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# Kinetic Stabilisation of a Molecular Strontium Hydride Complex using an Extremely Bulky Amidinate Ligand

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**Electronic Supplementary Information (24 pages)**

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## 1. Experimental

### General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Pentane was distilled over Na/K alloy (50:50), while hexane, toluene and THF were distilled over molten potassium. $^{1}H$, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra were recorded on either Bruker DPX300 or Bruker AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used or external $SiMe_4$. Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid state probe. FTIR spectra were collected for solid samples or Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out at the Science Centre, London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting materials $Ar^{\dagger}NH_2$,[1] and $K\{N(SiMe_3)_2\}$[2] were prepared by literature procedures, while $[MI_2(THF)_2]$ (M = Ca, Sr, Ba) were prepared by reactions of metal filings with iodine in tetrahydrofuran. All other reagents were used as received.

**$Ar^{\dagger}$NHC(O)Ad.** $Ar^{\dagger}NH_2$ (40 g, 86 mmol) and AdC(O)Cl (18 g, 90 mmol) were dissolved in 200 mL of dichloromethane, then triethylamine (18 mL, 133 mmol) added. This resulted in a colour change from brown to red. The mixture was allowed to stir overnight and was then washed with 1M $NaHCO_3$, followed by water (2 x 40 mL). The organic layer was separated and dried over $Na_2SO_4$, then filtered. Volatiles were removed from the filtrate *in vacuo* to give the product as a white powder (52 g, 98%). M.p. 196-197 ºC; $^{1}H$ NMR (300 MHz, $C_6D_6$, 298 K): δ = 0.92 (d, $^{3}J_{HH}$ = 6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.51 (m, 9H, Ad-*H*), 1.71 (m, 3H, Ad-*H*), 1.92 (m, 3H, Ad-*H*), 2.44 (sept, $^{3}J_{HH}$ = 6 Hz, 1H, C*H*(CH$_3$)$_2$), 5.93 (s, 2H C*H*Ph$_2$), 6.11 (s, 1H, N*H*), 6.91-7.17 (m, 22H, Ar*H*); $^{13}C\{^{1}H\}$ NMR (75 MHz, $C_6D_6$, 298 K): δ = 23.9 (CH(*C*H$_3$)$_2$), 28.6 (Ad-*C*), 34.1 (*C*H(CH$_3$)$_2$), 36.5 (Ad-*C*), 39.1 (Ad-*C*), 39.2 (Ad-*C*), 53.1 (*C*HPh$_2$), 126.7, 127.5, 128.7, 128.8, 129.0, 130.0, 130.1, 142.7, 144.2, 147.8 (Ar-*C*), 175.7 (*C*=O); IR *v*/cm$^{-1}$ (ATR): 3426 (w), 1663 (s), 1597 (m), 1181 (m), 1155 (m), 1102 (w), 1073 (m), 1030 (m), 669 (vs), 673 (m); acc. mass/ESI *m/z*: calc. 630.3736 found: 630.3732 ($MH^+$).

**$Ar^{\dagger}$NHC(O)Bu$^t$.** $Ar^{\dagger}NH_2$ (40 g, 86 mmol) was dissolved in 200 mL of dichloromethane and triethylamine (18 mL, 133 mmol) added. Bu$^t$COCl (13 mL, 105 mmol) was added slowly (Warning: exothermic), resulting in a colour change from brown to red. The mixture was allowed to stir overnight and was then washed with 1 M $NaHCO_3$ (40 mL) and water (2 x 40 mL). The organic layer was then dried over $Na_2SO_4$, then filtered. Volatiles were removed from the filtrate *in vacuo* to give the title compound as a white powder (46 g, 96%). M.p: 185-187°C; $^{1}H$ NMR (400 MHz,

$C_6D_6$, 298 K): δ = 0.91 (d, $^3J_{HH}$ = 8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.95 (s, 9H, Bu$^t$), 2.44 (sept, $^3J_{HH}$ = 8 Hz, 1H, C*H*(CH$_3$)$_2$), 5.92 (s, 2H, C*H*Ph$_2$), 6.11 (s, 1H, N*H*), 6.89 (s, 2H, Ar† *m*-Ar-*H*), 6.9-7.1 (m, 20H, Ar-*H*); $^{13}$C{H} NMR (100 MHz, $C_6D_6$, 298 K): δ = 23.9 (CH(*C*H$_3$)$_2$), 27.4 (C(*C*H$_3$)$_3$), 34.0 (*C*H(CH$_3$)$_2$), 39.1 (*C*(CH$_3$)$_3$), 53.0 (*C*HPh$_2$), 126.7, 127.4, 128.7, 129.9, 132.8, 142.6, 144.1, (Ar-*C*), 176.1 (N*C*O); IR *v*/cm$^{-1}$ (ATR): 3426 (w), 1680 (s), 1600 (m), 960 (w), 914 (w), 763 (s), 748 (s), 700 (vs), 651 (w), 631 (m), 609 (s); MS/ESI *m/z* (%): 552.32 (MH$^+$, 100).

**Ar†NCClAd.** Ar†NHC(O)Ad (50 g, 79 mmol) and $PCl_5$ (23 g, 111 mmol) were combined in a Schlenk flask. Toluene (30 mL) was added and the mixture was heated at reflux for 24h. The mixture was then evaporated to dryness and heated at 150 ºC under vacuum for 1h to remove unreacted $PCl_5$. This yielded the title compound as a brown, moisture sensitive solid (50 g, 98%). M.p. 199-200 ºC; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): 0.95 (d, $^3J_{HH}$ = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.51 (m, 6H, Ad-*H*), 1.79 (m, 9H, Ad-*H*), 2.49 (sept, $^3J_{HH}$ = 7 Hz, 1H, C*H*(CH$_3$)$_2$), 5.71 (s, 2H, C*H*Ph$_2$), 6.99-7.31 (m, 22H, Ar*H*); $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$, 298 K): 22.0 (CH(*C*H$_3$)$_2$), 26.6 (*C*H(CH$_3$)$_2$), 31.9 (Ad-*C*), 34.7 (Ad-*C*), 37.1 (Ad-*C*), 38.3 (Ad-*C*), 50.7 (*C*HPh$_2$), 124.5, 125.1, 126.5, 128.0, 128.5, 130.9, 140.7, 141.4, 142.0, 142.2, (Ar-*C*) 153.0 (Cl*C*N); IR *v*/cm$^{-1}$ (ATR): 1697 (s), 1598 (m), 1494 (s), 1077 (m), 1031 (m), 983 (m), 766 (m), 739 (s), 698 (vs); acc. MS/ESI *m/z*: calc for Ar†NC(OMe)AdH$^+$ (methanolysis product): 644.3892; found: 644.3876.

**Ar†NCClBu$^t$.** Synthesised using a similar procedure as for Ar†NCClAd, but using Ar†NHC(O)Bu$^t$ (32 g, 58 mmol), and $PCl_5$ (16.9 g, 81 mmol). Reaction yielded the title product as a pale brown, glassy solid (29 g, 85%). M.p: 176-178 °C; $^1$H NMR (400 MHz, $C_6D_6$, 298 K): δ = 0.94 (d, $^3J_{HH}$ = 8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.03 (s, 9H, Bu$^t$), 2.47 (sept, $^3J_{HH}$ = 8 Hz, 1H, C*H*(CH$_3$)$_2$), 5.68 (s, 2H, C*H*Ph$_2$), 6.96 (s, 2H, Ar† *m*-Ar-*H*), 7.00-7.20 (m, 20H, Ar-*H*); $^{13}$C{$^1$H} NMR (100 MHz, $C_6D_6$, 298 K): δ = 23.6 (CH(*C*H$_3$)$_2$), 27.8 (C(*C*H$_3$)$_3$), 33.6 (*C*H(CH$_3$)$_2$), 43.7 (*C*(CH$_3$)$_3$), 52.5 (*C*HPh$_2$), 128.1, 128.2, 128.4, 129.6, 132.6, 143.7, 143.9, 147.7 (Ar-*C*), 154.9 (Cl*C*N); IR *v*/cm$^{-1}$ (ATR): 1721 (s), 1682 (s). 1600 (m), 1158 (m), 1075 (m), 1030 (s), 930 (s), 895 (m), 760 (s), 739 (s), 689 (vs), 633 (m), 605 (s); MS/ESI *m/z* (%): (Ar†NC(OMe)Bu$^t$H$^+$ (methanolysis product) 566.34, 100).

**L$^{Ad}$H.** Ar†NCClAd (26 g, 40 mmol) and $DipNH_2$ (7.1g, 40 mmol) were combined in a Schlenk flask. Toluene (30 mL) and triethylamine (7.5 mL, 53 mmol) were added, resulting in formation of a white precipitate. This mixture was heated at reflux for 2 days, cooled, and 1M $NaHCO_3$ (30 mL) added. The mixture was transferred to a separating funnel and the organic layer was washed with water (2 x 30 mL). The organic layer was separated and volatiles removed *in vacuo* to give a sticky solid that was washed with MeOH (3 x 20 mL), yielding the title compound as a white powder (26 g, 82%). The washings were allowed to slowly evaporate yielding colourless crystals of the title compound (1.9g, 6%, combined yield 88%). M.p. 209-211 ºC; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = 0.91 (d, $^3J_{HH}$ = 6 Hz, 6H, Ar†-CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.37 (m, 6H, Ad-*H*), 1.47 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.52 (m, 6H, Ad-*H*), 1.59 (m, 3H, Ad-*H*), 2.45 (sept, $^3J_{HH}$ = 6 Hz, 1H, Ar†-C*H*(CH$_3$)$_2$), 3.63 (sept, $^3J_{HH}$ = 6 Hz, 2H, Dip-C*H*(CH$_3$)$_2$), 4.87 (s, 1H, N*H*), 6.29 (s, 2H, C*H*Ph$_2$), 6.89 (s, 2H, Ar† *m*-Ar-*H*), 6.90-7.30 (m, 23H, Ar-*H*). $^{13}$C{$^1$H} NMR (75MHz, $C_6D_6$, 298K): *δ* = 22.8 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 29.2 (*C*H(CH$_3$)$_2$), 34.1 (Ad-*C*), 36.4 (Ad-*C*), 40.0 (Ad-*C*), 43.6 (Ad-*C*), 53.3 (*C*HPh$_2$), 121.8, 122.9, 126.5, 126.7, 127.3, 129.6, 130.9, 136.2, 137.2, 143.6, 144.7, 147.7 (Ar-*C*), 155.8 (N*C*N); IR *v*/cm$^{-1}$ (ATR): 1621 (s), 1587 (m), 1383 (w), 1361 (w), 1313 (w), 1292 (w), 1258 (w), 1228 (w), 1182 (m), 1103 (m), 799 (m), 762 (s), 744 (m), 700 (vs); acc. MS/ESI *m/z*: calc: 789.5148, found: 789.5136 (MH$^+$).

**L$^{tBu}$H.** A similar procedure was used as for the synthesis of L$^{Ad}$H but using Ar†NCClBu$^t$ (32.0g, 58 mmol), NEt$_3$ (11.4 mL, 82 mmol) and DipNH$_2$ (16.2 mL, 15.2 mmol), yielded the the title compound as an off-white powder (36.4 g, 82 %). M.p: 158-160 °C; $^1$H NMR (400 MHz, $C_6D_6$, 298 K): δ = 0.71 (s, 9H, C(C*H*$_3$)$_3$), 0.91 (d, $^3J_{HH}$ = 8 Hz, 6H, Ar†CH(C*H*$_3$)$_2$), 1.22 (d, $^3J_{HH}$ = 8 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.42 (d, $^3J_{HH}$ = 4 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 2.44 (sept, $^3J_{HH}$ = 8 Hz, 1H, Ar†-C*H*(CH$_3$)$_2$), 3.59 (sept, $^3J_{HH}$ = 8 Hz, 2H, Dip-C*H*(CH$_3$)$_2$), 4.81 (s, 1H, N*H*), 6.30 (s, 2H, C*H*Ph$_2$), 6.88 (s, 2H, Ar† *m*-Ar-*H*), 7.05-7.30 (m, 23H, Ar*H*); $^{13}$C{H} NMR (100 MHz, $C_6D_6$, 298 K): δ = 22.8 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 25.5 (C(*C*H$_3$)$_3$), 29.1 (*C*H(CH$_3$)$_2$), 34.1 (*C*H(CH$_3$)$_2$), 40.1 (*C*(CH$_3$)$_3$), 53.2 (*C*HPh$_2$), 122.0, 123.0, 126.7, 126.8, 127.4, 128.5, 128.7, 130.9 136.0, 137.3, 143.6, 144.5, 146.3, 147.3 (Ar-*C*), 156.2 (N*C*N); IR *v*/cm$^{-1}$ (ATR): 1624 (s), 1587 (m), 1476 (s), 1449 (s), 1333 (w), 1285 (w), 1252 (w), 1236 (w), 1150 (m), 1100 (m), 1076 (m), 748 (s), 699 (vs), 650 (w), 627 (m), 606 (s); acc. MS/ESI *m/z*: calc: 711.4678, found: 711.4686 (MH$^+$).

**[K(L$^{Ad}$)].** L$^{Ad}$H (15 g, 19 mmol) was combined with KH (1.0g, 26 mmol) and K{N(SiMe$_3$)$_2$} (190 mg, 0.95 mmol), then dissolved in toluene (30 mL). The mixture was heated to 60 ºC for 16 h, then filtered. Volatiles were removed from the filtrate *in vacuo* to give the title compound as a light brown powder (14.1g, 90%). This was successfully used for subsequent syntheses, without further purification. M.p. 244-244 ºC, then blackens at 248 ºC; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = 1.04 (d, $^3J_{HH}$ = 6 Hz, 6H, Ar†-CH(C*H*$_3$)$_2$), 1.23 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.63 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.84 (m, 3H, Ad-*H*), 2.00 (m, 3H, Ad-*H*), 2.22 (m, 3H, Ad-*H*), 2.59 (sept, $^3J_{HH}$ = 6 Hz, 1H, Ar†-C*H*(CH$_3$)$_2$), 2.73 (m, 6H, Ad-*H*), 3.57 (sept, $^3J_{HH}$ = 6 Hz, 2H, Dip-C*H*(CH$_3$)$_2$), 6.36 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Dip *p*-Ar-*H*), 6.43 (s, 2H, C*H*Ph$_2$), 6.50-7.50 (m, 24H, Ar-*H*); $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 298 K): $\delta$ = 22.2, 24.4, 24.7 (CH(*C*H$_3$)$_2$), 29.7, 30.6 (*C*H(CH$_3$)$_2$), 34.0, 38.3, 43.5, 46.4 (Ad-*C*), 52.9 (*C*HPh$_2$), 117.0, 121.8, 125.8, 126.8, 129.0, 130.8, 138.7, 139.1, 141.0, 149.5, 151.9, 156.8 (Ar-*C*), 163.2 (N*C*N); MS/ESI *m/z* (%): 788.9 ($L^{ad}H_2^+$, 1).

**[$L^{tBu}$MgBu$^n$] (5).** MgBu$^n_2$ (1 M in hexane, 1.54 mL, 1.54 mmol) was added to a solution of $L^{tB}$H (500 mg, 0.63 mmol) in toluene (30 mL), and the mixture heated at 60 °C overnight. Volatiles were then removed *in vacuo*. The resultant white solid was extracted with 10 mL hexane then filtered. Concentration of the filtrate to *ca.* 2 mL followed by storage at -30 °C for 2 days resulted in the formation of colourless needles of **5** (260 mg, 47%). M.p: 172-175 °C; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = -1.08 (t, $^3J_{HH}$ = 8 Hz, 2H, MgC*H*$_2$), 0.90 (m, 7H, MgCH$_2$C*H*$_2$), 0.91 (m, 2H, MgC$_2$H$_4$C*H*$_2$), 0.98 (d, $^3J_{HH}$ = 7 Hz, 6H, Ar$^†$-CH(C*H*$_3$)$_2$), 1.14 (d, $^3J_{HH}$ = 7 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.19 (m, 3H, MgC$_3$H$_6$C*H*$_3$), 1.25 (s, 9H, Bu$^t$), 1.31 (d, $^3J_{HH}$ = 7 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 2.52 (sept, $^3J_{HH}$ = 6 Hz, 1H, Ar$^†$-C*H*(CH$_3$)$_2$), 3.50 (sept, $^3J_{HH}$ = 6 Hz, 2H, Dip-C*H*(CH$_3$)$_2$), 6.10 (s, 2H, C*H*Ph$_2$), 6.91-7.29 (m, 25H, Ar-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$, 298 K): δ = 6.2 (Mg*C*H$_2$) 14.4 (MgC$_3$H$_6$*C*H$_3$) 21.8, 24.2 (CH(*C*H$_3$)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 29.1 (C(*C*H$_3$)$_3$), 30.5 (*C*H(CH$_3$)$_2$), 31.5 (MgC$_2$H$_4$*C*H$_2$CH$_3$), 31.7 (MgCH$_2$*C*H$_2$), 33.9 (CH(*C*H$_3$)$_2$), 43.3 (*C*(CH$_3$)$_3$), 54.1 (*C*HPh$_2$), 123.0, 124.3, 126.5, 126.9, 128.4, 128.5, 130.3, 138.9, 142.5, 143.1, 143.5, 144.3 (Ar-*C*), 175.9 (N*C*N); IR *ν*/cm$^{-1}$ (ATR): 1599 (vs), 1242 (s), 1213 (s), 1176 (s), 1102 (s), 1076 (s), 1032 (s), 831 (m), 804 (m), 765 (s), 707 (vs); MS/ESI *m/z* (%): 710.6 ($L^{tB}H_2^+$, 38). N.B. A reproducible microanalysis of the compound could not be obtained as it consistently co-crystallised with small amounts (*ca.* 3%) of the amidine $L^{tBu}$H.

**[$L^{Ad}$MgBu$^n$] (6).** MgBu$^n_2$ (1 M in hexane, 1.4 mL, 1.4 mmol) was added to $L^{Ad}$H (500 mg, 0.63 mmol) dissolved in toluene (30 mL), and the mixture heated at 60 ºC overnight. Volatiles were then removed *in vacuo* and the white residue extracted into hexane (10 mL). This was filtered and the filtrate concentrated to *ca.* 2 mL, followed by storage at -30 ºC for 2 days. This resulted in the formation of colourless needles of **6** (330 mg, 60 %). M.p. 233-234 °C; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = -1.05 (t, $^3J_{HH}$ = 6Hz, 2H, MgC*H*$_2$), 0.90 (m, 3H, MgC$_3$H$_6$C*H*$_3$), 0.93 (d, $^3J_{HH}$ = 6 Hz, 6H, Ar$^†$-CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.16 (overlapping m, 4H, MgCH$_2$(C*H*$_2$)$_2$Me), 1.35 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.47 (m, 6H, Ad-*H*), 1.77 (s, 3H, Ad-*H*), 2.27 (s, 6H, Ad-*H*), 2.51 (sept, $^3J_{HH}$ = 6 Hz, 1H, Ar$^†$-C*H*(CH$_3$)$_2$), 3.56 (sept, $^3J_{HH}$ = 6 Hz, 2H, Dip-C*H*(CH$_3$)$_2$), 6.20 (s, 2H, C*H*Ph$_2$), 6.93-7.35 (m, 25H, Ar-*H*); $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 298 K): $\delta$ = 6.3 (Mg*C*H$_2$), 14.2 (MgC$_3$H$_6$*C*H$_3$), 22.0, 24.2 (CH(*C*H$_3$)$_2$), 26.1, 28.9 (*C*H(CH$_3$)$_2$), 29.2

(Ad-*C*), 31.5 ($Bu^n$-*C*$H_2$), 31.7 ($Bu^n$-*C*$H_2$), 33.9, 36.7, 40.3 (Ad-*C*), 54.1 (*C*$HPh_2$), 123.0, 124.1, 126.5, 126.9, 128.5, 130.0, 130.3, 131.2, 138.7, 142.2, 143.6, 144.4 (Ar-*C*), 175.6 (N*C*N); IR *v*/$cm^{-1}$ (Nujol): 1617 (m), 1600 (w), 1259 (s), 1227 (m), 1181 (w), 1091 (s), 1062 (s), 1030 (vs), 864 (w), 796 (s), 761 (s), 669 (vs); MS/ESI *m/z* (%): 788.8 ($L^{ad}H_2^+$, 28). N.B. A reproducible microanalysis of the compound could not be obtained as it consistently co-crystallised with small amounts (*ca.* 5%) of the amidine $L^{Ad}$H.

**[$L^{Ad}$Ca{N(SiMe$_3$)$_2$}] (7).** [$CaI_2(THF)_2$] (525 mg, 1.21 mmol), K{N($SiMe_3$)$_2$} (240 mg, 1.21 mmol) and [K($L^{Ad}$)] (1.00 g, 1.21 mmol) were combined in a Schlenk flask. THF (15 mL) was added and the mixture stirred for 4h at room temperature. Volatiles were removed *in vacuuo*, then toluene (20 mL) was added, and the mixture stirred for another 4h. Volatiles were removed under reduced pressure and the sticky residue extracted with pentane (25 mL), and the extract filtered. Removing volatiles from the extract under reduced pressure yielded **7** as an off white powder (290 mg, 24 %). A second crop was recovered by extracting the remaining residue with toluene (10 mL) and allowing for slow precipitation of a microcrystalline powder at -40 °C over several days (190 mg, 16%, combined yield, 40 %). M.p: 241-244 ºC; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = -0.02 (s, 18H, N{Si(C*H*$_3$)$_3$}$_2$) 1.04 (d, $^3J_{HH}$ = 6 Hz, 6H, Ar$^†$-CH(C*H*$_3$)$_2$), 1.20-1.34 (m, 6H, Ad-*H*) 1.36 (m, 12H, Dip-CH(C*H*$_3$)$_2$), 1.57 (s, 3H, Ad-*H*), 1.84 (s, 6H, Ad-*H*), 2.58 (sept, $^3J_{HH}$ = 6 Hz, 1H, Ar$^†$-C*H*(CH$_3$)$_2$), 3.57 (sept, $^3J_{HH}$ = 6 Hz, 2H, Dip-C*H*(CH$_3$)$_2$), 6.11 (s, 2H, C*H*Ph$_2$), 7.07-7.25 (m, 25H, Ar-*H*); $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 298 K): $\delta$ = 5.8 (N{Si(*C*H$_3$)$_3$}$_2$), 23.0, 24.3 (CH(*C*H$_3$)$_2$), 27.0, 28.9 (*C*H(CH$_3$)$_2$), 33.8, 36.4, 39.8, 47.9 (Ad-*C*), 53.3 (*C*HPh$_2$), 123.1, 123.7, 127.0, 127.5, 129.1, 129.7, 130.2, 130.4, 135.7, 141.1, 143.2, 147.5 (Ar-*C*), 174.4 (N*C*N); $^{29}$Si{$^1$H} NMR (80 MHz, $C_6D_6$, 298 K): $\delta$ = -15.8; IR *v*/$cm^{-1}$ (Nujol): 1597 (s), 1306 (w), 1264 (m), 1238 (m), 1183 (m), 1058 (s), 1038 (s), 1228 (w), 934 (m), 880 (m), 820 (s), 766 (m), 754 (m); MS/ESI *m/z* (%): 788.7 ($L^{Ad}H_2^+$, 25). N.B. A reproducible microanalysis of the compound could not be obtained as it consistently co-crystallised with small amounts (*ca.* 3%) of the amidine $L^{Ad}$H.

**[$L^{Ad}$Sr{N(SiMe$_3$)$_2$}] (8).** [$SrI_2(THF)_2$] (583 mg, 1.21 mmol), K{N($SiMe_3$)$_2$} (240 mg, 1.21 mmol) and [K($L^{Ad}$)] (1.00 g, 1.21mmol) were combined in a Schlenk flask. THF (15 mL) was added and the mixture stirred for 4h at room temperature. Volatiles were removed *in vacuo*, and toluene (20 mL) was added to the residue, before the mixture stirred for a further 4h. Volatiles were removed once more, and the sticky residue extracted with pentane (25 mL), and the extract filtered. Removing volatiles from the extract under reduced pressure yielded **8** as an off-white powder (320 mg, 26 %). A second crop was recovered by extracting the remaining residue with toluene (10 mL) and allowing for slow crystallization at -40 °C over several days (365 mg, 29%, combined yield, 55%). M.p: 191-193 ºC; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = -0.02 (s, 18H, N{Si(C*H*$_3$)$_3$}$_2$) 1.04 (d, $^3J_{HH}$ = 6 Hz, 6H, Ar$^†$-CH(C*H*$_3$)$_2$), 1.28 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.30 (m, 6H, Ad-*H*) 1.36 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.61 (s, 3H, Ad-*H*), 1.88 (s, 6H, Ad-*H*), 2.58 (sept, $^3J_{HH}$ = 6 Hz, 1H, Ar$^†$-C*H*(CH$_3$)$_2$), 3.58 (sept, $^3J_{HH}$ = 6 Hz, 2H, Dip-C*H*(CH$_3$)$_2$), 6.15 (s, 2H, C*H*Ph$_2$), 7.05-7.38 (m, 25H, Ar-*H*); $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 298 K): *δ* = 5.8 (N{Si(*C*H$_3$)$_3$}$_2$), 22.5, 24.3 (CH(*C*H$_3$)$_2$), 27.4, 28.8, 28.9 (*C*H(CH$_3$)$_2$), 33.7, 36.6, 40.0, 48.5 (Ad-*C*), 53.3 (*C*HPh$_2$), 122.6, 123.5, 127.0, 127.7, 129.0, 129.8, 130.7, 135.4, 140.1, 140.6, 143.5, 146.0, 148.7, 148.9 (Ar-*C*), 172.3 (N*C*N); $^{29}$Si{$^1$H} NMR (80 MHz, $C_6D_6$, 298 K): *δ* = -18.0; IR *ν*/cm$^{-1}$ (Nujol): 1613 (m), 1176 (w), 1108 (w), 1059 (m), 931 (m), 878 (m), 820 (m), 757 (m), 1058 (s), 1038 (s), 1228 (w), 934 (m), 880 (m), 820 (s), 696 (vs); MS/ESI *m/z* (%): 788.7 (L$^{Ad}$H$_2^+$, 14); anal. calc. for $C_{64}H_{81}SrN_3Si_2$: C, 74.19%, H, 7.88%, N, 4.06%. found: C, 74.41%, H, 7.80%, N, 3.96%.

**[L$^{Ad}$Ba{N(SiMe$_3$)$_2$}] (9).** [BaI$_2$(THF)$_2$] (695 mg, 1.21 mmol), K{N(SiMe$_3$)$_2$} (240 mg, 1.21 mmol) and [K(L$^{Ad}$)] (1.00 g, 1.21mmol) were combined in a Schlenk flask. THF (15 mL) was added and the mixture stirred for 4h at room temperature. Volatiles were removed *in vacuo*, toluene (10 mL) added, and the mixture stirred for another 4h. Volatiles were removed once more and the sticky residue extracted with pentane (20 mL), and the extract filtered. Removing volatiles from the extract under reduced pressure yielded **9** as an off-white powder (291 mg, 22 %). M.p: 184-186 ºC; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = 0.10 (s, 18H, N{Si(C*H*$_3$)$_3$}$_2$) 1.05 (d, $^3J_{HH}$ = 6 Hz, 6H, Ar$^†$-CH(C*H*$_3$)$_2$), 1.22 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.39 (d, $^3J_{HH}$ = 6 Hz, 6H, Dip-CH(C*H*$_3$)$_2$), 1.52 (m, 6H, Ad-*H*), 1.87 (s, 3H, Ad-*H*), 2.31 (s, 6H, Ad-*H*), 2.58 (sept, $^3J_{HH}$ = 6 Hz, 1H, Ar$^†$-C*H*(CH$_3$)$_2$), 3.53 (sept, $^3J_{HH}$ = 6 Hz, 2H, Dip-C*H*(CH$_3$)$_2$), 6.17 (s, 2H, C*H*Ph$_2$), 7.00-7.40 (m, 25H, Ar*H*). $^{13}$C{$^1$H} NMR (75 MHz, $C_6D_6$, 298 K): *δ* =6.8 (N{Si(*C*H$_3$)$_3$}$_2$), 23.4, 24.4, 26.7 (CH(*C*H$_3$)$_2$), 28.5, 29.3 (*C*H(CH$_3$)$_2$), 33.8, 36.9, 41.0, 49.1 (Ad-*C*), 50.0 (*C*HPh$_2$), 122.0, 123.5, 126.3, 127.0, 129.1, 129.3, 129.7, 129.9, 130.0, 130.4, 137.3, 139.6, 143.5, 147.5 (Ar-*C*), 167.3 (N*C*N); $^{29}$Si{$^1$H} NMR (80 MHz, $C_6D_6$, 298 K): *δ* = -18.3; IR *ν*/cm$^{-1}$ (Nujol): 1596 (m), 1173 (w), 1098 (w), 1078 (w), 1031 (s), 931 (m), 878 (m), 814 (s), 706 (s); MS/ESI *m/z* (%): 788.8 (L$^{Ad}$H$_2^+$, 29); anal. calc. for $C_{64}H_{81}BaN_3Si_2$: C, 70.79%, H, 7.52%, N, 3.87%. found: C, 70.63%, H, 7.65%, N, 3.66%.

**[L$^{tBu}$Mg(μ-H)]$_2$ (10).** PhSiH$_3$ (1.02 mL, 8.27 mmol) was added to **5** (2.90 g, 3.93 mmol) in toluene (20 mL). This mixture was heated to 60 ºC for 4h then filtered, and the filtrate concentrated to 3 mL. Hexane (30 mL) was added to the concentrate with vigourous stirring, resulting in a white precipitate. After 30 minutes, the suspension was filtered to yield **10** as a white solid (1.87 g, 60%). M.p: >260 °C; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = 0.71 (s, 18H, Bu$^t$), 1.06 (d, $^3J_{HH}$ = 7 Hz, 12H, Ar$^†$-CH(C*H*$_3$)$_2$), 1.09 (d, $^3J_{HH}$ = 7 Hz, 12H, Dip-CH(C*H*$_3$)$_2$), 1.27 (d, $^3J_{HH}$ = 7 Hz, 12H, Dip-

$CH(CH_3)_2$), 2.66 (sept, $^3J_{HH}$ = 7 Hz, 2H, Ar†-C*H*($CH_3)_2$), 3.52 (sept, $^3J_{HH}$ = 6 Hz, 4H, Dip-C*H*($CH_3)_2$), 3.86 (s, 2H, Mg*H*), 6.25 (s, 4H, C*H*$Ph_2$), 6.91–7.22 (m, 50H, Ar-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$, 298 K): δ = 22.7, 24.5, 26.5 (CH(*C*$H_3)_2$), 29.2 (C(*C*$H_3)_3$), 29.5, 34.0 (*C*H($CH_3)_2$), 42.5 (*C*($CH_3)_3$), 53.4 (*C*H$Ph_2$), 123.1, 124.4, 126.8, 126.9, 128.8, 129.7, 129.9, 130.4, 137.2, 142.3, 143.0, 143.4, 143.6, 145.7 (Ar-*C*), 177.8 (N*C*N); IR υ/$cm^{-1}$ (ATR): 1600 (m), 1494 (m), 1402 (s), 1317 (w), 1261 (s), 1097 (vs), 1030 (vs), 934 (w), 866 (m), 801 (s), 763 (m), 702 (s); MS/ESI *m/z* (%): 710.6 ($L^{tBu}H_2^+$, 21).

**[$L^{Ad}$Mg(μ-H)]$_2$ (11).** $PhSiH_3$ (1 mL, 5.8 mmol) was added to **6** (2.29g, 2.63 mmol) in toluene (20 mL). The mixture was heated to 60 ºC for 4h, filtered, and the filtrate concentrated to 3 mL. Hexane (30 mL) was added with vigourous stirring, resulting in a white precipitate. After 30 minutes, the suspension was filtered to give **11** as a white solid (520 mg, 26 %). M.p. >260 °C; $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = 0.97 (m, 6H, Ad-*H*), 1.04 (d br, $^3J_{HH}$ = 7 Hz, 12H, Ar†-CH(C*H*$_3)_2$), 1.09 (d, $^3J_{HH}$ = 7 Hz, 12H, Dip-CH(C*H*$_3)_2$), 1.19 (m, 9H, Ad-*H*), 1.32 (d, $^3J_{HH}$ = 7 Hz, 12H, Dip-CH(C*H*$_3)_2$), 1.45 (m, 9H, Ad-*H*), 1.72 (m, 6H, Ad-*H*), 2.68 (sept, $^3J_{HH}$ = 7 Hz, 2H, Ar†-C*H*($CH_3)_2$), 3.58 (sept, $^3J_{HH}$ = 6 Hz, 4H, Dip-C*H*($CH_3)_2$), 3.84 (s, 2H, Mg*H*), 6.25 (s, 4H, C*H*$Ph_2$), 6.93-7.50 (m, 50H, Ar-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$, 298 K): δ = 20.0, 22.4 (CH(*C*$H_3)_2$), 26.5 (Ad-*C*), 27.3, 32.0 (CH(*C*$H_3)_2$), 34.1, 36.8, 44.0 (Ad-*C*), 51.4 (*C*H$Ph_2$), 121.1, 122.1, 124.7, 125.9, 126.2, 126.9, 127.3, 127.4, 127.6, 127.8, 128.0, 128.3, 128.4, 134.8, 139.9, 140.6, 141.5, 141.8, 144.0 (Ar-*C*), 175.5 (N*C*N); IR υ/$cm^{-1}$ (Nujol): 1599 (m), 1264 (m), 1231 (w), 1179 (w), 1147 (m), 1111 (m), 1073 (w), 1062 (w), 1031 (m), 919 (m), 748(m), 715 (w), 699 (s), 644(m); MS/ESI *m/z* (%): 788.9 ($L^{ad}H_2^+$, 3). N.B. A reproducible microanalysis of the compound could not be obtained as it consistently co-crystallised with small amounts (*ca.* 3%) of the amidine $L^{Ad}$H. The molecular connectivity of the complex was confirmed by an X-ray crystal structure. The diffraction data were, however, of insufficient quality to publish the crystal structure here.

**[$L^{Ad}$Sr(μ-H)]$_2$ (12).** Compound **8** (80 mg, 0.078 mmol) was dissolved in hexane (5 mL). $PhSiH_3$ (0.020 mL, 0.016 mmoL) was added and the mixture allowed to stand at room temperature for 1h, then stored at -30 ºC overnight, yielding large colourless crystals of **8** (62 mg, 98%). M.p: decomposes slowly at R.T. $^1$H NMR (300 MHz, $C_6D_6$, 298 K): δ = 1.07 (d, $^3J_{HH}$ = 7 Hz, 12H, Ar†-CH(C*H*$_3)_2$), 1.31-1.56 (complex m, 54H, Ad-*H* and Dip-CH(C*H*$_3)_2$), 2.49 (sept, $^3J_{HH}$ = 7 Hz, 2H, Ar†-C*H*($CH_3)_2$), 3.59 (sept, $^3J_{HH}$ = 6 Hz, 4H, Dip-C*H*($CH_3)_2$), 4.90 (br, 2H, Sr*H*), 6.27 (s, 4H, C*H*$Ph_2$), 6.89-7.30 (m, 50H, Ar-*H*); $^1$H NMR (400 MHz, $d_8$-toluene, 253 K): δ = 0.92 (d, $^3J_{HH}$ = 7 Hz, 12H, Ar†-CH(C*H*$_3)_2$), 1.34 (d, $^3J_{HH}$ = 6 Hz, 12H, Dip-CH(C*H*$_3)_2$), 1.40 (m, 12H, Ad-*H*), 1.47 (d,

$^{3}J_{HH}$ = 6 Hz, 12H, Dip-CH(C*H*$_3$)$_2$), 1.71 (m, 6H, Ad-*H*), 1.93 (m, 12H, Ad-*H*), 2.58 (sept, $^{3}J_{HH}$ = 6 Hz, 2H, Ar$^†$-C*H*(CH$_3$)$_2$), 3.60 (sept, $^{3}J_{HH}$ = 6 Hz, 4H, Dip-C*H*(CH$_3$)$_2$), 5.41 (br, 2H, Sr*H*), 6.23 (s, 4H, C*H*Ph$_2$), 6.76-7.44 (complex, 50H, Ar-*H*); $^{13}$C{$^1$H} NMR (100 MHz, *d*$_8$-toluene, 253 K): 19.8 (Dip-CH(*C*H$_3$)$_2$), 24.3 (Ar$^†$-CH(*C*H$_3$)$_2$), 28.8 (Ar$^†$-*C*H(CH$_3$)$_2$), 28.9 (Ad-*C*), 33.5 (Dip-*C*H(CH$_3$)$_2$), 36.5 (Ad-*C*), 39.6 (Ad-*C*), 48.0 (Ad-*C*), 53.4 (*C*HPh$_2$), 122.3, 126.8, 129.0, 129.9, 130.2, 136.1, 137.4, 143.0, 132.9, 146.6, 147.3 (Ar-*C*, some signals obscured by solvent peaks), 170.5 (N*C*N); IR υ/cm$^{-1}$ (Nujol): 1600 (s), 1262 (s), 1235 (m), 1205 (w), 1183 (m), 1090 (m), 1076 (s), 1030 (w), 1018 (w), 962 (w), 931(m), 728 (m), 707 (s); MS/ESI *m/z* (%): 788.8 (L$^{ad}$H$_2^+$, 25); microanalysis of the compound was not possible due to its thermal instability.

## 2. X-Ray Crystallography

Crystals of Ar$^†$N(H)C(O)Ad **1S**, L$^{tBu}$H **2S**, L$^{Ad}$H **3S**, K(L$^{Ad}$) **4S**, **5**, **6**, **8**, **10** (two solvates) and **12** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either a Bruker X8 CCD diffractometer (λ = 0.71073 Å), or the Australian Synchrotron (λ = 0.71080 Å). The software package Blu-Ice[3] was used for synchrotron data acquisition, while the program XDS[4] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F$^2$ by full matrix least squares (SHELX97[5]) using all unique data. Hydrogen atoms are included in calculated positions (riding model), except the amine proton of **2S**, and the hydride ligands of **10**·(toluene)·(benzene)$_{0.5}$·(hexane)$_{0.75}$ and **12**, the atomic displacement and positional parameters a of which were refined isotropically. Structural parameters for **10** that are used in the main text were obtained from the solvate, **10**·(toluene)·(benzene)$_{0.5}$·(hexane)$_{0.75}$. The structural parameters for the other solvate are very similar. Flack parameters for chiral crystal structures were refined as 0(3) **2S**, 0.0029(8) **4S** and 0.046(6) **5**. Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

**Table S1.** Summary of Crystallographic Data for Compounds **1S-4S**, **5**, **6**, **8**, **10** (two solvates) and **12**.

| | **1S** | **2S** | **3S**·(toluene) | **4S**·(toluene)$_2$ | **5**·(hexane)$_{0.5}$ | **6**·(hexane)$_{0.5}$ |
|---|---|---|---|---|---|---|
| empirical formula | $C_{46}H_{47}NO$ | $C_{52}H_{58}N_2$ | $C_{65}H_{72}N_2$ | $C_{72}H_{79}KN_2$ | $C_{59}H_{73}MgN_2$ | $C_{65}H_{79}MgN_2$ |
| formula weight | 629.85 | 711.00 | 881.25 | 1011.47 | 834.50 | 912.61 |
| crystal system | Monoclinic | Orthorombic | Triclinic | Triclinic | Triclinic | Monoclinic |
| space group | $P2_1/n$ | $Pna2_1$ | $P$-1 | $P$-1 | P-1 | $P2_1/n$ |
| a (Å) | 8.5254(5) | 17.6472(9) | 10.7693(7) | 11.0746(5) | 10.617(2) | 10.920(2) |
| b (Å) | 25.7341(15) | 22.0745(11) | 13.8287(7) | 14.6742(6) | 13.060(3) | 36.006(7) |
| c (Å) | 16.0537(12) | 10.8828(6) | 18.7281(9) | 19.4655(8) | 18.769(4) | 13.878(3) |
| α (º) | 90 | 90 | 97.154(2) | 100.224(2) | 88.61(3) | 90 |
| β (º) | 100.564(2) | 90 | 93.116(2) | 99.400(2) | 78.20(3) | 103.99(3) |
| γ (º) | 90 | 90 | 112.207(2) | 108.468(2) | 77.65(3) | 90 |
| V (Å$^3$) | 3462.4(4) | 4239(4) | 2546(2) | 2870.0(2) | 2488.0(9) | 5294.9(18) |
| Z | 4 | 4 | 2 | 2 | 2 | 4 |
| T (K) | 123(2) | 123(2) | 123(2) | 123(2) | 100(2) | 123(2) |
| $\rho_{calcd}$ (g×cm$^3$) | 1.208 | 1.114 | 1.149 | 1.170 | 1.114 | 1.145 |
| μ (mm$^{-1}$) | 0.071 | 0.064 | 0.065 | 0.137 | 0.075 | 0.076 |
| F(000) | 1352 | 1536 | 952 | 1088 | 906 | 1980 |
| reflns collected | 51425 | 48025 | 43347 | 39562 | 16262 | 49026 |
| unique reflns | 6934 | 7078 | 10066 | 11357 | 8139 | 10788 |
| $R_{int}$ | 0.1064 | 0.0787 | 0.0688 | 0.0503 | 0.0911 | 0.0846 |
| R1 [I > 2σ(I)] | 0.0589 | 0.0503 | 0.0702 | 0.0532 | 0.0740 | 0.0746 |
| wR2 (all data) | 0.1627 | 0.1234 | 0.1996 | 0.1507 | 0.2128 | 0.1919 |
| largest peak and hole (e×Å$^{-3}$) | 0.25, -0.22 | 0.32, -0.25 | 1.41, -0.43 | 0.99, -0.45 | 0.51, -0.33 | 0.70, -0.39 |
| CCDC no. | 1589242 | 1589251 | 1589245 | 1589243 | 1589244 | 1589248 |

**Table S1 (contd.).** Summary of Crystallographic Data for Compounds **1S-4S**, **5**, **6**, **8**, **10** (two solvates) and **12**.

| | **8** | **10**·(toluene)·(benzene)$_{0.5}$ ·(hexane)$_{0.75}$ | **10**·(cyclohexane)$_2$ | **12**·(benzene)$_3$ |
|---|---|---|---|---|
| emp. form. | $C_{64}H_{81}N_3Si_2Sr$ | $C_{118.5}H_{137.5}Mg_2N_4$ | $C_{118}H_{144}Mg_2N_4$ | $C_{134}H_{146}N_4Sr_2$ |
| form. weight | 1036.12 | 1666.45 | 1666.99 | 1987.79 |
| crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic |
| space group | *P*2$_1$/*n* | *P*-1 | *P*-1 | *C*2/*c* |
| a (Å) | 11.9440(3) | 13.670(3) | 15.8039(4) | 36.5230(12) |
| b (Å) | 23.9840(6) | 17.829(4) | 16.4093(4) | 15.6316(6) |
| c (Å) | 20.6946(4) | 20.639(4) | 19.9724(5) | 22.9906(8) |
| α (º) | 90 | 99.12(3) | 91.713(1) | 90 |
| β (º) | 104.1470(10) | 94.20(3) | 104.171(1) | 126.8260(10) |
| γ (º) | 90 | 92.82(3) | 92.271(1) | 90 |
| V (Å$^3$) | 5748.5(2) | 4943.8(17) | 5013.7(2) | 10506.5(6) |
| Z | 4 | 2 | 2 | 4 |
| T (K) | 123(2) | 100(2) | 123(2) | 123(2) |
| $\rho_{calcd}$ (g×cm$^3$) | 1.197 | 1.119 | 1.104 | 1.257 |
| μ (mm$^{-1}$) | 1.020 | 0.075 | 0.074 | 1.070 |
| F(000) | 2208 | 1801 | 1808 | 4216 |
| reflns collected | 115948 | 33197 | 103397 | 171144 |
| unique reflns | 11289 | 16441 | 19892 | 10437 |
| $R_{int}$ | 0.0984 | 0.0328 | 0.0593 | 0.1058 |
| R1 [I > 2σ(I)] | 0.0432 | 0.0544 | 0.0538 | 0.0509 |
| wR2 (all data) | 0.1017 | 0.1549 | 0.1499 | 0.1408 |
| peak and hole (e×Å$^{-3}$) | 0.80, -0.69 | 0.80, -0.41 | 0.98, -0.34 | 0.60, -0.46 |
| CCDC no. | 1589246 | 1589250 | 1589247 | 1589249 |

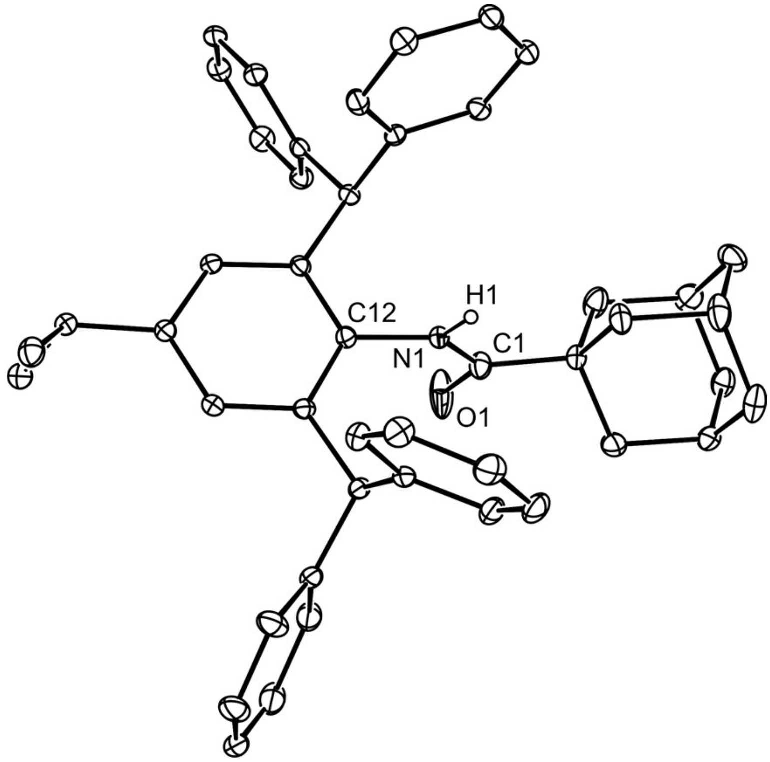


**Figure S1.** ORTEP diagram of Ar†N(H)C(O)Ad **1S** (20% thermal ellipsoids; hydrogen atoms, except H(1), omitted). Selected bond lengths (Å) and angles (°): O(1)-C(1) 1.217(3), N(1)-C(1) 1.344(3), O(1)-C(1)-N(1) 120.9(2), C(1)-N(1)-C(12) 124.3(2).

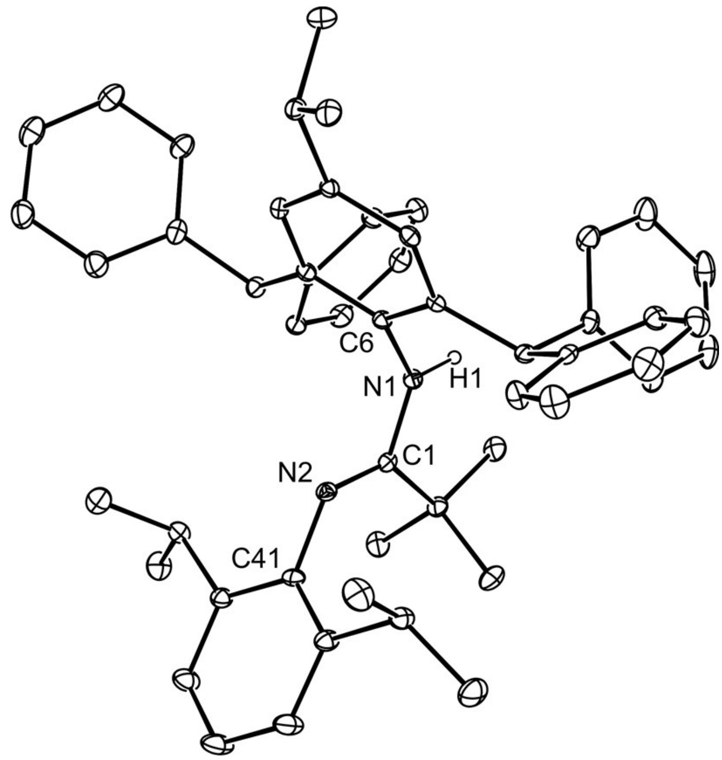


**Figure S2.** ORTEP diagram of $L^{tBu}H$ **2S** (20% thermal ellipsoids; hydrogen atoms, except H(1), omitted). Selected bond lengths (Å) and angles (°): C(1)-N(2) 1.283(3), N(1)-C(1) 1.376(3), N(2)-C(1)-N(1) 117.1(2).

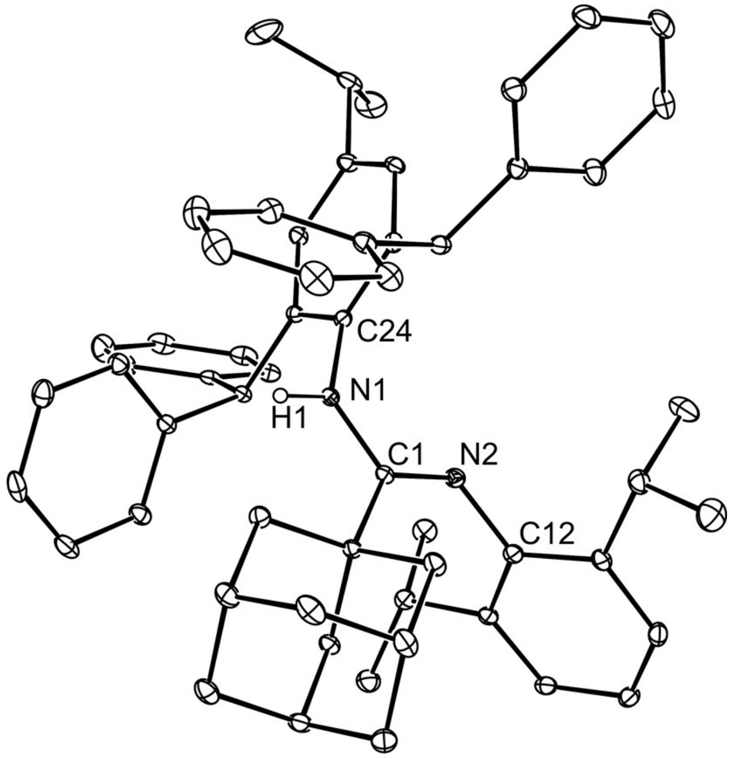


**Figure S3.** ORTEP diagram of $L^{Ad}H$ **3S** (20% thermal ellipsoids; hydrogen atoms, except H(1), omitted). Selected bond lengths (Å) and angles (°): N(1)-C(1) 1.363(3), C(1)-N(2) 1.289(3), N(2)-C(1)-N(1) 117.5(2).

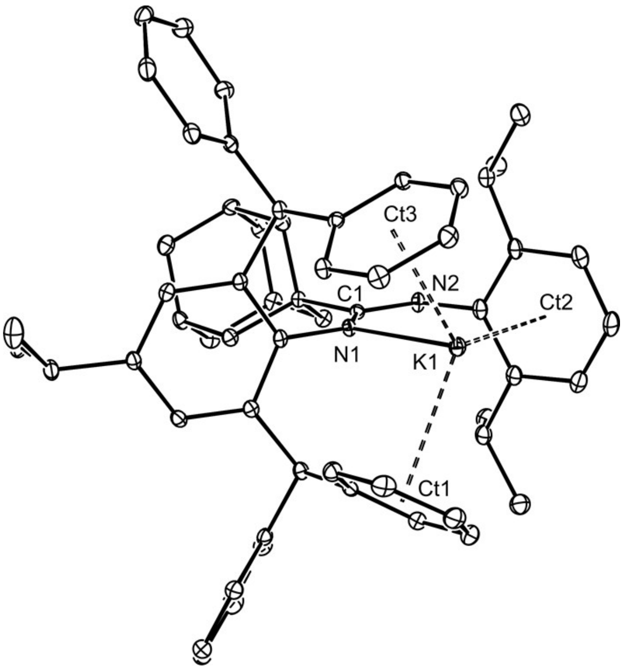


**Figure S4.** ORTEP diagram of [K($L^{Ad}$)] **4S** (20% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): K(1)-N(1) 2.7189(18), N(1)-C(1) 1.347(3), C(1)-N(2) 1.317(3), K(1)-Ct(1) 3.077(1), K(1)-Ct(2) 2.914(1), K(1)-Ct(3) 2.955(1), C(1)-N(1)-K(1) 126.94(13), N(2)-C(1)-N(1) 122.24(19).

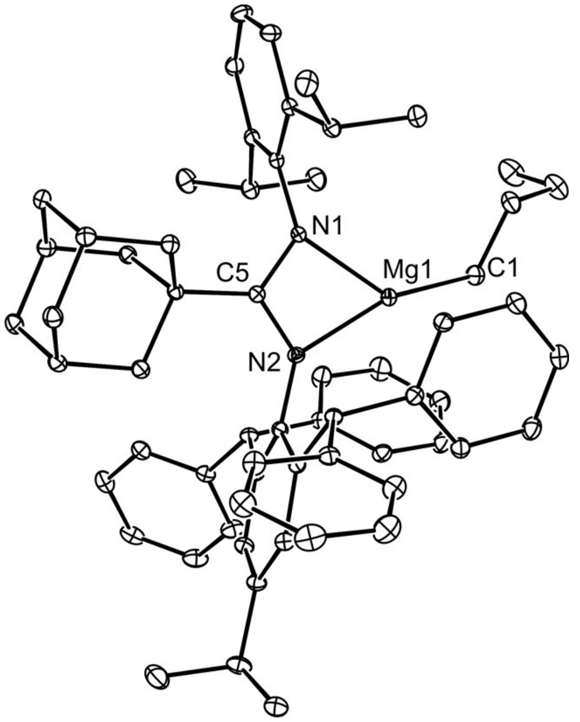


**Figure S5.** ORTEP diagram of [$L^{Ad}MgBu^{n}$] **6** (20% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)-N(2) 2.069(2), Mg(1)-N(1) 2.084(2), Mg(1)-C(1) 2.090(3), N(1)-C(5) 1.349(3), N(2)-C(5) 1.343(3), N(2)-Mg(1)-N(1) 64.16(8), N(2)-Mg(1)-C(1) 153.47(10), N(1)-Mg(1)-C(1) 131.69(10).

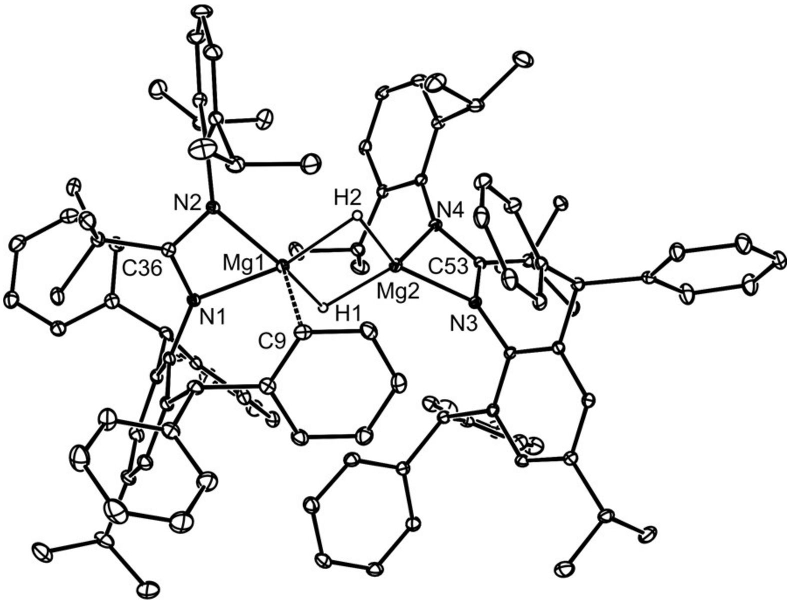


**Figure S6.** ORTEP diagram of [$L^{tBu}Mg(\mu\text{-}H)]_2$ **10** (cyclohexane solvate, 20% thermal ellipsoids; hydrogen atoms, except hydrides, omitted). Selected bond lengths (Å) and angles (°): Mg(1)-N(1) 2.0783(17), Mg(1)-N(2) 2.0795(18), Mg(1)-H(2) 1.969(15), Mg(1)-H(1) 1.896(15), Mg(2)-N(4) 2.0420(18), Mg(2)-N(3) 2.0602(17), Mg(2)-H(2) 1.941(15), Mg(2)-H(1) 1.885(14), Mg(1)-C(9) 2.616(2), N(1)-Mg(1)-N(2) 63.92(7), N(4)-Mg(2)-N(3) 64.92(7), H(2)-Mg(1)-H(1) 86.0(6), H(2)-Mg(2)-H(1) 87.1(6).

## 3. Computational Studies

Geometry optimizations were performed with the Gaussian09 suite of programs (revision D.02)[6] using the Becke's 3-parameter hybrid functional,[7] combined with the non-local correlation functional provided by Perdew/Wang.[8] The 6-311+G(d) all-electron basis set was used for both the magnesium and strontium atom, and the 6-31G(d) for the remaining atoms.[9] We have also considered in the present study dispersion effects, in particular the third generation of Grimme's dispersion corrections with Becke-Johnson damping model[10] on the B3PW91 geometries (single point calculations). All stationary points have been identified for minimum (Nimag=0) Natural population analysis (NPA) was performed using Weinhold's methodology.[11]

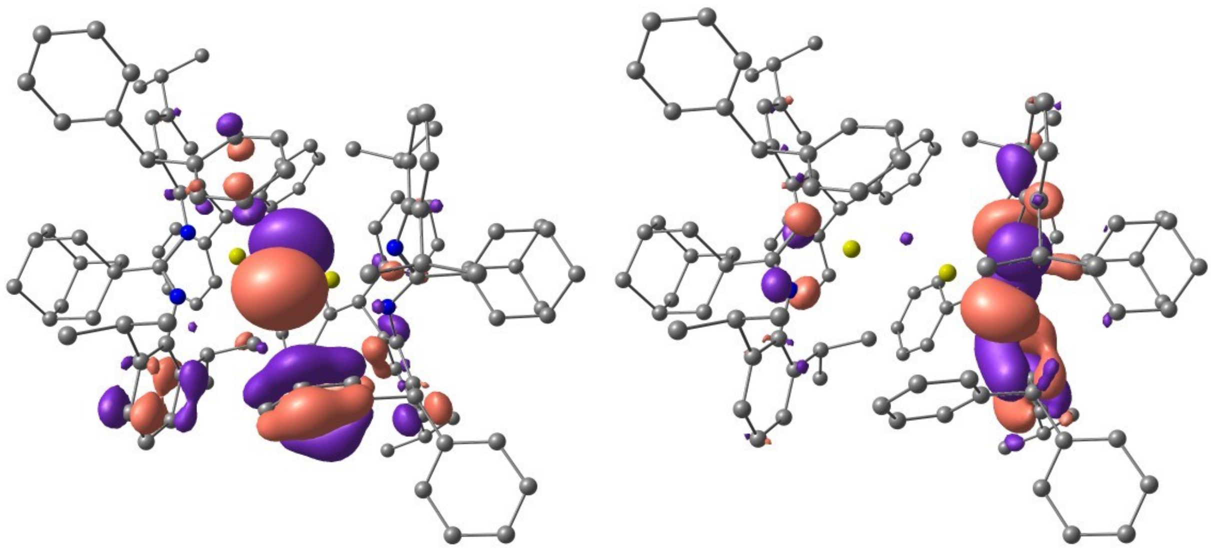

**Figure S7.** HOMO-8 (left) and HOMO (right) of compound **11**.

**Table S4.** Coordinates of the calculated structures at the B3PW91-D3BJ level.

**Compound 11**

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**Compound 12**

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