Supporting Information

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Anionic amido- N-heterocyclic carbenes; synthesis of covalently tethered lanthanide carbene complexes

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Experimental

General Procedures
All manipulations were carried out under a dry oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box unless otherwise stated. The solvents used (toluene, thf, diethyl ether) were degasses and purified by passage through activated alumina towers prior to use. Benzene-d6 was refluxed over potassium, and vacuum transferred prior to use. (2-Bromo-ethyl)-tert-butyl-ammonium bromide was prepared according to the literature.1 Other reagents were procured from Aldrich or Strem. Elemental analyses were determined by Mr. Stephen Boyer at London University.

1H and 13C NMR spectra were recorded on a Bruker AMX300 spectrometer, referenced internally to residual solvent proton resonance, and externally to TMS. Melting points were obtained in sealed glass capillaries under dinitrogen and are reported uncorrected.

Crystallographic X-ray data, were collected using Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART1000 CCD area detector diffractometer using o scans. Structure solution and refinement was carried out using the SHELXL suite of programs.2

Preparations

[H3LBr2] 1
In air, to a stirred suspension of (2-Bromo-ethyl)-tert-butyl-ammonium bromide (20g, 77mmol) in acetonitrile (300ml) was added tert-butyl imidazole (9.6g, 77mmol). The beige suspension was refluxed for 48 h, during which a brown precipitate formed. The precipitate was removed by filtration and the resulting colourless solution was cooled to -30°C for 18 h to afford colourless precipitate formed. This was isolated and recrystalised from acetonitrile to yield colourless 1 (13 g, 44 %). Crystals suitable for single crystal X-ray diffraction were grown from a chloroform solution at room temperature.

NMR/C6D6 δH 1.34 (1H, s, NH2+), 1.56 (9H, s, t-Bu), 1.75 (9H, s, t-Bu), 3.53 (2H, t, JCH2-CH2 5.5 Hz, CH2), 5.17 (2H, t, J 5.5 Hz, CH2), 7.39 (1H, d, J 3.8 Hz, CH), 7.72 (1H, d, J 3.6 Hz, CH), MS(ES) 224.31([H 2L]+, 100%) 225.31([H 3L]+, 22%).


[LiBr.H2LBr] 2
To a suspension of 1 (0.61 g, 1.6 mmol) in thf (30 ml) was added a solution of LiN{SiMe 3}2 (0.264 g, 1.6 mmol) in thf (5ml) dropwise over 30 minutes. The cream suspension was allowed to warm to room temperature over 12 h, during which time a became a pale orange solution. Filtration, and removal of volatiles from the filtrate under reduced pressure, afforded beige crystalline 2 (0.39 g, 61 %). Crystals suitable for single crystal X-ray diffraction were grown from a thf/toluene solution of 2 at room temperature.

NMR/CDC12 δH 0.88 (9H, s, t-Bu), 1.16 (9H, s, t-Bu), 2.58 (2H, t, JCH2-CH2 5.1 Hz, CH2), 4.15 (2H, t, JCH2-CH2 5.1 Hz, CH2), 6.07 (1H, s, CH), 6.44 (1H, s, CH), 10.94 (1H, s, CH). MS(ES) 224.21([H2L]+, 100%), 168.22([H2L-Bu]+, 35%).

[H2LBr] (salt-free 2)
Crystals of H2LBr suitable for single crystal X-ray diffraction were grown from a dilute, hot toluene extract of 2 at room temperature. NMR/C6D6 δH 1.07 (9H, s, t-Bu), 1.67 (9H, s, t-Bu), 2.11 (1H, s, NH), 3.1 (2H, t, JCH2-CH2 5.6 Hz, CH2), 4.64 (2H, t, JCH2-CH2 5.6 Hz, CH2), 7.43 (1H, s, CH), 7.77 (1H, s, CH), 10.05 (1H, s, CH).

[LiBr.HL] 3

To a magnetically stirred mixture of \(1\) (1 g, 2.5 mmol) and \(\text{LiN(SiMe}_3\}_2\) (0.87 g, 5 mmol) was added cooled \(\text{thf}\) (15 ml, -78 °C). The suspension was allowed to warm to room temperature over 6 h. After removal of volatiles under reduced pressure, extraction of the resultant beige solid with \(\text{thf}/\text{toluene}\), concentration and cooling of the solution to \(-30\ ^\circ\text{C}\) afforded \(3\) as a colourless solid (0.62 g, 77 %) NMR/C\(_6\text{D}_6\) \(\delta\)H 1.17 (9H, s, t-Bu), 1.62 (9H, s, t-Bu), 2.41 (2H, t, \(^3\text{J}_\text{HH} 8.9\) Hz, CH\(_2\)), 4.02 (2H, t, \(^3\text{J}_\text{HH} 4.69\) Hz, CH\(_2\)), 6.15 (1H, d, \(^3\text{J}_\text{HH} 1.41\) Hz, CH), 6.51 (1H, d, \(^3\text{J}_\text{HH} 1.61\) Hz, CH), \(\delta\)C 28.92 (t-Bu), 31.73 (t-Bu), 44.16 (CH\(_2\)), 51.12 (C(C\(_3\))N), 51.57 (C(C\(_3\))N), 68.43 (CH\(_2\)), 115.73 (CH), 119.42 (CH), 197.0 (Ccarbene).

MS(ES) 224.21 ([H\(_2\)L]+, 100%) 225.29 (7%) 168.19 ([H\(_2\)L-Bu]+, 40%).


\[\text{HL}\] \(4\)

To a mixture of \(1\) (5 g, 13 mmol), KH (1.04 g, 26 mmol), and KOBu \(^\dagger\) (0.15 g, 1 mmol) was added cooled \(\text{thf}\) (20 ml, -78°C). The suspension was allowed to warm to room temperature and refluxed for 48 h. The resultant brown solution was filtered and the volatiles removed from the filtrate under reduced pressure. The brown oil was purified by distillation (0.05 mbar, 100 °C) to yield analytically pure \(4\) as a colourless oil (3.36 g, 86 %). NMR/C\(_6\text{D}_6\) \(\delta\)H 0.95 (9H, s, t-Bu), 1.47 (9H, s, t-Bu), 2.81 (2H, q, \(^3\text{J}_\text{HH} 6.1\) Hz, CH\(_2\)), 3.96 (2H, t, \(^3\text{J}_\text{HH} 6.1\) Hz, CH\(_2\)), 6.59 (1H, s, \(^3\text{J}_\text{HH} 1.6\) Hz, CH), 6.69 (1H, s, \(^3\text{J}_\text{HH} 1.6\) Hz, CH), \(\delta\)C 28.2 (t-Bu), 30.43 (t-Bu), 43.38 (CH\(_2\)), 49.01 (C(C\(_3\))N), 51.55 (CH\(_2\)), 55 (C(C\(_3\))N), 114.35 (CH), 117.93 (CH), 211.0 (Ccarbene).


\[\text{Sm(L)(N\{SiMe}_3\}_2\}_2\] \(5\)

To a stirred, toluene suspension of \(3\) (0.5 g 1.62 mmol, 5 ml) was added a toluene solution of Sm(N\{SiMe\}_3\)_3 \(1.02\) g, 1.62 mmol, 10 ml). Over 12 h the solution darkened and a colourless precipitate formed. The solution was filtered and volatiles removed from the filtrate under reduced pressure to afford a yellow solid which was sublimed (0.05 torr, 110 °C) then recrystallised from diethyl ether to yield bright yellow crystals of \(5\) (0.22 g, 20 %). Crystals suitable for x-ray diffraction were grown by sublimation.

\(\delta\)C\(_{\text{cene}}\) 210 ppm, \(\delta\)P 57 ppm, \(2\text{J}_{\text{PY}} 6\) Hz.

\[\text{Y(L)(N\{SiMe}_3\}_2\}_2\] \(6\)

To a stirred, toluene suspension of \(3\) (0.5 g 1.62 mmol, 5 ml) was added a toluene solution of Y(N\{SiMe\}_3\)_3 \(1.02\) g, 1.62 mmol, 10 ml). Over 12 h the solution changed from pale yellow to pale pink. The solution was filtered and volatiles removed from the filtrate under reduced pressure to afford a pale pink solid which was sublimed (0.05 torr, 110 °C) then recrystallised from cold diethyl ether (-30°C) to yield colourless crystals of \(6\) (0.24 g, 25 %). Anal. Found C 43.32, H 8.71, N 9.64. Calc for C\(_{25}\)H\(_{60}\)N\(_5\)Si\(_4\)Sm\(_2\)Et\(_2\)O: C 49.32, H 8.56, N 9.92.

Displacement Reactions

A Youngs tap – equipped NMR tube was charged with a benzene-\(d_6\) solution of \(6\). Into the tube was syringed (liquids) or weighed (solids) an equimolar quantity of one of: \(\text{thf}\); \(\text{diethyl ether}\); \(\text{triphenyl phosphine}\); \(\text{trimethylamine oxide}\); \(\text{tetramethylethlenediamine (TMEDA)}\); or \(\text{triphenylphosphine oxide}\). After addition, the tube was sealed and shaken, and the monitored immediately, and then 24 h subsequently, by \(^{13}\text{C}\) NMR spectroscopy. The clearest indication of a successful displacement is the disappearance of the \(^1\text{J}_{\text{CY}}\) coupling. For \([6.\text{O=PPh}_3]\): \(\delta^{13}\text{C\(_{\text{cene}}\)} 210\text{ ppm}, \delta^{31}\text{P 57 ppm, }^{2}\text{J}_{\text{PY}} 6\) Hz.

X-ray crystallography

Internal codes:
H\(_3[\text{L}]\text{Br}_2\) 1 imtbbr
[\text{LiBr.H2LBr}] 2 tbaimc
[H\(_2\)LBr] (salt-free 2) incene
[LiBr.HL] 3 uoimat
---[HL] 4 (an oil, no xray) ----
[Sm(L)(N\{SiMe\}_3\}_2\)2] 5 smsitb
[Y(L)(N[SiMe3]2)2] 6 yimnbu

Data deposited at the Cambridge Crystallographic Data Centre
CCDC 218135 - 218140

Summary of Data CCDC 218135 ---------------
Authors: P.L.Arnold,S.A.Mungur,A.J.Blake,C.Wilson
Formula: C14 H30 Br2 Cl3 N3 O1
Unit cell parameters: a 6.6688(14) b 12.488(3) c 15.188(3)
    alpha 108.323(3) beta 99.873(3) gamma 104.700(3)
    space group P-1

Summary of Data CCDC 218136 ---------------
Authors: P.L.Arnold,S.A.Mungur,A.J.Blake,C.Wilson
Compound: H2LnBr
Formula: C13 H26 Br1 N3
Unit cell parameters: a 11.3134(14) b 10.8662(13) c 12.6709(15) beta 95.379(2)
    space group P21/c

Summary of Data CCDC 218137 ---------------
Authors: P.L.Arnold,S.A.Mungur,A.J.Blake,C.Wilson
Compound: LiBrH2LnBr
Formula: C26 H52 Br4 Li2 N6
Unit cell parameters: a 10.9033(11) b 15.0349(13) c 11.8786(12) beta 109.786(2)
    space group P21/n

Summary of Data CCDC 218138 ---------------
Authors: P.L.Arnold,S.A.Mungur,A.J.Blake,C.Wilson
Compound: LiBrHLn
Formula: C26 H50 Br2 Li2 N6
Unit cell parameters: a 17.4366(12) b 12.3407(8) c 14.5991(10)
    space group Pccn

Summary of Data CCDC 218139 ---------------
Authors: P.L.Arnold,S.A.Mungur,A.J.Blake,C.Wilson
Formula: C25 H60 N5 Si4 Sm1
Unit cell parameters: a 18.1374(12) b 11.6135(8) c 17.7363(12) beta 102.776(2)
space group P21/c

Summary of Data CCDC 218140  

Authors: P.L. Arnold, S.A. Mungur, A.J. Blake, C. Wilson


Formula: C25 H60 N5 Si4 Y1

Unit cell parameters: a 18.135(2) b 11.5446(14) c 17.661(2) beta 102.938(2)

space group P21/c

\[\text{[H}_3\text{LBr}_2\text{]} 1\]

\[\text{[LiBr.H}_2\text{LBr]} 2\]

\[\text{[H}_2\text{LBr]} \text{ (salt-free 2)}\]
\[ \text{LiBr.HL} \] 3

\[ \text{Sm(\text{SiMe}_3}_2\text{L}) \] 5

\[ \text{Y(\text{SiMe}_3}_2\text{L}) \] 6