

**Accessing low denticity coordination modes of a high denticity tripodal ligand to
complete its coordinative repertoire**

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Supporting Information

Experimental Section

General Remarks

All reactions and manipulations were carried out under a protective argon atmosphere using either standard Schlenk techniques or a glove box. All solvents were dried over Na/benzophenone and freshly distilled prior to use. $t\text{Bu}_2\text{Zn}$,¹ $t\text{Bu}_3\text{Ga}$ ² and Me_6TREN ³ were all synthesised according to literature procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 MHz spectrometer (operating at 400.03 MHz for ^1H and 100.58 MHz for ^{13}C). All ^{13}C NMR spectra were proton decoupled. Elemental analyses (C, H, N) were performed by Denise Gilmour, University of Strathclyde Elemental Analysis Service.

Synthesis of $\text{Zn}(t\text{Bu})_2N,N'$ - Me_6TREN , **1**.

Freshly prepared $(t\text{Bu})_2\text{Zn}$ (0.36 g, 2 mmol) was dissolved in hexane (3mL) and Me_6TREN (0.52 mmol, 2 mmol) was added via syringe. After stirring for ten minutes at room temperature this was cooled to -35°C and deposited the final product as a crop of colourless crystals (0.491 g, 60 %). **Note:** care should be taken when handling $(t\text{Bu})_2\text{Zn}$ and **1** as they are pyrophoric in air and smoke mildly even in an inert atmosphere. ^1H NMR (C_6D_6 , 300 K): 2.67 (t, 6 H, 7 Hz, $\text{Me}_6\text{TREN CH}_2$), 2.37 (t, 6 H, 7 Hz, $\text{Me}_6\text{TREN CH}_2$), 2.11 (s, 18 H, $\text{Me}_6\text{TREN CH}_3$), 1.22 ppm (s, 18 H, $\text{Zn}-t\text{Bu}$). ^{13}C NMR (C_6D_6 , 300 K): 58.0 ($\text{Me}_6\text{TREN CH}_2$), 53.2 ($\text{Me}_6\text{TREN CH}_2$), 46.2 ($\text{Me}_6\text{TREN CH}_3$), 32.6 ($\text{C}(\underline{\text{C}}\text{H}_3)_3$), 26.3 ($\underline{\text{C}}(\text{CH}_3)_3$). Elemental analysis calcd (%) for $\text{ZnN}_4\text{C}_{20}\text{H}_{48}$: C 58.59, H 11.80, N 13.66; found: C 57.39, H 12.09, N 13.88. More accurate elemental analyses could not be obtained due to the highly air-sensitive nature of the product.

Synthesis of [Ga(*t*Bu)₃]₃N-Me₆TREN, **2**.

(*t*Bu)₃Ga (0.30 mL, 1.5 mmol) was stirred in hexane (5 mL) and Me₆TREN (0.13 mL, 0.5 mmol) was added via syringe. After stirring this solution for ten minutes at room temperature it was cooled to -35°C and deposited the final product as a crop of colourless crystals (0.241 g, 51 %). ¹H NMR (C₆D₆, 300 K): 2.53 (m, 12 H, Me₆TREN CH₂ x 2), 2.16 (s, 18 H, Me₆TREN CH₃), 1.23 ppm (s, 81 H, Ga-*t*Bu). ¹³C NMR (C₆D₆, 300 K): 58.1 (Me₆TREN CH₂), 52.1 (Me₆TREN CH₂), 45.8 (Me₆TREN CH₃), 31.5 (C(CH₃)₃), 30.1 (C(CH₃)₃). Elemental analysis calcd (%) for Ga₃N₄C₄₈H₁₁₁: C 60.46, H 11.73, N 5.88; found: C 59.24, H 10.80, N 6.20. More accurate elemental analyses could not be obtained due to the highly air-sensitive nature of the product.

X-ray crystallography

Crystallographic data was collected at 123(2) K on Oxford Diffraction instruments with Mo K_α radiation (λ = 0.71073 Å). Crystallographic measurements were made with an Oxford Diffraction Xcalibur E diffractometer at 123(2) K with MoK_α monochromated radiation (λ = 0.71073 Å). The structures were solved and refined using SHELXS97⁴ and SHELXL97⁴.

Crystal data for **1**, C₂₀H₄₈N₄Zn, M_r = 409.99, triclinic, space group P $\bar{1}$, *a* = 8.9150(3), *b* = 11.3744(5), *c* = 13.6985(6) Å, α = 66.433(4)°, β = 77.519(3)°, γ = 72.686(4)°, *V* = 1208.01(9) Å³, *Z* = 2, μ = 1.026 mm⁻¹; 36079 reflections, 6738 unique, *R*_{int} 0.0311, final refinement with full-matrix least squares on *F*² gave *R* = 0.0246 (*F*, 6194 obs. data only) and *R*_w = 0.0610 (*F*², all data),) for 238 parameters, GOF = 1.060.

Crystal data for **2**, C₄₈H₁₁₁ Ga₃N₄, M_r = 953.57, hexagonal, space group P6₃, $a = b = 15.1685(3)$, $c = 14.0228(3)$ Å, $V = 2795.35(10)$ Å³, $Z = 2$, $\mu = 1.467$ mm⁻¹; 8948 reflections, 4154 unique, R_{int} 0.0254, final refinement with full-matrix least squares on F^2 gave $R = 0.0322$ (F , 3620 obs. data only) and $R_w = 0.0715$ (F^2 , all data), for 178 parameters, GOF = 1.056.

References

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