Carbon Monoxide and Isocyanide Complexes of Trivalent Uranium Metallocenes

M. del Mar Conejo,[a] Julian S. Parry,[a] Ernesto Carmona,*[a] Madeleine Schultz,[b] John G. Brennann,[b] Sharon M. Beshouri,[b] Richard A. Andersen,*[b] Robin D. Rogers,[c] Simon Coles,[d] and Michael Hursthouse[d]

Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday

Abstract: Organic isocyanide complexes of trivalent uranium metallocenes of the type $[Cp'_3U(CNR)]$, where $Cp' = C_5H_5$, MeC_5H_4, $Me_3CC_5H_4$, and $Me_3SiC_5H_4$ and R = Et; $Cp' = 1,3\text{-}(Me_3Si)_2C_5H_3$ and R = *t*Bu; $Cp' = Me_4C_5H$ and $R = 4\text{-}(MeO)C_6H_4$ and $2,6\text{-}Me_2C_6H_3$, have been isolated. When $Cp' = MeC_5H_4$ and $R = 2,6\text{-}Me_2C_6H_3$, both 1:1 and 1:2 adducts are obtained. The IR spectra show that $\tilde{\nu}_{CN}$ increases slightly for the alkyl isocyanide complexes and decreases slightly for the aryl isocyanide complexes relative to $\tilde{\nu}_{CN}$ for the free ligands. The uranium metallocenes form carbon monoxide adducts in which $\tilde{\nu}_{CO}$ moves to lower wavenumbers upon coordination (by 155 to 260 cm^{-1}). In only one case, however, can an adduct be isolated in crystalline form; $[(C_5Me_4H)_3U(CO)]$. The $\tilde{\nu}_{CO}$ stretching frequencies lie in the order $1,3\text{-}(Me_3Si)_2C_5H_3 > Me_3SiC_5H_4 > Me_3CC_5H_4 > C_5Me_4H$; $[(C_5Me_4H)_3U]$ is the best π donor in this series of metallocenes. Solution ^1H NMR spectra show that the adducts are fluxional and, in the case of $[(C_5Me_4H)_3U(L)]$ where L = CO or $4\text{-}(MeO)C_6H_4NC$, two fluxional processes can be observed: dissociation of L at relatively high temperature and cessation of ring rotation at low temperature. The crystal structures of the base-free metallocenes $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_3U]$ and $[(C_5Me_4H)_3U]$ show that these compounds are monomeric with idealized trigonal-planar geometry. The crystal structures of the $4\text{-}(MeO)C_6H_4NC$ and CO adducts of the latter metallocene are also described. All of the experimental studies reported herein are consistent with the view that the uranium metallocenes are better π donors than their cerium analogues, and the π-donating ability is dependent upon the ring substituents.

Keywords: carbonyl complexes · isocyanide complexes · metallocenes · uranium

Introduction

Carbon monoxide and organic isocyanides are well-known ligands for low-valent d-block transition metal compounds. Their effectiveness as σ donors decreases in the order CNR to CO, whereas their π-accepting capability follows the reverse order.[1] In d-block transition metal compounds the extent of π backbonding decreases as the net positive charge on the complex or the oxidation state of the metal center increases, which gives rise to the general view that metals in high oxidation state cannot bind to carbon monoxide. This perception has changed with the recent isolation of cationic carbonyl species such as $[Ir(CO)_6]^{3+}$[2] and $[M(CO)_4]^{2+}$ (M = Pd, Pt)[3] in which little π backbonding appears to exist.

The traditional view that actinide metals (An) cannot bind to carbon monoxide has changed recently[4] with the development of the chemistry of trivalent $[Cp'_3An]$ derivatives of sterically demanding cyclopentadienyl ligands.[5] A monocarbonyl complex of composition $[(Me_3SiC_5H_4)_3U(CO)]$ has been detected in the solid state and in hexane[6] and, although

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[a] Prof. E Carmona, Dr. M. del Mar Conejo, Dr. J. S. Parry
Departamento de Química Inorgánica
Instituto de Investigaciones Químicas, Universidad de Sevilla
Consejo Superior de Investigaciones Científicas
C/ Americo Vespuccio s/n
Isla de la Cartuja, E-41092 Sevilla (Spain)
Fax: (+34)■
E-mail: guzman@cica.es

[b] Prof. R. A. Andersen, M. Schultz, Dr. J. G. Brennann, Dr. S. M. Beshouri
Chemistry Department and Chemical Sciences Division of Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720 (USA)
E-mail: andersen@actinide.lbl.gov

[c] Prof. R. D. Rogers
Department of Chemistry, The University of Alabama
Tuscaloosa, AL, 35487 (USA)
E-mail: rdrogers@ua1vm.ua.edu

[d] Dr. S. Coles, Prof. M. B. Hursthouse
EPSRC National Crystallography service
Department of Chemistry University of Southampton
Highfield, Southampton SO17 1BJ (UK)
E-mail: m.b.hursthouse@soton.ac.uk

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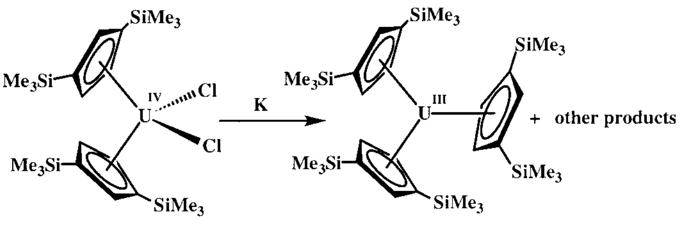
it loses the coordinated CO when exposed to vacuum, the $\tilde{\nu}_{CO}$ value of 1976 cm^{-1} suggests that the U^{III} metallocene, of f^3 electron configuration,[7] acts as a π donor. The related and isolable CNEt complex, which should be a good structural model for the CO adduct, shows a $\tilde{\nu}_{CN}$ stretching frequency shifted to slightly higher energy on coordination.[6] Use of the sterically more demanding tetramethylcyclopentadienyl ligand has resulted in the formation of an isolable carbonyl complex $[(C_5Me_4H)_3U(CO)]$.[8] The $\tilde{\nu}_{CO}$ value of 1880 cm^{-1} for the adduct seems unexpectedly low for a CO ligand which is shown by X-ray crystallography to be terminal.

Here we provide full details of the synthesis and characterization of some base-free trivalent uranium metallocenes $[Cp'_3U]$ that contain bulky cyclopentadienyl ligands, and we discuss their reactions with CO and various organic isocyanides.[9] The spectroscopic and structural results obtained support, in our view, the notion that the trivalent uranium metallocenes $[Cp'_3U]$ are good π donors and that the π-donating capability is modulated by the substituents on the cyclopentadienyl ligand.

Results

Base-free metallocenes: The new metallocenes $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_3U]$ (**1**) and $[(C_5Me_4H)_3U]$ (**2**) were prepared by synthetic routes that involved the reduction of the appropriate tetravalent uranium metallocene precursors. Complex **1** was obtained by a procedure similar to that used to generate the related $[(Me_3SiC_5H_4)_3U]$ and $[(Me_3CC_5H_4)_3U]$[9] complexes; that is by potassium reduction of $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_2UCl_2]$[10, 11] [Eq. (1)]. The tetramethylcyclopentadienyl derivative **2** was isolated following the reduction of $[(C_5Me_4H)_3UCl]$[8] by sodium naphthalene in tetrahydrofuran [Eq. (2)]. The precursor $[(C_5Me_4H)_3UCl]$ was independently synthesized by Cloke et al. during the progress of our work.[12]

Abstract in Spanish: *Los metalocenos de U^{III} de composición $[Cp'_3U]$ reaccionan con diversos isonitrilos orgánicos para formar los correspondientes complejos $[Cp'_3U(CNR)]$ ($Cp' = C_5H_5$, MeC_5H_4, $Me_3CC_5H_4$ y $Me_3SiC_5H_4$ y $R = Et$; $Cp' = 1,3\text{-}(Me_3Si)_2C_5H_3$ y $R = tBu$; $Cp' = MeC_5H_4$ y $R = 4\text{-}(MeO)C_6H_4$ y $2,6\text{-}Me_2C_6H_3$, $R = 2,6\text{-}Me_2C_6H_3$) aunque si $Cp' = MeC_5H_4$ y $R = 2,6\text{-}Me_2C_6H_3$ se puede aislar también el aducto 1:2. Los espectros de IR de estos compuestos ponen de manifiesto que el valor de $\tilde{\nu}_{CN}$ aumenta o disminuye ligeramente respecto al ligando libre según que R sea un grupo alquilo o arilo, respectivamente. La reacción análoga con el monóxido de carbono origina carbonilos de uranio de composición $[Cp'_3U(CO)]$ en los que $\tilde{\nu}_{CO}$ varía en el orden $1,3\text{-}(Me_3Si)_2C_5H_3 > Me_3SiC_5H_4 > Me_3CC_5H_4 > C_5Me_4H$, con una variación de entre 165 y 260 cm^{-1} en comparación con el CO libre. De ellos sólo el $[(C_5Me_4H)_3U(CO)]$ se puede aislar en forma de sólido cristalino. Se ha estudiado el comportamiento fluxional en disolución de algunos de los aductos $[(C_5Me_4H)_3U(L)]$, y se han determinado mediante difracción de rayos X las estructuras cristalinas de algunos de estos compuestos, entre ellas las del complejo de carbonilo $[(C_5Me_4H)_3U(CO)]$.*



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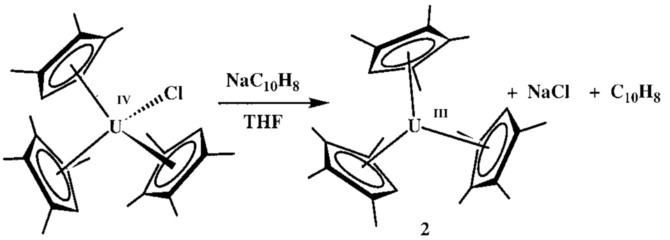

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(2)

Compound **1** is soluble in hexane and may be readily crystallized from this solvent at low temperatures. It is monomeric in the gas phase by mass spectrometry, and also in the solid state (see below). Its melting point of 232–235 °C is some 160 °C higher than that of the monosubstituted derivative $[(Me_3SiC_5H_4)_3U]$; a similar trend was noted between the same pair of cerium metallocenes.[13] This is presumably related to the way in which the substituted rings pack in the solid state; the monosubstituted derivative has more orientational degrees of freedom. In solution NMR spectra, the A_2B ring hydrogen atoms and the two $SiMe_3$ groups give single resonances whose chemical shifts change with temperature; the resonances are linear in T^{-1} and therefore follow the Curie–Weiss law. No change in line shape is detected over the temperature range of −80 to +80 °C, thus, average C_{3h} idealized symmetry is observed throughout this temperature range.

The solid-state structure of compound **1** is shown in Figure 1 (the crystal data are listed in Table 1), and even though the structure is not particularly well-defined (the crystal has pseudosymmetry and the silicon atom positions have large anisotropic thermal parameters) it clearly shows

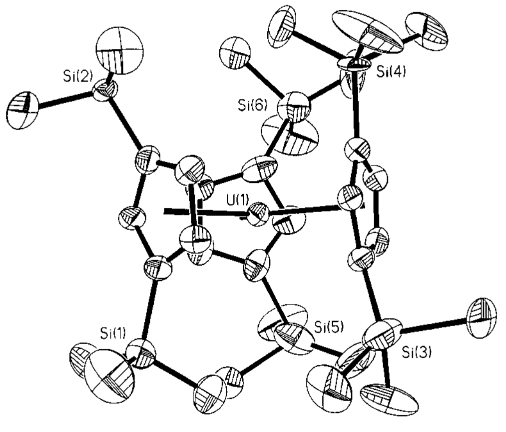


Figure 1. ORTEP drawing of $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_3U]$ (**1**). Important bond lengths [Å] and angles [°]: U–C(av) 2.82(5), U–C (centroid)(av) 2.54; Cp′(centroid)-U-Cp′(centroid)(av) 120.

Table 1. Crystal data and structure refinement.

Compound	**1**	**2**	**8d**	**8c**	**9d**
formula	$C_{33}H_{63}Si_6U$	$C_{27}H_{39}U$	$C_{35}H_{46}NOU$	$C_{27.6}H_{39}UN_{0.6}Cl_{0.4}$	$C_{28}H_{39}OU$
formula weight	866.4	601.61	734.78	631.43	629.62
crystal dimensions	irregular	0.4 × 0.4 × 0.1	0.19 × 0.11 × 0.02	0.15 × 0.15 × 0.03	0.21 × 0.14 × 0.11
crystal system	monoclinic	rhombohedral	monoclinic	orthorhombic	monoclinic
space group	*Ia* (no. 9)	*R*3 (no. 148)	*P*2(1) (no. 4)	*Fdd*2 (no. 43)	*P*2(1)/*c* (no. 14)
a [Å]	22.754 (7)	15.6845 (6)	9.2820 (2)	30.0219 (5)	10.581 (8)
b [Å]	11.341 (3)	15.6845 (6)	10.6698 (3)	30.0758 (5)	10.998 (4)
c [Å]	17.403 (3)	16.5106 (10)	15.4215 (4)	21.2675 (2)	21.069 (3)
α [°]	90	90	90	90	90
β [°]	105.77 (2)	90	94.8780 (1)	90	93.33 (3)
γ [°]	90	120	90	90	90
V [Å^3]	4321.9 (9)	3517.5 (3)	1521.06 (6)	19203.1 (4)	2448 (2)
Z	4	6	2	32	4
ρ_{calc} [g cm^{-3}]	1.33	1.704	1.604	1.747	1.709
F(000)	1748	1758	726	10336	1228
diffractometer	modified Picker	Smart	Smart	Smart	Fast-TV
μ(Mo$_{K\alpha}$) [cm^{-1}]	37.4	69.31	53.64	68.91	66.48
radiation [λ, Å]	0.71073	0.71073	0.71069	0.71069	0.71069
T [K]	296	173	124	112	120
scan technique	$\theta/2\theta$	$\theta/2\theta$	10 s scans of 0.3° in ω	10 s scans of 0.3° in ω	8 s scans of 0.25° in ω
$2\theta_{max}$	55	46.5	52.2	52.1	49.9
no. of reflections: total	10038	4788	6741	8268	9174
unique	5003	1137	3999	4315	3696
no. of observations	2793 [$I > 3\sigma$]	1060 [$I > 2\sigma$]	3049 [$I > 2\sigma$]	4315 [$I > 3\sigma$]	3696 [$I > 2\sigma$]
No. of variables	359	89	164	258	283
residuals: R	0.03	0.0282	0.069	0.038	0.0318
R_w	0.0326	0.0717	0.172	0.038	0.0689
R_{all}	0.102	0.0308	0.1021	0.0588	0.0475
maximum shift/error	< 0.01	< 0.02	0.04	< 0.01	< 0.01

that the metallocene is monomeric in the solid state. The Me_3Si groups are colinear with the molecular z axis, and the unique C–H atom pair of each cyclopentadienyl ring is oriented so as to define a molecule with idealized C_3 symmetry. Identical bond lengths and angles are observed in the cerium metallocene, although in the cerium case, one of the $(Me_3Si)_2C_5H_3$ groups is disordered in the crystal.[13] In the monomeric, monosubstituted derivative $[(Me_3SiC_5H_4)_3U]$, the three rings are ordered in the solid state with two of the Me_3Si groups oriented along the $(+z)$ axis and the third along the $(-z)$ axis.[14] In these two uranium metallocenes the U–C distances and the Cp′(centroid)-U-Cp′(centroid) angles are equal within the uncertainty in these values.

The reduction represented in Equation (2) is best effected in tetrahydrofuran as the solvent; crystallization from toluene provides black crystals of compound **2** in moderately good yields (ca. 70%). This complex is sparingly soluble in hexane, but more soluble in tetrahydrofuran and toluene. In solution the ^1H NMR spectrum of **2** gives rise to two signals at $\delta = 7.1$ and $\delta = -35.5$ (at 23 °C) that can be assigned to the ring methyl protons (6H:6H) together with another singlet at $\delta = -5.0$ (1H) corresponding to the unique CH of the ring. The spectrum is consistent with idealized C_{3h} symmetry and it does not undergo any significant change with temperature. As for **1**, the chemical shift of the signals vary linearly with T^{-1}, in accord with Curie–Weiss behavior.

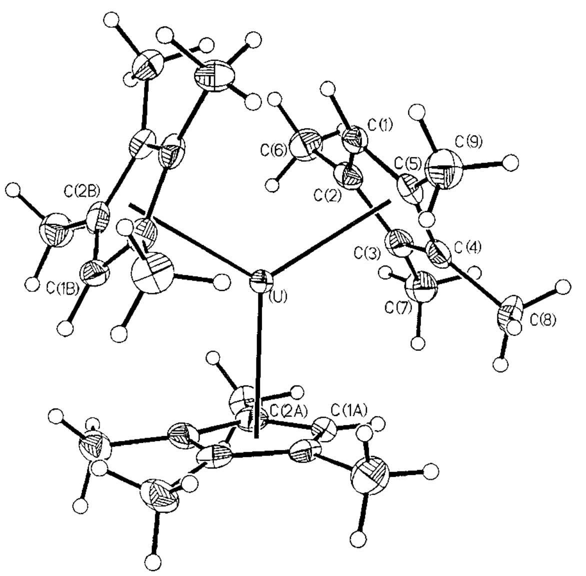
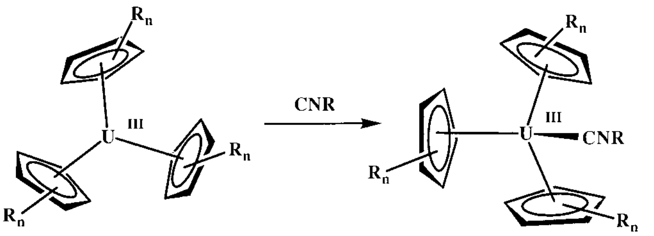


Figure 2. ORTEP drawing of $[(Me_4C_5H)_3U]$ (**2**). Important bond lengths [Å] and angles [°]: U–C(av) 2.77(5), U–C (centroid)(av) 2.523; Cp′(centroid)-U-Cp′(centroid)(av) 120. The hydrogen atoms are placed in ideal positions and not refined.

Compound **2** crystallizes from toluene at low temperatures in the space group $R\bar{3}$ (Figure 2). The uranium atom lies on a crystallographic threefold axis. Consequently (unlike its CO adduct discussed below, which exhibits a slight deviation from this geometry) the coordination environment is perfectly trigonal, with all the Cp′(centroid)-U-Cp′(centroid) angles equal to 120°. The C_5Me_4H ligands are arranged so that they define an idealized C_3 axis that passes through the uranium atom, and the Me substituents bend out of the Cp′ ring mean plane, away from the U center, with C6 (0.07 Å) and C9 (0.09 Å) bending less than C7 (0.22 Å) and C8 (0.23 Å). The U–Cp(centroid) distance of 2.52 Å is very close to that found in the recently reported [$(C_5Me_5)_3U$] complex (2.58 Å[15]); the slightly shorter distance may reflect the greater steric congestion about the U^{III} center in the latter compound.

Isocyanide complexes of [Cp'_3U]: In order to gain information about the electronic nature of the U^{III} center in the [Cp'_3U] metallocenes, several aliphatic and aromatic isocyanides adducts were prepared, [Eq. (3)] (Cp′ = C_5H_5 **3**, MeC_5H_4 **4**, $Me_3SiC_5H_4$ **5**, $Me_3CC_5H_4$ **6**, 1,3-$(Me_3Si)_2C_5H_3$ **7**, C_5Me_4H **8**. CNR: R = Me **8a**; R = Et **3**, **4a**, **5**, **6**; R = *i*Pr **8b**; R = *t*Bu **7**, **8c**; R = MeO-*p*-C_6H_4 **8d**; R = 2,6-$Me_2C_6H_3$ (Xyl) **4b**, **4c**, **8e**).[16]



(3)

All of the isocyanide complexes were made from the addition of an excess of CNR to the [Cp'_3U] complex in hexane, toluene, or diethyl ether. The reactions were instantaneous and the resulting red or violet adducts were crystallized from hexane (or toluene in the case of compounds **8** with the C_5Me_4H ligand) at low temperatures. They all have 1:1 stoichiometry with the exception of [$(MeC_5H_4)_3U(CNXyl)_n$](Xyl = 2,6-$Me_2C_6H_3$), for which both the 1:1 and the 1:2 adducts, **4b** and **4c**, respectively, have been isolated. Table 2 lists the isocyanide complexes that were obtained as crystalline solids, along with their $\tilde{\nu}_{CN}$ frequencies in the infrared spectrum. For comparative purposes, the analogous cerium isocyanides which are known to date are also included in order to illustrate quantitatively how [$Cp'_3U(CNR)$] differ from their 4f metallocene analogues in which the metal radii are similar.

Table 2. IR data of [$Cp'_3U(CNR)$] complexes.

Compound	$\tilde{\nu}$(CNR)[a]	Δ[b]	Δ[c]	References
[$(C_5H_5)_3U(CNEt)$] (**3**)	2170	+20		this work
[$(MeC_5H_4)_3U(CNEt)$] (**4a**)	2155	+5	+45	this work
[$(MeC_5H_4)_3U(CNXyl)$] (**4b**)	2060	−54	+90	this work
[$(MeC_5H_4)_3U(CNXyl)_2$] (**4c**)	2095	−19		this work
[$(Me_3SiC_5H_4)_3U(CNEt)$] (**5**)	2178	+28	+22	this work
[$(Me_3CC_5H_4)_3U(CNEt)$] (**6**)	2180	+30	+20	this work
{[1,3-$(Me_3Si)_2C_5H_3$]$_3$U(CN*t*Bu)} (**7**)	2140	+8	+30	this work
[$(C_5Me_4H)_3U(CNMe)$] (**8a**)	2165	+7		this work
[$(C_5Me_4H)_3U$(CN*i*Pr)] (**8b**)	2143	+3		this work
[$(C_5Me_4H)_3U$(CN*t*Bu)] (**8c**)	2127	−5		this work
[$(C_5Me_4H)_3U(CNC_6H_4$-*p*-OMe)] (**8d**)	2072	−50		this work
[$(C_5Me_4H)_3U(CNXyl)$] (**8e**)	2052	−62		this work
[$(MeC_5H_4)_3Ce(CNEt)$]	2200	+50		13
[$(MeC_5H_4)_3Ce$(CN*t*Bu)]	2175	+43		13
[$(MeC_5H_4)_3Ce(CNXyl)$]	2150	+36		13
[$(Me_3SiC_5H_4)_3Ce(CNEt)$]	2200	+50		13
[$(Me_3SiC_5H_4)_3Ce$(CN*t*Bu)]	2170	+38		13
[{1,3-$(Me_3Si)_2C_5H_3$}$_3$Ce(CN*t*Bu)]	2170	+38		13

[a] A single sharp, strong absorption in the Nujol mull spectra; cm^{-1}. [b] $\tilde{\nu}$(CNR) coordinated − $\tilde{\nu}$(CNR) free, using $\tilde{\nu}$(CNEt) = 2150, $\tilde{\nu}$(CN*t*Bu) = 2132, $\tilde{\nu}$(CNXyl) = 2114, $\tilde{\nu}$(CNMe) = 2158, $\tilde{\nu}$(CN*i*Pr) = 2140 and $\tilde{\nu}$(CNC_6H_4-*p*-OMe) = 2122 cm^{-1}. [c] $\tilde{\nu}$[$Cp'_3Ce(CNR)$] − $\tilde{\nu}$[$Cp'_3U(CNR)$].

In solution the isolated complexes **3**–**7** show averaged resonances in their ^{1}H NMR spectra over a temperature range of −80 to +80 °C, and the resonances obey the Curie–Weiss law with one exception, [$(MeC_5H_4)_3U(CNEt)$], in which the averaged chemical shifts are nonlinear in T^{-1}. The origin of this behavior is not known although the presence of a small amount of the 1:2 adduct seems to be the most reasonable explanation. The averaged chemical shifts show that, at least for **3**–**7**, the reaction illustrated in Equation (3) is an equilibrium reaction in the fast-exchange regime on the NMR time scale.

The isocyanide compounds **8** that contain an aromatic isocyanide (e.g. R = CNC_6H_4-*p*-OMe **8d**; R = CNXy **8e**) display reasonable thermal stability, similar to that of complexes **3**–**7**. For these two derivatives, $\tilde{\nu}_{CN} < 2100\ cm^{-1}$ and the decrease of the frequency found upon coordination is 50–60 cm^{-1} (see Table 2). However the alkyl isocyanide adducts (R = Me **8a**; R = *i*Pr **8b**; R = *t*Bu **8c**) are unstable in solution and decompose readily to produce the cyanide [$(C_5Me_4H)_3U(CN)$], although this latter compound has not been obtained in pure form. The rate of decomposition depends upon the R group, and parallels the stability of the radical R (see Experimental Section). Since there are several precedents for this or related decompositions both in organo d- and f-element chemistry[17] we have not investigated this transformation in more detail. An additional property of compounds **8** that has been studied is their fluxionality in solution; this will be described later.

Since [$(Me_3SiC_5H_4)_3U(CNEt)$] remains to date the only structurally characterized Cp'_3U^{III}-CNR complex,[6] we have determined the X-ray structures of some of the new isocyanides. Several crystal structures of the type $Cp'_2UX(CNR)_2$, in which the isocyanide ligands are nearly *trans* disposed and the other three ligands are located on equatorial sites in an idealized trigonal bipyramid, have been published.[18] Figure 3 shows the solid-state structure of compound **8d**. Compound **8d** crystallizes in the space group $P2_1$. Despite some twinning, useful information concerning the U-CNAr unit can be extracted. In **8d** the distance from the U atom to the isocyanide carbon atom (2.464(4) Å) is significantly shorter than in the [$Cp'_2UX(CNR)_2$] derivatives.[18] Interestingly, the U–C28 bond length in **8d** is only slightly longer than the U–CO distance found in the carbonyl adduct [$(C_5Me_4H)_3U(CO)$] (**9d**) (see below). These data and the large $\Delta\tilde{\nu}_{CN}$ shifts of about 50 and 60 cm^{-1} found in the adducts for **8d** and **8e**, respectively (see Table 2), unequivocally point to substantial $U^{III} \rightarrow$CNAr π-backbonding interaction.

An attempt to determine the structure of [$(C_5Me_4H)_3U$(CN*t*Bu)] (**8c**) indicated that the crystal contained in fact [$(C_5Me_4H)_3U(CN)$] and [$(C_5Me_4H)_3UCl$] (approximately 60 and 40 %, respectively). The origin of the latter has not been ascertained.[19] The molecules cocrystallize in the space group *Fdd*2, with the U atom lying on the pseudo-threefold axis.

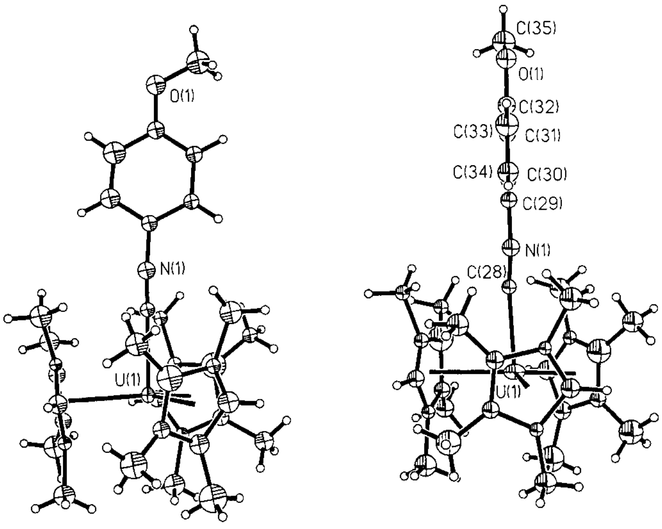


Figure 3. Two ORTEP perspectives of the $[(Me_4C_5H)_3U(CNC_6H_4\text{-}p\text{-}OMe)]$ (**8d**). Important bond lengths [Å] and angles [°]: U–C(av) 2.816(6), U–C(centroid)(av) 2.554, U–C(28) 2.464(4), C(28)–N 1.166(6); Cp′(centroid)-U-Cp′(centroid)(av) 119.6, U-C(28)-N 173.7 (9). The hydrogen atoms are placed in idealized positions and not refined.

There are two molecules in the asymmetric unit. The structural information regarding the fourth ligand is not precise owing to the mixture in the crystal (Figure 4). Nevertheless, this X-ray result provides additional support for the above-mentioned C–N bond rupture of the coordinated alkyl isocyanide ligand in compounds **8a**–**8c**.

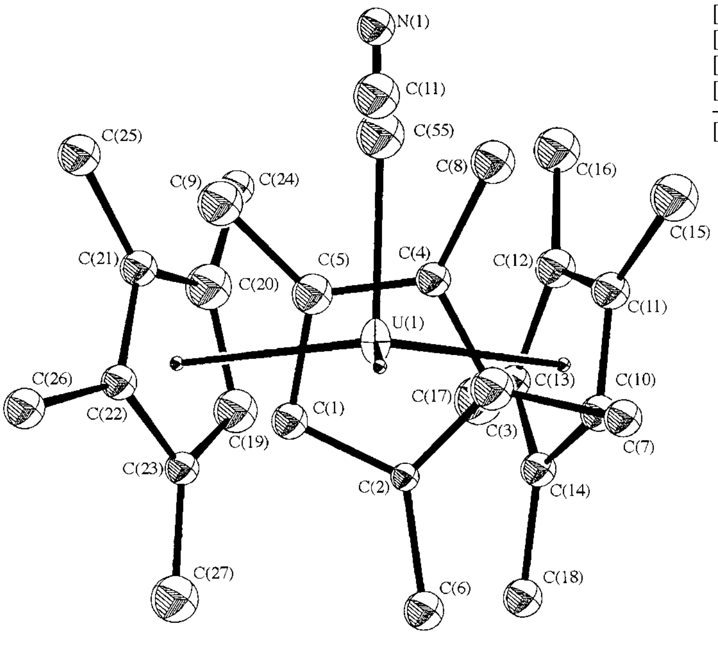
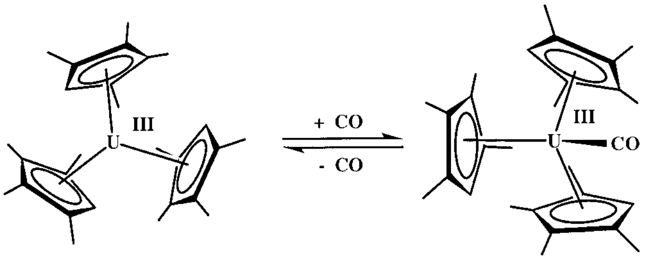


Figure 4. ORTEP drawing of $[(Me_4C_5H)_3U(CN)_{0.6}(Cl)_{0.4}]$(derived from the decomposition of **8c**). C55N and Cl1 are the superposition of CN and Cl group (atom) positions in the crystal. The refined occupancies are 60% CN and 40% Cl. The important bond lengths [Å] and angles [°]: U–C(av) 2.787(2), U–C(centroid) 2.497, U–C55 2.31(4); U-C55-N1 176(2).

Carbon monoxide complexes [Cp′$_3$U(CO)]: The base-free metallocenes [Cp′$_3$U] change color instantly when their solutions in hexane or toluene are exposed to an atmosphere of CO as a result of the formation of the corresponding adducts [Cp′$_3$U(CO)] (**9**) [Eq. (4); Cp′ = $Me_3SiC_5H_4$ **9a**, $Me_3CC_5H_4$ **9b**, 1,3-$(Me_3Si)_2C_5H_3$ **9c**, C_5Me_4H **9d**]. The metallocenes that contain Me_3Si and Me_3C change from green to



(4)

red, whereas the red-brown solutions of **2** become red-purple under these conditions. The coordination is reversible in all the cases and the adducts cannot be isolated except for the C_5Me_4H derivative **9d**, which is stable enough to be obtained as a crystalline solid. A change in the CO stretching frequency can be observed upon coordination and these frequencies are listed in Table 3. In the corresponding cerium metallocenes, the color does not change when solutions are exposed to an atmosphere of CO and no IR features associated with coordinated carbon monoxide are observed. In the solid state, $[(Me_3SiC_5H_4)_3U]$ (**9a**) takes up and releases CO when exposed to this gas and to vacuum, respectively. Moreover the CO stretching frequency is lower when ^{13}CO or $C^{18}O$ are employed (Table 3). All of these infrared data leave no doubt that the base-free uranium metallocenes [Cp′$_3$U] coordinate carbon monoxide to give compounds **9** and that the CO stretching frequencies decrease by about 155 to 260 cm^{-1}.

Table 3. IR data of [Cp′$_3$U(CO)] complexes.

Compound	$\tilde{\nu}$(CO)[a]	State	References
$[(Me_3SiC_5H_4)_3U(CO)]$ (**9a**)	1976	hexane	this work
$[(Me_3SiC_5H_4)_3U(^{13}CO)]$ (**9a′**)	1935	hexane	this work
$[(Me_3SiC_5H_4)_3U(CO)]$ (**9a**)	1969	KBr	6
$[(Me_3SiC_5H_4)_3U(^{13}CO)]$ (**9a′**)	1922	KBr	6
$[(Me_3CC_5H_4)_3U(CO)]$ (**9b**)	1960	hexane	this work
$[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_3U(CO)]$ (**9c**)	1988	methylcyclohexane	this work
$[(C_5Me_4H)_3U(CO)]$ (**9d**)	1880	Nujol	8
$[(C_5Me_4H)_3U(^{13}CO)]$ (**9d′**)	1840	Nujol	this work
$[(C_5Me_4H)_3U(C^{18}O)]$ (**9d″**)	1793	Nujol	this work

[a] cm^{-1}.

The tetramethylcyclopentadienyl complex **9d** has been isolated as a dark purple, almost black, crystalline solid. In solution it loses CO slowly to revert to the base-free metallocene **2**. The dissociative loss of carbon monoxide is accelerated by exposure to vacuum and for this reason, when the solvent is removed from solutions of **9d** carbon monoxide should be replenished periodically. However, under an atmosphere of carbon monoxide, **9d** is stable as a solid at room temperature for prolonged periods of time.[8] As specified in Table 3, $\tilde{\nu}_{CO}$ appears as an intense absorption at 1880 cm^{-1} in the solid state which shifts to about 1900 cm^{-1} in hexane solution. This corresponds to a lowering of $\tilde{\nu}_{CO}$ of about 260 to 240 cm^{-1} and can be taken as a clear indication of strong π-backdonation from the $[(C_5Me_4H)_3U]$ fragment to CO. In the ^{13}C-enriched carbonyl complex $[(C_5Me_4H)_3U(^{13}CO)]$, $\tilde{\nu}_{CO}$ is shifted to 1840 cm^{-1} in the solid-state IR spectrum.

The carbonyl **9d** is a fluxional molecule in solution. At 20 °C two very broad resonances ($\Delta\upsilon_{1/2} > 600$ Hz) at $\delta = 2.6$ (6H) and -12.1 (6H) arising from the ring methyl groups are observed, together with a sharper signal at $\delta = -2.7$ (1H) assigned to the C_5Me_4*H* protons. When the temperature is lowered, the signals change chemical shift but, in addition, those from the Me protons decoalesce to four equal-area resonances at low temperature. In accord with the structure proposed for these CO adducts and confirmed by X-ray studies (see below), the Me groups of each ring become nonequivalent and give rise to separate, well-defined peaks at $\delta = 24.8, -6.3, -5.5$, and 9.5 (3H each, data at -25 °C). In the temperature range from -70 to 0 °C, a plot of δ versus T^{-1} is linear, indicating Curie–Weiss behavior. Above room temperature (≥ 50 °C) the averaged chemical shifts of the Me protons are nonlinear in T^{-1}. In view of the chemical properties of **9d** described above, the most reasonable explanation for this appears to be an equilibrium between **9d** and the base-free metallocene **2** by dissociative loss of CO at high temperatures.

An X-ray study of complex **9d** at -123 °C shows that the crystals are monoclinic in the space group $P2_1/c$ (no. 14) (Figure 5). The U-C28-O angle is almost linear (175.2(6)°) and the U–CO bond length of 2.383(6) Å is significantly shorter than in the isocyanide adducts already discussed. This observation is in accord with the strong U–CO bonding interaction suggested by the IR data. Pertinent to the dynamic behavior exhibited by these $[(C_5Me_4H)_3U(L)]$ complexes (L = isocyanides or carbon monoxide) discussed in the following section, is the orientation of the three cyclopentadienyl rings; if the apex of the C_5Me_4H ligand is defined as the hydrogen-bearing ring carbon atom, the apices of the three rings are aligned in the same direction when viewed down the OC–U axis so that the threefold rotation axis coincides with this axis. This symmetry operation exchanges the rings, but cannot exchange the methyl groups on the β- or γ-ring carbon atoms. Thus, the four methyl groups are chemically inequivalent, as observed in the low-temperature ^{1}H NMR experiment.

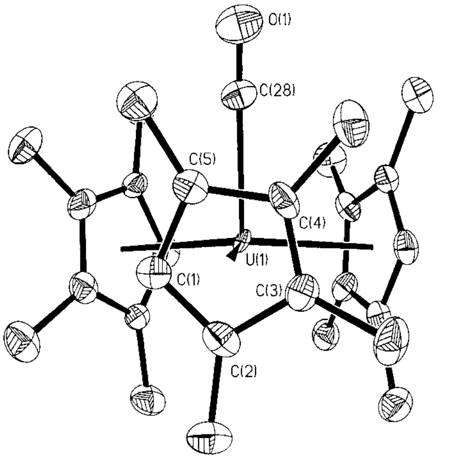


Figure 5. ORTEP drawing of $[(Me_4C_5H)_3U(CO)]$ (**9d**). Important bond lengths [Å] and angles [°]: U–C(av) 2.772(6), U–C(centroid)(av) 2.531, U–C(28) 2.383(6), C(28)–O(1) 1.142(7); Cp′(centroid)-U-Cp′(centroid) 118.8–120, U-C(28)-O 175.2(6).

Discussion

The difference Δ between $\tilde{\nu}_{CN}$ in a complex and in the free CNR ligand can be positive or negative and it is obviously related to the M–CNR bonding interaction.[20, 21] Generally Δ is negative when the metal is in a low oxidation state, which indicates that the isocyanide acts as an efficient π acceptor. In contrast, when bound to a metal in a high oxidation state (where there is little back-donation), the isocyanide releases electron density to the metal from an orbital on the carbon atom which has some antibonding character with respect to the C–N bond. As a result there is a strengthening of the C–N σ system which leads to positive values of Δ. Comparatively, aryl isocyanides are substantially better π acids than alkyl isocyanides and this difference is amplified when the isocyanide ligands are coordinated to high-valent metals, that is, to poor π-donor metal complexes.

As shown in Table 2, Δ values for the Ce^{III} isocyanide complexes are positive which suggests that the Ce^{III}–CNR interaction is mostly of the σ-type. Different trends are observed, however, for the $[Cp'_3U(CNR)]$ complexes. Firstly, in the compounds of the alkyl isocyanide ligands, Δ is also positive (except for compound **8c**, -5 cm^{-1}), albeit of smaller absolute value than in the Ce^{III} series, while for the aryl isocyanide derivatives, Δ values of about -50 to -60 cm^{-1} are observed. It is clear that the substituents on the isocyanide play the expected role in modulating $\tilde{\nu}_{CN}$. Electron-withdrawing groups reduce $\tilde{\nu}_{CN}$ upon coordination whilst electron donors raise it.

The substituents on the cyclopentadienyl ligand also affect $\tilde{\nu}_{CN}$ although less dramatically. For a given isocyanide in this series of compounds $\tilde{\nu}_{CN}$ values fall in the order $Me_3C \approx Me_3Si \approx (Me_3Si)_2 > H > Me > Me_4$. As the shifts are small and the reasons for them are a combination of σ and π effects within the CNR ligand, it is only possible to note the very general trend that electron-donating groups on the cyclopentadienyl ligand lower $\tilde{\nu}_{CN}$, presumably by making the metal center more electron-rich. This tendency is also observed in the carbonyl complexes, as explained below.

Another trend in the $\tilde{\nu}_{CN}$ stretching frequencies which we consider worth pointing out is that for a given adduct, $\tilde{\nu}_{CN}$ for the uranium complex is always less than that of its cerium analogue. In the case of the CNXyl adduct, this value (Δ′ in Table 2) is 90 cm^{-1} lower for uranium. This comparison clearly shows that uranium in the trivalent complexes is a better π donor than cerium in the analogous compounds. This tendency, along with the inability of the known cerium metallocenes to coordinate CO, clearly illustrates the difference between the 4f and 5f transition metal series. A similar ordering of π-donor trends was noted in bond-length comparisons between metallocenes of cerium and uranium with amine and phosphite donors.[22]

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As the uranium(III) metallocenes are π donors, their carbonyl complexes should exhibit $\tilde{\nu}_{CO}$ values below that of free CO. As shown in Table 3, this expectation is indeed fulfilled; however, as already indicated, only in the case of the C_5Me_4H derivative **2** can the corresponding adduct **9d** be isolated. The trend in $\tilde{\nu}_{CO}$ follows the order $(Me_3Si)_2 > Me_3Si > Me_3C > Me_4$. Clearly alkyl substituents in the Cp′ ring increase the electron density at the metal center and Me_3Si groups do not. Indeed four methyl groups reduce $\tilde{\nu}_{CO}$ by 80 cm^{-1} relative to a Me_3C group.

The isocyanide complexes **3**–**7** derived from the C_5H_5 and the mono- or disubstituted Cp′ ligands are dynamic on the ^1H NMR time scale to −80°C. The tetramethyl-substituted metallocenes that contain either an isocyanide or carbon monoxide ligand exhibit an interesting fluxionality which seems to be associated with the rotation of the C_5Me_4H ligands around the U–ring centroid axes. This behavior is similar for all compounds of this type. Since, as already described, the compounds that contain an alkyl isocyanide, **8a**–**8c**, decompose readily in solution, the present discussion will be limited to the aryl isocyanides **8d** and **8e**, and to the carbonyl complex **9d**. Figure 6 shows a plot of δ versus T^{-1} for the ring methyl ^1H NMR resonances of compound **8d** taken as a representative example. Sketch **A** depicts a view of one of the $[(C_5Me_4H)U(L)]$ fragments along the corresponding U–Cp(centroid) axis. In the slow exchange regime the four methyl groups of each C_5Me_4H ring are chemically inequivalent. Since the threefold U–L axis exchanges the rings, four equal area resonances (plus the signal from the CH unit) are expected and observed, in accord with the data in Figure 6. At higher temperatures they coalesce pairwise, so that above T_c two averaged resonances are observed in each case. The barriers to ring-site exchange in these adducts are 11.0 for **8d**, 9.4 for **8e**, and 11.5 kcal mol^{-1} for the carbonyl complex **9d**. The equilibration of the methyl groups bonded to the α- and β-C atoms with respect to the CH within each ring requires the generation of effective vertical planes of symmetry to give the adduct idealized C_{3v} symmetry. A free rotational motion of the rings that would align the ring C–H bonds with the U–L axis would explain the observed behavior.

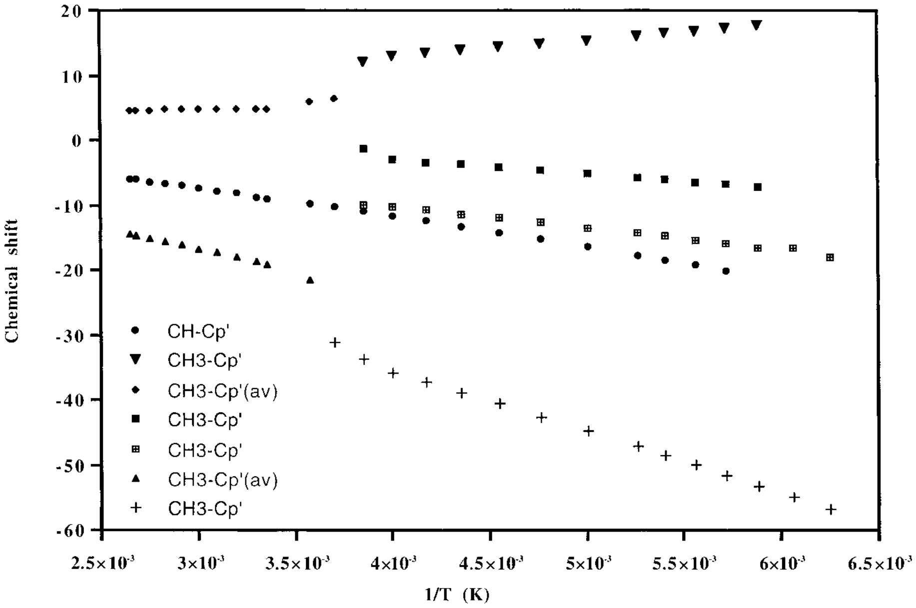
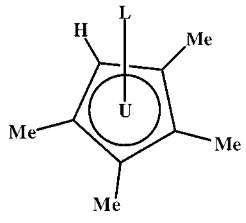


Figure 6. Plot of δ(ppm) versus 1/*T* for the complex $[(Me_4C_5H)_3U(CNC_6H_4\text{-}p\text{-}OMe)]$ (**8d**).



A

All of the data obtained for the $[Cp'_3U(L)]$ adducts point to the fact that uranium(III) metallocenes are better π donors than the cerium(III) analogues. This is due in part to the larger radii and therefore the lowered effect of the nuclear charge on the outermost electrons of the actinides as compared to the lanthanides, since f orbital involvement in metal–ligand bonding is greater for the actinides than for lanthanides. Presumably this effect is also true in the trivalent metallocenes.[24, 25] Thus the valence electrons on the uranium metallocenes are more polarizable than those on the cerium analogues, hence more of the electron density on uranium can populate the antibonding π orbitals of the π-acid ligand, which results in a lowering of $\tilde{\nu}_{CO}$ and $\tilde{\nu}_{CN}$ stretching frequencies in the former metallocene adducts. In a molecular orbital description, the empty metal orbital of the $[Cp'_3U]$ unit, which is of primarily $6dz^2$ character, accepts electron density from the ligand orbital localized on the carbon atom involved in the U–C σ bond.[25] For the π-component, the antibonding π orbitals of the molecule of CO (or CNR) can act as acceptors of electron density from the U 5f orbitals, perhaps hybridized with the U 6d orbitals. Since the electrons of the 5f metallocenes are higher in energy than those of the 4f metallocenes partly as a result of the metal nuclear charge, their orbital energies are closer in energy to those of the ligand acceptor orbitals and give rise to a larger overlap integral. In addition, relativistic effects destabilize the 5f orbitals more than the 4f orbitals, therefore bringing them closer in energy to the acceptor orbital of L, which augments the π donation. Regardless of the model used the net result is the same, the $[Cp'_3U]$ fragment is a better π donor than the $[Cp'_3Ce]$ fragment, and the donor properties can be significantly modulated by the substituents on the cyclopentadienyl ring.

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Experimental Section

All preparations and manipulations were carried out under oxygen-free argon with conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The petroleum used had a b.p. of 40–60 °C. The complexes $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_2UCl_2]$,[10, 11] $[(C_5Me_4H)_3UCl]$,[12] $[(C_5H_5)_3U(thf)]/NaCl$,[26] $[(MeC_5H_4)_3U(THF)]$,[27] $[(Me_3SiC_5H_4)_3U]$,[9a] and $[(Me_3CC_5H_4)_3U]$[9b] were prepared according to literature procedures. Microanalyses were obtained at Pascher Microanalytical Laboratory, Remagen (Germany), the analytical laboratories of the University of California (Berkeley), and the Microanalytical Service of the IIQ (Sevilla). Infrared spectra were recorded on Perkin-Elmer models 283 and 683, or Bruker, Vector 22 spectrometers. NMR spectra were recorded on JEOL FX-90QFT, Bruker AMX-300, AMX-500, DRX-400 and DRX-500 spectrometers. The ^1H and $^{13}C\{^1H\}$ resonances of the solvent were used as the internal standard, and the chemical shifts are reported relative to TMS.

$[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_3U]$ (1): The complex $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_2UCl_2]$ (3.00 g, 4.12 mmol) and potassium (0.35 g, 9.1 mmol) were suspended in hexane (60 mL) and heated to 80 °C. After stirring for one day, the dark-green cloudy solution was filtered. The volume of the filtrate was reduced to about 15 mL. Cooling to −20 °C produced green blocks (0.98 g). The volume of the mother liquor was reduced to 2 mL, and cooling to −20 °C produced a second crop of green blocks (0.67 g, 1.65 g total, 69 %). M.p. 232–235 °C; ^1H NMR (90 MHz, C_6D_6, 30 °C): $\delta = 20.8$ (s, 1H, C*H*-Cp′), −4.8 (s, 2H, C*H*-Cp′), −9.3 (s, 18H, Si*Me*$_3$-Cp′), ($\Delta\nu_{1/2}$ ca. 7–18 Hz); IR (Nujol, CsI): $\tilde{\nu} = 3075$(w), 3050(w), 1315(w), 1245(s), 1205(w), 1195(w), 1070(m), 915(s), 830(s), 770(m), 750(s), 685(m), 635(m), 610(w), 480(m), 375(m), 350(w), 325(w), 290(m), 240(w) cm^{-1}; MS($[M]^+$) : *m*/*z* (calcd, found) 865 (100, 100), 866 (67, 76), 867 (42, 48), 869 (6, 19); $C_{33}H_{63}Si_6U$ (865): calcd C 45.7, H 7.3; found C 45.5, H 7.2.

$[(C_5Me_4H)_3U]$ (2): Naphthalene (0.243 g, 1.90 mmol) was stirred over excess sodium in tetrahydrofuran (50 mL) for 16 h and then added slowly to $[(C_5Me_4H)_3UCl]$ (1.21 g, 1.90 mmol) at −80 °C. The mixture was allowed to warm to room temperature and stirred for 24 h, by which time it had become deep red. The solvent was removed in vacuo to yield a dark red mass. The reaction vessel was then immersed in a warm water bath (50 °C) under dynamic vacuum (0.05 Torr) for 2 h to remove naphthalene. During this time, the color of the solid lightened to a mottled orange-green. This was extracted with toluene (40+15 mL) and the extracts were filtered. Concentration of the resultant clear cherry red-brown solution to 20 mL produced small prisms on the flask wall. Cooling to −20 °C overnight yielded black crystals of **2** (0.62 g, 54 %); ^1H NMR (300 MHz, C_7D_8, 23 °C): $\delta = 7.4$, −35.5 (s, 6H each, C*H*$_3$-Cp′), −5.0 (s, 1H, C*H*-Cp′), ($\Delta\nu_{1/2}$ ca. 10–30 Hz); IR (Nujol, NaCl): $\tilde{\nu} = 3103$(m), 2721(m), 1327(m), 1018(s), 768(s) cm^{-1}; $C_{27}H_{39}U$ (601): calcd C 53.9, H 6.5; found C 53.4, H 6.4.

Synthesis of the U^{III} isocyanide adducts 3–8: The 1:1 adducts $[Cp'_3U(CNR)]$ were prepared by allowing the base-free $[Cp'_3U]$ compounds to react with the corresponding isocyanide ligands. Details are given below for the syntheses of $[\{1,3\text{-}(Me_3Si)_2C_5H_3\}_3U(CN\mathit{t}Bu)]$ (**7**) and $[(C_5Me_4H)_3U(CNXyl)]$ (**8e**) as representative examples.

Compound **1** (0.50 g, 0.58 mmol) was dissolved in hexane (50 mL), and *t*BuNC (0.07 mL, 0.05 g, 0.6 mmol) was added with a syringe. The color of the solution immediately changed from deep green to dark purple. After stirring for one hour, the solvent was removed under reduced pressure. The purple solid residue was dissolved in hexane (100 mL), and the solution was filtered. The volume of the filtrate was reduced to about 40 mL, and the solution was heated to redissolve the solid. Cooling to −20 °C produced purple blocks of **7** (0.20 g, 36 %). M.p. 230–232 °C; ^1H NMR (90 MHz, C_6D_6, 30 °C): $\delta = 0.4$ (s, 6H, C*H*-Cp′), −2.5 (s, 54H, Si*Me*$_3$-Cp′), 8.8 (s, 3H, C*H*-Cp′), −11.2 (s, 9H, *t*Bu), ($\Delta\nu_{1/2}$ ca. 10–22 Hz); IR (Nujol, CsI): $\tilde{\nu} =$ 3060(w), 2140(s), 1315(w), 1245(s), 1070(s), 925(s), 830(s), 815(w), 775(w), 750(m), 680(w), 630(m), 610(w), 480(w), 365(w), 290(w) cm^{-1}; $C_{36}H_{72}NSi_6U$ (924): calcd C 48.1, H 7.6, N 1.5; found C 46.8, H 7.6, N 1.4.

To complex **2** (0.34 g, 0.56 mmol) dissolved in toluene (35 mL) was added CNXyl (0.074 g, 0.56 mmol), dissolved in toluene (5 mL) and the resulting mixture was stirred at room temperature overnight. The solution was filtered and the filtrate was evaporated to a final volume of about 5 mL. Cooling to −30 °C produced dark blue, almost black, crystals of the adduct **8e** (0.41 g, 100 %). ^1H NMR (500 MHz, C_7D_8, 25 °C): $\delta = 8.2$, −21.6 (s, 18H, C*H*$_3$-Cp′) −13.6 (s, 3H, C*H*-Cp′), 17.2 (s, 1H, C*H*-Xyl), −2.7 (s, 2H, C*H*-Xyl), −16.7 (s, 6H, *Me*-Xyl), ($\Delta\nu_{1/2}$ ca. 50–300 Hz); IR (Nujol, NaCl): $\tilde{\nu} = 2718$(w), 2052(s), 1328(s), 1162(m), 1092(w), 1020(m), 772(s), 718(w) cm^{-1}; $C_{36}H_{48}NU$ (732): calcd C 59.5, H 6.6; found C 59.1, H 6.7.

$[(C_5H_5)_3U(CNEt)]$ (3): 42 % yield; ^1H NMR (90 MHz, C_6D_6, 36 °C): $\delta =$ −8.9 (s, 3H, CH$_2$*Me*), 14.1 (s, 15H, C*H*-Cp′), −55.3 (s, 2H, C*H*$_2$Me); IR (Nujol, CsI): $\tilde{\nu} = 2170$(m), 2160(m), 1720(w br), 1620(w br), 1346(m), 1260(m), 1090(m), 1050(w), 1008(s), 792(s), 765(s), 740(s), 495(m), 468(w), 400(w), 344(w), 210(s) cm^{-1}; $C_{18}H_{20}NU$ (488): calcd C 44.3, H 4.1, N 2.9; found C 44.0, H 4.4, N 2.6.

$[(MeC_5H_4)_3U(CNEt)]$ (4a): 28 % yield; m.p. 59–60 °C; ^1H NMR (90 MHz, C_6D_6, 34 °C): $\delta = -8.1$, −18.6 (s, 6H, C*H*-Cp′), −15.6 (s, 9H, *Me*-Cp′), −8.5 (s, 3H, CH$_2$*Me*), 59.3 (s, 2H, C*H*$_2$Me); IR (Nujol, CsI): $\tilde{\nu} = 2155$(s), 1339(m), 1090(w), 1028(m), 925(w), 847(w), 823(m), 765(s), 740(s), 610(w), 338(m), 215(w) cm^{-1}; $C_{21}H_{26}NU$ (530): calcd C 47.6, H 4.9, N 2.6; found C 47.3, H 4.9, N 2.2.

$[(MeC_5H_4)_3U(CNXyl)]$ (4b): 63 % yield; m.p. 73–76 °C; IR(Nujol, CsI): $\tilde{\nu} = 2060$(s), 1165(m), 1027(m), 923(w), 843(m), 812(m), 765(s), 745(s), 715(m), 605(m), 476(m), 387(w), 325(m), 262(w) cm^{-1}; $C_{27}H_{33}NU$ (609): calcd C 53.5, H 5.0, N 2.3; found C 53.2, H 6.2, N 2.0.

$[(Me_3SiC_5H_4)_3U(CNEt)]$ (5): 28 % yield; m.p. 112–115 °C; ^1H NMR (90 MHz, C_7D_8, 25 °C): $\delta = -1.1$, −18.9 (s, 6H, C*H*-Cp′), −6.3 (s, 27H, Si*Me*$_3$-Cp′), −8.8 (s, 3H, CH$_2$*Me*), 61.7 (s, 2H, C*H*$_2$Me); IR (Nujol, CsI): $\tilde{\nu} = 2178$(s), 2159(s), 1405(w), 1371(m), 1365(m), 1345(m), 1311(w), 1246(s), 1149(w), 1177(s), 1138(w), 1095(w), 1062(w), 1040(s), 902(s), 835(s), 765(s), 761(s), 690(m), 640(m), 625(m), 427(m), 322(m) cm^{-1}; $C_{27}H_{44}NSi_3U$ (704): calcd C 46.0, H 6.3, N 2.0; found C 45.9, H 6.3, N 1.9.

$[(Me_3CC_5H_4)_3U(CNEt)]$ (6): M.p. 123–126 °C; ^1H NMR (90 MHz, C_6D_6, 30 °C): $\delta = 0.0$, −24.2 (s, 6H, C*H*-Cp′), −6.8 (s, 27H, C*Me*$_3$-Cp′), −8.3 (s, 3H, CH$_2$*Me*), −57.7 (s, 2H, C*H*$_2$Me); $C_{30}H_{44}NU$ (657): calcd C 54.9, H 6.7, N 2.1; found C 55.0, H 6.6, N 2.0.

$[(C_5Me_4H)_3U(CNR)]$(8a–8c): These alkyl isocyanide derivatives (R = Me **8a**, *i*Pr **8b**, *t*Bu **8c**) were also prepared following a similar procedure, but because of their instability in solution the corresponding reaction mixtures were always maintained at temperatures below −30 °C. This study was only intended to observe the characteristic $\tilde{\nu}_{CN}$ associated with the coordinated isocyanide ligands in these adducts (2166 cm^{-1} **8a**, 2143 cm^{-1} **8b**, 2127 cm^{-1} **8c**) and therefore no attempts were made to investigate their decomposition to the cyanide derivative $(C_5Me_4H)_3U(CN)$ nor to isolate this species in a pure form.

Synthesis of the bis(isocyanide) adduct $[(MeC_5H_4)_3U(CNXyl)_2]$ (4c): Addition of 2,6-dimethylphenyl isocyanide (0.48 g, 3.3 mmol) to a solution of $[(MeC_5H_4)_3U(THF)]$ (0.64 g, 1.1 mmol) in diethyl ether gave an immediate color change to blue. The solvent was removed under reduced pressure, and the blue solid was extracted with hexane (30 mL). Cooling the filtrate (−20 °C) afforded blue plates (0.49 g, 20 %); m.p. 101–103 °C; ^1H NMR (90 MHz, C_6D_6, 31 °C): $\delta = -9.2$, 17.0 (s, 6H, C*H*-Cp′), −15.9 (s, 9H, *Me*-Cp′), −10.0 (s, 12H, *Me*-Xyl), 0.8 (t, 4H, C*H*-Xyl), 13.9 (d, 2H, C*H*-Xyl); IR (Nujol, CsI): $\tilde{\nu} = 2095$(s), 2065(s), 1177(m), 1078(w), 1060(w), 1040(w), 1025(m), 973(w), 925(w), 843(w), 811(m), 767(s), 759(s), 745(s), 715(m), 505(m), 465(m), 386(w), 322(w), 270(w) cm^{-1}; $C_{36}H_{40}N_2U$ (738): calcd C 58.6, H 5.3, N 3.8; found C 57.8, H 6.4, N 3.4.

Reaction of $[Cp'_3U]$ compounds with carbon monoxide: The base-free uranium metallocenes $[Cp'_3U]$ (Cp′ = $Me_3SiC_5H_4$, $Me_3CC_5H_4$, and $1,3\text{-}(Me_3Si)_2C_5H_3$) dissolved in hexane were exposed to an atmosphere of CO at room temperature and pressure and stirred for about 5 min. The resulting solutions were transferred to an IR cell under CO and the characteristic $\tilde{\nu}_{CO}$ stretching frequencies were measured. These values, including those obtained in the presence of ^{13}CO and $C^{18}O$, are given in Table 3.

A solution of $[(C_5Me_4H)_3U]$ (**2**) in toluene (0.97 g, 1.61 mmol, 40 mL) was stirred at room temperature under 1 atm of CO for about 10–15 min. The color changed from red-brown to purple. Cooling to −30 °C overnight provided dark purple-black prisms of the carbonyl adduct **9d** (0.64 g, 62 % yield). This complex loses CO slowly in solution. If partial evaporation of the solvent is needed to induce crystallization, the concentrated solutions should be exposed to CO for about 5–10 min before cooling to −30 °C. ^1H NMR (300 MHz, C_7D_8, 23 °C): $\delta = 2.6$, −12.1 (s, 6H, *Me*-Cp′), −2.7 (s, 1H, C*H*-Cp′); IR (Nujol, NaCl): $\tilde{\nu} = 1880$(s) cm^{-1}; $C_{28}H_{39}UO$ (629): calcd C 53.4, H 6.2; found C 53.5, H 6.3.

Crystal structure determinations of 1, 2, 8c, 8d, and 9d

Compound 1: The unit cell parameters for **1** were derived by a least-squares fit of the θ values of 19 reflections. Inspection of the intensity standards revealed a reduction of 3% of the original intensity. The data were corrected for this decay. Inspection of the systematic absences indicated possible space groups *Ia* and *I2/a*. The choice of the noncentric space group *Ia* was confirmed by the successful solution and refinement of the structure. The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques. There were no indications of hydrogen atoms in the final Fourier and there was no indication of secondary extinction in the high-intensity low-angle data. The final residuals for 359 variables refined against the 2793 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.03$, $wR = 0.0326$ and GOF = 1.07. The R value for the 5003 unique data was 0.102.

Compound 2: A brown single-crystal of this complex was mounted on a fiber and transferred to the goniometer. The crystal was cooled to $-100\,^{\circ}C$ during data collection. The space group was determined to be either the centric $R3$ or acentric $R\bar{3}$ from the systematic absences. The subsequent solution and successful refinement of the structure was carried out in the centric space group $R3$. A summary of data collection is given in Table 1. The geometrically constrained hydrogen atom was placed in a calculated position and allowed to ride on the bonded atom with B = 1.2* Ueqv (C(1)). The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (B = 1.2* Ueqv(C)). Refinement of nonhydrogen atoms was carried out with anisotropic temperature factors.

Compound 8c: The data was collected at $-161\,^{\circ}C$, cell constants and an orientation matrix obtained from a least-squares refinement of the measured positions of 4399 reflections with $I > 10\sigma$, in the range $4.0 > 2\theta < 52.3^{o}$ corresponded to an F-centered orthorhombic cell with the dimensions specified in Table 1. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded with Fourier techniques. The solution of the uranium atoms and the C_5Me_4H ligands was unproblematic; however the fourth ligands were assigned as Cl and CN based on the synthetic methodology and an examination of the packing diagram which indicated they could only be small ligands. Their occupancies were modeled as 40% Cl and 60% CN based on an examination of the Fourier map and the difference Fourier map. Subsequent refinement led to approximately equal thermal parameters for the Cl, C, and N atoms, which supports the occupancies in the model. The uranium atoms were refined anisotropically, while the rest of the non-hydrogen atoms were refined isotropically.

Compound 8d: Data were collected at $-149\,^{\circ}C$ on a pale green crystal. The cell constants and an orientation matrix were obtained from a least-squares refinement of the measured positions of 3196 reflections in the range $3.0 < 2\theta < 52.2^{o}$. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded with Fourier techniques. The three C_5Me_4H rings were restrained to be planar, the phenyl ring of the isocyanide was constrained to be hexagonal and restrained to be planar. The uranium atom was refined anisotropically; all other atoms were refined isotropically. Hydrogen atoms were included in calculated positions.

Compound 9d: A preliminary communication describing the formation of this complex and its structural characterization by X-ray techniques has already appeared.[8] The data were collected at 120 K on a FAST-TV area detector with an Oxford cryosystems cryostat, and processed by MADNESS software.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-114233–114236. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley Interscience, USA. **1988**.

[2] a) C. Bach, H. Willner, C. Wang, S. J. Rettig, J. Trotter, F. Aubke, *Angew. Chem.* **1996**, *108*, 2104; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1974; b) H. Willner, F. Aubke, *Angew. Chem.* **1997**, *109*, 2506; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2402.

[3] G. Hwang, C. Wang, F. Aubke, H. Willner, M. Bodenbinder, *Can. J. Chem.* **1993**, *71*, 1532.

[4] J. E. Ellis, W. Beck, *Angew. Chem.* **1995**, *107*, 2695; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2489.

[5] C. Janiak, H. Schumann, *Adv. Organomet. Chem.* **1991**, *33*, 291.

[6] J. G. Brennan, R. A. Andersen, J. L. Robbins, *J. Am. Chem. Soc.* **1986**, *108*, 33.

[7] a) B. E. Bursten, R. J. Strittmatter, *Angew. Chem.* **1991**, *103*, 1085; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1069; b) M. Pepper, B. E. Bursten, *Chem. Rev.* **1991**, *91*, 719.

[8] J. Parry, E. Carmona, S. Coles, M. Hursthouse, *J. Am. Chem. Soc.* **1995**, *117*, 2649.

[9] a) J. G. Brennan, R. A. Andersen, A. Zalkin, *Inorg. Chem.* **1986**, *25*, 1756; b) S. D. Stults, R. A. Andersen, A. Zalkin, *Organometallics* **1990**, *9*, 1623.

[10] P. C. Blake, M. F. Lappert, R. G. Taylor, *Inorg. Synth.* **1990**, *27*, 172.

[11] W. W. Lukens, S. M. Beshouri, L. M. Blosch, A. L. Stuart, R. A. Andersen, *Organometallics*, in press.

[12] F. G. N. Cloke, S. A. Hawkes, P. B. Hitchcock, P. Scott, *Organometallics* **1994**, *13*, 2895.

[13] S. D. Stults, R. A. Andersen, A. Zalkin, *Organometallics* **1990**, *9*, 115.

[14] A. Zalkin, J. G. Brennan, R. A. Andersen, *Acta Crystallogr. Sect. C* **1988**, *44*, 2104.

[15] W. J. Evans, K. J. Forrestal, J. W. Ziller, *Angew. Chem.* **1997**, *109*, 798; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 774.

[16] $Cp_3U(CNCy)$ is known; $\upsilon_{CN} = 2160\,cm^{-1}$. B. Kanellakopoulos, E. O. Fischer, E. Dornberger, E. Baumgartner, *J. Organomet. Chem.* **1970**, *24*, 507.

[17] a) R. Anwander, *Angew. Chem.* **1998**, *110*, 619; *Angew. Chem. Int. Ed.* **1998**, *37*, 599; b) W. J. Evans, D. K. Drummond *Organometallics* **1988**, *7*, 797; c) Y. Obora, T. Ohta, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 3745; d) G. Poszmik, P. J. Carroll, B. B. Wayland, *Organometallics* **1993**, *12*, 3410; e) R. Adam, C. Williers, M. Ephritikhine, M. Lance, M. Nierlich, J. Vigner, *J. Organomet. Chem.* **1993**, *445*, 99; f) W. W. Lukens, R. A. Andersen, *Organometallics* **1995**, *14*, 3435.

[18] a) A. Zalkin, S. M. Beshouri, *Acta Crystallogr. Sect. C* **1989**, *C45*, 1081; b) S. M. Beshouri, A. Zalkin, *Acta Crystallogr. Sect. C* **1989**, *45*, 1221.

[19] The U^{IV}-chloride complex may result from the reaction of **2** with chloride-containing impurities in the CNBu*t*, see: G. W. Gokel, R. P. Widera, W. P. Weber, *Org. Synth.* **1988**, *VI*, 232.

[20] a) A. C. Sarapu, R. F. Fenske, *Inorg. Chem.* **1975**, *14*, 247; b) M. H. Chisholm, D. L. Clark, D. Ho, J. C. Huffman, *Organometallics* **1987**, *6*, 532.

[21] a) P. M. Treichel, *Adv. Organomet. Chem.* **1973**, *11*, 21; b) Y. Yamamoto, *Coord. Chem. Rev.* **1980**, *32*, 193; c) E. Singleton, H. E. Oosthuizen, *Adv. Organomet. Chem.* **1983**, *22*, 207.

[22] J. G. Brennan, S. D. Stults, R. A. Andersen, A. Zalkin, *Organometallics* **1988**, *7*, 1329.

[23] For the sake of completeness, it should be mentioned that small amounts (5–10%) of an impurity are always present in the solutions of the above complexes. Interestingly this minor species is fluxional and its solution behavior is similar to that described above for the $[(C_5Me_4H)_3U(L)]$ adducts. We therefore propose C_3 symmetry for the molecules of this impurity which becomes effectively C_{3v} in the fast exchange regime. Although insufficiently characterized at present, it

appears to result from the reaction of either the base-free metallocene [$(C_5Me_4H)_3U$] or more likely the adducts [$(C_5Me_4H)_3U(L)$] with traces amounts of adventitious water.

[24] J. W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[25] a) B. E. Bursten, L. F. Rhodes, R. J. Strittmatter, *J. Am. Chem. Soc.* **1989**, *111*, 2756; b) B. E. Bursten, L. F. Rhodes, R. J. Strittmatter, *J. Am. Chem. Soc.* **1989**, *111*, 2758.

[26] a) D. C. Moody, J. D. Odom, *J. Inorg. Nucl. Chem.* **1979**, *41*, 553; b) D. G. Karraker, J. A. Stone, *Inorg. Chem.* **1972**, *11*, 1742; c) H. J. Wasserman, A. J. Zozulin, D. C. Moody, R. R. Ryan, K. V. Salazar, *J. Organomet. Chem.* **1983**, *254,* 305.

[27] a) J. G. Brennan, R. A. Andersen, A. Zalkin, *Inorg. Chem.* **1986**, *25*, 176; b) A. Zalkin, J. G. Brennan, *Acta Crystallogr. Sect. C* **1985**, *41*, 1295; c) J. G. Brennan, A. Zalkin, *Acta Crystallogr. Sect. C* **1985**, *41*, 1038.

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