Binuclear Pentamethylcyclopentadienyl Dirhodium Complexes with Pyrazolato and Diphenylphosphido Bridging Ligands†

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The reaction of $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-OMe})_2]BF_4$ [L = pyrazolate (pz), 3-methylpyrazolate, 3,5-dimethylpyrazolate or 3(5)-bromo-5(3)-methylpyrazolate] with $HPPh_2$ has been studied. Complexes of general formulae $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-OH})(\mu\text{-PPh}_2)]BF_4$, $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-PPh}_2)_2]BF_4$ and $[\{Rh(C_5Me_5)\}_2(\mu\text{-OH})_2(\mu\text{-PPh}_2)]BF_4$ were prepared and characterized by analytical and spectroscopic means. The crystal structure of $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})(\mu\text{-PPh}_2)_2]BF_4\cdot CHCl_3$ was determined. The rhodium atoms show pseudo-octahedral geometry and are separated by 3.473(1) Å. The μ-hydroxo complexes $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-OH})(\mu\text{-PPh}_2)]BF_4$ react with hydrochloric acid affording the corresponding μ-chloride compounds $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-Cl})(\mu\text{-PPh}_2)]BF_4$, which in turn have been also prepared from $[\{Rh(C_5Me_5)\}_2(\mu\text{-OH})_3]BF_4$, HL, $HPPh_2$ and HCl in 1:1:1:1 ratio. The crystal structure of $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})(\mu\text{-Cl})(\mu\text{-PPh}_2)]BF_4\cdot CHCl_3$ has been determined. Two $(C_5Me_5)Rh$ moieties are connected by three different anionic ligands, pz, Cl and PPh_2. The rhodium atoms are separated by 3.432(1) Å. Aged solutions of reaction mixtures of $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-OMe})_2]BF_4$ and $HPPh_2$ contain $[\{Rh(C_5Me_5)\}_2(\mu\text{-Ph}_2PO_2)_2(\mu\text{-PPh}_2)]BF_4$, the diphenylphosphinato ligands arising from $Ph_2P(O)OH$, an oxidation product of $HPPh_2$. The crystal structure of the solvate has been established. Two Ph_2PO_2 groups and a PPh_2 ligand bridge two $(C_5Me_5)Rh$ units. The rhodium–rhodium distance is 4.049(1) Å. The μ-hydrido complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-H})(\mu\text{-pz})(\mu\text{-PPh}_2)]$ has been prepared by treating $[\{Rh(C_5Me_5)\}_2(\mu\text{-OH})_3]BF_4$ with Hpz and $HPPh_2$ in refluxing propan-2-ol.

During the last decade there has been increasing interest in binuclear transition-metal complexes with organophosphido groups PR_2 as bridging ligands[1] mainly due to their low tendency to fragment into monometallic species and, consequently, to their potential use as bimetallic catalysts.[2] However, the $M\text{–}PR_2\text{–}M$ bridging unit has proved to be less inert than originally expected.[3] Several convenient methods of preparation of this type of complex have been developed.[4] Among them, reactions of lithiated phosphines or lithiated phosphine complexes with transition-metal complexes having halide ligands are the more extensively and successfully used.[5]

With regard to rhodium phosphido chemistry, although a variety of binuclear phosphido-bridged rhodium(I) complexes is known[6] and some diphenyl- and dimethyl-phosphido complexes of rhodium(II) have recently been communicated,[7] as far as we know, the only diphenylphosphidorhodium(III) complexes hitherto reported are $[\{Rh(C_5Me_5)\}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-X})]PF_6$ (X = PPh_2, Cl or SMe), prepared by Klingert and Werner[8] by protonation of the metal–metal bond of the corresponding rhodium(II) precursors with trifluoroacetic acid and the pyrazolato-bridged complexes $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-PPh}_2)_2]BF_4$, $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})_2(\mu\text{-PPh}_2)]BF_4$ and $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-OH})(\mu\text{-PPh}_2)]BF_4$ (L = pyrazolate type ligand), recently reported by us.[9]

On the other hand, we have shown that the tri-μ-hydroxo or tri-μ-methoxo complexes $[(ring)M(\mu\text{-OR})_3M(ring)]^+$ [(ring)M = $(C_5Me_5)Rh$, $(C_5Me_5)Ir$, $(p\text{-Pr}^iC_6H_4Me)Ru$; R = H or Me] react with strong mineral acids, in the presence of neutral ligands L′,[10] or acidic molecules, such as pyrazole-type ligands,[10a,11] affording complexes of general formulae $[(ring)L'M(\mu\text{-OR})_2ML'(ring)]^{2+}$ or $[(ring)M(\mu\text{-OR})_{3-x}(\mu\text{-L}')_xM(ring)]^+$ (x = 1 or 2) by protonation of one or two of the OR groups. Following our interest in this type of reactivity, we have attempted the preparation of μ-phosphido complexes by direct addition of a secondary phosphine to hydroxo- or methoxo-bridged compounds. In the present paper we report the preparation of new $(C_5Me_5)Rh^{III}$ complexes with diphenylphosphido and other anionic bridging ligands such as pyrazolate, hydroxide, chloride or hydride starting from μ-methoxo, $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-OMe})_2]BF_4$, or μ-hydroxo, $[\{Rh(C_5Me_5)\}_2(\mu\text{-OH})_3]BF_4$, complexes. The preparation and crystal structure of the diphenylphosphinato complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-Ph}_2PO_2)_2(\mu\text{-PPh}_2)]BF_4$ as well as the crystal structures of $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})(\mu\text{-PPh}_2)_2]BF_4\cdot CHCl_3$ and $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})(\mu\text{-Cl})(\mu\text{-PPh}_2)]BF_4\cdot CHCl_3$ are also reported.

Results and Discussion

We have recently reported that the reaction of the di-μ-methoxo complexes $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-OMe})_2]BF_4$ [L = pyrazolate (pz), 3-methylpyrazolate (mpz), 3,5-dimethylpyrazolate (dmpz), or 3(5)-bromo-5(3)-methylpyrazolate (bmpz)] with 2 equivalents of $HPPh_2$, in acetone, proceeds to give $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-OH})(\mu\text{-PPh}_2)]BF_4$ **1**–**4** respectively in moderate yield.[9] In this reaction, the di-μ-phosphido complexes $[\{Rh(C_5Me_5)\}_2(\mu\text{-L})(\mu\text{-PPh}_2)_2]BF_4$ (L = pz **5**, mpz **6** or bmpz **7**) were also formed although the dmpz derivative $[\{Rh(C_5Me_5)\}_2(\mu\text{-}$

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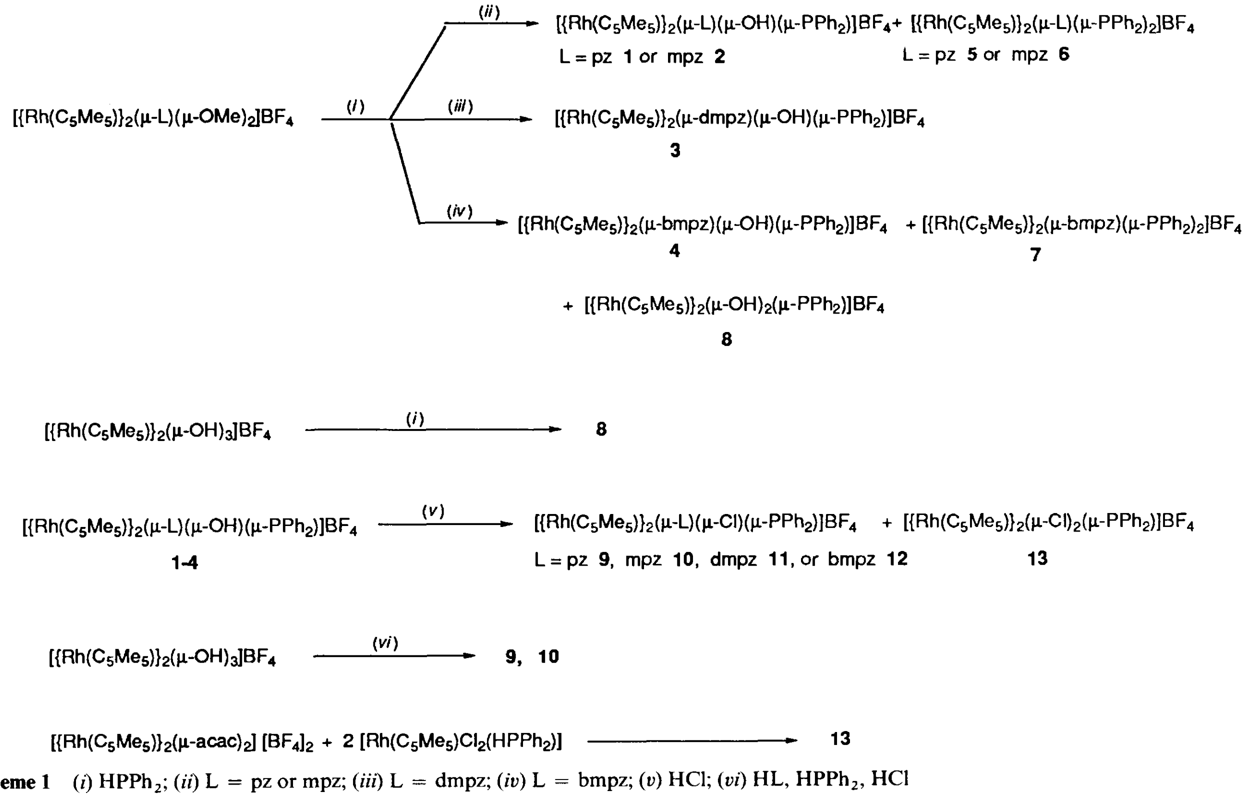
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

dmpz)(μ-PPh_2)$_2$]BF_4 was not detected. Compounds **6** and **7** have only been spectroscopically characterized but **5** could be isolated, by fractional crystallization, as red crystals in *ca.* 20% yield based on rhodium.[9] In particular, the ^1J(RhP) coupling constants for the latter complexes [97 (**5**), 99 (**6**) and 99 (**7**) Hz] are smaller than those found for other (C_5Me_5)Rh^{III} compounds with diphenylphosphide bridging ligands,[7c,9,12] but are comparable to those found for binuclear di-μ-phosphido complexes in which the Rh(μ-PPh_2)$_2$Rh core presents a folded molecular structure without a metal–metal bond.[2a,5a] In fact the molecular structure of **5** exhibits these features (see below).

When the aforementioned reaction was carried out starting from the bmpz derivative [{Rh(C_5Me_5)}$_2$(μ-bmpz)(μ-OMe)$_2$]-BF_4 the non-pyrazolate-containing di-μ-hydroxo compound [{Rh(C_5Me_5)}$_2$(μ-OH)$_2$(μ-PPh_2)]BF_4 **8** was also formed (Scheme 1). The formation of **8** implies hydrolysis of the methoxo groups of the starting material, most probably by traces of water from the solvent. Alkoxo groups have proven to be prone to hydrolysis in this type of complex.[9,10b,13,14] Complex **8** was characterized by analytical and spectroscopic means. In particular, its IR spectrum shows a very strong ν(OH) band at 3470 cm^{-1} and one triplet [δ 19.8, ^1J(RhP) = 127 Hz] and one doublet [δ 1.41, ^4J(PH) = 2.9 Hz, C_5Me_5] are the most relevant data of the ^{31}P and ^1H NMR spectra, respectively. It could be also prepared directly by adding $HPPh_2$ to an acetone solution of [{Rh(C_5Me_5)}$_2$(μ-OH)$_3$]BF_4.

When the ^{31}P-{^1H} NMR spectrum of the μ-hydroxo complex [{Rh(C_5Me_5)}$_2$(μ-pz)(μ-OH)(μ-PPh_2)]BF_4 **1** was recorded in chloroform small amounts of the μ-chloro compound [{Rh(C_5Me_5)}$_2$(μ-pz)(μ-Cl)(μ-PPh_2)]BF_4 **9** were detected. The chlorine atoms should be supplied by the solvent[15] and, in fact, when the above-described reaction between [{Rh(C_5Me_5)}$_2$(μ-pz)(μ-OMe)$_2$]BF_4 and 2 equivalents of $HPPh_2$ was performed in chlorinated solvents, such as chloroform or dichloromethane, the reaction mixture contained *ca.* 20% of **9** according to ^{31}P NMR measurements. In order to confirm this reactivity, we carried out the reaction of the μ-hydroxo complexes **1**–**4** with hydrochloric acid. Thus, in acetone, with equimolar amounts of aqueous HCl at room temperature, mixtures are obtained of the corresponding mono-μ-chloro complexes [{Rh(C_5Me_5)}$_2$(μ-L)(μ-Cl)(μ-PPh_2)]BF_4 (L = pz **9**, mpz **10**, dmpz **11** or bmpz **12**) and the di-μ-chloro derivative [{Rh(C_5Me_5)}$_2$(μ-Cl)$_2$(μ-PPh_2)]BF_4 **13**. We have not been able to purify efficiently complexes **9**–**12** from the mixture but we have characterized them by preparing **9** and **10** by an alternative route starting from [{Rh(C_5Me_5)}$_2$(μ-OH)$_3$]BF_4. This species reacts, in acetone, with Hpz or Hmpz, diphenylphosphine, and aqueous hydrochloric acid in 1 : 1 : 1 : 1 ratio rendering pure **9** and **10** in 48 and 52% yield, respectively. Complexes **11** and **12** were also prepared by this latter route but were contaminated by the di-μ-chloro complex **13**. Furthermore, we have prepared **13** by reaction, in acetone, of [{Rh(C_5Me_5)}$_2$(μ-acac)$_2$][BF_4]$_2$ (acac = acetylacetonate) with [Rh(C_5Me_5)Cl_2($HPPh_2$)] in 1 : 2 molar ratio. Scheme 1 summarizes all these reactions and in Table 1 are collected the relevant ^1H and ^{31}P-{^1H} NMR data for the new complexes. The ^{31}P-{^1H} NMR spectra consist of a triplet assigned to bridging PPh_2 ligands and their chemical shifts indicate that no appreciable Rh–Rh bonding occurs.[16] The ^1H NMR data are in accord with the proposed stoichiometries. In particular, they showed two different (C_5Me_5)Rh units for complexes **10** and **12** due to the unsymmetrical nature of their bridging diazolate ligands. In order to confirm the nature of the bridging chloride complexes **9**–**12** we determined the structure of **9** by a single-crystal X-ray diffraction study, the results of which are described later.

The ^{31}P-{^1H} NMR spectra of aged solutions containing the aforementioned reaction mixtures of the di-μ-methoxo complexes [{Rh(C_5Me_5)}$_2$(μ-L)(μ-OMe)$_2$]BF_4 with $HPPh_2$ (Scheme 1) show two new resonances: a singlet at δ 36.5 and a triplet centred at δ 23.5 with a coupling constant of 125 Hz. Both signals were only slightly broadened on removal of proton decoupling. From these solutions we have been able to isolate a red non-nitrogen-containing solid which was analysed as [{Rh(C_5Me_5)}$_2$(PPh_2)$_3O_4$]BF_4. In chloroform solution this red solid shows the above-mentioned ^{31}P-{^1H} NMR pattern and its ^1H NMR spectrum consists of a C_5Me_5 doublet centred at δ 1.10 and phenyl multiplet resonances from δ 6.9 to 8.0. The



Scheme 1 (*i*) $HPPh_2$; (*ii*) L = pz or mpz; (*iii*) L = dmpz; (*iv*) L = bmpz; (*v*) HCl; (*vi*) HL, $HPPh_2$, HCl

Table 1 Relevant NMR[a] data for complexes **8**–**15**

	^{1}H NMR				^{31}P-{^{1}H} NMR	
	C_5Me_5	H^{4b}	H^{3,5b}	Me^{3,5b}	δ(P)	^1J(RhP)
8 $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_2(\mu\text{-}PPh_2)]BF_4$	1.41 (d) ^4J(PH) = 2.9	—	—	—	19.8 (t)	127
9 $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4$	1.44 (d) ^4J(PH) = 2.9	6.37 (sq) ^3J(HH) ≈ ^5J(PH) = 2.1	7.57 (d)	—	47.8 (t)	114
10 $[\{Rh(C_5Me_5)\}_2(\mu\text{-}mpz)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4$	1.48 (br s) 1.46 (br s)	5.91 (br s)	c	2.25 (d)	51.7 (t)	115
11 $[\{Rh(C_5Me_5)\}_2(\mu\text{-}dmpz)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4$	1.47 (d) ^4J(PH) = 2.7	5.50 (s)	—	2.10 (s)	54.7 (t)	116
12 $[\{Rh(C_5Me_5)\}_2(\mu\text{-}bmpz)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4$	1.48 (br s) 1.50 (br s)	5.75 (s)	—	2.00 (s)	54.9 (t)	115
13 $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)]BF_4$	1.41 (d) ^4J(PH) = 2.6	—	—	—	28.6 (t)	117
14 $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Ph_2PO_2)_2(\mu\text{-}PPh_2)]BF_4$	1.10 (d) ^4J(PH) = 2.4	—	—	—	23.5 (t) 36.5 (s)	125
15 $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)(\mu\text{-}pz)(\mu\text{-}PPh_2)]BF_4$[d]	1.87 (d) ^4J(PH) = 2.4	5.43 (sq) ^3J(HH) ≈ ^5J(PH) = 2.0	6.55 (d)	—	141.1 (t)	113

[a] Measured in $CDCl_3$ (^{1}H) or $CDCl_3$–$CHCl_3$ (1 : 1 v/v) (^{31}P) at room temperature; chemical shifts relative to $SiMe_4$ (^{1}H) or 85% H_3PO_4 in D_2O (^{31}P) as external standards, J in Hz; s = singlet, br = broad, d = doublet, t = triplet, sq = pseudo-quartet. [b] Pyrazolate protons. [c] Obscured by the PPh_2 protons. [d] The ^{1}H NMR parameters of the hydride ligand are included in the text.

aliphatic : aromatic proton ratio was 1 : 1, in good agreement with the empirical formulation. Since spectroscopic and analytical data were not structurally diagnostic, we identified this compound as $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Ph_2PO_2)_2(\mu\text{-}PPh_2)]BF_4$ **14** by single-crystal X-ray diffraction (see below). The bridging Ph_2PO_2 ligands undoubtedly come from $Ph_2P(O)OH$, an oxidation product of the diphenylphosphine. In fact, a peak at δ *ca*. 27.7, assignable to free $Ph_2P(O)OH$,[17] was observed for some samples.

It is well known that hydride derivatives of transition metals can be prepared by hydrogen-transfer reactions from primary or secondary alcohols.[18] We have very recently prepared pentamethylcyclopentadienyl μ-hydrido complexes of iridium[19] and rhodium[11d] by using propan-2-ol as hydride source. This synthetic route also permits the preparation of mixed μ-phosphido-μ-hydrido $(C_5Me_5)Rh^{III}$ complexes. Thus, the reaction of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]BF_4$ with equimolecular amounts of Hpz and $HPPh_2$ in refluxing propan-2-ol afforded $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)(\mu\text{-}pz)(\mu\text{-}PPh_2)]BF_4$ **15** as the major product. However, a persistent problem was the presence of impurities, shown, by NMR spectroscopy, to be the di-μ-hydrido-μ-pyrazolato complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}pz)]BF_4$[11d] and the μ-pyrazolato-di-μ-phosphido complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}PPh_2)_2]BF_4$ **5**. Owing to the very similar properties of these three complexes, separation was very difficult indeed and we have not been able to prepare analytically pure samples of **15**. Other routes to this hydride, such as the reaction of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}pz)]BF_4$ with $HPPh_2$, did not give better results. In spite of that, we have undoubtedly characterized this complex by NMR spectroscopy. Thus, its ^{31}P-{^{1}H} NMR spectrum consists of one triplet centred at δ 141.1 with a coupling constant of 113 Hz. This chemical shift indicates that a rhodium–rhodium bond is present.[16] Besides the resonances for the C_5Me_5, pz, and PPh_2 ligands, the ^{1}H NMR spectrum (Table 1) shows the presence of a doublet of triplets centred at δ −11.7 assigned to a bridging hydride coupled to a phosphorus and two rhodium nuclei. The values of the couplings [^1J(RhH) = 20.5 and ^2J(PH) = 41.5 Hz] are in good agreement with those reported for other μ-hydrido $(C_5Me_5)Rh$ complexes.[8,11d]

The preparation of complex **13** according to the last reaction in Scheme 1 prompted us to attempt the synthesis of trinuclear pentamethylcyclopentadienyl phosphidorhodium complexes following a similar synthetic strategy: the reaction of the diphenylphosphine complex $[Rh(C_5Me_5)Cl_2(HPPh_2)]$ with dinuclear $(C_5Me_5)Rh$ compounds having μ-hydroxo or μ-methoxo groups which could be displaced by protonation. Nevertheless, only mixtures of the dinuclear products $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)]BF_4$ **13**, $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4$ **9**, $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}Cl)_2]BF_4$[11d] and $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)_2(\mu\text{-}Cl)]BF_4$[11d] were obtained by treating $[Rh(C_5Me_5)Cl_2(HPPh_2)]$ with the tri-μ-hydroxo or the di-μ-methoxo dinuclear complexes $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]BF_4$ or $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}OMe)_2]BF_4$.

Molecular Structures of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}PPh_2)_2]BF_4\cdot CHCl_3$ **5**$\cdot CHCl_3$, $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4\cdot CHCl_3$ **9**$\cdot CHCl_3$ *and* $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Ph_2PO_2)_2(\mu\text{-}PPh_2)]BF_4\cdot 0.22CHCl_3$ **14**$\cdot 0.22CHCl_3$.—Views of the structures of the cations of complexes **5**, **9** and **14** are shown in Figs. 1, 2 and 3, respectively. Important bond distances and angles are listed in Tables 2, 3 and 4, respectively.

In the structures of complexes **5** and **9** the two rhodium atoms are bridged by two diphenylphosphide and one pyrazolate group (**5**) and by one diphenylphosphide, one chloride, and one pyrazolate group (**9**). In both cases an η^5-bonded C_5Me_5 group completes the pseudo-octahedral 'three-legged piano stool' co-ordination commonly found for $(C_5Me_5)RhL(L')L''$ derivatives. The distances of the metal atoms to the centroids of the C_5Me_5 rings are 1.874(7) and 1.878(7) (complex **5**) and 1.823(4) and 1.821(5) Å (**9**). These distances are longer than those usually found for $(C_5Me_5)Rh$ complexes with pyrazolate bridging ligands,[10a,20,21] but compare well with those found for diphenylphosphido-bridged $C_5Me_5Rh^{III}$ systems.[7b,c,9] The methyl groups stay out of the plane through the five-membered rings, pointing away from the rhodium atoms. The C_5Me_5 rings are inclined to one another at angles of 19.9(3) (**5**) and 24.7(4)° (**9**). The Rh–Rh distances, 3.473(1) and 3.432(1) Å, for complexes **5** and **9** respectively, preclude any significant metal–metal interaction as anticipated from the relatively high-field values of their ^{31}P NMR chemical shifts.[16] The Rh–P bond distances, 2.341(2) (average for **5**) and 2.346(2) Å (average for **9**), are very similar to each other, compare well with the Rh^{III}–P bond distance found for the binuclear μ-diphenylphosphido complex $[(C_5Me_5)ClRh(\mu\text{-}Cl)(\mu\text{-}PPh_2)Rh(cod)]\cdot 0.5Et_2O$ (cod = cycloocta-1,5-diene) [2.346(1) Å][12] and are slightly longer than those found for the related di-μ-pyrazolato-μ-diphenylphosphido complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)_2(\mu\text{-}PPh_2)]BF_4$ [average 2.333(1) Å].[9] On the other hand, these bond distances are longer than the Rh–PPh_2 ones found in the

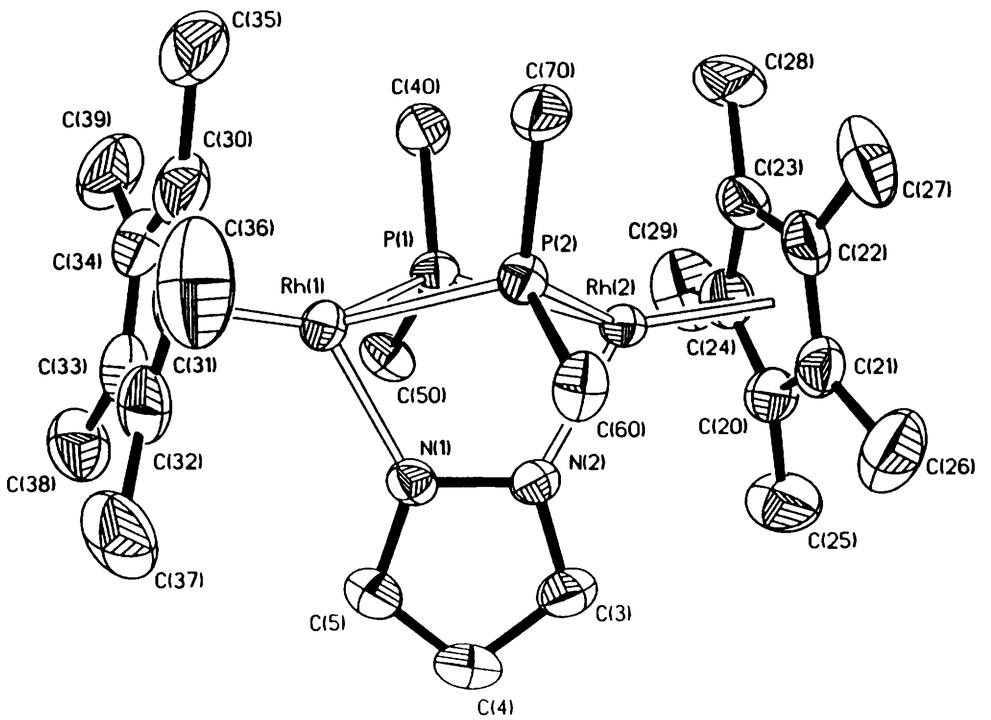


Fig. 1 View of the molecular structure of the cation of the complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})(\mu\text{-PPh}_2)_2]BF_4{\cdot}CHCl_3$ **5**$\cdot CHCl_3$, with the atomic numbering scheme. Only the *ipso*-carbons of the phenyl groups are shown for clarity

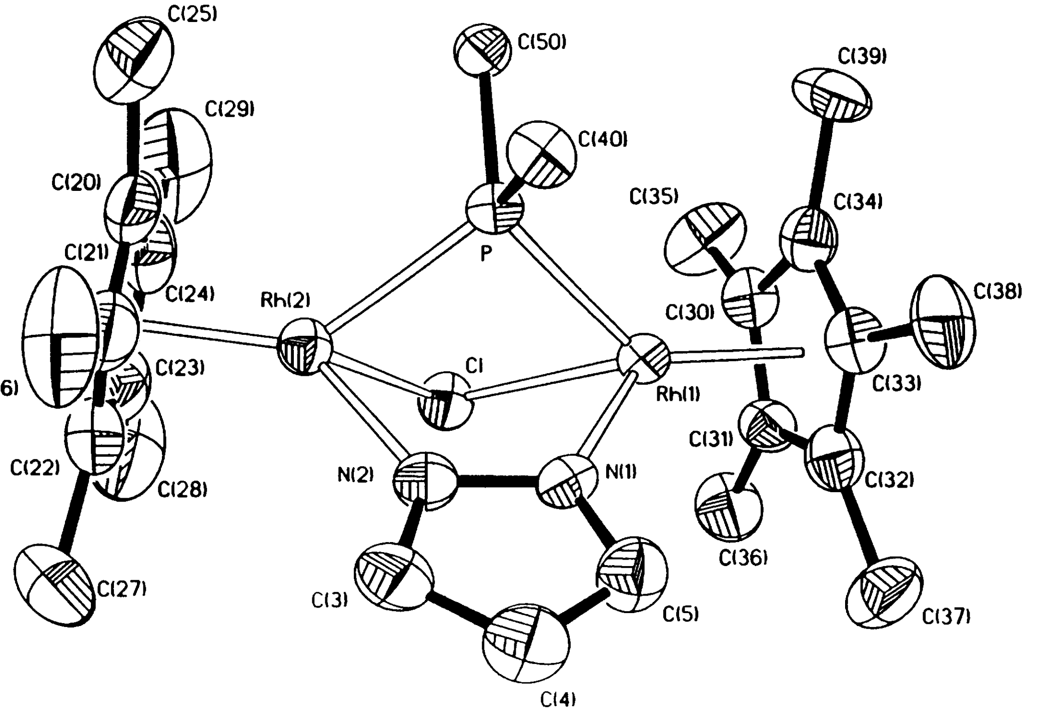


Fig. 2 View of the molecular structure of the cation of the complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})(\mu\text{-Cl})(\mu\text{-PPh}_2)]BF_4{\cdot}CHCl_3$ **9**$\cdot CHCl_3$, with the atomic numbering scheme. Details as in Fig. 1

pentamethylcyclopentadienylrhodium(II) complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-PMe}_2)(\mu\text{-PPh}_2)]$ [average 2.335(1) Å][7b] or in the trinuclear cyclopentadienyl Rh_2Ir cluster $[Rh_2Ir(C_5H_5)_2(\mu\text{-PPh}_2)(CO)_2(CF_3C_2CF_3)]$ [2.263(2) Å][22] in spite of the higher formal oxidation state of the rhodium atoms in complexes **5** and **9**. The angles around the P atoms reflect a distorted-tetrahedral geometry, the smallest values corresponding to Rh–P–Rh and C–P–C in both complexes.

The Rh–N bond distances 2.070(4) and 2.081(4) Å in complex **5** and 2.076(7) and 2.077(7) Å in **9** are comparable to those found in other binuclear pyrazolato-bridged $(C_5Me_5)Rh^{III}$ complexes such as $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})_2(\mu\text{-OH})]ClO_4$ [average 2.092(7) Å],[10a] $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})_2(\mu\text{-PPh}_2)]BF_4$ [average 2.092(4) Å],[9] and $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})_2(\mu\text{-Cl})]BF_4$ [average 2.091(9) Å],[21] as well as in the heterobinuclear RhRu complex $[(C_5Me_5)Rh\{\mu\text{-PO(OMe)}_2\}_2(\mu\text{-pz})Ru(C_6H_6)]ClO_4{\cdot}CH_2Cl_2$ [2.105(8) Å].[23] The Rh–Cl bond distances in complex **9** are 2.457(2) and 2.452(2) Å and fall in the range of Rh–Cl bond distances found in related μ-chloride $(C_5Me_5)Rh^{III}$ compounds.[12,20,21,24,25]

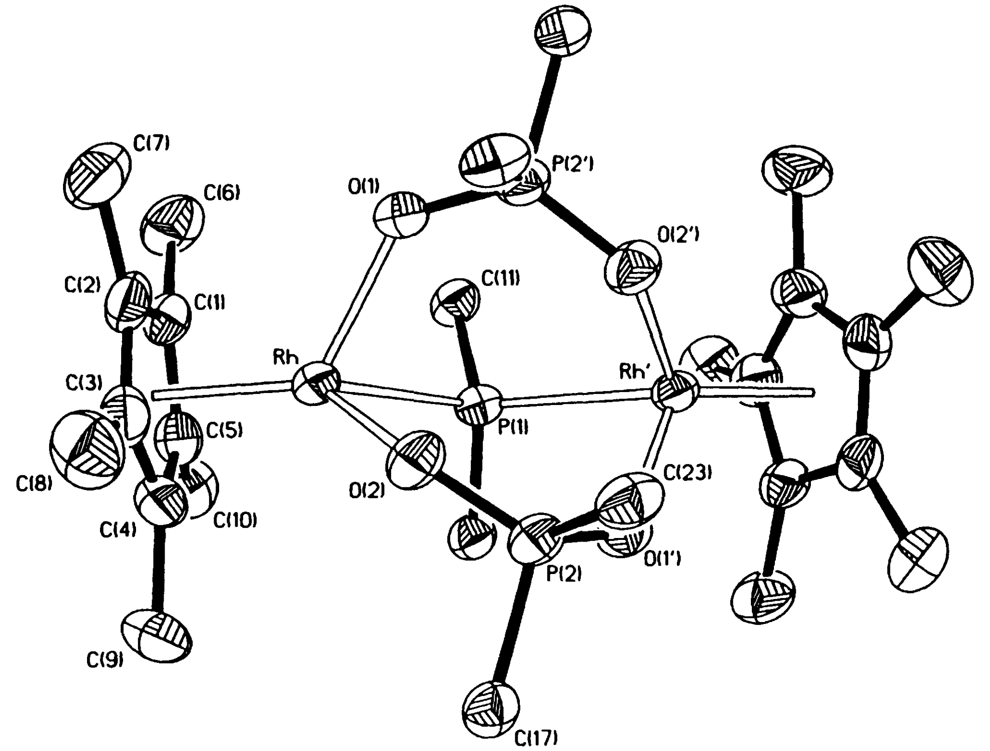


Fig. 3 View of the molecular structure of the cation of the complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Ph_2PO_2)_2(\mu\text{-}PPh_2)]BF_4\cdot0.22CHCl_3$ **14**·0.22CHCl$_3$, with the atomic numbering scheme. Details as in Fig. 1

Table 2 Relevant bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}PPh_2)_2]BF_4\cdot CHCl_3$ **5**·CHCl$_3$ *

Rh(1) ··· Rh(2)	3.473(1)	Rh(2)–P(1)	2.342(1)
Rh(1)–P(1)	2.339(2)	Rh(2)–P(2)	2.345(2)
Rh(1)–P(2)	2.341(1)	Rh(2)–N(2)	2.081(4)
Rh(1)–N(1)	2.070(4)	Rh(2)–G(2)	1.878(7)
Rh(1)–G(1)	1.874(7)	Rh(2)–C(20)	2.261(7)
Rh(1)–C(30)	2.187(7)	Rh(2)–C(21)	2.236(6)
Rh(1)–C(31)	2.247(9)	Rh(2)–C(22)	2.229(6)
Rh(1)–C(32)	2.264(6)	Rh(2)–C(23)	2.193(6)
Rh(1)–C(33)	2.232(6)	Rh(2)–C(24)	2.238(7)
Rh(1)–C(34)	2.236(6)	C(20)–C(21)	1.423(11)
C(30)–C(31)	1.445(10)	C(20)–C(24)	1.404(8)
C(30)–C(34)	1.450(11)	C(21)–C(22)	1.408(9)
C(31)–C(32)	1.410(11)	C(22)–C(23)	1.418(11)
C(32)–C(33)	1.445(11)	C(23)–C(24)	1.433(10)
C(33)–C(34)	1.393(9)		
N(1)–Rh(1)–P(1)	78.1(1)	N(2)–Rh(2)–P(1)	81.4(1)
N(1)–Rh(1)–P(2)	82.1(1)	N(2)–Rh(2)–P(2)	78.5(1)
N(1)–Rh(1)–G(1)	128.6(1)	N(2)–Rh(2)–G(2)	129.0(2)
P(1)–Rh(1)–P(2)	77.8(1)	P(1)–Rh(2)–P(2)	77.6(1)
P(1)–Rh(1)–G(1)	135.0(1)	P(1)–Rh(2)–G(2)	133.2(1)
P(2)–Rh(1)–G(1)	133.8(1)	P(2)–Rh(2)–G(2)	135.6(1)
Rh(1)–P(1)–Rh(2)	95.80(5)	Rh(1)–P(2)–Rh(2)	95.67(6)
Rh(1)–P(1)–C(40)	120.0(2)	Rh(2)–P(2)–C(60)	110.4(2)
Rh(2)–P(1)–C(40)	116.4(2)	Rh(1)–P(2)–C(60)	114.0(2)
Rh(1)–P(1)–C(50)	109.2(2)	Rh(2)–P(2)–C(70)	119.4(2)
Rh(2)–P(1)–C(50)	114.6(2)	Rh(1)–P(2)–C(70)	115.1(2)
C(40)–P(1)–C(50)	101.5(3)	C(60)–P(2)–C(70)	102.8(3)
Rh(1)–N(1)–N(2)	120.0(3)		

* G(1) and G(2) are the centroids of the C$_5$Me$_5$ rings.

Table 3 Relevant bond distances (Å) and angles (°) with e.s.d.s in parentheses for $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4\cdot CHCl_3$ **9**·CHCl$_3$ *

Rh(1) ··· Rh(2)	3.432(1)	Rh(2)–P	2.342(2)
Rh(1)–P	2.350(2)	Rh(2)–Cl(1)	2.452(2)
Rh(1)–Cl(1)	2.457(2)	Rh(2)–N(2)	2.077(7)
Rh(1)–N(1)	2.076(7)	Rh(2)–G(2)	1.821(5)
Rh(1)–G(1)	1.823(4)	Rh(2)–C(20)	2.173(10)
Rh(1)–C(30)	2.186(8)	Rh(2)–C(21)	2.125(11)
Rh(1)–C(31)	2.222(8)	Rh(2)–C(22)	2.224(10)
Rh(1)–C(32)	2.246(9)	Rh(2)–C(23)	2.218(11)
Rh(1)–C(33)	2.142(9)	Rh(2)–C(24)	2.154(10)
Rh(1)–C(34)	2.178(8)	C(20)–C(21)	1.427(17)
C(30)–C(31)	1.442(12)	C(20)–C(24)	1.410(16)
C(30)–C(34)	1.460(12)	C(21)–C(22)	1.408(17)
C(31)–C(32)	1.411(12)	C(22)–C(23)	1.355(17)
C(32)–C(33)	1.445(13)	C(23)–C(24)	1.441(16)
C(33)–C(34)	1.431(12)		
N(1)–Rh(1)–P	79.4(2)	N(2)–Rh(2)–P	80.4(2)
N(1)–Rh(1)–Cl(1)	86.8(2)	N(2)–Rh(2)–Cl(1)	85.9(2)
N(1)–Rh(1)–G(1)	130.8(2)	N(2)–Rh(2)–G(2)	131.9(2)
P–Rh(1)–Cl(1)	79.8(1)	P–Rh(2)–Cl(1)	80.1(1)
P–Rh(1)–G(1)	136.9(1)	P–Rh(2)–G(2)	135.3(2)
Cl(1)–Rh(1)–G(1)	124.6(1)	Cl(1)–Rh(2)–G(2)	124.8(2)
Rh(1)–P–Rh(2)	94.02(7)	Rh(1)–Cl(1)–Rh(2)	88.71(7)
Rh(1)–P–C(40)	113.1(3)	Rh(2)–P–C(40)	116.7(3)
Rh(1)–P–C(50)	115.7(3)	Rh(2)–P–C(50)	113.8(2)
C(40)–P–C(50)	104.0(4)	Rh(1)–N(1)–N(2)	119.9(5)

* G(1) and G(2) are the centroids of the C$_5$Me$_5$ rings.

Compound **14** has precise (*i.e.* crystallographically required) C_2 symmetry, the two-fold axis passing through P(1) and the mid-point of the Rh–Rh' segment. As shown in Fig. 3, the atoms in the basic asymmetric unit are labelled normally, while those in the 'other half' of the cation, which is related to the basic unit by the transformation $(x', y', z') = (y, x, \frac{1}{2} - z)$, are primed. The complex has two rhodium atoms separated by 4.049(1) Å and bridged by two diphenylphosphinato groups and one diphenylphosphide ligand. Each rhodium is η^5-bonded to a C$_5$Me$_5$ ligand, which completes its pseudo-octahedral co-ordination. The distance from the rhodium to the centroid of the corresponding C$_5$Me$_5$ ring is 1.811(2) Å. The distance is comparable to those found in complex **9**, slightly shorter

Table 4 Relevant bond distances (Å) and angles (°) with e.s.d.s in parentheses for $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Ph_2PO_2)_2(\mu\text{-}PPh_2)]BF_4\cdot0.22CHCl_3$ **14**·0.22CHCl$_3$ *

Rh···Rh′	4.049(1)	O(1)–P(2′)	1.508(3)
Rh–P(1)	2.398(1)	O(2)–P(2)	1.505(3)
Rh–O(1)	2.120(2)	P(1)–C(11)	1.837(3)
Rh–O(2)	2.146(2)	P(2)–C(17)	1.810(4)
Rh–G	1.811(2)	P(2)–C(23)	1.804(3)
Rh–C(1)	2.132(2)	C(1)–C(2)	1.454(4)
Rh–C(2)	2.228(4)	C(2)–C(3)	1.392(5)
Rh–C(3)	2.234(5)	C(3)–C(4)	1.446(4)
Rh–C(4)	2.150(5)	C(4)–C(5)	1.433(5)
Rh–C(5)	2.161(4)	C(5)–C(1)	1.428(4)
O(1)–Rh–O(2)	87.01(8)	Rh–P(1)–C(11)	106.03(11)
O(1)–Rh–P(1)	83.93(7)	Rh′–P(1)–C(11)	111.55(12)
O(2)–Rh–P(1)	94.23(6)	Rh–O(2)–P(2)	134.83(15)
O(1)–Rh–G	121.61(8)	O(2)–P(2)–O(1′)	118.21(13)
O(2)–Rh–G	123.35(9)	C(17)–P(2)–C(23)	106.27(15)
P(1)–Rh–G	132.85(5)	O(2)–P(2)–C(23)	108.30(14)
Rh–P(1)–Rh′	115.16(3)	O(2)–P(2)–C(17)	109.18(15)

* G is the centroid of the C_5Me_5 independent ring.

than those of **5** and falls in the range of those reported for $(C_5Me_5)Rh^{III}$ complexes.[9,10a,b,11b,20,21,24–29] The C_5Me_5 group has C–C ring distances (Table 4) suggesting some degree of localization into an ene–enyl form, as previously observed for some $(C_5Me_5)Rh^{III}$ complexes.[10a,12,20,30] The methyl substituents stay out of the plane through the five-membered rings bending away from the rhodium atoms. The different steric requirements of the bridging groups hold the two C_5Me_5 rings so that they are not parallel but inclined to one another at an angle of 35.4(1)°. The Rh–P bond distance, 2.398(1) Å, is significantly longer than those found in other $(C_5Me_5)Rh^{III}$ complexes with diphenylphosphido bridging ligands such as[9] $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)_2(\mu\text{-}PPh_2)]BF_4$ and complexes **5** and **9** in this work, which have average Rh–P values of 2.333(1), 2.341(2) and 2.346(2) Å, respectively. Additionally, the Rh–Rh separation in complex **14** is longer (by *ca.* 0.6 Å) than those found in the aforementioned diphenylphosphido complexes. Most probably, this is a consequence of the presence, in **14**, of two three-atom-bridging diphenylphosphinato ligands and causes elongation of the Rh–P bonds as well as opening of the Rh–P–Rh angles with respect to complexes **5**, **9** and $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)_2(\mu\text{-}PPh_2)]BF_4$ (Rh–P–Rh angles: 94.02(7)° in **9**, 95.67(6) and 95.80(5)° in **5**, 102.76(4)° in[9] $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)_2(\mu\text{-}PPh_2)]BF_4$ and 115.16(3)° in **14**). The Rh–O bond distances [2.120(2) and 2.146(2) Å] compare well with those found for μ-hydroxo[10a,b,31] and μ-methoxo[10a] pentamethylcyclopentadienyl complexes of rhodium(III). The structural features of the diphenylphosphinato ligands are comparable to those found in transition-metal complexes containing bridging diphenylphosphinate-*O,O′*.[32–35]

Experimental

Reagents and products were generally manipulated in Schlenk apparatus under an atmosphere of nitrogen or argon. Solvents were dried and distilled before use. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer (range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets, proton and ^{31}P NMR spectra on a Varian XL200 spectrometer operating at 80.9 (^{31}P) and 200.0 (^1H) MHz. The C, H and N analyses were carried out with a Perkin-Elmer 240B microanalyser. The complexes $[\{Rh(C_5Me_5)\}_2(\mu\text{-}L)(\mu\text{-}OMe)_2]BF_4$ (L = pz, mpz, dmpz or bmpz) were prepared as described by Oro *et al.*[10a] The tetrafluoroborate $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]BF_4$ was prepared by metathesis of the chloride salt[36] $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]Cl$ with $NaBF_4$, $[\{Rh(C_5Me_5)\}_2(\mu\text{-}acac)_2][BF_4]_2$ by the method of Maitlis and co-workers,[30] and $[Rh(C_5Me_5)Cl_2(HPPh_2)]$ by the method of Klingert and Werner.[7a]

Preparations.—$[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_2(\mu\text{-}PPh_2)]BF_4$ **8** *and* $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Ph_2PO_2)_2(\mu\text{-}PPh_2)]BF_4$ **14**. To a solution of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}bmpz)(\mu\text{-}OMe)_2]BF_4$ (100 mg, 0.125 mmol) in acetone (25 cm^3) was added $HPPh_2$ (44 μl, 0.250 mmol). After 20 min, precipitation of a yellow solid began and the resulting suspension was stirred for 15 min. The solid was filtered off, washed with acetone and diethyl ether, and dried under vacuum. It was characterized as complex **8**. Yield: 29 mg, 30% based on Rh. Ir (Nujol): ν(OH) 3470vs cm^{-1} (Found: C, 49.4; H, 5.6. Calc. for $C_{32}H_{42}BF_4O_2PRh_2$: C, 49.1; H, 5.4%). The mother-liquors were concentrated by partial vacuum-evaporation. Addition of diethyl ether afforded complex **14** as an orange solid. Recrystallization from chloroform–diethyl ether led to red crystals. Yield: 30 mg, 20% based on Rh (Found: C, 55.7; H, 5.3. Calc. for $C_{56}H_{60}BF_4O_4P_3Rh_2$: C, 56.0; H, 5.2%).

Complex **8** was also prepared as follows. To a solution of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]BF_4$ (93 mg, 0.150 mmol) in acetone (5 cm^3) was added $HPPh_2$ (260 μl, 1.50 mmol). The resulting solution was stirred for 30 min. The solid which precipitated was filtered off, washed with acetone and diethyl ether and vacuum dried. Yield: 20 mg, 17% based on Rh. This solid was identified as complex **8** by comparison of spectroscopic properties with those of an authentic sample prepared from $[\{Rh(C_5Me_5)\}_2(\mu\text{-}bmpz)(\mu\text{-}OMe)_2]BF_4$ as described above.

$[\{Rh(C_5Me_5)\}_2(\mu\text{-}L)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4$ (L = pz **9** *or* mpz **10**). A mixture of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]BF_4$ (150 mg, 0.240 mmol), the corresponding HL (0.240 mmol), $HPPh_2$ (43 μl, 0.244 mmol) and an aqueous solution of HCl (12.5 cm^3, 0.0190 mol dm^{-3}, 0.240 mmol) in acetone (20 cm^3) was stirred for 5 h. After partial vacuum-evaporation the orange solids which precipitated were filtered off, washed with water and diethyl ether and air dried. Recrystallization from dichloromethane–diethyl ether led to red crystals in both cases. Yields: 98 mg, 48% (**9**); 108 mg, 52% (**10**) (Found: C, 50.2; H, 5.6; N, 3.2. Calc. for $C_{35}H_{43}BClF_4N_2PRh_2$ **9**: C, 49.4; N, 5.1; N, 3.3. Found: C, 50.1; H, 5.2; N, 3.3. Calc. for $C_{36}H_{45}BClF_4N_2PRh_2$ **10**: C, 50.0; H, 5.2; N, 3.2%).

The related complexes $[\{Rh(C_5Me_5)\}_2(\mu\text{-}L)(\mu\text{-}Cl)(\mu\text{-}PPh_2)]BF_4$ (L = dmpz **11** or bmpz **12**) were also prepared by this method but an impurity shown by NMR spectroscopy to be $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)]BF_4$ **13** was present in the crude reaction product. We were not able to remove it efficiently.

Complexes **9**–**12** were also prepared as follows. To a solution of the corresponding compound $[\{Rh(C_5Me_5)\}_2(\mu\text{-}L)(\mu\text{-}OH)(\mu\text{-}PPh_2)]BF_4$ (0.090 mmol) in acetone (30 cm^3) was added an aqueous solution of HCl (4.7 cm^3, 0.0190 mol dm^{-3}, 0.090 mmol). The resulting solutions were stirred for 40 min. After partial vacuum evaporation, the orange solids which precipitated were filtered off, washed with water and diethyl ether and air dried. They are mixtures of complexes **9**–**12** with $[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)]BF_4$ **13** which could not be efficiently purified.

$[\{Rh(C_5Me_5)\}_2(\mu\text{-}Cl)_2(\mu\text{-}PPh_2)]BF_4$ **13**. A mixture of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}acac)_2][BF_4]_2$ (85 mg, 0.100 mmol) and $[Rh(C_5Me_5)Cl_2(HPPh_2)]$ (99 mg, 0.200 mmol) in acetone (20 cm^3) was stirred for 20 h. The solution was concentrated under reduced pressure. Addition of diethyl ether led to the precipitation of an orange solid which was filtered off, washed with diethyl ether and air dried. Yield: 85 mg, 52% (Found: C, 46.7; H, 5.0. Calc. for $C_{32}H_{40}BCl_2F_4N_2PRh_2$: C, 46.9; H, 4.9%).

$[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)(\mu\text{-}pz)(\mu\text{-}PPh_2)]BF_4$ **15**. To a solution of $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]BF_4$ (200 mg, 0.326 mmol), in propan-2-ol (40 cm^3), Hpz (22 mg, 0.326 mmol) and $HPPh_2$ (57 μl, 0.326 mmol) were added. The resulting solution was stirred under reflux for 20 h and then concentrated under reduced pressure. The addition of diethyl ether led to the precipitation of a red-maroon solid which was recrystallized from dichloro-

Table 5 Experimental data for the X-ray diffraction studies

	5·$CHCl_3$	**9**·$CHCl_3$	**14**·0.22$CHCl_3$
Formula	$C_{47}H_{53}BF_4N_2P_2Rh_2{\cdot}CHCl_3$	$C_{35}H_{43}BClF_4N_2PRh_2{\cdot}CHCl_3$	$C_{56}H_{60}BF_4O_4P_3Rh_2{\cdot}0.22CHCl_3$
M	1119.90	970.2	1208.90
Crystal system	Monoclinic	Orthorhombic	Trigonal
Space group	$P2_1/c$	*Pbca*	*R*3*c* (no. 167)
a/Å	17.286(2)	22.986(1)	22.8110(6)
b/Å	13.151(1)	20.044(1)	22.8110(6)
c/Å	22.856(3)	17.268(1)	52.611(3)
α/°	90	90	90
β/°	111.184(8)	90	90
γ/°	90	90	120
U/Å^3	4844.7(9)	7955.9(6)	23 708(3)
Z	4	8	18
D_c/g cm^{-3}	1.535	1.620	1.524
F(000)	2272	3904	11 100
μ/cm^{-1}	82.59	102.03	1.676
R^a	0.051	0.066	0.031
R'^b	0.057	0.059	0.036

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$.

Table 6 Final atomic coordinates with e.s.d.s in parentheses for the non-hydrogen atoms of complex **5**·$CHCl_3$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1)	0.232 02(2)	0.155 76(3)	−0.259 74(2)
Rh(2)	0.248 09(2)	0.391 07(3)	−0.323 40(2)
N(1)	0.343 0(3)	0.234 9(3)	−0.228 4(2)
N(2)	0.345 7(3)	0.333 8(3)	−0.247 1(2)
C(3)	0.421 9(4)	0.369 2(5)	−0.215 5(3)
C(4)	0.469 7(4)	0.293 8(6)	−0.177 2(3)
C(5)	0.418 4(4)	0.212 3(5)	−0.187 2(3)
C(20)	0.316 3(4)	0.520 5(5)	−0.348 7(3)
C(21)	0.263 6(4)	0.560 1(5)	−0.318 6(3)
C(22)	0.181 0(4)	0.537 2(5)	−0.356 2(4)
C(23)	0.181 7(4)	0.479 1(5)	−0.408 3(3)
C(24)	0.266 3(4)	0.471 0(5)	−0.403 9(3)
C(25)	0.408 1(5)	0.541 3(8)	−0.331 0(4)
C(26)	0.291 0(7)	0.625 2(7)	−0.260 8(5)
C(27)	0.105 7(6)	0.579 4(6)	−0.348 1(5)
C(28)	0.109 0(5)	0.453 4(7)	−0.466 0(4)
C(29)	0.294 5(7)	0.428 9(8)	−0.454 9(4)
C(30)	0.134 6(4)	0.046 4(5)	−0.264 7(4)
C(31)	0.176 8(5)	0.070 3(5)	−0.199 1(4)
C(32)	0.260 3(5)	0.039 8(5)	−0.181 6(3)
C(33)	0.271 3(4)	−0.005 4(5)	−0.235 7(3)
C(34)	0.194 6(4)	−0.006 0(5)	−0.284 7(3)
C(35)	0.043 3(5)	0.050 9(7)	−0.298 6(6)
C(36)	0.136 5(8)	0.107 9(7)	−0.154 8(5)
C(37)	0.322 9(7)	0.043 8(7)	−0.116 4(4)
C(38)	0.349 2(5)	−0.056 2(6)	−0.236 2(4)
C(39)	0.174 3(6)	−0.059 1(6)	−0.346 4(4)
P(1)	0.237 9(1)	0.219 8(1)	−0.353 5(1)
C(40)	0.157 2(4)	0.188 4(5)	−0.427 5(3)
C(41)	0.173 8(5)	0.189 9(6)	−0.483 1(3)
C(42)	0.119 9(7)	0.175 1(8)	−0.541 0(4)
C(43)	0.031 7(9)	0.160 8(10)	−0.542 9(6)
C(44)	0.013 0(6)	0.155 4(9)	−0.489 9(6)
C(45)	0.076 0(5)	0.168 5(6)	−0.430 5(4)
C(50)	0.329 9(4)	0.169 2(5)	−0.365 0(3)
C(51)	0.329 7(5)	0.071 4(6)	−0.389 6(3)
C(52)	0.401 1(6)	0.031 2(7)	−0.394 0(4)
C(53)	0.473 0(6)	0.085 9(8)	−0.375 8(4)
C(54)	0.474 8(5)	0.181 8(8)	−0.352 0(4)
C(55)	0.404 6(4)	0.224 5(6)	−0.346 1(3)
P(2)	0.177 2(1)	0.319 4(1)	−0.263 3(1)
C(60)	0.208 0(4)	0.382 2(4)	−0.186 2(3)
C(61)	0.270 5(5)	0.345 9(5)	−0.134 8(3)
C(62)	0.295 9(5)	0.398 5(7)	−0.077 7(4)
C(63)	0.257 5(5)	0.487 5(7)	−0.072 6(4)
C(64)	0.193 6(6)	0.525 4(6)	−0.123 9(4)
C(65)	0.169 1(4)	0.473 4(5)	−0.180 9(3)
C(70)	0.064 2(4)	0.326 0(5)	−0.291 7(3)
C(71)	0.019 5(4)	0.335 4(6)	−0.356 3(4)
C(72)	−0.066 6(5)	0.329 1(7)	−0.379 0(5)
C(73)	−0.108 1(5)	0.316 3(7)	−0.338 9(7)
C(74)	−0.065 3(6)	0.308 5(7)	−0.274 9(6)
C(75)	0.020 5(5)	0.314 3(6)	−0.251 2(4)
B	0.758 2(7)	0.244 2(7)	0.450 4(5)
F(1)	0.688 3(6)	0.234 2(10)	0.404 2(6)
F(2)	0.747 6(8)	0.323 1(7)	0.485 0(5)
F(3)	0.777 3(8)	0.160 1(7)	0.484 0(6)
F(4)	0.817 5(5)	0.269 1(6)	0.430 7(5)
C(6)	0.589 3(7)	0.243 5(9)	0.018 8(4)
Cl(1)	0.650 0(2)	0.248 8(2)	0.098 8(1)
Cl(2)	0.532 4(2)	0.354 2(3)	−0.005 2(1)
Cl(3)	0.524 7(3)	0.138 7(4)	0.003 1(3)

methane–diethyl ether. Proton and ^{31}P-{^1H} NMR spectra showed the presence of the complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz})(\mu\text{-}PPh_2)_2]BF_4$ **5** (≈15%). We were not able to remove this impurity efficiently.

X-Ray Crystallography.—Approximately prismatic crystals suitable for X-ray studies were obtained by slow diffusion of diethyl ether into chloroform solutions of the compounds. Red crystals of approximate dimensions 0.30 × 0.33 × 0.50 (**5**), 0.43 × 0.17 × 0.10 (**9**), and 0.68 × 0.43 × 0.28 mm (**14**) were used for the analyses. The crystallographic data for **5**·$CHCl_3$ **9**·$CHCl_3$, and **14**·0.22$CHCl_3$ are summarized in Table 5. Unit-cell parameters were determined from the setting angles of 101 (**5**) (θ < 45°), 100 (**9**) (θ < 45°) and 50 (**14**) (θ ⩽ 17°) carefully centred reflections. Data were collected at room temperature on Philips PW1100 or Siemens AED diffractometers, using graphite-monochromated Cu-Kα (**5** and **9**) or Mo-Kα (**14**) radiation and the ω–2θ scan type. All reflections with θ up to 65 (**5** and **9**) and 25° (**14**) were collected; of 8142 (**5**), 6740 (**9**) and 10 319 (**14**) measured reflections, 7110, 5158 and 4092 unique reflection having $I > 3\sigma(I)$ (**5** and **9**) or $> 2\sigma(I)$ (**14**) were considered observed and used in the analysis. Two standard reflections were monitored every 90 (**5** and **9**) and three every 55 min (**14**); no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied following the Walker and Stuart method[37] for **5** (maximum and minimum corrections 1.335–0.572) and **9** (1.190–0.553),

Table 7 Final atomic coordinates with e.s.d.s in parentheses for the non-hydrogen atoms of complex **9**·$CHCl_3$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	−0.054 88(2)	0.192 24(2)	0.210 56(3)	C(37)	−0.140 3(5)	0.0823 3(6)	0.308 4(7)
Rh(2)	0.091 29(2)	0.226 98(3)	0.206 95(4)	C(38)	−0.139 3(5)	0.084 4(5)	0.122 2(7)
Cl(1)	0.009 2(1)	0.266 1(1)	0.285 5(1)	C(39)	−0.145 8(5)	0.236 1(6)	0.068 0(5)
N(1)	0.005 1(3)	0.117 1(3)	0.232 2(4)	P	0.015 9(1)	0.216 6(1)	0.116 5(1)
N(2)	0.062 8(3)	0.131 4(3)	0.233 8(4)	C(40)	0.023 7(4)	0.150 9(4)	0.043 9(4)
C(3)	0.092 0(4)	0.073 8(5)	0.246 0(6)	C(41)	−0.018 3(4)	0.141 7(5)	−0.012 7(5)
C(4)	0.052 6(5)	0.022 4(4)	0.253 2(7)	C(42)	−0.013 8(5)	0.091 1(5)	−0.067 8(6)
C(5)	−0.001 2(4)	0.050 9(4)	0.243 0(6)	C(43)	0.033 9(6)	0.048 7(6)	−0.064 0(6)
C(20)	0.158 9(4)	0.272 4(6)	0.136 6(6)	C(44)	0.076 1(5)	0.057 5(5)	−0.008 7(7)
C(21)	0.180 4(5)	0.215 5(6)	0.177 1(7)	C(45)	0.072 1(4)	0.107 9(4)	0.046 3(5)
C(22)	0.180 3(4)	0.227 8(6)	0.257 4(7)	C(50)	0.003 3(4)	0.291 9(4)	0.059 7(5)
C(23)	0.156 6(5)	0.288 9(6)	0.268 5(6)	C(51)	0.015 4(5)	0.297 6(4)	−0.018 1(5)
C(24)	0.141 1(4)	0.317 4(5)	0.194 7(7)	C(52)	0.005 9(5)	0.357 4(5)	−0.057 3(6)
C(25)	0.159 3(7)	0.283 5(11)	0.051 5(8)	C(53)	−0.013 9(7)	0.411 6(6)	−0.018 6(7)
C(26)	0.210 1(6)	0.156 8(8)	0.137 2(15)	C(54)	−0.025 1(6)	0.407 4(5)	0.060 6(6)
C(27)	0.203 9(7)	0.183 4(10)	0.322 4(10)	C(55)	−0.016 0(5)	0.348 6(4)	0.098 9(5)
C(28)	0.145 2(8)	0.326 4(11)	0.343 0(10)	C(6)	0.792 9(6)	0.012 9(7)	0.561 2(8)
C(29)	0.117 3(8)	0.387 6(6)	0.182 2(13)	Cl(2)	0.778 8(2)	0.018 7(2)	0.660 0(2)
C(30)	−0.133 1(4)	0.253 9(4)	0.217 8(5)	Cl(3)	0.856 3(2)	−0.035 4(3)	0.546 8(3)
C(31)	−0.133 0(3)	0.209 7(4)	0.283 6(5)	Cl(4)	0.802 2(3)	0.092 9(2)	0.521 6(3)
C(32)	−0.135 0(4)	0.142 9(5)	0.258 2(6)	B	0.294 7(3)	0.429 7(3)	0.100 0(4)
C(33)	−0.133 4(4)	0.143 8(4)	0.174 6(5)	F(1)	0.264 5(15)	0.381 3(18)	0.148 0(21)
C(34)	−0.135 9(3)	0.211 7(4)	0.149 0(5)	F(2)	0.346 1(16)	0.427 0(18)	0.136 6(20)
C(35)	−0.138 9(5)	0.327 0(4)	0.221 6(7)	F(3)	0.273 4(18)	0.404 5(22)	0.038 0(25)
C(36)	−0.132 6(5)	0.233 1(6)	0.365 0(6)	F(4)	0.259 8(40)	0.479 5(49)	0.122 4(55)

Table 8 Final atomic coordinates with e.s.d.s in parentheses for the non-hydrogen atoms of complex **14**·$0.22CHCl_3$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Rh	0.392 13(1)	0.294 26(1)	0.261 41(1)	C(17)	0.454 4(2)	0.379 5(2)	0.185 5(1)
P(1)	0.286 84(4)	0.286 84(4)	0.250 00	C(18)	0.511 5(2)	0.371 7(2)	0.183 5(1)
P(2)	0.436 52(4)	0.410 22(4)	0.214 54(1)	C(19)	0.522 9(2)	0.345 9(2)	0.161 4(1)
O(1)	0.397 4(1)	0.365 3(1)	0.288 6(1)	C(20)	0.478 8(2)	0.327 2(2)	0.141 3(1)
O(2)	0.451 6(1)	0.378 9(1)	0.236 9(1)	C(21)	0.422 4(2)	0.334 0(2)	0.143 1(1)
C(1)	0.374 8(2)	0.214 2(2)	0.286 8(1)	C(22)	0.410 1(2)	0.360 3(2)	0.165 2(1)
C(2)	0.447 1(2)	0.262 2(2)	0.288 0(1)	C(23)	0.494 4(2)	0.500 4(2)	0.215 2(1)
C(3)	0.474 2(2)	0.268 1(2)	0.263 8(1)	C(24)	0.469 8(2)	0.544 2(2)	0.214 4(1)
C(4)	0.420 2(2)	0.223 7(2)	0.246 8(1)	C(25)	0.513 4(2)	0.614 7(2)	0.214 7(1)
C(5)	0.359 5(2)	0.187 5(2)	0.261 5(1)	C(26)	0.581 4(3)	0.639 9(2)	0.215 2(1)
C(6)	0.329 9(2)	0.192 8(2)	0.309 7(1)	C(27)	0.606 4(2)	0.596 3(2)	0.215 4(1)
C(7)	0.482 7(2)	0.297 9(2)	0.311 8(1)	C(28)	0.564 0(2)	0.527 3(2)	0.215 6(1)
C(8)	0.546 8(2)	0.312 8(2)	0.255 8(1)	B(1)	0.333 3	0.666 7	0.024 6(2)
C(9)	0.430 0(2)	0.210 0(2)	0.220 0(1)	F(1)	0.333 3	0.666 7	−0.002 2(1)
C(10)	0.296 0(2)	0.127 5(2)	0.252 8(1)	F(2)	0.390 7(1)	0.724 0(1)	0.032 8(1)
C(11)	0.229 9(2)	0.247 1(2)	0.277 1(1)	B(2)	0.000 0	0.000 0	−0.011 0(3)
C(12)	0.186 0(2)	0.178 0(2)	0.279 9(1)	F(3)	0.000 0	0.000 0	0.014 6(2)
C(13)	0.149 4(2)	0.152 7(2)	0.302 3(1)	F(4)	−0.051 6(3)	−0.060 9(3)	−0.019 1(1)
C(14)	0.156 8(2)	0.193 8(2)	0.322 0(1)	Cl(1)*	0.595 0(2)	0.333 3	0.083 3
C(15)	0.199 3(2)	0.262 5(2)	0.319 6(1)	C(29)*	0.666 7	0.333 3	0.069 8(6)
C(16)	0.235 8(2)	0.289 1(2)	0.297 2(1)				

* Solvent molecule.

and the ψ-scan technique[38] for **14** (transmission factors 0.771–0.704).

The three structures were solved by Patterson, DIRDIF,[39] and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all the non-hydrogen atoms (except BF_4^- for complex **9** and BF_4^- and the atoms of the solvent molecule for **14**). All hydrogen atoms of **5** and **9** were clearly located in the final ΔF map and refined isotropically; only the phenyl hydrogen atoms of the phosphide ligand of **14** were located in the ΔF map, the remaining ones being placed at their geometrically calculated positions (C–H 0.96 Å) and introduced in the final structure-factor calculations. At this stage of refinement a partial chloroform molecule was identified in the residual map of **14**; a fixed occupancy factor (0.111) was assigned to it for the subsequent cycles. The final cycles of refinement were carried out on the basis of 775 (**5**), 582 (**9**) and 321 (**14**) variables; after the last cycles, no parameter shifted by more than 0.25 (**5**), 0.36 (**9**) and 0.025 (**14**) e.s.d. The largest remaining peaks in the final difference map were equivalent to about 1.07 (**5**), 1.90 (**9**) and 0.68 e Å^{-3} (**14**). For complexes **5** and **9** a weighting scheme was chosen empirically to give no trends on $\langle w\Delta^2 \rangle$ *versus* $|F_o|$ or sin θ/λ. For **14** the following weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,538F^2$ was used. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref. 40. All calculations were carried out using the SHELX 76,[41] X-RAY 76[42] and DIRDIF[39] systems of crystallographic computer programs. The final atomic coordinates for the non-hydrogen atoms of **5**, **9** and **14** are given in Tables 6–8, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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