contain rows of intermolecular hydrogen bonds along the *a* and *b* axes, respectively. In compound (1), each molecule has both intra- and intermolecular hydrogen bonds with O···O distances 2·536 (6), 2·560 (6) and 2·553 (6), 2·562 (6) Å, and corresponding O—H···O angles 164 (6), 164 (6), and 174 (7), 163 (5)°, respectively. However, in compound (2), because of the *trans* conformation, only intermolecular hydrogen bonding is possible. Each molecule has two identical intermolecular hydrogen bonds with O···O distance 2·637 (4) Å and O—H···O angle 175 (5)°. The two bonds are related by a center of inversion as are those in the common carboxylic acid dimer. The molecules are hydrogen bonded throughout the crystal as depicted in Fig. 2(*b*).

In this series of compounds, the interesting structural features appear not only in the interaction between the olefin group and the metal ion, but also in the coplanarity of the atoms in the equatorial plane. It is apparent that compound (1) has much better coplanarity than compound (2) (χ^2 ratio of 1:10). Such deviation can be seen as a rotation of 11·23° of the fumaric acid molecule around the bond between the Fe atom and the ethylenic double bond; it corresponds to a rotation of only 3·9 (3) and 5·8 (4)° in compound (1). These rotations could be rationalized by the crystal lattice energy, intermolecular hydrogen bonding or a low-energy rotation barrier around the bond between the Fe atom and the ethylenic double bond. More work has to be performed before any definite conclusions can be drawn.

The authors thank the National Science Council of Taiwan for financial support of this work.

References

BROWN, C. J. (1966). *Acta Cryst.* **21**, 1–5.
GABE, E. J., LE PAGE, Y., WHITE, P. S. & LEE, F. L. (1987). *Acta Cryst.* A**43**, C294.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JAMES, M. N. & WILLIAMS, G. T. B. (1974). *Acta Cryst.* **30**, 1249–1257.
KRÜGER, C., BARNETT, B. L. & BRAUER, D. (1978). *The Organic Chemistry of Iron*, edited by E. A. K. VON GUSTORF, F.-W. GREVELS & I. FISCHLER, Vol. I, pp. 1–112. New York: Academic Press.
PEDONE, C. & SIRIGU, A. (1967). *Acta Cryst.* **23**, 759–762.

Acta Cryst. (1989). C**45**, 724–728

(η-8,9,10-Trinorbornadiene)[1,1,1-tris(diphenylphosphinomethyl)ethane-*P,P',P''*]rhodium Trifluoromethanesulfonate Methanol Solvate

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(*Received* 2 *February* 1988; *accepted* 26 *November* 1988)

Abstract. [Rh(C_7H_8)($C_{41}H_{39}P_3$)]$CF_3SO_3.CH_4O$, $C_{48}H_{47}P_3Rh^+CH_4O.CF_3O_3S^-$, $M_r = 1000·8$, monoclinic, $P2_1/c$, $a = 10·404$ (6), $b = 17·239$ (7), $c = 25·349$ (7) Å, $\beta = 90·95$ (6)°, $V = 4546$ (3) Å^3, $Z = 4$, $D_x = 1·460$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 5·7$ cm^{-1}, $F(000) = 2061$, $T = 293$ K, $R = 0·059$ for 7015 observed reflections. The Rh atom is pentacoordinated in a distorted square-pyramidal arrangement. The midpoints of the diolefinic coordinated double bonds and two P atoms of the tridentate phosphine ligand occupy equatorial sites, while the third P atom lies in the axial position.

Introduction. The coordination chemistry of the tripod-like tridentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, triphos, has been widely studied (Sacconi & Mani, 1982). Its geometry is such that it can only occupy three facial sites of a coordination polyhedron. As a consequence of its specific geometry, complexes with a stereochemistry and a reactivity not readily achievable with three unidentate ligands may be realized.

Since the catalytic activity of triphos complexes has not been extensively investigated, a study was undertaken on the synthesis, structure and reactivity of Rh^I and Rh^{III} triphos complexes of relevance to homogeneous hydrogenation such as hydrido, alkyl and olefin complexes.

The triphos ligand was found to stabilize pentacoordinated complexes of the type [Rh(diol)(triphos)]

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where diol = cyclooctadiene, norbornadiene, butadiene (Ott, 1986). The present work deals with the structure of $[Rh(nbd)(triphos)][F_3CSO_3]$, where nbd = norbornadiene.

Experimental. Crystals were obtained from CH_3OH. One molecule of CH_3OH per molecule of complex was found from the X-ray analysis; Nicolet *R*3 four-circle diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; crystal size $0{\cdot}24 \times 0{\cdot}16 \times 0{\cdot}60$ mm; unit-cell dimensions determined with 15 reflections ($20 \leq 2\theta \leq 26°$); 13 840 reflections measured in the range $3 \leq 2\theta \leq 56°$, $h = 0$ to 14, $k = 0$ to 23, $l = -34$ to 34; 7015 reflections with $I \geq 3\sigma(I)$ considered observed; ω-scan mode, with scan rate depending on the intensities. Three standards measured every 100 reflections, no significant change; data processed to yield values of I and $\sigma(I)$ (Bachechi, Zambonelli & Marcotrigiano, 1977); in the estimation of $\sigma(I)$ the uncertainty factor was $p = 0{\cdot}013$ as calculated from the variance of the standard reflections (McCandlish, Stout & Andrews, 1975). Corrections for Lorentz, polarization and for absorption. Structure solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o^2)+b|F_o|^2]$ minimized. Phenyl groups of the triphos ligand constrained to $6/mmm$ symmetry, d(C—C) = 1·395 and d(C—H) = 0·95 Å, C and H atoms with individual isotropic thermal parameters. All the other H atoms at calculated positions and refined riding on the corresponding C atoms. All the non-group non-H atoms were allowed to vibrate anisotropically (348 parameters refined). Convergence at $R = 0{\cdot}059$ and $wR = 0{\cdot}066$ ($S = 0{\cdot}24$); $(\Delta/\sigma)_{max} = 0{\cdot}04$; final difference map with $\Delta\rho$ in the range $\pm 0{\cdot}30$ e Å^{-3}. All calculations performed on the Data General Eclipse MV8000II computer using *SHELX*76 system (Sheldrick, 1976). Scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic parameters of the non-H atoms are given in Table 1.*

Table 1. *Final positional and thermal parameters of the non-*H *atoms*

$$U_{eq} = (1/6\pi^2)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{iso}/U_{eq}(Å^2)
Rh	0·49418 (4)	0·20480 (2)	0·13056 (2)	0·0264 (1)
P(1)	0·2989 (1)	0·2158 (1)	0·0864 (1)	0·0278 (3)
P(2)	0·5889 (1)	0·2604 (1)	0·0575 (1)	0·0314 (3)
P(3)	0·4744 (1)	0·3337 (1)	0·1652 (1)	0·0297 (3)
C(1)	0·3783 (5)	0·3687 (3)	0·0592 (2)	0·033 (1)
C(2)	0·3286 (7)	0·4392 (4)	0·0281 (3)	0·048 (2)
C(3)	0·2609 (5)	0·3174 (3)	0·0718 (2)	0·035 (1)
C(4)	0·4740 (5)	0·3253 (3)	0·0233 (2)	0·034 (1)
C(5)	0·4481 (5)	0·4017 (3)	0·1095 (2)	0·033 (1)
C(6)	0·1597 (4)	0·1775 (2)	0·1220 (2)	0·034 (1)
C(7)	0·1298 (4)	0·2099 (2)	0·1707 (2)	0·048 (1)
C(8)	0·0358 (4)	0·1759 (2)	0·2018 (2)	0·059 (2)
C(9)	−0·0282 (4)	0·1094 (2)	0·1842 (2)	0·055 (2)
C(10)	0·0018 (4)	0·0769 (2)	0·1355 (2)	0·059 (2)
C(11)	0·0957 (4)	0·1110 (2)	0·1044 (2)	0·050 (1)
C(12)	0·2811 (4)	0·1643 (2)	0·0235 (2)	0·032 (1)
C(13)	0·1934 (4)	0·1871 (2)	−0·0158 (2)	0·048 (1)
C(14)	0·1780 (4)	0·1426 (2)	−0·0613 (2)	0·056 (2)
C(15)	0·2504 (4)	0·0752 (2)	−0·0677 (2)	0·052 (2)
C(16)	0·3381 (4)	0·0524 (2)	−0·0285 (2)	0·055 (2)
C(17)	0·3534 (4)	0·0969 (2)	0·0171 (2)	0·046 (1)
C(18)	0·6524 (4)	0·1978 (3)	0·0054 (1)	0·048 (1)
C(19)	0·5880 (4)	0·1854 (3)	−0·0426 (1)	0·052 (2)
C(20)	0·6421 (4)	0·1376 (3)	−0·0807 (1)	0·063 (2)
C(21)	0·7606 (4)	0·1021 (3)	−0·0708 (1)	0·070 (2)
C(22)	0·8250 (4)	0·1145 (3)	−0·0228 (1)	0·063 (2)
C(23)	0·7709 (4)	0·1623 (3)	0·0153 (1)	0·050 (2)
C(24)	0·7320 (4)	0·3204 (3)	0·0679 (1)	0·036 (1)
C(25)	0·7743 (4)	0·3680 (3)	0·0271 (1)	0·053 (2)
C(26)	0·8816 (4)	0·4153 (3)	0·0349 (1)	0·066 (2)
C(27)	0·9467 (4)	0·4152 (3)	0·0835 (1)	0·064 (2)
C(28)	0·9044 (4)	0·3677 (3)	0·1242 (1)	0·062 (2)
C(29)	0·7971 (4)	0·3203 (3)	0·1164 (1)	0·049 (1)
C(30)	0·6065 (4)	0·3789 (2)	0·2033 (2)	0·038 (1)
C(31)	0·6451 (4)	0·4553 (2)	0·1945 (2)	0·052 (2)
C(32)	0·7412 (4)	0·4885 (2)	0·2261 (2)	0·066 (2)
C(33)	0·7987 (4)	0·4454 (2)	0·2667 (2)	0·065 (2)
C(34)	0·7602 (4)	0·3691 (2)	0·2756 (2)	0·064 (2)
C(35)	0·6641 (4)	0·3359 (2)	0·2439 (2)	0·052 (2)
C(36)	0·3437 (4)	0·3545 (2)	0·2118 (1)	0·035 (1)
C(37)	0·3461 (4)	0·3142 (2)	0·2595 (1)	0·050 (2)
C(38)	0·2468 (4)	0·3240 (2)	0·2952 (1)	0·060 (2)
C(39)	0·1453 (4)	0·3741 (2)	0·2832 (1)	0·056 (2)
C(40)	0·1429 (4)	0·4145 (2)	0·2355 (1)	0·045 (1)
C(41)	0·2421 (4)	0·4047 (2)	0·1998 (1)	0·037 (1)
C(42)	0·5375 (8)	0·0431 (4)	0·1535 (1)	0·055 (2)
C(43)	0·6241 (9)	0·1066 (5)	0·1327 (4)	0·081 (3)
C(44)	0·6547 (8)	0·1537 (5)	0·1727 (5)	0·095 (2)
C(45)	0·5804 (13)	0·1209 (5)	0·2196 (3)	0·097 (4)
C(46)	0·4480 (11)	0·1398 (5)	0·2027 (3)	0·087 (3)
C(47)	0·4221 (7)	0·0924 (5)	0·1623 (4)	0·072 (2)
C(48)	0·5886 (8)	0·0328 (4)	0·2085 (3)	0·063 (2)
S	0·8362 (3)	0·1237 (1)	0·3515 (1)	0·089 (1)
O(1)	0·7636 (18)	0·1805 (9)	0·3326 (9)	0·32 (1)
O(2)	0·7995 (10)	0·0679 (4)	0·3860 (4)	0·151 (4)
O(3)	0·8913 (21)	0·0915 (5)	0·3074 (5)	0·30 (1)
F(1)	1·0136 (14)	0·2251 (4)	0·3540 (5)	0·26 (1)
F(2)	0·9281 (12)	0·2097 (4)	0·4252 (4)	0·19 (1)
F(3)	1·0469 (12)	0·1314 (9)	0·4017 (9)	0·31 (1)
C(49)	0·9619 (15)	0·1743 (8)	0·3837 (6)	0·109 (5)
O(4)	0·4926 (20)	0·1106 (11)	0·3931 (7)	0·18 (1)
C(50)	0·4461 (26)	0·1777 (18)	0·3618 (8)	0·30 (2)

Discussion. The crystal structure consists of discrete $[Rh(nbd)(triphos)]^+$ cations and $[CF_3SO_3]^-$ anions with no short contacts between atoms of different ions. One molecule of CH_3OH solvent is present.

Perspective views of the cationic complex are shown in Figs. 1 and 2. Table 2 lists a selection of intramolecular distances and angles with their standard deviations.

The Rh atom is five-coordinated by the three P atoms of the triphos ligand and by the double bonds of the chelating norbornadiene ligand. The geometry of the inner coordination sphere of the cationic complex is illustrated in Fig. 3, which emphasizes the approximate square-pyramidal coordination environment of the Rh atom with P(3) assigned to the axial position. More exactly, because of the steric requirement of the bidentate diene ligand, which has a bite angle, MP(1)—Rh—MP(2)*, of only 66·3 (4)°, the overall coordi-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51546 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* MP(1) is the midpoint of C(43)=C(44) and MP(2) is the midpoint of C(46)=C(47).

nation geometry around the Rh atom can be regarded as almost midway between square pyramidal, with P(3) axial, and trigonal bipyramidal, with P(2) and MP(2) axial.

Square-pyramidal coordination geometries with similar distortions can be observed in some triphos complexes of Co and Ni with chelating ligands (Benelli, Di Vaira, Noccioli & Sacconi, 1976; Dapporto, Midollini, Orlandini & Sacconi, 1976; Bianchini, Meli & Orlandini, 1982) (Table 3). As can be noticed, the bite angles of the five bidentate ligands in Table 3 are comparable as are the deviations from the ideal geometry on the basal plane of the coordination square pyramid, while the values of the P(3)—Rh—MP angles [123·2 (3) and 114·5 (2)°] are greater with respect to the corresponding P(3)—*M*—*L* angles in the other triphos complexes. The two midpoints of the coordinated double bonds are far out of the ideal basal plane of the square pyramid [1·15 (1) and 0·78 (1) Å]. The bulky nbd can be accommodated in the Rh coordination sphere as a chelating ligand only with the plane through the olefinic C atoms so inclined with respect to the basal plane of the square pyramid as to lie parallel to the P(1)–P(2)–P(3) face of the square pyramid. With the plane, which contains the double bonds, so oriented, the olefinic C atoms can be maintained at about 2·2 Å from the Rh atom only with a shift which brings the double-bond midpoints out of the basal plane of the square pyramid.

A rotation of the nbd ligand with respect to the triphos ligand, which would favour a trigonal bipyramidal coordination with one coordinated double bond equatorial and the other axial, is prevented by short contacts which would be established between the H atoms of nbd and those of the phenyl rings of the triphos ligand.

The related complex $[Rh(nbd)(C_3triphos)]^+$, where C_3triphos is the tripod-like tridentate ligand $Ph_2PCH(CH_2PPh_2)_2$ (Bachechi, Ott & Venanzi, 1989) presents a trigonal bipyramidal coordination. The C_3 triphos ligand seems more flexible than the triphos ligand and nbd can be accommodated in the rhodium coordination sphere with one double bond axial and the other equatorial.

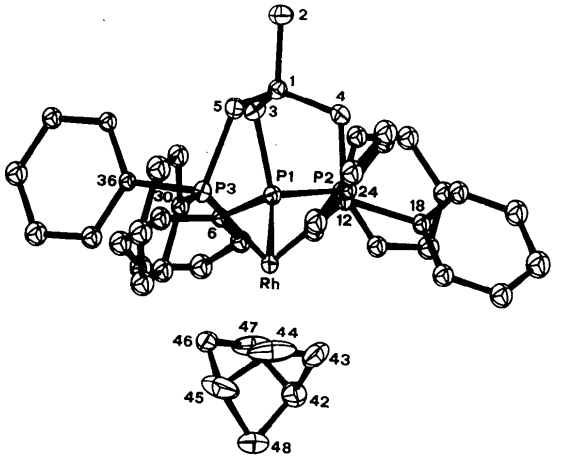

Fig. 1. Perspective view of the complex cation $[Rh(nbd)(triphos)]^+$. The ellipsoids represent 30% probability.

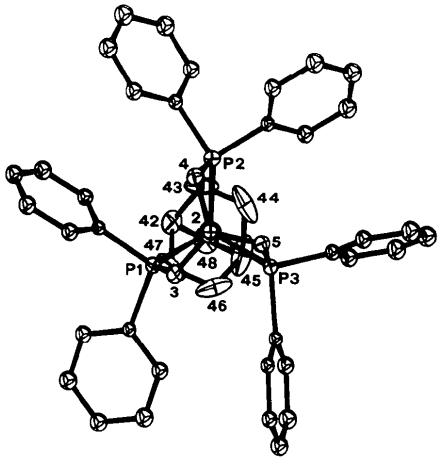

Fig. 2. Perspective view of the complex cation $[Rh(nbd)(triphos)]^+$ along the pseudo C_3 axis. The ellipsoids represent 30% probability.

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

Rh–P(1)	2·311 (1)	P(3)–C(5)	1·851 (5)
Rh–P(2)	2·319 (1)	P(3)–C(30)	1·841 (4)
Rh–P(3)	2·399 (1)	P(3)–C(36)	1·851 (4)
Rh–MP(1)*	2·055 (9)	C(1)–C(2)	1·535 (8)
Rh–MP(2)*	2·115 (9)	C(1)–C(3)	1·545 (8)
Rh–C(43)	2·166 (7)	C(1)–C(4)	1·553 (7)
Rh–C(44)	2·157 (7)	C(1)–C(5)	1·564 (8)
Rh–C(46)	2·205 (6)	C(42)–C(43)	1·517 (10)
Rh–C(47)	2·233 (7)	C(42)–C(48)	1·495 (10)
P(1)–C(3)	1·833 (5)	C(43)–C(44)	1·334 (14)
P(1)–C(6)	1·842 (4)	C(44)–C(45)	1·536 (15)
P(1)–C(12)	1·832 (4)	C(45)–C(46)	1·472 (15)
P(2)–C(4)	1·842 (5)	C(45)–C(48)	1·547 (11)
P(2)–C(18)	1·838 (4)	C(46)–C(47)	1·334 (13)
P(2)–C(24)	1·829 (4)	C(47)–C(42)	1·491 (11)

P(1)–Rh–P(2)	87·8 (1)	Rh–P(3)–C(36)	118·8 (1)
P(1)–Rh–P(3)	91·2 (1)	C(5)–P(3)–C(30)	103·4 (2)
P(1)–Rh–MP(1)*	145·1 (3)	C(5)–P(3)–C(36)	105·2 (2)
P(1)–Rh–MP(2)*	95·6 (3)	C(30)–P(3)–C(36)	97·6 (2)
P(2)–Rh–P(3)	87·1 (1)	P(1)–C(3)–C(1)	114·8 (4)
P(2)–Rh–MP(1)*	99·0 (3)	P(2)–C(4)–C(1)	115·7 (4)
P(2)–Rh–MP(2)*	158·0 (3)	P(3)–C(5)–C(1)	116·8 (4)
P(3)–Rh–MP(1)*	123·2 (3)	C(3)–C(1)–C(2)	107·4 (5)
P(3)–Rh–MP(2)*	114·5 (2)	C(3)–C(1)–C(4)	111·2 (4)
MP(1)–Rh–MP(2)*	66·3 (4)	C(3)–C(1)–C(5)	113·5 (4)
Rh–P(1)–C(3)	111·2 (2)	C(4)–C(1)–C(2)	107·1 (5)
Rh–P(1)–C(6)	115·2 (1)	C(4)–C(1)–C(5)	111·1 (4)
Rh–P(1)–C(12)	117·2 (1)	C(5)–C(1)–C(2)	106·2 (5)
C(3)–P(1)–C(6)	105·9 (2)	C(42)–C(43)–C(44)	108·1 (8)
C(3)–P(1)–C(12)	105·6 (2)	C(43)–C(44)–C(45)	104·3 (7)
C(6)–P(1)–C(12)	100·6 (2)	C(44)–C(45)–C(46)	100·1 (6)
Rh–P(2)–C(4)	110·2 (2)	C(44)–C(45)–C(48)	101·0 (8)
Rh–P(2)–C(18)	119·6 (2)	C(46)–C(45)–C(48)	102·6 (8)
Rh–P(2)–C(24)	118·3 (1)	C(45)–C(46)–C(47)	105·2 (7)
C(4)–P(2)–C(18)	104·9 (2)	C(45)–C(48)–C(42)	91·9 (5)
C(4)–P(2)–C(24)	104·1 (2)	C(46)–C(47)–C(42)	108·2 (7)
C(18)–P(2)–C(24)	97·7 (2)	C(47)–C(42)–C(43)	97·2 (5)
Rh–P(3)–C(5)	108·7 (2)	C(47)–C(42)–C(48)	101·7 (7)
Rh–P(3)–C(30)	121·1 (1)	C(48)–C(42)–C(43)	101·9 (7)

* MP(1) is the midpoint of C(43)=C(44) and MP(2) the midpoint of C(46)=C(47).

The distances from the Rh atom to the olefinic C atoms [2·166 (7), 2·157 (7), 2·205 (6), 2·233 (7) Å] and to the midpoints of the coordinated double bonds [2·06 and 2·12 Å] are consistent with values previously reported but the coordinated double bonds C(43)=C(44) and C(46)=C(47), both 1·334 (13) Å, seem little affected by the coordination. Although coordination generally leads to a lengthening of the C=C bond towards values ranging around 1·400 Å, other short C=C bond distances with comparable metal-to-olefin distances can be observed in distorted square-planar complexes of diene ligands: 1·362 (8) and 1·357 (8) Å in [Rh(cyclooctadiene)(PPh_2CHCH_3-$CHCH_3PPh_2$)]$^+$ (Ball & Payne, 1977), 1·359 (10) and 1·375 (10) Å in [Rh(nbd)(norphos)*]$^+$ (Kyba, Davis, Juri & Shirley, 1981), 1·386 (6) Å in [$RuCl_2$(norbornadiene)($C_6H_5NH_2$)$_2$] (Manoli, Gaughan & Ibers, 1974).

In the related [Rh(nbd)(C_3triphos)]$^+$ complex the metal-to-olefin distances are comparable [2·07 and 2·14 Å] but the C=C bond lengths present the usual lengthening on coordination [1·392 (13) and 1·432 (13) Å] according to the pattern observed in trigonal bipyramidal complexes of diene ligands.

* norphos = (−)-(*R,R*)-*exo*-2-*endo*-3-bis(diphenylphosphino)bicyclo[2.2.1]heptene.

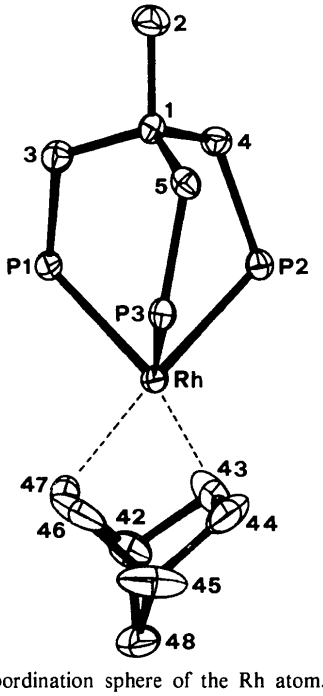

Fig. 3. Inner coordination sphere of the Rh atom. The diagram emphasizes the relationship of the coordination geometry to a square-pyramidal arrangement. The ellipsoids represent 30% probability.

Table 3. *Coordination geometry* (°) *of some square-pyramidal triphos complexes*

	[Rh(nbd)-(triphos)]$^+$ (*a*)	[Co(BH_4)-(triphos)] (*b*)	[Co(SO_4)-(triphos)] (*c*)	[Co(S_2CO)-(triphos)] (*d*)	[Si(SeO_4)-(triphos)] (*c*)
P(1)–*M*–P(2)	87·8 (1)	89·6 (2)	88·7 (2)	89·0 (3)	88·5 (2)
P(1)–*M*–P(3)	91·2 (1)	91·3 (2)	90·6 (2)	91·6 (2)	90·8 (2)
P(1)–*M*–*L*(1)	145·1 (3)	155·7 (61)	157·0 (4)	155·5 (4)	153·3 (5)
P(1)–*M*–*L*(2)	95·6 (3)	109·1 (55)	96·9 (4)	97·2 (3)	93·4 (5)
P(2)–*M*–P(3)	87·1 (1)	93·3 (2)	92·5 (2)	91·6 (3)	92·1 (2)
P(2)–*M*–*L*(1)	99·0 (3)	93·3 (67)	98·3 (4)	93·5 (3)	99·2 (5)
P(2)–*M*–*L*(2)	158·0 (3)	159·5 (57)	161·2 (3)	165·6 (3)	161·0 (5)
P(3)–*M*–*L*(1)	123·2 (3)	112·6 (60)	110·8 (4)	112·6 (3)	114·2 (6)
P(3)–*M*–*L*(2)	114·5 (2)	94·5 (60)	105·3 (4)	101·2 (3)	106·8 (5)
L(1)–*M*–*L*(2)	66·3 (4)	66·3 (88)	70·1 (5)	75·5 (3)	71·3 (7)

M = Rh, Co, Ni; *L* = MP, H, O, S, O, respectively.
References: (*a*) present work; (*b*) Dapporto, Midollini, Orlandini & Sacconi (1976); (*c*) Benelli, Di Vaira, Noccioli & Sacconi (1976); (*d*) Bianchini, Meli & Orlandi (1982).

The other bond distances and angles within the nbd ligand do not differ significantly from the results of previous structural investigations on chelating nbd ligands. The C—C bond distances average to 1·51 Å. The bond angles can be divided into three sets: the C(sp^2)—C(sp^3)—C(sp^3) angles average to 106·5°, the angles centred at the bridgehead C atoms average to 100·8° and the angle at the C atom of the bridging apex, *i.e.* C(42)—C(48)—C(45), is 91·9 (5)°.

The two basal Rh—P bond distances [2·311 (2) and 2·319 (1) Å] fall in the middle of the Rh—P range generally observed in tertiary phosphine complexes of Rh^I while the apical Rh—P(3) [2·399 (1) Å] seems to be one of the longest Rh—P bond distances observed (Muir & Ibers, 1969; Nappier, Meek, Kirchner & Ibers, 1973).

Dimensions in the triphos ligand are normal with the small deviations from the ideal geometry generally found in triphos complexes (Bachechi, Janser & Venanzi, 1985). The angles at the P atoms can be divided into four sets: the Rh—P—C_{aryl} angles with average 118·1 (8)°, the Rh—P—C_{alkyl} angles with average 110 (1)°, the C_{alkyl}—P—C_{aryl} angles with average 104·9 (9)° and the C_{alkyl}—P—C_{alkyl} angles with average 99 (2)°. In the aliphatic chains the P—C—C angles average 116 (1)° as in most triphos complexes.

As with other structures, the $CF_3SO_3^-$ anion has a fairly large thermal motion or disorder which results in low precision in the bond distances and angles. The sulfonate group has average S—O bond distance of 1·35 (3) Å and average O—S—O bond angle of 114 (11)°. The C—S bond distance is 1·760 (14) Å. The —CF_3 group is tetrahedral with average C—F bond distance of 1·26 (2) Å and average bond angle at the C atom of 109 (5)°. The S—O and C—F bond distances deviate considerably from those determined for the $CF_3SO_3^-$ anions in other compounds (Bino, Hesse & Kuppers, 1980; Delaplane, Lundgren & Olovsson, 1975; De Simone & Glick, 1978). The $CF_3SO_3^-$ anion has a staggered conformation and the F—C—S—O

torsion angles for F and O atoms in *trans* positions are 175 (1), 178 (1) and 176 (1)°.

References

BACHECHI, F., JANSER, P. & VENANZI, L. M. (1985). *J. Organomet. Chem.* **296**, 229–242.

BACHECHI, F., OTT, J. & VENANZI, L. M. (1989). *Acta Cryst.* In the press.

BACHECHI, F., ZAMBONELLI, L. & MARCOTRIGIANO, G. (1977). *J. Cryst. Mol. Struct.* **7**, 11–20.

BALL, R. G. & PAYNE, N. C. (1977). *Inorg. Chem.* **16**, 1187–1191.

BENELLI, C., DI VAIRA, M., NOCCIOLI, G. & SACCONI, L. (1976). *Inorg. Chem.* **16**, 182–187.

BIANCHINI, C., MELI, A. & ORLANDINI, A. (1982). *Inorg. Chem.* **24**, 4166–4169.

BINO, A., HESSE, K. F. & KUPPERS, H. (1980). *Acta Cryst.* B**36**, 723–725.

DAPPORTO, P., MIDOLLINI, S., ORLANDINI, A. & SACCONI, L. (1976). *Inorg. Chem.* **15**, 2768–2774.

DELAPLANE, R. G., LUNDGREN, J. O. & OLOVSSON, I. (1975). *Acta Cryst.* B**31**, 2202–2207, 2208–2213.

DE SIMONE, R. E. & GLICK, M. D. (1978). *Inorg. Chem.* **17**, 3574–3577.

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

KYBA, E. P., DAVIS, R. L., JURI, P. N. & SHIRLEY, K. R. (1981). *Inorg. Chem.* **20**, 3616–3623.

MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* A**31**, 245–249.

MANOLI, J., GAUGHAN, A. P. & IBERS, J. A. (1974). *J. Organomet. Chem.* **72**, 247–259.

MUIR, K. W. & IBERS, J. A. (1969). *Inorg. Chem.* **8**, 1921–1928.

NAPPIER, T. E., MEEK, D. W., KIRCHNER, R. M. & IBERS, J. A. (1973). *J. Am. Chem. Soc.* **95**, 4194–4210.

OTT, J. (1986). PhD thesis, ETH Zentrum, Zürich, Switzerland.

SACCONI, L. & MANI, F. (1982). In *Transition Metal Chemistry*, Vol. 8, edited by G. A. NELSON & B. N. FIGGIS. New York: M. Decker.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1989). C**45**, 728–730

Di-*tert*-butyl(glycylglycinato)tin(IV) Monohydrate

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(*Received* 23 *May* 1988; *accepted* 7 *November* 1988)

Abstract. $[Sn(C_4H_6N_2O_3)(C_4H_9)_2].H_2O$, $M_r = 381{\cdot}0$, monoclinic, $P2_1/n$, $a = 8{\cdot}895$ (6), $b = 14{\cdot}092$ (7), $c = 13{\cdot}653$ (8) Å, $\beta = 93{\cdot}17$ (5)°, $V = 1709$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}481$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}5$ mm^{-1}, $F(000) = 776$, $T = 291$ (1) K, final $R = 0{\cdot}063$ for 1872 unique reflections [$F \geq 3{\cdot}0\sigma(F)$]. The polyhedron around Sn is a distorted trigonal bipyramid formed by two equatorial $C(CH_3)_3$ groups and the tridentate, nearly planar, glycylglycinate ligand. The equatorial Sn—$N_{peptide}$ bond is short: 2·085 (8) Å. The $(CH_3)_3C$—Sn—$C(CH_3)_3$ bond angle is 121·7 (4)°, the O—Sn—N_{amino} bond angle is only 149·6 (3)°. The molecules are connected through a hydrogen-bond network involving hydrogen bonds between water and NH_2 and $CO_{peptide}$ and $CO_{carboxylate}$ groups as well as hydrogen bonds between NH_2 and $CO_{carboxylate}$ groups of neighbouring molecules.

Introduction. Previous structural studies of diorganotin derivatives of dipeptides R_2SnX (H_2X = dipeptide), some of which exhibit antileukaemic properties (Huber & Barbieri, 1986), demonstrated that Sn has a distorted trigonal-bipyramidal environment and that the bond angles in the polyhedron around Sn are more or less different depending on the type of R and X [R = Ph = C_6H_5, X = GlyGly = glycylglycinate (Huber, Haupt, Preut, Barbieri & Lo Giudice, 1977); R = Me = CH_3, X = GlyMet = glycylmethionate (Preut, Mundus, Huber & Barbieri, 1986); R = Cy = C_6H_{11}, X = GlyAla = glycylalaninate, GlyGly (Vornefeld, Huber, Preut & von Angerer, 1989); R = n-Bu = n-C_4H_9, X = GlyVal = glycylvalinate (Preut, Mundus, Huber & Barbieri, 1989)]. The molecules are linked by hydrogen bonds. In this context we found it worthwhile to study the function of the water molecule in the hydrogen-bonding system of the title compound with two voluminous R groups at Sn, which we synthesized recently as a first example of an R_2SnX hydrate. We also wanted to find out if the water molecule might even coordinate to Sn as we observed recently in an R_2Sn

0108-2701/89/050728-03$03.00 © 1989 International Union of Crystallography