Supporting Information to

Three different product types from reactions of lithiated cyclic aminals with trivalent organometal chlorides †

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Preparative Procedures and Analytical Data

**Compound 3.** 56 mg (0.25 mmol) bis(2-lithio-3-methyl-1,3-diazacyclohex-1-yl)methane was dissolved in 12 mL toluene. To this solution 110 mg (0.25 mmol) of solid [YCpCl₂·3thf] was slowly added under rapid stirring within 5 min. The reaction mixture was allowed to stir over at ambient temperature. After filtration, the solution was concentrated and the colourless complex could be crystallised by layering pentane onto the toluene solution. Yield: 26.4 mg (0.03 mmol, 13 %). ¹H NMR (600 MHz, d₈-thf): δ = 6.22 ppm (s, 10H, Cp), 3.17 (br, 2H, NCH(eq)₂N), 3.07 (m, 2H, NCH(eq)₂CH₂), 2.85 (m, 4H, NCH(eq)₂CH₂), 2.71 (m, 2H, NCH(eq)₂CH₂), 2.61 (br, 2H, NCH(ax)₂N), 2.41 (s, 6H, NCH₃), 2.33 (s, 6H, NCH₃), 2.07 (m, 2H, CH₂C(H(eq))₂CH₂), 1.70 (m, 2H, NCH(ax)₂CH₂), 1.58 (m, 2H, NCH(ax)₂CH₂), 1.50 (m, 4H, NCH(ax)₂CH₂). ¹³C{¹H} NMR (151 MHz, d₈-thf): δ = 109.8 ppm (Cp), 92.3 (LiC), 92.0 (LiC), 85.1 (YC, ¹J₆C-Y = 7.8 Hz), 77.4 (NCH₂CH₂), 75.5 (NCH₂N), 58.8 (NCH₂CH₂, ²J₆C-Y = 1.9 Hz), 55.8 (NCH₂CH₂), 55.3 (NCH₂CH₂), 52.5 (NCH₂CH₂, ²J₆C-Y = 1.6 Hz), 50.5 (NCH₂CH₂), 49.3 (NCH₂N), 45.7 (NCH₃), 45.5 (NCH₃), 42.2 (NCH₂CH₂), 26.2 (NCH₂CH₂), 22.5 (NCH₂CH₂). ⁷Li NMR (194 MHz, d₈-thf, 25°C): δ = -0.07 ppm. Mr = 813.42, found C 47.34, H 6.66, N 13.55%, C₃₂H₅₄Cl₂Li₂N₈Y₂ requires C 47.25, H 6.69, N 13.78%.

**Compound 4.** 60 mg (0.15 mmol) of the bis{(2,4,6-trimethyl-2,4,6-triazacyclohex-1-yl)lithium}·(1,3,5-trimethyl-1,3,5-triazacyclohexan) was dissolved in 12 mL toluene. To this solution 76 mg (0.3 mmol) of solid [YCp₂Cl] was slowly added under rapid stirring within 5 min. The reaction mixture was allowed to stir over at ambient temperature. After filtration, the solution was stored at ambient temperature for 2 weeks. The product was obtained as colourless crystals. Yield: 22.0 mg (0.06 mmol, 37 % (referring to the consumption of one equivalent of lithiated tmtac in 1). ¹H NMR (600 MHz, d₈-thf, 25°C): δ = 5.84 (s, 10 H, Cp), 3.95 (d, 2H, NCH₂(eq)N), 2.93 (d, 2H, NCH₃(ax)N),
2.88 (2H, NCH₂CH), 2.86 (s, 1H, NCHN), 2.60 (s, 3H, NCH₃), 2.30 ppm (s, 9H, TMTAC-NCH₃).

¹³C{¹H} NMR (151 MHz, d₈-thf, 25°C): δ = 108.7 (Cp), 84.0 (CH), 78.6 (NCH₂N), 57.0 (NCH₂CH, ²J_C-Y = 2.5 Hz), 43.9 (NCH₃, ²J_C-Y = 1.7 Hz), 39.9 (TMTAC-NCH₃), 39.4 (TMTAC-NCH₃). Mᵣ = 390.35, found C 58.68, H 7.66, N 12.53%, C₁₈H₂₉N₄Y·0.₅(C₇H₈) requires C 59.17, H 7.62, N 12.84%.

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¹³C{¹H} NMR (151 MHz, d₈-thf, 25°C): δ = 108.7 (Cp), 84.0 (CH), 78.6 (NCH₂N), 57.0 (NCH₂CH, ²J_C-Y = 2.5 Hz), 43.9 (NCH₃, ²J_C-Y = 1.7 Hz), 39.9 (TMTAC-NCH₃), 39.4 (TMTAC-NCH₃). Mᵣ = 390.35, found C 58.68, H 7.66, N 12.53%, C₁₈H₂₉N₄Y·0.₅(C₇H₈) requires C 59.17, H 7.62, N 12.84%.

**Compound 5.** A solution of di-tert.-butylgallium chloride (4.38 g, 20.0 mmol) in 50 mL of hexane was added dropwise to a suspension of compound 1 (3.99 g, 10.0 mmol) in 50 mL hexane at −78 °C. The reaction mixture was stirred overnight while warming to ambient temperature. The mixture was filtered and the solid residue washed twice with two portions of 5 mL hexane. After one week of storage at −20°C grew colourless crystals of 5; yield 1.92 g (43%, 8.53 mmol). ¹H NMR (500 MHz, C₆D₆): δ = 1.21 (s, 36H, (CH₃)₃C), 2.81 (d, 6H, ²J_HH = 1.28 Hz, NCH₃), 9.04 ppm (br q, 2H, ²J_HH = 1.54 Hz, CH=N); ¹³C{¹H}-NMR (125 MHz, C₆D₆): δ = 22.1 ((CH₃)₃C), 32.3 ((CH₃)₃C), 54.7 (NCH₃), 224.1 ppm (C≡N); Mᵣ = 225.10 g/mol, found C 53.21, H 9.60, N 6.32 %, C₂₀H₄₄Ga₂N₂ requires C 53.14, H 9.81, N 6.20 %.
Crystallographic structure determinations

The structures were solved by direct methods and refined by full-matrix least squares cycles (program SHELX-97\textsuperscript{14}). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications. Copies of the data can be obtained from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) CCDC 778691 (3), 778692 (4) and 783496 (5).

Crystal data for 3: C\textsubscript{32}H\textsubscript{54}Cl\textsubscript{2}Li\textsubscript{2}N\textsubscript{8}Y\textsubscript{2}, monoclinic, \textit{P}2\textsubscript{1}/\textit{n}, \textit{a} = 8.477(1), \textit{b} = 21.345(1), \textit{c} = 10.802(1) Å, \textit{β} = 105.850(1)\textdegree, \textit{V} = 1880.3(1) Å\textsuperscript{3}, \textit{Z} = 2, \textit{ρ}\textsubscript{ber.} = 1.437 g cm\textsuperscript{-3}, \textit{λ} = 0.71073 Å, \textit{θ}\textsubscript{max.} = 27.5\textdegree, \textit{T} = 100(2) K, \textit{μ} = 3.246 mm\textsuperscript{-1}. 42960 measured, 4288 independent refl. \textit{(R}\textsubscript{int} = 0.0450). 316 parameters, \textit{R} = 0.0241 for 3789 refl. with \textit{I}>2\textsigma(\textit{I}) and \textit{wR}\textsubscript{2} = 0.0588 for all 4288 data. Max./min. residual peaks 0.52/−0.46 e Å\textsuperscript{-3}.

Crystal data for 4: C\textsubscript{18}H\textsubscript{29}N\textsubscript{4}Y·(0.5 C\textsubscript{7}H\textsubscript{8}), monoclinic, \textit{C}2\textsubscript{\textit{m}}, \textit{a} = 25.885(2), \textit{b} = 12.584(2), \textit{c} = 17.235(2) Å, \textit{β} = 129.264(3)\textdegree, \textit{V} = 4346.3(6) Å\textsuperscript{3}, \textit{Z} = 8, \textit{ρ}\textsubscript{ber.} = 1.334 g cm\textsuperscript{-3}, \textit{λ} = 1.54178 Å, \textit{θ}\textsubscript{max.} = 72.2\textdegree, \textit{T} = 225(2) K, \textit{μ} = 3.855 mm\textsuperscript{-1}. 27268 measured, 4337 independent refl. \textit{(R}\textsubscript{int} = 0.0198). 284 parameters, \textit{R} = 0.0262 for 4117 refl. with \textit{I}>2\textsigma(\textit{I}) and \textit{wR}\textsubscript{2} = 0.0735 for all 4337 data. Max./min. residual peaks 1.07/−0.38 e Å\textsuperscript{-3}. Half a disordered toluene molecule per formula unit was corrected for using the SQUEEZE procedure of PLATON\textsuperscript{15}.

Crystal data for 5: C\textsubscript{20}H\textsubscript{44}Ga\textsubscript{2}N\textsubscript{2}, monoclinic, \textit{P}2\textsubscript{1}/\textit{c}, \textit{a} = 8.9080(1), \textit{b} = 12.3329(2), \textit{c} = 11.6776(2) Å, \textit{β} = 108.7611(9)\textdegree, \textit{V} = 1214.75(3) Å\textsuperscript{3}, \textit{Z} = 2, \textit{ρ}\textsubscript{ber.} = 1.236 g cm\textsuperscript{-3}, \textit{λ} = 0.71073 Å, \textit{θ}\textsubscript{max.} = 30.0\textdegree, \textit{T} = 100(2) K, \textit{μ} = 2.222 mm\textsuperscript{-1}. 37072 measured, 3544 independent refl. \textit{(R}\textsubscript{int} = 0.028). 116 parameters, \textit{R} = 0.0253 for 3250 refl. with \textit{I}>2\textsigma(\textit{I}) and \textit{wR}\textsubscript{2} = 0.0680 for all 3544 data. Max./min. residual peaks 0.81/−0.48 e Å\textsuperscript{-3}.

\textsuperscript{14} "A short history of SHELX", Sheldrick, G.M. (2008), Acta Crystal. A64, 112-122
\textsuperscript{15} Spek, A. L. (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands