ChemComm

Structure and reactions of a metallacyclic complex containing a remarkably long uranium–carbon bond

Rita Boaretto, Paul Roussel, Andrew J. Kingsley, Ian J. Munslow, Christopher J. Sanders, Nathaniel W. Alcock and Peter Scott*

Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL. E-mail: peter.scott@warwick.ac.uk

Received (in Basel, Switzerland) 11th May 1999, Accepted 17th July 1999

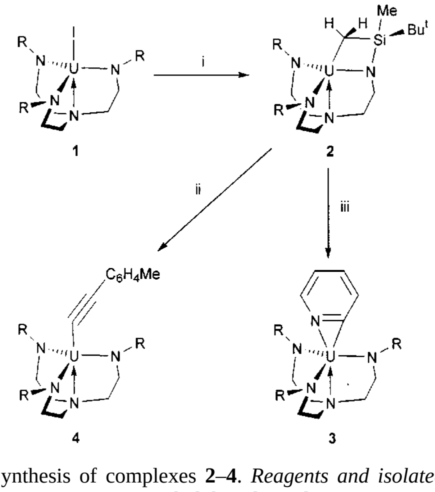
The intramolecular metalation of a β-silyl methyl group in [U{N($CH_2CH_2NSiMe_2Bu^t)_3$}(CH_2Ph)] occurs rapidly, despite the conformational demands of the triamidoamine ligand, to produce a highly strained metallacycle (U–C *ca.* 2.75 Å); this complex reacts cleanly with a range of carbon and other acids to give, for example, an alkynyl with a bent (156°) U–C≡C unit.

Intramolecular C–H activation of ligands is relatively common among early actinide complexes, including those containing bulky alkyls,[1] amides,[2] phosphides[3] and phenoxides.[4] Molecular models suggested that triamidoamine[5] [($RNCH_2CH_2)_3N$)]$^{3-}$ complexes of metals with large van der Waals radii would be less prone to such reactions because of conformational restrictions (*vide infra*), and might instead undergo *inter*molecular reactions with hydrocarbons. With this in mind we set out to synthesise species such as [{($RNCH_2CH_2)_3N$}MR′] (M = U, Th; R′ = H, alkyl). While we have prepared a wide range of triamidoamine complexes containing bonds between the early actinides and other elements,[6] the synthesis of M–C σ bonds proved troublesome. For example, reactions of the uranium and thorium chlorides [{($RNCH_2CH_2)_3N$}MCl] (R = $SiMe_3$) and related compounds with a wide variety of metal alkyls led to the formation of intractable yellow mixtures. More recently however we have shown that the bulkier triamidoamine (where R = $SiMe_2Bu^t$, henceforth NN′$_3$), forms much more synthetically useful complexes with the f elements.[7,8] Use of this ligand has allowed us to isolate an extremely reactive and structurally fascinating metallacyclic uranium complex which is an excellent starting material for the synthesis of other organometallic compounds.

Treatment of [U(NN′$_3$)I][7] **1** with a stoichiometric amount of lithium or potassium alkyl in pentane afforded brown solutions from which extremely air-sensitive orange–brown crystals of **2** were isolated by filtration and cooling to −30 °C (Scheme 1). This product was the same irrespective of the alkylating agent used, although optimum yields (71% isolated) were obtained by use of lithium neopentyl or potassium benzyl in toluene. When this latter reaction was performed in an NMR tube and monitored by ^1H NMR spectroscopy, smooth and quantitative conversion of **1** to **2** with co-production of toluene was observed within minutes at ambient temperature. Interestingly, the presumed intermediate species [U(NN′$_3$)CH_2Ph] immediately decomposed to the metallacycle **2** and was not detected. The rapidity of this reaction is quite surprising; by comparison, conversion of the titanium[9] and molybdenum[10] triamidoamines [{($Me_3SiNCH_2CH_2)_3N$}TiBu^S] and [{($Me_3SiNCH_2CH_2)_3N$}MoH] to their respective metallacycles occurs only slowly and at elevated temperatures. Similarly, Andersen's metallacycle [U{N($SiMe_3)_2$}$_2${N($SiMe_3$)(CH_2SiMe_2)}] is produced by thermolysis of [U{N($SiMe_3)_2$}$_3$X] (X = H, Me).[2]

Single crystals of **2** were grown from a saturated solution of the pure compound in pentane and the molecular structure (Fig. 1) was determined by X-ray crystallography.† The U–C(108) distance of 2.752(11) Å is significantly longer than any other U–C σ-bond hitherto recorded; the usual range is *ca.* 2.4–2.55 Å,[12] although distances of *ca.* 2.60 Å have been measured in complexes of chelating phosphorus ylids.[13] The metallacyclic phosphide [$Cp^*_2U(CH_2SiMe_2PSiMe_3)$][3] and amide [$Cp^*_2Th_2(CF_3SO_3)_3(NSiMe_3)(CH_2SiMe_2NSiMe_3)$][14] contain M–C–Si–N rings similar to that in **2** but the M–C distances of 2.415(20) and 2.43(5) Å are well within the range observed for their acyclic counterparts. Schrock's (triamidoamine)molybdenum metallacycle[10] adopts a similar conformation to **2**, but the Mo–C bond is only *ca.* 0.08 Å longer than those in acyclic alkyls.

An important feature of the structure of **2** is the orientation of the $SiMe_2$ groups at Si(12) and Si(13) which bring one methyl group from each, C(114) and C(119), toward the otherwise open face of the uranium centre. The non-bonded U–C distances of 3.056(14) and 3.218(10) Å, respectively, are consistent with the presence of C–H→U agostic interactions.[15] The maximum deviations of any atom from the least-squares planes [U, N(12), Si(12), C(114)], [U, N(13), Si(13), C(119)] and [U, N(11), Si(11), C(108)] are 0.08, 0.05 and 0.06 Å respectively.



Scheme 1 Synthesis of complexes **2**–**4**. *Reagents and isolated yields*: i, KPh, toluene, 71%; ii, *p*-methylphenylacetylene, pentane, 80%; iii, pyridine, pentane, recrystallisation from hexamethyldisiloxane, 80%.

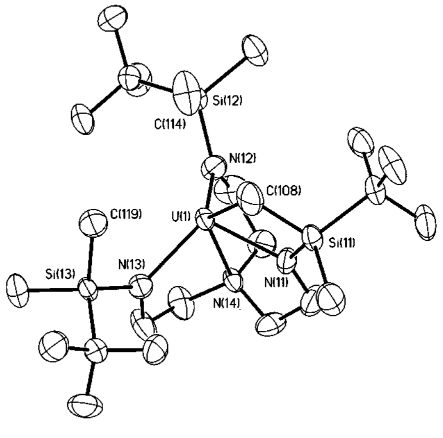


Fig. 1 Thermal ellipsoid plot of the molecular structure of **2**; hydrogen atoms omitted.

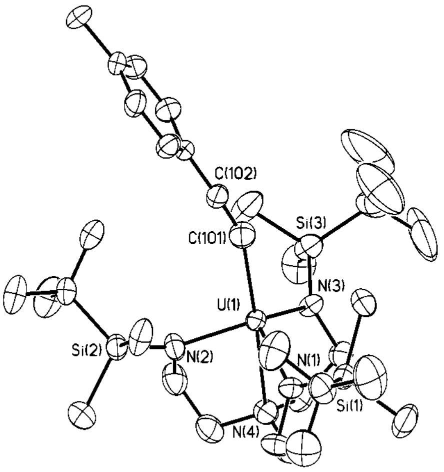


Fig. 2 Thermal ellipsoid plot of the molecular structure of **4**; hydrogen atoms omitted.

The ^1H NMR spectrum of **2** recorded in d_8-toluene contains a total of 22 peaks indicating that the product is chiral. Of these, 20 peaks are readily assigned to methyl and *tert*-butyl groups or diastereotopic methylene protons in the ligand backbone. Relatively broad peaks, at $\delta -35.34$ and -52.34 are assigned to the Si–CH$_2$–U group on the basis of a selective deuteration study.‡ Other spectroscopic and analytical data are also in accord with the structure proposed for **2**.

The metallacycles $[\{(Me_3Si)_2N\}_2M\{N(SiMe_3)(SiMe_2CH_2)]$ (M = U, Th) have been used extensively as starting materials for a wide range of complexes.[16] Accordingly, we have found that **2** reacts cleanly with acids HX under very mild conditions to form a range of U–X bonds with concomitant regeneration of the symmetric triamidoamine framework.

Reactions of **2** with trimethylamine hydrochloride, diethylamine and Bu^{t}OH give the complexes $[(NN_3')UCl]$, $[(NN_3')U(NEt_2)]$[7] and $[(NN_3')U(OBu^t)]$[17] in essentially quantitative yields. Similarly, reaction of **2** with pyridine proceeds rapidly at room temperature to give the brown crystalline η^2-pyridyl complex **3** and *p*-methylphenylacetylene gives the yellow–green alkynyl $[U(NN_3')(\eta^1\text{-}C{\equiv}CC_6H_4Me)]$ **4**.

The molecular structure of **4** is shown in Fig. 2. The angle U–C(101)–C(102) of 156.4(6)° is significantly lower than the range found for the few structurally characterised non-bridging alkynyls of the f elements (170–176°).[18] Perhaps the alkynyl uranium fragment in **4** bends in order to allow for increased U–C π-overlap. We are currently investigating this and other related phenomena.

Hence, although the conformational constraints of the triamidoamine ligand do not prevent intramolecular C–H activation of the somewhat acidic β-silyl methyl groups in $[U(NN'_3)R]$, the metallacycle **2** thus formed is an excellent starting material for the generation of a range of highly crystalline organometallic complexes of uranium.

P. S. wishes to thank EPSRC for a Project Studentship and SmithKline Beecham for a CASE award (to C. J. S.), Pfizer (UK) Ltd for a CASE award to I. J. M., Universitá degli Studi di Ferrara for support of R. B., and BNFL for both a CASE award (to P. R.) and postdoctoral fellowship (to A. J. K.). We thank EPSRC and Siemens Analytical Instruments for grants in support of the diffractometer.

Notes and references

† *Crystal data*: $C_{24}H_{56}N_4Si_3U$ **2**: M = 723.03, triclinic, space group $P\bar{1}$, a = 12.7602(5), b = 13.3286(5), c = 13.3902(5) Å, α = 119.3350(10), β = 109.0980(10), γ = 92.8980(10)°, U = 1813.56(12) Å^3 (by least squares refinement on 9181 reflection positions), T = 180(2) K, Z = 2, μ(Mo-Kα) = 4.590 mm^{-1}, 11113 reflections measured, 8070 unique (R_{int} = 0.0296), R_1 [for 6567 reflections with $I > 2\sigma(I)$] = 0.0459, wR_2 = 0.1206.

$C_{33}H_{64}N_4Si_3U$ **4**: M = 839.18, monoclinic, space group $P2_1/c$, a = 17.3244(10), b = 12.7945(10), c = 18.6257(15) Å, β = 97.7090(10)°, U = 4091.2(5) Å^3 (by least squares refinement on 7606 reflection positions), T = 180(2) K, Z = 4, μ(Mo-Kα) = 4.080 mm^{-1}, 24202 reflections measured, 9593 unique (R_{int} = 0.0922), R_1 [for 8001 reflections with $I > 2\sigma(I)$] = 0.0559, wR_2 = 0.1533. Data were collected on a Siemens SMART CCD. The structures were solved by direct methods with additional light atoms found by Fourier methods. Atoms N(13) and C(119) in **2** were refined anisotropically.

CCDC 182/1350. See http://www.rsc.org/suppdata/cc/1999/1701/ for crystallographic files in .cif format.

‡ Addition of dry D_2 to a sample of **2** in toluene-d^8 leads to deuteration at ambient temperature over a period of hours of all SiMe$_2$ groups and the metallacyclic CH$_2$ *via* sequential σ-bond metathesis reactions. Andersen's metallacycle is fully deuterated under these conditions. See ref. 2.

1 C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108**, 425.

2 S. J. Simpson, H. W. Turner and R. A. Andersen, *Inorg. Chem.*, 1981, **20**, 2991.

3 S. W. Hall, J. C. Huffman, M. M. Miller, L. R. Avens, C. J. Burns, D. S. J. Arney, A. F. England and A. P. Sattelberger, *Organometallics*,1993, **12**, 752.

4 D. L. Clark, S. K. Grumbine, B. L. Scott and J. G. Watkin, *Organometallics*, 1996, **15**, 949.

5 R. R. Schrock, *Acc. Chem. Res.*, 1997, **30**, 99; J. G. Verkade, *Acc. Chem. Res.*, 1993, **26**, 483.

6 P. Roussel, P. B. Hitchcock, N. D. Tinker and P. Scott, *Chem. Commun.*, 1996, 2053; P. Scott and P. B. Hitchcock. *J. Chem. Soc., Chem. Commun.*, 1995, 579; P. Scott and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 1995, 603.

7 P. Roussel, N. W. Alcock, R. Boaretto, A. J. Kingsley, I. J. Munslow, C. J. Sanders and P. Scott, *Inorg. Chem.*, in press.

8 P. Roussel and P. Scott, *J. Am. Chem. Soc.*,1998, **120**, 1070; P. Roussel, N. W. Alcock and P. Scott, *Inorg. Chem.*, 1998, **37**, 3435.

9 C. C. Cummins, R. R. Schrock and W. M. Davis, *Organometallics*, 1992, **11**, 1452.

10 R. R. Schrock, S. W. Seidel, N. C. Mösch-Zanetti, K.-Y. Shih, M. B. O'Donoghue, W. M. Davis and W. M. Reiff, *J. Am. Chem. Soc.*, 1997, **119**, 11 876.

11 G. Perego, M. Cesari, F. Farina and G. Lugli, *Acta Crystallogr., Sect. B*, 1976, **32**, 3034; P. G. Edwards, R. A. Andersen and A. Zalkin, *Organometallics*, 1984, **3**, 293; J. L. Stewart and R. A. Andersen, *J. Chem. Soc., Chem. Commun.*, 1987, 1846; M. Wedler, F. Knosel, F. T. Edelmann and U. Behrens, *Chem. Ber.*, 1992, **125**, 1313.

12 R. E. Cramer, S. Roth, F. Edelmann, M. A. Bruck, K. C. Cohn and J. W. Gilje, *Organometallics*, 1989, **8**, 1192.

13 R. J. Butcher, D. L. Clark, S. K. Grumbine and J. G. Watkin, *Organometallics*, 1995, **14**, 2799.

14 M. Müller, V. C. Williams, L. H. Doerrer, M. A. Leech, S. A. Mason, M. L. H. Green and K. Prout, *Inorg. Chem.*, 1998, **37**, 1315; see also citation in ref. 4.

15 S. J. Simpson and R. A. Andersen, *J. Am. Chem. Soc.*, 1981, **103**, 4063; A. Dormond, A. el Bouadili and C. Moise, *J. Chem. Soc., Chem. Commun.*, 1985, 914; A. Dormond, A. A. Aalti, A. el Bouadili and C. Moise, *Inorg. Chim. Acta*, 1987, **139**, 171; D. M. Barnhart, D. L. Clark, S. K. Grumbine and J. G. Watkin, *Inorg. Chem.*,1995, **34**, 1695; D. M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman and J. G. Watkin, *Inorg. Chem.*, 1995, **34**, 5416; D. M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman and J. G. Watkin, *Inorg. Chem.*, 1994, **33**, 3939; D. L. Clark and J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 1766; J. M. Berg, D. L. Clark, J. C. Huffman, D. E. Morris, A. P. Sattelberger, W. E. Streib, W. G. Vandersluys and J. G. Watkin, *J. Am. Chem. Soc.*, 1992, **114**, 10 811.

16 P. Roussel, P. B. Hitchcock, N. D. Tinker and P. Scott, *Inorg. Chem.*,1997, **36**, 5716.

17 J. L. Atwood, C. F. Hains Jnr., M. Tsutsui and A. E. Gebala, *J. Chem. Soc., Chem. Commun.*, 1973, 452; J. L. Atwood, M. Tsutsui, N. Ely and A. E. Gebala, *J. Coord. Chem.*, 1976, **5**, 209; W. J. Evans, T. A. Ulibarri, L. R. Chamberlain, J. W. Ziller and D. Alvarez Jnr., *Organometallics*, 1990, **9**, 2124; W. J. Evans, R. A. Keyer and J. W. Ziller, *Organometallics*, 1993, **12**, 2618; W. J. Evans, G. W. Rabe and J. W. Ziller, *J. Organomet. Chem.*, 1994, **21**, 483.

Communication 9/03783G