

Magnesium and zinc complexes of functionalised, saturated N-heterocyclic carbene ligands; carbene lability and functionalisation, and lactide polymerisation catalysis.

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Structure of [HL^P.KN^{''}]

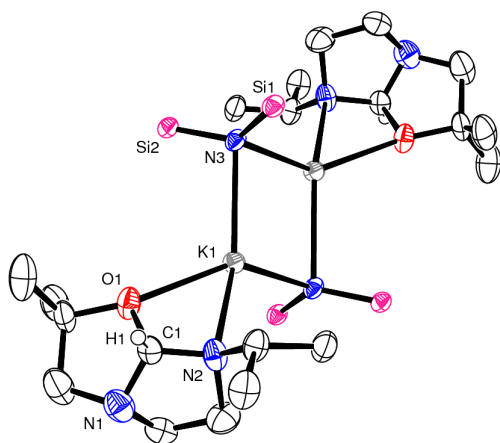


Figure S1. Displacement ellipsoid drawing of the molecular structure of [HL^P.KN^{''}] (50 % probability ellipsoids). Silicon bound carbon atoms and hydrogen atoms omitted for clarity (except on C1).

The structure is dimeric in the solid state, based around two bridging KN^{''} groups forming a K₂N₂ core residing over a crystallographic inversion centre, with the coordination sphere of each potassium being completed through coordination to the oxygen and one of the nitrogen atoms of the ligand. The imidazolinium iodide starting material has been singly deprotonated, with no inclusion of any iodide containing residues, and the resulting ligand intermediate forms a bicyclic adduct structure, with the formerly imidazolinium CH now forming the central imidazolidine unit.

Synthesis of [MgCl(L^D)]

To a stirred solution of (HL^D) (390 mg, 1.28 mmol) in toluene (10 mL) was added dropwise MeMgCl (0.43 mL, 1.28 mmol; 3.0 M in thf) immediately resulting in effervescence and generation of a white precipitate. The reaction mixture was stirred for 1 h at rt before being allowed to settle. The solid was filtered off, washed with toluene (2 x 5 mL) and dried *in vacuo* to afford [MgCl(L^D)] as a colourless powder. Yield: 470 mg (100 %). ¹H

NMR (C_5D_5N); δ 7.41 (t, 1H, $^3J = 8$ Hz, 4- C_6H_3), 7.21 (d, 2H, $^3J_{HH} = 8$ Hz, 3,5- C_6H_3), 3.64 (m, 4H, $NH-CH_2CH_2-N(H)Dipp$), 3.50 (s, 2H, $HOCMe_2-CH_2$), 3.38 (sept, 2H $^2J_{HH} = 7$ Hz, $CH-(CH_3)_2$), 1.43 and 1.14 (d, 6 H each, $^3J_{HH} = 7$ Hz, $CH-(CH_3)_2$), 1.03 (s, 6H, $CH-(CH_3)_2$). ^{13}C ; 212.8 ($C_{carbene}$), 148.3, 138.1, 129.4 and 124.9 (C_6H_3), 70.7 ($C-(CH_3)_2$), 61.5 ($HOCMe_2-CH_2$), 54.1 and 53.4 ($NH-CH_2CH_2-N(H)Dipp$), 29.7 ($C-(CH_3)_2$), 28.7 ($CH-(CH_3)_2$), 26.0 and 25.1 ($CH-(CH_3)_2$).

Structure of $[Zn(L^M)_2]$

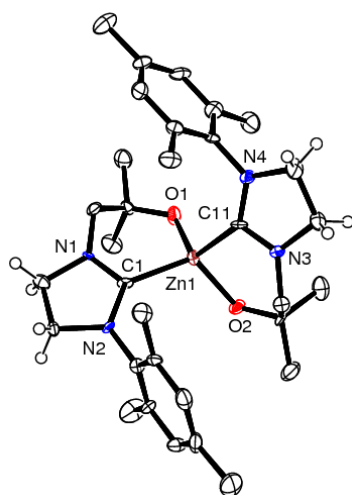


Figure S2. Displacement ellipsoid drawing of the molecular structure of $[Zn(L^M)_2]$ (50 % probability ellipsoids). Hydrogen atoms omitted for clarity (except on the NHC backbone carbons).

The complex consists of two bidentate alkoxy-carbene ligands bound to the zinc centre, and the geometry at the four coordinate metal is distorted-tetrahedral. Due to difficulties with the quality of the data collected; the structure was modelled using DELU and SIMU restraints and the disagreeable reflection 26 0 0 was omitted. C17 is refined isotropically; on attempted anisotropic refinement, it becomes a ‘non-positive definite’ indicating that the Anisotropic Displacement Parameters for this atom have refined to values that are not mathematically sound.

Table SI1 X-ray data Summarised

	$[HL^P.KN'']$	$[Zn(L^M)_2]$
Crystal data		
Chemical formula	$C_{16}H_{38}KN_3OSi_2$	$C_{32}H_{46}N_4O_2Zn$
M_r	383.77	584.10
Cell setting, space group	Triclinic, $P-1$	Monoclinic, $C2/c$
Temperature (K)	150 (2)	93 (2)
a, b, c (Å)	9.9490 (4), 10.9970 (5), 12.2370 (5)	45.089 (4), 11.2093 (9), 12.7221 (11)

$\alpha, \beta, \gamma (^{\circ})$	95.194 (2), 111.793 (2), 108.661 (2)	104.578 (2)
$V (\text{\AA}^3)$	1143.97 (8)	6222.9 (9)
Z	2	8
$D_x (\text{Mg m}^{-3})$	1.114	1.247
Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\mu (\text{mm}^{-1})$	0.34	0.82
Crystal form, colour	Block, colourless	Block, colourless
Crystal size (mm)	$0.65 \times 0.45 \times 0.30$	$0.19 \times 0.13 \times 0.06$
Data collection		
Diffractionmeter	Bruker SMART APEX CCD area detector	Bruker SMART APEX CCD area detector
Data collection method	ω -scans	ω -scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.584	?
$T_{\max}$	0.746	?
No. of measured, independent and observed reflections	13380, 5406, 4732	19344, 4017, 2934
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.042	0.134
$\theta_{\max} (^{\circ})$	29.0	25.4
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.108, 0.240, 1.29	0.071, 0.188, 0.86
No. of reflections	5406 reflections	4017 reflections
No. of parameters	220	352
H-atom treatment	Riding	Mixture of independent and constrained refinement
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 4.806P]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.1063P)^2 + 78.112P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.00	0.042
$\Delta\rho_{\max}, \Delta\rho_{\min} (\text{e \AA}^{-3})$	1.11, -0.43	0.56, -0.45
Extinction method	SHELXL	
Extinction coefficient	0.00	
Computer programs: SMART (Siemens, 1993); SAINT (Siemens, 1995); SIR-92 (Giacovazzo, 1994); SHELXL-97 (Sheldrick, 1997); ORTEP (Farrugia, 1997); enCIFer (Allen et. al., 2004).		