

Dibenzyl[1,2-bis(dimethylphosphino)ethane]bis(cyclopentadienyl)thorium(IV)

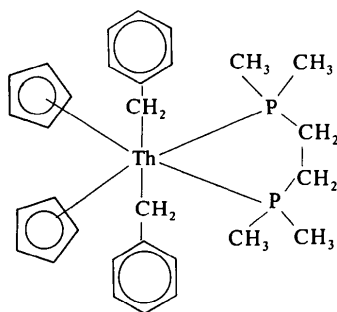
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Abstract. $[\text{Th}(\text{C}_5\text{H}_5)_2(\text{C}_7\text{H}_7)_2(\text{C}_6\text{H}_{16}\text{P}_2)]$, $M_r = 694.64$, triclinic, $P\bar{1}$, $a = 13.104(4)$, $b = 11.124(4)$, $c = 10.518(4)$ Å, $\alpha = 89.90(3)$, $\beta = 92.99(3)$, $\gamma = 110.16(3)^\circ$, $V = 1437.1$ Å³, $Z = 2$, $D_x = 1.605$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 179.1$ cm⁻¹, $F(000) = 680$, $T = 296$ K, $R = 0.028$ for 4021 unique reflections with $F^2 > \sigma(F^2)$ of 4279 total unique data. Distances (Å) are: ave. Th–C(Cp) 2.83 ± 0.05 ; Th–C(benzyl) 2.648 (6), 2.666 (7); Th–P 3.142 (2), 3.237 (2); Th–Cp(ring) 2.56, 2.59. The cyclopentadienyl rings are *trans* to the bidentate ligand, in agreement with Keppert's rules for six-coordinate complexes. There are no interactions between the Th atom and the aryl ring.

Introduction. In the preceding paper (Zalkin, Brennan & Andersen, 1987) the X-ray crystal structures of $(\text{C}_5\text{H}_5)_2\text{Th}(X)_2 \cdot (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$, where X is CH_3 or Cl , were described and the geometry of the complexes was rationalized on the basis of Keppert's rules (Keppert, 1977). In our synthetic studies we prepared the benzyl analogue, $X = (\text{CH}_2\text{C}_6\text{H}_5)$, the structure of which is of considerable interest since the benzylic group often behaves as an η^3 - or η^4 -benzylic ligand towards actinide centers, e.g. *ortho*- and *ipso*-carbon–uranium distances are shorter than the sum of the van der Waals radii of the elements (Mintz, Moloy, Marks & Day, 1982; Edwards, Andersen & Zalkin, 1984).



Experimental. The complex was made by the reaction of $[\text{Th}(\text{C}_5\text{H}_5)_2\text{Cl}_2(\text{C}_6\text{H}_{16}\text{P}_2)]$ with benzyllithium at 228 K (Brennan, 1985). Crystals suitable for the X-ray

study were grown from a toluene:pentane (1:1) mixture at 203 K. Yellow air-sensitive crystals were sealed inside quartz capillaries under argon. Crystal $0.18 \times 0.19 \times 0.25$ mm with six faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 36 reflections, $40 < 2\theta < 80^\circ$; analytical absorption correction, range 5.39 to 20.85; max. $(\sin\theta)/\lambda = 0.56$ Å⁻¹; h –13 to 13, k 0 to 12, l –11 to 11; three standard reflections, average decay 5%, intensities adjusted accordingly; 6932 data, 4279 unique, $R_{\text{int}} = 0.030$; structure solved by Patterson and Fourier methods; refined on F , f' and f'' terms included, 394 parameters; positional coordinates of all the hydrogen atoms were estimated and, with the exception of the 16 dimethylphosphinoethane hydrogen atoms, were refined in the least-squares refinements with isotropic thermal parameters; dimethylphosphinoethane H-atom parameters included but not refined; anisotropic thermal parameters for non-hydrogen atoms; large anisotropies in the thermal parameters of C(27) and C(28) and a short C–C bond length suggest disorder in the dimethylphosphinoethane ligand, $R = 0.031$ for 4279 data; $R = 0.028$ for 4021 reflections for which $F^2 > \sigma(F^2)$; $wR = 0.033$; $S = 1.3$; $w = [\sigma(F)]^{-2}$, $p = 0.045$ in calculation of $\sigma(F^2)$; max. $(\text{shift}/\sigma) < 0.04$; empirical extinction correction, $F_{\text{corr}} = (1 + kI)$, $k = 2.3 \times 10^{-7}$; max. and min. of ΔF synthesis 1.3 and -1.1 e Å⁻³; atomic f , f' and f'' for neutral Th, Cl, P and C, and spherical bonded H from *International Tables for X-ray Crystallography* (1974); local unpublished programs and *ORTEP* (Johnson, 1965).

Atomic parameters are listed in Table 1,* and distances and angles are listed in Table 2. Fig. 1 shows the molecule and numbering scheme.

Discussion. The stereochemistry of the title compound is similar to that of the methyl and chloro analogues

* Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positions, distances and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43410 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å²)
$$B_{eq} = \sum_i \sum_j B_{ij} a_i^* a_j^* a_j / 3.$$

	x	y	z	B _{eq} /B
Th	0.17689 (1)	0.35991 (2)	0.23254 (1)	3.436 (6)
P(1)	0.26019 (14)	0.13689 (16)	0.31568 (17)	5.00 (5)
P(2)	0.18855 (13)	0.31165 (16)	0.53572 (13)	4.56 (5)
C(1)	0.0117 (5)	0.4689 (6)	0.2200 (6)	4.6 (2)
C(2)	0.0439 (5)	0.4718 (6)	0.3488 (6)	4.4 (2)
C(3)	0.1481 (5)	0.5634 (6)	0.3676 (6)	4.8 (2)
C(4)	0.1805 (5)	0.6163 (6)	0.2467 (6)	4.7 (2)
C(5)	0.0961 (5)	0.5578 (6)	0.1600 (6)	4.9 (2)
C(6)	0.1371 (7)	0.2188 (9)	-0.0065 (7)	6.7 (3)
C(7)	0.2450 (8)	0.2391 (10)	0.0235 (7)	6.7 (3)
C(8)	0.3046 (8)	0.3665 (11)	0.0181 (7)	7.6 (4)
C(9)	0.2328 (11)	0.4303 (10)	-0.0143 (7)	8.3 (4)
C(10)	0.1289 (10)	0.3379 (11)	-0.0288 (7)	7.0 (4)
C(11)	0.0053 (6)	0.1506 (7)	0.2696 (8)	5.3 (2)
C(12)	-0.1021 (5)	0.1615 (6)	0.2362 (6)	4.7 (2)
C(13)	-0.1457 (6)	0.1491 (7)	0.1096 (7)	5.9 (2)
C(14)	-0.2417 (6)	0.1717 (8)	0.0783 (8)	6.5 (3)
C(15)	-0.3002 (6)	0.2020 (8)	0.1692 (9)	6.8 (3)
C(16)	-0.2610 (6)	0.2107 (8)	0.2943 (9)	6.4 (3)
C(17)	-0.1651 (5)	0.1902 (7)	0.3268 (7)	5.5 (2)
C(18)	0.3814 (5)	0.4691 (7)	0.3201 (7)	5.0 (2)
C(19)	0.4275 (5)	0.6076 (6)	0.3027 (7)	5.1 (2)
C(20)	0.4234 (5)	0.6947 (7)	0.3966 (7)	5.5 (2)
C(21)	0.4600 (6)	0.8293 (8)	0.3768 (10)	7.0 (3)
C(22)	0.5042 (7)	0.8734 (9)	0.2649 (12)	8.3 (4)
C(23)	0.5122 (8)	0.7922 (10)	0.1708 (11)	8.3 (4)
C(24)	0.4761 (7)	0.6620 (8)	0.1916 (9)	6.8 (3)
C(25)	0.4034 (7)	0.1612 (9)	0.2979 (9)	7.6 (3)
C(26)	0.1955 (8)	-0.0235 (8)	0.2436 (9)	7.8 (3)
C(27)	0.2423 (10)	0.0979 (9)	0.4833 (8)	8.5 (4)
C(28)	0.2601 (9)	0.1997 (11)	0.5691 (8)	8.7 (4)
C(29)	0.0635 (6)	0.2476 (8)	0.6191 (6)	6.7 (3)
C(30)	0.2672 (7)	0.4392 (9)	0.6473 (7)	7.7 (3)
H(1)C(1)	-0.058 (5)	0.417 (6)	0.179 (6)	4.3 (13)*
H(2)C(2)	-0.002 (5)	0.424 (6)	0.408 (6)	4.2 (13)*
H(3)C(3)	0.193 (5)	0.589 (6)	0.445 (7)	5.7 (16)*
H(4)C(4)	0.259 (5)	0.689 (5)	0.230 (5)	4.0 (12)*
H(5)C(5)	0.102 (5)	0.586 (6)	0.082 (6)	4.4 (13)*
H(6)C(6)	0.068 (7)	0.119 (9)	0.003 (8)	8.6 (23)*
H(7)C(7)	0.277 (7)	0.163 (9)	0.039 (8)	8.7 (22)*
H(8)C(8)	0.400 (7)	0.396 (8)	0.043 (8)	8.8 (22)*
H(9)C(9)	0.242 (6)	0.533 (8)	-0.037 (7)	7.3 (18)*
H(10)C(10)	0.068 (6)	0.341 (7)	-0.052 (7)	5.4 (17)*
H(11)C(13)	-0.104 (5)	0.132 (6)	0.035 (7)	5.6 (15)*
H(12)C(14)	-0.266 (6)	0.167 (7)	-0.002 (7)	6.4 (18)*
H(13)C(15)	-0.378 (7)	0.237 (8)	0.132 (8)	8.7 (22)*
H(14)C(16)	-0.297 (6)	0.228 (7)	0.348 (7)	5.6 (18)*
H(15)C(17)	-0.131 (6)	0.206 (7)	0.411 (7)	5.8 (16)*
H(16)C(20)	0.392 (7)	0.660 (9)	0.495 (9)	9.2 (23)*
H(17)C(21)	0.448 (7)	0.891 (9)	0.460 (9)	9.0 (24)*
H(18)C(22)	0.551 (4)	0.982 (5)	0.284 (5)	3.6 (11)*
H(19)C(23)	0.552 (8)	0.845 (9)	0.110 (9)	9.5 (26)*
H(20)C(24)	0.489 (6)	0.607 (7)	0.118 (7)	6.7 (18)*
H(37)C(11)	0.022 (6)	0.087 (7)	0.218 (7)	6.0 (16)*
H(38)C(11)	0.019 (5)	0.144 (6)	0.343 (7)	4.7 (15)*
H(39)C(18)	0.398 (5)	0.450 (6)	0.394 (6)	4.2 (14)*
H(40)C(18)	0.429 (6)	0.431 (7)	0.282 (7)	7.1 (19)*

* Atoms refined isotropically.

(Zalkin, Brennan & Andersen, 1987). This is expected on the bases of Keppert's rules (Keppert, 1977) since a Th-ring centroid distance of 2.57 Å is less than the averaged Th-C(benzyl) bond distance of 2.657 (5) Å, and the ligand with the shortest metal-ligand bond will prefer to occupy the site *trans* to the bidentate ligand. The averaged Th-C(benzyl) distance is longer than the equivalent Th-C(CH₃) distance in the methyl analogue of 2.573 (6) Å (Zalkin, Brennan & Andersen, 1987). This is consistent with previous structural results which show that the uranium or thorium benzyl bond length is *ca* 0.1 Å longer than the equivalent metal-carbon (*sp*³-hybridized) distance (Perego, Cesari, Farina &

Table 2. Selected bond distances (Å) and angles (°)

Th-C(1)	2.820 (6)	Th-C(10)	2.780 (7)
Th-C(2)	2.794 (6)	Th-C(11)	2.666 (7)
Th-C(3)	2.818 (6)	Th-C(18)	2.648 (6)
Th-C(4)	2.841 (6)	Th-Cp(1)*	2.561
Th-C(5)	2.841 (6)	Th-Cp(2)	2.591
Th-C(6)	2.893 (7)	Th-P(1)	3.142 (2)
Th-C(7)	2.912 (7)	Th-P(2)	3.237 (2)
Th-C(8)	2.864 (7)	P(2)1P(1)	3.394 (4)
Th-C(9)	2.772 (7)		
P(1)-Th-P(2)	64.26 (5)	Th-C(11)-C(12)	115.5 (5)
P(1)-Th-C(11)	71.26 (17)	Th-C(18)-C(19)	108.0 (3)
P(1)-Th-C(18)	73.39 (16)	Th-P(1)-C(25)	117.53 (30)
P(2)-Th-C(11)	75.13 (17)	Th-P(1)-C(26)	119.80 (30)
P(2)-Th-C(18)	71.77 (17)	Th-P(1)-C(27)	112.88 (28)
C(11)-Th-C(18)	139.30 (23)	C(25)-P(1)-C(26)	100.9 (4)
Cp(1)-Th-Cp(2)	115.9	C(25)-P(1)-C(27)	103.2 (5)
Cp(1)-Th-C(11)	100.9	C(26)-P(1)-C(27)	99.8 (4)
Cp(1)-Th-C(18)	102.6	Th-P(2)-C(28)	109.85 (27)
Cp(1)-Th-P(1)	154.9	Th-P(2)-C(29)	119.79 (24)
Cp(1)-Th-P(2)	90.8	Th-P(2)-C(30)	121.45 (27)
Cp(2)-Th-C(11)	99.6	C(28)-P(2)-C(29)	104.5 (4)
Cp(2)-Th-C(18)	99.3	C(28)-P(2)-C(29)	98.4 (5)
Cp(2)-Th-P(1)	89.1	C(29)-P(2)-C(30)	99.8 (4)
Cp(2)-Th-P(2)	153.2		

* Cp(1) and Cp(2) represent the centroids of cyclopentadienyl atoms C(1)-C(5) and C(6)-C(10) respectively.

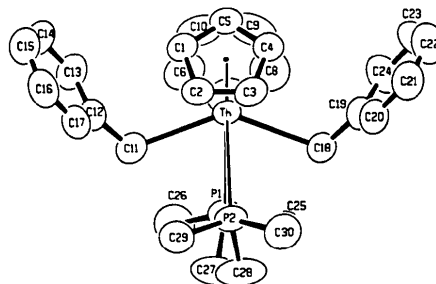


Fig. 1. ORTEP (Johnson, 1965) view of the title compound showing the atomic numbering scheme; 50% probability ellipsoids.

Lugli, 1976; Edwards, Andersen & Zalkin, 1984).

The two independent Th-P distances are significantly different, with an averaged distance of 3.19 (3) Å. The Th-P distance is substantially longer than that found in the chloro [3.122 (1) Å] and methyl [3.147 (1) Å] analogues (Zalkin, Brennan & Andersen, 1987). In all three complexes the averaged Th-C(C₅H₅) distances are equal within experimental error. The long Th-P distances can be rationalized most easily as a steric effect since the benzyl group is larger than a methyl group which prevents the phosphine from getting closer to the thorium atom in the benzyl derivative.

The principal reason for investigating the structure of the benzyl derivative was to examine the interaction, if any, between the actinide metal center and the aryl-ring carbon atoms. There are no thorium-carbon contacts shorter than 3.2 Å and the Th-C(18)-C(19), Th-C(11)-C(12) angles are normal. This is consistent with the explanation advanced previously (Edwards, Andersen & Zalkin, 1984) which suggested that the η³- or η⁴-benzylic interactions are relatively weak (on the

order of solvation energies or crystal packing energies) and that they are a manifestation of the desire of the large electropositive actinide metals to maximize their coordination numbers and to minimize the intramolecular ligand–ligand repulsions. The molecular structure is a compromise between these two conflicting tendencies. In the molecule described here, the thorium atom is coordinatively saturated and no benzylic interactions are observed.

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References

- BRENNAN, J. G. (1985). PhD Thesis. Univ. of California at Berkeley.
 EDWARDS, P. G., ANDERSEN, R. A. & ZALKIN, A. (1984). *Organometallics*, **3**, 293–298.
International Tables for X-ray Crystallography (1974). Vol. IV; Table 2.2, pp. 71–102. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KEPPERT, D. L. (1977). *Prog. Inorg. Chem.* **23**, 1–65.
 MINTZ, E. A., MOLOY, K. G., MARKS, T. J. & DAY, V. W. (1982). *J. Am. Chem. Soc.* **104**, 4692–4695.
 PEREGO, G., CESARI, M., FARINA, F. & LUGLI, G. (1976). *Acta Cryst.* **B32**, 3034–3039.
 ZALKIN, A., BRENNAN, J. G. & ANDERSEN, R. A. (1987). *Acta Cryst.* **C43**, 418–420.

Acta Cryst. (1987). **C43**, 423–425

Struktur von *N*-(4-Methoxybenzyliden)-2-methoxybenzylammonium Hexachloro-titanat(IV) Dibenzol

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Abstract. $2\text{C}_{16}\text{H}_{18}\text{NO}_2^+ \cdot \text{TiCl}_6^{2-} \cdot 2\text{C}_6\text{H}_6$, $M_r = 929.50$, monoclinic, $C2/c$, $a = 26.721$ (4), $b = 13.789$ (3), $c = 13.740$ (3) Å, $\beta = 112.05$ (4)°, $V = 4692.4$ Å³, $Z = 4$, $D_x = 1.316$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å $\mu = 5.642$ cm⁻¹, $F(000) = 1928$, $T = 293$ K, $R = 0.043$ for 1767 significant [$I > 3\sigma(I)$] reflections. The crystal structure consists of the ionic compound $[\text{C}_{16}\text{H}_{18}\text{NO}_2]^+ [\text{TiCl}_6]^{2-}$ and benzene as solvent in the ratio 1:2. In the centrosymmetric anion, Ti has a distorted octahedral coordination with Ti–Cl distances 2.309 (1)–2.351 (1) Å. Bond distances in the cation are in good agreement with literature values.

Einleitung. Einige Komplexe mit Schiffchen Basen dienen als Modell für den Energie-Transfer in biologischen Systemen, als Sauerstoff-Carrier und als Katalysatoren für biologische Reaktionen (Hughes, 1981). Im Rahmen unserer Untersuchungen über die Reaktionen von TiCl_4 mit Schiffchen Basen (Bastida, Sousa, Gayoso & Romero, 1982; Sousa, De la Fuente, Gayoso & Bastida, 1982; Rodriguez, Sousa, Gayoso, Bastida & Romero, 1983; Sousa, Macias, Gayoso & Romero, 1983) berichten wir im folgenden über die

Struktur eines Komplexes, der bei der Reaktion von *N*-(4-methoxybenzyliden)-2-methoxybenzylamin mit TiCl_4 entsteht.

Experimentelles. Rote, würfelförmige Kristalle; $0,2 \times 0,2 \times 0,25$ mm, in eine Kapillare abgefüllt. Buerger Präzessionsaufnahmen zeigen die Laue-Symmetrie $2/m$ und die Auslöschungsregeln hkl nur vorhanden für $h + k = 2n$, $h0l$ nur vorhanden für $l = 2n$; Raumgruppe Cc oder $C2/c$, letztere bestätigte sich durch die Verfeinerungsrechnungen. Registrierung der Reflexintensitäten auf dem Automatischen Vierkreisdiffraktometer CAD-4 (Fa. Enraf-Nonius, Delft), Mo $K\alpha$, Graphitmonochromator, Gitterkonstanten durch Verfeinerung der θ -Werte von 25 Reflexen hoher Beugungswinkel ($7 < \theta < 16^\circ$). 6667 Intensitäten erfasst, ω/θ scan, $\theta_{\max} < 23^\circ$, $0 < h < 29$, $-15 < k < 15$, $-15 < l < 15$; drei Kontrollreflexe alle 60 min, Intensitätsabnahme 0,768% pro Stunde, daher Korrektur für lineare Zersetzung; LP-Korrektur, empirische Absorptionskorrektur, Transmissionsfaktoren 0,886–0,989 (North, Phillips & Mathews, 1968), 3493 symmetrieunabhängige Reflexe ($R_{\text{int}} = 0,030$), davon