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[1,2-Bis(dimethylphosphino)ethane]bis(cyclopentadienyl)dimethylthorium(IV) and [1,2-Bis(dimethylphosphino)ethane]dichlorobis(cyclopentadienyl)thorium(IV)

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Abstract. [Th(CH$_3$)$_2$(C$_5$H$_5$)$_2$(C$_6$H$_{16}$P$_2$)] (1), $M_r =$ 542·44, monoclinic, $P2_1/n$, $a = 18·485$ (4), $b = $ 14·118 (4), $c = 8·258$ (2) Å, $\beta = 91·05$ (2)°, $V = $ 2154·7 Å^3, $Z = 4$, $D_x = 1·672$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 73·0$ 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); Th–Cp 2·59, 2·57. [Th(C$_5$H$_5$)$_2$Cl$_2$(C$_6$H$_{16}$P$_2$)] (2), $M_r = 583·28$, monoclinic, $P2_1/n$, $a = $ 18·268 (2), $b = 14·237$ (6), $c = 7·996$ (3) Å, $\beta = $ 92·27 (4)°, $V = 2078·0$ Å^3, $Z = 4$, $D_x = 1·864$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70173 Å, $\mu = 78·3$ cm^{-1}, $F(000) = $ 1104, $T = 296$ K, $R = 0·020$ for 2361 unique reflections with $I > \sigma(I)$. 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); Th–Cp 2·56, 2·54. The structures of (1) and (2) are crystallographically isomorphous and were investigated to study their six-coordinate stereochemistry. The cyclopentadienyl rings are *trans* to the bidentate ligand.

Introduction. Compounds of the type (C$_5$H$_5$)$_2$-M(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 intramolecular 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$_2$Y$_2$-(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$_5$H$_5$)$_2$Th(X)$_2$.[(CH$_3$)$_2$PCH$_2$-CH$_2$P(CH$_3$)$_2$] where X = Cl, CH$_3$ (this paper) and where X = CH$_2$C$_6$H$_5$ (Zalkin, Brennan & Andersen, 1987) are described.
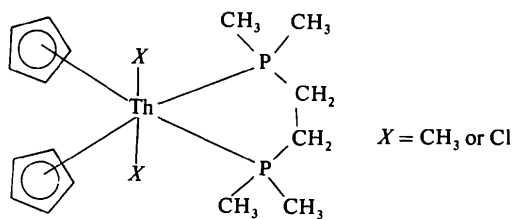
Experimental. The dimethyl complex (1) was made by the reaction of (2) with methyllithium at 228 K (Brennan, 1985). Colorless crystals suitable for X-ray studies were picked from the crystals obtained by crystallization from a toluene:pentane (1:4) solution at 203 K. The dichloro complex (2) was synthesized from the reaction of sodium cyclopentadienide with ThCl$_4$.(CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$ in a tetrahydrofuran solution at 203 K and crystallized from toluene. Crystals suitable for X-ray studies were grown from toluene:diethyl ether (6:4) at 253 K. The air-sensitive crystals were sealed inside quartz capillaries under

argon. Crystal $0.19 \times 0.25 \times 0.32$ mm with six faces (1), $0.22 \times 0.25 \times 0.37$ mm with 12 faces (2); modified Picker automatic diffractometer (1), Enraf–Nonius CAD-4 (2); graphite monochromator; cell dimensions from 20 reflections, $20 < 2\theta < 34°$ (1), 24 reflections, $20 < 2\theta < 32°$ (2); analytical absorption correction, range 1.47 to 1.93 (1), 3.26 to 4.66 (2); 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 standard's intensities from average, intensities adjusted isotropically; 7611 (1), 2929 $[I > \sigma(I)]$ (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 four 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 $I > \sigma(I)$ (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 calculation of $\sigma(F^2)$; max. (shift/σ) < 0.004; empirical extinction correction, $F_{corr} = (1 + kI)$, $k = 1.7 \times 10^{-9}$ (1), 1.9 $\times$ 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 for X-ray Crystallography* (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

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \Sigma_i \Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j / 3.$$

	x	y	z	B_{eq}
Compound (1)				
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)
Compound (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 bond distances* (Å) *and angles* (°)

	Compound (1)		Compound (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–Cp(1)*	2.593	Th–Cp(1)	2.564
Th–Cp(2)	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)
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')†	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)

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

† Primed atoms are the disordered counterparts of C(13) and C(14).

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. Figs. 1 and 2 show the molecules and numbering schemes.

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 C₅H₅⁻ ligand is larger than that of a chloride or methyl group (Bagnall & Xing-fu, 1982), is that the cyclopentadienyl groups should be *trans* to each other and the anionic ligands should be *trans* to the chelating phosphine ligands. This is clearly not the case in (1), (2) and in the benzyl analogue (Zalkin, Brennan & Andersen, 1987). 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 are determined by the $M—X$ and $M—Y$ distances. Monodentate ligands with the shortest metal–ligand distances will occupy the less sterically crowded sites *trans* 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 UCl₂{N[Si(CH₃)₃]}₂.(CH₃OCH₂-CH₂OCH₃) (McCullough, Turner, Andersen, Zalkin & Templeton, 1981). A similar geometry is observed for (1) even though the Th–ring centroid distance is essentially equal to that of the Th—C(CH₃). 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.

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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 Document Supply Centre as Supplementary Publication No. SUP 43409 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
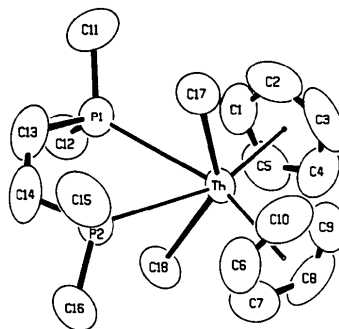

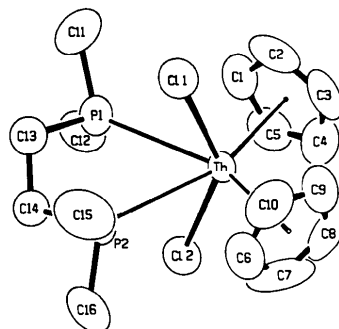Fig. 1. *ORTEP* (Johnson, 1965) view of (1) showing the atomic numbering scheme; 50% probability ellipsoids.

Fig. 2. *ORTEP* (Johnson, 1965) view of (2) showing the atomic numbering scheme; 50% probability ellipsoids; disordered atoms C(13') and C(14') not included.

The averaged Th—P distances in (1) and (2) are 3·147 (1) and 3·121 (1) Å, respectively. These distances are in the range found in Th(CH₂C₆H₅)₄·-[(CH₃)₂PCH₂CH₂P(CH₃)₂] of 3·17 ± 0·02 Å (Edwards, Andersen & Zalkin, 1984).

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