were refined anisotropically for a total of 262 parameters. $R = 0{\cdot}028$, $wR = 0{\cdot}035$, GOF = 1·2, where non-Poisson $w^{-1} = [\sigma^2(I) + (0{\cdot}04I)^2]/4F^2$; final $(\Delta/\sigma)_{\max} < 0{\cdot}01$, $\rho_{\max} = 0{\cdot}24\,(5)$ and $\rho_{\min} = -0{\cdot}21\,(5)$ e Å^{-3} on final difference map. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974) and programs used were those of Enraf–Nonius (1982) *SDP*.* Table 1 gives the atomic coordinates and Table 2 gives selected bond distances and angles. Figs. 1 and 2 show the complexes with the numbering schemes.

Related literature. The structures of three similar dimanganese complexes have been reported recently: one with a —C(Me)(OSiMe$_3$)— unit bridging the two cp rings (Cordes, Durham & Askew, 1989*a*), one with a —C(CH$_3$)(OH)— bridge (Cordes, Durham & Askew, 1989*b*) and one with a —C(O)CH═C(CH$_3$)— bridge (Cordes, Durham & Askew, 1989*b*). The structure of a related monomeric manganese complex has been reported by Berndt & Marsh (1963).

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References

BERNDT, A. F. & MARSH, R. E. (1963). *Acta Cryst.* **16**, 118–123.

CORDES, A. W., DURHAM, B. & ASKEW, E. (1989*a*). *Acta Cryst.* C**45**, 1231–1232.

CORDES, A. W., DURHAM, B. & ASKEW, E. (1989*b*). *Acta Cryst.* C**45**, 1229–1231.

Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KOLOBOVA, N. E., VALUEVA, Z. P., ANISIMOV, K. N. & SULEIMANOV, G. Z. (1978). *Bull. Acad. Sci. USSR Div. Chem. Sci.* **27**, 787–790.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

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* Tables of anisotropic temperature factors, H-atom positions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52089 (35 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 Acetonitriletris(triphenylphosphine)rhodium(I) Tetraphenylborate

BY WILLIAM CLEGG

Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, England

AND C. DAVID GARNER AND SUSAN HEYWORTH

Department of Chemistry, The University, Manchester M13 9PL, England

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Abstract. $[Rh(C_2H_3N)\{P(C_6H_5)_3\}_3][B(C_6H_5)_4]$, $M_r = 1250{\cdot}1$, triclinic, $P\overline{1}$, $a = 12{\cdot}095\,(1)$, $b = 15{\cdot}594\,(2)$, $c = 18{\cdot}482\,(2)$ Å, $\alpha = 105{\cdot}971\,(5)$, $\beta = 93{\cdot}856\,(8)$, $\gamma = 99{\cdot}580\,(6)°$, $V = 3281{\cdot}0$ Å^3, $Z = 2$, $D_x = 1{\cdot}265$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54184$ Å, $\mu = 3{\cdot}17$ mm^{-1}, $F(000) = 1300$, $T = 295$ K, $R = 0{\cdot}0402$ for 7864 unique observed reflections. The structure consists of discrete cations and anions. The Rh atom in the cation has essentially square-planar coordination, with the Rh—P bond *trans* to the acetonitrile ligand [2·262 (1) Å] significantly shorter than those *cis* to it [2·315 (1) and 2·361 (1) Å]. The Rh—N bond length is 2·045 (3) Å. There is a small distortion of the square-planar coordination towards tetrahedral, with deviations of atoms from the RhP$_3$N mean plane of: Rh −0·027 (1), P(1) −0·146 (1), P(2) 0·134 (1), P(3) −0·140 (1), N(4) 0·180 (4) Å, and with in-plane compression of P—Rh—N angles and expansion of P—Rh—P angles from ideal values of 90°. The acetonitrile ligand is essentially linearly coordinated [Rh—N—C = 171·8 (3)°].

Experimental. The compound was obtained in an attempt to prepare a salt of the $[Rh(PPh_3)_3(\text{pyridine})]^+$ cation; pyridine was replaced by acetonitrile during recrystallization from this solvent. Crystal size 0·13 × 0·23 × 0·27 mm, Stoe–Siemens diffractometer, unit-cell parameters from 2θ values

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} matrix.

	x	*y*	*z*	U_{eq}
Rh	1555·8 (2)	3200·8 (2)	2111·4 (1)	32·0 (1)
P(1)	2381·7 (7)	2267·1 (6)	2711·6 (5)	36·0 (3)
P(2)	686·2 (7)	3835·2 (6)	3113·6 (4)	34·0 (3)
P(3)	791·9 (6)	3885·0 (6)	1284·9 (4)	32·8 (3)
C(112)	3334 (2)	2681 (2)	4232 (1)	51 (1)
C(113)	3330	2648	4978	64 (2)
C(114)	2381	2186	5196	63 (2)
C(115)	1435	1758	4667	61 (2)
C(116)	1438	1791	3921	52 (2)
C(111)	2388	2253	3703	41 (1)
C(122)	1184 (3)	845 (2)	1498 (2)	75 (2)
C(123)	825	−64	1077	115 (3)
C(124)	1118	−750	1358	113 (3)
C(125)	1769	−527	2059	93 (3)
C(126)	2128	382	2480	64 (2)
C(121)	1836	1068	2199	44 (1)
C(132)	4493 (2)	3324 (1)	2783 (2)	52 (2)
C(133)	5657	3494	2758	62 (2)
C(134)	6229	2772	2564	68 (2)
C(135)	5637	1879	2396	71 (2)
C(136)	4473	1710	2421	58 (2)
C(131)	3901	2432	2614	41 (1)
C(212)	2728 (2)	4920 (2)	3799 (1)	53 (1)
C(213)	3586	5374	4389	71 (2)
C(214)	3489	5281	5113	72 (2)
C(215)	2535	4735	5246	67 (2)
C(216)	1677	4282	4656	51 (1)
C(211)	1773	4374	3932	40 (1)
C(222)	320 (2)	5664 (2)	3573 (1)	52 (1)
C(223)	−319	6331	3576	67 (2)
C(224)	−1363	6106	3132	67 (2)
C(225)	−1769	5213	2685	57 (2)
C(226)	−1129	4546	2682	46 (1)
C(221)	−85	4771	3126	39 (1)
C(232)	−954 (2)	3442 (1)	4043 (1)	53 (2)
C(233)	−1797	2872	4262	63 (2)
C(234)	−2104	1956	3850	65 (2)
C(235)	−1567	1609	3219	58 (2)
C(236)	−723	2179	3000	46 (1)
C(231)	−417	3095	3412	40 (1)
C(312)	1238 (2)	2866 (1)	−120 (1)	54 (2)
C(313)	1735	2717	−792	70 (2)
C(314)	2442	3433	−946	71 (2)
C(315)	2651	4298	−427	66 (2)
C(316)	2155	4447	245	54 (2)
C(311)	1448	3731	398	42 (1)
C(322)	−1259 (2)	2690 (2)	1097 (1)	50 (1)
C(323)	−2324	2229	726	66 (2)
C(324)	−2801	2475	123	68 (2)
C(325)	−2213	3182	−110	62 (2)
C(326)	−1149	3643	261	50 (1)
C(321)	−672	3397	865	37 (1)
C(332)	207 (1)	5643 (2)	1533 (1)	47 (1)
C(333)	488	6588	1821	69 (2)
C(334)	1556	7003	2210	74 (2)
C(335)	2343	6473	2312	60 (2)
C(336)	2062	5529	2024	44 (1)
C(331)	994	5114	1634	36 (1)
N(4)	2603 (3)	2775 (3)	1319 (2)	52 (1)
C(41)	3276 (4)	2624 (4)	933 (2)	64 (2)
C(42)	4169 (6)	2442 (7)	455 (4)	118 (4)
B	4055 (4)	1403 (3)	7316 (2)	45 (2)
C(512)	1930 (2)	1640 (2)	7135 (1)	55 (2)
C(513)	816	1380	6790	64 (2)
C(514)	517	633	6145	66 (2)
C(515)	1332	147	5845	65 (2)
C(516)	2446	408	6189	54 (2)
C(511)	2746	1154	6834	45 (1)
C(522)	4942 (2)	2940 (2)	8418 (1)	55 (2)
C(523)	5250	3884	8697	74 (2)
C(524)	5070	4423	8227	88 (3)
C(525)	4582	4019	7478	84 (3)
C(526)	4274	3074	7200	65 (2)
C(521)	4454	2535	7669	47 (1)
C(532)	3014 (2)	614 (2)	8275 (1)	63 (2)
C(533)	3028	214	8864	87 (3)
C(534)	4052	118	9197	92 (3)
C(535)	5062	421	8942	84 (2)
C(536)	5048	820	8353	69 (2)
C(531)	4024	916	8020	53 (1)
C(542)	5669 (3)	1493 (2)	6393 (2)	83 (2)
C(543)	6380	1095	5894	120 (4)
C(544)	6377	166	5735	130 (5)
C(545)	5663	−363	6076	110 (3)
C(546)	4952	35	6575	78 (2)
C(541)	4955	963	6734	58 (2)

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

Rh—P(1)	2·361 (1)	Rh—P(2)	2·262 (1)
Rh—P(3)	2·315 (1)	Rh—N(4)	2·045 (3)
N(4)—C(41)	1·130 (6)	C(41)—C(42)	1·456 (9)
P(1)—Rh—P(2)	95·0 (1)	P(1)—Rh—P(3)	167·6 (1)
P(2)—Rh—P(3)	96·4 (1)	P(1)—Rh—N(4)	82·3 (1)
P(2)—Rh—N(4)	169·6 (1)	P(3)—Rh—N(4)	87·3 (1)
Rh—N(4)—C(41)	171·8 (3)	N(4)—C(41)—C(42)	178·3 (5)

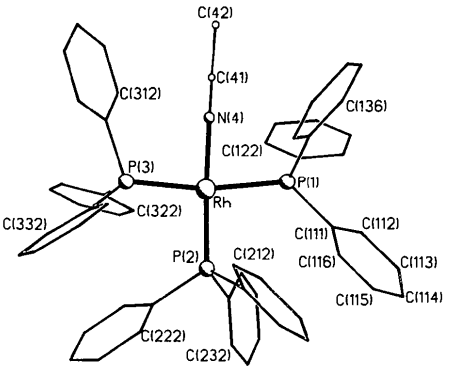

Fig. 1. Structure of the cation showing the numbering scheme. H atoms are omitted. The numbering of atoms of other phenyl rings follows the same pattern as the one shown.

of 32 reflections (30–40°) measured at ±*ω*. Data collection in *ω*/*θ* scan mode with on-line profile fitting (Clegg, 1981), $2\theta_{max}$ 115°, index ranges h $-13 \rightarrow 13$, k $-17 \rightarrow 17$, l $0 \rightarrow 20$; and h $0 \rightarrow 13$, k $-17 \rightarrow 17$, l $-20 \rightarrow 0$; no significant variation in intensities of three standard reflections, semi-empirical absorption corrections (transmission 0·427–0·614), 13 253 reflections measured, 8792 unique, 7864 with $F > 4\sigma_c(F)$ (σ_c from counting statistics only), $R_{int} = 0{\cdot}040$.

Structure solution by Patterson and difference syntheses, blocked-cascade least-squares refinement on F, weighting $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 11 - 33G + 71G^2 - 18H + 7H^2 + 11GH$ [$G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$ (Wang & Robertson, 1985)], anisotropic thermal parameters for all non-H atoms, rigid ideal hexagons (C—C = 1·395 Å) for phenyl groups, H atoms constrained [C—H 0·96 Å on ring-angle external bisectors, $U(\text{H}) = 1{\cdot}2U_{eq}(\text{C})$], extinction parameter $x = 1{\cdot}3\ (2) \times 10^{-6}$ [$F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$]. $R = 0{\cdot}0402$, $wR = 0{\cdot}0414$, $S = 1{\cdot}23$ for 623 parameters, mean $\Delta/\sigma = 0{\cdot}01$, max. $\Delta/\sigma = 0{\cdot}21$, $\Delta\rho_{max} = 0{\cdot}50$,

$\Delta\rho_{min} = -0.45$ 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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References

Bennett, M. A. & Longstaff, P. A. (1965). *Chem. Ind.* (*London*), p. 846.

Bennett, M. J. & Donaldson, P. B. (1977). *Inorg. Chem.* **16**, 655–660.

Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Osborn, J. A., Jardine, F. H., Young, J. F. & Wilkinson, G. (1966). *J. Chem. Soc. A*, pp. 1711–1732.

Pimblett, G., Garner, C. D. & Clegg, W. (1985). *J. Chem. Soc. Dalton Trans.* pp. 1977–1980.

Sheldrick, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Revision 5. Univ. of Göttingen, Federal Republic of Germany.

Wang, H. & Robertson, B. E. (1985). *Structure and Statistics in Crystallography*, edited by A. J. C. Wilson, pp. 125–136. New York: Adenine Press.

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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)

By David A. Grossie*

Department of Chemistry, Wright State University, Dayton, Ohio 45435, *USA*

and William H. Watson

FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, *USA*

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Abstract. $[AgNO_3(C_{18}H_{15})]$, $M_r = 448.17$, orthorhombic, $P2_12_12_1$, $a = 13.452$ (4), $b = 15.086$ (2), $c = 8.650$ (2) Å, $V = 1755.4$ (12) Å^3, $Z = 4$, $D_x = 1.696$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 12.33$ cm^{-1}, $F(000) = 896$, $T = 293$ K, final $R = 0.052$ 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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* Author to whom correspondence should be addressed.

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