COMMUNICATION

Dalton
www.rsc.org/dalton

Pyridyl donor induced 1,3-silyl migration in metal complexes of the guanidine CyHNC{N(SiMe$_3$)Py}NCy, Py = 2-(6-MeC$_5$H$_3$N)† ‡

Marcus L. Cole and Peter C. Junk *

School of Chemistry, Monash University, Clayton, Vic 3800, Australia.
E-mail: Peter.Junk@sci.monash.edu.au; Fax: +61(0)399054597; Tel: +61(0)399054570

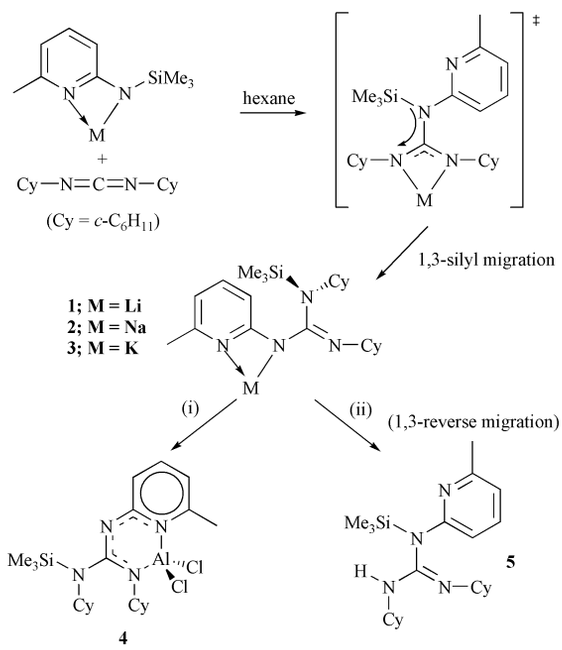
Received 4th April 2003, Accepted 6th May 2003
First published as an Advance Article on the web 12th May 2003

The insertion of 1,3-dicyclohexylcarbodiimide into a group 1 metallated 2-(trimethylsilyl)aminopyridine occurs with a 1,3-silyl shift of the intended guanidinate. An aluminium complex of the modified ligand, which exhibits *pseudo* β-diketiminate binding of the metal centre, exemplifies the coordinative versatility of this new multi *N*-donor system.

The chemistry of amidinate ligands, [(RN)$_2$CR]$^-$ (R^1/R^2 = alkyl, aryl, silyl), has seen a flurry of interest resulting from the global search for monoanionic ligands capable of supporting diverse catalytic assemblies.[1,2] The related guanidinate ligand class; [(R^{1}N)C(NR^{2}R^3)(NR^4)]$^-$, can similarly access numerous coordination modes and offers bountiful steric and electronic control from their facile incorporation of directed combinations of substituents.[3] With this in mind, several groups have reported the structural chemistry of *s*-, *p*-, *d*-, and *f*-block species based upon symmetrical (R^1 = R^4, R^2 = R^3) guanidinates.[1–3] To our knowledge, no attempt to functionalise the CN$_3$ core of these species, *e.g.* the incorporation of pendant functionalities, has been made.[4] This approach has reaped rich dividends in amidinate chemistry where modification of both structure[5] and catalytic activity[6] have been observed courtesy of augmentative nitrogen donors.

Our long-term interest in the amidinate[7] and substituted 2-amidopyridine[8] chemistry of *s*- and *f*-block elements gave us a particular interest in combining these two areas to assess the structural and chemical implications to species that encompass both. Accordingly, the typical preparation of guanidinate complexes *via* the addition of a group 1 bis(trimethylsilyl)amide across 1,3-dicyclohexylcarbodiimide (DCC)[9] was modified to incorporate a 2-pyridyl donor (see Scheme 1). Here we describe the outcome of this initiative and discuss the implications of donor inclusion upon the intended guanidinate backbone nitrogen.

Addition of lithium, sodium or potassium 2-(trimethylsilyl)-amido-6-methylpyridine[8,10] to hexane solutions of DCC resulted in near quantitative formation of colourless highly hydrocarbon soluble species (Scheme 1) that were isolated as pmdien (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) (**1**), bis(dme) (**2**), or pmdien and diethyl ether (**3**) adducts (resp.) after addition of pmdien and/or extraction into dme/diethyl ether. ^{1}H NMR and FTIR spectroscopy‡§ of all three species confirm their formulae and indicate the absence of a strong C=N stretch at 2120 cm^{-1} and formation of strong absorptions at *ca.* 1650 cm^{-1} consistent with the conversion of the carbodiimide to a species of lower bond order. However, the placement of this stretch at approx. 170 cm^{-1} higher than the C=N absorption of typical thf-adducted group 1 guanidinates (*e.g.* R^1/R^4 = Cy (C$_6$H$_{11}$), R^2/R^3 = SiMe$_3$; *ca.* 1480 cm^{-1})[9b] implies the new species could contain a localised imine bond inconsistent with the intended composition.



Scheme 1 (i) Et$_2$O, AlCl$_3$, −MCl; (ii) hexane/Et$_2$O, HCl, −MCl.

An X-ray structure determination of **2** (Fig. 1)¶ suggests that rather than isolating the expected guanidinate (see transient species Scheme 1) a 1,3-silyl migration occurs following insertion of DCC into the metal-amide. This mimics direct insertion

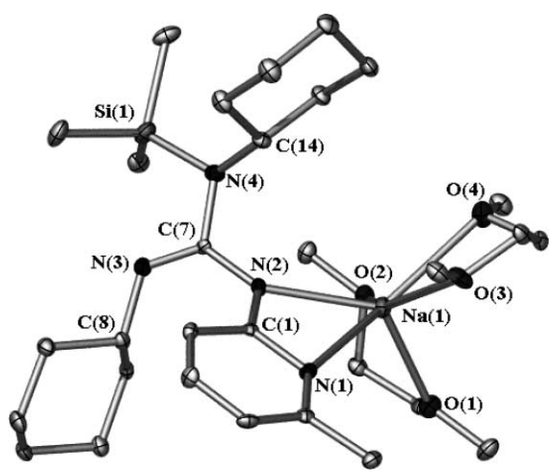


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Na(1)–N(1) 2.535(3), Na(1)–N(2) 2.394(3), N(2)–C(7) 1.384(4), N(3)–C(7) 1.303(5), N(4)–C(7) 1.411(4), N(1)–Na(1)–N(2) 55.0(1), N(1)–C(1)–N(2) 114.2(3), N(2)–C(7)–N(3) 129.8(3), N(2)–C(7)–N(4) 117.4(3), N(3)–C(7)–N(4) 112.4(3), C(7)–N(3)–C(8) 122.1(3).

† Dedicated to the memory of Sam M. Liddiard, a true friend and colleague.
‡ Electronic supplementary information (ESI) available: spectroscopic data for **1**, **3** and **5**. See http://www.rsc.org/suppdata/dt/b3/b303772j/

DOI: 10.1039/b303772j

into the N–$SiMe_3$ bond (**1**–**3**) and retains the imine suggested by FTIR. The foremost feature of the new system is the preferential binding of sodium by the amido-pyridine donor set in preference to the conventional DCC derived chelate. This results in-spite of an adjacent 'free' guanidinate *N,N′*-donor, rendering both the imine and amine donors redundant.

The inclusion of amide, pyridyl, amine and imine functionalities within one system invites speculation regarding the nature of binding with metals of increased size and/or decreased electropositivity. Correspondingly, solutions of **1**–**3** were added to ethereal aluminium trichloride. The resulting species, **4**, (see Scheme 1) was isolated quantitatively as small colourless block-like crystals.¶ The position of the FTIR C=N stretch of **4** is placed at lower frequency than those of **1**–**3**, at 1619 cm^{-1},§ indicating potential participation of the C=N moiety in metal binding. The ^{27}Al NMR of **4** indicates a four coordinate Al centre (96.3 ppm)[11] and the ^{13}C NMR spectrum, like those of **1**–**3**, suggests the presence of two distinct sets of cyclohexyl groups. The retention of the silyl group upon the cyclohexylamine moiety could explain this, however, were the initial migration to be reversible the potentially asymmetric nature of the intended *N*-substituted backbone could confer comparable chemical inequivalence.

The molecular structure of **4** (Fig. 2)¶ exemplifies the coordinative dexterity of the new ligand system. Unlike **1**–**3**, **4** describes a rearrangement of the group 1 binding motif rendering a *pseudo* β-diketiminate donor set. This unit comprises the original amidopyridine as well as the imine functionality, which leads to an expected lengthening of the imine C=N bond (*e.g.* **2**; 1.303(5) Å, **4**; 1.361(2) Å) and opening of the N_{amide}–C–$N_{pyridyl}$ angle (*e.g.* **2**; 114.2(3)°, **4**; 123.2(1)°). Geometrically, compound **4** resembles β-diketiminates coordinated to an aluminium dichloride subunit, *e.g.* $[AlCl_2\{C(H)\{C(CH_3)N(p\text{-tolyl})\}_2\}]$ (**6**),[12] with a bite angle approaching tetrahedral ideality (**6**; 99.4(1)°, **4**; 99.2(1)°). This is in stark contrast to known guanidinate species, *e.g.* $[AlCl_2\{(N^iPr)_2C\{N(SiMe_3)_2\}\}]$,[13a] which exhibit bite angles in the range 71.4–72.7°.[13] This countenances the binding mode chosen. To our knowledge the N_3C_2 anion donor of **4** is the first of its type and represents the only example of a β-pyridyl substituted ketiminate.

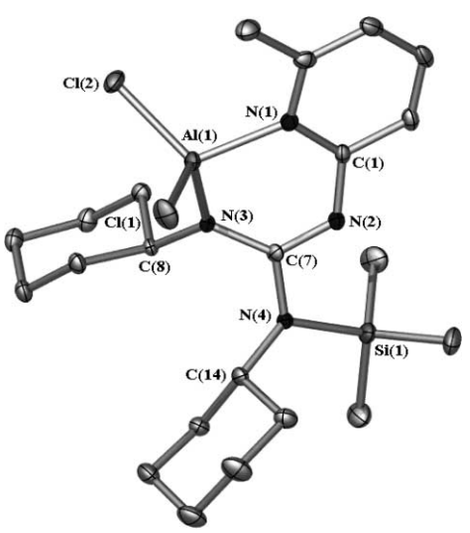


Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.917(2), Al(1)–N(3) 1.837(2), N(3)–C(7) 1.361(2), N(2)–C(7) 1.321(2), N(4)–C(7) 1.392(2), N(1)–Al(1)–N(3) 99.2(1), N(1)–C(1)–N(2) 123.2(1), N(3)–C(7)–N(2) 124.0(2), N(2)–C(7)–N(4) 114.7(1), C(7)–N(3)–C(8) 118.1(1).

While 1,3-migrations proliferate the nitrile and isonitrile chemistries of both silylated amides and alkyls,[2,14,15,16] there is no precedent for analogous shifts in related C–N double bond chemistry. Perhaps the most heavily utilised example of the aforementioned migration is Sanger's synthesis of 1,3-bis(trimethylsilyl)benzamidinates *via* the insertion of benzonitrile into group 1 bis(trimethylsilyl)amides.[17] In view of two recent examples that incorporate the related iminate ligand, *e.g.* $[Ti_2(\mu\text{-}O)_2\{C(Ph)\{N(SiMe_3)_2\}_2\}_3\{N{=}C(Ph)N(SiMe_3)_2\}]$,[18] the shift that gives rise to this symmetrical ligand appears reversible. Surprisingly, we are unaware of any reports that describe the conversion of 1,3-bis(trimethylsilyl)benzamidinate to a neutral species using a protic source. In this vein ethereal hydrogen chloride was added to **1**–**3** liberating MCl and the neutral protonated ligand, **5** (Scheme 1). For **1**, the isolation of this precursor as a co-crystallate of $[\{LiCl(pmdien)\}_2]$ permitted a structure determination that confirmed a reverse silyl shift.‡[19] As no-such rearrangement occurs during the preparation, or use of, group 1 guanidinates bearing the $N(SiMe_3)_2$ group, *e.g.* $[(Cy)NC\{N(SiMe_3)_2\}N(Cy)]^-$,[9] we assert that the presence of a supplementary 2-pyridyl group in **1**–**4**, and consequent 2-amidopyridine donor, instructs the observed migration.

We are currently evaluating the inorganic chemistry of guanidine **5** and investigating similar rearrangements during the insertion of DCC into alternative mono(trimethylsilyl) substituted amides bearing augmentative functionalities.

We thank the Australian Research Council (ARC) for their continued financial support (Discovery grant DP0211090).

Notes and references

§ Selected spectroscopic data for **2**: ^{1}H NMR (C_6D_6, 300 K): δ 0.64 (s, 9H, Si(CH_3)$_3$), 0.93–1.97 (m, 22H, Cy-*H*), 2.20 (s, 3H, CH_3), 3.09 (s, 6H, CH_3, dme), 3.17 (s, 4H, CH_2, dme), 5.94 (d, 1H, Py-*H*, $^2J_{CH}$ 7.0 Hz), 6.32 (d, 1H, Py-*H*, $^2J_{CH}$ 8.4 Hz), 7.03 (m, 1H, Py-*H*). ^{13}C NMR (C_6D_6, 300 K): δ 6.8 (s, Si(CH_3)$_3$), 25.3, 25.5, 25.6, 26.5, 27.2, 35.4, 35.9, 36.6, 55.7 (s, Cy-*C* and CH_3), 59.1 (s, CH_3, dme), 71.7 (s, CH_2, dme), 104.4, 107.5, 128.7, 136.7, 155.4, 163.6 (s, N_3C and Py-*C*). IR (Nujol) ν/cm^{-1}: 762m, 782m, 845s br, 946s, 1056s, 1158m, 1232s br, 1588s br, 1650s. For **4**: ^{1}H NMR (C_6D_6, 300 K): δ 0.40 (s, 9H, Si(CH_3)$_3$), 0.81–2.29 (m, 22H, Cy-*H*), 2.61 (s, 3H, CH_3), 5.79 (d, 1H, Py-*H*, $^2J_{CH}$ 7.3 Hz), 6.52 (d, 1H, Py-*H*, $^2J_{CH}$ 7.7 Hz), 6.74 (m, 1H, Py-*H*). ^{13}C NMR (C_6D_6, 300 K): δ 4.6 (s, Si(CH_3)$_3$), 15.9 (s, CH_3), 23.9, 25.9, 26.0, 26.5, 27.3, 27.7, 34.7, 35.6 (s, Cy-*C*), 116.1, 120.7, 141.2, 153.1, 157.8, 166.6 (s, N_3C and Py-*C*). ^{27}Al NMR (C_6D_6, 300 K, external $[Al(H_2O)_6]^{3+}$ reference): δ 96.3 (br s, $\nu_{1/2}$ 215 Hz). IR (Nujol) ν/cm^{-1}: 682m sh, 778m, 841s br, 970m, 1104s br, 1248s br, 1563s br, 1619s.

¶ *Crystal data*: For **2** ($C_{30}H_{57}N_4O_4Si_1Na_1$): M = 588.88, monoclinic, $P2_1$ (No. 4), a = 10.943(2), b = 12.892(3), c = 12.249(2) Å, β = 91.84(3)°, V = 1727.2(6) Å^3, T = 123(2) K, μ(Mo-Kα) = 0.118 mm^{-1}, independent ref. = 6179 (R_{int} = 0.1125), $R1$ (for 3585 reflections with $I > 2\sigma(I)$) = 0.0593, $wR2$ (all data) 0.0985. For **4** ($C_{22}H_{37}Cl_2N_4Si_1Al_1$): M = 485.53, monoclinic, $C2/c$ (No. 15), a = 31.997(6), b = 9.1761(18), c = 21.752(4) Å, β = 125.82(3)°, V = 5178.4(18) Å^3, T = 123(2) K, μ(Mo-Kα) = 0.348 mm^{-1}, independent ref. = 6305 (R_{int} = 0.0730), $R1$ (for 4860 reflections with $I > 2\sigma(I)$) = 0.0492, $wR2$ (all data) 0.1293. CCDC reference numbers 203278 and 203279. See http://www.rsc.org/suppdata/dt/b3/b303772j/ for crystallographic data in .cif or other electronic format.

1 J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.
2 F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403.
3 P. J. Bailey and S. Pace, *Coord. Chem. Rev.*, 2001, **214**, 91.
4 During the submission of this Communication a report detailing the ethylene tethering of two guanidines appeared as an advance article: T-G. Ong, G. P. A. Yap and D. S. Richeson, *Organometallics*, 2003, 387.
5 (*a*) D. Doyle, Y. K. Gunko, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 2000, 4093 and references therein; (*b*) S. Bambirra, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2001, **20**, 782 and references therein.
6 M. J. R. Brandsma, E. A. C. Brusee, A. Meetsma, B. Hessen and J. H. Teuben, *Eur. J. Inorg. Chem.*, 1998, 1867.
7 M. L. Cole, D. J. Evans, P. C. Junk and M. K. Smith, *Chem. Eur. J.*, 2003, **9**, 415 and references therein.
8 J. Baldamus, M. L. Cole, U. Helmstedt, E. Hey-Hawkins, C. Jones, P. C. Junk, F. Lange and N. A. Smithies, *J. Organomet. Chem.*, 2003, **665**, 33 and references therein.

9 (*a*) Y. Zhou, G. P. A. Yap and D. S. Richeson, *Organometallics*, 1998, **17**, 4387; (*b*) G. R. Giesbrecht, A. Shafir and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1999, 3601.
10 M. L. Cole and P. C. Junk, unpublished material.
11 R. Benn and A. Rufinska, *Angew. Chem. Int. Ed.*, 1986, **25**, 861.
12 B. Qian, D. L. Ward and M. R. Smith, *Organometallics*, 1998, **17**, 3070.
13 (*a*) S. L. Aeilts, M. P. Coles, D. C. Swenson, R. F. Jordan and V. G. Young, *Organometallics*, 1998, **17**, 3265; (*b*) C-C. Chang, C-S. Hsiung, H-L. Su, B. Srinivas, M. Y. Chiang, G-H. Lee and Y. Wang, *Organometallics*, 1998, **17**, 1595.
14 P. B. Hitchcock, M. F. Lappert and D-S. Liu, *J. Organomet. Chem.*, 1995, **488**, 241.
15 A. R. Brook and A. R. Basindale, in *Rearrangements in Ground and Excited States*, Academic Press, New York, 1980, vol. 2, pp. 149–227.
16 P. C. Andrews, D. R. Armstrong, M. MacGregor, R. E. Mulvey and D. Reed, *J. Chem. Soc., Chem. Commun.*, 1989, 1341.
17 A. R. Sanger, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 351.
18 (*a*) J. R. Hagadorn and J. Arnold, *Inorg. Chem.*, 1997, **36**, 2928; (*b*) J. R. Hagadorn and J. Arnold, *Organometallics*, 1998, **17**, 1355.
19 Crystallographic details of [{LiCl(pmdien)}$_2$].2(**5**) will be published at a later date.