

Supplementary data

Bent metal carbene geometries in amido N-heterocyclic carbene complexes

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Experimental

General Procedures

All manipulations were carried out under a dry oxygen-free nitrogen atmosphere using standard Schlenk techniques, or in a MBraun Unilab glove box, unless otherwise stated. Solvents (hexane, toluene, diethyl ether and thf) were purified by passage through activated alumina towers and degassed with nitrogen prior to use. d_6 -Benzene was distilled from potassium and degassed by three freeze-pump-thaw cycles prior to use. Other reagents were procured from Aldrich or Strem and used without further purification. Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University.

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX300 spectrometer, referenced internally to residual solvent proton resonance, and externally to TMS. Crystallographic X-ray data were collected variously using Bruker SMART 1000 or APEX CCD area detector diffractometers ($\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$) using ω scans. Structure solution and refinement was carried out using the SHELXTL suite of programs.¹

¹ Bruker, 1997, SHELXTL 5.10. Bruker AXS Inc., Madison, Wisconsin, USA. G. M. Sheldrick, Acta Cryst A, 1990, 46, 467. G. M. Sheldrick, 1997, SHELXL97, University of Goettingen, Germany.

Preparation of [LiL] 1a

*n*BuLi (3.04 ml, 7.61 mmol) was added to a cold (−78 °C) solution of HL (1.70 g, 7.61 mmol) in thf (5 ml), during which time the solution turned red. The solution was allowed to warm slowly to room temperature and stirred for 18 hours. Volatiles were removed *in vacuo* to give a sticky red solid. The product was dissolved in diethyl ether (10 ml) and stored at −30 °C overnight to afford **1a** as a crop of colourless crystals suitable for an X-ray diffraction study. Yield: (0.82 g, 80 %). Anal. Calcd for C₂₆H₄₈Li₂N₆: C, 68.10; H, 10.55; N, 18.33 %. Found C, 67.95; H, 10.75; N, 18.16 %. ¹H NMR (300 MHz, *d*₆-benzene, 298 K): δ 1.35 (s, 18H, *t*Bu), 1.37 (s, 18H, *t*Bu), 3.83 (m, br, 8H, CH₂), 6.35 (s, 2H, CH), and 6.49 (s, 2H, CH). ¹³C{¹H} NMR (75 MHz, *d*₆-benzene, 298 K): δ 31.65 (*t*Bu), 33.12 (*t*Bu), 52.35 (NCMe₃), 54.36 (CH₂), 55.1 (CH₂), 55.92 (NCMe₃), 115.46 (CH), 120 (CH), and 198.71 (C_{carbene}).

Preparation of [LiL^{mes}] 1b

As above, but using *n*BuLi (4.20 ml, 6.72 mmol) and L^{mes}H₃Br₂ (1.00 g, 2.24 mmol). The product **1b** was isolated from toluene stored at −30 °C overnight as a colourless solid. Yield: (0.49 g, 75 %). ¹H NMR (300 MHz, *d*₆-benzene, 298 K): δ 1.48 (s, 9H, *t*Bu), 1.98 (s, 6H, 2xCH₃), 2.07 (s, 3H, CH₃), 4.37 (s, 2H, CH₂), 6.17 (s, 1H, CH), 6.53 (s, 1H, CH), and 6.67 (s, 2H, CH). One CH₂ signal (2H) is obscured by the *para*-methyl signal.

Preparation of [MgL₂] 2

A solution of Me₂Mg (0.21 g, 3.78 mmol) in THF (4 ml) was added dropwise to a cold (−78 °C) solution of LH (1.69 g, 7.57 mmol) in THF (10 ml). The solution was allowed to warm to room temperature and stirred for 18 hrs, during which time the pale yellow solution became dark orange. Volatiles were removed *in vacuo* to afford a tan coloured powder. The product was washed with diethyl ether (5 ml), and the resulting microcrystalline precipitate isolated by filtration. The mother liquor was stored at −30 °C overnight to give a crop of colourless crystals of [MgL₂], **2**. Combined yield: 1.29 g, 73 %. Crystals suitable for an X-ray diffraction study were grown from cold (5 °C) diethyl

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ether. Anal. Calcd for $C_{26}H_{48}MgN_6$: C, 66.58; H, 10.32; N, 17.92 %. Found: C, 66.35; H, 10.59; N, 18.52 %. 1H NMR (300 MHz, d_6 -benzene, 298 K): δ 1.48 (s, 18H, *t*Bu), 1.70 (s, 18H, *t*Bu), 3.75 (m, 4H, CH_2), 3.96 (m, 2H, CH_2), 4.12 (m, 2H, CH_2), 6.30 (d, $^3J_{HH} = 1.7$ Hz, 2H, CH), and 6.44 (d, $^3J_{HH} = 1.7$ Hz, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, d_6 -benzene, 298 K): δ 29.24 (*t*Bu), 29.64 (*t*Bu), 47.81 (CH_2), 52.53 (NCMe₃), 55.17 (NCMe₃), 57.44 (CH_2), 113.74(CH), 120.15 (CH), and 185.39 (C_{carbene}).

Preparation of [UO₂L₂] 3a

THF (2 ml) was added to a mixture of **1a** (0.10 g, 0.41 mmol) and UO₂Cl₂·thf₂ (0.10 g, 0.21 mmol) to give an immediate dark brown colour. The solution was stirred for 18 hours, volatiles were then removed *in vacuo* to give a brown solid. The product was dissolved in toluene/hexane (2/2 ml) and stored at -30 °C overnight to afford dark red crystals of **3a** suitable for an X-ray diffraction study. Yield: (0.60 g, 31 %). Anal. Calcd for $C_{26}H_{48}N_6O_2U \cdot \frac{1}{2}C_6H_5CH_3$: C, 49.12; H, 7.00; N, 10.42 %. Found: C, 44.09; H, 6.81; N, 10.60 %. FTIR (KBr pellet, cm^{-1}): 2810, 1590, 1219, 1168, 980, 929, 893, 759, 724. *Major isomer*: 1H NMR (300 MHz, d_6 -benzene, 298 K): δ 1.51 (s, 18H, *t*Bu), 1.57 (s, 18H, *t*Bu), 3.97 (dd, $^3J_{HH} = 5.4$ Hz, $^2J_{HH} = 13.0$ Hz, 2H, CH_2), 5.15 (dt, $^3J_{HH} = 6.0$ Hz, $^2J_{HH} = 13.0$ Hz, 2H, CH_2), 6.34 (d, $^3J_{HH} = 1.7$ Hz, 2H, CH), 6.65 (d, $^3J_{HH} = 1.7$ Hz, 2H, CH), 6.66 (dt, $^3J_{HH} = 5.5$ Hz, $^2J_{HH} = 13.0$ Hz, 2H, CH_2), and 8.22 (dd, $^3J_{HH} = 4.9$ Hz, $^2J_{HH} = 13.0$ Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, d_6 -benzene, 298 K): δ 30.99 (*t*Bu), 34.42 (*t*Bu), 54.79 (CH_2), 57.63 (NCMe₃), 58.06 (NCMe₃), 60.23 (CH_2), 116.76(CH), 120.56 (CH), and 262.80 (C_{carbene}). *Minor isomer 1*: 1H NMR (300 MHz, d_6 -benzene, 298 K): δ 1.47 (s, 18H, *t*Bu), 1.63 (s, 18H, *t*Bu), 2.81 (dt, $^3J_{HH} = 6.1$ Hz, $^2J_{HH} = 12.9$ Hz, 2H, CH_2), 3.87 (dd, $^3J_{HH} = 5.4$ Hz, $^2J_{HH} = 13.6$ Hz, 2H, CH_2), 5.47 (dt, $^3J_{HH} = 5.6$ Hz, $^2J_{HH} = 13.0$ Hz, 2H, CH_2), 6.31 (d, $^3J_{HH} = 1.8$ Hz, 2H, CH), 8.93 (dd, 2H, CH_2). One CH signal (2H) is obscured by signals from the major isomer. *Minor isomer 2*: 1H NMR (300 MHz, d_6 -benzene, 298 K): δ 1.39 (s, 18H, *t*Bu), 1.76 (s, 18H, *t*Bu), 4.96 (dt, $^3J_{HH} = 6.4$ Hz, $^2J_{HH} = 12.9$ Hz, 2H, CH_2), 5.80 (d, $^3J_{HH} = 6.0$ Hz, 2H, CH), 8.14 (dd, $^3J_{HH} = 6.0$ Hz, $^2J_{HH} = 13.4$ Hz, 2H, CH_2), 9.31 (d, $^3J_{HH} = 1.7$ Hz, 2H, CH). Two CH_2 signals (4H) are obscured by signals from the major isomer.

Preparation of $[UO_2L^{mes}_2]$ **3b**

As above, but using **1b** (0.12 g, 0.41 mmol) and $UO_2Cl_2 \cdot 2thf_2$ (0.10 g, 0.21 mmol). Red crystals of **3b** suitable for an X-ray diffraction study were obtained from a toluene/hexane (2/2 ml) mix stored at $-30\text{ }^\circ\text{C}$ overnight. Yield: (0.11 g, 65 %). FTIR (KBr pellet, cm^{-1}): 2958, 1610, 1560, 1490, 1400, 1364, 1202, 1099, 1035, 933, 848, 736. ^1H NMR (300 MHz, d_6 -benzene, 298 K): δ 0.94 (s, 18H, *t*Bu), 2.07 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 3.02 (m, 4H, CH_2), 3.58 (m, 4H, CH_2), 6.21 (d, $^3J_{\text{HH}} = 1.6\text{ Hz}$, 2H, CH), 6.24 (d, $^3J_{\text{HH}} = 1.4\text{ Hz}$, 2H, CH), 6.65 (s, 2H, CH), 6.64 (s, 2H, CH).

X-Ray Crystallography

Crystals were coated in perfluoropolyether oil, mounted on a glass fibre tipped goniometer, then fitted on the diffractometer.