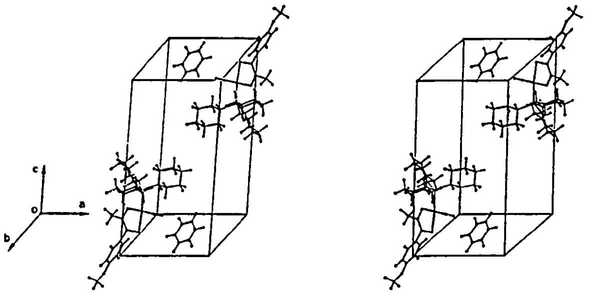

Fig. 2. Stereoscopic view of the molecular packing.

cone angles and bonding characteristics. The present substitution pattern and geometrical parameters compare well with those of carbonyl(thioacetylacetonato)(triphenylphosphine)rhodium(I) and other complexes (Botha, Basson & Leipoldt, 1987), carbonyl(2-pyridinethiolato *N*-oxide-*κO*,*κS*)(triphenylphosphine)rhodium(I) (Basson, Leipoldt, Roodt & Preston, 1991) and [1,1-diphenylhydrazido(2−)-N^2]bis(*N*-methylbenzothiohydroxamato)oxomolybdenum(VI) (Fitzroy, Fallon, Murray, Frederiksen & Tiekink, 1990).

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Structure of Carbonyl(*N*-hydroxy-*N*-nitrosobenzenaminato-*O*,*O'*)(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhodium(I)

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Abstract. $[Rh(C_6H_5N_2O_2)(CO)(C_5H_9O_3P)]$, $M_r = 416.1$, monoclinic, $P2_1/c$, $a = 11.990\,(1)$, $b = 6.195\,(1)$, $c = 20.906\,(3)$ Å, $\beta = 92.857\,(10)°$, $V = 1550.8\,(4)$ Å^3, $Z = 4$, $D_m = 1.78\,(1)$, $D_x = 1.78$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 12.12$ cm^{-1}, $T = 295$ K, $F(000) = 832$, final $R = 0.0525$ for 2909 observed reflections. The ligand atoms are arranged in a distorted square-planar array around the Rh atom. The cyclic phosphite is situated *trans* to the hydroxo O atom. The least-squares plane containing the ring atoms of the bidentate ligand forms a dihedral angle of 5.7 (4)° with the least-squares plane of the coordinated atoms. Bond distances are Rh—O(nitroso) = 2.026 (5), Rh—O(hydroxo) = 2.059 (4), Rh—P = 2.156 (2) and Rh—C = 1.772 (9) Å.

Experimental. The title complex was prepared by mixing equimolar amounts of the cyclic phosphite and $[Rh(cupf)(CO)_2]$ (cupf = cupferron anion, $C_6H_5N_2O_2^-$) (Goswami & Singh, 1980) in acetone, evaporation of the solvent and recrystallization from 1:1 benzene/*n*-propanol at room temperature to yield yellow needles. The density was determined by flotation in NaI solution. A crystal with dimensions 0.075 × 0.125 × 0.5 mm was used for data collection on an Enraf–Nonius CAD-4F diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The $\omega/2\theta$-scan technique was used with variable scan width $\Delta\omega = (0.59 + 0.34\tan\theta)°$, a scan speed maximum of 4.12° min^{-1} in ω and a maximum scan time of 60 s per reflection. The unit-cell parameters were determined with a least-squares fit of 25 reflections with $6 < \theta < 17°$. All possible reflections with $0.07 < \sin\theta/\lambda < 0.70$ Å^{-1} in the index ranges $0 \le h \le 16$, $0 \le k \le 8$, $-29 \le l \le 29$ gave 3940 unique reflections of which 2909 were considered as observed with $I > 3.0\sigma(I)$. No equivalent reflections were measured. An

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Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Rh	2910.0 (1)	4480.3 (1)	5924.0 (2)	53.9 (1)
P	4282 (2)	6640 (3)	6153.6 (8)	49.9 (4)
O(1)	2596 (7)	6617 (13)	4681 (3)	134 (2)
O(2)	1727 (4)	2084 (8)	5808 (2)	66 (1)
O(3)	2945 (4)	3075 (8)	6800 (2)	65 (1)
O(4)	4661 (5)	8264 (9)	5627 (2)	81 (1)
O(5)	4145 (4)	8157 (9)	6756 (2)	75 (1)
O(6)	5404 (4)	5425 (7)	6354 (3)	70 (1)
N(1)	2242 (5)	1448 (10)	6863 (3)	65 (1)
N(2)	1673 (4)	1012 (9)	6355 (3)	54 (1)
C(1)	2765 (8)	5722 (16)	5161 (4)	93 (3)
C(2)	5632 (7)	9603 (13)	5799 (3)	78 (2)
C(3)	5098 (6)	9561 (12)	6926 (3)	66 (2)
C(4)	6364 (6)	6759 (11)	6546 (4)	67 (2)
C(5)	6026 (6)	9161 (9)	6488 (3)	51 (1)
C(6)	7048 (7)	10545 (12)	6686 (4)	72 (2)
C(11)	925 (6)	−823 (11)	6354 (3)	58 (2)
C(12)	159 (8)	−1024 (16)	5855 (4)	96 (3)
C(13)	−538 (9)	−2832 (19)	5835 (5)	118 (3)
C(14)	−471 (8)	−4296 (16)	6318 (5)	95 (3)
C(15)	291 (7)	−4059 (14)	6819 (5)	86 (2)
C(16)	1012 (7)	−2292 (13)	6846 (4)	73 (2)

Table 2. *Selected interatomic bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Rh—P	2.156 (2)	Rh—O(2)	2.059 (4)
Rh—O(3)	2.026 (5)	Rh—C(1)	1.772 (9)
P—O(4)	1.574 (5)	P—O(5)	1.587 (5)
P—O(6)	1.579 (5)	O(2)—N(2)	1.325 (6)
O(3)—N(1)	1.325 (7)	N(2)—N(1)	1.264 (7)
N(2)—C(11)	1.448 (8)	C(1)—O(1)	1.155 (9)
O(4)—C(2)	1.460 (8)	O(5)—C(3)	1.466 (8)
O(6)—C(4)	1.458 (7)	C(2)—C(5)	1.516 (8)
C(3)—C(5)	1.497 (10)	C(4)—C(5)	1.546 (9)
C(5)—C(6)	1.535 (8)		

P—Rh—O(2)	170.8 (1)	P—Rh—O(3)	94.8 (1)
O(2)—Rh—O(3)	77.3 (2)	P—Rh—C(1)	88.3 (2)
O(2)—Rh—C(1)	99.9 (3)	O(3)—Rh—C(1)	175.6 (3)
Rh—P—O(4)	119.0 (2)	Rh—P—O(5)	115.8 (2)
O(4)—P—O(5)	102.8 (3)	Rh—P—O(6)	113.2 (2)
O(4)—P—O(6)	102.6 (3)	O(5)—P—O(6)	101.1 (3)
Rh—O(2)—N(2)	108.9 (3)	Rh—O(3)—N(1)	115.6 (4)
O(2)—N(2)—N(1)	124.7 (5)	O(2)—N(2)—C(11)	116.7 (5)
N(1)—N(2)—C(11)	118.5 (6)	O(3)—N(1)—N(2)	113.5 (5)
Rh—C(1)—O(1)	174.4 (10)	P—O(4)—C(2)	116.4 (4)
P—O(5)—C(3)	115.7 (4)	P—O(6)—C(4)	117.0 (4)
O(4)—C(2)—C(5)	109.8 (5)	O(5)—C(3)—C(5)	110.4 (5)
O(6)—C(4)—C(5)	108.9 (5)	C(2)—C(5)—C(3)	110.2 (6)
C(2)—C(5)—C(4)	108.5 (6)	C(3)—C(5)—C(4)	108.1 (6)
C(2)—C(5)—C(6)	111.2 (5)	C(3)—C(5)—C(6)	110.5 (6)
C(4)—C(5)—C(6)	108.3 (6)		

empirical absorption correction (North, Phillips & Mathews, 1968) was made with a minimum correction factor of 0.95 and a maximum of 0.99. The mean intensity of three standard reflections, measured every 3600 s of X-ray exposure, varied from the initial value by −1.5%. The intensity data were corrected for this effect. The structure was solved by the heavy-atom method using *SHELXS*86 (Sheldrick, 1990) and subjected to full-matrix least-squares refinement on F with 203 positional and anisotropic displacement parameters using *SHELX*76 (Sheldrick, 1976). The H-atom positions were calculated riding on the adjacent C atoms assuming C—H = 1.08 Å and refined with an overall isotropic temperature factor. Neutral-atom scattering factors (Cromer & Mann, 1968) and anomalous-dispersion corrections for Rh were taken from *International Tables for X-ray Crystallography* (1962, Vol. III, p. 216). Final $R = 0.0525$, $wR = 0.0541$, unit weights. S was not calculated; $(\Delta\rho)_{max} = 1.4$ and $(\Delta\rho)_{min} = -0.92$ e Å^{-3}; positional $(\Delta/\sigma)_{max} = 0.016$. Final atomic coordinates* are given in Table 1 and main geometrical parameters in Table 2. A perspective view (Johnson, 1976) of the molecule with atomic labels is shown in Fig. 1 and a stereoscopic view of the molecules in the unit cell in Fig. 2.

Related literature. Phosphines in general substitute only one of the CO groups *trans* to the ligand atom with the largest *trans* influence in [$Rh(LL')(CO)_2$] complexes (LL' = uninegative bidentate ligands having S, N or O donor atoms). A *trans* influence

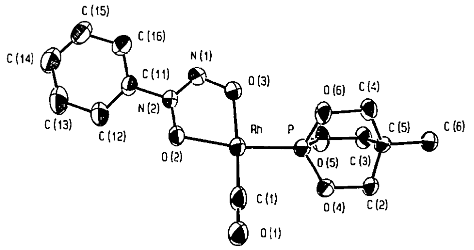

Fig. 1. Perspective view of the molecule with atom labels (H atoms omitted for clarity).

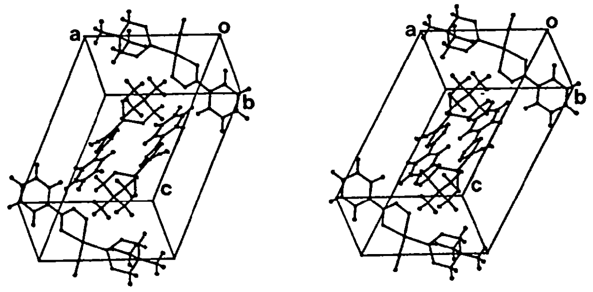

Fig. 2. Stereoscopic view of the molecules in the unit cell.

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* Lists of least-squares planes, anisotropic displacement parameters, structure factors, complete bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54444 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0217]

order of S > N > O, as measured by Rh—P distances, was thus established (Botha, Basson & Leipoldt, 1987). For bidentate ligands having the same donor atoms, like β-diketones, it was also found that the donor atom nearest to the most electronegative substituent has the largest *trans* influence. Exceptions to this phenomenon have been found in structure determinations, such as (1,1,1-trifluoro-5,5,5-trimethylpentanedionato)(carbonyl)(triphenylphosphine)-rhodium(I) (Leipoldt, Basson & Potgieter, 1986), and could be ascribed to steric intervention of bulky groups on the bidentate ligand preventing the formation of the expected isomer. The structure of [Rh(cupf)(CO)(PPh$_3$)] (Basson, Leipoldt, Roodt & Venter, 1986) also showed the normal expected isomer with P *trans* to the nitroso O atom. The present complex with a much less bulky but stronger π-bonding P ligand [cone angle = 101° compared to 145° of PPh$_3$ (Tolman, 1977)] unexpectedly gave the other isomer compared to [Rh(cupf)(CO)(PPh$_3$)]. This result is still under investigation.

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Structure of ^{t}BuCO-Gly-Glyψ[CH$_2$—N$^+$H$_2$]NHEt.BPh$_4^-$

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Abstract. *N*-(*tert*-Butylcarbonylglycylaminoethyl)-*N*-(ethyl)ammonium tetraphenylborate, $C_{11}H_{24}N_3O_2^+.C_{24}H_{20}B^-$, $M_r = 549.57$, triclinic, $P\bar{1}$, $a = 11.567$ (2), $b = 11.922$ (2), $c = 14.484$ (3) Å, $\alpha = 70.99$ (2), $\beta = 74.83$ (2), $\gamma = 59.33$ (1)°, $V = 1613.1$ Å^3, $Z = 2$, $D_x = 1.13$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 4.69$ cm^{-1}, $\mu R_{\max} \ll 1$, $F(000) = 592$, $T = 293$ K, $R = 0.058$ for 3491 observed reflections. This pseudopeptide is folded by a short N$^+$—H···O=C hydrogen bond (N3···O1 = 2.81 Å) which closes a ten-membered ring. This results in a β-turn structure that can be classified as type II on the basis of the conformational angles for the N-terminal glycine. The conformational angles φ_1, ψ_1, φ_2 and ψ_2 are −53.4 (6), 139.7 (4), 91.5 (5) and −62.6 (6)° respectively.

Experimental. Crystal size 0.20 × 0.10 × 0.18 mm, X-ray data were collected at room temperature on Enraf–Nonius CAD-4 automatic diffractometer, with Cu $K\alpha$ radiation up to θ value of 70° ($\omega/2\theta$-scanning mode). Cell parameters refined by least squares on the basis of 25 independent θ values in the range 20–30°. 6108 reflections measured ($h = -14$ to 14, $k = -14$ to 14, $l = 0$ to 17), 3491 with $F_o > 3\sigma(F_o)$ were used for all calculations. Three standards (212, 022, 002) measured every 2 h showed no deviations greater than 2% in intensity. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

Structure solved by direct methods, using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least-squares procedure on *F* (*SHELX*; Sheldrick, 1976). *E* maps revealed all the non-H atoms, and the H atoms appeared in difference maps. Refined parameters were calculated using

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