

Table 1. Atomic parameters

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
U	0.18863 (2)	0.11824 (2)	0.35897 (1)	3.339 (6)
Br	0.20423 (9)	0.32988 (8)	0.31666 (3)	6.40 (3)
Si1	-0.04814 (17)	-0.12204 (21)	0.39988 (7)	4.88 (6)
Si2	0.02958 (18)	0.10755 (20)	0.23520 (7)	4.59 (6)
Si3	0.44003 (18)	-0.08801 (18)	0.41748 (7)	4.79 (7)
Si4	0.30450 (20)	0.36631 (21)	0.44719 (8)	5.68 (7)
N1	-0.0751 (6)	0.2705 (6)	0.39312 (20)	5.1 (2)
N2	0.4408 (5)	0.1163 (6)	0.28308 (21)	5.5 (2)
C1	-0.0078 (6)	0.0171 (6)	0.32377 (25)	3.9 (2)
C2	0.0352 (6)	-0.0609 (6)	0.35467 (23)	3.9 (2)
C3	0.1379 (6)	-0.0997 (6)	0.33657 (25)	4.1 (2)
C4	0.1548 (6)	-0.0474 (6)	0.29623 (24)	3.7 (2)
C5	0.0640 (6)	0.0292 (6)	0.28696 (22)	3.7 (2)
C6	0.3734 (6)	0.1462 (7)	0.41853 (24)	4.2 (2)
C7	0.3434 (6)	0.0323 (6)	0.42288 (22)	3.9 (2)
C8	0.2362 (7)	0.0345 (7)	0.44315 (24)	4.0 (2)
C9	0.2049 (6)	0.1444 (6)	0.45058 (22)	4.2 (2)
C10	0.2899 (6)	0.2171 (6)	0.43543 (22)	3.9 (2)
C11	0.0051 (7)	0.2264 (6)	0.38401 (25)	4.7 (2)
C12	0.3708 (6)	0.1122 (8)	0.30743 (25)	5.4 (2)
C13	-0.1774 (8)	0.3305 (9)	0.4045 (3)	6.8 (3)
C14	0.5317 (7)	0.1299 (7)	0.25126 (29)	5.7 (3)
C15	-0.1787 (7)	-0.1862 (8)	0.37371 (28)	6.8 (3)
C16	-0.0956 (8)	-0.0163 (8)	0.44006 (28)	7.0 (3)
C17	0.0324 (8)	-0.2327 (8)	0.4300 (3)	8.1 (3)
C18	0.1632 (7)	0.1462 (7)	0.20699 (26)	6.3 (3)
C19	-0.0592 (7)	0.2296 (7)	0.24854 (27)	6.5 (3)
C20	-0.0574 (8)	0.0197 (8)	0.19556 (27)	7.3 (3)
C21	0.4795 (8)	-0.1160 (8)	0.35979 (28)	7.6 (3)
C22	0.5758 (7)	-0.0600 (9)	0.4497 (3)	7.8 (3)
C23	0.3701 (9)	-0.2108 (8)	0.4393 (4)	10.1 (4)
C24	0.3462 (10)	0.3811 (9)	0.5074 (3)	10.0 (4)
C25	0.1702 (9)	0.4444 (8)	0.4381 (4)	8.9 (4)
C26	0.4186 (9)	0.4271 (8)	0.4141 (4)	10.1 (4)
C27	-0.1685 (12)	0.4458 (12)	0.3910 (5)	14.2 (7)
C28	-0.2720 (11)	0.2769 (14)	0.3779 (5)	15.3 (7)
C29	-0.1970 (12)	0.3198 (13)	0.4513 (4)	14.2 (6)
C30	0.5678 (8)	0.2492 (8)	0.2525 (3)	7.7 (4)
C31	0.4829 (9)	0.0971 (10)	0.2059 (3)	10.2 (4)
C32	0.6292 (9)	0.0546 (9)	0.2667 (4)	10.4 (5)
H1	-0.079 (5)	0.055 (5)	0.3259 (20)	4.2 (16)†
H2	0.183 (5)	-0.157 (5)	0.3478 (19)	3.9 (16)†
H3	0.208 (5)	-0.059 (5)	0.2780 (18)	2.5 (13)†
H4	0.440 (5)	0.171 (5)	0.4059 (19)	3.6 (15)†
H5	0.202 (5)	-0.029 (5)	0.4498 (19)	2.8 (15)†
H6	0.134 (5)	0.166 (5)	0.4625 (18)	3.0 (13)†

†  $B_{iso}$ .

**Related literature.** The U<sup>III</sup> dimer, [UBr{C<sub>5</sub>H<sub>3</sub>[Si(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>}]<sub>2</sub>, has been synthesized and structurally characterized (Blake, Lappert, Taylor, Atwood &

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

Cp1-U	2.520	C5-U	2.787 (7)
Cp2-U	2.514	C6-U	2.784 (7)
Br-U	2.8761 (10)	C7-U	2.798 (7)
C11-U	2.662 (8)	C8-U	2.769 (7)
C12-U	1.697 (7)	C9-U	2.777 (7)
C1-U	2.788 (7)	C10-U	2.819 (7)
C2-U	2.825 (7)	C11-N1	1.128 (8)
C3-U	2.789 (7)	C12-N2	1.126 (8)
C4-U	2.777 (7)		
Br-U-C11	75.65 (17)	C12-U-Cp1	86.97
Br-U-C12	72.73 (20)	C12-U-Cp2	99.22
C11-U-C12	148.09 (25)	Cp1-U-Cp2	129.08
Br-U-Cp1	118.73	C11-N1-C13	178.4 (9)
Br-U-Cp2	112.16	C12-N2-C14	176.2 (10)
C11-U-Cp1	94.41	U-C11-N1	177.1 (7)
C11-U-Cp2	96.44	U-C12-N2	173.1 (7)

Cp1 and Cp2 represent the centers of cyclopentadienyl rings C1-C5 and C6-C10 respectively.

Zhang, 1987). The ability of isocyanides to act as good donor ligands toward uranium metal centers has been previously observed (Kanellakopoulos, Fischer, Dornberger & Baumgartner, 1970).

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Structure of [Ag(PPh<sub>3</sub>)<sub>4</sub>]PF<sub>6</sub>

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**Abstract.** Tetrakis(triphenylphosphine)silver hexafluorophosphate, [Ag{P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}]<sub>4</sub>PF<sub>6</sub>,  $M_r = 1302.01$ ,

trigonal,  $R\bar{3}$ ,  $a = 14.330$  (6),  $b = 14.330$  (6),  $c = 51.57$  (1) Å,  $V = 9171$  (5) Å<sup>3</sup>,  $Z = 6$ ,  $D_x = 1.414$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 5.139$  cm<sup>-1</sup>,  $F(000) = 4008$ ,  $T = 292$  K,  $R = 0.0401$

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for 2687 unique observed reflections. The anion adopts  $\bar{3}$  symmetry and the metal atom lies on a special position of symmetry 3 coordinated by two types of ligands. The P atom of one of the triphenylphosphine ligands is positioned on the same 3 axis as the metal and thus one of the phenyl rings is crystallographically independent. One other triphenylphosphine ligand situated off the axis completes the asymmetric unit for the cation.

**Experimental.** The title compound, which can be synthesized directly by mixing four equivalents of PPh<sub>3</sub> with Ag(PF<sub>6</sub>), was unexpectedly obtained in a reaction of ReCl<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>, Mo( $\eta^6$ -PhPMe<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>3</sub> and Ag(PF<sub>6</sub>) in benzene. The addition of hexane to this solution resulted in the formation of white crystals; one of an irregular geometry of dimensions 0.3 × 0.4 × 0.4 mm was mounted on a glass fiber. Cell constants were derived from least-squares refinement based on 25 reflections having 25 < 2 $\theta$  < 35°. Intensity data were collected at variable scan speeds (2–20° min<sup>-1</sup>), which depended on a pre-scan count with a skip option, using the  $\omega$ -scan technique with 4 ≤ 2 $\theta$  ≤ 55° ( $h = 0$  to 19,  $k = 0$  to 19,  $l = -68$  to 68) on a Nicolet P3/F equivalent diffractometer using graphite-monochromated Mo K $\alpha$  radiation. Three standard reflections (0,6,24, 5,3,16, 6,2,20), measured every 100 reflections, showed small (< 0.2%) random variations. Data were corrected for Lorentz and polarization effects, and for absorption effects based on  $\psi$  scans using the empirical method of North, Phillips & Mathews (1968);  $T_{\min} = 0.9735$ ,  $T_{\max} = 0.9992$ . There are 84274/12 reflections in the sphere; however, due to the skip option and the insertion of an index restriction after 945 reflections were collected ( $-h + k + l = 2n$  only present), only 3906 data were collected and averaged to 2687 unique observed reflections ( $F_o^2 >$

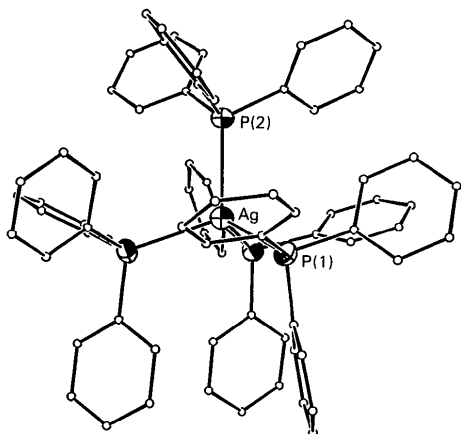


Fig. 1. An ORTEP drawing (Johnson, 1965) of [Ag(PPh<sub>3</sub>)<sub>4</sub>]<sup>+</sup> showing a partial atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level and spheres have been drawn with arbitrary radii.

Table 1. Positional and equivalent isotropic thermal parameters and their e.s.d.'s for [Ag(PPh<sub>3</sub>)<sub>4</sub>]PF<sub>6</sub>

The equivalent isotropic displacement parameter is:  $\frac{1}{3}[a^2u^2B_{11} + b^2v^2B_{22} + c^2w^2B_{33} + 2ab(\cos\gamma)u^*v^*B_{12} + 2ac(\cos\beta)u^*w^*B_{13} + 2bc(\cos\alpha)v^*w^*B_{23}]$ .

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Ag	0.667	0.333	0.08521 (1)	2.845 (6)
P(1)	0.52472 (6)	0.38856 (6)	0.10227 (2)	2.61 (2)
P(2)	0.667	0.333	0.03404 (3)	2.54 (2)
C(111)	0.5188 (3)	0.4010 (3)	0.13730 (7)	3.13 (8)
C(112)	0.4244 (3)	0.3732 (4)	0.15037 (9)	5.4 (1)
C(113)	0.4271 (4)	0.3938 (5)	0.1768 (11)	7.6 (2)
C(114)	0.5216 (5)	0.4380 (4)	0.19016 (9)	6.9 (2)
C(115)	0.6149 (4)	0.4629 (4)	0.17758 (9)	5.3 (1)
C(116)	0.6139 (3)	0.4453 (3)	0.15127 (8)	4.1 (1)
C(121)	0.3865 (2)	0.2869 (3)	0.09347 (7)	2.76 (8)
C(122)	0.3557 (3)	0.1787 (3)	0.09714 (9)	4.1 (1)
C(123)	0.2560 (4)	0.0982 (3)	0.0892 (11)	5.2 (1)
C(124)	0.1855 (3)	0.1237 (4)	0.07764 (9)	4.9 (1)
C(125)	0.2133 (3)	0.2299 (3)	0.07433 (9)	4.8 (1)
C(126)	0.3134 (3)	0.3107 (3)	0.08226 (8)	3.69 (9)
C(131)	0.5322 (2)	0.5124 (3)	0.09041 (7)	2.80 (8)
C(132)	0.5687 (3)	0.5458 (3)	0.06537 (8)	3.70 (9)
C(133)	0.5694 (3)	0.6344 (3)	0.05461 (8)	4.5 (1)
C(134)	0.5335 (3)	0.6911 (3)	0.06885 (9)	4.8 (1)
C(135)	0.4984 (4)	0.6611 (3)	0.0937 (11)	5.2 (1)
C(136)	0.4980 (3)	0.5724 (3)	0.10473 (8)	4.4 (1)
C(211)	0.5401 (3)	0.2365 (3)	0.01875 (7)	2.77 (8)
C(212)	0.4452 (3)	0.2277 (3)	0.02814 (8)	3.53 (9)
C(213)	0.3477 (3)	0.1575 (3)	0.01692 (9)	4.4 (1)
C(214)	0.3436 (3)	0.0953 (4)	-0.0039 (11)	4.9 (1)
C(215)	0.4362 (4)	0.1037 (4)	-0.01338 (9)	5.2 (1)
C(216)	0.5347 (3)	0.1733 (3)	-0.00222 (8)	4.0 (1)
P(11)	0.000	0.000	0.000	3.38 (4)
P(22)	0.333	0.667	0.167	4.65 (5)
F(11)	0.0339 (2)	0.1018 (2)	0.01775 (6)	7.21 (9)
F(22)	0.4245 (4)	0.7498 (4)	0.14954 (9)	14.1 (2)

Table 2. Selected bond lengths (Å) and valence angles (°)

Numbers in parentheses are e.s.d.'s in the least significant digits.

Ag	P(1)	2.674 (1)	P(1)	C(131)	1.828 (4)		
Ag	P(2)	2.639 (2)	P(2)	C(211)	1.822 (3)		
P(1)	C(111)	1.821 (4)	P(11)	F(11)	1.579 (3)		
P(1)	C(121)	1.835 (3)	P(22)	F(22)	1.534 (4)		
P(1)	Ag	P(2)	109.21 (2)	C(111)	P(1)	C(131)	102.7 (2)
Ag	P(1)	C(111)	115.8 (2)	C(121)	P(1)	C(131)	101.7 (2)
Ag	P(1)	C(121)	111.3 (1)	Ag	P(2)	C(211)	115.6 (1)
Ag	P(1)	C(131)	119.5 (1)	C(211)	P(2)	C(211)	102.6 (2)
C(111)	P(1)	C(121)	103.8 (2)				

3 $\sigma F_o^2$ );  $R_{\text{merge}}(F_o) = 0.017$ . Scattering factors, including anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). All computations were carried out using the SDP/V package of programs (B. A. Frenz & Associates, Inc., 1985). The structure was solved by direct methods and subjected to full-matrix least-squares refinement. All non-H atoms were refined anisotropically. H atoms were added at calculated positions and then refined freely.  $wR = \{[\sum w(|F_o| - |F_c|)^2] / [\sum w(F_o)^2]\}^{1/2}$  was minimized, where  $w = \sigma^2(|F_o|)^{-1}$ ; the final  $R$  value was 0.0401,  $wR = 0.0492$  and  $S = 1.194$  for 334 variables. The largest shift/e.s.d. in the final least-squares cycle was 0.16; the maximum residual electron density in the difference Fourier map was 0.745 e Å<sup>-3</sup>. The molecule and the atomic labeling scheme are shown in Fig. 1.

Final positional and equivalent isotropic thermal parameters are shown in Table 1;\* some selected bond distances and angles are listed in Table 2.

**Related literature.** The crystal structures of  $[\text{Ag}(\text{PPh}_3)_4]$  with  $\text{ClO}_4^-$  and  $[\text{SnPh}_2(\text{NO}_3)_2(\text{Cl}, \text{NO}_3)]^-$  as anions have been reported (Engelhardt, Pakawatchai, White & Healy, 1985; Pelizzi, Pelizzi & Tarasconi, 1984).

\*Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete intramolecular bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51750 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Structure of Tricarbonyl( $\eta$ -cyclopentadienyl)[(2,3,7,8,12,13,17,18-octaethylporphinato)thallio(III)]molybdenum(0)

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**Abstract.**  $[\text{MoTi}(\text{C}_5\text{H}_5)(\text{C}_{36}\text{H}_{44}\text{N}_4)(\text{CO})_3]$ ,  $[(\text{oep})\text{TiMo}(\text{CO})_3\text{Cp}]$ ,  $M_r = 982.22$ , triclinic,  $P\bar{1}$ ,  $a = 12.883$  (2),  $b = 14.021$  (2),  $c = 15.350$  (2) Å,  $\alpha = 59.40$  (1),  $\beta = 59.98$  (1),  $\gamma = 67.61$  (1)°,  $V = 2036.6$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.601$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.071073$  Å,  $\mu = 0.52$  cm<sup>-1</sup>,  $F(000) = 976$ ,  $R(F) = 0.0214$ ,  $wR(F) = 0.0254$ ,  $\text{GOF} = 0.464$  for 6096 reflections.  $[(\text{oep})\text{TiMo}(\text{CO})_3\text{Cp}]$  has two coordinated metal units, which are linked by a single covalent bond; the Ti–Mo bond distance is 2.829 (1) Å. The average Ti–N distance is 2.294 (5)  $\pm$  0.02 Å and the Ti atom lies 1.000 (1) Å above the four-N-atom plane towards the Mo atom. The average Mo–CO distance is 1.973 (6)  $\pm$  0.002 Å.

**Experimental.** Crystals were prepared according to Guilard *et al.* (1988). A black crystal, 0.25  $\times$  0.32  $\times$  0.20 mm, of  $[(\text{oep})\text{TiMo}(\text{CO})_3\text{Cp}]$  recrystallized from toluene/heptane was mounted on a CAD-4 diffrac-

tometer. Unit-cell dimensions at room temperature were obtained from accurate angle values of 25 reflections with  $10 < \theta < 22^\circ$  using monochromated Mo  $K\alpha$  radiation. 7410 reflections were measured up to  $(\sin\theta)/\lambda = 0.60$  Å<sup>-1</sup> at room temperature ( $-15 \leq h \leq 15$ ,  $-16 \leq k \leq 16$ ,  $0 \leq l \leq 18$ );  $\bar{2}45$ ,  $\bar{5}36$ ,  $\bar{2}15$  standard reflections monitored every 2 h;  $\omega$ - $2\theta$  scan; scan width  $1.0^\circ + 0.35^\circ \tan\theta$ ; scan speed  $v$ :  $0.55 < v < 1.65^\circ \text{ min}^{-1}$ . No decay was observed and no absorption correction was applied. 6096 reflections [ $I \geq 3\sigma(I)$ ], corrected for Lorentz and polarization effects, were used to solve the structure. The structure was solved by interpretation of the Patterson map; all non-H atoms were refined anisotropically; H atoms were located at their calculated positions. At convergence ( $\Delta/\sigma$  max. = 0.10 for  $U_{33}$  of Ti), a residual Fourier map (*SHELX76*; Sheldrick, 1976) gave a maximum peak of 0.52 e Å<sup>-3</sup>. The weighting scheme used was  $w^{-1} = \sigma^2(F) + 0.0054F^2$ . Atomic scattering factors were taken from *SHELX76* and from *International Tables for X-ray Crystallography* (1974).

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