

Insertion of Isocyanides into Actinoid–Carbon Bonds of Tris- and Bis-cyclopentadienyluranium Mono- and Di-alkyls

Alain Dormond,* Abdel Aziz Elbouadili, and Claude Moïse

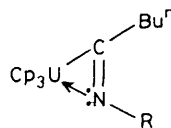
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (LA 33), Faculté des Sciences Gabriel, 6, boulevard Gabriel, 21100 Dijon, France

Isocyanides react readily with UCp_3R and $U(C_5Me_5)_2RCl$ (Cp = cyclopentadienyl, R = alkyl) to give iminoalkyl insertion compounds; with $U(C_5Me_5)_2R_2$, only one insertion reaction occurs, the second metal–carbon bond does not react; i.r. spectra of the insertion compounds exhibit unusually low CN stretching frequencies indicative of strong metal–nitrogen bonding which causes non-equivalence in the Cp groups in the n.m.r. spectrum of $UCp_3\{\eta^2-CN(C_6H_3Me_2-2,6)Bu^n\}$.

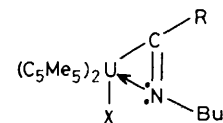
There has been interest recently in the insertion of carbon monoxide into the actinoid–carbon bonds of $M(C_5Me_5)_2R_2$ or MCp_3R (M = Th, U; R = alkyl, dialkylamido, or H; Cp = cyclopentadienyl) to give dihapto-acyl compounds.^{1,2} We report here a new insertion reaction of isocyanides (isoelectronic with CO) into the uranium–carbon bonds of UCp_3R , $U(C_5Me_5)_2RCl$, and $U(C_5Me_5)_2Me_2$ (R = alkyl).

The UCp_3Me complex did not react with isocyanides but UCp_3Bu^n ³ reacted readily at low temperature, affording quantitatively the insertion products (**1a–c**). In the same way, the dialkyl compound $U(C_5Me_5)_2Me_2$ ⁴ reacted with t-butylisocyanide to give the monoinsertion product (**2a**). No further

insertion occurred, even in the presence of an excess of isocyanide. It seems likely that the bulky nature of the $U\{C(Me)NBut^t\}$ moiety prevents further reaction. Neverthe-



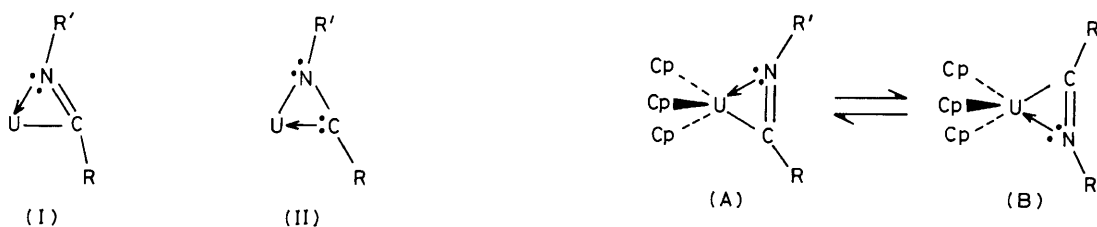
- (1) **a**; $R = Bu^t$
b; $R = C_6H_{11}$
c; $R = C_6H_3Me_2-2,6$



- (2) **a**; $R = Me, X = Me$
b; $R = Me, X = Cl$
c; $R = Bu^n, X = Cl$

Table 1. ^1H N.m.r. signal assignments for (1) and (2) in C_6D_6 .

Compound	δ		
	Cp protons	Alkyl groups	Imine groups
(1a)	-13.0 (s, 15H)	35.67 (m, 2H), 20.85 (m, 2H), 8.68 (m, 2H), 5.83 (t, 3H)	-5.55 (s, 9H)
(1b)	-12.38 (s, 15H)	53.32 (m, 2H), 46.07 (m, 2H), 18.12 (m, 2H), 12.25 (t, 3H)	7.89 (m, 1H), -3.47 (m, 1H), -5.81 (m, 4H), -6.72 (m, 1H), -19.38 (m, 2H), -25.11 (m, 2H)
(1c)	-10.5 (br., 15H) ^a	53.38 (m, 2H), 40.55 (m, 2H), 21.41 (m, 2H), 12.28 (t, 3H)	-29.58 (s, 6H), -2.40 (d, 2H, <i>m</i>) 0.06 (t, 1H, <i>p</i>)
(2a)	-3.15 (s, 30H)	U-CH ₃ -151.0 (s, 3H), C-CH ₃ 49.5 (s, 3H)	-12.85 (s, 9H)
(2b)	-0.37 (s, 30H)	42.7 (s, 3H)	2.45 (s, 9H)
(2c)	-0.54 (s, 30H)	33.82 (m, 2H), 31.42 (m, 2H), 12.63 (m, 2H), 8.03 (t, 3H)	-3.34 (s, 9H)

^a At 70°C.

less, the remaining U-Me group was reactive towards reagents such as CCl_4 or CHCl_3 giving the monochloride (2b). This compound was directly obtained from $\text{U}(\text{C}_5\text{Me}_5)_2\text{MeCl}$.⁴

Compound (2c) was obtained quantitatively from $\text{U}(\text{C}_5\text{Me}_5)_2\text{Bu}^n\text{Cl}$ [prepared from $\text{U}(\text{C}_5\text{Me}_5)_2\text{Cl}_2$ and Bu^nLi (1 equiv.) in tetrahydrofuran (THF) at -70°C]. The latter was not isolated and at room temperature formed quantitatively the deep green $\text{U}^{\text{III}}(\text{C}_5\text{Me}_5)_2\text{Cl}\cdot\text{THF}$ complex.⁵

The structure of the insertion compounds was established by i.r. and n.m.r. spectroscopy. The i.r. spectra showed a broad intense band at *ca.* 1600 cm^{-1} † attributable to $\nu(\text{CN})$ ⁶ while there was no band at *ca.* 1960 cm^{-1} attributable to a co-ordinated isocyanide group. The CN stretching frequency is substantially lower than that of typical transition metal iminoalkyls^{7,8} (*ca.* $1680\text{--}1700\text{ cm}^{-1}$). This decrease in frequency is of the same order as the decrease in $\nu(\text{CO})$ in going from the transition metal-dihapto-acyls (*ca.* $1550\text{--}1600\text{ cm}^{-1}$)⁹ to compounds with CO inserted in the actinoid-carbon bonds (*ca.* $1450\text{--}1500\text{ cm}^{-1}$)^{1,2} and suggests predominance of the carbene-like structure (II) over that depicted in (I).

As is typical of U^{IV} organometallics, all the complexes exhibit substantial n.m.r. isotropic shifts and, as a consequence of the short $5f^2$ electron spin-lattice relaxation times, narrow line widths. After insertion of RNC, the *n*-butyl and methyl groups showed a dramatic deshielding (from *ca.* 200 p.p.m. for the α -protons to 20 p.p.m. for the δ -protons) and in the n.m.r. spectrum of (2a) two distinct methyl resonances are present, the shift of the unreacted methyl group being almost

unchanged. The isocyanide proton resonances are significantly shifted under the influence of the neighbouring paramagnetic uranium centre, in good agreement with an iminoalkyl structure. The cyclopentadienyl and pentamethylcyclopentadienyl proton resonances are moderately shifted.

The signal for the cyclopentadienyl protons of (1c) was not detected in its n.m.r. spectrum recorded at room temperature but at $+70^\circ\text{C}$ it appeared as a broad singlet at $\delta -10$ and at low temperature (-55°C) as two sharp singlets of relative intensities 5 ($\delta +42.6$) and 10 ($\delta -41.4$). All spectral changes were reversed upon raising the temperature and were independent of concentration (Table 1).

Throughout these experiments the line shape of the butyl, methyl, and aromatic protons effectively remained the same. This behaviour cannot be interpreted as an (A) \rightleftharpoons (B) equilibrium.¹ The geometry of Cp_3XY structures appears to be tetrahedral if the Cp centroids and the midpoint of the CN bond are taken to represent vertices of a polyhedron;¹⁰ therefore, the three free rotating Cp groups must be equivalent and the (A) and (B) structures are enantiomeric [the alkyl and aryl protons in (1c) show only one set of signals even at low temperature]. The splitting of the Cp peaks into two signals is thus a result of a restricted rotation of the Cp groups about the uranium midpoint of the C-N bond axis (rotation of the $\eta^5\text{-C}_5\text{H}_5$ about the five fold axis, a process known to have a low barrier,¹¹ remains unchanged).

The barrier to rotation of the Cp rings can be estimated at the coalescence temperature (80°C). The isotropic shifts of the Cp resonances were found to obey an approximate Curie relationship (a plot of δ vs. $1/T$ is linear) below the coalescence temperature and extrapolation of these data yielded $\Delta\delta = 2000\text{ Hz}$ and $\tau_c = 2.25 \times 10^{-4}$ at the coalescence temperature.¹² The $\Delta G^\ddagger = (1/\tau_c) = kT/h e^{-\Delta G^\ddagger/RT}$ for -Cp rotation was thus estimated to be $62.2 \pm 5\text{ kJ mol}^{-1}$. Such a barrier to rotation induced by the bulky dimethylphenyl group is only possible for a short U-N distance and strong U-N bonding.

In conclusion, we have shown that the U-C bond is very reactive towards isocyanides. The iminoalkyl insertion compounds show a strong metal-nitrogen interaction and bulky

† In a typical experiment, to a solution of UCp_3Bu^n (0.5 g) in 20 ml of toluene, *t*-butylisocyanide (0.17 g) in 5 ml of toluene was added slowly at -40°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 and stored overnight at -20°C . After filtration, the brown, very air-sensitive crystals of (1a) (90% yield) were washed with $2 \times 2\text{ ml}$ of pentane and dried *in vacuo*.

‡ $\nu(\text{CN})$, (Nujol): (1a) 1596; (1b), (1c) 1598; (2a) 1610; (2b), (2c) 1608 cm^{-1} .

isocyanide groups prevent a second insertion in the $U(C_5Me_5)_2R_2$ complexes.

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