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The inverse sandwich complex $[(K(18\text{-crown-}6))_2Cp][CpFe(CO)_2]$ – unpredictable redox reactions of $[CpFe(CO)_2]I$ with the silanides $Na[SiRtBu_2]$ (R = Me, *t*Bu) and the isoelectronic phosphanyl borohydride $K[PtBu_2BH_3]$†

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The dimeric iron carbonyl $[CpFe(CO)_2]_2$ and the iodosilanes tBu_2RSiI were obtained from the reaction of $[CpFe(CO)_2]I$ with the silanides $Na[SiRtBu_2]$ (R = Me, *t*Bu) in THF. By the reactions of $[CpFe(CO)_2]I$ and $Na[SiRtBu_2]$ (R = Me, *t*Bu) the disilanes $tBu_2RSiSiRtBu_2$ (R = Me, *t*Bu) were additionally formed using more than one equivalent of the silanide. In this context it should be noted that reduction of $[CpFe(CO)_2]_2$ with $Na[SitBu_3]$ gives the disilanes $tBu_3SiSitBu_3$ along with the sodium ferrate $[(Na(18\text{-crown-}6))_2Cp][CpFe(CO)_2]$. The potassium analogue $[(K(18\text{-crown-}6))_2Cp][CpFe(CO)_2]$ (orthorhombic, space group $Pmc2_1$), however, could be isolated as a minor product from the reaction of $[CpFe(CO)_2]I$ with $[K(18\text{-crown-}6)][PtBu_2BH_3]$. The reaction of $[CpFe(CO)_2]_2$ with the potassium benzophenone ketyl radical and subsequent treatment with 18-crown-6 yielded the ferrate $[K(18\text{-crown-}6)][CpFe(CO)_2]$ in THF at room temperature. The crown ether complex $[K(18\text{-crown-}6)][CpFe(CO)_2]$ was analyzed using X-ray crystallography (orthorhombic, space group $Pna2_1$) and its thermal behaviour was investigated.

Introduction

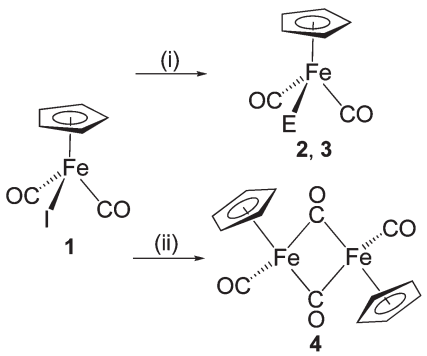
In the past few decades cyclopentadienyliron dicarbonyl complexes have gained significant importance as model systems in organometallic chemistry. On the one hand the $[CpFe(CO)_2]$-fragment is an ideal candidate to investigate substitution reactions because it can act as a nucleophile (*e.g.* $M[CpFe(CO)_2]$; M = alkali metal), as an electrophile (*e.g.* $[CpFe(CO)_2]X$; X = halogen) or as a radical (*e.g.* $[CpFe(CO)_2]_2$),[1] on the other hand its electronic properties can be related to the carbonyl IR stretching frequencies[2] as well as to the ^{13}C NMR shifts of the carbonyl[3] and cyclopentadienido[4] carbon atoms.

In a preceding study[5] we have already made a comparison of cyclopentadienyliron dicarbonyl complexes with two series of isoelectronic and largely isosteric ligands, namely PPh_2Me,[6] $[PPh_2BH_3]^-$,[6] and $[SiPh_2Me]^-$[7] and $SPtBu_3$,[8] $[SPtBu_2BH_3]^-$[8] and $[SSitBu_3]^-$.[9] In this report we have concluded that, with respect to electron donor strength, phosphanyl borohydrides occupy an intermediate position between phosphanes (weakest donors) and silyl ligands (strongest donors).[5] The same is true for the thio derivatives, although the differences are smaller.[5]

The purpose of this paper is now to examine the reactivity of $[CpFe(CO)_2]I$ towards the silanides $Na[SiRtBu_2]$ (R = Me, *t*Bu)[5,10,11] and to make a comparison with the chemical behaviour of the isoelectronic phosphanyl borohydride $K[PtBu_2BH_3]$. In the course of these investigations we studied additionally the thermal and chemical behaviour of the ferrate $[K(18\text{-crown-}6)][CpFe(CO)_2]$.

Results and discussion

Recently we have reported that preparation of the phosphanyl borohydride homologue can best be achieved by introducing the



Scheme 1 Reactivity of $[CpFe(CO)_2]I$ towards the silanides $Na[SiRtBu_2]$ (R = Me, *t*Bu) and the isoelectronic phosphanyl borohydride $K[PR_2BH_3]$ (R = Ph, *t*Bu). (i) K[E] (**2**, E = PPh_2BH_3; **3**, E = $PtBu_2BH_3$. (ii) M[E]; M[E] = $Na[SiRtBu_2]$ (R = Me, *t*Bu), $K[PtBu_2BH_3]$).

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†CCDC 832033 (**$[(K(18\text{-crown-}6))_2Cp][5]$**), 832034 (**$[K(18\text{-crown-}6)][5]$**), 832031 (**6**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt00031h

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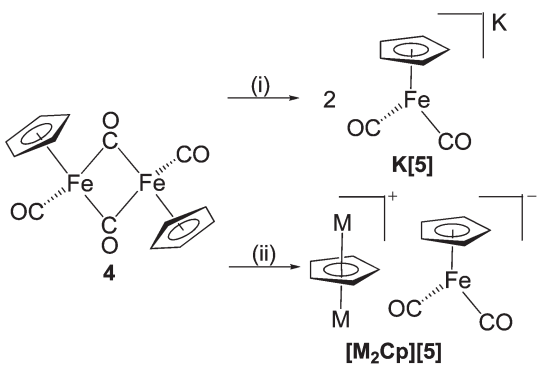
preformed ligands, rather than assembling them with the phosphorus atom connected to a metal fragment.[5] Therefore treatment of $[CpFe(CO)_2]I$ with $K[PPh_2BH_3]$[6] in THF resulted in nearly quantitative formation of the desired compound (Scheme 1).[5]

In pursuit of complexes of the type $[CpFe(CO)_2]SiR_3$ (R = alkyl), $[CpFe(CO)_2]I$ (**1**) was first treated with one equivalent of the sodium silanides $Na[SiMe\textit{t}Bu_2]$[5] and $Na[Si\textit{t}Bu_3]$.[10,11] The NMR spectra of these reactions, however, indicate that it is not practical to prepare the cyclopentadienyliron dicarbonyl silanides $[CpFe(CO)_2]SiR\textit{t}Bu_2$ by the same routes as applied for isoelectronic phosphanyl borohydrides. The spectroscopically identifiable silicon-containing products are $\textit{t}Bu_2RSiI$[11–13] and $\textit{t}Bu_2RSiSiR\textit{t}Bu_2$[14,15] (R = Me, *t*Bu), respectively, indicating that a redox reaction took place. The identity of $\textit{t}Bu_2RSiI$ and $\textit{t}Bu_2RSiSiR\textit{t}Bu_2$ (R = Me, *t*Bu), respectively, was confirmed by comparison with authentic samples. The ^{13}C NMR spectra of both reaction solutions showed that **1** had been completely consumed, and new signals appeared which could be assigned to the dimer $[CpFe(CO)_2]_2$ (**4**), Na[Cp], the corresponding disilane $\textit{t}Bu_2RSiSiR\textit{t}Bu_2$ (R = Me, *t*Bu), and the related iodo silane $\textit{t}Bu_2RSiI$ (R = Me, *t*Bu). Due to the presence of paramagnetic species, the signals which were observable in the ^1H NMR spectra of the reaction solutions are broadened. Moreover, by varying the molar ratio of **1** and $Na[Si\textit{t}Bu_3]$ from 1 : 1 to 1 : 5, the NMR signals of the dimer **4** could not be detected any more while the amount of paramagnetic components increased. The dimer **4** was isolable in 42% yield by a 1 : 1 reaction of $Na[SiMe\textit{t}Bu_2]$ and **1**. It is remarkable that treatment of **1** with 0.5 molar equivalents of $Na[Si\textit{t}Bu_3]$ already gave $\textit{t}Bu_3SiI$ and **4** that had been produced in 1 : 1 reactions, but in contrast to equimolar reactions, no disilane $\textit{t}Bu_3SiSi\textit{t}Bu_3$ was thereby formed.

The reaction of **1** with $[K(18\text{-crown-6})][P\textit{t}Bu_2BH_3]$ which represents a stronger and a sterically more demanding phosphanyl borohydride than $[PPh_2BH_3]^-$ gives **3** however along with the ferrate **[(K(18-crown-6))$_2$Cp][5]** as its minor product. Obviously, a fragmentation reaction of the $[CpFe(CO)_2]$ moiety with liberation of K[Cp] had additionally taken place. Thus the question arises as to what are the factors leading to this decomposition. Interestingly, a very similar degradation of the $[CpFe(CO)_2]$ moiety takes place when **4** is treated with $Na[Si\textit{t}Bu_3]$. We found that the reaction of **4** with $Na[Si\textit{t}Bu_3]$ gives the disilane $\textit{t}Bu_3SiSi\textit{t}Bu_3$ and the ferrate $[CpFe(CO)_2]^-$ as well as the cyclopentadienide anion (Scheme 2). Apparently, these products are formed by an β-addition of $Na[Si\textit{t}Bu_3]$ to **4** (oxidative addition of $Na[Si\textit{t}Bu_3]$ to dinuclear **4**) and a subsequent substitution reaction with the liberation of the cyclopentadienide anion (Scheme 2). In this context it should be noted that Fe(II) compounds with bulky σ-donating substituents are paramagnetic and undergo easily a reductive elimination by which elementary iron is formed (*e.g.* $Fe(Si\textit{t}Bu_3)_2$[16] decomposes at temperatures below −20 °C). It has been shown that demetallation of half-sandwich complexes with liberation of the $[Cp]^-$ anion takes place in the presence of strong reduction agents such as sodium metal in hexamethylphosphoramide or potassium in the presence of 18-crown-6 and naphthalene.[17] We reported on the successful decomplexation of cyclopentadienide from cymantrene, which is the analogous Mn complex of **4**, by treatment with potassium metal in the presence of naphthalene and tetramethylethylenediamine.[18]



Scheme 2 Reduction behaviour of $[CpFe(CO)_2]_2$ (**4**). (i) Potassium benzophenone ketyl radical. (ii) $M[Si\textit{t}Bu_3]$ (M = Na); $M[P\textit{t}Bu_2BH_3]$ (M = K).

In order to prove the stability of the cyclopentadienyl dicarbonyl ferrate anion we decided to examine additionally the thermal behaviour of **[K(18-crown-6)][5]**. At first we synthesized the ferrate **[K(18-crown-6)][5]** from **4** and potassium benzophenone ketyl radical by a slightly modified literature procedure[19] (Scheme 2). Single crystals of **[K(18-crown-6)][5]** were grown from a 1 : 1 mixture of **K[5]** and 18-crown-6 in THF at room temperature.

Upon heating of **[K(18-crown-6)][5]** to 120 °C no decomposition was observed either in benzene nor in THF, we can therefore conclude that **[K(18-crown-6)][5]** is thermostable under the conditions by which we observed $[Cp]^-$ liberation during the reaction of **4** with $Na[Si\textit{t}Bu_3]$.

We have reported that the silyl complex $[CpFe(CO)_2]SiMePh_2$ (**6**) can be obtained in moderate yield by the reaction of **K[5]** with $Ph_2MeSiCl$.[5] However, when **K[5]** was treated with the sterically hindered bromosilanes $\textit{t}Bu_2MeSiBr$[12] and $\textit{t}Bu_3SiBr$[11] as well as with supersilyl triflate $\textit{t}Bu_3SiO_3SCF_3$,[20] no substitution reaction could be detected even after two months at room temperature.

The inverse sandwich complex **[(K(18-crown-6))$_2$Cp][5]** (shown in Fig. 1; selected bond lengths and angles see figure caption), crystallizes in the orthorhombic space group $Pmc2_1$ with a half molecule of the ferrate and a half molecule of benzene in the asymmetric unit (Fig. 2). The inverse sandwich cation in **[(K(18-crown-6))$_2$Cp][5]** consists of two [K(18-crown-6)] units and one Cp ring.[21] The central cyclopentadienyl ring is η^5-coordinated to the two crown ether-encapsulated potassium cations (Fig. 1). Therefore each K atom is connected to the six O atoms of the crown ether and to five C atoms of the Cp ring. The K–C distances range from 3.055(13) to 3.081(12) Å.[22] The distances between the centre of gravity of the Cp ring and the two K atoms are 2.841 and 2.849 Å, respectively.[23] These distances are comparable to those reported for other compounds containing KCp units. The averaged C–C bond lengths of the Cp ligand of $[(K(18\text{-crown-6}))_2Cp]^+$ is 1.398(19) Å. The structural parameters of the ferrate anion in **[(K(18-crown-6))$_2$Cp][5]** are related to those found in **[K(18-crown-6)][5]** and the determined values are typical for the anion $[CpFe(CO)_2]^-$.[24]

X-Ray quality crystals of the ferrate **[K(18-crown-6)][5]** were grown from a THF solution of a 1 : 1 mixture of unsupported **[K][5]** and 18-crown-6 at room temperature. Complex

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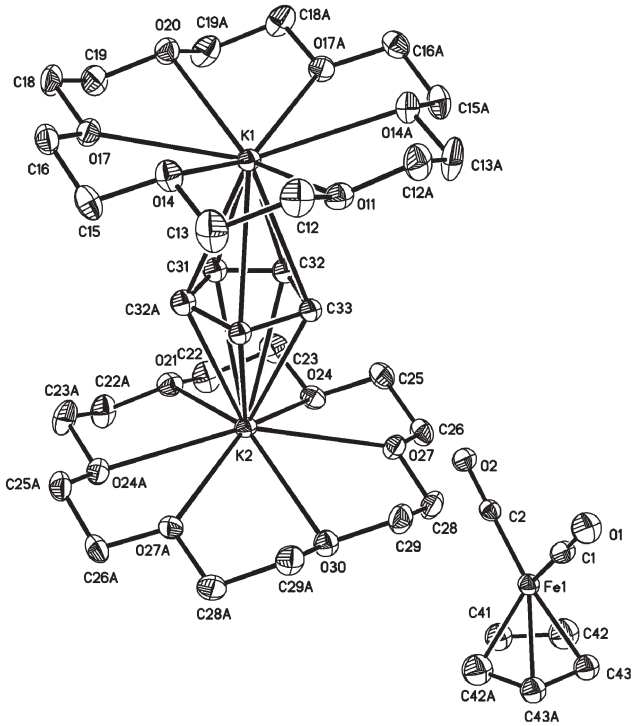

Fig. 1 Molecular structure of **[(K(18-crown-6))$_2$Cp][5]** in the solid state. Selected bond lengths [Å] and bond angles [°]: K(1)–O(17) 2.840 (3), K(1)–O(11) 2.906(4), K(1)–O(14) 2.929(3), K(1)–O(20) 2.969(4), K(1)–C(31) 3.064(13), K(1)–C(32) 3.073(8), K(1)–C(31′) 3.080(12), K(1)–C(33) 3.081(7), K(2)–O(27) 2.853(3), K(2)–O(21) 2.892(5), K(2)–O(24) 2.939(3), K(2)–O(30) 2.941(4), K(2)–C(31) 3.055(13), K(2)–C(32′) 3.073(8), K(2)–C(32) 3.078(8), K(2)–C(31′) 3.081(12), O(11)–C(12) 1.432(5), Fe(1)–C(2) 1.727(6), Fe(1)–C(1) 1.735(7), Fe(1)–C(41′) 2.089 (12), Fe(1)–C(43′) 2.104(7), Fe(1)–C(42′) 2.117(7), Fe(1)–C(41) 2.120 (14), Fe(1)–C(42) 2.122(11), Fe(1)–C(43) 2.131(10), C(1)–O(1) 1.187 (8), C(2)–O(2) 1.188(7), C(2)–Fe(1)–C(1) 89.5(3), O(1)–C(1)–Fe(1) 178.8(6), O(2)–C(2)–Fe(1) 178.9(5).

[K(18-crown-6)][5] crystallizes in the orthorhombic space group $Pna2_1$ with one molecule in the asymmetric unit (Fig. 3). In contrast to the structure of **[(K(18-crown-6))$_2$Cp][5]**, the ferrate **[K(18-crown-6)][5]** displays contact ion pairs in the solid state. Each K atom is surrounded by one ferrate anion and one crown ether molecule. In summary, the ferrate **[K(18-crown-6)][5]** features one contact of a K centre with the carbonyl group and six strong K–O interactions with the crown ether, which gives a coordination number of seven for the K centre. It is remarkable that the distance between the K atom and the C atom of the carbonyl ligand is shorter than that to the O atom. The distances between the O atoms of the crown ether and the K centre are in good agreement with those observed in other 18-crown-6 complexes of related potassium salts.[25] The K–Fe distance in **[K(18-crown-6)][5]** (K–Fe 3.576 Å) is shorter than that found in the potassium ferrate **[(K(18-crown-6))$_2$Cp][5]** (K–Fe 7.722 Å). The metrical parameters of **[K(18-crown-6)][5]** are listed in the caption of Fig. 3.

X-Ray quality crystals of a new polymorph of **6** were grown from a pentane solution at ambient temperature. The complex **6** crystallizes in two crystallographically independent molecules in the asymmetric unit of the monoclinic space group $P2/c$ from

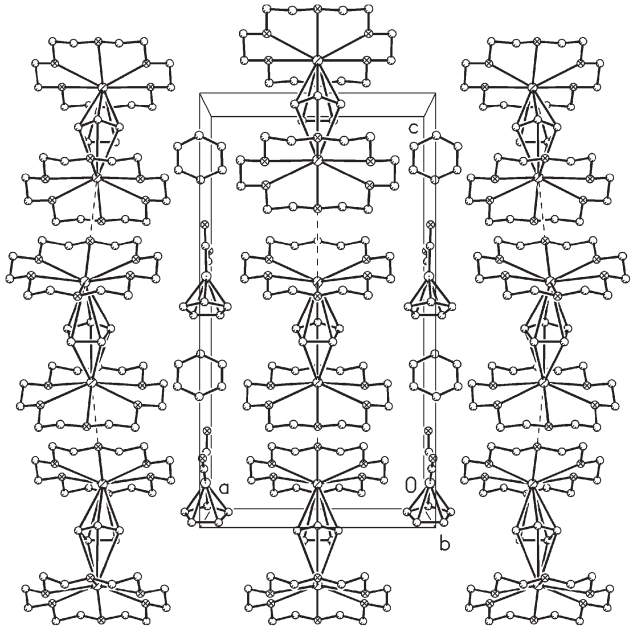

Fig. 2 Crystal packing diagram of **[(K(18-crown-6))$_2$Cp][4]** together with one benzene molecule .

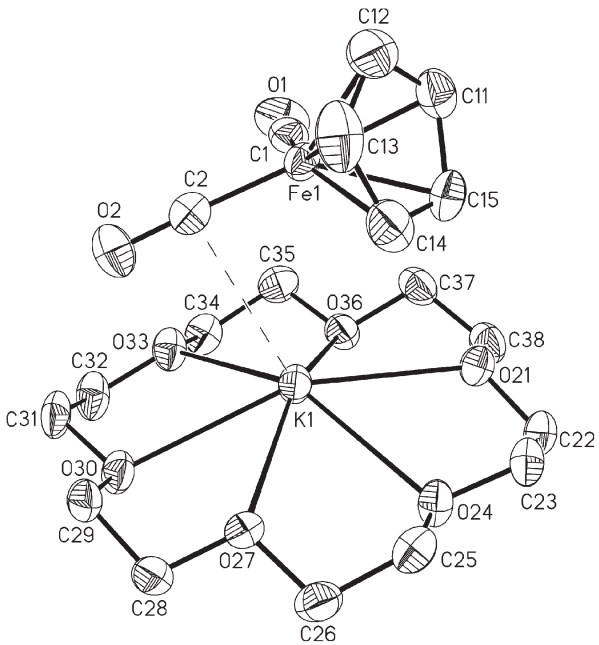

Fig. 3 Molecular structure of **[K(18-crown-6)][5]** in the solid state. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Fe(1)–C(1) 1.714(2), Fe(1)–C(2) 1.719(2), Fe(1)–C(11) 2.086(2), Fe(1)–C(13) 2.104(3), Fe(1)–C(15) 2.104(2), Fe(1)–C(14) 2.113(2), Fe(1)–C(12) 2.119(2), Fe(1)–K(1) 3.5764(5), K(1)–O(24) 2.8523(17), K(1)–O(21) 2.8549(17), K(1)–O(33) 2.8697(16), K(1)–O(36) 2.8819(17), K(1)–O(27) 2.8843 (15), K(1)–O(30) 2.9214(17), K(1)–C(2) 3.288(2), C(1)–O(1) 1.179(3), C(2)–O(2) 1.184(3), C(1)–Fe(1)–C(2) 90.40(11), C(2)–Fe(1)–K(1) 66.33 (8), O(1)–C(1)–Fe(1) 178.6(2), O(2)–C(2)–Fe(1) 178.3(2), O(2)–C(2)–K(1) 93.29(15).

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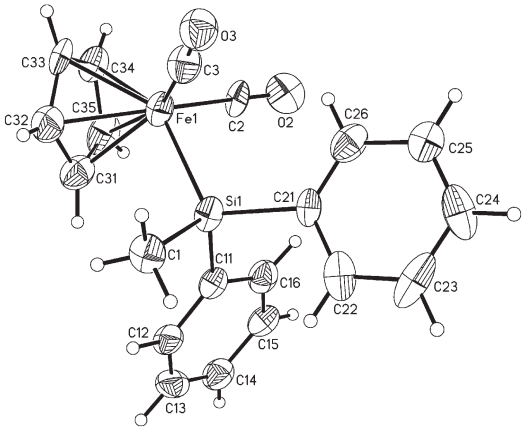

Fig. 4 Solid-state structure of one of two crystallographic independent molecules of **6** in the solid state. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Fe(1)–C(2) 1.748(14), Fe(1)–C(3) 1.751(17), Fe(1)–C(35) 2.082(17), Fe(1)–C(31) 2.083(19), Fe(1)–C(33) 2.108(16), Fe(1)–C(34) 2.122(14), Fe(1)–C(32) 2.124(19), Fe(1)–Si(1) 2.326(5), Si(1)–C(11) 1.884(16), Si(1)–C(1) 1.888(15), Si(1)–C(21) 1.938(15), C(2)–O(2) 1.145(18), C(3)–O(3) 1.156(19), O(2)–C(2)–Fe(1) 178.4(16), O(3)–C(3)–Fe(1) 176.6(17), C(2)–Fe(1)–C(3) 98.4(8).

pentane (Fig. 4; selected bond lengths and angles see caption of Fig. 4).[26] The structural parameters of this polymorph are comparable with those of **6** which was crystallized from benzene.[5]

Experimental section

General procedures

All experiments were carried out under dry argon or nitrogen with strict exclusion of air and moisture using standard Schlenk techniques or a glove box. The solvents (benzene, diethylether, hexane, pentane, tetrahydrofuran) were distilled from sodium/benzophenone prior to use. The NMR spectra were recorded on a Bruker AM 250, a Bruker DPX 250, a Bruker Avance 300 and a Bruker Avance 400 spectrometer. A JASCO FT/IR 4200 spectrometer was used for the IR spectra.

Synthesis of [K(18-crown-6)][5]

Potassium pieces (156 mg, 4 mmol) were added to a solution of benzophenone (728 mg, 4 mmol) in THF (20 cm^3) at room temperature. Immediately the potassium benzophenone ketyl radical was formed. Addition of an excess of **3** (759 mg, 2.2 mmol) to this solution resulted in disappearance of the characteristic deep blue colour of the potassium benzophenone ketyl radical. The reaction mixture was stirred for a further 12 h at room temperature, during which an orange-red precipitate formed. The orange-red solid was isolated by filtration. After washing the precipitate with benzene (8 × 3 cm^3), analytically pure **K[5]** remained as an orange-red microcrystalline solid (362 mg, 47% yield).

At room temperature 18-crown-6 (106 mg, 0.40 mmol) was added to a slurry of unsupported **K[5]** (42 mg, 0.20 mmol) in THF (10 cm^3). The mixture was stirred for 1 h at room temperature. After filtering, single crystals of **[K(18-crown-6)][5]** were grown from the filtrate after 5 days at room temperature. Yield: 73 mg (76%). **[K(18-crown-6)][5]**: IR: $\tilde{\nu}$ = 1727, 1874 cm^{-1} (CO). Found: C, 47.38; H, 6.24. $C_{19}H_{29}FeKO_8$ requires C, 47.51; H, 6.08.

Reaction of 1 with Na[SiMe*t*Bu$_2$]

A solution of Na[SiMe*t*Bu$_2$] (A: 63 mg, 0.36 mmol; B: 162 mg, 0.92 mmol) in THF (A: 1 cm^3, B: 3 cm^3) was added to a cooled solution (−78 °C) of **1** (A: 218 mg, 0.72 mmol; B: 278 mg, 0.92 mmol) in THF (5 cm^3). After warming to room temperature overnight, an NMR sample was taken. In the ^{1}H NMR spectrum of mixture A, resonances were observable which could be assigned to *t*Bu$_2$MeSiI and **3**. The signals of the disilane *t*Bu$_2$MeSiSiMe*t*Bu$_2$ were additionally found in the ^{1}H NMR and ^{29}Si NMR spectrum of approach B (*t*Bu$_2$MeSiSiMe*t*Bu$_2$: $\delta_{Si}\{^1H\}$ (49.7 MHz; C_6D_6; Me_4Si) 7.1). Due to paramagnetic components in mixture B, the signals in the NMR spectra are broadened.

Work-up of **4** from mixture B: All volatiles were removed *in vacuo*. The residue was extracted into pentane. After filtering, **4** was crystallized from pentane. Yield: 137 mg (42%).

Preparation of an authentic sample of *t*Bu$_2$MeSiI

To an ice-cooled solution of *t*Bu$_2$MeSiH (430 mg, 2.71 mmol) in CH_2Cl_2 (8 cm^3) was added dropwise a solution of I_2 (720 mg, 2.84 mmol) in CH_2Cl_2 (8 cm^3). The solution was warmed to room temperature and stirred overnight. Volatiles were removed at room temperature/70 torr to give a solid. *t*Bu$_2$MeSiI: δ_H (250.1 MHz; C_6D_6; Me_4Si) 0.48 (3 H, s, Me), 0.99 (18 H, s, *t*Bu). $\delta_C\{^1H\}$ (62.9 MHz; C_6D_6; Me_4Si) −2.3 (Si*Me*), 21.1 (*C*Me$_3$), 28.1 (C*Me*$_3$). $\delta_{Si}\{^1H\}$ (49.7 MHz; C_6D_6; Me_4Si) 40.7 (*t*Bu$_2$MeSiI). Found: C, 38.03; H, 7.45. $C_9H_{21}ISi$ requires C, 37.53; H, 7.22.

Reaction of 1 with Na[Si*t*Bu$_3$]

A solution of Na[Si*t*Bu$_3$] (A: 8 mg, 0.036 mmol; B: 23 mg, 0.104 mmol; C: 89 mg, 0.401 mmol) in THF (A: 0.1 cm^3; B: 0.3 cm^3; C: 1 cm^3) was added to a solution of **1** (A: 20 mg, 0.066 mmol; B: 31 mg, 0.102 mmol; C: 24 mg, 0.079 mmol) in THF (5 cm^3) at room temperature. In the ^{1}H NMR spectrum of method A, resonances were observable which could be assigned to *t*Bu$_3$SiI[11] and **4**. Additionally the signals of the disilane *t*Bu$_3$SiSi*t*Bu$_3$[15] were found in the ^{1}H NMR and in the ^{29}Si NMR spectrum of method B (*t*Bu$_3$SiSi*t*Bu$_3$: $\delta_{Si}\{^1H\}$ (49.7 MHz; C_6D_6; Me_4Si) 35.0). Due to paramagnetic components, no signals were observable for method C, whereas the signals in the NMR spectra of mixture B were broadened.

Formation of [(K(18-crown-6))$_2$Cp][5]

When the reaction solution of **1** with [K(18-crown-6)][P*t*Bu$_2$BH$_3$] in 1 : 1 stoichiometry was left to stand for several weeks, a few crystals of the composition [(K(18-crown-6))$_2$Cp][CpFe(CO)$_2$] (**[(K(18-crown-6))$_2$Cp][5]**) could be isolated. Due to the low yield of these species, no further characterization could be undertaken.

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Table 1 Crystal data and experimental details for **[(K(18-crown-6))$_2$Cp][5]** and **[K(18-crown-6)][5]**

	[(K(18-crown-6))$_2$Cp][5]	[K(18-crown-6)][5]
Empirical formula	$C_{42}H_{64}FeK_2O_{14}$	$C_{19}H_{29}FeKO_8$
Formula weight	926.98	480.37
Temperature/K	173(2)	173(2)
Crystal size/mm^3	0.35 × 0.33 × 0.32	0.28 × 0.26 × 0.23
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pmc2_1$	$Pna2_1$
a/Å	11.4260(13)	14.9080(5)
b/Å	9.8741(8)	10.4189(4)
c/Å	21.0967(16)	14.3622(6)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	2380.2(4)	2230.81(15)
Z	2	4
Calcd. density/ Mg m^{-3}	1.293	1.430
μ/mm^{-1}	0.552	0.903
Index ranges	$-13 \le h \le 13$, $-10 \le k \le 11$, $-25 \le l \le 22$	$-16 \le h \le 18$, $-12 \le k \le 12$, $-17 \le l \le 17$
θ-range/°	3.57 to 25.57	3.36 to 25.67
No. of reflns Collected	8991	26 783
No. of indep. reflns	4207	4176
R_{int}	0.0355	0.0770
Goodness-of-fit (F^2)	1.037	0.972
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0499, wR_2 = 0.1317	R_1 = 0.0267, wR_2 = 0.0554
R_1, wR_2 indices (all data)	R_1 = 0.0547, wR_2 = 0.1352	R_1 = 0.0311, wR_2 = 0.0565
Largest diff. peak and hole/e Å^{-3}	0.555 and −0.482	0.172 and −0.162

Reaction of 4 with Na[Si*t*Bu$_3$]

A solution of Na[Si*t*Bu$_3$] (124 mg, 0.56 mmol) in THF (1.4 cm^3) was added to a solution of **4** (89 mg, 0.25 mmol) and 18-crown-6 (119 mg, 0.45 mmol) in 5 cm^3 benzene at ambient temperature and stirred for 2 days during which a dark precipitate formed. After filtration, crystals of the ferrate were grown from the filtrate at room temperature. Yield: 145 mg (71%). **[(Na(18-crown-6))$_2$Cp][5]**: IR: $\tilde{\nu}$ = 1786, 1876 cm^{-1} (CO). *m*/*z* (ESI$^+$) (%): 636.6 (100), 637.6 (45.4), 638.7 (10.2), [(Na(18-crown-6))$_2$Cp]$^+$, calcd for [(Na(18-crown-6))$_2$Cp]$^+$ 639.3 (100), 640.3 (32.4), 641.3 (7.6), 287.3 (100), 288.2 (12.5) [Na(18-crown-6)]$^+$, calcd for [Na(18-crown-6)]$^+$ 287.2 (100), 288.2 (13.5). Found: C, 52.75; H, 7.25. $C_{36}H_{60}FeNa_2O_{14}$ requires C, 52.82; H, 7.39.

Crystal structure determinations of [(K(18-crown-6))$_2$Cp][5], and [K(18-crown-6)][5], and 6

Data collections for **[(K(18-crown-6))$_2$Cp][5]**, **[K(18-crown-6)][5]**, and **6** were performed on a STOE IPDS-II two-circle diffractometer with graphite-monochromated MoK_α-radiation (λ = 0.71073 Å). The structures were solved with direct methods and refined against F^2 by full-matrix least-squares calculations (Table 1). Absorption corrections were performed with the MULABS option in PLATON.[27] All non-H atoms have been refined anisotropically, whereas the H atoms have been treated with a riding model.

CCDC reference numbers: CCDC 832033 (**[(K(18-crown-6))$_2$Cp][5]**), 832034 (**[K(18-crown-6)][5]**), 832031 (**6**).

Conclusions

The dimeric iron carbonyl **4** and the iodosilanes *t*Bu$_2$RSiI were obtained from the reaction of [CpFe(CO)$_2$]I with the silanides Na[SiR*t*Bu$_2$] (R = Me, *t*Bu) in THF. In the case of 1 : 1 approaches the disilanes *t*Bu$_2$RSiSiR*t*Bu$_2$ (R = Me, *t*Bu) were additionally formed. Reduction of **4** with Na[Si*t*Bu$_3$] gives the disilanes *t*Bu$_3$SiSi*t*Bu$_3$ along with the ferrate **[(Na(18-crown-6))$_2$Cp][5]**. The inverse sandwich complex **[(K(18-crown-6))$_2$Cp][5]** was isolated as a minor product from the reaction of **1** with [K(18-crown-6)][P*t*Bu$_2$BH$_3$]. In addition we prepared **[K(18-crown-6)][5]** and investigated its thermal behaviour. The paramagnetic ferrate **[K][5]** was obtained from the reaction of **4** with the potassium benzophenone ketyl radical in THF at room temperature. Subsequent treatment of the reaction mixture with 18-crown-6 yielded **[K(18-crown-6)][5]**. The solid-state structure of **[K(18-crown-6)][5]** features contact ion pairs of the complexed potassium cation and the ferrate anion. It is remarkable that the distance between the K cation and the C atom of the carbonyl ligand is shorter than that between the K atom and O atom of the carbonyl group of ferrate anion.

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