Syntheses and *X*-Ray Crystal Structures of Lithium and Chromium(II) Complexes of the Tri-t-butylmethoxide Ligand

Jan Hvoslef, Håkon Hope, Brendan D. Murray, and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616, U.S.A.

The syntheses and *X*-ray crystal structures of Li and Cr^{II} complexes of the tri-t-butylmethoxide ligand are described, these are $[\{Li(OCBu^t_3)(thf)\}_2]$ and $[Cr(OCBu^t_3)_2{\cdot}LiCl(thf)_2]$ (thf = tetrahydrofuran); the latter compound has a rare distorted T-shaped geometry at chromium and when dissolved in n-hexane gives LiCl and a complex that analyses as $[Cr(OCBu^t_3)_2(thf)_2]$.

A number of recent publications have shown that transition metal compounds with bulky alkoxide substituents display some interesting properties. For example, use of the 2,6-di-t-butylphenoxide and related ligands has led to (i) C–H bond activation,[1] (ii) formation of benzyne intermediates during aryl isomerizations,[2] and (iii) isolation of Cr^{II} and Mn^{II} compounds which are thought to have low co-ordination numbers.[3] In addition, use of the large $-OCHBu^t_2$ group has afforded new alkoxides of $Cr^{III, IV}$, Mn^{II}, Fe^{III}, Co^{II}, and Cu^{I}.[4]

Here we report the isolation and crystal structures of the new metal derivatives (**1**) and (**2**) of the very crowded $-OCBu^t_3$ ligand. The starting material, Bu^t_3COH, was synthesized according to the procedure given by Syper,[5] and quantitatively converted into a solution containing $LiOCBu^t_3$ by treatment with Bu^nLi (1 equiv.) in n-hexane–thf (thf = tetrahydrofuran). Removal of the solvent *in vacuo* and recrystallization of the residue from minimum quantities of n-hexane afforded (**1**) in 70% isolated yield (m.p. 116 °C).

$[\{Li(OCBu^t_3)(thf)\}_2]$ (**1**) $[Cr(OCBu^t_3)_2{\cdot}LiCl(thf)_2]$ (**2**)

The chromium(II) derivative (**2**) was synthesized by adding a solution formed from the addition of n-butyl-lithium (19 mmol, 10.5 cm³ of 1.8 M Bu^nLi in n-hexane) to Bu^t_3COH (18.9 mmol) in ether (20 cm³) to a slurry of $CrCl_3$ (6.3 mmol) in thf (30 cm³). The solution was stirred for 18 h, its volume then reduced to 20 cm³ and filtered. Cooling below 0 °C for 24 h afforded large emerald green crystals of (**2**).

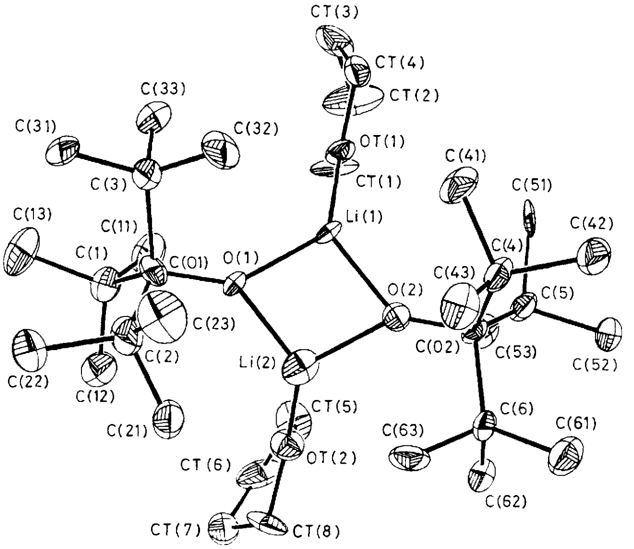

Figure 1. Molecular structure of (**1**). Principal dimensions not given in the text are: Li(1)–OT(1), 1.963(10); Li(2)–OT(2), 2.009(11); C(O1)–O(1), 1.393(7); C(O2)–O(2), 1.391(7); C(5)–C(51), 1.555(8) Å; Li(1)–O(1)–Li(2), 79.3(5); O(1)–Li(1)–O(2), 98.7(4); O(1)–Li(1)–OT(1), 124.3(5); C(O1)–O(1)–Li(1), 142.2(4); Li(1)–O(2)–Li(2), 79.3(5); C(1)–C(O1)–O(1), 107.9(5)°. Hydrogen atoms have been omitted for clarity.

The crystal structures of both (**1**) and (**2**) have been determined by *X*-ray diffraction, and are illustrated in Figures 1 and 2.‡ *Crystal data:* (**1**) at 140 K are: orthorhombic space group $Pbc2_1$; $a = 10.685(1)$, $b = 16.884(3)$, $c = 19.558(3)$ Å; $U = 3546.4$ Å³; $D_c = 1.05$ g cm⁻³ for $Z = 4$; $\mu = 0.60$ cm⁻¹; 2409 unique data [1343 with $F > 6\sigma(F)$] with Mo-K_α radiation ($\lambda = 0.71069$ Å) and the ω scan technique; $R = 0.042$ for the 1373 reflections used. (**2**) (140 K); triclinic, space group $P\bar{1}$; $a = 12.633(12)$, $b = 12.898(8)$, $c = 12.998(18)$ Å; $\alpha = 61.47(8)$, $\beta = 80.06(9)$, $\gamma = 81.73(6)°$; $D_c = 1.16$ g cm⁻³ for

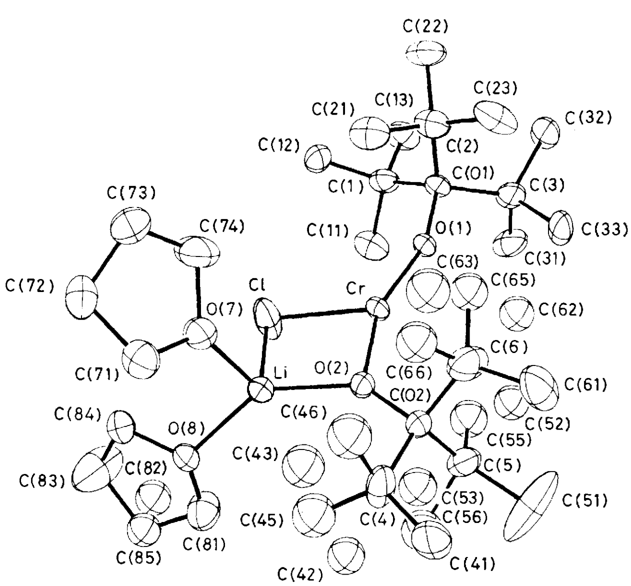

Figure 2. Molecular structure of (**2**). Principal dimensions not given in the text are: Cr–Cl, 2.324(2); Li–Cl, 2.417(8); Li–O(2), 1.920(11); Li–O(7), 1.958(12); C(O1)–O(1), 1.404(5); avg. C(O1)–C(1,2,3), 1.634(10) Å; O(2)–Cr–Cl, 91.1; Cl–Li–O(2), 90.1(4); Li–Cl–Cr, 77.6(2); Li–O(2)–Cr, 98.9(3); Cr–O(1)–C(O1), 158.0(4); Cl–Cr–O(1), 110.9(1)°. Hydrogen atoms have been omitted for clarity.

---

‡ Figure 2 illustrates the disorder found in the hydrocarbon portion of the bridging $-OCBu^t_3$ and in one of the thf molecules. We were unable to avoid this phenomenon by using different solvents for crystallization, since this invariably led to the isolation of crystals of $[Cr(OCBu^t_3)_2(thf)_2]$. However, the interesting part of the geometry of (**2**) concerns the core atoms only, and the data, refined to a final R value of 0.058, indicate that there is no reason to believe the geometry in the hydrocarbon part of the bridging alkoxide is significantly different from that in the terminal ligand, or from the values found in (**1**).

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

$Z = 2$; $U = 1828.2$ Å^3; $\mu = 4.3$ cm^{-1}; 3166 unique data with $F > 6\sigma(F)$, Mo-K_α radiation and ω scan; $R = 0.058$.

Compound (**1**) has a roughly planar central core of two lithium (three-co-ordinate) and two oxygen atoms. The structure differs from the previously reported compound, $[\{Li(OC_6H_2Me\text{-}4,Bu^t{}_2\text{-}2,6)(OEt_2)\}_2]$,[6] in that the ligated thf oxygen atoms and the $CBu^t{}_3$ groups deviate from the central core plane on opposite sides. The Li–O distances in (**1**) are quite short, 1.835(10), 1.852(9), 1.846(11), and 1.830(12) Å, similar to the values of 1.849(11) and 1.867(10) Å in the aryloxo compound above.[6]

There is a considerable degree of strain in the t-butyl groups in both (**1**) and (**2**). Around the most crowded carbon atom in (**1**), C(O1), the angles are 110.3(5), 111.9(5), and 112.7(5)° and the C–C distances 1.632(9), 1.653(9), and 1.620(9) Å. The terminal $OCBu^t{}_3$ group in (**2**) has bond distances and angles that are quite similar. Similar distortion has been noted in crystals of tri-t-butyl *p*-nitrobenzoate[7] and in the gas phase by the electron diffraction study of tri-t-butylmethane.[8]

The structure of (**2**) is interesting in several respects, being the first structurally characterized example of a three co-ordinate chromium(II) compound. The geometry at chromium is best described as distorted T-shaped owing to the extremely wide O(1)–Cr–O(2) angle of 157.9(2)°. All the atoms forming the core [O(1), O(2), Cr, Cl, Li] are coplanar but as in (**1**) the thf oxygen atoms deviate significantly from the plane. The co-ordination at the Li atom is severely distorted from tetrahedral owing to steric effects. The O–Li–O angles vary from 90.1(4) to 139.1(5)°, and the Li–O bond lengths from 1.920(11) to 2.023(10) Å. The Li $\cdots$ Cl distance is close to the sum of their ionic radii.[9] The Cr–O(1) distance, 1.881(4) Å, is longer than those found in $[LiCr(OCHBu^t{}_2)_4(thf)]$, 1.823(4) Å, or in $[Cr(OCHBu^t{}_2)_4]$, 1.771(3) Å.[4] This may be attributed to the lower oxidation state of the central metal atom in (**2**). The bridging Cr–O(2) distance, 1.991(3) Å, is similar to those found in $[\{Cr(\eta^5\text{-}C_5H_5)(OBu^t)\}_2]$,[10] which is dimeric with a formal Cr–Cr single bond.

When (**2**) is dissolved in hexane, LiCl is eliminated and a blue-green crystalline complex is obtained. The complex gave an elemental analysis consistent with the formulation $[Cr(OCBu^t{}_3)_2(thf)_2]$, m.p. 196—200 °C (decomp.), the structure of which may be similar to that of *trans*-$[Cr\{N(SiMe_3)_2\}_2(thf)_2]$.[11] Chromium alkoxides of the type $[Cr(OR)_2(thf)_2]$ (where OR is 2,6-di-t-butylphenolate or 2,4,6-tri-t-butylphenolate) have been reported but no crystal structure data has been presented.[3] We are currently examining this new complex and the properties of the $-OCBu^t{}_3$ ligand with later first row transition metals by *X*-ray diffraction methods.[12]

We thank the N.S.F. and the Norwegian Council for Sciences and Humanities for generous financial support; J. H. is on leave from the University of Oslo, Norway.

Received, 1st August 1983; Com. 1032

References

1 L. Chamberlain, J. Keddington, I. P. Rothwell, and J. C. Huffman, *Organometallics*, 1982, **1**, 1538.

2 L. Chamberlain and I. P. Rothwell, *J. Am. Chem. Soc.*, 1983, **105**, 1665.

3 B. Horvarth and E. G. Horvarth, *Z. Anorg. Allg. Chem.*, 1979, **457**, 51; B. Horvarth, R. Möseler, and E. G. Horvarth, *ibid.*, 1979, **449**, 41.

4 M. Bochmann, G. Wilkinson, G. B. Young, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 1863.

5 L. Syper, *Roczniki. Chimi.*, 1973, **47**, 433.

6 B. Çetinkaya, I. Gümrükçü, M. F. Lappert, J. L. Atwood, and R. Shakir, *J. Am. Chem. Soc.*, 1980, **102**, 2086.

7 P.-T. Cheng, S. C. Nyburg, C. Thankachan, and T. T. Tidwell, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 654; T. T. Tidwell, *Tetrahedron*, 1978, **34**, 1855.

8 H. B. Burgi and L. S. Bartell, *J. Am. Chem. Soc.*, 1972, **94**, 5236.

9 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

10 M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, *Inorg. Chem.*, 1978, **18**, 120.

11 D. C. Bradley, M. B. Hursthouse, C. W. Newing, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1972, 567.

12 B. D. Murray and P. P. Power, to be published.