Insertion of Isocyanides into Actinoid–Nitrogen Bonds of Biscyclopentadienyluranium Mono- and Bis-(dialkylamides)

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Isocyanides react readily with $Ucp_2(NEt_2)_2$ (cp = cyclopentadienyl) and $U(C_5Me_5)_2(NEt_2)Cl$ giving iminoalkylamido insertion compounds: starting from $Ucp_2(NEt_2)_2$ and an excess of isocyanide or from the monoinserted compound, a second insertion occurs, affording the highly symmetrical bis(iminoalkylamido) compounds; ^1H n.m.r. data indicate the importance of a 'carbenoid' resonance hybrid and nitrogen lone-pair donation to the 'carbenoid' carbon atom.

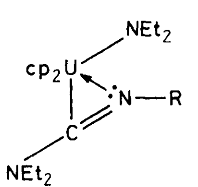
In a recent paper, we reported the facile insertion of isocyanides into the uranium–carbon bond of tris- and bis-(cyclopentadienyl)uranium alkyls to give dihapto-iminoalkyl compounds.[1] We have now studied the reactivity of a type of actinoid–element bond which is likely to be more resistant towards insertion reactions than the corresponding alkyls† and we report here the first examples of isocyanide insertions into a d or f element metal-to-nitrogen bond and the properties of the resulting 'metalloamidines'[4] closely related to the analogous carbamoyls.[5]

The $Ucp_2(NEt_2)_2$ (cp = cyclopentadienyl)[6] complex reacted at low temperature with one equivalent of CNC_6H_{11} or $CNC_6H_3Me_2$-2,6 and the monoinsertion products (**1a,b**) were quantitatively obtained.

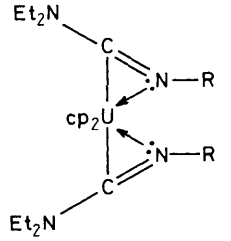
Despite the increased steric bulk around the actinoid ion, the monoinserted compound reacted readily at room temperature with a second equivalent of isocyanide to give the thermally stable bis(iminoalkylamido) compounds (**2a,b**). Using t-butyl isocyanide, no reaction occurred, even if a large excess of isocyanide was used.

The more sterically hindered mono(diethylamido): Ucp_3-NEt_2[7] or bis(diethylamido): $U(C_5Me_5)_2(NEt_2)_2$[5] did not react with isocyanides whereas the mono(diethylamido): $U(C_5Me_5)_2(NEt_2)Cl$[4] reacted slowly with an excess of CNC_6H_{11} at room temperature affording (**3**) quantitatively. (Using $CNC_6H_5Me_2$-2,6, a slow reaction occurred in refluxing toluene with noticeable decomposition while $CNBu^t$ did not react.)

The relative reactivities of U–C and U–N bonds with respect to isocyanide insertions were examined in an intramolecular competition experiment. Starting from $U(C_5Me_5)_2(NEt_2)Me$‡ [prepared from $U(C_5Me_5)_2(NEt_2)Cl$ and MeLi, 1 equiv., in pentane at −70 °C], insertion initially occurred into the metal–carbon σ-bond to give the η^2-iminoalkyl (**4**) and efforts to introduce further t-butyl or cyclohexyl isocyanide into the metal nitrogen bond have failed.



(**1**)



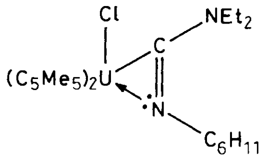
(**2**)

a; R = C_6H_{11}
b; R = $C_6H_3Me_2$-2,6

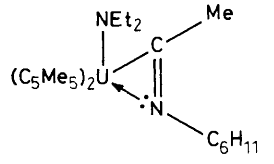
The structures of the insertion compounds§ were established by i.r. and n.m.r. spectroscopy. The i.r. spectra showed no bands at 1960 cm^{-1} attributable to a co-ordinated isocyanide group, while a broad band appeared near 1640 cm^{-1} for the bis(cyclopentadienyls) (**1**) and (**3**) and at 1690 cm^{-1} for the bis(pentamethylcyclopentadienyl) compound (**3**).¶

These frequency transitions were assigned to modes which are predominantly C=N stretching in character. They appear at wavelengths higher than the organic amidines[8] (*ca.* 1620 cm^{-1}), but similar to those of transition metal η^2-iminoalkyls[9,10] and substantially higher than the transition metal σ-iminoalkyls[11] and suggest by analogy to actinoid–iminoalkyls[1] the η^2-co-ordination of the inserted C=N functionalities.

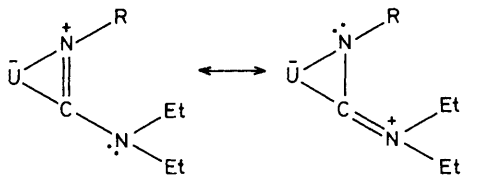
^1H N.m.r. data are given in Table 1; all of the described U^{IV} complexes exhibit large isotropic shifts and generally narrow line widths. After insertion of RNC, all spectra show non-



(**3**)



(**4**)



(A) (B)

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† As an example, mean bond dissociation energies for ZrR_4 compounds vary from 54 (R = CH_2Bu^t) to 74 (R = Me) to 82 (R = NEt_2) kcal mol^{-1} (1 cal = 4.184 J) (ref. 2) and it is well known that trends in actinoid(IV) ligand bond energies closely parallel trends in Zr^{IV} ligand bond energies (ref. 3).

‡ ^1H N.m.r. data (C_6D_6): δ 32 (br, $w_{\frac{1}{2}}$ *ca.* 200 Hz, 4H, CH_2), 7.41 (t, br, $w_{\frac{1}{2}}$ *ca.* 30 Hz, 6H, Me), 2.44 (s, 30H, C_5Me_5), −134 (s, 3H, Me).

§ In a typical experiment, to a solution of $Ucp_2(NEt_2)_2$ (1.02 g) in 20 ml of pentane, cyclohexyl isocyanide (0.218 g; 0.02 mol) in 10 ml of pentane was added slowly at −30 °C. The mixture was stirred for 1 h and its temperature was allowed to rise to room temperature. Solvent was removed, and the mixture, concentrated to 5 ml, was stored overnight at −70 °C. After filtration, the yellow-brown extremely air-sensitive and very soluble (pentane) crystals of (**1a**) (50% yield) were washed with 2 ml of pentane and dried *in vacuo*. All compounds give satisfactory elemental analysis.

¶ ν(CN), Nujol (**1a**) 1645; (**1b**) 1640; (**2a**) 1650; (**2b**) 1645; (**3**) 1690; (**4**) 1625 cm^{-1}.

Table 1. ^{1}H N.m.r. signal assignments for inserted compounds (C_6D_6, 25 °C, Jeol FX100 or Brucker 400 WM).

Compound	C_5H_5 or C_5Me_5 protons	NEt_2 groups	Imine groups
(1a)	−19.80 (s, 10H)	25.08 (q, 4H),^{a} 9.23 (t, 6H),^{a} 2.54 (br, 4H, $w_{\frac{1}{2}}$ 40 Hz), 1.14 (br, 6H, $w_{\frac{1}{2}}$ 30 Hz)	+4.79 (m, 1H), −2.59 (m, 1H), −4.18 (m, 3H), −5.47 (m, 2H), −18.55 (m, 2H), −20.32 (m, 2H)
(1b)	−25.3 (br, 10H, $w_{\frac{1}{2}}$ 80 Hz)^b	4.85^b (br, 4H, $w_{\frac{1}{2}}$ 200 Hz), 16.82^b (br, 6H, $w_{\frac{1}{2}}$ 135 Hz), 62.53 (q, 2H),^{a} 19.39 (t, 3H),^{a} −1.55^c (q, 2H), −0.50 (t, 3H)^a	−0.53 (t, 1H), −0.90 (d, 2H), −28.32 (s, 6H)
(2a)	−18.39 (s, 10H)	51.45^c (br, 4H, $w_{\frac{1}{2}}$ *ca.* 100 Hz), 11.5^c (br, 6H, $w_{\frac{1}{2}}$ *ca.* 80 Hz), 8.0^c (br, 4H, $w_{\frac{1}{2}}$ *ca.* 60 Hz), −2.95^c (br, 6H, $w_{\frac{1}{2}}$ *ca.* 50 Hz)	34.51 (m, 2H), 6.18 (m, 4H), 4.88 (m, 4H), 3.90 (m, 2H), 3.09 (m, 4H), 1.39 (m, 4H), −40.84 (m, 2H)
(2b)	−30.65^c (s, 10H, $w_{\frac{1}{2}}$ *ca.* 20 Hz)	44.2^c (br, 4H, $w_{\frac{1}{2}}$ *ca.* 100 Hz) 14.8^c (t, 6H)^a 24.59^c (br, 4H, $w_{\frac{1}{2}}$ *ca.* 80 Hz) 17.05^c (br, 6H, $w_{\frac{1}{2}}$ *ca.* 60 Hz)	3.34^c (br, 2H, $w_{\frac{1}{2}}$ *ca.* 25 Hz), 0.70^c (br, 4H, $w_{\frac{1}{2}}$ *ca.* 25 Hz), −6.34^c (br, 12H, $w_{\frac{1}{2}}$ *ca.* Hz)
(3)	0.33 (s, 30H)	12.43 (q, 2H),^{a} −1.23 (t, 3H)^a 6.23^c (q, 2H), 4.27 (t, 3H)^a	50.97 (m, 1H), 6.63 (m, 2H), 5.07 (m, 2H), 2.53 (m, 2H), 2.13 (m, 1H), −0.43 (m, 1H), −3.57 (m, 2H)
(4)	−2.98 (s, 30H)	11.80 (q, 4H),^{a} 40.38 (t, 6H)^a	34.03^d (s, 3H), 2.53 (m, 1H), −5.62 (m, 1H), −8.0 (m, 2H), − 10.80 (m, 2H), −21.29 (m, 2H), −23.50 (m, 1H), −29.29 (m, 2H)

^{a} J = 7 Hz. ^{b} Recorded at 80 °C. ^{c} Good resolved signals at 80 °C. ^{d} Inserted Me group.

equivalent alkyl functionalities‖ for the inserted NEt_2 groups. This behaviour indicates that the rotation of the alkyl groups about the CN bond is slow on the n.m.r. time scale at room temperature. This barrier was attributed to multiple CN bonding and the resonance hybrid (B) is stabilized by the η^2-co-ordination.[12]

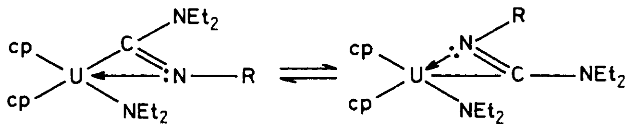
No significant broadening of the signals occurred when the temperature was raised, indicating a high value of the $\Delta G^‡$ for CN rotation [$\Delta G^‡ > 23$ kcal mol^{-1} (1 cal = 4.184 J) for the analogous carbamoyls[3]].

The signals of the cyclopentadienyl and unreacted NEt_2 protons of (**1b**) appear very broadened even at 80 °C. This behaviour can be interpreted as an equilibrium (C) $\rightleftharpoons$ (D).[12] The geometry of the $cp_2U[C(NEt_2)NR]NEt_2$ structures appears to be tetrahedral if the midpoint of the CN bond, the cp centroids, and the NEt_2 group are taken to represent the vertices of a polyhedron; the [C(NEt_2)NR] group has two possible orientations on the 'equatorial girdle' and structures (C) and (D) are diastereoisomeric.

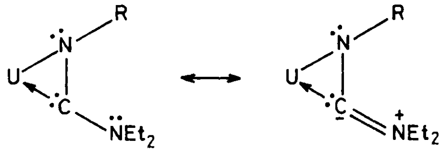
Moreover, the broadening of the NEt_2 signals can provide evidence of a restricted rotation about the U–N bond due to an interaction between the lone pair of the nitrogen atom and an empty orbital of the metallic nucleus.

It is noteworthy that the cyclohexyl protons in spectra of (**1a**), (**3a**), and (**4**) appear within 50 p.p.m. of each other and well resolved multiplets corresponding to a locked conformation of the cyclohexyl ring are obtained.[13]

The considerable shift observed for the cyclohexyl protons compared to a diamagnetic compound implies the neighbouring of the paramagnetic atom[14] and as a consequence a very



(C) (D)



(E) (F)

short U–N bond distance. This fact suggests, as with organo-actinoid iminoalkyl or carbamoyl complexes, the predominance of a resonance hybrid with carbenoid character. Moreover, the spectroscopic data indicate that a resonance hybrid (F) with delocalization of the nitrogen lone pair into the carbenoid carbon must play an important role in the bonding.

The spectra of the bisinserted compounds (**2a**) and (**2b**) appeared remarkably simple. Only one set of signals for the two cp, cyclohexyl or dimethylphenyl, and diethylamido protons were recorded. This suggests that the complexes may possess a pseudo C_2 axis as has been previously established by Marks *et al.* for analogous dicarbamoyl compounds.[3]

The regioselectivity of the insertion reaction into the metal–carbon bond in the $U(C_5Me_5)_2(NEt_2)Me$‖ compound has been unambiguously established by n.m.r. spectroscopy: as expected for an insertion into the uranium–methyl bond, the

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‖ Only one set of broad signals was observed for the inserted NEt_2 protons in (**1a**). This trend seems indicative of a lower barrier to rotation about the CN bond.

methyl protons were dramatically deshielded[1] (δ 168) while the NEt_2 protons showed only one quartet and one triplet.

In conclusion, we have shown that the U–N bond, known to be very reactive toward carbon monoxide insertion, is reactive toward the more bulky isocyanides, affording two new classes of mono- and bis-inserted compounds.

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