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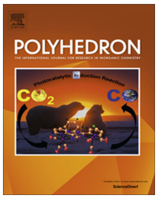

Synthesis and characterization of sterically encumbered aluminum thiolato complexes with rare Al/S/halide structural motifs

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ABSTRACT

The reaction of the bulky lithium terphenyl thiolates LiSAr^{Me6} (Ar^{Me6} = C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$) and LiSAr^{iPr4} (Ar^{iPr4} = C_6H_3-2,6-(C_6H_3-2,6-iPr$_2$)$_2$) with $AlBr_3$ in PhMe or Et_2O resulted in the formation of two new lithium aluminum thiolate salts LiAl(SAr^{Me6})$_2$Br$_2$·PhMe **1**, [LiAl(SAr^{Me6})Br$_3$]$_2$ **2**, and the etherate Al(SAr^{iPr4})Br$_2$(OEt$_2$) **3**. Compounds **1**–**3** were structurally characterized and analyzed by ^{1}H, ^{13}C NMR and IR spectroscopy. In further investigations the reduction of **1** and **2** with KC_8 or Rieke's magnesium in different solvent systems afforded the compounds KAl(SAr^{Me6})$_3$H·2PhMe **4** and LiAl(SAr^{Me6})Br$_{0.36}$I$_{1.64}$(2-THF)·PhMe **5**. All of the compounds described herein contain four-coordinate aluminum atoms with distorted tetrahedral geometries.

1. Introduction

Over the last two decades, a large variety of sterically-demanding ligands has been used to stabilize heavier main group organometallic compounds with unusual oxidation states, bonding, and coordination numbers. The group 13 metals Al–Tl have been prominent in these investigations [1,2]. In addition, group 13 metal derivatives of group 16 element ligands –ER (E = O, S, Se; R = organic group) have been investigated for their potential applications in the formation of binary materials [3,4] as well as in MOCVD (metal organic chemical vapour deposition) [5–7]. The synthesis and characterization of several group 13 metal thiolates have been reported. For example derivatives with aryl substituents such as Trip (C_6H_2-2,4,6-iPr$_3$) or Mes* (Mes* = C_6H_2-2,4,6-tBu$_3$) have been shown to have lower coordination numbers. For example the tristhiolato complexes M(SMes*)$_3$ (M = Al, Ga, In) [8,9] feature trigonal planar coordination at the metals. In addition, structural and spectroscopic data for the compounds Al(SMes*)$_2$R (R = nBu, tBu), Ga(Mes$^*_2$)(SR) (R = Me, Ph), Ga(SMes*)$_2$$n$Bu and [$tBu_2$AlSTrip]$_2$ indicate that M–S p–p π-bonding is weak with an upper limit of 22–38 kJ/mol to the π-bond energy. In the case of Mes$^*_2$GaSMe and Mes$^*_2$GaSPh restricted rotation barriers around the M–S bond were detected [10]. Reactions of the aluminumhydride (Mes*AlH$_2$)$_2$ with S(SiMe$_3$)$_2$ resulted in a dimeric chalcogenide derivative (Mes*AlS)$_2$ with three-coordinate aluminum atoms and two-coordinate sulfur atoms [11].

Gallium and indium derivatives of sterically demanding chalcogenolate ligands with m-terphenyl substituents have been studied also. These compounds were obtained by two different routes: in the first route, treatment of ArMMAr (M = Ga, In) (Ar = Ar^{iPr4} = C_6H_3-2,6-(C_6H_3-2,6-iPr$_2$)$_2$) with elemental sulfur in toluene afforded dimeric gallium and indium thiolates; in the second route reaction of LiSAr^{iPr4} with InCl in toluene (PhMe) resulted in a dimeric indium thiolate with an In_2S_2 core [12]. In general, aluminum thiolate compounds display high melting points above 300 °C indicating exceptionally high thermal stability. However, for aluminum chalcogenolates neither ArSAlAlSAr nor ArSAlCl are available as stable compounds. To synthesize organoaluminumthiolates, salt metathesis reactions with preformed thiolates are generally used. Herein we report on the reactivity of the ligands LiSAr^{Me6} and LiSAr^{iPr4} with $AlBr_3$ and investigate reductions of the products using reducing agents such as KC_8 and Rieke's magnesium [13].

2. Experimental

2.1. General procedures

All manipulations were carried out with the use of modified Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All solvents were dried by the method of Grubbs and degassed three times prior to use. $AlBr_3$ was sublimed prior to use. HSAr^{Me6} [14] and HSAr^{iPr4} [15] were prepared according to literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian 600 MHz instrument and referenced to the C_6D_6 solvent. Melting points were recorded in glass

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capillaries sealed under N_2 and are uncorrected. IR data were recorded in the range 4000–200 cm^{-1} as a Nujol mull between CsI plates using a Perkin Elmer PE-1430 spectrometer.

2.2. $LiAl(SAr^{Me6})_2Br_2\cdot PhMe$ (**1**)

$LiSAr^{Me6}$ (1.41 g, 4 mmol) in PhMe (ca. 25 mL) was added dropwise over 30 minutes to a toluene solution (ca. 20 mL) of $AlBr_3$ (0.53 g, 2 mmol) cooled to ca. 0 °C with an ice bath. A white precipitate formed immediately. After 45 minutes, the solution was allowed to warm to ambient temperature and was stirred for one day. The solution was filtered over celite and all volatile components were removed under reduced pressure. The colorless residue was extracted with PhMe (ca. 40 mL) and was concentrated to ca. 15 mL and stored at ca. 7 °C for 2 days to produce colorless cube-like crystals of **1** (1.32 g, 1.35 mmol, 68% based on aluminum, m. p. 308–310 °C).

^1H NMR (599.7 MHz, C_6D_6, 294 K): $\delta = 2.11$ (s, 24H, *o*-CH_3), 2.17 (s, 12H, *p*-CH_3), 6.80 (s, 8H, $C_6H_2Me_3$), 6.83 (d, 4H, *m*-C_6H_3, $^3J_{H,H} = 7.62$ Hz), 6.97 (t, 2H, *p*-$C_6H_{3,}$ $^3J_{H,H} = 7.62$ Hz);

$^{13}C\{^1H\}$ NMR (150.8 MHz, C_6D_6, 296 K): 21.3 (*p*-CH_3), 21.7 (*o*-CH_3), 125.7 (*p*-C_6H_3), 127.1 (*m*-$C_6H_2Me_3$), 128.4 (*m*-C_6H_3), 128.6 (*o*-C_6H_3), 129.2 (*o*-$C_6H_2Me_3$), 129.3 (*p*-$C_6H_2Me_3$), 137.0 (*i*-$C_6H_2Me_3$), 137.9 (*i*-C_6H_3).

FT-IR (nujol, cm^{-1}): 1590 (m, sharp), 1540 (w, medium), 1430 (strong, broad), 1355 (strong, medium), 1035 (w, sharp), 155 (w, sharp), 1065 (w, sharp), 1015 (m, medium), 835 (s, sharp), 825 (s, sharp), 780 (s, sharp), 725 (s, sharp), 715 (s, sharp), 705 (s, sharp), 670 (w, sharp), 560 (w, sharp), 440 (m, sharp), 400 (s, sharp), 380 (s, sharp), 345 (m, sharp), 320 (w, medium), 265 (w, medium), 220 (w, sharp).

2.3. $[LiAl(SAr^{Me6})Br_3]_2$ (**2**)

$LiSAr^{Me6}$ (0.70 g, 2 mmol) in PhMe (ca. 12.5 mL) was added dropwise over 30 minutes to a PhMe solution (ca. 20 mL) of $AlBr_3$ (0.53 g, 2 mmol) cooled to ca. 0 °C with an ice bath. A white precipitate formed immediately. After 45 minutes, the solution was allowed to warm to ambient temperatures and was stirred for one day. The solution was filtered over celite and all volatile components were removed under reduced pressure. The colorless residue was extracted with PhMe (ca. 40 mL), concentrated to ca. 15 mL and stored at ca. −20 °C for 2 days to produce X-ray quality, colorless rod-like crystals of **2** (1.313 g, 1.06 mmol, 53% based on aluminum).

^1H and $^{13}C\{^1H\}$ NMR spectroscopy were prevented by the low solubility of **2** in solvents with which it did not react. m.p. >250 °C.

FT-IR (nujol, cm^{-1}): 1606 (s, sharp), 1562 (m, medium), 1455 (s, broad), 1380 (s, broad), 1085 (m, medium), 1110 (m, medium), 1092 (m, medium), 1034 (s, broad), 980 (m, sharp), 918 (m, sharp), 874 (s, sharp), 856 (s, sharp), 808 (s, sharp), 781 (m, sharp), 751 (s, sharp), 735 (s, sharp), 728 (s, sharp), 592 (m, sharp), 518 (m, sharp), 485 (s, medium), 442 (s, sharp), 405 (s, medium), 378 (s, medium), 345 (s, medium), 325 (s, medium), 270 (m, broad), 248 (m, sharp).

2.4. $Al(SAr^{iPr4})Br_2(OEt_2)$ (**3**)

$LiSAr^{iPr4}$ (0.87 g, 2 mmol) in diethyl ether (ca. 50 mL) was added dropwise over 30 minutes to a diethyl ether solution (ca. 15 mL) of aluminum tribromide (0.53 g, 2 mmol) cooled to ca. −78 °C with a dry ice ethanol bath. Within 4 hours, the solution was allowed to warm to ambient temperatures and was stirred for two days. The solution was filtered with a filter-tipped cannula and all volatile components were removed under reduced pressure. The colorless residue was extracted with hexane (ca. 40 mL) and was concentrated to ca. 12 mL. Colorless plate-like crystals of **3** formed after 10 hours at room temperature (0.58 g, 0.84 mmol, 42%, m.p. 163–165 °C).

^1H NMR (599.7 MHz, C_6D_6, 294 K): $\delta = 0.49$ (t, 6H, CH_3, OEt_2, $^3J_{H,H} = 6.98$ Hz), 1.14 (d, 12H, CH_3, *o*-$CH(CH_3)_2$ $^3J_{H,H} = 6.81$ Hz), 1.54 (d, 12H, CH_3, *o*-$CH(CH_3)_2$, $^3J_{H,H} = 6.77$ Hz), 3.07 (sept, 4H, CH, *o*-$CH(CH_3)_2$, $^3J_{H,H} = 6.63$ Hz), 3.25 (quart, 4H, CH_2, OEt_2, $^3J_{H,H} = 6.95$ Hz), 7.13 (t, 1H, *p*-C_6H_3, $^3J_{H,H} = 7.38$ Hz), 7.25 (d, 4H, *m*-C_6H_3-2,6-*i*Pr_2, $^3J_{H,H} = 7.07$ Hz), 7.25 (d, 2H, *m*-C_6H_3, $^3J_{H,H} = 7.07$ Hz), 7.31 (t, 2H, *p*-C_6H_3-2,6-*i*$Pr_{2,}$ $^3J_{H,H} = 7.31$ Hz).

$^{13}C\{^1H\}$ NMR (150.8 MHz, C_6D_6, 296 K): 13.3 (CH_3, OEt_2), 24.3 (*o*-$CH(CH_3)_2$), 26.5 (*o*-$CH(CH_3)_2$), 31.2 (*o*-$CH(CH_3)_2$), 70.1 (CH_2, OEt_2)), 123.3 (*p*-C_6H_3), 125.7 (*m*-C_6H_3-2,6-*i*Pr_2), 128.4 (*m*-C_6H_3), 131.2 (*o*-C_6H_3), 133.4 (*o*-C_6H_3-2,6-*i*Pr_2), 140.7 (*p*-C_6H_3-2,6-*i*Pr_2), 146.3 (*i*-C_6H_3-2,6-*i*Pr_2), 147.3 (*i*-C_6H_3)

FT-IR (nujol, cm^{-1}): 1575 (w, sharp), 1445 (strong, broad), 1380 (strong, broad), 1360 (strong, sharp), 1325 (m, sharp), 1285 (w, sharp), 1090, (m, sharp), 1055 (m, sharp), 1040 (m, sharp), 990 (s, broad), 870 (strong, sharp), 865 (m, sharp), 820 (m, sharp), 805 (s, sharp), 790 (s, sharp), 755 (s, sharp), 515 (m, sharp), 435 (m, sharp), 415 (m, sharp).

2.5. $KAl(SAr^{Me6})_3H\cdot 2PhMe$ (**4**)

Method **A**: A suspension of KC_8 (0.141 g, 1.04 mmol) in PhMe (ca. 20 mL) was cooled to ca. −78 °C. To this suspension was added dropwise a solution of $LiAl(SAr^{Me6})_2Br_2\cdot PhMe$ (0.78 g, 0.8 mmol) dissolved in PhMe (ca. 30 mL). The reaction mixture was slowly warmed to room temperature and stirred for 48 h at room temperature resulting in a colorless reaction mixture. The solution was filtered over celite, concentrated to ca. 12 mL and stored at ca. −20 °C to give colorless plate-like crystals (0.208 g (0.162 mmol, 20% based on aluminum, m. p. 316–319 °C).

Method **B**: A suspension of KC_8 (0.224 g, 1.7 mmol) in Et_2O (ca. 20 mL) was cooled to ca. −78 °C. To this suspension was added dropwise a solution of $LiAlBr_2(SAr^{Me6})_2\cdot PhMe$ (0.77 g, 0.79 mmol) dissolved in Et_2O (ca. 30 mL). The reaction mixture was slowly warmed to room temperature and stirred for 48 h at room temperature resulting in a colorless reaction mixture. The solution was concentrated to dryness and extracted in ca. 40 mL of PhMe. Concentration to ca. 12 mL and storage at −20 °C yielded **3** (0.198 g, 0.154 mmol, 19% based on aluminum, m. p. 316–319 °C).

^1H NMR (599.7 MHz, C_6D_6, 294 K): $\delta = 2.12$ (s, 24H, *o*-CH_3), 2.19 (s, 12H, *p*-CH_3), 3.19 (s, 1H, Al-H), 6.87 (s, 8H, $C_6H_2Me_3$), 6.91 (d, 4H, *m*-C_6H_3, $^3J_{H,H} = 7.62$ Hz), 7.01 (t, 2H, *p*-$C_6H_{3,}$ $^3J_{H,H} = 7.62$ Hz).

$^{13}C\{^1H\}$ NMR (150.8 MHz, C_6D_6, 296 K): 20.3 (*p*-CH_3), 21.2 (*o*-CH_3), 125.5 (*p*-C_6H_3), 125.7 (*m*-$C_6H_2Me_3$), 128.4 (*m*-C_6H_3), 128.6 (*o*-C_6H_3), 129.0 (*o*-$C_6H_2Me_3$), 129.3 (*p*-$C_6H_2Me_3$), 136.3 (*i*-$C_6H_2Me_3$), 137.5 (*i*-C_6H_3).

FT-IR (nujol, cm^{-1}): ν_{Al-H} 1905 (m, sharp), 1602 (m, sharp), 1555 (w, medium), 1450 (s, broad), 1382 (m, sharp), 1370 (s, sharp), 1250 (w, medium), 1030 (s, sharp), 840 (s, sharp), 790 (s, sharp), 766 (m, sharp), 736 (s, sharp), 718 (s, sharp), 582 (s, sharp), 455 (m, medium), 390 (m, medium), 325 (m, medium), 245 (m, sharp).

2.6. $LiAl(SAr^{Me6})Br_{0.36}I_{1.64}(2THF)\cdot PhMe$ (**5**)

Preparation of Rieke's magnesium via the KI-activated method [16]: $MgCl_2$ (0.24 g, 2.5 mmol), K (0.186 g, 4.75 mmol), and KI (0.415 g, 2.5 mmol) were weighed out in a drybox and suspended in ca. 20 mL THF. The mixture was refluxed for 3 h during which time the activated Mg formed. The solution was cooled to room temperature and used immediately. The suspension of Rieke's magnesium in THF was cooled to ca. 0 °C. To this suspension was added dropwise a PhMe solution of $[LiAl(SAr^{Me6})Br_3]_2$ prepared *in situ* (ca. 50 mL) according to 2.3. and stirred for 30 min. at ca. 0 °C. The reaction mixture was allowed to warm to room