic Mn(II) complexes with an appreciable zero-field splitting. Such a single one-line spectrum devoid of any hyperfine structure has been interpreted as arising from a Mn(II) complex with a neighboring atom magnetic interaction [14].

Mössbauer Spectra

The ^{57}Fe Mössbauer spectrum of the chloride complex of tripodal phosphine ligand shows a single sharp absorption peak with no quadrupole splitting (Fig. 2). The observed isomer shift value, δ 0.48 mm s^{-1}, is in good agreement with the values reported previously (from −0.2 to +0.4 mm s^{-1}) for low-spin iron(II) complexes [15,16]. Hence, the Mössbauer spectral datum supports the trigonalbipyramidal structure of the complex.

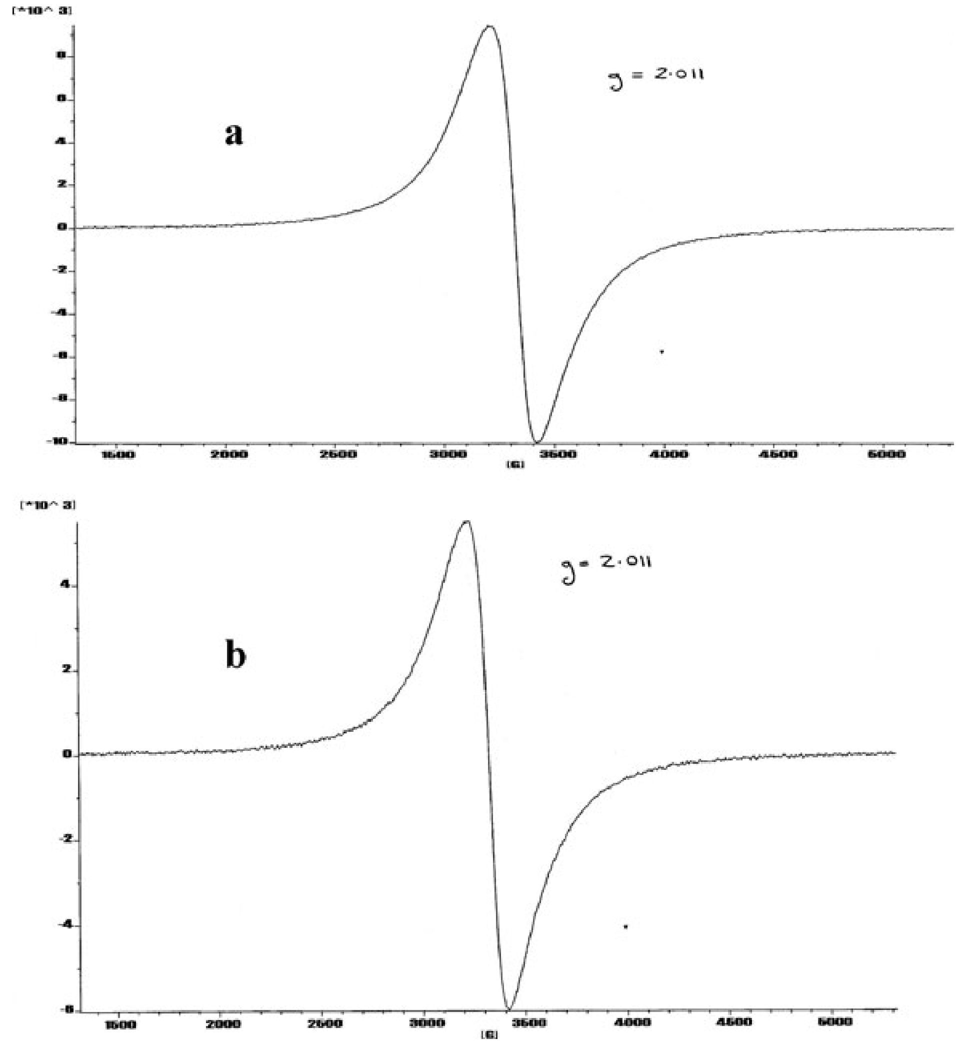

FIGURE 1 Polycrystalline ESR spectrum of complex **1**: (a) RT and (b) 120 K.

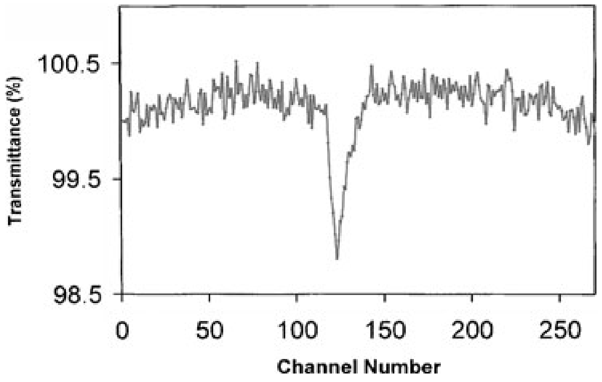

FIGURE 2 The Mössbauer spectrum of complex **2** [$FeCl_2\{(Ph_2PMe_2Si)_3CH\}$].

Magnetic Moment

Room-temperature magnetic moments of complexes **1** and **2** show that metals are in low spin in the solid state. The complex **1**′s μ_B value, which is equal to 1.68 BM, agrees well with a trigonal bipyramidal geometry around a low spin Mn^{2+} ion. On the other hand, the μ_B value for complex **2**, 2.02 BM, is lower than expected for low spin Fe^{2+} with two unpaired electrons (2.83 BM). The low value of magnetic moment is attributed to antiferromagnetic interactions. This observation corroborates well with the ESR findings of complex **1**.

Electronic Spectra

The UV spectrum of the ligand in DMF shows a prominent band at λ_{max} 271 nm. The electronic spectrum of paramagnetic complex **1** showed a similar band of ligand origin. The complex does not absorb in the visible region as is typical for other Mn(II) complexes.

The high spin trigonal bipyramidal Fe(II) complexes are expected to show two bands in the near infrared for the expected one-electron transition

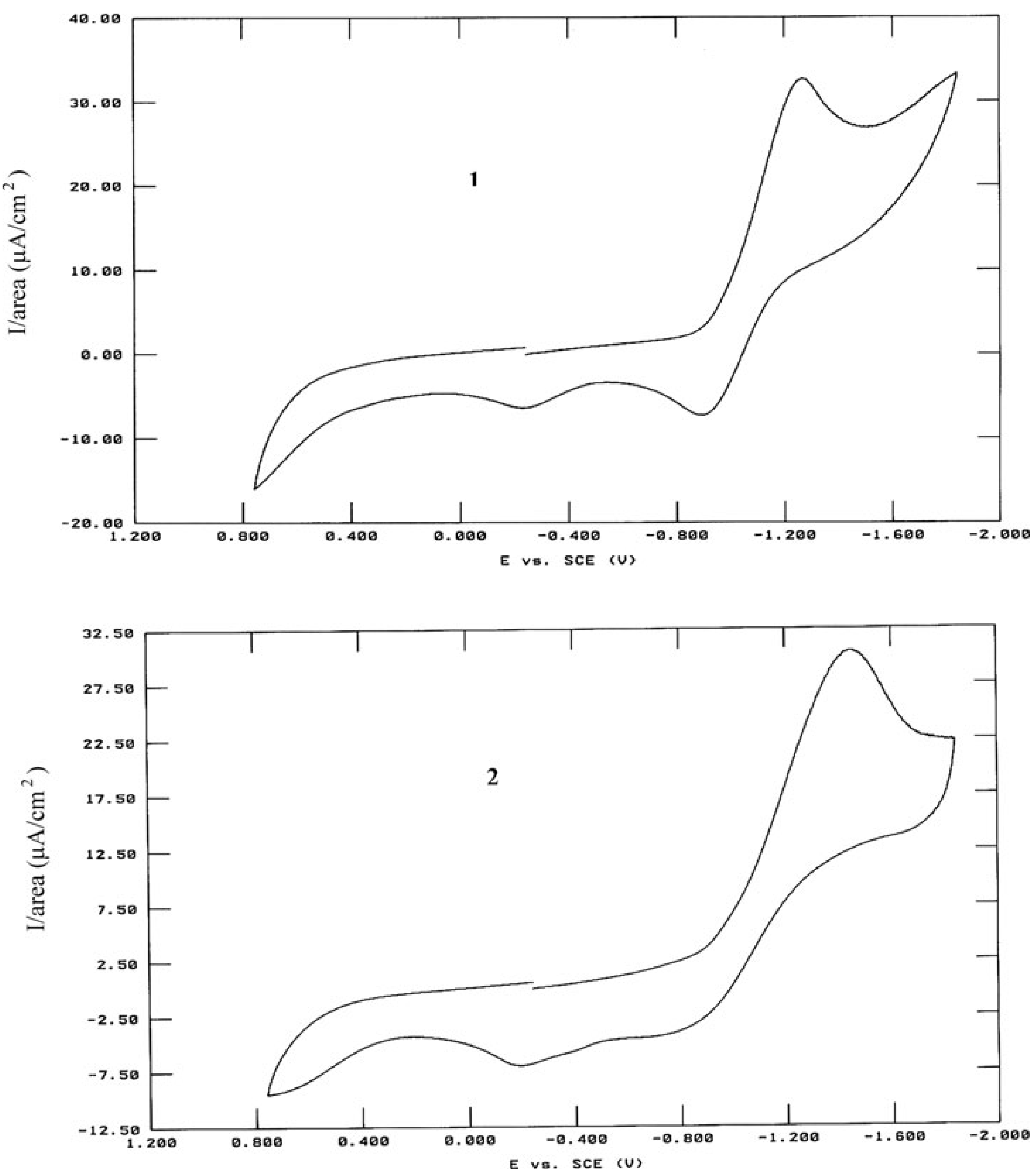

FIGURE 3 Cyclic voltammogram of complexes **1** and **2**(0.1 mM) in DMF at 100 mV s^{-1}.

with configuration $(e'')^3$ $(e')^2$ (a'_1): $^5E' \rightarrow {}^5E''$; $^5A' \rightarrow {}^5E''$ [17]. In the present investigation, the electronic spectrum of complex **2** showed no absorption in the visible region; instead, it exhibited an intense absorption in the UV region at 273 nm similar to that of the free ligand.

Cyclic Voltammetry

The electrochemical behavior of the complexes **1** and **2** has been studied by cyclic voltammetry in DMF using a glassy carbon/Pt electrode under dry nitrogen atmosphere at room temperature. In the cyclic voltammogram of complex **1** and **2**(Fig. 3; Table 1), a quasi-reversible wave at $E_{pc} = -1.31$; $E_{pa} = -0.86$ V for **1** and a single irreversible reduction wave at $E_{pc} = -1.55$ V for **2** versus SCE with the 50–500 mV s^{-1} scan rates are observed. These are attributed to Mn(II) to Mn(0) and Fe(II) to Fe(0) reductions, respectively [18]. The cathodic peak potential value for **2** is more negative than that of **1** indicating that the

TABLE 1 Cyclic Voltammetric Data[a] of Complexes 1 and 2

	*Mn-Complex (**1**)*			*Fe-Complex (**2**)*		
Scan Rate (mV s^{-1})	*E_{pc} (V)*	*E_{pa} (V)*	*I_{pc} (μA)*	*E_{pc} (V)*	*E_{pa} (V)*	*I_{pc} (μA)*
50	−1.22	−0.93 −0.23	23.9	−1.41	−0.18	21.1
100	−1.27	−0.90 −0.23	32.6	−1.44	−0.19	30.4
200	−1.32	−0.86 −0.19	42.2	−1.56	−0.16	42.0
300	−1.34	−0.83 −0.16	48.5	−1.62	−0.16	49.8
500	−1.40	−0.78 −0.13	58.8	−1.73	−0.14	64.5

[a] Recorded in 10^{-4} M DMF solution, $[NEt_4][ClO_4]$, 0.1 M, working electrodes: glassy carbon for **1** and platinum for **2**.

complex **2** is more stabilized on the CV time scale. The linear plot of the cathodic peak current (I_{pc}) versus the square root of the scan rate ($\nu^{1/2}$) passes close to the origin (Fig. 4), indicating that the electrode process is mainly diffusion controlled. An irreversible anodic peak at $E_{pa} = -0.18$ (**1**) and -0.16 (**2**) V could be assigned to the oxidation of the ligand on the electrode surface. Controlled-potential electrolysis for complexes **1** and **2** in the DMF solution at −1.31 V for **1** and −1.55 V for **2** involved the passage of 1.80 eq. of charge, indicating two-electron reduction of mononuclear manganese and iron species.

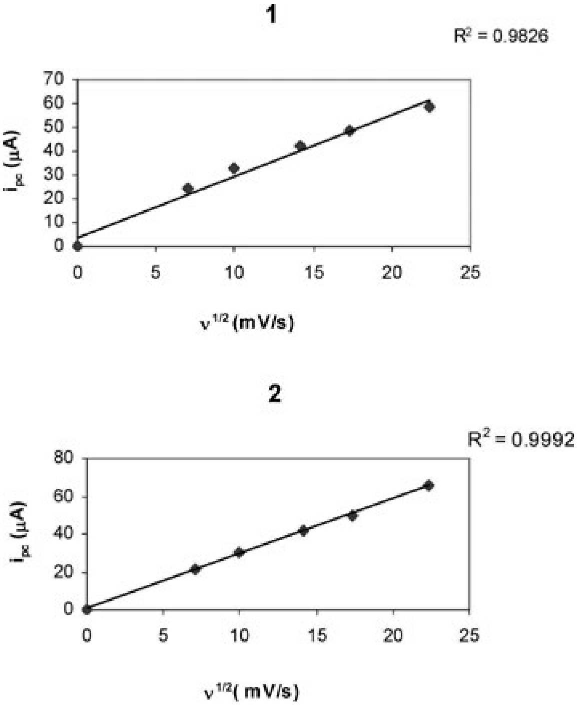

FIGURE 4 A plot of i_{pc} vs. $\nu^{1/2}$ for **1** and **2**, $C = 1.0 \times 10^{-4}$ mol dm^{-3}.

Efforts to grow a single crystal did not succeed, and this precluded a single crystal X-ray determination.

Proposed Structure of the Complex

The analytical, spectral, and electrochemical evidences suggest that both complex **1** and **2** have the formula $[MCl_2\{HC(SiMe_2PPh_2)_3\}]$, and the basic structure (Fig. 5) consists of three shared six-membered puckered metallacycles made of M, P, Si, C, Si, and P in the mentioned order; the metal and the carbon atoms are being common to all the three rings. The metal atom in the structure thus gets a trigonal bipyramidal environment with one Cl and two P atoms occupying the corners of a trigonal plane, and the remaining Cl and P atoms occupy the two trans positions on the axis. The two Cl atoms are thus cis to one another. The carbon, silicon, and phosphorus atoms of the ligand $HC(SiMe_2PPh_2)_3$ retain their tetrahedral configuration in the complex. A similar structure for complexes $[MnCl_2L]$ (L = tripod nitrogen ligand), $[FeP(CH_2PR_2)_3Cl]^+$, and $[Fe(terpy)X_2]$ (terpy= 2, 2′, 2″-terpyridine; X = Cl, Br,

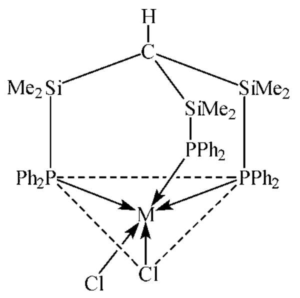

FIGURE 5 Proposed structure of $[MCl_2\{(Ph_2PMe_2Si)_3CH\}]$ (**1**,**2**).

I, NCS) has earlier been reported in the literature [19–21].

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