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Alkyl and Aryl Compounds of Iridium and Rhodium. XX [1]. Preparation and Characterization of Mesitylbis(trimethylphosphite)triphenylphosphinerhodium(I) and Mesityltris(trimethylphosphite)rhodium(I)

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The reaction of $Rh(2,4,6\text{-}Me_3C_6H_2)(CO)(PPh_3)_2$ *with* $P(OMe)_3$ *gave* cis-$Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_2(PPh_3)$ *(***I***) and* $Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_3$ *(***II***). Crystals of* **I** *are triclinic, space group* $P\bar{1}$, *with* $a = 982.2(5)$, $b = 1026.9(7)$, $c = 1868.3(11)$ *pm*, $\alpha = 81.61(5)$, $\beta = 78.62(5)$, $\gamma = 73.37(5)°$, *and* $Z = 2$. *The structure was solved from diffractometer data by the heavy-atom method and anisotropically refined by block-matrix least-squares procedures to* $R = 0.046$ $(R_w = 0.053)$ *for 4930 unique reflections. Complex* **II** *crystallizes in the monoclinic system, space group* $P2_1/n$, *with* $a = 842.2(4)$, $b = 1759.0(9)$, $c = 1831.1(9)$ *pm*, $\beta = 92.32(5)°$, *and* $Z = 4$. *The structure was solved by Patterson techniques and refined by full-matrix least-squares methods employing a mixed thermal model. The final discrepancy indexes* $R = 0.072$ *and* $R_w = 0.077$ *are based on 4223 independent diffractometer data. The geometry of both* **I** *and* **II** *can be described as planar with a slight distortion to tetrahedral.* $Rh\text{–}P(OMe)_3$ *distances in* **I** *are 222.3(1) (*trans*-ligand* PPh_3*) and 222.1(2) pm, whilst in* **II** $Rh\text{–}P(OMe)_3$ *bonds* trans *to each other are 224.3(2) and 226.5(2) pm, the value of* $d[Rh\text{–}P(OMe)_3]$ trans *to mesityl being 223.4(2) pm. There is no obvious correlation between metal–phosphite bond lengths and* $^1J[Rh\text{–}P(OMe)_3]$ *coupling constants which are 190.9 Hz (*trans*-ligand mesityl) and 280.5 Hz (*trans*-ligand* PPh_3*) in* **I** *and, respectively, 188.4 Hz (*trans*-ligand mesityl) and 250.6 Hz (*trans*-ligand* $P(OMe)_3$*) in* **II**.

Introduction

In a series of previous papers [2–4] we have demonstrated that *ortho*-alkyl substituted iridium aryls $Ir[ArCH_2R\text{-}(2)](CO)(PR_3)_2$ react smoothly with $R_nP(OR)_{3-n}$ ligands to form metallacyclic hydrido complexes of general formula $\overline{IrH[C(O)\text{–}Ar\text{–}C}HR\text{-}(2)][R_nP(OR)_{3-n}]_3$. With the initial objective of extending the scope of this CO-insertion/C–H addition reaction to corresponding organorhodium compounds, we have recently been investigating the $Rh[C_6H_2Me_3\text{-}(2,4,6)](CO)(PPh_3)_2/P(OMe)_3$ system. We did not detect any cyclometallated product, *e.g.* $\overline{RhH[C(O)C_6H_2C}H_2\text{-}(2)\text{-}Me_2\text{-}(4,6)][P(OMe)_3]_3$, but instead obtained and structurally characterized the two phosphite substituted mesityl rhodium(I) species $Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_2(PPh_3)$ (I) and $Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_3$ (II).

Experimental

General Procedures and Instrumentation

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried according to recommended methods and were distilled under nitrogen prior to use.

^{31}P NMR spectra were collected in toluene on a Bruker WH 90 instrument operating at 36.44 MHz. The spectra were referenced to an external H_3PO_4 standard (downfield positive). Calculations of theoretical spectra were performed using the LAOCN3 program [5].

X-ray measurements were made at 20 ± 2 °C on a Syntex $P2_1$ diffractometer.

Preparation of Complexes

Trimethyl phosphite (1.5 ml) was added to a solution of 1.16 g (1.5 mmol) of $Rh(2,4,6\text{-}Me_3C_6H_2)(CO)(PPh_3)_2$ [6] in toluene (15 ml). This mixture was stirred at room temperature for 15 hours and then filtered and concentrated *in vacuo* to give an oily residue which was re-dissolved in hexane (15 ml). Crystallization at 0 °C yielded large white crystals of triphenylphosphine which were removed by filtration.

The filtrate was allowed to stand at −30 °C for several days which caused the separation of 0.72–0.85 g (66–77%) of $Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_3$ (II) as well-shaped yellow prisms. These were col-

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lected by decantation, washed with 2 × 1 ml of cold hexane and dried *in vacuo*.

Small orange crystals of complex **I**, $Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_2(PPh_3)$, were deposited from the concentrated mother liquor upon prolonged standing at −30 °C; yield: 0.09–0.14 g (10–16%).

Anal. Calcd. for $C_{33}H_{44}O_6P_3Rh$ (732.5), **I**: C, 54.11; H, 6.05. Found: C, 54.28; H, 6.09. Calcd. for $C_{18}H_{38}O_9P_3Rh$ (594.3), **II**: C, 36.38; H, 6.44. Found: C, 36.41; H, 6.47.

X-ray Studies

Single crystals of the title compounds, suitable for X-ray work, were grown by re-crystallization of the complexes from hexane. The specimens used had approximate dimensions of 0.1 × 0.1 × 0.1 mm.

Crystal Data

From diffractometry with Mo-Kα radiation (λ = 71.069 pm):

Complex **I**. Triclinic; space group $P\bar{1}$; $a = 982.2(5)$, $b = 1026.9(7)$, $c = 1868.3(11)$ pm, $\alpha = 81.61(5)$, $\beta = 78.62(5)$, $\gamma = 73.37(5)°$, $V = 1762 \times 10^6$ pm^3; $Z = 2$, $D_c = 1.380$ g cm^{-3}; $\mu = 5.84$ cm^{-1}; F(000) = 760.

Complex **II**. Monoclinic; space group $P2_1/n$; $a = 842.2(4)$, $b = 1759.0(9)$, $c = 1831.1(9)$ pm, $\beta = 92.32(5)°$, $V = 2710 \times 10^6$ pm^3; $Z = 4$, $D_c = 1.456$ g cm^{-3}; $\mu = 7.56$ cm^{-1}; F(000) = 1232.

Data Collection

Three dimensional X-ray intensities were measured by the $\theta - 2\theta$ scan technique using graphite-monochromated Mo-Kα radiation. The scan speed was variable depending on the count rate. Two standard intensities were monitored every 98 reflections and showed no significant decrease during data collection. In this way a total of 5758 independent data was collected within the range $2° < 2\theta < 50°$ for complex **I**. Of these, 4930 had $I > 1.96\sigma(I)$ and were considered to be observed. For complex **II**, the intensities of 4786 unique reflections with $3° < 2\theta < 50°$ were measured of which 4223, having $F_o > 3\sigma(F_o)$, were employed in the subsequent analysis. The data were corrected for Lorentz and polarization effects but not for absorption.

Structure Solving and Refinement

The positional parameters of the rhodium atoms were determined by Patterson techniques. Subsequent difference Fourier maps revealed all of the remaining non-hydrogen atoms.

The structural model resulting for **I** was refined by anisotropic block-diagonal least-squares procedures using unit weights. The following final discrepancy indexes were obtained: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o = 0.046$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.053$.

The structure of **II** was refined by full-matrix least-squares methods employing a mixed thermal model with oxygen and carbon isotropic. The ΔF syntheses revealed high temperature factors of the oxygen atoms of the $(MeO)_3P(3)$ ligand, as well as three additional peaks near P(3) which were about half as high as those of the oxygens attached to P(1) and P(2). This fact was attributed to the existence of a two-fold orientational disorder of the P–O–C bonds around the Rh–P(3) axis. Two sets of oxygen positions, O(31), O(32), O(33) and O(31*), O(32*), O(33*), with each pair sharing the same methyl carbon (*cf.* [7]) were therefore introduced, the site occupation factors being compelled to sum unity. Since the population parameters refined to 0.504 and 0.496 for the respective sets, split-atom occupancies fixed at 0.5 were adopted in the final cycles which converged at $R = 0.072$ and $R_w = 0.077$ (w = 1).

All calculations were performed employing the SHELX program system with scattering factors from the sources given therein [8]. Final atomic positions and selected bond lengths and angles are presented in Tables I–III. Listings of thermal parameters and of observed and calculated structure factors are available from the Editor upon request.

TABLE I. Fractional Atomic Coordinates with E.S.D.'s for $Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_2(PPh_3)_2$ (I).

Atom	x/*a*	y/*b*	z/*c*
Rh	0.1043(1)	0.3014(1)	0.2843(1)
P(1)	−0.0201(2)	0.2980(2)	0.3973(1)
P(2)	−0.0615(2)	0.4705(2)	0.2375(1)
P(3)	0.2713(2)	0.2918(2)	0.1764(1)
O(11)	0.0644(5)	0.2670(4)	0.4653(2)
O(12)	−0.1314(5)	0.4395(5)	0.4172(2)
O(13)	−0.1120(5)	0.1881(5)	0.4236(2)
O(21)	−0.2186(5)	0.4488(5)	0.2557(3)
O(22)	−0.0375(6)	0.4902(6)	0.1503(3)
O(23)	−0.1000(6)	0.6257(5)	0.2548(3)
C(1)	0.2459(6)	0.1294(6)	0.3297(3)
C(2)	0.3576(6)	0.1419(6)	0.3635(3)
C(3)	0.4506(7)	0.0276(7)	0.3945(3)
C(4)	0.4356(8)	−0.1028(8)	0.3921(4)
C(5)	0.3268(8)	−0.1184(6)	0.3593(4)
C(6)	0.2326(6)	−0.0024(6)	0.3279(3)
C(7)	0.3796(7)	0.2814(7)	0.3661(3)
C(8)	0.5386(10)	−0.2291(9)	0.4263(5)
C(9)	0.1177(8)	−0.0245(7)	0.2914(4)
C(11)	0.0976(8)	0.1381(8)	0.5102(4)
C(12)	−0.2086(10)	0.4590(9)	0.4923(4)
C(13)	−0.2232(8)	0.1867(9)	0.3841(5)
C(21)	−0.3523(8)	0.5421(10)	0.2603(6)
C(22)	−0.1040(12)	0.6027(11)	0.1042(5)
C(23)	−0.0351(10)	0.6756(8)	0.3016(5)
C(311)	0.4594(6)	0.1960(6)	0.1809(3)
C(312)	0.5680(7)	0.2619(7)	0.1752(4)

(continued on facing page)

TABLE I *(continued)*

Atom	x/*a*	y/*b*	z/*c*
C(313)	0.7079(8)	0.1846(9)	0.1842(5)
C(314)	0.7387(8)	0.0442(10)	0.1984(4)
C(315)	0.6322(8)	−0.0227(7)	0.2035(3)
C(316)	0.4912(7)	0.0534(6)	0.1947(3)
C(321)	0.2389(6)	0.2118(6)	0.1025(3)
C(322)	0.1062(7)	0.1868(7)	0.1075(4)
C(323)	0.0782(9)	0.1245(8)	0.0521(4)
C(324)	0.1867(10)	0.0852(8)	−0.0080(4)
C(325)	0.3189(9)	0.1097(8)	−0.0132(4)
C(326)	0.3469(7)	0.1734(7)	0.0418(3)
C(331)	0.2919(7)	0.4609(6)	0.1350(4)
C(332)	0.2966(9)	0.5005(9)	0.0602(4)
C(333)	0.3101(11)	0.6358(11)	0.0346(6)
C(334)	0.3197(11)	0.7206(10)	0.0834(8)
C(335)	0.3157(10)	0.6789(8)	0.1576(6)
C(336)	0.3004(8)	0.5479(7)	0.1839(4)

TABLE II. Fractional Atomic Coordinates with E.S.D.'s for Rh(2,4,6-$Me_3C_6H_2$)[$P(OMe)_3$]$_3$ (II).

Atom	x/*a*	y/*b*	z/*c*
Rh	0.2885(1)	0.2591(1)	0.5496(1)
P(1)	0.2256(3)	0.1677(1)	0.6306(1)
P(2)	0.2906(3)	0.3498(1)	0.6350(1)
P(3)	0.3861(4)	0.3338(1)	0.4628(1)
O(11)	0.2537(7)	0.0784(3)	0.6150(3)
O(12)	0.3321(7)	0.1729(4)	0.7044(3)
O(13)	0.0460(7)	0.1641(4)	0.6573(4)
O(21)	0.2335(7)	0.4359(4)	0.6163(3)
O(22)	0.4559(8)	0.3778(4)	0.6721(4)
O(23)	0.1849(7)	0.3299(4)	0.7041(3)
O(31)	0.3024(14)	0.4127(6)	0.4445(8)
O(31*)	0.3568(16)	0.4238(5)	0.4664(6)
O(32)	0.4777(13)	0.3030(7)	0.3933(5)
O(32*)	0.2743(16)	0.3279(9)	0.3843(6)
O(33)	0.5572(12)	0.3641(8)	0.5034(7)
O(33*)	0.5533(13)	0.3206(9)	0.4271(8)
C(1)	0.2887(9)	0.1731(4)	0.4689(4)
C(2)	0.1550(10)	0.1604(5)	0.4212(4)
C(3)	0.1557(11)	0.1004(5)	0.3691(5)
C(4)	0.2855(11)	0.0543(5)	0.3643(5)
C(5)	0.4201(10)	0.0654(5)	0.4097(5)
C(6)	0.4196(9)	0.1243(4)	0.4618(4)
C(7)	0.0054(12)	0.2090(6)	0.4249(5)
C(8)	0.2829(13)	−0.0115(6)	0.3073(6)
C(9)	0.5720(11)	0.1351(5)	0.5095(5)
C(11)	0.1419(12)	0.0356(6)	0.5686(6)
C(12)	0.3030(14)	0.1226(7)	0.7669(7)
C(13)	−0.0765(13)	0.2151(6)	0.6324(6)
C(21)	0.0761(14)	0.4445(7)	0.5842(7)
C(22)	0.5828(13)	0.3242(7)	0.6839(6)
C(23)	0.1756(13)	0.3804(6)	0.7677(6)
C(31)	0.3855(14)	0.4721(7)	0.4015(6)
C(32)	0.3637(16)	0.2853(9)	0.3286(8)
C(33)	0.7024(19)	0.3510(11)	0.4675(9)

TABLE III. Selected Bond Lengths (pm) and Angles (°).

Bond	Distance	Atoms	Angle
Rh(2,4,6-$Me_3C_6H_2$)[$P(OMe)_3$]$_2$(PPh_3):			
Rh–P(1)	222.3(1)	P(1)–Rh–P(2)	95.1(1)
Rh–P(2)	222.1(2)	P(1)–Rh–P(3)	169.6(1)
Rh–P(3)	232.9(1)	P(2)–Rh–P(3)	93.9(1)
Rh–C(1)	209.6(5)	P(1)–Rh–C(1)	82.8(1)
		P(2)–Rh–C(1)	174.1(2)
		P(3)–Rh–C(1)	88.7(1)
Rh(2,4,6-$Me_3C_6H_2$)[$P(OMe)_3$]$_3$:			
Rh–P(1)	226.5(2)	P(1)–Rh–P(2)	92.5(1)
Rh–P(2)	223.4(2)	P(1)–Rh–P(3)	169.1(1)
Rh–P(3)	224.3(2)	P(2)–Rh–P(3)	94.9(1)
Rh–C(1)	211.5(7)	P(1)–Rh–C(1)	87.5(2)
		P(2)–Rh–C(1)	179.5(2)
		P(3)–Rh–C(1)	85.0(2)

Results and Discussion

Perspective views of the molecules also defining the atomic numbering schemes used are given in Figs. 1 and 2.

The geometry of both **I** and **II** can be described as planar with a slight distortion to tetrahedral. Thus the *trans*-P–Rh–P angles are reduced to 169.6° in **I** and to 169.1° in **II**. These distortions are, however, smaller than those of [$Rh(PMe_3)_4$]$^+$, RhCl(PMe_3)$_3$, and RhCl(PPh_3)$_3$ in which *trans*-P–Rh–P angles ranging from 148.3 to 164.0° have been observed [10, 11]. In the latter cases, the deviations from the expected planar coordination have been ascribed to intramolecular phosphine repulsions. The smaller extent of tetrahedral distortion found for the

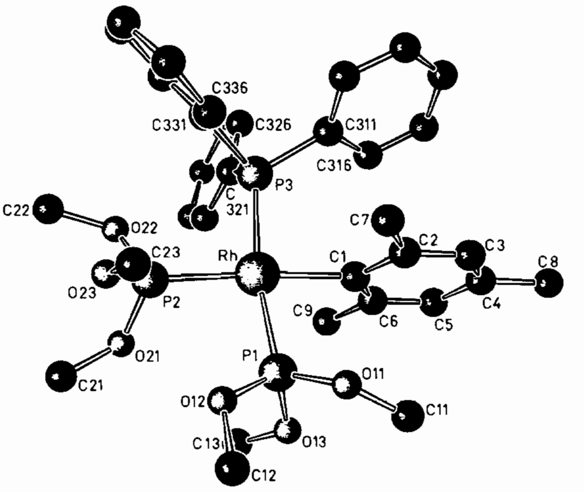

Fig. 1. SCHAKAL [9] computer drawn representation of the *cis*-Rh(2,4,6-$Me_3C_6H_2$)[$P(OMe)_3$]$_2$(PPh_3) molecule.

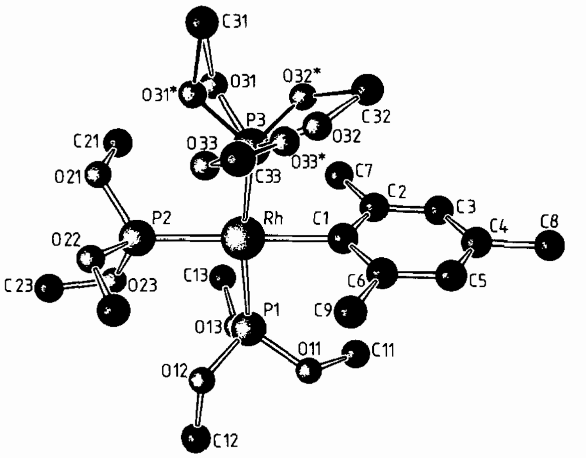

Fig. 2. SCHAKAL plot [9] of the $Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_3$ molecule including the orientational disorder of the P–O–C bonds around the Rh–P(3) axis.

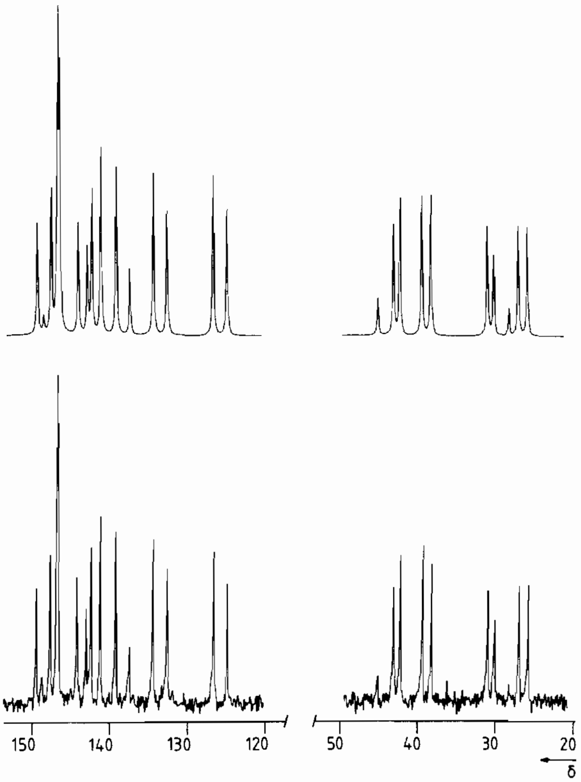

Fig. 3. Below: experimental *ABMX* ^{31}P NMR spectrum of *cis*-$Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_2(PPh_3)$ (P_A *trans* to mesityl, P_B *trans* to PPh_3, $P_M = PPh_3$, $X = {}^{103}Rh$). Above: simulated spectrum; spectral parameters used in calculation are: $\delta(P_A) = 144.9$, $\delta(P_B) = 135.5$, $\delta(P_M) = 35.1$; $^2J(P_AP_B) = 67.7$, $^2J(P_AP_M) = -51.1$, $^2J(P_BP_M) = 461.5$, $^1J(RhP_A) = 190.9$, $^1J(RhP_B) = 280.5$, $^1J(RhP_M) = 146.1$ Hz.

molecules of **I** and **II** may therefore reflect the steric flexibility of the $P(OMe)_3$ ligand which can also be inferred from Tolman's cone angles decreasing in the series $PPh_3 > PMe_3 > P(OMe)_3$ [12].

The rhodium–phosphite distances of **I** and **II** (table III) are considerably longer than those of the dimer $(C_8H_{12})RhCl_2Rh[P(OPh)_3]_2$ (d[Rh–P(OPh)$_3$] = 214.2 pm [13]) in which the *trans*-ligand is a chloride. This bond-lengthening is obviously due to the well-known *trans*-bond weakening influence of C- and P-donor ligands, and a similar effect exerted upon d[M–P(OR)$_3$] has previously been reported for various phosphite complexes of Ir(III) [2, 14–16].

Although the Rh–P(OMe)$_3$ distances of both **I** and **II** do not seem to depend upon the nature of the respective *trans*-ligands (Table III) the $^1J[Rh–P(OMe)_3]$ coupling constants do so to a marked degree. Thus the *ABMX* and *AB*$_2$X ^{31}P NMR spectra of **I** (Fig. 3) and **II** (Fig. 4) afforded $^1J(RhP)$ parameters of 190.9 and 188.4 Hz for the ^{31}P nuclei *trans* to the aryl group, the values of $^1J[Rh–P(OMe)_3]$ in

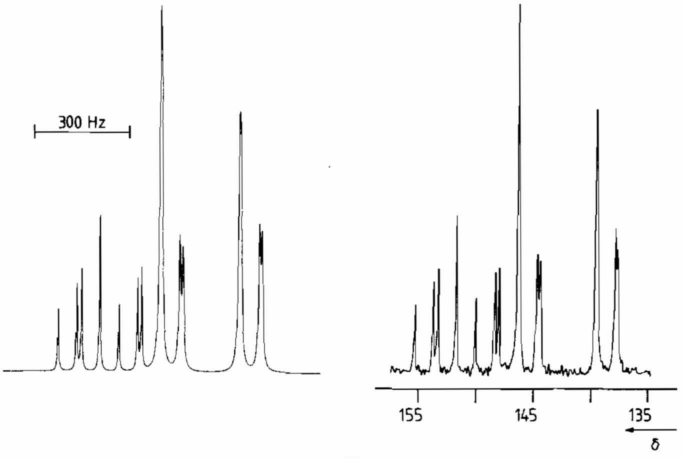

Fig. 4. Right: experimental *AB*$_2$X ^{31}P NMR spectrum of $Rh(2,4,6\text{-}Me_3C_6H_2)[P(OMe)_3]_3$ (P_A *trans* to mesityl, P_B's mutually *trans*, $X = {}^{103}Rh$). Left: simulated spectrum; spectral parameters used in calculation are: $\delta(P_A) = 150.1$, $\delta(P_B) = 142.1$; $^2J(P_AP_B) = 65.6$, $^1J(RhP_A) = 188.4$, $^1J(RhP_B) = 250.6$ Hz.

the *trans*-R–Rh–P moieties being 280.5 Hz (**I**) and 250.6 Hz (**II**). It therefore appears that there is no simple correspondence between d(Rh–P) and ^1J(Rh–P) in these systems. This situation can be compared with results obtained by Muir and co-workers for a series of *cis*-$PtCl_2(PEt_3)L$ complexes in which the ^1J(Pt–P) couplings also bear little relationship to d(Pt–P) distances [17].

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References

1 Part XIX: E. Arpac, F. Mirzaei, A. Yardimcioglu and L. Dahlenburg, *Z. Anorg. All. Chem.*, in press.
2 K. von Deuten and L. Dahlenburg, *Transition Met. Chem., 5,* 222 (1980).
3 L. Dahlenburg and F. Mirzaei, *J. Organomet. Chem., 251,* 103 (1983).
4 L. Dahlenburg, *J. Organomet. Chem., 251,* 215-(1983).
5 S. M. Castellano, in D. F. DeTar (Ed.), 'Computer Programs for Chemistry', Vol. I, p. 10: LAOCN3; Benjamin, New York, 1968.
6 L. Dahlenburg, F. Mirzaei and A. Yardimcioglu, *Z. Naturforsch., 37b,* 310 (1982).
7 R. Uson, P. Lahuerta, J. Reyes, L. A. Oro, C. Foces-Foces, F. H. Cano and S. Garcia-Blanco, *Inorg. Chim. Acta, 42,* 75 (1980).
8 G. Sheldrick, SHELX 76. Program for Crystal Structure Determination, University of Cambridge, England, 1976.
9 E. Keller, SCHAKAL. A FORTRAN Program for Graphic Representations of Molecular Models, University of Freiburg, F.R.G., 1980.
10 M. J. Bennett and P. B. Donaldson, *Inorg. Chem., 16,* 655 (1977).
11 R. A. Jones, F. Mayor Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 511 (1980).
12 C. A. Tolman, *Chem. Rev., 77,* 313 (1977).
13 J. Coetzer and G. Gafner, *Acta Cryst., 826,* 985 (1970).
14 J. M. Guss and R. Mason, *J. Chem. Soc., Dalton Trans.*, 2193 (1972).
15 M. J. Nolte, E. Singleton and E. van der Stok, *J. Organomet. Chem., 142,* 387 (1977).
16 M. J. Nolte, E. Singleton and E. van der Stok, *J. Chem. Soc., Chem. Commun.*, 973 (1978).
17 L. Manojlovic-Muir, K. W. Muir and T. Solomun, *J. Organomet. Chem., 142,* 265 (1977).