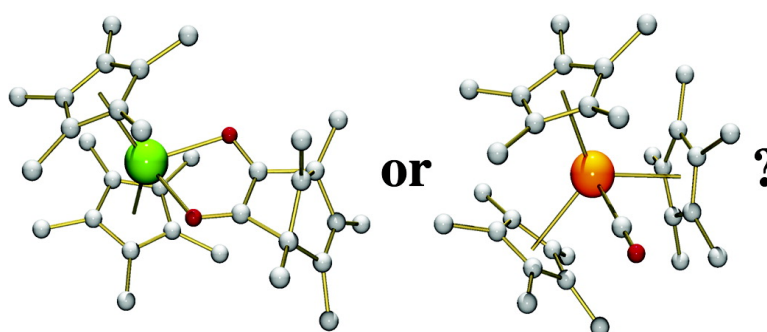Article

Comparative Reactivity of Sterically Crowded nf (CMe)Nd and (CMe)U Complexes with CO: Formation of a Nonclassical Carbonium Ion versus an f Element Metal Carbonyl Complex

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Comparative Reactivity of Sterically Crowded nf³ (C₅Me₅)₃Nd and (C₅Me₅)₃U Complexes with CO: Formation of a Nonclassical Carbonium Ion versus an f Element Metal Carbonyl Complex

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Abstract: Sterically crowded isoelectronic nf³ (C₅Me₅)₃M complexes of neodymium and uranium, compounds which have unconventionally long metal ligand distances, are found to react very differently with CO as a substrate. The 4f³ complex (C₅Me₅)₃Nd reacts with CO to form a nonclassical carbonium ion complex, (C₅Me₅)₂Nd(O₂C₇Me₅), which contains a three-coordinate planar carbon. (C₅Me₅)₃U reacts with CO to form an even more crowded CO adduct through a reaction type never observed before for (C₅Me₅)₃M compounds. The rare uranium carbonyl complex, (C₅Me₅)₃U(CO), has ν_{CO} = 1922 cm^{-1} and a U−C(CO) distance of 2.485(9) Å.

Introduction

Recent efforts in f element chemistry have provided a new class of compounds, the (C₅Me₅)₃M complexes, which have unusually long metal ligand bonds.[1−4] Although long metal ligand distances are known in f element complexes containing agostic interactions,[5] they generally involve only one or two interactions and the rest of the bonds are normal and predictable based on ionic radii.[6−10] In contrast, in the sterically crowded (C₅Me₅)₃M complexes, all of the metal ligand bonds are longer than conventional distances. The isolation of over 14 crystallographically characterized (C₅Me₅)₃M complexes[1] demonstrates that an entire series of long bond organometallics can be isolated under the proper conditions.

These sterically crowded complexes provide an opportunity to develop new reaction chemistry with traditional components. For example, the (C₅Me₅)₃M compounds contain pentamethylcyclopentadienyl ligands that are not simple spectator ligands. These C₅Me₅ rings have unusual reactivity in that they participate in reactions traditionally found for alkyl ligands[11]

(e.g., small molecule insertion chemistry, olefin polymerization, hydrogenation, and ring opening) as well as reduction chemistry via a (C₅Me₅)$^{-1}$/(C₅Me₅) redox couple in a reaction called sterically induced reduction.[12]

Recent synthetic advances have provided the first opportunity to compare isoelectronic 4f versus 5f reactivity in this unusual class of complexes.[2,3] Comparisons of lanthanide versus actinide reactivity are of interest in terms of separation of highly radioactive actinides from lanthanide components in spent nuclear fuel.[13−15] Variations in reactivity can depend on the difference in the radial extension of the 4f versus 5f valence orbitals and the accompanying effects.[16] This approach has led to numerous recent calculations evaluating 4f versus 5f bonding.[17−23] Unfortunately, because few isomorphous and isoelectronic 4fⁿ/5fⁿ pairs exist, it is difficult to make direct experimental comparisons of lanthanide versus actinide reactivity.[24−29]

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We report here a direct comparison of the nf^3 systems, (C$_5$Me$_5$)$_3$Nd and (C$_5$Me$_5$)$_3$U, using as a substrate CO, which has independently interesting f element chemistry. Historically, actinide/CO complexes were of interest in isotope separation because M(CO)$_x$ complexes of transition metals are volatile.[30] However, the hard oxophilic f elements typically have a low binding affinity for the soft π bonding CO ligand, and carbonyl complexes did not readily form. Instead, CO generally reacts with f element complexes via insertion into M$-$C and M$-$H bonds.[31–40] To date, only a few f element metal carbonyl complexes have been spectroscopically observed,[29,41,42] and only one molecular carbonyl complex of an f element, (C$_5$Me$_4$H)$_3$-U(CO), has been crystallographically characterized.[42] In addition to the 4f^3 versus 5f^3 reactivity comparisons and f element CO chemistry described here, we also report a new type of reaction for the sterically crowded class of (C$_5$Me$_5$)$_3$M complexes.

Experimental Section

The complexes described in the following are extremely air and moisture sensitive. Synthesis and manipulations of these compounds were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. THF, toluene, and hexanes were saturated with Ar and passed through a GlassContour column.[43] Benzene-d_6 was distilled over a NaK alloy and benzophenone. Ultrahigh purity CO (Airgas) was passed through a microporous fiberglass purification column (Airgas). (C$_5$Me$_5$)$_3$Nd[2] and (C$_5$Me$_5$)$_3$U[3] were prepared as previously described. NMR experiments were conducted with a Bruker 400 MHz spectrometer. IR samples were analyzed either as thin films using an ASI ReactIR1000 or as KBr pellets, Nujol mulls, or in C$_6$H$_6$ solutions using a Perkin-Elmer 2000 FT-IR. Elemental analyses were provided by Desert Analytics or Analytische Laboratorien.

(C$_5$Me$_5$)$_2$Nd(O$_2$C$_7$Me$_5$), 1. In an argon-filled glovebox free of coordinating solvents, a Fisher Porter high-pressure reaction vessel was charged with (C$_5$Me$_5$)$_3$Nd[2] (70 mg, 0.127 mmol), 10 mL of toluene, and a stir bar. The apparatus was attached to a vacuum manifold, evacuated to the vapor pressure of the solvent, and pressurized with 20 psi of CO. After several minutes, the olive-green solution turned

dark red. After an hour, the stirred solution was a mint-green color. The reaction was stirred for an additional 17 h, and no further color change was observed. The vessel was depressurized and brought into the glovebox. The solvent was removed by rotary evaporation to yield **1** as a blue-green powder (74 mg, 96%) (similar results were obtained when this reaction was run at 1 atm). X-ray quality crystals of **1** were grown from a toluene solution at −45 °C after 24 h. ^{1}H NMR (C$_6$D$_6$): δ 6.4 (s, 15H, C$_5$Me$_5$), 6.0 (s, 15H, C$_5$Me$_5$), 3.1 (s, 3H, CH$_3$), 2.0 (s, 6H, CH$_3$), −5.2 (s, 6H, CH$_3$). ^{13}C (C$_6$D$_6$): δ −12.7, −11.5, 1.4, 6.8, 11.5, 67.6, 70.1, 136.9, 284.4, 289.0 [(C$_5$Me$_5$)$_2$Sm(O$_2$C$_7$Me$_5$) also displayed only 10 of the expected 11 signals].[40] IR (KBr): 2964 s, 2902 s, 2851 s, 1441 s, 1402 w, 1370 s, 1302 w, 1107 m, 1066 w, 1015 w, 974 w, 723 w, 692 w, 635 w cm^{-1}. Anal. Calcd for C$_{32}$H$_{45}$-NdO$_2$: C, 63.43; H, 7.49; Nd, 23.8. Found: C, 62.74; H, 7.66; Nd, 24.50.

(C$_5$Me$_5$)$_3$U(CO), 2. In an argon-filled glovebox free of coordinating solvents, a flask fitted with a high-vacuum greaseless stopcock was charged with a solution of (C$_5$Me$_5$)$_3$U[3] (62 mg, 0.096 mmol) dissolved in toluene (ca. 3 mL). The flask was attached to a vacuum line, and the solution was degassed by freeze−pump thawing (3×). Excess CO (1 atm) was introduced into the flask, and within 6 h a microcrystalline black solid precipitated. The solvent was removed under vacuum, and **2** was isolated (61 mg, 95%). X-ray quality crystals of **2** were grown under 1 atm of CO from a saturated solution of **2** dissolved in a ca. 3:1 mixture of toluene/hexane at room temperature within 12 h. ^{1}H NMR (C$_6$D$_6$, 298 K): δ 0.25 (s, 15H, C$_5$Me$_5$). IR (KBr): 2966 s, 2905 s, 2855 s, 1922 vs, 1438 m, 1377 m, 1257 w, 1066 w, 1016 m, 946 w, 803 w, 675 w cm^{-1}. IR (C$_6$H$_6$ solution): 1925 (ν_{CO}) cm^{-1}. Anal. Calcd for C$_{31}$H$_{45}$OU: C, 55.46; H, 6.70; U, 35.46. Found: C, 55.77; H, 6.50; U, 35.57.

X-ray Data Collection, Structure Solution, and Refinement for 1. A crystal of approximate dimensions 0.20 × 0.20 × 0.50 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[44] program package was used to determine the unit-cell parameters and for data collection. The raw frame data were processed using SAINT[45] and SADABS[46] to yield the reflection data file. Subsequent calculations were carried out using the SHELX-TL[47] program. The systematic absences were consistent with the orthorhombic space group *Pnma*, which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[48] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, R1 = 0.024 and wR2 = 0.0507 and GOF = 1.215 for 262 variables refined against all 3710 data. **1** is isomorphous with previously reported (C$_5$Me$_5$)$_2$Sm-(O$_2$C$_7$Me$_5$).[40]

X-ray Data Collection, Structure Solution, and Refinement for 2. A brown crystal of approximate dimensions 0.18 × 0.19 × 0.30 mm was mounted on a glass fiber and handled as described for **1**. The systematic absences were consistent with the hexagonal space group *P*6$_3$/*m*, which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[48] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a site of $\bar{6}$ symmetry. The carbonyl ligand was disordered. Atoms C(7) and O(1) were included with partial site-occupancy-factors (1/6) to

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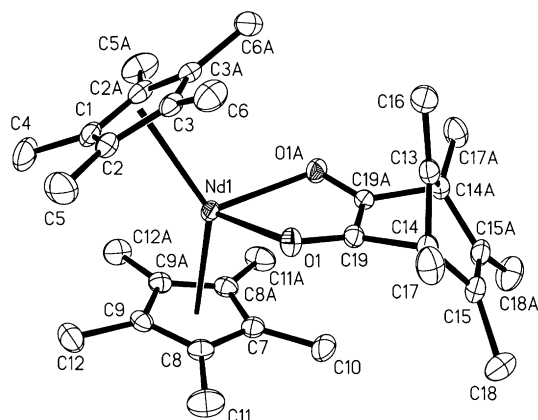(48) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

Figure 1. A thermal ellipsoid plot of **1**, (C₅Me₅)₂Nd(O₂C₇Me₅).

account for an equal distribution over two sites. At convergence, wR2 = 0.0425 and GOF = 1.148 for 58 variables refined against 1167 data. (As a comparison for refinement on F, R1 = 0.0161 for those 1098 data with $I > 2.0\sigma(I)$.)

Results

Olive-green (C₅Me₅)₃Nd[2] reacts with CO in toluene to form a hexane soluble mint-green compound, **1**, which can be isolated in greater than 95% yield. Although Nd(III) is paramagnetic, the ¹H NMR spectrum of **1** contained five observable signals in a 5:5:2:2:1 ratio, consistent with CO insertion into a Nd−C(η^1-C₅Me₅) bond. To our knowledge, the only published example of CO inserting into a M−C₅Me₅ bond occurs when CO reacts with (C₅Me₅)₃Sm to form the nonclassical carbonium ion complex, (C₅Me₅)₂Sm(O₂C₇Me₅).[40] The intensities of the ¹H NMR signals as well as the number of peaks in the ¹³C NMR spectrum and the IR absorptions for **1** are consistent with the corresponding data for (C₅Me₅)₂Sm(O₂C₇Me₅).

An X-ray diffraction study revealed that **1** was (C₅Me₅)₂Nd-(O₂C₇Me₅) (eq 1, Figure 1), a complex isomorphous with the previously reported samarium compound.

$$ \text{(1)} $$
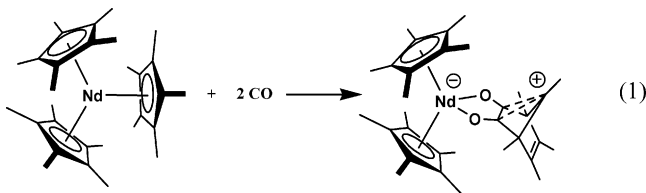
Because Sm and Nd differ in radius by only 0.031 Å,[49] it is not surprising that the bond distances and angles in both structures are identical within experimental error. The Nd−C(C₅-Me₅) bond distances in **1** range from 2.740(2) to 2.781(3) Å. These are conventional distances as expected for a complex that does not have the steric crowding of its precursor (C₅Me₅)₃Nd, which has Nd−C(C₅Me₅) bonds ranging from 2.8146(13) to 2.927(2) Å.[2]

As in (C₅Me₅)₂Sm(O₂C₇Me₅), **1** appears to contain a nonclassical carbonium ion[50,51] involving the trigonal planar C(13). No hydrogen was observed near C(13), and the angles around C(13) sum to 359.94°. C(13) is oriented toward the C(19)−C(19a) double bond in that C(13)−C(14)−C(19) is 76.38(14)° while
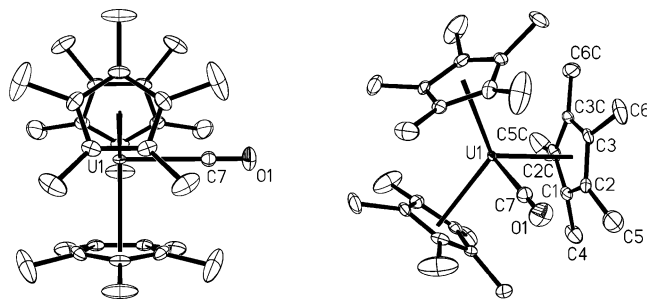
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Figure 2. Two orientations of (C₅Me₅)₃U(CO) with thermal ellipsoids drawn to 50% probability.

C(13)−C(14)−C(15) is 105.0(2)°. The 1.430(3) Å C(19)−C(19A) bond is longer than the C(15)−C(15A) bond, 1.329(4) Å, which is consistent with delocalization of the electron pair to stabilize the carbocationic center at C(13).[52] These structural data are very similar to those in the bridged bishomocyclopropenyl cation, 2,3-dimethyl-7-phenyl-2-norbornen-7-ylium hexafluoroantimonate(V), [C₇H₆(Me)₂Ph]⁺[SbF₆]⁻,[52] as well as its neutral boron analogue, [BC₆Me₆Ph(BPhC₂Me₂)],[53,54] each of which have the bridgehead atom analogous to C(13) tipped toward the unsaturated bond analogous to C(19)−C(19a).

In contrast to the neodymium reaction, addition of CO to brown solutions of (C₅Me₅)₃U[3] in benzene at room temperature caused an immediate color change to almost black. Monitoring the reaction by ¹H NMR spectroscopy showed quantitative conversion of (C₅Me₅)₃U to a new complex, **2**, after 6 h. Isolation of **2** as a microcrystalline solid was achieved upon removal of solvent under vacuum, but **2** is not stable as a solid for extended time periods under vacuum. The ¹H NMR spectrum of **2** differed from that of **1** in that only a single resonance at δ 0.25 ppm was observed, a result inconsistent with CO insertion into a U−(C₅Me₅) bond to form a 5f³ analogue of **1**. The IR spectrum of **2** showed a strong absorption at 1922 cm⁻¹ in a KBr pellet and at 1917 cm⁻¹ as a Nujol mull. This absorption was assigned as a CO stretch because the KBr spectrum of the ¹³CO analogue of **2** displayed an absorption at 1877 cm⁻¹, close to the predicted value of 1879 cm⁻¹.

Crystals of **2** suitable for X-ray crystallographic analysis were grown at room temperature under 1 atm of CO, and the structural analysis identified **2** as the uranium carbonyl (C₅Me₅)₃U(CO), Figure 2, eq 2. The U−C(C₅Me₅) bond distances in **2** (range,

$$ \text{(2)} $$
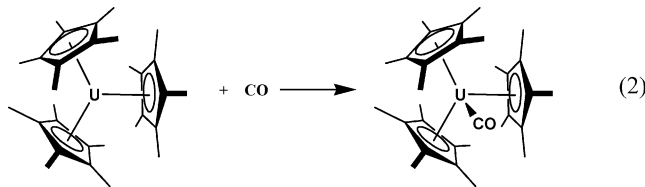
2.821(2)−2.927(3) Å; average 2.85(4) Å, U−ring centroid 2.587 Å) are similar to the large distances in other sterically crowded (C₅Me₅)₃M complexes.[1] The 120° ring centroid−U−ring centroid angle and 90° ring centroid−U−C(CO) angles in **2** are identical to those in the sterically crowded (C₅Me₅)₃UCl,[55] (C₅-

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Me$_5$)$_3$UF,[55] and (C$_5$Me$_5$)$_3$ThH.[56] The CO ligand is disordered over the molecular mirror plane that bisects the three symmetrically equivalent C$_5$Me$_5$ rings, a common feature in (C$_5$-Me$_5$)$_3$MZ complexes. The U$-$C$-$O angle is rigorously 180° because CO lies on a symmetry axis and the 2.485(9) Å U$-$C(CO) distance is considerably longer than the only other U$-$C(CO) distance in the literature, 2.383(6) Å in (C$_5$Me$_4$H)$_3$U-(CO).[42] Within the error limits on the 1.13(1) Å C(7)$-$O bond, the distance is indistinguishable from the C$-$O bond length in (Me$_4$C$_5$H)$_3$U(CO), 1.142(7) Å,[42] and free CO, 1.128 Å.[57] Refinement of the X-ray data on **2** as an isocarbonyl,[58,59] (C$_5$-Me$_5$)$_3$U(OC), gave poorer agreement than the carbon bound model. This is consistent with the prediction made by Bursten and co-workers that the isocarbonyl would be less stable and that the U(CO) binding would be preferred in the theoretical (C$_5$H$_5$)$_3$U(CO) complex.[60]

The fact that **2** has a ν_{CO} absorption 40 cm^{-1} lower than the ν_{CO} = 1976 cm^{-1} of (Me$_3$SiC$_5$H$_4$)$_3$U(CO),[41] the first example of a spectroscopically characterized molecular uranium carbonyl, is consistent with the greater electron-donating ability of the C$_5$Me$_5$ ligand relative to Me$_3$SiC$_5$H$_4$. However, one would also expect **2** to have a lower ν_{CO} than observed for (C$_5$Me$_4$H)$_3$U-(CO), ν_{CO} = 1880 cm^{-1}. The fact that the ν_{CO} in **2** is approximately 40 cm^{-1} higher than that in the latter compound may be a reflection of the unusually long U$-$C(CO) bond in **2**.

The binding of carbon monoxide to (C$_5$Me$_5$)$_3$U is reversible. The loss of CO from **2** in the solid state at $<10^{-3}$ atm was monitored by IR spectroscopy by disappearance of the CO signal. The half-life for the complex is approximately 12 h. Complex **2** also loses CO in C$_6$D$_6$ to form (C$_5$Me$_5$)$_3$U under both Ar and H$_2$. Additionally, no insertion into a U$-$C(C$_5$Me$_5$) bond was observed even at increased CO pressure (up to 80 psi) or when irradiated with a medium-pressure mercury lamp.

Discussion

The reaction of (C$_5$Me$_5$)$_3$Nd with CO to form (C$_5$Me$_5$)$_2$Nd-(O$_2$C$_7$Me$_5$), **1**, is directly parallel with the reactivity of (C$_5$Me$_5$)$_3$-Sm. The isolation of **1** shows that formation of a nonclassical carbonium ion complex was not specific to samarium or to any special chemistry that could arise from Sm(II) intermediates.[61] Likewise, the stability and isolability of **1** demonstrate that the formation of a nonclassical carbonium ion complex in solution at room temperature is also not limited to the single samarium example. In retrospect, the similarity in size of Nd and Sm and the accompanying similarity in steric crowding of their (C$_5$Me$_5$)$_3$M complexes suggests that they should react analogously with CO. However, the reaction of the sterically similar (C$_5$Me$_5$)$_3$U is different.

Despite the isomorphous nature of these sterically crowded f element complexes, whose reactivity is often dominated by steric factors, parallel 4f^3 and 5f^3 reactivity is not observed for

(C$_5$Me$_5$)$_3$Nd and (C$_5$Me$_5$)$_3$U. Hence, the reaction of (C$_5$Me$_5$)$_3$U with CO to form (C$_5$Me$_5$)$_3$U(CO), **2**, not only reveals a rare example of a crystallographically characterizable molecular f element carbonyl, but it also shows that there can be major differences in reactivity between 4f versus 5f isoelectronic and isomorphous compounds in this sterically crowded class.

Typical variations in 4f and 5f reactivity involve small degrees of difference in similar reactions. Most typically, this involves differences in stability constants for coordination of polydentate ligands.[14,63-65] Equations 1 and 2 comprise a rare case in which the 4f versus 5f reaction chemistry is significantly different. The difference in reactivity of (C$_5$Me$_5$)$_3$Nd and (C$_5$Me$_5$)$_3$U with CO is consistent with the common assumptions that the actinides are less ionic and softer than the lanthanides, and that the 5f orbitals have a greater radial extension than the 4f orbitals.[16]

Equation 2 also represents a new type of reaction available to (C$_5$Me$_5$)$_3$M complexes. These sterically crowded molecules had not previously been observed to undergo adduct formation, eq 3. These crowded molecules typically react to reduce steric

$$(C_5Me_5)_3M + L \rightarrow (C_5Me_5)_3ML \qquad (3)$$

congestion, not increase it. Interestingly, the U$-$C(C$_5$Me$_5$) bond lengths in (C$_5$Me$_5$)$_3$U and (C$_5$Me$_5$)$_3$U(CO) are similar. Hence, CO adduct formation does not strongly perturb the steric crowding in the already reactive and sterically strained (C$_5$-Me$_5$)$_3$U unit.

Equation 2 also demonstrates important steric differences between (C$_5$Me$_5$)$_3$U and (C$_5$Me$_4$H)$_3$U[29] despite a difference of only one methyl substituent per ring. (C$_5$Me$_4$H)$_3$U has trigonal planar C$_5$Me$_4$H rings,[29] and coordination of CO involves a ligand rearrangement to a pseudotetrahedral geometry in (C$_5$Me$_4$H)$_3$-U(CO).[42] This occurs because the less crowded H positions in each of the rings can tip toward the adjacent rings, thus accommodating the incoming CO ligand. This is not observed in the fully substituted (C$_5$Me$_5$)$_3$U. As a consequence, **2** has a longer U$-$CO bond, a higher ν_{CO} frequency, and requires 6 h for complete reactions, whereas (C$_5$Me$_4$H)$_3$U reacts instantaneously with CO.

These results suggest that (C$_5$Me$_5$)$_3$U is unique in that it is sterically crowded enough to participate in CO insertion chemistry like (C$_5$Me$_5$)$_3$Ln complexes, but its 5f^3 U(III) electron configuration allows adduct formation to occur. It is electronically similar to (C$_5$Me$_4$H)$_3$U, but its more sterically crowded nature allows it to do similar chemistry without ligand rearrangement or distortion of its structure. This allows (C$_5$Me$_5$)$_3$U to make adducts of traditionally weakly bonding ligands at distances even greater than the rarely observed U$-$C bond in (C$_5$Me$_4$H)$_3$U(CO).

Conclusion

The isoelectronic 4f^3 and 5f^3 Nd(III) and U(III) centers display significantly different reaction chemistry with CO in their isomorphous (C$_5$Me$_5$)$_3$M complexes. Hence, this special class of sterically crowded molecules allows a major differentiation

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of lanthanide versus actinide reaction chemistry. The formation of $(C_5Me_5)_2Nd(O_2C_7Me_5)$ shows that stabilization of nonclassical carbonium ions is not limited to a single samarium complex and that the unusual insertion chemistry of the typically ancillary C_5Me_5 ligand is still available to $(C_5Me_5)_3Nd$, a complex known to be less reactive than $(C_5Me_5)_3Sm$.[66] The formation of $(C_5Me_5)_3U(CO)$ demonstrates that simple adduct formation is another viable reaction pathway for $(C_5Me_5)_3M$ complexes. The structure of $(C_5Me_5)_3U(CO)$ shows that nontraditional f element ligands such as CO can bind to f elements even at long distances if the proper coordination environment is present. The unique

nature of $(C_5Me_5)_3U$ should make it ideal to study other f element small molecule interactions. ∎

Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles; listing of observed and calculated structure factor amplitudes for compounds **1** and **2** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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