Thermally stable potassium N-heterocyclic carbene complexes with alkoxide ligands, and a polymeric crystal structure with distorted, bridging carbenes

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Supplementary data

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 degassed and purified by passage through activated alumina towers prior to use. Benzene-d_6 and pyridine-d_5 were refluxed over potassium, and vacuum transferred prior to use. Other reagents were procured from Aldrich or Strem. Elemental analyses were determined by Mr. Stephen Boyer at London University.

^{1}H and ^{13}C 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 ω scans. Structure solution and refinement was carried out using the SHELXTL suite of programs.[1]

Preparations

Syntheses of [H_2L^1]I, [H_2L^2]Br, [H_2L^3]I are described in the literature.[2]

[KL^1] 1

To a cold, magnetically stirred, cream slurry of [H_2L^1]I in thf (15.03 g, 48.8 mmol, 50 ml, -50 ˚C) was added a cold suspension of KH in thf (6.05 g, 151.3 mmol, 30 ml, -50 ˚C) dropwise over ten minutes. During the addition gas evolution was observed, and the solution darkened slightly. The mixture was allowed to warm to room temperature, with stirring, over 13 h. After this time, the orange solution was isolated from the pale grey powder by filtration, and the thf washings of the powder (3 x 10 ml thf) combined with the filtrate. Concentration of the solution to 30 ml afforded an orange oil, to which 60 ml of pentane was added to precipitate a cream powder. This powder was isolated by filtration and washed with pentane (3 x 20 ml) to afford [KL^1] **1** in 73 % yield (7.84 g). Spectroscopy (^{1}H NMR) of the crude reaction mixture shows the reaction is quantitative. Powdered **1** is deliquescent.

Single crystals of **1** were grown by slow evaporation of a thf solution of **1** at 25 ˚C (5.0 g, 0.8 ml).

^{1}H-NMR (C_6D_6, 300 MHz): δ ppm 6.58 (s, 1H, NC*H*CHN) 6.46 (s, 1H, NCHC*H*N) 4.42 (sept, 1H, NC*H*$(CH_3)_2$) 3.90 (s, 1H, NCH_2) 1.30 (s, 6H, C$(CH_3)_2$) 1.28 (d, 6H, NCH$(CH_3)_2$).
^{13}C{^{1}H}-NMR (C_6D_6, 75 MHz): δ ppm 208.4 (NCN) 121.5 (N*C*CN) 113.9 (NC*C*N) 70.1 (*C*$(CH_3)_2$) 66.3 (NCH_2) 51.6 (N*C*H$(CH_3)_2$) 32.5 (NCH$(CH_3)_2$) 22.1 (C$(CH_3)_2$.
Anal. Calcd. for $C_{10}H_{17}N_2OK$: C 54.51, H 7.78, N 12.71. Found C 54.77, H 7.93, N 12.59. Calcd. for $[C_{10}H_{17}N_2OK]_8$[thf]: C 54.98, H 7.91, N 12.21. (EI)MS m/z: 284 ($[K(CN(CH_2)N(Pr^i)CHCH)_2]^+$, 16 %), 256 ($[K(CNN(Pr^i)CHCH)_2H]^+$, 4 %), 226 ($[K(C\{N(CH_2)CH\}_2)_2]^+$, 8 %), 212 ($[K(C\{N(CH_2)NCHCH)_2]^+$, 20 %),

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[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.

[2] P. L. Arnold, M. Rodden, K. M. Davis, A. C. Scarisbrick, A. J. Blake, and C. Wilson, *Chem. Commun.*, 2004, 1612.

194 ([$K_2(OPr^i)_2$]$^+$ 24 %), 173 (45 %), 72 ([NHPr^{i}CH]$^+$ 100 %). MPt. 134-6 ° (dec). IR (fluorocarbon oil mull) ν (cm^{-1}): 1654.8 (w), 1400.5 (m), 1388.7 (w). 1349.3 (w), 1200.6 (s), 793.0 (m), 521.6 (m), 598.6 (s).

[KL^2], 1a

Procedure as for [KL^1].
Characterising data:
^{1}H-NMR (pyridine-*d5*, 300 MHz): δ ppm 6.96 (d, 1H, ^{3}J=1.2 Hz, NC*H*CHN) 6.69 (d, 1H, ^{3}J=1.2 Hz, NCHC*H*N) 4.07 (s, 2H, NC*H*$_2$) 3.66 (s, 3H, NC*H*$_3$) 1.37 (s, 6H, C(C*H*$_3$)$_2$).
^{13}C{^{1}H}-NMR (pyridine-*d5*, 75 MHz): δ ppm 211.6 (NCN) 122.2 (N*C*CN) 118.7 (NC*C*N) 70.6 (*C*(CH$_3$)$_2$) 67.3 (N*C*H$_2$) 37.7 (N*C*H$_3$) 33.5 (C(*C*H$_3$)$_2$).
MPt. 100-2 ° (dec). IR (fluorocarbon oil mull) ν (cm^{-1}): 1577.3 (w), 1419.2 (m), 1392.4 (w). 1361.3 (w), 1202.6 (s), 798.3 (m), 526.7 (m).

[KL^3] 1b

Procedure as for [KL^1].
Characterising data:
^{1}H-NMR (C_6D_6, 300 MHz): δ ppm 6.40 (s, 1H, NC*H*CHN) 6.25 (s, 1H, NCHC*H*N) 3.74 (dd, 2H NC*H*$_2$) 3.58 (dd, 1H, NCH$_2$C*H*) 3.37 (s, 3H, NC*H*$_3$) 1.02 (s, 9H, C(C*H*$_3$)$_3$).
^{13}C{^{1}H}-NMR (pyridine-*d5*, 75 MHz): δ ppm 211.1 (NCN) 121.1 (N*C*CN) 120.8 (NC*C*N) 87.2 (CH$_2$C*H*O) 60.7 (N*C*H$_2$) 38.8 (N*C*H$_3$) 37.9 (*C*(CH$_3$)$_3$) 28.3 (C(*C*H$_3$)$_3$).
MPt. 122-4 ° (dec). IR (fluorocarbon oil mull) ν (cm^{-1}): 1590.5 (w), 1474.0 (m), 1391.4 (w). 1348.6 (w), 1204.2 (s), 791.7 (m), 519.8 (m).

[HL^1] 2

A flask was charged with a stirrer bar and a mixture of [H_2L^1]I (7.45 g, 24.2 mmol) and KH (1.0 equiv., 0.968 g, 24.2 mmol) and cooled to -80 °C with stirring. Addition of thf (40 ml) afforded a cream suspension. During the addition gas evolution was observed, and the solution darkened slightly. The mixture was allowed to warm to room temperature, with stirring, over 48 h. After this time, the orange solution was isolated from the pale cream powder by filtration, and the thf washings of the powder (2 x 10 ml thf) combined with the filtrate. Concentration of the solution to one fifth of the total volume, the storage at –30 °C for 24 hours afforded a mass of colourless clumps of crystals which were isolated and washed with thf (1 x 5 ml) and pentane (4 x 5 ml), the dried to yield a pale yellow powder [HL] **2** in 64 % yield (2.83 g). Spectroscopy (^{1}H NMR) of the crude reaction mixture shows the reaction is quantitative. The compound is very hygroscopic.

^{1}H-NMR (C_6D_6, 300 MHz): δ ppm 7.77 (br s, fwhm 37 Hz, 1H, NC*H*N) 6.43 (s, 1H, NC*H*CHN) 6.38 (s, 1H, NCHC*H*N) 4.24 (sept, 1H, ^{3}J=7.5 Hz) NC*H*(CH$_3$)$_2$) 3.66 (s, 2H, NC*H*$_2$) 1.31 (s, 6H, C*H*$_3$)$_2$) 1.23 (d, 6H, ^{3}J=7.5 Hz, NCH(C*H*$_3$)$_2$).
^{1}H-NMR (thf, 300 MHz): δ ppm 6.75 (s, 1H, NC*H*N) 6.79 (br s, 1H, NC*H*CHN) 6.73 (s, 1H, NCHC*H*N) 4.28 (sept, 1H, ^{3}J=7 Hz) NC*H*(CH$_3$)$_2$) 3.67 (s, 2H, NC*H*$_2$) 1.27 (d, 6H, ^{3}J=7.5 Hz, NCH(C*H*$_3$)$_2$) 0.97 (s, 6H, C*H*$_3$)$_2$).
^{1}H-NMR (pyridine-d_5, 300 MHz): δ ppm 7.72 (br s, 1H, NC*H*N) 6.95 (d, 1H, NC*H*CHN, ^{3}J=7 Hz) 6.87 (s, 1H, NCHC*H*N, ^{3}J=7 Hz) 4.27 (sept, 1H, ^{3}J=8 Hz) NC*H*(CH$_3$)$_2$) 3.83 (s, 2H, NC*H*$_2$) 1.13 (d, 6H, ^{3}J= 8 Hz, NCH(C*H*$_3$)$_2$) 1.07 (s, 6H, C*H*$_3$)$_2$).
^{13}C{^{1}H}-NMR (C_6D_6, 75 MHz): δ ppm 198.7.0 (NCN) 120.7 (N*C*CN) 115.0 (NC*C*N) 69.8 (NCH$_2$*C*) 60.7 (N*C*H$_2$) 52.0 (N*C*H(CH$_3$)$_2$) 27.7, 23.9 (NCH(*C*H$_3$)$_2$), (C(*C*H$_3$)$_2$).
^{13}C{^{1}H}-NMR (thf, 75 MHz): δ ppm 202.4 (NCN) 121.2 (N*C*CN) 115.5 (NC*C*N) 69.7 (NCH$_2$*C*) 60.8 (N*C*H$_2$) 52.3 (N*C*H(CH$_3$)$_2$) 27.4, 24.0 (NCH(*C*H$_3$)$_2$), (C(*C*H$_3$)$_2$).
^{13}C{^{1}H}-NMR (pyridine-d_5, 75 MHz): δ ppm 202.0 (NCN) 122.9 (N*C*CN) 117.3 (NC*C*N) 71.1 (NCH$_2$*C*) 62.1 (N*C*H$_2$) 53.4 (N*C*H(CH$_3$)$_2$) 29.0, 25.1 (NCH(*C*H$_3$)$_2$), (C(*C*H$_3$)$_2$).
MS (ES): m/z 182 ([M]$^+$, 100 %). Anal. Calcd. for $C_{10}H_{18}N_2O\cdot0.25H_2O$: C 64.30, H 9.98, N 14.99. Found C 64.21, H 9.94, N 14.91.

[HL^2], 2a

Procedure as for [HL^1].
Characterising data: ^{1}H-NMR (C6D6, 300 MHz): δ ppm 6.09 (s, 1H, NC*H*CHN) 6.03 (s, 1H, NCHC*H*\N) 5.38 (br s, 1H, NC*H*N) 3.44 (s, 2H, NCH$_2$) 3.11 (s, 3H, NCH$_3$) 1.17 (s, 6H, C(CH$_3$)$_2$).

$^{13}C\{1H\}$-NMR (C_6D_6, 75 MHz): δ ppm 150.4 (N*C*N) 122.9 (N*C*CN) 120.7 (NC*C*N) 69.3(*C*(CH_3)$_2$) 60.9 (N*C*H_2) 36.9 (N*C*H_3) 28.2 (C(*C*H_3)$_2$).

Crystallography

A single crystal was mounted in a film of RS3000 perfluoropolyether on a dual-stage glass fibre and transferred to the diffractometer. X-ray diffraction data were collected using Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART1000 CCD area detector diffractometer at the University of Nottingham.

Data for 1

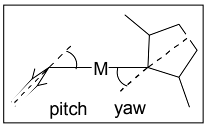

Table of pitch and yaw angles for **1**

Bond	Pitch	Yaw
K1-C31	40.9	10.0
K2-C21	42.8	7.2
K3-C71	20.9	7.4
K4-C11	8.9	5.1
K5-C41	13.1	6.9
K6-C81	35.8	6.3
K7-C51	51.9	12.2
K8-C61	16.8	2.7

Selected distances and angles
K1 O3 2.648(3)
K1 O1 2.657(3)
K1 O2 2.737(3)
K1 O100 2.983(4)
K1 C31 2.983(5) . pitch 40.9 yaw 10
K1 C26 3.409(5)
K1 C15 3.536(4)
K1 K2 3.6246(14)
K1 K4 3.7287(15)
K1 K3 3.7310(16)
K2 O2 2.579(3)
K2 O1 2.606(3)
K2 O4 2.679(3)
K2 C21 3.052(5) . pitch 42.8 yaw 7.2
K2 C42 3.081(4)
K2 C12 3.143(4)
K2 C43 3.528(5)
K2 K4 3.7862(16)
K2 K3 3.8727(15)
K3 O1 2.631(3)
K3 O4 2.634(3)
K3 O3 2.657(3)
K3 C71 3.128(4) . from other tetramer pitch 20.9 yaw 7.4
K3 C37 3.438(6)
K3 C47 3.466(5)
K3 C45 3.491(5)
K3 K4 3.7012(14)
K4 O2 2.638(3)
K4 O3 2.642(3)
K4 O4 2.717(3)
K4 C11 3.158(4) . from other tetramer pitch 8.9 yaw 5.1
K4 C27 3.334(5)
K4 C36 3.430(6)
K4 C45 3.505(4)
K4 C25 3.524(5)
K5 O7 2.624(3)
K5 O6 2.664(3)
K5 O5 2.706(3)
K5 C41 3.066(5) . from other tetramer pitch 13.1 yaw 6.9
K5 C57 3.451(5)

K5 C65 3.529(5)
K5 K7 3.6555(16)
K5 K8 3.7133(14)
K5 K6 3.8081(14)
K6 O8 2.586(3)
K6 O7 2.631(3)
K6 O6 2.656(3)
K6 C81 2.945(5) . pitch 35.8 yaw 6.3
K6 C62 3.132(5)
K6 C72 3.160(4)
K6 K8 3.6587(16)
K6 K7 3.7347(16)
K7 O5 2.543(3)
K7 O8 2.631(3)
K7 O6 2.673(3)
K7 C51 2.994(5) . pitch 51.9 yaw 12.2
K7 C86 3.399(6)
K7 K8 3.6857(15)
K8 O7 2.647(3)
K8 O5 2.686(3)
K8 O8 2.698(3)
K8 C61 3.054(4) . from other tetramer pitch 16.8 yaw 2.7
K8 C87 3.384(5)
K8 C75 3.506(4)
K8 C56 3.538(6)

Portion of the polymeric structure: