mercury lamp through a cutoff filter ($\lambda > 360$ nm). The reaction was followed by the infrared spectrum. The formation of the ketene 7 was confirmed by comparison of the infrared spectrum of matrix-isolated authentic sample. For the ultraviolet absorption, the argon-diluted sample was deposited on a sapphire window cooled at 10 K and irradiated with the wavelength greater than 360 nm. The ultraviolet spectrum was taken at periodic intervals.

Photolysis of 4 in Argon Matrix in the Presence of Methanol. The sample was deposited on a CsI window cooled at 20 K together with Ar and methanol (Ar:methanol = 730:30). The matrix was irradiated with $\lambda > 360$ nm. The infrared spectrum after the photolysis was completely identical with that obtained in the absence of methanol except for the bands of methanol. The matrix was warmed slowly to room temperature, and the volatile products were collected in a trap cooled by liquid nitrogen. Gc–MS revealed the presence of **12a** (8%), **7** (74%), and **9a** (18%).

Photolysis of 4 in Hydrocarbon Matrix at 77 K. A mixture of 4 (ca. 0.1 mg) and 3-methylpentane (5 mL) was placed in a quartz UV cell and degassed for several times. The mixture was cooled to 77 K, and the resulting matrix was irradiated ($\lambda > 360$ nm) through the windows of a quartz Dewar. The ultraviolet absorption was taken at periodic intervals. An absorption band with a maximum of 293 nm appeared and grew on irradiation time. The isopentane/methylcyclohexane (3:1) matrix containing 4 also resulted in the appearance of band with a maximum of 293 nm due to 8 at 77 K on irradiation ($\lambda > 360$ nm).

Photolysis of 4 in Methanol/2-Methyltetrahydrofuran Matrix at 77 K. A mixture of 4 (326 mg, 1.34 mmol), methanol (4 mL), and 2-methyltetrahydrofuran (4 mL) was cooled to 77 K. The resulting matrix was irradiated through a Pyrex tube with a high-pressure mercury lamp for 9 h. Separation of the reaction mixture by GLC gave **7** (11%), **12a** (4%), and methoxysilane **9c** (83%).

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Registry No. 4, 79251-24-4; 7, 79251-25-5; 8, 79251-29-9; **9a**, 79251-30-2; **9b**, 79251-28-8; **9c**, 79251-32-4; **12a**, 79251-26-6; **12b**, 79257-68-4; 10, 79251-31-3; 14, 110046-19-0; MeOSi(Me)$_2$CH(SiMe$_3$)CO$_2$Me, 79251-27-7; bis(pentamethyldisilanyl)thiane, 110077-40-2; benzophenone, 119-61-9.

Synthesis, Reactivity, and Electrochemical Behavior of [η^5-(Alkoxysilyl)cyclopentadienyl]iron Dicarbonyl Complexes

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The binuclear iron complexes [(η^5-C$_5$H$_4$SiMe$_2$OEt)Fe(CO)$_2$]$_2$ (1) and [(η^5-C$_5$H$_4$(CH$_2$)$_3$Si(OMe)$_3$)Fe(CO)$_2$]$_2$ (2) have been prepared by thermal reaction between the cyclopentadienylalkoxysilane C$_5$H$_5$SiMe$_2$OEt or C$_5$H$_5$(CH$_2$)$_3$Si(OMe)$_3$ and Fe(CO)$_5$ in good yield. From these compounds new mononuclear iron complexes are formed. The oxidation of 1 and 2 with ferricinium hexafluorophosphate in the presence of PPh$_3$ gives the cationic complexes [(η^5-C$_5$H$_4$SiMe$_2$OEt)Fe(CO)$_2$PPh$_3$]PF$_6$ (3) and [(η^5-C$_5$H$_4$(CH$_2$)$_3$Si(OMe)$_3$)Fe(CO)$_2$PPh$_3$]PF$_6$ (4). The anions [(η^5-C$_5$H$_4$SiMe$_2$OEt)Fe(CO)$_2$]$^-$ (5) and [(η^5-C$_5$H$_4$(CH$_2$)$_3$Si(OMe)$_3$)Fe(CO)$_2$]$^-$ (6) were obtained by treatment of 1 and 2 with potassium benzophenone ketyl. The compounds are characterized by ^{1}H and ^{13}C NMR and IR spectroscopy. The electrochemistry of the dinuclear compounds 1 and 2 indicates that two-electron oxidation products are stable on the voltammetry time scale. However, the results show that the kinetic stability of the oxidation products is very dependent upon the donor properties of the solvent and the nature of the ring substituents.

Introduction

In the last years, there has been considerable interest focused on the multiple functionalization of the cyclopentadienyl ligand, which often results in considerable kinetic stabilization of its complexes with transition metals,[1,2] and, depending on the desired oxidation state, this may result in thermodynamic stabilization as well. It is known, from a redox viewpoint, that permethylation on the η^5-C$_5$H$_5$ ring leads to the stabilization of the higher oxidation states.[3-5] However, recently, it has been found that η^5-C$_5$Ph$_5$ ligand is capable of stabilizing lower oxidation states because of the electron-withdrawing ability of phenyl ring substituent.[6-9]

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Table I. IR Bands [ν(CO)] of the Synthesized and Related Complexes[a]

complex	solid[b]	CH_2Cl_2	THF
1	2000 w, 1958 vs, 1920 w, 1784 m, 1758 vs, 1737 sh	1995 vs, 1954 s, 1774 vs	1991 vs, 1950 s, 1779 vs
2	1989 vs, 1946 vs,[c] 1803 w, 1775 vs	1987 vs, 1945 m, 1765 vs	1982 vs, 1947 s, 1777 vs
3	2046 vs, 2003 vs, 1961 sh	2057 vs, 2015 vs	2054 vs, 2009 vs
4	2048 vs, 2002 vs	2054 vs, 2003 vs	2050 vs, 1998 vs
5			1859 vs, 1773 vs
6			1861 vs, 1771 vs
$[FP]_2$[d]	1975 vs, 1933 vs, 1801 w, 1766 vs	1999 vs, 1960 m, 1777 vs	1994 vs, 1951 s, 1784 vs

[a] In cm^{-1}. [b] Nujol mull. [c] Liquid film. [d] $[Fp]_2 = [(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, this work.

We are interested in the synthesis of new organometallic complexes that contain alkoxysilane- and siloxane-[10]functionalized cyclopentadienyl ligands, in order to analyze the influence of the Si–O–Si groups on the kinetic stability of the complexes.

On the other hand, the hydrolyzable alkoxysilane-substituted organometallic complexes will be suitable moieties for attachment to inorganic support materials in organometallic catalysis. In fact, the immobilization of homogeneous catalysts has become of increasing interest,[11-13] and one of the possibilities of "heterogenization" of transition-metal complexes by using organic or inorganic supports[14,15] is their coordination via cyclopentadienyl ligands. However, the functionalization of inorganic supports in this way is limited by the fact that the only modifiers known so far have been cyclopentadienyl groups directly bound to silicon.[16,17]

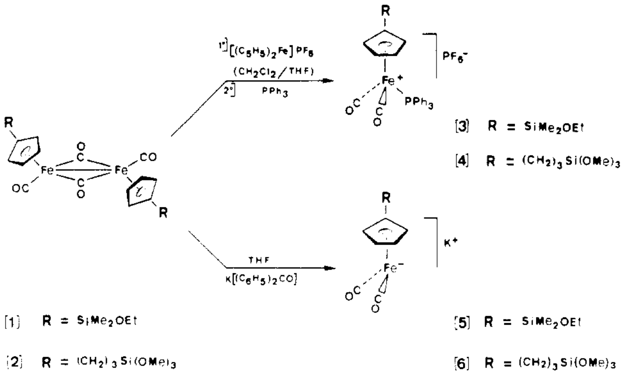
It is interesting to note that it has been shown that the catalytic properties of heterogenized complexes are significantly affected by the length of the space separating the support surface from the anchoring ligand.[18,19]

We report here full details of the synthesis and characterization of new binuclear (silyl-substituted cyclopentadienyl)iron complexes $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]_2$ (1) and $[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3)Fe(CO)_2]_2$ (2), of the related cationic mononuclear derivatives $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2PPh_3]PF_6$ (3) and $[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3)Fe(CO)_2PPh_3]PF_6$ (4), and of the monoanionic complexes $K[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]$ (5) and $K[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3)Fe(CO)_2]$ (6). In addition, the electrochemical behavior in various solvents of the binuclear complexes 1 and 2 is reported and discussed.

Results and Discussion

The new binuclear iron complexes 1 and 2 (Scheme I) can be synthesized conveniently by reaction of the respective silyl-substituted cyclopentadiene, $C_5H_5SiMe_2OEt$ and $C_5H_5(CH_2)_3Si(OMe)_3$, with $Fe(CO)_5$, in decane or xylene as solvents, at temperatures around 130 °C. In these preparations it is necessary to remove unreacted starting materials and byproducts by column chromatography (neutral alumina, *n*-hexane/THF, 2/1). In pure form, complex 1 exists as dark red, air-stable crystals,[20] whereas 2 is a red liquid at room temperature.

Scheme I



It is known that the oxidative cleavage of the Fe–Fe bond in the binuclear complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ can be accomplished by chemical reagents as $AgBF_4$,[22] $FeCl_3$,[23] O_2/HBF_4,[24] or Ph_3C^+ [25] or electrochemical oxidation.[26] Recently, Catheline and Astruc[27] have reported that the ferricinium cation can be used as oxidant to synthesize the cationic complexes $[(\eta^5\text{-}C_5R_5)Fe(CO)_2L]^+$ (R = H or Me; L = solvent or ligand).

In our case we found that ferricinium hexafluorophosphate, $[(\eta^5\text{-}C_5H_5)_2Fe]^+PF_6^-$, is a very efficient and clean reagent for effecting the transformation of eq 1, with 1 as well as with 2.

$$[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2 + [(\eta^5\text{-}C_5H_5)_2Fe]^+PF_6^- \xrightarrow{THF/CH_2Cl_2} 2[(\eta^5\text{-}C_5H_4R)Fe(CO)_2THF]^+PF_6^- \quad (1)$$

$$R = SiMe_2OEt,\ (CH_2)_3Si(OMe)_3$$

In practice, this oxidation proceeds at room temperature in THF to give the complexes $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2THF]PF_6$, which were characterized by IR spectroscopy but were not isolated. To the CH_2Cl_2/THF solution of these intermediate complexes was added an excess of PPh_3 (2/1), and the complexes $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2PPh_3]PF_6$ (3) and $[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3Fe(CO)_2PPh_3]PF_6$ (4) could be isolated. Both cationic complexes 3 and 4 were isolated as air-stable, crystalline solids.

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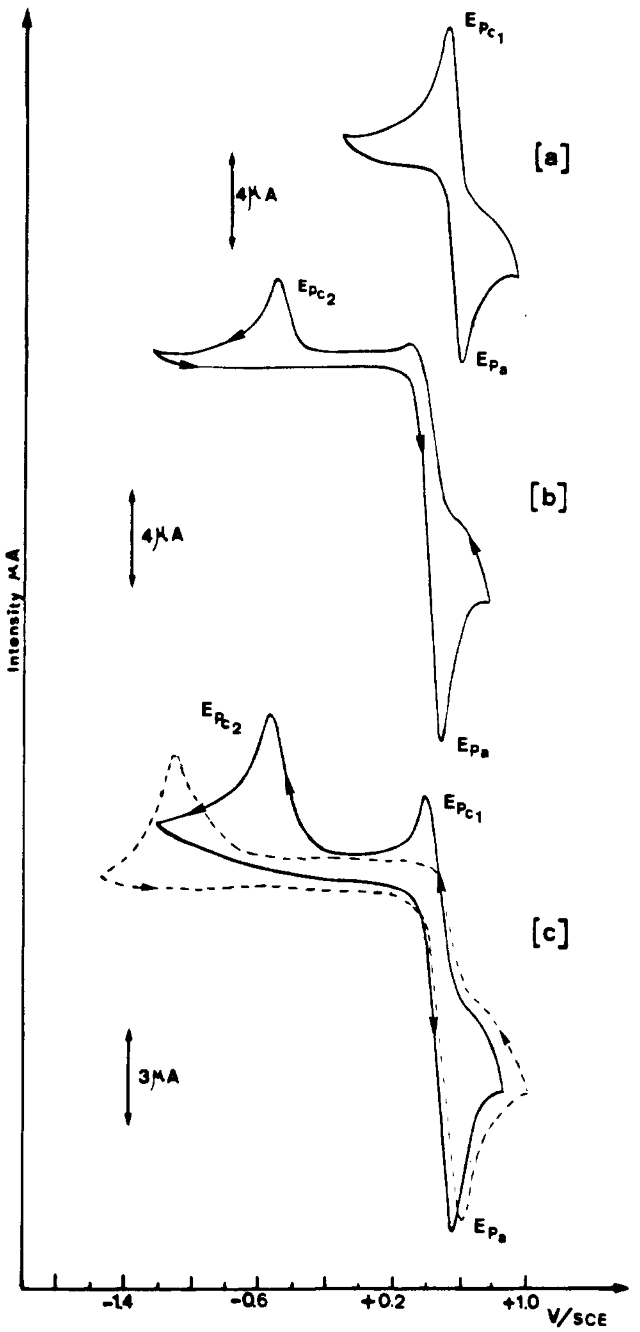

Figure 1. Cyclics voltammograms in CH_2Cl_2 at a platinum electrode for (a) $[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3Fe(CO)_2]_2$ (2) (scan rate = 0.1 V s^{-1}), (b) $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]_2$ (1) (scan rate = 0.1 V s^{-1}), and (c) $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]_2$ [scan rate = 0.5 V s^{-1} (—)] and $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]_2$ in presence of PPh_3 [scan rate = 0.5 V s^{-1} (- - -)].

The dimers 1 and 2 could be rapidly and cleanly reduced by using potassium benzophenone ketyl (Scheme I) in THF solution at room temperature.[28] The pure anionic complexes 5 and 6 were isolated as orange, air-sensitive powdery solids.

The IR spectra of these products show bands corresponding to ν(SiOR) (1190–812 cm^{-1}) (a set of bands), ν($SiMe_2$) (1280, 790 cm^{-1}), and ν($SiCH_2$) (1250, 760 cm^{-1}).[29,30] The ν(CO) frequencies either in the solid or in solution for compounds 1–6, and selected reference compounds are listed in Table I. The electron-donating capacity of the (alkoxysilyl)cyclopentadienyl ligands is reflected in the values of ν(CO), which are smaller than those in the corresponding complexes with unsubstituted cyclopentadienyl ligands.

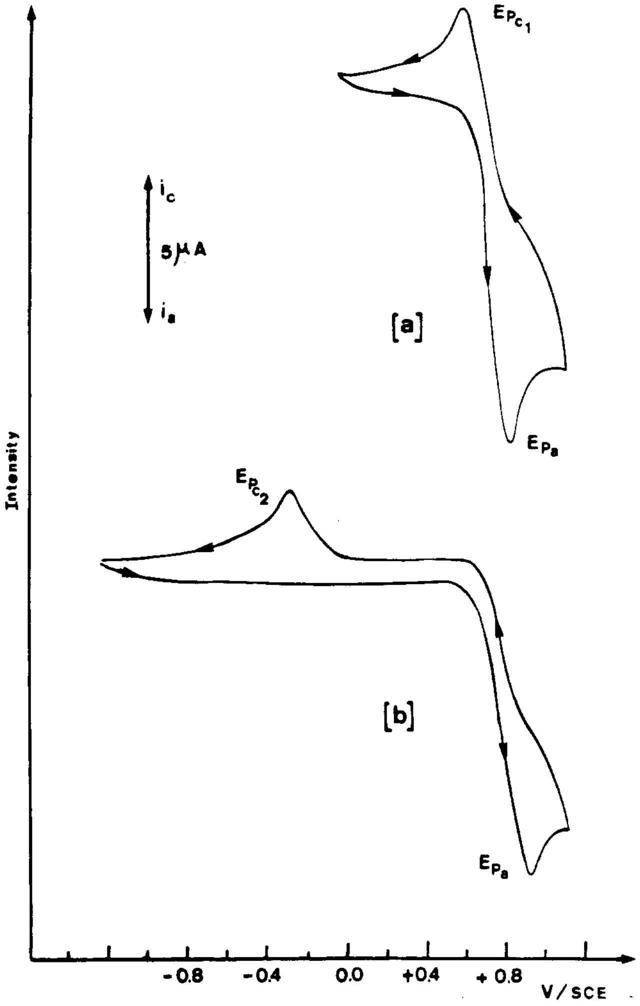

Figure 2. Cyclics voltammograms in THF at a platinum electrode for (a) $[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3)Fe(CO)_2]_2$ (2) (scan rate = 0.5 V s^{-1}) and (b) $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]_2$ (1) (scan rate = 0.2 V s^{-1}).

Electrochemistry

Ambient-temperature cyclic voltammograms (CVs) of compounds 1 and 2 in 0.1 M [n-Bu_4N][PF_6] in dichloromethane and THF solutions at a platinum disk electrode are shown in Figures 1 and 2, at different scan rates. The anodic and cathodic peak voltages are listed in Table II. Potentiostatic coulometry and comparisons of the limiting currents, obtained from rotating disk electrode (RDE) voltammograms between 1 and 2, respectively, with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ indicate a two-electron-transfer process. The CV curves reveal that in CH_2Cl_2 the electron transfers involved are reversible, the peak separation ΔE_p, being about 70 mV at 0.1 V s^{-1}. The peak current ratio, $i_{p_c}/i_{p_a} = 1$ (i_{p_c} = cathodic return peak current; i_{p_a} = anodic peak current), at all scan rates indicates that for 2 a chemically reversible process takes place and a dication, stable on the cyclovoltammetry time scale, is generated. Attempts to isolate the dication by exhaustive electrolysis or chemical oxidation with ferricinium hexafluorophosphate were not useful. In both cases, as the reaction progressed, it is observed (monitoring by IR) that the bands corresponding to the ν(CO) bridge disappear and

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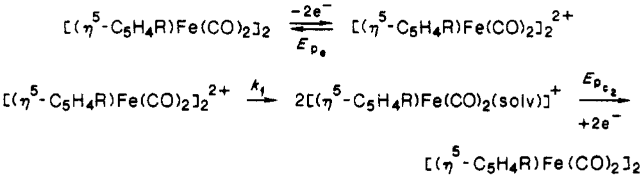
Table II. Electrochemical Data for the Compounds[a]

		oxidations					reductions		
compd	solv	E_{p_a}	$E_{p_{c1}}$	$E_{p_{c2}}$	i_a/i_c	n	E_{p_c}	E_{p_a}	n
1	CH_2Cl_2	+0.70	+0.63	−0.30	0.60	2	−1.76	...	2
	THF	+0.92		−0.50		2	−1.48	−0.94	2
2	CH_2Cl_2	+0.67	+0.61	...	1.10	2	−2.10[b]	...	2
	THF	+0.80	+0.71	−0.62[b]	0.65	2	−1.98	−0.92	2
3	CH_2Cl_2						−1.04	+0.90	1
	THF						−0.92	+0.93	1
4	CH_2Cl_2						−1.10	+0.70	1
	THF						−1.00	+0.87	1

[a] Peak potentials, E_p, in V; i_a/i_c denotes the peak current ratio, and n is the determined number of electrons. [b] Ill-defined peak. [c] In CH_2Cl_2 vs SCE, ferrocene/ferricinium couple, E_{p_a} = +0.55 V and E_{p_c} = +0.49 V. In THF vs SCE, ferrocene/ferricinium couple, E_{p_a} = +0.51 V and E_{p_c} = +0.45.

Scheme II[a]



[a] R = $SiMe_2OEt$ (1) in CH_2Cl_2; R = $(CH_2)_3Si(OMe)_3$ (2) in THF.

new bands at 2066 and 2019 cm^{-1} appear. These are characteristic of $[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3)Fe(CO)_2(CH_2Cl_2)]^+$.

The dication derived from 1 undergoes decomposition on the voltammetry time scale; at scan rates $v \leq 0.10$ V s^{-1}, no reduction peak is seen after the scan reversal passes the anodic peak. When the potential scan rate is increased, the cathodic peak is detected (Figure 1c). Using the method of Nicholson,[31] we are able to estimate the rate constant for the decomposition of the dication $[1]^{2+}$ from the change in the ratio of the cathodic and anodic peak current with the scan rate as $k_f = 2.3 \pm 0.5$ s^{-1}. On cyclic voltammograms where the oxidation products of 1 undergo significant chemical decomposition, another reduction peak $E_{p_{c2}}$ appears near −0.30 V vs SCE on the cathodic return scan. The chemical or electrochemical formation of the monocation is confirmed by spectrophotometric examination of the solutions obtained in the same way as indicated for 2. The ν(CO) bridge band at 1774 cm^{-1} disappears, and new bands at 2068 and 2023 cm^{-1} appear. These are due to the cationic species $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2(CH_2Cl_2)]^+$. The CVs of these solutions show a pair of cathodic and anodic peaks at −0.34 and +0.68 V. The potentials of these peaks are nearly identical with the anodic and cathodic peak potentials of the dimer obtained under the same conditions. These results are consistent with an electrochemical EC mechanism (Scheme II).

Addition of PPh_3 to the solutions of all the complexes modifies significantly the CV curves obtained (Figure 1c). On CV it is observed that the reduction peaks mentioned above disappear and new reduction peaks appear at −1.04 and −1.10 V vs SCE in CH_2Cl_2 on the cathodic return scan of 1 and 2, respectively. The cathodic peak voltages are identical with the reduction peak potential observed, respectively, in the CV of dichloromethane solutions of the chemically obtained **3** and **4**. The formation of these cations was proved by IR spectroscopic examination of solutions obtained by electrochemical oxidation of dimers 1 and 2 in presence of PPh_3. On the other hand, the products of reduction steps are the dimers. When the scan is extended to −2.20 V, other peaks are found and these coincide with the reduction peak potentials of the dimers 1 and 2 (see below).

The stability of the dications $[1]^{2+}$ and $[2]^{2+}$ is critically solvent-dependent. From CV curves, the ratio i_{p_c}/i_{p_a} indicates that the chemical step corresponding to the decomposition of $[1]^{2+}$ and $[2]^{2+}$ species is accelerated as the solvent donor capacity increases.[32] In THF, for compound 2, the ratio i_{p_c}/i_{p_a} is near unity at 1 V s^{-1} and decreases at low scan rates. The average first-order constant, k_f, for the decomposition reaction of $[1]^{2+}$, calculated by using the method of Nicholson[31] is 1.2 ± 0.5 s^{-1}. In contrast, the decomposition of $[1]^{2+}$ in THF is such that i_{p_c}/i_{p_a} is about zero, even with scan rates as high as 5 V s^{-1}. In this case, another reduction peak appears near −0.50 V vs SCE (Figure 2), which cannot be associated with the reversible system because of the large peak separation. This cathodic peak, E_{p_c}, can be attributed to the reduction of $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2THF]^+$ derived from an irreversible fast decomposition reaction of the dication[33] (EC mechanism). In presence of PPh_3, the cathodic peak $E_{p_{c2}}$ shifts to −0.92 V. This voltage value is identical with the cathodic peak displayed by CV of THF solutions of complex **3**.[33] The electrochemical behavior of 1 in THF is analogous to that is shown for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.[34] For complex 2 on CV, where the oxidation products undergo significant chemical decomposition, a second broad peak is also observed at about −0.62 V vs SCE.

This behavior is adequately explained by Scheme II; the formation of the corresponding monocations $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2THF]^+$ and $[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3Fe(CO)_2THF]^+$ by chemical or electrochemical oxidation is proved with IR spectroscopic examination of solutions. The addition of PPh_3 causes the disappearance of the reversible reduction peak and shifts the second cathodic peak $E_{p_{c2}}$ to −1.00 V, which is identical with the reduction peak of **4**.[33]

In all cases, the two-electron oxidation products follow an EC mechanism, where the dications undergo an irreversible first-order decomposition reaction. However, this decomposition is more rapid for complex 1 in both solvents. This is related, probably, with the different electron donor ability of the ring silicon substituents, and it is in accord with the ν(CO) values (Table I) and oxidation peak potentials observed (Table II). The greater electron-donating ability of the propyltrimethoxysilane substituent explains the more easy oxidation of complex 2. In addition, the UV–visible spectrum of complex 2 shows a decrease in the energy of the visible band 1, λ = 348 nm; 2, λ = 352 nm),

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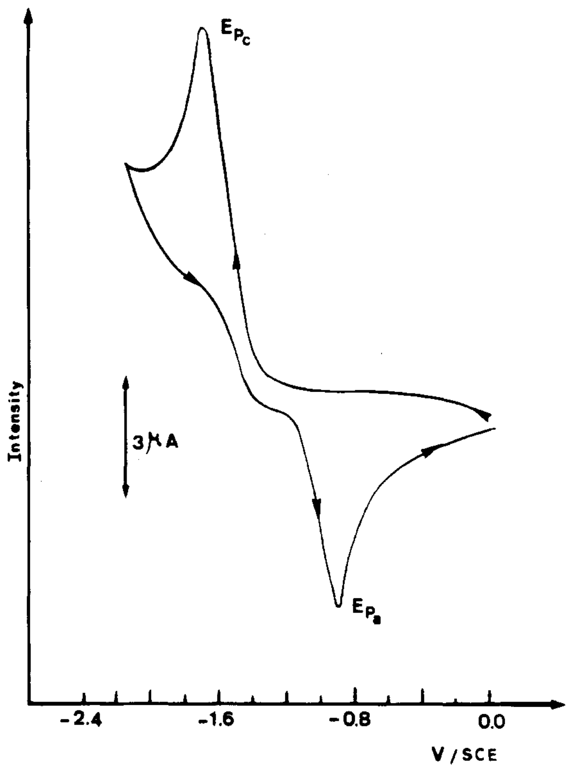

Figure 3. Cyclic voltammogram in THF at a platinum electrode for $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]_2$ (1) (scan rate = 0.2 V s^{-1}).

which agrees with the relative ease of electron removal from HOMO, in accordance with the electrochemical behavior.

On the other hand, the higher electron density in the cation $[2]^{2+}$ enhances its kinetic stability, making it possible to detect it on the CV time scale in donor solvents such as THF. A similar behavior has been displayed in the reactivity of transition-metal complexes with ligands of pronounced electron-donating properties, such as peralkylcyclopentadienes.[1] In this way, the electrochemical behavior of 1 and 2 is very different from that shown by the parent compound $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.[34]

The electrochemical reduction of complexes 1 and 2 also has been examined by cyclic voltammetry. The CV of compound 1 in THF solution, Figure 3, shows a pair of cathodic and anodic peaks corresponding to an irreversible system. The behavior of complex 2 is similar (see Table II). Potentiostatic coulometry and comparisons of the RDE voltammograms with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ indicate that the reduction process corresponds to a two-electron transfer.

The products of the electroreduction are the respective anions 5 and 6. This was proved by IR spectroscopic examination of the solutions obtained by exhaustive electroreduction. The oxidation peaks correspond to oxidation of these anions to the dimers. This conclusion is supported by the CV of the chemically prepared anions, carried out under the same conditions, which display also a pair of anodic and cathodic peaks, identical with the peak potentials of the dimers. Upon goint to lower temperatures (-25 °C) and/or higher sweep rates (3 V s^{-1}), the oxidation of the dianion was not detected.

The electrochemical irreversibility of the reductions is confirmed by the magnitude of the slopes in the plots of E_p vs log v (v = scan rate), which are significantly larger than those expected for a reversible process.[35]

Therefore, the two-electron reduction of the dimers probably follows an EC mechanism where the reduction products undergo a fast irreversible decomposition reaction:

$$[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2 \xrightarrow{+2e^-} 2[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]^-$$

$$R = SiMe_2OEt,\ (CH_2)_3Si(OMe)_3$$

In dichloromethane solvent, the anion seems to be unstable since the cathodic peaks are observed (Table II) but no anodic peak is detected in the CV curves.

Experimental Section

General Data. All reactions and manipulations of complexes, reagents, and solvents were carried out under oxygen-free nitrogen by using Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen just before use. Dichloromethane and *n*-hexane were distilled from phosphorus pentoxide. Xylene was distilled from sodium before use. Decane was distilled under nitrogen before use. Infrared spectra were a recorded at 4000–200 cm^{-1} on a Nicolet 5DX, FT-IR spectrophotometer, using Nujol and hexachlorobutadiene mulls, between CsI windows. The solution spectra (THF or CH_2Cl_2) were examined in a 0.1-mm liquid cell with KBr windows. In all cases the solvent absorptions were substracted by use of the software of the spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-200-5Y (200 MHz, FT mode) instrument. The NMR chemical shifts are reported in parts per million (δ) with reference to internal tetramethylsilane. Elemental analyses were performed by the center for microanalyses of the Centro Nacional de Química Orgânica at Madrid.

[γ-(Trimethoxysilyl)propyl]cyclopentadiene was prepared[36] by reaction between (γ-chloropropyl)trimethoxysilane, $Cl(CH_2)_3Si(OMe)_3$, and sodium cyclopentadienide. The $C_5H_5(CH_2)_3Si(OMe)_3$ was purified by fractional distillation in vacuo using a Vigreux column, bp 85 °C at 0.5 mmHg. The (dimethylethoxysilyl)cyclopentadiene was synthesized by a literature procedure.[16,17]

For the purifications via column chromatography, neutral alumina (Fluka), pretreated at 250 °C and at 10^{-3} mmHg was used for compounds 1 and 2. In the case of complexes 5 and 6 silica (Merck), pretreated with Me_3SiCl, in C_6H_6, according to the literature procedure,[37] was used.

Electrochemical Measurements. Cyclic voltammetric measurements were carried out by the use of a Metrohm VA-Scanner, in conjunction with a Metrohm VA-detector and a Linseis LY-17100 X-Y recorder. Fast scan cyclic voltammograms are recorded on a Hitachi VC-6015 digital storage oscilloscope. The coulometric experiments were carried out with a Beckman Electroscan 30 instrument. The electrochemical measurements were performed in a three-electrode cell, with a platinum disk working electrode, a platinum wire auxiliary electrode, and a aqueous saturated calomel electrode (SCE) as a reference electrode. The reference electrode was separated from the test solution by a Vycor frit and a bridge of $[n\text{-}Bu_4N]PF_6$ (0.1 M) in the corresponding solvent. The $[n\text{-}Bu_4N]PF_6$ supporting electrolyte was prepared by metathesis of $n\text{-}Bu_4I$ with NH_4PF_6 in hot acetone and recrystallized thrice from ethanol. The resulting white crystals were dried in vacuo at 50–70 °C. A sample solution containing a metal complex (10^{-3} M) and a supporting electrolyte, $[n\text{-}Bu_4N]PF_6$ (0.1 M), was deaerated with prepurified nitrogen prior to measurements. For bulk electrolysis work, the working electrode was a platinum mesh electrode.

Preparation of $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2]_2$ (1). A mixture of $C_5H_5SiMe_2OEt$ (10.00 g, 59.5 mmol) and $Fe(CO)_5$ (10 mL, 74 mmol), in 40 mL of degassed xylene, was refluxed for 24 h under oxygen-free nitrogen. The dark red reaction mixture was allowed to cool and filtered to remove decomposition materials, and then the solvent and the unreacted $Fe(CO)_5$ were removed in vacuo. The crude product was dissolved in degassed THF, and the red

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[35] Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790.

[36] Deschler, U., personal communication.

[37] Wartmann, J.; Deuel, H. *Helv. Chim. Acta* **1959**, *42*, 1166.

solution obtained was filtered on a chromatography column (neutral alumina, 3 × 30 cm). Elution with THF gave a simple dark red band that was collected and concentrated to 20 mL. Hexane (60 mL) was added and the solution cooled to −50 °C for 2 days. Filtration gave 7 g (65%) of **1** as dark red crystals. The compound was recrystallized from THF/*n*-hexane (1/3) mixture: ^{1}H NMR ($CDCl_3$) δ 0.5 (s, 12 H, $SiCH_3$), 1.2 (t, 6 H, EtO), 3.7 (q, 4 H, CH_2O), 4.54 (t, 4 H, C_5H_4), 4.97 (t, 4 H, C_5H_4); ^{13}C NMR ($CDCl_3$) δ −1.42 (s, CH_3Si), 10.33 (s, EtO), 50.50 (s, CH_2O), 94.29, 93.00 (s, C_5H_4), 89.50 (s, C_5H_4-carbon bond to Si). Anal. Calcd for $C_{22}H_{30}O_6Si_2Fe_2$: C, 47.31; H, 5.37; Fe, 20.07. Found: C, 47.14; H, 5.47; Fe, 20.45.

Preparation of [(η^5-$C_5H_4(CH_2)_3Si(OMe)_3$)Fe(CO)$_2$]$_2$ (2). A mixture of $C_5H_5(CH_2)_3Si(OMe)_3$ (10.00 g, 44 mmol) and $Fe(CO)_5$ (8 mL, 60 mmol) in 30 mL of degassed decane was heated at 130 °C for 24 h, under oxygen-free nitrogen. The dark red reaction mixture that formed was allowed to cool, filtered to remove decomposition materials, and then placed on a chromatography column (neutral alumina, 3 × 30 cm). Elution with *n*-hexane/THF (2/1) gave an initial yellow band, which contained the unreacted $Fe(CO)_5$, and a second red band, eluted with THF, which was collected. The solvent was removed in vacuo from the red THF solution to give **2** as a red liquid in 60% yield: ^{1}H NMR ($CDCl_3$) δ 0.70 (m, 4 H, CH_2Si), 1.98 (m, br, 4 H, CH_2), 3.60 (s, 18 H, $Si(OMe)_3$), 5.10 (t, br, 4 H, C_5H_4), 5.58 (t, br, 4 H, C_5H_4); ^{13}C NMR ($CDCl_3$) δ 8.92 (s, CH_2Si), 26.25 (s, CH_2), 50.24 (s, $Si(OMe)_3$), 54.15 (s, CH_2), 88.23, 87.36 (s, C_5H_4). Anal. Calcd for $C_{26}H_{38}O_{10}Si_2Fe_2$: C, 46.01; H, 5.60; Fe, 16.52. Found: C, 45.93; H, 5.86; Fe, 16.16.

Preparation of [(η^5-$C_5H_4SiMe_2OEt$)Fe(CO)$_2$PPh$_3$]$^+$PF$_6^-$ (3). **1** (1.00 g, 1.8 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]^+PF_6^-$ (1.18 g, 3.6 mmol) were stirred in 90 mL of CH_2Cl_2/THF (2/1) for 24 h at room temperature. The reaction was monitored by IR spectroscopy. The initial bands of **1** at 1995, 1954, and 1774 cm^{-1} gave way to new bands at 2068 and 2022 cm^{-1} which correspond to the cationic complex $[(\eta^5\text{-}C_5H_4SiMe_2OEt)Fe(CO)_2THF]^+PF_6^-$, which was not isolated. At this point, PPh_3 (1.88 g, 7.2 mmol) was added. The mixture was stirred at room temperature for 24 h and then heated at 50 °C for 4 h. The IR spectrum showed new bands at 2057 and 2015 cm^{-1}, indicating the formation of the new phosphine-substituted cationic complex **3**. The reaction mixture was filtered, and the resulting red-orange solution was concentrated to 20 mL. Addition of 60 mL of diethyl ether caused the formation of a solid, which was filtered, washed with ether, and dried in vacuo. The solid was recrystallized from CH_2Cl_2/ether (1/3), giving **3** as yellow-gray crystals (70%): ^{1}H NMR ($CDCl_3$) δ 0.63 (s, H, $SiCH_3$), 1.45 (t, 3 H, EtO), 3.60 (q, 2 H, CH_2O), 5.27 (t, 2 H, C_5H_4), 5.63 (t, 2 H, C_5H_4), 7.54 (m, 15 H, Ph). Anal. Calcd for $C_{29}H_{30}F_6O_3P_2SiFe$: C, 50.73; H, 4.37; Fe, 8.16. Found: C, 50.55; H, 4.18; Fe, 7.96.

Preparation of [(η^5-$C_5H_4(CH_2)_3Si(OMe)_3$)Fe(CO)$_2$PPh$_3$]$^+$PF$_6^-$ (4). Under the same conditions of **3**, 1 g (1.5 mmol) of **2** and $[(\eta^5\text{-}C_5H_5)_2Fe]^+PF_6^-$ (1.00 g, 3.0 mmol) were stirred for 48 h. The progress of the reaction was monitored by IR spectroscopy. The initial bands of **2** at 1987, 1945, and 1765 cm^{-1} disappeared and gave way to new bands at 2063 and 2017 cm^{-1} which correspond to the cationic complex $[(\eta^5\text{-}C_5H_4(CH_2)_3Si(OMe)_3Fe(CO)_2THF]^+PF_6^-$ which was not isolated. PPh_3 (1.57 g, 6 mmol) was added, and the mixture was stirred 24 h at room temperature and then 3 h at 50 °C. The solution was filtered and concentrated to give a yellow-brown oil which was treated with ether and set aside at −50 °C for several hours. The yellow crystalline solid that formed was collected by filtration to give pure **4** (60%): ^{1}H NMR ($CDCl_3$) δ 0.82 (m, 2 H, CH_2Si), 2.05 (m, 2 H, CH_2), 3.50 (m, 2 H, CH_2), 5.32 (br, 2 H, C_5H_4), 5.70 (br, 2 H, C_5H_4), 7.83 (m, br, 15 H, Ph). Anal. Calcd for $C_{31}H_{34}O_5F_6P_2SiFe$: C, 49.86; H, 4.56; Fe, 7.50. Found: C, 49.20; H, 4.32; Fe, 7.15.

Preparation of K[(η^5-$C_5H_4SiMe_2OEt$)Fe(CO)$_2$] (5). Potassium benzophenone ketyl was prepared by magnetically stirring benzophenone (0.65 g, 3.6 mmol) and small freshly cut pieces of potassium metal (0.14 g, 3.6 mmol) in 65 mL of dry and degassed THF. The blue mixture was stirred for 16 h to ensure complete solubilization of the potassium. **1** (1.00 g, 1.8 mmol) was added rapidly, and the mixture was stirred for 8 h at room temperature. The blue color gradually disappeared, and an orange solution resulted. The reaction progress was monitored by IR spectroscopy. The bands of the initial dimer **1** at 1991, 1950, and 1779 cm^{-1} disappeared, but two new bands at 1859 and 1773 cm^{-1} grew in corresponding to anion **5**. At this point, the isolation of **5** can be accomplished by two methods. **Method a.** The solution was column chromatographed on pretreated silica.[37] Elution with THF gave initially a minor red band, which contained some unreacted dimer **1**, and secondly a major orange band, which was collected. Concentration to 20 mL was followed by addition of diethyl ether to cause formation of an orange solid which was collected by filtration to give **5** as an orange powdery solid in 35% yield. **Method b.** The isolation of **5** was performed by concentration of the THF reaction mixture to 15 mL. Addition of 30 mL of *n*-hexane and cooling at −50 °C for 24 h caused the formation of an orange solid that was collected by filtration and washed quickly with THF and then with *n*-hexane, giving **5** in 63% yield. Anal. Calcd for $C_{12}H_{15}O_3SiKFe$: C, 43.64; H, 4.54; Fe, 16.97. Found: C, 43.15; H, 4.10; Fe, 16.68.

Preparation of K[(η^5-$C_5H_4(CH_2)_3Si(OMe)_3$)Fe(CO)$_2$] (6). A similar procedure was used with **2** (1.20 g, 1.8 mmol), benzophenone (0.65 g, 3.6 mmol), and potassium metal (0.14 g, 3.6 mmol). Complex **6** was obtained as an orange powder solid. Method a gave a 30% yield while method b gave **6** in 70% yield. Anal. Calcd for $C_{13}H_{19}O_5SiKFe$: C, 41.27; H, 5.02; Fe, 14.81. Found: C, 41.65; H, 5.60; Fe, 14.20.

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Registry No. **1**, 66214-83-3; **2**, 110373-32-5; **3**, 110373-36-9; **4**, 110373-38-1; **5**, 110373-33-6; **6**, 110373-34-7; $C_5H_5SiMe_2OEt$, 38556-71-7; $Fe(CO)_5$, 13463-40-6; $C_5H_5(CH_2)_3Si(OMe)_3$, 71808-68-9; $[(\eta^5\text{-}C_5H_5)_2Fe]^+PF_6^-$, 11077-24-0; benzophenone, 119-61-9.