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 [Ag(PPh$_3$)$_4$] with ClO$_4^-$ and [SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)]$^-$ as anions have been reported (Engelhardt, Pakawatchai, White & Healy, 1985; Pelizzi, Pelizzi & Tarasconi, 1984).

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* 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(η-cyclopentadienyl)[(2,3,7,8,12,13,17,18-octaethylporphinato)thallio(III)]molybdenum(0)

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Abstract. [MoTl(C$_5$H$_5$)(C$_{36}$H$_{44}$N$_4$)(CO)$_3$], [(oep)-TlMo(CO)$_3$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^3, $Z = 2$, $D_x = 1.601$ g cm^{-3}, λ(Mo $K\alpha$) = 0.071073 Å, $\mu = 0.52$ cm^{-1}, $F(000) = 976$, $R(F) = 0.0214$, $wR(F) = 0.0254$, GOF = 0.464 for 6096 reflections. [(oep)TlMo(CO)$_3$Cp] has two coordinated metal units, which are linked by a single covalent bond; the Tl—Mo bond distance is 2.829 (1) Å. The average Tl—N distance is 2.294 (5) ±0.02 Å and the Tl 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) ±0.002 Å.

Experimental. Crystals were prepared according to Guilard *et al.* (1988). A black crystal, 0.25 × 0.32 × 0.20 mm, of [(oep)TlMo(CO)$_3$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 $10 < \theta < 22°$ using monochromated Mo $K\alpha$ radiation. 7410 reflections were measured up to $(\sin\theta)/\lambda = 0.60$ Å^{-1} at room temperature ($-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $0 \leq l \leq 18$); $\overline{2}4\overline{5}$, $\overline{5}3\overline{6}$, $\overline{2}1\overline{5}$ standard reflections monitored every 2 h; ω–2θ scan; scan width $1.0° + 0.35°\tan\theta$; scan speed v: $0.55 < v < 1.65°$ 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 (Δ/σ max. = 0.10 for U_{33} of Tl), a residual Fourier map (*SHELX*76; Sheldrick, 1976) gave a maximum peak of 0.52 e Å^{-3}. The weighting scheme used was $w^{-1} = \sigma^2(F) + 0.0054F^2$. Atomic scattering factors were taken from *SHELX*76 and from *International Tables for X-ray Crystallography* (1974).

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Table 1. *Positional parameters and equivalent isotropic temperature factors and their e.s.d.'s*

	x	y	z	B_{eq}*(Å²)
Tl	0.17325 (1)	0.18077 (1)	0.27612 (1)	2.953 (5)
Mo	0.34602 (3)	0.30627 (3)	0.21025 (3)	3.61 (1)
O(1)	0.2459 (4)	0.4260 (3)	0.0254 (3)	8.5 (2)
O(2)	0.5820 (4)	0.3725 (4)	0.0032 (3)	8.6 (2)
O(3)	0.4995 (3)	0.0747 (3)	0.2020 (4)	9.7 (2)
N(1)	0.1243 (3)	0.1814 (3)	0.1518 (2)	3.6 (1)
N(2)	0.2469 (3)	-0.0022 (2)	0.2943 (2)	3.32 (9)
N(3)	0.0962 (3)	0.0874 (3)	0.4642 (2)	3.30 (9)
N(4)	-0.0254 (3)	-0.2707 (2)	0.3214 (2)	3.4 (1)
C(1)	0.0488 (3)	0.2658 (3)	0.1026 (3)	3.8 (1)
C(2)	0.0739 (3)	0.2602 (3)	0.0019 (3)	3.8 (1)
C(3)	0.1667 (3)	0.1707 (3)	-0.0084 (3)	3.7 (1)
C(4)	0.1985 (3)	0.1226 (3)	0.0862 (3)	3.6 (1)
C(5)	0.2850 (3)	0.0279 (3)	0.1107 (3)	3.7 (1)
C(6)	0.3077 (3)	-0.0314 (3)	0.2065 (3)	3.7 (1)
C(7)	0.3940 (3)	-0.1343 (3)	0.2307 (3)	3.9 (1)
C(8)	0.3844 (4)	-0.1651 (3)	0.3340 (3)	4.0 (1)
C(9)	0.2919 (3)	-0.0804 (3)	0.3733 (3)	3.6 (1)
C(10)	0.2533 (4)	-0.0807 (3)	0.4756 (3)	4.0 (1)
C(11)	0.1627 (3)	-0.0035 (3)	0.5179 (3)	3.5 (1)
C(12)	0.1251 (3)	-0.0076 (3)	0.6269 (3)	3.8 (1)
C(13)	0.0351 (3)	0.0827 (3)	0.6350 (3)	3.8 (1)
C(14)	0.0169 (3)	0.1407 (3)	0.5329 (3)	3.5 (1)
C(15)	-0.0672 (3)	0.2386 (3)	0.5072 (3)	3.7 (1)
C(16)	-0.0871 (3)	0.2991 (3)	0.4103 (3)	3.5 (1)
C(17)	-0.1788 (3)	0.3980 (3)	0.3896 (3)	4.0 (1)
C(18)	-0.1732 (3)	0.4263 (3)	0.2883 (3)	3.9 (1)
C(19)	-0.0751 (3)	0.3473 (3)	0.2450 (3)	3.5 (1)
C(20)	-0.0389 (3)	0.3446 (3)	0.1436 (3)	3.7 (1)
C(25)	0.0022 (4)	0.3328 (4)	-0.0696 (3)	4.8 (1)
C(26)	-0.1177 (5)	0.2962 (5)	-0.0242 (4)	6.8 (2)
C(27)	0.2236 (4)	0.1275 (4)	-0.0961 (3)	4.8 (1)
C(28)	0.1730 (6)	0.0271 (5)	-0.0633 (5)	8.4 (2)
C(29)	0.4725 (4)	-0.1959 (4)	0.1561 (4)	5.2 (2)
C(30)	0.4052 (6)	-0.2646 (4)	0.1583 (5)	8.1 (2)
C(31)	0.4592 (4)	-0.2591 (4)	0.3963 (4)	5.1 (1)
C(32)	0.5487 (5)	-0.2224 (5)	0.4015 (5)	6.8 (2)
C(33)	0.1807 (5)	-0.0936 (4)	0.7078 (3)	5.2 (2)
C(34)	0.3007 (6)	-0.0691 (6)	0.6819 (5)	8.8 (3)
C(35)	-0.0315 (4)	0.1192 (4)	0.7290 (3)	5.1 (2)
C(36)	0.0175 (6)	0.2131 (5)	0.7103 (5)	8.6 (3)
C(37)	-0.2578 (4)	0.4582 (4)	0.4660 (4)	5.5 (2)
C(38)	-0.1881 (6)	0.5324 (5)	0.4558 (6)	8.6 (3)
C(39)	-0.2553 (4)	0.5168 (3)	0.2325 (4)	4.7 (1)
C(40)	-0.3623 (5)	0.4739 (4)	0.2573 (5)	7.1 (2)
C(50)	0.3930 (7)	0.3048 (6)	0.3386 (6)	10.2 (3)
C(51)	0.3781 (6)	0.4133 (6)	0.2668 (5)	7.8 (2)
C(52)	0.2631 (7)	0.4521 (5)	0.2719 (5)	8.7 (3)
C(53)	0.1976 (5)	0.3636 (7)	0.3516 (6)	8.8 (3)
C(54)	0.2770 (8)	0.2714 (5)	0.3949 (4)	8.6 (3)
C(55)	0.2789 (4)	0.3783 (4)	0.0960 (4)	5.0 (2)
C(56)	0.4952 (4)	0.3471 (4)	0.0784 (4)	5.8 (2)
C(57)	0.4376 (4)	0.1585 (4)	0.2056 (4)	5.7 (2)

* Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as:

$$(4/3) [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

Final residuals are $R(F) = 0.021$; $wR(F) = 0.0254$; $GOF = 0.464$. Fractional coordinates and equivalent isotropic temperature factors are given in Table 1;* bond lengths and angles are listed in Table 2; Fig. 1 is the *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule.

Related literature. For a review of metal–metal bonding in metalloporphyrin chemistry, see Guilard, Lecomte &

*Lists of observed and calculated structure factors, anisotropic thermal parameters, positional and isotropic temperature factors for H atoms and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51795 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances (Å) and bond angles (°)*

Tl—Mo	2.8289 (5)	Mo—Cp*	2.010
Tl N(1)	2.285 (5)	Mo—C(50)	2.321 (8)
Tl—N(2)	2.289 (4)	Mo—C(51)	2.310 (8)
Tl—N(3)	2.306 (3)	Mo—C(52)	2.346 (8)
Tl—N(4)	2.297 (3)	Mo—C(53)	2.337 (8)
		Mo—C(54)	2.337 (8)
		Mo—C(O1)	1.975 (6)
		Mo—C(O2)	1.972 (4)
		Mo—C(O3)	1.973 (5)
		C(O1)—O(1)	1.145 (8)
		C(O2)—O(2)	1.141 (5)
		C(O3)—O(3)	1.152 (6)
N(1)—C(1)	1.367 (5)	C(7)—C(8)	1.365 (7)
N(1)—C(4)	1.374 (6)	C(7)—C(29)	1.505 (7)
N(2)—C(6)	1.363 (7)	C(8)—C(9)	1.457 (5)
N(2)—C(9)	1.370 (5)	C(8)—C(31)	1.502 (6)
N(3)—C(11)	1.357 (5)	C(9)—C(10)	1.388 (7)
N(3)—C(14)	1.362 (5)	C(10)—C(11)	1.396 (5)
N(4)—C(16)	1.371 (6)	C(11)—C(12)	1.467 (7)
N(4)—C(19)	1.373 (5)	C(12)—C(13)	1.363 (5)
C(1)—C(2)	1.451 (8)	C(12)—C(33)	1.489 (6)
C(1)—C(20)	1.391 (5)	C(13)—C(14)	1.450 (6)
C(2)—C(3)	1.378 (5)	C(13)—C(35)	1.503 (7)
C(2)—C(25)	1.502 (7)	C(14)—C(15)	1.398 (5)
C(3)—C(4)	1.456 (7)	C(15)—C(16)	1.389 (7)
C(3)—C(27)	1.490 (7)	C(16)—C(17)	1.448 (5)
C(4)—C(5)	1.389 (5)	C(17)—C(18)	1.364 (7)
C(5)—C(6)	1.393 (6)	C(17)—C(37)	1.510 (7)
C(6)—C(7)	1.449 (5)	C(18)—C(19)	1.451 (5)
C(18)—C(39)	1.498 (6)	C(19)—C(20)	1.401 (7)
C(25)—C(26)	1.516 (9)	C(27)—C(28)	1.52 (2)
C(29)—C(30)	1.51 (1)	C(31)—C(32)	1.48 (2)
C(33)—C(34)	1.52 (2)	C(35)—C(36)	1.52 (1)
C(37)—C(38)	1.52 (1)	C(39)—C(40)	1.51 (1)
C(50)—C(51)	1.362 (9)	C(50)—C(54)	1.42 (1)
C(51)—C(52)	1.35 (1)	C(52)—C(53)	1.40 (1)
C(53)—C(54)	1.40 (1)		
Mo—Tl—N(1)	121.65 (7)	N(1)—Tl—N(2)	79.4 (1)
Mo—Tl—N(2)	115.91 (9)	N(1)—Tl—N(3)	128.3 (1)
Mo—Tl—N(3)	110.1 (1)	N(1)—Tl—N(4)	79.1 (1)
Mo—Tl—N(4)	115.4 (2)	N(2)—Tl—N(3)	79.1 (1)
C(55)—Mo—C(56)	80.3 (2)	N(2)—Tl—N(4)	128.4 (1)
C(55)—Mo—C(57)	105.5 (3)	N(3)—Tl—N(4)	78.6 (2)
C(56)—Mo—C(57)	78.0 (2)	Tl—Mo—C(55)	72.3 (2)
Mo—C(55)—O(1)	174.7 (5)	Tl—Mo—C(56)	132.6 (2)
Mo—C(56)—O(2)	178.0 (7)	Tl—Mo—C(57)	73.4 (2)
Mo—C(57)—O(3)	174.1 (7)	Tl—Mo—Cp*	110.6
C(1)—N(1)—C(4)	107.6 (4)	C(6)—N(2)—C(9)	107.7 (3)
C(11)—N(3)—C(14)	107.5 (4)	C(16)—N(4)—C(19)	107.0 (3)
N(1)—C(1)—C(4)	109.6 (3)	N(1)—C(1)—C(20)	124.9 (5)
C(2)—C(1)—C(20)	125.5 (4)	C(1)—C(2)—C(3)	106.9 (4)
C(1)—C(2)—C(25)	125.1 (3)	C(3)—C(2)—C(25)	127.7 (5)
C(2)—C(3)—C(4)	106.4 (4)	C(2)—C(3)—C(27)	128.1 (4)
C(4)—C(3)—C(27)	125.5 (3)	N(1)—C(4)—C(3)	109.4 (4)
N(1)—C(4)—C(5)	124.7 (4)	C(3)—C(4)—C(5)	125.7 (4)
C(4)—C(5)—C(6)	128.5 (5)	N(2)—C(6)—C(5)	124.1 (3)
N(2)—C(6)—C(7)	109.6 (4)	C(5)—C(6)—C(7)	126.3 (4)
C(6)—C(7)—C(8)	106.9 (4)	C(6)—C(7)—C(29)	124.9 (4)
C(8)—C(7)—C(29)	128.1 (3)	C(7)—C(8)—C(9)	106.7 (3)
C(7)—C(8)—C(31)	129.5 (4)	C(9)—C(8)—C(31)	123.6 (5)
N(2)—C(9)—C(8)	109.1 (5)	N(2)—C(9)—C(10)	125.5 (3)
C(8)—C(9)—C(10)	125.4 (4)	C(9)—C(10)—C(11)	127.4 (4)
N(3)—C(11)—C(10)	125.2 (4)	N(3)—C(11)—C(12)	109.5 (3)
C(10)—C(11)—C(12)	125.3 (4)	C(11)—C(12)—C(13)	106.3 (4)
C(11)—C(12)—C(33)	124.7 (3)	C(13)—C(12)—C(33)	129.1 (4)
C(12)—C(13)—C(14)	106.9 (4)	C(12)—C(13)—C(35)	127.7 (5)
C(14)—C(13)—C(35)	125.5 (3)	N(3)—C(14)—C(13)	109.9 (4)
N(3)—C(14)—C(15)	124.9 (5)	C(13)—C(14)—C(15)	125.2 (4)
C(14)—C(15)—C(16)	127.9 (5)	N(4)—C(16)—C(15)	124.5 (4)
N(4)—C(16)—C(17)	109.8 (4)	C(15)—C(16)—C(17)	125.6 (4)
C(16)—C(17)—C(18)	106.7 (4)	C(16)—C(17)—C(37)	124.5 (5)
C(18)—C(17)—C(37)	128.7 (3)	C(17)—C(18)—C(19)	107.1 (3)
C(17)—C(18)—C(39)	127.7 (4)	C(19)—C(18)—C(39)	125.1 (5)
N(4)—C(19)—C(18)	109.4 (4)	N(4)—C(19)—C(20)	124.4 (3)
C(18)—C(19)—C(20)	126.3 (4)	C(1)—C(20)—C(19)	127.8 (4)
C(2)—C(25)—C(26)	113.1 (3)	C(3)—C(27)—C(28)	113.1 (4)
C(7)—C(29)—C(30)	113.2 (5)	C(8)—C(31)—C(32)	114.1 (4)
C(12)—C(33)—C(34)	112.3 (4)	C(13)—C(35)—C(36)	112.8 (4)
C(17)—C(37)—C(38)	111.0 (5)	C(18)—C(39)—C(40)	111.8 (4)
C(51)—C(50)—C(54)	106.2 (7)	C(50)—C(51)—C(52)	112.2 (7)
C(51)—C(52)—C(53)	106.8 (5)	C(52)—C(53)—C(54)	108.0 (7)
C(50)—C(54)—C(53)	106.8 (6)		

Numbers in parentheses are e.s.d.'s in the least significant digits.
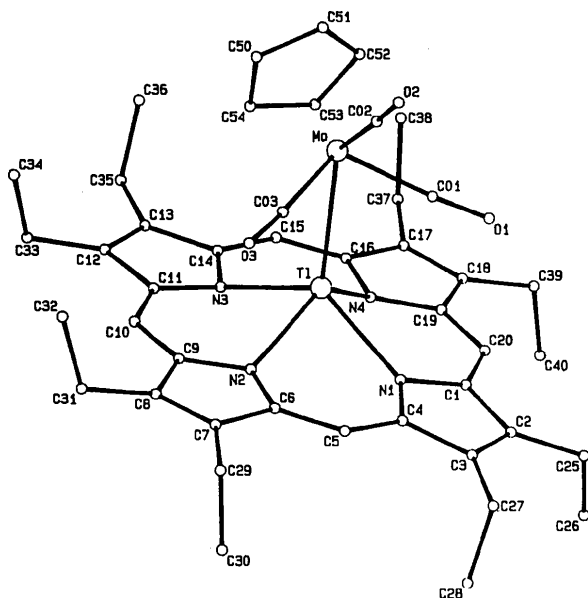* Cp: center of the cyclopentadienyl ring.

Fig. 1. *PLUTO* drawing of [(oep)TlMo(CO)₃Cp].

Kadish (1987), Brothers & Collman (1986) and references therein.

The crystal structures containing a hetero metal–metal bond in the metalloporphyrin series are: [(oep)-SnFe(CO)₄] (Barbe, Guilard, Lecomte & Gerardin, 1984), Sn=Fe = 2·491 (1) Å; [(tetraphenylporphinato)Sn{Mn(CO)₄HgMn(CO)₅}].0·5CH₂Cl₂ (Onaka *et al.*, 1985), Sn–Mn = 2·554 (3) Å; [(oep)InMn-(CO)₅] (Guilard, Mitaine, Moïse, Lecomte, Boukhris,

Swistak, Tabard, Lacombe, Cornillon & Kadish, 1987), In–Mn = 2·705 (1) Å; [(oep)RhIn(oep)] (Jones, Carrol & Wayland, 1986), Rh–In = 2·584 (2) Å; [(oep)-TlMn(CO)₅] (Guilard *et al.*, 1988), Tl–Mn = 2·6994 (9) Å; [(oep)InMo(CO)₃Cp] (Lecomte, Habbou, Mitaine, Richard & Guilard, 1989), In–Mo = 2·890 (1) Å.

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Structure of Tricarbonyl(η-cyclopentadienyl)[(2,3,7,8,12,13,17,18-octaethylporphinato)indio(III)]molybdenum(0) at 100 (5) K

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Abstract. [InMo(C₅H₅)(C₃₆H₄₄N₄)(CO)₃], [(oep)-InMo(CO)₃Cp], $M_r = 892·67$, triclinic, $P\bar{1}$, $a = 12·679$ (5), $b = 13·895$ (5), $c = 15·239$ (8) Å, $\alpha = 58·81$ (4), $\beta = 59·46$ (4), $\gamma = 67·85$ (4)°, $V = 1954·5$ Å³, $Z = 2$, $D_x = 1·516$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 0·17$ cm⁻¹, $F(000) = 912$, $T = 100$ K,

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