Insertion of 2,6-Dimethylphenyl Isocyanide into the U–N Bond of $[U(\eta\text{-}C_5H_5)_3(NEt_2)]$. Crystal Structure of $[U(\eta\text{-}C_5H_5)_3\{C(NEt_2){=}NC_6H_3Me_2\text{-}2,6\}]$†

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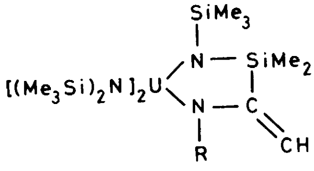
Insertion of $CNC_6H_3Me_2$-2,6 into the U–N bonds of $[U(\eta\text{-}C_5H_5)_2(NEt_2)_2]$ and $[U(\eta\text{-}C_5H_5)_3(NEt_2)]$ has been observed, leading to the formation of iminocarbamoyl derivatives. The structure of one of the resulting complexes $[U(\eta\text{-}C_5H_5)_3\{C(NEt_2){=}NC_6H_3Me_2\text{-}2,6\}]$ has been determined by *X*-ray analysis; this shows that the $[C(NEt_2){=}NC_6H_3Me_2\text{-}2,6]^-$ anion is η^2-co-ordinated and the C=N double bond lies perpendicular to the U–M axis (where M is the midpoint of the C=N bond). ^1H N.m.r. shows that the C_5H_5 protons are magnetically inequivalent. Some evidence of the insertion of $CNC_6H_3Me_2$-2,6 into the U–P bond of $[U(\eta\text{-}C_5H_5)_3(PPh_2)]$ is also reported.

Insertion reactions of small dipolar molecules such as CO into U–C and U–N bonds have been successfully developed, giving η^2-acyl and η^2-imidoyl derivatives respectively.[1–3] The isoelectronic molecules of isocyanide RNC have been shown to insert into the U–C bonds of $[U(\eta\text{-}C_5H_5)_3R]$ and $[U(\eta\text{-}C_5Me_5)_2R(X)]$ (R = alkyl, X = Cl) with formation of the analogous iminoacyl derivatives,[4,5] while with $[\overline{U(CH_2SiMe_2N}SiMe_3)\{N(SiMe_3)_2\}]$ the cyclic derivative (I) (R = Bu^t) was obtained.[3] Recently it was reported by Dormond *et al.*[6] that isocyanides insert into the U–N bond of $[U(\eta\text{-}C_5H_5)_2(NEt_2)_2]$ but not of $[U(\eta\text{-}C_5H_5)_3(NEt_2)]$; the inertness in the latter case was imputed to steric reasons.[6] In the course of our investigations of insertion reactions we have found, in contrast to this last observation, that *o*-xylyl isocyanide readily inserts into the U–N bond of $[U(\eta\text{-}C_5H_5)_3(NEt_2)]$ to give an iminocarbamoyl derivative; in addition the same reaction has been carried out with $[U(\eta\text{-}C_5H_5)_3(PPh_2)]$.

Here we describe these reactions, the spectroscopic characterization of the products obtained, and the first structural determination of an iminocarbamoyl derivative, *i.e.* $[U(\eta\text{-}C_5H_5)_3\{C(NEt_2){=}NC_6H_3Me_2\text{-}2,6\}]$.


(I)

Experimental

The manipulation of uranium(IV) organometallic derivatives and the preparation of samples were carried out under a controlled atmosphere inside a suitable dry-box. Solvents were appropriately purified and dried prior to use.[7] Compounds UCl_4,[8a] $[U(\eta\text{-}C_5H_5)_3Cl]$,[8b] $[U(\eta\text{-}C_5H_5)_3(NEt_2)]$,[8c] $[U(\eta\text{-}C_5H_5)_2(NEt_2)_2]$,[8d] and $[U(\eta\text{-}C_5H_5)_3(PPh_2)]$[8c] were synthesized according to published procedures. Commercially available alkyl or aryl isocyanides were used as supplied.

Carbon, H, N, and U analyses were carried out by Dornis und Kolbe Mikroanalytisches Laboratorium, Mulheim (West Germany). Proton n.m.r. spectra were recorded with a Varian FT-80A spectrometer (solvents: $[^2H_6]$benzene or $[^2H_8]$-toluene; C_6D_5H as internal standard; chemical shifts relative to $SiMe_4$). Infrared spectra were recorded with a Perkin-Elmer 580B apparatus (Nujol mulls sandwiched between KBr plates in sealed air-tight O-ring holders). Near-i.r.–visible and mass spectra (electron impact = 70 eV, probe temperature 80 °C) were recorded with Cary 17D and ZAB 2F VG Organic Ltd. spectrometers respectively.

Reaction of $[U(\eta\text{-}C_5H_5)_2(NEt_2)_2]$ **(1)** *with* $CNC_6H_3Me_2$-2,6.—Complex **(1)** (1 mmol) dissolved in Et_2O (20 cm^3) was treated with $CNC_6H_3Me_2$-2,6 (2 mmol) at room temperature. After stirring for 24 h the solvent was removed under vacuum. The resulting green residue was washed several times with small portions of n-hexane and dried under vacuum to yield the *product* $[U(\eta\text{-}C_5H_5)_2\{C(NEt_2){=}NC_6H_3Me_2\text{-}2,6\}_2]$ **(2)** (80%) (Found: C, 55.85; H, 6.20; N, 7.20; U, 30.90. Calc. for $C_{36}H_{48}N_4U$: C, 55.80; H, 6.25; N, 7.25; U, 30.70%). I.r.: $\nu_{max.}$ at 1 590w, 1 510vs, 1 375vs, 1 365s, 1 350vs, 1 295m, 1 260s, 1 205m, 1 165s, 1 105m, 1 090m, 1 080s, 1 060m, 1 030w, 1 010s, 860m, 800m, 785s, 760vs, 660m, 590w, and 510w cm^{-1}. Mass spectrum: *m/z* 774 (M^+); other characteristic ions at 571 $[U(\eta\text{-}C_5H_5)_2\{C(NEt_2){=}NC_6H_3Me\text{-}2,6\}]^+$, 438 $[U(\eta\text{-}C_5H_5)_2N(CH_2CH_2)_2]^+$, 383 $[U(\eta\text{-}C_5H_5)_2NH]^+$, 368 $[U(\eta\text{-}C_5H_5)_2]^+$, and 303 $[U(\eta\text{-}C_5H_5)]^+$. Near-i.r.–visible (toluene): $\lambda_{max.}$ at 1 400, 1 200, 1 180, 1 090, 1 030, 960, 910, 870, 750, 660, 620, and 580 nm. ^1H N.m.r. (C_6D_6, T = 27 °C): δ −32.57 (10 H, br, $W_{\frac{1}{2}}$ 25, C_5H_5), −6.97 (12 H, br, $W_{\frac{1}{2}}$ 50, Me_2-2,6), 24.66 (4 H, br, $W_{\frac{1}{2}}$ 50, CH_3CH_2N), 13.33 (6 H, br, $W_{\frac{1}{2}}$ 38, CH_3CH_2N), 16.82 (6 H, br, $W_{\frac{1}{2}}$ 76, CH_3CH_2N), and 41.32 (4 H, $W_{\frac{1}{2}}$ 280 Hz, CH_3CH_2N) (it was not possible to detect $C_6H_3Me_2$-2,6); ($[^2H_8]$toluene, T = 70 °C): δ −26.99 (10 H, br, C_5H_5), −5.17 (12 H, br, Me_2-2,6), −1.29 (4 H, br, $H^{3,5}$), 2.45 (2 H, br, H^4), 21.33 (4 H, br, CH_3CH_2N), 14.53 (6 H, br, CH_3CH_2N), 36.43 (4 H, br, CH_3CH_2N), and 11.69 (6 H, br, CH_3CH_2N).

Reaction of $[U(\eta\text{-}C_5H_5)_3(NEt_2)]$ **(3)** *with* CNC_6H_3-

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† Tris(η-cyclopentadienyl)[η^2-diethylamino(2,6-dimethylphenylimino)methyl]uranium(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Me_2-2,6.—The isocyanide (1 mmol) was added to an Et_2O solution (20 cm^3) of (**3**) (1 mmol) and the mixture stirred for 24 h. The resulting solid was filtered off and washed with small portions of Et_2O. After drying, the yellow product was positively identified as the insertion product [U(η-C_5H_5)$_3$-{C(NEt_2)=N$C_6H_3Me_2$-2,6}] (**4**) (Found: C, 52.90; H, 5.35; N, 4.35; U, 37.30. Calc. for $C_{28}H_{34}N_2U$: C, 52.85; H, 5.40; N, 4.40; U, 37.40%). I.r.: $\nu_{max.}$ at 1 535vs, 1 365vs, 1 295w, 1 260m, 1 245w, 1 200w, 1 170s, 1 105m, 1 080m, 1 050m, 1 010s, 860m, 770vs, 670w, and 590w cm^{-1}. Mass spectrum: m/z 636 (M^+); other characteristic primary ion (constant linked scan experiment) at 571 ($M^+ - C_5H_5$). Near-i.r.–visible (Et_2O): $\lambda_{max.}$ at 1 390, 1 340, 1 300, 1 240, 1 190, 1 150, 1 130, 1 060, 1 040, 760, 680, 640, 580, 560, and 440 nm. ^1H N.m.r. (C_6D_6, T = 27 °C): δ 27.07 (5 H, s, C_5H_5), −31.8 (10 H, s, C_5H_5), −26.01 (6 H, s, Me_2-2,6), −0.69 (2 H, d, $H^{3,5}$), −1.01 (1 H, t, H^4), 6.12* (3 H, t, $\mathrm{C}H_3\mathrm{CH_2N}$), 8.66* (2 H, q, $\mathrm{CH_3C}H_2\mathrm{N}$), 23.97 (3 H, t, $\mathrm{C}H_3\mathrm{CH_2N}$), and 70.74 (2 H, q, $\mathrm{CH_3C}H_2\mathrm{N}$). The two signals indicated by asterisks have been assigned to protons of the same ethyl group by double-resonance experiments.

From a saturated solution in Et_2O a single crystal was obtained; it was sealed in a glass capillary and analyzed by *X*-ray diffraction.

Syntheses of [U(η-C_5D_5)$_3$(NEt_2)] (**3-D**) *and* [U(η-C_5D_5)$_3$-{C(NEt_2)=N$C_6H_3Me_2$-2,6}] (**4-D**).—Tl(C_5D_5) was obtained following the known procedure.[8e] The extent of deuteriation in the cyclopentadienyl rings was determined by mass spectrometry to be in the order of 80%. Tl(C_5D_5) was then used to prepare compound (**3-D**), following the same procedure used for (**3**). The insertion product (**4-D**) was obtained following the same procedure for (**4**) but using [U(η-C_5D_5)$_3$(NEt_2)]. Both deuteriated compounds (**3-D**) and (**4-D**) were characterized by their ^1H n.m.r. chemical shifts. The shifts occur at the same position and with the appropriate intensity ratios as their non-deuteriated analogues (**3**) and (**4**) respectively: of course the ^1H signals of the C_5D_5 rings show very reduced intensity due to the extent of deuteriation.

Reaction of [U(η-C_5H_5)$_3$(PPh_2)] (**5**) *with* CNC_6H_3-Me_2-2,6.—Compound (**5**) (1 mmol) dissolved in toluene (20 cm^3) was treated at room temperature with CN$C_6H_3Me_2$-2,6 (1 mmol) with stirring. After 24 h the resulting solution was reduced to 5 cm^3 under vacuum and n-hexane (25 cm^3) was added. The suspension was filtered to give [U(η-C_5H_5)$_3$-{C(PPh_2)=N$C_6H_3Me_2$-2,6}] (**6**) as a brown solid, which was washed several times with small portions of n-hexane, dried *in vacuo*, and characterized (Found: C, 55.80; H, 4.55; N, 2.05; U, 33.75. Calc. for $C_{35}H_{34}NPU$: C, 57.70; H, 4.55; N, 1.85; U, 31.75%). I.r.: $\nu_{max.}$ at 1 510vs, 1 160s, 1 090s, 1 010vs, 990m, 835m, 780vs, 720m, 690vs, 650m, 600m, 510s, and 475m cm^{-1}. ^1H N.m.r. (C_6D_6, T = 37 °C): δ 29.49(t), 14.6(t), 12.1(t), 0.66(t), −1.81(d), and −28.29(s). Absence of other signals and the intensities of those observed do not allow their assignments.

Crystal-structure Determination of [U(η-C_5H_5)$_3${C(NEt_2)=N$C_6H_3Me_2$-2,6}] (**4**).—A crystal fragment of maximum dimension 0.2 mm was used to collect intensity data on a Philips four-circle diffractometer using monochromated Mo-K_α radiation. Accurate lattice parameters were obtained from the settings of 25 medium-angle reflections.

Crystal data. $C_{28}H_{34}N_2U$, M = 636, monoclinic, space group $P2_1/c$, a = 13.438(6), b = 8.446(7), c = 21.981(5) Å, β = 102.14(3)°, U = 2 439 Å^3, D_c = 1.73 g cm^{-3}, Z = 4, $F(000)$ = 1 232, and μ(Mo-K_α) = 100.5 cm^{-1}.

Intensities up to θ = 30° were measured, using a scan speed of 2° min^{-1} and a θ–2θ scan width. Of the 4 724 reflections measured, 2 982 with $I > 3\sigma(I)$ were considered observed and used in subsequent calculations. Corrections were made for Lorentz polarization and for absorption.[9] The intensities of two standard reflections were monitored at intervals and showed that the crystal remained stable during irradiation. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to a final conventional residue R of 0.071. The ring carbon atoms were refined as rigid bodies (C–C = 1.395 Å for phenyl and 1.420 Å for cyclopentadienyl rings). The cyclopentadienyl carbon atoms are very anisotropic, consistent with the usual large librational motion associated with these rings.[10] A final difference Fourier map showed no peaks greater than ±0.6e Å^{-3} except for some residual peaks at 2.1e Å^{-3} around the U atom. The maximum shift in the refined parameters was 0.3σ in the last cycle. Atomic scattering factors for neutral atoms were from ref. 11, those for U being corrected for anomalous dispersion.[12] Fractional atomic parameters are given in Table 1, bond distances and angles in Table 2.

Table 1. Fractional atomic co-ordinates for [U(η-C_5H_5)$_3${C(NEt_2)=N$C_6H_3Me_2$-2,6}] (**4**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
U	0.180 87(6)	0.396 04(9)	0.403 34(3)
N(1)	0.260 27(111)	0.429 25(155)	0.318 82(70)
N(2)	0.420 85(118)	0.300 69(224)	0.354 85(80)
C(11)	0.051 59(174)	0.556 55(508)	0.308 21(129)
C(12)	0.056 89(174)	0.660 85(508)	0.359 46(129)
C(13)	0.004 33(174)	0.589 22(508)	0.401 98(129)
C(14)	−0.033 45(174)	0.440 64(508)	0.377 02(129)
C(15)	−0.004 25(174)	0.420 45(508)	0.319 06(129)
C(1)	0.224 27(176)	0.079 85(224)	0.397 18(133)
C(2)	0.235 16(176)	0.111 43(224)	0.461 70(133)
C(3)	0.136 56(176)	0.136 39(224)	0.473 69(133)
C(4)	0.064 73(176)	0.120 22(224)	0.416 59(133)
C(5)	0.118 93(176)	0.085 28(224)	0.369 30(133)
C(6)	0.241 44(161)	0.480 98(252)	0.528 64(77)
C(7)	0.201 92(161)	0.622 41(252)	0.497 83(77)
C(8)	0.270 40(161)	0.673 91(252)	0.460 74(77)
C(9)	0.352 25(161)	0.564 32(252)	0.468 63(77)
C(10)	0.334 36(161)	0.445 08(252)	0.510 60(77)
C(16)	0.325 73(137)	0.356 61(186)	0.360 90(85)
C(17)	0.483 38(183)	0.215 14(315)	0.408 54(114)
C(18)	0.504 34(206)	0.041 17(380)	0.394 73(152)
C(19)	0.472 90(156)	0.342 00(306)	0.304 19(108)
C(20)	0.531 79(180)	0.502 12(341)	0.318 12(128)
C(21)	0.257 43(97)	0.478 81(135)	0.256 56(41)
C(22)	0.268 53(97)	0.637 36(135)	0.241 48(41)
C(23)	0.256 13(97)	0.682 78(135)	0.179 32(41)
C(24)	0.232 63(97)	0.569 65(135)	0.132 24(41)
C(25)	0.221 53(97)	0.411 11(135)	0.147 32(41)
C(26)	0.233 92(97)	0.365 69(135)	0.209 48(41)
C(27)	0.219 36(168)	0.192 03(288)	0.224 57(103)
C(28)	0.293 57(197)	0.764 47(285)	0.291 69(128)

Results and Discussion

The U–N bonds of both [U(η-C_5H_5)$_2$(NEt_2)$_2$] (**1**) and [U(η-C_5H_5)$_3$(NEt_2)] (**3**) {and probably also the U–P bond of [U(η-C_5H_5)$_3$(PPh_2)] (**5**)} activate the isocyanide to give the corresponding insertion products. In our hands (**1**) gives (**2**) as reported by Dormond *et al.*,[6] while (**3**), in contrast to their observations, reacts quantitatively at room temperature in organic solvents with CN$C_6H_3Me_2$-2,6 to form [U(η-C_5H_5)$_3$-{C(NEt_2)=N$C_6H_3Me_2$-2,6}] (**4**). Complexes (**2**) and (**4**) are very air sensitive, thermally stable products which are soluble in ether and aromatic solvents, and less soluble in aliphatic solvents. This reaction, reflecting the features of

Table 2. Bond lengths (Å) and angles (°) for [U(η-C_5H_5)$_3${C(NEt_2)=$NC_6H_3Me_2$-2,6}] (4)*

U–N(1)	2.35(2)	U–C(11)	2.78(2)
U–C(16)	2.35(2)	U–C(12)	2.83(3)
U–M	2.26	U–C(13)	2.87(3)
U–Cp(1)	2.52	U–C(14)	2.84(2)
U–Cp(2)	2.54	U–C(15)	2.78(3)
U–Cp(3)	2.55	N(1)–C(16)	1.29(2)
U–C(1)	2.74(2)	N(1)–C(21)	1.42(2)
U–C(2)	2.75(2)	N(2)–C(16)	1.40(2)
U–C(3)	2.82(2)	N(2)–C(17)	1.48(3)
U–C(4)	2.85(2)	N(2)–C(19)	1.48(3)
U–C(5)	2.81(2)	C(17)–C(18)	1.54(4)
U–C(6)	2.80(2)	C(19)–C(20)	1.56(4)
U–C(7)	2.79(2)	C(22)–C(28)	1.53(3)
U–C(8)	2.81(2)	C(26)–C(27)	1.52(2)
U–C(9)	2.83(2)		
U–C(10)	2.82(2)		
M–U–Cp(1)	103	C(16)–N(1)–C(21)	135(2)
M–U–Cp(2)	100	N(1)–C(16)–N(2)	126(2)
M–U–Cp(3)	112	C(16)–N(2)–C(17)	118(2)
Cp(1)–U–Cp(2)	117	C(16)–N(2)–C(19)	126(2)
Cp(1)–U–Cp(3)	112	C(17)–N(2)–C(19)	116(2)
Cp(2)–U–Cp(3)	111	C(2)–C(17)–C(18)	114(2)
N(1)–U–C(16)	32(1)	N(2)–C(19)–C(20)	111(2)
U–N(1)–C(16)	74(1)	U–N(1)–C(21)	151(1)
U–C(16)–N(1)	74(1)	U–C(16)–N(2)	160(1)

* Cp(1), Cp(2), and Cp(3) designate the centroids of the C(1)—C(5), C(6)—C(10), and C(11)—C(15) cyclopentadienyl rings; M designates the mid-point of the N(1)—C(16) distance.

the corresponding CO insertion into U–C and U–N bonds as well as the insertion of RNC into U–C, represents a further indication of the co-ordinative and electronic unsaturation of the uranium atom which in such a way reaches a co-ordination number as high as 11, since the resulting insertion ligand is η^2-co-ordinated.

The formulations of the products arise from analytical, spectroscopic, and [for (4)] *X*-ray crystallographic data.

Spectroscopic Data.—Complex (2) presents the same properties as found by Dormond *et al.*[6] except for the i.r. band ascribed to ν(CN) which in our case occurs at 1 510 cm^{-1} instead of 1 645 cm^{-1}; (4) and (6) show ν(CN) at 1 535 and 1 510 cm^{-1} respectively. In our opinion these are typical values of η^2-co-ordinated insertion ligands; in fact all the structurally characterized η^2-iminoalkyl complexes show i.r. absorptions in the range 1 500—1 600 cm^{-1}.[13,*] Thus in these complexes a behaviour analogous to that of CO inserted compounds has been observed. In addition (2), (4), and (6) present the bands corresponding to the other groups of the molecule, while bands near 2 000 cm^{-1} indicating co-ordinated isocyanide ligands are absent. Rather intense peaks corresponding to the parent ion appear in the mass spectra of (2) and (4) but while (2) easily loses one of the two η^2-C(NEt_2)=$NC_6H_3Me_2$-2,6 groups, (4) loses first a cyclopentadienyl group; thus the [U(η-C_5H_5)$_2${C(NEt_2)$_2$=$NC_6H_3Me_2$-2,6}]$^+$ ion is produced in the fragmentation pattern both of (2) and (4) as shown below.

[U(η-C_5H_5)$_2${C(NEt_2)=$NC_6H_3Me_2$-2,6}$_2$]$^+$ − C(NEt_2)=$NC_6H_3Me_2$-2,6

↓

[U(η-C_5H_5)$_2${C(NEt_2)=$NC_6H_3Me_2$-2,6}]$^+$

↑

[U(η-C_5H_5)$_3${C(NEt_2)=$NC_6H_3Me_2$-2,6}]$^+$ − C_5H_5

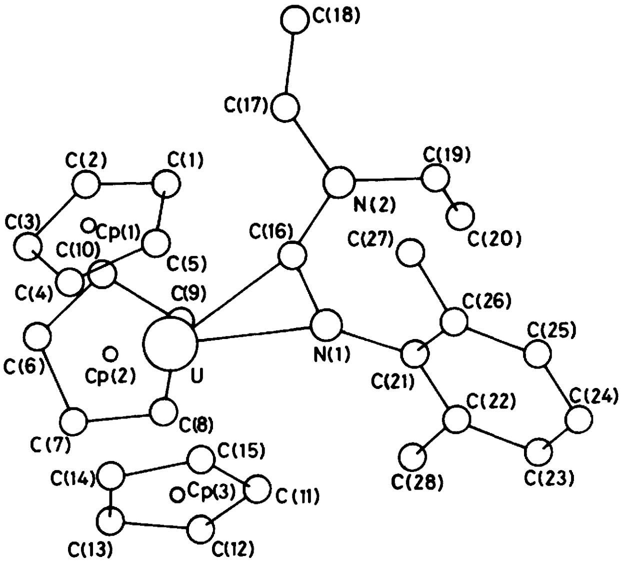
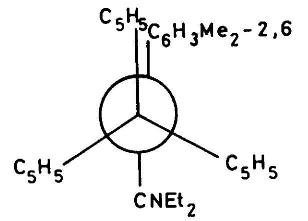


Figure 1. Molecular structure of [U(η-C_5H_5)$_3${C(NEt_2)=$NC_6H_3Me_2$-2,6}] (4)

The room-temperature ^1H n.m.r. spectra of (2), (4), and (6) show large isotropic shifts typical of paramagnetic uranium(IV) complexes. The signals of (2) are similar to those of ref. 6 while those of (4) indicate particularly interesting behaviour. The protons of the C_5H_5 groups give rise to two singlets (2:1 intensity ratio) 58.9 p.p.m. apart; their unequivocal assignment was possible by comparison with the ^1H n.m.r. spectrum of [U(η-C_5D_5)$_3${C(NEt_2)=$NC_6H_3Me_2$-2,6}] (4-D) which lacks the two signals ascribed to the cyclopentadienyl protons. Such a feature is probably due to the absence of free rotation of the η^2-iminocarbamoyl ligand so that the three C_5H_5 groups are no longer magnetically equivalent, as represented in the Newmann projection shown above. This is one of the very rare examples of [U(η-C_5H_5)$_3$X] systems in which the C_5H_5 protons give rise to two different n.m.r. signals and unique to our knowledge in which this phenomenon is observed at room temperature. Moreover, the protons of the ethyl groups also present two different sets of resonances; here these groups are not magnetically equivalent as found in (2) and in the carbamoyl derivative [U(η-C_5H_5)$_3${C(O)NEt_2}],[2] and it is likely that the partial double-bond character of the C-NEt_2 bond, formed by delocalization of the lone pair of electrons of the nitrogen atom, hampers the free rotation around the C–N axis. The set of sharp signals observed for (6) seems incomplete for the expected formulation [U(η-C_5H_5)$_3${C(PPh_2)=$NC_6H_3Me_2$-2,6}].



Crystal Structure of [U(η-C_5H_5)$_3${C(NEt_2)=$NC_6H_3Me_2$-2,6}] (4). The molecular structure of (4) is shown in Figure 1

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* The only exceptions are the complexes [Mo(η-C_5H_5)(CO)$_2${η^2-C(CH_3)=NCH_3}] and [Mo(η-C_5H_5)(CO)$_2${η^2-C(CH_3)=N-C_6H_5}] whose absorptions lie between 1 680 and 1 720 cm^{-1}.[13d]

Table 3. Comparison of selected U–C, U–N, C=N bond distances (Å)

Compound	U–C	Ref.
$[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(NEt_2)=NC_6H_3Me_2\text{-}2,6\}]$	2.35	This work
$[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(Me)=NC_6H_{11}\}]$	2.36	5
$[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(CHPMePh_2)=NC_6H_{11}\}]$	2.44	15
$[U(\eta\text{-}C_5H_5)_3Bu^t]$	2.426	17
	U–N	
$[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(NEt_2)=NC_6H_3Me_2\text{-}2,6\}]$	2.35	This work
$[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(Me)=NC_6H_{11}\}]$	2.40	5
$[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(CHPMePh_2)=NC_6H_{11}\}]$	2.31	15
$[U(\eta\text{-}C_5H_5)_3(NPh_2)]$	2.29	18
$[AsPh_4][U(\eta\text{-}C_5H_5)_3(NCS)_2]$	2.50—2.46	19(*b*)
$[U(\eta\text{-}C_5H_5)_3(NCMe)_2]_2[UO_2Cl_4]$	2.61—2.58	19(*a*)
$[\{U(NEt_2)_4\}_2]$	2.28—2.57*	20
	C=N	
$[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(NEt_2)=C_6H_3Me_2\text{-}2,6\}]$	1.29	This work
$[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(Me)=NC_6H_{11}\}]$	1.25	5
$[Mo(\eta\text{-}C_5H_5)(CO)_2\{\eta^2\text{-}C(Me)=NC_6H_5\}]$	1.233	13(*d*)
$[Mo(\eta\text{-}C_5H_5)(CO)_2\{P(OMe)_3\}(\sigma\text{-}MeCNC_6H_5)]$	1.266	13(*d*)
$[Zr(OC_6H_3Bu^t{}_2\text{-}2,6)_2\{\eta^2\text{-}C(Bu^t)=NCH_2C_6H_5\}_2]$	1.286	13(*b*)
$[Y(\eta\text{-}C_5H_5)_2\{\eta^2\text{-}CH=NC(Me)_3\}_2]$	1.275	13(*c*)

* For bridging $N\langle^{U}_{U}$ bond.

and consists of discrete molecular units, with intermolecular distances generally corresponding to van der Waals contacts. In each molecule three η^5-bonded C_5H_5 rings and one η^2-bonded $C(NEt_2)=NC_6H_3Me_2\text{-}2,6$ ligand are co-ordinated to the uranium atom so that the overall geometry is pseudo-tetrahedral if the midpoint of the C(16)–N(1) bond and the C_5H_5 centroids are considered as the vertices. Thus, the co-ordination geometry in (4) resembles, with some obvious differences, that of the perfectly tetrahedral molecule $[U(\eta\text{-}C_5H_5)_4]$,[14] in which the S_4 symmetry is allowed by the four equivalent ligands, whereas the structure as a whole can be strictly compared with those of $[U(\eta\text{-}C_5H_5)_3\{C(CHPMePh_2)=NC_6H_{11}\}]$[15] and $[U(\eta\text{-}C_5H_5)_3\{C(Me)=NC_6H_{11}\}]$.[5] The U atom lies 2.53 Å (mean value) out of the C_5H_5 planes, comparable to 2.55 Å found in $[U(\eta\text{-}C_5H_5)_4]$, and the average U–C distance of 2.808 Å for the 15 η^5-ring carbons compares favourably with 2.807 Å (mean) in $[U(\eta\text{-}C_5H_5)_4]$[14] and with 2.81 Å (mean) in $[U(\eta\text{-}C_5H_5)_3(OCCHPMePh_2)]$.[16] Moreover U, C(21), N(1), C(16), and N(2) are almost coplanar (the last four are perfectly coplanar) with dihedral angles of 34 and 31° with the planes defined by two C_5H_5 rings and 89° with that of the third. Furthermore, contact distances indicate that, apart from the presence of the xylyl and ethyl substituents, the above mentioned atoms lie on a pseudo mirror plane which also includes C(11). In Figure 2 the structure is projected along the M–U axis and presents two C_5H_5 rings, namely C(1)–C(5) and C(6)–C(10), symmetrically inclined to the U, C(21), N(1), C(16), N(2) plane which perpendicularly intersects the third, C(11)–C(15), cyclopentadienyl ring. A similar structural feature is observed in $[U(\eta\text{-}C_5H_5)_3\{C(Me)=NC_6H_{11}\}]$[5] where the corresponding mirror plane is determined by space-group symmetry. The angles C(16)–N(1)–C(21) and N(1)–C(16)–N(2) are 135 and 126° respectively, whereas other significant angles are 126° for C(16)–N(2)–C(19), 116° for C(17)–N(2)–C(19), and 118° for C(16)–N(2)–C(17).

The most interesting aspect of this molecule is the mode of ligation of the iminocarbamoyl ligand, for which a comparison of related bond distances existing in the literature is reported in Table 3. Both C(16) and N(1) are bonded to the uranium atom; their bond distances are the same (2.35 Å), forming an isosceles triangle with the C(16)–N(1) bond. The U–C bond distance is similar to that in $[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(Me)=NC_6H_{11}\}]$ and $[U(\eta\text{-}C_5H_5)_3(OCCHPMePh_2)]$,[16] for which a U–C partial double bond character has been suggested, but shorter than in $[U(\eta\text{-}C_5H_5)_3Bu^t]$[17] and the insertion derivative $[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(CHPMePh_2)=NC_6H_{11}\}]$ for which a single U–C bond character has been suggested.[15] Thus the present U–C bond could also have the partial character of a double bond. The U–N bond can be considered in the same way, whose distance is intermediate between that of $[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(Me)=NC_6H_{11}\}]$ and those of $[U(\eta\text{-}C_5H_5)_3\{\eta^2\text{-}C(CHPMePh_2)=NC_6\text{-}$

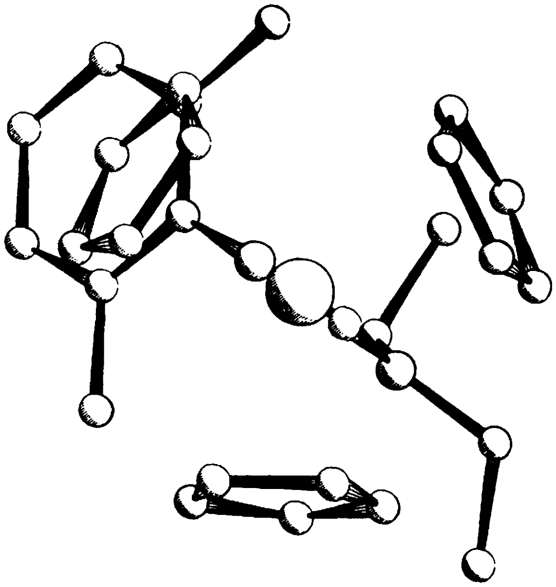
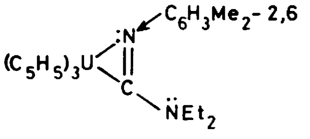


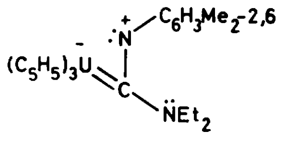
Figure 2. Projection of $[U(\eta\text{-}C_5H_5)_3\{C(NEt_2)=NC_6H_3Me_2\text{-}2,6\}]$ along the U–M direction

$H_{11}\}]$ and $[U(\eta\text{-}C_5H_5)_3(NPh_2)]$[18] for which a U–N bond order between 1 and 2 has been proposed; in any case the U–N bond observed here is far shorter than that of a typical U–N co-ordination bond $\{$*e.g.* of $[U(\eta\text{-}C_5H_5)_3(NCMe)_2]_2[UO_2Cl_4]$[19] in which the uranium ion is similarly eleven-co-ordinate$\}$. Such a bonding mode of the iminocarbamoyl ligand to the uranium ion through partially double U–C(16) and U–N(1) bonds justifies the hypothesis of the rigidity around the U–M axis [M = midpoint of the C(16)–N(1) bond] which causes the C_5H_5 protons to be magnetically inequivalent, thus explaining their n.m.r. behaviour. Similarly the different shifts of the protons of the two ethyl groups bonded to N(2) may be accounted for on the basis of a C(16)–N(2) partial double bond character; in fact the distance observed (1.40 Å) is shorter than (1.48 Å) N(2)–C(17) and N(2)–C(19) (Table 2) which compare well with other similar bonds (*cf.* N–C bonds ranging from 1.47 to 1.49 Å in $[\{U(NEt_2)_4\}_2]$[20]). This situation can be illustrated by the Newmann projection and the resonance form (**D**).

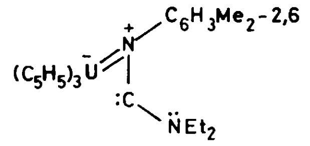
The other N–C bond, *i.e.* N(1)–C(21) has a distance consistent with a normal N–C_{aryl} bond. The N(1)–C(16) bond length is comparable to other C–N double bonds of similar compounds as shown in Table 3 and is in accord with an sp^2-hybridized nitrogen atom doubly bonded to C(16). On the basis of the above considerations the resonance structures (**A**)—(**D**) may be plausible for complex (**4**). Such electronic formulae point out: (*a*) the formal negative charge on the uranium atom which is reflected by the larger U–C_5H_5 average distance (2.808 Å) as observed in similar compounds[21] compared with the U–C_5H_5 distance of other $[U(\eta\text{-}C_5H_5)_3X]$ complexes,[22] where a typical U–X bond has been proposed; (*b*) the significant double character of the C(16)–N(2) bond due to delocalization of the N(2) lone pair; (*c*) both U–N(1) and U–C(16) are shorter than usual single bonds suggesting partial double bond character.



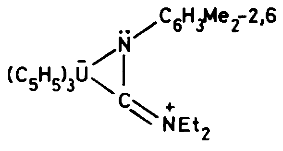
(**A**)



(**B**)



(**C**)



(**D**)

In conclusion our results complete those reported by Dormond *et al.*[6] and provide the first example of a structurally characterized complex obtained by the insertion of an isocyanide molecule into a U–N bond. Evidence of such an insertion into a U–P bond has also been obtained, confirming the general ability of a U–X (X = σ ligand) bond to activate dipolar molecules. Similar experiments on isocyanide insertion into a U–H bond are in progress.[23]

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