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# New complexes with M–Si–O or M–Si–S linkages (M = Fe or Co)

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## Abstract

$Ph_2XSiFe(CO)_2Cp$ [X = *p*-tolylS (**1a**), MeO (**1b**)] and Ph[2-$MeOC_6H_4$]$XSiFe(CO)_2Cp$ [X = Cl (**2a**), OMe (**2b**)] have been fully characterised, including X-ray crystal structure determinations for **1a**, **1b** and **2a**. None of the examples showed any tendency for migration of the X groups from silicon to iron, with elimination of silylene. However, very ready loss of the X groups was seen in the electrospray mass spectra, suggesting formation of the cationic silylene–iron complex ions is favoured. This was especially so for **2a** and **2b**, where intramolecular stabilisation of the silicon centre from the 2-OMe group is possible. The stable siloxane $O[SiPh_2\{Co(CO)_4\}]_2$ was also characterised; the X-ray crystal structure analysis shows a Si–O–Si bond angle of 153°. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Cobalt; Iron; Silylene; Siloxane complex; Thia-siloxane

## 1. Introduction

The 1,2-migration of a group X from silicon to a transition metal in compounds containing $M–SiR_2X$ units has been frequently invoked to explain rearrangement processes, especially those where metal-silylenes are probable intermediates [1–3]. Only recently however has this been directly observed, by Mitchell and Tilley in the reversible interconversion of $(Et_3P)_2Pt(H)$-$Si(SBu^t)_2OTf$ and $[(Et_3P)_2Pt(\mu\text{-}SBu^t)Si(H)(SBu^t)]^+$ via H-migration [4]. More commonly, the systems in which 1,2-migrations are indirectly most strongly implicated are those involving disilanes, where migration of the β-silyl group to the metal generates silyl/silylene intermediates [5]. Examples of this type are known for many transition metals [1].

So far there appear to be no definite examples in which an –OR or –SR group transfers from silicon to a transition metal. Migration involving a Si–O bond may be implicated in the metal-catalysed disproportionation of $O(SiMe_2H)_2$ into $Me_2SiH_2$ and polysiloxanes, though other mechanisms can be proposed [6]. A related example is the reaction of $O(SiH_3)_2$ with $Co_2(CO)_8$ to give products such as $Si[Co_2(CO)_7]_2$ without Si–O bonds [7]. Transfer of –SR is perhaps even more likely, given the 1,2-migration of an H-group described above, since Si–H and Si–S bonds have similar strengths (e.g. Si–H 320–340 kJ $mol^{-1}$, Si–S 314 kJ $mol^{-1}$ [8]).

There are now several examples of species with M–Si–O linkages described in the literature, with varying properties. Greene and Curtis tentatively characterised the siloxane $O[SiMe_2\{Co(CO)_4\}]_2$, but found it to be extremely unstable [9]. In contrast, species such as $(MeO)_3SiCo(CO)_4$ are apparently readily handled [10]. Braunstein [11] has developed extensive chemistry of bi-metallic compounds based on $(MeO)_3Si$ groups acting as bridging ligands. More recently, stable metallosilanol and metallosiloxane compounds have been reported, including derivatives $(Me_5C_5)(PMe_3)(OC)_2$-$MSiR_2(OH)$ (M = Cr, Mo, W) from Malisch's group [12], and osmium examples from Roper's laboratory [13]. Both mono- and octa-$Co(CO)_4$ derivatives of octasilasesquioxane have been characterised [14], following earlier work with smaller cyclosiloxanes [15].

This present paper describes some new complexes with $L_nM$–Si–OR or $L_nM$–Si–SR bonds. The fragment $L_nM$ chosen was mainly $Cp(CO)_2Fe$ since this is the best studied for silyl group migration. The supporting groups on the silicon were Ph since these stabilise silylene intermediates better than Me. One example incorporating $Co(CO)_4$ was also synthesised since this

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group appears to encourage silyl migration under very mild conditions [3].

## 2. Experimental

### 2.1. General

All manipulations were carried out in an oxygen-free $N_2$ atmosphere with carefully dried solvents in standard Schlenk equipment. $Ph(2\text{-}MeOC_6H_4)SiCl_2$ was prepared by coupling ortholithiated anisole with $Ph_2SiCl_2$, and $(Ph_2HSi)_2O$ by hydrolysis of $Ph_2HSiCl$. $Co_2(CO)_8$ was freshly sublimed before use while $[Fe(CO)_2Cp]_2$ was used as received. “TolS” refers specifically to *p*-tolylthio group.

### 2.2. Instrumentation

Infrared spectra were recorded on a Digilab FTS-40 FTIR spectrophotometer. NMR spectroscopy was performed using a Bruker AC300P Multinuclear FT spectrometer. Routine electrospray mass spectra (ESMS) were obtained on a VG Platform II spectrometer operating under standard conditions. EDESI mass spectra were collected using a Micromass Quattro LC instrument, in positive-ion mode. Samples were introduced directly to the source at 4 μl $min^{-1}$ via a syringe pump as MeCN–MeOH solutions. Data collection was carried out in continuum mode. The cone voltage was initially set at 0 V and was increased by increments of 1 V after every scan up to a maximum of 200 V.

Elemental analysis was performed by the Campbell Microanalytical Laboratory, University of Otago. Melting points were measured on a Reichart Thermopan melting point apparatus and are uncorrected.

### 2.3. Reactions

#### 2.3.1. Preparation of $Ph_2ClSiFe(CO)_2Cp$

This known compound was prepared in 60% yield from $Na[Fe(CO)_2Cp]$ and $Ph_2SiCl_2$ in THF. M.p. 88–89 °C (Lit. 89–94 °C [16] or 95–96 °C [17]), IR: $\nu$ CO (petroleum spirits) 2015 (s), 1965 (s) $cm^{-1}$; $^1H$-NMR: $\delta$ 7.68, 7.35 (m, 10H, $C_6H_5$), $\delta$ 4.80 (s, 5H, $C_5H_5$); $^{13}C$-NMR: $\delta$ 214.5 (*C*O), $\delta$ 142.3 (*ipso*), 133.6 (*ortho*), 129.1 (*para*), 127.8 (*meta*) ($C_6H_5$), $\delta$ 85.5 ($C_5H_5$); ESMS: (MeCN–$H_2O$), *m*/*z* 418 (100%) $[M-Cl+MeCN+H_2O]^+$; 400 (45%) $[M-Cl+MeCN]^+$; 377 (35%) $[M-Cl+H_2O]^+$; 359 (40%) $[M-Cl]^+$.

#### 2.3.2. Preparation of $Ph_2(TolS)SiFe(CO)_2Cp$ (**1a**)

To a stirred THF solution (30 ml) of $Ph_2ClSiFe(CO)_2Cp$ (0.683 g, 1.73 mmol) was added Na[STol] (0.253 g, 1.73 mmol). After 2 days stirring, the IR spectrum of the reaction solution showed complete conversion to a new species. The solvent was evaporated and replaced with ether (30 ml). The solution was filtered, petroleum spirits (10 ml) was added and the mixture was concentrated to ca. 5 ml, and stored at −20 °C. Yellow crystals of $Ph_2(TolS)SiFe(CO)_2Cp$ were formed (0.400 g, 48%). M.p. 133 °C. Anal. Found: C, 63.59; H, 4.61. Calc. for $C_{26}H_{22}FeO_2SSi$ requires: C, 64.73; H, 4.60%; HRMS: Anal. Found: 482.046, required 482.0459, IR: $\nu$ CO (THF) 2005 (s), 1953 (s) $cm^{-1}$; $^1H$-NMR: $\delta$ 7.67, 7.30 (m, 10H, $C_6H_5$), $\delta$ 6.99 (d, $J=7.8$ Hz, 2H, $C_6H_4$), $\delta$ 6.79 (d, $J=8.1$ Hz, 2H, $C_6H_4$), $\delta$ 4.63 (s, 5H, $C_5H_5$), $\delta$ 2.19 (s, 3H, $CH_3$); $^{13}C$-NMR: $\delta$ 214.3 (*C*O), 141.4–127.6 (m, $C_6H_5$, $C_6H_4$), $\delta$ 85.0 ($C_5H_5$), $\delta$ 21.0 ($CH_3$); FABMS: *m*/*z*: 482 (7%) $[M+H]^+$, 454 (68%) $[M+H-CO]^+$, 426 (100%) $[M+H-2CO]^+$, 359 (74%) $[M-STol]^+$, 304 (33%) $[M-STol-2CO]^+$. Attempted purification by chromatography on silica led to extensive decomposition, the only product isolated being $[Fe_2(\mu\text{-}STol)_2(CO)_2Cp_2]^+$ (identified spectroscopically: ESMS *m*/*z* 544 $[M^+]$; IR $\nu$(CO) (THF) 1972 $cm^{-1}$; ESR: $g_{iso}$ 2.004, $\Delta p-p$ 10G, cf. Ref. [18]) with an unidentified anion.

#### 2.3.3. Preparation of $Ph_2(MeO)SiFe(CO)_2Cp$ (**1b**)

A THF solution (10 ml) of $Ph_2ClSiFe(CO)_2Cp$ (0.501 g, 1.27 mmol) was treated with a methanolic solution of NaOMe (0.82 ml, containing 1.25 mmol NaOMe). The reaction was left to stir overnight. The solvent was replaced with ether, the solution was filtered and left to crystallise at 4 °C. Small, thin yellow crystals of $Ph_2(MeO)SiFe(CO)_2Cp$ formed (0.399 g, 81%). M.p. 99 °C; Anal. Found: C, 61.57; H, 4.71. Calc. for $C_{20}H_{18}FeO_2Si$ requires C, 61.55; H, 4.65%; IR: $\nu$ CO (THF) 1998 (s), 1943 (s) $cm^{-1}$; $^1H$-NMR: $\delta$ 7.60, 7.34 (m, 5H, $C_6H_5$), $\delta$ 4.65 (s, 5H, $C_5H_5$), $\delta$ 3.48 (s, 3H, $OCH_3$); $^{13}C$-NMR: $\delta$ 214.9 (*C*O), $\delta$ 142.6 (*ipso*), 133.9 (*ortho*), 128.7 (*para*), 127.7 (*meta*) ($SiC_6H_5$), $\delta$ 84.5 ($C_5H_5$), $\delta$ 52.2 ($OCH_3$); $^{29}Si$-NMR: $\delta$ 57.2, ESMS (MeCN–$H_2O$): Cone 20 V: *m*/*z* 408 (100%) $[M+NH_4]^+$, 391 (40%) $[M+H]^+$; Cone 40 V: *m*/*z* 400 $[M-OMe+MeCN]^+$. More detailed ESMS information about fragmentation processes for this compound is presented in Section 3.

#### 2.3.4. Preparation of $Ph(2\text{-}MeOC_6H_4)ClSiFe(CO)_2Cp$ (**2a**)

$[Fe(CO)_2Cp]_2$ (0.71 g, 2.00 mmol) in THF (20 ml) was reduced with sodium amalgam (1%) to $Na[Fe(CO)_2Cp]$. The resulting solution was transferred by syringe into a Schlenk flask at 0 °C containing $Ph(2\text{-}MeOC_6H_4)SiCl_2$ (1.3 g, 4.6 mmol) in ether (10 ml). The stirred solution was allowed to return to room temperature and left overnight. The solvent was removed under vacuum and replaced with ether (30 ml). The solution was passed through a filter stick to remove

NaCl and the solvent removed once more. Chromatography (silica, $CH_2Cl_2$–petroleum spirit 1:5) provided a bright yellow band which was collected and recrystallised from ether–petroleum spirit to provide pale yellow crystals of Ph(2-MeO$C_6H_4$)ClSiFe$(CO)_2$Cp. (0.54 g, 32%). M.p. 108–110 °C; Anal. Found: C, 56.37; H, 4.02. Calc. for $C_{20}H_{17}ClFeO_3Si$ requires C, 56.56; H, 4.03%. IR: $\nu$ CO (petroleum spirit) 2016 (s), 1967 (s) $cm^{-1}$. $^1$H-NMR: $\delta$ 7.9–6.8 (m, 9H, $C_6\mathit{H}_5$, $C_6\mathit{H}_4$), $\delta$ 4.72 (s, 5H, $C_5\mathit{H}_5$), $\delta$ 3.68 (s, 3H, $OC\mathit{H}_3$); $^{13}$C-NMR: $\delta$ 214.0, 213.9 (2*C*O), $\delta$ 142.5–109.9 (m, $\mathit{C}_6H_5$ and $\mathit{C}_6H_4$), $\delta$ 85.5 ($\mathit{C}_5H_5$), $\delta$ 60.3 ($\mathit{C}H_3$); ESMS: (MeCN–$H_2O$) *m/z* 429 $[M - Cl + OH + Na]^+$, 425, $[M - Cl + 2H_2O]$, 407 $[M - Cl + H_2O]^+$.

### *2.3.5. Preparation of Ph[2-(MeO)$C_6H_4$](MeO)SiFe$(CO)_2$Cp (**2b**)*

A THF solution (10 ml) of Ph[2-(MeO)$C_6H_5$]-ClSiFe$(CO)_2$Cp (0.174 g, 0.410 mmol) was treated with a methanolic solution of NaOMe (3.6 ml, containing 0.45 mmol NaOMe). After 14 h the solvent was evaporated and the residue was extracted with ether. After filtration the solution was stored at −25 °C to give ragged yellow crystals of Ph[2-(MeO)$C_6H_4$](MeO)SiFe-$(CO)_2$Cp (0.077 g, 45%). M.p. 176–179 °C; IR: $\nu$ CO (THF) 2001 (s), 1946 (s) $cm^{-1}$; $^1$H-NMR: $\delta$ 7.58, 7.27 (m, 5H, $C_6\mathit{H}_5$), $\delta$ 6.9 (m, 4H, $C_6\mathit{H}_4$), $\delta$ 4.65 (s, 5H, $C_5\mathit{H}_5$), $\delta$ 3.66 (s, 3H, $OC\mathit{H}_3$), $\delta$ 3.44 (s, 3H, $SiOC\mathit{H}_3$); ESMS: (MeCN–$H_2O$); *m/z* 421 $[M + H]^+$.

### *2.3.6. Reaction of $(Ph_2HSi)_2O$ with $Co_2(CO)_8$ (**3**)*

To a Schlenk flask was added $(PhH_2Si)_2O$ (0.562 g, 1.47 mmol), $Co_2(CO)_8$ (0.500 g, 1.46 mmol) and petroleum spirits (25 ml). The mixture was stirred overnight at room temperature to produce a pale brown solution with some white precipitate. The solvent was removed under vacuum, and the residue was washed with small quantities of petroleum spirit to remove unreacted $Co_2(CO)_8$. The crude product was extracted from small amounts of $Co_4(CO)_{12}$ with $Et_2O$, and this solution was evaporated slowly to yield large, colourless crystals of $O[SiPh_2\{Co(CO)_4\}]_2$ (0.874 g, 83%). IR $\nu$(CO): (petroleum spirits, $cm^{-1}$) 2097 (m), 2096 (m), 2036 (m), 2035 (m), 2014 (vs), 2005 (s), 1998 (s). The compound was further characterised by an X-ray crystal structure determination.

## *2.4. X-ray crystallography*

For compounds **1a** and **2a**, unit cell parameters and intensity data were collected using a Siemens SMART CCD diffractometer, using standard collection procedures, with monochromatic Mo–$K_\alpha$ X-rays (0.71073 Å). Corrections for absorption and other effects were carried out with SADABS [19]. For **1b** and **3**, data were collected on a Nicolet R3 four-circle diffractometer and corrected for absorption by a $\phi$ scan method. All other calculations used the SHELX97 programs [20]. The structures were solved by direct methods, and developed routinely with refinement based on $F^2$. All non-hydrogen atoms were assigned anisotropic temperature factors, and hydrogen atoms were included in calculated positions. Selected bond parameters are in the captions to Figs. 1, 3–5.

### *2.4.1. Crystal data for $Ph_2$(TolS)SiFe$(CO)_2$Cp (**1a**)*

$C_{26}H_{22}FeO_2SSi$, $M_r$ 482.44, triclinic, $P\bar{1}$, $a = 8.5754(2)$, $b = 9.9558(2)$, $c = 14.7730(3)$ Å, $\alpha = 81.066(1)$, $\beta = 75.044(1)$, $\gamma = 68.367(1)°$, $V = 1130.15(4)$ Å$^3$, $D_{calc} = 1.418$ g $cm^{-3}$, $Z = 2$, $F(000) = 500$, μ(Mo–$K_\alpha$) 0.833 $mm^{-1}$, $T_{max}$ 1.000, $T_{min}$ 0.7217, crystal size $0.44 \times 0.37 \times 0.09$ $mm^3$. *T* 148 K.

A total of 13 606 reflections, 3751 unique ($R_{int}$ 0.0378) were collected $2 < \theta < 25°$. Final $R_1$ 0.0575 (data with $I > 2\sigma(I)$), 0.0606 (all data), $wR_2$ 0.1722, goodness-of-fit 1.030, final $\Delta e$ $+1.20/-0.51$.

### *2.4.2. Crystal data for $Ph_2$(MeO)SiFe$(CO)_2$Cp (**1b**)*

$C_{20}H_{18}FeO_3Si$, $M_r$ 390.28, monoclinic, $C2/c$, $a = 31.67(3)$, $b = 7.609(4)$, $c = 17.35(2)$ Å, $\beta = 122.85(5)°$, $V = 3512(5)$ Å$^3$, $D_{calc} = 1.476$ g $cm^{-3}$, $Z = 8$, $F(000) = 1616$, μ(Mo–$K_\alpha$) 0.91 $mm^{-1}$, $T_{max}$ 0.86, $T_{min}$ 0.71, crystal size $0.82 \times 0.53 \times 0.12$ $mm^3$. *T* 141 K.

A total of 2357 reflections, 2097 unique ($R_{int}$ 0.0497) were collected $2 < \theta < 22.5°$. Final $R_1$ 0.0532 (data with $I > 2\sigma(I)$), $wR_2$ 0.1256, goodness-of-fit 1.036, final $\Delta e$ $+0.96/-0.37$.

### *2.4.3. Crystal data for Ph(2-MeO$C_6H_4$)ClSiFe$(CO)_2$Cp (**2a**)*

$C_{20}H_{17}ClFeO_3Si$, $M_r$ 424.73, monoclinic, $P2_1/n$, $a = 9.0901(1)$, $b = 14.6719(2)$, $c = 15.0469(2)$ Å, $\beta = 107.38(1)$, $V = 1915.20(4)$ Å$^3$, $D_{calc} = 1.473$ g $cm^{-3}$, $Z = 4$, $F(000) = 872$, μ(Mo–$K_\alpha$) 1.006 $mm^{-1}$, $T_{max}$ 0.8496, $T_{min}$ 0.7853, crystal size $0.42 \times 0.28 \times 0.22$ $mm^3$. *T* 203 K.

A total of 19 366 reflections, 4462 unique ($R_{int}$ 0.0335) was collected $2 < \theta < 28°$. Final $R_1$ 0.0371 (data with $I > 2\sigma(I)$), 0.0446(all data), $wR_2$ 0.0889, goodness-of-fit 1.063, final $\Delta e$ $+1.09/-0.47$.

### *2.4.4. Crystal data for $O[SiPh_2\{Co(CO)_4\}]_2$ (**3**)*

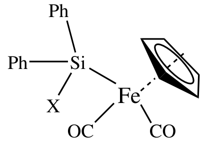
$C_{32}H_{20}Co_2O_9Si_2$, $M_r$ 722.52, triclinic, $P\bar{1}$, $a = 10.362(3)$, $b = 10.383(5)$, $c = 17.331(5)$ Å, $\alpha = 74.42(2)$, $\beta = 80.87(5)$, $\gamma = 61.34(2)°$, $V = 1575.1(10)$ Å$^3$, $D_{calc} = 1.523$ g $cm^{-3}$, $Z = 2$, $F(000) = 732$, μ(Mo–$K_\alpha$) 1.183 $mm^{-1}$, $T_{max}$ 0.897, $T_{min}$ 0.809, crystal size $0.72 \times 0.36 \times 0.18$ $mm^3$. *T* 141 K.

A total of 5234 reflections, 4921 unique ($R_{int}$ 0.0376) was collected $2 < \theta < 24°$. Final $R_1$ 0.0481 (data with $I > 2\sigma(I)$), $wR_2$ 0.0978, goodness-of-fit 1.029, final $\Delta e$ $+0.38/-0.36$.

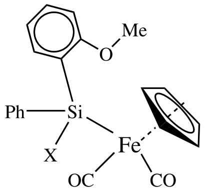
## 3. Results and discussion

### 3.1. Ph$_2$(TolS)Fe(CO)$_2$Cp (**1a**)

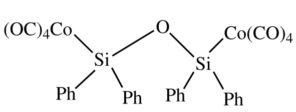
This compound was readily prepared from ClPh$_2$SiFe(CO)$_2$Cp, on reaction with a stoichiometric amount of Na[STol] in THF. The yellow crystalline material is essentially air-stable, but attempted chromatography on silica led to rapid decomposition, giving among other products the known radical cation [Fe$_2$(CO)$_2$Cp$_2$(STol)$_2$]$^+$, characterised by its ESMS, its $\nu$(CO) spectrum and its characteristic ESR spectrum [18]. While this formally involves a transfer of the thiol group from silicon to iron, the reaction was non-specific, so mechanistic discussion is unwarranted.



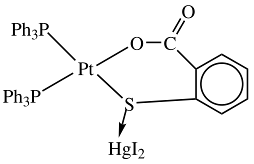
**1a** X = S(tolyl-*p*)
**1b** X = OMe



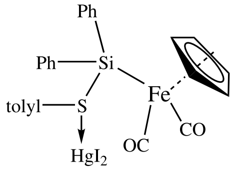
**2a** X = Cl
**2b** X = OMe



**3**



**(4)**



**(5)**

In an attempt to induce a migration reaction, Ph$_2$(TolS)SiFe(CO)$_2$Cp was thermolysed or photolysed, in the presence of HMPA to trap any silylene intermediates. However, only slow decomposition to intractable products was observed, suggesting that the deoligomerisation reaction observed for disilyl complexes of Fe(CO)$_2$Cp does not have a parallel with Si–S bonds.

It is known that Pt(II) thiolate complexes form stable adducts via a bridging S atom to mercury(II) halides, as in **4** [21]. It was therefore of interest to see if the S atom of Ph$_2$(TolS)SiFe(CO)$_2$Cp behaved similarly, to give complex **5**. When Ph$_2$(TolS)SiFe(CO)$_2$Cp and HgI$_2$ were mixed in $d^6$-DMSO in a NMR tube, the $^1$H signals from the Cp protons shifted by + 0.36 ppm, and the tolyl-group protons also shifted markedly. These changes are consistent with the formation of an adduct of the type **5**. However all attempts to isolate the adduct were thwarted. A yellow solid was formed which contained Hg, I and tolyl groups, and probably contained (TolS)HgI (or the corresponding symmetrised equivalents), while the solution showed carbonyl-region infrared peaks which were consistent with Ph$_2$ISiFe(CO)$_2$Cp. All this points to the initial formation of **5**, but further reaction exchanges the Si–S bond (possibly via a silylene) for a Si–I one. However the system did not provide anything other than this tentative information.

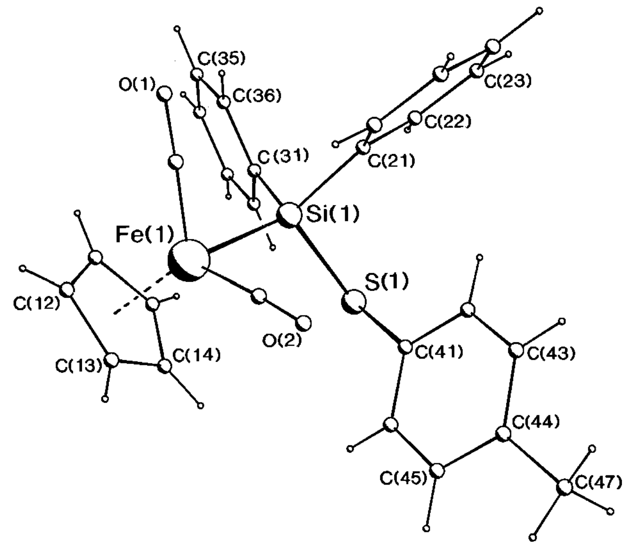


Fig. 1. The structure of Ph$_2$(TolS)SiFe(CO)$_2$Cp. Bond parameters include: Fe(1)–Si(1) 2.296(2), Si(1)–S(1) 2.180(2), Fe(1)–C$_{cp}$ (av) 2.097(6) Å; Fe(1)–Si(1)–S(1) 113.68, Si(1)–S(1)–C(41) 102.8(2), Fe(1)–Si(1)–C(21) 118.1(2), Fe(1)–Si(1)–C(31) 112.0(2)°.

The X-ray structure determination of Ph$_2$(TolS)SiFe(CO)$_2$Cp was undertaken since the only previous examples related to this were (TolS)$_{3-n}$(Tf)$_n$SiRu(PMe$_3$)$_2$Cp*, [(TolS)$_2$(MeCN)SiRu(PMe$_3$)$_2$Cp*]$^+$ and [(TolS)(phen)SiRu(PMe$_3$)$_2$Cp*]$^{2+}$ from Tilley's group [22], and Ph$_2$(PhS)SiRhH$_2$(PMe$_3$)$_3$ [23]. The structure is illustrated in Fig. 1, which shows the expected arrangement about both the Fe and Si atoms. The orientation of the tolyl group is towards the metal fragment, which appears unusual but is presumably the result of crystal packing interactions on a flexible bond. The closest intramolecular approach between the two fragments, O(2)···C(41) (3.39 Å) is essentially the sum of the van der Waals radii for the two atoms, so there is no barrier to the observed orientation. The Fe–Si bond length is 2.296(2) Å, which can be compared to those in the only other two molecules of the type Ph$_2$XSiFe(CO)$_2$Cp to have been determined, X = F 2.278(1) Å [24] and X = OMe 2.292(2) Å (see Section 3.2). The trend in the order STol > OMe > F is that expected on electronegativity grounds. The Si–S bond length of 2.180(2), and the Si–S–C bond angle of 102.8(2)° are both slightly

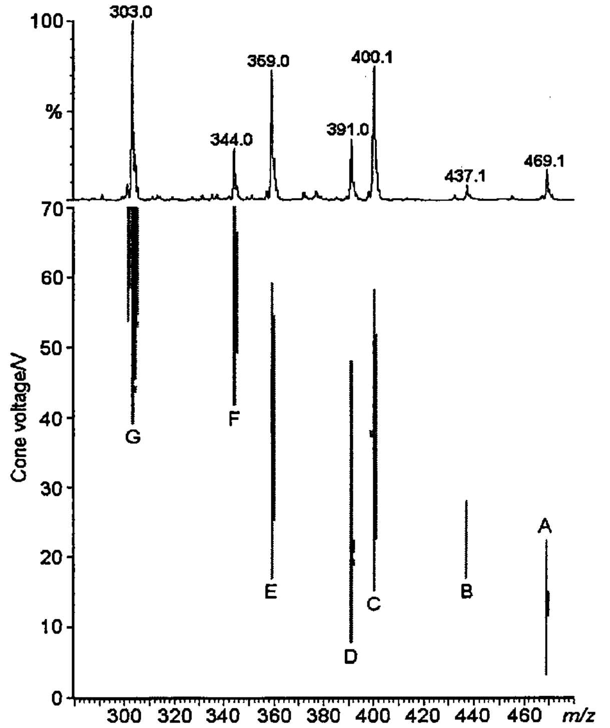


Fig. 2. Positive-ion EDESI-MS map [27] of $Ph_2(MeO)SiFe(CO)_2Cp$, run in a mobile phase of MeCN–MeOH with traces of DMSO present.

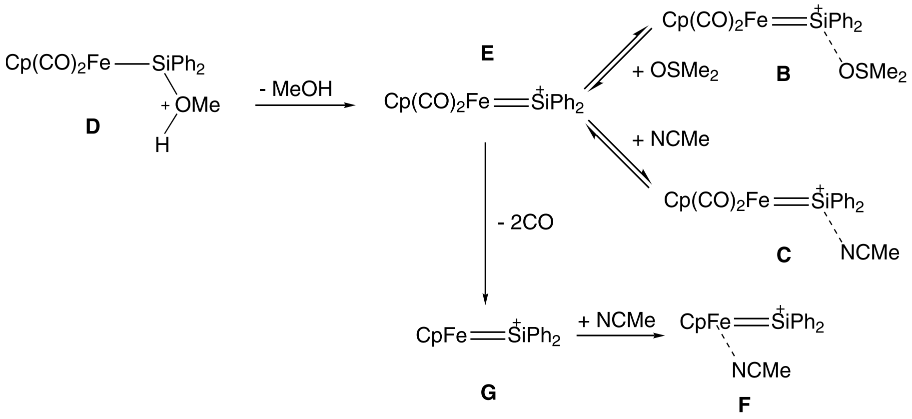
larger than the corresponding parameters in $Ph_3SiSPh$ (2.156 Å and 99.5°, respectively [25]), but the differences are not chemically significant.

### 3.2. $Ph_2(MeO)SiFe(CO)_2Cp$ (**1b**)

This compound was readily prepared in good yield from Na[OMe] and $Ph_2ClSiFe(CO)_2Cp$ in THF, showing no tendency to undergo base cleavage of the Fe–Si bond [26]. The spectroscopic characterisation given in Section 2 is as expected and only the ESMS merit further discussion. When run in $MeCN-H_2O$ at low cone voltages, the main peaks observed corresponded to $[M+H]^+$ and $[M+NH_4]^+$ arising from chemical ionisation by attachment of $H^+$ or $NH_4^+$, presumably at the oxygen atom of the methoxy group. More interesting is the behaviour at higher cone voltages, where the fragmentation patterns can yield some revealing information. At low cone voltage settings, fragmentation of the complexes is minimised and the electrospray ionisation mass spectra consist of ions derived from the intact parent molecule, sometimes also incorporating a molecule of the solvent used as a mobile phase. The appearance of $[M+H+\text{solvent}]^+$ ions is strongly dependent on how good a donor the solvent is, so acetonitrile, pyridine and dimethylsulfoxide (DMSO) are common adducts whereas water, methanol and dichloromethane are less frequently observed. These adducts are the first to disappear as the fragmentation energy (cone voltage) is increased. Further fragmentation generally consists of the loss of neutral fragments from the pseudo-molecular ion. These features can all be observed in the energy-dependent electrospray ionisation mass spectrum (EDESI-MS) [27] of $Ph_2(MeO)SiFe(CO)_2Cp$ (Fig. 2).

This data presentation technique provides a two-dimensional map of cone voltage versus $m/z$ ratio, and allows visualisation of the entire fragmentation pattern in a convenient format. $Ph_2(MeO)SiFe(CO)_2Cp$ was analysed in an acetonitrile–methanol solution, with trace amounts of DMSO present, and the fragmentation processes are summarised in Scheme 1.

At the lowest cone voltage, only the ion $[M+H+\text{DMSO}]^+$ is observed (**A**). The DMSO adduct is observed rather than MeCN or MeOH, because DMSO is a superior donor. As the cone voltage is increased, the ion $[M+H]^+$ (**D**) makes an appearance, following loss of the loosely attached solvent. At ~ 15 V, three more ions appear, all silylene species resulting from elimination of methanol from the parent ion. The three are $[Ph_2Si{=}Fe(CO)_2Cp]^+$ (**E**) at 359 $m/z$, with the base-stabilised species $[(MeCN)Ph_2Si{=}Fe(CO)_2Cp]^+$ (**C**) at 400 $m/z$ and $[(DMSO)Ph_2Si{=}Fe(CO)_2Cp]^+$ (**B**) at 437 $m/z$.



Scheme 1.

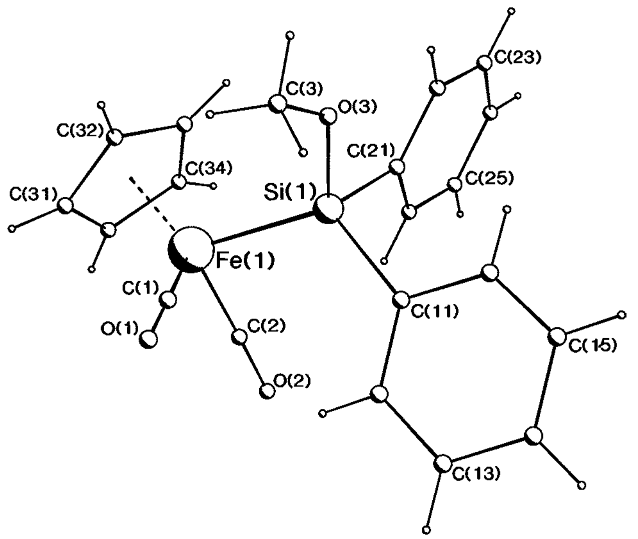


Fig. 3. The structure of $Ph_2(MeO)SiFe(CO)_2Cp$. Bond parameters include: Fe(1)–Si(1) 2.293(3), Si(1)–O(3) 1.656(5), C(3)–O(3) 1.421(8), Fe(1)–$C_{cp}$ (av) 2.093(7) Å; Fe(1)–Si(1)–O(3) 112.3(2), Si(1)–O(3)–C(3) 125.7(4), Fe(1)–Si(1)–C(11) 116.1(2), Fe(1)–Si(1)–C(21) 114.9(2)°.

The last two results from collisions with gas-phase solvent molecules subsequent to methanol elimination. **C** is much more intense than **B** now, because there is no time for an equilibrium to be set up which the better donor can dominate. EDESI-MS/MS [27] experiments show that **B** does not derive directly from **A**; if **A** is selected and subjected to fragmentation in an argon-filled collision cell, **B** does not appear at all. At ~40 V, both CO ligands are lost simultaneously to form $[Ph_2Si{=}FeCp]^+$ (**G**). A proportion of these ions react with MeCN to form $[Ph_2Si{=}FeCp(MeCN)]^+$ (**F**), with the MeCN possibly attached to the coordinatively unsaturated iron rather than the silicon atom.

The crystal structure of complex **1b** was determined for comparison with that of $Ph_2(TolS)SiFe(CO)_2Cp$ (**1a**) discussed above. This is shown in Fig. 3. The two molecules are similar overall, other than the relative conformation of the STol/OMe groups in the respective examples. The Fe–Si bond lengths are not significantly different despite the more electronegative substituent in the OMe example, a feature that usually leads to bond shortening. The Si–O bond in **1b** is 1.656(5) Å which is shorter than expected by comparison with the Si–S bond of **1a** (2.180(2) Å) and the difference in covalent radii of O and S (0.3–0.4 Å), but this is not unusual for bonds to Si where Si–O bonds are shortened relative to Si–S by stronger π bonding. The wider Si–O–C bond of 125.7(4)° in **1b** compared to the Si–S–C bond of 102.8(2)° in **1a** is also usual for silyl ethers.

### 3.3. $Ph(2\text{-}MeOC_6H_4)XSiFe(CO)_2Cp$ (X = Cl, OMe)

These compounds were prepared because they have an *ortho*-OMe group on one of the aryl rings that is positioned so that it can interact with the silicon atom, stabilising a silylene centre if one is formed. Ogino has shown that *ortho*-$CH_2NMe_2$ groups can stabilise iron–silylenes using this approach [23].

The chloro example $Ph(2\text{-}MeOC_6H_4)ClSiFe(CO)_2Cp$ was prepared analogously to $Ph_2ClSiFe(CO)_2Cp$. It could be chromatographed on silica which suggested that the Si–Cl bond is relatively unreactive, and this was confirmed by the lack of any reaction at the Si–Cl bond with Na[STol]. However it did react with $[OMe]^-$ to give the corresponding methoxy-silyl species $Ph(2\text{-}MeOC_6H_4)(MeO)SiFe(CO)_2Cp$.

In the ESMS of $Ph(2\text{-}MeOC_6H_4)(OMe)SiFe(CO)_2Cp$ in $MeCN{-}H_2O$, the main peak at low cone voltages was the $[M+H]^+$ ion, formed presumably by attachment at the OMe oxygen atom, together with some solvated $[M+H+H_2O]^+$. However as the cone voltage was increased, loss of MeOH readily occurred to generate a strong signal from the silylene cation $[Ph(2\text{-}MeOC_6H_4)Si{=}Fe(CO)_2Cp]^+$, together with increasing amounts of $[Ph(2\text{-}MeOC_6H_4)Si{=}Fe(CO)_nCp]^+$ ($n = 1$, 0) under more forcing conditions. In this case, EDESI-MS studies of $Ph(2\text{-}MeOC_6H_4)(OMe)SiFe(CO)_2Cp$ showed that the pendant OMe group prevents coordination of donors including acetonitrile, pyridine and DMSO after the elimination of methanol. This observation is strong evidence that the pendant OMe group provides a degree of intramolecular stabilisation by coordination to the silicon centre, certainly enough to prevent association of other bases.

In an attempt to reproduce the ESMS results on a preparative scale, $Ph(2\text{-}MeOC_6H_4)(MeO)SiFe(CO)_2Cp$, was sealed in an NMR tube with $[Me_3O]BF_4$ in $CDCl_3$, in the hope that the MeO group on silicon would be eliminated as $Me_2O$. However no reaction took place, even after several days at room temperature.

The X-ray crystal structure of $Ph(2\text{-}MeOC_6H_4)ClSiFe(CO)_2Cp$ (**2a**) was undertaken to see if there was any tendency for the silicon atom to become five-coordinate. Fig. 4 shows that the *ortho*-OMe group is orientated so that the oxygen atom is pointing towards the silicon atom, and there are indications of a weak bonding intramolecular interaction between these atoms. The Si···O distance of 2.991 Å is shorter than the sum of the van der Waals radii for Si and O at 3.6 Å, though much longer than the sum of the covalent radii of about 1.84 Å. The C(21)–C(26)–O(3) angle is 115.5°, suggesting the methoxy group is drawn towards the silicon to shorten the O···Si distance. The Cl on the Si atom lies opposite the site where the O···Si interaction is developing. Comparison with the structure of $MeC(O)N(SiMe_2Cl)_2$ which has Si–Cl bonds to both four- and five-coordinate silicon atoms [28] shows that the value of 2.115 Å for the Si–Cl distance in $Ph(2\text{-}MeOC_6H_4)ClSiFe(CO)_2Cp$ is longer than the Si–Cl bond to the tetrahedral silicon atom (2.050 Å) though

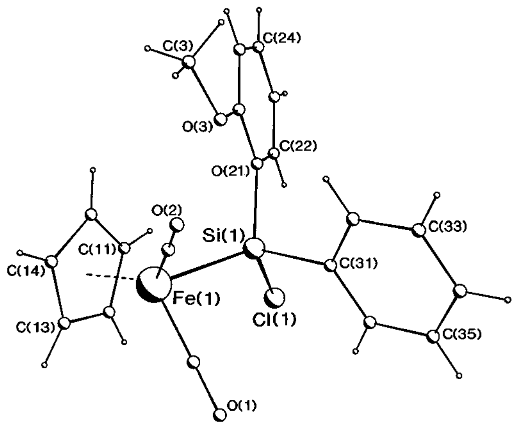


Fig. 4. The structure of Ph(2-MeOC$_6$H$_4$)ClSiFe(CO)$_2$Cp. Bond parameters include: Fe(1)–Si(1) 2.2698(2), Si(1)–Cl(1) 2.1151(7), Fe(1)–C$_{cp}$ (av) 2.093(2) Å, Si(1)···O(3) 2.991 Å; Fe(1)–Si(1)–Cl(1) 108.09(3), C(26)–O(3)–C(3) 118.8(2), C(21)–C(26)–O(3) 115.5(2)°.

much shorter than the Si–Cl *trans* to O on the five-coordinate Si (2.348 Å). This is significant, since a major factor determining the tendency for five-coordination at silicon is the capacity for a Si–X bond to be stretched, which is facile for X = Cl [29]. Finally, the sum of the angles about the silicon atom for the potentially equatorial groups [Fe–Si–C(21), Fe–Si–C(31) and C(21)–Si–C(31)] is 342.2°, midway between tetrahedral (328°) and planar (360°). All of this points to a weak bonding O···Si interaction, poised to stabilise the silicon centre once the *trans* group is lost in the mass spectrometer.

The Fe–Si bond in Ph(2-MeOC$_6$H$_4$)ClSiFe(CO)$_2$Cp is 2.2698(6) Å, surprisingly shorter than even Ph$_2$FSiFe(CO)$_2$Cp (2.278(1) Å [24]). Based on electronegativity grounds alone, a bond length comparable to that of Ph$_2$(MeO)SiFe(CO)$_2$Cp (2.292(2) Å) might have been expected. This may be related to the small distortion towards trigonal bipyramidal geometry, with the Fe in a pseudo-equatorial site, induced by the *ortho*-OMe group interaction.

### 3.4. O[SiPh$_2${Co(CO)$_4$}]$_2$

The early report of O[SiMe$_2${Co(CO)$_4$}]$_2$ described it as extremely unstable, decomposing slowly even at − 78 °C [9]. Since 1,2 silyl-migration reactions of R$_5$Si$_2$Co(CO)$_4$ have been shown to be extremely facile [3], it was of interest to synthesise a stable example of a heteroatom-substituted silyl–cobalt compound. Accordingly, we reacted O(SiPh$_2$H)$_2$ with Co$_2$(CO)$_8$ and obtained good yields of O[SiPh$_2${Co(CO)$_4$}]$_2$. This showed none of the instability of the methyl analogue, since it was readily isolated. The solid was even stable for considerable periods in air, although in solution it proved to be moderately air-sensitive. The reasons for the remarkable difference in behaviour between the methyl and phenyl examples are not obvious, but are presumably attributable to the steric protection provided by the phenyl groups. The molecule is very crowded and perhaps is prevented from adopting a conformation where a migration reaction is possible, if this is involved in the decomposition process.

The carbonyl region infrared spectra of O[SiPh$_2${Co(CO)$_4$}]$_2$ showed doubling of the normal pattern found for terminal Co(CO)$_4$ groups. This is unlikely to arise from coupling between the two ends of the molecule and suggests perhaps that two conformers exist in solution. To determine the solid state structure an X-ray study was carried out. The crystal contains discrete molecules, as shown in Fig. 5. As expected, the backbone of the molecule consists of two silicon atoms, both tetrahedrally coordinated, joined in a Si–O–Si linkage. Each silicon atom is further bonded to two phenyl rings and to a cobalt atom which has trigonal bipyramidal coordination, the silicon occupying an axial site. One parameter of interest is the Si–O–Si angle of 153.4(2)°, which is surprisingly bent given the fact that other bulky disiloxanes (e.g. O(SiPh$_3$)$_2$ [30], O[SiMeF{Fe(CO)$_2$Cp}]$_2$ [31], O[Si(OBu$^t$)$_3$]$_2$ [32] and O[SiCl$_2${C(SiMe$_3$)$_3$}]$_2$ [33]) all show linear Si–O–Si bonds. It is generally assumed that the linear arrangement is stabilised by Si···O π-bonding, and consistent with these ideas, the Si–O bond length in O[SiPh$_2${Co(CO)$_4$}]$_2$ of 1.630(3) Å is closer to that in O(SiH$_3$)$_2$ (Si–O–Si 142.2(3)°, Si–O 1.634 Å [34]) than to O[SiMeF{Fe(CO)$_2$Cp}]$_2$ (Si–O–Si 180°, Si–O 1.603 Å [31]).

The Co–Si bonds (2.348 Å average) are relatively long, with previous values for simple R$_3$SiCo(CO)$_4$ ranging from 2.254 to 2.38 Å [35]. This is presumably because of the bulk of the substituents in **3**.

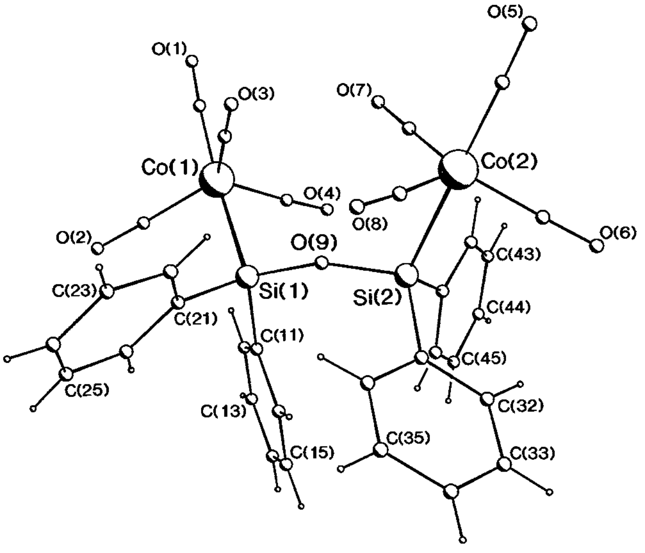


Fig. 5. The structure of O[SiPh$_2$(Co(CO)$_4$)]$_2$. Bond parameters include: Co(1)–Si(1) 2.341(2), Co(2)–Si(2) 2.354(2), Si(1)–O(9) 1.630(3), Si(2)–O(9) 1.629(3) Å; Si(1)–O(9)–Si(2) 153.4(2)°.

In the solid state, molecules of $O[SiPh_2\{Co(CO)_4\}]_2$ adopt a *gauche* configuration for the two cobalt-containing groups, with interlocking of CO groups and Ph substituents. A possible explanation for the complex IR spectrum in solution is that there is also an *anti* configuration which interchanges slowly on the IR time scale, giving rise to doubled peaks. This seems more likely than coupling of vibrational modes across the two halves of the molecule.

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 172420–172423 for **1a**, **1b**, **2a** and **3**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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