$\Delta\rho_{\rm min} = -0{\cdot}45$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974); *SHELXTL* (Sheldrick, 1985) and local computer programs.

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, selected bond lengths and angles in Table 2.* The cation structure is shown in Fig. 1.

Related literature. The structure of the tetrafluoroborate salt of the same cation has been reported by Pimblett, Garner & Clegg (1985), together with a comparison with the two known forms of 'Wilkinson's catalyst' $[RhCl(PPh_3)_3]$ (Bennett & Longstaff, 1965; Osborn, Jardine, Young & Wilkinson, 1966; Bennett & Donaldson, 1977). The structure of the cation reported here, while being more precise because there is no disorder in the anion, is not significantly different from the earlier result, except for a slightly greater tetrahedral distortion of the square-planar coordination of Rh.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and complete bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52096 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Nitrato(triphenylphosphine oxide)silver(I)

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Abstract. $[AgNO_3(C_{18}H_{15})]$, $M_r = 448{\cdot}17$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}452$ (4), $b = 15{\cdot}086$ (2), $c = 8{\cdot}650$ (2) Å, $V = 1755{\cdot}4$ (12) Å^3, $Z = 4$, $D_x = 1{\cdot}696$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 12{\cdot}33$ cm^{-1}, $F(000) = 896$, $T = 293$ K, final $R = 0{\cdot}052$ for 1862 observed reflections. The Ag atom is five coordinate, forming a distorted square-based pyramid. It is bound to the O of the triphenylphosphine oxide, to two O atoms of one nitrate group, and to two O atoms of a symmetry-related nitrate group. Bond distances around the Ag atom range from 2·261 to 2·697 Å and the Ag—O—P bond angle is 133·3 (4)°.

Experimental. Synthesis by dissolving equimolar amounts of silver nitrate and triphenylphosphine oxide in hot absolute ethanol, hot-filtered and allowed to evaporate; colorless rectangular crystal (0·34 × 0·40 × 0·40 mm); Enraf–Nonius CAD-4 diffractometer system, ω:2θ scanning technique, variable scan speed (0·6–5·6° min^{-1}), Mo $K\alpha$ radiation, and a graphite monochromator; lattice parameters by least squares utilizing 25 accurately centered reflections (θ = 8 to 12°); three reflections (323, 542, 632) measured every 2 h revealed no significant change (< 1·5%); 4288 unique reflections measured ($1 < \theta < 35°$; range of *hkl*: 0→21, 0→24, 0→13), 1862 with $I > 3\sigma(I)$; Lorentz, polarization and numerical absorption (correction = 1·444–1·543) cor-

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Table 1. *Atomic positional and equivalent isotropic thermal* ($Å^2 \times 10^3$) *parameters for nitrato(triphenylphosphine oxide)silver*(I)

$$U_{eq} = (U_{11} + U_{22} + U_{33} + U_{12}\cos\gamma + U_{13}\cos\beta + U_{23}\cos\alpha)/3.$$

	x	y	z	U_{eq}
Ag	0·80389 (6)	0·06485 (7)	0·95803 (10)	71·8 (5)
O(1)	0·6977 (7)	0·1410 (5)	0·7780 (8)	74 (5)
O(2)	0·7498 (6)	0·0190 (4)	0·6803 (9)	58 (4)
O(3)	0·6501 (7)	0·1007 (6)	0·5515 (9)	91 (6)
N	0·6991 (7)	0·0876 (5)	0·6697 (9)	52 (5)
O(4)	0·9633 (4)	0·1051 (5)	0·9138 (6)	55 (4)
P	1·0569 (1)	0·0948 (2)	1·0036 (2)	35 (1)
C(11)	1·1427 (6)	0·1787 (6)	0·9429 (10)	38 (4)
C(12)	1·2442 (7)	0·1703 (7)	0·9573 (13)	55 (6)
C(13)	1·3076 (8)	0·2322 (7)	0·8951 (13)	59 (6)
C(14)	1·2714 (8)	0·3025 (7)	0·8172 (12)	59 (6)
C(15)	1·1702 (8)	0·3132 (7)	0·8016 (12)	55 (6)
C(16)	1·1072 (7)	0·2511 (6)	0·8636 (12)	52 (6)
C(21)	1·0353 (6)	0·1066 (6)	1·2080 (9)	39 (4)
C(22)	0·9963 (7)	0·0331 (7)	1·2891 (10)	49 (5)
C(23)	0·9666 (7)	0·0417 (8)	1·4430 (12)	66 (6)
C(24)	0·9726 (8)	0·1258 (8)	0·5150 (10)	66 (7)
C(25)	1·0147 (7)	0·1968 (7)	1·4341 (11)	62 (6)
C(26)	1·0443 (6)	0·1873 (7)	1·2814 (10)	46 (5)
C(31)	1·1154 (6)	−0·0091 (6)	0·9740 (10)	40 (4)
C(32)	1·0881 (8)	−0·0593 (7)	0·8519 (12)	61 (6)
C(33)	1·1347 (10)	−0·1425 (9)	0·8243 (16)	82 (9)
C(34)	1·2108 (9)	−0·1703 (8)	0·9191 (19)	87 (10)
C(35)	1·2385 (8)	−0·1192 (7)	1·0441 (16)	65 (7)
C(36)	1·1896 (7)	−0·0415 (6)	1·0694 (12)	56 (5)

Table 2. *Interatomic distances* (Å) *and valence angles* (°) *for nitrato(triphenylphosphine oxide)silver*(I)

Ag—O(1)	2·405 (8)	C(21)—C(22)	1·413 (13)
Ag—O(2)	2·603 (8)	C(21)—C(26)	1·379 (13)
Ag—O(4)	2·261 (6)	C(22)—C(23)	1·396 (13)
Ag—O(2*)	2·413 (7)	C(23)—C(24)	1·416 (17)
Ag—O(3*)	2·697 (9)	C(24)—C(25)	1·399 (16)
O(4)—P	1·488 (6)	C(25)—C(26)	1·387 (13)
P—C(11)	1·791 (9)	C(31)—C(32)	1·350 (13)
P—C(21)	1·801 (8)	C(31)—C(36)	1·385 (13)
P—C(31)	1·772 (9)	C(32)—C(33)	1·423 (17)
C(11)—C(12)	1·376 (12)	C(33)—C(34)	1·377 (19)
C(11)—C(16)	1·376 (13)	C(34)—C(35)	1·379 (19)
C(12)—C(13)	1·374 (14)	C(35)—C(36)	1·362 (14)
C(13)—C(14)	1·348 (15)	O(1)—N	1·235 (10)
C(14)—C(15)	1·378 (15)	O(2)—N	1·243 (11)
C(15)—C(16)	1·372 (14)	O(3)—N	1·232 (12)
O(1)—Ag—O(2)	50·5 (2)	C(13)—C(14)—C(15)	119·8 (10)
O(1)—Ag—O(4)	109·0 (3)	C(14)—C(15)—C(16)	119·5 (9)
O(1)—Ag—O(2*)	126·1 (3)	C(11)—C(16)—C(15)	121·5 (9)
O(1)—Ag—O(3*)	140·6 (3)	P—C(21)—C(22)	118·0 (7)
O(2)—Ag—O(4)	100·4 (2)	P—C(21)—C(26)	121·7 (7)
O(2)—Ag—O(2*)	120·8 (2)	C(22)—C(21)—C(26)	119·8 (8)
O(2)—Ag—O(3*)	95·5 (2)	C(21)—C(22)—C(23)	120·5 (9)
O(4)—Ag—O(2*)	124·0 (2)	C(22)—C(23)—C(24)	119·1 (10)
O(4)—Ag—O(3*)	94·7 (3)	C(23)—C(24)—C(25)	119·3 (9)
O(2*)—Ag—O(3*)	49·0 (3)	C(24)—C(25)—C(26)	120·9 (10)
Ag—O(4)—P	133·3 (4)	C(21)—C(26)—C(25)	120·3 (9)
O(4)—P—C(11)	108·6 (4)	P—C(31)—C(32)	119·2 (7)
O(4)—P—C(21)	111·5 (3)	P—C(31)—C(36)	123·1 (7)
O(4)—P—C(31)	113·1 (4)	C(32)—C(31)—C(36)	117·6 (8)
C(11)—P—C(21)	108·8 (4)	C(31)—C(32)—C(33)	120·4 (10)
C(11)—P—C(31)	107·2 (4)	C(32)—C(33)—C(34)	119·7 (12)
C(21)—P—C(31)	107·5 (4)	C(33)—C(34)—C(35)	119·9 (11)
P—C(11)—C(12)	123·3 (7)	C(34)—C(35)—C(36)	118·4 (11)
P—C(11)—C(16)	118·8 (6)	C(31)—C(36)—C(35)	123·8 (10)
C(12)—C(11)—C(16)	117·5 (8)	O(1)—N—O(2)	119·7 (8)
C(11)—C(12)—C(13)	121·2 (9)	O(1)—N—O(3)	121·1 (9)
C(12)—C(13)—C(14)	120·4 (10)	O(2)—N—O(3)	119·2 (8)

rections applied; 25 non-H positions from earlier investigation (Grossie, 1982) refined using *SFLSX* (Hall, Spadaccini, Olthof-Hazekamp & Dreissig, 1988); H-atom positions were calculated and additively constrained to each C atom, $B = 5{\cdot}0$ Å^2; final refinement including 226 parameters converged, $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0{\cdot}052$, $wR = 0{\cdot}059$, $S = 2{\cdot}32$, $w = 1/\sigma^2(|F_o|)$, max. shift/e.s.d. in final least-squares cycle $6{\cdot}48 \times 10^{-3}$, max. and min. peaks in final ΔF map 1·4 and $-1{\cdot}4$ e Å^{-3}, in vicinity of the Ag atom; R factor for all 4288 reflections is 0·131. Investigation used the *XTAL* system of crystallographic programs (Hall & Stewart, 1988; Grossie, 1988) on a Zenith 248 personal computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters and U_{eq} values are presented in Table 1,* while interatomic distances and valence angles are given in Table 2.

An *ORTEP* (Davenport, Hall & Dreissig, 1988; Johnson, 1970) drawing of the molecule is shown in Fig. 1.

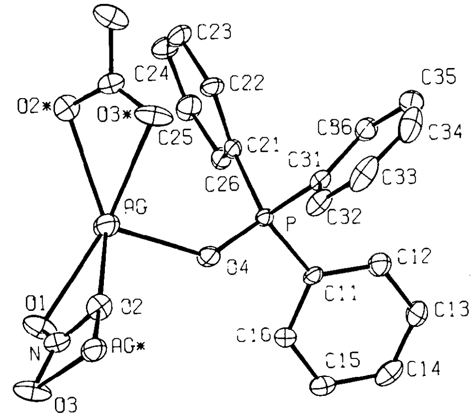

Fig. 1. *ORTEP* drawing of nitrato(triphenylphosphine oxide)-silver. O2* and O3* are nitrate O-atom positions in the asymmetric unit at $\frac{1}{2}-x, -y, \frac{1}{2}+z$ and Ag* is the Ag-atom position in the asymmetric unit at $\frac{3}{2}-x, -y, z-\frac{1}{2}$.

Related literature. With most divalent first-row transition-metal perchlorates the resultant product of reaction with a phosphine oxide is the formation of a complex in which the metal is bonded to four phosphine oxides (Cotton & Bannister, 1960; Bannister & Cotton, 1960*a*). If the metal nitrate is used, the complex formed has the metal atom coordinated by both the phosphine oxide and the nitrate (Bannister & Cotton, 1960*b*). The crystal structure of the

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* Lists of H-atom coordinates, anisotropic thermal parameters, least-squares planes, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52070 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

organic ligand, triphenylphosphine oxide, has been extensively investigated in its many crystal modifications, most recently by Spek (1987) and Baures & Silverton (1990).

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(η-1,5-Cyclooctadiene)iodomethyl(2,4-pentanedionato-*O*,*O*′)iridium(III)

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Abstract. $[\mathrm{Ir(C_5H_7O_2)(I)(CH_3)(C_8H_{12})}]$, $M_r = 541{\cdot}45$, monoclinic, $P2_1/c$, $a = 7{\cdot}879\ (7)$, $b = 16{\cdot}639\ (2)$, $c = 11{\cdot}856\ (2)$ Å, $\beta = 99{\cdot}36\ (4)°$, $V = 1533{\cdot}5\ (3)$ Å^3, $Z = 4$, $D_m = 2{\cdot}34\ (1)$, $D_x = 2{\cdot}344$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 112{\cdot}4$ cm^{-1}, $F(000) = 1012$, final $R = 0{\cdot}075$ for 2377 absorption-corrected reflections. This structure determination confirms the *trans* oxidative addition of $\mathrm{CH_3I}$ to [Ir(acac)(cod)]. The Ir—C(olefinic) distances range from 2·14 (2) to 2·19 (2) Å with an average of 2·17 (2) Å. Ir—C(methyl) = 2·17 (3), Ir—I = 2·833 (3) and both Ir—O distances are 2·05 (2) Å. Both the methyl C and I atoms are displaced towards the acac ring-atom plane [C—Ir—I = 156·6 (7)°] probably owing to steric restrictions imposed by H atoms on the olefinic C atoms.

Experimental. The complex was prepared from [Ir(acac)(cod)] and a tenfold molar excess $\mathrm{CH_3I}$ in acetone, vacuum distillation of the solvent and subsequent recrystallization by slow evaporation of a petroleum ether (b.p. 353–373 K) solution. Density of the yellow needle-shaped crystals was determined by the flotation method in thallous formate solution. Crystal size 0·11 × 0·12 × 0·2 mm, Enraf–Nonius CAD-4F diffractometer, graphite monochromator, Mo $K\alpha$ radiation, $\omega/2\theta$-scan technique, variable scan width where $\Delta\omega = (0{\cdot}58 + 0{\cdot}34\tan\theta)°$, scan rate 5·49° min^{-1} in ω, unit-cell parameters from least-squares refinement of 25 reflections with $6 < \theta < 20°$, measuring range $3 < \theta < 25°$, empirical absorption corrections (North, Phillips & Mathews, 1968), with minimum correction factor 0·65 and maximum 0·99, three standard reflections measured every 3600 s of X-ray exposure time varied −1·9%, all possible reflections with $\sin\theta/\lambda < 0{\cdot}60$ Å^{-1} in the index ranges $0 < h < 9$, $0 < k < 19$, $-14 < l < 14$. 2780 unique reflections of which 2377 observed reflections with $I > 2{\cdot}0\sigma(I)$ were used for all calculations (*XRAY*72, Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on F (163 variables). H atoms were not placed. Neutral-atom scattering factors (Cromer &

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