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Preliminary communication

Five-coordinate silicon: synthesis, dynamic behaviour and structure of a cyclic anionic trifluorosilicate forming part of a transition metal complex; crystal structure of 18-crown-6 potassium [η^4-(1,4-diphenylbutadienylene)-tricarbonyliron]trifluorosilicate

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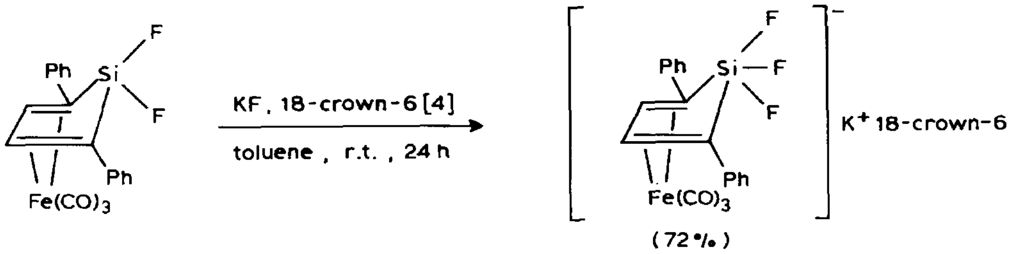
Abstract

Reaction of potassium fluoride with (η^4-1,1-difluoro-2,5-diphenylsilacyclopentadiene)tricarbonyliron (**1**) gave the transition metal complex **2** incorporating a pentacoordinated anionic silicate. The crystal structure analysis and the variable ^{19}F NMR of complex **2**, 18-crown-6 potassium [η^4-(1,4-diphenylbutadienylene)tricarbonyliron]trifluorosilicate, are reported and its dynamic behaviour discussed.

Recently, Damrauer et al. described an easy method of preparing acyclic fluorosilicates, $[R_nSiF_{5-n}]^-$ as their 18-crown-6 potassium salts [1]. We have extended this method to a reaction of difluorosilane within a transition metal complex, viz. (1,1-difluoro-2,5-diphenylsilacyclopentadiene)tricarbonyliron (**1**) [2]. Treatment of **1** with one equivalent of a 1/1 mixture of KF and 18-crown-6 in toluene at room



(1) (2)

Scheme 1. Synthesis of the 18-crown-6 potassium [η^4-(1,4-diphenylbutadienylene)tricarbonyliron]trifluorosilicate (**2**).

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Selected bond lengths (Å) and bond angles (°) for 18-crown-6 potassium [η^4-(1,4-diphenylbutadienylene)tricarbonyliron]trifluorosilicate (**2**)

Si–F(1)	1.633(8)	Si–C(4)	1.968(13)
Si–F(2)	1.668(8)	Si–C(7)	1.894(12)
Si–F(3)	1.621(8)		
C(4)–Si–F(2)	175.2(5)	C(4)–Si–F(1)	92.5(5)
F(1)–Si–F(3)	108.8(4)	C(4)–Si–F(3)	94.5(5)
F(1)–Si–C(7)	125.0(5)	F(2)–Si–F(1)	89.0(4)
F(3)–Si–C(7)	126.3(5)	F(2)–Si–F(3)	89.4(4)
C(4)–Si–C(7)	82.4(5)	F(2)–Si–C(7)	93.1(5)

temperature gave a good yield (72%) of the 18-crown-6 potassium [η^4-(1,4-diphenylbutadienylene)tricarbonyliron]trifluorosilicate (**2**) [3*] (Scheme 1).

The ^{1}H NMR spectrum of **2** is dominated by a 24-proton singlet from the crown moiety; in addition, there is a characteristic splitting of the aromatic protons signals upon pentacoordination, as observed previously by Damrauer et al. [1]. In deuteroacetone solution, at 30 °C, the ^{19}F NMR spectrum of **2** shows a sharp singlet at -114 ppm [3*] relative to $CFCl_3$, indicating fast permutational isomerization of the fluorine atoms and the singlet persists down to -105 °C. Thus, **2** undergoes intramolecular exchange over a large range of temperature (30 to -105 °C), indicative of a low activation barrier; applying the Eyring equation, we conclude that the activation barrier is less than 6 kcal mol^{-1}. In sharp contrast, acyclic trifluorodiphenyl- and trifluoromethylphenyl-silicates were found to give two different fluorine signals at low temperatures in the ratio $F_a/F_e = 2/1$ ($\Delta G = 11.7$ and 9.9

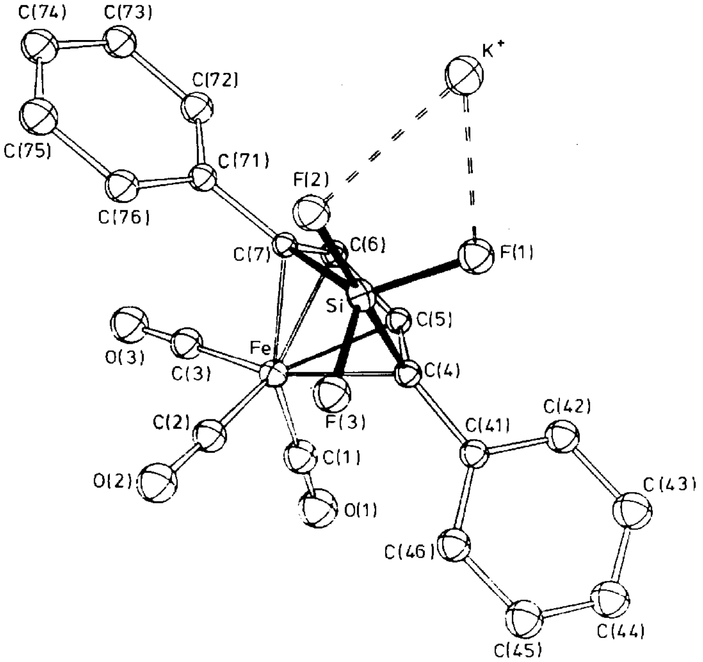
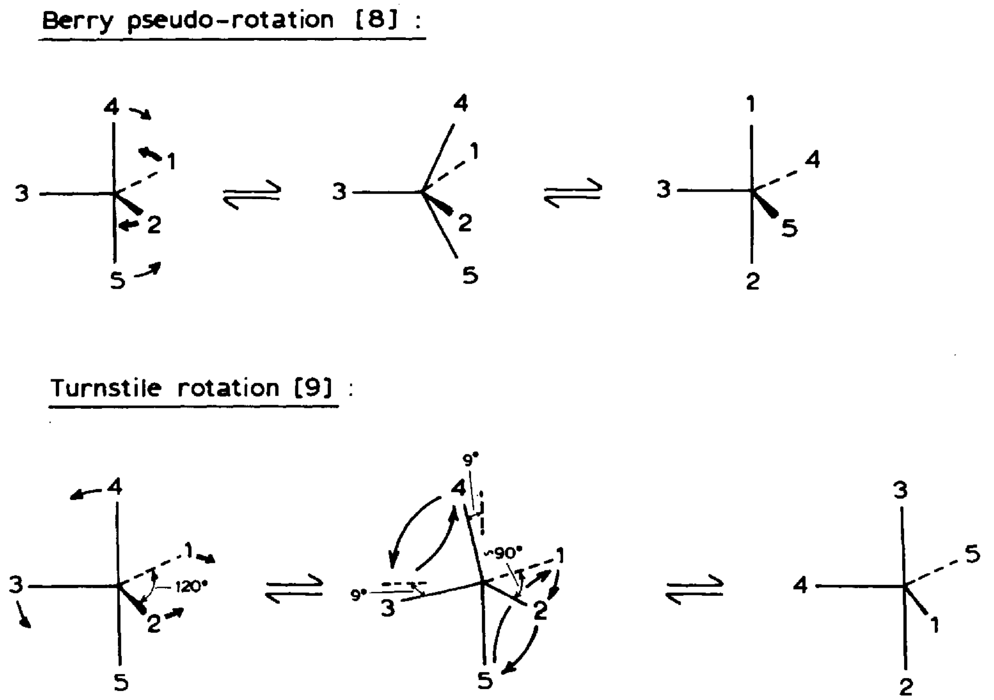


Fig. 1. ORTEP view of 18-crown-6 potassium [1,4-diphenylbutadienylene)tricarbonyliron]trifluorosilicate (**2**).



Scheme 2. Berry pseudo-rotation and turnstile processes.

kcal mol^{-1}, respectively); these were ascribed to equatorial and axial environments in a typical trigonal bipyramidal structure [1].

The crystal structure of **2** shows that the environment of the silicon atom is essentially trigonal bipyramidal [5*], with the five-membered ring occupying axial–equatorial positions, as expected. Bond lengths and angles about silicon are listed in Table 1, and Fig. 1 shows an ORTEP view of the molecule.

The molecular geometry is very close to those of acyclic $R_2SiF_3^-$; the bond lengths show no special features (Table 1) and most of the angles are consistent with the literature data [3*,4]. Slight interactions between the potassium cation and the fluorine atoms F(1) and F(2) (K ··· F distances 2.762(7) and 2.638(7) Å) results in some lengthening of the corresponding Si–F bonds and inequivalence of the two equatorial bonds Si–F(1) and Si–F(3); this interaction seems stronger than with the oxygen atoms of the crown-ether (bonding distances range from 2.81(1) to 2.93(1) Å).

A more detailed analysis of the structure of **2** reveals two interesting features:

(1) of the equatorial–axial angles, the C(4)–Si–C(7) angle of the silole (82.4(5)°) is slightly smaller than that in related complexes (~ 90°) [7], indicating special steric requirements of the five membered ring structures.

(2) of the equatorial angles, the F(1)–Si–F(3) angle deviates markedly from the ideal value of 120° and is lowered to 108.8(4)°.

The intramolecular ligand exchanges observed with pentacoordinated species can be described mechanistically in terms of either Berry pseudorotation or a turnstile process (Scheme 2).

Examination of the molecular structure of **2** reveals that a permutational isomerization of **2**, by Berry pseudorotation must traverse a high energy barrier because of the severe steric constraints imposed on the trigonal bipyramidal geometry by the silole ring structure (C(4)–Si–C(7) 82.4°). In contrast, the structure of **2** places it close to a turnstile barrier configuration. The latter needs a bending of two equatorial bonds towards each other in the equatorial plane until the original 120° angle between them has become about 90°; the F(1)–Si–F(3) angle (108.8(4)°) reflects such a motion. Hence, relative internal rotations of the pair (C(4) and C(7)) relative to the trio (F(1), F(2) and F(3)) seem likely to account for the observed fluorine equivalence in **2**. Similar studies of the analogous trimethoxysilicate are now in progress.

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3 *$C_{38}H_{36}O_9F_3SiFeK$, (2)*: m.p. 205°C; ^1H NMR (acetone-d_6, TMS) δ (ppm) 7.5–6.8 (m, 10H, aromatic) 5.65 (q, ^4J(H–F) 2–3 Hz, 2H, ethylenic) 3.6 (s, 24H, 18-crown-6); ^{19}F NMR (acetone-d_6, $CFCl_3$) δ (negative shifts to high field) −114 ppm (t, ^4J(F–H) 2.5 Hz); IR (hexane) ν(C≡O) 1990, 2053 cm^{-1}. Anal. Found: C, 51.18; H, 5.14. Calc: C, 50.82; H, 4.95%.

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5 *Crystal structure analysis of 2*: $P2_{1/c}$, a 13.890(2), b 15.432(2), c 16.580(3) Å, β 105.02(2)°, V 3432.6 Å^3, $Z = 4$, $R = 0.045$ for 1185 independent reflections with $F > 2.6\sigma(F)$ (Enraf–Nonius CAD-4 diffractometer, Mo-K_α). A list of atomic coordinates and all crystal data may be obtained from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, U.K.

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