Supporting Information

Tris(2-dimethylaminoethyl)amine: A simple new tripodal polyamine ligand for Group 1 metals

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1. General Experimental Details.

The ligand Me_6TREN was prepared according to the method of Britovsek *et al.*[1] Lithium and sodium hexamethyldisilazide salts, *2,4,6*-trimethylphenol, *2,6*-di(*tert*-butyl)-*4*-methylphenol were bought from Aldrich and used without further purification.

All the reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glove-box techniques. All solvents were freshly distilled from suitable drying agents and degassed prior to use (toluene over sodium/benzophenone and dichloromethane over calcium hydride, hexane was eluted over activated alumina columns and stored under argon).

^{1}H NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer at room temperature and referenced to residual protio solvent peaks, unless otherwise stated. ^{7}Li{^{1}H} NMR spectra were recorded on a Bruker 400 MHz or Bruker 500 MHz and referenced to a external 1M LiCl solution in D_2O. Benzene-d_6 and toluene-d_8 (Aldrich) were degassed and stored over 4Å molecular sieves. Coupling constants *J* are given in Hertz.

2. Preparation and Characterisation of Complex 1.

2.1 Preparation and spectroscopic data.

$LiN(SiMe_3)_2$ (0.440 g, 2.6 mmol) was dissolved in toluene (10 ml), to which Me_6TREN (0.600 g, 2.6 mmol) was slowly added. The resulting solution was stirred for one hour, then all solvents were removed under vacuum and the resulting white solid was washed with hexane (2 x 10 mL) (yield 0.686 g, 67%). X-ray quality crystals were grown on cooling hexane

solutions of the complex at 253 K. Found C, 53.50; H, 11.70; N, 18.50. $C_{18}H_{48}N_5LiSi_2$ requires C, 54.36; H, 12.17; N 17.62. ^{1}H NMR (C_6D_6): 0.33 (s, 18H, 2 x Si*Me*$_3$), 1.92 (m, 6H, 3 x NC*H*$_2$CH$_2$NMe$_2$), 2.02 (s, 18H, 3 x N*Me*$_2$), 2.28 (m, 6H, 3 x C*H*$_2$NMe$_2$) ppm. ^{1}H NMR (tol-d_8): 0.49 (s, 18H, 2 x Si*Me*$_3$), 1.79 (m, 6H, 3 x NC*H*$_2$CH$_2$NMe$_2$), 2.00 (s, 18H, 3 x N*Me*$_2$), 2.18 (m, 6H, 3 x C*H*$_2$NMe$_2$) ppm. ^{7}Li{^{1}H} NMR (tol-d_8): 0.56 ppm.

2.2 Crystallographic data for 1.

Data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å), and the structure were solved by direct methods and refined on all F^2 data using SHELXL-97 suite of programs, with hydrogen atoms included in idealised positions and refined using the riding model.[2]

*X-Ray data for **1***: $C_{18}H_{48}LiN_5Si_2$, M = 397.73, colourless prism, 0.40 x 0.40 x 0.30 mm^3, monoclinic, space group P2$_1$/n, a = 15.9460(1), b = 10.2750(2), c = 16.7070(2) Å, $\alpha = \gamma = 90$, $\beta = 103.690(1)^o$, V = 2659.59(6) Å^3, Z = 4, D_c = 0.993 g/cm^3, F_{000} = 888, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2)K, $2\theta_{max}$ = 55.1º, 41474 reflections collected, 41482 unique [R(int) = 0.0000]. *Final GooF* = 1.066, R1 = 0.0790, *w*R2 = 0.1993, *R* indices based on 30685 reflections with I >2sigma(I) (refinement on F^2), 249 parameters, CCDC 769779. Optimal convergence of the structural model was achieved when pseudo-merohedral twinning (32%) of 180 degrees about the -1 0 1 direct lattice direction was accounted for.

3. Preparation and Characterisation of Complex 2

3.1 Preparation and spectroscopic data.

$LiN(SiMe_3)_2$ (0.440 g, 2.6 mmol) was dissolved in hexane (12 ml), to which Me_6TREN (0.300 g, 1.3 mmol) and *2,4,6*-trimethylphenol (0.350 g, 2.6 mmol) were added. The resulting solution was stirred for one hour, and then allowed to stand at room temperature. X-ray quality crystals were grown overnight, decanted from solution and dried under vacuum (0.420 g, 43%). Found C, 69.00; H, 9.97; N, 10.90. $C_{60}H_{104}Li_4N_8O_4$ requires C, 69.98; H, 10.19; N 10.89. ^{1}H NMR (tol-d^8, 298K): 1.94 (s, 36H, 6 x NMe_2), 2.02 (bs, 12H, 6 x CH_2NMe$_2$), 2.22 [s, 24H, 8 x *o*-Me(Ar)], 2.35 (bs, 12H, 6 x NCH_2CH$_2$NMe$_2$), 2.33 [s, 12H, 4 x *p*-Me(Ar)] ppm. ^{1}H NMR (C_6D_6): 6.93 (s, 2H, 2 x Ar-H), 2.15 [s, 12H, 4 x *p*-Me(Ar)], 2.27 [s, 24H, 8 x *o*-Me(Ar)], 2.22 (bs, 12H, 6 x NCH_2CH$_2$NMe$_2$), 1.87 (bs, 48H, 6 x NCH_2CH$_2$NMe$_2$ + 6 x NMe_2) ppm. ^{7}Li{^{1}H} NMR (C_6D_6) 1.09 (bs), 0.27 (bs) ppm.

3.2 Crystallographic data for 2.

Data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å), and all structures were solved by direct methods and refined on all F^2 data using SHELXL-97 suite of programs, with hydrogen atoms included in idealised positions and refined using the riding model.[2]

X-Ray data for ***2***: $C_{60}H_{104}Li_4N_8O_4$, M = 1029.27, colourless prism, 0.25 x 0.15 x 0.15 mm^3, triclinic, space group P-1, a = 10.3310(3), b = 12.0130(3), c = 14.1840(4) Å, α = 69.1400(10), β = 77.1830(10), γ = 75.7100(10)^o, V = 1576.51(7) Å^3, Z = 1, D_c = 1.084 g/cm^3, F_{000} = 564, Mo-

Kα radiation (λ = 0.71073 Å), T = 150(2)K, $2\theta_{max}$ = 50.0º, 16806 reflections collected, 5527 unique [R(int) = 0.0421]. *Final GooF* = 1.024, R1 = 0.0763, *w*R2 = 0.1982, *R* indices based on 4344 reflections with I >2sigma(I) (refinement on F^2), 355 parameters, CCDC 769780.

4. Preparation and Characterisation of Complex 3

4.1 Preparation and spectroscopic data.

$NaN(SiMe_3)_2$ (0.490 g, 2.6 mmol) was dissolved in toluene (10 ml), to which Me_6TREN (0.600 g, 2.6 mmol) and *2,4,6*-trimethylphenol (0.70 g, 5.2 mmol) were added. The resulting solution was stirred for one hour, then approximately 50% of the solution was removed *in-vacuo* and allowed to stand at room temperature. X-ray quality crystals were grown overnight, decanted from solution and dried under vacuum (1.145 g, 84%). Found C, 67.50; H, 9.67; N, 10.70. $C_{30}H_{53}N_4NaO_2$ requires C, 68.64; H, 10.19; N 10.68. ^{1}H NMR (C_6D_6): 1.76 [s, 12H, 4 x *o*-Me(Ar)], 1.99 (s, 18H, 3 x NMe_2), 2.33 (s, 6H, 3 x NCH_2), 2.42 [s, 12H, 3 x CH_2NMe_2 + 2 x *p*-Me(Ar)], 6.95 (s, 4H, 4 x Ar-H), 10.96 (bs, 1H, O-H) ppm.

4.2 Crystallographic data for 3.

Data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å), and all structures were solved by direct methods and refined on all F^2 data using SHELXL-97 suite of programs, with hydrogen atoms included in idealized positions and refined using the riding model.[2]

X-Ray data for ***3***: $C_{30}H_{53}N_4NaO_2$, M = 524.75, colourless prism, 0.22 x 0.14 x 0.09 mm^3, monoclinic, space group C2/c, a = 25.660(11), b =

25.9020(13), c = 19.7360(10) Å, $\alpha = \gamma = 90$, β = 95.970(2)°, V = 13049.3(11) Å^3, Z = 16, D_c = 1.068 g/cm^3, F_{000} = 4608, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2)K, $2\theta_{max}$ = 50.2º, 43029 reflections collected, 11197 unique [R(int) = 0.1894]. *Final GooF* = 1.035, R1 = 0.1052, *w*R2 = 0.2106, *R* indices based on 5119 reflections with I >2sigma(I) (refinement on F^2), 719 parameters, CCDC 769781. The asymmetric unit consists of two disordered molecules of **3**. One of the independent molecules exhibits a disorder over two sites in one of the methylene groups of an arm of the Me_6TREN ligand, which could be modelled in approximately 1:1 ratio. The second independent molecule exhibits a disorder over two sites on the *2,4,6*-tri(methyl)phenol molecule in approximately 2:1 ratio, with both rings sharing the *p*-Me group.

5. Preparation and Characterisation of Complex 4

5.1 Preparation and spectroscopic data.

$NaN(SiMe_3)_2$ (0.490 g, 2.6 mmol) was dissolved in hexane (15 ml) and toluene (10 ml), to which Me_6-TREN (0.600 g, 2.6 mmol) and *2,6*-di(*tert*butyl)-*4*-methylphenol (0.570 g, 2.6 mmol) were added. The resulting solution was stirred for one hour, and then allowed to stand at room temperature. X-ray quality crystals were grown overnight, decanted from solution and dried under vacuum (0.870 g, 71%). Found C, 66.90; H, 10.70; N, 11.60. $C_{27}H_{53}N_4NaO$ requires C, 68.58; H, 11.31; N 11. 68. ^{1}H NMR (C_6D_6): 1.84 (bs, 18H, 3 x NMe_2), 1.96 [s, 24H, 3 x NCH_2 + 2 x ^{t}Bu(Ar)], 2.00 (m, 6H, 3 x NCH_2), 2.65 [s, 3H, *p-Me*(Ar)], 7.39 (s, 2H, Ar-*H*) ppm.

5.2 Crystallographic data for 4.

Data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å), and all structures were solved by direct methods and refined on all F^2 data using SHELXL-97 suite of programs, with hydrogen atoms included in idealised positions and refined using the riding model.[2]

*X-Ray data for **4***: $C_{27}H_{53}N_4NaO$, M = 472. 72, colourless prism, 0.7 x 0.6 x 0.5 mm^3, orthorhombic, space group Pbca, a = 9.9720(2), b = 17.6940(3), c = 34.0110(7) Å, $\alpha = \beta = \gamma = 90^o$, V = 6001.1(2) Å^3, Z = 8, D_c = 1.046 g/cm^3, F_{000} = 2096, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2)K, $2\theta_{max}$ = 55.92º, 29677 reflections collected, 6706 unique [R(int) = 0.0664]. *Final GooF* = 1.025, R1 = 0.0705, *w*R2 = 0.1748, *R* indices based on 4802 reflections with I >2sigma(I) (refinement on F^2), 310 parameters, CCDC 769782.

6. References

1. G. J. P. Britovsek, J. England and A. J. P. White, *Inorg. Chem.*, 2005, **44**, 8125.
2. G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.