$0.005004|F|^2]^{-1}$ (*SHELX76*; Sheldrick, 1976). $f$, $f'$, $f''$ from *International Tables for X-ray Crystallography* (1974, Vol. IV). HC21, HC22, HC51, HC52 atoms, visible in difference syntheses, have been refined without constraints; the remaining hydrogens were included at calculated positions and refined with geometrical constraints. Final $R = 0.067$, $wR = 0.07$, max. shift/e.s.d. = 0.17, max. and min. heights in final difference Fourier synthesis: 0.96 and $-1.25$ e Å$^{-3}$. A VAX 750 computer was used.

The molecular structure with the atomic numbering is shown in Fig. 1 and the final positional and thermal parameters are listed in Table 1.* Bond lengths, bond angles and torsion angles (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) are listed in Table 2. Crystal packing is shown in Fig. 2.

**Related literature.** The five-membered ring adopts an envelope conformation (Duax & Norton, 1975, 1984) instead of the half-chair conformation found in the pyracetam crystal (Pritzkow, 1983). The asymmetry parameter $C_s = 2.0$ (3) indicates a small distortion of the mirror symmetry.

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* Lists of structure factors, anisotropic thermal parameters, all bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54547 (45 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Structure of Carbonyl(4-methoxy-*N*-methylbenzothiohydroxamato-*κO*,*κS*)(tricyclohexylphosphine)rhodium(I) Benzene Solvate

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**Abstract.** $[Rh(C_9H_{10}NO_2S)(CO)\{P(C_6H_{11})_3\}].C_6H_6$, $M_r = 685.7$, triclinic, $P\bar{1}$, $a = 9.764$ (2), $b = 10.185$ (2), $c = 19.885$ (3) Å, $\alpha = 80.03$ (1), $\beta = 87.87$ (1), $\gamma = 61.94$ (1)°, $V = 1716.5$ (5) Å$^3$, $Z = 2$, $D_m = 1.31$ (1), $D_x = 1.33$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $\mu = 6.24$ cm$^{-1}$, $T = 295$ K, $F(000) = 720$, final $R = 0.0503$ for 4858 observed reflections. The complex has approximate square-planar geometry about the Rh atom with the P and S atoms in a *trans* orientation. The O—Rh and S—Rh bonds form an angle of 83.4 (1)°. The least-squares planes consisting of the chelate ring atoms and *N*-substituted C atom on the one hand, and coordinated atoms, including O of CO, on the other hand, form a dihedral angle of 2.1 (5)°. The least-squares plane of the benzene C atoms forms a dihedral angle of 37.2 (5)° with the above-defined coordination plane. Bond distances are Rh—O = 2.029 (4), Rh—S = 2.306 (2), Rh—P = 2.290 (1) and Rh—C = 1.787 (6) Å.

**Experimental.** The substituted thiohydroxamate ligand was prepared according to methods described by Jensen & Pedersen (1961) and Jensen, Buchardt & Christophersen (1967). The precursor complex, $[Rh(C_9H_{10}NO_2S)(CO)_2]$, was obtained by adding a slight excess of ligand to $[RhCl(CO)_2]_2$ in dimethylformamide. The title complex was prepared by mixing equimolar amounts of $PCy_3$ and $[Rh(C_9H_{10}NO_2S)(CO)_2]$ in benzene, boiling the solution with activated carbon and evaporating the filtrate to an oily residue. This was dissolved in 70/30 ($v/v$) benzene/hexane which on slow evaporation at room temperature gave light-yellow tabular crystals. The density was determined by flotation in NaI solution. A crystal with dimensions 0.15 × 0.05 × 0.18 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 $\Delta\omega =$

0108-2701/92/010169-03$03.00

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 | 8652 (1) | 8079 (1) | 7937 (1) | 38.6 (1) |
| P | 8829 (2) | 7787 (2) | 6815 (1) | 35.3 (3) |
| S | 8753 (2) | 8310 (2) | 9065 (1) | 50.4 (3) |
| N | 11457 (6) | 6185 (6) | 8807 (2) | 52 (1) |
| O | 5418 (5) | 10433 (6) | 7631 (3) | 78 (1) |
| O(1) | 10879 (5) | 6436 (5) | 8161 (2) | 55 (1) |
| O(2) | 13097 (6) | 6005 (6) | 11922 (2) | 78 (1) |
| C | 6678 (7) | 9506 (7) | 7752 (3) | 52 (1) |
| C(1) | 10613 (7) | 6972 (7) | 9263 (3) | 48 (1) |
| C(2) | 11313 (7) | 6705 (6) | 9960 (3) | 46 (1) |
| C(3) | 11669 (8) | 7751 (7) | 10144 (3) | 56 (2) |
| C(4) | 12273 (8) | 7560 (7) | 10795 (3) | 58 (2) |
| C(5) | 12497 (7) | 6315 (7) | 11273 (3) | 54 (1) |
| C(6) | 12114 (8) | 5262 (7) | 11092 (3) | 60 (2) |
| C(7) | 11521 (7) | 5461 (7) | 10445 (3) | 54 (1) |
| C(8) | 13380 (10) | 7099 (9) | 12143 (4) | 81 (2) |
| C(9) | 13065 (8) | 4990 (9) | 8909 (4) | 76 (2) |
| C(11) | 7076 (6) | 7860 (6) | 6446 (3) | 37 (1) |
| C(12) | 6537 (7) | 6825 (7) | 6896 (3) | 51 (1) |
| C(13) | 4920 (7) | 7169 (8) | 6650 (3) | 59 (2) |
| C(14) | 4883 (8) | 7024 (8) | 5907 (3) | 62 (2) |
| C(15) | 5444 (7) | 8032 (8) | 5461 (3) | 54 (1) |
| C(16) | 7070 (7) | 7681 (7) | 5697 (3) | 49 (1) |
| C(21) | 9029 (6) | 9328 (6) | 6247 (3) | 38 (1) |
| C(22) | 7586 (7) | 10858 (6) | 6178 (3) | 50 (1) |
| C(23) | 7828 (8) | 12098 (7) | 5729 (3) | 59 (2) |
| C(24) | 9212 (8) | 12190 (7) | 6000 (4) | 66 (2) |
| C(25) | 10664 (8) | 10690 (8) | 6057 (4) | 66 (2) |
| C(26) | 10433 (7) | 9440 (7) | 6513 (3) | 50 (1) |
| C(31) | 10595 (6) | 6060 (6) | 6694 (3) | 39 (1) |
| C(32) | 10538 (7) | 4601 (6) | 7011 (3) | 52 (1) |
| C(33) | 12131 (8) | 3231 (7) | 7020 (3) | 63 (2) |
| C(34) | 12769 (8) | 3116 (7) | 6319 (4) | 63 (2) |
| C(35) | 12791 (7) | 4569 (7) | 5988 (4) | 60 (2) |
| C(36) | 11207 (7) | 5939 (7) | 5974 (3) | 51 (1) |
| C(44) | 6022 (12) | 1765 (12) | 1358 (6) | 103 (3) |
| C(55) | 7402 (13) | 1041 (14) | 1690 (5) | 100 (3) |
| C(66) | 8401 (12) | −331 (15) | 1567 (5) | 107 (3) |
| C(77) | 8014 (14) | −1016 (12) | 1133 (7) | 114 (4) |
| C(88) | 6585 (16) | −251 (17) | 786 (6) | 117 (4) |
| C(99) | 5551 (11) | 1169 (15) | 914 (6) | 113 (3) |

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

| | | | |
|---|---|---|---|
| Rh—P | 2.290 (1) | Rh—S | 2.306 (2) |
| Rh—O(1) | 2.029 (4) | Rh—C | 1.787 (6) |
| P—C(21) | 1.853 (5) | P—C(11) | 1.852 (5) |
| P—C(31) | 1.841 (5) | S—C(1) | 1.688 (6) |
| O(1)—N | 1.357 (6) | C(1)—C(2) | 1.493 (7) |
| C(1)—N | 1.310 (7) | N—C(9) | 1.459 (7) |
| C(5)—O(2) | 1.360 (7) | O(2)—C(8) | 1.406 (8) |
| C—O | 1.146 (7) | | |
| P—Rh—S | 173.8 (1) | P—Rh—O(1) | 91.4 (1) |
| S—Rh—O(1) | 83.4 (1) | P—Rh—C | 89.2 (2) |
| S—Rh—C | 96.0 (2) | O(1)—Rh—C | 178.9 (2) |
| Rh—P—C(21) | 112.4 (2) | Rh—P—C(11) | 113.8 (2) |
| C(21)—P—C(11) | 103.4 (2) | Rh—P—C(31) | 111.2 (2) |
| C(21)—P—C(31) | 104.2 (2) | C(11)—P—C(31) | 111.3 (2) |
| Rh—S—C(1) | 97.7 (2) | Rh—O(1)—N | 116.9 (3) |
| S—C(1)—C(2) | 119.6 (4) | S—C(1)—N | 120.7 (4) |
| C(2)—C(1)—N | 119.7 (5) | O(1)—N—C(1) | 121.3 (5) |
| O(1)—N—C(9) | 112.1 (5) | C(1)—N—C(9) | 126.6 (5) |
| C(5)—O(2)—C(8) | 117.8 (5) | Rh—C—O | 179.2 (6) |

$(0.41 + 0.34\tan\theta)$°, a maximum scan speed of 3.3° $\min^{-1}$ in $\omega$ and a maximum scan time of 60 s per reflection. The unit-cell parameters were determined from a least-squares fit of 25 reflections with $15 < \theta < 17$°. The intensity measuring range was $3 < \theta < 27$°. An empirical absorption correction (North, Phillips & Mathews, 1968) was made with a minimum correction factor of 0.975 and a maximum of 0.999. The mean intensity of three standard reflections, measured every 3600 s of X-ray exposure, gave a total loss of 7.1% during 61 h exposure. The intensity data were corrected for this decay. All possible reflections with $0.07 < (\sin\theta)/\lambda < 0.64$ Å$^{-1}$ in the index ranges $0 < h < 11$, $-12 < k < 12$, $-23 < l < 23$ gave 6430 unique reflections of which 4858 were considered observed with $I > 3.0\sigma(I)$. No equivalent reflections were measured. The structure was solved by the heavy-atom method using *SHELXS*86 (Sheldrick, 1990) and subjected to anisotropic full-matrix least-squares refinement on $F$ with 377 positional and thermal 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 $R = 0.0503$, $wR = 0.0524$ with unit weights. $(\Delta\rho)_{max} = 0.97$ and $(\Delta\rho)_{min} = -0.59$ e Å$^{-3}$, $(\Delta/\sigma)_{max} = 0.88$ and positional $(\Delta/\sigma)_{max} = 0.38$. Final atomic coordinates* are given in Table 1, main geometrical parameters in Table 2, a perspective view (Johnson, 1976) with atomic labels in Fig. 1 and a stereoscopic view of the molecular packing in Fig. 2.

**Related literature.** The purpose of the present structure investigation was to determine the specific isomer formed when only one carbonyl group in complexes of the type [Rh($LL'$)(CO)$_2$]($LL'$ = uninegative bidentate ligands having S, N or O donor atoms) is substituted by phosphines having different

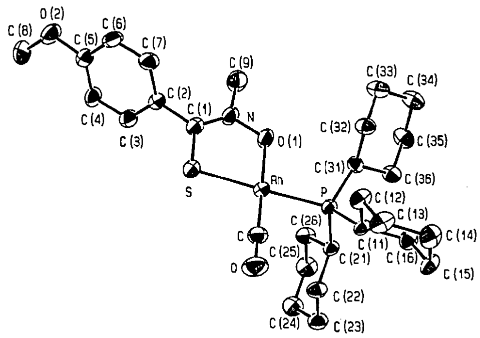

Fig. 1. Perspective view and atomic labelling of the molecule (H atoms omitted for clarity).

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* Lists of least-squares planes and deviations, anisotropic thermal parameters, bond distances and angles, H-atom parameters, and structure factors, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54458 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0215]

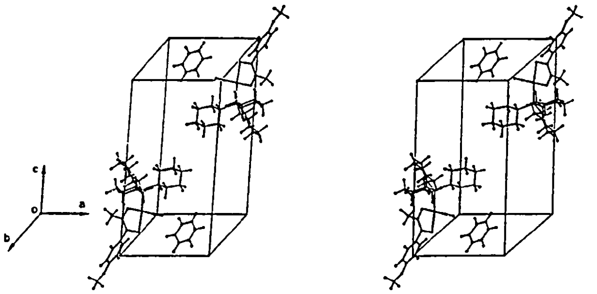

Fig. 2. Stereoscopic view of the molecular packing.

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-$\kappa O,\kappa S$)(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$^{-3}$, $\lambda$(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 $\omega$ 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