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Uranium(IV) Complexes with the Oxygen Tripod Ligand $L^- = CpCo[P(O)(OEt)_2]_3^-$. X-ray Crystal Structure of L_2UCl_2

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Reaction of UX_4 with NaL ($L = (C_5H_5)Co[P(O)(OEt)_2]_3$) gave the complexes LUX_3 ($X = BH_4$ (**1**), Cl (**2**)). The trichloride **2** reacted with NaL or TlCp ($Cp = C_5H_5$) to afford respectively the compounds L_2UCl_2 (**3**) and $LCpUCl_2$ (**4**). Crystals of **3** belong to space group $P2_1/c$. The unit cell has $a = 13.229$ (4) Å, $b = 20.011$ (2) Å, $c = 21.080$ (1) Å, $\beta = 103.97$ (3)°, $V = 5415$ (3) Å^3 and contains four molecules. For the 2321 independent reflections with $I > 3\sigma(I)$, the final conventional and weighted discrepency factors are 0.052 and 0.054, respectively. The geometry of the UO_6Cl_2 core is intermediate between a bicapped trigonal prism and a square antiprism. The average U-Cl distance is 2.728 (8) Å, and the average U-O distance is 2.36 (5) Å.

Introduction

The anionic half-sandwich complex $(C_5H_5)Co[P(O)(OEt)_2]_3^-$ (hereafter abbreviated as L^-) is an oxygen tripod ligand that has been coordinated to a great number of metals, giving ML_2 and ML_2^+ compounds,[2] and to a variety of organometallic fragments[3] in various oxidation states. The ligand L has been crystallographically characterized as its sodium salt $(NaL)_3 \cdot 2H_2O$[4] and its lithium salt $(LiL)_2$.[5] This monoanionic six-electron ligand is formally equivalent to the cyclopentadienyl and the tris(pyrazolyl)borate $[HB(pz)_3^-]$ anions, and its cone angle (160°) is comparable with that of $C_5Me_5^-$ (146°) and $HB(pz)_3^-$ (180°).

We thought that this tripod ligand, because of its low position in the spectrochemical series,[6] near the hydroxide and fluoride ions, which makes it distinctly different from both $C_5Me_5^-$ and $HB(pz)_3^-$, would be interesting for the preparation of stable uranium derivatives. Here we present the syntheses of the first U(IV) complexes LUX_3 ($X = BH_4$ (**1**), Cl (**2**)), L_2UCl_2 (**3**), and $LCpUCl_2$ (**4**) ($Cp = C_5H_5$); we also describe the X-ray crystal structure of **3**.

Results and Discussion

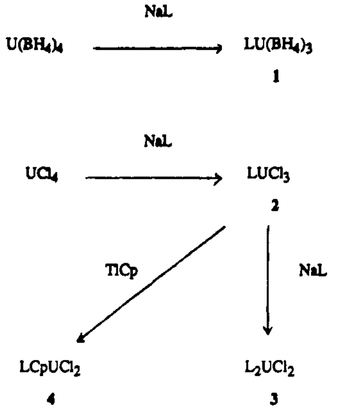
Preparation. Reaction of $U(BH_4)_4$ with 1 mol equiv of NaL in toluene at 20 °C afforded immediately the tris(borohydride) compound $LU(BH_4)_3$ (**1**) (Scheme I); the latter was isolated in 80% yield as light green crystals after filtration, partial evaporation of the solvent, and crystallization from toluene-pentane. The trichloride analogue **2** was similarly prepared in 50% yield from UCl_4 in tetrahydrofuran.

In contrast to **1** (See Experimental Section), complex **2** rapidly and cleanly reacted with the stoichiometric amount of NaL or TlCp in THF to yield respectively, after the usual work up and crystallization from pentane or toluene, yellow crystals of L_2UCl_2 (**3**) (45%) and green crystals of $LCpUCl_2$ (**4**) (30%).

Compounds **1**, **2**, and **4** should be kept under inert atmosphere, but **3** is stable in air and can even be dissolved in water without decomposition. The complexes were characterized on the basis of elemental analysis and ^1H NMR spectroscopic data and by single-crystal crystallographic studies in the case of **3** and **4**.

NMR Spectra of the Complexes. The ^1H NMR spectra of **1** and **2** in THF-d_8 at 30 °C exhibited three signals, a singlet, a multiplet, and a triplet, with an intensity ratio of 5:12:18, which were respectively assigned to cyclopentadienyl, the six equivalent methylene, and the six equivalent methyl groups of the ligand L. The methylene protons are diastereotopic, and in addition to geminal and vicinal proton-proton coupling they show virtual coupling to three phosphorous nuclei. The spectrum of **1** also showed a quartet at δ 56.6 ($J_{BH} = 85$Hz) corresponding to the three equivalent borohydride ligands.

Scheme I. Synthesis of Compounds **1-4** ($L = CpCo[P(O)(OEt)_2]_3$



The spectrum of L_2UCl_2 (**3**) at 30 °C was similar to the ones of the complexes **1** and **2**. At -20 °C, the CH_3 triplet and the CH_2 multiplet signal broadened, and at -65 °C, the spectrum showed, in addition to the singlet corresponding to the cyclopentadienyl group (5 H), a set of six signals of equal intensity (6 × 2 H) and a second set of three signals also of equal intensity (3 × 6 H), which were respectively attributed to the methylene and the methyl protons. Spin saturation transfer experiments[7] revealed that all the CH_3 and all the CH_2 groups are still exchanging. The nonrigidity of the coordination polyhedron around uranium obviously gives the ligands L time-averaged C_{3v} symmetry at 30 °C whereas at -65 °C the NMR spectrum is in accord with the C_{2v} molecular symmetry observed in the solid-state structure. In Chart I is shown how six nonequivalent methylene (a-f) and three nonequivalent methyl (A-C) positions arise in the ligand L when the C_{3v} symmetry is lowered to C_{2v}.

The coordination polyhedron of uranium in $LCpUCl_2$ (**4**) is more rigid than that in L_2UCl_2 (**3**). The ^1H NMR spectrum of **4** at 30 °C already revealed three signals corresponding to the three sets of anisochronous methyl groups. The spectrum of **4** at -70 °C is well resolved and corresponds to a static structure with C_s symmetry as observed in the crystal structure. By irradiation, it was possible to associate each CH_3 triplet signal with one pair of CH multiplet resonances. For example, the triplet

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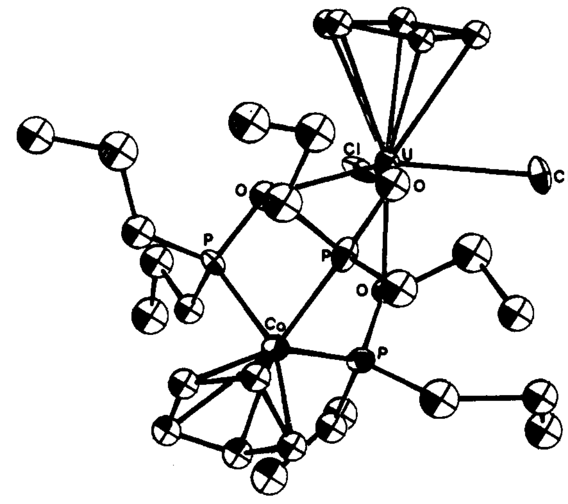
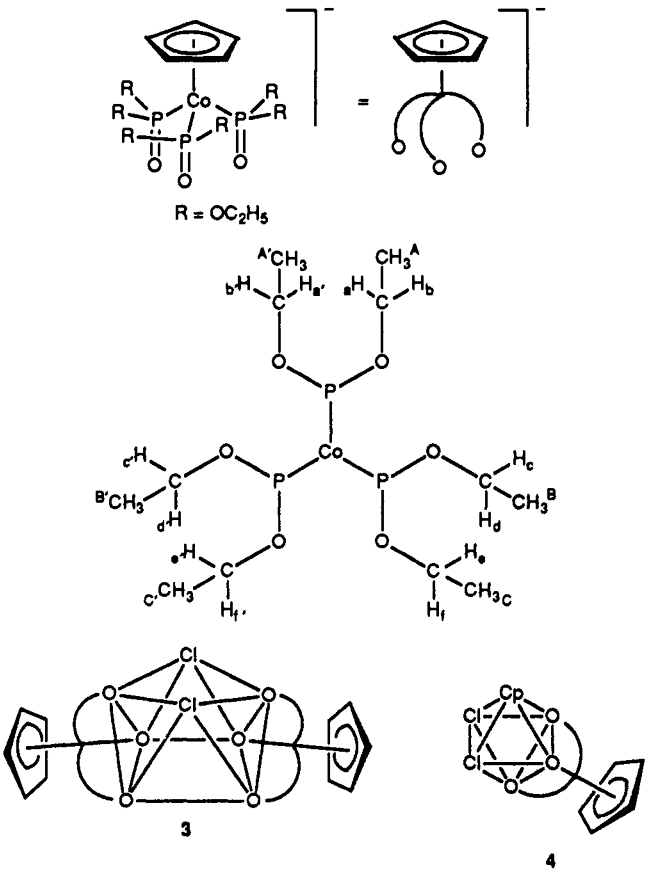


Figure 1. ORTEP diagram of the crystal structure of 4.

Chart I. Representations of the C_{3v} Tripod Ligand L (Primed Atoms Related by the Plane of Symmetry) and of the Square-Antiprism and Octahedral Environments of the U Atom in Compounds 3 and 4



at δ 11.51 (J = 7 Hz) was coupled with the two multiplets at δ 35.02 and 30.31 and was transformed into a doublet when one of these two signals was irradiated. These facts indicated that compounds 3 and 4 adopt preferentially a geometry in which one of the planes of symmetry of the C_{3v} tripod ligand is also a plane of symmetry of the complex (Chart I). This would be the case if the ligands of 3 and 4 were respectively in the square antiprismatic and the octahedral arrangements shown in Chart I. The structures of 3 and 4 have been determined by X-ray crystallography.

X-ray Crystal Structure of L_2UCl_2. Crystals of 4 belong to space group $P2_1/n$ with a = 11.758 (2) Å, b = 19.882 (4) Å, c = 14.187 (5) Å, β = 91.23 (2)°, D_{calc} = 1.82 g·cm^{-3}, and Z = 4. The refinement fitting 984 unique data ($I > 3\sigma(I)$) led to a final R index of 0.09. An ORTEP diagram of 4 is shown in Figure 1. The structure could not be determined with good accuracy and will not be presented here in details. However, it unambiguously revealed the pseudooctahedral configuration of the complex with the cyclopentadienyl group and one leg of the tripod ligand occupying the axial positions and the equatorial plane containing the two cis chlorine atoms and the two other legs of the ligand L.

Table I. Crystallographic Data for 3

$C_{34}H_{70}Cl_2Co_2O_{18}P_6U$	1379.6
space group	$P2_1/c$
a, Å	13.229 (4)
b, Å	20.011 (2)
c, Å	21.080 (1)
β, deg	103.97 (3)
V, Å^3	5415 (3)
Z	4
D_{calc}, g cm^{-3}	1.66
cryst dimens, mm	0.35 × 0.20 × 0.10
μ(Mo Kα), cm^{-1}	37.66
radiation (λ, Å)	Mo Kα (0.71073)
2θ range, deg	2.40
scan mode	$\omega/2\theta$
tot. no. of indep reflcns	5208
no. of reflcns used, $I > 3\sigma(I)$	2321
no. of variables	308
$R = (\sum\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.052
$R_w = [(\sum w[\lvert F_o\rvert - \lvert F_c\rvert]^2)/\sum w\lvert F_o\rvert^2]^{1/2}$ [a]	0.054

[a] $w = 4F_o^2/[\sigma_o^2(F_o^2) + (pF^2)^2]$; p = 0.04.

Table II. Selected Bond Distances (Å) and Angles (deg) for 3

(1) U Environment

U–Cl(1)	2.735 (5)	U–Cl(2)	2.721 (5)
U–O(17A)	2.35 (1)	U–O(17B)	2.39 (1)
U–O(27A)	2.41 (1)	U–O(27B)	2.33 (1)
U–O(37A)	2.326 (9)	U–O(37B)	2.36 (1)
Cl(1)–U–Cl(2)	97.9 (2)		
O(17A)–U–O(27A)	70.8 (3)	O(17B)–U–O(27B)	73.9 (3)
O(17A)–U–O(37A)	74.1 (3)	O(17B)–U–O(37B)	73.8 (3)
O(27A)–U–O(37A)	74.0 (3)	O(27B)–U–O(37B)	71.6 (3)

(2) $(C_5H_5)Co[P(O)(OEt)_2]_3$ Ligand

	A	B
Co–P(1)	2.164 (6)	2.148 (6)
Co–P(2)	2.155 (5)	2.159 (6)
Co–P(3)	2.157 (6)	2.171 (6)
Co–C(1)	2.12 (2)	2.15 (2)
Co–C(2)	2.10 (2)	2.13 (2)
Co–C(3)	2.10 (2)	2.12 (2)
Co–C(4)	2.08 (2)	2.12 (2)
Co–C(5)	2.10 (2)	2.07 (2)
P(1)–O(11)	1.63 (1)	1.59 (1)
P(1)–O(14)	1.63 (1)	1.59 (1)
P(1)–O(17)	1.52 (1)	1.48 (1)
P(2)–O(21)	1.59 (1)	1.60 (1)
P(2)–O(24)	1.60 (1)	1.61 (1)
P(2)–O(27)	1.49 (1)	1.54 (1)
P(3)–O(31)	1.61 (1)	1.60 (2)
P(3)–O(34)	1.63 (1)	1.62 (2)
P(3)–O(37)	1.514 (9)	1.52 (1)
Co–P(1)–O(11)	112.3 (5)	107.8 (5)
Co–P(1)–O(14)	104.2 (5)	112.5 (6)
Co–P(1)–O(17)	120.2 (5)	117.8 (5)
Co–P(2)–O(21)	111.9 (5)	114.4 (5)
Co–P(2)–O(24)	108.0 (5)	107.1 (6)
Co–P(2)–O(27)	118.8 (5)	118.3 (5)
Co–P(3)–O(31)	107.9 (5)	109.7 (6)
Co–P(3)–O(34)	113.1 (5)	105.3 (5)
Co–P(3)–O(37)	115.8 (5)	119.8 (5)

The crystallographic data for 3 appear in Tables I–III, and an ORTEP diagram of the molecule is shown in Figure 2. The crystal structure consists of discrete mononuclear units at general positions in the unit cell. The uranium atom is surrounded by two chloride and two oxygen tripod ligands to give a coordination number of

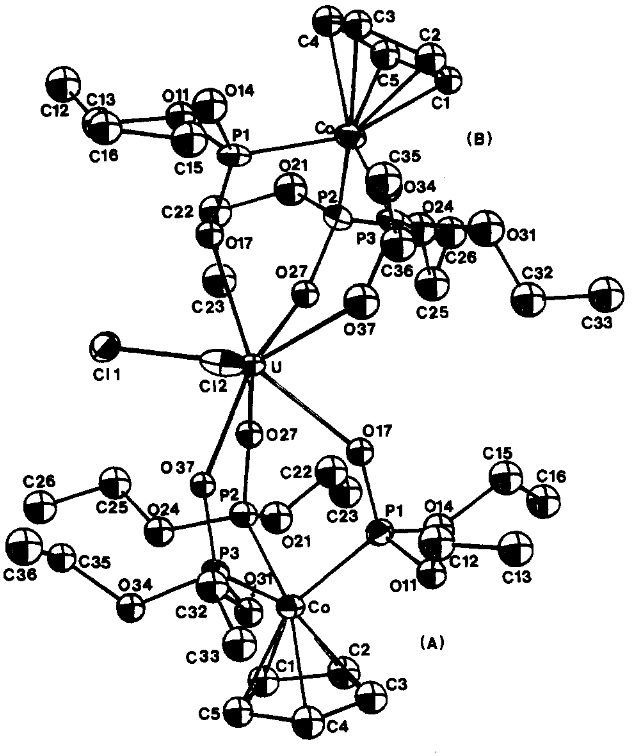


Figure 2. ORTEP diagram of the crystal structure of 3.

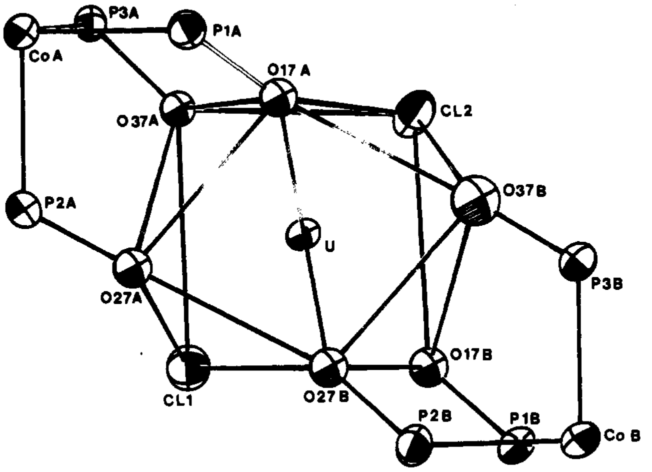


Figure 3. View of complex 3, showing the coordination geometry (distorted bicapped trigonal prism or square antiprism). The OEt and Cp groups have been omitted for clarity.

8. The geometry of the primary coordination sphere (Figure 3) may be seen either as a distorted bicapped trigonal prism (formed by the two parallel triangles O(17A), O(37A), Cl(2) and O(17B), O(27B), Cl(1), the U atom being at 1.60 Å from these planes and O(27A) and O(37B) capping two nearly rectangular faces of the prism) or a distorted square antiprism (O(37A), Cl(2), O(17B), and Cl(1) are nearly coplanar to within ±0.45 Å and parallel to the O(17A), O(37B), O(27B), O(27A) mean plane by ±0.28 Å, the U atom being at 1.37 Å from these planes). The U–O distances range between 2.41 (1) and 2.33 (1) Å, and the U–Cl distances are 2.735 (5) and 2.721 (5) Å. The U–O distances seem relatively short when compared with the U–N distances ($U-N_{av}$ = 2.55 Å) in the isostructural tris(pyrazolyl)borate complex $[HB(pz)_3]_2UCl_2$.[8] The U–Cl distances on the other hand are longer than in $[HB(pz)_3]_2UCl_2$ ($U-Cl_{av}$ = 2.63 Å) and $[C_5H_3(SiMe_3)_2]_2UCl_2$ ($U-Cl_{av}$ = 2.57 Å).[9]

Table III. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, Å^2
U	–0.18165 (6)	0.22701 (5)	0.19796 (5)	3.47 (2)[a]
Cl(1)	–0.1923 (4)	0.2860 (3)	0.3132 (3)	6.1 (2)[a]
Cl(2)	–0.1134 (4)	0.1047 (3)	0.2465 (4)	6.5 (2)[a]
Co(A)	0.0901 (2)	0.3390 (2)	0.1649 (2)	3.91 (8)[a]
C(1A)	0.163 (2)	0.434 (1)	0.178 (1)	5.5 (6)
C(2A)	0.130 (2)	0.416 (1)	0.108 (1)	5.4 (6)
C(3A)	0.184 (2)	0.355 (1)	0.099 (1)	5.0 (6)
C(4A)	0.246 (2)	0.336 (1)	0.161 (1)	5.6 (6)
C(5A)	0.234 (2)	0.381 (1)	0.212 (1)	4.8 (6)
P(1A)	–0.0087 (4)	0.2738 (4)	0.0943 (3)	4.3 (2)[a]
P(2A)	–0.0442 (4)	0.3839 (3)	0.1885 (3)	4.2 (2)[a]
P(3A)	0.0980 (4)	0.2647 (3)	0.2401 (3)	3.7 (1)[a]
O(11A)	0.0579 (9)	0.2183 (8)	0.0649 (7)	5.2 (4)
O(14A)	–0.054 (1)	0.3218 (8)	0.0315 (7)	5.6 (4)
O(17A)	–0.0960 (9)	0.2352 (7)	0.1126 (6)	4.3 (3)
O(21A)	–0.080 (1)	0.4504 (8)	0.1474 (7)	6.0 (4)
O(24A)	–0.008 (1)	0.4149 (7)	0.2605 (7)	4.7 (3)
O(27A)	–0.1394 (9)	0.3422 (7)	0.1840 (6)	4.0 (3)
O(31A)	0.1695 (9)	0.2043 (6)	0.2259 (6)	4.1 (3)
O(34A)	0.1623 (9)	0.2899 (7)	0.3118 (6)	4.4 (4)
O(37A)	–0.0055 (8)	0.2385 (6)	0.2481 (6)	3.2 (3)
C(12A)	0.045 (2)	0.147 (1)	0.077 (1)	8.1 (8)
C(13A)	0.053 (2)	0.110 (2)	0.019 (2)	12 (1)
C(15A)	–0.130 (2)	0.293 (1)	–0.026 (1)	8.6 (8)
C(16A)	–0.143 (2)	0.358 (2)	–0.072 (2)	12 (1)
C(22A)	–0.163 (2)	0.452 (2)	0.093 (1)	9.5 (9)
C(23A)	–0.174 (2)	0.521 (2)	0.066 (2)	12 (1)
C(25A)	–0.085 (2)	0.454 (1)	0.287 (1)	8.1 (8)
C(26A)	–0.031 (2)	0.472 (2)	0.353 (2)	9.9 (9)
C(32A)	0.175 (2)	0.142 (1)	0.268 (1)	6.4 (7)
C(33A)	0.262 (2)	0.102 (1)	0.256 (1)	6.5 (7)
C(35A)	0.109 (2)	0.296 (1)	0.367 (1)	5.3 (6)
C(36A)	0.133 (2)	0.235 (1)	0.410 (1)	7.1 (7)
Co(B)	–0.5082 (2)	0.1733 (2)	0.1015 (2)	4.76 (9)[a]
C(1B)	–0.617 (1)	0.170 (1)	0.007 (1)	4.7 (6)
C(2B)	–0.604 (2)	0.104 (1)	0.037 (1)	4.8 (6)
C(3B)	–0.628 (2)	0.102 (1)	0.098 (1)	5.3 (6)
C(4B)	–0.664 (2)	0.174 (1)	0.111 (1)	5.3 (6)
C(5B)	–0.655 (1)	0.208 (1)	0.057 (1)	4.4 (6)
P(1B)	–0.4423 (4)	0.1673 (3)	0.2050 (3)	4.6 (2)[a]
P(2B)	–0.4414 (4)	0.2714 (4)	0.0992 (3)	4.8 (2)[a]
P(3B)	–0.3710 (5)	0.1262 (4)	0.0821 (4)	5.8 (2)[a]
O(11B)	–0.5085 (9)	0.2147 (7)	0.2402 (7)	4.6 (3)
O(14B)	–0.464 (1)	0.0973 (8)	0.2348 (8)	6.9 (4)
O(17B)	–0.3303 (9)	0.1824 (7)	0.2291 (7)	4.0 (3)
O(21B)	–0.501 (1)	0.3296 (8)	0.1275 (7)	6.2 (4)
O(24B)	–0.461 (1)	0.2928 (8)	0.0236 (8)	7.4 (5)
O(27B)	–0.3259 (9)	0.2815 (7)	0.1336 (6)	4.5 (3)
O(31B)	–0.385 (1)	0.1191 (9)	0.0048 (9)	8.2 (5)
O(34B)	–0.376 (1)	0.0488 (9)	0.1044 (9)	8.8 (5)
O(37B)	–0.264 (1)	0.1542 (7)	0.1127 (7)	5.0 (4)
C(12B)	–0.476 (2)	0.225 (1)	0.311 (1)	7.4 (7)
C(13B)	–0.552 (2)	0.269 (1)	0.332 (1)	7.7 (7)
C(15B)	–0.384 (2)	0.049 (1)	0.265 (1)	7.1 (7)
C(16B)	–0.374 (2)	0.045 (1)	0.336 (1)	8.3 (8)
C(22B)	–0.465 (2)	0.364 (1)	0.190 (1)	7.8 (8)
C(23B)	–0.396 (2)	0.423 (1)	0.180 (1)	8.0 (8)
C(25B)	–0.423 (2)	0.360 (2)	0.001 (1)	9.8 (9)
C(32B)	–0.315 (2)	0.148 (1)	–0.030 (1)	9.4 (9)
C(26B)	–0.526 (2)	0.392 (2)	–0.028 (2)	12 (1)
C(33B)	–0.316 (2)	0.092 (2)	–0.082 (2)	12 (1)
C(35B)	–0.276 (2)	0.003 (2)	0.110 (2)	10.2 (9)
C(36B)	–0.327 (3)	–0.059 (2)	0.129 (2)	15 (1)

[a] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\vec{a}_i\vec{a}_j$.

The Cp rings of the L ligands are planar to within 0.02 Å, and the average C–C distances have usual values for cycle A (1.46 (3) Å) and cycle B (1.45 (4) Å). The Co atom is surrounded by three P atoms (average Co–P = 2.16 (1) Å) and one η^5-cyclopentadienyl ligand (U–Cp(centroid) = 1.60 (1) Å), which form

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a three legged piano stool; the P–Co–Cp(centroid) angles range from 123 (1) to 126 (1)° whereas the P–Co–P angles range from 90 (1) to 91 (1)° for the A and B ligands.

We have seen that these square antiprismatic and octahedral structures of **3** and **4** are also those which are preferentially adopted by the complexes in solution.

Concluding Remarks

We have described here the first uranium(IV) complexes of the oxygen tripod ligand L^-. In view of the rich and novel organometallic chemistry of uranium,[10] we would be especially interested to see whether these compounds form σ-alkyl derivatives and how oxygen tripod ligands in lieu of pentamethylcyclopentadienyl ligands alter the a priori high affinity of uranium for oxygen.

Experimental Section

General Methods. Microanalyses were carried out by the Analytical Laboratories at Engelskirchen, FRG. The ^1H NMR spectra were recorded on a Bruker W60 (FT) instrument. Deuteriated solvents were dried over Na/K alloy. The paramagnetic shifts are relative to tetramethylsilane (δ 0 ppm).

All experiments were carried out under argon in Schlenk type glassware attached to a high-vacuum line or used in a glovebox. Solvents were thoroughly dried and deoxygenated by standard methods and were distilled immediately prior to use. UCl_4,[11] $U(BH_4)_4$,[12] and TlCp[13] were prepared by published methods. $(NaL)_3{\cdot}2H_2O$ was synthesized according to the literature method;[14] a toluene solution of this hydrate was kept on 4-Å molecular sieves for 2 h, and the anhydrous salt NaL was obtained after evaporation of the solution.

Preparation. $\{CpCo[P(O)(OEt)_2]_3\}U(BH_4)_3$ (1). A 50-mL round-bottom flask was charged with $U(BH_4)_4$ (40.1 mg, 0.13 mmol) and NaL (79.8 mg, 0.14 mmol), and toluene (20 mL) was condensed into it under vacuum at −78 °C. The mixture was stirred at 20 °C for 30 min. The solution was filtered, and its volume was reduced to 1 mL; after addition of pentane (5 mL) light green crystals of **1** were formed. The product was filtered and dried under vacuum. Yield: 97 mg, 87%. Anal. Calcd for $C_{17}H_{47}CoO_9P_3U$: C, 24.96; H, 5.79; P, 11.36; B, 3.96. Found: C, 24.82; H, 5.64; P, 11.29; B, 3.83. ^1H NMR (THF-d_8, 303 K): δ 56.6 (br q, J_{BH} = 85 Hz, 12 H, BH_4), 7.76 (s, 5 H, Cp), 2.41 (m, 12 H, CH_2), 0.18 (t, J = 7 Hz, 18 H, CH_3). IR (Nujol): 2420, 2390, 2180, and 2110 cm^{-1} (BH_4).

$\{CpCo[P(O)(OEt)_2]_3\}UCl_3$ (2). A 50-mL round-bottom flask was charged with UCl_4 (110 mg, 0.29 mmol) and NaL (160 mg, 0.29 mmol), and THF (20 mL) was condensed into it under vacuum at −78 °C. The mixture was stirred at 20 °C for 20 min; the solution was filtered and evaporated to dryness. The solution obtained after extraction of the residue with a 1:1 mixture of toluene and THF (25 mL) was filtered and evaporated to dryness, leaving a green powder that was washed with pentane (5 mL) and then recrystallized from THF–pentane. The yellow crystals of **2** were filtered out, washed with pentane (2 mL), and dried under vacuum. Yield: 130 mg, 51%. Anal. Calcd for $C_{17}H_{35}Cl_3CoO_9P_3U$: C, 23.21; H, 4.01; P, 10.56; Cl, 12.09. Found: C, 22.83; H, 3.87; P, 10.26; Cl, 12.09. ^1H NMR (THF-d_8, 303 K): δ 6.45 (s, 5 H, Cp), 3.04 (m, 12 H, CH_2), 0.50 (t, J = 7 Hz, 18 H, CH_3).

$\{CpCo[P(O)(OEt)_2]_3\}_2UCl_2$ (3). A 50-mL round-bottom flask was charged with UCl_4 (90 mg, 0.24 mmol) and $(NaL)_3{\cdot}2H_2O$ (280 mg, 0.50 mmol of NaL), and THF (30 mL) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at 20 °C for 30 min. The solution was filtered and evaporated to dryness, and the residue was extracted with toluene (25 mL). After filtration and evaporation of the solution, the yellow powder was recrystallized from toluene–pentane, giving yellow needles of **3**. The product was filtered out and dried under vacuum. Yield: 150 mg, 45%. These crystals were suitable for X-ray analysis. Compound **3** was similarly isolated from the reaction of **2** with 1 mol equiv of NaL. Anal. Calcd for $C_{34}H_{70}Cl_2Co_2O_{18}P_6U$: C, 29.60; H, 5.11; P, 13.47; Cl, 5.14. Found: C, 29.30; H, 5.06; P, 13.61; Cl, 4.94. ^1H NMR (THF-d_8, 303 K): δ 10.05 (s, 5 H, Cp), 1.71 (br, $w_{1/2}$ = 25 Hz, 12 H, CH_2), −0.50 (br t, J = 7 Hz, 18 H, CH_3). ^1H NMR (THF-d_8, 208 K): δ 10.90 (s, 5 H, Cp), 13.91 and 9.03 (br, 2 H + 2 H, CH) coupled with the signal at 3.88 (br, 3 H, CH_3), 12.63 and 10.41 (br, 2 H + 2 H, CH) coupled with the signal at 4.49 (br, 3 H, CH_3), −20.64 and −21.67 (br, 2 H + 2 H, CH) coupled with the signal at −13.27 (br, 3 H, CH_3). The half-height width of the CH and CH_3 signals is ca. 20 Hz.

$\{CpCo[P(O)(OEt)_2]_3\}CpUCl_2$ (4). A 50-mL round-bottom flask was charged with **2** (128 mg, 0.09 mmol) and TlCp (42 mg, 0.15 mmol), and THF (20 mL) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred at 20 °C for 1 h. After evaporation to dryness, the residue was extracted with a 1:1 mixture of THF–toluene (20 mL); the solution was filtered and evaporated to dryness, and the green powder was recrystallized from toluene. The green crystals were filtered out, washed with pentane (5 mL), and dried under vacuum. Yield: 25 mg, 30%. Analyses are in agreement with the formula **4**·$^1/_2$NaCl. Anal. Calcd for $C_{22}H_{40}Cl_{2.5}CoO_9P_3Na_{0.5}U$: C, 28.15; H, 4.29; P, 9.90; Cl, 9.44. Found: C, 28.39; H, 4.37; P, 10.10; Cl, 9.11. The mother liquors were concentrated to ca. 5 mL, and crystals of **4**, suitable for X-ray analysis, were formed. ^1H NMR (THF-d_8, 303 K): δ 29.03 (br, 2 H, CH), 25.30 (br, 2 H, CH), 22.50 (s, 5 H, U–Cp), 9.93 (br, 6 H, CH_3), 8.49 (s, 5 H, Co–Cp), −4.13 (br, 6 H, CH_3), −5.10 (br, 6 H, CH_3), −5.83 (br, 2 H, CH), −8.51 (br, 2 H, CH), −10.97 (br, 4 H, CH). ^1H NMR (THF-d_8, 203 K): δ 35.02 and 30.31 (m, 2 H + 2 H, CH) coupled with the signal at 11.51 (t, J = 7 Hz, 6 H, CH_3), 27.88 (s, 5 H, U–Cp), 9.34 (s, 5 H, Co–Cp), −8.47 and −11.38 (m, 2 H + 2 H, CH) coupled with the signal at −5.04 (t, J = 7 Hz, 6 H, CH_3), −14.99 (m, 4 H, CH) coupled with the signal at −6.65 (t, J = 7 Hz, 6 H, CH_3).

Reactions of 1 with NaL and TlCp. Attempts to prepare the complex $L_2U(BH_4)_2$ by reaction of **1** with 1 mol equiv of NaL gave several products that could not be separated.

An NMR tube was charged with **1** (8 mg, 0.01 mmol) and TlCp (3 mg, 0.012 mmol), and toluene-d_8 (0.5 mL) was condensed into it under vacuum at −78 °C. After 48 h, the ^1H NMR spectrum showed the formation of $LCpU(BH_4)_2$. ^1H NMR (toluene-d_8, 303 K): δ 43.96, 39.06, −10.80, −15.21, −19.47, and −19.78 (s, 6 × 2 H, CH), 15.08, −6.38, and −9.01 (s, 3 × 3 H, CH_3), 33.00 (s, 5 H, U–Cp), 9.24 (s, 5 H, Co–Cp), −85.40 (q, J_{BH} = 85 Hz, 8 H, BH_4). Other minor products were also formed, and the borohydride analogue of **4** was not isolated pure.

X-ray Crystallographic Analysis of 3. Single crystals of **3** were grown from toluene–pentane. A selected crystal was collected and sealed in the glovebox in a thin-walled glass capillary. X-ray intensity data were collected at 22 °C on an Enraf-Nonius CAD-4 automatic diffractometer equipped with a graphite monochromator. Cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°; they are given in Table I together with relevant information concerning experimental conditions and details of the structure solutions and refinements. An empirical absorption was applied.[15] After correction for Lorentz and polarization effects, 2321 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. All calculations were performed on a micro VAX II computer using the Enraf-Nonius Structure Determination Package.[16] The U atom position was derived from a Patterson map, and the remaining non-hydrogen atoms were located from subsequent least-squares refinement and difference Fourier syntheses. Final full-matrix least-squares refinement cycles using anisotropic temperature factors for U, Cl, Co, and P atoms converged to $R = 0.052$ and $R_w = 0.054$. H atoms were not included in the refinement. Atomic scattering factors for neutral atoms as well as anomalous scattering contributions were taken from ref 17. The final positional and thermal parameters with standard deviations are presented in Table III.

Supplementary Material Available: Tables of anisotropic thermal parameters and additional bond distances and angles (7 pages); a table of F_o vs F_c values (9 pages). Ordering information is given on any current masthead page.

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