Triamidoamine complexes of scandium, yttrium and the lanthanides

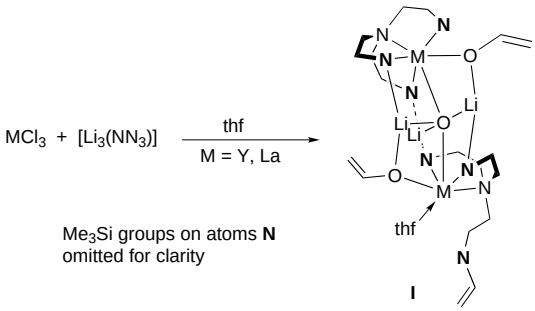
Paul Roussel, Nathaniel W. Alcock and Peter Scott*†

Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL

Synthesis of the simple triamidoamine complexes of the group 3 and lanthanide elements is achieved for the first time by reaction of $[Li_3(NN'_3)(thf)_3]$ [NN'_3 = $N(CH_2CH_2NSiMe_3)_3$] with the metal trichlorides; the 'ate' complexes $[M(NN'_3)ClLi(thf)_3]$ (M = Sc, Y, La) thus produced are converted smoothly to $[M(NN'_3)]$ on sublimation *in vacuo*.

The quadridentate triamidoamines $[N(CH_2CH_2NR)_3]^{3-}$ are established as an important class of ligand for the main group, transition and actinide elements. The complexes formed have unique properties as a result, for example, of the formation of a single, sterically protected fifth coordination site.[1] Most recently we have reported the complexation of dinitrogen to a (triamidoamine)uranium centre; an unprecedented feat for an actinide element.[2]

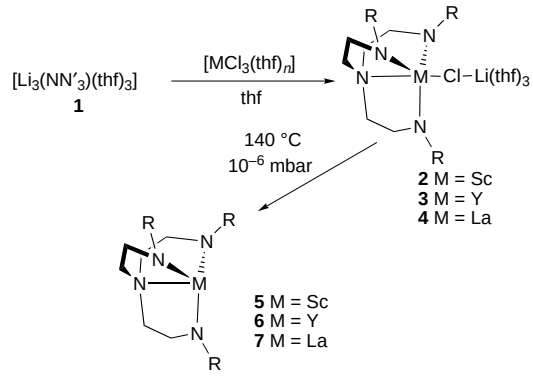
Reported attempts to synthesise the group 3 and lanthanide triamidoamines have thus far led to isolation of a novel trigonal monopyramidal lithium compound,[3] or the formation of the unusual product **I** below.[4]



The triamidoamine ligand $[N(CH_2CH_2NR)_3]$ (R = $SiMe_3$) would be expected to have a lower steric demand than the closely related fragment $\{N(SiMe_3)_2\}_3$ because of the constraints of the tripodal chelate structure. The actinide complexes $[U\{N(CH_2CH_2NSiMe_3)_3\}X]$ for example tend to have dimeric or distorted structures unless strong π-donor ligands X are used[5] while the compounds $[U\{N(SiMe_3)_2\}_3X]$ are monomeric.[6] The more sterically demanding triamidoamines R = $SiPr^i_3$ and $SiMePh_2$ form complexes which, in our experience, are difficult to isolate and unreactive. The ligand R = $SiMe_2Bu^t$[7] (henceforth NN'_3) however represents a suitable compromise between steric demand and synthetic utility. In its complexes with the actinides, three *tert*-butyl groups are oriented such that they encircle the equatorial plane in three-fold symmetric (trigonal pyramidal) structures and thus stabilise this geometry while allowing reactivity at the remaining axial site.[8] The complexes are crystalline, soluble and volatile. Using this type of ligand we have synthesised for the first time the simple group 3 and lanthanide triamidoamines.

Reaction of pure $[Li_3(NN'_3)(thf)_3]$ **1** with anhydrous $[MCl_3(thf)_n]$ (M = Sc, Y, La) in thf leads to rapid dissolution of the metal halide and formation of the analytically pure, colourless 'ate' complexes $[M(NN'_3)ClLi(thf)_3]$ (M = Sc **2**, Y **3**, La **4**) in near quantitative yields (Scheme 1).‡

Single crystals of the yttrium compound **3** were grown by slow cooling of a concentrated solution in pentane. The



Scheme 1 Synthesis of complexes **2**–**7**

molecular structure shown in Fig. 1 was determined by X-ray diffraction.§ The crystallographically threefold symmetric (triamidoamine)yttrium fragment is distorted from trigonal monopyramidal geometry by the displacement of the yttrium atom 0.67 Å out of the plane defined by the three amido nitrogen atoms. In the related triamides $[M\{N(SiMe_3)_2\}_3]$ (M = Sc, Eu[9] Y,[10] Nd,[11] Yb[12]) the metal atoms all lie 0.4 Å above the plane regardless of the ionic radius of the metal.[13] The apical amino N(1)–Y bond length in **3** is 2.588(4) Å. The amido N(1)–Y bond length of 2.231(2) Å is comparable to 2.226(6) Å found in $[Y\{N(SiMe_3)_2\}_3]$. The Y–Cl bond of 2.6526(16) Å is slightly longer than 2.55 and 2.598(2) Å observed in the 'ate' complexes $[Y\{N(SiMe_3)_2\}_3Cl][Li(thf)_4]$ and $[YR_3ClLi(Et_2O)_3]$ [R = $CH(SiMe_3)_2$], respectively,[10] presumably as a result of the *trans* effect of the amino N(1).

Heating compounds **2**–**4** to 140 °C and 10^{-6} mbar led to the distillation of pure colourless $[M(NN'_3)]$ (M = Sc **5**, Y **6**, La **7**) which solidified on cooling.‡ Trigonal monopyramidal triamidoamine complexes of the first row transition metals have been

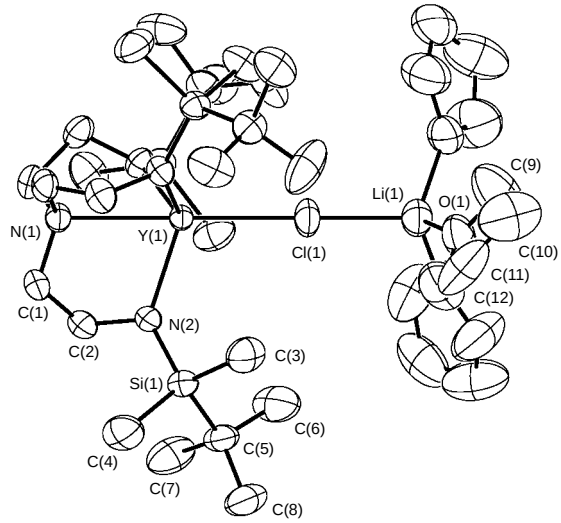


Fig. 1 Thermal ellipsoid plot of the molecular structure of **3**; hydrogen atoms omitted

synthesised,[7,14] but similar complexes of the second and third row have not been detected despite their implication in dinitrogen activation processes.[15] We cannot at present exclude the possibility of an agostic C–H–Y interaction in the apical coordination site, although no unusual NMR or IR shifts were observed.

Variable temperature NMR spectra of **2** in [$^2H_8$]toluene solution show that an equilibrium is established between the 'ate' complex [Sc(NN′$_3$)ClLi(thf)$_3$] **2** and [Sc(NN′$_3$)] **5** with the ratio [**5**] : [**2**] = 1 : 2.0 at 293 K. For the yttrium compounds, the ratio [**6**] : [**3**] is 1 : 22 while for lanthanum the base-free compound [La(NN′$_3$)] is not observed up to *ca*. 373 K. Thus the increase in atomic radius from Sc^{III} (0.89 Å) to Ln^{III} (1.17 Å) is accompanied by increased stability of the 'ate' complex; a good example of the prevalence of steric over electronic effects in lanthanide chemistry.

Complexes analogous to **2**–**7** are readily prepared for all of the stable lanthanides; we will report the trends in magnetic and spectroscopic properties of these compounds in due course. They have potential applications as regioselective Lewis acid catalysts by virtue of their single, sterically protected coordination site; related chiral titanatranes are effective enantioselective catalysts.[16] For the moment, we have shown that with suitable choice of ligand substituent, the elusive triamidoamine complexes of scandium and the rare earth elements can be synthesised.

P. S. wishes to thank the EPSRC for a Project Studentship, BNFL for a CASE award (to P. R.), and Pfizer Ltd. and SmithKline Beecham for support.

Notes and References

* E-mail: peter.scott@warwick.ac.uk

† *Characterising data*: for **2**: ^{1}H NMR (293 K, [$^2H_6$]benzene, see text), δ 3.7 (br m, 12 H, thf), 3.56 (t, 6 H, CH_2), 2.68 (t, 6 H, CH_2), 1.40 (m, 12 H, thf), 1.23 (s, 27 H, Bu^t), 0.43 (s, 18 H, $SiMe_2$). ^{13}C{^{1}H} NMR (293 K, [$^2H_6$]benzene), δ 68.59 (thf), 65.91 (CH_2), 45.99 (CH_2), 28.61 (C*Me*$_3$), 25.48 (thf), 21.65 (*C*Me$_3$), −2.41 ($SiMe_2$). ^{7}Li{^{1}H} NMR (293 K, [$^2H_6$]benzene), δ 1.80 (br s). MS (EI) as for **5**. For **3**: ^{1}H NMR (293 K, [$^2H_6$]benzene, see text), δ 3.56 (m, 15 H, CH_2 and thf), 2.64 (t, 6 H, CH_2), 1.4 (m, 12 H, thf), 1.22 (s, 27 H, Bu^t), 0.41 (s, 18 H, $SiMe_2$). ^{13}C{^{1}H} NMR (293 K, [$^2H_6$]benzene), δ 68.69 (thf), 65.15 (CH_2), 46.01 (CH_2), 28.67 (C*Me*$_3$), 25.46 (thf), 21.34 (*C*Me$_3$), −3.32 ($SiMe_2$). ^{7}Li{^{1}H} NMR (293 K, [$^2H_6$]benzene), δ 0.38 (s). MS (EI) as for **6**. For **4**: ^{1}H NMR (293 K, [$^2H_8$]toluene, see text), δ 3.62 (br m, 12 H, thf), 3.54 (t, 6 H, CH_2), 2.72 (t, 6 H, CH_2), 1.36 (m, 12 H, thf), 1.11 (br s, 27 H, Bu^t), 0.16 (br s, 18 H, $SiMe_2$). ^{13}C{^{1}H} NMR (293 K, [$^2H_8$]toluene), δ 68.44 (thf), 47.25 (CH_2), 27.96 (C*Me*$_3$), 25.45 (thf), 20.89 (*C*Me$_3$), 14.27 (CH_2), −4.32 ($SiMe_2$). ^{7}Li{^{1}H} NMR (293 K, [$^2H_6$]benzene), δ 1.80 (br s). ^{139}La{^{1}H} (298 K, [$^2H_6$]benzene), δ 1035.2 (s). MS (EI) as for **7**. For **5**: ^{1}H NMR (293 K, [$^2H_8$]toluene), δ 3.32 (t, 6 H, CH_2), 2.56 (t, 6 H, CH_2), 1.01 (s, 27 H, Bu^t), 0.13 (s, 18 H, $SiMe_2$). ^{13}C{^{1}H} NMR (293 K, [$^2H_8$]toluene), δ 58.84 (CH_2), 45.11 (CH_2), 27.61 (C*Me*$_3$), 20.40 (C*Me*$_3$), −3.82 ($SiMe_2$). MS (EI) *m/z* 530 (63%, M$^+$), 515 (14%, M$^+$ − Me), 473 (100%, M$^+$ − Bu^t). For **6**: ^{1}H NMR (293 K, [$^2H_8$]toluene), δ 3.39 (t, 6 H, CH_2), 2.57 (t, 6 H, CH_2), 1.00 (s, 27 H, Bu^t), 0.08 (s, 18 H, $SiMe_2$). ^{13}C{^{1}H} NMR (293 K, [$^2H_8$]toluene), δ 57.23 (CH_2), 45.88 (CH_2), 27.49 (C*Me*$_3$), 20.40 (*C*Me$_3$), − 4.23 ($SiMe_2$). MS (EI) *m/z* 574 (45%, M$^+$), 559 (12%, M$^+$ − Me), 517 (80%, M$^+$ − Bu^t). For **7**: ^{1}H NMR (293 K, [$^2H_8$]toluene), δ 3.57 (t, 6 H, CH_2), 2.71 (t, 6 H, CH_2), 1.00 (s, 27 H, Bu^t), 0.08 (s, 18 H, $SiMe_2$). ^{13}C{^{1}H} NMR (293 K, [$^2H_8$]toluene), δ 57.48 (CH_2), 47.65 (CH_2), 27.44 (C*Me*$_3$), 20.37 (*C*Me$_3$), −4.59 ($SiMe_2$). MS (EI) *m/z* 624 (16%, M$^+$), 609 (7%, M$^+$ − Me), 567 (33%, M$^+$ − Bu^t).

§ *Crystal data* for **3**. $C_{36}H_{81}ClLiN_4O_3Si_3Y$, M = 833.62, cubic, space group $Pa\bar{3}$, a = 21.486(2) Å, U = 9919.0(16) Å^3 (by least squares refinement on 6602 reflection positions), Z = 8, D_c = 1116 Mg m^{-3}, F(000) = 3600. Colourless needle 0.52 × 0.16 × 0.14 mm at 180(2) K, final R_1, wR_2 and S were 0.0486, 0.0961 and 1.070. CCDC 182/797.

1 J. G. Verkade, *Acc. Chem. Res.*, 1993, **26**, 483; *Coord. Chem. Rev.*, 1994, **137**, 233; R. R. Schrock, *Acc. Chem. Res.*, 1997, **30**, 9; *Pure Appl. Chem.*, 1997, **69**, 2197.
2 P. Roussel and P. Scott, *J. Am. Chem. Soc.*, 1998, **120**, 1070.
3 D. Zhibang, V. G. Young and J. G. Verkade, *Inorg. Chem.*, 1995, **34**, 2179.
4 H. C. Aspinall and M. R. Tillotson, *Inorg. Chem.*, 1996, **35**, 2163.
5 P. Scott and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 1995, 603; *J. Chem. Soc., Chem. Commun.*, 1995, 579; P. Roussel, P. B. Hitchcock, N. D. Tinker and P. Scott, *Inorg. Chem.*, 1997, **36**, 5716.
6 H. W. Turner, R. A. Andersen, A. Zalkin and D. H. Templeton, *Inorg. Chem.*, 1979, **18**, 1221.
7 C. C. Cummins, J. Lee, R. R. Schrock and W. M. Davis, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1501.
8 P. Roussel, P. B. Hitchcock, N. D. Tinker and P. Scott, *Chem. Commun.*, 1996, 2053.
9 J. S. Ghotra, M. B. Hursthouse and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1973, 669.
10 M. Westerhausen, M. Hartmann, A. Pfitzner and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1995, **621**, 837.
11 R. A. Andersen, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1978, **17**, 2317.
12 P. J. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek, *Coord. Chem. Rev.*, 1977, **24**, 1.
13 K. N. Raymond and C. W. Eigenbrot, *Acc. Chem. Res.*, 1980, **13**, 276.
14 C. Rosenberger, R. R. Schrock and W. M. Davis, *Inorg. Chem.*, 1997, **36**, 123.
15 K.-Y. Shih, R. R. Schrock and R. Kempe, *J. Am. Chem. Soc.*, 1994, **116**, 8804.
16 W. A. Nugent, T. V. Rajanabu and M. J. Burk, *Science*, 1993, **259**, 479.

Received in Basel, Switzerland, 8th December 1997; 7/08785C