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The First Metal-Oxo Cluster Containing Lithium and Bismuth

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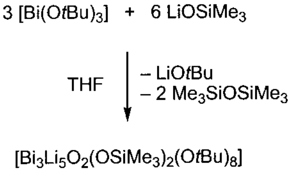
The reaction of $[Bi(OtBu)_3]$ with $LiOSiMe_3$ gave the heterobimetallic bismuth-oxo cluster $[Bi_3Li_5(\mu_5\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_6]$ (**1**) after elimination of $Me_3SiOSiMe_3$. The cage compound **1** is the first example of a mixed-metal alkoxide/siloxide composed of lithium and bismuth. Crystals of **1**·2 C_7H_8 and **1**·1.5 THF suitable for X-ray single crystal structure analysis were obtained by crystallisation from toluene and THF, respectively. Both solvates crystallise in the orthorhombic space group *Pmmn* with Z = 2. The lattice constants are $a = 16.267(3)$ Å, $b = 17.126(3)$ Å and $c = 12.155(2)$ Å (**1**·2 C_7H_8) and $a = 16.353(2)$ Å, $b = 17.156(1)$ Å and $c = 12.256(1)$ Å (**1**·1.5 THF). In both compounds the solvent molecules occupy channels along the *c*-axis. The basic molecular unit is best described as a face-sharing double cubane $[BiLi_5(\mu_4\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2]$ which is coordinated by two $[Bi(OtBu)_3]$ molecules. The compound is kinetically labile in solution and readily decomposes in 1,1,2,2-tetrachloroethane with elimination of 1,1,2-trichloroethylene.

Introduction

Heterometallic bismuth-oxo compounds including element combinations such as Bi/Mo/O,[1,2] Bi/Ti/O,[3] Bi/Sr/Ta/O[4] as well as Bi/V/O[5] have found various applications as ferroelectric devices, oxide ion conductors, non-toxic pigments, catalysts and catalyst models. We are interested in novel precursors for bismuth-containing materials and therefore we have started to systematically explore the chemistry of bismuth silanolates[6] which has been scarcely reported before.[7,8] The synthesis of one of the most promising precursors, $[Bi(OSiMe_3)_3]$, was published in 1968 starting from $BiCl_3$ and $NaOSiMe_3$.[8] Our attempts to reproduce the synthetic procedure did not result in the pure bismuth tris(trimethylsilanolate). We always observed sodium contamination of the final material and isolated several heterobimetallic sodium bismuth-oxo clusters.[9] The formation of such heterobimetallic cage compounds composed of bismuth and sodium is not surprising given the similar ionic radii [$r(Bi^{3+})$ = 117 pm; $r(Na^+)$ = 116 pm; coordination number CN = 6],[10] and the rich and variable coordination chemistry of both atom types. Indeed, several such heterobimetallic alkoxides composed of sodium and bismuth were synthesized previously.[11,12] In addition, heterobimetallic bismuth alkoxides including metals such as potassium,[12] barium,[13] vanadium,[14] titanium,[15] molybdenum,[2,16] and terbium[17] were reported. Mixed-metal carboxylates/alkoxides are also known for some transition metals.[18] However, to the best of our knowledge no heterobimetallic alkoxide containing lithium as the lightest metal atom [$r(Li^+)$ = 73 pm; CN = 4][10] and bismuth, the heaviest stable element of the periodic table, was reported before. The only cage compound we are aware of is $[Li_2Bi_2(NtBu)_2(thf)_2]$.[19] Notably, the reaction of $[Bi(OtBu)_3]$ with NaO*t*Bu and KO*t*Bu was reported to give $[Bi_2Na_4O(OtBu)_8]$ and $[BiK(OtBu)_4]$, respectively, whereas no reaction was observed with LiO*t*Bu.[12] This prompted us to look at the reaction of $[Bi(OtBu)_3]$ with $LiOSiMe_3$ as an alternative method for the synthesis of $[Bi(OSiMe_3)_3]$ by ligand exchange.

Results and Discussion

The metathesis reaction of $[Bi(OtBu)_3]$ with $LiOSiMe_3$ was expected to provide the bismuth silanolate $[Bi(OSiMe_3)_3]$. However, the reaction according to Equation (1) gave the heterometallic bismuth-oxo cluster $[Bi_3Li_5(\mu_5\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_6]$ (**1**) (Figure 1) with high yield (> 90%). Both GC-MS and ^{29}Si NMR of the reaction solution from which compound **1** had been filtered off revealed the formation of $Me_3SiOSiMe_3$. Apparently, the trimethylsiloxy groups are the source for the μ_5-oxygen atoms in compound **1**. Similarly, we did ob-



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serve recently that $Me_3SiOSiMe_3$ is eliminated by the reaction of $BiCl_3$ with $NaOSiMe_3$ and also upon thermally induced decomposition of $[Bi(OSiMe_3)_3]$.[9,20] Notably, elimination of di-*tert*-butyl ether was reported to take place upon reaction of $[Bi(OtBu)_3]$ with NaO*t*Bu but not with LiO*t*Bu.[12]

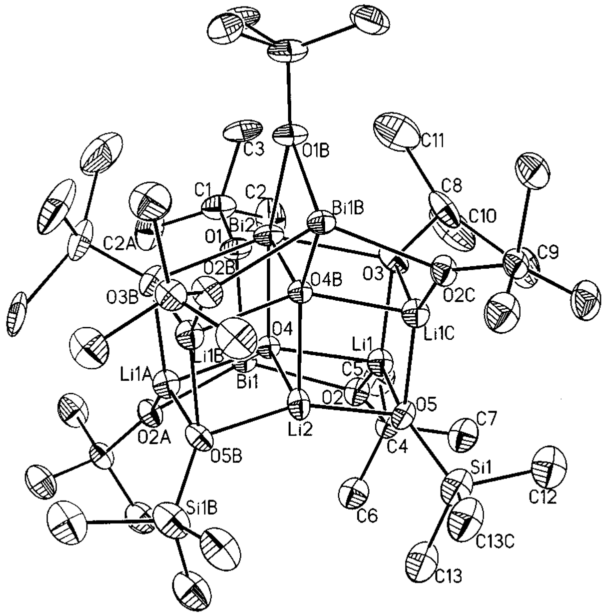

Figure 1. View of the molecular structure of $[Bi_3Li_5(\mu_5\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_6]$ (**1**) showing the atom numbering scheme (ORTEP drawing with 30% probability ellipsoids). Selected bond lenghts [Å] and angles [°] associated with Li (for Bi see also Figure 3): Li(1)–O(2) 1.865(13), Li(1)–O(3) 1.992(13), Li(1)–O(4) 2.087(12), Li(1)–O(5) 1.925(12), Li(2)–O(5) 1.897(8), Li(2)–O(4) 2.10(2); O(2)–Li(1)–O(3) 128.3(7), O(2)–Li(1)–O(4) 86.5(5), O(2)–Li(1)–O(5) 133.7(7), O(3)–Li(1)–O(4) 86.9(5), O(3)–Li(1)–O(5) 97.9(5), O(4)–Li(1)–O(5) 98.7(6), O(4)–Li(2)–O(4B) 84(1), O(4)–Li(2)–O(5) 99.1(5), O(5)–Li(2)–O(5B) 155(2), Li(1)–O(4)–Li(2) 76.6(4), Li(1)–O(5)–Li(2) 85.6(7), Li(1)–O(3)–Li(1C) 80.3(7), Li(1)–O(3)–Bi(2) 96.5(4), Li(2)–O(4)–Bi(2) 97.5(5), Li(2)–O(4)–Bi(1) 144.1(5), Bi(1)–O(1)–Bi(2) 96.9(2), Bi(1)–O(4)–Bi(2) 118.4(3). Symmetry operations used to generate equivalent atoms: A = $-x + 1/2$, y, z; B = $-x + 1/2$, $-y + 3/2$, z; C = x, $-y + 3/2$, z.

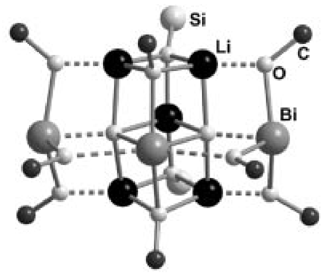

Figure 2. Ball and stick model of the face sharing double-cubane $[BiLi_5(\mu_4\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2]$ coordinated by $[Bi(OtBu)_3]$. Methyl groups omitted for clarity. The dimensions of the spheres do not correlate with the effective ionic radii of the atoms.

The molecular structure of compound **1** is best described to consist of the face-sharing double-cubane $[BiLi_5(\mu_4\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2]$ and two $[Bi(OtBu)_3]$ molecules which are coordinated to the heterocubane through their oxygen atoms as well as the bismuth atoms (Figure 2). The incorporation of the large bismuth atom results in distortions from an ideal face-centred double cubane structure.

As a result of the high symmetry of compound **1** only two distinct lithium and bismuth atoms, respectively, are observed. Both lithium atoms are coordinated to four oxygen atoms and adopt a coordination geometry, which is best described as distorted trigonal bipyramid with one vertex being unoccupied. For Li(1) this vertex is in axial and for Li(2) it is in equatorial position. Slight differences in the Li–O bond lengths are observed depending on the bridging mode of the oxygen atoms. The shortest Li–O bond lengths are observed for μ_2-O*t*Bu [Li(1)–O(2) 1.865(13) Å] followed by μ_3-$OSiMe_3$/μ_3-O*t*Bu [Li(1)–O(3) 1.992(13) Å, Li(1)–O(5) 1.925(12) Å, Li(2)–O(5) 1.897(8) Å] and μ_5-O [Li(1)–O(4) 2.087(12) Å, Li(2)–O(4) 2.10(2) Å]. Irregular coordination polyhedra are observed for both bismuth atoms. The coordination geometry at Bi(1) might be described as a distorted *pseudo*-trigonal bipyramid BiO_4X with the lone pair X occupying an axial position (Figure 3). The Bi–O bond lengths are in the range 2.087(6)–2.242(5) Å with the shortest bond lengths found in axial position. As a result of the stereochemical activity of the lone pair the torsion angle Bi(1)–O(1)–O(2A)–O(2) amounts to 22°. A [4+2]-coordination is observed for Bi(2) with a short Bi–O bond length of 2.087(6) Å for Bi(1)–O(4), a bond length of 2.331(7) Å for Bi(2)–O(3) and a longer bismuth–oxygen distance of 2.683(7) Å for Bi(2)···O(1). In first approximation the polyhedron might be described as strongly distorted *pseudo*-pentagonal bipyramid BiO_6X with a stereochemically active lone pair occupying a position within the pentagonal plane. Consequently, the O(3)–Bi(2)–O(3B) angle decreases from 180° to 146.4(3)° and the O(1)–Bi(2)–O(1B) angle increases from 144° to 146.0(3)°.

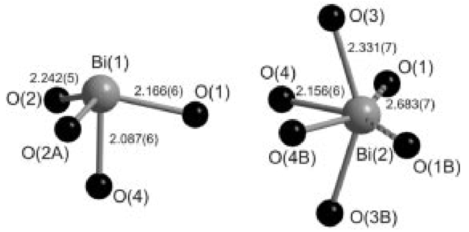

Figure 3. View of the bismuth–oxygen polyhedra observed for Bi(1) and Bi(2) including distances given in Å. Selected O–Bi–O angles [°]: O(1)–Bi(1)–O(2) 108.9(1), O(1)–Bi(1)–O(4) 78.3(2), O(2)–Bi(1)–O(2A) 128.6(2), O(2)–Bi(1)–O(4) 77.5(1); O(1)–Bi(2)–O(1B) 146.0(3), O(1)–Bi(2)–O(3) 94.9(1), O(1)–Bi(2)–O(4) 66.4(2), O(3)–Bi(2)–O(3B) 146.4(3), O(3)–Bi(2)–O(4) 77.3(1), O(4)–Bi(2)–O(1B) 147.6(2), O(4)–Bi(2)–O(4B) 81.3(3). Symmetry operations used to generate equivalent atoms: *A* = $-x + 1/2$, y, z; *B* = $-x + 1/2$, $-y + 3/2$, z.

The heterometallic bismuth-oxo cluster crystallises from both toluene and THF in form of the solvates $\mathbf{1}\cdot 2\ C_7H_8$ and $\mathbf{1}\cdot 1.5$ THF, respectively. In the solid state the metal-oxo clusters, which have a brick-like shape with approximate dimensions of $12\times 11\times 11$ Å^3 (atom to atom distance), arrange in such a way that channels along the *c-axis* are formed. Solvent molecules occupy these channels. In Figure 4 a packing diagram of **1**·2 C_7H_8 leaving the voids unoccupied is shown. The diameter of the channels amounts to approximately 6 Å (atom to atom distance). The THF solvate **1**·1.5 THF shows similar crystallographic data.

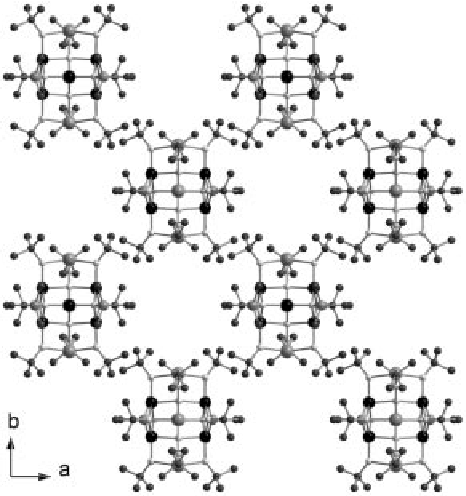

Figure 4. Packing diagram of **1**·2 C_7H_8 in the solid state. The solvent molecules which occupy the channels along the *c*-axis are removed for clarity.

The moisture-sensitive compound dissolves in solvents such as CD_2Cl_2, $C_2D_2Cl_4$, CCl_4, toluene and THF at room temperature, but its solubility is significantly decreased at lower temperature. The ^1H NMR spectrum of a [D$_6$]toluene solution of **1** is rather complex and shows a vast number of signals which are grouped in the regions (a): δ = 0.22–0.52 ppm and (b): δ = 1.05–1.67 ppm with an overall integral ratio of approximately 1:4 (see Figure S1 in the Supporting Information). Similarly, complex ^1H NMR spectra are observed in other solvents such as 1,1,2,2-tetrachlorethane and CCl_4. These spectra are not compatible with the structure of compound **1** observed in the solid state. Thus we conclude that in solution the metal-oxo cluster is kinetically labile and gives a mixture of metal (oxo)alkoxides. This hypothesis is further supported by a comparison of the IR spectra of the solid material **1** and its saturated CCl_4 solution (Figure S2). Decomposition of compound **1** in 1,1,2,2-[D$_2$]tetrachloroethane under base-catalysed elimination of DCl to give [D]-1,1,2-trichloroethylene was observed at room temperature overnight. Heating of a 1,1,2,2-tetrachlorethane solution significantly enhances this process and a colourless solid containing chloride and bismuth was obtained.[21] In contrast compound **1** is stable in CCl_4 and heating a toluene solution of **1**·1.5 THF at reflux and subsequent crystallisation at –20 °C gave single crystals of the toluene solvate **1**·2 C_7H_8.

Conclusion

In contrast to heterometallic sodium/bismuth oxoalkoxides and oxosilanolates those of lithium were not reported so far. We anticipated that formation of lithium derivatives is less likely as a result of the great difference of the ionic radii of lithium and bismuth. However, metathesis reaction of [Bi(O*t*Bu)$_3$] with $LiOSiMe_3$ gave the novel heterometallic metal-oxo cluster [$Bi_3Li_5(\mu_5\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_6$] (**1**) instead of [$Bi(OSiMe_3)_3$]. Formation of the metal-oxo cluster **1** proceeds through elimination of $Me_3SiOSiMe_3$. It should be noted that our attempts to prepare [$Bi(OSiMe_3)_3$] by salt elimination using $BiCl_3$ and $MOSiMe_3$ (M = Li, Na, K) also failed.[9] Apparently, the ready formation of $Me_3SiOSiMe_3$ makes the salt metathesis unfavourable for the synthesis of bismuth tris(trimethylsilanolate) even with the small lithium cation. However, heterometallic bismuth compounds might be suitable precursors for novel mixed metal oxide materials prepared through mild non-aqueous procedures.

Experimental Section

General Remarks: Solvents were distilled from appropriate drying agents prior to use (THF, Et_2O and toluene from sodium; $C_2D_2Cl_4$, CD_2Cl_2 and CCl_4 from CaH_2). All manipulations were carried out under argon using the Schlenk-type technique. [Bi(O*t*Bu)$_3$][22] and $LiOSiMe_3$[23] were prepared according to literature procedures. Elemental analyses were performed on a LECO-CHNS-932 analyser. The deviation from the calculated values results from the moisture sensitivity of the compound. NMR experiments were performed using a Bruker DPX 300, DRX 400 and DRX 500. Chemical shifts δ are given in ppm and were referenced against Me_4Si (^1H, ^{29}Si). The ^{29}Si NMR of the reaction solution was recorded with a D_2O capillary as external lock reference. NMR experiments were carried out in sealed NMR tubes. IR spectra were obtained from a Bruker FTIR IFS 28 spectrometer. The IR spectra were run as Nujol mulls and absorption bands assigned to the compound are listed in the range 400–1500 cm^{-1}. Decomposition of compound **1** in 1,1,2,2-tetrachloroethane to give 1,1,2-trichloroethylene and a colourless solid (**A**) was observed. GC-MS (Perkin–Elmer Turbomass Gold) of the supernatant solution revealed the formation of 1,1,2-trichloroethylene and *t*BuOH. The amount of 1,1,2-trichloroethylene was negligible in freshly distilled 1,1,2,2-tetrachlorethane. According to an EDX analysis (Hitachi FEG S 4500) the inhomogeneous solid material (**A**) contains Bi and Cl with a ratio in the range 1:2.8–4.8.

[$Bi_3Li_5(\mu_5\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_6$] (1): A solution of $LiOSiMe_3$ (15.36 g, 0.16 mmol) in 200 mL Et_2O was added to a solution of [Bi(O*t*Bu)$_3$] (22.84 g, 0.05 mmol) in 250 mL THF at room temperature and the reaction mixture was stirred overnight to give a cloudy yellow solution. After filtration the amount of solvent was reduced to approximately 100 mL and fractional crystallisation at –20 °C gave colorless crystals of **1**·1.5 THF. The ^{29}Si NMR of the supernatant solution showed a signal at 7.4 ppm assigned to $Me_3SiOSiMe_3$ and a second signal at 9.9 ppm assigned to $LiOSiMe_3$. The combined crystalline fractions (24.99 g, 92% based on Bi) were dried in vacuo to remove the THF and to leave a colourless amorphous solid. Comparison of the IR spectra of the single crystals **1**·1.5 THF and the amorphous material **1** indicates removal of the guest molecules THF without collapse of the molecular structure (see Supporting Information). Single crystals suitable for X-ray crystallography were obtained from both THF and toluene by dissolution of the amorphous material and subsequent crystallisation at –20 °C. Analytical data of **1**: $C_{38}H_{90}Bi_3Li_5O_{12}Si_2$ (1456.93): calcd. C 31.3, H 6.2; found C 30.7, H 6.7. ^1H NMR

(500.13 MHz, $C_2D_2Cl_4$): δ = 0.02–0.06 ($OSiMe_3$), 1.22–1.28 (O*t*Bu), 1.36–1.40 ppm (O*t*Bu). ^1H NMR (400.13 MHz, $[D_8]$toluene): δ = 0.22–0.52 ($OSiMe_3$), 1.05–1.67 (O*t*Bu). ^{29}Si NMR (79.49 MHz, CD_2Cl_2): δ = –3.8, –3.9, –4.2 ppm (major signal), –4.3, –4.6. IR $\tilde{\nu}$ = 1357 (s), 1241 (m), 1229 (m), 1191 (s), 1020 (s), 984 (s), 941 (s), 918 (m), 828 (m), 752 (w), 742 (w), 639 (w), 576 (m), 546 (m), 528 (m), 480 (w), 463 (w), 445 cm^{-1} (w).

X-ray Crystallography: Intensity data for the colorless crystal **1**·2 C_7H_8 were collected with a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α radiation at 173 K. The data collection covered almost the whole sphere of reciprocal space with three sets at different κ-angles and 307 frames via ω-rotation (Δ/ω = 1°) at two times 75 s per frame. The crystal–detector distance was 3.4 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections there was no indication for any decay. The structure was solved by direct methods SHELXS97[24] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97.[25] The H atoms were placed in geometrically calculated positions using a riding model with U_{iso} constrained at 1.2 times U_{eq} of the carrier C atom for non-methyl and 1.5 times U_{eq} of the carrier C atom for methyl groups. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from the International Tables for X-ray Crystallography. An absorption correction was applied with a multi-scan method using SCALEPACK[26] (T_{min} = 0.385, T_{max} = 0.572). Disorder was found for two *tert*-butyl groups. The methyl group C3 (0.25, *y*, *z*) is disordered over two position and refined on a normal position with an occupancy of 0.5. Three methyl groups (C9–C11) on special position (*x*, 0.75, *z*) were refined with occupancies of 0.2 (C9), 0.9 (C10), and 0.4 (C11). All atoms of the solvent molecules toluene were isotropically refined with an occupancy of 0.25. Further details are listed in Table 1.

Table 1. Crystallographic data for $[Bi_3Li_5(\mu_5\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_6]\cdot 2C_7H_8$ (**1**·2 C_7H_8).

Compound	**1**·2 C_7H_8
Empirical formula	$C_{52}H_{106}Bi_3Li_5O_{12}Si_2$
Formula weight	1641.19
Crystal system	orthorhombic
Space group	*Pmmn*
a [Å]	16.267(3)
b [Å]	17.126(3)
c [Å]	12.155(2)
Volume [Å^3]	3386(1)
Z	2
$\rho_{calcd.}$ [g cm^{-3}]	1.610
Absorption coefficient [mm^{-1}]	7.860
Crystal size [mm]	0.15 × 0.12 × 0.08
Theta range for data collection [°]	3.94 to 27.45
Reflections collected	11338
Independent reflections	4110 [R_{int} = 0.038]
Goodness-of-fit on F_2	0.938
R [$I > 2\sigma(I)$]	0.0277
wR_2 (all data)	0.0661
Largest diff. peak and hole [e·Å^{-3}]	1.140/–1.209

CCDC-273897 (for **1**·2 C_7H_8) and -288998 (for **1**·1.5 THF) 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.

Supporting Information (for details see the footnote on the first page of this article): Figure S1: NMR spectra of $[Bi_3Li_5(\mu_5\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_6]$ (**1**). Figure S2: IR spectra of $[Bi_3Li_5(\mu_5\text{-}O)_2(\mu_3\text{-}OSiMe_3)_2(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_6]$ (**1**).

Acknowledgments

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