

Crystal Structures of $(\text{MeC}_5\text{H}_4)_3\text{M}(\text{L})$ ($\text{M} = \text{Uranium or Cerium}$; $\text{L} = \text{Quinuclidine or P}(\text{OCH}_2)_3\text{CEt}$). Evidence for Uranium to Phosphorus π -Back-Bonding

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The synthesis and X-ray crystal structure of $(\text{MeC}_5\text{H}_4)_3\text{M}(\text{L})$, where M is Ce or U and L is $\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$ or $\text{P}(\text{OCH}_2)_3\text{CEt}$, are described. Crystals of $(\text{MeC}_5\text{H}_4)_3\text{U}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$ are triclinic of space group $P\bar{1}$ with $Z = 2$. For the uranium complex, $a = 10.604$ (4) Å, $b = 13.552$ (6) Å, $c = 8.333$ (4) Å, $\alpha = 100.20$ (4)°, $\beta = 74.78$ (4)°, and $\gamma = 104.13$ (4)° at 23 °C; the calculated density is 1.751 g/cm³. The structure was refined by full-matrix least squares to a conventional R factor of 0.022 [4209 data, $F^2 > 2\sigma(F^2)$]. For the cerium compound, $a = 10.609$ (4) Å, $b = 13.586$ (5) Å, $c = 8.348$ (5) Å, $\alpha = 100.15$ (4)°, $\beta = 74.75$ (4)°, and $\gamma = 104.01$ (3)° at 23 °C; the calculated density is 1.451 g/cm³. The structure was refined by full-matrix least squares to a conventional R factor of 0.024 [4516 data, $F^2 > 2\sigma(F^2)$]. The uranium(III) and cerium(III) atoms are each bonded to three cyclopentadienyl rings; the average U-C and Ce-C distances are 2.82 ± 0.03 and 2.85 ± 0.03 Å, respectively. The U-N and Ce-N distances are 2.764 (4) and 2.789 (3) Å, respectively. Crystals of $(\text{MeC}_5\text{H}_4)_3\text{U}[\text{P}(\text{OCH}_2)_3\text{CEt}]$ and $(\text{MeC}_5\text{H}_4)_3\text{Ce}[\text{P}(\text{OCH}_2)_3\text{CEt}]$ are orthorhombic of space group $P2_12_12_1$ with $Z = 4$. The structure of the two isomorphous complexes were determined by single-crystal X-ray diffraction methods and refined by full-matrix least squares. For the uranium complex, $a = 13.122$ (5) Å, $b = 16.363$ (5) Å, $c = 10.922$ (4) Å at 23 °C; the calculated density is 1.806 g/cm³; the final R factor is 0.044 [2292 data, $F^2 > 3\sigma(F^2)$]. For the cerium complex, $a = 13.163$ (7) Å, $b = 16.443$ (7) Å, and $c = 10.976$ (4) Å at 23 °C; the calculated density is 1.509 g/cm³; the final R factor is 0.046 [3195 data, $F^2 > 3\sigma(F^2)$]. The metal atom is tetrahedrally bound to the three cyclopentadienyl rings and a phosphorus atom. The U-P and Ce-P distances are 2.988 (6) and 3.086 (3) Å, respectively; the average U-C and Ce-C distances are 2.80 ± 0.05 and 2.82 ± 0.03 Å, respectively. The metal to Lewis base bond lengths are rationalized in terms of U-P π -back-bonding and the lack of π -back-bonding in both of the amine complexes and in the cerium phosphite complex.

The concept of metal-ligand bond strength and the evolution of a ligand displacement series is a fundamental problem in metal chemistry. The pioneering work of Chatt and Pearson, in which metals are classified as class a (hard) or class b (soft), is based upon measuring equilibrium quotients in solution.¹ In general, those metals that have a high coordinative affinity for nitrogen or oxygen donor atoms relative to those with phosphorus or sulfur donor atoms are classified as class a or hard acceptors. For class b or soft acceptors the opposite is true. The f-block metals are classified as class a acceptors in aqueous solution mainly on the basis of the nonexistence of phosphine complexes and the large number of complexes with nitrogen and oxygen donor ligands. Several phosphorus complexes of the actinide and lanthanide metals have been isolated recently and the concept that phosphines cannot yield isolable complexes with the f-block metals is no longer tenable.² The observation of isolable f-metal phosphine complexes, however, does not address their classification as class a or class b acceptors; ligand competition experiments are required to establish a solution displacement series. Quantitative studies on $\text{Cp}_3\text{Yb}(\text{L})$ have shown that PEt_3 is approximately as good a base as is pyrrolidine.^{2j} Studies in this laboratory have shown that the ligand displacement series toward $(\text{RC}_5\text{H}_4)_3\text{M}$ ($\text{M} = \text{Ce or U}$) is phosphine > amine.³ Further, in competition between $(\text{RC}_5\text{H}_4)_3\text{U}$ and $(\text{RC}_5\text{H}_4)_3\text{Ce}$ for a given ligand, uranium always prefers the class b donor over cerium.^{3c} The trivalent uranium, 5f³ electronic structure, and the trivalent cerium, 4f¹ electronic structure, metallocenes were chosen since these metals have similar sizes and therefore steric

effects will be minimized.⁴ In order to test the similar size postulate, we have examined the crystal structures of the series $(\text{MeC}_5\text{H}_4)_3\text{M}(\text{L})$, where M is U and L is Me_3P ,^{5a} tetrahydrothiophene,^{5b} and *p*-(dimethylamino)pyridine^{5c} and where M is Ce and L is Me_3P .^{5d} The structure of $\text{Cp}_3\text{U}(\text{tetrahydrofuran})$ has been published.^{5e} In this paper

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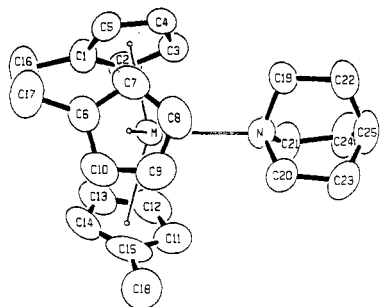


Figure 1. ORTEP drawing of $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{U}\cdot\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$.

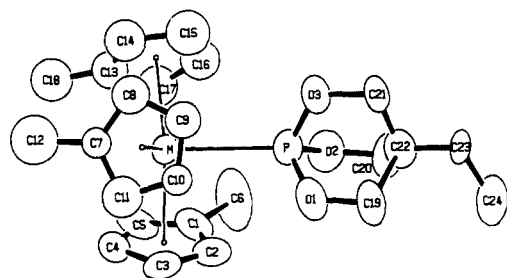


Figure 2. ORTEP drawing of $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{U}\cdot\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$ ($\text{M} = \text{U}$). Only one conformation of the disordered ring C(7)-C(11) is shown.

we report the crystal structures of the molecules $(\text{MeC}_5\text{H}_4)_3\text{M}(\text{L})$ where M is uranium or cerium and L is the tied-back phosphite and amine, $\text{P}(\text{OCH}_2)_3\text{Cet}$ and $\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$, respectively, and evolution of the concept of U-P π -back-bonding.

Synthesis and Crystallographic Studies

The uranium and cerium compounds were made by ligand displacement from $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{THF})$ or $(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{THF})$. The synthetic and characterization details are in the Experimental Section. The quinuclidine complexes $(\text{MeC}_5\text{H}_4)_3\text{M}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$, where M is U or Ce, are isostructural. They crystallize in the triclinic crystal system in space group $P\bar{1}$. One ORTEP drawing is shown in Figure 1 for the uranium compound. The numbering of the atoms in the cerium compound is identical with those used for the uranium compound. The phosphite complexes $(\text{MeC}_5\text{H}_4)_3\text{M}[\text{P}(\text{OCH}_2)_3\text{Cet}]$, where M is U or Ce, are also isostructural. They crystallize in the orthorhombic crystal system in space group $P2_12_12_1$. An ORTEP diagram is shown in Figure 2, and the atom numbering scheme is the same for the uranium and cerium compounds. Positional parameters are in Tables I and II, bond lengths and angles are in Tables III and IV, and crystal data are in Tables V and VI. All four molecules have a similar geometry that is based upon an idealized tetrahedron with three sites filled by the MeC_5H_4 ring centroids and the other position filled by the Lewis base.

The bond properties for the four molecules are very similar. The averaged M-C distances range from 2.85 ± 0.03 to 2.80 ± 0.05 Å, the metal to MeC_5H_4 ring centroid distance ranges from 2.58 to 2.53 Å, and the ring centroid-metal-ring centroid angles range from 116° to 119° . The averaged ring centroid-metal-Lewis base angle is 101° in the quinuclidine compounds and 95° in the phosphite complexes. These values are not statistically significantly different, due mainly to the large spread in metal-carbon ring distances which is further complicated by the disorder of one MeC_5H_4 ring in both phosphite complexes. The near equivalence of these bond parameters is consistent with our contention that the radii of trivalent uranium and

Table I. Positional Parameters with Estimated Standard Deviations

atom	x	y	z
$(\text{CH}_3\text{C}_5\text{H}_4)_3\text{U}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$			
U	0.16548 (2)	0.25147 (1)	0.21294 (2)
N	-0.0996 (4)	0.21080 (28)	0.3828 (5)
C(1)	0.3507 (5)	0.1244 (4)	0.1811 (7)
C(2)	0.2325 (5)	0.0547 (4)	0.1617 (6)
C(3)	0.1371 (5)	0.0588 (3)	0.3163 (6)
C(4)	0.1977 (5)	0.1310 (4)	0.4327 (6)
C(5)	0.3286 (5)	0.1707 (4)	0.3486 (6)
C(6)	0.3600 (6)	0.4236 (4)	0.2992 (7)
C(7)	0.2721 (6)	0.4015 (4)	0.4549 (6)
C(8)	0.1473 (6)	0.4222 (4)	0.4588 (7)
C(9)	0.1587 (7)	0.4583 (4)	0.3062 (8)
C(10)	0.2894 (6)	0.4593 (4)	0.2106 (7)
C(11)	0.0285 (7)	0.2354 (6)	-0.0472 (7)
C(12)	0.0825 (7)	0.1498 (5)	-0.0762 (6)
C(13)	0.2191 (7)	0.1786 (5)	-0.1256 (6)
C(14)	0.2524 (7)	0.2837 (5)	-0.1261 (6)
C(15)	0.1366 (9)	0.3200 (5)	-0.0806 (7)
C(16)	0.4820 (7)	0.1411 (6)	0.0481 (9)
C(17)	0.5080 (7)	0.4219 (7)	0.2442 (11)
C(18) ^a	0.0911 (16)	0.4285 (12)	-0.0711 (20)
C(18')	0.406 (3)	0.3259 (24)	-0.165 (4)
C(19)	-0.1106 (5)	0.1968 (4)	0.5618 (7)
C(20)	-0.1642 (6)	0.2973 (4)	0.3821 (8)
C(21)	-0.1800 (6)	0.1162 (4)	0.3064 (8)
C(22)	-0.2545 (7)	0.1951 (6)	0.6700 (9)
C(23)	-0.3155 (6)	0.2715 (5)	0.4609 (10)
C(24)	-0.3201 (6)	0.0871 (5)	0.4189 (10)
C(25)	-0.3476 (6)	0.1767 (5)	0.5484 (10)
$(\text{CH}_3\text{C}_5\text{H}_4)_3\text{Ce}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$			
Ce	0.16556 (1)	0.25123 (1)	0.21241 (2)
N	-0.10155 (24)	0.21105 (19)	0.3845 (3)
C(1)	0.3515 (3)	0.12328 (27)	0.1825 (5)
C(2)	0.2335 (4)	0.05429 (25)	0.1641 (5)
C(3)	0.1382 (3)	0.05784 (24)	0.3159 (4)
C(4)	0.1984 (3)	0.12887 (27)	0.4318 (4)
C(5)	0.3288 (3)	0.16867 (29)	0.3499 (5)
C(6)	0.3608 (4)	0.42497 (26)	0.2997 (5)
C(7)	0.2723 (4)	0.40253 (28)	0.4536 (5)
C(8)	0.1492 (4)	0.42362 (29)	0.4588 (5)
C(9)	0.1579 (5)	0.45925 (26)	0.3102 (6)
C(10)	0.2891 (4)	0.46104 (25)	0.2113 (5)
C(11)	0.0279 (5)	0.2351 (5)	-0.0493 (5)
C(12)	0.0835 (5)	0.1487 (3)	-0.0784 (5)
C(13)	0.2195 (5)	0.1781 (3)	-0.1291 (4)
C(14)	0.2523 (3)	0.2835 (4)	-0.1300 (4)
C(15)	0.1360 (6)	0.3203 (4)	-0.0841 (5)
C(16)	0.4824 (5)	0.1405 (4)	0.0506 (7)
C(17)	0.5075 (5)	0.4239 (5)	0.2454 (9)
C(18) ^a	0.0962 (11)	0.4233 (9)	-0.0759 (15)
C(18')	0.3919 (20)	0.3233 (15)	-0.1804 (24)
C(19)	-0.1119 (4)	0.1976 (3)	0.5610 (5)
C(20)	-0.1657 (4)	0.29701 (28)	0.3833 (5)
C(21)	-0.1811 (4)	0.1156 (3)	0.3098 (6)
C(22)	-0.2558 (4)	0.1943 (5)	0.6684 (6)
C(23)	-0.3165 (4)	0.2727 (4)	0.4632 (7)
C(24)	-0.3221 (4)	0.0875 (4)	0.4224 (8)
C(25)	-0.3482 (4)	0.1784 (4)	0.5503 (7)

^a C(18) and C(18') represent a disordered atom refined with half-occupancy in two positions.

cerium are identical for molecules with the same coordination number.

The M-N distances in the quinuclidine complexes are similar: the U-N and Ce-N distances are 2.764 (4) and 2.789 (3) Å, respectively. The shorter U-N distance, by 0.023 Å (6σ), relative to the Ce-N distance is consistent with the shorter, averaged U-C distance relative to the averaged Ce-C distance (Table III), even though the latter distances are not statistically significant. In the phosphite complexes the U-P distances of 2.988 (6) Å is 0.098 Å shorter than the Ce-P distance of 3.086 (3) Å. On the basis of the M-N bond length data discussed above, a U-P

Table II. Positional Parameters with Estimated Standard Deviations

atom	x	y	z
$(CH_3C_5H_4)_3U[P(OCH_2)_3CC_2H_5]$			
U	0.10577 (5)	0.20386 (4)	0.26633 (5)
P	0.1146 (5)	0.32846 (27)	0.0667 (4)
O(1)	0.1165 (10)	0.2920 (7)	-0.0684 (8)
O(2)	0.0183 (9)	0.3910 (8)	0.0561 (11)
O(3)	0.2060 (10)	0.3918 (8)	0.0629 (12)
C(1)	-0.1028 (17)	0.2061 (13)	0.2089 (19)
C(2)	-0.0550 (15)	0.1779 (13)	0.1022 (20)
C(3)	-0.0164 (16)	0.0985 (15)	0.1327 (19)
C(4)	-0.0395 (14)	0.0803 (11)	0.2576 (19)
C(5)	-0.0938 (17)	0.1478 (15)	0.3017 (20)
C(6)	-0.1627 (4)	0.2918 (14)	0.2238 (23)
C(7)	0.2686 (25)	0.0938 (19)	0.2933 (26)
C(8)	0.3206 (29)	0.1689 (20)	0.286 (3)
C(9)	0.303 (3)	0.1991 (24)	0.165 (3)
C(10)	0.247 (3)	0.1364 (23)	0.104 (3)
C(11)	0.218 (4)	0.0704 (24)	0.1833 (29)
C(12)	0.266 (4)	0.0358 (26)	0.403 (4)
C(7') ^a	0.2836	0.1379	0.3186
C(8') ^a	0.3199	0.2035	0.2419
C(9')	0.283 (3)	0.1830 (24)	0.1214 (23)
C(10')	0.226 (5)	0.110 (3)	0.110 (4)
C(11')	0.246 (4)	0.0799 (20)	0.2304 (29)
C(12')	0.207 (4)	-0.0029 (22)	0.278 (4)
C(13)	0.0879 (17)	0.2469 (12)	0.5148 (17)
C(14)	0.1904 (19)	0.2674 (14)	0.4811 (21)
C(15)	0.1893 (22)	0.3390 (15)	0.3940 (23)
C(16)	0.0804 (18)	0.3519 (13)	0.3879 (18)
C(17)	0.0155 (16)	0.2955 (16)	0.4516 (18)
C(18)	0.0632 (16)	0.1812 (14)	0.6050 (20)
C(19)	0.1161 (19)	0.3472 (10)	-0.1737 (15)
C(20)	0.0179 (15)	0.4486 (12)	-0.0501 (17)
C(21)	0.2087 (17)	0.4535 (13)	-0.0362 (18)
C(22)	0.1190 (15)	0.4389 (10)	-0.1212 (14)
C(23)	0.1303 (13)	0.5000 (10)	-0.2223 (15)
C(24)	0.0480 (20)	0.4938 (15)	-0.3229 (22)
$(CH_3C_5H_4)_3Ce[P(OCH_2)_3CC_2H_5]$			
Ce	0.10957 (5)	0.20103 (4)	-0.26770 (5)
P	0.1156 (4)	0.32925 (17)	-0.06257 (23)
O(1)	0.1179 (8)	0.2929 (5)	0.0723 (6)
O(2)	0.0227 (6)	0.3927 (5)	-0.0526 (7)
O(3)	0.2099 (6)	0.3897 (6)	-0.0578 (8)
C(1)	-0.0988 (9)	0.2056 (9)	-0.2064 (10)
C(2)	-0.0509 (10)	0.1714 (8)	-0.1014 (11)
C(3)	-0.0126 (10)	0.0954 (9)	-0.1326 (13)
C(4)	-0.0406 (10)	0.0793 (8)	-0.2564 (12)
C(5)	-0.0920 (10)	0.1470 (9)	-0.3015 (11)
C(6)	-0.1571 (11)	0.2878 (10)	-0.2169 (15)
C(7)	0.2677 (20)	0.0865 (15)	-0.2818 (27)
C(8)	0.3224 (23)	0.1679 (18)	-0.2859 (26)
C(9)	0.3100 (25)	0.2116 (19)	-0.176 (4)
C(10)	0.2598 (24)	0.1419 (19)	-0.1116 (23)
C(11)	0.2202 (26)	0.0673 (18)	-0.171 (3)
C(12)	0.2759 (28)	0.0200 (19)	-0.3802 (29)
C(7')	0.2917 (23)	0.1181 (19)	-0.3206 (22)
C(8')	0.3207 (23)	0.1929 (20)	-0.2656 (25)
C(9')	0.2944 (18)	0.1825 (18)	-0.1338 (20)
C(10')	0.2297 (26)	0.1169 (21)	-0.1013 (27)
C(11')	0.2457 (25)	0.0735 (17)	-0.219 (3)
C(12')	0.2084 (27)	-0.0075 (19)	-0.270 (4)
C(13)	0.0907 (11)	0.2435 (9)	-0.5148 (12)
C(14)	0.1928 (14)	0.2660 (11)	-0.4814 (16)
C(15)	0.1846 (16)	0.3353 (12)	-0.3978 (19)
C(16)	0.0863 (11)	0.3515 (9)	-0.3847 (12)
C(17)	0.0183 (11)	0.2960 (11)	-0.4573 (13)
C(18)	0.0662 (13)	0.1826 (11)	-0.6090 (16)
C(19)	0.1188 (13)	0.3495 (6)	0.1716 (10)
C(20)	0.0239 (10)	0.4486 (7)	0.0483 (11)
C(21)	0.2108 (10)	0.4512 (9)	0.0381 (11)
C(22)	0.1197 (11)	0.4377 (6)	0.1249 (9)
C(23)	0.1327 (10)	-0.5009 (7)	0.2288 (11)
C(24)	0.0526 (14)	0.4973 (10)	0.3278 (14)

^a Atom in fixed position.

Table III. Selected Distances (Å) and Angles (deg)

$(CH_3C_5H_4)_3U[N(CH_2CH_2)_3CH]$			
Bond Distances			
U-N	2.764 (4)	U-C(12)	2.797 (5)
U-C(1)	2.848 (5)	U-C(13)	2.776 (5)
U-C(2)	2.857 (5)	U-C(14)	2.810 (5)
U-C(3)	2.815 (5)	U-C(15)	2.876 (5)
U-C(4)	2.792 (4)	N-C(19)	1.508 (6)
U-C(5)	2.802 (5)	N-C(20)	1.497 (6)
U-C(6)	2.837 (5)	N-C(21)	1.496 (6)
U-C(7)	2.846 (5)	U-Cp ₁ ^a	2.56
U-C(8)	2.814 (5)	U-Cp ₂	2.55
U-C(9)	2.786 (5)	U-Cp ₃	2.57
C-C(10)	2.804 (5)	U-C _{av}	2.82 ± 0.03
C-C(11)	2.862 (5)		
Bond Angles			
N-U-Cp ₁	100.9	Cp ₁ -U-Cp ₂	117.0
N-U-Cp ₂	101.3	Cp ₁ -U-Cp ₃	115.7
N-U-Cp ₃	101.4	Cp ₂ -U-Cp ₃	116.2
U-N-C(25)	178.5 (2)		
$(CH_3C_5H_4)_3Ce[N(CH_2CH_2)_3CH]$			
Bond Distances			
Ce-N	2.789 (3)	Ce-C(12)	2.815 (4)
Ce-C(1)	2.868 (3)	Ce-C(13)	2.804 (4)
Ce-C(2)	2.871 (3)	Ce-C(14)	2.841 (4)
Ce-C(3)	2.834 (3)	Ce-C(15)	2.911 (4)
Ce-C(4)	2.816 (3)	N-C(19)	1.488 (5)
Ce-C(5)	2.832 (3)	N-C(20)	1.490 (4)
Ce-C(6)	2.866 (3)	N-C(21)	1.498 (4)
Ce-C(7)	2.859 (4)	Ce-Cp ₁ ^a	2.58
Ce-C(8)	2.838 (4)	Ce-Cp ₂	2.58
Ce-C(9)	2.815 (4)	Ce-Cp ₃	2.59
Ce-C(10)	2.835 (3)	Ce-C _{av}	2.85 ± 0.03
Ce-C(11)	2.882 (4)		
Bond Angles			
N-Ce-Cp ₁	100.9	Cp ₁ -Ce-Cp ₂	117.0
N-Ce-Cp ₂	101.0	Cp ₁ -Ce-Cp ₃	115.8
N-Ce-Cp ₃	101.6	Cp ₂ -Ce-Cp ₃	116.2
Ce-N-C(25)	178.2 (2)		

^aCp₁, Cp₂, and Cp₃ represent the ring centers of cyclopentadienyl rings C(1)-C(5), C(6)-C(10), and C(11)-C(15), respectively.

distance of ca. 3.06 Å was expected. Hence we can say, with confidence, that the U-P distance in the phosphite complex is shorter than expected by ca. 0.07 Å.

Table VII shows a list of compounds of the type $(RC_5H_4)_3M(L)$ with the M-L distances and the parameters Δ , which is defined as $[M-L] - [U-L]$, and Δ' , which is defined as $[UC_{av}-UL] - [MC_{av}-ML]$. Within a given pair of molecules, the parameter Δ' is defined to compensate for the change in U-C(centroid) and M-C(centroid) distances caused by different metal radii. When $\Delta' = 0$, the U-L and lanthanide to Lewis base bond lengths are identical with those predicted by ionic radii summation. When $\Delta' > 0$, the U-L bond length is shorter than that of the lanthanide to ligand distance. The large uncertainty in the averaged metal-ring carbon distance causes large uncertainty in Δ' . The parameter Δ , rather than Δ' , is used in the following discussion. Choosing Δ or Δ' leads to the same qualitative result. With first-row nitrogen and oxygen donors (class a or hard donors) the U-L and Ce-L distances are the same and Δ is between 0.01 and 0.02. With second-row donors, class b or soft donors, the U-P bond lengths are shorter than the lanthanide to phosphorus bond lengths. This perturbation is consistent with a stronger U-P, relative to Ce-P, bond that is consistent with the equilibrium quotient studies.³ Hence the U-P bond is stronger and shorter than the Ce-P bond in solution and in the solid state, respectively.

Table IV. Selected Interatomic Distances (Å) and Angles (deg)

(CH ₃ C ₅ H ₄) ₃ U[P(OCH ₂) ₃ CC ₂ H ₅]			
Bond Distances			
U-Cp(1)	2.521	P-O(1)	1.59 (1)
U-Cp(2)	2.544	P-O(2)	1.63 (1)
U-Cp(2')	2.490	P-O(3)	1.59 (1)
U-Cp(3)	2.517	O(1)-C(19)	1.46 (2)
U-C _{av}	2.80 (5)	O(2)-C(20)	1.50 (2)
U-P	2.988 (6)	O(3)-C(21)	1.48 (2)
Bond Angles			
Cp(1)-U-Cp(2)	119.3	U-P-O(1)	115.0 (5)
Cp(1)-U-Cp(2')	121.6	U-P-O(2)	116.8 (5)
Cp(1)-U-Cp(3)	120.3	U-P-O(3)	119.6 (5)
Cp(2)-U-Cp(3)	116.9	O(1)-P-O(2)	100.5 (7)
Cp(2')-U-Cp(3)	115.5	O(1)-P-O(3)	102.0 (8)
Cp(1)-U-P	95.7	O(2)-P-O(3)	100.1 (7)
Cp(2)-U-P	95.0	P-O(1)-C(19)	120 (1)
Cp(2')-U-P	92.4	P-O(2)-C(20)	117 (1)
Cp(3)-U-P	98.1	P-O(3)-C(21)	119 (1)
(CH ₃ C ₅ H ₄) ₃ Ce[P(OCH ₂) ₃ CC ₂ H ₅]			
Bond Distances			
Ce-Cp(1)	2.548	P-O(1)	1.597 (7)
Ce-Cp(2)	2.554	P-O(2)	1.611 (9)
Ce-Cp(2')	2.523	P-O(3)	1.591 (9)
Ce-Cp(3)	2.540	O(1)-C(19)	1.43 (1)
Ce-C _{av}	2.82 (3)	O(2)-C(20)	1.44 (1)
Ce-P	3.086 (3)	O(3)-C(21)	1.46 (2)
Bond Angles			
Cp(1)-Ce-Cp(2)	119.12	Ce-P-O(1)	114.6 (4)
Cp(1)-Ce-Cp(2')	122.08	Ce-P-O(2)	118.0 (4)
Cp(1)-Ce-Cp(3)	119.99	Ce-P-O(3)	118.5 (4)
Cp(2)-Ce-Cp(3)	118.01	O(1)-P-O(2)	100.6 (6)
Cp(2')-Ce-Cp(3)	114.94	O(1)-P-O(3)	101.5 (6)
Cp(1)-Ce-P	94.65	O(2)-P-O(3)	100.8 (5)
Cp(2)-Ce-P	94.07	P-O(1)-C(19)	118.3 (8)
Cp(2')-Ce-P	94.48	P-O(2)-C(20)	117.8 (8)
Cp(3)-Ce-P	98.25	P-O(3)-C(21)	117.0 (9)

^aCp(1), Cp(2), Cp(2'), and Cp(3) represent the centroids of cyclopentadienyl rings C(1)-C(5), C(7)-C(11), C(7')-C(11'), and C(13)-C(17). The averaged U-C and Ce-C distances include the ordered and disordered rings as do the averaged centroid-M-centroid angle.

An explanation for the observed bond length trend is to postulate metal to ligand π -bonding in the uranium compounds and to postulate that the interaction between (MeC₅H₄)₃Ce and the Lewis base are σ -only or purely electrostatic interactions. The σ -only language implies a molecular orbital or covalent description of the metal to ligand bonding whereas the electrostatic term implies that the metal to ligand interaction is governed by Coulomb's law. A preference for either language is irrelevant for our purposes since both lead to the same net result; i.e., for class a donors, (MeC₅H₄)₃Ce and (MeC₅H₄)₃U behave similarly. On the other hand, the shorter U-L bond lengths relative to Ce-L bond lengths, when L is a phosphine or phosphite, may be rationalized by postulating uranium to phosphorus π -bonding which is absent in the lanthanide complexes. Consistent with the postulate of U-L π -bonding is the observation that the CO stretching frequency in (Me₃SiC₅H₄)₃U(CO) of 1976 cm⁻¹ is ca. 170 cm⁻¹ lower than that in free carbon monoxide^{3c} and that neither (Me₃SiC₅H₄)₃Ce nor (Me₃SiC₅H₄)₃Nd form complexes with carbon monoxide.^{3b} Further, the U-C(CNEt) bond length in (Me₃SiC₅H₄)₃U(CNEt) of 2.57 (3) Å is 0.08 (2) Å shorter than the equivalent bond length in Cp₃Pr(CN-cHex). As listed in Table VII, Δ' for this pair of isocyanides is 0.11. This is a significant shortening of the U-C bond length relative to Pr-C since Δ' is 0 for Cp₃U-(THF) and Cp₃Pr(THF).

Table V. Crystallographic Summary and Data Processing

	(CH ₃ C ₅ H ₄) ₃ U[N-(CH ₂ CH ₂) ₃ CH]	(CH ₃ C ₅ H ₄) ₃ Ce[N(CH ₂ CH ₂) ₃ CH]
<i>a</i> , Å	10.604 (4)	10.609 (4)
<i>b</i> , Å	13.552 (6)	13.586 (5)
<i>c</i> , Å	8.333 (4)	8.348 (5)
α , deg	100.20 (4)	100.15 (4)
β , deg	74.78 (4)	74.75 (4)
γ , deg	104.13 (4)	104.01 (3)
cryst syst		triclinic
space group		P1
<i>V</i> , Å ³	1112.0	1118.2
<i>d</i> (calcd), g/cm ⁻³	1.751	1.451
<i>Z</i>		2
temp, °C		23
empirical formula	C ₂₅ H ₃₄ NU	C ₂₅ H ₃₄ NCe
<i>f</i> (000)	566	498
<i>fw</i>	586.59	488.68
color	red	yellow
X-ray	Mo K α (graphite monochromated)	
wavelength (K α_1 , K α_2), Å		0.70930, 0.71359
cryst size, mm	0.14 × 0.22 × 0.45	0.17 × 0.24 × 0.26
abs coeff, cm ⁻¹	69.25	20.76
abs corr range	2.36-4.16	1.39-1.72
cryst decay corr range	0.95-1.03	0.96-1.08
diffractometer		modified Picker FACS-1
2 θ limits, deg		4-55
<i>hkl</i> limits	<i>h</i> -13, 13; <i>k</i> -17, 17; <i>l</i> -10, 10	
scan type		θ -2 θ
scan width, deg		1.40 + 0.693 tan θ
no. of stds		3
freq of stds		250
no. of scan data	10337	10337
no. of unique reflctns	5170	5173
<i>R</i> _{int} ^b	0.020	0.016
no. of nonzero weighted (wtd) data	4209 (<i>F</i> ² > 2 σ)	4516 (<i>F</i> ² > 2 σ)
<i>p</i> ^c	0.04	0.050
extinct <i>k</i> ^d	4.34 × 10 ⁻⁸	1.31 × 10 ⁻⁷
max % extinctn corr	4.7	10.2
no. of parameters	243	324
<i>R</i> (nonzero wtd dta) ^e	0.022	0.024
<i>R</i> _w ^f	0.028	0.032
<i>R</i> (all data)	0.036	0.031
goodness of fit ^g	1.04	1.08
max shift-esd	0.02	0.03
max, min residuals, e/Å ³	1.44, -0.81	0.78, -0.61

^aUnit-cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo K α components of 21 reflections (21 < 2 θ < 33°) for compound on the left and 33 reflections (23 < 2 θ < 35°) for compound on the right. ^b*R*_{int} = agreement factor between equivalent or multiply measured reflections = $\sum_j [F^2(hkl)_j - \langle F^2(hkl) \rangle] / \sum_i [F^2(hkl)_i]$. ^cIn the least squares, the assigned weights to the data are 1.0/[$\sigma(F)$]² were derived from $\sigma(F)^2 = [S^2 + (pF^2)^2]$, where *S*² is the variance due to counting statistics and *p* is assigned a value that adjusts the weights of the stronger reflections such that their weighted residuals are comparable to those of the weak ones. ^dSimple extinction correction has the form (*F*_o)_{corr} = (1 + *kI*)*F*_o, where *I* is the uncorrected intensity and *F*_o is the observed scattering amplitude. ^e*R* = $\sum(|F_o| - |F_c|) / \sum|F_o|$. ^f*R*_w = $\sqrt{[\sum w(|F_o| - |F_c|)^2] / \sum wF_o^2}$. ^g σ_1 = error in observation of unit weight = $\sqrt{[\sum w(|F_o| - |F_c|)^2] / (NO - NV)}$, where NO is the number of observations and NV is the number of variables.

The postulate of M-L π -bonding when M is a low-valent d-transition metal and L is carbon monoxide, an isocyanide, phosphite, or trifluorophosphine⁷ is not particularly controversial,^{1,8} though alternative views have been

(7) Attempts to make (MeC₅H₄)₃U(PF₃) from reaction of (MeC₅H₄)₃U(THF) and PF₃ yields (MeC₅H₄)₃UF as the only isolated product; see Experimental Section for details.

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Table VI. Crystallographic Summary and Data Processing

	$(\text{CH}_3\text{C}_5\text{H}_4)_3\text{U}-$ $[\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5]$	$(\text{CH}_3\text{C}_5\text{H}_4)_3\text{Ce}-$ $[\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5]$
a , Å	13.122 (5)	13.163 (7)
b , Å	16.363 (5)	16.443 (7)
c , Å	10.922 (4)	10.976 (4)
cryst syst	orthorhombic	
space group	$P2_12_12_1$	
V , Å ³	2345.1	2375.6
d_{calcd} , g/cm ³	1.806	1.509
Z	4	
temp, °C	23.0	
empirical formula	$\text{C}_{24}\text{H}_{32}\text{O}_3\text{PU}$	$\text{C}_{24}\text{H}_{32}\text{O}_3\text{PCe}$
$f(000)$	1228	1092
fw	637.53	539.61
color	brown	yellow
reflectn rules	$h00, h = 2n; 0k0, k = 2n; 00l, l = 2n$	
wavelength ($K\alpha_1, K\alpha_2$), Å	0.70930, 0.71359	
cryst size, mm	0.12 × 0.25 × 0.32	0.50 × 0.54 × 0.70
μ , cm ⁻¹	61.00	20.32
abs corr range	1.91–4.11	2.38–2.91
cryst decay corr range	0.92–1.04	0.95–1.01
2θ limits, deg	4.5–55.1	4.5–50.1
hkl limits	$h 0, 15; k 0, 21; l \pm 14$	$h 0, 15; k 0, 19; l \pm 13$
scan type	θ - 2θ	
scan width, deg	1.25 + 0.693 tan θ	1.40 + 0.693 tan θ
no. of stds	3	
no. of reflectns between stds	250	
no. of scan data	5487	4546
no. of unique reflectns	5097	4204
no. of nonzero weighted (wtd) data	2292	3195
	$(F^2 > 3\sigma(F^2))$	$(F^2 > 3\sigma(F^2))$
R^b	0.04	0.04
extinctn k^c	2.1×10^{-7}	3.6×10^{-9}
max % extinctn corr	9.1	0.1
no. of parameters	220	226
R (nonzero wtd data) ^d	0.044	0.046
R_w^e	0.045	0.059
R (all data)	0.16	0.071
goodness of fit ^f	1.23	1.72
max shift/esd in least-squares	0.02	0.08
max, min in diff map, e/Å ³	1.9, -2.7	0.7, -0.7

^a Unit-cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo $K\alpha$ components of 28 reflections ($2\theta < 31^\circ$) for the uranium complex and 22 reflections ($2\theta < 2\theta < 34^\circ$) for the cerium complex. ^{b–g} See Table V, footnotes b–g, respectively.

advanced.⁹ The postulate of M–L π -bonding in alkylphosphines is rather controversial.¹⁰ The results of several systematic X-ray crystal structure studies have been interpreted in terms of metal–ligand π -back-bonding.¹¹ In the case of the f-transition metals described in this paper, the most unifying model is one in which the trivalent uranium metallocenes can engage in π -back-bonding with ligands that have acceptor orbitals available; a symmetry orbital description has been given.^{3c} In contrast π -bonding is not required to rationalize the bond lengths in the trivalent 4f-transition-metal metallocene Lewis base complexes.

Experimental Section

All operations were done under nitrogen. Microanalyses were performed by the microanalytical laboratory of this department.

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Table VII. Bond Lengths in $(\text{RC}_5\text{H}_4)_3\text{M}(\text{L})$ Compounds

compound	M–L, Å	Δ , Å	Δ' , Å	ref
$(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{quin})^c$	2.787 (3)			this work
$(\text{MeC}_5\text{H}_4)_3\text{U}(\text{quin})^c$	2.764 (4)	0.022 (4)	0.00	this work
$(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{PMe}_3)$	3.074 (6)			5d
$(\text{MeC}_5\text{H}_4)_3\text{U}(\text{PMe}_3)$	2.972 (6)	0.102 (6)	0.07	5a
$(\text{MeC}_5\text{H}_4)_3\text{Ce}-$ $[\text{P}(\text{OCH}_2)_3\text{CET}]$	3.086 (3)			this work
$(\text{MeC}_5\text{H}_4)_3\text{U}-$ $[\text{P}(\text{OCH}_2)_3\text{CET}]$	2.988 (6)	0.098 (6)	0.09	this work
$(\text{C}_5\text{H}_5)_3\text{Pr}(\text{THF})$	2.56 (1)			6a
$(\text{C}_5\text{H}_5)_3\text{U}(\text{THF})$	2.55 (1)	0.01 (1)	0.00	5e
$(\text{C}_5\text{H}_5)_3\text{Pr}(\text{CN-cHex})$	2.65 (1)			6b
$(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}(\text{CNET})$	2.57 (2)	0.08 (2)	0.11	3c

^a $\Delta = \text{ML} - \text{UL}$ ($\text{M} = \text{Ce}$ or Pr). ^b $\Delta' = [(\text{U}-\text{C}_{av}) - \text{UL}] - [(\text{M}-\text{C}_{av}) - \text{ML}]$. ^c quin = quinuclidine, $\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}$.

The ¹H and ¹³C NMR spectra were measured at 89.56 and 22.50 MHz, respectively, on a JEOL-FX90Q instrument and are reported in δ values relative to tetramethylsilane with positive values to high frequency. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 580 machine.

$(\text{MeC}_5\text{H}_4)_3\text{Ce}(\text{THF})$. Sodium cyclopentadienide (26.4 mL of a 1.25 M solution in tetrahydrofuran, 33.0 mmol) was added to a suspension of cerium trichloride (2.71 g, 11.0 mmol) in tetrahydrofuran (60 mL). The yellow suspension was stirred for 12 h. The solvent was removed under reduced pressure, the yellow residue was extracted with diethyl ether (150 mL) and filtered, and the filtrate was concentrated to ca. 80 mL. Cooling the filtrate to -20°C yielded yellow needles (3.7 g, 80% yield), mp 142–146 °C dec. Anal. Calcd for $\text{C}_{22}\text{H}_{29}\text{CeO}$: C, 58.8; H, 6.50. Found: C, 58.7; H, 6.42. IR: 1320 w, 1260 m, 1238 w, 1165 m, 1075 m, 1045 s, 1030 s, 1015 s, 970 w, 927 m, 860 s, 820 s, 750 s, 665 m, 610 m, 550 w, 470 w, 400 w, 320 m, 210 s cm^{-1} . ¹H NMR (C_6D_6 , 36°C): δ 10.19 (6 H, $\nu_{1/2} = 20$ Hz), 8.66 (6 H, $\nu_{1/2} = 20$ Hz), -1.41 (9 H, $\nu_{1/2} = 5$ Hz), -4.93 (4 H, $\nu_{1/2} = 8$ Hz), -11.26 (4 H, $\nu_{1/2} = 20$ Hz). The last two resonances shifted toward the diamagnetic region of the spectrum upon addition of tetrahydrofuran.

$(\text{MeC}_5\text{H}_4)_3\text{Ce}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$. Toluene (60 mL) was added to quinuclidine (0.19 g, 1.7 mmol) and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{THF}$ (0.75 g, 1.7 mmol). The yellow solution was stirred for 2 h during which time the solution became yellow-green. The toluene was removed slowly under reduced pressure. The yellow-green residue was dissolved in toluene (60 mL), filtered, and the filtrate was concentrated to ca. 50 mL. Cooling the filtrate to -20°C afforded yellow needles (0.50 g, 53% yield), mp 156–159 °C dec. Anal. Calcd for $\text{C}_{25}\text{H}_{34}\text{CeN}$: C, 61.5; H, 7.01; N, 2.87. Found: C, 61.5; H, 7.03; N, 2.93. IR: 1310 m, 1272 w, 1235 w, 1198 m, 1150 w, 1112 w, 1043 s, 1035 m, 1030 m, 1010 w, 990 m, 973 m, 927 m, 895 w, 853 w, 822 s, 820 m, 810 s, 780 s, 750 s, 610 m, 570 w, 540 w, 475 w, 400 w, 323 m, 220 s cm^{-1} . ¹H NMR (C_6D_6 , 28°C): δ 12.16 (6 H, $\nu_{1/2} = 15$ Hz), 6.90 (6 H, $\nu_{1/2} = 15$ Hz), -1.95 (9 H, $\nu_{1/2} = 5$ Hz), -3.48 (1 H, $\nu_{1/2} = 9$ Hz), -4.32 (6 H, $\nu_{1/2} = 12$ Hz), -11.14 (6 H, $\nu_{1/2} = 23$ Hz).

$(\text{MeC}_5\text{H}_4)_3\text{Ce}[\text{P}(\text{OCH}_2)_3\text{CET}]$. To the phosphite (0.20 g, 1.2 mmol) and $(\text{MeC}_5\text{H}_4)_3\text{Ce}\cdot\text{THF}$ (0.55 g, 1.2 mmol) was added toluene (60 mL). The yellow-green solution was stirred for 2 h. The toluene was removed slowly under reduced pressure. The yellow-green residue was dissolved in diethyl ether (50 mL) and filtered, and the filtrate was concentrated to ca. 30 mL. Cooling the filtrate to -20°C yielded yellow bricks (0.31 g, 47% yield), mp 170–171 °C. Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{CeO}_3\text{P}$: C, 53.4; H, 5.98; P, 5.74. Found: C, 53.4; H, 6.12; P, 5.99. IR: 1690 m, 1610 w, 1300 m, 1260 w, 1237 w, 1188 m, 1170 w, 1150 s, 1060 w, 1040 s, 970 m, 955 s, 860 w, 848 s, 820 s, 760 s, 730 s, 642 s, 620 m, 565 w, 532 m, 497 m, 468 m, 420 w, 409 m, 370 m, 350 m, 330 s, 250 m, 230 s cm^{-1} . ¹H NMR (C_6D_6 , 33°C): δ 10.28 (12 H, $\nu_{1/2} = 40$ Hz), -1.64 (6 H, $\nu_{1/2} = 4$ Hz), -1.92 (3 H, t, $J = 7$ Hz), -2.28 (9 H, $\nu_{1/2} = 8$ Hz), -2.51 (2 H, q, $J = 7$ Hz).

$(\text{MeC}_5\text{H}_4)_3\text{U}[\text{N}(\text{CH}_2\text{CH}_2)_3\text{CH}]$. Toluene (10 mL) was added to an intimate mixture of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{THF})^{12}$ (1.0 g, 1.8 mmol) and quinuclidine (0.50 g, 4.3 mmol). The solution was stirred for 10 min, the toluene was removed, and the brown solid was extracted with a hexane/toluene (50:10) mixture at 55°C . The extract was cooled to -25°C , and the dark red needles (0.25 g,

23% yield) were collected; mp 159–162 °C dec. ^1H NMR (C_6D_6 , 28 °C): δ -10.14 (6 H), -10.78 (6 H), -11.09 (6 H), -14.27 (9 H), -14.64 (6 H), -28.64 (6 H). The resonances due to the quinuclidine ligand are the second, third, and sixth since these shift toward the diamagnetic region of the spectrum upon addition of excess quinuclidine. The line width of the resonances is ca. 5–15 Hz wide except the resonance at δ -28.64 which is ca. 32 Hz wide at half-height. ^{13}C NMR (C_6D_6 , 32 °C): δ 277.21 (d, $J_{\text{CH}} = 163$ Hz), 273.28 (d, $J_{\text{CH}} = 163$ Hz), 249.15 (s), 13.94 (q, $J_{\text{CH}} = 141$ Hz), -17.93 (t, $J_{\text{CH}} = 131$ Hz), -83.87 (q, $J_{\text{CH}} = 125$ Hz), -122.6 (br). Anal. Calcd for $\text{C}_{25}\text{H}_{34}\text{NU}$: C, 51.2; H, 5.84; N, 2.39. Found: C, 50.6; H, 5.73; N, 2.29. The infrared spectrum is essentially identical with that of the cerium analogue.

(MeC₅H₄)₃U[P(OCH₂)₃CeT]. A solution of the phosphite (0.50 g, 3.1 mmol) in diethyl ether (20 mL) was added to (MeC₅H₄)₃U·THF (1.3 g, 2.3 mmol) in diethyl ether (20 mL). A red precipitate appeared immediately. The diethyl ether was removed under reduced pressure, and the dark red solid was extracted with hot toluene (20 mL × 2). Cooling (-20 °C) the extract afforded red crystals (0.64 g, 44% yield), mp >300 °C. ^1H NMR (C_6D_6 , 28 °C): δ -3.92 (2 H, t, $J = 7.8$ Hz), -5.78 (3 H, q, $J = 7.8$ Hz), -8.03 (6 H), -10.73 (6 H), -17.88 (6 H), -21.11 (9 H). Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{OPU}$: C, 45.2; H, 5.06; P, 4.86. Found: C, 45.2; H, 5.08; P, 4.73. The infrared spectrum is essentially identical with that of its cerium analogue.

(MeC₅H₄)₃UF. The (MeC₅H₄)₃U·THF (1.5 g, 2.7 mmol) was dissolved in toluene (20 mL). The Schlenk tube was exposed to vacuum and then the flask was connected to a metal vacuum line which was connected to a cylinder containing trifluorophosphine. The flask was opened to the PF₃ atmosphere. The color of the solution changed from brown to green. The flask was stirred for 4 h, the volatile material was removed under reduced pressure, and the green residue was crystallized from toluene (ca. 15 mL, -20 °C) as light green crystals in 19% (0.26 g) yield; mp 198–202 °C. ^1H NMR (C_6D_6 , 27 °C): δ 5.61 (2 H), -2.11 (3 H), -19.25 (3 H). ^{13}C NMR (C_6D_6 , 27 °C): δ 221.4 (d), 173.8 (d), 151.4 (s), -6.87 (q). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{FU}$: C, 43.7; H, 4.28. Found: C, 43.8; H, 4.38. IR: 1061 w, 1045 w, 1028 m, 973 w, 930 w, 890 w, 840 m, 770 s, 720 m, 610 w, 467 s, 344 m, 236 m cm^{-1} . The absorption at 467 cm^{-1} was assigned to the U–F stretching frequency by comparison with (MeC₅H₄)₃UCl. The unsubstituted derivative Cp₃UF is known.¹³

X-ray Crystallography of the Quinuclidine Complexes.

The crystals, because of their sensitivity to the atmosphere, were sealed inside thin-walled quartz capillaries. Intensities were collected on a modified Picker FACS-I diffractometer equipped with a Mo X-ray tube and a graphite monochromator. The data were corrected for crystal decay, absorption (analytical method),¹⁴ and Lorentz and polarization effects. Details of the data collection and results are shown in Table V. The metal atomic positions were located with the use of three-dimensional Patterson maps; subsequent least-squares refinements and electron density maps revealed the locations of all of the non-hydrogen atoms. The structures were refined by full-matrix least squares. Scattering factors¹⁵ were adjusted for anomalous dispersion. In the uranium complex the non-methyl hydrogen atoms were placed in estimated positions at 0.98 Å from the bonding carbon atom and were

included with fixed isotropic thermal parameters, but not refined, in the least-squares calculations. In the cerium complex the positional and isotropic thermal parameters of all but three non-methyl hydrogen atoms were included in the least-squares procedures; the parameters of three of the hydrogen atoms would not converge to reasonable values and were included with estimated but fixed values. In both structures the methyl carbon atom, C(18), is disordered between two positions on the cyclopentadiene ring; positional parameters for this methyl carbon were entered as two half atoms in two locations as C(18) and C(18'). Anisotropic thermal parameters were assigned to all the non-hydrogen atoms with the exception of the disordered ones which were assigned isotropic thermal parameters.

X-ray Crystallography of the Phosphite Complexes. The crystals, because of their sensitivity to the atmosphere, were sealed inside thin-walled quartz capillaries. Intensities were collected on a modified Picker FACS-I diffractometer equipped with a Mo X-ray tube and a graphite monochromator. The data were corrected for crystal decay, absorption (analytical method),¹⁴ and Lorentz and polarization effects. Details of the data collection and results are shown in Table VI. The heavy-atom positions were located with the use of three-dimensional Patterson maps; subsequent least-squares refinements and electron density maps revealed the locations of all of the non-hydrogen atoms. The structures were refined by full-matrix least squares; hydrogen atoms were not included; scattering factors¹⁵ were adjusted for anomalous dispersion. With anisotropic temperature factors on all of the atoms, the least-squares refinement resulted in large and unrealistic thermal parameters for the atoms in the methylcyclopentadienyl groups C(7)–C(12) and C(13)–C(18), and even after these atoms were refined with isotropic thermal parameters, the bond distances in these groups were poor and the refinement of their parameters were not converging. An electron density map calculated through the plane of this ring showed a continuum of electron density with many poorly resolved peaks. To accommodate this disorder, two half-occupancy methylcyclopentadienyl groups were introduced into the structure. To accomplish the convergence of the least-squares procedures, the atoms in these groups were refined with distance restraints,¹⁶ and the positional parameters of atoms C(7') and C(8'), in the uranium complex, were fixed. Because the space group is polar, both sets of enantiomorphic structures were refined; the weighted *R* factors for the two conformations were 0.045 and 0.061 for the uranium complex and 0.059 and 0.062 for the cerium complex. The positional parameters given in Table VI are for the conformations with the lowest *R* factors.

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Supplementary Material Available: Tables of thermal parameters, estimated hydrogen atom positions, least-squares planes additional distances, additional angles, and distance restraints (16 pages); listings of observed structure factors and their discrepancies from the calculated values, (75 pages). Ordering information is given on any current masthead page.

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