Terminal OH-Containing Alumoxane

Synthesis, Structural Characterization, and Reaction of the First Terminal Hydroxide-Containing Alumoxane with an [$\{Al(OH)\}_2(\mu\text{-}O)$] Core**

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Dedicated to Professor Alan H. Cowley
on the occasion of his 70th birthday

Considerable attention has been focused on the investigations of their structure and mode of catalytic activity of alumoxanes since the discovery of methylalumoxane (MAO) as a highly active cocatalyst in ethylene and propylene polymerization by group 4 metallocenes in 1980.[1] The role of MAO seems clear,[2] but the molecular structure of the active alumoxane species remains an open question. In the course of numerous investigations of the controlled hydrolysis of aluminum compounds, some alumoxanes have been isolated and structurally characterized by introducing bulky alkyl or aryl groups in place of methyl groups,[3] but none of them perform as well as MAO in the metallocene mediated olefin polymerization. Although three coordinate aluminum sites are present in the compounds in which oligomerization is sterically hindered by bulky ligands,[4] alumoxanes containing terminal hydroxide are very rare.

Recently we demonstrated that the liquid ammonia/toluene two phase system is highly effective for the hydrolysis and ammonolysis of transition metal compounds. The organozirconium oxide and hydroxide clusters [$\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot(C_7H_8)$,[5] [$(Cp^*Zr)_6(\mu_4\text{-}O)(\mu\text{-}O)_4(\mu\text{-}OH)_8]\cdot 2(C_7H_8)$,[6] and related systems[7] were prepared by the hydrolysis and ammonolysis of metal chlorides in a liquid ammonia/toluene two-phase system at low temperatures. More recently, the first hydrolysis by a main-group metal halide in a two phase system led to an unprecedented congener of boronic acid $LAl(OH)_2$ (**1**; L = HC[(CMe)(2,6-iPr$_2$C$_6$H$_3$N)]$_2$).[8] Herein we report on the synthesis of the first dinuclear alumoxane that contains a terminal hydroxide and a six-membered alumoxane with a three coordinate Al center and two coordinate O atoms.

The reaction of $LAlI_2$ (**2**) with KOH that contained 10–15% H_2O (1.0:0.71 molar ratio of pure KOH) and KH (1.0:1.4 molar ratio) in liquid ammonia and toluene at −78 °C results in the complete removal of iodide and the formation of

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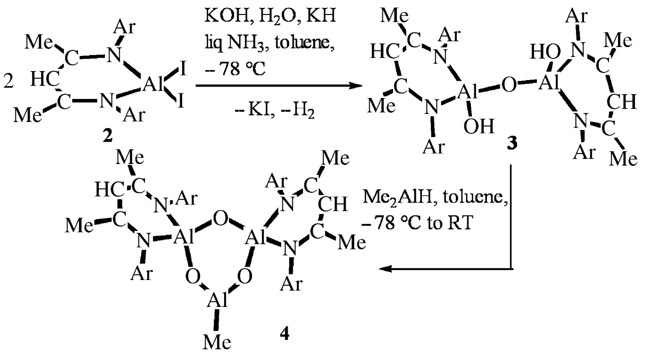
β-diketiminatoalumoxane $[\{LAl(OH)\}_2(\mu\text{-}O)]\cdot 0.5(C_7H_8)\cdot C_6H_{14}$ (**3**; Scheme 1). A proposed mechanism for the formation of **3** is similar to that of **1**.[8] In this reaction dihydroaluminum **1** is obtained as an intermediate in the first steps. Meanwhile, we assume that the amidohydroaluminum $\{LAl(OH)(NH_2)\}$ intermediate is formed because of the excess of the starting material **2**. After intermolecular ammonia elimination, the two intermediates are converted to **3**. However, no $\{LAl(OH)(NH_2)\}$ was found after the reaction was complete. Moreover, it is well documented that ammonolysis of aluminum triiodide yields potassium aluminate $KAl(NH_2)_4$ in the presence of K or $K(NH_2)$ in liquid ammonia.[9] We suppose that the excess of **2** and the intermediate $[LAl(OH)(NH_2)]$ react with KNH_2 (resulting from the reaction of KH and NH_3), thus leading to insoluble or noncrystalline products under the above condition. Furthermore, increase of the molar ratio of **2**:(KOH+H_2O), such as 1.0 to 1.5, led to the mixture of products **1** and **3**. Therefore, we assume that the liquid ammonia/toluene two phase system and the excess of **2** and KH in this reaction are essential for the formation of **3**, and the bulky L ligand on aluminum is stabilizing the terminal hydroxide-containing alumoxane. Further reaction of **3** with Me_2AlH (1.0:1.0 molar ratio) in toluene results in the formation of trimeric alumoxane $[(LAl)_2(MeAl)(\mu\text{-}O)_3]\cdot 2\,C_7H_8$ (**4**; Scheme 1). The steric hindrance of the L ligands attached to two Al atoms leads to the coordinatively unsaturated third Al atom in **4**.



Ar = 2,6-$iPr_2C_6H_3$

Scheme 1. Synthesis of **3** and **4**.

Compounds **3** and **4** are colorless crystalline solids with melting points of 265 and 152 °C, respectively. No decomposition or polymerization was observed when **3** or **4** were kept in the toluene solution or as solids in a glove box. The most intense peak in the EI mass spectrum of **3** appears at m/z 905 $[M^+-0.5\,C_7H_8-C_6H_{14}-H_2O-Me]$, and the signal at 938 (42%) is assigned to the $[M^+-0.5\,C_7H_8-C_6H_{14}]$ fragment. Compound **4** exhibits the fragments $[M^+-2\,C_7H_8]$, $[M^+-2\,C_7H_8-Me]$ and $[L^+-Me]$ at 979 (56), 964 (48) and 403 (100), respectively. In the IR spectrum of **3**, a sharp band (3716 cm^{-1}) for the stretching frequency of the free hydroxide is observed.

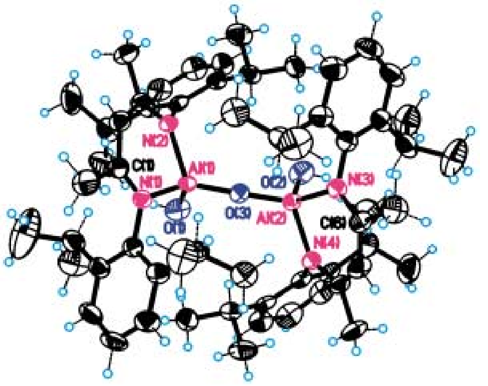


Figure 1. The crystal structure of **3**. The toluene and hexane molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)-O(1) 1.738(3), Al(1)-O(3) 1.698(3), Al(2)-O(2) 1.741(3), Al(2)-O(3) 1.694(3), Al(1)-N(1) 1.912(3), Al(1)-N(2) 1.928(3), Al(2)-N(3) 1.911(3), Al(2)-N(4) 1.919(3); O(1)-Al(1)-O(3) 112.33(14), O(1)-Al(1)-N(1) 111.76(15), O(1)-Al(1)-N(2) 106.84(13), N(1)-Al(1)-N(2) 95.64(13), Al(1)-O(3)-Al(2) 143.84(16).

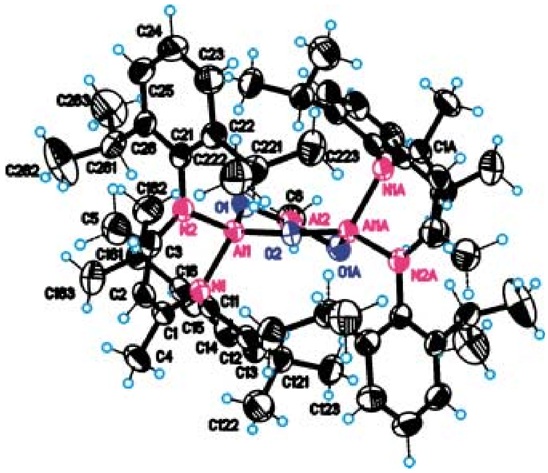


Figure 2. The crystal structure of **4**. The two toluene molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)-O(1) 1.726(2), Al(1)-O(2) 1.7122(16), Al(2)-O(1) 1.708(2), Al(1)-N(1) 1.930(3), Al(1)-N(2) 1.909(2); O(1)-Al(1)-O(2) 108.28(11), O(1)-Al(1)-N(1) 101.23(11), O(1)-Al(1)-N(2) 125.16(11), N(1)-Al(1)-N(2) 95.26(11), Al(1)-O(1)-Al(2) 117.69(13), Al(1)-O(2)-Al(1A) 125.73(18), O(1)-Al(2)-O(1A) 115.53(16).

The molecular structures of **3** and **4**[10] are shown in Figure 1 and Figure 2, respectively. Compounds **3** and **4** crystallize in the monoclinic space groups *P*2(1)/*n* and *C*2/*c*, respectively. Compound **3** contains a bent AlOAl species without a center of symmetry. Each of the Al atoms exhibits a highly distorted tetrahedral geometry with two nitrogen atoms of the ligand L, an OH group and one (μ-O) unit. The two ligands L adopt an approximately staggered *anti* conformation (the angles between the N(1)Al(1)N(2) and N(3)Al(2)N(4) planes are 87.70°), and the bulky *ortho* substituents (2,6-$iPr_2C_6H_3$) of the ligands L are arranged *trans* to each other at the same side of the two Al centers, which minimizes the steric repulsion between the two ligands. The OH groups are bent out of the Al(1)O(3)Al(2) plane (31.26° and 30.71°) towards the opposite side where the 2,6-$iPr_2C_6H_3$ substituents are oriented. The Al-(μ-O) bond lengths (1.698(3) and 1.694(3) Å) are comparable, and the

Al-(μ-O)-Al angle (143.84(16)°) is significantly smaller than those found in compounds $[\{[(Me_3Si)_2HC]_2Al\}_2(\mu\text{-}O)]$ (1.6877(4) Å; 180°),[11] $[\{(t\text{Bu})_2Al[NH(Me)CH_2CH_2NMe_2]\}_2](\mu\text{-}O)$ (1.690(7) Å; 173.0(4)°),[12] and $[\{HC[(CMe)(NMe)]_2AlCl\}_2(\mu\text{-}O)]$ (1.6770(6) Å; 180°).[13] The Al–OH bond lengths (1.738(3) and 1.741(3) Å) of **3** are significantly longer than those in **1** (1.6947(15) and 1.7107(16) Å),[8] but considerably shorter than those of the Al–(μ-OH) and Al–(μ_3-OH) bonds exhibited by compounds $[(Ph_2Si)_2O_3]_4Al_4(\mu\text{-}OH)_4$ (1.787(3) to 1.814(3) Å, average 1.800 Å),[14] $[\{Mes_2Al(\mu\text{-}OH)\}_2]\cdot 2\,THF$ (1.822 Å; Mes = mesityl),[3e] and $[Al_5(t\text{Bu})_5(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CPh)_2]$ (Al–(μ_3-OH), 1.914(5) to 2.086(4) Å; Al–(μ-OH), 1.820(3) to 1.828(3) Å).[15] The Al–N bond lengths (1.912(3) and 1.928(3) Å) are longer than those observed in **1** (1.8881(17) and 1.8903(16) Å) and $[\{HC[(CMe)(NMe)]_2AlCl\}_2(\mu\text{-}O)]$ (1.8611(16) and 1.8617(16) Å).[13]

The structure of **4** contains two four coordinate Al and one three coordinate Al linked by μ-oxo bridges to form a highly distorted six-membered $(AlO)_3$ ring. The coordination sphere of Al(1), Al(1A) or Al(2) is completed by two nitrogen atoms of L or one Me group, respectively. The Al(2)–(μ-O) bond lengths (1.708(2) Å) are slightly shorter than those of Al(1)–(μ-O) and Al(1A)-(μ-O) (1.7122(16) and 1.726(2) Å) in **4**, but longer than those in **3** and other dimeric compounds containing an $\{Al_2(\mu\text{-}O)\}$ unit. Furthermore, the Al–(μ-O) bond lengths of **3** are considerable shorter than those of the Al–(μ-OH) bonds found in the six-membered ring compound $[(t\text{Bu})_2Al(\mu\text{-}OH)]_3$ (1.846(3) to 1.851(2) Å) and in a complex containing three coordinate Al centers $[(t\text{Bu})_2Al\{\mu\text{-}OAl(t\text{Bu})_2\}]_2$ (1.750(3) to 1.871(4) Å).[4a]

It has been demonstrated that compounds with linear centrosymmetric $\{Al_2(\mu\text{-}O)\}$ building units have significant Al-(μ-O) double bond character.[16] Compound **3** contains a bent $\{Al_2(\mu\text{-}O)\}$ unit but short Al-(μ-O) bonds, which should increase the steric interaction between the bulky L groups on adjacent aluminum atoms. The calculated molecular electrostatic potential (MESP) isosurface of **3** is presented in Figure 3.[17] The negative potential regions ($-20\ \text{kcal mol}^{-1}$) of the lone pairs arrange outside of the one bridged and two terminal oxygen atoms, which interact with the π electrons of the two aryl rings. Because of this interaction the π electron density in the MESP map of the two aromatic rings becomes stronger. The bending of the Al-O-Al bond (143.86°) leads to an effective overlap of the lone pairs of the oxygen atoms with the π electrons of the two aromatic rings. The argument that the lone pair electron density of the bridged oxygen atom is partially transferred to the aromatic rings is supported by the partial double bond character of the Al-(μ-O) bonds.

Because of the Lewis acidic Al^{3+} centers, the OH groups of **3** are expected to function as Brönsted acids. The solid state IR spectrum (Nujol) of **3** exhibits a sharp band ($3716\ \text{cm}^{-1}$) for the OH groups, which is similar to that found for the free OH groups of compound **1** ($3727\ \text{cm}^{-1}$). Therefore, **3** contains free and strong Brönsted acidic OH groups.[18] Furthermore, these protons of the OH groups are expected to resonate at very low field in the ^{1}H NMR spectrum. However, no resonance was observed at low field in the ^{1}H NMR spectrum of **3**. It can be clearly seen that the protons of the two OH groups are surrounded by the two aromatic rings because of the high π electron density of the aromatic rings in **3** (Figure 3). As a result the aromatic rings give rise to unusual shielding, which causes the two OH protons to resonate at high field ($\delta = -0.30$ ppm).

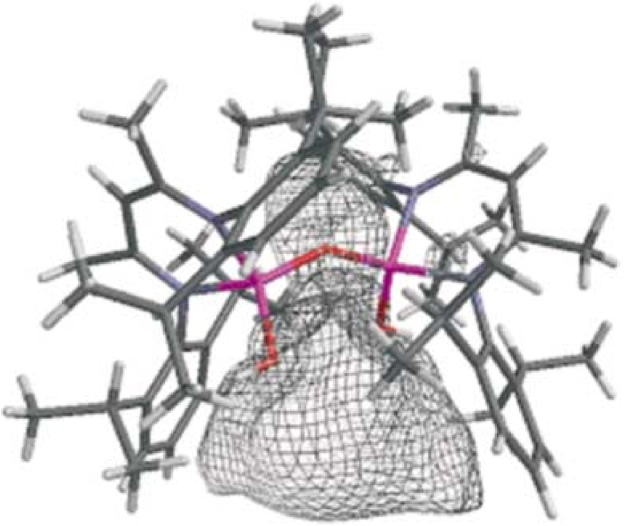


Figure 3. The calculated molecular potential isosurfaces ($-20\ \text{kcal mol}^{-1}$) for **3** (area: 150.67 Å^2, volume: 95.19 Å^3) at the HF/STO-3G level, showing the interaction of the lone pairs on the oxygen atoms and the π electrons of the aromatic rings.

It has been traditionally proposed that alumoxanes containing three coordinate Al centers are strong Lewis acids and vital for the catalytic activity. Although **4** contains a three coordinate Al center, no catalytic activity was observed when **4** was used as a cocatalyst for the dimethylzirconocene polymerization of ethylene in toluene solution at room temperature. This result is in agreement with that obtained by Barron and co-workers, although they used no methyl-containing aluminum three coordinate species.[19]

Herein, we present the hydrolysis of an aluminum compound that involves a liquid NH_3/toluene two phase system and yields the hitherto unknown $[\{LAl(OH)\}_2(\mu\text{-}O)]$ species. The partial transfer of the lone pair electron density of the three O atoms of **3** results in the formal double bond character of the Al–(μ-O) bonds and in a stronger electron density of the two aromatic rings with the consequence that the two Brönsted acidic OH protons resonate at very high field in the ^{1}H NMR spectrum. Because of the presence of the Brönsted acidic OH groups, **3** should react with organometallic compounds, which provides possibilities in the field of design and synthesis of low molecular weight organoaluminum-containing compounds, such as **4**, and newer and unusual applications in the catalysis of olefins. Such an investigation is currently underway in our laboratories.

Experimental Section

Synthesis of **3**: Ammonia (40 mL) was condensed onto a suspension of **2** (1.50 g, 2.15 mmol), KOH (KOH > 85 %, H_2O 10–15 %; 0.10 g, 1.52 mmol KOH (85 %), 0.83 mmol H_2O (15 %)) and KH (0.12 g, 3.00 mmol) in toluene (80 mL) at −78 °C while the reaction mixture was stirred. The mixture was stirred continuously for an additional 1 h at this temperature. The excess ammonia was then allowed to evaporate from the reaction mixture over a period of 4 h. During this time the mixture was warmed slowly to room temperature. After filtration and subsequent concentration (to 5 mL) in vacuo, hexane (5 mL) was added to the filtrate. The resulting colorless solution was kept at −20 °C for two days to give colorless crystals of **3** (0.56 g). Yield 67 % (according to O containing reactants). Mp: 265 °C; IR (Nujol): $\tilde{\nu}$ = 3716, 1549, 1534, 1439, 1401, 1383, 1317, 1226, 1176, 1099, 1023, 975, 935, 873, 798, 760 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6; the sample isolated from toluene was used, in which one molecule of aluminum dimer contains one molecule of toluene): δ = 7.24–7.00 (m, *Ph*Me and *Ar*), 4.87 (s, 2H, γ-C*H*), 3.73 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 3.57 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*Me$_2$), 3.24 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 3.12 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*Me$_2$), 2.10 (s, 3H, Ph*Me*), 1.55 (d, $^3J_{HH}$ = 7.5 Hz, 6H, CH*Me*$_2$), 1.50 (s, C*Me*), 1.48 (d, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$), 1.45 (s, C*Me*) (18H), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.14, 1.13 (dd, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 0.82 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$), 0.73 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH*Me*$_2$), −0.30 ppm (s, 2H, O*H*); EI-MS: *m*/*z* (%): 938 (42) [$M^+ - 0.5\,C_7H_8 - C_6H_{14}$], 920 (19) [$M^+ - 0.5\,C_7H_8 - C_6H_{14} - H_2O$], 905 (100) [$M^+ - 0.5\,C_7H_8 - C_6H_{14} - H_2O - Me$]; elemental analysis calcd (%) for $C_{67.5}H_{102}Al_2N_4O_3$ (1071.5): C 75.7, H 9.6, N 5.2; found: C 75.1, H 9.4, N 5.2.

Synthesis of **4**: Me_2AlH (20 % in heptane, 0.29 g, 1.0 mmol) was added to the solution of **3** (1.07 g, 1.0 mmol) in toluene (60 mL) at −78 °C while the reaction mixture was stirred. The mixture was warmed slowly to room temperature and stirred continuously overnight at this temperature. After filtration and subsequent concentration (to 5 mL) in vacuo, the resulting colorless solution was kept at −20 °C for two weeks to give colorless crystals of **4** (0.61 g). After concentration of the filtrate to 3 mL, the solution was kept at −20 °C for three days and an additional crop of **4** (0.12 g) was formed. Yield 0.73 g (63 %). Mp: 152 °C; IR (Nujol): $\tilde{\nu}$ = 1550, 1533, 1466, 1382, 1318, 1252, 1178, 1024, 936, 904, 884, 798, 760, 729 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6): δ = 7.31–6.99 (m, *Ph*Me and *Ar*), 4.87 (s, 2H, γ-C*H*), 4.15 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*Me$_2$), 3.33 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 3.11, 3.06 (dsept, $^3J_{HH}$ = 6.8 and 6.7 Hz, 4H, C*H*Me$_2$), 2.10 (s, 6H, Ph*Me*), 1.58 (d, $^3J_{HH}$ = 6.5 Hz, 6H, CH*Me*$_2$), 1.48 (s, 6H, C*Me*), 1.46 (s, 6H, C*Me*), 1.42, 1.38 (dd, $^3J_{HH}$ = 6.8 and 6.9 Hz, 18H, CH*Me*$_2$), 1.12, 1.09 (dd, $^3J_{HH}$ = 7.0 and 7.1 Hz, 12H, CH*Me*$_2$), 0.87 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH*Me*$_2$), 0.72 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH*Me*$_2$), −1.48 ppm (s, 3H, *Me*); EI-MS: *m*/*z* (%): 979 (56) [$M^+ - 2\,C_7H_8$], 964 (48) [$M^+ - 2\,C_7H_8 - Me$], 403 (100) [L−Me]; elemental analysis calcd. for $C_{73}H_{101}Al_3N_4O_3$ (1163.5): C 75.3, H 8.7, N 4.8; found: C 74.5, H 8.7, N 4.8.

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[10] a) Crystal data for **3**: Single crystals of **3** suitable for X-ray structural analysis were obtained from a solution of toluene and hexane by maintaining the reaction mixture at −20 °C for one week. $C_{67.5}H_{102}Al_2N_4O_3$, M_r = 1071.49, monoclinic, space group *P*2(1)/*n*, a = 13.731(3) Å, b = 21.352(4) Å, c = 22.877(5) Å, β = 103.58(3)°, V = 6520.0(1) Å^3, Z = 4, ρ_{calcd} = 1.092 Mg m^{-3}, $F(000)$ = 2340, λ = 0.71073 Å, T = 203(2) K, $\mu(Mo_{K\alpha})$ = 0.090 mm^{-1}. Of the 16982 measured reflections, 8498 were independent (R_{int} = 0.0844). The final refinement converged at $R1$ = 0.0657 for $I > 2\sigma(I)$, $wR2$ = 0.1908 for all data. The final difference Fourier synthesis gave a min./max. residual electron density −0.425/+0.347 e Å^{-3}; b) Crystal data for **4**: Single crystals of **4** suitable for X-ray structural analysis were obtained from a solution of toluene by maintaining the reaction mixture at −20 °C for two weeks. $C_{73}H_{101}Al_3N_4O_3$, M_r = 1163.52, monoclinic, space group *C*2/*c*, a = 19.515(3) Å, b = 14.738(2) Å, c = 24.414(5) Å, β = 102.974(10)°, V = 6842.6(19) Å^3, Z = 4, ρ_{calcd} = 1.129 Mg m^{-3}, $F(000)$ = 2520, λ = 0.71073 Å, T = 200(2) K, $\mu(Mo_{K\alpha})$ = 0.103 mm^{-1}. Of the 5788 measured reflections, 5670 were independent (R_{int} = 0.0982). The final refinement converged at $R1$ = 0.0672 for $I > 2\sigma(I)$, $wR2$ = 0.2049 for all data. The final difference Fourier synthesis gave a min./max. residual electron density −0.457/+0.669 e Å^{-3}; c) Data for the structures **3** and **4** were collected on a Stoe-Siemens-AED2 four-circle diffractometer. Intensity measurements were performed on a rapidly cooled crystal with the dimensions 0.8 × 0.6 × 0.5 mm^3 in the range $7.04 \leq 2\theta \leq 45.02°$ and 1.0 × 0.5 × 0.4 mm^3 in the range $7.00 \leq 2\theta \leq 49.90°$ for **3** and **4**, respectively. The structures were solved by direct methods (SHELXS-97)[20] and refined with all data by full-matrix least-squares on F^2. The hydrogen atoms of C−H bonds were placed in idealized positions. CCDC 212660 and 212661 (**3** and **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cam-

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