

Supplementary information for:

Structural and epr characterisation of single electron and alkyl transfer products from reaction of dimethyl magnesium with bulky α -diimine ligands.

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General Procedures.

All the air/moisture sensitive experimental work was performed under N₂ using standard Schlenk techniques on a vacuum line under dry, oxygen free, nitrogen. Some experimental work and characterisations were carried out in a nitrogen filled glove box (Saffron), fitted with oxygen and water scavenging columns. All solvents were dried and deoxygenated before use. Solvents and reagents where commercially available were purchased from Aldrich, Acros or Fischer. With exception of NMR solvents which were purchased from Goss Scientific. Diethylether, toluene, hexane, benzene, and THF were all distilled from Na/benzophenone under a nitrogen atmosphere. NMR solvents were degassed using three freeze-pump-thaw cycles and stored over molecular sieves. The diimine ligands were placed under vacuum and then under nitrogen before complexation reactions. Elemental analyses were performed by sealing aluminium capsules containing approx. 1mg of compound under nitrogen in the glove box, and determined using a Perkin Elmer 2400 CHN Analyser. NMR were recorded on a Gemini 200MHz, Bruker 200Mhz, Bruker 250MHz and Bruker GPX 360MHz spectrometers. IR spectra were obtained on a Perkin Elmer Paragon 1000 FT-IR spectrometer as potassium bromide discs or as liquid thin films. EPR spectra were recorded on a Bruker ER200D spectrometer at room temperature.

[Mg(μ_2 -Me){(2,6-¹Pr₂Ph)BIAN}]₂ (2)

A solution of MgMe₂ (0.503 g, 1.004 mmoles) in Et₂O (35 cm³) was added by cannula to an Et₂O (25 cm³) solution of the ligand **1** (0.116 g, 2.133 mmoles). A colour change of orange to black to dark red was observed. The reaction mixture was sonicated in an ultrasound cleaning bath for 5 mins and then left to stir overnight. The solution was filtered through celite. The filtrate was layered with hexane and stored at -26°C for 2 days providing a small crop of red crystals which X-ray structure analysis showed to be [Mg(μ_2 -Me){(2,6-¹Pr₂Ph)BIAN}]₂.(C₆H₄)_{1.25} (0.12 g, 10 %). Satisfactory elemental analysis could not be obtained which we attribute to the extreme air sensitivity of **6**. For the epr spectrum an Et₂O (25 cm³) solution of **1** (40 mg, 0.081 mmoles) was stirred overnight and MgMe₂ (4 mg, 0.073 mmoles) in Et₂O (25 cm³), was added by cannula. A colour change of orange to black to dark red was observed. A sample of the solution was transferred to a quartz flat cell in the glove box and the EPR analysis undertaken. The EPR analysis parameters were CF 3440,

Gain 3.2×10^4 , Mod 4 Gpp, SW 200, Phase 0° , Power 100 mW, Freq 9.71 GHz; after simulation using WinEPR: $g=2.0117$, $2N a^N=4.6$, Lorentzian line width 4.7 G.

[Mg(μ_2 -CH₃){(2,6-ⁱPr₂Ph)NCMe}]₂ (4)

A solution of ligand **3** (2.173 g, 10.8 mmoles) in Et₂O (25 cm³) was added to an Et₂O (25 cm³) solution of MgMe₂ (0.585 g, 5.37 mmoles) with stirring. An orange solution formed. The solution was allowed to stir for 1h. A portion of the solution (1.7 cm³) was diluted with Et₂O (48 cm³) and a sample of the solution was placed in a flat quartz cell for EPR analysis in the glove box and the EPR spectrum recorded. The EPR analysis parameters were CF 3440, Gain 4×10^4 , Mod 4 Gpp, SW 200, Phase 180° , Power 100 mW, Freq 9.71 GHz; after simulation using WinEPR: $g=2.0123$, $2N a^N=5.54$, $6H a^H=5.54$, Lorentzian line width 4.00 G.

[Mg(μ_2 -Me){(2,6-ⁱPr₂Ph)NC(Me)₂C(Me)N(2,6-ⁱPr₂Ph)}] (5)

MgMe₂ (0.300 g, 5.518 mmoles) was dissolved in THF (1cm³) and toluene (10cm³) and then frozen in liquid nitrogen. A chilled solution of **63** (2.287 g, 5.62 mmole) in toluene (10cm³) and THF (0.2cm³) was added via cannula, and the reaction mixture allowed to gradually melt and warm to room temperature. The clear orange solution was allowed to stand at room temperature overnight and placed in the freezer at -22°C the next day. After 5 days red block crystals were formed which X-ray structure analysis showed to be [Mg(μ_2 -Me){(2,6-ⁱPr₂Ph)NC(Me)₂C(Me)N(2,6-ⁱPr₂Ph)}] (C₇H₈.C₄H₈O) (0.510 g, 16%).

CHN: Found C 78.63, H 10.15, N 5.99; C₆₀H₉₂N₄Mg₂ requires C 78.50, H 10.10, N 6.10. **IR** (Nujol, cm⁻¹): ($\nu_{\text{C=N}}$): 1589.2; 1609.8. **¹H NMR** (360.13 MHz, THF-*d*₈): δ - 1.79 (s, 3H, MgCH₃), 1.01 (d, $J = 6.81\text{Hz}$, 6H, (ⁱPr-CH₃)), 1.11 (d, $J = 6.84\text{Hz}$, 6H, (ⁱPr-CH₃)), 1.19 (d, $J = 7.04\text{Hz}$, 6H, (ⁱPr-CH₃)), 1.21 (d, $J = 6.91\text{Hz}$, 6H, (ⁱPr-CH₃)), 1.27 (s, 6H, (C(CH₃)₂)), 2.25 (s, 3H, (N=C(CH₃))), 3.02 (sept, $J = 6.81\text{Hz}$, 4H, (ⁱPr-CH)), 3.98 (sept, $J = 6.89\text{Hz}$, 4H, (ⁱPr-CH)), 6.75 (t, $J = 7.32\text{Hz}$, 4H, *o*-ArCH), 6.91 (d, $J = 7.55\text{Hz}$, 8H, *m*-ArCH), 7.13-7.19 (m, 12H, ArCH), **¹³C NMR** (90.55 MHz, THF-*d*₈): 19.04 (s, CH₃), 24.33 (s, CH₃), 24.56 (s, CH₃), 24.66 (s, CH₃), 27.04 (s, CH₃), 28.38 (s, CH), 28.72 (s, CH), 30.12 (s), 32.65 (s), 121.67 (s, CH), 123.11 (s,

CH), 124.62 (s, CH), 126.54 (s, CH), 128.89 (s, CH), 129.01 (s, CH), 140.09 (s, C),
150.12 (s, C).

The epr spectra were simulated with WINepr and the resulting hyperfine coupling constants and line widths are provided in the experimental section. The simulated and experimental spectra are shown below.

