3841 unique reflections, 2840 of which had $F \geq 4.0\sigma(F)$. The structure was solved via direct methods in space group $P\bar{1}$ and $\Delta\rho$ maps. It was refined (on F) using full-matrix least squares with anisotropic displacement parameters for all non-H atoms and for each molecule a common isotropic one for the H atoms, which were placed in geometrically calculated positions (C—H 0·96 Å). 309 parameters were refined. Weights $w = 1.0/[\sigma^2(F) + (0.004849F^2)]$ led to a featureless analysis of variance in terms of $\sin\theta$ and F_o. The refinement converged to $S = 1.16$, $R = 0.074$, $wR = 0.077$, $(\Delta/\sigma)_{max} = 0.018$ (no extinction correction). The largest peaks in final $\Delta\rho$ map were ± 3.7 (9) e Å^{-3}, near W. The poor quality of the weakly reflecting crystal could be a reason for the high R value. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were: *PARST* (Nardelli, 1983), *SHELXTL-Plus* (Sheldrick, 1987), *PCK*83 (Williams, 1984), *PLATON* (Spek, 1982), *MISSYM* (Le Page, 1987). The two independent molecules and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the unit-cell contents is in Fig. 2. Positional parameters and the

equivalent values of the anisotropic displacement parameters for the non-H atoms are given in Table 1.* Bond lengths and bond angles are given in Table 2.

Related literature. For the preparation of the compound see Naumann & Varbelow (1990).

References

Le Page, Y. (1987). *J. Appl. Cryst.* 20, 264–269.
Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.
Naumann, D. & Varbelow, H.-G. (1990). In the press.
Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet *R3m/V* crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
Spek, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. Sayre. Oxford: Clarendon Press.
Williams, D. E. (1984). *PCK*83. A crystal and molecular packing analysis program. Univ. of Louisville; QCPE Program No. 481. Dept. of Chemistry, Indiana Univ., Indiana, USA.

Structure of a Trinuclear Rhodium(I) Complex, [cis-Rh(CO)(PPh3)]3(μ_3-O)(μ_3-OCMe3)

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Abstract. μ_3-*tert*-Butoxy-1,2,3-tricarbonyl-μ_3-oxo-1,2,3-tris(triphenylphosphine)trirhodium, [Rh3(CO)3(O)(C4H9O){(C6H5)3P}3], $M_r = 1268.7$, monoclinic, $P2_1/n$, $a = 12.728$ (6), $b = 21.392$ (6), $c = 21.741$ (11) Å, $\beta = 100.29$ (4)°, $V = 5824$ (4) Å^3, $Z = 4$, $D_x = 1.45$ g cm^{-3}, $\lambda(\text{Mo }K\bar{\alpha}) = 0.710730$ Å, $\mu = 9.5$ cm^{-1}, $F(000) = 2560$, $T = 296$ K, $R(F) = 5.3$, $R(wF) = 6.6\%$ for 5466 data with $|F_o| > 4.0\sigma(|F_o|)$. The molecule consists of three *cis*-Rh(CO)(PPh3) units which are linked together symmetrically by a capping μ_3-oxo ligand (*trans* to the three CO ligands) and a capping μ_3-*tert*-butoxy ligand (*trans* to the three PPh3 ligands). Bond lengths are

Rh—PPh3 = 2·231 (3)–2·236 (3) Å, Rh—CO = 1·796 (13)–1·818 (12) Å, Rh—(μ_3-O) = 2·045 (5)–2·053 (6) Å and Rh—(μ_3-OCMe3) = 2·144 (6)–2·163 (6) Å; non-bonding Rh···Rh distances are 2·888 (2)–2·995 (2) Å. Each rhodium(I) center is in a slightly distorted square-planar coordination environment. The [Rh(CO)P]3(μ_3-O)(μ_3-OCC3) core of the molecule possesses approximate C_{3v} symmetry.

Experimental. The title compound, [cis-Rh(CO)(PPh3)]3(μ_3-O)(μ_3-OCMe3), was obtained, in low yield, as an unexpected product during attempts to synthesize *trans*-Rh(PPh3)2(CO)(OCMe3) [from

reaction of *trans*-Rh(PPh$_3$)$_2$(CO)Cl and NaOCMe$_3$ in toluene]. Efforts are currently underway to determine unambiguously the source of the μ_3-oxo ligand. Meanwhile we report, below, the results of an X-ray diffraction study on [*cis*-Rh(CO)(PPh$_3$)]$_3$(μ_3-O)(μ_3-OCMe$_3$). A burnt orange crystal of approximate size $0.15 \times 0.3 \times 0.6$ mm was selected from a small sample grown by vapor diffusion (pentane into a benzene solution). The crystal was sealed into a thin-walled glass capillary in an inert (Ar) atmosphere and was mounted and aligned accurately on a Syntex *P*2$_1$ automated four-circle diffractometer. Determination of unit-cell parameters (from the Mo $K\overline{\alpha}$ components of 25 reflections with $2\theta = 25$–$30°$), Laue symmetry (2/*m*) and the orientation matrix were performed as described previously (Churchill, Lashewycz & Rotella, 1977). Data were collected with Mo $K\alpha$ radiation for $2\theta = 4.0$–$45.0°$ $\{[(\sin\theta)/\lambda]_{max} = 0.539$ Å^{-1}, $0 \le h \le 13$, $0 \le k \le 23$, $-23 \le l \le 22\}$. Data were collected by the coupled θ(crystal)–2θ(counter) method at $3.0°$ min^{-1} over the symmetrical range $2\theta(K\alpha_1) - 1.0°$ to $2\theta(K\alpha_2) + 1.0°$. Three standard reflections were measured after every batch of 97 reflections. The systematic absences *h0l* for $h + l = 2n + 1$ and *0k0* for $k = 2n + 1$ uniquely define the centrosymmetric monoclinic space group *P*2$_1$/*n*. A total of 7816 data were corrected for Lorentz and polarization effects. Examination of ψ-scan data indicated that an absorption correction was not appropriate (variation in transmission being of the same magnitude, *i.e.* ±3%, as variations in the standards). Data were merged [$R(I) = 5.1$%] to a unique set of 6790 reflections. Any datum with *I*(net) < 0 was assigned an $|F_o|$ value of zero. Those 5466 data with $|F_o| > 4.0\sigma(|F_o|)$ were used in the subsequent refinement.

The positions of the three Rh and three P atoms were determined from an *E* map. Least-squares refinement of positional and isotropic thermal parameters of these six atoms led to $R(F) = 25.4$%. The remaining non-H atms were located from a series of difference Fourier syntheses. H atoms of the phenyl rings and the *tert*-butyl group were included using a riding model (with idealized trigonal and staggered tetrahedral geometry, respectively); assigned values were d(C—H) $= 0.96$ Å (Churchill, 1973) and $U = 0.08$ Å^2. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all 72 non-H atoms led to convergence (max. $\Delta/\sigma = 0.04$) with $R(F) = 5.3$%, $R(wF) = 6.6$% and GOF $= 1.46$ for 650 variables refined against those 5466 data with $|F_o| > 4.0\sigma(|F_o|)$. [$R(F) = 7.1$% and $R(wF) = 7.9$% for all 6790 data.] A final difference Fourier map showed $\Delta\rho$ from -0.54 to $+0.94$ e Å^{-3} and two higher peaks ($+1.41$ e Å^{-3} at -0.0156, 0.5439, 0.0163 and $+1.34$ e Å^{-3} at 0.0639, 0.5025, 0.0402) close to 0,

1/2, 0. Attempts to include these features as a solvent molecule were not successful. A listing of atomic coordinates is given in Table 1.*

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

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

	x	y	z	$U_{eq}(\text{Å}^2)$
Rh(1)	0.13159 (6)	0.26751 (3)	0.89679 (3)	0.0367 (3)
Rh(2)	0.11262 (6)	0.19131 (3)	0.78570 (3)	0.0352 (3)
Rh(3)	-0.08114 (5)	0.25138 (3)	0.82046 (3)	0.0344 (3)
P(1)	0.1867 (2)	0.2352 (1)	0.9948 (1)	0.0378 (9)
P(2)	0.1572 (2)	0.0903 (1)	0.7843 (1)	0.0400 (9)
P(3)	-0.2216 (2)	0.2082 (1)	0.8528 (1)	0.0413 (9)
O(1)	0.0387 (4)	0.1931 (3)	0.8622 (3)	0.0323 (20)
O(2)	0.0672 (4)	0.2861 (3)	0.7996 (3)	0.0353 (21)
O(3)	0.2551 (8)	0.3831 (4)	0.9332 (5)	0.1025 (44)
O(4)	0.2271 (8)	0.2100 (4)	0.6804 (5)	0.0975 (43)
O(5)	-0.2350 (6)	0.3348 (4)	0.7439 (4)	0.0873 (37)
C(1)	0.0942 (8)	0.2522 (5)	1.0478 (5)	0.0450 (37)
C(2)	0.0060 (9)	0.2891 (6)	1.0256 (6)	0.0741 (52)
C(3)	-0.0630 (11)	0.3033 (7)	1.0680 (10)	0.1120 (85)
C(4)	-0.0436 (15)	0.2823 (9)	1.1287 (9)	0.1149 (91)
C(5)	0.0393 (13)	0.2465 (7)	1.1472 (7)	0.0881 (65)
C(6)	0.1085 (10)	0.2302 (5)	1.1081 (6)	0.0635 (47)
C(7)	0.2162 (7)	0.1516 (4)	1.0086 (4)	0.0374 (32)
C(8)	0.2897 (8)	0.1314 (5)	1.0602 (5)	0.0526 (40)
C(9)	0.3065 (9)	0.0690 (5)	1.0716 (5)	0.0570 (43)
C(10)	0.2510 (9)	0.0262 (6)	1.0321 (5)	0.0571 (44)
C(11)	0.1787 (8)	0.0455 (5)	0.9812 (5)	0.0454 (37)
C(12)	0.1619 (7)	0.1080 (4)	0.9691 (4)	0.0401 (35)
C(13)	0.3124 (8)	0.2713 (5)	1.0327 (4)	0.0432 (35)
C(14)	0.3995 (9)	0.2651 (5)	1.0020 (5)	0.0628 (45)
C(15)	0.4950 (8)	0.2912 (6)	1.0265 (6)	0.0712 (52)
C(16)	0.5076 (12)	0.3234 (7)	1.0793 (8)	0.0978 (68)
C(17)	0.4230 (12)	0.3307 (8)	1.1113 (7)	0.1075 (72)
C(18)	0.3274 (10)	0.3041 (6)	1.0869 (5)	0.0746 (52)
C(19)	0.0607 (7)	0.0329 (4)	0.8001 (4)	0.0394 (34)
C(20)	0.0624 (9)	-0.0294 (5)	0.7837 (5)	0.0613 (46)
C(21)	-0.0110 (11)	-0.0714 (5)	0.7972 (6)	0.0738 (53)
C(22)	-0.0869 (10)	-0.0518 (6)	0.8297 (6)	0.0766 (57)
C(23)	-0.0921 (9)	0.0087 (6)	0.8473 (6)	0.0756 (55)
C(24)	-0.0185 (8)	0.0521 (5)	0.8300 (5)	0.0538 (41)
C(25)	0.1911 (11)	0.0622 (5)	0.7120 (5)	0.0589 (46)
C(26)	0.1108 (13)	0.0421 (6)	0.6651 (6)	0.0803 (58)
C(27)	0.1399 (20)	-0.0243 (8)	0.6062 (7)	0.1265 (102)
C(28)	0.2476 (24)	-0.0303 (8)	0.5974 (10)	0.1398 (130)
C(29)	0.3244 (17)	-0.0507 (8)	0.6459 (8)	0.1114 (88)
C(30)	0.2973 (12)	-0.0656 (6)	0.7023 (6)	0.0789 (58)
C(31)	0.2790 (7)	-0.0718 (5)	0.8408 (4)	0.0414 (35)
C(32)	-0.3362 (8)	0.1211 (5)	0.8733 (5)	0.0532 (41)
C(33)	0.4286 (9)	0.1083 (6)	0.9155 (6)	0.0644 (48)
C(34)	0.4629 (9)	0.0472 (6)	0.9283 (6)	0.0641 (48)
C(35)	0.4068 (9)	-0.0007 (6)	0.8968 (6)	0.0667 (49)
C(36)	0.3130 (9)	0.0105 (5)	0.8528 (5)	0.0567 (42)
C(37)	-0.2051 (7)	0.1783 (4)	0.9334 (4)	0.0415 (35)
C(38)	-0.1082 (8)	0.1493 (5)	0.9594 (5)	0.0477 (38)
C(39)	-0.0949 (9)	0.1253 (5)	1.0180 (5)	0.0596 (44)
C(40)	-0.1740 (10)	0.1296 (6)	1.0524 (5)	0.0634 (48)
C(41)	-0.2700 (11)	0.1568 (6)	1.0278 (5)	0.0728 (53)
C(42)	-0.2848 (9)	0.1812 (6)	0.9685 (5)	0.0628 (46)
C(43)	-0.2785 (7)	0.1423 (5)	0.8035 (5)	0.0443 (36)

Table 1 (cont.)

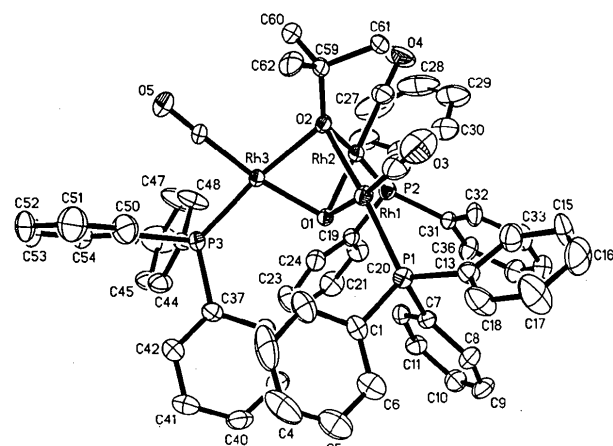|	x	y	z	$U_{eq}(Å^2)$
C(44)	−0·3447 (9)	0·0985 (5)	0·8250 (5)	0·0599 (43)
C(45)	−0·3881 (10)	0·0511 (6)	0·7869 (6)	0·0774 (54)
C(46)	−0·3674 (14)	0·0473 (8)	0·7277 (7)	0·1179 (80)
C(47)	−0·2986 (15)	0·0894 (8)	0·7071 (7)	0·1242 (83)
C(48)	−0·2550 (11)	0·1378 (6)	0·7452 (6)	0·0774 (54)
C(49)	−0·3350 (8)	0·2622 (6)	0·8534 (5)	0·0552 (43)
C(50)	−0·3185 (11)	0·3178 (6)	0·8823 (6)	0·0750 (54)
C(51)	−0·4001 (14)	0·3575 (7)	0·8833 (8)	0·1055 (78)
C(52)	−0·4994 (14)	0·3441 (10)	0·8583 (9)	0·1103 (87)
C(53)	−0·5183 (11)	0·2885 (9)	0·8304 (8)	0·0941 (70)
C(54)	−0·4399 (9)	0·2474 (6)	0·8269 (6)	0·0680 (44)
C(59)	0·0815 (7)	0·3412 (4)	0·7631 (5)	0·0474 (38)
C(60)	0·0271 (8)	0·3311 (5)	0·6955 (5)	0·0601 (44)
C(61)	0·2018 (7)	0·3507 (5)	0·7637 (5)	0·0624 (44)
C(62)	0·0377 (9)	0·3979 (4)	0·7915 (6)	0·0636 (46)
C(63)	0·2072 (10)	0·3384 (5)	0·9199 (6)	0·0650 (47)
C(64)	0·1816 (9)	0·2015 (5)	0·7211 (6)	0·0578 (44)
C(65)	−0·1762 (7)	0·3028 (5)	0·7745 (5)	0·0496 (38)

Fig. 1. *ORTEP*II view of [cis-Rh(CO)(PPh₃)]₃(μ_3-O)(μ_3-OCMe₃). Note that the Rh—C—O systems are labeled Rh(1)—C(63)—O(3), Rh(2)—C(64)—O(4) and Rh(3)—C(65)—O(5).

Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s*

Rh(1)—Rh(2)	2·888 (2)		Rh(1)—Rh(3)	2·932 (2)
Rh(1)—P(1)	2·231 (3)		Rh(1)—O(1)	2·045 (5)
Rh(1)—O(2)	2·163 (6)		Rh(1)—C(63)	1·818 (12)
Rh(2)—Rh(3)	2·995 (2)		Rh(2)—P(2)	2·236 (3)
Rh(2)—O(1)	2·053 (6)		Rh(2)—O(2)	2·144 (6)
Rh(2)—C(64)	1·796 (13)		Rh(3)—P(3)	2·234 (3)
Rh(3)—O(1)	2·052 (5)		Rh(3)—O(2)	2·152 (6)
Rh(3)—C(65)	1·800 (10)			
P(1)—C(1)	1·825 (11)		P(1)—C(7)	1·840 (9)
P(1)—C(13)	1·834 (9)		P(2)—C(19)	1·812 (10)
P(2)—C(25)	1·806 (12)		P(2)—C(31)	1·841 (9)
P(3)—C(37)	1·844 (10)		P(3)—C(43)	1·839 (10)
P(3)—C(49)	1·851 (11)		O(2)—C(59)	1·450 (12)
O(3)—C(63)	1·144 (15)		O(4)—C(64)	1·157 (16)
O(5)—C(65)	1·139 (13)			

Rh(2)—Rh(1)—Rh(3)	61·9 (1)		Rh(2)—Rh(1)—P(1)	126·1 (1)
Rh(3)—Rh(1)—P(1)	127·2 (1)		Rh(2)—Rh(1)—O(1)	45·3 (2)
Rh(3)—Rh(1)—O(1)	44·4 (1)		P(1)—Rh(1)—O(1)	99·9 (2)
Rh(2)—Rh(1)—O(2)	47·6 (2)		Rh(3)—Rh(1)—O(2)	47·0 (2)
P(1)—Rh(1)—O(2)	171·9 (2)		O(1)—Rh(1)—O(2)	72·0 (2)
Rh(2)—Rh(1)—C(63)	131·5 (4)		Rh(3)—Rh(1)—C(63)	130·1 (4)
P(1)—Rh(1)—C(63)	86·2 (4)		O(1)—Rh(1)—C(63)	173·7 (4)
O(2)—Rh(1)—C(63)	101·9 (4)		Rh(1)—Rh(2)—Rh(3)	59·8 (1)
Rh(1)—Rh(2)—P(2)	125·0 (1)		Rh(3)—Rh(2)—P(2)	129·9 (1)
Rh(1)—Rh(2)—O(1)	45·1 (1)		Rh(3)—Rh(2)—O(1)	43·1 (1)
P(2)—Rh(2)—O(1)	100·6 (2)		Rh(1)—Rh(2)—O(2)	48·2 (2)
Rh(3)—Rh(2)—O(2)	45·9 (2)		P(2)—Rh(2)—O(2)	172·4 (2)
O(1)—Rh(2)—O(2)	72·2 (2)		Rh(1)—Rh(2)—C(64)	127·3 (3)
Rh(3)—Rh(2)—C(64)	133·2 (3)		P(2)—Rh(2)—C(64)	86·9 (3)
O(1)—Rh(2)—C(64)	171·7 (4)		O(2)—Rh(2)—C(64)	100·2 (4)
Rh(1)—Rh(3)—Rh(2)	58·3 (1)		Rh(1)—Rh(3)—P(3)	125·5 (1)
Rh(2)—Rh(3)—P(3)	130·0 (1)		Rh(1)—Rh(3)—O(1)	44·2 (1)
Rh(2)—Rh(3)—O(1)	43·2 (2)		P(3)—Rh(3)—O(1)	100·5 (2)
Rh(1)—Rh(3)—O(2)	47·3 (1)		Rh(2)—Rh(3)—O(2)	45·7 (2)
P(3)—Rh(3)—O(2)	172·2 (2)		O(1)—Rh(3)—O(2)	72·1 (2)
Rh(1)—Rh(3)—C(65)	134·7 (3)		Rh(2)—Rh(3)—C(65)	128·6 (4)
P(3)—Rh(3)—C(65)	86·0 (3)		O(1)—Rh(3)—C(65)	171·7 (4)
O(2)—Rh(3)—C(65)	101·6 (4)			
Rh(1)—P(1)—C(1)	114·4 (3)		Rh(1)—P(1)—C(7)	118·4 (3)
C(1)—P(1)—C(7)	103·1 (5)		Rh(1)—P(1)—C(13)	113·5 (3)
C(1)—P(1)—C(13)	104·0 (4)		C(7)—P(1)—C(13)	101·5 (4)
Rh(2)—P(2)—C(19)	118·0 (3)		Rh(2)—P(2)—C(25)	115·8 (4)
C(19)—P(2)—C(25)	102·4 (5)		Rh(2)—P(2)—C(31)	112·6 (3)
C(19)—P(2)—C(31)	104·3 (4)		C(25)—P(2)—C(31)	101·9 (5)
Rh(3)—P(3)—C(37)	118·8 (3)		Rh(3)—P(3)—C(43)	112·8 (3)
C(37)—P(3)—C(43)	104·7 (4)		Rh(3)—P(3)—C(49)	114·4 (4)
C(37)—P(3)—C(49)	99·6 (5)		C(43)—P(3)—C(49)	104·8 (5)
Rh(1)—O(1)—Rh(2)	89·6 (2)		Rh(1)—O(1)—Rh(3)	91·4 (2)
Rh(2)—O(1)—Rh(3)	93·7 (2)		Rh(1)—O(2)—Rh(2)	84·2 (2)
Rh(1)—O(2)—Rh(3)	85·6 (2)		Rh(2)—O(2)—Rh(3)	88·4 (2)
Rh(1)—O(2)—C(59)	128·4 (5)		Rh(2)—O(2)—C(59)	128·9 (6)
Rh(3)—O(2)—C(59)	126·6 (5)		Rh(1)—C(63)—O(3)	178·6 (12)
Rh(2)—C(64)—O(4)	177·6 (10)		Rh(3)—C(65)—O(5)	178·0 (10)

The analytical form of the appropriate neutral-atom scattering factors was corrected for both the real (f') and imaginary (f'') components of anomalous dispersion using the values compiled in *International Tables for X-ray Crystallography*, (1974, Vol. IV, pp. 99–101, 149–150). The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = (\sigma|F_o|)^2 + (0\cdot001|F_o|^2)$. An empirical correction for secondary extinction was also applied to the data in the form $|F_{o,corr}| = |F_{o,uncorr}|[1\cdot0 + 0\cdot002\chi|F_{o,uncorr}|^2/(\sin2\theta)]^{-1/4}$; the value obtained for χ was 0·00007 (3).
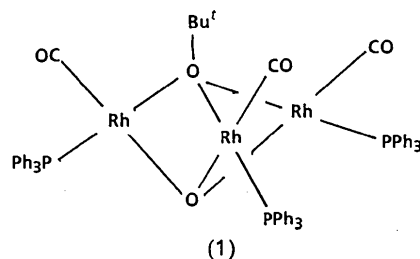
Computer programs used were the UCI-modified version of the *UCLA Crystallographic Package* (1984) and the Nicotet XRD *SHELXTL-Plus* program set (Sheldrick, 1987). The molecular structure and atomic labeling scheme are depicted in Fig. 1. Bond lengths and angles are compiled in Table 2.

The crystal consists of discrete, ordered molecular units of [cis-Rh(CO)(PPh₃)]₃(μ_3-O)(μ-OCMe₃) which are mutually separated at van der Waals distances; there are no abnormal intermolecular contacts.

Related literature. The overall geometry of [cis-Rh(CO)(PPh₃)]₃(μ_3-O)(μ_3-OCMe₃) may be represented by (1).

(1)

To the best of our knowledge, such a structure is unique in rhodium(I) chemistry. We have previously reported the structure of a mononuclear rhodium(I) phenoxide complex, *trans*-Rh(PPh₃)₂(CO)(OC₆H₅) (Bernard, Churchill, Janik & Atwood, 1990) in which Rh—OC₆H₅ = 2·044 (2) Å. However, the overall core structure of (I) is perhaps most similar to that of Rh₃(μ-Cl)₃[μ-H₃CN(PF₂)₂]₃ (Mague & Johnson, 1990; Mague, Johnson & Lloyd, 1989) in which three non-bonded rhodium(I) centers are held in a triangular arrangement at distances of 3·0755 (4)–3·1180 (4) Å (with molecular C_{3v} symmetry) *via* sets of bridging chloro and bis(difluorophosphino)-methylamine ligands. It should be noted that the non-bonding Rh⋯Rh distances of 2·888 (2)–2·995 (2) Å in the present complex are not dramatically longer than the Rh—Rh bond lengths of

2·701 (8)–2·796 (8) Å found in Rh₄(CO)₉(μ-CO)₃ (Wei, 1969).

References

BERNARD, K. A., CHURCHILL, M. R., JANIK, T. S. & ATWOOD, J. D. (1990). *Organometallics*, **9**, 12–16.

CHURCHILL, M. R. (1973). *Inorg. Chem.* **12**, 1213–1214.

CHURCHILL, M. R., LASHEWYCZ, R. A. & ROTELLA, F. J. (1977). *Inorg. Chem.* **16**, 265–271.

MAGUE, J. T. & JOHNSON, M. P. (1990). *Acta Cryst.* C46, 129–131.

MAGUE, J. T., JOHNSON, M. P. & LLOYD, C. L. (1989). *J. Am. Chem. Soc.* **111**, 5012–5013.

SHELDRICK, G. M. (1987). *SHELXTL-Plus.* Release 3.4 for Nicolet *R3m/V* crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

UCLA Crystallographic Package (1984). Univ. of California, Los Angeles, USA.

WEI, C. H. (1969). *Inorg. Chem.* **8**, 2384–2397.

Structure of Triaqua[1,2-benzenedicarboxylato(2 −)](2,2′-bipyridine)nickel(II) Monohydrate

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Abstract. [Ni(C₈H₄O₄)(C₁₀H₈N₂)(H₂O)₃].H₂O, M_r = 451·06, orthorhombic, $P2_12_12_1$, $a = 24·487 (13)$, $b = 22·043 (8)$, $c = 7·510 (2)$ Å, $V = 4054 (3)$ Å³, $Z = 8$, $D_x = 1·478$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 10·0$ cm⁻¹, $F(000) = 1872$, room temperature, $R = 0·058$ for 3987 independent reflections having $I > 2\sigma(I)$. In the asymmetric part of the unit cell there are two discrete units nearly related by a center of symmetry. Both Ni atoms are in a distorted octahedral environment. The 1,2-benzenetetracarboxylate(2 −) anions act as monodentate ligands.

Experimental. Blue, needle-like (0·18 × 0·09 × 0·08 mm) crystals suitable for X-ray determination were obtained from dilute aqueous solutions containing equimolar amounts of Ni(NO₃)₂, 2,2′-bipyridine and sodium phthalate. 18 reflections with $12·4 < \theta <$

19·6° were used for measuring lattice parameters. Data were collected on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan, intensity measurement to $2\theta_{max} = 42°$ ($0 \le h \le 34$, $0 \le k \le 30$, $0 \le l \le 10$). Two standard reflections, no significant intensity variation, 4888 reflections were measured, 3987 observed [$I > 2\sigma(I)$] reflections were used for refinements. Data were corrected for Lorentz and polarization, not for absorption.

The positions of the Ni atoms were found by the Patterson method and the rest of the non-H atoms were located by alternate cycles of difference Fourier maps and isotropic least-squares refinement (on F). After anisotropic refinement was carried out in two blocks for non-H atoms, positions of H atoms were calculated and included in the model at fixed posi-