Intercalation of Oxide into $[Zr(C_5Me_5)F_3]$

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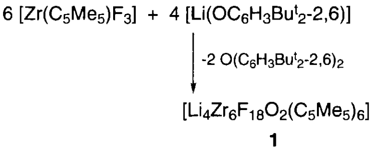
The reaction of lithium 2,6-di-*tert*-butylphenoxylate and trifluoro(pentamethylcyclopentadienyl)zirconium in a molar ratio of 2:3 leads to $[Li_4Zr_6F_{18}O_2(C_5Me_5)_6]$ which can be viewed as an interstitial oxide compound of $[Zr(C_5Me_5)F_3]$.

Large clusters based on fluorine-bridged organometallic units provide the opportunity to isolate inorganic solids, which exist otherwise only as large three-dimensional aggregates. This was previously shown in the case of NaF and MgF_2 embedded in a titanium–fluorine cage.[1] Similarly, fluorine ions can be trapped using $[Ti(C_5Me_5)F_3]$ and NaF as shown in $[\{[(C_5Me_5)TiF_3]\text{-}F\}_2Na]^-Na^+$.[2] With the synthesis of $[Li_4Zr_6F_{18}O_2(C_5Me_5)_6]$ **1**, we show for the first time that oxide can be intercalated in a zirconium fluorine complex.†

For the preparation of **1** we employed the observation that in reactions with lithium alkoxides containing electron-rich organic groups cleavage of the carbon–oxygen bond occurs.[3] Thus, we treated lithium 2,6-di-*tert*-butylphenoxylate with trifluoro(pentamethylcyclopentadienyl)zirconium in a molar ratio of 2:3.‡

Compound **1** crystallises with 2 molecules of toluene,§ the aromatic protons of which appear as a multiplet at *ca.* δ 7 in the ^1H NMR spectrum,¶ while the methyl of the toluene appears as a singlet at δ 1.34. The hydrogen atoms of the pentamethylcyclopentadienyl moiety give rise to a series of characteristic signals (δ 2.10 and 2.03). The ^7Li NMR spectrum shows a multiplet (around δ −2.26) which is made up of a quintet due to coupling with four fluorine atoms and a quartet from those lithium atoms bonded to three fluorine atoms (and one oxygen). In the ^{19}F NMR spectrum the lines are too broad (*ca.* 100 Hz) to show the splitting arising from the coupling to the lithium atoms. The ten fluorine atoms bonded between one zirconium and one lithium atom give rise to a multiplet at δ 21, while the signal due to the four bridging fluorine atoms is found at δ −56.5. The two terminal fluorine atoms account for the appearance of a signal at δ 50.



$$6\,[Zr(C_5Me_5)F_3] + 4\,[Li(OC_6H_3Bu^t_2\text{-}2,6)] \xrightarrow{-2\,O(C_6H_3Bu^t_2\text{-}2,6)_2} \underset{\mathbf{1}}{[Li_4Zr_6F_{18}O_2(C_5Me_5)_6]}$$

Scheme 1

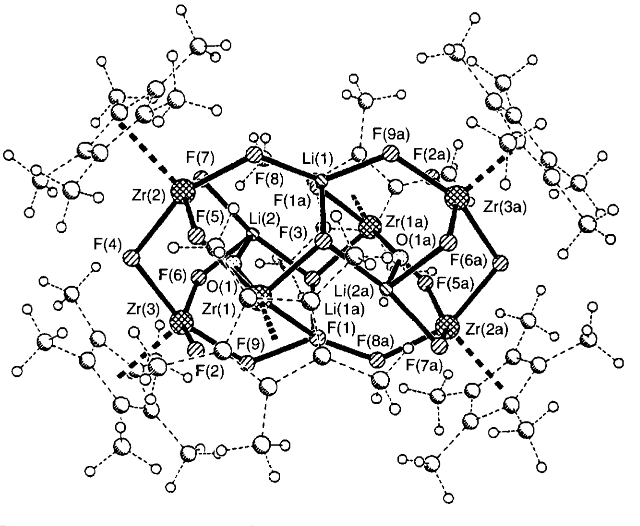


Fig. 1 Molecular structure of $[Li_4Zr_6F_{18}O_2(C_5Me_5)_6]$. The toluene molecules were disordered and have been omitted for clarity. Selected bond distances (Å) and angles (°) of **1**: Zr(1)–O(1) 2.129(4), O(1)–Li(2) 2.027(10), Zr(1)–F(1) 2.061(3), Zr(1)–F(3) 2.051(4), Li(2)–F(6) 1.951(11), Li(2)–F(7) 1.952(10), Li(1)–F(3) 1.930(10), Li(1)–F(8) 1.816(11), Li(1)–F(9a) 1.823(11), Zr(3)–F(2) 2.149(3), Zr(1)–O(1)–Li(2) 148.6(3), F(7)–Li(2)–F(3a) 168.2(6), F(8)–Li(1)–F(9a) 135.1(7), Li(1)–F(3)–Zr(1) 123.8(4).

In the crystal[4]‖ of **1**, pentamethylcyclopentadienyl units shield the zirconium atoms [Zr–C_5Me_5 (centre) av. 2.245 Å], whereas the lithium atoms are not bonded to an organic substituent. The overall appearence of the metal–fluorine backbone of the complex can be described as a 'waisted ellipsoid'. Two oxygen atoms are intercalated in the cavity, both being bound at the same distance to one zirconium (2.129 Å) and one lithium (2.028 Å) atom, respectively. One type of lithium atom is bound additionally to three fluorine atoms (1.952 and 2.028 Å) but a fourth fluorine atom is quite close (2.087 Å) distorting the tetrahedral geometry of lithium to quasi-trigonal bipyramidal. The second type of lithium atom is almost tetrahedrally surrounded by four fluorine atoms. However, the bond lengths to the fluorine atoms along the long axis of the ellipsoid are considerably shorter (1.820 Å on average) than all other lithium–fluorine bonds in the crystal (av. 1.935, 1.952, 2.028 Å). The angle between these fluorine atoms [F(8)–Li(1)–F(9a)] is 135°, consequently leading to significant Li–F bond strain. The average bond distance between zirconium and fluorine atoms is 1.995 Å where the fluorine also bridges to a lithium atom, and 2.019 Å where it bridges to another zirconium atom. Both are considerably shorter than in the tetramer $[Zr(C_5Me_5)F_3]_4$ (2.10–2.18 Å).[5] There are only two terminal fluorine atoms bonded to zirconium (2.149 Å).

Questions arise, such as why the backbone is so compressed and the lithium atoms possess their unusual surrounding. We notice that all zirconium atoms have coordination number five in a distorted square-pyramidal geometry. In the direction of the sixth coordination site the central oxygen is found at a distance only slightly longer (2.189 Å av.) than the Zr–O bond in the complex (2.129 Å). Even if there is no real bond, this leads to a considerable reduction of size of the complex. The resulting octahedral environment of the oxygen and the shortening of the bond distances are typical for compounds with interstitially bonded atoms as found in other complexes.[6]

Compound **1** is a stepping stone of a rapidly growing field which arises from the symbiosis of inorganic solids and organometallic compounds.

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Footnotes

† There is no reaction of $[Zr(C_5Me_5)F_3]$ and Li_2O due to the high lattice energy of Li_2O.

‡ The reaction was performed under dry nitrogen. Solvents were freshly distilled from sodium and degassed prior to use. *Preparation of* $[Li_4Zr_6F_{18}O_2(C_5Me_5)_6]$ **1**. $[Zr(C_5Me_5)F_3]$ (1.70 g, 6.00 mmol) and $[Li(OC_6H_3Bu^t_2\text{-}2,6)]$ (0.84 g, 4.00 mmol) were mixed in the solid state and after addition of toluene (30 cm^3) the solution was stirred at 70 °C for 2 d. The white solid obtained was separated and recrystallised from thf (20 cm^3). Yield: 1.18 g (64%). Mass spectrum: *m/z* 1625 ($M^+ - C_5Me_5$, 10%), 262 [$Zr(C_5Me_5)F_2$, 100] (Found: C, 43.7, H, 5.9, F, 18.4. $C_{60}H_{90}F_{18}Li_4O_2Zr_6\cdot C_7H_8$ requires C, 43.5, H, 5.3, F, 18.5%). $\delta_H(C_6D_6)$ 7.05–6.95 (5 H, m, C_6H_5), 2.10–2.03 (90 H, m, 6 C_5Me_5), 1.34 (3 H, s, Me).

δ_{Li} (thf–C_6D_6) −2.32 [qnt, J_{12}(Li–F) 40 Hz], −2.2 [q, J_{12}(Li–F) 40 Hz]. δ_F(C_6D_6) 50 (2 F, s), 21 (10 F, s), −56 (4 F, s), −100 (2 F, s). IR (Nujol, CsI) ν/cm^{-1} 1390vs, 1072s, 580vs (Zr–F).

§ The non-crystalline compound contains one molecule of toluene.

¶ NMR: Bruker AM 250; $SiMe_4$ for ^1H, $CFCl_3$ for ^{19}F and LiCl for ^7Li NMR were used as standards, respectively. EI mass spectra were measured on Finnigan MAT 8230 and Varian MAT CH5 instruments at 70 eV. IR spectra were obtained on a Bio-Rad FTS 7 spectrophotometer as Nujol mulls between CsI plates. The Analytical Laboratory of the Institute of Inorganic Chemistry of the University of Göttingen performed the elemental analyses.

|| *Crystal structure solution and refinement*: diffraction data were collected on a Siemens-Stoe AED four-circle diffractometer at 153 K with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods with SHELX-86 and refined by full-matrix least squares on F^2 (SHELX-93). Non-hydrogen atoms were refined anisotropically and hydrogen atoms inserted in calculated positions.

Crystal data: $C_{74}H_{106}F_{18}Li_4O_2Zr_6 \cdot 2C_7H_8$, M = 1944.7, triclinic, space group $P\bar{1}$, a = 11.993(3), b = 12.358(3), c = 15.442(4) Å, α = 66.28(3), β = 82.86(3), γ = 75.59(3)°, U = 2.0286(9) nm^3, Z = 1, D_c = 1.592 Mg m^{-3}, μ_{calc} = 0.825 mm^{-1}, $F(000)$ = 980, crystal size 0.4 × 0.4 × 0.3 mm, 9707 collected reflections, 7129 independent reflections, goodness of fit 1.041, refinement converged with $R1$ = 0.0525 and $wR2$ = 0.1200 [$I > 2\sigma(I)$], and for all data $R1$ = 0.0750 and $wR2$ = 0.1377.

Atomic coordinates, bond lengths, bond angles and displacement parameters have been deposited at the Cambridge Crystallographic Centre. Further details of the crystal structure investigation may be obtained from the Fachinformatsionszentrum Karlsrühe, D-76344 Eggenstein-Leopoldshafen-2, Germany, on quoting the depository number CSD-404291. See Information for Authors, Issue No. 1.

References

1 F.-Q. Liu, A. Kuhn, R. Herbst-Irmer, D. Stalke and H. W. Roesky, *Angew. Chem.*, 1994, **106**, 577; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 555.

2 H. W. Roesky, M. Sotoodeh and M. Noltemeyer, *Angew. Chem.*, 1992, **104**, 869; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 864.

3 A. Künzel, F.-Q. Liu, M. Sokolow, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt and I. Uson, *J. Chem. Soc., Dalton Trans.*, in the press.

4 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; G. M. Sheldrick, University of Göttingen.

5 A. Herzog, F.-Q. Liu, H. W. Roesky, A. Demsar, K. Keller, M. Noltemeyer and F. Pauer, *Organometallics*, 1994, **13**, 1251.

6 See, for example: V. W. Day, T. A. Eberspacher, W. G. Klemperer, R. P. Planalp, P. W. Schiller, A. Yagasaki and B. Zhong, *Inorg. Chem.*, 1993, **32**, 1629; W. G. Klemperer and B. Zhong, *Inorg. Chem.*, 1993, **32**, 5821; R. D. Adams and W. Wu, *Organometallics*, 1993, **12**, 1238; R. A. T. Gould, K. L. Craighead, J. S. Wiley and L. H. Pignolet, *Inorg. Chem.*, 1995, **34**, 2902; T. R. Mohs, G. P. A. Yap, A. L. Rheingold and E. A. Maatta, *Inorg. Chem.*, 1995, **34**, 9.