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Stabilization of a Diamagnetic Sc^IBr Molecule in a Sandwich-Like Structure[†]

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*Summary: Reaction of a new β-diketiminato derivative of scandium, $LScBr_2$ (L = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$), with $(C_3H_5)MgBr$ gave the unexpected scandium complex $(LMgBr)_2ScBr$ (**1**), whose structure was established by X-ray analysis, liquid and solid-state NMR, EPR, UV−vis, and magnetic measurements. Correlation of all results leads to the conclusion that the formal oxidation state of scandium in this complex is one (Sc(I)) having no unpaired electrons.*

Compounds of the early transition metals in low oxidation states have attracted much attention due to their unusual properties (i.e. potential new catalysts) and as pure scientific curiosities. Nevertheless, there are few examples of such complexes known, preferentially prepared by metal vapor synthetic techniques.[1] By this route, several subvalent scandium complexes have been obtained by Nixon et al.[2] One particular exception is the first subvalent lanthanum compound, prepared by Lappert et al.[3] By exploring the chemistry of scandium complexes containing a new β-diketiminato ligand, which has been developed in our group,[4] we obtained a subvalent scandium complex whose preparation and characterization is reported herein. The reaction of a THF solution of $LScBr_2$ (L is a β-diketiminato ligand that possesses two pendant arms, $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$)[5] with 2 equiv of $(C_3H_5)MgBr$ in diethyl ether is accompanied by a color change from yellow to dark brown at room temperature after a few hours.[6] When the solvent was removed and the remaining solid extracted with toluene, a dark blue solution was obtained, from which suitable crystals of **1** for X-ray measurement were grown. The molecular structure of **1** has been determined by X-ray crystallography (see the Supporting Information) and is shown in Figure 1. (The compound crystallizes with one molecule of toluene.)[7]

As far as the structure is concerned, there are several interesting features. The molecular symmetry is C_{2v}. The two LMgBr frames surround the scandium atom symmetrically in a sandwich-like structure, having a certain similarity with Cp_2ScCl, where the Cp groups are arranged in a bent fashion (the distance from Sc to the C_3N_2 ligand frame is 1.76 Å).[8] The coordination number of scandium in **1** is 11. The Sc−Br(1) bond length of **1** is longer by 0.19 Å compared with that of $LScBr_2$, as a consequence of the larger radius of Sc(I) in comparison with Sc(III). The stronger bonds between scandium and nitrogen atoms compared with those of scandium and carbon atoms are seen from the structural data (see Figure 1). The scandium atom is only 0.16 Å out of the plane formed by N(1), N(1)#2, N(1)#3, and N(1)#1. Interestingly, the Sc−C(1) and Sc−C(2) bond lengths for **1** are comparable with the Sc−C (enclosed in the benzene-like ring) bond lengths for $[(\eta^5\text{-}P_3C_2tBu_2)Sc(\mu\text{-}\eta^6{:}\eta^6\text{-}P_3C_3tBu_3)Sc(\eta^5\text{-}P_3C_2tBu_2)$ (2.450(5) Å).[2] The N(1)−C(1) bond length is slightly longer than that in $LScBr_2$ by roughly 0.05 Å, as a consequence of the higher coordination number for nitrogen atoms from the ligand frame. However, no significant differences have been observed for the C(1)−C(2) bond lengths of **1** in

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[†] Dedicated to Professor Ekkehard Winterfeldt on the occasion of his 70th birthday.

[1] (a) Cloke, G. N. *Chem. Soc. Rev.* **1993**, 17 and references therein. (b) Corbett, J. D. *Inorg Chem.* **2000**, *39*, 5178 and references therein.

[2] (a) Arnold, L. P.; Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7630. (b) Arnold, L. P.; Cloke, F. G. N.; Nixon, J. F. *Chem. Commun.* **1998**, 797.

[3] Cassani, M. C.; Duncalf, D. J.; Lappert, F. M. *J. Am. Chem. Soc.* **1998**, *120*, 12958.

[4] Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *J. Organomet. Chem.* **2002**, *643−644*, 47.

[5] (a) Neculai, A. M.; Roesky, H. W.; Neculai, D.; Magull, J. *Organometallics* **2001**, *26*, 5501. (b) Neculai, D.; Neculai, A. M.; Roesky, H. W.; Magull, J. *J. Chem. Soc., Dalton Trans.*, submitted for publication.

[6] Compound **1** was synthesized by the following procedure: to a solution of $LScBr_2$ (0.5 g, 0.99 mmol) in 20 mL of THF was added 2 mL of $(C_3H_5)MgBr$ (1 M in ether, 2 mmol) at 0 °C. The mixture was left to react for an additional 5 h while it reached room temperature. In the meantime the color of the suspension changed from yellow to dark brown. Then, all the volatiles were removed under vacuum, and 25 mL of toluene was added. The precipitate was filtered off, to give a dark blue solution that was concentrated to approximately 10 mL. Blue-green crystals of **1** formed overnight. The crystals were separated, washed with small amounts of toluene, and dried under vacuum (0.125 g, 25.8%). Anal. Calcd for $(C_{17}H_{35}N_4MgBr)_2ScBr\cdot 0.5C_7H_8$: C, 46.41; H, 7.68; N, 11.54. Found: C, 46.44; H, 7.57; N, 10.60 (composition due to the drying procedure).

[7] Crystal data for $\mathbf{1}\cdot C_7D_8$: $C_{41}H_{78}Br_3Mg_2N_8Sc$, dark green, M_r = 1016.42, T = 133 K, orthorhombic, space group *Cmcm*, a = 21.5760(12) Å, b = 12.9704(7) Å, c = 17.7340(8) Å, V = 4962.8(4) Å^3, Z = 4, D_c = 1.360 g cm^{-3}. The final R factor was 0.0315 for 2073 reflections with $I_o > 2\sigma(I_o)$ (R_w = 0.0346 for all 26 177 data). GOF = 1.107.

[8] Atwood, J. L.; Smith, K. D. *J. Chem. Soc., Dalton Trans.* **1973**, 2487.

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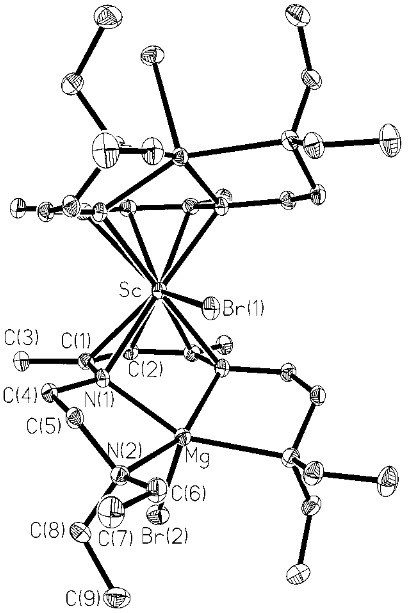
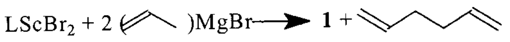


Figure 1. Molecular structure of **1**. Solvent and protons were omitted for clarity. Selected bond lengths (Å): Sc−Br(1) = 2.800(1), Sc−N(1) = 2.274(2), Sc−C(1) = 2.413(3), Sc−C(2) = 2.431(4), N(1)−C(1) = 1.385(3), C(1)−C(2) = 1.411(3), Mg−N(1) = 2.142(2), Mg−N(2) = 2.345(2), Mg−Br(2) = 2.534(1). Selected bond angles (deg): N(1)−C(1)−C(2) = 121.0(2), C(1)−C(2)−C(1)#2 = 129.1(4), N(1)#1−Sc−N(1) = 102.91(11), C(1)−Sc−C(1)#1 = 86.65(12), C(2)−Sc−C(2)#3 = 83.45(19), N(1)−Sc−Br(1) = 85.85(6), N(1)−Mg−Br(2) = 98.98(7), N(1)−Mg−N(2) = 79.76(8), N(2)−Mg−N(2)#2 = 110.62(12).[9]

comparison with those from $LScBr_2$. The magnesium atoms are pentacoordinated. All the nitrogen atoms that are coordinated to magnesium are involved in a square-pyramidal geometry around the metal center. The magnesium atom lies out of the N(1), N(1)#2, N(2)#2, N(2) plane by 0.40 Å in the direction of the bromine atom. The Mg−N bond lengths are not equal, due to the different bonding modes of the nitrogen to magnesium atoms. The Mg−N(1) bond length is slightly different from those encountered in similar compounds, previously reported.[10] The Mg−Br(2) bond length (2.53 Å) demonstrates the more covalent nature of this bond (the sum of ionic radii for Mg^{2+} and Br^- is 2.60 Å).

Complex **1** is very air- and moisture sensitive, as is proved by its immediate decolorization upon exposure to air. The composition of the unanticipated molecular formula $(LMgBr)_2ScBr$ that resulted from the X-ray structural analysis is consistent with ^1H, ^{13}C, and ^{45}Sc NMR data in solution.[11] The elemental analysis was determined for $(LMgBr)_2ScBr$ with half a molecule of toluene. It is noteworthy that all the hydrogen atoms can be assigned with one major upfield shift (2 ppm), namely, the hydrogen atom bonded directly to the backbone, C(Me)C*H*C(Me); in addition, the resonance of the ^{45}Sc NMR spectrum is shifted upfield from 335.0 ppm in $LScBr_2$ to 167.5 ppm in **1**. Temperature-dependent NMR experiments showed that **1** started to decompose irreversibly in solution from 50 °C onward, but a certain degree of decomposition is also observed at 28 °C (see the Supporting Information). In addition, the decomposition was confirmed with mass spectral investigations, where only the fragment LMgBr could be assigned.[12] Furthermore, in the UV−vis spectrum, an absorption at 570 nm (C_6D_6) was observed ($\epsilon = 0.18 \times 10^4$). Intriguingly, compound **1** showed no paramagnetic behavior by any means,[13] as one could expect by taking into account the previous subvalent complex of scandium prepared by Nixon et al.[2] Therefore, to investigate any possible structural changes of **1** in solution compared to the solid state**,** additional solid-state NMR experiments were conducted under magic angle spinning (MAS)[14] conditions. A Floquet analysis[15] of the resulting ^{45}Sc spinning sideband spectra resulted in an isotropic chemical shift value that is consistent with the results obtained in solution. Likewise, the ^{13}C chemical shifts observed under MAS conditions corroborate with the data obtained in solution. However, to demonstrate that indeed a redox reaction took place, a GC-MS experiment was designed. For this purpose the reaction was carried out in deuterated THF and all the volatiles were collected. The corroboration of the GC-MS and ^1H NMR spectrum of the volatiles revealed that 1,5-hexadiene was the only byproduct, which clearly shows that a redox reaction took place (see Scheme 1). Still, the exact amount of 1,5-hexadiene and the nature of the other side products of the reaction could not be isolated and characterized.

Scheme 1



In summary, we have achieved the first crystallographically and spectroscopically characterized subvalent organoscandium compound with all the valence electrons paired, **1**, which we formulate as a Sc^IBr species bridged by two neutral η^5-LMgBr moieties. The η^5 coordination of the LMgBr is preferred, due to the better shielding of the scandium atom compared to η^2 coordination. An alternative formulation of compound **1** as $[LMgBr]^-{}_2Sc^{3+}Br^-$, as a consequence of the perhaps “noninnocent” nature of the LMgBr, can be invoked, but it seems to us less plausible in the light of the proofs presented above. Calculations concerning the complex **1** as well as its chemical reactivity are currently underway.

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[9] Symmetry transformations used to generate equivalent atoms: (#1) $-x, y, z$; (#2) $x, y, -z + 3/2$; (#3) $-x, y, -z + 3/2$.

[10] Chisholm, M. H.; Huffman, J. C.; Phomhrai, K. *J. Chem. Soc., Dalton Trans.* **2001**, 224.

[11] Solution NMR data for **1**: ^1H NMR (500 MHz, C_6D_6, 300 K) δ 3.63 (br, 4 H; $Et_2NCH_2\mathit{CH_2}$), 3.49 (br, 8 H, $N\mathit{CH_2}CH_3$), 3.2 (t, 4 H, $Et_2NCH_2\mathit{CH_2}$), 2.82 (s, 2 H, C(Me)*CH*C(Me)), 2.6 (br, 8 H, $N\mathit{CH_2}CH_3$), 2.41 (d, 4 H, $Et_2N\mathit{CH_2}CH_2$), 2.28 (d, 4 H, $Et_2N\mathit{CH_2}CH_2$), 1.82 (s, 12 H, $C\mathit{CH_3}$), 0.91 (br, 24 H, $NCH_2\mathit{CH_3}$); ^{13}C NMR (125 MHz, C_6D_6, 300 K) δ 129.27, 92.81, 55.11, 45.78, 44.29, 20.87, 9.5; ^{45}Sc NMR (121 MHz, referenced to $[Sc(H_2O)_6]^{3+}$ in D_2O, C_6D_6, 300 K) δ 167.5.

[12] EI-MS (*m*/*z* (relative intensity, %)): 400 ($LMgBr^+$, 5), 314 ($LMgBr^+ - C_5H_{12}N$, 50), 86 ($C_5H_{12}N$, 100).

[13] Compound **1** showed only diamagnetic behavior in the solid state when magnetic measurements were employed. When temperature-dependent EPR was recorded for a toluene solution of **1**, no signal was observed (−70 °C to room temperature).

[14] Andrew, E. R.; Bradbury A.; Eades, R. G. *Nature* **1958**, *182*, 1659. Experiments were conducted at 400 and 600 MHz (^1H resonance frequency) resonance frequencies employing 4 mm triple-resonance MAS probe heads. The results will be published elsewhere.

[15] Baldus, M.; Levante, T. O.; Meier, B. H. *Z. Naturforsch.* **1994**, *49*, 88.

Supporting Information Available: Text giving experimental procedures and characterization data and figures giving NMR temperature-dependent spectra of **1** in the ranges 0.75−1.9 and 2.3−4.4 ppm. This material is available free of charge via the Internet at http://pubs.acs.org.

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