Host–Guest Complexes

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Cyclic Dimethylsiloxanes as Pseudo Crown Ethers: Syntheses and Characterization of $Li(Me_2SiO)_5[Al\{OC(CF_3)_3\}_4]$, $Li(Me_2SiO)_6[Al\{OC(CF_3)_3\}_4]$, and $Li(Me_2SiO)_6[Al\{OC(CF_3)_2Ph\}_4]$**

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In memory of Chunying Liao

Although the chemistry of silicon is notably different from that of carbon,[1] parallels between the chemistry of the two elements continue to emerge, for example, the recent syntheses of a proposed Si≡Si triple bond,[2] persilaaromatic rings,[3] silylium ions,[4] and silaadamantane.[5] However, few stable adducts of silicon ethers (for example, $(Me_3Si)_2O$) have been prepared,[6] and there have been no reports of direct reactions of metal ions with cyclic dimethylsiloxanes D_n ($D_n = (Me_2SiO)_n$, $n = 1$–40)[7] or related compounds, in contrast to the extensive and selective reaction of metal ions with the structurally similar crown ethers.[8] Silacrown ethers containing one or two Me_2SiO units have a drastically reduced ability to bind metal cations compared to crown ethers.[9] This observation has been attributed to the low basicity of oxygen in siloxane compounds,[10] the reasons for which are of continuing interest.[11] Nevertheless, two examples[12] of $[KD_7]^+$ ions were unexpectedly isolated from reactions in the presence of silicone grease,[13] although the mechanisms of the reactions are unclear. In a reaction designed to give $Se_6Ph_2[Al_F]_2$ ($[Al_F] = Al\{OC(CF_3)_3\}_4$) from $Se_4(AsF_6)_2$, 2 $Li[Al_F]$, and Se_2Ph_2 in the presence of silicone grease, we unexpectedly obtained crystals of $LiD_6[Al_F]$. Subsequently, we prepared $LiD_5[Al_F]$, $LiD_6[Al_F]$, and $LiD_6[Al_{PhF}]$ ($[Al_{PhF}] = Al\{OC(CF_3)_2Ph\}_4$) in high yield by the reaction of $Li[Al_F]$ or $Li[Al_{PhF}]$ with D_5 or D_6 in CH_2Cl_2 solution [Eq. (1)].

$$\mathrm{LiX} + \mathrm{D}_n \xrightarrow[\mathrm{RT}]{\mathrm{CH_2Cl_2}} \mathrm{LiD}_n\mathrm{X} \qquad (1)$$

$X = [Al_F]$ ($n = 5$ or 6) or $[Al_{PhF}]$ ($n = 6$)

These results, and the calculated energies of related reactions of alkali-metal cations with cyclic dimethysiloxanes imply the existence of a new class of host–guest complexes for the cyclic siloxanes that is similar to, but less extensive than, that for the crown ethers; for example, the reaction of $Li[Al_{PhF}]$ and D_5 in CH_2Cl_2 did not give the expected product $LiD_5[Al_{PhF}]$.[14] In addition, these findings imply that new classes of metal complexes of cyclosiloxane analogues (for example, cyclophosphazenes) may be prepared by using metal salts of large weakly coordinating anions, which minimize lattice-energy changes and cation–anion interactions.[15]

The IR and Raman spectra of the moisture-sensitive, thermally stable, colorless salts $LiD_5[Al_F]$, $LiD_6[Al_F]$, and $LiD_6[Al_{PhF}]$ showed the characteristic peaks of the anions, as well as peaks very similar to those of the siloxane reactants. Electron ionization mass spectrometry (EI-MS) and chemical analysis of the products were consistent with the given formulations. The $^{29}Si\{^1H\}$ NMR signals of $LiD_6[Al_{PhF}]$ ($\delta = -10.14$ ppm) and $LiD_6[Al_F]$ ($\delta = -9.22$ ppm) in liquid SO_2 were different from that of D_6 ($\delta = -22.69$ ppm), implying the presence of the $[LiD_6]^+$ ion, or an equilibrium mixture of $[LiD_6]^+$, Li^+, and D_6.[16] The $^{29}Si\{^1H\}$ NMR chemical shift of $LiD_5[Al_F]$ ($\delta = -21.28$ ppm) is similar to that of D_5 ($\delta = -21.67$ ppm), indicating complete dissociation of the complex into Li^+, $[Al_F]^-$, and D_5 in liquid SO_2. This observation is consistent with the less negative estimated energy ($\Delta E = -210\ \mathrm{kJ\,mol^{-1}}$, HF/6-31G*) for the reaction of $Li[Al_F]$ with D_5 [Eq. (2)] compared to that for the corresponding reaction with D_6 ($\Delta E = -242\ \mathrm{kJ\,mol^{-1}}$; Scheme 1).[17]

$$\mathrm{Li[Al_F]_{(s)}} + \mathrm{D_{5(l)}} \rightarrow \mathrm{LiD_5[Al_F]_{(s)}} \qquad (2)$$

A preliminary single-crystal X-ray diffraction (XRD) study of $LiD_5[Al_F]$[18] clearly showed that the structure of the $[LiD_5]^+$ ion is very similar to that calculated by ab initio and density functional theory (DFT) methods (Figure 1, Table 1). The solid-state structures of the $[LiD_6]^+$ ions (Figure 2) in both $LiD_6[Al_F]$ and $LiD_6[Al_{PhF}]$ are similar,[19,20] but the cation in $LiD_6[Al_F]$ more clearly resembles the ideal gas-phase structure, in which the Li^+ ion is in the plane of the Si_6O_6 ring. The distortion from the ideal structure results from $Li^+\cdots F^{\delta-}$ interactions between the cations and the anions. The strength of these interactions, which can be judged by calculating their

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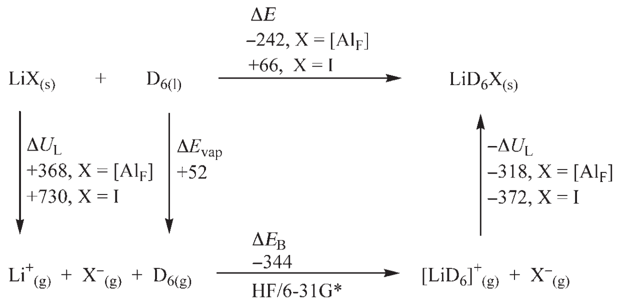

Scheme 1. Born–Haber cycle for the reaction of LiX (X = $[Al_F]$ or I) with D_6. Lattice energies ΔU_L, energy of vaporization ΔE_{vap}, binding energies ΔE_B (calculated at the HF/6-31G* level of theory), and energies of formation ΔE are given in $kJ\,mol^{-1}$.

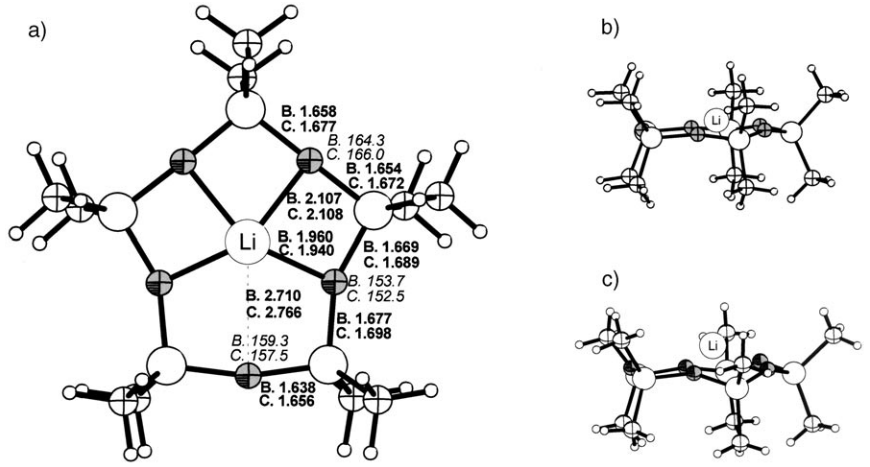

Figure 1. a) Top view and b) side view of the optimized C_s geometry of the $[LiD_5]^+$ ion; interatomic distances [Å] (bold) and angles [°] (italic) calculated at the HF/6-31G* (B) and B3LYP/6-31G* (C) levels of theory are indicated. c) Side view of the $[LiD_5]^+$ ion in the preliminary crystal structure of $LiD_5[Al_F]$. $D_5 = (Me_2SiO)_5$; $[Al_F] = Al\{OC(CF_3)_3\}_4$. Large open Si, filled crossed O, open crossed C, small open H.

bond valence s (in valence units vu),[21] is greater in the salt of the more basic $[Al_{PhF}]^-$ ion ($s = 0.125$ vu) than in $LiD_6[Al_F]$ ($s = 0.041$ vu), leading to a greater displacement of the Li^+ ion out of the Si_6O_6 plane in $LiD_6[Al_{PhF}]$ (0.423(3) Å) than in $LiD_6[Al_F]$ (0.13(1) Å), and to a slightly stronger coordination of four oxygen atoms to the Li^+ ion in $LiD_6[Al_F]$ (Li–O 2.03(2)–2.07(1) Å; $s = 0.81$ vu) than in $LiD_6[Al_{PhF}]$ (Li–O 2.059(3)–2.099(4) Å; $s = 0.77$ vu). Related compounds with five-coordinate Li^+ ions include Li([12]crown-4)Cl (Li–O 2.128(2) Å) and Li([12]crown-4)$[CF_3SO_2N(CH_2)_3OCH_3]$ (Li–O 2.080(3)–2.187(3) Å).[22] The cyclohexaphosphonitrile ring, which is isoelectronic to cyclohexasiloxane, acts as a macrocyclic ligand to Cu^{2+} and Co^{2+} in the ions $[\{N_6P_6(NMe_2)_{12}\}MCl]^+$ (M = Cu, Co).[23] In these cations, the metal atoms are coordinated by four nitrogen atoms of the cyclohexaphosphazene ring and one chlorine atom, in a coordination geometry that is similar to that of the lithium atoms in $LiD_6[Al_{PhF}]$.

The average Si–O_{NC} bond lengths and Si-O_{NC}-Si angles involving the noncoordinating oxygen atoms (O_{NC}) in the $[LiD_6]^+$ ions of $LiD_6[Al_F]$ and $LiD_6[Al_{PhF}]$ (Figure 2c, Table 1) are similar to those found for the oxygen atoms in D_6 by electron diffraction (ED).[24] For the coordinating oxygen atoms, however, the average Si–O bond lengths are slightly longer, and the average Si-O-Si angles are smaller. The average Si–C bond lengths for the silicon atoms adjacent to two coordinating oxygen atoms are similar to those for the silicon atoms adjacent to only one coordinating oxygen atom. The average lengths of all the Si–C bonds in the $[LiD_6]^+$ ions are slightly shorter than that in D_6 (Table 1). These differences are consistent with a strong electrostatic interaction between the lithium and oxygen atoms,[25] and an induced polarization of the $p^2(O) \rightarrow \sigma^*(Si{-}CH_3)$ interactions, which leads to a slight weakening of the Si–O bonds and a slight strengthening of the Si–C bonds (Figure 3). The calculated natural bond orbital (NBO) charges support this picture: upon coordination of D_6 to the Li^+ ion, the charge on the coordinating oxygen atoms becomes more negative, the charge on the $SiMe_2$ fragments

Table 1: Experimental and calculated average distances [Å] and angles [°] for the $[LiD_5]^+$ and $[LiD_6]^+$ ions, and for the free D_5 and D_6 molecules.

	Symmetry	Method	Li–O	Si–O	Si–O_{NC}[a]	Si–C[b]	Si-O_{NC}-Si	Si-O-Si
D_5	C_s	HF/6-31G*			1.632	1.874	159.0	
	C_s	B3LYP/6-31G*			1.654	1.876	152.7	
	D_{5d}[c]	ED[d]			1.620(2)	1.845(4)	146.5(1)	
	C_s[c]	XRD[e]			1.629(1)	1.845(2)	148.0(1)	
$[LiD_5]^+$	C_s	HF/6-31G*	2.034	1.664	1.638	1.862	159.3	159.0
	C_s	B3LYP/6-31G*	2.023	1.684	1.656	1.863	157.5	159.2
D_6	C_2	HF/6-31G*			1.632	1.874	158.2	
	C_2	B3LYP/6-31G*			1.656	1.876	153.7	
	D_{3d}[c]	ED[d]			1.622(1)	1.846(1)	149.6(1)	
$[LiD_6]^+$	C_2	HF/6-31G*	2.042	1.671	1.631	1.865	151.5	143.5
	C_2	B3LYP/6-31G*	2.023	1.692	1.651	1.867	149.3	142.9
	C_2[c]	XRD ($[Al_F]^-$)	2.06(1)	1.661(6)	1.617(7)	1.837(1)	151.1(5)	141.1(4)
	C_2[c]	XRD ($[Al_{PhF}]^-$)	2.078(3)	1.655(1)	1.620(2)	1.836(2)	146.5(1)	141.7(1)

[a] The subscript NC denotes noncoordinating O atoms; O atoms without subscripts are coordinated to Li atoms. [b] Average length for all Si–C bonds. [c] Approximate symmetries. [d] The gas-phase structures of D_5 and D_6 were determined by electron diffraction (ED); the final structures are not well defined.[24] [e] The single-crystal structure of D_5 was determined by X-ray diffraction (XRD): S. Parson, D. Rankin, P. Wood, private communication to the Cambridge Structural Database, CCDC-247844, The Cambridge Crystallographic Data Centre, **2004**.

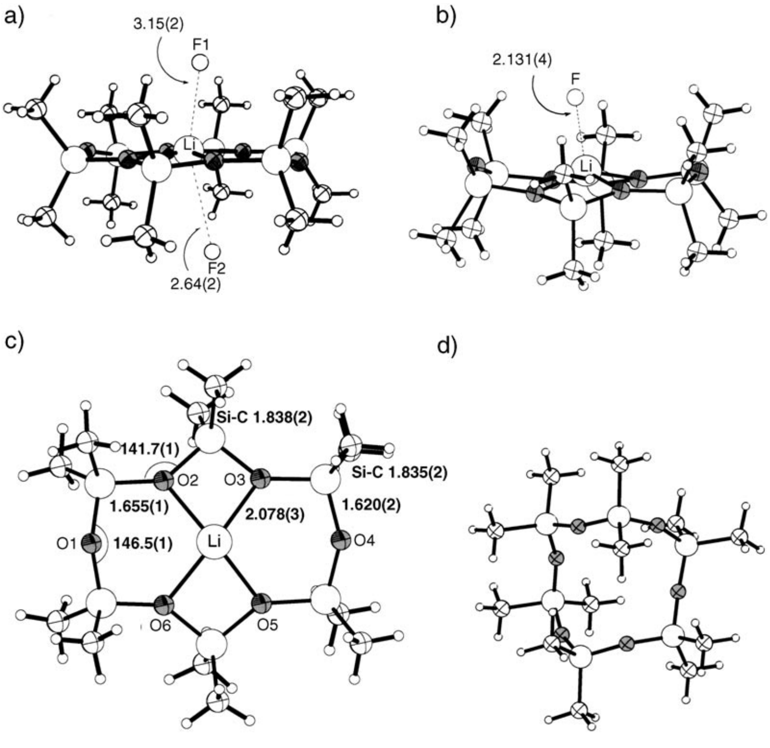

Figure 2. a) Side view of the $[LiD_6]^+$ ion in $LiD_6[Al_F]$. b) Side view and c) top view of the $[LiD_6]^+$ ion in $LiD_6[Al_{PhF}]$; average interatomic distances [Å] (Li–O, Si–O, Si–O_{NC}, O_2Si–C, and $O(O_{NC})Si$–C; the subscript NC denotes noncoordinating O atoms; O atoms without subscripts are coordinated to the Li atom) and angles [°] (Si-O-Si and Si-O_{NC}-Si) are indicated. d) Optimized C_2 geometry of D_6 at the HF/6-31G* level of theory. $D_6 = (Me_2SiO)_6$; $[Al_F] = Al\{OC(CF_3)_3\}_4$; $[Al_{PhF}] = Al\{OC(CF_3)_2Ph\}_4$. Large open Si, filled crossed O, open crossed C, small open H.

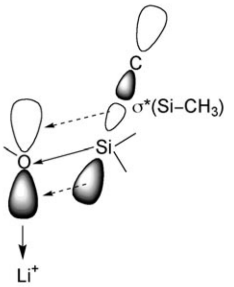

Figure 3. Schematic representation of the polarization of the O–Si bond and the $p^2(O) \rightarrow \sigma^*(Si\text{-}CH_3)$ interaction upon coordination of D_6 to Li^+ in the $[LiD_6]^+$ ion.

becomes more positive, and the charge on lithium becomes slightly less than 1, which implies a very small amount of Li–O covalent bonding (Table 2). Further calculations on $[MD_6]^+$ (M = Na, K) imply that replacement of the Li^+ ion by the less polarizing Na^+ and K^+ ions increases the positive charge on the metal atom, decreases the positive charge on the $SiMe_2$ fragments, and decreases the negative charge on the coordinating oxygen atoms. In contrast, there is little change in the C–O bond lengths and C-O-C angles in [18]crown-6 upon coordination to alkali-metal cations,[25] consistent with the absence of $p^2 \rightarrow \sigma^*$ hyperconjugation in the crown ether.

The structure of D_6 was determined in the gas phase by ED.[24] This study suggested that the D_6 ring is puckered, with some methyl groups pointing inward (see Figure 2d for the geometry of D_6 calculated at the HF/6-31G* level of theory). Rotation of the inner methyl groups outward produces a larger cavity at the center of the ring, which is occupied by Li^+ in the $[LiD_6]^+$ ion (the calculated geometry of $[LiD_6]^+$ is similar to that of the cation in $LiD_6[Al_F]$, Figure 2a). Upon coordination of the Li^+ ion, the Si_6O_6 framework of D_6 becomes nearly planar. However, in $LiD_6[Al_{PhF}]$, stronger Li···F and H···F contacts cause some deformation (bending) of the Si_6O_6 plane (Figure 2b).[26]

Table 2: Average atomic and fragment NBO charges (*q*) for D_6 and its alkali-metal complexes $[MD_6]^+$ (M = Li, Na, Rb), calculated at the B3LYP/6-31G* level of theory.

	D_6	$[LiD_6]^+$	$[NaD_6]^+$	$[KD_6]^+$
symmetry	C_2	C_2	D_{3h}	C_{6v}
$q(M^+)$		0.932	0.962	0.978
$q(O_{NC}{}^{[a]})$	−1.275	−1.271		
$q(O)$		−1.316	−1.303	−1.297
$q(SiMe_2)$	1.275	1.313	1.309	1.301
$\Delta q(SiMe_2)^{[b]}$	0	0.038	0.034	0.026

[a] The subscript NC denotes noncoordinating O atoms; O atoms without subscripts are coordinated to M atoms. In $[NaD_6]^+$ and $[KD_6]^+$, the M atoms are coordinated by all O atoms equally. See Supporting Information for details. [b] Difference between the average charges $q(SiMe_2)$ of $[MD_6]^+$ and of free D_6.

The syntheses of the $LiD_5[Al_F]$, $LiD_6[Al_F]$, and $LiD_6[Al_{PhF}]$ salts are the first examples of the preparation of host–guest complexes directly from cyclic dimethylsiloxanes, alkali-metal ions, and weakly coordinating anions. Their structures imply that the cyclic dimethylsiloxanes (D_5 and D_6) act as pseudo crown ethers and provide rare examples of silicon ethers behaving as Lewis bases. The counterpoise-corrected binding energies for the alkali-metal complexes $[MD_6]^+$ exhibit a remarkable similarity to that for [18]crown-6 (Figure 4):[27] for both sets of complexes (in the gas phase), the binding energies become less negative with increasing size of the alkali-metal cation. However, the binding affinity of D_6 calculated at the HF/3-21G level is approximately 100 kJ mol^{-1} less than that of [18]crown-6, reflecting the lower basicity of the siloxanes. Thus, the reaction of $D_{6(l)}$ with $LiI_{(s)}$ is thermodynamically unfavorable ($\Delta E = +66$ kJ mol^{-1}; Scheme 1).[28] However, replacement of I^- by the larger ion $[Al_F]^-$ reduces the unfavorable change in lattice energy on

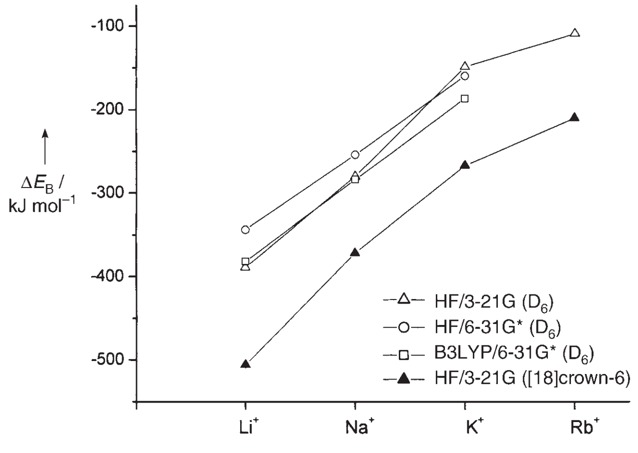

Figure 4. Binding energies ΔE_B (counterpoise corrected) of D_6 and [18]crown-6 with alkali-metal cations.

going from LiX to LiD_6X ($\Delta U_L(LiX) - \Delta U_L(LiD_6X) = +358\ kJ\,mol^{-1}$ for $X = I$ and $+50\ kJ\,mol^{-1}$ for $X = [Al_F]$), and the energy of formation of $LiD_6[Al_F]_{(s)}$ from $Li[Al_F]_{(s)}$ and $D_{6(l)}$ is $\Delta E = -242\ kJ\,mol^{-1}$ (Scheme 1). Thus, a new class of salts with cyclosiloxane–metal cations and weakly coordinating anions can be anticipated.

Experimental Section

$LiD_5[Al_F]$: CH_2Cl_2 (50 mL) was added to D_5 (0.45 mL, 1.16 mmol) over solid $Li[Al_F]$ (0.985 g, 1.01 mmol) in a 100-mL Schlenk flask. The resulting colorless, clear solution was concentrated to saturation by stirring overnight at room temperature. Large crystals were obtained after 1 day at −20 °C. The solvent was removed under vacuum, and the crystallized product was washed three times with *n*-hexane. Yield: 1.25 g (90 %, based on $Li[Al_F]$). $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, RT): $\delta = -21.28$ ppm (m, D_5); $^{13}C\{^1H\}$ NMR (100.6 MHz, SO_2, RT): $\delta = 0.893$ ppm (s, D_5); ^1H NMR (400.0 MHz, SO_2, RT): $\delta = 0.125$ ppm (s, D_5); ^{19}F NMR (376.3 MHz, SO_2, RT): $\delta = -74.113$ ppm (s, $Li[Al_F]$); ^{27}Al NMR (104.2 MHz, SO_2, RT): $\delta = 35.107$ ppm (s, $Li[Al_F]$); ^7Li NMR (155.4 MHz, SO_2, RT): $\delta = -0.288$ ppm (s, $Li[Al_F]$). FT-IR (KBr, solid, RT, $\tilde{\nu}$ assigned to $[LiD_5]^+$ marked with *, e.g. 2972 (w),*): $\tilde{\nu} = 2972$ (w),* 2907 (w),* 1626 (w), 1356 (s),* 1301 (s), 1275 (s),* 1236 (s), 1215 (vs), 1163 (m), 1026 (s; ϑ_{as}(SiOSi)),* 971 (vs), 855 (m),* 825 (s),* 808 (s),* 752 (m; ϑ_a(SiC2)),* 726 (s; ϑ_s(SiC2)),* 709 (m),* 666 (w; ϑ_s(SiOSi)),* 572 (w), 568 (m), 555 (m), 534 (m), 439 (m), 401 cm^{-1} (m). FT-Raman (RT, $\tilde{\nu}$ assigned to $[LiD_5]^+$ marked with *): $\tilde{\nu} = 2975$ (m; ϑ_a(CH)),* 2914 (s; ϑ_s(CH)),* 1494 (w), 1402 (w), 1276 (w), 797 (w),* 745 (w),* 536 (m), 321 (w), 164 cm^{-1} (w). EI-MS (30 eV): *m*/*z* (%): 539 (20) $[M^+ - D_5 - OC(CF_3)_3 - C_2F_8O]$, 522 (33) $[M^+ - D_5 - C(CF_3)_3 - 3CF_3 - F]$, 354 (100) $[M^+ - Li[Al_F] - Me = D_5^+ - Me]$. Elemental analysis (%) calcd: C 23.24, H 2.25; found: C 23.37, H 2.47. M.p.: 216 °C (decomp).

$LiD_6[Al_F]$: The preparation of $LiD_6[Al_F]$ was similar to that of $LiD_5[Al_F]$ ($Li[Al_F]$ 0.808 g, 0.830 mmol; D_6 0.50 mL, 1.08 mmol; CH_2Cl_2 50 mL). Yield: 1.12 g (95 %, based on $Li[Al_F]$). $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, RT): $\delta = -9.22$ ppm (s, $SiMe_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, SO_2, RT): $\delta = 120.011$ (q, $J(C,F) = 291$ Hz, 3 C, CF_3), 79.219 (s, 1 C, $OCCF_3$), 0.202 ppm (s, 3 C, $SiMe_2$); ^1H NMR (400.0 MHz, SO_2, RT): $\delta = 0.296$ ppm (s, $SiMe_2$); ^{19}F NMR (376.3 MHz, SO_2, RT): $\delta = -75.193$ ppm (s, $[Al_F]$); ^{27}Al NMR (104.2 MHz, SO_2, RT): $\delta = 34.998$ ppm (s, $[Al_F]$); ^7Li NMR (155.4 MHz, SO_2, RT): $\delta = 0.190$ ppm (s). IR (KBr, neat, RT, $\tilde{\nu}$ assigned to $[LiD_6]^+$ marked with *): $\tilde{\nu} = 2965$ (m),* 2916 (w),* 1537 (w), 1494 (w),* 1408 (m),* 1377 (w),* 1352 (s), 1300 (s), 1276 (s),* 1241 (s), 1216 (s), 1167 (s), 1132 (m), 1087 (s; ϑ_{as}(SiOSi)),* 1010 (s), 968 (s), 853 (s),* 822 (s),* 794 (s; ϑ_a(SiC2)),* 752 (m; ϑ_a(SiC2)),* 724 (s; ϑ_s(SiC2)),* 665 (w; ϑ_s(SiOSi)),* 619 (m; ϑ_s(SiOSi)),* 560 (m), 532 (m), 441 (m), 396 cm^{-1} (s). Raman (RT, $\tilde{\nu}$ assigned to $[LiD_6]^+$ marked with *): $\tilde{\nu} = 2975$ (s; ϑ_a(CH)),* 2915 (vs; ϑ_s(CH)),* 1495 (w), 797 (w),* 745 (w),* 542 (m), 320 (w), 168 cm^{-1} (w). EI-MS (30 eV): *m*/*z* (%): 539 (15) $[M^+ - D_6 - OC(CF_3)_3 - C_2F_8O]$, 522 (31) $[M^+ - D_6 - C(CF_3)_3 - 3\,CF_3 - F]$, 354 (100) $[M^+ - Li[Al_F] - Me = D_6^+ - Me]$. Elemental analysis (%) calcd: C 23.72, H 2.56; found C 23.77, H 2.60. M.p. 286 °C (decomp).

$LiD_6[Al_{PhF}]$: CH_2Cl_2 (20 mL) was transferred onto D_6 (0.45 mL, 0.97 mmol) over solid $Li[Al_{PhF}]$ (0.956 g, 0.95 mmol) in a 100-mL Schlenk flask. The resulting yellowish, clear solution was stirred overnight at room temperature. *n*-Hexane (40 mL) was added to the solution, and a large amount of crystals was obtained after 1 day at −20 °C. The crystals were separated by filtration, and the filtrate was further concentrated to one third, producing more crystals, which were washed with *n*-hexane. Total yield: 1.17 g (85 %, based on $Li[Al_{PhF}]$). $^{29}Si\{^1H\}$ NMR (79.4 MHz, SO_2, RT): $\delta = -10.14$ ppm (s, $SiMe_2$); $^{13}C\{^1H\}$ NMR (100.6 MHz, SO_2, RT): $\delta = 0.454$ (s, $SiMe_2$), 80.085 (s, $OC(CF_3)_2Ph$), 125.763 (q, $J(C,F) = 291$ Hz, CF_3), 128.186 (s, *ortho*-C_6H_5), 128.688(s, *meta*-C_6H_5), 129.206 (s, *para*-C_6H_5), 136.069 ppm (s, *ipso*-C_6H_5); ^1H NMR (400.0 MHz, SO_2, RT): $\delta = 0.288$ (s, 36 H, $SiMe_2$), 7.898 (m, 8 H, *meta*-C_6H_5), 7.330 (m, 4 H, *para*-C_6H_5), 7.233 ppm (m, 8 H, *ortho*-C_6H_5); ^{19}F NMR (376.3 MHz, SO_2, RT): $\delta = -74.119$ ppm (s, $[Al_{PhF}]$); ^{27}Al NMR (104.2 MHz, SO_2, RT): $\delta = 29.552$ ppm (s, $[Al_{PhF}]$); ^7Li NMR (155.4 MHz, SO_2, RT): $\delta = 0.180$ ppm (s). FT-IR (KBr, neat, RT, $\tilde{\nu}$ assigned to $[LiD_6]^+$ marked with *): $\tilde{\nu} = 3666$ (w), 3576 (w), 3062 (vw), 2963 (w),* 2899 (vw),* 1622 (m), 1502 (w), 1485 (w), 1446 (m),* 1412 (w),* 1331 (m), 1305 (s), 1266 (vs),* 1223 (s), 1193 (vs), 1198 (vs), 1133 (s), 1078 (s; ϑ_{as}(SiOSi)),* 1026 (s), 1001 (s; ϑ_{as}(SiOSi)),* 996 (vs), 966 (vs), 932 (s), 915 (m), 855 (s),* 821 (s),* 795 (s; ϑ_a(SiC2)),* 761 (m), 743 (m), 713 (vs), 688 (m),* 658 (m; ϑ_s(SiOSi)),* 619 (w), 559 (w), 538 (w), 495 (w), 435 (m), 396 cm^{-1} (m). FT-Raman (RT, $\tilde{\nu}$ assigned to $[LiD_6]^+$ marked with *): $\tilde{\nu} = 3084$ (s), 2967 (s; ϑ_a(CH)),* 2909 (vs; ϑ_s(CH)),* 1604 (w), 1495 (w), 1171 (w), 1038 (m), 1005 (m),* 786 (w), 735 (w), 619 (w),* 542 cm^{-1} (m). EI-Ms (30 eV): *m*/*z* (%): 918 (92) $[M^+ - D_6 - CF_3 - F]$, 901 (100) $[M^+ - D_6 - CF_3 - 2F]$, 429 (40) $[M^+ - Li[Al_{PhF}] - Me = D_6^+ - Me]$. Elemental analysis (%) calcd: C 39.72, H 3.89; found: C 39.70, H 3.84. M.p.: 132 °C (decomp).

The following are given in the Supporting Information: general experimental techniques; a description of the reaction designed to produce $Se_6Ph_2[Al_F]_2$, from which crystals of $LiD_6[Al_F]$ were isolated; a comparison of the FT-IR, FT-Raman, and NMR spectra of $LiD_5[Al_F]$, $LiD_6[Al_F]$, and $LiD_6[Al_{PhF}]$ with those of the reactants; different views of the crystal structures of $LiD_5[Al_F]$, $LiD_6[Al_F]$, and $LiD_6[Al_{PhF}]$; and details of the calculations.

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[19] Structure determination of $LiD_6[Al_F]$: Bruker AXS P4/SMART 1000 diffractometer, graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(1)$ K, $P\bar{1}$, $Z = 4$, $a = 11.0053(19)$, $b = 22.828(4)$, $c = 24.398(5)$ Å, $\alpha = 101.660(4)$, $\beta = 102.974(3)$, $\gamma = 103.558(3)°$, $V = 5592.7(18)$ Å^3, $\rho_{calcd} = 1.664$ mg m^{-3}, $2\theta_{max} = 50.0°$, 26311 reflections collected, 17449 independent reflections, 1485 parameters, $R1(I{>}2\sigma) = 0.1049$, $R1$(all data) = 0.1422. There are two symmetry-independent $[LiD_6]^+$ ions in $LiD_6[Al_F]$, one of which is shown in Figure 2a. The main difference between the two cations is the differing strength of their Li⋯F contacts (3.02(2) and 3.19(2) Å for the $[LiD_6]^+$ ion not shown in Figure 2a). The structure of $LiD_6[Al_F]$ was not well determined, owing to severe rotational disorder in the anion, which prevents precise comparison with that of $LiD_6[Al_{PhF}]$.

[20] Structure determination of $LiD_6[Al_{PhF}]$: Bruker AXS P4/SMART 1000 diffractometer, graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(1)$ K, $P\bar{1}$, $Z = 2$, $a = 11.9673(9)$, $b = 15.9362(12)$, $c = 17.7554(12)$ Å, $\alpha = 88.198(2)$, $\beta = 87.127(2)$, $\gamma = 72.045(1)^o$, $V = 3216.8(4)$ Å^3, $\rho_{calcd} = 1.498$ mg m^{-3}, $2\theta_{max} = 55.0°$, 22472 reflections collected, 14017 independent reflections, 823 parameters, $R1(I{>}2\sigma) = 0.0416$, $R1$(all data) = 0.0667. CCDC-291338 ($LiD_6[Al_F]$) and CCDC-291339 ($LiD_6[Al_{PhF}]$)contain 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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