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Communication

Unsolvated $[KFl(SiPh_3)]_n$ (Fl = fluorenyl): A supramolecular chain structure assembled exclusively through $K\cdots C{-}\pi$-bonding

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ABSTRACT

Unsolvated potassium 9-triphenylsilylfluorenide, $[KFl(SiPh_3)]_n$ (**3**, Fl = fluorenyl), has been prepared in 89% yield by metalation of 9-fluorenyltriphenylsilane (**2**) with potassium hydride in toluene/THF and structurally characterized by X-ray diffraction. In the solid state, compound **3** comprises a linear chain structure. Due to the absence of coordinating solvent molecules, supramolecular self-assembly occurs solely *via* $K\cdots C{-}\pi$-bonding.

1. Introduction

Fluorenyl ligands (Fl) play an important role in the synthesis of highly efficient Group 4 [1] and lanthanide [2] metallocene catalysts for olefin polymerization. Such catalytically active metallocene complexes are generally made by metathetical reactions between Group 4 or rare-earth metal halides and the corresponding alkali metal fluorenides. The solid state structures of alkali metal fluorenides have been the subject of detailed structural investigations in recent years [3]. The vast majority of the structurally characterized examples are solvated species containing coordinated Lewis bases such as Et_2O [3f], DME (1,2-dimethoxyethane) [3j], TMEDA (N,N,N′,N′-tetramethylethylenediamine) [3b], PMDTA (N,N,N′,N″,N″-pentamethyldiethylenetriamine) [3b,d] or 18-crown-6 [3i,j,m]. In contrast, the structures of unsolvated alkali metal fluorenides have been studied to a much lesser extent. Notable are reports on the solid-state structures of the unsubstituted base-free derivatives LiFl [3g] and NaFl [3h]. We report here the synthesis and structural characterization of the unsolvated potassium derivative of 9-fluorenyltriphenylsilane which in the solid state comprises an unusual supramolecular chain structure assembled exclusively through $K\cdots C{-}\pi$-bonding.

2. Results and discussion

Scheme 1 illustrates the synthetic route leading to the title compound potassium 9-triphenylsilylfluorenide, $[KFl(SiPh_3)]_n$ (**3**). The starting material, 9-fluorenyltriphenylsilane (**2**), was first reported almost sixty years ago by Gilman and Miller [4a,b]. We obtained compound **2** in high yield (82%) by a slight modification of the original preparation [4a,b] *via* metalation of fluorene (**1**) with *n*-butyllithium followed by treatment of the LiFl intermediate with Ph_3SiCl. In an earlier report, the anion of **2** had already been studied in solution [4c]. It was generated by deprotonation of **2** with $CH_3SOCH_2^-K^+$ in DMSO-d_6 and its ^1H and ^{13}C NMR spectra were measured. In order to isolate a crystalline material, the deprotonation reaction of **2** was carried out with the use of potassium hydride. Treatment of **2** with KH in THF according to Scheme 1 directly afforded the potassium fluorenide $[KFl(SiPh_3)]_n$ (**3**) in 89% yield.

NMR spectra (^1H and ^{13}C) clearly showed the absence of coordinated THF in the product despite the fact that the preparation had been carried out in the presence of THF. Large, yellow-green X-ray quality single-crystals of **3** were grown by carefully layering the filtered reaction mixture with *n*-pentane and allowing the mixture to stand undisturbed over a period of *ca.* 2 weeks. Crystal data and structure refinement details are listed in Table 1, and selected bond lengths and angles for **3** are summarized in Table 2. Fig. 1 depicts the supramolecular chain structure of **3**, while the coordination environment around potassium is illustrated in Fig. 2.

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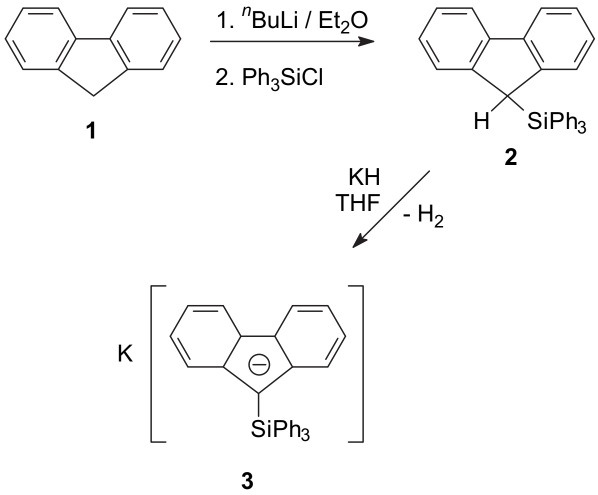

Scheme 1. Synthetic route to 9-fluorenyltriphenylsilane (**2**) and potassium 9-triphenylsilylfluorenide, $[KFl(SiPh_3)]_n$ (**3**).

The X-ray structural analysis confirmed the presence of an unsolvated potassium fluorenide. In the solid state, compound **3** comprises a linear chain structure of the type $[KFl(SiPh_3)]_n$. Due to the absence of coordinating solvent molecules, supramolecular self-assembly occurs solely *via* K···C–π-bonding. Such K···C–π-bonding is not uncommon and has been found in very different classes of potassium compounds containing aromatic ring systems. It often occurs when the central potassium ion is sterically unsaturated and in need of increasing its formal coordination number [5]. Three different π-systems are coordinated to the central potassium ion, involving all three phenyl rings of the triphenylsilyl substituent. On one side, the ligand is η^5-bonded to potassium *via* the formally anionic central cyclopentadienyl moiety of the fluorenyl system with K–C(1) being the shortest distance (3.014(3) Å). On the same side, the coordination is complemented by an allyl-like η^3-interaction with one of the phenyl rings. Supramolecular self-assembly into a polymeric linear chain structure (Fig. 1) is accomplished through η^6–π-interactions with two phenyl rings of neighboring triphenylsilylfluorenyl groups. Thus the unique overall coordination of the $[Fl(SiPh_3)]^-$ anions can be best described as μ-η^3:η^5:η^6:η^6-bridging. The K–C distances differ significantly, falling in the range of 3.010(3) (K–C(1))–3.469(4) (K–C(31)) Å, but are still in the normal range reported earlier for solvated potassium fluorenides [3] and various other potassium compounds involving π-interactions with aromatic rings [5].

Table 1
Crystal data and structure refinement for $[KFl(SiPh_3)]_n$ × 05. toluene (**3**).

Identification code	zabah	
Empirical formula	$C_{69}H_{54}K_2Si_2$	
Formula weight	1017.50 g/mol	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P−1	
Unit cell dimensions	a = 7.9070(5) Å	α = 92.100(3)°
	b = 9.4621(6) Å	β = 90.576(3)°
	c = 37.571(2) Å	γ = 111.749(3)°
Volume	2608.3(3) $Å^3$	
Z	2	
Density (calculated)	1.296 mg/m^3	
Absorption coefficient	0.272 mm^{-1}	
F(000)	1068	
Crystal size	0.35 × 0.15 × 0.07 mm^3	
Theta range for data collection	1.08–26.37°	
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $-46 \le l \le 46$	
Reflections collected	23374	
Independent reflections	10570 [R(int) = 0.0582]	
Completeness to theta = 26.37°	99.4%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	10570/114/697	
Goodness-of-fit on F^2	1.087	
Final *R* indices [I > 2sigma(I)]	$R1 = 0.0676, wR2 = 0.1328$	
R indices (all data)	$R1 = 0.0983, wR2 = 0.1432$	
Largest diff. peak and hole	0.475 and −0.430 e $Å^{-3}$	

Table 2
Selected bond lengths [Å] and angles [°] for $[KFl(SiPh_3)]_n$ (**3**). The compound (**3**) crystallizes with 2 molecules in the asymmetric unit.

K–C(1)	3.014(3)	K′–C(1′)	3.010(3)
K–C(2)	3.074(3)	K′–C(13′)	3.101(3)
K–C(13)	3.141(3)	K′–C(2′)	3.107(3)
K–C(26)	3.206(3)	K′–C(19′)	3.229(3)
K–C(25)	3.221(3)	K′–C(26′)	3.238(3)
K–C(19)	3.243(4)	K′–C(14′)	3.246(3)
K–C(24)	3.256(4)	K′–C(25′)	3.265(3)
K–C(7)	3.263(4)	K′–C(8′)	3.271(3)
K–C(14)	3.274(3)	K′–C(7′)	3.292(3)
K–C(20)	3.300(3)	K′–C(18′)	3.294(4)
K–C(8)	3.301(3)	K′–C(20′)	3.298(3)
K–C(18)	3.306(4)	K′–C(15′)	3.299(4)
K–C(15)	3.328(4)	K′–C(24′)	3.329(4)
K–C(27)	3.342(4)	K′–C(17′)	3.368(4)
K–C(23)	3.374(4)	K′–C(21′)	3.369(3)
K–C(17)	3.381(4)	K′–C(16′)	3.379(4)
K–C(16)	3.391(5)	K′–C(31′)	3.416(3)
K–C(21)	3.404(4)	K′–C(23′)	3.421(4)
K–C(22)	3.462(4)	K′–C(22′)	3.438(4)
K–C(31)	3.469(4)	K′–C(27′)	3.467(4)
Si–C(1)#1	1.814(3)	Si’–C(1′)	1.818(3)
Si–C(20)	1.879(3)	Si’–C(20′)#2	1.884(3)
Si–C(14)	1.881(3)	Si’–C(14′)#2	1.885(3)
Si–C(26)#1	1.897(3)	Si’–C(26′)	1.895(3)
C(1)#1–Si–C(20)	114.78(15)	C(1′)–Si’–C(20′)#2	114.00(15)
C(1)#1–Si–C(14)	113.85(16)	C(1′)–Si’–C(14′)#2	113.41(15)
C(20)–Si–C(14)	100.39(14)	C(20′)#2–Si’–C(14′)#2	100.16(14)
C(1)#1–Si–C(26)#1	110.09(14)	C(1′)–Si’–C(26′)	110.53(14)
C(20)–Si–C(26)#1	108.16(15)	C(20′)#2–Si’–C(26′)	109.85(14)
C(14)–Si–C(26)#1	109.05(15)	C(14′)#2–Si’–C(26′)	108.37(15)

Symmetry transformations used to generate equivalent atoms: #1 - x − 1, y, z #2 -x + 1, y, z.

Notably, the crystal structure of **3** differs largely from those of the unsubstituted base-free derivatives LiFl [3g] and NaFl [3h]. The crystal lattice of the parent lithium fluorenide is built up of subunits in which two lithium ions are encapsulated by two nearly planar and parallel arranged carbanions, whereas solvent-free fluorenylsodium forms the salt-like structure $Na_2[NaFl_3]$, containing the novel trigonal $[NaFl_3]^{2-}$ anion [3h]. In contrast, the crystal structure of **3** comprises the supramolecular $[KFl(SiPh_3)]_n$ chains. As illustrated in Fig. 3, these polymeric chains are found in a parallel alignment without leaving any larger pores in the crystal lattice.

In summarizing the results reported here, unsolvated potassium 9-triphenylsilylfluorenide, $[KFl(SiPh_3)]_n$ (**3**, Fl = fluorenyl), is readily

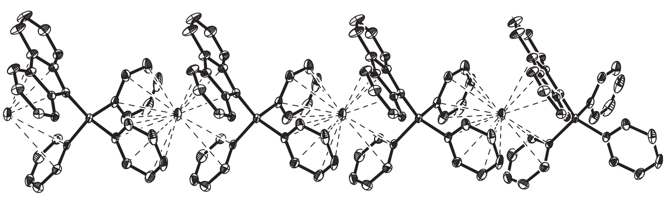

Fig. 1. ORTEP view of the supramolecular chain structure of $[KFl(SiPh_3)]_n$ (**3**) with thermal ellipsoids at the 50% probability level (H atoms are not shown for clarity).

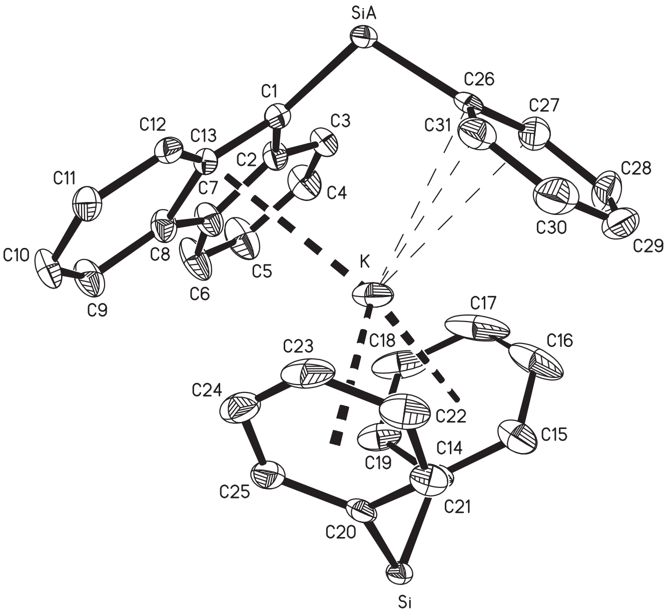

Fig. 2. Coordination environment around potassium in $[KFl(SiPh_3)]_n$ (**3**).

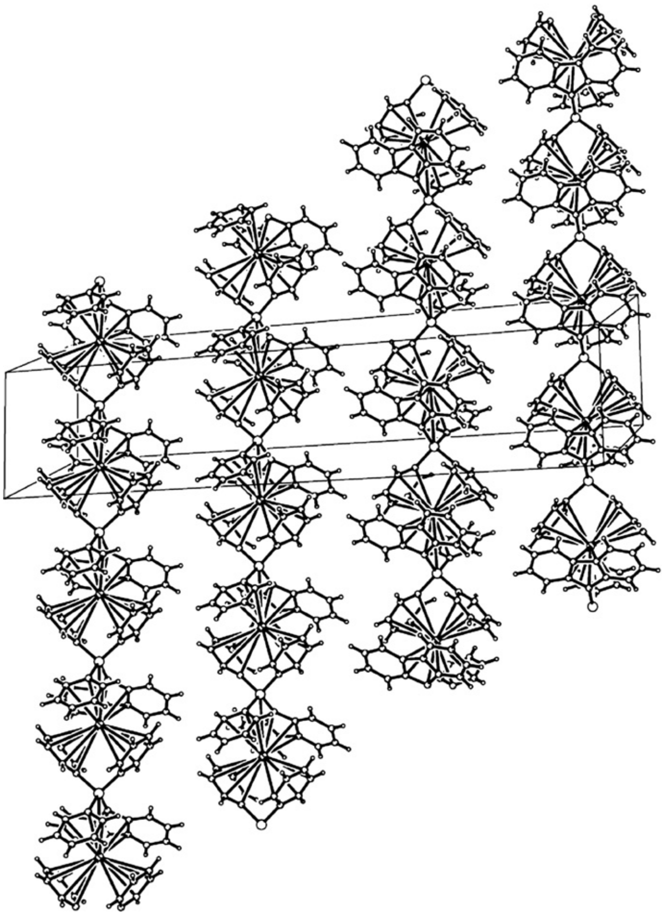

Fig. 3. Parallel alignment of the supramolecular chains of $[KFl(SiPh_3)]_n$ (**3**) in the crystal structure.

accessible in high yield (89%) by metalation of 9-fluorenyltriphenylsilane (**2**) with potassium hydride in toluene/THF. X-ray diffraction revealed a linear chain structure in the solid state. Due to the absence of coordinating solvent molecules, supramolecular self-assembly occurs solely *via* K···C–π-bonding. Compound **3** can be expected to be a useful precursor for the synthesis of transition metal complexes containing the triphenylsilylfluorenyl ligand.

3. Experimental section

3.1. General procedures

The reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. All solvents were distilled from sodium/benzophenone under nitrogen atmosphere prior to use. All glassware was oven-dried at 140 °C for at least 24 h, assembled while hot, and cooled under vacuum prior to use. The starting materials fluorene and Ph_3SiCl were purchased from commercial suppliers and used as received. Potassium hydride (Aldrich) was freed from mineral oil by washing with *n*-pentane under argon, dried in vacuum and stored in the dry-box. NMR spectra were recorded in THF-d_8 or C_6D_6 solutions on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts were referenced to TMS. Microanalyses were performed using a Leco CHNS 923 apparatus. The intensity data of **3** were collected on a Bruker CDD SMART diffractometer with Mo K_α radiation. The data were collected with the Bruker SMART [6] program using ω-scans. The space group was determined with Bruker SAINT [6] program. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [7].

*3.2. Modified synthesis of 9-fluorenyltriphenylsilane (**2**) [4c]*

To a solution of fluorene (13.5 g, 80 mmol) in diethyl ether (200 mL) was added at −30 °C a 1.6 M solution of *n*-butyllithium in *n*-hexane (50 mL, 80 mmol). The mixture was allowed to warm to room temperature and was stirred for 12 h. After filtration, solid Ph_3SiCl (23.6 g, 80 mmol) was added and stirring was continued for 1 h. The reaction mixture was carefully hydrolyzed with cold water (*ca.* 100 mL) and the organic phase was separated and dried over $MgSO_4$. Filtration and evaporation to dryness followed by rinsing with *n*-pentane (3 × 50 mL) afforded **2** as a colorless solid in 82% yield (27.9 g). M.p. 184 °C. Analysis ($C_{31}H_{24}Si$, $Mw = 424.61$ g/mol): C 88.00 (calcd. 87.69), H 5.50 (5.70) %. IR (KBr): ν_{max} 3435 (w br), 3066 (w), 3049 (w), 3001 (w), 2929 (w), 2851 (w), 2361 (vw), 1951 (vw br), 1907 (vw br), 1588 (8w), 1569 (w), 1484 (w), 1474 (w), 1442 (s), 1427 (vs), 1334 (w), 1303 (w), 1186 (w), 1178 (m), 1156 (w), 1107 (vs), 1028 (m), 997 (m), 888 (w), 825 (w), 778 (vs), 736 (vs), 698 (vs), 620 (m), 580 (m), 519 (vs), 495 (s), 485 (s), 447 (m), 424 (m) cm^{-1}. ^1H and ^{13}C NMR (THF-d_8) were in excellent agreement with those reported in the literature [4c].

*3.3. Synthesis of potassium 9-triphenylsilylfluorenide, $[KFl(SiPh_3)]_n$ (**3**)*

To a suspension of KH (0.1 g, 2.5 mmol) in THF (10 mL) was added a solution of **2** (1.06 g, 2.5 mmol) in THF/toluene (1:1, 20 mL) and the mixture was stirred for 2 h at 80 °C, causing gas evolution (H_2) and the development of an orange color. The solution was filtered through a thin layer of Celite filter aid, and the clear orange filtrate was carefully layered with *n*-pentane (15 mL) and left to stand undisturbed for 2 weeks. During that time large, yellow-green crystals grew, which were isolated by decanting the liquid and drying in an argon stream. The resulting crystals of the toluene solvate were directly suitable for X-ray diffraction. Thorough drying *in vacuo* afforded the toluene-free material as an orange powder.

Yield: 1.03 g (89%). M.p. *ca.* 150 °C (dec.). Analysis ($C_{31}H_{23}KSi$, *Mw* = 462.70 g/mol): C 80.93 (calcd. 80.47), H 5.06 (5.01)%. IR (KBr): ν_{max} 3437 (vw br), 3066 (w), 3017 (w), 2922 (vw), 1961 (vw br), 1905 (vw br), 1845 (vw br), 1715 (w), 1611 (w), 1601 (w), 1589 (w), 1571 (w), 1479 (w), 1453 (m), 1428 (vs), 1325 (m), 1296 (s), 1261 (w), 1217 (m), 1184 (m), 1150 (m), 1118 (vs), 1028 (m), 1014 (m), 996 (m), 976 (m), 920 (w), 738 (s), 726 (s), 712 (vs), 700 (vs), 517 (vs), 445 (m). ^1H NMR (DMSO-d_6, 400.1 MHz, 25 °C): $\delta = 7.89$ (d, 2H, H-4 and H-6), 7.59 (m, 11H, H-1, H-8 + C_6H_5), 7.29 (m, 6H, C_6H_5), 7.19 (t, 2H, H-2 and H-7), 7.18 (dd, 2H, H-3 and H-6) ppm. ^{13}C NMR (DMSO-d_6, 100.6 MHz, 25 °C): $\delta = 142.83$ (C-10 and C-13), 141.10 (C-11 and C-12), 134.80 (*m*-C_6H_5), 134.11 (*ipso*-C_6H_5), 128.84 (*p*-C_6H_5), 128.26 (C-2 and C-7), 128.15 (C-3 and C-5), 126.73 (C-8), 126.55 (C-1), 125.11 (*o*-C_6H_5), 119.92 (C-4), 76.88 (C-9) ppm.

Acknowledgements

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Appendix A. Supplementary material

CCDC 795641 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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