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Ferrocenyl Compounds Containing Two Hypervalent Silicon Species. Electrochemical Studies

Genevieve Cerveau, Claude Chuit, Ernest Colomer, Robert J. P. Corriu,* and Catherine Reyé

Laboratoire "Hétérochimie et Aminoacides", URA CNRS 1097, Institut de Chimie Fine, Université de Montpellier II, Place Eugène-Bataillon, F-34095 Montpellier Cedex 5, France

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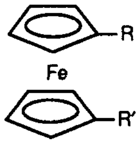
Summary: Mono- and bis-pentacoordinated systems, with either silatrane or catecholate units, were obtained in good yields from 1,1′-bis(trimethoxysilyl)ferrocene. Electrochemical study of these compounds showed a significant reduction in the redox potential Fe^{II}/Fe^{III} when the silicon atom is pentacoordinated, in contrast to the small increase in this potential in ferrocenes bearing tetracoordinated silicon substituents.

Since the pioneer work of Frye,[1] hypervalent species of silicon have received much attention.[2-6] Recently, a new route to fluorosilicates has been reported[7] and extended to alkoxosilicates[8] and even to hydridoalkoxosilicates.[9] Novel systems have also been described: pentacoordinated silicon compounds containing organometallic groups[10,11] and pentacoordinated catecholates bearing functional substituents.[12,13]

In this paper we report the synthesis of compounds containing two hypervalent silicon atoms in the same molecule and an unexpected electrochemical effect introduced by the hypervalent structure at silicon.

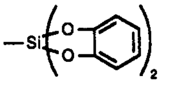
Dilithioferrocene is easily prepared from ferrocene,[14] and the subsequent reaction with chlorotrimethoxysilane[15] leads to 1,1′-bis(trimethoxysilyl)ferrocene (**1**) (eq 1),[16,17] which can be reduced into 1,1′-disilylferrocene (**2**).[18]

Table I. Spectral Data and Redox Potentials for Complexes 1–6[a]

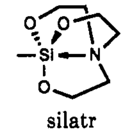


compd no.	R	R′	^{29}Si NMR	mass data for ^{56}Fe, *m/e*	$E_{1/2}$, V[23]
	H	H			+0.4
1	Si(OMe)$_3$	Si(OMe)$_3$	–47.40[b]	426 (mol. peak)	+0.55
2	SiH$_3$	SiH$_3$	–62.20[e]	246 (mol. peak)	+0.61
3	Si(OMe)$_3$	Si(cat)	–45.70[c] –80.27	549 (A$^-$)	+0.31
4	Si(cat)	Si(cat)	–78.63[c]	711 (A^{2-}K$^+$)	+0.07
5	Si(OMe)$_3$	silatr	–46.23[d] –74.57	479 (mol. peak)	+0.21
6	silatr	silatr	–69.69[b]	532 (mol. peak)	–0.07

[a] Structures for Si(cat) and silatr are as follows.

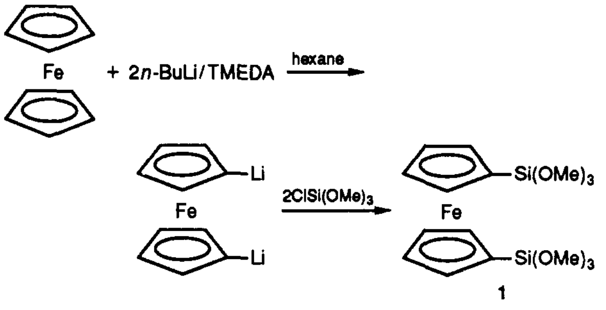


Si(cat)



silatr

[b] In CDCl$_3$. [c] In CD$_3$OD. [d] In CD$_2$Cl$_2$. [e] In CDCl$_3$; q, $J_{\mathrm{Si,H}}$ = 201 Hz.



(1)

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(16) Complex 1: 15 mmol of 1,1′-dilithioferrocene[14] (from 2.79 g of ferrocene) in 125 mL of hexane was added dropwise to 5.5 g (35 mmol) of ClSi(OMe)$_3$ in 30 mL of hexane at 0 °C. The reaction mixture was warmed to room temperature and was stirred for 16 h. After this time the solution was filtered and the solvent was evaporated in vacuo. Unreacted ferrocene was sublimed, and the residue was distilled. A 10-g amount (52%) of 1 was recovered; bp 145–147 °C (~7 Pa). ^{1}H NMR (CDCl$_3$): δ 4.42 and 4.24 (2 × 2 H, 2 t, C_5H_4), 3.63 (9 H, s, OCH_3). ^{13}C NMR (CDCl$_3$): δ 74.4 and 72.7 (C-2 and C-3), 72.2 (C-1), 51.2 (OCH_3). Anal. Calcd for $C_{16}H_{26}FeO_6Si_2$: C, 45.09; H, 6.11; Fe, 13.11; Si, 13.15. Found: C, 45.00; H, 6.01; Fe, 12.96; Si, 13.55. A similar method has been reported for the analogous ethoxy derivative.[17]

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Reactions of **1** with catechol or with triethanolamine are highly selective: either the mono- (**3** and **5**) or the bis-pentacoordinated systems (**4** and **6**) can be obtained in almost quantitative yields[19-22] (eqs 2–5).

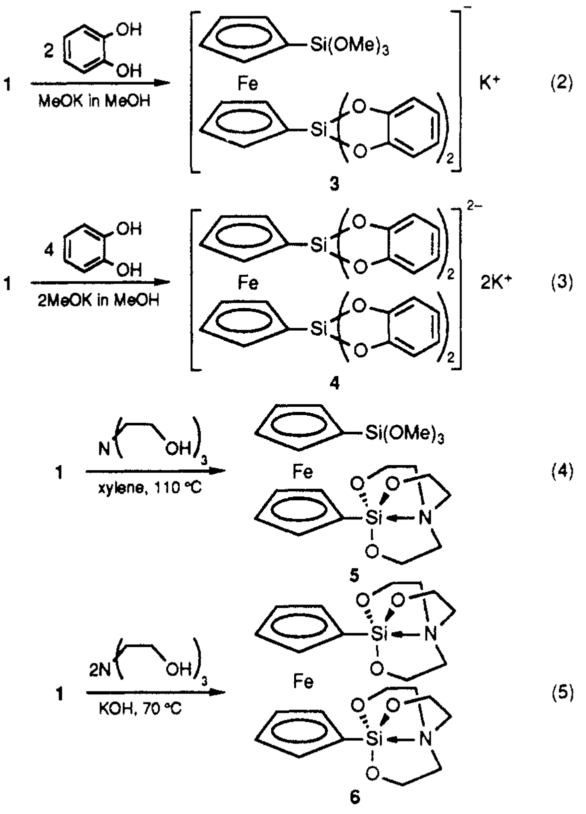

Table II. Variation of $E_{1/2}$ (V) of Compounds 1–9 with Respect to That of Ferrocene and 1,1′-Bis(trimethoxysilyl)ferrocene (1)[a]

compd no.	R	R′	$\Delta E_{1/2}$[b]	$\Delta E_{1/2}$[c]
1	$Si(OMe)_3$	$Si(OMe)_3$	+0.15	
2	SiH_3	SiH_3	+0.21	+0.06
3	$Si(OMe)_3$	Si(cat)	−0.09	−0.24
4	Si(cat)	Si(cat)	−0.33	−0.48
5	$Si(OMe)_3$	silatr	−0.19	−0.34
6	silatr	silatr	−0.47	−0.62
7	NMe_2	NMe_2	−0.54	
8	$COCH_3$	$COCH_3$	+0.48	
9	$SiMe_3$	$SiMe_3$	+0.09	−0.06

[a] See Table I for drawings of ferrocene derivatives and ligands. [b] With respect to ferrocene. [c] With respect to 1.

The catecholates **3** and **4** and the silatrane **6** were isolated as orange powders; **5** was obtained as a viscous oil. These complexes gave satisfactory spectroscopic data (Table I). In particular, the ^{29}Si NMR chemical shifts are found in the usual range for anionic pentacoordinated silicates and neutral pentacoordinated silicon compounds.[4] Complexes **3** and **5**, bearing a tetra- and a pentacoordinated silicon atom, exhibit two ^{29}Si resonances, which are within the range of chemical shifts observed for $PhSi(OMe)_3$ (−57.5 ppm), sodium bis(benzene-1,2-diolato)phenylsilicate (−87.3 ppm), and phenylsilatrane (−81.7 ppm).[4] Mass spectra were recorded in the FAB negative mode for **3** and **4** and in the EI mode for **1**, **5** and **6**. A detailed interpretation of the mass spectral data of the compounds presented here will be given elsewhere.[23]

An electrochemical study[24] of these compounds shows an interesting electronic effect: a significant lowering of the redox potential corresponding to the reversible Fe^{II}/Fe^{III} transition is observed in the case of the anionic and neutral pentacoordinated compounds **3**–**6**, in contrast to the small increase in the case of 1,1′-bis(trimethoxysilyl)ferrocene (**1**). Thus, the coordination number at silicon has a drastic importance on its electronic properties: electron withdrawing in the case of tetracoordination and electron releasing with pentacoordination, whatever the geometry.

The introduction of trimethoxysilyl groups in ferrocene shifts the redox potential of iron from +0.40 to +0.55 V (a value similar to that obtained for 1,1′-bis(triethoxysilyl)ferrocene, $E_{1/2}$ = +0.6 V (SCE),[17] corresponding to the introduction of an electron-withdrawing group[25]). On the other hand, the introduction of hypervalent groups shifts this potential toward lower values: the substitution of one trimethoxysilyl group in **1** by one pentacoordinated bis(catecholate) unit results in a shift of −0.24 V for **3** and the substitution of both groups in a lowering of −0.48 V for **4**. In the case of silatrane units, the replacement of both $Si(OMe)_3$ groups leads to a shift of −0.62 V (−0.34 V for the replacement of only one group). The much lower values observed for iron oxidation in **4** (+0.07 V) and in **6** (−0.07 V) correspond to an increase of electron density at iron and suggest that these groups behave as electron donors toward ferrocene, as observed for other electron donor substituents; i.e., $E_{1/2}$ = −0.23 V (SCE) in the case of 1,1′-bis(dimethylamino)ferrocene.[26] Since the half-wave

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(18) Complex **2**: 10.22 g (24 mmol) of **1** in 10 mL of ether was added dropwise to a suspension of 2.7 g (71 mmol) of $LiAlH_4$ in 150 mL of ether at 0 °C. The reaction mixture was refluxed for 2 h. After this time the solution was cooled and was added dropwise to an excess of 1 M HCl at 0 °C. The organic compound was extracted with ether, and complex **2** was isolated by distillation. A 4.8-g amount (81%) of **2** was recovered; bp 57–59 °C (~2 Pa). ^1H NMR (CCl_4): δ 4.30 (m, cyclopentadienyl), 4.18 (s and m, SiH_3 and cyclopentaidenyl) (the proximity of the signals does not allow for integration). Anal. Calcd for $C_{10}H_{14}FeSi_2$: C, 48.81; H, 5.69; Fe, 22.72; Si, 22.78. Found: C, 48.95; H, 5.92; Fe, 22.40; Si, 22.71.

(19) Complex **3**: 0.35 g (5 mmol) of MeOK, 2.13 g (5 mmol) of **1**, and 1.1 g (10 mmol) of catechol in 40 mL of methanol were heated at 70 °C for 2 h. The solvent was evaporated in vacuo, and the residue was washed with ether to give 2.38 g (81%) of an orange powder. ^1H NMR (CD_3OD): δ 6.8–6.5 (8 H, m, aromatic), 4.39 and 4.13 (2 × 4 H, 2 m, C_5H_4), 3.55 (9 H, s, OCH_3). ^{13}C NMR (CD_3OD): δ 150.5, 119.1, and 111.5 (aromatic), 76.7–68.8 (10 signals, cyclopentadienyl), 45.2 (OCH_3).

(20) Complex **4**: 1.4 g (20 mmol) of MeOK, 4.26 g (10 mmol) of **1**, and 4.4 g (40 mmol) of catechol in 100 mL of methanol were treated as above. A 6.8-g amount (90%) of an orange powder was obtained. ^1H NMR (CD_3OD): δ 6.78–6.55 (16 H, m, aromatic), 4.01 and 3.71 (2 × 4 H, 2 t, C_5H_4). ^{13}C NMR (CD_3OD): δ 149.1, 117.5, and 109.8 (aromatic), 75.1 and 69.8 (C-2 and C-3), 69.5 (C-1).

(21) Complex **5**: 2.13 g (5 mmol) of **1** and 0.68 g (4.5 mmol) of triethanolamine in 30 mL of xylene were heated at 110 °C for 8 h. After this time the mixture was stirred at room temperature for 14 h and 30 mL of methanol was added. The solvents were distilled at atmospheric pressure to leave a waxy residue, which was washed several times with pentane. **5** was obtained as a viscous brown oil (1.95 g, 81%). ^1H NMR (CCl_4): δ 4.25 and 4.13 (2 × 4 H, 2 m, C_5H_4), 3.73 (6 H, m, OCH_2), 3.60 (9 H, s, OCH_3), 2.70 (6 H, m, NCH_2). ^{13}C NMR (CD_2Cl_2) δ 76.3–66.8 (10 signals, cyclopentadienyl), 57.9 (OCH_2), 51.5 (NCH_2), 51.2 (OCH_3). Anal. Calcd for $C_{19}H_{29}FeNO_6Si_2$: C, 47.61; H, 6.06; N, 2.92. Found: C, 45.30; H, 5.63; N, 3.32.

(22) Complex **6**: 2.13 g (5 mmol) of **1**, 1.35 g (9 mmol) of triethanolamine, and 50 mg of KOH were heated at 70 °C for 2 h. A solid was obtained. The methanol formed in the reaction was pumped off, and the residue was washed with pentane and crystallized from CH_2Cl_2/MeOH. A 1.98-g amount (74%) of an orange powder was obtained. ^1H NMR ($CDCl_3$): δ 4.32–3.92 (8 H, m, C_5H_4), 3.71 (12 H, m, OCH_2), 2.69 (12 H, m, NCH_2). ^{13}C NMR ($CDCl_3$): δ 77.6 and 74.2 (C-2 and C-3), 71.8 (C-1), 58.7 (OCH_2), 52.0 (NCH_2). Anal. Calcd for $C_{22}H_{32}FeN_2O_6Si_2$: C, 49.64; H, 6.02; N, 5.26. Found: C, 48.30; H, 5.99; N, 5.21.

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oxidation potentials, $E_{1/2}$, observed for substituted ferrocenes clearly reflect the electron-donating or -accepting properties of the substituents,[27] it is interesting to point out the drastic effect due to pentacoordination at silicon (Table II). In the case of **6**, the shift ($\Delta E_{1/2} = -0.47$ V) is similar to that observed for 1,1'-bis(dimethylamino)ferrocene (**7**; $\Delta E_{1/2} = -0.54$ V).[26,27] Strong electron-withdrawing substituents show an effect of the same magnitude, but in the opposite sense ($\Delta E_{1/2} = 0.48$ V for 1,1'-diacetylferrocene (**8**)[25]). In contrast, the groups $Si(OMe)_3$ ($\Delta E_{1/2} = 0.15$ V) in **1**, $SiMe_3$ ($\Delta E_{1/2} = 0.09$ V) in 1,1'-bis(trimethylsilyl)ferrocene (**9**),[28] and SiH_3 ($\Delta E_{1/2} = 0.21$ V) in 1,1'-disilylferrocene (**2**) behave as weakly electron-attracting species.

In conclusion, we have reported the very easy synthesis of molecules containing two hypervalent silicon species. These hypervalent anionic and neutral silicon moieties behave as electron donors, in contrast to the electron-withdrawing effect of the $Si(OMe)_3$ groups, although in both cases silicon is surrounded by oxygen atoms.

At the present time, the interpretation is not obvious since very little is known about the electronic effect of hypervalent silicon substituents. However, ab initio calculations[29] performed on pentacoordinated silicon compounds have shown that the electron density is spread on the surrounding ligands. The silicon atom behaves as an electron donor and thus becomes positively charged. This explanation could account for the lower redox potentials observed. In the case of the silatranes a strong transmission of electron density from nitrogen to iron via silicon, due to the bis-apical positions in the trigonal bipyramid, could be suggested.

Further work is in progress for the preparation of other models in order to understand better the behavior of silicon in hypervalent species.

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Synthesis of a New Heterobinuclear Iron–Ruthenium Complex, $(CO)_3Fe(\mu\text{-}\eta^4\text{-}C(O)C(Ph){=}C{=}CH_2)Ru(CO)Cp$, and Its Reactions To Give Trinuclear Metal Clusters

Chris E. Shuchart, George H. Young,† and Andrew Wojcicki*
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Mario Calligaris‡ and Giorgio Nardin
Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy

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Summary: The reaction of the new ruthenium–propargyl complex $PhC{\equiv}CCH_2Ru(CO)_2Cp$ (**1**) with $Fe_2(CO)_9$ in THF at 0 °C or in diethyl ether at reflux temperature affords a novel heterobinuclear metal–(allenylcarbonyl) complex, $(CO)_3Fe(\mu\text{-}\eta^4\text{-}C(O)C(Ph){=}C{=}CH_2)Ru(CO)Cp$ (**2**), as the major product. In contrast, reaction between $PhC{\equiv}CCH_2Fe(CO)_2Cp$ and $Fe_2(CO)_9$ yields $(CO)_3Fe[\eta^4\text{-}C(O)C(Ph){\cdots}C(Fe(CO)_2Cp){\cdots}CH_2]$ (**4**). A mechanism for the formation of **2** and **4** is proposed which is somewhat analogous to that for [3 + 2] cycloaddition reactions of metal–propargyl complexes with neutral electrophiles. **2** reacts with $Fe_2(CO)_9$ to give the trinuclear Fe_2Ru clusters $Fe_2(CO)_6RuCp(\mu_2\text{-}CO)_2(\mu_3\text{-}\eta^1\text{-}CCH{=}CHPh)$ (**3**) and $Fe_2(CO)_6Ru(CO)Cp(\mu_3\text{-}\eta^3\text{-}C(Ph){=}C{=}CH_2)$ (**5**) as the major products and with $Pt(PPh_3)_2(C_2H_4)$ to afford two FeRuPt complexes. The structures of **2**, **4**, and **5** were determined by X-ray crystallography.

The chemistry of transition-metal–propargyl complexes $RC{\equiv}CCH_2ML_n$ is highlighted by the reactions with protic acids to give the metal–allene cations $[(\eta^2\text{-}CH_2{=}C{=}CHR)ML_n]^+$ and with various uncharged electrophiles E=Nu (e.g., SO_2, $(CN)_2C{=}C(CN)_2$ (TCNE), and $ClSO_2NCO$, inter alia) to afford the [3 + 2] cycloadducts $\overline{CH_2NuEC(R){=}C}ML_n$ (E = electrophilic part and Nu = nucleophilic part of E=Nu).[1,2] A more recent development is the use of propargyl complexes in conjunction with metal carbonyls in the synthesis of heterobinuclear and -trinuclear metal compounds containing bridging alkyne and allenyl ligands.[3-5] In this communication we report (i) an extension of the latter reactions to the synthesis of other types of binuclear metal compounds, (ii) the apparent mechanistic relationship among these diverse reactions of metal–propargyl complexes, and (iii) the use of a new FeRu complex in the preparation of trinuclear metal clusters.

The first known ruthenium–propargyl complex, $PhC{\equiv}CCH_2Ru(CO)_2Cp$ (**1**), was obtained by reduction of $[Ru(CO)_2Cp]_2$ with $NaK_{2.8}$ in THF followed by addition of $PhC{\equiv}CCH_2Cl$ at −78 °C. Warming to room temperature, removing the solvent, and crystallizing from hexane afforded a light yellow solid in 70% yield.[6-8] **1** undergoes

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† Present address: B. F. Goodrich Research and Development Center, Brecksville, OH 44141.

‡ To whom inquiries concerning the X-ray crystallographic work should be addressed.

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(6) Selected spectroscopic data for **1**: IR (THF) ν(CO) 2014 (s), 1959 (s), $\nu(C{\equiv}C)$ 2182 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.33 (s, Cp), 2.17 (s, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 200.7 (CO), 101.2, 81.6 ($C{\equiv}C$), −26.4 (CH_2).

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