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Carbonyl-κC-[tris(diphenylphosphinoyl)methanido-$\kappa^2 O,O'$][tris(*o*-tolyl)phosphine-κP]rhodium(I), $[Rh(C\{P(O)Ph_2\}_3)(CO)\{P(o\text{-}Tol)_3\}]$

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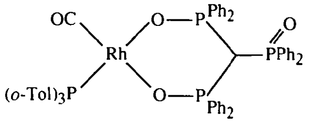
Abstract

The title compound, $[Rh(C_{37}H_{30}P_3O_3)(C_{21}H_{21}P)(CO)]$, has approximate square-planar coordination geometry around the Rh atom. The significant difference [0.012 (3) Å] in the Rh—O bond lengths is due to the slightly different *trans* influence of $P(o\text{-}Tol)_3$ and CO. This suggests that the longer Rh—O bond [*trans* to $P(o\text{-}Tol)_3$] will be preferentially substituted during intramolecular fluxional coordination behaviour of the tripodal ligand.

Comment

This structure determination forms part of an extension of our studies of square-planar rhodium(I) complexes (Basson, Leipoldt, Roodt & Preston, 1991) of the form $[Rh(L,L')(CO)(PR_3)]$ (where L,L' is a monoanionic bidentate ligand) to include tripodal ligands of the form $[Ph_2P(X)][Ph_2P(Y)][Ph_2P(Z)]CH$ (hereafter HTris*XYZ*, where *X*, *Y* and *Z* are Group VIB elements). Rhodium(I) and iridium(I) complexes containing the $TrisO_3^-$ ligand have been found to be efficient catalysts for the cyclotrimerization and hydrosilylation of acetylenes (Tanke & Crabtree, 1990). Oxidative addition very often forms part of a catalytic cycle and in this context we are studying the mechanisms of oxidative addition of iodomethane to various Rh^I complexes formulated above. Structural results are sometimes of immense value as an aid in formulating the intimate nature of reaction mechanisms (Leipoldt, Basson, Roodt & Purcell, 1992) and the possible *trans* influence of $P(o\text{-}Tol)_3$ in the title complex, (I), concerned us in view of its unusual reactivity towards a number of common organic solvents and the known fluxional behaviour between the coordinated and uncoordinated arms in bidentate $TrisS_3^-$ complexes (Browning, Beveridge, Bushnell & Dixon, 1986).



(I)

The Rh atom in (I) displays the usual square-planar geometry with the tripodal ligand coordinated in the bidentate mode *via* two O atoms. The C atom of the carbonyl group is situated 0.343 (4) Å from the plane defined by Rh, O1, O2 and P4. The Rh—P distance of 2.231 (1) Å is within the range 2.232 (2)–2.245 (2) Å

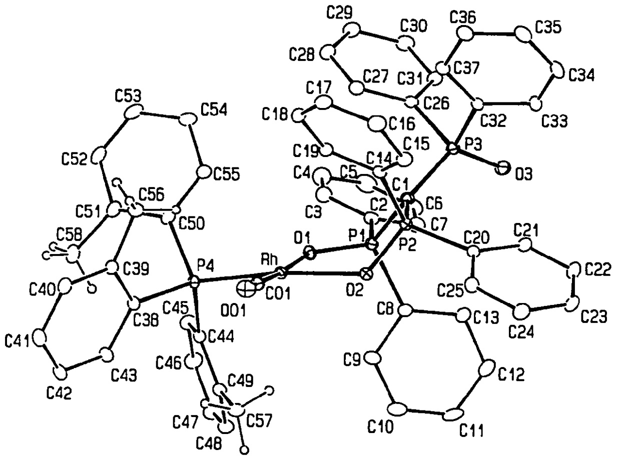


Fig. 1. The molecular structure of the title complex showing 50% probability ellipsoids. Phenyl ring H atoms are omitted for clarity.

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found for carbonyltriphenylphosphinerhodium(I) complexes containing exclusively oxygen donor atoms in the bidentate ligand (Graham, Lamprecht, Potgieter, Roodt & Leipoldt, 1991). The O1—Rh—O2 ligand bite angle of 84.92 (8)° is relatively small compared to the bite angles found for the sterically more crowded sulfur equivalent, $TrisS_3^-$, which are usually greater than 90° (Browning, Dixon, Hilts, Meanwell & Wang, 1991; Grim & Kettler, 1991). The chelating ligand adopts a distorted boat configuration with P1 and O2 at the prows. The methine C atom C1 displays sp^2 character and is displaced by only 0.139 (3) Å from the plane formed by P1, P2 and P3, but the chelate-ring angle P1—C1—P2 deviates significantly from 120°. This indicates that the two coordinating arms of the ligand are 'pulled together' on coordination to the metal, a phenomenon which has also been observed for $[Rh(CO)(PPh_3)(TrisS_3)].Me_2CO$ (Smit, Basson, Roodt & Steynberg, 1994).

Experimental

$[Rh(cod)(TrisO_3)]$ (cod = cyclooctadiene) (Tanke & Crabtree, 1990) was dissolved in tetrahydrofuran and CO gas bubbled through the solution. To the $[Rh(CO)_2(TrisO_3)]$ that formed *in situ* was added 1.1 equivalents of tris(*o*-tolyl)phosphine. The title compound (I) was obtained by the addition of hexane. Crystals were obtained from a saturated nitromethane solution at 293 K. The density D_m was measured by flotation in aqueous NaI.

Crystal data

$[Rh(C_{37}H_{30}P_3O_3)(C_{21}H_{21}P)(CO)]$
$M_r = 1050.78$
Triclinic
$P\bar{1}$
$a = 11.069\,(2)$ Å
$b = 14.426\,(3)$ Å
$c = 16.561\,(4)$ Å
$\alpha = 81.64\,(2)°$
$\beta = 105.19\,(2)°$
$\gamma = 94.05\,(2)°$
$V = 2523.5\,(9)$ Å^3
$Z = 2$
$D_x = 1.383$ Mg m^{-3}
$D_m = 1.372$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 30–40°$
$\mu = 4.309$ mm^{-1}
$T = 293\,(2)$ K
Rectangular
0.44 × 0.12 × 0.10 mm
Yellow

Data collection

Syntex $P\bar{1}$ diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*CSD*; Akselrud, Grin, Zavalii, Pecharsky & Fundamensky, 1989)
$T_{min} = 0.379$, $T_{max} = 0.703$
6574 measured reflections
6574 independent reflections

6471 observed reflections $[I > 2\sigma(I)]$
$\theta_{max} = 57.46°$
$h = 0 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 17$
3 standard reflections monitored every 100 reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.0359$
$wR(F^2) = 0.0973$
$S = 1.044$
6471 reflections
617 parameters
H atoms treated using a riding model with an overall $U_{iso} = 0.084\,(2)$ Å^2

$w = 1/[\sigma^2(F_o^2) + (0.0700P)^2 + 1.2000P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.335$
$\Delta\rho_{max} = 0.82$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
Rh	0.57963 (2)	0.68356 (2)	0.35755 (1)	0.04101 (11)
P1	0.30729 (7)	0.75807 (6)	0.26057 (5)	0.0446 (2)
P2	0.40306 (7)	0.62349 (6)	0.18377 (5)	0.0434 (2)
P3	0.22506 (8)	0.77651 (6)	0.06800 (5)	0.0494 (2)
P4	0.68375 (7)	0.77468 (5)	0.45275 (5)	0.0417 (2)
O1	0.4321 (2)	0.7751 (2)	0.32352 (14)	0.0506 (5)
O2	0.4576 (2)	0.59794 (14)	0.27820 (13)	0.0463 (5)
O3	0.0876 (2)	0.7575 (2)	0.0535 (2)	0.0649 (7)
C01	0.7069 (3)	0.6076 (2)	0.3755 (2)	0.0497 (8)
O01	0.7851 (3)	0.5567 (2)	0.3811 (2)	0.0792 (8)
C1	0.3199 (3)	0.7258 (2)	0.1650 (2)	0.0459 (7)
C2	0.2234 (3)	0.8656 (2)	0.2440 (2)	0.0526 (8)
C3	0.2919 (4)	0.9477 (3)	0.2625 (3)	0.0675 (10)
C4	0.2316 (5)	1.0305 (3)	0.2532 (3)	0.0899 (14)
C5	0.1028 (6)	1.0315 (4)	0.2275 (3)	0.095 (2)
C6	0.0350 (5)	0.9511 (4)	0.2099 (3)	0.0844 (13)
C7	0.0931 (4)	0.8679 (3)	0.2181 (3)	0.0673 (10)
C8	0.2175 (3)	0.6701 (2)	0.3114 (2)	0.0501 (8)
C9	0.2560 (4)	0.6466 (3)	0.3980 (2)	0.0613 (9)
C10	0.1913 (5)	0.5790 (3)	0.4384 (3)	0.0752 (12)
C11	0.0878 (5)	0.5349 (3)	0.3943 (3)	0.0820 (14)
C12	0.0463 (4)	0.5581 (3)	0.3079 (3)	0.0807 (13)
C13	0.1120 (3)	0.6259 (3)	0.2658 (3)	0.0644 (10)
C14	0.5342 (3)	0.6366 (2)	0.1361 (2)	0.0470 (7)
C15	0.5627 (4)	0.5736 (3)	0.0891 (2)	0.0625 (9)
C16	0.6737 (4)	0.5842 (3)	0.0641 (3)	0.0763 (12)
C17	0.7584 (4)	0.6555 (3)	0.0877 (3)	0.0751 (12)
C18	0.7315 (4)	0.7190 (3)	0.1347 (2)	0.0680 (10)
C19	0.6199 (3)	0.7101 (3)	0.1575 (2)	0.0570 (9)
C20	0.3109 (3)	0.5194 (2)	0.1519 (2)	0.0491 (8)
C21	0.1895 (4)	0.5215 (3)	0.1042 (2)	0.0668 (10)
C22	0.1224 (4)	0.4379 (3)	0.0885 (3)	0.0869 (14)
C23	0.1754 (4)	0.3534 (3)	0.1201 (3)	0.0792 (12)
C24	0.2965 (4)	0.3507 (3)	0.1690 (3)	0.0738 (11)
C25	0.3638 (4)	0.4334 (3)	0.1843 (2)	0.0628 (9)
C26	0.2617 (3)	0.9016 (2)	0.0568 (2)	0.0516 (8)
C27	0.3805 (3)	0.9391 (3)	0.0862 (2)	0.0611 (9)
C28	0.4051 (4)	1.0342 (3)	0.0749 (3)	0.0739 (12)
C29	0.3103 (4)	1.0939 (3)	0.0344 (3)	0.0792 (12)
C30	0.1919 (4)	1.0580 (3)	0.0039 (3)	0.0839 (13)
C31	0.1679 (4)	0.9625 (3)	0.0146 (3)	0.0690 (11)
C32	0.2765 (3)	0.7373 (2)	−0.0168 (2)	0.0513 (8)
C33	0.1928 (4)	0.6829 (3)	−0.0702 (2)	0.0693 (10)
C34	0.2235 (5)	0.6528 (3)	−0.1374 (3)	0.0817 (13)
C35	0.3376 (5)	0.6771 (3)	−0.1524 (3)	0.0766 (12)
C36	0.4214 (4)	0.7319 (3)	−0.1018 (3)	0.0735 (11)
C37	0.3911 (3)	0.7617 (3)	−0.0340 (2)	0.0619 (9)
C38	0.8387 (3)	0.7437 (2)	0.5212 (2)	0.0441 (7)
C39	0.9432 (3)	0.7443 (2)	0.4877 (2)	0.0465 (7)
C40	1.0583 (3)	0.7220 (2)	0.5442 (2)	0.0583 (9)
C41	1.0719 (3)	0.7007 (3)	0.6292 (3)	0.0659 (10)
C42	0.9707 (4)	0.7011 (3)	0.6618 (2)	0.0661 (10)
C43	0.8544 (3)	0.7226 (2)	0.6084 (2)	0.0552 (8)
C44	0.5842 (3)	0.7792 (2)	0.5247 (2)	0.0453 (7)

C45	0.5398 (3)	0.8649 (3)	0.5317 (2)	0.0601 (9)
C46	0.4603 (4)	0.8705 (3)	0.5823 (3)	0.0764 (12)
C47	0.4216 (4)	0.7908 (3)	0.6254 (3)	0.0730 (11)
C48	0.4615 (3)	0.7059 (3)	0.6178 (2)	0.0613 (9)
C49	0.5435 (3)	0.6968 (2)	0.5686 (2)	0.0487 (8)
C50	0.7141 (3)	0.8953 (2)	0.4052 (2)	0.0492 (8)
C51	0.7871 (3)	0.9648 (2)	0.4486 (3)	0.0568 (9)
C52	0.8204 (4)	1.0454 (3)	0.4002 (3)	0.0734 (12)
C53	0.7825 (4)	1.0583 (3)	0.3143 (4)	0.0797 (13)
C54	0.7060 (4)	0.9927 (3)	0.2717 (3)	0.0733 (11)
C55	0.6726 (3)	0.9117 (3)	0.3179 (2)	0.0590 (9)
C56	0.9394 (3)	0.7715 (3)	0.3957 (2)	0.0598 (9)
C57	0.5803 (4)	0.5997 (2)	0.5647 (2)	0.0643 (10)
C58	0.8314 (4)	0.9598 (3)	0.5425 (3)	0.0778 (12)

Table 2. *Selected geometric parameters* (Å, °)

Rh—C01	1.783 (3)	P2—O2	1.521 (2)
Rh—O1	2.082 (2)	P2—C1	1.742 (3)
Rh—O2	2.094 (2)	P3—O3	1.489 (2)
Rh—P4	2.2313 (10)	P3—C1	1.761 (3)
P1—O1	1.526 (2)	C01—O01	1.151 (4)
P1—C1	1.755 (3)		
C01—Rh—O1	174.02 (12)	O3—P3—C1	116.56 (15)
C01—Rh—O2	92.70 (12)	P1—O1—Rh	124.27 (13)
O1—Rh—O2	84.92 (8)	P2—O2—Rh	125.43 (12)
C01—Rh—P4	93.69 (11)	O01—C01—Rh	174.8 (3)
O1—Rh—P4	89.38 (7)	P2—C1—P1	110.2 (2)
O2—Rh—P4	170.38 (6)	P2—C1—P3	127.1 (2)
O1—P1—C1	114.76 (14)	P1—C1—P3	120.7 (2)
O2—P2—C1	109.71 (14)		

Data collection and cell refinement: Syntex $P\bar{1}$ software. Structure solution: *SHELXS*86 (Sheldrick, 1990) to obtain the position of the heavy atom and *SHELXL*93 (Sheldrick, 1993) to solve the structure *via* successive Fourier maps. Structure refinement: *SHELXS*86. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and least-squares-planes data have been deposited with the IUCr (Reference: MU1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Dinuclear Palladium Compound, [$Pd_2(PPh_3)_2(SC_2H_4S)_2$]

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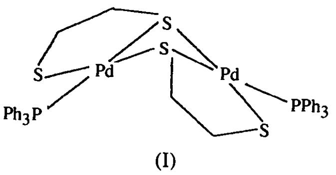
(*Received* 18 *August* 1994; *accepted* 23 *December* 1994)

Abstract

The title compound, bis(μ-1,2-ethanedithiolato-S,S':S)-bis[(triphenylphosphine)palladium(II)], is a dimer where the Pd atoms are linked by two S atoms, one from each $SC_2H_4S^{2-}$ ligand; each Pd atom is four-coordinate (one P and three S atoms) with a distorted square-planar geometry. The Pd···Pd distance is 3.038 (2) Å, and the average Pd—S and Pd—P distances are 2.332 (5) and 2.281 (5) Å, respectively.

Comment

The nickel group compounds with mixed sulfur and phosphine ligands have attracted attention because of their relevance and importance to a wide variety of chemical and industrial systems. Up to now, some dinuclear compounds with mixed thiolate and phosphine ligands, such as [$Pd_2(SC_6F_5)_2(PPh_3)_2$] (Fenn & Segrott, 1972), [$Pt_2(SCH_2Ph)_4(PMePh_2)_2$] (Bird, Siriwardane, Lai & Shaver, 1982) and [$\{Pt_2(SCH_2CH_2CMe{=}CH_2)_2\}_2(PPh_3)_2I_2$] (Abel *et al.*, 1990), have been structurally characterized. We have recently reported dinickel compounds: [$Ni_2(PPh_3)_2(SC_2H_4S)_2$] (Cao, Huang, Lei, Hong & Liu, 1992) and [$Ni_2(PPh_3)_2(SC_3H_6S)_2$] (Cao, Huang, Lei, Kang, Hong & Liu, 1992). Here, we report the crystal structure of [$Pd_2(PPh_3)_2(SC_2H_4S)_2$], (I), which is isomorphic with [$Ni_2(PPh_3)_2(SC_2H_4S)_2$] and consists of two palladium quadrilaterals sharing a common edge.



(I)

The two Pd atoms are bridged by two S atoms, one from each $SCH_2CH_2S^{2-}$ ligand. Each Pd atom is surrounded by one P and three S atoms in an approximately square-planar arrangement. Fig. 1 shows the structure with the atomic numbering scheme.