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Extending the coordination capabilities of tertiary phosphines and arsines: preparation, molecular structure, and reactivity of dinuclear rhodium complexes with PR_3 and AsR_3 in a doubly bridging coordination mode

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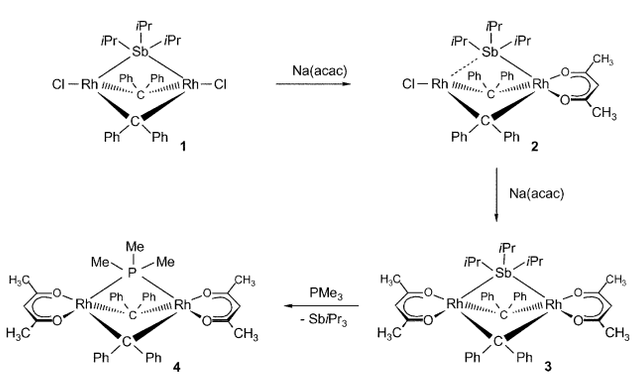
The reactions of $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CPh_2)_2(\mu\text{-}PR_3)]$ (PR_3 = PMe_3 **4**, PMe_2Ph **7**, PEt_3 **8**) with an equimolar amount of Me_3SiX (X = Cl, Br, I) afforded the unsymmetrical complexes $[Rh_2X(\kappa^2\text{-acac})(\mu\text{-}CPh_2)_2(\mu\text{-}PR_3)]$ **5**, **9**–**12**, which contain the phosphine in a semi-bridging coordination mode. From **4** and excess Me_3SiCl, the tetranuclear complex $[\{Rh_2Cl(\mu\text{-}Cl)(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)\}_2]$ **6** was obtained. In contrast, the reaction of **4** with an excess of Me_3SiX (X = Br, I) yielded the dinuclear complexes $[Rh_2X_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)]$ **13**, **14** in which, as shown by the X-ray crystal structure analysis of **14**, the bridging phosphine is coordinated in a truly symmetrical bonding mode. While related compounds with PEt_3 and PMe_2Ph as bridging ligands were prepared on a similar route, the complex $[Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}P\textit{i}Pr_3)]$ **19** was obtained from the mixed-valence species $[(P\textit{i}Pr_3)Rh(\mu\text{-}CPh_2)_2Rh(\kappa^2\text{-acac})_2]$ **17** and HCl. The reaction of $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ **3** with $AsMe_3$ gave the related $Rh(\mu\text{-}AsMe_3)Rh$ compound **21**. With Me_3SiCl, the acac ligands of **21** can be replaced stepwise by chloride to give $[Rh_2Cl(\kappa^2\text{-acac})(\mu\text{-}CPh_2)_2(\mu\text{-}AsMe_3)]$ **23** and $[\{Rh_2Cl(\mu\text{-}Cl)(\mu\text{-}CPh_2)_2(\mu\text{-}AsMe_3)\}_2]$ **24**, the latter being isomorphous to the phosphine-bridged dimer **6**.

Tertiary phosphines PR_3 with R = alkyl or aryl belong like CO to the most well-known ligands in coordination chemistry. While with regard to CO not only numerous metal complexes with terminal but also with doubly bridging carbonyl ligands have been described, the general knowledge is that tertiary phosphines (and tertiary arsines AsR_3 and stibines SbR_3 as well) behave exclusively as terminal coordinated ligands.[1,2]

In attempting to obtain a dinuclear palladium compound with $Pd(\mu\text{-}PF_3)Pd$ as the core unit, Balch *et al*. reported in 1990 the preparation and structural characterization of a cationic Pd_3 complex consisting of a nearly equilateral triangle of palladium atoms bridged at the edges by diphenylphosphinomethane ligands and capped by the *triply* bridging phosphorus atom of PF_3.[3] More recently, we found in the context of our studies on the reactivity of carbenerhodium(I) compounds,[4] that the bis(stibine) derivatives *trans*-$[RhCl(=CRR')(Sb\textit{i}Pr_3)_2]$ generate upon heating dinuclear rhodium(I) complexes such as $[Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ **1** with $[Rh(\mu\text{-}Sb\textit{i}Pr_3)Rh]$ as a building block.[5] After initial attempts to substitute the triisopropylstibine in **1** by a tertiary phosphine failed,[5] we circumvented the difficulties by the sequence of reactions shown in Scheme 1. The crucial observation was that replacing the chloro ligands in **1** by acetylacetonate (acac) changes the reactivity of the starting material significantly and provides the opportunity to substitute $Sb\textit{i}Pr_3$ for PMe_3 without fragmentation of the dinuclear core. However, while according to the NMR data (the ^{31}P NMR spectrum of **4** shows a sharp triplet in the temperature range of −60 °C to +25 °C) there was no doubt, that the PMe_3 ligand should occupy a symmetrical doubly bridging position, the X-ray crystal structure analysis of **4** revealed that in the solid the distances between the phosphorus and the two rhodium centers differ by 0.30 Å.[6]



Scheme 1

In order to find out how strongly the *anionic* ligands influence the binding of the bridging ligands, we attempted to reconvert the $Rh(\kappa^2\text{-acac})$ to RhX units (X = Cl, Br, I) and thus to reduce both the coordination number and the steric crowding at the metal centers. The present paper reports the synthesis and structural characterization of dichloro-, dibromo- and diiodorhodium complexes not only with PMe_3 but also with PMe_2Ph, PEt_3, $P\textit{n}Bu_3$ and $P\textit{i}Pr_3$ as bridging ligands, the conversion of some $Rh_2(\kappa^2\text{-acac})_2$ to corresponding $Rh_2X(\kappa^2\text{-acac})$ derivatives containing semi-bridging phosphines, and the preparation of the first representatives with trimethylarsine in a doubly bridging coordination mode. Some preliminary results of this work have already been communicated.[7]

Results and discussion

A dimer with two $[Rh(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)Rh]$ subunits

Taking the preference of Si–O bond formation into consideration, we treated the bis(κ^2-acac) compound **4** with an excess of Me_3SiCl in benzene at room temperature with the aim to replace the acac by the chloro ligands. A slow reaction, accompanied by a gradual change of color from brown to red, takes place which gives a product **6**, correctly analyzing as $[Rh_2Cl_2(CPh_2)_2(PMe_3)]$, in 91% yield. The red solid is only slightly air-sensitive, insoluble in pentane and diethyl ether, and moderately soluble in benzene and dichloromethane. If the reaction of **4** with Me_3SiCl is carried out in the molar ratio of 1 : 1, the unsymmetrical complex **5** (Scheme 2) is obtained, which has originally been prepared from **2** and PMe_3 by bridge-ligand exchange.[6] According to the X-ray crystal structure analysis, the trimethylphosphine occupies in **5** a semi-bridging position, the phosphorus atom being 0.6 Å nearer to the rhodium center with the acac than to that with the chloro ligand.[8]

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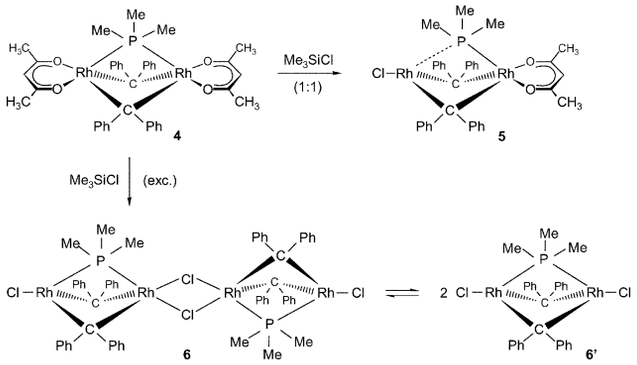


Scheme 2

While we anticipated, owing to the ^{1}H and ^{13}C NMR spectra, that compound **6** possesses a structure analogously to the stibine-bridged complex **1**, the X-ray crystal structure analysis revealed that in the lattice two dinuclear moieties are connected *via* two bridging chlorides to give a Rh_4 species with a chain-like $ClRh_2Cl_2Rh_2Cl$ core (Fig. 1). Moreover, the midpoint of the planar $Rh(\mu\text{-}Cl)_2Rh$ fragment is a center of symmetry. While the coordination geometry around Rh(1) is distorted tetrahedral, that around Rh(2) is best described as square-pyramidal with the phosphorus atom P(1) in the apical position. The structure of the fragment $[ClRh(\mu\text{-}CPh_2)(\mu\text{-}PMe_3)RhCl_2]$ is thus similar to that of the unsymmetrical molecule **5**.[6] Besides the Rh(1)–Rh(2) distance of 2.5054(2) Å (2.4993(2) Å for the second independent molecule found in the asymmetric unit), which differs only slightly to that of the stibine-bridged compound **1** (2.5349(5) Å), the most important structural features of **6** are the Rh–P bond lengths. They are 2.3625(6) and 2.4826(6) Å in the molecule shown in Fig. 1 and 2.3890(6) and 2.4173(6) Å in the second molecule (Table 1). Most noteworthy, the difference between the two Rh–P distances is in each case much less than for the bis(acac) complex **4**, indicating that – at least in the crystal lattice – the type of the anionic ligands bonded to rhodium influences significantly the position of the bridging phosphine unit. Due to the similarity of the Rh–Rh and Rh–P distances, the bond angles of the Rh_2P triangle are nearly the same and deviate only marginally from the 60° value. As expected, the bond length Rh(1)–Cl(1) is considerably shorter than the distances Rh(2)–Cl(2) and Rh(2)–Cl(2A), the latter differing in both independent molecules by less than 0.03 Å.

Although cryoscopic measurements with a saturated solution of **6** in benzene confirm that under these conditions the tetranuclear compound is present (calc.: *M* 1370.5; found: *M* 1310), the ^{31}P NMR spectrum of **6** in C_6D_6 at room temperature is concentration-dependent. The spectrum of a nearly saturated solution (4 mmol l^{-1}) exhibits a somewhat broadened triplet at δ −24.6 (assigned to tetranuclear **6**) which after lowering the concentration to 0.1 mmol l^{-1} transforms into a sharp triplet with a chemical shift of δ −20.4 (assigned to dinuclear **6′**). Since the data in CD_2Cl_2 are quite similar (a broadened triplet being observed at δ −23.1 for a concentrated and a sharp triplet at δ −15.7 for a diluted solution), we conclude that both in benzene and dichloromethane a rapid equilibrium between the Rh_4 and the Rh_2 species exists (see Scheme 2). At low concentrations the Rh_2 species **6′** dominates. At 193 K in toluene-d_8, the ^{31}P NMR spectrum displays a doublet of doublets at δ −30.4 (assigned to **6**), which indicates that under these conditions the conversion of **6** to **6′** is slowed down on the NMR time scale.

Tertiary phosphines in semi-bridging and truly symmetrical doubly bridging positions

The reactivity of **4** toward Me_3SiBr and Me_3SiI is similarly to that of the same starting material toward Me_3SiCl. With equimolar amounts of the substrates, the unsymmetrical complexes **9** and **10** are formed (Scheme 3) and isolated as dark red (**9**) or dark brown (**10**) solids in nearly quantitative yields. An alternative procedure consists in the reaction of **5** with NaBr or NaI in acetone which equally affords **9** and **10** in good to excellent yields. Both **9** and **10** are thermally less stable than **5** but can be stored at room temperature under argon for weeks. The same is true for the $Rh_2Cl(\kappa^2\text{-acac})$ compounds **11** and **12**, which are obtained from **7** or **8** and Me_3SiCl in the molar ratio of 1 : 1. As was already reported,[6] the PEt_3 derivative **12** is also accessible from **2** and PEt_3. The ^{31}P NMR spectra of **9** and **10** display, similarly to the spectrum of **5**, one doublet of doublets with ^{103}Rh–^{31}P coupling constants that differ for **9** by 93.3 and for **10** by 111.7 Hz (see, for comparison, **5**: ΔJ = 84.3 Hz). Since for transition-metal complexes containing terminal phosphine ligands, the size of the coupling constant $^{1}J(Rh,P)$ can be correlated to a first approximation to the Rh–P bond lengths,[9] it is conceivable that the difference in the distances between the phosphorus atom of the semi-bridging trimethylphosphine and the two rhodium centers is larger in **9** and particularly in **10** than in **5**. It should be mentioned that for compound $[(\kappa^2\text{-acac})Rh(\mu\text{-}CPh_2)_2(\mu\text{-}CO)Rh(PMe_3)(\kappa^2\text{-acac})]$, formed from **4** and CO, in which the PMe_3 ligand occupies a terminal position, the ^{103}Rh–^{31}P coupling constants are, respectively, 129.1 and 7.6 Hz.[10]

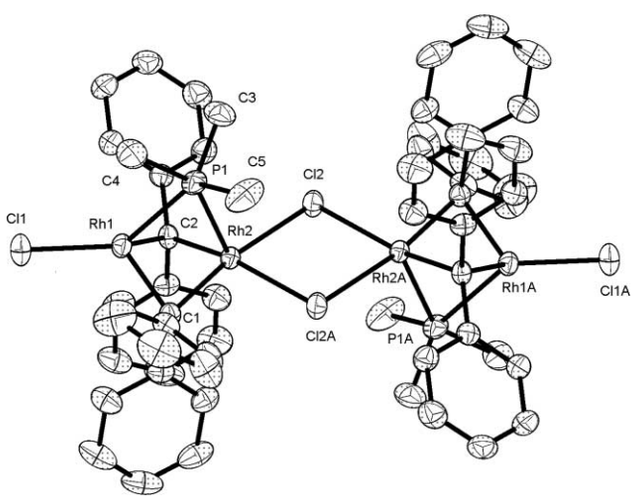
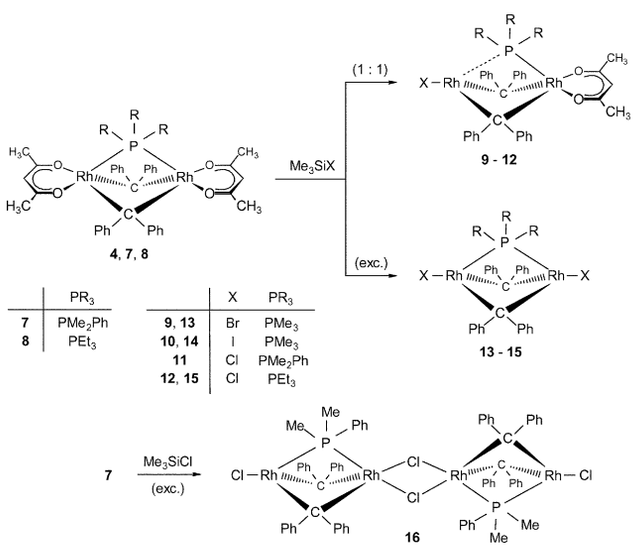


Fig. 1 An ORTEP plot of one of the centrosymmetric dimers of rhodium complex **6**[20] (symmetry operation used to generate equivalent atoms: $-x, -y + 2, -z$).



Scheme 3

Table 1 Selected bond lengths (Å) and angles (°) for compound **6** (there are two independent molecules **6a** and **6b** in the asymmetric unit; values for **6b** are in square brackets)

Rh(1)–Rh(2)	2.5054(2) [2.4993(2)]	Rh(1)–Cl(1)	2.3088(6) [2.2979(6)]
Rh(1)–P(1)	2.4826(6) [2.4173(6)]	Rh(2)–Cl(2)	2.4961(5) [2.4911(5)]
Rh(2)–P(1)	2.3625(6) [2.3890(6)]	Rh(2)–Cl(2A)	2.4636(5) [2.4685(6)]
Rh(1)–C(1)	1.988(2) [1.992(2)]	P(1)–C(3)	1.815(3) [1.811(3)]
Rh(1)–C(2)	1.968(2) [1.978(2)]	P(1)–C(4)	1.816(3) [1.814(3)]
Rh(2)–C(1)	2.044(2) [2.038(2)]	P(1)–C(5)	1.839(3) [1.841(3)]
Rh(2)–C(2)	2.051(2) [2.046(2)]		
Rh(1)–P(1)–Rh(2)	62.217(15) [62.662(15)]	C(1)–Rh(2)–Cl(2)	170.77(6) [173.90(6)]
P(1)–Rh(2)–Rh(1)	61.245(16) [59.225(15)]	C(2)–Rh(2)–Cl(2A)	159.02(6) [152.20(6)]
P(1)–Rh(1)–Rh(2)	56.538(14) [58.114(15)]	Cl(1)–Rh(1)–Rh(2)	167.894(19) [172.29(2)]
Rh(1)–C(1)–Rh(2)	76.83(7) [76.65(7)]	Cl(2A)–Rh(2)–Cl(2)	77.733(19) [77.89(2)]
Rh(1)–C(2)–Rh(2)	77.08(7) [76.77(7)]	Rh(2A)–Cl(2)–Rh(2)	102.267(19) [102.11(2)]

The reactions of **4** with a twofold excess of Me_3SiBr or Me_3SiI proceed quite slowly and afford in toluene after 24 h (X = Br) or 2 h (X = I) at room temperature the dibromo and diiodo complexes **13** and **14** in 90–92% isolated yield. In contrast to **6**, the ^{31}P NMR spectra of **13** and **14** are independent of the concentration of the solution and display in each case a sharp triplet at δ −18.3 (**13**) and δ −20.8 (**14**), respectively. However, while the ^{31}P NMR spectrum of **14** remains unchanged by lowering the temperature to 193 K, the corresponding spectrum of **13** changes and at 193 K shows together with the triplet at δ −17.5 a doublet of doublets at δ −31.8. If we take the data reported for **6** and **6′** into account, the appearance of these two signals indicate that in the case of **13** at low temperature apart from the dinuclear compound **13** also the tetranuclear species [BrRh(μ-CPh_2)$_2$(μ-PMe_3)Rh(μ-Br)$_2$-Rh(μ-CPh_2)$_2$(μ-PMe_3)RhBr] is present. At 193 K, the equilibrium between the monomer and the dimer is obviously very slow on the NMR time scale and thus both the Rh_2 and the Rh_4 complexes can be observed.

The expectation that, owing to the ^{31}P NMR data, the PMe_3 ligand in **14** occupies, even in the solid, a truly symmetrical bridging position was confirmed by an X-ray crystal structure analysis. As shown in Fig. 2, the molecule contains a C_2 axis passing through the phosphorus atom and the midpoint of the Rh–Rh distance. Therefore, the structure of **14** is quite similar to that of the stibine-bridged compound **1**.[5] The I–Rh–Rh–I axis in **14** is nearly linear with bond angles Rh(1)–Rh(1A)–I(1A) = Rh(1A)–Rh(1)–I(1) = 174.37(2)° (Table 2). The Rh–P bond lengths are 2.412(3) Å and thus lie between those of the bis(acac) derivative **4** (2.2707(7) and 2.5700(8) Å).[6] We note that for the chain-like Rh_4Cl_4 complex **6** the Rh–P distances in each of the dinuclear subunits differ by *ca*. 0.07 Å.

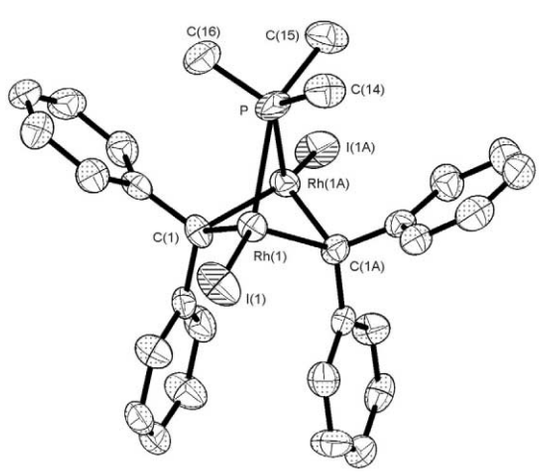
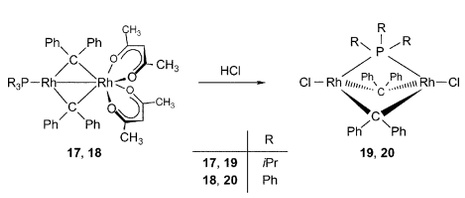


Fig. 2 An ORTEP plot of rhodium complex **14**[20] (symmetry operation used to generate equivalent atoms: $-x + 2/3$, $-x + y + 1/3$, $-z + 5/6$; there is a disorder of the methyl groups bonded to phosphorus)

The reactions of **7** and **8** with an excess of Me_3SiCl also lead to a displacement of the acac ligands by chloride. In both cases, deeply colored solids **15** and **16** are obtained of which **15** is much better soluble in benzene than **16**. The ^{31}P NMR spectrum of **15** displays (in C_6D_6) a sharp triplet at δ 6.0 which does not change either at higher concentrations of the solution or at lowering the temperature to 193 K. Therefore, we assume that under the experimental conditions only the dinuclear complex, probably having a similar structure as **14**, exists. The ^{31}P NMR spectrum of **16** shows (in CD_2Cl_2) at room temperature a broadened triplet at δ −17.0 (with ^1J(Rh,P) = 101.7 Hz) which at 193 K becomes a doublet of doublets with ^{103}Rh–^{31}P coupling constants of, respectively, 139.8 and 68.6 Hz. These data indicate that in the case of the PMe_2Ph-bridged complex the tetranuclear compound **16** dominates at low temperatures while at room temperature it is in equilibrium with the corresponding Rh_2 species. It should be mentioned that attempts to prepare **15** and **16** from **1** and PEt_3 or PMe_2Ph by ligand exchange failed.

After we confirmed that PMe_3, PMe_2Ph and PEt_3 can behave as doubly bridging ligands, we finally also succeeded with transferring the more bulky P*i*Pr$_3$ from a terminal into a bridging position. In our previous studies on the reactivity of **1** (the precursor of compound **3**) toward Lewis bases, we discovered that this complex reacts with P*i*Pr$_3$ to give *trans*-[RhCl(=CPh_2)(P*i*Pr$_3$)$_2$].[5] In contrast, treatment of **3** with P*i*Pr$_3$ does not lead to cleavage of the Rh(μ-CPh_2)Rh bridges and affords by migration of one acac ligand from one metal center to the next the interesting mixed-valence compound **17** in excellent yield.[11] Since it is conceivable that this reaction proceeds *via* the phosphine-bridged species [Rh$_2$(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-P*i*Pr$_3$)], we attempted to trap this intermediate by replacing the acac ligands for chloride. Thus, the mixed-valence complex **17** (Scheme 4) was treated with an excess of Me_3SiCl but on this route a mixture of products was formed. A clean reaction occurred, however, if a solution of HCl in benzene was dropped under vigorous stirring to a solution of **17** in the same solvent at room temperature. After removal of the volatile materials, the required complex **19** was isolated as a red, moderately air-stable solid in 91% yield. In the same way, the PPh_3 counterpart **20** could be generated from **18**. It contained, however, even after recrystallization from acetone some impurities (*ca*. 10%) and was thus characterized by spectroscopic techniques. The ^{13}C NMR spectra of **19** and **20** display a triplet for the CPh_2 carbon atoms at δ 180.7 (**19**) and δ 191.2 (**20**) with a ^{103}Rh–^{13}C coupling



Scheme 4

Table 2 Selected bond lengths (Å) and angles (°) for compound **14**

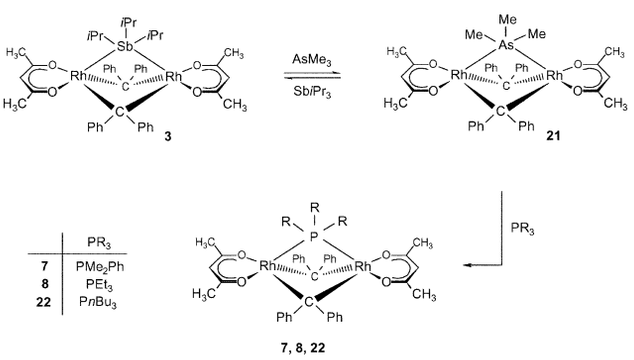
Rh(1)–C(1)	2.004(9)	Rh(1)–P	2.413(3)
Rh(1)–C(1A)	2.008(9)	Rh(1A)–P	2.413(3)
Rh(1A)–C(1)	2.004(9)	Rh(1)–I(1)	2.5981(10)
Rh(1)–Rh(1A)	2.5042(14)		
Rh(1)–C(1)–Rh(1A)	77.2(3)	I(1)–Rh(1)–P	126.88(6)
C(1)–Rh(1)–C(1A)	87.1(4)	I(1)–Rh(1)–C(1)	126.1(2)
I(1)–Rh(1)–Rh(1A)	174.37(2)	I(1)–Rh(1)–C(1A)	125.5(3)
Rh(1)–P–Rh(1A)	62.53(10)	C(1)–Rh(1)–Rh(1A)	51.3(2)
C(1)–Rh(1)–P	89.5(3)	C(1A)–Rh(1)–Rh(1A)	51.5(3)
C(1A)–Rh(1)–P	89.6(3)	P–Rh(1)–Rh(1A)	58.74(5)

constant of 28.6 Hz. Since the ^{31}P NMR spectra of **19** and **20** also show a sharp triplet at, respectively, δ 14.9 (**19**) and δ 9.8 (**20**), there is no doubt that the more bulky phosphines P*i*Pr$_3$ and PPh$_3$ can equally be linked to two rhodium centers in a doubly bridging position.

Trimethylarsine as a semi-bridging and a doubly bridging ligand

While the stibine-bridged compound **1** reacts smoothly with P*i*Pr$_3$ and PPh$_3$, it is inert toward the corresponding arsines As*i*Pr$_3$ and AsPh$_3$ and does not form by bridge cleavage the square-planar compounds *trans*-[RhCl(=CPh$_2$)(AsR$_3$)$_2$]. A slow reaction takes place if **1** is treated with AsMe$_3$ but in this case a mixture of products results which could not be separated by fractional crystallization or column chromatography.

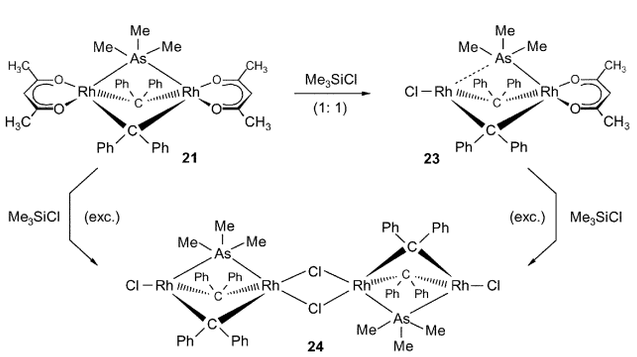
The successful route to bind AsMe$_3$ in a doubly bridging position was similar to that found for PMe$_3$.[6] Treatment of the bis(κ^2-acac) derivative **3** with trimethylarsine in benzene leads to an equilibrium between **3** and the AsMe$_3$ counterpart, which even in the presence of a large excess of the arsine could not be completely shifted to the side of the required product. However, in hexane as solvent (in which **21** is only sparingly soluble) the arsine-bridged complex **21** precipitates and is obtained in 85% isolated yield (Scheme 5). The light brown solid (the composition of which has been confirmed by elemental analysis and a FAB mass spectrum) is thermally more stable than the PMe$_3$ analogue **4** and can be stored under argon at low temperatures for weeks. In benzene or acetone solution it decomposes quite readily. The ^{1}H and ^{13}C NMR spectra of **21** indicate that the two acac as well as the two CPh$_2$ ligands are equivalent and thus we assume that the trimethylarsine occupies a symmetrical doubly bridging position.



Scheme 5

In contrast to **4**, the AsMe$_3$ counterpart **21** is rather labile and reacts not only with Sb*i*Pr$_3$ but also with tertiary phosphines such as PMe$_2$Ph, PEt$_3$ and P*n*Bu$_3$ by bridge-ligand exchange. While compounds **7** and **8** could be prepared, similarly to **4** (see Scheme 1), from **3** and PMe$_2$Ph or PEt$_3$, respectively, attempts to obtain **22** in the same way (benzene, room temperature) resulted in the formation of the mixed-valence compound [(P*n*Bu$_3$)Rh(μ-CPh$_2$)$_2$Rh(κ^2-acac)$_2$].[12] Although we postulated that this molecule is generated *via* **22**, we failed to fully characterize this isomer. The procedure to isolate the phosphine-bridged complex **22** consists in treatment of a solution of **21** in toluene at −50 °C with one equivalent of P*n*Bu$_3$, followed by warming to 0 °C and stirring the reaction mixture at this temperature under reduced pressure for 20 min. Under these conditions, the volatile trimethylarsine (bp 52 °C) is removed and the product **22** isolated as a brown solid in 89% yield. Due to the three C$_4$ chains at the phosphorus atom, **22** is much better soluble in organic solvents than the PMe$_3$ analogue. The ^{31}P NMR spectrum of **22** (in C$_6$D$_6$) displays a sharp triplet at δ −9.6 with a ^1J(Rh,P) coupling constant that is identical to that of **8**. We note that both **7** and **8** are obtained from **21** in much better yields than from **3** as the precursor.

Similarly to the PMe$_3$ analogue **4**, compound **21** reacts in benzene with Me$_3$SiCl in the molar ratio of 1 : 1.1 to give the dinuclear complex **23** (Scheme 6), probably containing the arsine in a semi-bridging coordination mode. As already observed for the PMe$_3$-counterparts **4** and **5**, the unsymmetrical species **23** (isolated as a brown solid in 88% yield) is significantly more stable than **21** and does not decompose in benzene even after storing for three days.



Scheme 6

Replacing the remaining acac ligand of **23** by chloride is more difficult and, even with a large excess of Me$_3$SiCl, the formation of **24** occurs only slowly at room temperature. After removal of the volatiles, the dichloro derivative has been isolated as a red–brown solid in 91% yield. As shown by the X-ray crystal structure analysis, the AsMe$_3$-bridged compound **24** is isomorphous to **6** and also possesses the midpoint of the Rh(μ-Cl)$_2$Rh unit as a center of symmetry (Fig. 3). Analogously to **6**, the half dimer structure is found twice in the asymmetric unit. The Rh–Rh distance in each dinuclear subunit is 2.5225(3) Å (2.5271(3) Å in the second independent molecule) which is slightly larger than in **6**. The two Rh–As bond lengths in each subunit differ somewhat (0.05 Å in one molecule and 0.10 Å in the other) reflecting the inequivalence of the "outer" and "inner" metal centers of the ClRh$_2$Cl$_2$Rh$_2$Cl chain (Table 3). Not only the arsine but also the two diphenylcarbene ligands are linked to Rh(1) and Rh(2) in a slightly unsymmetrical fashion. Therefore, no mirror plane exists along the Cl(1)–Rh(1)–Rh(2) axis. As expected, the terminal distance Rh(1)–Cl(1) is significantly shorter than the distances Rh(2)–Cl(2) and Rh(2)–Cl(2A) in the centre of the molecule. Regarding the unit cell of **24**, it should be mentioned that there are no

Table 3 Selected bond lengths (Å) and angles (°) for compound **24** (there are two independent molecules **24a** and **24b** in the asymmetric unit; values for **24b** are in square brackets)

Rh(1)–Rh(2)	2.5225(3) [2.5271(3)]	Rh(1)–Cl(1)	2.3006(7) [2.3108(6)]
Rh(1)–As(1)	2.5372(3) [2.5777(3)]	Rh(2)–C(1)	2.048(2) [2.055(2)]
Rh(2)–As(1)	2.4899(3) [2.4757(3)]	Rh(2)–C(14)	2.046(2) [2.047(2)]
Rh(1)–C(1)	1.989(2) [1.973(2)]	Rh(2)–Cl(2)	2.4662(7) [2.4917(6)]
Rh(1)–C(14)	1.983(2) [1.994(2)]	Rh(2)–Cl(2A)	2.4895(7) [2.4669(6)]
Rh(1)–As(1)–Rh(2)	60.225(9) [59.970(9)]	Rh(1)–Rh(2)–Cl(2)	144.647(17) [138.145(16)]
As(1)–Rh(1)–Rh(2)	58.958(8) [58.011(8)]	C(1)–Rh(2)–Cl(2)	96.89(7) [96.17(6)]
As(1)–Rh(2)–Rh(1)	60.817(9) [62.018(8)]	C(14)–Rh(2)–Cl(2A)	94.43(6) [95.11(6)]
Rh(1)–C(1)–Rh(2)	77.32(8) [77.68(8)]	Cl(1)–Rh(1)–Rh(2)	173.55(2) [170.13(2)]
Rh(1)–C(14)–Rh(2)	77.51(8) [77.39(8)]	Cl(2A)–Rh(2)–Cl(2)	78.52(2) [78.43(2)]
C(1)–Rh(1)–C(14)	91.66(9) [91.73(9)]	Rh(2A)–Cl(2)–Rh(2)	101.48(2) [101.57(2)]
C(1)–Rh(2)–C(14)	88.19(9) [87.92(9)]		

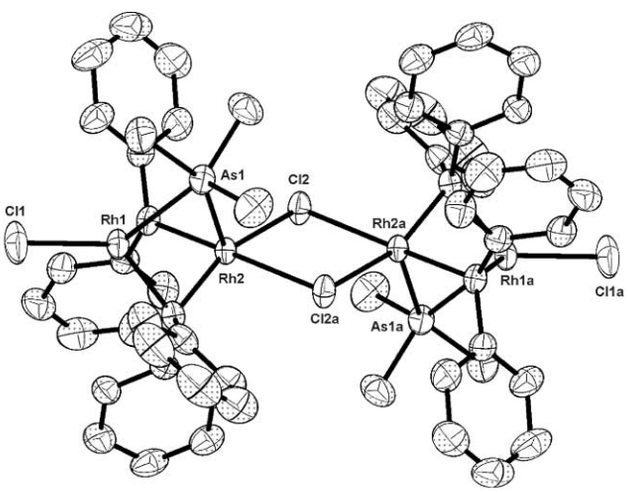


Fig. 3 An ORTEP plot of one of the centrosymmetric dimers of rhodium complex **24**[20] (symmetry operation used to generate equivalent atoms: $-x + 1, -y, -z + 1$).

contacts either between the terminal chloride Cl(1) and the corresponding Rh–Cl fragment of a neighbouring Rh_2 subunit or between Cl(1) and the benzene molecules incorporated in the crystal. We also note that the ^1H and the ^{13}C NMR spectra of **24** (in CD_2Cl_2) remain unchanged in the temperature range between 193 and 333 K, indicating that under these conditions probably no dissociation of the tetranuclear Rh_4 to the dinuclear Rh_2 species takes place.

Conclusion

The present investigation closes a gap in the field of coordination chemistry. After it had been supposed for decades that tertiary phosphines, arsines and stibines behave exclusively as terminal ligands, it was only recently that this postulate became weakened. The preparation of the Balch compound with the triply bridging PF_3[3] and the discovery of compound **1** (according to Caulton "the first outsider")[13] as well as its $SbMe_3$, $SbEt_3$ and $Sb(CH_2Ph)_3$ analogues[5,14] was followed by the isolation and structural characterization of **4** and **5** and has now culminated in the synthesis of the first arsine-bridged species **21**, **23** and **24**. Apart from the preparation of these new Rh(μ-$AsMe_3$)Rh complexes, the most noteworthy feature of this work is that with respect to tertiary phosphines not only PMe_3 but also the more bulky analogues PMe_2Ph, PEt_3, P*n*Bu_3, P*i*Pr_3 and PPh_3 can be forced to bind to two metal centers in a doubly bridging position. That in general a bonding mode such as M(μ-ER_3)M with E = P, As, Sb should not be regarded in principle as thermodynamically unfavorable, was recently pointed out by Braunstein and Boag who took the isolobal analogy between PR_3 and SiR_3^- as well as the existence of various silyl-bridged transition-metal compounds into consideration.[15] Thus, it is well possible that the preparation of complexes such as **1**–**16** and **19**–**24** might only be the first step into a new field. The recent discovery by Reau and co-workers[16] that the phosphorus atom of substituted phospholes is able to bridge two palladium centers in a symmetrical fashion undoubtedly supports this prediction.

Experimental

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **3**,[11] **4**,[6] **7**,[17] **8**,[17] **17**,[11] and **18**[11] were prepared as described in the literature. Melting points were measured by differential thermal analysis (DTA). NMR spectra were recorded (if not otherwise stated) at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a IFS 25 FT-IR infrared spectrometer, and mass spectra on a Finnigan MAT 90 (70 eV) or on a Hewlett-Packard G 1800 GCD instrument. Coupling constants are given in hertz. Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broadened signal.

Preparations

[$Rh_2Cl(\kappa^2$-acac)(μ-$CPh_2)_2$(μ-PMe_3)] 5. A solution of **4** (54 mg, 0.07 mmol) in benzene (10 cm^3) was treated with Me_3SiCl (0.008 cm^3, 0.07 mmol) and stirred for 1 h at room temperature. The solvent was evaporated *in vacuo*, the remaining red–brown solid was washed twice with 3 cm^3 portions of pentane–diethyl ether (1 : 1) and dried; yield 47 mg (94%). The product was characterized by comparison of the ^1H and ^{31}P NMR data with those of an authentic sample.[6]

[{Rh_2Cl_2(μ-$CPh_2)_2$(μ-PMe_3)}$_2$] 6. A solution of **4** (129 mg, 0.16 mmol) in benzene (20 cm^3) was treated with Me_3SiCl (0.23 cm^3, 1.81 mmol) and stirred for 24 h at room temperature. The solvent was evaporated *in vacuo*, the remaining red solid was washed twice with 5 cm^3 portions of diethyl ether and dried; yield 99 mg (91%). Alternatively, compound **6** can also be prepared from **5** (518 mg, 0.69 mmol) and Me_3SiCl (1.0 cm^3, 7.88 mmol) in benzene (70 cm^3); yield 436 mg (92%); mp 126 °C (decomp.) (Found: C, 49.24; H, 6.18; mol. weight (benzene) 1310. $C_{58}H_{58}Cl_4P_2Rh_4$ requires: C, 49.53; H, 6.24%; mol. weight 1370.5). NMR (C_6D_6): δ_H (400 MHz, 4 mmol l^{-1}) 7.87, 7.66 (8 H, both m, *ortho*-H of C_6H_5), 6.83 (4 H, m, *meta*-H of C_6H_5), 6.74 (2 H, m, *para*-H of C_6H_5), 6.65 (6 H, m, *meta*-H and *para*-H of C_6H_5), 0.88 [18 H, d, J(P,H) 10.6, PCH_3]; δ_H (200 MHz, 0.1 mmol l^{-1}) 7.62 (8 H, m, *ortho*-H of C_6H_5), 6.70 (12 H, m, *meta*- and *para*-H of C_6H_5), 0.69 [18 H, d, J(P,H) 10.6, PCH_3]; δ_C (100.6 MHz, 4 mmol l^{-1}) 187.8 (m, CPh_2), 153.5 [d, J(P,C) 3.8, *ipso*-C of C_6H_5], 152.3 (s, *ipso*-C of C_6H_5), 128.5, 127.6, 127.5, 127.0, 126.9, 124.8 (all s, C_6H_5), 23.5 [d, J(P,C) 40.0 Hz, PCH_3]; δ_P (81.0 MHz, 4 mmol l^{-1}) −24.6 [br t, J(Rh,P) 109.3]; δ_P (81.0 MHz, 0.1 mmol l^{-1}) −20.4 [t, J(Rh,P) 109.3]; NMR (CD_2Cl_2): δ_P (81.0 MHz, 8 mmol l^{-1}) −23.1 [br t, J(Rh,P) 109.4]; δ_P (81.0 MHz, 0.1 mmol l^{-1}) −15.7 [t, J(Rh,P) 109.3]; NMR (toluene-d_8): δ_P (81.0 MHz, 2 mmol l^{-1}, 293 K): −21.3

[t, J(Rh,P) 111.9]; δ_P (81.0 MHz, 2 mmol l^{-1}, 233 K) −26.0 (br m); δ_P (81.0 MHz, 2 mmol l^{-1}, 193 K) −30.4 [dd, J(Rh,P) 128.4, J(Rh′,P) 95.4].

[$Rh_2Br(\kappa^2$-acac)(μ-$CPh_2)_2$(μ-PMe_3)] 9. (a) A solution of **4** (132 mg, 0.16 mmol) in toluene (20 cm^3) was treated dropwise at −50 °C with Me_3SiBr (0.021 cm^3, 0.16 mmol). After the solution was warmed to room temperature, it was stirred for 30 min. The solvent was evaporated *in vacuo*, the remaining residue was washed twice with 2 cm^3 portions of diethyl ether, and then recrystallized from acetone (5 cm^3) at −60 °C. Dark red crystals precipitated, which were separated from the mother-liquor and dried; yield 118 mg (92%). (b) A solution of **5** (56 mg, 0.07 mmol) in acetone (25 cm^3) was treated with NaBr (15 mg, 0.15 mmol) and stirred for 2 h at room temperature. The solvent was evaporated *in vacuo*, and the residue was extracted twice with 20 cm^3 portions of pentane–dichloromethane (1 : 1). The combined extracts were brought to dryness *in vacuo*, and the remaining residue was recrystallized from acetone (3 cm^3) at −60 °C. Dark red crystals; yield 53 mg (89%); mp 144 °C (decomp.) (Found: C, 51.07; H, 4.57. $C_{34}H_{36}BrO_2PRh_2$ requires: C, 51.47; H, 4.57%). IR (KBr): (CO_{acac}) 1580, 1522 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.96 (4 H, m, *ortho*-H of C_6H_5), 7.20 (6 H, m, *meta*- and *para*-H of C_6H_5), 7.04 (4 H, m, *ortho*-H of C_6H_5), 6.71 (6 H, m, *meta*-H and *para*-H of C_6H_5), 5.80 (1 H, s, CH of acac), 2.23 (6 H, s, CH_3 of acac), 0.92 [9 H, dd, J(P,H) 10.8, J(Rh,H) 0.6, PCH_3]; δ_C (100.6 MHz) 189.3 (s, CO of acac), 174.1 [ddd, J(Rh,C) 30.5, J(Rh′,C) 21.0, J(P,C) 4.8, CPh_2], 153.3 [d, J(P,C) 1.9, *ipso*-C of C_6H_5], 153.2 (s, *ipso*-C of C_6H_5), 127.6, 127.1, 126.6, 125.7, 125.5, 124.7 (all s, C_6H_5), 100.8 [d, J(Rh,C) 1.9, CH of acac], 28.2 (s, CH_3 of acac), 22.0 [d, J(P,C) 40.0, PCH_3]; δ_P (162.0 MHz) −27.3 [dd, J(Rh,P) 157.7, J(Rh′,P) 64.4].

[$Rh_2I(\kappa^2$-acac)(μ-$CPh_2)_2$(μ-PMe_3)] 10. (a) This compound was prepared as described for **9**, from **4** (99 mg, 0.12 mmol) and Me_3SiI (0.017 cm^3, 0.12 mmol) in toluene (20 cm^3). A dark brown microcrystalline solid was obtained; yield 96 mg (94%). (b) A solution of **5** (71 mg, 0.09 mmol) in acetone (25 cm^3) was treated with NaI (14 mg, 0.09 mmol) and stirred for 2 h at room temperature. The solvent was evaporated *in vacuo*, and the residue was extracted twice with 20 cm^3 portions of pentane–dichloromethane (1 : 1). The combined extracts were brought to dryness *in vacuo*, and the remaining residue was recrystallized from acetone (3 cm^3) at −60 °C. Dark brown crystals; yield 59 mg (74%); mp 116 °C (decomp.) (Found: C, 49.01; H, 4.54. $C_{34}H_{36}IO_2PRh_2$ requires: C, 48.60; H, 4.32%). NMR (CD_2Cl_2): δ_H (400 MHz) 8.02 (4 H, m, *ortho*-H of C_6H_5), 7.17 (6 H, m, *meta*- and *para*-H of C_6H_5), 7.10 (4 H, m, *ortho*-H of C_6H_5), 6.72 (6 H, m, *meta*- and *para*-H of C_6H_5), 5.79 (1 H, s, CH of acac), 2.22 (6 H, s, CH_3 of acac), 0.92 [9 H, d, J(P,H) 11.2, PCH_3]; δ_C (100.6 MHz) 189.4 (s, CO of acac), 171.5 [ddd, J(Rh,C) 31.5, J(Rh′,C) 20.0, J(P,C) 4.3, CPh_2], 153.1 (s, *ipso*-C of C_6H_5), 152.9 [d, J(P,C) 1.9, *ipso*-C of C_6H_5], 127.5, 127.1, 126.6, 125.8, 125.7, 125.3 (all s, C_6H_5), 100.7 (s, CH of acac), 28.2 (s, CH_3 of acac), 21.2 [d, J(P,C) 41.0, PCH_3]; δ_P (162.0 MHz) −22.3 [dd, J(Rh,P) 165.2, J(Rh′,P) 53.5].

[$Rh_2Cl(\kappa^2$-acac)(μ-$CPh_2)_2$(μ-PMe_2Ph)] 11. This compound was prepared as described for **5**, from **7** (60 mg, 0.07 mmol) and Me_3SiCl (0.01 cm^3, 0.07 mmol) in benzene (10 cm^3). An orange microcrystalline solid was obtained; yield 52 mg (93%); mp 63 °C (decomp.) (Found: C, 57.39; H, 5.08. $C_{39}H_{38}ClO_2PRh_2$ requires: C, 57.76; H, 4.72%). IR (KBr): ν(CO_{acac}) 1576, 1522 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.93 (4 H, m, *ortho*-H of C_6H_5), 7.37, 7.22, 7.13, 6.66, 6.58 (21 H, all m, C_6H_5), 5.81 (1 H, s, CH of acac), 2.26 (6 H, s, CH_3 of acac), 1.15 [6 H, d, J(P,H) 10.8, PCH_3]; δ_C (100.6 MHz) 189.2 (s, CO of acac), 174.6 [ddd, J(Rh,C) 30.5, J(Rh′,C) 20.0, J(P,C) 3.8, CPh_2], 154.0 (s, *ipso*-C of CC_6H_5), 132.0 [d, J(P,C) 55.3, *ipso*-C of PC_6H_5], 129.8 [d, J(P,C) 2.9, *para*-C of PC_6H_5], 129.1 [d, J(P,C) 9.5, *ortho*- or *meta*-C of PC_6H_5], 128.6 [d, J(P,C) 10.5, *ortho*- or *meta*-C of PC_6H_5], 127.8, 127.1, 126.6, 125.6, 125.5, 124.6 (all s, C_6H_5), 101.1 (s, CH of acac), 28.1 (s, CH_3 of acac), 18.7 [d, J(P,C) 43.9, PCH_3]; δ_P (162.0 MHz) −29.3 [dd, J(Rh,P) 152.6, J(Rh′,P) 69.8].

[$Rh_2Cl(\kappa^2$-acac)(μ-$CPh_2)_2$(μ-PEt_3)] 12. This compound was prepared as described for **5**, from **8** (60 mg, 0.07 mmol) and Me_3SiCl (0.01 cm^3, 0.07 mmol) in benzene (10 cm^3). A dark brown solid was obtained; yield 50 mg (90%). The product was characterized by comparison of the ^1H and ^{31}P NMR data with those of an authentic sample.[12]

[Rh_2Br_2(μ-$CPh_2)_2$(μ-PMe_3)] 13. A solution of **4** (100 mg, 0.12 mmol) in benzene (20 cm^3) was treated with Me_3SiBr (0.03 cm^3, 0.25 mmol) and stirred for 24 h at room temperature. A gradual change of color from red–brown to red occurred. The volatiles were evaporated *in vacuo*, the residue was dissolved in acetone (4 cm^3) and the solution was stored for 12 h at −25 °C. Red crystals precipitated, which were separated from the mother-liquor and dried; yield 88 mg (92%); mp 63 °C (decomp.) (Found: C, 44.44; H, 4.03. $C_{29}H_{29}Br_2PRh_2$ requires: C, 44.99; H, 3.78%). NMR (CD_2Cl_2): δ_H (400 MHz) 7.43 (4 H, m, *ortho*-H of C_6H_5), 7.24, 6.80 (16 H, both m, *ortho*-, *meta*- and *para*-H of C_6H_5), 1.08 [9 H, d, J(P,H) 10.6, PCH_3]; δ_C (100.6 MHz) 188.6 (m, CPh_2), 152.5 [d, J(P,C) 3.8, *ipso*-C of C_6H_5], 150.5 (s, *ipso*-C of C_6H_5), 129.0, 127.8, 127.4, 126.9, 126.7, 123.2 (all s, C_6H_5), 22.9 [d, J(P,C) 40.0, PCH_3]; δ_P (162.0 MHz, 293 K) −18.3 [t, J(Rh,P) 108.5]; δ_P (81.0 MHz, 193 K) −17.5 [t, J(Rh,P) 108.0], −31.8 [br dd, J(Rh,P) 132.2, J(Rh′,P) 76.3].

[Rh_2I_2(μ-$CPh_2)_2$(μ-PMe_3)] 14. This compound was prepared as described for **13**, from **4** (214 mg, 0.26 mmol) and Me_3SiI (0.067 cm^3, 0.53 mmol) in benzene (20 cm^3); reaction time 2 h. A red microcrystalline solid was obtained; yield 205 mg (90%); mp 80 °C (decomp.) (Found: C, 39.72; H, 3.52. $C_{29}H_{29}I_2PRh_2$ requires: C, 40.12; H, 3.37%). NMR (CD_2Cl_2): δ_H (300 MHz) 7.54 (4 H, m, *ortho*-H of C_6H_5), 7.24, 6.88, 6.75 (16 H, all m, *ortho*-, *meta*- and *para*-H of C_6H_5), 1.02 [10.5, d, J(P,H) PCH_3]; δ_C (75.5 MHz) 184.9 (m, CPh_2), 152.2 [d, J(P,C) 4.0, *ipso*-C of C_6H_5], 150.1 (s, *ipso*-C of C_6H_5), 128.8, 127.9, 127.4, 127.2, 126.9, 123.3 (all s, C_6H_5), 22.8 [d, J(P,C) 39.3, PCH_3]; δ_P (81.0 MHz) −22.1 [t, J(Rh,P) 104.2].

[Rh_2Cl_2(μ-$CPh_2)_2$(μ-PEt_3)] 15. This compound was prepared as described for **6**, from **8** (145 mg, 0.17 mmol) and Me_3SiCl (5.0 cm^3, 39.4 mmol) in benzene (20 cm^3). A red microcrystalline solid was obtained; yield 103 mg (85%); mp 85 °C (decomp.) (Found: C, 53.11; H, 5.09. $C_{32}H_{35}Cl_2PRh_2$ requires C, 52.84; H, 4.85%). NMR (C_6D_6): δ_H (400 MHz) 7.80, 7.57 (8 H, both m, *ortho*-H of C_6H_5), 6.70 (10 H, m, *meta*- and *para*-H of C_6H_5), 6.59 (2 H, m, *para*-H of C_6H_5), 0.77 (15 H, m, PCH_2CH_3); δ_C (100.6 MHz) 186.7 (m, CPh_2), 153.7 [d, J(P,C) 2.9, *ipso*-C of C_6H_5], 151.8 (s, *ipso*-C of C_6H_5), 128.6, 128.3, 127.7, 127.4, 127.0, 123.5 (all s, C_6H_5), 22.0 [d, J(P,C) 34.3, PCH_2], 9.3 [d, J(P,C) 4.8, PCH_2CH_3]; δ_P (162.0 MHz) 4.8 [t, J(Rh,P) 102.5].

[{Rh_2Cl_2(μ-$CPh_2)_2$(μ-PMe_2Ph)}$_2$] 16. This compound was prepared as described for **6**, from **7** (82 mg, 0.09 mmol) and Me_3SiCl (1.0 cm^3, 7.88 mmol) in benzene (30 cm^3). A red–brown microcrystalline solid was obtained; yield 47 mg (67%); mp 118 °C (decomp.) (Found: C, 54.30; H, 4.25. $C_{34}H_{31}Cl_2PRh_2$ requires C, 54.65; H, 4.18%). NMR (CD_2Cl_2): δ_H (400 MHz) 7.52, 7.38, 7.31, 7.23, 6.84, 6.74 (25 H, all m, C_6H_5), 1.38 [6 H, d, J(P,C) 10.6, PCH_3]; δ_C (100.6 MHz) 187.0 (m, CPh_2), 153.2 [d, J(P,C) 3.8, *ipso*-C of CC_6H_5], 151.7 (s, *ipso*-C of CC_6H_5), 131.3 [d, J(P,C) 2.9, *para*-C of PC_6H_5], 129.8 [d, J(P,C) 9.5, *ortho*- or *meta*-C of PC_6H_5], 129.4 [d, J(P,C) 10.5, *ortho*- or

meta-C of PC_6H_5], 128.8, 127.7, 127.3, 126.7, 126.6, 123.6 (all s, C_6H_5), 19.9 [d, *J*(P,C) 43.9, PCH_3], signal of *ipso*-C atom of PC_6H_5 could not be exactly located; δ_P (162.0 MHz, 293 K) −17.0 [br t, *J*(Rh,P) 101.7]; δ_P (81.0 MHz, 193 K) −26.8 [dd, *J*(Rh,P) 139.8, *J*(Rh′,P) 68.6].

[Rh_2Cl_2(μ-CPh_2)$_2$(μ-P*i*Pr_3)] 19. A solution of **17** (105 mg, 0.12 mmol) in benzene (100 cm^3) was treated under vigorous stirring with a 0.16 M solution of HCl in benzene (7.32 cm^3, 1.17 mmol) at room temperature. A change of color from greenish to red occurred. The solvent was evaporated *in vacuo*, the remaining red–brown residue was washed three times with 3 cm^3 portions of diethyl ether (0 °C) and dried; yield 82 mg (91%); mp 119 °C (decomp.) (Found: C, 54.85; H, 5.40. $C_{35}H_{41}Cl_2PRh_2$ requires C, 54.64; H, 5.37%). NMR (CD_2Cl_2): δ_H (400 MHz, 263 K) 7.47, 7.22, 7.10, 6.73 (20 H, all m, C_6H_5), 1.45–1.10 (21 H, br m, $PCHCH_3$); δ_C (100.6 MHz, 263 K) 180.7 [t, *J*(Rh,C) 28.6, *C*Ph_2], 152.4, 152.1 (both s, *ipso*-C of C_6H_5), 127.8, 127.3, 127.1, 127.0, 126.1, 122.9 (all s, C_6H_5), 28.4 (m, P*C*HCH_3), 20.7 (m, $PCHCH_3$); δ_P (162.0 MHz, 263 K) 14.9 [t, *J*(Rh,P) 92.6].

Generation of [Rh_2Cl_2(μ-CPh_2)$_2$(μ-PPh_3)] 20. A solution **18** (139 mg, 0.14 mmol) in benzene (100 cm^3) was treated under vigorous stirring with a 0.16 M solution of HCl in benzene (8.70 cm^3, 1.39 mmol) at room temperature. The solvent was evaporated *in vacuo*, the remaining red–brown residue was washed three times with 3 cm^3 portions of diethyl ether (0 °C) and dried. The NMR data revealed that a mixture of products was formed with **20** as the dominating species (*ca.* 80%). Since attempts to separate the by-products by fractional crystallization or column chromatography failed, **20** was characterized spectroscopically. Typical data: NMR (CD_2Cl_2): δ_C (100.6 MHz) 191.2 [t, *J*(Rh,C) 28.6, *C*Ph_2], 152.4, 151.6 (both s, *ipso*-C of CC_6H_5; δ_P (162.0 MHz) 9.8 [t, *J*(Rh,P) 103.6].

[Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-$AsMe_3$)] 21. A suspension of **3** (553 mg, 0.56 mmol) in hexane (20 cm^3) was treated with $AsMe_3$ (0.108 cm^3, 1.00 mmol) and stirred for 6 h at room temperature. A clear solution was formed, which was stored for 15 h at −78 °C. Light brown crystals precipitated, which were separated from the mother-liquor, washed three times with 3 cm^3 portions of hexane and dried; yield 408 mg (85%; mp 105 °C (decomp.) (Found: C, 54.44; H, 5.11. $C_{39}H_{43}AsO_4Rh_2$ requires C, 54.69; H, 5.06%). IR (KBr): (CO_{acac}) 1581, 1518 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 8.23, 7.32 (8 H, both m, *ortho*-H of C_6H_5), 7.05, 6.73 (12 H, both m, *meta*- and *para*-H of C_6H_5), 5.50 (2 H, s, CH of acac), 1.95 (12 H, s, CH_3 of acac), 0.88 (9 H, s, $AsCH_3$): δ_H (100.6 MHz, 233 K) 188.0 (s, CO of acac), 172.7 [t, *J*(Rh,C) 22.4, *C*Ph_2], 155.1, 154.9 (both s, *ipso*-C of C_6H_5), 126.9, 126.1, 125.8, 124.9, 124.4, 124.2 (all s, C_6H_5), 99.5 (s, CH of acac), 27.8 (s, CH_3 of acac), 18.0 (s, $AsCH_3$). MS (FAB, 2-nitrophenyloctyl ether): *m*/*z* (relative intensity) 856 (12, M^+), 736 (100, $M^+ - AsMe_3$).

[Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-P*n*Bu_3)] 22. A solution of **21** (67 mg, 0.08 mmol) in toluene (10 cm^3) was treated at −50 °C with P*n*Bu_3 (0.02 cm^3, 0.08 mmol) and after warming to 0 °C stirred for 20 min under reduced pressure (*ca.* 20 mbar). All volatile materials were evaporated *in vacuo*. The remaining brown solid was washed twice with 2 cm^3 portions of pentane (0 °C) and dried; yield 65 mg (89%); mp 69 °C (decomp.) (Found: C, 54.44; H, 5.11. $C_{48}H_{61}O_4PRh_2$ requires C, 54.69; H, 5.06%). IR (KBr): (CO_{acac}) 1586, 1518 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz, 253 K) 7.86 (4 H, m, *ortho*-H of C_6H_5), 7.09, 6.86, 6.64 (16 H, all m, C_6H_5), 5.67 (2 H, s, CH of acac), 2.07 (12 H, s, CH_3 of acac), 1.26, 1.00 (18 H, all m, CH_2 of P*n*Bu_3), 0.74 (9 H, m, CH_3 of P*n*Bu_3); δ_C (100.6 MHz, 253 K) 187.9 (s, CO of acac), 174.0 [t, *J*(Rh,C) 24.1, *C*Ph_2], 156.4 [d, *J*(P,C) 1.9, *ipso*-C of C_6H_5], 156.2 (s, *ipso*-C of C_6H_5), 132.5, 130.0, 128.3, 127.4, 126.3, 126.0, 125.0, 124.1, 123.9 (all s, C_6H_5), 99.6 (s, CH of acac), 29.4 [d, *J*(P,C) 31.5, PCH_2], 28.3 (s, CH_3 of acac), 26.7 [d, *J*(P,C) 4.8, CH_2 of P*n*Bu_3], 23.3 [d, *J*(P,C) 16.2, CH_2 of P*n*Bu_3], 13.5 (s, CH_3 of P*n*Bu_3); δ_P (162.0 MHz, 253 K) 13.6 [t, *J*(Rh,P) 103.6]; NMR (C_6D_6): δ_P (81.0 MHz, 293 K) −9.6 [t, *J*(Rh,P) 104.3].

[Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-PMe_2Ph)] 7. This compound was prepared as described for **22**, from **21** (242 mg, 0.28 mmol) and PMe_2Ph (0.04 cm^3, 0.28 mmol) in toluene (10 cm^3). A red–brown microcrystalline solid was obtained; yield 227 mg (92%). The product was characterized by comparison of the ^1H and ^{31}P NMR data with those of an authentic sample.[12]

[Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-PEt_3)] 8. This compound was prepared as described for **22**, from **21** (372 mg, 0.43 mmol) and PEt_3 (0.063 cm^3, 0.43 mmol) in toluene (10 cm^3). A red–brown microcrystalline solid was obtained; yield 365 mg (98%). The product was characterized by comparison of the ^1H and ^{31}P NMR data with those of an authentic sample.[12]

[Rh_2Cl(κ^2-acac)(μ-CPh_2)$_2$(μ-$AsMe_3$)] 23. A solution of **21** (76 mg, 0.09 mmol) in benzene (10 cm^3) was treated with Me_3SiCl (0.012 cm^3, 0.10 mmol) and stirred for 1 h at room temperature. The solvent was evaporated *in vacuo*, the remaining brown solid was washed twice with 5 cm^3 portions of pentane–diethyl ether (10 : 1) and dried; yield 62 mg (88%); mp 105 °C (decomp.) (Found: C, 51.12; H, 4.58. $C_{34}H_{36}AsClO_2Rh_2$ requires C, 51.51; H, 4.58%). IR (KBr): (CO_{acac}) 1580, 1519 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 8.36, 7.42 (8 H, both m, *ortho*-H of C_6H_5), 7.04 (4 H, m, *meta*-H of C_6H_5), 6.91 (2 H, m, *para*-H of C_6H_5), 6.63 (6 H, m, *meta*-H and *para*-H of C_6H_5), 5.41 (1 H, s, CH of acac), 1.89 (6 H, s, CH_3 of acac), 0.62 (9 H, s, $AsCH_3$); δ_C (100.6 MHz) 189.1 (s, CO of acac), 178.2 [dd, *J*(Rh,C) 27.2, *J*(Rh′,C) 20.0, *C*Ph_2], 154.7, 153.9 (both s, *ipso*-C of C_6H_5), 127.7, 127.3, 126.7, 126.4, 126.2, 124.9 (all s, C_6H_5), 101.0 (s, CH of acac), 28.0 (s, CH_3 of acac), 18.6 (s, $AsCH_3$).

[{Rh_2Cl_2(μ-CPh_2)$_2$(μ-$AsMe_3$)}$_2$] 24. (a) A solution of **21** (82 mg, 0.10 mmol) in benzene (2 cm^3) was treated with Me_3SiCl (2.0 cm^3, 15.7 mmol) and stirred for 4 h at room temperature. A small part of a red–brown solid precipitated. The volatile materials were evaporated *in vacuo*, the remaining red–brown solid was washed twice with 2 cm^3 portions of benzene and 5 cm^3 portions of diethyl ether and dried; yield 63 mg (90%). (b) Under the same conditions as used for (a), the reaction of **23** (75 mg, 0.09 mmol) and Me_3SiCl (2.0 cm^3, 15.7 mmol) gave the same product; yield 65 mg (93%); mp 120 °C (decomp.) (Found: C, 51.76; H, 4.48. $C_{58}H_{58}As_2Cl_4Rh_2 \cdot 2C_6H_6$ requires C, 52.07; H, 4.37%). NMR (CD_2Cl_2): δ_H (400 MHz) 7.75 (4 H, m, *ortho*-H of C_6H_5), 7.24, 6.86, 6.76 (16 H, all m, C_6H_5), 1.19 (s, $AsCH_3$); δ_C (100.6 MHz) 153.2, 152.4 (both s, *ipso*-C of C_6H_5), 128.4, 128.2, 127.6, 127.2, 126.7, 126.4, 124.7 (all s, C_6H_5), 20.5 (s, $AsCH_3$); signal for the *C*Ph_2 carbon atoms could not be exactly located.

Crystallography

Single crystals of **6** and **24** (both containing two independent molecules of the complex and two molecules of benzene in the asymmetric unit) were grown from benzene at room temperature, and those of **14** (containing two thirds of a molecule of acetone in the asymmetric unit) from a saturated solution in acetone at −25 °C. Crystal data collection parameters are summarized in Table 4. The data were collected on a Bruker Smart Apex diffractometer with D8-Goniometer using monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were corrected by Lorentz and polarization effects, and empirical absorption corrections were applied. The structures of **6** and **14** were solved by the Patterson method, and the structure of **24** was solved by direct methods (SHELXS-97).[18]

Table 4 Crystal data for complexes **6**, **14** and **24**

	6	**14**	**24**
Formula	$C_{58}H_{58}Cl_4P_2Rh_4 \cdot 2C_6H_6$	$C_{29}H_{29}I_2PRh_2 \cdot 2/3C_3H_6O$	$C_{58}H_{58}Cl_4As_2Rh_4 \cdot 2C_6H_6$
M	1526.64	906.83	1614.54
Crystal size/mm	0.40 × 0.40 × 0.20	0.30 × 0.17 × 0.16	0.67 × 0.66 × 0.63
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	$P2_1/c$ (no. 14)	$R\bar{3}c$ (no. 167)	$P2_1/c$ (no. 14)
Cell dimens. determn.	8804 rflns., $2.303 < \theta < 28.246°$	9283 rflns., $2.431 < \theta < 24.492°$	8282 rflns., $2.292 < \theta < 28.146°$
a/Å	22.2854(11)	22.9416(17)	22.4012(13)
b/Å	15.1150(7)	22.9416(17)	15.2521(9)
c/Å	19.2895(9)	31.230(3)	19.4838(11)
α/°	90	90	90
β/°	101.8780(10)	90	102.535(10)
γ/°	90	120	90
V/Å^3	6358.4(5)	14235(2)	6498.3(7)
Z	4	18	4
D_c/g cm^{-3}	1.595	1.904	1.650
T/K	173(2)	173(2)	173(2)
μ/mm^{-1}	1.280	3.066	2.214
Scan method	ω	ω	ω
2θ(max.)/°	50.00	50.28	50.00
No. of reflections measured	60158	53403	35365
No. of unique reflections (R_{int})	11183 (0.0228)	2818 (0.0787)	10588 (0.0154)
No. of observed reflections	10525 ($I > 2\sigma(I)$)	2780 ($I > 2\sigma(I)$)	10117 ($I > 2\sigma(I)$)
No. of reflections used for refinement	3072	2818	3216
No. of parameters refined	727	188	727
Final R indices	$R1 = 0.0228$, $wR2 = 0.0541$ [a] ($I > 2\sigma(I)$)	$R1 = 0.0643$, $wR2 = 0.1368$ [a] ($I > 2\sigma(I)$)	$R1 = 0.0222$, $wR2 = 0.0531$ [a] ($I > 2\sigma(I)$)
R indices (all data)	$R1 = 0.0249$, $wR2 = 0.0551$ [a]	$R1 = 0.0649$, $wR2 = 0.1371$ [a]	$R1 = 0.0246$, $wR2 = 0.0540$ [a]
Residual electron density/e Å^{-3}	0.472/−0.351	1.526/−1.043	0.664/−0.356

[a] $w^{-1} = [\sigma^2F_o^2 + (0.0265P)^2 + 4.0856P]$ (**6**), $w^{-1} = [\sigma^2F_o^2 + (0.0186P)^2 + 644.7705P]$ (**14**), $w^{-1} = [\sigma^2F_o^2 + (0.0437P)^2 + 4.9135P]$ (**24**), where $P = (F_o^2 + 2F_c^2)/3$.

Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-97).[19] The positions of all hydrogen atoms were calculated according to ideal geometry and refined using the riding method.

CCDC reference numbers 178267 (**6**), 202931 (**14**) and 178268 (**24**).

See http://www.rsc.org/suppdata/dt/b3/b314734g/ for crystallographic data in CIF or other electronic format.

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