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BIS(CYCLOPENTADIENYL)DIMETHYLTHORIUM(IV) [BIS(DIMETHYLDIPHOSPHINO)ETHANE] AND BIS(CYCLOPENTADIENYL)DICHLOROTHORIUM(IV) [BIS(DIMETHYLDIPHOSPHINO)ETHANE]
$(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$,
$(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

A. Zalkin, J.G. Brennan, and R.A. Andersen

September 1986

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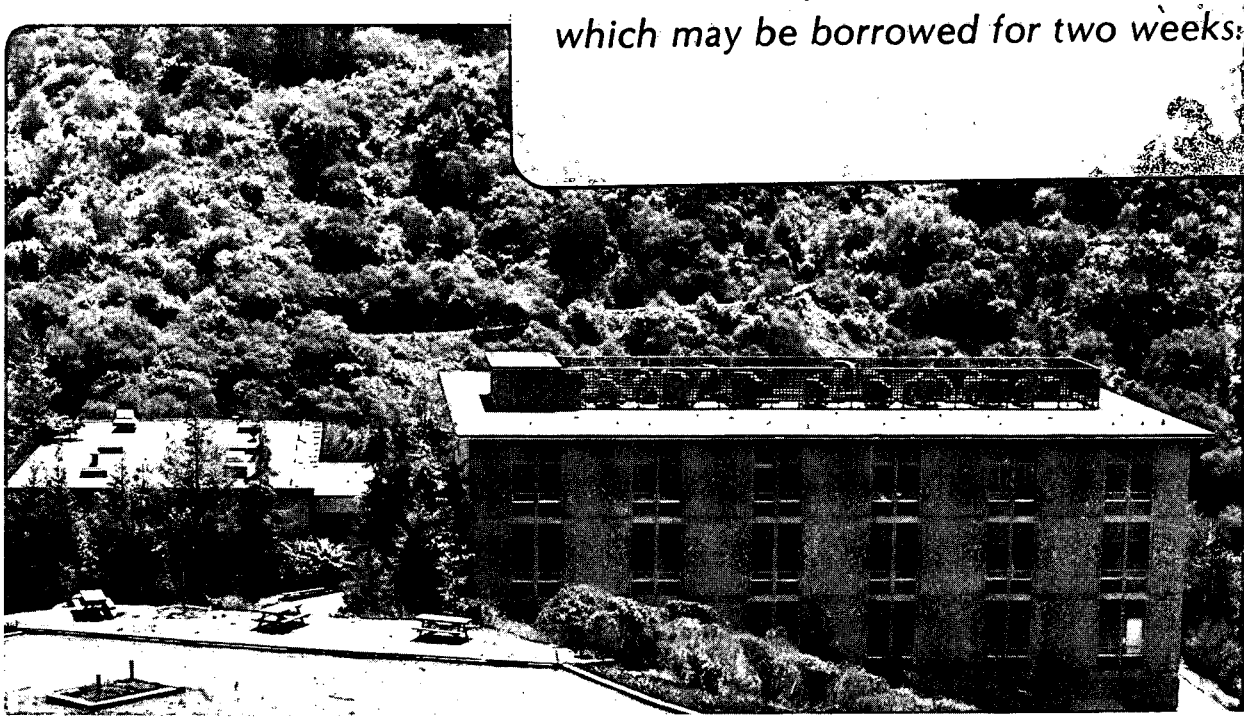

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Bis(cyclopentadienyl)dimethylthorium(IV)[bis(dimethyldiphosphino)ethane] and Bis(cyclopentadienyl)dichlorothorium(IV)[bis(dimethyldiphosphino)ethane]

$(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$, $(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

By Allan Zalkin, John G. Brennan & Richard A. Andersen

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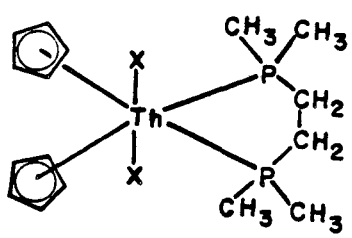
Abstract. $(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$ (1) M_r= 542.44, monoclinic, $P2_1/n$, a = 18.485(4), b = 14.118(4), c = 8.258(2) Å, β = 91.05(2)°, V = 2154.7 $Å^3$, Z = 4, D_x = 1.672 g cm^{-3}, λ(MoKα)=0.71073 Å, μ = 73.0 cm^{-1}, F(000) = 1040, T = 296 K, R = 0.026 for 2521 unique reflections with $F^2>2\sigma(F^2)$. Distances (Å) are: Th-C(Cp) 2.84 ± 0.03; Th-C(methyl) 2.562(8), 2.583(7); Th-P 3.146(2), 3.147(2) Å; Th-Cp 2.59, 2.57 Å. $(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$ (2) M_r= 583.28, monoclinic, $P2_1/n$, a = 18.268(2), b = 14.237(6), c = 7.996(3) Å, β = 92.27(4)°, V = 2078.0 $Å^3$, Z = 4, D_x = 1.864 g cm^{-3}, λ(MoKα)=0.71073 Å, μ = 78.3 cm^{-1}, F(000)= 1104, T = 296 K, R = 0.020 for 2361 unique reflections with I>σ(I). Distances (Å) are: Th-C(Cp) 2.80 ± 0.02; Th-Cℓ 2.707(2), 2.708(2); Th-P 3.121(2), 3.122(2) Å; Th-Cp 2.56, 2.54 Å. The structures of (1) and (2) are crystallographically isomorphous and were done to study their six-coordinate stereochemistry. The cyclopentadienyl rings are trans to the bidentate ligand.

Introduction. Compounds of the type $(C_5H_5)_2M(X)_2(L)$ where M is thorium or uranium, X is an anionic ligand such as halide or alkyl, and L is a neutral, bidentate phosphine ligand were prepared in order to examine the details of inter- and intra-molecular ligand exchange in solution. The stereochemistry of these six coordinate compounds (defining the centroid of the cyclopentadienyl ring as occupying a coordination site) in the solid state was essential since two idealized geometries are possible for MX_2Y_2-(bidentate ligand), that is either the X ligands or the Y ligands are trans to the bidentate ligand. For comparison the X-ray structures of $(C_5H_5)_2Th(X)_2\cdot[(CH_3)_2PCH_2CH_2P(CH_3)_2]$ where X = Cℓ, CH_3 (this paper) and where X = $CH_2C_6H_5$ (Zalkin. Brennan. Andersen, 1986) are described.



X = CH_3 or Cℓ

Experimental. The dimethyl complex (1) was made by the reaction of (2) with methyllithium at -45°C (Brennan, 1985). Colorless crystals suitable for X-ray studies were picked from the crystals obtained by crystallization from a toluene:pentane (1:4) solution at -70°C. The dichloro complex (2) was synthesized from the reaction of sodium cyclopentadienide with $ThCℓ_4\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$ in a tetrahydrofuran solution at -70°C and crystalllized from toluene. Crystals suitable for X-ray studies were grown from toluene:diethyl ether (6:4) at -20°C. The air sensitive crystals were sealed inside quartz capillaries under argon. Crystal 0.19 x 0.25 x 0.32 mm with 6 faces (1), 0.22 x 0.25 x 0.37 mm with 12 faces (2); modified Picker automatic diffractometer (1), Enraf-Nonius CAD-4 (2); graphite monochromator; cell dimensions from 20 reflections, 20° < 2θ < 34° (1), 24

reflections, 20°< 2θ < 32° (2); analytical absorption correction, range 1.47 to 1.83 (1), 3.26 to 4.66; max. $(\sin\theta)/\lambda$ = 0.60 $Å^{-1}$(1), 0.54 $Å^{-1}$(2); h -22 to 22, k 0 to 16, ℓ -9 to 9 (1); h -19 to 19, k 0 to 15, ℓ 0 to 8 (2); three standard reflections, [0.4%, 0.4%, 0.3% (1)], [1.3%, 1.7%, 1.2% (2)] variation in standards intensities from average, intensities adjusted isotropically; 7611 (1), 2929 [(I > σ(I)] (2) data, 3817 (1), 2361 (2) unique , R_{int}= 0.029 (1), 0.020 (hk0,$\bar{h}$k0) (2); structure solved by Patterson and Fourier methods; refined on F, 190 (1), 188 (2) parameters; 26 hydrogen positions (1) and 30 hydrogen positions (including 4 disordered positions) (2) in calculated locations with fixed isotropic thermal parameters; anisotropic thermal parameters for non-hydrogen atoms except for disordered atoms in (2); R = 0.060 for 3817 data (1); R = 0.026 for 2521 reflections for which $F^2>2\sigma(F^2)$ (1); R = 0.020 for 2361 reflections for which I>σ(I) (2); wR = 0.028 (1), 0.027 (2); S = 1.1 (1), 1.6 (2); w = $[\sigma(F)]^{-2}$, p = 0.035 (1), 0.020 (2) in calc. of $\sigma(F^2)$; max (shift/σ) < 0.004; empirical extinction correction, F_{corr}= (1 + kI), k = 1.7×10^{-9}(1), 1.9×10^{-7}(2); max. and min. of ΔF synthesis 0.9 and -0.8 e $Å^{-3}$(1), 0.4 and -0.5 e $Å^{-3}$(2); atomic f for neutral Th, Cℓ, P, and C, and spherical bonded H from International Tables (1974); local unpublished programs and ORTEP (Johnson, 1965). Large anisotropic thermal parameters for C(13) and C(14) as well as a shortened C-C distance between these atoms suggests disorder in the backbone of the dimethylphosphinoethane ligand. In the dichloro complex (2) these atoms were treated as half atoms in two distinct positions and refined with restrained distances (Waser, 1963) (P-C 1.86(1); C-C 1.54(1) Å) and with isotropic thermal parameters, whereas in (1) these carbon atoms were refined with anisotropic thermal parameters; either way of treating these atoms resulted in the same agreement factors. The temperature factors

of the phosphorus atoms are a little larger than and about as isotropic as the thorium atoms, which suggests that they are not disordered, however, the terminal phosphorus methyl group carbon atoms have large anisotropic thermal parameters and are likely disordered in a synchronous fashion with C(14) and C(15) through the pivotal phosphorus atom.

Atomic parameters are listed in Table 1,* and distances and angles are listed in Table 2. Figures 1 & 2 show the molecules and numbering schemes.

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*Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positions, distances and angles, least-squares planes, and ORTEP drawings have been deposited with the British Library Lending Division as Supplementary Publication No. (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The geometry of 1 and 2, at first glance, is contra-intuitive since the sterically largest ligands should try to get farthest from each other. The expectation, based upon the concept that the steric size (cone angle) of the $C_5H_5^-$ ligand is larger than that of a chloride or methyl group (Bagnall and Xing-fu, 1982), is that the cyclopentadienyl groups should be <u>trans</u> to each other and the anionic ligands should be <u>trans</u> to the chelating phosphine ligands. This is clearly not the case in 1, 2, and in the benzyl analogue (Zalkin, Brennan & Andersen, 1986). This situation has been analyzed by Keppert (1977). In six coordinate molecules of the type $M(X)_2(Y)_2$ (bidentate ligand) the locations of X relative to Y is determined by the M-X and M-Y distances. Monodentate ligands with the shortest metal-ligand distance will occupy the less sterically crowded sites <u>trans</u> to the

bidentate ligand. In the compounds 2, and the benzyl analogue, the Th-ring centroid distance is shorter than the Th-C(benzyl) or the Th-Cℓ bond distance. Hence the ligand with the shortest bond distance is located trans to the bidentate ligand in accord with Keppert's prediction. A similar explanation was proposed for the stereochemistry of $UC\ell_2\{N[Si(CH_3)_3]\}_2\cdot(CH_3OCH_2CH_2OCH_3)$, (McCullough, Turner, Andersen, Zalkin & Templeton, 1981). A similar geometry is observed for compound 1 even though the Th-ring centroid distance is essentialy equal to that of the Th-C(CH_3). This suggests that the application of Keppert's rules to compounds with cyclopentadienyl ligands may not be universally appropriate and the rules should serve only as a guide to stereochemical predictions.

The averaged Th-P distance in 1 and 2 are 3.147 ± 0.001 Å and 3.121 ± 0.001 Å, respectively. These distances are in the range found in $Th(CH_2C_6H_5)_4\cdot[(CH_3)_2PCH_2CH_2P(CH_3)_2]$ of 3.17 ± 0.02 Å (Edwards, Andersen & Zalkin, 1984).

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Table 1. Atomic Parameters

$$B_{eq} = \Sigma_i \Sigma_j B_{ij} a_i^* a_j^* a_i \cdot a_j / 3, \quad Å^2.$$

$$(C_5H_5)_2(CH_3)_2Th \cdot (CH_3)_2PCH_2CH_2P(CH_3)_2$$

Atom	x	y	z	$B_{eq}(Å^2)$
Th	0.10278(1)	0.18457(2)	0.17906(3)	3.642(6)
P(1)	0.12141(11)	0.35769(16)	-0.05635(27)	5.37(6)
P(2)	0.25767(10)	0.20883(15)	0.03265(26)	5.08(6)
C(1)	-0.0213(5)	0.3063(7)	0.1659(16)	7.0(3)
C(2)	-0.0446(5)	0.2234(12)	0.1046(13)	8.3(4)
C(3)	-0.0466(5)	0.1579(7)	0.2250(24)	9.0(5)
C(4)	-0.0237(6)	0.2027(10)	0.3626(14)	7.9(4)
C(5)	-0.0073(4)	0.2935(8)	0.3280(15)	6.9(3)
C(6)	0.1985(6)	0.0315(8)	0.2473(17)	7.8(4)
C(7)	0.1891(6)	0.0748(7)	0.3888(16)	7.9(4)
C(8)	0.1183(8)	0.0566(9)	0.4369(12)	8.4(4)
C(9)	0.0871(6)	0.0038(8)	0.3172(20)	8.3(4)
C(10)	0.1362(9)	-0.0112(7)	0.2019(13)	8.5(4)
C(11)	0.0599(6)	0.3730(8)	-0.2315(11)	8.3(4)
C(12)	0.1206(5)	0.4759(6)	0.0293(13)	8.0(3)
C(13)	0.2082(6)	0.3541(8)	-0.1612(14)	9.4(4)
C(14)	0.2681(5)	0.3231(8)	-0.0677(15)	10.3(4)
C(15)	0.2898(5)	0.1255(9)	-0.1190(13)	9.6(4)
C(16)	0.3362(4)	0.2140(7)	0.1685(12)	7.6(3)
C(17)	0.0900(5)	0.1241(6)	-0.1126(10)	6.4(3)
C(18)	0.1712(4)	0.3126(6)	0.3446(10)	6.1(2)

Table 1. Atomic Parameters (continued)

$(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

Atom	x	y	z	$B_{eq}(Å^2)$
Th	0.10512(1)	0.18258(1)	0.16923(2)	3.133(6)
P(1)	0.12195(9)	0.35857(12)	-0.05896(22)	5.09(5)
P(2)	0.25928(8)	0.20910(13)	0.02111(22)	4.99(5)
C(1)	-0.0239(3)	0.2933(5)	0.1423(11)	6.1(2)
C(2)	-0.0466(3)	0.2029(6)	0.0970(11)	6.9(3)
C(3)	-0.0416(4)	0.1506(5)	0.2430(15)	7.3(3)
C(4)	-0.0149(4)	0.2063(8)	0.3699(10)	7.5(3)
C(5)	-0.0059(4)	0.2923(6)	0.3086(11)	6.2(2)
C(6)	0.2047(4)	0.0417(7)	0.2634(15)	8.2(3)
C(7)	0.1782(9)	0.0736(6)	0.4105(16)	10.7(4)
C(8)	0.1072(6)	0.0419(7)	0.4099(11)	8.5(3)
C(9)	0.0928(4)	-0.0040(5)	0.2691(13)	6.9(3)
C(10)	0.1528(6)	-0.0049(5)	0.1802(9)	7.2(3)
C(11)	0.0631(5)	0.3704(6)	-0.2478(9)	8.0(3)
C(12)	0.1122(4)	0.4724(4)	0.0423(11)	6.9(2)
C(13)	0.2044(5)	0.3509(10)	-0.1849(15)	5.17(27)*
C(14)	0.2696(6)	0.3324(7)	-0.0591(15)	4.76(24)*
C(15)	0.2931(4)	0.1194(8)	-0.1165(11)	10.4(4)
C(16)	0.3372(3)	0.2249(6)	0.1667(10)	7.1(2)
Cℓ(1)	0.08841(9)	0.12385(11)	-0.15195(19)	5.77(5)
Cℓ(2)	0.17713(9)	0.31184(11)	0.36194(19)	5.19(4)
C(13')	0.2198(6)	0.3772(8)	-0.1076(18)	5.40(28)*
C(14')	0.2560(8)	0.2870(8)	-0.1594(15)	6.3(3)*

* Isotropically refined disordered atoms.

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

Cp $ThMe_2 \cdot Me_2PCH_2CH_2PMe_2$			Cp $ThCl_2 \cdot Me_2PCH_2CH_2PMe_2$		
Th	- C(1)	2.866(8)	Th	- C(1)	2.837(6)
Th	- C(2)	2.834(9)	Th	- C(2)	2.824(6)
Th	- C(3)	2.820(9)	Th	- C(3)	2.804(6)
Th	- C(4)	2.821(8)	Th	- C(4)	2.788(6)
Th	- C(5)	2.849(8)	Th	- C(5)	2.824(6)
Th	- C(6)	2.843(9)	Th	- C(6)	2.791(7)
Th	- C(7)	2.802(9)	Th	- C(7)	2.776(7)
Th	- C(8)	2.803(9)	Th	- C(8)	2.777(7)
Th	- C(9)	2.813(10)	Th	- C(9)	2.785(6)
Th	- C(10)	2.838(9)	Th	- C(10)	2.808(6)
Th	- C(18)	2.583(7)	Th	- Cℓ(1)	2.707(2)
Th	- C(17)	2.562(8)	Th	- Cℓ(2)	2.708(2)
Th	- CC(1)	2.593	Th	- Cp(1)	2.564
Th	- Cp(1)	2.573	Th	- Cp(2)	2.544
Th	- P(1)	3.146(2)	Th	- P(1)	3.122(2)
Th	- P(2)	3.147(2)	Th	- P(2)	3.121(2)
P(2)	- P(1)	3.352(3)	P(2)	- P(1)	3.332(3)

$Cp_2ThMe_2 \cdot Me_2PCH_2CH_2PMe_2$			$Cp_2ThCl_2 \cdot Cl_2PCH_2CH_2PMe_2$		
P(1) -Th	-P(2)	64.36(5)	P(1) -Th	-P(2)	64.52(5)
P(1) -Th	-C(17)	71.76(20)	P(1) -Th	-Cℓ(1)	72.75(5)
P(1) -Th	-C(18)	74.05(20)	P(1) -Th	-Cℓ(2)	74.35(6)
P(2) -Th	-C(17)	75.18(20)	P(2) -Th	-Cℓ(1)	75.33(6)
P(2) -Th	-C(18)	71.78(18)	P(2) -Th	-Cℓ(2)	73.05(5)
C(17)-Th	-C(18)	140.04(28)	Cℓ(1)-Th	-Cℓ(2)	141.63(5)
Cp(1)-Th	-Cp(2)	116.1	Cp(1)-Th	-Cp(2)	113.9
Cp(1)-Th	-C(18)	98.9	Cp(1)-Th	-Cℓ(1)	101.2

Cp(1)-Th	-C(17)	101.4	Cp(1)-Th	-Cℓ(2)	98.7
Cp(1)-Th	-P(1)	90.4	Cp(1)-Th	-P(1)	91.3
Cp(1)-Th	-P(2)	154.5	Cp(1)-Th	-P(2)	155.6
Cp(2)-Th	-C(17)	99.4	Cp(2)-Th	-Cℓ(1)	99.6
Cp(2)-Th	-C(18)	102.0	Cp(2)-Th	-Cℓ(2)	101.8
Cp(2)-Th	-P(1)	153.4	Cp(2)-Th	-P(1)	154.7
Cp(2)-Th	-P(2)	89.3	Cp(2)-Th	-P(2)	90.3
Th -P(1)	-C(11)	120.3(4)	Th -P(1)	-C(11)	119.26(28)
Th -P(1)	-C(12)	118.2(3)	Th -P(1)	-C(12)	116.14(26)
Th -P(1)	-C(13)	112.1(3)	Th -P(1)	-C(13)	111.9(4)
C(11)-P(1)	-C(12)	100.9(5)	C(11)-P(1)	-C(12)	102.7(4)
C(11)-P(1)	-C(13)	99.5(5)	C(11)-P(1)	-C(13)	91.2(5)
C(12)-P(1)	-C(13)	102.9(5)	C(12)-P(1)	-C(13)	113.0(5)
Th -P(2)	-C(14)	112.0(3)	Th -P(2)	-C(14)	110.3(4)
Th -P(2)	-C(15)	120.2(3)	Th -P(2)	-C(15)	118.7(3)
Th -P(2)	-C(16)	119.2(3)	Th -P(2)	-C(16)	117.90(24)
C(14)-P(2)	-C(15)	102.7(6)	C(14)-P(2)	-C(15)	114.2(5)
C(14)-P(2)	-C(16)	98.9(5)	C(14)-P(2)	-C(16)	91.0(4)
C(15)-P(2)	-C(16)	100.6(5)	C(15)-P(2)	-C(16)	101.5(4)
			Th -P(1)	-C(13')[b]	110.7(4)
			C(11)-P(1)	-C(13')	110.7(5)
			C(12)-P(1)	-C(13')	94.4(4)
			Th -P(2)	-C(14')	111.9(4)
			C(15)-P(2)	-C(14')	87.1(5)
			C(16)-P(2)	-C(14')	115.6(5)

[a] Cp(1) and Cp(2) represent the centroids of cyclopentadienyl atoms C(1)-C(5) and C(6)-C10) respectively.

[b] Primed atoms are the disordered counterparts of C(13) and C(14).

Figure 1. ORTEP (Johnson, 1965) of $(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$ (1) showing the atomic numbering scheme; 50% probability ellipsoids.

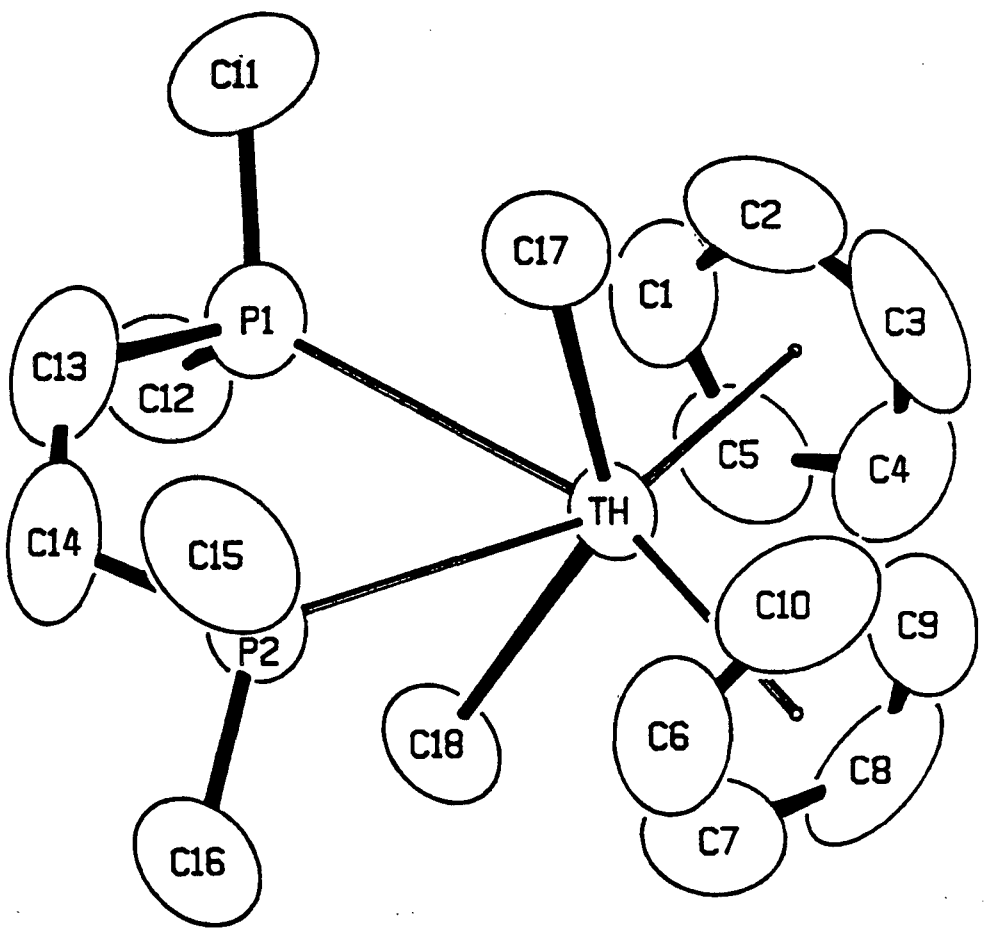
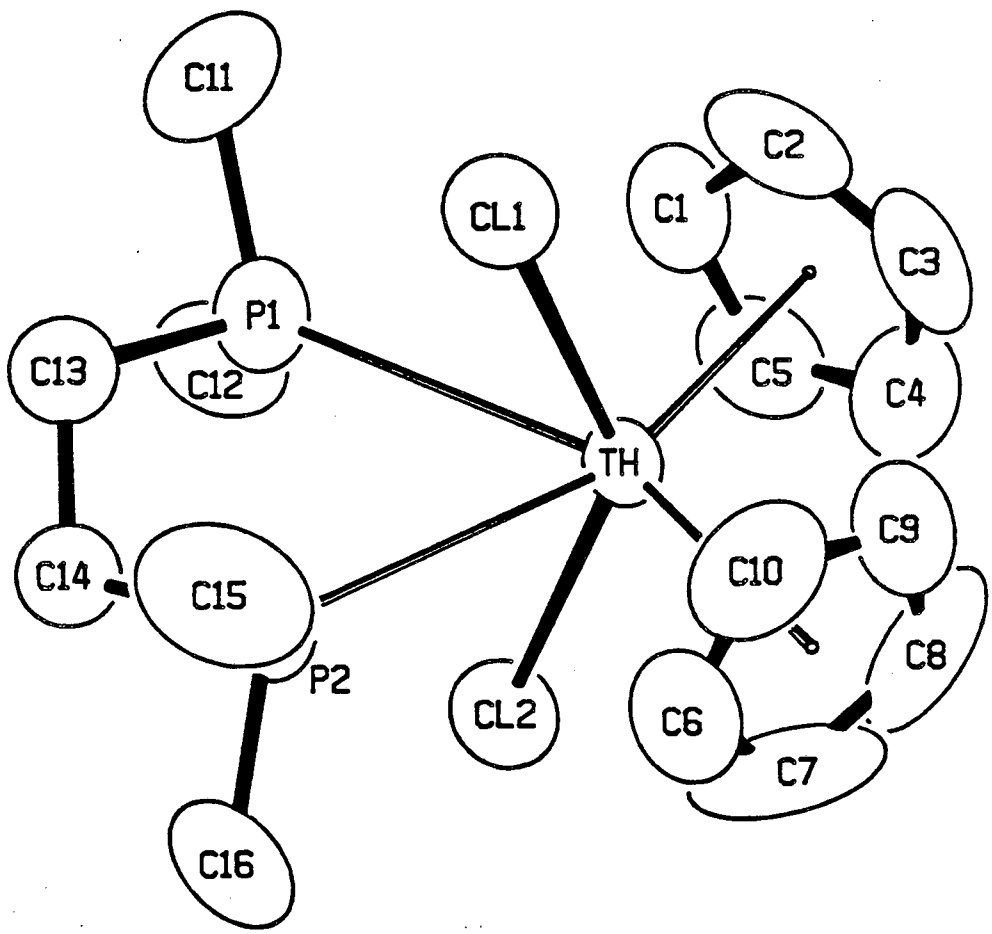


Figure 2. ORTEP (Johnson, 1965) of $(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$ (2) showing the atomic numbering scheme; 50% probability ellipsoids; disordered atoms C(13') & C(14') not included.



Supplemental Material

for

Bis(cyclopentadienyl)dimethylthorium(IV)bis(dimethyldiphosphino)ethane and Bis(cyclopentadienyl)dichlorothorium(IV)bis(dimethyldiphosphino)ethane

$(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$, $(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

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Abstract. $(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$ (1) M_r= 542.44, monoclinic, $P2_1/n$, a = 18.485(4), b = 14.118(4), c = 8.258(2) A, β = 91.05(2)°, V = 2154.7 A^3, Z = 4, D_x = 1.672 g cm^{-3}, λ(MoKα)=0.71073 A, μ = 73.0 cm^{-1}, F(000) = 1040, T = 296 K, R = 0.026 for 2521 unique reflections with $F^2>2\sigma(F^2)$. Distances (A) are: Th-C(Cp) 2.84 ± 0.03; Th-C(methyl) 2.562(8), 2.583(7); Th-P 3.146(2), 3.147(2) A; Th-Cp 2.59, 2.57 A. $(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$ (2) M_r= 583.28, monoclinic, $P2_1/n$, a = 18.268(2), b = 14.237(6), c = 7.996(3) A, β = 92.27(4)°, V = 2078.0 A^3, Z = 4, D_x = 1.864 g cm^{-3}, λ(MoKα)=0.71073 A,μ = 78.3 cm^{-1}, F(000)= 1104, T = 296 K, R = 0.020 for 2361 unique reflections with I>σ(I). Distances (A) are: Th-C(Cp) 2.80 ± 0.02; Th-Cℓ 2.707(2), 2.708(2); Th-P 3.121(2), 3.122(2) A; Th-Cp 2.56, 2.54 A. The structures of (1) and (2) are crystallographically isomorphous and were done to study their six-coordinate stereochemistry. The cyclopentadienyl rings are trans to the bidentate ligand.

Supplemental Table 1. Anisotropic Thermal Parameters (A^2)[a]

$(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Th	3.101(10)	3.775(11)	4.067(12)	-0.017(12)	0.522(7)	-0.166(13)
P(1)	4.75(10)	5.22(10)	6.14(12)	0.30(8)	0.57(8)	1.12(9)
P(2)	3.73(8)	5.96(12)	5.61(10)	0.46(8)	1.28(7)	0.19(8)
C(1)	4.6(4)	6.6(5)	10.0(7)	1.7(4)	2.5(4)	2.3(6)
C(2)	4.3(5)	12.4(9)	8.1(7)	2.1(5)	-0.7(4)	-2.0(7)
C(3)	4.0(4)	5.5(6)	17.5(12)	-0.7(4)	2.9(6)	-1.7(7)
C(4)	5.9(5)	10.0(8)	7.8(6)	2.8(5)	3.2(5)	2.7(6)
C(5)	4.1(4)	7.4(6)	9.2(7)	1.8(4)	1.5(4)	-2.3(5)
C(6)	6.7(6)	5.7(5)	11.1(8)	1.5(5)	2.5(6)	1.6(5)
C(7)	7.9(6)	5.4(5)	10.3(7)	0.9(5)	-2.9(6)	1.5(5)
C(8)	11.2(8)	8.1(7)	6.0(5)	3.8(6)	3.1(5)	3.3(5)
C(9)	6.6(6)	6.7(6)	11.6(9)	-1.2(5)	-0.3(6)	3.1(6)
C(10)	13.3(9)	4.3(5)	7.9(7)	2.4(6)	-1.5(7)	-0.2(4)
C(11)	10.0(7)	8.8(6)	6.2(5)	1.5(5)	-0.8(5)	1.2(5)
C(12)	7.7(5)	5.5(5)	10.6(7)	-0.2(4)	-2.0(5)	1.6(5)
C(13)	7.6(6)	10.0(7)	10.6(7)	0.5(5)	2.7(5)	4.7(6)
C(14)	4.6(4)	12.6(9)	13.9(9)	0.4(5)	2.9(5)	7.7(7)
C(15)	6.3(5)	12.8(8)	9.7(7)	0.3(5)	2.5(5)	-4.8(6)
C(16)	4.4(4)	9.6(7)	8.8(6)	-0.4(4)	0.3(4)	-0.3(5)
C(17)	7.5(5)	5.9(5)	5.8(4)	-1.0(4)	-0.5(4)	-1.5(4)
C(18)	5.7(4)	6.9(5)	5.6(4)	-1.6(4)	0.4(3)	-2.4(4)

Supplemental Table 2. Anisotropic Thermal Parameters (A^2) (continued)

$(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Th	2.794(11)	3.274(11)	3.371(11)	0.002(6)	0.606(7)	-0.103(7)
Cℓ(1)	6.62(8)	6.17(9)	4.53(7)	-1.44(7)	0.22(6)	-1.59(7)
Cℓ(2)	5.32(7)	5.96(8)	4.32(7)	-1.03(6)	0.49(6)	-1.39(6)
P(1)	4.79(8)	4.51(7)	6.02(9)	0.26(6)	0.95(7)	1.20(7)
P(2)	3.56(7)	6.15(8)	5.37(8)	0.61(6)	1.63(6)	0.64(7)
C(1)	3.73(29)	5.9(4)	8.7(5)	1.63(26)	2.0(3)	1.9(4)
C(2)	2.71(26)	9.1(5)	8.8(5)	0.89(29)	-0.14(28)	-2.8(4)
C(3)	3.3(3)	6.0(4)	12.8(7)	-0.07(27)	2.3(4)	2.3(5)
C(4)	4.8(4)	11.3(6)	6.7(4)	2.3(4)	3.3(3)	2.0(5)
C(5)	4.4(3)	7.6(4)	6.7(4)	0.89(29)	1.46(29)	-2.3(4)
C(6)	4.5(3)	6.7(5)	13.2(8)	1.2(3)	0.3(4)	5.1(5)
C(7)	16.5(10)	4.6(4)	10.4(7)	0.3(5)	-9.3(7)	0.8(4)
C(8)	13.1(7)	7.3(5)	5.3(4)	4.2(5)	3.9(5)	3.0(4)
C(9)	5.9(4)	4.4(3)	10.3(6)	-0.17(28)	0.8(4)	2.6(4)
C(10)	9.9(5)	4.6(3)	7.1(4)	2.8(4)	0.9(4)	0.3(3)
C(11)	10.2(5)	7.9(5)	5.9(4)	1.1(4)	-0.2(4)	1.6(4)
C(12)	6.3(4)	4.0(3)	10.2(5)	-0.39(26)	-1.8(3)	0.3(3)
C(15)	6.7(4)	16.1(8)	8.4(5)	1.8(5)	2.1(4)	-5.7(6)
C(16)	4.3(3)	8.3(4)	8.8(5)	-1.1(3)	1.1(3)	-1.5(4)

[a] The anisotropic temperature factor has the form:

$$\exp[-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \cdots].$$

Supplemental Table 3. Estimated Hydrogen Positional and Isotropic Thermal Parameters (A^2) [a] $(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

Atom	x	y	z	B
H(1)	-0.0153	0.3643	0.1071	10.0
H(2)	-0.0574	0.2125	-0.0074	10.0
H(3)	-0.0616	0.0928	0.2142	10.0
H(4)	-0.0198	0.1744	0.4682	10.0
H(5)	0.0106	0.3403	0.4030	10.0
H(6)	0.2425	0.0308	0.1875	10.0
H(7)	0.2245	0.1119	0.4468	10.0
H(8)	0.0960	0.0772	0.5350	10.0
H(9)	0.0382	-0.0193	0.3144	10.0
H(10)	0.1282	-0.0463	0.1035	10.0
H(11)	0.0791	0.4209	-0.3018	10.0
H(12)	0.0134	0.3928	-0.1947	10.0
H(13)	0.0556	0.3145	-0.2890	10.0
H(14)	0.0720	0.4919	0.0583	10.0
H(15)	0.1379	0.5200	-0.0487	10.0
H(16)	0.1513	0.4773	0.1243	10.0
H(17)	0.2185	0.4170	-0.1988	10.0
H(18)	0.2028	0.3124	-0.2524	10.0
H(19)	0.3090	0.3184	-0.1376	10.0
H(20)	0.2779	0.3696	0.0146	10.0
H(21)	0.3010	0.0662	-0.0675	10.0
H(22)	0.3323	0.1506	-0.1680	10.0
H(23)	0.2527	0.1161	-0.2000	10.0
H(24)	0.3772	0.2361	0.1102	10.0
H(25)	0.3460	0.1518	0.2107	10.0
H(26)	0.3264	0.2563	0.2562	10.0

[a] The isotropic temperature factor has the form $\exp[-B(\sin\theta/\lambda)^2]$.

Supplemental Table 3. (continued)

$(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

Atom	x	y	z	B
H(1)	-0.0212	0.3475	0.0675	10.0
H(2)	-0.0630	0.1810	-0.0141	10.0
H(3)	-0.0547	0.0844	0.2539	10.0
H(4)	-0.0042	0.1869	0.4854	10.0
H(5)	0.0112	0.3468	0.3741	10.0
H(6)	0.2544	0.0514	0.2256	10.0
H(7)	0.2043	0.1109	0.4966	10.0
H(8)	0.0729	0.0517	0.4992	10.0
H(9)	0.0458	-0.0325	0.2357	10.0
H(10)	0.1574	-0.0353	0.0716	10.0
H(11)	0.0126	0.3830	-0.2164	10.0
H(12)	0.0805	0.4223	-0.3159	10.0
H(13)	0.0642	0.3119	-0.3126	10.0
H(14)	0.1285	0.5219	-0.0329	10.0
H(15)	0.0607	0.4825	0.0665	10.0
H(16)	0.1421	0.4735	0.1463	10.0
H(17)	0.1992	0.2994	-0.2657	10.0
H(18)	0.2116	0.4101	-0.2445	10.0
H(19)	0.2686	0.3769	0.0335	10.0
H(20)	0.3159	0.3382	-0.1161	10.0
H(21)	0.3368	0.1426	-0.1699	10.0
H(22)	0.3052	0.0630	-0.0513	10.0
H(23)	0.2550	0.1045	-0.2023	10.0
H(24)	0.3482	0.1654	0.2235	10.0
H(25)	0.3797	0.2450	0.1049	10.0
H(26)	0.3255	0.2728	0.2491	10.0
H(17')[a]	0.2225	0.4223	-0.1984	10.0
H(18')	0.2460	0.4012	-0.0071	10.0
H(19')	0.3060	0.2996	-0.1943	10.0
H(20')	0.2278	0.2574	-0.2520	10.0

[a] Primed atoms are disordered counterparts to atoms H(17)-H(20).

Supplemental Table 4. Additional Distances(Å)

$Cp_2ThMe_2 \cdot Me_2PCH_2CH_2PMe_2$		$Cp_2ThCl_2 \cdot Me_2PCH_2CH_2PMe_2$	
P(1) - C(11)	1.837(9)	P(1) - C(11)	1.827(8)
P(1) - C(12)	1.813(9)	P(1) - C(12)	1.824(7)
P(1) - C(13)	1.837(10)	P(1) - C(13)	1.847(10)
P(2) - C(14)	1.825(10)	P(2) - C(14)	1.881(9)
P(2) - C(15)	1.826(10)	P(2) - C(15)	1.810(8)
P(2) - C(16)	1.820(9)	P(2) - C(16)	1.817(7)
C(1) - C(2)	1.344(14)	C(1) - C(2)	1.396(9)
C(1) - C(5)	1.370(14)	C(1) - C(5)	1.357(11)
C(2) - C(3)	1.358(16)	C(2) - C(3)	1.384(11)
C(3) - C(4)	1.362(15)	C(3) - C(4)	1.362(12)
C(4) - C(5)	1.349(13)	C(4) - C(5)	1.332(10)
C(6) - C(7)	1.333(13)	C(6) - C(7)	1.366(14)
C(6) - C(10)	1.347(14)	C(6) - C(10)	1.316(11)
C(7) - C(8)	1.398(14)	C(7) - C(8)	1.374(13)
C(8) -C(9)	1.358(15)	C(8) - C(9)	1.319(12)
C(9) - C(10)	1.344(14)	C(9) - C(10)	1.329(11)
C(13)- C(14)	1.409(14)	C(13) - C(14)	1.551(12)
		P(1) - C(13')[a]	1.864(10)
		P(2) - C(14')	1.819(11)
		C(13')- C(14')	1.511(12)

Supplemental Table 4. (continued)

$Cp_2ThMe_2 \cdot Me_2PCH_2CH_2PMe_2$		$Cp_2ThC\ell_2 \cdot Me_2PCH_2CH_2PMe_2$	
H(1) - C(1)	0.959	H(1) - C(1)	0.979
H(2) - C(2)	0.963	H(2) - C(2)	0.977
H(3) - C(3)	0.963	H(3) - C(3)	0.978
H(4) - C(4)	0.962	H(4) - C(4)	0.977
H(5) - C(5)	0.961	H(5) - C(5)	0.980
H(6) - C(6)	0.960	H(6) - C(6)	0.979
H(7) - C(7)	0.960	H(7) - C(7)	0.978
H(8) - C(8)	0.961	H(8) - C(8)	0.979
H(9) - C(9)	0.961	H(9) - C(9)	0.979
H(10)- C(10)	0.961	H(10) - C(10)	0.977
H(11)- C(11)	0.964	H(11) - C(11)	0.982
H(12)- C(11)	0.958	H(12) - C(11)	0.978
H(13)- C(11)	0.955	H(13) - C(11)	0.981
H(14)- C(12)	0.959	H(14) - C(12)	0.979
H(15)- C(12)	0.957	H(15) - C(12)	0.979
H(16)- C(12)	0.961	H(16) - C(12)	0.978
H(17)- C(13)	0.961	H(17) - C(13)	0.980
H(18)- C(13)	0.960	H(18) - C(13)	0.980
H(19)- C(14)	0.961	H(19) - C(14)	0.975
H(20)- C(14)	0.960	H(20) - C(14)	0.980
H(21)- C(15)	0.960	H(21) - C(15)	0.977
H(22)- C(15)	0.957	H(22) - C(15)	0.978
H(23)- C(15)	0.959	H(23) - C(15)	0.981
H(24)- C(16)	0.958	H(24) - C(16)	0.978
H(25)- C(16)	0.962	H(25) - C(16)	0.980
H(26)- C(16)	0.958	H(26) - C(16)	0.979
		H(17')- C(13')[a]	0.971
		H(18')- C(13')	0.979
		H(19')- C(14')	0.982
		H(20')- C(14')	0.980

[a] Primed atoms are disordered counterparts to atoms C(13), C(14) and H(17)-H(20).

Supplemental Table 5. Additional Angles

$Cp_2ThMe_2 \cdot Me_2PCH_2CH_2PMe_2$		$Cp_2ThCl_2 \cdot Me_2PCH_2CH_2PMe_2$	
Atoms	Angle(°)	Atoms	Angle(°)
C(2) -C(1) - C(5)	107.8(10)	C(2) -C(1) -C(5)	107.6(7)
C(1) -C(2) - C(3)	109.3(10)	C(1) -C(2) -C(3)	105.6(7)
C(2) -C(3) - C(4)	106.4(10)	C(2) -C(3) -C(4)	108.9(7)
C(3) -C(4) - C(5)	109.5(10)	C(3) -C(4) -C(5)	107.9(8)
C(1) -C(5) - C(4)	107.1(10)	C(1) -C(5) -C(4)	109.9(7)
C(7) -C(6) - C(10)	109.0(10)	C(7) -C(6) -C(10)	109.3(8)
C(6) -C(7) - C(8)	107.6(10)	C(6) -C(7) -C(8)	104.7(7)
C(7) -C(8) - C(9)	106.3(09)	C(7) -C(8) -C(9)	108.8(8)
C(8) -C(9) - C(10)	108.6(10)	C(8) -C(9) -C(10)	108.7(8)
C(6) -C(10)- C(9)	108.5(10)	C(6) -C(10) -C(9)	108.5(8)
P(1) -C(13)- C(14)	115.8(08)	P(1) -C(13) -C(14)	106.2(8)
P(2) -C(14)- C(13)	115.8(08)	P(2) -C(14) -C(13)	107.1(8)
		P(1) -C(13')-C(14')[a]	111.7(9)
		P(2) -C(14')-C(13')	107.6(9)

[a] Primed atoms are counterparts to C(13) & C(14).

Supplemental Table 6. Least-squares Planes

$(C_5H_5)_2(CH_3)_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

Plane No. 1

Equation of plane: 17.46930 a - 3.71855 b - 1.74192 c = -1.79523

Distance to the plane from atoms

in the plane			not in the plane	
atom	d(Å)	σ(d)	atom	d(Å)
C(1)	-0.0042	(169)	Th	2.592(7)
C(2)	0.0039	(218)		
C(3)	0.0018	(238)		
C(4)	-0.0040	(181)		
C(5)	0.0041	(159)		

Plane No. 2

Equation of plane: -5.42084 a 11.74148 b - 3.84877 c = -1.65146

Distance to the plane from atoms

in the plane			not in the plane	
atom	d(Å)	σ(d)	atom	d(Å)
C(6)	-0.0068	(177)	Th	2.572(7)
C(7)	0.0075	(173)		
C(8)	-0.0064	(183)		
C(9)	0.0028	(203)		
C(10)	0.0041	(206)		

$(C_5H_5)_2C\ell_2Th\cdot(CH_3)_2PCH_2CH_2P(CH_3)_2$

Plane No. 1

Equation of plane: 17.33518 a -3.41437 b + -1.93801 c = -1.69297

Distance to the plane from atoms

in the plane			not in the plane	
atom	d(Å)	σ(d)	atom	d(Å)
C(6)	0.0131	(138)	Th	2.564(5)
C(7)	-0.0056	(110)		
C(8)	0.0013	(110)		
C(9)	0.0036	(114)		
C(10)	-0.0126	(143)		

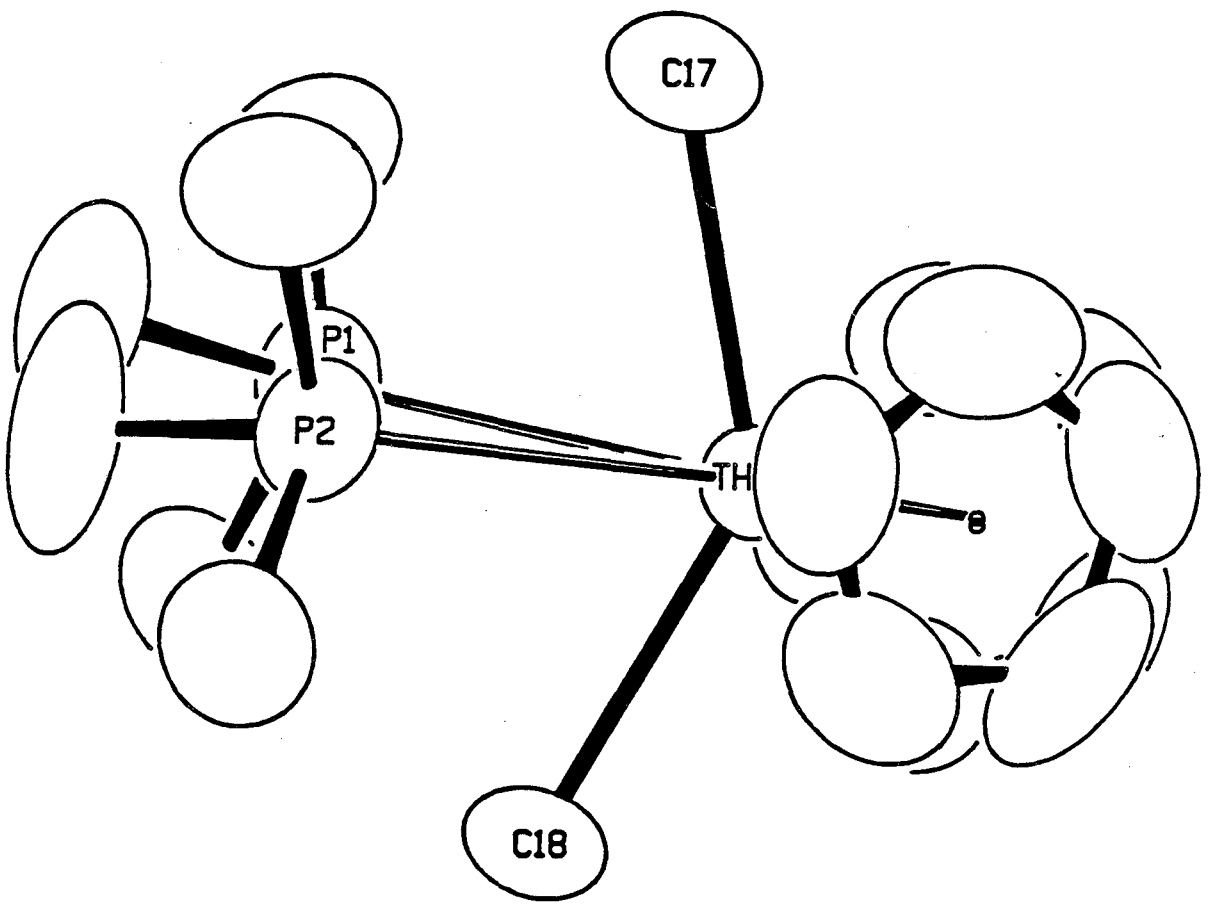
Plane No. 2

Equation of plane: - 5.15826 a + 12.07150 b - 3.49565 c = -1.47343

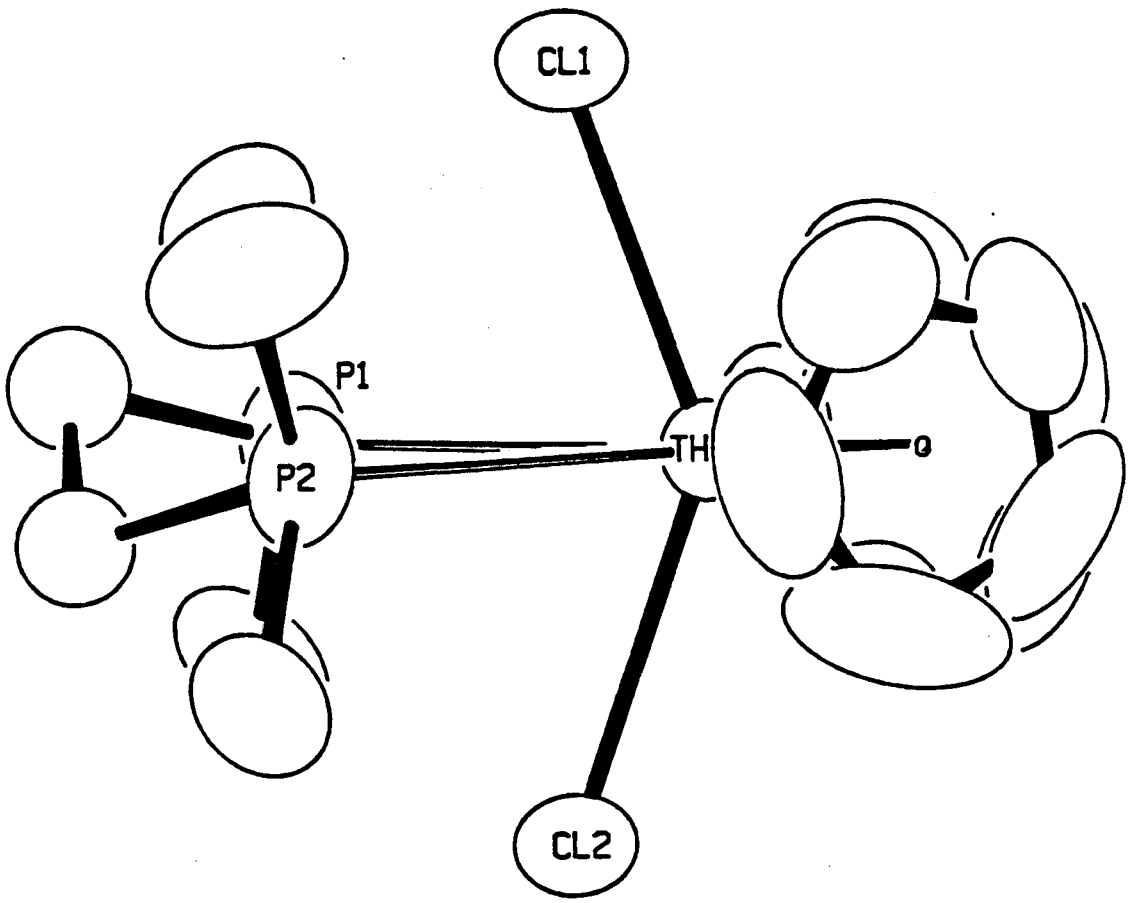
Distance to the plane from atoms

in the plane			not in the plane	
atom	d(Å)	σ(d)	atom	d(Å)
C(1)	0.0060	(131)	Th	2.544(6)
C(2)	-0.0070	(145)		
C(3)	0.0077	(189)		
C(4)	0.0003	(156)		
C(5)	-0.0039	(134)		

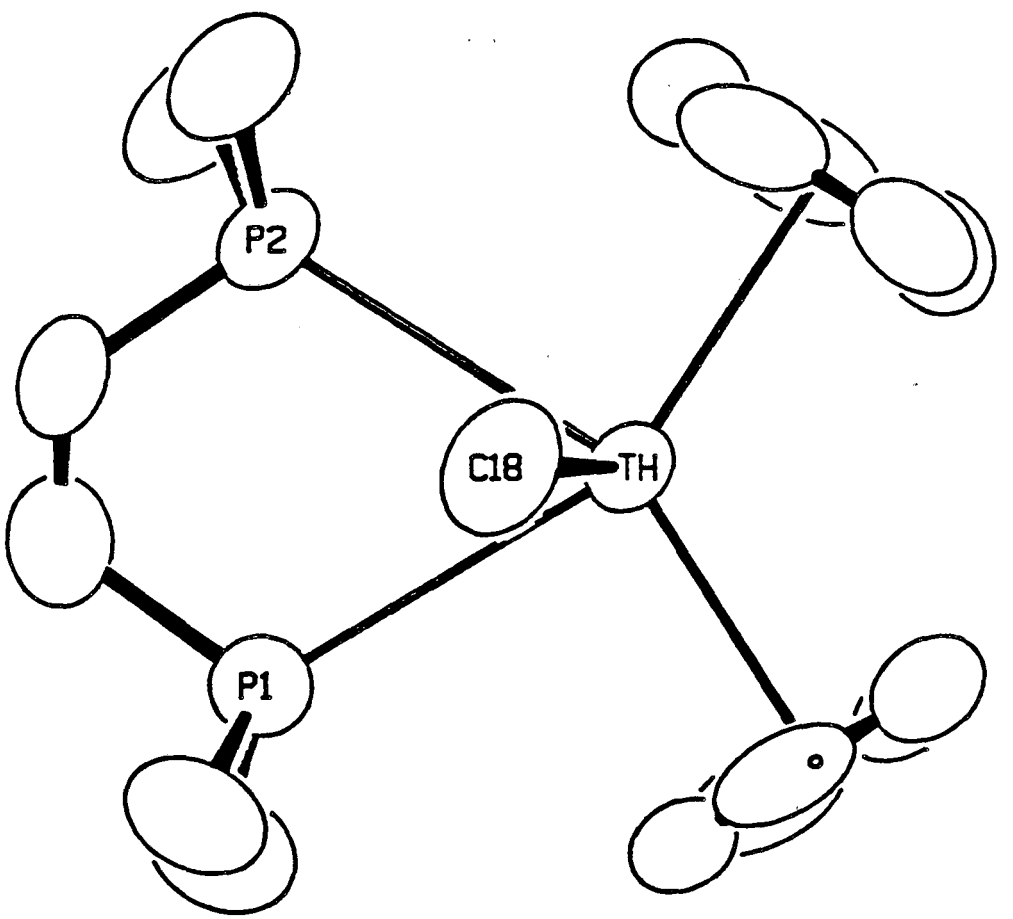
Supplemental Fig. 1. ORTEP drawing of compound **1** viewed down a line connecting the centroids of the Cp rings.



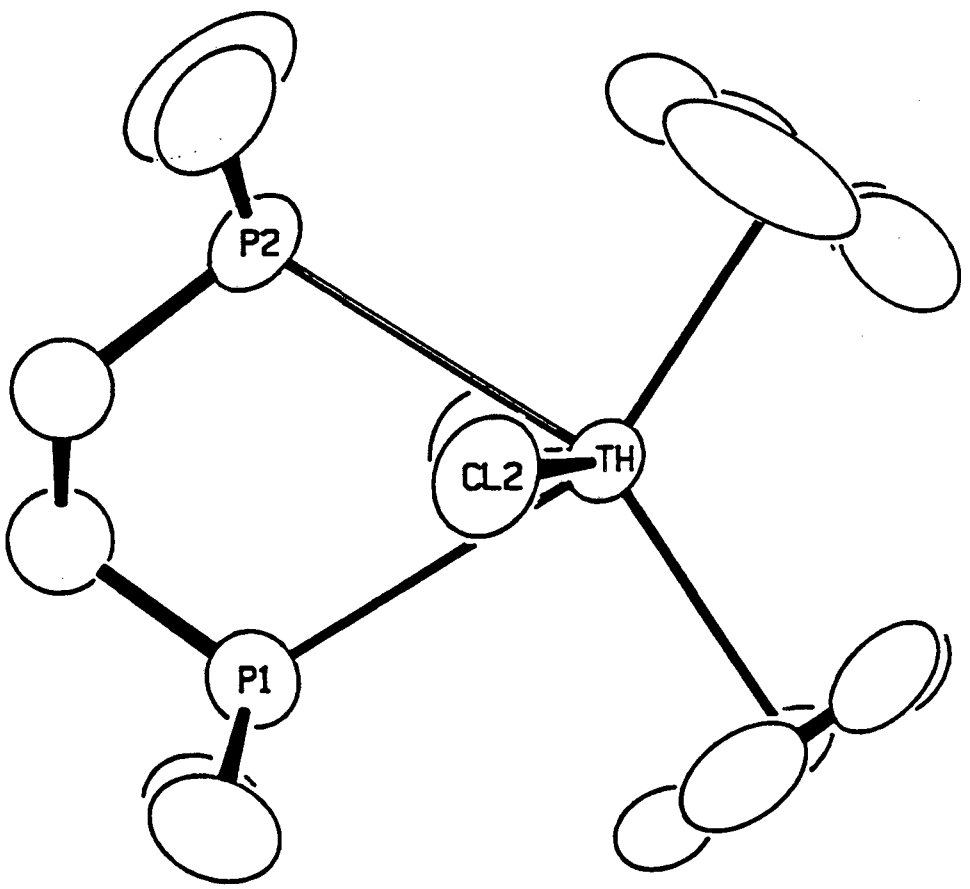
Supplemental Fig. 2. ORTEP drawing of molecule **2** viewed down a line connecting the centroids of the Cp rings; disordered atoms C(13') & C(14') not included.



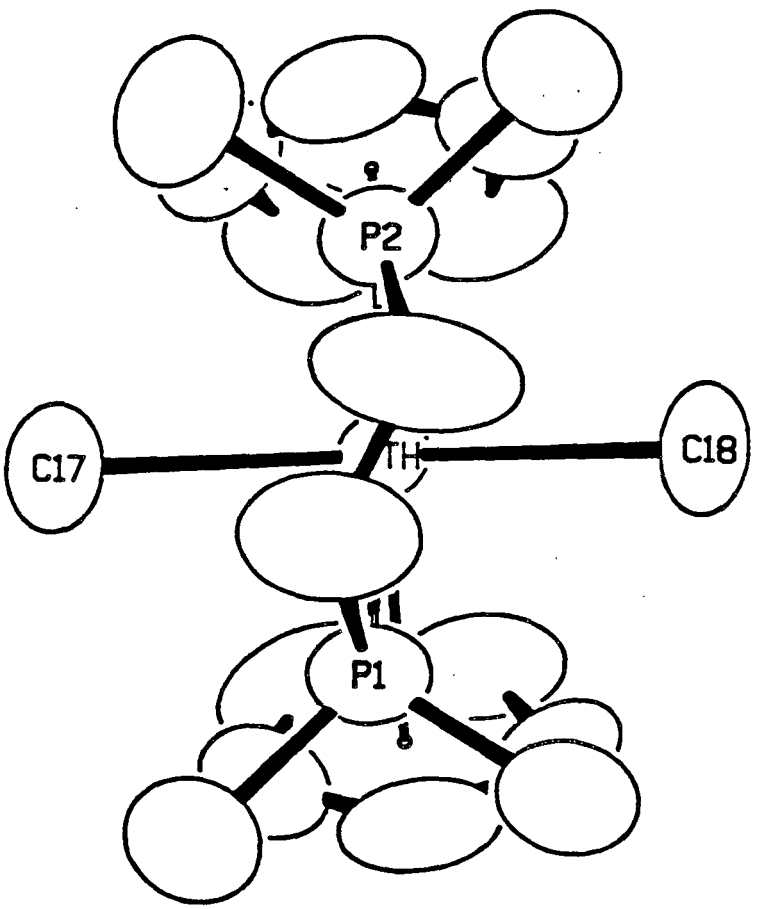
Suppplemental Fig 3. ORTEP drawing of molecule 1 viewed in a direction edge on to the Cp rings.



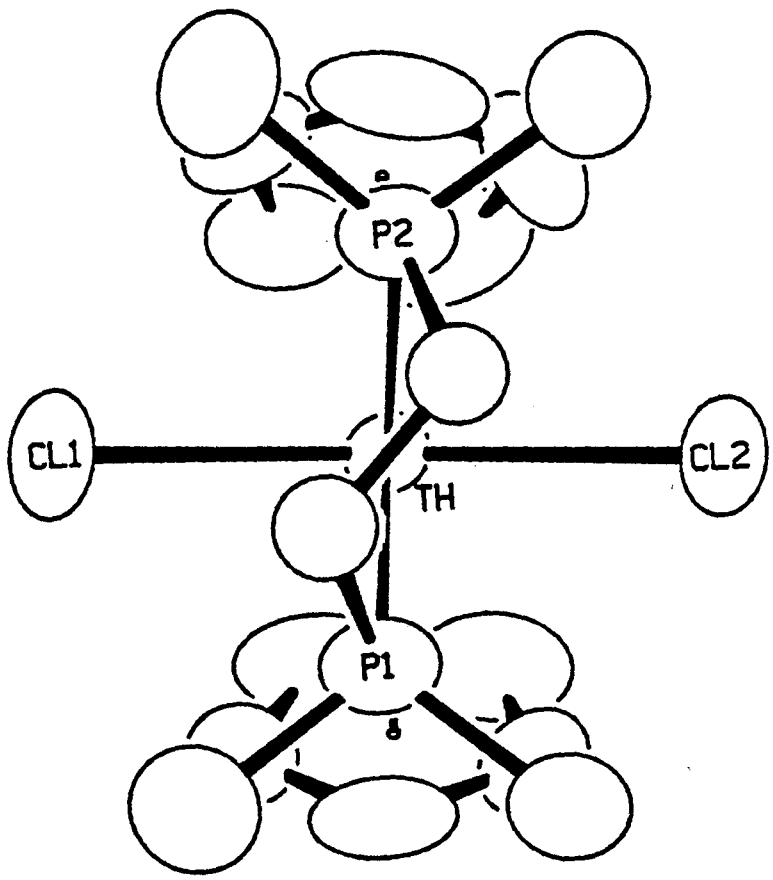
Supplemental Fig. 4. ORTEP drawing of molecule 2 viewed in a direction edge on to the Cp rings.



Supplemental Fig. 5. ORTEP drawing of molecule 1 viewed down a pseudo-2-fold axis.



Supplemental Fig 6. ORTEP drawing of molecule 2 viewed down a pseudo-2-fold axis.



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