COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Bent metal carbene geometries in amido *N*-heterocyclic carbene complexes†

Shaheed A. Mungur,[a] Stephen T. Liddle,[a] Claire Wilson,[a] Mark J. Sarsfield[b] and Polly L. Arnold*[a]

[a] *School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD. E-mail: Polly.Arnold@Nottingham.ac.uk; Fax: 44 115 9513563; Tel: 44 115 9513437*

[b] *British Nuclear Fuels plc, Nuclear Science & Technology Services B170, Sellafield, Cumbria, UK CA20 1PG*

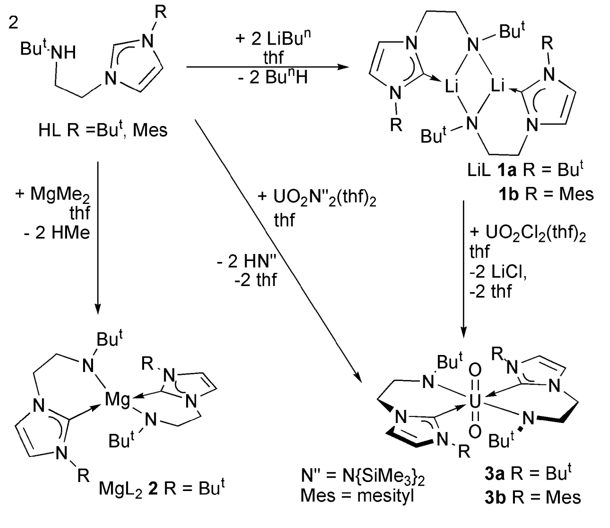
Received (in Cambridge, UK) 2nd July 2004, Accepted 1st September 2004
First published as an Advance Article on the web 15th October 2004

Lithium(I) and uranium(VI) amido-tethered Bu^t-substituted *N*-heterocyclic carbene (NHC) complexes exhibit very distorted metal–carbene bonds; the corresponding magnesium(II) and mesityl-substituted NHC uranium(VI) complexes are undistorted; the distortion does not affect the ligand binding strength, suggesting a dominance of electrostatic character in closed-shell electropositive metal–carbene bonds.

Imidazol-2-ylidenes, or *N*-heterocyclic carbenes (NHCs) [C{NRCH}$_2$], are neutral donor ligands that bind, with negligible back-bonding, to almost all metals in the periodic table.[1] Increasingly, the strongly σ-basic NHCs find use as additives in homogeneous, Lewis acidic metal-catalysed processes.[2] Whilst there has been no study of the trends in bonding and reactivity of early, or electropositive, metal–NHC complexes, and only one reported study of the reactivity of the early metal–NHC bond,[3] the assumption that carbenes bind to early metals as a simple two-electron donor has already been challenged by density functional theoretical studies based on observed crystallographic data.[4]

We have been studying the use of *N*-anionic functional groups pendant to the NHC to provide a 'tether' by which an electropositive metal may be bound more strongly to the soft carbene centre.[3] We recently reported the synthesis of an amino-functionalised NHC ligand HL, Scheme 1, and showed for the first time how the coordination of the amido group aids in the synthesis and manipulation of electropositive metal adducts.

Herein, we report the synthesis of the first amido-NHC complexes of lithium, magnesium, and uranium cations, and compare the observed deformation of the ligated metal carbene fragment (from the anticipated trigonal planar carbon geometry) for these closed shell metal cations. The uranyl ion [UO$_2$]$^{2+}$, which binds ligands exclusively in the equatorial plane, and whose vibrational spectrum is very sensitive to the strength of the equatorial ligands,[5] provides an ideal structural core at which to study whether this carbene distortion reduces the binding strength, or whether electrostatics dominate the bonding to these electropositive metals.



Scheme 1 Synthesis of lithium, magnesium, and uranium amido-*N*-heterocyclic carbene complexes.

The amino-carbene HL is readily deprotonated by an equivalent of lithium *n*-butyl in hexane–thf, Scheme 1, yielding [LiL] **1a** as a waxy colourless solid,†‡ or half an equivalent of dimethylmagnesium, yielding colourless crystalline [MgL$_2$] **2**,‡ Scheme 1. The lithium salt is particularly air- and moisture-sensitive. Crystalline samples of **1a** smoke in air, and react violently (smoking and decomposing to a black solid) when ground as a powder in the glove box in fluorocarbon oil (fomblin), presumably breaking carbon–fluorine bonds. Complexes **1** and **2** are the first reported s-block complexes of NHC ligands with an N-bound anionic functional group. Crystals suitable for single crystal X-ray diffraction of **1a** and **2** were grown from diethyl ether solutions; see Fig. 1.

Remarkably, neither complex retains coordinated solvent molecules.[6] The lithium salt forms instead a discrete dimer, *via* bridging amido groups, and displays no interactions with neighbouring molecules, despite its very open coordination sphere, and the flexibility of the L chelate. Normally, homoleptic lithium amides crystallise in polymeric ladder-type structures; this salt may be regarded as a carbene-solvated amido-bridged Li(I) dimer.[7]

The most interesting feature of the structure of **1a** is the severe distortion of the carbene NCN–Li bond. Whilst the lithium amine analogue [LiBr·HL] is also dimeric, and has a short Li–C distance, the Li–C–[ring centroid] angle is close to linear, 161.8°, but this angle in **1a** is 147.9°.

The two components of this distortion, both pitch and yaw, (summarised in Fig. 3) are equally large, even though both carbene chelates contain a flexible (CH$_2$)$_2$ backbone. The Li–C distances in **1a** are the shortest yet reported for NHC complexes, and compare closely with those observed in lithiated aryl compounds, which also show structural deviations at the anionic carbon. In the structure of unsolvated LiPh the Li cations are bent 36° and 27° out of the phenyl planes, but form part of a σ$_2$-bridging Li$_2$–C$_2$ core with Li–C distances of 2.322 Å.[8]

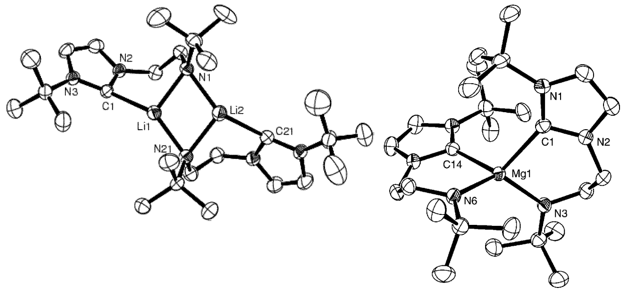


Fig. 1 Thermal ellipsoid drawing of **1a** and **2** (50% probability). Selected distances (Å) and angles (°) **1a**: Li(1)–C(1) 2.124(4), Li(2)–C(21) 2.162(4), Li(1)–C(1)–centroid$_{NHC}$ 149.3. **2**: Mg(1)–C(1) 2.263(2), Mg(1)–C(14) 2.2697(16), Mg(1)–C(1)–centroid$_{NHC}$167.5.

---

† Electronic supplementary information (ESI) available: synthetic details for all complexes described. See http://www.rsc.org/suppdata/cc/b4/b410074c/

DOI: 10.1039/b410074c

Despite the diagonal relationship between Li^+ and Mg^{2+}, and the same size of Li^+ and Mg^{2+} (Shannon radii 0.59 and 0.57 Å respectively), the Mg(II) carbene complex **2** shows virtually no distortion about the M–CN_2 fragment. It forms a bis(ligand) chelate with short Mg–N bonds,[9] and average Mg–C bonds (compared with other Mg–NHC complexes).[10] The Mg–C bonds are longer by 0.1 Å than the Li–C bonds, but the proximity of the ligand *tert*-butyl groups may prevent a closer approach of the carbene.

Treatment of $[UO_2Cl_2(thf)_2]$ with two equivalents of **1** in thf (or treatment of $[UO_2(N\{SiMe_3\}_2)_2(thf)_2]$ with two equivalents of HL in toluene) affords red $[UO_2L_2]$ **3a**. For additional comparison, and because organometallic uranyl complexes are so rare,[11] the *N*-mesityl salt **1b**† was also made and treated with $[UO_2Cl_2(thf)_2]$, to afford **3b**. Complex **3a** forms in 90% of the *trans*-NHC isomer (and 10% presumed *cis*-NHC, not isolated), according to ^1H NMR spectroscopy, while **3b** forms exclusively the *trans*-NHC isomer.

A single crystal X-ray diffraction study of both complexes **3**,‡ Fig. 2, shows that the former is distorted in the same manner as **1a**, whilst the latter is not at all, as with **2**. However, the metal–carbene distances are all 2.64 Å (within standard uncertainties) in **3a**, **3b**, and the monodentate NHC adduct $[UO_2([C\{NMesCH\}_2])_2]$. The mesityl groups in **3b** pack neatly in the *trans* conformation, implying that the asymmetric NHC group can bend to accommodate steric factors, such as a preferred *trans* isomer.

Importantly, the uranyl stretch in the UO_2^{2+} complexes **3** allows us to confirm that the amido-carbene ligands bind equally well to the metal in both conformations. The asymmetric ν_3 uranyl stretch is observed in the FTIR spectrum at 929 and 933 cm^{-1} for **3a** and **3b** respectively; the values of ν_3 exhibited by reported uranyl coordination complexes fall within a range of about 100 cm^{-1}. The analogous stretch in $[UO_2Cl_2[C\{NMesCH\}_2])_2]$ is 938 cm^{-1}.

We can attribute the bent geometry of the bound carbene either to a partial rehybridisation at carbon, the involvement of other π-type orbitals (see introduction), or to the presence of a strongly polarised electrostatic bond to the electropositive metal which does not have an angular dependence. Fig. 3 summarises the degree of bend at the carbene carbon in each complex. The lithium–carbene bonds are significantly shorter than the magnesium–carbene distances, despite the severe distortion at carbon. Further, the differences in pitch and yaw, but similarities in bond length and UO_2 vibrational spectra of the two uranyl complexes suggests that the NHC group can bend to accommodate steric factors without reducing the strength of the electrostatic bonding interaction. It is notable that one monodentate NHC adduct $[Y(C\{NMeCH\}_2)N''_3]$ ($N'' = N\{SiMe_3\}_2$) displays a deviation of 8°, but the complex also contained agostic interactions that could have contributed to the asymmetry in the structure.[12] We also measured an 8° angle in the complex $[Y(L)N''_2]$,[3] and note that the lithium alkoxy-carbene $[Li([OCHBu^tCH_2(1\text{-}C\{NCHCHNBu^t\})])\cdot LiI]$ which also has a flexible C_2-alkyl backbone, has a very short Li–C distance, 2.135 Å, and a yaw of 19°, although we have no related structures with which to compare this.[2a]

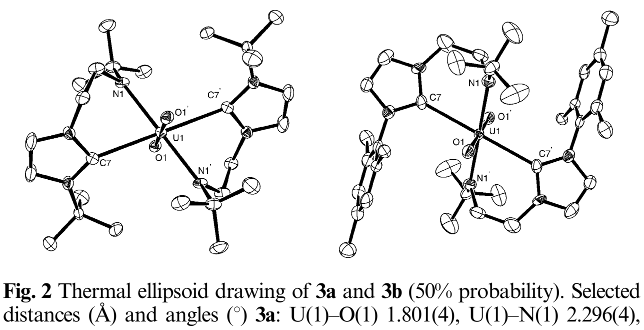


Fig. 2 Thermal ellipsoid drawing of **3a** and **3b** (50% probability). Selected distances (Å) and angles (°) **3a**: U(1)–O(1) 1.801(4), U(1)–N(1) 2.296(4), U(1)–C(7) 2.640(5), U(1)–C(7)–centroid$_{NHC}$ 158.3. **3b**: U(1)–O(1) 1.802(5), U(1)–N(1) 2.277(6), U(1)–C(7) 2.633(7), U(1)–C(7)–centroid$_{NHC}$ 169.4.

complex:	**1a**	**2**	**3a**	**3b**
pitch (°):	18	2	23	9
	20	4		
yaw (°):	20	10	17	3
	22	11		

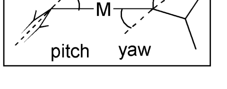


Fig. 3 Measured pitch and yaw of M–CN_2C_2 fragments of **1a** to **3b** (°).

To conclude, the first s-block (lithium and magnesium) and uranium amido *N*-heterocyclic carbene complexes have been made. These show significant distortion of the metal–carbene bond from the anticipated trigonal planar hybridisation without any significant reduction in the strength of the metal–carbene bond, implying that bonding is predominantly electrostatic in nature. The lithium complex binds the carbene in preference to thf molecules in the solid state and solution, forming very short M–C bonds, despite the large distortion. The uranyl complexes provide new examples of rare organometallic uranyl species, and a means of monitoring the strength of the bound NHC group.

We thank the EPSRC (PLA, STL, SAM), BNFL (MJS), the Nuffield Foundation, and the Royal Society for financial support.

Notes and references

‡ Crystal data **1**: $C_{26}H_{48}Li_2N_6$, $M = 458.58$, orthorhombic, space group *Pbca*, $a = 10.6274(13)$, $b = 19.835(3)$, $c = 28.003(3)$ Å, $U = 5903(1)$ Å^3, $Z = 8$, $D_c = 1.032$ g cm^{-3}, $\mu = 0.061$ mm^{-1} (Mo Kα, $\lambda = 0.71073$ Å), $T = 150$ K, R ($F^2 > 2\sigma$) = 0.0495, R_w (F^2 all data) = 0.1378, goodness-of-fit = 0.909 for all 5024 unique data (41265 measured, $R_{int} = 0.1060$, $2\theta < 50°$) and 304 refined parameters. **2**: $C_{26}H_{48}MgN_6$, $M = 469.01$, monoclinic, space group *C*2/*c*, $a = 11.4773(8)$, $b = 17.5050(13)$, $c = 28.222(2)$ Å, $\beta = 95.341(2)°$, $U = 5645.4(7)$ Å^3, $Z = 8$, $D_c = 1.104$ g cm^{-3}, $\mu = 0.087$ mm^{-1} (Mo Kα, $\lambda = 0.71073$ Å), $T = 150$ K, R ($F^2 > 2\sigma$) = 0.0455, R_w (F^2 all data) = 0.1252, goodness-of-fit = 1.027 for all 6476 unique data (24105 measured, $R_{int} = 0.0317$, $2\theta < 52°$) and 325 refined parameters. **3a**: $C_{29.5}H_{51.5}N_6O_2U$, $M = 760.30$, triclinic, space group $P\bar{1}$, $a = 11.473(5)$, $b = 11.700(5)$, $c = 13.665(5)$ Å, $\alpha = 66.755(5)$, $\beta = 80.951(5)$, $\gamma = 78.183°$ $U = 1643.7(12)$ Å^3, $Z = 2$, $D_c = 1.536$ g cm^{-3}, $\mu = 4.971$ mm^{-1} (Mo Kα, $\lambda = 0.71073$ Å), $T = 150$ K, R ($F^2 > 2\sigma$) = 0.0303, R_w (F^2 all data) = 0.0785, goodness-of-fit = 1.014 for all 6649 unique data (13270 measured, $R_{int} = 0.0302$, $2\theta < 52°$) and 352 refined parameters. **3b**: $C_{36}H_{52}N_6O_2U$, $M = 838.87$, monoclinic, space group *C*2/*c*, $a = 22.899(5)$, $b = 10.128(5)$, $c = 15.221(5)$ Å, $\beta = 97.608(5)°$, $U = 3499(2)$ Å^3, $Z = 4$, $D_c = 1.592$ g cm^{-3}, $\mu = 4.679$ mm^{-1} (Mo Kα, $\lambda = 0.71073$ Å), $T = 150$ K, R ($F^2 > 2\sigma$) = 0.0363, R_w (F^2 all data) = 0.0819, goodness-of-fit = 1.017 for all 3085 unique data (12229 measured, $R_{int} = 0.0784$, $2\theta < 50°$) and 211 refined parameters. CCDC 244355–244358. See http://www.rsc.org/suppdata/cc/b4/b410074c/ for crystallographic data in .cif or other electronic format.

1 W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1291; J. C. Green, R. G. Scurr, P. L. Arnold and F. G. N. Cloke, *Chem. Commun.*, 1997, 1963; M. Niehues, G. Erker, G. Kehr, P. Schwab, R. Frohlich, O. Blacque and H. Berke, *Organometallics*, 2002, **21**, 2905.

2 (*a*) P. L. Arnold, M. Rodden, K. M. Davis, A. C. Scarisbrick, A. J. Blake and C. Wilson, *Chem. Commun.*, 2004, 1612; (*b*) H. Y. Zhou, E. J. Campbell and S. T. Nguyen, *Org. Lett.*, 2001, **3**, 2229.

3 P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed.*, 2003, **42**, 5981.

4 C. D. Abernethy, G. M. Codd, M. D. Spicer and M. K. Taylor, *J. Am. Chem. Soc.*, 2003, **125**, 1128; P. Shukla, J. A. Johnson, D. Vidovic, A. H. Cowley and C. D. Abernethy, *Chem. Commun.*, 2004, 360; H. Nakai, X. L. Hu, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Inorg. Chem.*, 2004, **43**, 855.

5 M. J. Sarsfield, H. Steele, M. Helliwell and S. J. Teat, *Dalton Trans.*, 2003, 3443.

6 R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufalli, C. P. Butts, E. Linehan, J. M. Oliva, A. G. Orpen and M. J. Quayle, *Chem. Commun.*, 1999, 241.

7 M. Vestergren, J. Ericsson, G. Hilmersson and M. Hakånsson, *J. Organomet. Chem.*, 2003, **682**, 172.

8 R. E. Dinnebier, U. Behrens and F. Olbrich, *J. Am. Chem. Soc.*, 1998, **120**, 1430.

9 P. J. Bailey, C. M. E. Dick, S. Fabre and S. Parsons, *Dalton Trans.*, 2000, 1655; W. Clegg, L. Horsburgh, R. E. Mulvey, M. J. Ross, R. B. Rowlings and V. Wilson, *Polyhedron*, 1998, **17**, 1923.

10 A. J. Arduengo III, H. V. Rasika-Dias, R. Davidson and R. L. Harlow, *J. Organomet. Chem.*, 1993, **462**, 13.

11 The other example is also an NHC adduct: W. J. Oldham, Jr., S. M. Oldham, B. L. Scott, K. D. Abney, W. H. Smith and D. A. Costa, *Chem. Commun.*, 2001, 1348.

12 W. A. Herrmann, F. C. Munck, G. R. J. Artus, O. Runte and R. Anwander, *Organometallics*, 1997, **16**, 682.