As shown in Scheme I, operation of the allowed [1,5]-sigmatropic shift could explain both experimental observations. Indeed this mechanism interchanges enantiomeric asymmetric forms in a single step whereas the same process in **1b** would give a higher energy alternate symmetric isomer, thus accounting for the higher energy (slower rate) for the rearrangement in **1b**. It is also clear that the allowed process would exchange the two axial carbonyl groups of the *mer* isomer **1a** in apparent harmony of the experimental results. However a closer examination of the figure reveals that, contrary to the requirements of the [1,5]-sigmatropic shifts, the two processes (ring-whizzing and CO exchange) are not coupled. For instance in the −29 °C spectrum the carbon signals of **1a** have virtually coalesced, whereas the carbonyl resonances show little broadening. Since it does not occur via symmetry-allowed [1,5]-shifts, a simple explanation for the low-temperature ring-whizzing motion in both **1a** and **1b** could be a 1,2-sliding movement of the rigid Os(CO)$_3$SnPh$_3$ moiety over the π-surface of the cycloheptatrienyl ring[7] (left-hand side of Scheme I). This then leaves the large difference in fluxionality between **1a** and **1b** unanswered. Also the specific exchange of only two carbonyls in **1a** at higher temperatures is surprising and implies perhaps the onset of the "allowed" [1,5]-sigmatropic shifts.

Work is underway to fully quantify the energetics of the different exchange processes and to resolve the ambiguities and questions raised by the experimental results concerning the applicability of the symmetry rules to this type of (η^3-C$_7$H$_7$)ML$_4$ compounds.

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(7) (a) Confirmation of the 1,2-metal shift in **1a** has been secured by both spin saturation transfer (Kiel, G.-Y., unpublished results) and selective inversion-recovery experiments (Muhandiram, D. R.; McClung, R. E. D., personal communication). (b) The slower coalescence of the carbon-4 signal in **1b** (Figure 1, T = −29 °C) indicates that 1,2-metal shift operates in this isomer as well. Symmetry rule on the other hand would predict an overall 1,3-metal shift since two consecutive [1,5]-sigmatropic shifts are required for return to the original molecule. Thus it appears that the high energy of the putative alternate symmetric intermediate aborts the Woodward–Hoffmann path and opens up simple 1,2-slide of the metal in **1b** also.

Uranium–Carbon Multiple-Bond Chemistry. 9.[1] The Insertion of Ph—N=C=O into the Uranium–Carbon Bond of Cp$_3$U=CHP(Ph)(R)(Me) To Form Cp$_3$U[(NPh)(O)CCHP(Ph)(R)(Me)]

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Summary: The reaction of Cp$_3$U=CHP(CH$_3$)(R)(C$_6$H$_5$) (**1a**, R = CH$_3$; **1b**, R = C$_6$H$_5$) with Ph—N=C=O gives Cp$_3$U[(NPh)(O)CCHP(CH$_3$)(C$_6$H$_5$)(R)] (**2a**, R = CH$_3$; **2b**, R = C$_6$H$_5$). The crystal structure of **2a**, space group $P2_1/c$ with a = 13.402 (2) Å, b = 11.653 (1) Å, c = 23.209 (3) Å, β = 112.18 (1)°, V = 3357.3 (8) Å^3, Z = 4, R = 5.79%, and R_G = 6.48%, has been determined. It is the first Cp$_3$UXY complex with a four-membered chelate ring to be structurally characterized.

Carbon dioxide inserts into both transition-metal-[2-4] and actinide–carbon[5] single bonds to form new carbon–carbon single bonds, thus producing carboxylates. The insertion of other hetereocumulenes, including isocyanates, R—N=C=O, that are analogous to CO$_2$ are also important.[6] In contrast to the extensive chemistry with metal–carbon single bonds, very little is knwon about the behavior of CO$_2$ or its analogues with metal–carbon multiple bonds. While the addition of hetereocumulenes to matel–carbon multiple bonds[7] has been reported and an insertion occurs during a rather complex reaction of CyNCO with a tungsten alkylidene,[8] no compound that results from the insertion of a single heterocumulene molecule into a structurally characterized metal–carbon multiple bond has yet been described.

We are interested in utilizing the oxygen and nitrogen affinity of actinides to activate small molecules. In this regard we have determined that the α-carbon atom in Cp$_3$U=CHPMePhR (Me = CH$_3$; Ph = C$_6$H$_5$; **1a**, R = Me; **1b**, R = Ph) is a strong nucleophile[9] and that polar-unsaturated molecules including CO,[10] RCN,[11] RNC,[12] and metal carbonyls[1,13] will insert into the uranium carbon multiple bond of **1**. A common feature in all these insertion reactions is the formation of a complex in which the heteroatom is tightly bound to uranium and which contains a carbon–carbon multiple bond formed from the four electrons of the U=C bond. The resulting metal–carbonyl insertion products will undergo further reactions which include C–O bond cleavage,[14] carbonyl coupling,[15] and metal migration.[1] On the basis of this chemistry we expected that CO$_2$, or CO$_2$ analogues such as R—N=C=O, might also insert into the uranium–carbon multiple bond of **1**. Such reactions would be particularly interesting because they would represent a new facet of f-element–CO$_2$ and related chemistry.

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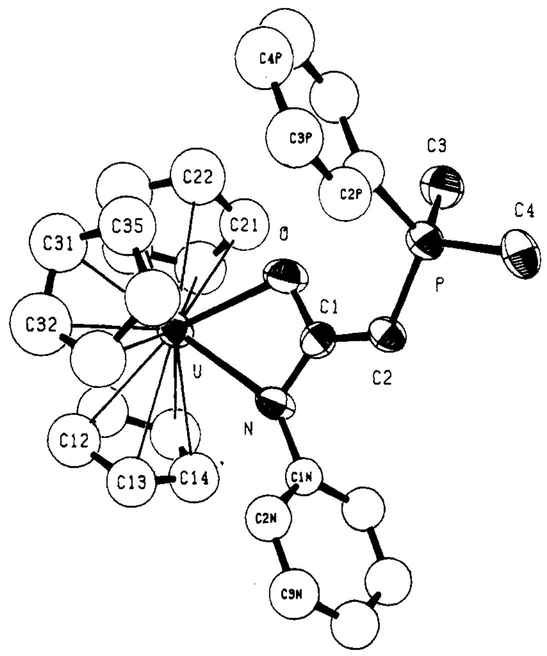


Figure 1. An ORTEP drawing of $Cp_3U[(NPh)(O)CCHPMe_2Ph]$ (**2a**). Some important bond distances (Å) and angles (°): U–Cp(mean), 2.84 (2); U–O, 2.34 (1); U–N, 2.45 (1); O–C(1), 1.33 (2), N–C(1), 1.35 (2); C(1)–C(2), 1.40 (2); P–C(2), 1.71 (1); P–C(3), 1.82 (2); N–U–O, 55.2 (3); N–C(1)–O, 112 (1); C(1)–O–U, 98.8 (8); C(1)–N–U, 93.5 (8); C(1)–C(2)–P, 118 (1).

The reaction of equimolar amounts of Ph—N=C=O and Cp_3U=CHPMe$_2$Ph for 5 h at −78 C in toluene solution followed by warming to room temperature and evaporation of the solvent produces a brown solid, **2a**. Upon recrystallization from a saturated toluene solution to which a few drops of heptane were added, **2a** was obtained in 69% yield. A similar reaction between Cp_3U=CHPMePh$_2$ and Ph—N=C=O produces **2b**.[16] The structure of **2a** was determined by X-ray crystallography[17] (space group $P2_1/c$, unit cell parameters a = 13.405 (2) Å, b = 11.653 (1) Å, c = 23.209 (3) Å, β = 112.18 (1)°, V = 3357.3 (8) Å^3). A summary of the crystal parameters, data collection, and refinement and lists of bond distances and angles, positional and thermal parameters, and the observed and calculated structure factors are given, respectively, in Tables I–IV (supplementary material).

The structure of **2a** is illustrated in Figure 1. The ligand coordinates to the pyramidal Cp_3U^+ group in a manner that minimizes steric interaction (Figure 2). The U–O bond distance, 2.34 (1) Å, is longer than 2.27 (1) Å in $Cp_3U(\eta^2\text{-OC})CHPMePh_2$[10] and 2.05 (1) Å in $[(Me_5C_5)_2U(OMe)]_2PH$[18] but close to 2.373 (5) Å for *tert*-butoxy groups bridged between two uranium atoms in $U_3(O)(OCMe_3)_{10}$[19] and 2.363 (8) Å in $(SCN)_4U(OC(Me)N(i\text{-}Pr)_2)_4$.[20] The U–N separation, 2.45 (1) Å, is similar to the U–N distances of 2.46 (1) and 2.57 (1) Å of the bridging diethylamido groups in $U(NEt_2)_4$,[21] of 2.40 (1) and 2.36 (1) Å in $Cp_3U(N_2C_3H_3)$,[22] and of 2.44 (1) Å in $(SCN)_4U(OC(Me)N(i\text{-}Pr)_2)_4$.[20] The U–N and U–O distances in **2a** are thus consistent with single bonds to donor atoms that carry a partial negative charge. The O—C(1) distance, 1.33 (2) Å, is longer than a typical C=O distance, 1.23 Å, but shorter than an sp^3-hybridized C—O single bond length, 1.43 Å. Likewise, the N–C(1) bond length, 1.35 (2) Å, lies between single-, 1.47 Å, and double-bond, 1.26 Å, distances. Thus both O–C(1) and N–C(1) contain some multiple-bond character. Multiple or ylidic bond character is indicated by the P–C(2) bond distance, 1.71 (1) Å, which is significantly shorter than 1.82 (2) and 1.83 (2) Å for the two P–Me bonds and 1.831 (8) Å for P–C(1P). The C(1)–C(2) distance, 1.40 (2) Å, also indicates multiple-, C=C, bond character. In view of these structural parameters, the bonding in **2** (**2a**, R = Me; **2b**, R = Ph) can be described by

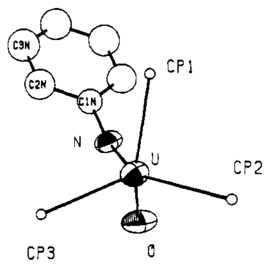
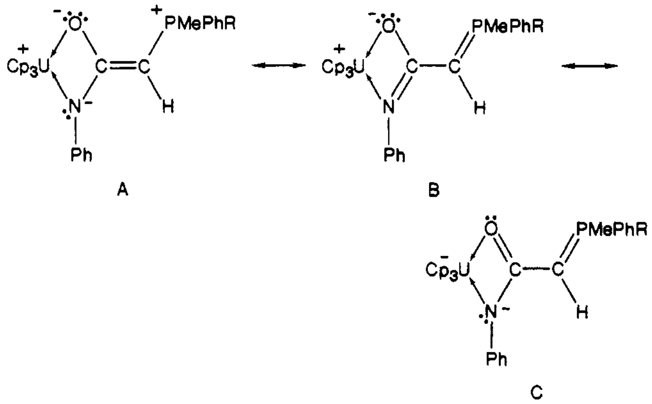


Figure 2. An ORTEP drawing of $Cp_3U[(NPh)(O)CCHPMe_2Ph]$ (**2a**), viewed down the U–C(1) axis. Many atoms have been deleted for clarity. CP represents the centroid of a cyclopentadienide group.



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[16] **2a**: ^1H NMR (toluene-d_8, 300 MHz, 23 °C, ppm): PPh (ortho), 16.96 (dd, 2 H, J_{HCCH} = 7 Hz, J_{PCCH} = 12 Hz), PPh (meta), 11.00 (t, 2 H, J_{HCCH} = 7 Hz), PPh (para), 10.27 (t, 1 H, J_{HCCH} = 7 Hz), PMe, 14.35 (d, 6 H, J_{PCH} = 13 Hz) NPh(para), 3.40 (t, 1 H, J_{HCCH} = 7 Hz), NPh(meta), 2.50 (t, 2 H, J_{HCCH} = 7 Hz), NPh(ortho), −16.06 (d, 2 H, J_{HCCH} = 7 Hz), PCH=, 1.82 (d, 1 H, J_{PCH} = 25 Hz), Cp_3U, −10.69 (s, 15 H); IR (thin film on NaCl plates; 1100–1600 cm^{-1}: 1591 (w), 1485 (s, sh), 1474 (s), 1360 (m), 1287 (w). **2b**: ^1H NMR (toluene-d_8, 300 MHz, 23 °C, ppm): PPh(ortho), 16.04 (dd, 4 H, J_{HCCH} = 7 Hz, J_{PCCH} = 12 Hz), PPh(meta), 10.66 (t, 4 H, J_{HCCH} = 7 Hz), PPh(para), 10.00 (t, 2 H, J_{HCCH} = 7 Hz), PMe, 15.73 (d, 3 H, J_{PCH} = 13 Hz), NPh(para), 3.56 (t, 1 H, J_{HCCH} = 7 Hz), NPh(meta), 2.74 (t, 2 H, J_{HCCH} = 7 Hz), NPh(ortho), −15.25 (d, 2 H, J_{HCCH} = 7 Hz), PCH=, 1.85 (d, 1 H, J_{PCH} = 24 Hz), Cp_3U, −10.69 (s, 15 H). Satisfactory analysis was not obtained for 2. Even crystallographic quality crystals yielded low values for nitrogen and carbon.

[17] A single crystal of **2a** was mounted in a glass capillary and sealed under nitrogen. X-ray data, collected at ambient temperature using a Syntex P1 diffractometer, was corrected for absoption by using PROCESS, a computer program for empirical absorption correction of X-ray data, obtained from R. Bau, University of Southern California, and modified by M. Carrie, University of Hawaii, 1986. The heavy atom was located by using MULTAN-80, a system of computer programs for direct methods solution of crystal structures from X-ray data by P. Main, 1980, and the remaining atoms were located in series of difference Fourier maps and least-squares refinements using SHELX-76, a system of computer programs for X-ray structure determination of G. M. Sheldrick, 1976. In **2a** the Cp groups, the phenyl groups, and the toluene solvate molecule were refined isotropically as rigid bodies by using the standard parameters contained in SHELX-76: all remaining atoms were refined anisotropically to yield the final error indices of R = 5.79% and R_G = 6.48%.

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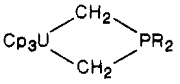
where A is the major form but where B and C also contribute significantly. As predicted by this bonding description O, N, C(1), C(2), and C(1N) are coplanar (Table V (supplementary material)). A related compound has been prepared by the reduction of Ph—N=C=O with $(MeC_5H_4)_3U$.[23] In this complex, $[(MeC_5H_4)_3U]_2(\mu\text{-}\eta^1,\eta^2\text{-}PhNCO)$, the U–N, 2.36 (2) Å, N–C, 1.31 (2) Å, and O–C, 1.36 (2) Å, distances are indistinguishable from those in **2a**.

There are not many Cp_3UXY complexes.[22,24] Some with monodentate, trans X and Y ligands have been reported,[24–28] but, with the exception of those with three-membered chelate rings,[10,11,22,23,29–31] no *cis*-Cp_3UXY complexes have been structurally characterized.[32] Since a theoretical model that considers steric effects[36] predicts that Cp_3U complexes of both *trans*-Cp_3UXY and *cis*-Cp_3UXY complexes, containing a three-membered chelate ring, will be more stable than Cp_3U complexes with larger chelate rings, the characterization of **2a** as the first *cis*-Cp_3UXY complex with a four membered chelate ring is particularly significant. In accord with the predictions that molecules of this type should be very sterically crowded,[36] the bite distance in the ligand, 2.22 (2) Å, is short, the average C(Cp)–U distance, 2.84 (2) Å, is long, and the Cp(centroid)–U–Cp(centroid) angles have been compressed from about 117°, typical for Cp_3U–X complexes, to 112°, 115°, and 110°.

We have earlier postulated[37] that



is an intermediate in the formation of $Cp_3U{=}CHP(Me)(R)_2$ from Cp_3UCl and $Li(CH_2)(CH_2)PR_2$. The existance of the four-membered chelate ring in **2** supports this hypothesis.

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Supplementary Material Available: Table I, crystal, data collection, and reduction parameters, Table II, bond distances and bond angles, Table III, positional and thermal parameters for $Cp_3U[(NPh)(O)CCHPMe_2Ph]{\cdot}C_7H_8$, and Table V, distances from the O, N, C(1), C(2), C(1N) least-squares plane (4 pages); Table IV, observed and calculated structure factors for $Cp_3U[(NPh)(O)CCHPMe_2Ph]{\cdot}C_7H_8$ (19 pages). Ordering information is given on any current masthead page.

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The Slip-Fold Distortion of π-Bound Indenyl Ligands. Dynamic NMR and X-ray Crystallographic Studies of (η-Indenyl)RhL_2 Complexes[†]

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Summary: Crystal and molecular structures of two $(\eta\text{-}C_9H_7)RhL_2$ complexes, L = $\eta\text{-}C_2H_4$ (**2a**) (R = 0.031, R_w = 0.039) and L = PMe_3 (**2b**) (R = 0.026, R_w = 0.032), are reported. Values of the indenyl ring slip parameter, Δ, are 0.161 and 0.201 Å, respectively, indicating significantly greater slip-fold distortion for **2b** than for **2a**. Comparison with the known structure of $(\eta\text{-}C_9H_7)Rh(\eta\text{-}$duroquinone) (**2c**) for which Δ = 0.046 Å suggests a correlation between ligand σ-donor/π-acceptor capabilities and the degree of slip-fold distortion. The degree of distortion is also correlated with the ^{13}C NMR chemical shift of the ring junction carbon atoms and with the barrier to indenyl ring rotation. The latter has been studied in solution by dynamic FTNMR spectroscopy using $(\eta\text{-}1\text{-}CH_3C_9H_6)RhL_2$ complexes. Larger barriers result from increased distortions; $\Delta G^{\ddagger}_{253}$ = 11.20 ± 0.03 kcal mol^{-1} for $(\eta\text{-}1\text{-}CH_3C_9H_6)Rh(PMe_3)_2$.

There has been considerable recent interest in the enhanced reactivity of η^5-indenyl transition-metal complexes toward ligand substitution and related reactions compared with their $\eta^5\text{-}C_5R_5$ analogues.[1–4] This rate enhancement is believed to be related to the relative ease of ring slippage from η^5 to η^3.[1–4] Our interest in stoichiometric[5] and catalytic[6] reactions of η^5-indenyl rhodium complexes prompted a detailed investigation of factors effecting ground-state slip-fold distortions and related ligand dynamics in a series of (η-indenyl)RhL_2 complexes.

We recently reported[7] the first example of hindered indenyl-ring rotation in an unusual $(\eta\text{-}C_9H_7)RhLL'$ complex (1) wherein L = CO, L′ = $(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)Cr(\mu\text{-}CO)_2(CO)$, and the observed $\Delta G^{\ddagger}$ was ca. 10.8 kcal mol^{-1}.

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