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Monocyclooctatetraenyluranium(IV) borohydrides. Crystal structure of $(\eta\text{-}C_8H_8)U(BH_4)_2(OPPh_3)$

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Abstract

$U(BH_4)_4$ has been shown to react with $(COT)_2U$ (COT = η-C_8H_8) or cyclooctatetraene to give the monocyclooctatetraenyl complex $(COT)U(BH_4)_2$ (III), which has been converted into the Lewis base adducts $(COT)U(BH_4)_2L$ (L = PPh_3, V; THF, VI; $OPPh_3$, VII) and the mixed ring derivatives (COT(Cp)U(BH_4)L (Cp = η-C_5H_5; L = THF; $OPPh_3$. VIII). The crystal structure of VII shows it to have a three-legged piano stool configuration.

Introduction

Bis(cyclooctatetraenyl)uranium (IV) compounds have been extensively studied since the preparation of uranocene, $(COT)_2U$ (COT = η-C_8H_8) (I), in 1968 [1]. However, well characterized mono-COT uranium complexes, which might show a more varied chemistry, were unknown until recently, when Sattelberger et al. prepared $(COT)U[N(SiMe_3)_2]_2$ from $(COT)UCl_2(THF)_2$ (THF = tetrahydrofuran) [2]. We describe below an alternative route to such monocyclooctatetraenyluranium derivatives, from the borohydride precursor $(COT)U(BH_4)_2$ (III) and also present the crystal structure of $(COT)U(BH_4)_2(OPPh_3)$ (VII).

Results and discussion

Synthesis of $(COT)U(BH_4)_2$ (III); evidence for the bridged mono-COT intermediate $(BH_4)_3U(COT)U(BH_4)_3$ (IV)

The poorly soluble uranocene (I) reacted immediately in toluene with a stoechiometric amount of $U(BH_4)_4$ (II) to give a red solution, which after 15 min at 20 °C deposited a greenish powder of $(COT)U(BH_4)_2$ (III); the yield was nearly quantitative. Compound III was also prepared in good yield by photolysis or thermolysis of

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II in toluene or mesitylene in the presence of a slight excess of cyclooctatetraene. Again we observed the initial formation of a red solution, which subsequently deposited small green needles of III.

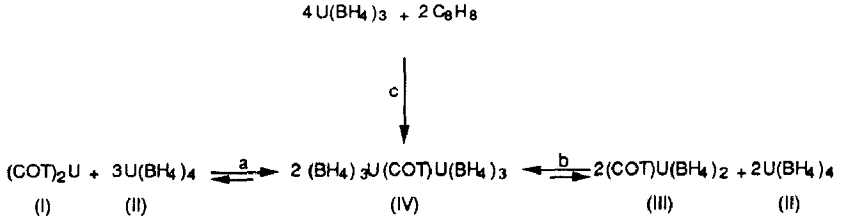
$$(COT)_2U + U(BH_4)_4 \rightarrow 2(COT)U(BH_4)_2 \leftarrow 2C_8H_8 + 2U(BH_4)_4$$

(I) (II) (III) (II)

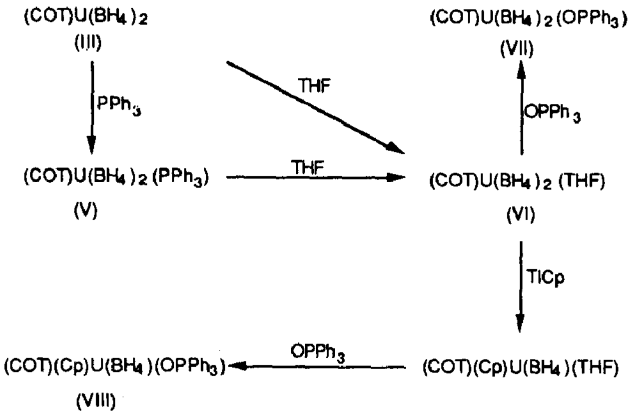
The insolubility of III in non-coordinating solvents suggests a polymeric structure; the formulation $[(COT)U(BH_4)_2]_n$ was deduced from the elemental analyses and the formation of soluble adducts with Lewis bases (vide infra).

The ^1H NMR spectrum of the red solution exhibited, in addition to the signals of I and II, a quartet at 80.57 ppm (J 80 Hz) and a singlet at -24.98 ppm, with relative intensities 24/8, and these were tentatively assigned to the COT bridged compound $(BH_4)_3U(COT)U(BH_4)_3$ (IV). A few examples of bimetallic complexes with a bridged COT ligand have been reported: $[(Me_2NCH_2CH_2NMe_2)Li]_2[C_8H_6(1,4\text{-}SiMe_3)_2]$ [3] and the triple-decker sandwich anion $(COT)_3Ti_2^{2-}$ [4]. Stable toluene solutions of IV were made up by various routes (Scheme 1): (a) by treating I with an excess of II, (b) by making an equimolecular mixture of II and III, (c) by treating $U(BH_4)_3$ (in the form of $U(BH_4)_3$ (mesitylene) [5]) with cyclooctatetraene. All these reactions took place at 20 °C, and in all cases the major product IV was formed in good yield but it could not be isolated pure, free from I, II or III ([IV]/[II] 65/35). It is clear, from the equilibria shown in Scheme 1, that IV may be an observable intermediate during the synthesis of III. When the latter was prepared from an equimolecular mixture of I and II, uranocene (I), which is not very soluble in toluene, first reacted with an excess of II to give IV (equilibrium a); equilibrium b was then shifted towards the formation of III by the subsequent reaction of II with I. Reduction of II to give $U(BH_4)_3$ was achieved both by photolysis [6] and by thermolysis [7]; reaction c, between the uranium tris(borohydride) and cyclooctatetraene, gave IV, and in this case, displacement of equilibrium b was caused by the reduction of II.

Preparation of III from I represents the first synthesis of a mono-COT complex from a bis(annulene)uranium derivative [8], ($(COT)UCl_2(THF)_2$ was isolated from the reaction of UCl_3 with cyclooctatetraene in THF [2]), and resembles that of the thorium compounds $(COT)ThX_2(THF)_2$ ($X = Cl, BH_4$), which were obtained by refluxing an equimolecular mixture of $(COT)_2Th$ and ThX_4 in tetrahydrofuran [8,9]. In contrast to the free base compound III, the THF adduct $(COT)U(BH_4)_2(THF)$ (VI) could not be easily prepared from II: prolonged refluxing in THF was necessary, and concomitant formation of $U(BH_4)_3(THF)_n$ [5] (by reaction of II with I) and/or cyclooctatetraene polymers (reaction of II with C_8H_8) was observed.



Scheme 1.



Scheme 2.

Recently the substituted mono-COT complex [η-$C_8H_6(1,4\text{-}SiMe_3)_2$]$U(BH_4)_2$ was synthesized by treatment of the $UCl_4/2LiBH_4$ mixture with the potassium salt of the corresponding cyclooctatetraene dianion [3]. The similar reaction with K_2COT was not straight forward, and gave high yield of uranocene [9].

Synthesis of the Lewis base adducts (COT)U(BH$_4$)$_2$L (L = PPh$_3$, V; THF, VI; OPPh$_3$, VII) and (COT)(Cp)U(BH$_4$)(OPPh$_3$) (VIII)

Addition of a small excess (ca. 2 equiv.) of PPh_3 or THF to a suspension of III in toluene led to the formation of (COT)$U(BH_4)_2(PPh_3)$ (V) and (COT)$U(BH_4)_2$(THF) (VI), both of which crystallized from toluene/pentane (Scheme 2). The NMR spectra (Table 1) revealed that V and VI rapidly exchange their PPh_3 or THF ligands with the corresponding free molecules. The triphenylphosphine ligand of V

Table 1

^1H NMR spectra of the complexes [a]

Compound	COT ligand	BH_4 ligands	other ligands
(COT)$U(BH_4)_2(PPh_3)$ (V)	−35.88(s, 8H)	140(br, 800, 8H)	0.89 (s, 6H, *o*.Ph) 5.7 (m, 9H, *m*- and *p*-Ph)
(COT)$U(BH_4)_2$(THF) (VI)	−33.35(s, 8H)	126.21(q, 83, 8H)	−6.71 (s, 4H, β-THF) −23.30 (s, 4H, α-THF)
(COT)$U(BH_4)_2(OPPh_3)$ (VII)	−28.82(s, 8H)	71.63(q, 83, 8H)	7.07 (m, 15H, Ph)
(COT)(Cp)$U(BH_4)$(THF) ·THF [b]	−47.60(s, 8H)	−33.81(br, 110, 4H)	−65.42 and −21.45 (s, 4H+4H, coordinated THF) 1.32 and 4.71 (s, 4H+4H, free THF) 24.50 (s, 5H, Cp)
(COT)(Cp)$U(BH_4)(OPPh_3)$ (VIII)	−29.99(s, 8H)	−13.71(q, 75, 4H)	−1.73 (br, 65, 6H, *o*-Ph) 5.77 (br, 30, 6H, *m*-Ph) 6.60 (br, 25, 3H, *p*-Ph) 8.13 (s, 5H, Cp)

[a] V and VI in toluene-d_8, VII and VIII in THF-d_8; δ relative to TMS (multiplicity, J or half height width in Hz, intensity, assignment). [b] In toluene-d_8 at −70 °C; spin saturation transfer was observed between the free and coordinated THF signals.

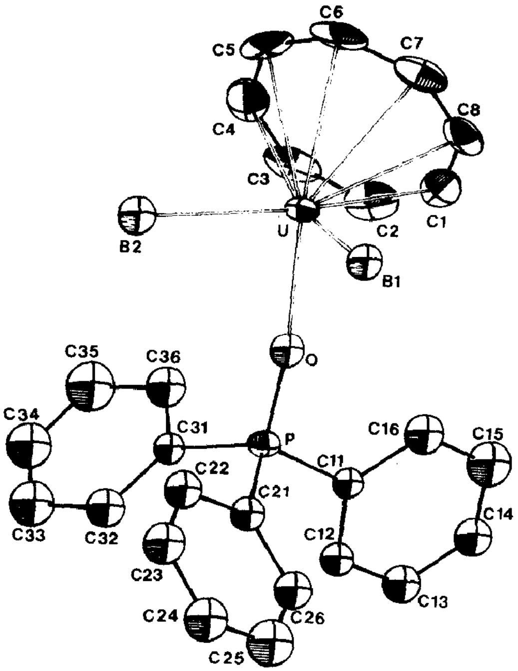


Fig. 1. ORTEP drawing of monocyclooctatetraenyluranium (VII).

was readily displaced by THF to give VI, which was treated with a stoichiometric amount of triphenylphosphine oxide to give (COT)U$(BH_4)_2(OPPh_3)$ (VII), which was isolated as red crystals from THF/pentane in 80% yield.

It is noteworthy that III is a rare example of an organoactinide compound which, like $(MeCp)_3U$, is able to accommodate either a phosphine oxide or a phosphine ligand [10]. Phosphine complexes of the *f* elements are not numerous, and most of them are trivalent uranium derivatives containing the more basic PR_3 ligands [11]. Compound V is, to our knowledge, the first triphenylphosphine complex of an actinide; however, the solution of this compound in toluene was not indefinitely stable, and after 3 h at 20 °C, precipitation of III and liberation of free PPh_3 were observed (see Experimental).

Metathesis of the borohydride ligands of VI with $NaN(SiMe_3)_2$ in toluene gave the diamide derivative (COT)U$[N(SiMe_3)_2]_2$ [2] in quantitative yield (NMR experiment). Compound VI was treated with TlCp (Cp = η-C_5H_5) in THF, and after the usual work up, a red THF solvate of (COT)(Cp)U(BH_4)(THF) was crystallized from THF/pentane. In the presence of 1 equiv. of $OPPh_3$, the latter complex was readily transformed into (COT)(Cp)U$(BH_4)(OPPh_3)$ (VIII), which was isolated as red crystals from THF/pentane (30% from VI). Compound VIII was also obtained in quantitative yield (NMR) by treating VII with TlCp. The only other mixed ring organoactinide complexes previously reported are $[(COT)(C_5Me_5)ThCl]_2$ and its derivatives [12].

X-ray crystal structure of (COT)U$(BH_4)_2(OPPh_3)$ (VII)

Compound VII is the first monocyclooctatetraenyluranium compound to have been crystallographically characterized. An ORTEP [13] drawing is shown in Fig. 1;

selected bond distances and angles are listed in Table 2. The structure consists of discrete molecules which adopt a three legged piano stool configuration: the three angles B(1)–U–B(2), B(1)–U–O and B(2)–U–O are respectively 93.9(5), 88.5(4), and 90.4(4)°, and the three angles B(1)–U–COT, B(2)–U–COT and O–U–COT (where COT is the centroid of the ring) are 125.6(5), 125.0(4), and 122.9(3)°. The short U–B distances (2.57(1) and 2.66(1) Å) are characteristic of tridentate BH_4 ligands [14]. The C_8H_8 ligation in VII is not much different from that in I. The COT ring is planar (the C atoms are within ±0.03 Å of the best least squares plane) and the U atom lies at 1.98(1) Å from this plane. The mean U–C bond distance is 2.68(1) Å and the mean C–C bond distance is 1.38(4) Å; the corresponding values in uranocene are 2.647 and 1.392 Å, respectively [1].

Experimental

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 chemical shifts are given as δ values relative to tetramethylsilane. The ^1H NMR spectra are given in Table 1.

All experiments were carried out under argon in Schlenk type glassware on a high vacuum line or in a glove box. Photolysis was performed in a quartz vessel with a 1000 W UV lamp (Hg, medium pressure). Solvents were thoroughly dried and deoxygenated by the standard methods and distilled immediately prior to use. $(COT)_2U$ [1], $U(BH_4)_4$ [15], $U(BH_4)_3$(mesitylene) [5], $NaN(SiMe_3)_2$ [16] TlCp [17] were prepared by published methods. Cyclooctatetraene (Merck) was distilled. PPh_3 (Prolabo) and $OPPh_3$ (Schuchardt) were used without purification.

Syntheses

(COT)U(BH$_4$)$_2$ (III). (a) A 100 ml round bottom flask was charged with I (820 mg) and II (528 mg) and toluene (50 ml) was condensed into it under vacuum at −78°C. The mixture was stirred at 20°C. A red solution was immediately obtained, I dissolved progressively, and a green powder separated. After 1 h, the green powder was filtered off, dried under vacuum, and shown to be III (1170 mg, 87%).

(b) A solution of II (220 mg) and cyclooctatetraene (320 mg) in mesitylene (13 ml) was heated under reflux for 5 min. The red solution deposited green needles of III, which were filtered off, washed with toluene, and dried under vacuum (220 mg, 79%). A similar mixture of II and C_8H_8 was refluxed in toluene for 72 h to give III in 43% yield.

(c) A solution of II (240 mg) and cyclooctatetraene (400 mg) in toluene (25 ml) was irradiated at 20°C for 12 h. The red solution deposited green needles of III, which were filtered off and dried under vacuum (200 mg, 66%). Analysis. Found: C, 25.61; H, 4.17; B, 5.68. $C_8H_{16}B_2U$ calcd.: C, 25.84; H, 4.34; B, 5.81%.

Formation of (BH$_4$)$_3$ U(COT)U(BH$_4$)$_3$ (IV). The ^1H NMR spectrum (toluene-d_8, 30°C) of the red solution which was observed during the various preparations of III exhibited two signals at 80.57 ppm (q, 80, 24H, BH_4) and −24.98 ppm (s, 8H, COT), which were attributed to IV. Toluene-d_8 (0.5 ml) was condensed into an NMR tube containing either I (5 mg) and II (10 mg), II (5 mg) and III (6.3 mg) or

$U(BH_4)_3$(mesitylene) (10 mg) and C_8H_8 (3 mg). The NMR spectra indicated the formation of IV; the ratio [IV]/[II] was equal to ca. 65/35 (by integration of the BH_4 signals). Solids were invariably observed in the NMR tubes (green needles of III or emerald crystals of I).

(COT)U(BH$_4$)$_2$(PPh$_3$) (V). A 50 ml round bottom flask was charged with III (103 mg) and PPh_3 (144 mg) and toluene (15 ml) was condensed in under vacuum at −78 °C. The mixture was stirred for 5 h at 20 °C until a red solution was obtained (use of 2 equiv. of PPh_3 was necessary to bring about complete dissolution of III, and when 1 equiv. of the phosphine was used only half of the III dissolved). The NMR spectrum in toluene-d_8 of the mixture obtained after evaporation of an aliquot (0.5 ml) of the red solution was similar to that of V (Table 1), except that the phenyl protons signals integrated for 30H and the *ortho*-hydrogens peak was shifted towards its diamagnetic position (δ 2.47 ppm). Coalescence of this signal was observed at −95 °C. The solution was then filtered and the volume of toluene was reduced to 10 ml and pentane (20 ml) was condensed in. Green microcrystals of V separated within a few minutes, and these were filtered off and dried under vacuum (97 mg, 55%). The microcrystals were not completely soluble in toluene and contained a small amount (ca. 5%) of III and this was also reflected in the elemental analysis. After 3 h at 20 °C, a solution of V deposited green crystals of III and the NMR spectrum showed the formation of free PPh_3([V]/[PPh_3] 0.83).

(COT)U(BH$_4$)$_2$(THF) (VI). THF (ca. 1 ml) was condensed into a 50 ml round bottom flask containing III (80 mg) in toluene (20 ml) at −78 °C. The red solution was evaporated to dryness and the residue recrystallized from toluene/pentane as red microcrystals of VI, which were filtered off and dried under vacuum (80 mg, 83%). It was confirmed that a stoichiometric amount of THF is sufficient to dissolve

Table 2

Selected bond distances (Å) and angles (°) for compound VII

Environment of uranium		COT ring	
U-B(1)	2.57(1)	C(1)-C(2)	1.39(2)
U-B(2)	2.66(1)	C(2)-C(3)	1.39(2)
U-O	2.27(1)	C(3)-C(4)	1.42(3)
U-COT [a]	1.98(1)	C(4)-C(5)	1.36(2)
U-C(1)	2.68(2)	C(5)-C(6)	1.46(3)
U-C(2)	2.68(2)	C(6)-C(7)	1.31(2)
U-C(3)	2.68(1)	C(7)-C(8)	1.34(2)
U-C(4)	2.68(2)	C(8)-C(1)	1.38(2)
U-C(5)	2.69(1)		
U-C(6)	2.67(2)	C(1)-C(2)-C(3)	134(2)
U-C(7)	2.66(2)	C(2)-C(3)-C(4)	134(2)
U-C(8)	2.68(2)	C(3)-C(4)-C(5)	137(2)
		C(4)-C(5)-C(6)	134(2)
O-U-B(1)	88.5(4)	C(5)-C(6)-C(7)	132(2)
O-U-B(2)	90.4(4)	C(6)-C(7)-C(8)	140(2)
B(1)-U-B(2)	93.9(5)	C(7)-C(8)-C(1)	134(1)
COT-U-B(1)	125.6(5)	C(8)-C(1)-C(2)	136(1)
COT-U-B(2)	125.0(4)		
COT-U-O	122.9(3)		

[a] COT is the centroid of the C_8H_8 ring.

III in toluene. Analysis. Found: C, 32.20; H, 5.29; B, 4.95. $C_{12}H_{24}B_2OU$ calcd.: C, 32.46; H, 5.45; B, 4.87%.

(COT)U(BH$_4$)$_2$(OPPh$_3$) (VII). A 50 ml round bottom flask was charged with III (68 mg) or VI (70 mg) and $OPPh_3$ (51 mg) and THF (10 ml) was condensed in under vacuum at −78 °C. The mixture was stirred at 20 °C for 15 min and the solvent then evaporated off. Recrystallization of the residue from THF/pentane gave red microcrystals of VII (98 mg, 80%), which were filtered off and dried under vacuum. Analysis. Found: C, 47.68; H, 4.62; B, 3.05; P, 4.60. $C_{26}H_{31}B_2POU$ calcd.: C, 48.03; H, 4.80; B, 3.32; P, 4.76%.

(COT)(Cp)U(BH$_4$)(OPPh$_3$) (VIII). (a) A 50 ml round bottom flask was charged with VI (130 mg) or III (110 mg) and TlCp (80 mg). THF (15 ml) was condensed in under vacuum at −78 °C. The mixture was stirred at 20 °C for 2 h then filtered, and the solvent was evaporated off. Recrystallization of the residue from THF/pentane gave red microcrystals of the mono-THF-solvate of (COT)(Cp)U(BH_4)(THF) (100 mg, 65%), which was characterized from its NMR spectrum. (Table 1). Another 50 ml round bottom flask was charged with this solvate (90 mg), $OPPh_3$ (42 mg) and THF (10 ml) was condensed in at −78 °C under vacuum. The mixture was stirred at 20 °C for 15 min; then the solvent was evaporated off and the residue recrystal-

Table 3

Crystallographic data and experimental details for compound VII

Crystal data	
Cryst. dimensions (mm)	0.40 × 0.30 × 0.25
Color	red
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	15.447(12)
b (Å)	16.967(8)
c (Å)	19.477(5)
V (Å^3)	5105(8)
Z	8
D_{calc} (g cm^{-3})	1.69
μ(Mo-K_α) (cm^{-1})	61.06
Data collection	
Radiation	Mo-K_α (λ 0.71073 Å)
θ limits (°)	1–23
Scan type	$\omega/2\theta$
Monochromator	graphite
reflections measured	
h	0, 16
k	0, 18
l	0, 20
Reflections collected	
total	4070
unique	3534
with I > 3 σ(I)	1752
Final values	
$R(F)$	0.037
$R_w(F^2)(\omega = 0.04)$ [a]	0.042

[a] $w = 1/(\sigma F_o)^2$ and $\sigma F_o^2 = [\sigma(I)^2 + (pF^2)^2]^{1/2}$; $p = 0.04$.

lized from THF/pentane, to give red microcrystals of VIII (105 mg, 87% from IV). Analysis. Found: C, 52.92; H, 4.61; B, 1.46; P, 4.18. $C_{31}H_{32}BPOU$ calcd.: C, 53.16; H, 4.60; B, 1.54; P, 4.42%.

(b) Toluene-d_8 (0.5 ml) was condensed into an NMR tube containing VII (10 mg) and TlCp (4.5 mg). After 10 min the NMR spectrum revealed a near quantitative formation of VIII.

X-ray crystal structure of VII

A single crystal was introduced into a thin-walled Lindemann glass tube in an inert atmosphere dry-box. Data were collected on an Enraf–Nonius CAD4 automatic diffractometer equipped with a graphite monochromator. Cell dimensions were obtained by a least-squares refinement of the setting angles of the 25 reflections with θ between 8 and 12°. Intensities were corrected for Lorentz polarization effects and absorption (using the empirical DIFABS method [18]). The structure was solved by the heavy-atom method and refined by full-matrix least-squares (F).

Table 4

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their e.s.d. for compound VII

Atom	*x*	*y*	*z*	B (Å^2) ^{a}
U	0.05449(3)	0.08000(3)	0.20153(2)	2.818(8) ★
P	0.0621(3)	0.1868(2)	0.3722(2)	3.13(7) ★
O	0.0499(6)	0.1454(5)	0.3031(4)	3.9(2)
C(1)	−0.098(1)	0.143(1)	0.1665(7)	6.0(4) ★
C(2)	−0.040(1)	0.2055(9)	0.1653(8)	6.3(4) ★
C(3)	0.040(1)	0.2169(8)	0.1344(7)	6.3(4) ★
C(4)	0.094(1)	0.169(1)	0.0926(7)	7.9(5) ★
C(5)	0.092(1)	0.094(1)	0.0671(6)	8.3(5) ★
C(6)	0.031(1)	0.029(1)	0.0732(7)	7.2(5) ★
C(7)	−0.046(1)	0.0241(9)	0.1019(7)	5.8(4) ★
C(8)	−0.100(1)	0.0675(9)	0.1400(7)	5.1(4) ★
C(11)	−0.0352(7)	0.2356(7)	0.3939(6)	3.1(3)
C(12)	−0.0411(9)	0.2901(8)	0.4480(6)	4.0(3)
C(13)	−0.1174(9)	0.3295(9)	0.4615(7)	5.0(4)
C(14)	−0.187(1)	0.3177(9)	0.4213(7)	5.4(4)
C(15)	−0.188(1)	0.266(1)	0.3678(8)	7.0(4)
C(16)	−0.110(1)	0.2211(9)	0.3546(8)	5.5(4)
C(21)	0.0902(9)	0.1192(8)	0.4399(7)	3.5(3)
C(22)	0.1637(9)	0.0714(8)	0.4314(7)	4.7(3)
C(23)	0.190(1)	0.019(1)	0.4815(7)	5.7(4)
C(24)	0.145(1)	0.0178(9)	0.5405(8)	5.8(4)
C(25)	0.075(1)	0.0605(9)	0.5505(9)	6.8(5)
C(26)	0.0431(9)	0.1154(9)	0.5006(7)	4.7(3)
C(31)	0.1467(7)	0.2579(8)	0.3675(6)	3.2(3)
C(32)	0.2097(9)	0.2660(9)	0.4168(7)	5.1(3)
C(33)	0.276(1)	0.3230(9)	0.4066(9)	7.4(5)
C(34)	0.276(1)	0.368(1)	0.3518(8)	7.2(5)
C(35)	0.214(1)	0.364(1)	0.3019(9)	8.4(5)
C(36)	0.146(1)	0.3081(9)	0.3085(7)	5.6(4)
B(1)	0.016(1)	−0.047(1)	0.2666(9)	4.0(4)
B(2)	0.224(1)	0.060(1)	0.2153(8)	4.4(4)

^{a}★ means: $B_{eq} = \frac{4}{3}[\Sigma_i \Sigma_j \beta_{ij} \vec{a}_i \vec{a}_j]$.

The H atoms of the COT and phenyl rings were included in the refinement at calculated positions (C–H 0.95 Å, B 6 $Å^2$); they were not refined but constrained to ride on their C atoms. The H atoms of the BH_4 groups were not located; the U, P, and C atoms of the COT ring were refined anisotropically. All calculations were performed on a MicroVax II computer with the Enraf–Nonius Structure Determination Package [19]. Analytical scattering factors for neutral atoms [20] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3. Selected bond lengths and angles are listed in Table 2 and final position parameters in Table 4. A complete list of bond lengths and angles and a table of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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