

Preparation and Crystal Structure of the Addition Compound MeLi·U[OCH(CMe₃)₂]₄, a Compound with a Uranium to Carbon σ-Bond

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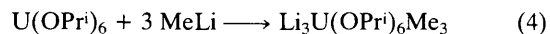
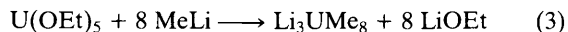
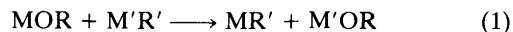
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Reaction of MeLi and U[OCH(CMe₃)₂]₄ gives the addition compound, LiU(Me)[OCH(CMe₃)₂]₄ which in the solid state has a geometry based upon square pyramidal uranium with the apical site occupied by a methyl group and the four basal sites being occupied by oxygen atoms of the alkoxide ligand, two of which form bridges to the lithium atom.

Reaction of metal alkoxides with organolithium or other main-group metal alkyls will give either substitution (equation 1) or addition (equation 2) products. In d-block transition metal chemistry, ligand substitution is usually observed¹ whereas with p-block metals addition reactions are usually observed.² In uranium chemistry both reaction types have been observed using spectroscopic methods (equations 3 and 4).³ The addition compounds of the p-block metals are of considerable utility in organic synthesis and have been called super-bases owing to their ability to deprotonate hydrocarbons whose *pK_a* are in the range of 35–50.^{2a} Further, addition compounds derived from metal alkyls and lanthanide alkoxides have found use in stereospecific organic synthesis.⁴ Even though addition compounds have demonstrated their synthetic utility, no crystal structure information is available and their constitution in the solid state is unknown. In this communication we present structural details for the addition compound formed by reaction of MeLi and U[OCH(CMe₃)₂]₄.

Addition of LiOCH(CMe₃)₂⁵ to UCl₄ in diethyl ether (4 : 1 molar ratio) gives a grey solution from which a pink-purple solid may be crystallized from pentane at –80 °C in *ca.* 50% yield. The solid was identified as U[OCH(CMe₃)₂]₄ (m.p.

105–107 °C, sublimation temperature, 90–95 °C at 10^{–3} mm Hg) by satisfactory analytical and mass spectroscopic data, *M*⁺ 810, and ¹H n.m.r. spectroscopy (C₆D₆, 20 °C) δ 32.12 (4 H, *ν*₃ 8 Hz) and 0.14 (72 H, *ν*₃ 8 Hz). The magnetic susceptibility of the alkoxide shows Curie–Weiss behaviour from 5 to 120 K with *μ* = 2.59 *μ*_B (θ = –16.8 K) and from 140 to 280 K with *μ* = 2.71 *μ*_B (θ = –32.8 K), consistent with tetravalent uranium.



Addition of 1 mol. equiv. of MeLi to U[OCH(CMe₃)₂]₄ in hexane gives a pale green solution from which purple crystals of LiU(Me)[OCH(CMe₃)₂]₄, m.p. 160–165 °C, may be isolated by crystallization from toluene (–15 °C) in *ca.* 35% yield. The addition compound gives a satisfactory elemental analysis and a (*M* – 7)⁺ ion in the mass spectrum. An ORTEP diagram is shown in Figure 1.†

The complex is based upon two-co-ordinate lithium and five-co-ordinate uranium with the geometry of the uranium being near that of a square pyramid with the methyl occupying the apical site with a U–C(Me) distance of 2.465(7) Å. The oxygen atoms occupy the basal site with an averaged U–O (terminal) distance of 2.103 ± 0.002 Å and U–O (bridging) distance of 2.262 ± 0.004 Å. The averaged O–U–C(Me) angle is 98.4 ± 0.6°, the basal O(1)–U–O(3), O(3)–U–O(4), and O(2)–U–O(4) angles averaged 94.1 ± 2.7°, the O(1)–U–O(2) angle is 72.7(1)°, and the averaged O(1)–U–O(4) and O(2)–U–O(3) angle is 158.9 ± 0.5°. The U–C and U–O distances are normal for tetravalent uranium compounds.⁶

The solution properties of the addition compound suggest that the compound dissociates as shown in equation (5). A

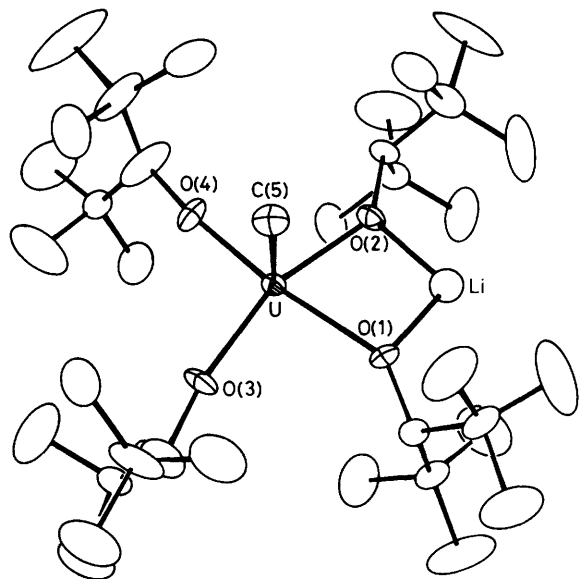
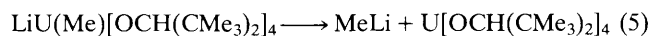


Figure 1. The carbon atoms have the same number as the oxygen atoms to which they are bonded. U–O(1) 2.268(4), U–O(2) 2.256(4), U–O(3) 2.101(4); U–O(4) 2.104(5), Li–O(1) 1.84(1), Li–O(2) 1.82(2), Li ··· U 3.07(1) Å, O(1)–U–O(2) 72.7(1), O(2)–U–O(4) 92.5(2), O(3)–U–O(4) 97.8(2), O(1)–U–O(3) 92.0(2), Li–O(2)–U 97.1(4), Li–O(1)–U 96.0(5), O(2)–Li–O(1) 94.2(6), Li–O(1)–C(1) 120.8(6), Li–O(2)–C(2) 121.3(5), U–O(1)–C(1) 143.0(3), U–O(2)–C(2) 141.6(4), U–O(3)–C(3) 169.0(6), U–O(4)–C(4) 175.0(5)°. The ellipsoids are 30% probability.

† *Crystal data:* C₃₇H₇₉LiO₄U, *M* = 832, monoclinic, space group *P*2₁/*c*, *a* = 11.648(2), *b* = 15.866(2), *c* = 23.405(3) Å, β = 105.29(1)°, *U* = 4172(1) Å³, *D_c* = 1.32 g cm^{–3}, *Z* = 4, Mo–K_α radiation, λ = 0.71073 Å, μ(Mo–K_α) = 37.15 cm^{–1}. The structure was solved by a combination of Patterson and Fourier methods and refined using 4354 unique reflections [*F*_o² > 3σ(*F*_o²)] measured on a CAD-4 diffractometer (2θ_{max} 45°). An empirical absorption correction was applied to the data, all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed into the structure factor calculations in idealized positions but they were not refined. The final difference Fourier map suggested possible alternative positions for O(3) and O(4) and their attached carbon atoms though this disorder could not be modelled. The *R* value is 0.0305 for 383 variables refined against 4352 data, *R_w* = 0.0408 and g.o.f. = 1.998. Atomic co-ordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, issue No. 1.

freshly prepared sample in C₆D₆ or C₇D₈ shows resonances in the ¹H n.m.r. spectrum (200 MHz, + 20 °C) at δ 32.2 and 0.12, each with $\nu_{\frac{1}{2}}$ of ca. 10 Hz, due to the methyne and methyl protons of U[OCH(CMe₃)₂]₄ and resonances at δ 38.2 ($\nu_{\frac{1}{2}}$ 112 Hz), -2.52 ($\nu_{\frac{1}{2}}$ 28 Hz), and -204 ($\nu_{\frac{1}{2}}$ 120 Hz) in area ratio of 2:36:1.5. The latter resonance is in the region of U-C σ-bonds⁷ and the other two resonances are presumably due to methyne and methyl protons of the alkoxide in LiU(Me)[OCH(CMe₃)₂]₄. The two large resonances due to the t-butyl protons in U[OCH(CMe₃)₂]₄ and LiU(Me)[OCH(CMe₃)₂]₄ are in an area ratio of 1:1.8. This suggests that in hydrocarbon solvents the reaction shown in equation (5) takes place, assuming that methyl-lithium is not detected owing to its insolubility. The spectrum changes irreversibly on heating and on cooling the resonances that are identified as being due to U[OCH(CMe₃)₂]₄ do not change shape, though their chemical shift is temperature dependent as expected for a paramagnetic compound, and those resonances due to the addition compound broaden into the base-line by -40 °C. Clearly the solution constitution is not identical with the solid state constitution and inferences made on the basis of a spectroscopic study in a single phase must be treated conservatively.



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