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Uranium(IV) bis(amido), imido and bis(acetylide) complexes: synthesis, molecular structure, solution dynamics and interconversion reactions

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Reactions of $[UMe_2(C_5Me_5)_2]$ with primary aromatic or aliphatic amines led to the rapid formation of monomeric uranium(IV) complexes $[U(C_5Me_5)_2(NHR)_2]$ (R = 2,6-dimethylphenyl **1**, Et **2** or Bu^t **3**). The compounds were characterized by standard techniques and for **1**, by X-ray diffraction. In co-ordinating solvents like tetrahydrofuran (thf) compound **1** reacted intramolecularly releasing one primary amine and forming the imidouranium(IV) $[U(C_5Me_5)_2\{N(C_6H_3Me_2\text{-}2,6)\}]\cdot$thf **4**, whereas in non-co-ordinating solvents the base-free $[U(C_5Me_5)_2\{N(C_6H_3Me_2\text{-}2,6)\}]$ **5** was obtained. The thf in **4** was found not to be in equilibrium with bulk solvents, and different proton chemical shifts for the adducted base were observed as a function of temperature following a Curie–Weiss behaviour. σ-Bond metathesis reactions of the bis(amido) and/or imido complexes with terminal alkynes produced the bis(acetylide) complexes $[U(C_5Me_5)_2(C{\equiv}CR)_2]$ (R = Ph **6** or Bu^t **7**) active species for the regioselective oligomerization of terminal alkynes, which can be prepared also from the reaction of $[UMe_2(C_5Me_5)_2]$ with 2 equivalents of the corresponding terminal alkyne. Reactivity studies show the possible interconversion among these bis(amido), imido and bis(acetylide) complexes.

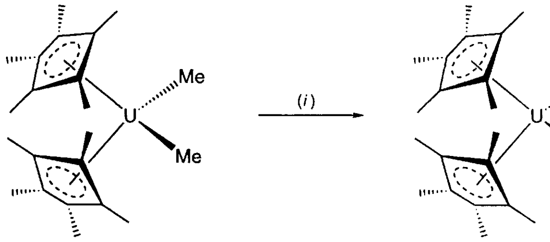
Many metal imido complexes (M=NR) in the middle of the transition series (Group 5–10 triads) are known, but in most of these compounds the M=N linkages are notoriously inert,[1] despite the implication that imido species could be involved in the ammoxidation of propylene, the Haber ammonia synthesis and the reduction of nitriles and hydrazines.[2] The reactivity of osmium imido complexes[3] and of early transition-metal imido/bis(amido)[4] complexes suggests that moving away from the middle of the Periodic Table may vary the properties of the metal–ligand bond in these compounds and improve the chances of using them in amido, imido transfer reactions or as intermediates in the formation of carbyl complexes. Recently we have shown that organoactinide complexes of the type $[An(C_5Me_5)_2(NR)]\cdot$thf (thf = tetrahydrofuran) $[An(C_5Me_5)(NHR)_2]$ and $[An(C_5Me_5)_2(C{\equiv}CR)_2]$ (An = Th or U) can be employed as effective homogeneous catalysts in the synthesis of highly useful organic molecules like imines/enamines[5] and enynes[6] respectively. Comparative studies show that, for organoactinide complexes, the reactivity toward the formation of imines/enamines is higher than for the isolobal early transition metals and different for the formation of enynes.[7]

We present here the synthesis of several monomeric bis(pentamethylcyclopentadienyl)uranium(IV) bis(amido) complexes, the simple conversion into the corresponding imido compound after intramolecular elimination of an amine, and the reactivity of these imido and bis(amido) complexes toward terminal acetylenes. To our knowledge, bis(pentamethylcyclopentadienyl)actinide(IV) bis(amido) complexes have not been structurally characterized so far.

Results and Discussion

Synthesis of bis(pentamethylcyclopentadienyl)uranium(IV) bis(amido) complexes

Treatment of $[UMe_2(C_5Me_5)_2]$ with 2 equivalents of NH_2R in thf gives the compounds $[U(C_5Me_5)(NHR)_2]$ (R = 2,6-dimethylphenyl **1**, Et **2** or Bu^t **3**) as dark red to black crystals (Scheme 1).[8] These reactions can be run quantitatively (as indicated by ^{1}H NMR spectroscopy) on a gram scale and the products crystallized from hot hexane although their high solubility precluded isolation in yields higher than *ca.* 35%, even from hexane at −78 °C. Complexes **1**–**3** are remarkable monomeric compounds, with two secondary amide ligands bearing reasonably unreactive hydrogen atoms.† They are fairly stable at room temperature and do not form dimeric complexes and free amine in non-co-ordinating solvents.[8c,10] Attempts to trap the corresponding mono(methylamido) intermediate complex using only 1 mol of amine were unsuccessful indicating that the σ-bond metathesis of the second uranium–methyl bond is very fast (even at −78 °C) and/or the monomethyl complex undergoes disproportionation allowing us only to observe the bis(amido) or the starting dimethyl complexes (Scheme 2).‡[,10b]



1 R = $C_6H_3Me_2$-2,6
2 R = Et
3 R = Bu^t

Scheme 1 (*i*) $2NH_2R$, thf, 298 K, $-2CH_4$

Crystal structure of $[U(C_5Me_5)_2\{NH(C_6H_3Me_2\text{-}2,6)\}_2]$

Suitable crystals of complex **1** were obtained from a hot hexane solution cooled slowly to room temperature. Fig. 1 shows an ORTEP[12] drawing of the structure with the atom numbering

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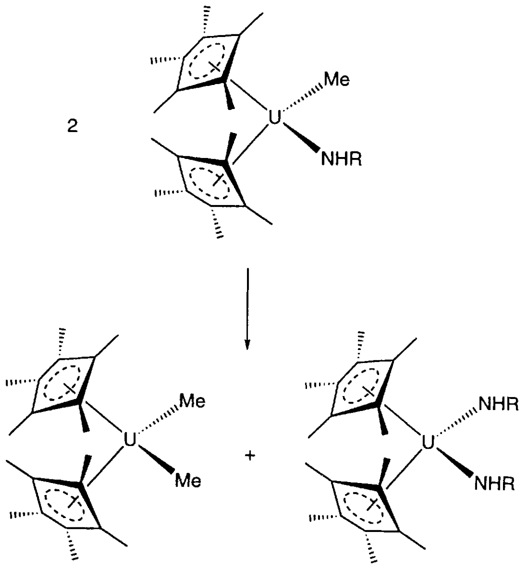
† For $[Ln(C_5Me_5)_2(NHMe)(NH_2Me)]$ where the amine hydrogens scramble with the amido hydrogen.[9]

‡ For a similar zirconium complex see ref. 11.



Scheme 2 (*i*) thf, 298 K

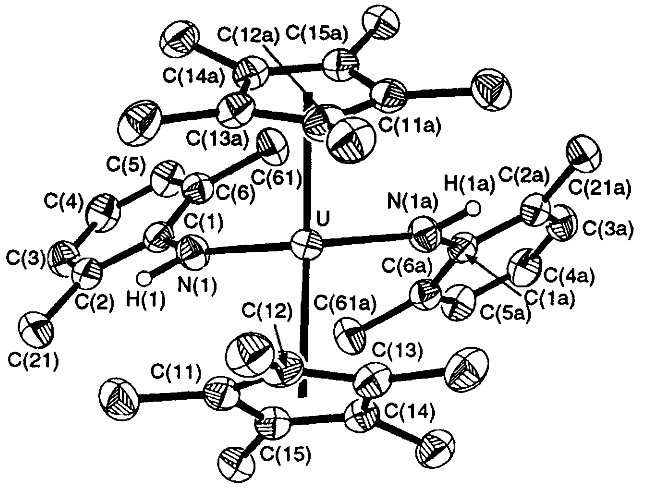


Fig. 1 An ORTEP drawing of the tetrahedral uranium(IV) bis(amido) complex **1** with atom numbering scheme. All thermal vibrational ellipsoids encompass 30% of the electron density

scheme. Bond lengths and selected angles are given in Table 1. The X-ray structural analysis reveals that single crystals of **1** are composed of discrete mononuclear $[U(C_5Me_5)_2(NHR)_2]$ molecules. The uranium(IV) ion, lying on a two-fold symmetry axis, adopts the familiar 'bent sandwich' actinide co-ordination geometry,[10a,11] being π bonded to two C_5Me_5-ligands and σ bonded to two NHR^- ligands. The $U(C_5Me_5)_2$ portion of each monomeric unit is unexceptional with an average C–C ring distance of 1.41(2,5,20)* Å,[13] C–CH_3 distance of 1.52(2,4,20) Å and U–C ring distance of 2.78(2,4,20) Å. The ring centroid–U–ring centroid angle of 127.8° is much smaller than those in other early organo-f-element complexes and comparable to those of the zirconium ring-bridged cyclopentadienyl systems, allowing the N–U–N angle of 111.0(3) to be much larger than in any structurally characterized organo-f-element complexes.[13,14] In addition, this angle is manifested in the N···N non-bonded distance of 3.737 Å similar to that of $[La(C_5Me_5)_2(NHMe)(NH_2Me)]$.[9] When compared (after correction for trivalent eight-co-ordinate ionic radii),†,[15] with Ln–N (Ln = lanthanide) distances in previously characterized lanthanide amido complexes $[Y(C_5Me_5)_2\{N(SiMe_3)_2\}]$ 2.415(5) (calc.), 2.274(5) (actual);[16] $[Y\{SiMe_2(C_5H_4)(C_5H_3R)\}\{N(SiMe_3)_2\}]$ (R = 1*S*,2*S*,5*R*-menthyl) 2.423(3) Å (calc.), 2.283(7) (actual);[17] $[Sm\{SiMe_2(C_5H_4)(C_5H_3R')\}\{N(SiMe_3)_2\}]$ (R′ = 1*S*,2*S*,5*R*-neomenthyl) 2.381(5) Å (calc.), 2.300(5) Å (actual);[17] $[\{(C_5H_4Me)_2Yb(NH_2)\}_2]$ 2.49(1) Å (calc.), 2.31(1) (actual),[18] the present U–NHR distance is ≈0.1 Å shorter. The U–N bond is in fact comparable to that in tetrakis(diphenylamido)uranium(IV), 2.27(3) Å.[8e] Interestingly, the U–N bond is even slightly shorter, after correction for effective ionic radii,[15] than the Hf–N bond length of 2.36(1) Å [2.027(8) Å actual] in $[Hf(C_5Me_5)_2H(NHMe)]$,[19] and the Zr–N bond length of 2.412(4) Å [2.092(3) actual] in $[Zr(C_5H_5)_2(NHPh)][O_3SCF_3]$.[20] These complexes are all suggested to have M–N (M = Zr or Hf) multiple-bond character. It is noteworthy that the U–NHR bond length in the bis(amido) complex is 0.22 Å larger than in the corresponding organothorium imido complex (Th = NR) bearing the same R group.[7a]

Table 1 Bond lengths (Å) and selected angles (°) for complex **1**

U–N(1)	2.267(6)	C(2)–C(21)	1.502(11)
U–C(11)	2.801(7)	C(3)–C(4)	1.362(12)
U–C(12)	2.791(6)	C(4)–C(5)	1.392(13)
U–C(13)	2.731(5)	C(5)–C(6)	1.369(6)
U–C(14)	2.751(5)	C(6)–C(61)	1.503(13)
U–C(15)	2.800(6)	C(11)–C(12)	1.393(10)
U–N(1a)	2.267(6)	C(11)–C(15)	1.410(7)
U–C(11a)	2.802(7)	C(11)–C(111)	1.507(11)
U–C(12a)	2.792(6)	C(12)–C(13)	1.409(9)
U–C(13a)	2.733(5)	C(12)–C(121)	1.535(7)
U–C(14a)	2.751(5)	C(13)–C(14)	1.420(8)
U–C(15a)	2.800(6)	C(13)–C(131)	1.503(11)
N(1)–C(1)	1.424(7)	C(14)–C(15)	1.391(9)
C(1)–C(2)	1.430(12)	C(14)–C(141)	1.521(7)
C(1)–C(6)	1.413(10)	C(15)–C(151)	1.537(10)
C(2)–C(3)	1.386(8)		

N(1)–U–N(1a)	111.0(3)	N(1a)–U–C(13)	95.3(2)
N(1)–U–C(11)	80.0(2)	N(1a)–U–C(14)	83.9(2)
N(1)–U–C(12)	107.5(2)	N(1a)–U–C(15)	104.4(2)
N(1)–U–C(13)	125.8(2)	N(1)–U–C(11a)	131.6(2)
N(1)–U–C(14)	105.0(2)	N(1a)–U–C(11a)	80.1(2)
N(1)–U–C(15)	78.6(2)	C(11)–U–C(11a)	128.7(2)
C(11)–U–C(12)	28.9(2)	U–N(1)–C(1)	150.6(5)
C(12)–U–C(13)	29.5(2)	U–N(1a)–C(1a)	150.6(5)
C(13)–U–C(14)	30.0(2)	U–N(1)–C(6)	120.9(4)
C(11)–U–C(15)	29.2(1)	C(1)–N(1)–C(6)	30.4(4)
C(14)–U–C(15)	29.0(2)	C(1)–C(2)–C(3)	118.7(7)
C(11)–U–C(13)	48.6(2)	C(1)–C(2)–C(21)	121.9(5)
N(1a)–U–C(11)	131.5(2)	C(2)–C(1)–C(3)	30.1(3)
N(1a)–U–C(12)	124.8(2)		

When compared with other early transition metals or lanthanides a major difference lies in the relative orientation of the NR groups. In the uranium bis(amido) complex, the *ipso*-carbon lies in the plane formed by N–U–N [N(1a)–U–N(1)–C(1) dihedral angle = 0.2°(8)] in contrast to the alkyl groups of $[Hf(C_5Me_5)_2H(NHMe)]$, $[Zr(C_5H_5)_2(NHPh)][O_3SCF_3]$ and $[La(C_5Me_5)_2(NHMe)(NH_2Me)]$ are rotated 63(3), 74.4(5) and 66(1)° out of the equatorial girdle, respectively. The relatively obtuse U–N(1)–C(1) angle 150.6(5)° suggests the absence of any U–CH_3 agostic interaction [no U–C(CH_3) is less than 3.5 Å], and is larger than the M–N–C angles of 145.5(7) and 133.4(3)° observed in $[Hf(C_5Me_5)_2H(NHMe)]$ and $[Zr(C_5H_5)_2(NHPh)][O_3SCF_3]$ respectively.

The crystal structure of the similar complex $[Hf(C_5Me_5)_2H(NHMe)]$ was determined by Bercaw and co-workers[19] in

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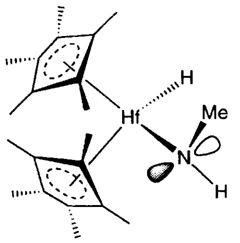
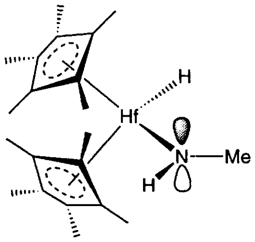
* The first number in parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the maximum deviation from the average value and the number of individual measurements which are included in the average value.

† Representative eight-co-ordinate effective ionic radii: La^{III}, 1.160; Sm^{III}, 1.079; Yb^{III}, 0.985; Hf^{IV}, 0.83; and Zr^{IV}, 0.84 Å.



A



B

order to assess the importance of the π bonding in d^0 permethylhafnocene amido complexes. The observed rotation of the NMe group out of the H–Hf–N plane was interpreted as a means to maximize overlap between the nitrogen lone pair (located in the p$_z$ orbital) and the metal lowest unoccupied molecular orbital (LUMO) **A**.[21] Although favoured electronically, this orientation is sterically disfavoured over that in **B**, as a result of non-bonding interactions with the NMe and ring methyls.

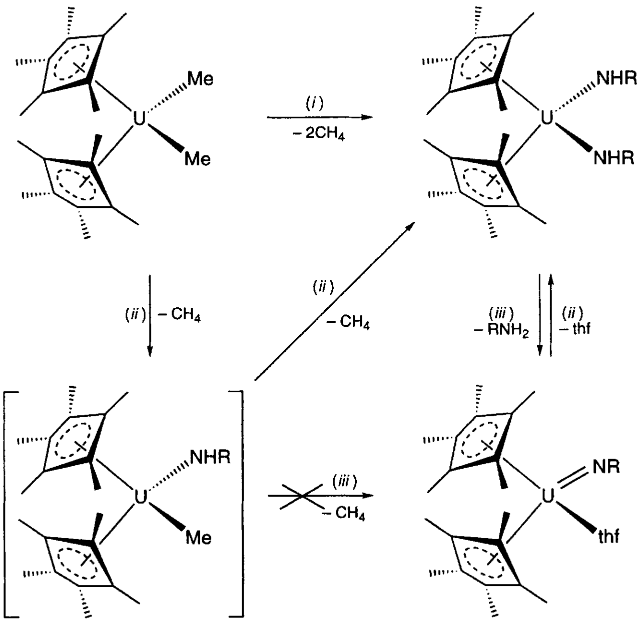
The observed orientation of the phenyl rings in complex **1** is favourable compared with the solution-derived structures of [AnCl(C$_5$Me$_5$)$_2$(NEt$_2$)] and [An(C$_5$Me$_5$)$_2$(NEt$_2$)$_2$] (An = U or Th), for which geometries of type **B** were implied.[8b] The preferred geometry can be additionally manifested by the solution NMR spectrum of complex **1** where the two *o*-methyl groups and *m*-hydrogens are inequivalent even at 347 °C, indicating that the ligands lie in deep potentials and there is no free rotation of the 2,6-dimethylphenyl moiety to scramble structures **A** and **B**. Furthermore, it is possible also that the structures of these 5f^n complexes are sterically dominated and/or that other valence orbitals are involved.

Reactivity studies of the [U(C$_5$Me$_5$)$_2$(NHR)$_2$] complexes

An alternative route for the preparation of complexes **2** and **3** was tested by using **1** as the starting material. Addition of an excess of NH$_2$Et or NH$_2$Bu^t to a thf solution of **1**, at room temperature, results in the quantitative formation of complexes **2** and **3** respectively. In hot thf, complex **1** undergoes a rapid and clean intramolecular elimination of an amine yielding the corresponding uranium imide–base adduct **4** (Scheme 3).[22] For a bulky amido substituent R we have been able to characterize the monomeric adduct and compare it to the analogous thorium imido complex of which we have determined the structure in the solid state and in solution.[5,7a]

The ^{1}H NMR dynamics of complex **4** show that the thf signals of the adduct change dramatically from those corresponding to co-ordinated thf towards those for free thf with temperature (δ −36.0 to −25.0 and −13.5 to −8.5 for the OCH$_2$ and CH$_2$, from 203 to 293 K respectively), which implies that at higher temperatures the solvent is bound loosely. It is worth pointing out that there is no scrambling of the adducted base with bulk solvents and the large shifts follow a Curie–Weiss paramagnetic temperature dependence indicating no temperature-dependent equilibria in solution.[23] The preparation of the base-free uranium imido complex **5** was accomplished by starting from [UMe$_2$(C$_5$Me$_5$)$_2$] and the corresponding amine in hexane at 343 K, whereas complexes **2**, **3**, **6** and **7** were synthesized in thf solutions.

We recently reported that organoactinides are efficient catalysts for the stereospecific oligomerization of terminal alkynes[6] and the novel intermolecular hydroamination of terminal alkynes with aliphatic amines (Scheme 5).[7] Based on the difference in the ^{1}H NMR spectra (see Experimental section) and on the same kinetic behaviour of the complexes **4** and **5** for the intermolecular hydroamination of terminal alkynes, we believe that **5** has a monomeric structure.*[8c] The



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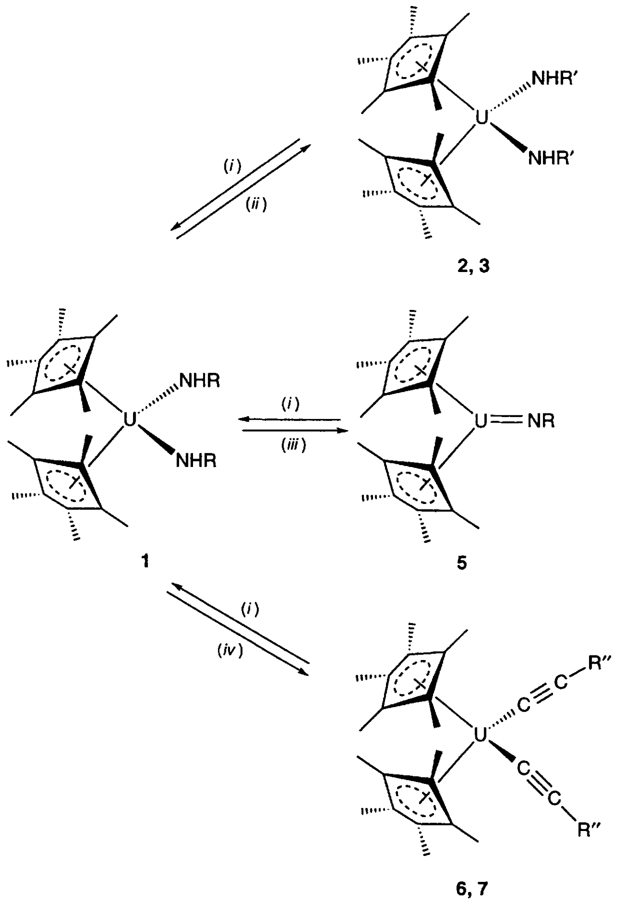
Scheme 3 Synthesis of bis(pentamethylcyclopentadienyl)-amido and -imido complexes. (*i*) 2NH$_2$R; (*ii*) NH$_2$R; (*iii*) thf



Scheme 4 Reactivity and interconversion reactions of bis(pentamethylcyclopentadienyl)uranium bis(amido), imido and carbyl complexes. R = C$_6$H$_3$Me$_2$-2,6, R′ = Et or Bu^t, R″ = Ph or Bu^t. (*i*) NH$_2$R; (*ii*) NH$_2$R′; (*iii*) hexane; (*iv*) HC≡CR″

possible use of these bis(amido) organoactinide complexes as starting materials for the synthesis of bis(acetylide) complexes

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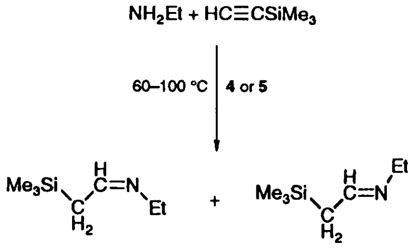
* Complex **4** or **5** exhibit the same-first order kinetics in the intermolecular hydroamination of terminal alkynes.

Table 2 Summary of crystal and refinement data for complex **1**

Formula	$C_{36}H_{50}N_2U$
M	748.8
T/K	293
Crystal system, space group	Monoclinic, $C2/c$
Colour, habit	Black, isometric
a/Å	22.392(4)
b/Å	10.942(2)
c/Å	16.193(3)
β/°	126.92(2)
U/Å^3	3172.2(10)
Z	4
D_c/Mg m^{-3}	1.568
F(000)	1488
Crystal dimensions/mm	0.3 × 0.3 × 0.3
μ/mm^{-1}	5.143
Scan mode	ω
Scan width/°	1.2
2θ limits/°	3–60
h, k, l ranges	−31 to 25, 0–15, 0–22
No. reflections	
Total	5709
Unique (R_{int})	4602 (0.0127)
Observed [$F > 3.0\sigma(F)$]	3836
Absorption correction	Semiempirical
No. parameters	217
Goodness of fit	1.63
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0000F^2$
Final R indices	$R = 0.0420$, $wR = 0.0320$, $R' = 0.0359$
(all data)	$R = 0.0542$, $wR = 0.0328$
Largest difference peak, hole/e Å^{-3}	1.04, −1.02
Largest and mean Δ/σ	1.387, 0.080



Scheme 5

was tested (Scheme 4). We found that the reaction of **1** with an excess of terminal alkynes gave quantitative yields of the bis(carbyl) complexes **6** and **7**. An excess of the alkyne is necessary because the metathesis reaction is an equilibrium.

Conclusion

This investigation has shown that it is possible to synthesize and characterize monomeric bis(pentamethylcyclopentadienyl)-uranium bis(amido) complexes from primary amines. These complexes yield corresponding base-adduct and base-free imido complexes. Furthermore, the bis(amido) and imido complexes which are active species for the oligomerization and/or intermolecular hydroamination of terminal alkynes can be used as starting materials for the synthesis of carbyl complexes.

Experimental

Materials and methods

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum [10^{-5} Torr (*ca.* 1.33 × 10^{-3} Pa)] line, or in a nitrogen-filled Vacuum Atmospheres glove-box with a medium-capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under argon from sodium–benzophenone, hydrocarbon solvents (toluene, hexane) under nitrogen from Na/K alloy. All solvents for vacuum-line manipulations were stored *in vacuo* over Na/K alloy in resealable bulbs. Amine and acetylenic compounds (Aldrich) were dried over activated molecular sieve, degassed and freshly vacuum transferred. The compound [$UMe_2(C_5Me_5)_2$] was prepared according to the literature.[10b]

Physical measurements

The NMR spectra were recorded on a Bruker AM 200 spectrometer referenced to internal solvent resonances and reported relative to tetramethylsilane. The experiments were conducted in Teflon valve-sealed tubes (J-Young). Samples were prepared in a glove-box or after vacuum transfer of the solvent in a high-vacuum line. Deuteriated solvents were dried over Na/K alloy and degassed by freeze–thaw cycles on a high-vacuum line.

Crystallography

The single crystal of compound **1** was grown from a saturated hexane solution. A Siemens P4 diffractometer (graphite-monochromized Mo-Kα radiation, λ = 0.710 73 Å) was used. The crystal and data collection parameters are given in Table 2. Three reflections were measured periodically (every 100) as orientation and intensity control and no significant variations were observed. The structure was solved by the Patterson method and refined by full-matrix least squares on F using the program SHELXTL PLUS[24] on an Iris Indigo computer. Methyl hydrogens were refined using the riding model, isotropic U values refined in groups with a common U value. Aromatic and NH hydrogens were isotropically refined.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the

CCDC for this material should quote the full literature citation and the reference number 186/23.

Preparations

$[U(C_5Me_5)_2\{NH(C_6H_3Me_2\text{-}2,6)\}_2]$. The complex $[UMe_2(C_5Me_5)_2]$ (200 mg, 0.37 mmol) and $NH_2(C_6H_3Me_2\text{-}2,6)$ 90.0 mg, 0.74 mmol) were dissolved in thf (20 cm^3) and heated to 343 K (bath temperature) for 5 h. The solvent was then removed at high vacuum. Hexane (20 cm^3) was added and the suspension warmed to 313 K. The reaction mixture was filtered over a D3 frit whilst warm. The solids were washed with two 10 cm^3 portions of cold hexane and dissolved in hexane (10 cm^3) at 347 K. Crystallization from the hot solution afforded 95 mg (0.13 mmol) dark red cubic crystals of complex **1**. Yield: 35% calculated on $[UMe_2(C_5Me_5)_2]$ (Found: C, 57.20; H, 6.60; N, 3.80. $C_{36}H_{50}N_2U$ requires C, 57.75; H, 6.70; N, 3.75%). ^{1}H NMR (C_6D_{12}, 296 K): δ 8.85 (d, 2 H, 7.0 *m*-H), 5.44 (s, 30 H, C_5Me_5), 4.10 (d, 2 H, $^3J_{HH}$ = 7.0, *m*-H), 2.70 (t, 2 H, $^3J_{HH}$ = 7.0 Hz, *p*-H), −0.78 (s, 6/3 H, CH_3), −22.4 (s, 6/3 H, CH_3) and −52.0 (s, br, 2 H, NH).

$[U(C_5Me_5)_2(NHEt)_2]$ 2. In an NMR tube, $[UMe_2(C_5Me_5)_2]$ (22 mg, 0.04 mmol) and NH_2Et (9.0 mg, 0.2 mmol) were dissolved in thf (1.0 cm^3). The reaction occurs spontaneously. For its completion the mixture was heated to 343 K (bath temperature) for 10 min. Then the solvent and the excess of ethylamine were removed at high vacuum to obtain complex **2** quantitatively.

Alternatively, in an NMR tube complex **1** (10 mg 0.014 mmol) and NH_2Et (5 mg, 0.11 mmol) were dissolved in thf (1.0 cm^3) and heated to 343 K (bath temperature) for 1 h. Then the solvent and excess of ethylamine were removed at high vacuum. ^{1}H NMR (C_4D_8O, 296 K): δ 1.18 (s, 30 H, C_5Me_5), 0.05 (t, 6 H, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3), −4.7 (br, 4 H, CH_2CH_3) and −76.50 (s, br, 2 H, NH).

$[U(C_5Me_5)_2(NHBu^t)_2]$ 3. As above, the reaction of $[UMe_2(C_5Me_5)_2]$ (22 mg, 0.04 mmol) and NH_2Bu^t (14 mg, 0.2 mmol) afforded complex **3** quantitatively. ^{1}H NMR (C_4D_8O, 296 K): δ 2.49 (s, 30 H, C_5Me_5), −3.74 (s, 18 H, Bu^t) and −64.30 (s, br, 2 H, NH).

$[U(C_5Me_5)_2\{N(C_6H_3Me_2\text{-}2,6)\}]\cdot$thf 4. The complex $[UMe_2(C_5Me_5)_2]$ (510 mg, 0.95 mmol) and $NH_2(C_6H_3Me_2\text{-}2,6)$ (115 mg, 0.95 mmol) were dissolved in thf (40 cm^3) and heated to 363 K (bath temperature) for 12 h. Then the solvent was removed at high vacuum. Hexane (30 cm^3) was added and the mixture filtered over a G3 frit. Repeated recrystallization from hot hexane solution afforded 125 mg (0.18 mmol) dark amber flakes of complex **4**. After the first crystallization 450 mg {64 mmol, 67% yield calculated on $[UMe_2(C_5Me_5)_2]$} of **4** were obtained as a black powder.

Alternatively, in an NMR tube, complex **1** (10 mg, 0.014 mmol) was dissolved in thf (1.0 cm^3) and heated to 343 K (bath temperature) for 2 h for completion. Then the solvent was removed at high vacuum. ^{1}H NMR (C_6D_{12}, 297 K): δ 37.0 (br, 2 H, *m*-H), 14.3 (t, 1 H, $^3J_{HH}$ = 7.0 Hz, *p*-H), 5.4 (br, 6 H, CH_3), −1.5 (s, 30 H, C_5Me_5), −13.8 (br, 4 H, CH_2CH_2O) and −26.8 (br, 4 H, CH_2CH_2O).

$[U(C_5Me_5)_2\{N(C_6H_3Me_2\text{-}2,6\}]$ 5. The complex $[UMe_2(C_5Me_5)_2]$ (200 mg, 0.37 mmol) and $NH_2(C_6H_3Me_2\text{-}2,6)$ (45.0 mg, 0.74 mmol) were dissolved in hexane (20 cm^3) and heated to 343 K (bath temperature) overnight. Then the mixture was filtered while warm. The solids were washed with two 10 cm^3 portions of cold hexane. Complex **5** was obtained as a black powder. ^{1}H NMR (C_6D_{12}, 296 K): δ 26.8 (d, 2 H, $^3J_{HH}$ = 7.0, *m*-H), 7.3 (t, 1 H, $^3J_{HH}$ = 7.0 Hz, *p*-H), 6.0 (s, 6 H, CH_3) and −5.4 (s, 30 H, C_5Me_5).

$[U(C_5Me_5)_2(C{\equiv}CPh)_2]$ 6. The complex $[UMe_2(C_5Me_5)_2]$ (22 mg, 0.04 mmol) and phenylacetylene (20 mg, 0.2 mmol) were dissolved in thf (1.0 cm^3) in an NMR tube. The mixture was heated to 343 K (bath temperature) for 30 min. Then the solvent and excess of phenylacetylene were removed at high vacuum, giving complex **6** quantitatively.

Alternatively, as described above, the reaction of complex **1** (10 mg, 0.014 mmol) and phenylacetylene (10 mg, 0.1 mmol) in thf (1.0 cm^3) afforded pure compound **6**. ^{1}H NMR (C_4D_8O, 296 K): δ 22.8 (d, 4 H, $^3J_{HH}$ = 7.0, *o*-H), 13.1 (t, 2 H, $^3J_{HH}$ = 7.0, *p*-H), 12.3 (t, 4 H, $^3J_{HH}$ = 7.0 Hz, *m*-H) and 3.0 (s, 30 H, C_5Me_5).

$[U(C_5Me_5)_2(C{\equiv}CBu^t)_2]$ 7. Complex **7** was synthesized quantitatively as described above. ^{1}H NMR (C_4D_8O, 296 K): δ 5.95 (s, 30 H, C_5Me_5) and −3.85 (s, 18 H, Bu^t).

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