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β-Diketiminate Stabilized Magnesium Hydroxide, Heterobimetallic, and Halide Complexes: Synthesis and X-ray Structural Studies

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Abstract. The controlled hydrolysis of heteroleptic magnesium amide, $LMgN(SiMe_3)_2$ (L = $CH[C(Me)N(2,6\text{-}iPr_2C_6H_3)]_2$) with water afforded the corresponding hydroxide $[LMg(OH)\cdot THF]_2$ as air and moisture sensitive compound. The presence of a sterically bulky *β*-diketiminate ligand prevents the self-condensation reaction of this hydroxide complex. Single crystal X-ray analysis shows that the hydroxide is dimeric in the solid state. Reaction of the magnesium amide or $LMg(Me)\cdot OEt_2$ with LAlMe(OH) generates the heterobimetallic species containing the Mg–O–Al moiety. Additionally, the reaction of methylmagnesiumchloride with the free ligand leads to complex L'MgCl (L' = $CH[Et_2NCH_2CH_2N(CMe)]_2$). As revealed by the crystal structure, L'MgCl is a solvent free monomeric magnesium chloride complex that is analogues to the Grignard reagent.

Introduction

In recent years, the *β*-diketiminate ligands have emerged as potential spectator ligands, in view of their strong binding to metals, their tunable steric and electronic effects, and diversity in bonding modes.[1] Usage of this ligand has witnessed an impressive growth in main group metal chemistry in the last decade. A very important breakthrough, particularly in the alkaline earth metal chemistry, has been the synthesis of *β*-diketiminate stabilizied magnesium(I) complexes by *Jones* and coworkers.[2] In this paper we are discussing a facile route for the synthesis and characterization of *β*-diketiminate stabilized magnesium hydroxide, heterobimetallic, and halide complexes.

There is a great interest in the synthesis and characterization of novel main group hydroxide complexes due to their potential application as precursor for the synthesis of heterobi- and heteropolymetallic compounds that can act as versatile catalysts in organic transformations.[3, 4] In addition, the hydroxide complexes can function as model compounds for the insoluble or unstable metal hydroxides $M(OH)_x$. In view of these applications, we have reported earlier on the syntheses and reaction chemistry of various molecular hydroxide complexes such as the N-bonded silanetriol[3,4] $RSi(OH)_3$ (R = $2,6\text{-}iPr_2C_6H_3NSiMe_3$), the Al^{III} and Ga^{III} dihydroxides $LM'(OH)_2$,[5,6] and the Al^{III} and Ga^{III} monohydroxide[7] by tailor-made synthetic strategies and unveiled their reactivity. Recently, our group also reported a unprecedented germylene hydroxide LGe(OH), which contains a hydroxyl group attached to a Ge^{II} atom.[8] These examples portray the evolution of the groups 13 and 14 hydroxide chemistry. Nevertheless, the organometallic hydroxide chemistry with respect to group 2 elements is still at its infancy. This is partly due to the higher percentage of the ionic character in the M–OH (M = an alkaline earth metal) bond and also due to a fast ligand exchange, although very recently we have reported hydrocarbon soluble heavier alkaline earth metal hydroxides $[LCa(OH)\cdot THF]_2$ and $[LSr(OH)\cdot THF_{1.5}]_2$.[9]

The magnesium hydroxide[10a] complex $\{[Tp^{Ar,Me}]Mg(\mu\text{-}OH)\}_2$ (Ar = $p\text{-}tBuC_6H_4$) stabilized by the *tris*(1-pyrazolyl)hydroborate ($Tp^{Ar,Me}$) ligand was prepared by *Parkin* et al. Another example of a magnesium hydroxide $[LMg(OH)\cdot THF]_2\cdot 4THF$ was obtained by *Bochmann* and coworkers.[10b] The latter compound was isolated by serendipity, when $LMg(\eta^1\text{-}C_3H_5)(THF)$ was kept at –26 °C for crystallization and it lacks a direct synthetic route. In view of the increasing importance of the heteroleptic complexes in polymerization reactions,[11] we attempted for the synthesis of a magnesium complex that contains both the halide and *β*-diketiminate ligand. In accordance with the theoretical studies on RM–MR complexes[12] of group 2 elements, the *β*-diketiminate stabilized group 2 metal halides could also be considered as promising precursor to prepare compounds with low valent group 2 elements containing a metal-metal bond.[2,13]

Results and Discussion

Compound $[LMg(OH)\cdot THF]_2$ (**1**) was prepared by the reaction of $LMgN(SiMe_3)_2$[14] with a stoichiometric amount of water at –20 °C (Scheme 1). Compound **1** is a white solid soluble in toluene, THF, and sparingly soluble in benzene. It was char-

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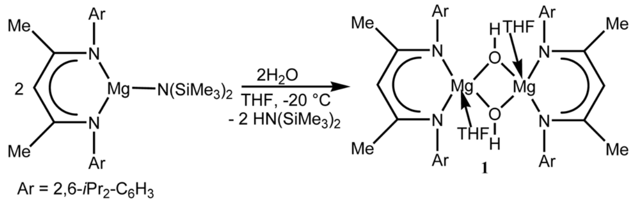
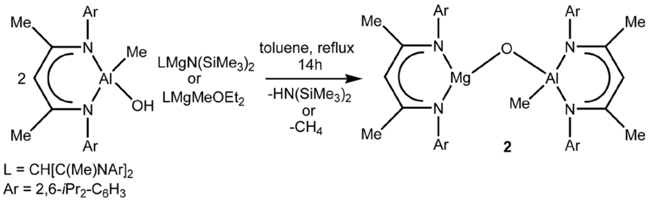
acterized by IR, ^{1}H NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. In the IR spectrum a sharp absorption around 3741 cm^{-1} can be attributed to the O–H stretching frequency. The ^{1}H NMR spectrum of **1** exhibits a resonance at –0.46 ppm for MgO–H. The base peak in the EI mass spectrum of **1** at *m*/*z* 916 corresponds to molecular ion [M$^+$]. The X-ray molecular structure of **1** is in agreement with that of *Bochmann* et al.[10b]



Scheme 1. Synthesis of *β*-diketiminate stabilized magnesium hydroxide **1**.

In our earlier report we have shown that soluble molecular compounds with Mg–O–Al skeleton are achieved by the reaction of Mg[N(SiMe$_3$)$_2$]$_2$ with aluminum monohydroxide.[15] This work was further extended by using LMgMe·OEt$_2$[16] or LMg–N(SiMe$_3$)$_2$.[14] The reaction of LAl(Me)OH[7b] with a stoichiometric amount of LMgMe·OEt$_2$[16] or LMg–N(SiMe$_3$)$_2$[14] in toluene at reflux temperature results in the formation of compound LMg–O–Al(Me)L (**2**) in excellent yield (Scheme 2). Compound **2** is a colorless crystalline solid that melts in the range 259–262 °C. It was characterized by ^{1}H NMR, IR spectroscopy, elemental analysis, EI mass spectrometry, and X-ray structural analysis. The ^{1}H NMR spectrum of **2** exhibits the Al–*Me* resonance at –1.42 ppm. The backbone protons of the ligand resonate at 4.82 and 4.92 ppm. Other resonances are typical for the *β*-diketiminate ligand. The EI mass spectrum of **2** reveals that the most intense peak appears at *m*/*z* 901 and corresponds to the loss of one methyl group from the molecular ion, [M$^+$ – Me].



Scheme 2. Preparation of *β*-diketiminate magnesium-aluminum oxide **2**.

X-ray quality crystals for **2**·THF were obtained after several attempts from a toluene/THF solution. The asymmetric unit contains both **2**·THF and LAl(Me)OH. Compound **2**·THF and LAl(Me)OH crystallize in the monoclinic space group *C*2/*c* (Table 1, Figure 1 shows only **2**·THF). The X-ray structural analysis of **2**·THF revealed that the magnesium and aluminum atoms are connected by a bridging oxygen atom. Interestingly, the magnesium and aluminum atoms are each arranged in a C_3N_2M six-membered ring. The arrangement around the magnesium, as well as the aluminum atom, is tetrahedrally distorted. The Mg–O distances (1.851(1)–2.095(1) Å) are in agreement with the Mg–O bond lengths in compounds L(Me)Al–O–Mg(THF)$_2$–N(SiMe$_3$)$_2$ and L(Me)Al–O–Mg(THF)$_2$–O–Al(Me)L (1.854–2.085 Å).[15] The Mg(1)–O(1)–Al(1) bond angle (157.62(1)°) is similar to those found in compounds L(Me)Al–O–Mg(THF)$_2$–N(SiMe$_3$)$_2$ and

Table 1. Crystallographic data for the X-ray structural analyses of compounds **2** and **3**.

parameter	**2**·THF·LAl(Me)OH	**3**·0.5 toluene
empirical formula	$C_{93}H_{138}Al_2MgN_6O_3$	$C_{20.50}H_{39}ClMg\,N_4$
formula weight	1466.36	401.32
T /K	100(2)	100(2)
crystal system	monoclinic	monoclinic
CCDC No	789418	789419
Space group	*C*2/*c*	$P2_1/c$
a /	20.462(2)	17.111(1)
b /	18.184(1)	7.133(1)
c /	47.396(3)	19.709(1)
α /°	90	90
β /°	100.98(2)	110.70(2)
γ /°	90	90
V /Å^3	17312(2)	2017.2(6)
Z	8	4
ρ_{calc} /Mg·m^{-3}	1.125	1.185
μ /mm^{-1}	0.092	0.210
F(000)	6400	876
reflections collected	52737	36297
Independent reflection	15817	4273
data/restraints/ parameters	15817/2/999	4273/0/266
GooF	0.0481, 0.1149	0.0303, 0.0796
$R1$, $wR2[I > 2\sigma(I)]^{a,\,b)}$	0.0593, 0.1208	0.0329, 0.0812
$R1$, $wR2$ (all data)	1.028	1.049
largest diff peak, hole /*e*·Å^{-3}	0.595, –0.348	0.575, –0.257

a) $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; b) $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$

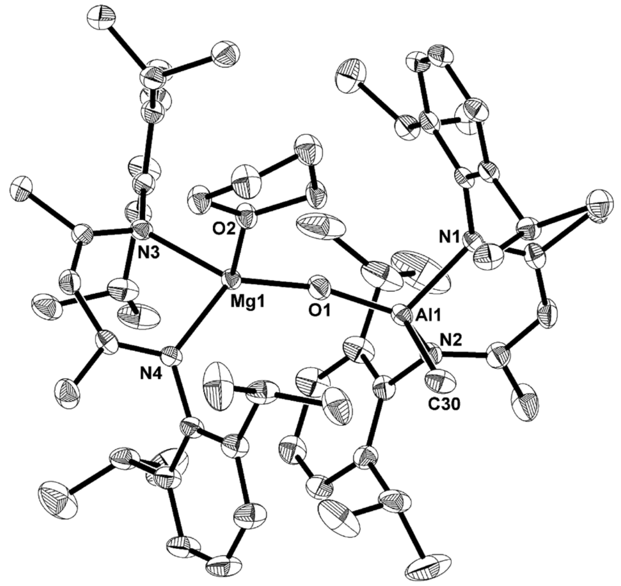
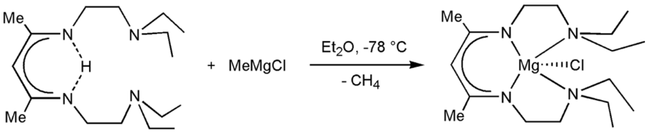


Figure 1. Molecular crystal structure of compound LMg(THF)(μ–O)Al(Me)L (**2**) depicted at 50 % probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /°: Mg(1)–O(1) 1.857(2), Mg(1)–N(3) 2.103(2), Mg(1)–N(4) 2.093(2), Al(1)–O(1) 1.684(1), Al(1)–N(1) 1.977(2), Al(1)–N(2) 1.945(2); Mg(1)–O(1)–Al(1) 157.62(1), N(1)–Al(1)–N(2) 93.56(1), N(3)–Mg(1)–N(4) 90.99(1).

L(Me)Al–O–Mg(THF)$_2$–O–Al(Me)L (Mg–O–Al av. bond angle 157.1°). The Al–C and Al–O distances are 1.982(2) and 1.684(2) Å respectively, which are in good agreement with those observed in [OCMeCHCMeNAr]$_2$AlMe (Ar = 2,6-iPr$_2$C$_6$H$_3$) (Al–C 1.975(2) Å) and [HC(CMeNMe)$_2$AlCl]$_2$(μ-O) (Al–O 1.677(2) Å).[17,18]

A clean reaction of L'H[19] (L' = CH[Et$_2$NCH$_2$CH$_2$N(CMe)]$_2$) with MeMgCl in diethyl ether at –78 °C leads to the evolution of methane gas, and the formation of compound L'MgCl (**3**) (Scheme 3). Compound **3** is a colorless solid and melts at 158–162 °C. It was characterized by ^{1}H NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray crystal structure analysis. The ^{1}H NMR spectrum of **3** exhibits a resonance at 4.74 ppm for the γ-H proton. The other chemical shifts are typical for the ligand L'. Moreover, the molecular ion of **3** was detected at m/z = 354.



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Scheme 3. Preparation of *β*-diketiminate magnesiumchloride L'MgCl (**3**).

Single crystals of **3** suitable for X-ray structural analysis were obtained from toluene with a small amount of THF solution. The compound crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit and half a molecule of disordered toluene located on a crystallographic inversion center (Figure 2, Table 1). The core of this structure is MgN$_4$Cl. The magnesium atom is surrounded by four nitrogen atoms of the monoanionic *β*-diketiminate ligand, and an axial chlorine atom. So, the magnesium atom is pentacoordinate and the coordination around the metal atom is distorted square pyramidal. The Mg–Cl bond length (2.360(1) Å) is shorter than that found in LMgI·OEt$_2$ (2.689(2) Å),[20] and [LFe(μ-Cl)$_2$]Mg(THF)$_4$ (2.520(1) Å).[21] The N(1)–Mg(1)–N(2) bond angle is compressed to 88.16(1)° due to the rigid ligand backbone, whereas the N(2)–Mg(1)–Cl(1) angle opens up to 109.47(1)°. The bond angle of N(2)–Mg(1)–N(1) (88.16(1)°) is more acute than that found in LMgI·OEt$_2$ (93.1°).

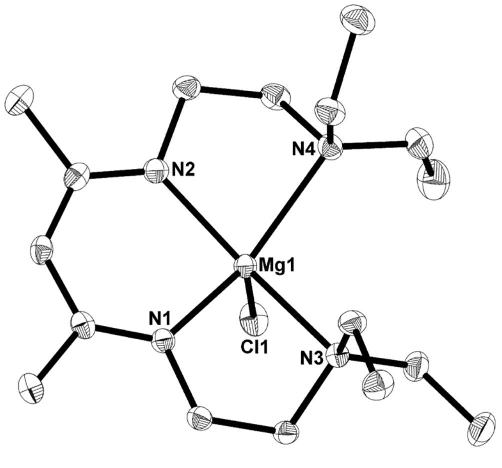

Figure 2. Molecular crystal structure of compound L'MgCl (**3**) depicted at 50 % probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /°: Mg(1)–N(1) 2.083(2), Mg(1)–N(2) 2.081(2), Mg(1)–N(3) 2.285(2), Mg(1)–N(4) 2.329(2), Mg(1)–Cl(1) 2.360(1); N(2)–Mg(1)–N(1) 88.16(1), N(2)–Mg(1)–Cl(1) 109.47(1), N(2)–Mg(1)–N(4) 78.47(1), N(1)–Mg(1)–N(3) 78.96(1), N(3)–Mg(1)–N(4) 97.51(1).

Conclusion

A facile route is described for the synthesis of a well-defined magnesium hydroxide complex of the formula [LMg(OH)·THF]$_2$ that is soluble in organic solvents. Access to this hydroxide could also be of interest in sol-gel coatings, and as polymerization catalyst. The heterobimetallic compound LMg(THF)–O–Al(Me)L has been prepared by the reaction of LMgN(SiMe$_3$)$_2$ or LMgMe·OEt$_2$ with LAl(Me)OH, in which the oxygen atom is linked to two six- membered MC$_3$N$_2$ (M = Mg, Al) rings. Furthermore, solvent free L'MgCl was prepared. The reduction of L'MgCl is ongoing in our laboratory and will be published in due course.

Experimental Section

All manipulations were performed under a dry and oxygen free atmosphere (N$_2$) using standard Schlenk techniques or inside a MBraun MB 150-GI glove box. All solvents were distilled from Na/benzophenone prior to use. Chemicals were purchased commercially and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 200 MHz instrument and referenced to the deuterated solvent in case of the ^{1}H and ^{13}C NMR spectra. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 450 instrument.

Preparation of Compound 1: Degassed and distilled water (46 μL, 2.55 mmol) was added to a solution of LMgN(SiMe$_3$)$_2$ (1.52 g, 2.53 mmol) in THF (30 mL) at –20 °C, and afterwards allowed to warm to room temperature. After stirring at room temperature for 15 min, the slurry was dried in vacuo. The resulting solid of **1** was washed with n-hexane (10 mL) and finally dried in vacuo. Yield: (0.810 g, 1.528 mmol, 60 %). Mp: 336–340 °C. C$_{58}$H$_{84}$Mg$_2$N$_4$O$_2$ (916): C 75.89, H 9.22, N 6.10; found: C 75.50, H 9.19, N 6.14 %. **^{1}H NMR** (200 MHz, C$_6$D$_6$, 25 °C, SiMe$_4$): –0.46 (s, 2 H, Mg–O*H*), 0.88 (d, J = 6.9 Hz, 24 H, CH(C*H*$_3$)$_2$), 1.11 (d, J = 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$), 1.30 (m, 8 H, O–CH$_2$–C*H*$_2$), 1.54 (s, 12 H, C*H*$_3$), 3.14 (sept, J = 6.8 Hz, 8 H, C*H*(CH$_3$)$_2$), 3.57 (m, 8 H, O–C*H*$_2$–CH$_2$), 4.81 (s, 2 H, *γ*-C*H*), 7.11 (s, 12 H, *m-*, *p*-Ar–*H*) ppm. **^{1}H NMR** (500 MHz, [D$_8$]THF, 25 °C, SiMe$_4$): –1.41 (s, 2 H, Mg–O*H*), 0.89 (d, J = 6.9 Hz, 24 H, CH(C*H*$_3$)$_2$), 1.01 (d, J = 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$), 1.43 (s, 12 H, C*H*$_3$), 1.80 (m, 8 H, O–CH$_2$–C*H*$_2$), 2.97 (sept, 8 H, J = 6.9 Hz, C*H*(CH$_3$)$_2$), 3.70 (m, 8 H, O–C*H*$_2$–CH$_2$), 4.63 (s, 2 H, *γ*-C*H*), 7.11 (s, 12 H, *m-*, *p*-Ar–*H*) ppm; **^{13}C{^{1}H} NMR** (125.75 MHz, C$_6$D$_6$, 25 °C, SiMe$_4$): 19–23, 26, 28.2, 29.5, 96, 70, 127–145 ppm. **EI-MS** (70 eV): m/z (%): 916 (100) [M$^+$]. **IR** (Nujol) $\tilde{\nu}$ = 3741 (MgO–H), 3669, 1624, 1552, 1315, 1176, 1100, 1022, 931, 794, 759, 703 cm^{-1}.

Preparation of Compound 2: LAl(Me)OH (0.47 g, 1.0 mmol) dissolved in toluene (20 mL) was added drop by drop at room temperature to a stirred solution of $LMgN(SiMe_3)_2$ (0.60 g, 1.0 mmol) or $LMgMe{\cdot}OEt_2$ (0.530 g, 1.0 mmol) in toluene (20 mL). The solution was set to reflux for 14 h. After removal of all the volatiles in vacuo compound **2** remained as a solid. Yield (0.82 g, 89 %). Mp: 259–262 °C. $C_{59}H_{85}AlMgN_4O$ (916): C 77.29, H 9.28, N 6.11; found: C 76.77, H 9.13, N 6.06 %. **^{1}H NMR** (200 MHz, C_6D_6, 25 °C, $SiMe_4$): –1.42 (s, 3 H, Al–CH_3), 1.08 (d, 12 H, $CH(CH_3)_2$), 1.22 (d, 24 H, $CH(CH_3)_2$), 1.31 (d, 12 H, $CH(CH_3)_2$), 1.52 (s, 6 H, CH_3), 1.64 (s, 6 H, CH_3), 3.25 (sept, 6 H, $CH(CH_3)_2$)), 3.75 (sept, 2 H, $CH(CH_3)_2$)), 4.82 (s, 1 H, γ-CH), 4.92 (s, 1 H, γ-CH), 7.08–7.16 (m, 12 H, *m*-, *p*–Ar–H) ppm; **^{13}C{^{1}H} NMR** (125.75 MHz, C_6D_6, 25 °C, $SiMe_4$): –3.3, 25.4, 25.5, 26.1, 26.2, 35.5, 43.2, 97.3, 141.3, 147.5. **EI-MS** (70 eV): *m*/*z* (%): 901 (100) [M^+ – Me], 916 (6) [M^+]. **IR** (Nujol) $\tilde{\nu}$ = 1860, 1795, 1733, 1619, 1530, 1440, 1318, 1261, 1176, 1100, 1021, 955, 798, 760, 722, 623 cm^{-1}.

Preparation of Compound 3: To a solution of L'H (1.04 g, 3.3 mmol) in diethyl ether (15 mL) was slowly added drop by drop a solution of MeMgCl (3 m in THF, 1.04 mL, 3.3 mmol) in diethyl ether (20 mL) at –78 °C. The stirring was continued for 1 h at this temperature. When the solution was allowed to warm to room temperature, an evolution of methane gas was observed, and stirring was continued at ambient temperature for 12 h. The volatiles were removed in vacuo and the residue was washed with *n*-pentane (15 mL). The solid was dissolved in toluene (20 mL) and overnight storage of this solution at –32 °C resulted in colorless crystals of **3**. Yield: 1.20 g (63.5 %). Mp: 158–162 °C. $C_{20.5}H_{39}ClMgN_4$ (401.32): C 61.35, H 9.79, N 13.96; found: C 60.89, H 9.56, N 13.75 %. **^{1}H NMR** (200 MHz, C_6D_6, 25 °C, $SiMe_4$): 0.8 (t, 12 H, CH_2CH_3), 1.81 (s, 6 H, CH_3), 2.61 (t, 4 H, CH_2CH_2N),), 2.62–2.68 (q, 8 H, CH_3CH_2N), 3.01 (t, 4 H, CH_2CH_2N), 4.74 (s, 1 H, γ-CH) ppm; **^{13}C{^{1}H} NMR** (125.75 MHz, C_6D_6, 25 °C, $SiMe_4$): 15.4, 17.1, 22.2, 23.1, 40.3, 47.8, 93.2, 140.2, 145.6 ppm. **EI-MS** (70 eV): *m*/*z* (%): 354 (5) $[M]^+$, 319 (15) $[M – Cl]^+$, 86 (100) $[C_5H_{12}N]^+$

Crystal Structure Determination

Shock cooled crystals were selected and mounted under nitrogen atmosphere using the X-TEMP.[22] The data for **2**·THF was collected at 100(2) K using a INCOATEC Mo Microsource[23] with Quazar mirror optics and APEX II detector with a D8 goniometer. The data of **3**·0.5 toluene was measured using a Bruker TXS-Mo rotating anode with Helios mirror optics and APEX II detector with a D8 goniometer. Both diffractometers were equipped with a low-temperature device and used Mo-K_α radiation, λ = 0.71073 Å. The data of **2**·THF and **3**·0.5toluene were integrated with SAINT[24] and an empirical absorption (SADABS) was applied.[25] The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[26] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to equal to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and isotropic displacement parameters restraints. CCDC-789418, -789419 contain the supplementary crystallographic data for compounds **2** and **3** of 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.

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