The remarkable efficiency of *N*-heterocyclic carbenes in lanthanide(III)/actinide(III) differentiation

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The capacity of NHC molecules to discriminate between trivalent lanthanide and actinide ions was revealed by competition reactions of analogous U(III) and Ce(III) compounds with $C_3Me_4N_2$ and a comparison of the crystal structures of the corresponding carbene adducts.

N-heterocyclic carbenes (NHCs) derived from imidazolium salts have gained a prominent position in coordination and organometallic chemistry for their capacity to bind as two-electron donors to almost all metals in the periodic table, whatever their oxidation state, and for their expanding use in the field of homogeneous catalysis.[1] It is generally accepted that the metal–NHC bond is very strong, with a pronounced ionic character and negligible π back-donation in its covalent part. However, quantum chemical calculations have indicated that the contribution of π back-donation is more important in the gold complex $AuCl(C_3H_4N_2)$ than in its silver analogue, a difference explained by relativistic effects.[2] Density functional theory studies have suggested that the NHC ligand in $U\{N(SiMe_3)_2\}_3(C_3Me_4N_2)$,[3] a rare example of an actinide–carbene complex,[4] is able to act as a π-acceptor and thereby ensure the stabilization of the electron-rich uranium(III) ion. On the other hand, it was demonstrated that in the $Cr(CO)_5L$ complexes, NHCs and phosphines are nucleophilic and soft ligands, the nucleophilicity and softness of NHCs being slightly larger than those of phosphines.[5] These indications of the π-accepting ability and softness of NHCs led us to consider these molecules as potentially useful for the discrimination of trivalent lanthanide and actinide ions. This represents a challenging problem in both its fundamental aspects and potential applications, especially the partitioning of spent nuclear fuel.[6] It is noteworthy that NHC complexes have been found to form upon the dissolution of metal salts in *N*,*N*′-dialkylimidazolium based room temperature ionic liquids, investigated in the development of novel nuclear processing and separation technologies.[4a] The differentiation of these ions should originate from the modestly enhanced covalency of actinide–ligand bonding compared to lanthanides, and should be favoured by the stronger interaction between the softer (or less hard) 5f ion and the soft, π-accepting ligands.[7] With these ideas in mind, we studied the coordination of the NHC ligand $C_3Me_4N_2$ to analogous uranium(III) and cerium(III) complexes. Comparison of the crystal structures of the resulting carbene compounds and competition reactions revealed the much stronger affinity of the NHC ligand for the actinide than the lanthanide ion.

Addition of 1 mol equiv. of $C_3Me_4N_2$ to $U(C_5Me_5)_2I(py)$[8] in toluene led to the immediate substitution of the pyridine ligand to give the carbene complex $U(C_5Me_5)_2I(C_3Me_4N_2)$ (**1**), which was isolated as dark green crystals in 70% yield. Orange crystals of the cerium analogue $Ce(C_5Me_5)_2I(C_3Me_4N_2)$ (**2**) were similarly obtained from $Ce(C_5Me_5)_2I$. In the presence of 1 mol equiv. of NHC, the trivalent metallocenes $M(C_5H_4Bu^t)_3$ (M = U[9] and Ce[10]) were readily and almost quantitatively transformed in toluene into their carbene adducts $M(C_5H_4Bu^t)_3(C_3Me_4N_2)$ (M = U (**3**) and Ce (**4**)), crystallizing from this solvent as dark brown and yellow crystals respectively. After the tris(amide) compound $U\{N(SiMe_3)_2\}_3(C_3Me_4N_2)$ and its tris(aryloxide) derivative $U\{(^{Ad}ArO)_3tacn\}(C_3Me_4N_2)$ ((^{Ad}ArO)$_3$tacn = 1,4,7-tris(3-*tert*-butyl-5-adamantyl-2-hydroxybenzyl)-1,4,7-triazacyclononane),[3] complexes **1** and **3** form new examples of uranium(III) compounds containing a *N*-heterocyclic carbene ligand, and are the first organometallic ones.[11] Meanwhile **2** and **4** are the first carbene complexes of cerium. Compounds **1–4** gave satisfactory elemental analyses (C, H and N) and were characterized by ^1H NMR spectroscopy† and X-ray diffraction analysis.‡

Crystals of the analogous uranium and cerium complexes are isomorphous. Views of the uranium compounds **1** and **3** are shown in Fig. 1 and Fig. 2 respectively, together with selected bond lengths.

The metal coordination geometry is the familiar pseudo-tetrahedral arrangement found in the series of complexes $M(C_5H_4R)_3L$ and $M(C_5Me_5)_2XL$.[12] In compounds **1–4** the planar

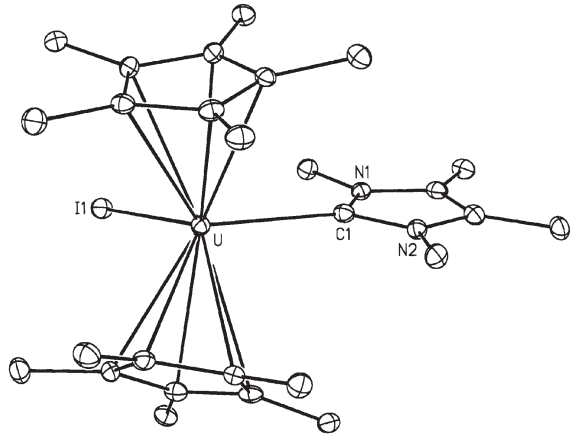

Fig. 1 Structure of **1**. Selected bond lengths (Å) (the corresponding values for the cerium analogue **2** are in square brackets): <U–C(C_5Me_5)> 2.80(2) [2.81(2)], U–C1 2.687(5) [2.724(4)], U–I1 3.1266(4) [3.1595(4)], C1–N1 1.357(7) [1.368(5)], C1–N2 1.362(7) [1.358(5)].

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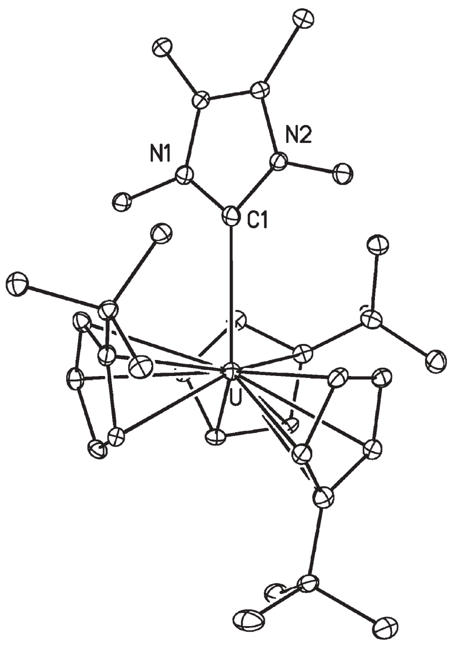

Fig. 2 Structure of **3**. Selected bond lengths (Å) (the corresponding values for the cerium analogue **4** are in square brackets): <U–C($C_5H_4Bu^t$)> 2.86(7) [2.89(7)], U–C1 2.768(5) [2.797(4)], C1–N1 1.374(6) [1.372(6)], C1–N2 1.372(6) [1.380(5)].

NHC ligand, with rms deviations in the range 0.02–0.04 Å, defines the pseudo-plane of symmetry that also contains the iodine atom in **1** and **2** and the *ipso* carbon atom of one of the three $C_5H_4Bu^t$ groups in **3** and **4**. The M–C(cyclopentadienyl) and M–I distances are unexceptional; the U–I and Ce–I bond lengths of 3.1266(4) and 3.1595(4) Å in **1** and **2** are similar to the average M–I distances in $MI_3(bipy)_2(py)$ (3.22(3) and 3.23(3) Å for M = U and Ce respectively)[13] and $[MI_2(OPPh_3)_4][I]$ (3.151(7) and 3.17(3) Å for M = U and Ce respectively).[14] The U–C(carbene) distance of 2.687(5) Å in **1** is shorter than the corresponding 2.768(5) Å in **3**, in agreement with the smaller coordination number. These values can be compared with those of 2.672(5) and 2.789(14) Å in the aforementioned tris(amide) and tris(aryloxide) uranium(III) carbene complexes respectively.[3]

Comparison of the crystal structures of **1** and **2**, and of **3** and **4** shows that the U–I and U–C(carbene) distances are shorter by *ca.* 0.03 Å than the Ce–I and Ce–C(carbene) distances, while the ionic radius of uranium(III) is 0.02 Å longer than that of cerium(III).[15] Such deviations of U–X distance (X = I, N and P) from a purely ionic bonding model, which have been observed in a variety of analogous uranium(III) and lanthanide(III) complexes,[13,14,16] are accounted-for by the presence of a stronger, more covalent interaction between the actinide and the soft and π-accepting ligands. In other words, the NHC molecule, because of its softness and π-accepting capability, has a stronger affinity for the 5f ion than the 4f ion. This assumption was confirmed by competition reactions in solution, studied by ^1H NMR spectroscopy.

The remarkable strength of the bond between the NHC and the trivalent 4f or 5f ion is evident from the ^1H NMR spectra of **1–4** in thf or pyridine. They show that the $C_3Me_4N_2$ ligand was not displaced by σ-donor oxygen and nitrogen containing solvents. In contrast, the pyridine ligand of $M(C_5Me_5)_2I(py)$ and $M(C_5H_4Bu^t)_3(py)$ (M = U, Ce) is almost totally dissociated in thf solution. The spectra of **1** and **2** indicate that the four methyl substituents of the NHC ligand are magnetically inequivalent, in agreement with the crystal structures. Complexes **3** and **4** are more fluxional than **1** and **2** since their spectra at room temperature exhibit broad resonances, corresponding to the cyclopentadienyl and carbene ligands. It is only below −50 °C that the set of 12 individual signals can be resolved, indicating that **3** and **4** in solution adopt the same rigid C_s structure found in the solid state. Addition of $C_3Me_4N_2$ to 1 mol equiv. of both $U(C_5Me_5)_2I$ and $Ce(C_5Me_5)_2I$ in thf gave the two carbene compounds **1** and **2** in the relative proportions 80 : 20 at 23 °C, and 90 : 10 at −60 °C. Complexes **1** and **2** were obtained in the same molar ratio from a 1 : 1 mixture of $U(C_5Me_5)_2I$ and **2**. The competition reaction between $U(C_5H_4Bu^t)_3$ and $Ce(C_5H_4Bu^t)_3$ with the NHC ligand also revealed the selective formation of the U(III) carbene complex **3**. The relative proportions of **3** and **4** could not be measured with precision at 23 °C because of the broadness and overlap of the NMR signals. At −60 °C the molar ratio of **3** to **4** was 90 : 10. These results clearly demonstrate that the NHC ligand has a much stronger affinity for uranium(III) than cerium(III). By comparison with the other molecules considered for the differentiation of the model complexes $U(C_5H_4R)_3$ and $Ce(C_5H_4R)_3$ (*i.e.* phosphine,[16e] phosphite,[16e] isonitrile[17] and azine[16c,18] ligands), the NHC ligand is by far the most efficient, presenting simultaneously the strongest affinity and the highest selectivity for the U(III) compound. The selective complexation of the uranium metallocenes over the cerium metallocenes by $C_3Me_4N_2$ in thf can only be compared with that of UX_3 selection over CeX_3 (X = I, OTf) by 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (Rbtp) molecules in pyridine, which preferably give the tris(Rbtp) complex $[U(Rbtp)_3][X]_3$.[16c] Currently these terdentate nitrogen ligands are the most promising extractants available for the hydrometallurgical reprocessing of nuclear waste.

In conclusion, the reactions of $C_3Me_4N_2$ with $M(C_5Me_5)_2I$ and $M(C_5H_4Bu^t)_3$ (M = U, Ce) afforded the first organometallic uranium(III) carbene complexes and the first carbene complexes of cerium(III). In the process, a novel aspect of the NHC ligand's chemistry, *i.e.* their high efficiency in differentiating between trivalent 4f and 5f ions, was revealed.

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Notes and references

† Syntheses and characterizing data. **$U(C_5Me_5)_2I(C_3Me_4N_2)$ (1)**: An NMR tube was charged with $U(C_5Me_5)_2I(py)$ (33.0 mg, 0.046 mmol), $C_3Me_4N_2$ (5.7 mg, 0.046 mmol) and toluene (0.4 mL). Dark green crystals of **1** were deposited from the resulting solution. A further batch of crystals were obtained after standing at 6 °C. The crystals were filtered off and dried under vacuum (24.5 mg, 70%). δ_H NMR (200 MHz, 23 °C, [$^2H_8$]thf) 0.68 (30 H, C_5Me_5), −10.49, −11.19, −46.82 and −53.99 (4 × 3 H, $C_3Me_4N_2$). Found: C, 42.78; H, 5.60; N, 3.75. $C_{27}H_{42}N_2IU$ requires C, 42.69; H, 5.57; N, 3.69%. **$Ce(C_5Me_5)_2I(C_3Me_4N_2)$ (2)**: An NMR tube was charged with $Ce(C_5Me_5)_2I$ (25.0 mg, 0.046 mmol), $C_3Me_4N_2$ (6.2 mg, 0.05 mmol) and toluene (0.4 mL). The tube containing the resulting orange solution was immersed in an ultrasound bath (80 W, 40 kHz) and after 2 h, orange crystals of **2** were deposited. A further batch of crystals were obtained after

standing at 6 °C. The crystals were filtered off and dried under vacuum (22.2 mg, 73%). δ_H NMR (200 MHz, 23 °C, [$^2H_8$]thf) 5.84 (30 H, C_5Me_5), −2.45, −2.60, −19.59 and −22.70 (4 × 3 H, $C_3Me_4N_2$). Found: C, 48.87; H, 6.23; N, 4.14. $C_{27}H_{42}N_2ICe$ requires C, 49.01; H, 6.40; N, 4.23%. **$U(C_5H_4Bu^t)_3(C_3Me_4N_2)$ (3)**: An NMR tube was charged with $U(C_5H_4Bu^t)_3$ (33.4 mg, 0.055 mmol), $C_3Me_4N_2$ (6.2 mg, 0.050 mmol) and toluene (0.4 mL). The resulting solution rapidly deposited brown crystals of **3** which were filtered off, washed with pentane and dried under vacuum (39.1 mg, 98%). δ_H NMR (200 MHz, −72 °C, [$^2H_8$]thf) 21.43 (2 H, CH), 8.89 (2 H, CH), 8.47 (2 H, CH), 1.95 (18 H, Bu^t), −6.35 (6 H, Me), −6.69 (2 H, CH), −15.18 (3 H, Me), −21.38 (9 H, Bu^t), −30.13 (2 H, CH), −34.81 (2 H, CH), −42.22 (3 H, Me). Found: C, 56.09; H, 6.91; N, 3.94. $C_{34}H_{51}N_2U$ requires C, 56.26; H, 7.08; N, 3.86%. **$Ce(C_5H_4Bu^t)_3(C_3Me_4N_2)$ (4)**: The complex was prepared by the method described for **3** from $Ce(C_5H_4Bu^t)_3$ (33.9 mg, 0.067 mmol) and $C_3Me_4N_2$ (7.5 mg, 0.060 mmol) and was isolated as a yellow powder (40.4 mg, 96%). δ_H NMR (200 MHz, −72 °C, [$^2H_8$]thf) 20.73, 18.16, 14.27 and 11.52 (4 × 2 H, CH), 10.11 (3 H, Me), 3.79 (18 H, Bu^t), −0.14 (3 H, Me), −3.56 (2 H, CH), −4.07 (3 H, Me), −5.72 (9 H, Bu^t), −20.78 (3 H, Me), −36.23 (2 H, CH). Found: C, 64.93; H, 8.18; N, 4.51. $C_{34}H_{51}N_2Ce$ requires C, 65.04; H, 8.19; N, 4.46%.

‡ Crystal data for **1** $C_{27}H_{42}IN_2U$: M = 759.56, monoclinic, a = 9.1421(4), b = 16.3732(9), c = 18.7094(10) Å, β = 101.260(3)°, V = 2746.6(2) Å^3, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 7.050 mm^{-1}. 18055 reflections measured, 4960 unique (R_{int} = 0.083) which were used in all calculations. Final R values: R_1 = 0.031 [4013 reflections with $I > 2\sigma(I)$], wR_2 = 0.072 (all data). Crystal data for **2**: $C_{27}H_{42}CeIN_2$: M = 661.65, monoclinic, a = 9.1078(5), b = 16.4318(15), c = 18.7200(16) Å, β = 101.209(5)°, V = 2748.2(4) Å^3, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 2.795 mm^{-1}. 42837 reflections measured, 5194 unique (R_{int} = 0.098) which were used in all calculations. Final R values: R_1 = 0.033 [4377 reflections with $I > 2\sigma(I)$], wR_2 = 0.068 (all data). Crystal data for **3**: $C_{34}H_{51}N_2U$: M = 752.80, orthorhombic, a = 8.9326(3), b = 11.2965(6), c = 30.8373(14) Å, V = 3111.7(2) Å^3, space group $P2_12_12_1$, Z = 4, μ(Mo-Kα) = 5.240 mm^{-1}, 20444 reflections measured, 5838 unique (R_{int} = 0.051) which were used in all calculations. Final R values: R_1 = 0.025 [5499 reflections with $I > 2\sigma(I)$], wR_2 = 0.057 (all data). Crystal data for **4**: $C_{34}H_{51}CeN_2$: M =627.89, orthorhombic, a = 8.9399(4), b = 11.3123(9), c = 30.971(2) Å, V = 3132.1(4) Å^3, space group $P2_12_12_1$, Z = 4, μ(Mo-Kα) = 1.477 mm^{-1}, 28747 reflections measured, 5939 unique (R_{int} = 0.067) which were used in all calculations. Final R values: R_1 = 0.030 [5131 reflections with $I > 2\sigma(I)$], wR_2 = 0.049 (all data). The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and were processed with DENZO-SMN.[19] The structures were solved and refined with the SHELXTL package.[20] Absorption effects were corrected empirically with the program DELABS in PLATON.[21] CCDC 259874–259877. See http://www.rsc.org/suppdata/cc/b5/b503526k/ for crystallographic data in CIF or other electronic format for compounds **1–4**.

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