FRENZ, B. A. (1985). *Structure Determination Package.* College Station, Texas 77840, USA, and Enraf–Nonius, Delft, The Netherlands, revised locally by Dr F. J. HOLLANDER.

IBERS, J. A. & SNYDER, R. G. (1962). *Acta Cryst.* **15**, 923–930.

International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

OBERHANSLI, W. & DAHL, L. F. (1965). *Inorg. Chem.* **4**, 150–157.

PICKARDT, J. & STÜHLER, H. O. (1980). *Chem. Ber.* **113**, 1623–1626.

STÜHLER, H. O. & PICKARDT, J. (1981). *Z. Naturforsch. Teil B*, **36**, 315–321.

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Structure of (α–2-η-Benzyl)(*P,P,P′,P′*-tetra-*tert*-butylethylenebisphosphine)rhodium(I)

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Abstract. $[\mathrm{Rh(C_7H_7)(C_{18}H_{40}P_2)}]$, $M_r = 512\cdot50$, triclinic, $P\bar{1}$, $a = 9\cdot5973\,(8)$, $b = 10\cdot4471\,(15)$, $c = 14\cdot3667\,(15)$ Å, $\alpha = 88\cdot46\,(1)$, $\beta = 83\cdot92\,(1)$, $\gamma = 67\cdot95\,(1)°$, $V = 1327\cdot5\,(3)$ Å^3, $Z = 2$, $D_m = 1\cdot29$, $D_x = 1\cdot283$ g cm^{-3}, Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å), $\mu = 7\cdot59$ cm^{-1}, $F(000) = 544$, $T = 295$ K, $R = 0\cdot022$, $wR = 0\cdot033$ for 3152 independent reflections with $F_o > 3\sigma(F_o)$. The Rh atom is in a distorted square-planar environment in which two coordination sites are occupied by an allylic bond to the benzyl ligand. The benzyl ligand is unsymmetrically bound: the Rh—C(6) and Rh—C(7) distances are 2·371 (2) and 2·162 (2) Å, respectively. The non-allylic portion of the ligand exhibits the expected bond-length alternation.

Introduction. The title compound, $[(\eta^3\text{-}\mathrm{C_6H_5CH_2})\mathrm{Rh}\{(\{(\mathrm{CH_3})_3\mathrm{C}\}_2\mathrm{P})_2\mathrm{C_2H_4}\}]$, is the product of the reaction of $[(\mu\text{-}\mathrm{Cl})\mathrm{Rh}\{(\{(\mathrm{CH_3})_3\mathrm{C}\}_2\mathrm{P})_2\mathrm{C_2H_4}\}]_2$ and benzyllithium. The fluxional nature of the product in solution is confirmed by the equivalence of the two *ortho* and *meta* C atoms in the ^{13}C NMR spectrum (Del Paggio, 1986; Del Paggio, Andersen & Muetterties, 1987). In this crystal structure determination, the title compound is shown to be an approximately square-planar complex. The diene-like bond-length alternation between those C atoms not involved in allylic bonding is consistent with a simple resonance model of ligand bonding and is typical of η^3-benzyl complexes (Cotton & LaPrade, 1968; Behrens & Weiss, 1975; Becker & Stille, 1978; Sonada, Bailey & Maitlis, 1979).

Experimental. The complex $[(\eta^3\text{-}\mathrm{C_6H_5CH_2})\mathrm{Rh}\{(\{(\mathrm{CH_3})_3\mathrm{C}\}_2\mathrm{P})_2\mathrm{C_2H_4}\}]$, prepared as described previously (Del Paggio, 1986; Del Paggio, Andersen & Muetterties, 1987), was crystallized from pentane. The density was measured by flotation in $\mathrm{CH_3CN/H_2O/KI}$. An orange parallelepiped crystal measuring $0\cdot45 \times 0\cdot25 \times 0\cdot15$ mm was mounted in a 0·3 mm quartz capillary under argon. Data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Accurate cell dimensions and orientation matrix were obtained by centering 24 reflections (12 Friedel pairs) with $27 \le 2\theta \le 30°$. 3791 reflections were collected, of which 3463 were independent and 3152 were observed based on $I > 3\sigma(I)$. The θ–2θ scan mode was used ($3 \le 2\theta \le 45°$) and the index ranges were $0 \le h \le 10$, $-11 \le k \le 11$, and $-15 \le l \le 15$. Intensity checks every 2 h on three standard reflections indicated no significant decay. ψ scans on four reflections yielded an average maximum variation in intensity of 3·2%; thus, no absorption correction was applied.

The data were reduced and the structure solved using the *Enraf–Nonius Structure Determination Package* (Frenz, 1985). The structure was refined in space group $P\bar{1}$; initial positions of the Rh and two P atoms were determined from a three-dimensional Patterson map. H atoms (not refined) were included at idealized positions with a C—H distance of 0·95 Å and with isotropic thermal parameters set at 1·3 times those of the corresponding C atom. Full-matrix least-squares refinement of positional and anisotropic thermal parameters of non-H atoms converged at $R = 0\cdot022$, $wR = 0\cdot033$ and $S = 1\cdot813$. A secondary-extinction parameter was not included in final refinements. The function mini-

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mized was $\sum w||F_o| - |F_c||^2$ where $w = 1/\sigma^2(F_o)$ and $\sigma^2(F_o) = [\sigma^2(I) + (pF_o^2)^2]/2F_o^2$. A value of $p = 0{\cdot}03$ was chosen to prevent overweighting of strong reflections. In the final difference Fourier map $(\Delta\rho)_{max} = 0{\cdot}32$ and $(\Delta\rho)_{min} = -0{\cdot}30$ e Å^{-3}. Max. $\Delta/\sigma = 0{\cdot}03$. 253 variables were refined.* Atomic scattering factors are taken from *International Tables for X-ray Crystallography* (1974).

Table 1. *Positional parameters and their e.s.d.'s*

	x	*y*	*z*	*B**(Å^2)
Rh	0·14655 (2)	−0·05049 (2)	−0·23023 (1)	2·792 (4)
P(1)	0·20520 (6)	0·13972 (6)	−0·22157 (4)	2·85 (1)
P(2)	0·39204 (7)	−0·17768 (6)	−0·24018 (4)	2·95 (1)
C(1)	−0·0517 (3)	−0·0914 (3)	−0·2645 (2)	4·21 (6)
C(2)	−0·0825 (3)	−0·0726 (3)	−0·3600 (2)	5·52 (8)
C(3)	−0·1798 (3)	0·0470 (4)	−0·3903 (2)	6·86 (9)
C(4)	−0·2554 (3)	0·1609 (4)	−0·3294 (3)	6·73 (9)
C(5)	−0·2251 (3)	0·1491 (3)	−0·2379 (3)	6·06 (9)
C(6)	−0·1205 (3)	0·0257 (3)	−0·2050 (2)	4·53 (7)
C(7)	0·0592 (3)	−0·2133 (3)	−0·2318 (2)	4·80 (7)
C(8)	0·4968 (3)	−0·0660 (3)	−0·2165 (2)	3·58 (6)
C(9)	0·4138 (3)	0·0833 (2)	−0·2433 (2)	3·48 (6)
C(10)	0·1589 (3)	0·2276 (3)	−0·1018 (2)	4·14 (6)
C(11)	0·1915 (4)	0·3596 (3)	−0·0967 (2)	5·61 (8)
C(12)	0·2552 (4)	0·1232 (3)	−0·0348 (2)	5·29 (8)
C(13)	−0·0083 (4)	0·2577 (4)	−0·0668 (2)	5·87 (8)
C(14)	0·1409 (3)	0·2808 (2)	−0·3127 (2)	3·55 (6)
C(15)	−0·0212 (4)	0·3796 (3)	−0·2864 (2)	5·42 (8)
C(16)	0·1427 (3)	0·2066 (3)	−0·4042 (2)	4·47 (7)
C(17)	0·2423 (3)	0·3635 (3)	−0·3322 (2)	4·92 (7)
C(18)	0·4802 (3)	−0·2555 (3)	−0·3604 (2)	3·93 (6)
C(19)	0·6448 (4)	−0·3568 (3)	−0·3661 (2)	6·09 (9)
C(20)	0·4722 (3)	−0·1355 (3)	−0·4251 (2)	4·78 (7)
C(21)	0·3831 (4)	−0·3265 (3)	−0·3997 (2)	5·84 (8)
C(22)	0·4603 (3)	−0·3187 (3)	−0·1500 (2)	4·06 (6)
C(23)	0·6289 (4)	−0·3683 (3)	−0·1372 (2)	5·40 (8)
C(24)	0·3722 (4)	−0·2557 (3)	−0·0560 (2)	5·44 (8)
C(25)	0·4219 (4)	−0·4420 (3)	−0·1727 (3)	6·18 (8)

* The thermal parameter given for anisotropically refined atoms is the equivalent isotropic thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$, where *a, b, c* are real-cell parameters and *B(i,j)* are anisotropic betas.

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and torsional angles* (°)

Rh—P(1)	2·269 (1)	P(1)—Rh—P(2)	88·23 (2)
Rh—P(2)	2·219 (1)	P(1)—Rh—C(6)	106·72 (5)
Rh—C(1)	2·208 (2)	P(1)—Rh—C(7)	172·15 (6)
Rh—C(6)	2·371 (2)	P(2)—Rh—C(6)	163·80 (6)
Rh—C(7)	2·162 (2)	P(2)—Rh—C(7)	99·36 (6)
C(1)—C(2)	1·427 (3)	C(6)—Rh—C(7)	65·51 (8)
C(2)—C(3)	1·344 (4)	C(2)—C(1)—C(7)	123·0 (2)
C(3)—C(4)	1·405 (4)	C(6)—C(1)—C(7)	120·0 (2)
C(4)—C(5)	1·371 (4)	C(1)—C(2)—C(3)	121·7 (2)
C(5)—C(6)	1·410 (3)	C(2)—C(3)—C(4)	121·6 (2)
C(1)—C(7)	1·427 (3)	C(3)—C(4)—C(5)	118·7 (2)
C(1)—C(6)	1·413 (3)	C(4)—C(5)—C(6)	120·8 (2)
		C(1)—C(6)—C(5)	120·6 (2)

P(2)	Rh	P(1)	C(9)	7·36 (9)	Rh	P(1)	C(9)	C(8)	−26·9 (2)
P(1)	Rh	P(2)	C(8)	9·15 (9)	Rh	P(2)	C(8)	C(9)	−28·1 (2)
P(2)	C(8)	C(9)	P(1)	35·3 (2)					

Discussion. The final atomic coordinates are listed in Table 1 and selected bond distances and angles are given in Table 2. Fig. 1 is a view of the molecule showing the atomic numbering scheme.

The 16-electron Rh^{I} (d^8) complex exhibits pseudo-square-planar geometry with two adjacent coordination sites occupied by the allylic ligand. The P(1)—Rh—P(2) angle is close to the ideal value of 90°; the small bite of the allylic ligand, however, causes distortion of the remaining angles. There is a dihedral angle of 6° between the planes defined by Rh—P(1)—P(2) and Rh—C(6)—C(7), and the Rh atom itself is 0·075 Å above the P(1)—P(2)—C(6)—C(7) least-squares plane. In addition, P(1) and C(7) are above this plane, while P(2) and C(6) are located below the plane. These features indicate that the deviation from planarity in this molecule involves both bending and twisting at the Rh center.

Rh bonding to (η^3-$C_6H_5CH_2$) is not completely symmetrical. The Rh—C(6) distance is 0·209 Å longer than Rh—C(7), which is consistent with the difference in electron densities on C(6) and C(7) as determined by extended Hückel molecular-orbital calculations (Bleeke, Burch, Coulman & Schardt, 1981). This bond-length difference is comparable to the 0·21 Å difference between analogous bonds found in $[(\eta^3\text{-}CH_3C_6H_4\text{-}CH_2)Mo(C_5H_5)(CO)_2]$ (Cotton & La Prade, 1968), but it is significantly less than the 0·325 Å difference found in $[\{\eta^3\text{-}(CH_3)_5C_6CH_2\}Rh(P\{OCH(CH_3)_2\}_3)_2]$ (Burch, Muetterties & Day, 1982) and the 0·372 Å difference found in $[(\eta^3\text{-}C_6H_5CH_2)Co\{P(OCH_3)_3\}_3]$ (Bleeke, Burch, Coulman & Schardt, 1981). In addition, the Rh—P bond *trans* to C(7) [Rh—P(1)] is slightly longer (0·050 Å) than that *trans* to C(6) [Rh—P(2)], as is the case with $[\{\eta^3\text{-}(CH_3)_5C_6CH_2\}Rh(P\{OCH(CH_3)_2\}_3)_2]$.

The benzyl ligand itself exhibits an 'allyl-diene' distortion which has been observed in similar complexes

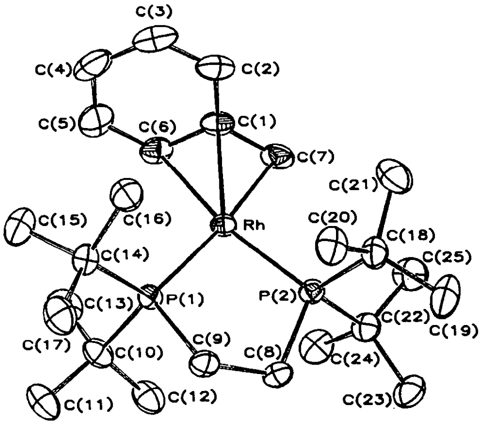

Fig. 1. Molecular structure of $[(\eta^3\text{-}C_6H_4CH_2)\text{-}Rh\{(\{(CH_3)_3C\}_2P)_2C_2H_4\}]$ showing the atomic numbering scheme. Ellipsoids represent 30% probability surfaces.

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* 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 44316 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Cotton & LaPrade, 1968; Behrens & Weiss, 1975; Becker & Stille, 1978; Sonada, Bailey & Maitlis, 1979). The C(2)—C(3) and C(4)—C(5) bond lengths are significantly shorter than the remainder of the C—C distances in the ligand, suggesting the double-bond localization of a diene. The difference between the averages of longer and shorter bond lengths is 0·058 Å for $[(\eta^3\text{-}C_6H_5CH_2)Rh\{(\{(CH_3)_3C\}_2P)_2C_2H_4\}]$; on this basis, the magnitude of the 'allyl-diene' distortion is comparable to that observed in $[\{\eta^3\text{-}(CH_3)_5C_6CH_2\}\text{-}Rh(P\{OCH(CH_3)_2\}_3)_2]$ (0·055 Å), $[(\eta^3\text{-}C_6H_5CH_2)Co\text{-}\{P(OCH_3)_3\}_3]$ (0·057 Å), and $[\{\eta^3\text{-}C_6H_5CH(C_2H_5)\}\text{-}Rh(1,5\text{-cyclooctadiene})]$ (0·065 Å) (Stuhler & Pickardt, 1981). The η^3 coordination of the benzyl ligand in solution and the fluxionality of the complex have been established by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectroscopy (Del Paggio, 1986; Del Paggio, Andersen & Muetterties, 1987).

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References

Becker, Y. & Stille, J. K. (1978). *J. Am. Chem. Soc.* **100**, 845–850.

Behrens, U. & Weiss, E. (1975). *J. Organomet. Chem.* **96**, 399–433, 435–450.

Bleeke, J. R., Burch, R. R., Coulman, C. L. & Schardt, B. C. (1981). *Inorg. Chem.* **20**, 1316–1318.

Burch, R. R., Muetterties, E. L. & Day, V. W. (1982). *Organometallics*, **1**, 188–197.

Cotton, F. A. & LaPrade, M. D. (1968). *J. Am. Chem. Soc.* **90**, 5418–5422.

Del Paggio, A. A. (1986). PhD thesis, Univ. of California, Berkeley, CA 94720, USA.

Del Paggio, A. A., Andersen, R. A. & Muetterties, E. L. (1987). *Inorg. Chem.* In the press.

Frenz, B. A. (1985). *Enraf–Nonius Structure Determination Package*. College Station, TX, USA and Enraf–Nonius, Delft, The Netherlands. Revised locally by Dr F. J. Hollander.

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

Sonada, A. Bailey, P. M. & Maitlis, P. M. (1979). *J. Chem. Soc. Dalton Trans.* pp. 346–350.

Stuhler, H. D. & Pickardt, H. (1981). *Z. Naturforsch. Teil B*, **36**, 315–321.

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Monoclinic and Triclinic Forms of [1,2-Bis(diphenylphosphino)propane](η^6-methyldiphenylphosphine)(methyldiphenylphosphine)molybdenum(0) Benzene Solvate

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Abstract. $[Mo(C_{13}H_{13}P)_2(C_{27}H_{26}P_2)]_2.C_6H_6$, $M_r = 1895·8$, triclinic, $P\bar{1}$, $a = 13·808\ (2)$, $b = 15·860\ (3)$, $c = 23·315\ (5)$ Å, $\alpha = 103·18\ (2)$, $\beta = 102·45\ (1)$, $\gamma = 96·79\ (1)°$, $U = 4779\ (4)$ Å^3, $Z = 2$, $D_x = 1·317$ Mg m^{-3}, $\mu(Mo\ K\alpha) = 0·43$ mm^{-1}, $F(000) = 1972$, $T = 298$ K, $R = 0·081$ for 6515 observed $[I > 3\sigma(I)]$ reflections. $[Mo(C_{13}H_{13}P)_2(C_{27}H_{26}P_2)].C_6H_6$, $M_r = 987·0$, monoclinic, $P2_1/a$, $a = 19·165\ (9)$, $b = 13·154\ (10)$, $c = 20·195\ (9)$ Å, $\beta = 105·09\ (4)°$, $U = 4916\ (9)$ Å^3, $Z = 4$, $D_x = 1·333$ Mg m^{-3}, $\mu(Mo\ K\alpha) = 0·43$ mm^{-1}, $F(000) = 2056$, $T = 298$ K, $R = 0·093$ for 2268 observed $[I > 3\sigma(I)]$ reflections. The triclinic form contains two independent molecules in the asymmetric unit. One molecule has the configurations *S*(*exo*-P), *S*(prophos) and the other *S*(*exo*-P), *R*(prophos) for the phosphine ligands. Thus all possible combinations of the possible configurations of the phosphine ligands (*SS*, *RR*, *RS* and *SR*) are present in the centrosymmetric unit cell. There is one molecule of benzene solvent in the asymmetric unit. In the asymmetric unit of the monoclinic form the molecule has the configurations *S*(*exo*-P), *S*(prophos) and the unit cell contains only *SS* and *RR* molecules. There is one molecule of benzene solvent per Mo in this form.

Introduction. Formation of η^6-arylphosphine molybdenum complexes is thought to occur *via* an intramolecular σ to π rearrangement of an octahedral disolvated tetraphosphine molybdenum intermediate (Frizzell, Luck, Morris & Peng, 1985). In the series of compounds $[Mo(\eta^6\text{-}PhPMePh)(P\text{—}P)(PMePh_2)]$ (P—P = chelating diphosphine) the dangling P atom of the

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