Synthesis, Characterization, and Electrochemistry of Dicyclopentadienylsiloxane-bridged Dicarbonyldi-iron

Moisés Morán,* Isabel Cuadrado, and José R. Masaguer
Departamento de Química, C-VIII, Facultad de Ciencias, Universidad Autónoma, Cantoblanco, 28049-Madrid, Spain
José Losada
Departamento de Química Inorgánica y Analítica, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid, Spain

The new metal–metal bonded binuclear iron complexes $[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]$ [R = R′ = Me, *n* = 1 (**1**) or 2 (**2**); R = Me, R′ = Ph, *n* = 1 (**3**)] have been prepared in good yield by reaction between dicyclopentadienylsiloxanes, $C_5H_5(RR'SiO)_nSiRR'C_5H_5$ (R = R′ = Me, *n* = 1 or 2; R = Me, R′ = Ph, *n* = 1), and $[Fe(CO)_5]$. Oxidation of (**1**)—(**3**) with $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ in the presence of PPh_3 gives the dicationic complexes $[\{Fe(CO)_2(PPh_3)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}][PF_6]_2$ [R = R′ = Me, *n* = 1 (**7**) or 2 (**8**); R = Me, R′ = Ph, *n* = 1 (**9**)]. The dianionic complexes $K_2[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]$ [R = R′ = Me, *n* = 1 (**10**) or 2 (**11**); R = Me, R′ = Ph, *n* = 1 (**12**)] were obtained by treating (**1**)—(**3**) with potassium diphenylketyl. The new binuclear iron complexes have been characterized by ^1H and ^{13}C n.m.r. and i.r. spectroscopy. The electrochemistry of compounds (**1**)—(**3**) indicates that two-electron oxidation products are stable on the voltammetric time-scale. Their kinetic stability depends upon the solvent donicity. The final products are dication complexes which do not contain carbonyl bridges (**4**)—(**6**).

Considerable attention is presently being focused on the synthesis and study of a variety of metal–metal bonded transition-metal complexes.[1–5] A large number of them have been found to function as unique catalysts or catalyst precursors, and it is hoped that some may offer new possibilities for activating organic or inorganic molecules by co-operative involvement of their active positions.[6] In this way, dinuclear complexes are related to several important catalytic processes such as heterogeneous Fischer-Tropsch reactions, olefin metathesis, or alkylene polymerization.[4]

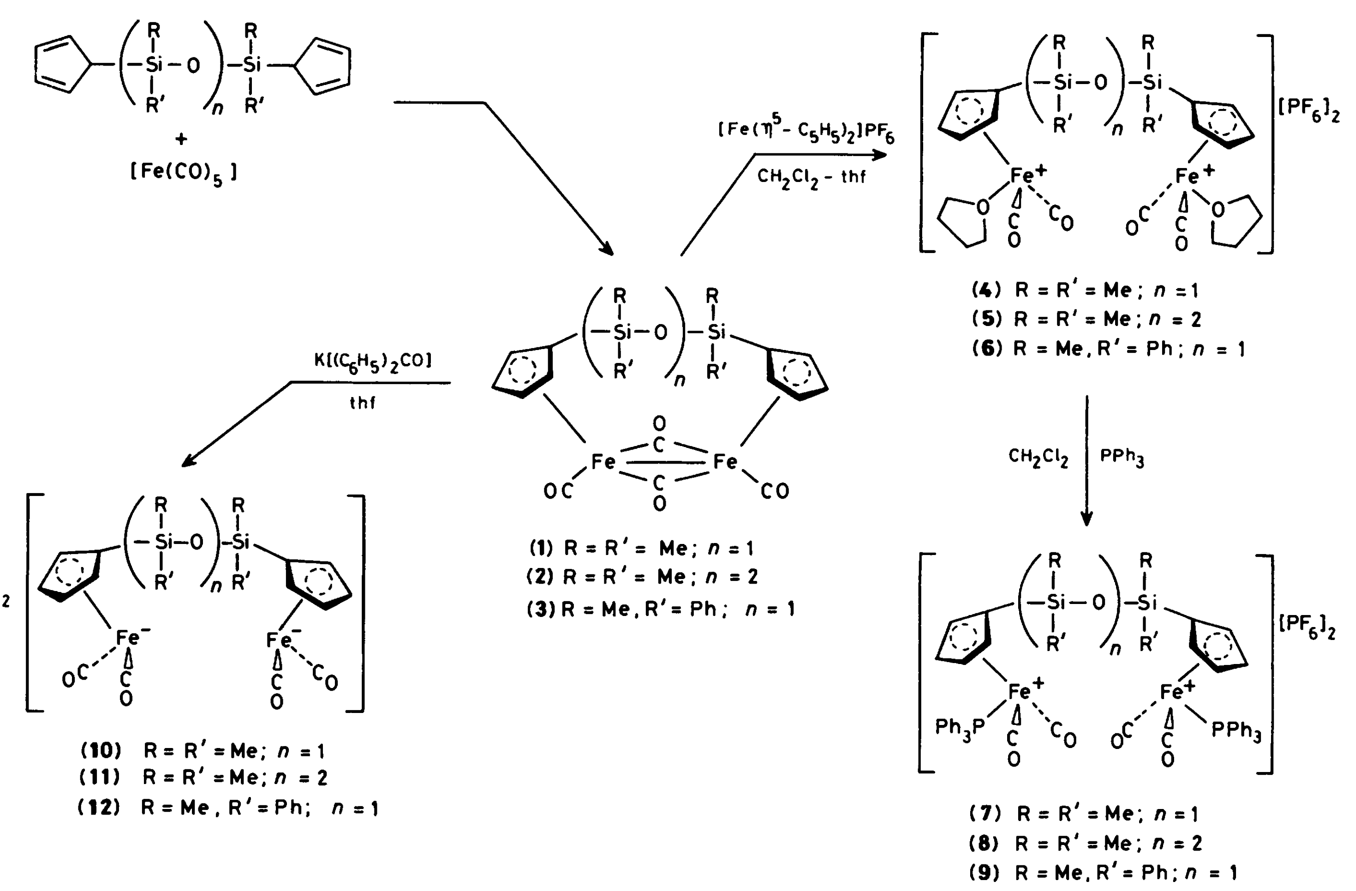
Some of the interesting organometallic metal–metal bonded systems are bridged binuclear iron complexes. These systems are well suited for studying interactions between two metal reaction sites, since being bridge linked inherently retains the two metals in close proximity. The only linked binuclear iron complexes described until now have a dicyclopentadienylsilane link and/or a bridging diphosphine ligand.[7–10] But as yet, there are no binuclear complexes containing cyclopentadienylsiloxane as linkage between two iron atoms.

Siloxanes have a special interest because they are potential catalyst supports; the poly(phenylmethylsiloxanes), $(\text{–OSiPhMe–})_n$, have been used as substrates for metal atoms to form polymeric π-arene complexes attached to the silicone backbone.[11,12] An alternative method of attaching metals indirectly to a silicone chain involves the use of silicones with pendant cyclopentadienyl groups. These ligands are effective anchoring groups since the metal is strongly bound by the η^5-co-ordination.[13,14] Polymers of these types and related titanium complexes in which the cyclopentadienyl rings of titanocene dichloride are bridged have been reported.[15] The cyclopentadienyl-siloxanes and -silanes are considered to be interesting new materials for metal vapour synthesis, possibly providing a route to liquid phase cyclopentadienyl-functionalized catalyst systems in which the active sites could be amenable to specific tailoring and precise characterization.[16]

Taking into account all these factors, we have prepared the new siloxane bridged-cyclopentadienyl binuclear species $[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]$ [R = R′ = Me, *n* = 1 (**1**) or 2 (**2**); R = Me, R′ = Ph, *n* = 1 (**3**)] (Scheme) in which the –Si–O–Si– units behave as chemically non-interactive links between the two cyclopentadienyl rings and hence maintain the two metal centres in close proximity, even when the bonding between the two iron atoms is destroyed by oxidation or reduction processes, resulting in the cationic binuclear complexes $[\{Fe(CO)_2(thf)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}][PF_6]_2$ [R = R′ = Me, *n* = 1 (**4**) or 2 (**5**); R = Me, R′ = Ph, *n* = 1 (**6**), thf = tetrahydrofuran] and $[\{Fe(CO)_2(PPh_3)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}][PF_6]_2$ [R = R′ = Me, *n* = 1 (**7**) or 2 (**8**); R = Me, R′ = Ph, *n* = 1 (**9**)], or the dianion complexes $K_2[\{Fe(CO)_2\}\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]$ [R = R′ = Me, *n* = 1 (**10**) or 2 (**11**); R = Me, R′ = Ph, *n* = 1 (**12**)]. We report here full details on the synthesis, characterization, and properties of these compounds and in addition the electrochemical behaviour in CH_2Cl_2 or thf is reported and discussed.

Results and Discussion

Reaction of one equivalent of the chlorosiloxane $Cl(RR'SiO)_nSiRR'Cl$ (R = R′ = Me, *n* = 1 or 2; R = Me, R′ = Ph, *n* = 1) with two equivalents of sodium cyclopentadienide, in thf solution, gives the siloxane-substituted cyclopentadienes $C_5H_5(SiRR'O)_nSiRR'C_5H_5$. After isolation they are treated directly with $Fe(CO)_5$, in decane or xylene (isomer mixture) as solvents, at *ca.* 130 °C to form the new siloxane-bridged binuclear Fe–Fe bonded complexes (**1**)—(**3**) (Scheme). In these preparations it is necessary to remove unreacted products or decomposition materials by column chromatography. Complexes (**1**)—(**3**) are isolated pure as red air-stable crystals and display characteristic i.r. and n.m.r. spectral data similar to those of the related silane-bridged binuclear systems $[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4SiMe_2C_5H_4\}]$,[7] and $[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4Me_2Si(CH_2)_2SiMe_2C_5H_4\}]$[8] and the silylcyclopentadienyl iron dimers $[\{Fe(CO)_2(\eta^5\text{-}C_5H_4R'')\}_2]$ [R″ = $SiMe_2(OEt)$ or $(CH_2)_3Si(OMe)_3$].[17] The relatively high yield of compound (**2**) (*ca.* 55%) compared to (**1**) and (**3**) (*ca.* 30%) indicates that a longer siloxane chain in the cyclopentadienyl bridge is advantageous in the synthesis.



Scheme 1.

Table 1. Analytical[a] and physical data for the complexes

Complex	Colour	Analysis (%)			ν(CO)/cm^{-1}	
		C	H	Fe	CH$_2$Cl$_2$	*b*, *c*
(1) $[\{Fe(CO)_2\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4Me_2SiOSiMe_2C_5H_4)]$	Red	44.9 (44.6)	4.3 (4.1)	23.6 (23.1)	1 993vs, 1 950w, 1 771vs	2 001vs, 1 962w, 1 784s[b]
(2) $[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(Me_2SiO)_2SiMe_2C_5H_4\}]$	Red	42.8 (43.0)	4.2 (4.6)	20.5 (20.1)	1 994vs, 1 953s, 1 773vs	1 996vs, 1 957vs, 1 785vs[b]
(3) $[\{Fe(CO)_2\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4MePhSiOSiMePhC_5H_4)]$	Red	55.7 (55.3)	3.6 (3.9)	18.3 (18.1)	1 996vs, 1 954w, 1 772vs	2 002vs, 1 963w, 1 785s[b]
(4) $[\{Fe(CO)_2(thf)\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4Me_2SiOSiMe_2C_5H_4)][PF_6]_2$	*d*				2 064vs, 2 016vs	
(5) $[\{Fe(CO)_2(thf)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(Me_2SiO)_2SiMe_2C_5H_4\}]\text{-}[PF_6]_2$	*d*				2 065vs, 2 017vs	
(6) $[\{Fe(CO)_2(thf)\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4MePhSiOSiMePhC_5H_4)]\text{-}[PF_6]_2$	*d*				2 067vs, 2 019vs	
(7) $[\{Fe(CO)_2(PPh_3)\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4Me_2SiOSiMe_2C_5H_4)]\text{-}[PF_6]_2$	Yellow	48.1 (48.5)	3.9 (3.7)	8.8 (8.3)	2 054vs, 2 010vs	2 051vs, 2 008vs[c]
(8) $[\{Fe(CO)_2(PPh_3)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(Me_2SiO)_2SiMe_2C_5H_4\}]\text{-}[PF_6]_2$	Yellow-brown	48.7 (48.9)	4.3 (4.1)	8.4 (8.1)	2 053vs, 2 010vs	2 050vs, 2 007vs[c]
(9) $[\{Fe(CO)_2(PPh_3)\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4MePhSiOSiMePhC_5H_4)]\text{-}[PF_6]_2$	Yellow	53.8 (54.0)	3.5 (3.8)	8.0 (7.8)	2 056vs, 2 013vs	2 052vs, 2 008vs[c]
(10) $K_2[\{Fe(CO)_2\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4Me_2SiOSiMe_2C_5H_4)]$	Orange	38.8 (39.1)	3.3 (3.6)	20.5 (20.3)		1 855s, 1 845(sh), 1 762vs[c]
(11) $K_2[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(Me_2SiO)_2SiMe_2C_5H_4\}]$	Orange	37.3 (37.7)	4.4 (4.0)	7.8 (7.6)		1 854s, 1 846s, 1 770s[c]
(12) $K_2[\{Fe(CO)_2\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4MePhSiOSiMePhC_5H_4)]$	Red-orange	48.4 (48.1)	3.7 (3.5)	16.5 (16.3)		1 858s, 1 770s, 1 761s[c]

[a] Required values are given in parentheses. [b] In cyclohexane. [c] In thf. [d] Not isolated.

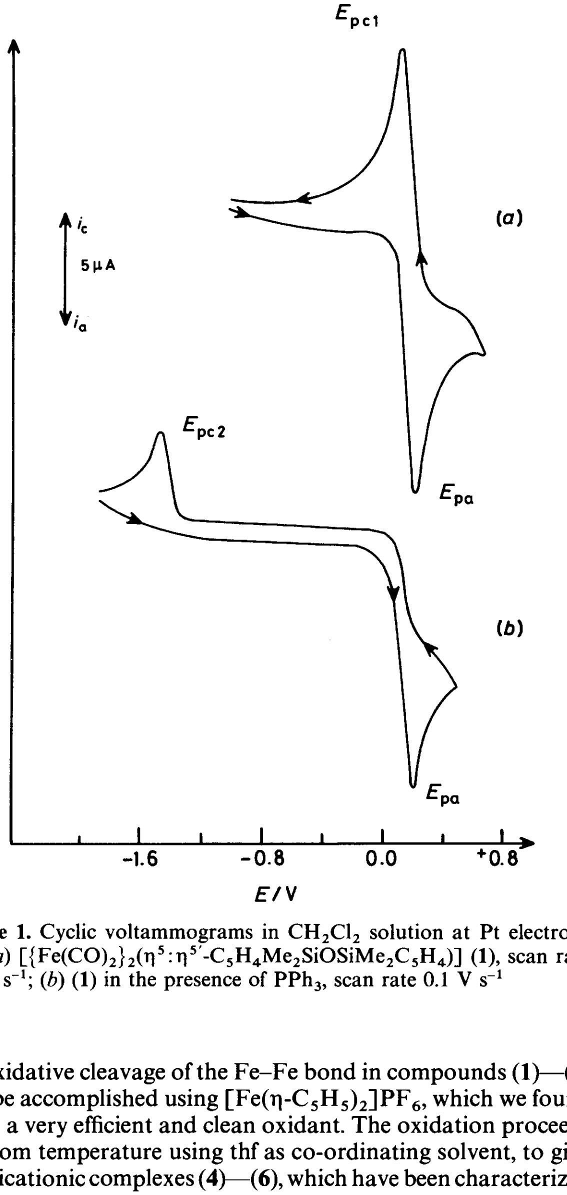


Figure 1. Cyclic voltammograms in CH_2Cl_2 solution at Pt electrode for: (*a*) [$\{Fe(CO)_2\}_2(\eta^5:\eta^{5'}\text{-}C_5H_4Me_2SiOSiMe_2C_5H_4)$] (**1**), scan rate 0.1 V s^{-1}; (*b*) (**1**) in the presence of PPh_3, scan rate 0.1 V s^{-1}

Oxidative cleavage of the Fe–Fe bond in compounds (**1**)—(**3**) can be accomplished using [$Fe(\eta\text{-}C_5H_5)_2$]PF_6, which we found to be a very efficient and clean oxidant. The oxidation proceeds at room temperature using thf as co-ordinating solvent, to give the dicationic complexes (**4**)—(**6**), which have been characterized by i.r. spectroscopy (see Experimental section and Table 1), but not isolated. They are excellent intermediates for the preparation of the phosphine dicationic analogues (**7**)—(**9**), which are formed by adding an excess (2:1) of PPh_3 to a CH_2Cl_2–thf solution of the intermediates. This step needs gentle warming at 35—40 °C for several hours to effect the complete substitution of thf by the triphenylphosphine ligand. The $(RR'SiO)_nSiRR'$ groups behave as chemically non-interactive links between the two cyclopentadienyl rings and hence keep the two iron centres in close proximity. Compounds (**7**)—(**9**) are air-stable yellow crystals.

Compounds (**1**)—(**3**) are rapidly and cleanly reduced, using potassium diphenylketyl as cleavage reagent in thf solution at room temperature (Scheme). The same method has been used to synthesize K[$Fe(CO)_2(\eta^5\text{-}C_5H_5)$],[18] and we have also found that K[$(C_6H_5)_2CO$] is a very efficient reagent for reducing [$\{Fe(CO)_2(\eta^5\text{-}C_5H_4R'')\}_2$] [R″ = $SiMe_2(OEt)$ or $(CH_2)_3Si(OMe)_3$][17] into their respective monoanions K[$Fe(CO)_2(\eta^5\text{-}C_5H_4R'')$]. It is interesting to note that in the related binuclear dicyclopentadienylsilane-bridged systems, the dianions [$\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4SiMe_2C_5H_4\}$]$^{2-}$ and [$\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4Me_2Si(CH_2)_2SiMe_2C_5H_4\}$]$^{2-}$ (obtained by treatment with Na/Hg)[7,8] are used '*in situ*' for further reactions, usually alkylation with CH_3I or allyl halides.[8,19] In our case, the formation of Na_2[$\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}$] salts was difficult, probably because large contact surfaces of Na/Hg were necessary to effect the complete reduction due to low solubility of the dimers, especially (**1**) and (**2**), in thf at room temperature; thus long reaction times were necessary, which caused partial progressive decomposition of the anions. However, this feature is not observed when potassium diphenylketyl is used, the reduction being complete in 30 min. The dianion complexes (**10**)—(**12**) are isolated pure as orange or red-orange powdery solids; they must be handled and stored under nitrogen since exposure to air rapidly forms the precursor dimers (**1**)—(**3**) respectively.

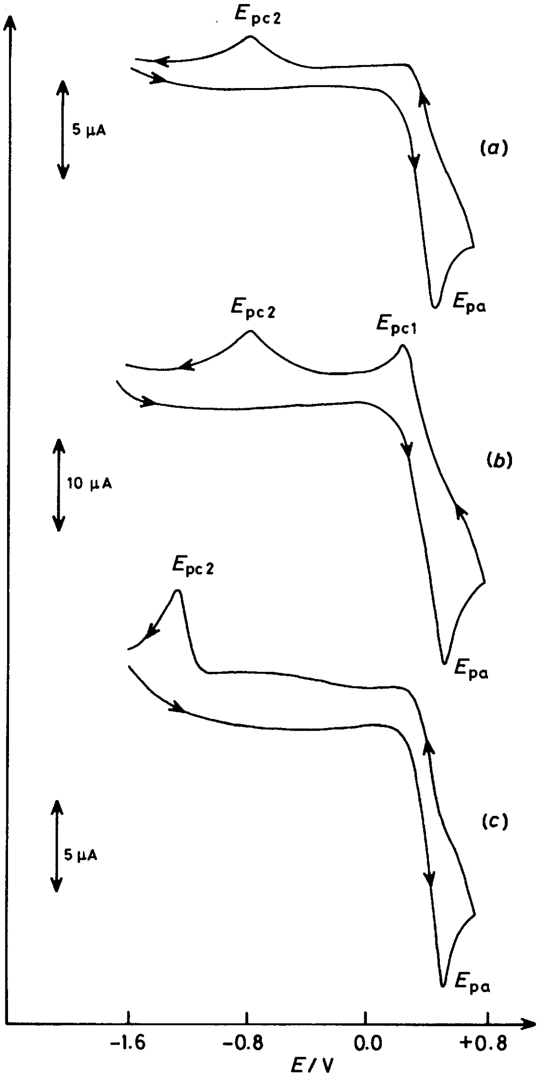


Figure 2. Cyclic voltammograms in thf solution, at Pt electrode for: (*a*) [$\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(Me_2SiO)_2SiMe_2C_5H_4\}$] (**2**), scan rate 0.1 V s^{-1}; (*b*) (**2**), scan rate 0.8 V s^{-1}; (*c*) (**2**) in the presence of PPh_3, scan rate 0.1 V s^{-1}

All the complexes synthesized show characteristic strong i.r. bands for the siloxane chain at[20,21] 1 100—1 000 [ν_{asym}(SiOSi)], 1 280—1 255 [$\delta(SiCH_3)$], and 1 180—1 100 cm^{-1} [δ(SiPh)]. Frequencies corresponding to the carbonyl stretching vibrations, ν(CO), in solution for compounds (**1**)—(**12**) are listed in Table 1. The shifts to lower frequencies when compared to the unsubstituted analogues [$\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2$] [ν(CO)-($CH_2Cl_2$): 1 998, 1 959, and 1 775 cm^{-1}] reflect the electron-

Table 2. Cyclic voltammetric[a] data for the complexes at 200 mV s^{-1}

		Oxidation						Reduction		
Compound	Solvent	E_{pa}	E_{pc1}	E_{pc2}	i_a/i_c	n[b]	k_f[c]/s^{-1}	E_{pc}	E_{pa}	n[b]
(1)	CH_2Cl_2	+0.18	+0.13		1	2		−2.39		2
	thf	+0.44		−0.82		2	2.3	−2.24	−1.38	2
(2)	CH_2Cl_2	+0.14	+0.09		1	2		−2.43		2
	thf	+0.42		−0.88		2	2.1	−2.26	−1.40	2
(3)	CH_2Cl_2	+0.26	+0.20		1			−2.32		2
	thf	+0.48		−0.78		2	2.4	−2.10	−1.32	2
(7)	CH_2Cl_2							−1.64	+0.20	
	thf							−1.32	+0.41	
(8)	CH_2Cl_2							−1.67	+0.18	
	thf							−1.37	+0.38	
(9)	CH_2Cl_2							−1.52	+0.24	
	thf							−1.38	+0.44	

[a] At platinum electrode. Potentials quoted *vs.* $[Fe(\eta^5-C_5H_5)_2]^+$–$[Fe(\eta^5-C_5H_5)_2]$ couple. [b] Number of electrons (coulometric experiments). [c] Rate constant of the decomposition step at −30 °C.

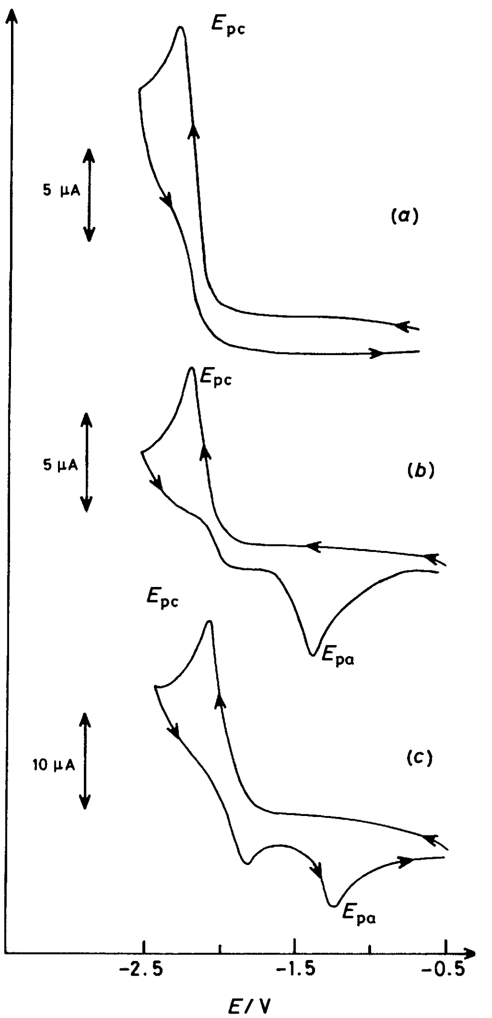


Figure 3. Cyclic voltammograms, at Pt electrode for: (*a*) $[\{Fe(CO)_2\}_2(\eta^5:\eta^{5'}-C_5H_4Me_2SiOSiMe_2C_5H_4)]$ **(1)**, in CH_2Cl_2 solution, scan rate 0.1 V s^{-1}; **(1)**, in thf solution, scan rate 0.1 V s^{-1}; (*c*) **(1)**, in thf solution at −30 °C, scan rate 0.8 V s^{-1}

releasing effect of the SiRR′ substituted rings, which is greater for $SiMe_2$ than SiMePh substituents. For the dianion compounds **(10)**—**(12)**, the ν(CO) splitting observed in thf solution can be attributed to ion-pair formation. A similar effect has been observed for the anion $[Fe(CO)_2(\eta^5-C_5H_5)]^-$.[18,22]

Electrochemical Studies.—Ambient-temperature cyclic voltammograms (c.v.) of compounds **(1)**—**(3)** in (0.1 mol dm^{-3} $[NBu^n{}_4]PF_6$) dichloromethane or thf solutions at a platinum disc electrode are shown in Figures 1—3, at different scan rates. The anodic and cathodic peak potentials are listed in Table 2. Potentiostatic coulometry and comparisons of limiting currents obtained from rotating disc electrode (r.d.e.) voltammograms between **(1)**—**(3)** and $[\{Fe(CO)_2(\eta^5-C_5H_5)\}_2]$ indicate two-electron transfer. Cyclic voltammetry shows that **(1)**—**(3)** undergo reversible two-electron oxidation in CH_2Cl_2 (Figure 1). These electrochemical processes, and those described later, are diffusion controlled with the anodic current function ($i_{pa}/v^{\frac{1}{2}}$) independent of scan rate (v) over the range 0.1—1 V s^{-1}. The peak separation at 100 mV s^{-1} was *ca.* 50 mV. The ratio of cathodic to anodic currents $i_{pa}/i_{pc} = 1$ over the scan range studied and indicates that for compounds **(1)**—**(3)** chemically reversible processes take place and stable dications, in the c.v. time-scale, are formed. However, attempts to isolate these dications, not containing carbonyl bridges, by means of exhaustive electrolysis or chemical oxidation with $[Fe(\eta^5-C_5H_5)_2]PF_6$ were unsuccessful. In all cases, as the reaction proceeds the i.r. bands corresponding to the bridging carbonyls of **(1)**—**(3)** disappear and new bands characteristic of the dications $[\{Fe(CO)_2(solvent)\}_2\{\eta^5:\eta^{5'}-C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]^{2+}$ (Table 1) appear.

Addition of PPh_3 to these solutions of **(1)**—**(3)** significantly modifies the c.v. curves (Figure 1); the reversible systems disappear and new reduction peaks (E_{pc2}) can be observed at the potentials listed in Table 2. These cathodic peak potentials are identical to the reduction peak potentials observed in the c.v. curves of CH_2Cl_2 solutions of the chemically obtained cations **(7)**—**(9)** respectively. The formation of these cations was demonstrated by i.r. spectroscopic monitoring of solutions obtained by exhaustive electrochemical oxidation of dimers **(1)**—**(3)** in the presence of PPh_3.

In thf the electrochemical behaviour is very different. At high scan rates ($v \geqslant 800$ mV s^{-1}) chemically reversible systems can be observed (Figure 2) (at $v = 5$ V s^{-1} the i_{pc}/i_{pa} ratio is *ca.* 0.8). Over the range 50—700 mV s^{-1} irreversible processes, corresponding to two-electron transfers, take place. The stability of these dications in thf has been checked by obtaining c.v.s at low temperatures (−30 °C); the i_{pc}/i_{pa} ratio is close to unity at 1 V s^{-1} and decreases at lower sweep rates. The average values of the first-order constants, k_f, for the decompositions of $(\mathbf{1})^{2+}$—$(\mathbf{3})^{2+}$, calculated using the method of Nicholson and Shain,[23] are listed in Table 2. Thus differing substituents on the siloxane chain do not generate significant differences in the decomposition rates of these cations.

Exhaustive electrolysis of the dimers in thf leads to the formation of the cations (**4**)—(**6**), which are also obtained by chemical oxidation. Their formation was evidenced by i.r. spectroscopy (Table 1) and cyclic voltammetric control of solutions obtained from bulk electrolytic oxidations. The cyclic voltammograms display a pair of cathodic and anodic peaks, their potentials being identical with the peak potentials of the dimers (**1**)—(**3**).

In the presence of PPh_3 the cathodic peaks shift to more negative potentials (Figure 2). The processes remain irreversible even at lower temperatures (−30 °C) and for higher sweep rates (5 V s^{-1}), suggesting the formation of the cations (**7**)—(**9**).

These results are consistent with an electrochemical (e.c.) mechanism as shown below. Therefore the electrochemical oxidation of (**1**)—(**3**) is very different from that shown by $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$.[24] Similarly, distinctive behaviour has been found for $[Fe_2(CO)_2\{Ph_2P(CH_2)_nPPh_2\}(\eta^5:\eta^{5'}\text{-}C_5H_4SiMe_2C_5H_4)]$ (n = 1—3), where electrochemical oxidation takes place in two one-electron steps.[10]

$$\begin{tikzcd}
{[\{Fe_2(\mu\text{-}CO)(CO)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]} \arrow[r, shift left, "-2e^-"] & {[\{Fe(\mu\text{-}CO)(CO)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]^{2+}} \arrow[l, shift left, "E_{pa}"] \arrow[d, "k_f"] \\
 & {[\{Fe(CO)_2(solvent)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]^{2+}} \arrow[ul, "+2e^-", "E_{pc2}"']
\end{tikzcd}$$

The electrochemical reduction of compounds (**1**)—(**3**) has also been examined by cyclic voltammetry. The c.v. curves in thf solutions (Figure 3) show a pair of cathodic and anodic peaks corresponding to an irreversible process with a large potential peak separation (Table 2). Potentiostatic coulometry and comparisons of the r.d.e. voltammograms with $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ indicate that the reduction corresponds to two-electron transfers.

The products of the electroreduction are the anions (**10**)—(**12**), which do not contain carbonyl bridges. These anions have been synthesized and isolated chemically. The electroreductive formation of (**10**)—(**12**) is evidenced by i.r. spectroscopic monitoring of solutions obtained by exhaustive electrolysis. In addition cyclic voltammograms recorded from solutions of the chemically prepared anions, carried out under the same conditions, display a pair of anodic and cathodic waves, their peak potentials being identical with those of the dimers (**1**)—(**3**).

At lower temperatures and/or higher sweep rates, oxidation peaks corresponding to dianions with carbonyl bridges are detected (Figure 3).

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

Therefore, the two-electron reductions of the dimers probably follow an e.c. mechanism where the reduction products undergo a fast irreversible decomposition, see below.

$$\begin{tikzcd}
{[\{Fe(\mu\text{-}CO)(CO)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]} \arrow[r, "+2e^-"] & {[\{Fe(\mu\text{-}CO)(CO)\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]^{2-}} \arrow[d, "fast"] \\
 & {[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]^{2-}}
\end{tikzcd}$$

In dichloromethane as solvent the anion seems to be unstable since the cathodic peaks are observed (Figure 3), but any anodic peak is detected in the c.v. curves.

These results are similar to those found in the electrochemical reduction of $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ at mercury and platinum electrodes,[25–27] but indicate different behaviour from $[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4SiMe_2C_5H_4\}]$ which is reduced in two one-electron steps, at a mercury electrode.[7]

Experimental

All reactions and manipulations were carried out under oxygen-free nitrogen using Schlenk techniques. Tetrahydrofuran (thf) and diethyl ether were distilled from sodium diphenylketyl under nitrogen just before use. Dichloromethane was distilled from phosphorus pentoxide. Xylene was distilled from sodium before use. Infrared spectra were recorded in the range 4 000—200 cm^{-1} on a Nicolet 5DX FT-IR spectrophotometer using Nujol or hexachlorobutadiene mulls between CsI windows. The solution spectra were examined in a 0.1-mm cell with KBr windows. The proton and carbon n.m.r. spectra were recorded on a Bruker WH-200-SY (200 MHz, Fourier-transform mode) spectrometer. Chemical shifts (δ) are reported in p.p.m. with reference to internal $SiMe_4$.

The chlorosiloxanes $Cl(Me_2SiO)_nSiMe_2Cl$ (n = 1 or 2) were prepared by controlled partial hydrolysis of $SiMe_2Cl_2$ in diethyl ether–1,4-dioxane.[28] Controlled partial hydrolysis of $SiMePhCl_2$ in diethyl ether affords ClSiMePhOSiMePhCl.[29] These chlorosiloxanes react readily with sodium cyclopentadienide to give $C_5H_5(SiRR'O)_nSiRR'C_5H_5$ (R = R′ = Me; R = Me, R′ = Ph).[15]

The electrochemical apparatus, techniques, and measurements have been described previously.[30] All potentials are quoted against the $[Fe(\eta^5\text{-}C_5H_5)_2]^+$–$[Fe(\eta^5\text{-}C_5H_5)_2]$ couple.

Synthesis of Complexes $[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}\text{-}C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]$.—The preparation of (**1**) is described in detail below. The procedures for (**2**) and (**3**) were similar (Table 1).

Crude $C_5H_5SiMe_2OSiMe_2C_5H_5$, previously prepared as above from $ClMe_2SiOSiMe_2Cl$ (14.20 g, 70 mmol) and $Na(C_5H_5)$ (12.3 g, 140 mmol), was dissolved in dry, degassed xylene (25 cm^3) and $[Fe(CO)_5]$ (19.2 cm^3, 142 mmol) was added. The mixture was heated at 130 °C for 24 h. The red mixture was allowed to cool to room temperature, filtered to remove decomposition materials, and the solvent removed in vacuum. Any unreacted $[Fe(CO)_5]$ was collected in the low-temperature trap. The crude products were dissolved in thf–n-hexane (1:2) and the resulting red solution placed on a chromatography column (neutral alumina, 3 × 30 cm). Elution with hexane developed an initial clear yellow band which was rejected, and after elution with thf gave a red band which was collected. This was concentrated to 15 cm^3 and n-hexane (50

cm^3) added. The solution was cooled to -50 °C for 2 d. Filtration afforded (**1**) as red crystals.

(**1**), $\delta_H(CDCl_3)$ 0.35 (12 H, s, $SiCH_3$), 4.40 (4 H, t, C_5H_4), 5.40 (4 H, t, C_5H_4); $\delta_C(CDCl_3)$ 1.21 (s, CH_3), 93.2, 94.6 (s, C_5H_4), 211.0 (s, CO). (**2**), $\delta_H(CDCl_3)$ 0.40 (18 H, s, $SiCH_3$), 4.42 (4 H, t, C_5H_4), 4.96 (4 H, t, C_5H_4); $\delta_C(CDCl_3)$ 1.2 (s, $SiCH_3$), 93.0, 94.3 (s, C_5H_4), 210 (s, CO). (**3**), $\delta_H(CDCl_3)$ 0.61 (6 H, s, $SiCH_3$), 4.4 (4 H, t, C_5H_4), 5.1 (4 H, t, C_5H_4), 7.3 (10 H, br m, Ph); $\delta_C(CDCl_3)$ 1.30 (s, $SiCH_3$), 96.4, 96.6 (s, C_5H_4), 127.6, 133.2 (s, Ph), 209.6 (s, CO).

Synthesis of the Dicationic Complexes $[\{Fe(CO)_2(PPh_3)\}_2\{\eta^5:\eta^{5'}-C_5H_4(RR'SiO)_nSiRR'C_5H_4\}][PF_6]_2$.—The preparation of (**7**) is described in detail below. The procedures for (**8**) and (**9**) were similar.

Compound (**1**) (1 g, 2.05 mmol) and $[Fe(\eta^5-C_5H_5)_2]PF_6$ (1.40 g, 4.20 mmol) were stirred in CH_2Cl_2–thf (2:1) (80 cm^3) for 24 h at room temperature. The reaction was monitored by i.r. spectroscopy. The initial ν(CO) bands of (**1**) at 1 994, 1 953, and 1 773 cm^{-1} disappear and give way to new bands at 2 065 and 2 018 cm^{-1}, which correspond to the dicationic bridged complex (**4**) which is not isolable. To this solution PPh_3 (1.10 g, 4.20 mmol) was added. The mixture was stirred for 3 h at room temperature, then heated to 40 °C for 3 h, and finally stirred overnight at room temperature to ensure complete substitution. The i.r. spectrum then showed two new bands at 2 054 and 2 010 cm^{-1}, indicating the formation of the cation (**7**). The red-orange solution was filtered and concentrated to 15 cm^3. Addition of diethyl ether (50 cm^3) caused formation of a solid which was filtered off, washed several times with ether (10 cm^3), and dried in vacuum. The solid was recrystallized from CH_2Cl_2–ether (1:3), giving yellow crystals of (**7**).

(**7**), $\delta_H(CDCl_3)$ 0.50 (12 H, s, $SiCH_3$), 4.42 (4 H, t, C_5H_4), 5.42 (4 H, t, C_5H_4), 7.56 (30 H, m, Ph). (**8**), $\delta_H(CDCl_3)$ 0.51 (18 H, s, $SiCH_3$), 4.51 (4 H, t, C_5H_4), 5.16 (4 H, t, C_5H_4), 7.57 (30 H, m, Ph). (**9**), $\delta_H(CDCl_3)$ 0.70 (6 H, s, $SiCH_3$), 4.48 (4 H, t, C_5H_4), 5.20 (4 H, t, C_5H_4), 7.52 (40 H, br m, Ph).

Synthesis of the Dianion Complexes $K_2[\{Fe(CO)_2\}_2\{\eta^5:\eta^{5'}-C_5H_4(RR'SiO)_nSiRR'C_5H_4\}]$.—The preparation of (**10**) is described in detail below, (**11**) and (**12**) were obtained similarly.

Potassium diphenylketyl 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 thf (25 cm^3) at room temperature. The blue mixture was stirred for 5 h to ensure complete solubilization of the potassium metal. Compound (**1**) (0.87 g, 1.8 mmol) was rapidly added, and the mixture stirred at room temperature; the progressive disappearance of the blue colour of the potassium benzophenone was observed. The reaction was monitored by i.r. spectroscopy. After 12 h the initial bands of the dimer at 1 992, 1 951, and 1 771 cm^{-1} had completely disappeared, to be replaced by new strong bands at 1 855, 1 846, and 1 762 cm^{-1} corresponding to the dianion (**10**). The solution was filtered and the solvent removed *in vacuo* to 15 cm^3. Addition of diethyl ether resulted in the formation of a solid which was collected by filtration, to give (**10**) as an orange, very air-sensitive solid.

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