

Communications to the Editor

Synthesis and Single Crystal X-ray Diffraction Study on the First Isolable Carbonyl Complex of an Actinide, (C₅Me₄H)₃U(CO)

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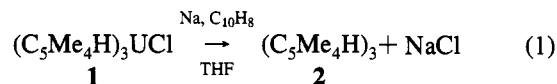
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Almost all transition metals form stable complexes with carbon monoxide.¹ In contrast, there are no reports of analogous molecular actinide carbonyl compounds that have been obtained in a pure state. As such, these compounds have been traditionally regarded as too unstable and/or too labile to isolate.² This is despite the fact that there are numerous examples of insertion of CO into actinide M–X bonds,³ a prerequisite of which probably involves prior coordination of CO.⁴

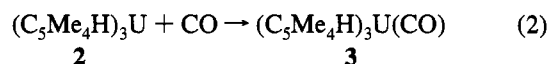
Apart from low-temperature matrix isolation studies,⁵ the only known molecular actinide carbonyl complex is the uranium derivative (Me₃SiC₅H₄)₃U(CO),⁶ reported by Andersen and co-workers in 1986. This compound, formed on exposure of (Me₃SiC₅H₄)₃U to CO, exhibits ν_{CO} at the relatively low value of ca. 1976 cm⁻¹. However, it readily loses CO, both in solution and in the solid state. Its preparation, and that of other U(III) derivatives containing π acid ligands,⁷ suggest that molecular actinide–CO complexes might be isolable species, a hypothesis that also finds theoretical support.⁸ We wish to report that the duodecamethyl metallocene (C₅Me₄H)₃U (**2**) provides an electronic and steric environment that enables the synthesis and

structural characterization by X-ray methods of the first isolable carbonyl complex of an actinide element, (C₅Me₄H)₃U(CO).

Uranium tetrachloride reacts smoothly with 3 equiv of KC₅-Me₄H in tetrahydrofuran at room temperature to afford the corresponding hydrocarbon soluble, crystalline compound (C₅-Me₄H)₃UCl (**1**), independently synthesised by Scott *et al.* during the progress of our work.⁹ We find that **1** is readily reduced by sodium naphthalenide in tetrahydrofuran to yield the corresponding hydrocarbon-soluble, black, crystalline trivalent metallocene (C₅Me₄H)₃U (**2**) (eq 1).¹⁰



Saturated cherry red-brown solutions of **2** turn purple immediately when stirred under ca. 1 atm of CO at room temperature and yield dark purple-black prisms of the CO adduct (C₅Me₄H)₃U(CO) (**3**) upon cooling to –20 °C (eq 2).¹¹ The



reaction appears quantitative by ¹H NMR spectroscopy.¹² The IR spectrum of **3** is dominated by an intense carbonyl stretching absorption, which appears at 1880 cm⁻¹ in the solid state and at 1900 cm⁻¹ in petroleum ether solution. This suggests a strong U → CO π-backbonding interaction, presumably between the U 5f π and the CO π* orbitals.⁸ Although the three C₅Me₄H rings would be expected to make the U(III) center in **2** more electron rich than that in (Me₃SiC₅H₄)₃U,¹³ the lowering of ν_{CO} in solution by 76 cm⁻¹ in comparison with that of Andersen's complex is somewhat surprising.

When toluene solutions of **3** are treated to prolonged exposure to vacuum, they eventually revert back to the original color of **2**. However, solutions sealed under an atmosphere of CO are stable for at least 2 months at ambient temperature, with no detectable signs of decomposition. Moreover, solid samples

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(10) Naphthalene (0.243 g, 1.90 mmol) was stirred over excess sodium in tetrahydrofuran (50 mL) for 16 h and then added slowly at –80 °C to **1** (1.21 g, 1.90 mmol). 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 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%). Anal. Calcd for C₂₇H₃₉U: C, 53.91; H, 6.49. Found: C, 53.38; H, 6.45. ¹H NMR (C₆D₅CD₃, 300 MHz, +23 °C): 2 signals assigned to the Me resonances are observed at δ 7.4 (18H) and δ –35.5 (18H), while the ring protons resonate at δ –5.0 (3H), with Δν_{1/2} ranging between ca. 10 and 30 Hz.

(11) Anal. Calcd for C₂₈H₃₉UO: C, 53.42; H, 6.20. Found: C, 53.52; H, 6.27.

(12) ¹H NMR (C₆D₅CD₃, 300 MHz): the molecule is fluxional in solution; at 23 °C, two broad resonances (Δν_{1/2} > 600 Hz) assigned to the Me protons are observed at δ 2.6 (18H) and δ –12.1 (18H), together with a relatively sharp signal assigned to the ring protons at δ –2.7 (3H, Δν_{1/2} = 13 Hz). Variable-temperature magnetic susceptibility studies on this compound will be reported at a later stage.

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§ Address correspondence regarding X-ray structure determination to this author.

(1) For some recent general reviews on transition metal–carbonyl chemistry, see: (a) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (b) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. See also: *J. Organomet. Chem.* **1990**, *383* (special volume dedicated to metal–carbonyl chemistry).

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(4) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1984**, *23*, 1633.

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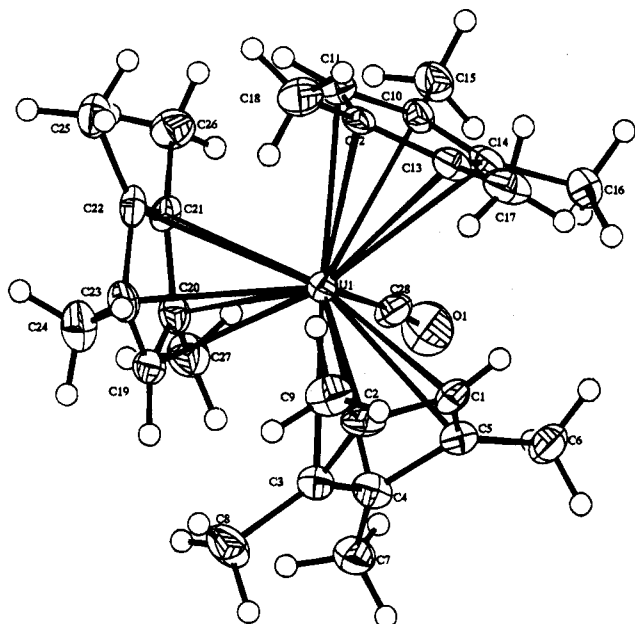


Figure 1. Molecular structure of $(C_5Me_4H)_3U(CO)$ at 120 K; 50% probability ellipsoids are given for non-hydrogen atoms. Selected interatomic distances (\AA): U–C28, 2.383(6); C28–O1, 1.142(7); U–Cp'1(dummy centroid), 2.528; U–Cp'2, 2.535; U–Cp'3, 2.531.

of **3** are stable for at least 2 months in the solid state at room temperature under an Ar or N_2 atmosphere and show no evidence of decomposition when exposed for 5 h to dynamic vacuum. This has allowed the full characterization of **3**, including a single crystal X-ray study.¹⁴ The molecular structure of **3** is presented in Figure 1 in the form of a SNOOPI plot. The molecule possesses pseudo- C_{3v} symmetry, and, as expected, the carbonyl ligand is bonded through the carbon atom. If the apex of the C_5Me_4H ligand is defined as the hydrogen-bearing ring carbon atom, then the apices of the Cp' rings (Cp' = tetramethylcyclopentadienyl anion) are aligned in the same direction when viewed down the OC–U axis. This arrangement serves to minimize sterically unfavorable intramolecular Me–Me interactions with the Me substituents on the proximate ring and can also be observed with $(C_5Me_4H)_3UCl$.⁹ The U–C (Cp') distances range from 2.71 to 2.89 \AA , and the U–Cp' ring

centroid distances are all $2.53 \pm 0.005 \text{ \AA}$. The Cp'–U–Cp' ring centroid angles range from 118.8° to 120.0° . The Cp' rings are planar (maximum deviations from the ring mean plane are, for ring 1, C1–C5, 0.016 \AA ; for ring 2, C10–C14, 0.052 \AA ; for ring 3, C19–C23, 0.007 \AA), while the methyl substituents deviate from the ring mean plane, bending away from the uranium atom. Undoubtedly, the most interesting feature of the molecule is the U–CO unit: the U–C–O angle is almost linear, at $175.2(6)^\circ$, and is characterized by a relatively short U–C separation of 2.383(6) \AA . This distance is approximately 0.19 \AA shorter than the U–C(CNEt) separation of 2.57(3) \AA in $(Me_3SiC_5H_4)_3U(CNEt)$, where significant π -backbonding has been postulated,^{6,7} and is in accord with the strong U–CO bonding interaction suggested by the IR data. Finally, the C–O distance at 1.142(7) \AA is similar to that found in $(C_5Me_5)_2Ti(CO)_2$ (1.149 \AA).¹⁵

In conclusion, we have demonstrated that, under appropriate conditions and with a suitable choice of coligands, uranium carbonyl complexes can be isolated. Our results question the current view of actinide carbonyls as unstable or unisolable entities. Preliminary results indicate that the electron-rich metal center in **2** may give rise to a correspondingly rich and diverse chemistry, an area which we are now exploring. In addition, we are presently extending this chemistry to other M–Cp'–based complexes (M = Th, U) as well as to mixed-ring ligand systems.

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Supplementary Material Available: Tables of positional parameters, thermal parameters, bond lengths and bond angles, and crystal data for **3** (5 pages); observed and calculated structure factors (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) Data were collected at 120 K on a FAST-TV area detector using an OXFORD CRYOSYSTEMS cryostat and processed by MADNESS software. Crystal data for **3**: monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$, $a = 10.581(8) \text{ \AA}$, $b = 10.998(4) \text{ \AA}$, $\beta = 93.33(3)^\circ$, $V = 2448(2) \text{ \AA}^3$, $R_1 = 0.0318$, $wR_2 = 0.0689$ for 3696 reflections with $I > 2\sigma(I)$ and 283 parameters at 120 K.

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