Supporting Information

For

Unusual reactivity in organoaluminum and NHC chemistry: deprotonation of AlMe₃ by a NHC moiety involving the formation of a sterically bulky NHC/AlMe₃ Lewis adduct

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Experimental Details

General Procedures. All experiments were carried out under N₂ using standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene, pentane, and tetrahydrofuran were collected after going through drying columns (SPS apparatus, MBraun) and stored over activated molecular sieves (4 Å) for 24h in a glovebox prior to use. CH₂Cl₂, CD₂Cl₂, and C₆D₆ were distilled from CaH₂, degassed under a N₂ flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. All deuterated solvents were obtained from Eurisotop (CEA, Saclay, France). All other chemicals were purchased from Aldrich and were used as, with the exception of free carbene 1,3-di-*tert*-butylimidazolin-2-ylidene (1) purchased from T.C.I. Europe Corporation. The NMR spectra were recorded on Bruker AC 300 or 400 MHz NMR spectrometers , in Teflon-valved J-Young NMR tubes at ambient temperature, unless otherwise indicated. ¹H and ¹³C chemical shifts are reported vs. SiMe₄ and were determined by reference to the residual ¹H and ¹³C solvent peaks. Elemental analysis for all compounds were performed at the Services de Microanalyse of the Université de Strasbourg (Strasbourg France).

Synthesis of the Al-NHC complex η^1 -*C*-[{(N^tBu)C}₂C]AlMe₃ (2). In a glovebox, a precooled pentane solution (-35 °C, 5 mL) of free carbene 1,3-di-*tert*-butylimidazolin-2-ylidene (300.0 mg, 1.66 mg) was added dropwise via a pipette to a precooled (-35 °C) pentane solution (5 mL) of AlMe₃ (120.0 mg, 1.66 mmol) under vigorous stirring. The resulting colorless solution was allowed to warm to room temperature provoking, upon warming, the massive precipitation of a colorless solid. The latter suspension was stirred for 2h at room temperature after which it was filtered through a glass frit. The collected colorless solid was dried *in vacuo* to afford compound **2** as an analytically pure solid (343 mg, 82% yield). X-ray quality crystals were grown from a 1/10 CH₂Cl₂/pentane solution cooled -35 °C. Anal. Calcd for C₁₇H₁₉NO₂ (252.37): C 66.63; H 11.58; N 11.10; found: C, 66.27; H 11.71.

¹H NMR (300 MHz, CD₂Cl₂): $\delta = -0.73$ (s, 9H, Al*Me*), 1.73 (s, 18H, ^{*t*}Bu), 7.18 (s, 2H, CH). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): $\delta -0.8$ (Al*Me*₃), 31.4 (^{*t*}Bu), 59.1 (^{*t*}Bu), 117.4 (CH), 174.3 (C_{carbene}).

Synthesis of the "abnormal" Al-NHC complex 3. In a glovebox, a toluene (5 mL) solution of the analytically pure normal Al-NHC complex 2 (100 mg, 0.40 mmol) was stirred at room temperature for 20h. The solution was then evaporated to dryness to yield pure complex 3 (96 mg, 96% yield). X-ray quality crystals were grown from a 1/10 CH₂Cl₂/pentane solution cooled -35 °C. Anal. Calcd for C₁₇H₁₉NO₂ (252.37): C 66.63; H 11.58; N 11.10; found: C, 66.85; H 11.32. ¹H NMR (300 MHz, CD₂Cl₂): δ = -0.93 (s, 9H, Al*Me*), 1.62 (s, 9H, ^{*t*}Bu), 1.68 (s, 9H, ^{*t*}Bu), 7.13 (d, ⁴*J*_{HH} = 2 Hz, 1H, CH), 8.00 (d, ⁴*J*_{HH} = 2 Hz, 1H, CH). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ -6.1 (Al*Me*₃), 29.9 (^{*t*}Bu), 30.4 (^{*t*}Bu), 57.2 (^{*t*}Bu), 59.1 (^{*t*}Bu), 126.8 (CH), 128.6 (CH), 155.9 (C_{carbene}).

Synthesis of the liquid ionic species [1,3-di-*tert*-butylimidazolium][Me₃Al(μ^3 -CH₂)(AlMe₂)₂(μ^2 -CH₃)] (4). In a glove box, a dichloromethane solution (1 mL) of AlMe₃ (5 equiv., 2.00 mmol, 158.0 mg) was added at room temperature via a pipette to a stirring dichloromethane solution of the "normal" Al-NHC adduct complex 2 (100 mg, 0.40 mmol). The resulting colorless solution was stirred for 20h at room temperature and the volatiles were removed *in vacuo* to afford a colorless liquid, which was identified as salt species 4 on the basis of ¹H and ¹³C NMR data, X-ray crystallographic and elemental analysis. While compound 4 is liquid at room temperature, X-ray quality crystals of the salt species 4 could however be grown at -35 °C from a concentrated 10/1 pentane/CH₂Cl₂. Due to the dynamic behaviour of the aluminate anion Me₃Al(μ^3 -CH₂)(AlMe₂)₂(μ^2 -CH₃)⁻ in solution at room temperature, ¹³C {¹H} and DEPT NMR were recorded both at room temperature and at – 30

°C; these data are consistent with the aluminate anion in complex 2 essentially retaining its solid-state structure in solution.

Data for complex 4. Anal. Calcd for C₂₀H₄₇Al₃N₂ (396.56): C 60.57; H 11.95; N 7.06; found: C, 60.82; H 11.63. ¹H NMR (300 MHz, CD₂Cl₂): δ -0.83 (br, 26H, Al*Me* and Al*CH*₂), 1.71 (s, 18H, ^{*t*}Bu), 7.49 (s, 1H, CH), 8.19 (s, 1H, CH). ¹H NMR (400 MHz, CD₂Cl₂, 243 K): δ -1.04 (br. s, 2H, Al*CH*₂), -0.88 (br. s, 24H, AlMe), 1.74 (s, 18H, ^{*t*}Bu), 7.42 (s, 1H, CH), 8.15 (s, 1H, CH). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 243 K): δ -6.1 (Al*Me*₃), 29.9 (^{*t*}Bu), 30.4 (^{*t*}Bu), 57.2 (^{*t*}Bu), 59.1 (^{*t*}Bu), 126.8 (CH), 128.6 (CH), 155.9 (C_{carbene}). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 243 K): δ -6.4 (Al*C*H₂), -5.3 (Al*Me*), -4.5 (Al*Me*), 30.2 (^{*t*}Bu), 61.4 (^{*t*}Bu), 121.2 (CH), 129.4 (CH). **X-ray crystallographic analysis.** Single crystals of complexes **2**, **3** and **4** were mounted on a Nonius Kappa-CCD area detector diffractometer ($Mo \ K\alpha \ \lambda = 0.71073 \ \text{Å}$). The complete conditions of data collection (Denzo software) and structure refinements are given in table S1. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software.¹ The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Most of the hydrogen atoms were generated according to stereo-chemistry and refined using a riding model in SHELXL97 except those for atoms C(9) and C(11) in complex **3** and for atoms C(1)and C(17) in complex **4** (see the corresponding cif files). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC 752342-752344. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Formula	$C_{14}H_{29}AlN_2$ (2)	$C_{14}H_{29}AlN_{2}$ (3)	$C_{20}H_{47}Al_{3}N_{2}$ (4)
Formula weight	252.37	252.37	396.54
Crystal system	Monoclinic	Orthorhombic	monoclinic
Crystal size	0.32 0.19 0.10	0.30 0.15 0.11	0.20 0.20 0.10
Crystal Color	Colorless	Colorless	Colorless
Space group	P 2 ₁ /c	P n m a	$P 2_1/c$
a (Å)	9.4995(6)	15.7347(9)	12.036(1)
b (Å)	15.0660(10)	9.7457(3)	12.480(1)
c (Å)	11.2880(5)	10.8668(6)	19.024(2)
α (°)	90	90	90
β (°)	95.311(3)	90	105.60(5)
γ (°)	90	90	90
$\dot{V}(\dot{A}^3)$	1608.60(16)	1666.38(14)	2752.3(8)
Ζ	4	4	4
Density (g.cm ⁻³)	1.042	1.006	0.957
μ (Mo K α) (mm ⁻¹)	0.111	0.107	0.143
F(000)	560	560	880
Data collection			
Temperature (K)	173(2)	173(2)	173(2)
Theta min - max	2.15 - 27.48	2.28 - 27.48	2.22 - 27.51
Dataset[h, k, l]	-12/9, -18/19, -14/14	-20/18, -11/12, -14/12	-15/15, 0/16, 0/24
Tot., Uniq. Data, R(int)	12590, 3681, 0.1073	10157, 2018, 0.0789	9071, 6229, 0.00
Observed data (> 2σ)	2542	1364	2975
Refinement			
Nreflections, Nparameters	3681, 164	2018, 114	6229, 238
R2, R1, wR2,	0.0850, 0.0512, 0.1398	0.1001, 0.0586, 0.1578	0.1512, 0.0688, 0.2057,
wR1, Goof	0.1242, 1.041	0.1379, 1.029	0.1687, 0.937
Max. and Av. Shift/Error	0.000, 0.000	0.000, 0.000	0.000, 0.000
Min, Max. Res Dens. (e.A ⁻³)	-0.298, 0.307	-0.307, 0.366	-0.504, 0.537

 Table S1 : Crystal data and refinement details for complexes 2, 3 and 4.

¹ Sheldrick G.M. SHELXL97, University of Göttingen, Germany, **1997**.