A New Family of Dinuclear Rhodium Complexes Containing Tertiary Phosphanes in a Semibridging or Doubly Bridging Bonding Mode

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Dedicated to Professor Lord Lewis on the occasion of his 75th birthday

Abstract: The reactions of $[Rh_2Cl(\kappa^2\text{-acac})(\mu\text{-CPh}_2)_2(\mu\text{-Sb}i\text{Pr}_3)]$ (**3**) and $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-CPh}_2)_2(\mu\text{-Sb}i\text{Pr}_3)]$ (**4**) with PMe_3 lead to exchange of the bridging ligand and afford the novel PMe_3-bridged counterparts **5** and **6**, in which the phosphane occupies a semibridging (**5**) or a doubly bridging (**6**) position. In both cases, the bonding mode was confirmed crystallographically. Treatment of **6** with CO causes a shift of PMe_3 from a bridging to a terminal position and gives the unsymmetrical complex $[(\kappa^2\text{-acac})Rh(\mu\text{-CPh}_2)_2(\mu\text{-CO})Rh(PMe_3)(\kappa^2\text{-acac})]$ (**7**). Similarly to **5** and **6**, the related compounds **10** and **11** with one or two acac-f_3 ligands were prepared. While both PEt_3 and $P\textit{n}Bu_3$ react with **3** by exchange of the bridging stibane for phosphane to give compounds **12** and **13**, the reactions of **4** with $PMePh_2$ and $P\textit{n}Bu_3$ afford the mixed-valent Rh^0Rh^{II} complexes $[(PR_3)Rh(\mu\text{-CPh}_2)_2Rh(\kappa^2\text{-acac})_2]$ (**17**, **18**) in high yields. In contrast, treatment of **4** with PEt_3 and PMe_2Ph generates the phosphane-bridged compounds $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-CPh}_2)_2(\mu\text{-PR}_3)]$ (**14**, **15**) exclusively. Stirring a solution of **14** (R = Et) in benzene for 15 h at room temperature leads to complete conversion to the mixed-valent isomer **16**. The reaction of **6** with an equimolar amount of CR_3CO_2H (R = F, H) or phenol in the molar ratio of 1:10 results in substitution of one acac by one trifluoroacetate, acetate, or phenolate ligand without disturbing the $[Rh_2(\mu\text{-CPh}_2)_2(\mu\text{-PR}_3)]$ core. From **6** and an excess of CR_3CO_2H, the symmetrical bis(trifluoroacetato) and bis(acetate) derivatives $[Rh_2(\kappa^2\text{-O}_2CCR_3)_2(\mu\text{-CPh}_2)_2(\mu\text{-PMe}_3)]$ (**21**, **22**) were obtained.

Keywords: carbene ligands · mixed-valent compounds · O ligands · P ligands · rhodium

Introduction

In the context of our studies on the reactivity of square-planar carbenerhodium(I) complexes *trans*-$[RhCl(=CRR')(L)_2]$ ($L = PR_3$, AsR_3, SbR_3),[1] we recently observed that the bis(stibane) derivatives *trans*-$[RhCl(=CRR')(Sb\textit{i}Pr_3)_2]$ are thermally labile and, on heating in benzene at 60 °C, undergo partial elimination of $Sb\textit{i}Pr_3$ to generate dinuclear rhodium(I) complexes with a $[Rh(\mu\text{-Sb}i\text{Pr}_3)Rh]$ building block in excellent yields.[2] Since the bridging coordination mode of trialkylstibanes was not only new but rather unexpected,[3] we were surprised that these compounds with rhodium(I) in a distorted tetrahedral coordination environment are remarkably stable and decompose at temperatures around 190 °C or even higher. Moreover, in explorative studies we found that the bridging $Sb\textit{i}Pr_3$ ligand can be replaced by CO, $CN\textit{t}Bu$, or SbR_3 (R = Me, Et) without breaking the $[Rh(\mu\text{-CRR}')_2Rh]$ core.[2] The terminal chloro ligands in **2**, prepared from **1** by thermolysis (Scheme 1), could also be substituted stepwise by acetylacetonate (acac) to give the unsymmetrically and symmetrically bridged complexes **3** and **4**, respectively.[4,5]

Since **2** undergoes ligand exchange of SbR_3 for $Sb\textit{i}Pr_3$, we hoped to replace $Sb\textit{i}Pr_3$ by tertiary phosphanes PR_3. However, the initial attempts completely failed. Treatment of **2** with $P\textit{i}Pr_3$, $P\textit{i}Pr_2Ph$, $P\textit{i}PrPh_2$, PPh_3, or $PMePh_2$ did not afford $[Rh_2Cl_2(\mu\text{-CPh}_2)_2(\mu\text{-PR}_3)]$ but gave the corresponding mononuclear complexes *trans*-$[RhCl(=CPh_2)(PR_3)_2]$ by displacement of the stibane and cleavage of the carbene bridges. Even when these reactions were monitored in an NMR tube, no signals for a possible intermediate containing a $[Rh(\mu\text{-PR}_3)Rh]$ moiety could be observed. Despite this failure we continued our research and found most recently that the use of the acac-substituted compounds **3** and **4** instead of **2** as starting materials changes the reactivity of the stibane-bridged dinuclear species significantly and allows the isolation of transition metal complexes with various tertiary phosphanes coordinated in a doubly bridging mode.

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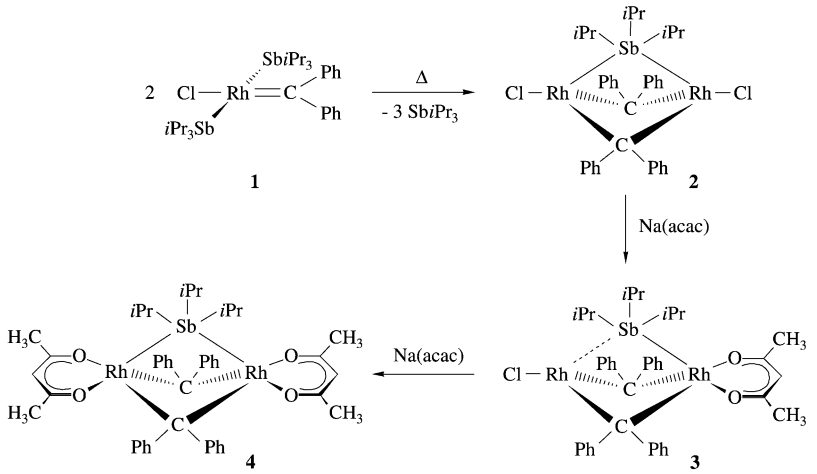
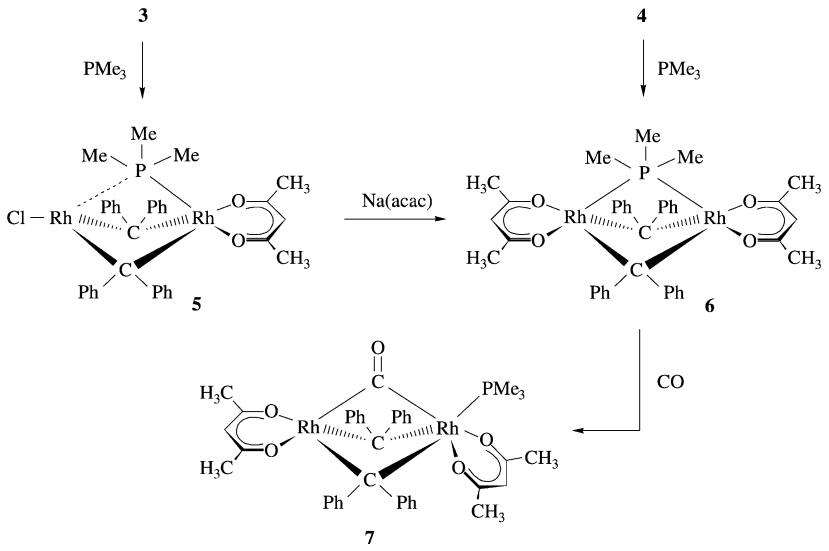


Scheme 1. Synthesis of **4**.

Herein we report the preparation and characterization of unsymmetrical and symmetrical dirhodium compounds with PMe_3, PEt_3, $PnBu_3$, and PMe_2Ph as bridging ligands, the conversion of some of them into mixed-valent Rh_2 isomers, and the substitution of one or both acac moieties of $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)]$ by other mono- or bidentate ligands. A short communication on first steps of this study has already appeared.[4]

Results and Discussion

Preparation of complexes of the general formula $[Rh_2XX'(\mu\text{-}CPh_2)_2(\mu\text{-}PR_3)]$: In contrast to bulky $PiPr_3$, which not only reacts with **2** but also with **3** by bridge cleavage, the smaller PMe_3 behaves differently. Treating a solution of **3** in either pentane/diethyl ether or dichloromethane at −78 °C with an equimolar amount of PMe_3, followed by warming to room temperature, leads to a gradual change of color from dark red to red-brown and gives **5** in about 85% yield (Scheme 2). The ^{31}P NMR spectrum of **5** (in C_6D_6) displays a doublet of doublets at $\delta = -36.4$ ppm with $^1J(Rh,P)$ coupling constants of 147.5 and 81.4 Hz. Compared with **7** (see below), these values clearly indicate that the PMe_3 ligand is not linked to one of the metal centers in a terminal fashion. The proposed unsymmetrical structure is supported by the ^{13}C NMR spectrum of **5**, in which the resonance for the equivalent carbene carbon atoms appears as a doublet of doublets of doublets with two different $^1J(Rh,C)$ coupling constants of 30.5 and 20.7 Hz and one small $^2J(P,C)$ coupling constant of 3.6 Hz. Not only the carbene but also the methyl carbon atoms of the phosphane are equivalent on the NMR timescale, giving rise to a sharp doublet at $\delta = 22.4$ ppm with $^1J(P,C) = 40.7$ Hz.



Scheme 2. Synthesis of **7**.

The X-ray crystal structure analysis of **5** (Figure 1) confirms that the PMe_3 ligand, similar to the $SbiPr_3$ ligand in **3**,[6] occupies a semibridging rather than a terminal position.[7] Apart from the different Rh1–P and Rh2–P distances, characteristic features are in particular the bond angles in the Rh_2P triangle, which are significantly smaller than 90°. In the case of a nonbridging arrangement, the angle Rh1-Rh2-P should be considerately larger than 90°. Owing to the higher coordination number of Rh1 compared to Rh2, not only the phosphane but also the two diphenylcarbene ligands are linked to the metal centers in an unsymmetrical fashion. The distances Rh2–C1 and Rh2–C2 are about 0.11 Å shorter than those from Rh1 to C1 and C2, quite similar to the situation found for **3**.[6] However, in contrast to **3** the acac ligand in **5** is coordinated in a symmetrical mode. The molecular fragment O1,O2,Rh1,Rh2 is almost planar, whereas the Rh1-Rh2-Cl axis is slightly bent (172.30(4)°), the bending being comparable to that in **3** (171.55(3)°). The three P–C distances are nearly the same and lie in the range of rhodium(I) compounds with a terminal PMe_3 ligand.[8] The methyl groups of the phosphane are in a staggered conformation with respect to Cl and the oxygen atoms O1 and O2. The Rh1–Rh2 bond length of 2.5318(8) Å in **5** is rather short, but similar to those of other dinuclear rhodium(I) complexes, including **2**, with a metal–metal bond.[6,9]

Compound **5** reacts not only with Tl(acac)[4] but also with Na(acac) in a molar ratio of 1:4 in acetone at room temperature

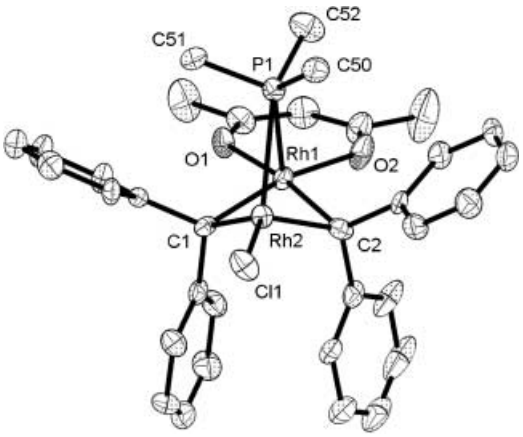


Figure 1. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Rh1–Rh2 2.5318(8), Rh1–P1 2.2406(15), Rh2–P1 2.8410(14), Rh1–C1 2.060(5), Rh1–C2 2.057(5), Rh2–C1 1.939(5), Rh2–C2 1.949(5), Rh1–O1 2.115(3), Rh1–O2 2.116(4), Rh2–Cl 2.3072(15); Rh1-P1-Rh2 58.34(4), P1-Rh1-Rh2 72.78(4), P1-Rh2-Rh1 48.88(4), Rh1-Rh2-Cl 172.30(4), Rh1-C1-Rh2 78.49(16), Rh1-C2-Rh2 78.36(18), C1-Rh1-C2 86.77(19), C1-Rh2-C2 93.3(2), O1-Rh1-O2 85.42(13).

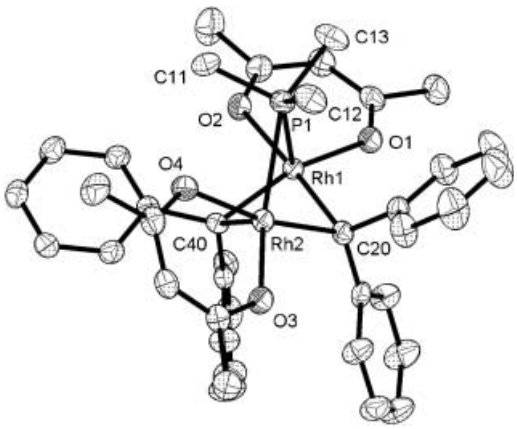


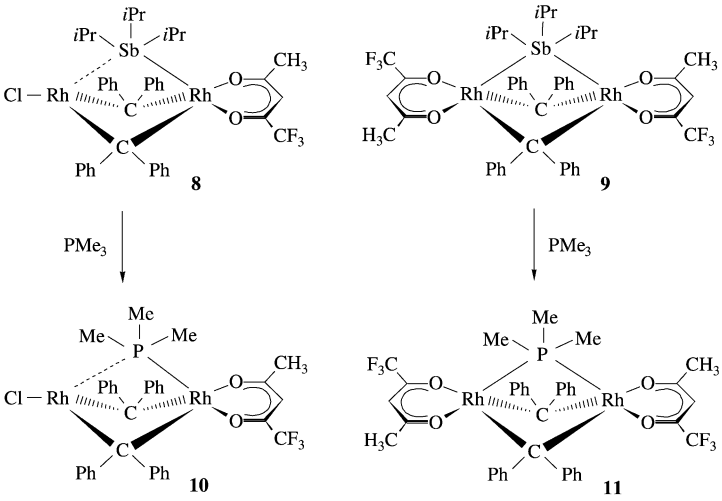
Figure 2. Molecular structure of **6**. Selected bond lengths [Å] and angles [°]: Rh1–Rh2 2.5281(5), Rh1–P1 2.2707(7), Rh2–P1 2.5700(8), Rh1–C20 2.069(3), Rh1–C40 2.038(2), Rh2–C20 1.995(2), Rh2–C40 1.974(3), Rh1–O1 2.1138(18), Rh1–O2 2.1596(19), Rh2–O(3) 2.0760(19), Rh2–O(4) 2.2097(19); Rh1-P1-Rh2 62.61(2), P1-Rh1-Rh2 64.50(2), P1-Rh2-Rh1 52.890(19), Rh1-C20-Rh2 76.90(9), Rh1-C40-Rh2 78.09(9), C20-Rh1-C40 84.55(10), C20-Rh2-C40 88.23(10), O1-Rh1-O2 84.11(7), O(3)-Rh2-O(4) 83.67(7).

by substitution of the chloro for the acetylacetonato ligand to give dinuclear complex **6** (see Scheme 2). An alternative procedure to obtain **6** consists of the substitution of Sb*i*Pr$_3$ in **4** by PMe$_3$; in both cases the yields are excellent. The pale brown, moderately air sensitive **6** is readily soluble in benzene, acetone, and dichloromethane, but less so in pentane and diethyl ether. The symmetrical complex **6** is thermally less stable than its unsymmetrical counterpart **5**, as was also observed for **3** and **4**. Regarding the spectroscopic data of **6**, we note that in contrast to **5** the ^{31}P NMR spectrum does not display a doublet of doublets but a sharp triplet, which illustrates that the PMe$_3$ ligand is coordinated to both rhodium centers in an identical mode. The ^1J(Rh,P) coupling constant is 110.6 Hz, which is about midway between the two coupling constants found for **5** (147.5 and 81.4 Hz). The ^{13}C NMR resonance for the bridging carbene carbon atoms appears as a doublet of triplets at $\delta =$ 170.7 ppm, which is slightly upfield (by 4 ppm) compared with **5**.

The X-ray crystal structure of **6** is shown in Figure 2. Although the two Rh–P bond lengths are not exactly the same, the difference of about 0.3 Å is only half of that in **5**. Since neither the ^{31}P nor the ^{1}H NMR spectrum of **6** is temperature-dependent, it is conceivable that the small deviation from ideal symmetry of the sterically hindered molecule in the crystal is due to steric reasons or packing effects. In our opinion the more important fact is that the bond angles Rh1-Rh2-P, Rh2-Rh1-P, and Rh1-P-Rh2 deviate by at most 7.1° from the value of 60° required for an isosceles triangle. The coordination geometry of both rhodium centers corresponds to a distorted square pyramid, with the difference that for the polyhedron around Rh1 the P atom and for the polyhedron around Rh2 the carbene C atom C40 is in the apical position. The two planar six-membered rings formed by the metal atoms and the acac ligands lie not in the same plane but are twisted; the dihedral angle between the two planes is 30.2°. In contrast to the distances Rh1–O1 and Rh1–O2, which are nearly the same (difference: ca. 0.04 Å), the bond lengths Rh2–O3 and Rh2–O4 differ by about 0.13 Å, which may also reflect steric crowding in the molecule.

Compound **6** is highly reactive toward carbon monoxide. Passing a slow stream of CO through a solution of **6** in benzene causes an almost instantaneous change of color from red-brown to light red and affords, after evaporation of the solvent, the dinuclear complex **7** in 95% yield (isolated product). The IR spectrum of **7** displays a ν(CO) band at 1829 cm^{-1}, the position of which is characteristic for a doubly bridging CO ligand. The presence of a terminal PMe$_3$ ligand in **7** is confirmed by the splitting of the ^{31}P NMR resonance, which appears as a doublet of doublets with one large (129.7 Hz) and one small (7.6 Hz) ^{31}P–^{103}Rh coupling constant. For **5**, which contains a semibridging CO group, the values are 147.5 and 81.4 Hz, respectively. The ^{13}C NMR spectrum of **7** shows one doublet of doublets of doublets at $\delta = 203.8$ ppm and one triplet at $\delta = 159.8$ ppm for the ^{13}C nuclei of the carbene carbon atoms; the splitting pattern of the former, with ^2J(P,C) = 77.3 Hz, indicates that it belongs to the *C*Ph$_2$ atom *trans* to the PMe$_3$ ligand.

Compounds **8** and **9**, which contain acac-f$_3$ instead of acac ligands, behave similarly to **3** and **4** and react with an equimolar amount of PMe$_3$ in hexane/diethyl ether or benzene to give dinuclear complexes **10** and **11** in 72–78% yield (Scheme 3). As already observed for **5** and **6**, the unsymmetrical compound **10** is considerably more stable than its symmetrical counterpart. While the ^{31}P NMR spectrum of **10** displays a doublet of doublets, that of **11** shows a sharp triplet with a ^1J(Rh,P) coupling constant that is virtually identical to that of **6**. Since the chemical shifts and the splitting pattern of the signals in the ^{1}H and ^{13}C NMR spectra of **10** and **11** are quite similar to those of **5** and **6**, we assume that there is also a strict analogy in the bonding mode of the PMe$_3$ ligand in the two pairs of complexes.

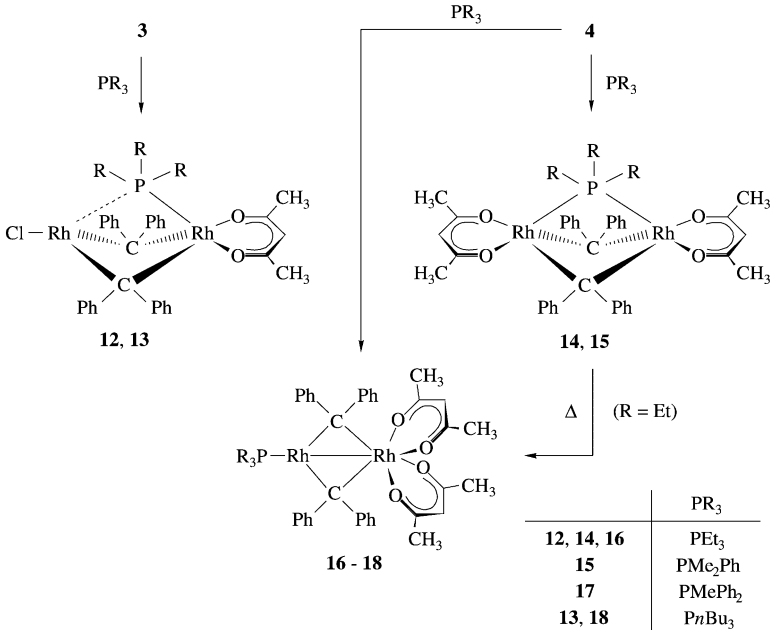


Scheme 3. Reactions of **8** and **9** with PMe_3 to give **10** and **11**, respectively.

The different behavior of 3 and 4 toward PEt_3 and $PnBu_3$: In contrast to PMe_3, the more bulky $PiPr_3$ reacts with the stibane precursor **3** to give a mixture of products, among which the known complex *trans*-[RhCl(=CPh_2)($PiPr_3$)$_2$], but no species with a bridging $PiPr_3$, could be detected. Following this observation, we were prompted to study the reactivity toward **3** of phosphanes whose sizes, indicated by their cone angles,[10] lie between those of PMe_3 and $PiPr_3$. Thus, treatment of **3** with PEt_3 under the same conditions as used for the preparation of **5** gave the analogous dinuclear compound **12** as a dark brown solid in 81% yield (Scheme 4). The somewhat larger $PnBu_3$ behaved analogously, although in this case besides the desired complex **13** some by-products were also obtained. Attempts to separate these by-products from **13** by fractional crystallization failed. Since using more than one equivalent of $PnBu_3$ or performing the reaction at lower temperatures did not improve the result, compound **13** was characterized spectroscopically. Similarly to **5** and **12**, the ^{31}P NMR spectrum of **13** displays the expected doublet of doublets at $\delta = -9.9$ ppm, which indicates that most probably the $PnBu_3$ ligand occupies a semibridging position. The ^1J(Rh,P) coupling constants are 139.8 and 73.7 Hz and differ only marginally from those found for **5** and **12**.

An interesting situation arises if the symmetrical complex **4** is treated with PEt_3 and $PnBu_3$. The reaction of **4** with PEt_3 in diethyl ether at −30 to 0 °C gives, after low-temperature crystallization from OEt_2, the symmetrical PEt_3-bridged compound **14** in 61% yield of isolated product (Scheme 4). The reaction of **4** with $PnBu_3$ under exactly the same conditions afforded a mixture of products, among which [Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-P*n*Bu_3)] is the predominant species. However, this complex could not obtained in analytically pure form by this route.[11] If the reaction of **4** with $PnBu_3$ in C_6D_6 is monitored in an NMR tube and not stopped after [Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-P*n*Bu_3)] has been generated, subsequent slow rearrangement to isomer **18** can be observed. On a preparative scale, the reaction of **4** with a twofold excess of $PnBu_3$ in benzene gives, after two days at room temperature, the mixed-valent complex **18** in 91% yield of isolated product. The PEt_3 counterpart **16** is accessible either by the same route or can be obtained nearly quantitatively by stirring a solution of **14** in benzene for 15 h at 25 °C. Complexes **16** and **18** are brownish green or brown air-stable solids, the chemical properties and spectroscopic data of which are very similar to those of the analogues [($PiPr_3$)Rh(μ-CPh_2)$_2$Rh(κ^2-acac)$_2$] and [(PPh_3)Rh(μ-CPh_2)$_2$Rh(κ^2-acac)$_2$], respectively. These complexes were prepared from **4** and $PiPr_3$ or PPh_3 in a similar way; the $PiPr_3$ derivative was characterized by crystallography.[6] The ^{31}P NMR spectra of **16** and **18** both display a typical doublet of doublets with one large (264.9 and 269.5 Hz, respectively) and one small (4.8 and 5.1 Hz, respectively) ^{31}P–^{103}Rh coupling constant.

The dominant role of the size of the reacting phosphane is also evident in the reactions of **4** with PMe_2Ph and $PMePh_2$. While the smaller ligand PMe_2Ph generates exclusively the phosphane-bridged compound **15** (see Scheme 4), the larger ligand $PMePh_2$ produces the unsymmetrical complex **17** in 86% yield. In contrast to the rearrangement of **14** to **16**, attempts to convert **15** to the mixed-valent isomer [(PMe_2Ph)Rh(μ-CPh_2)$_2$Rh(κ^2-acac)$_2$] remained unsuccessful. We also failed to detect the supposed intermediate [Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-$PMePh_2$)] in the re-



Scheme 4. Behavior of **3** and **4** to PR_3.

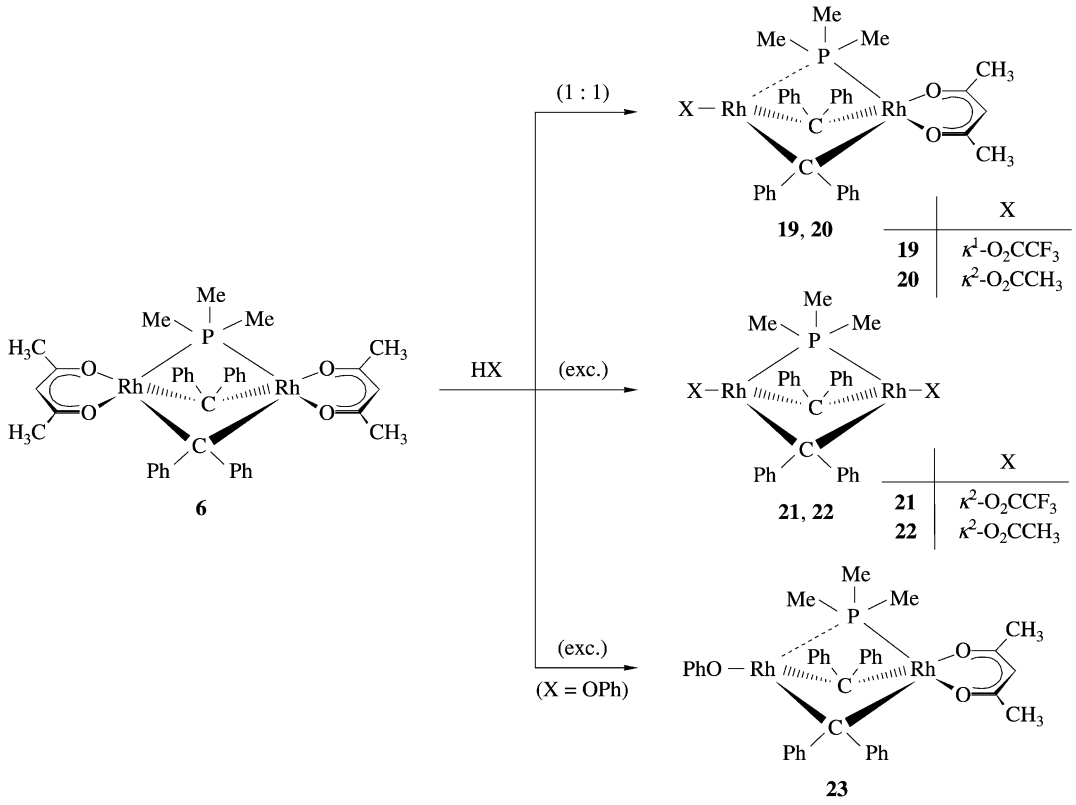
action of **4** with $PMePh_2$, which seems to be as labile as the undetected species $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CPh_2)_2(\mu\text{-}P\textit{i}Pr_3)]$.[6]

With regard to the mechanism for the isomerization of the PR_3-bridged compounds to the mixed-valent isomers, we briefly investigated the kinetics of the conversion of **14** to **16**. In C_6D_6 at 293.5 K the reaction is strictly first order with $k = 9.41(5) \times 10^{-5}\ s^{-1}$ and $\Delta G^{*} = 94.5(5)\ kJ\,mol^{-1}$. We therefore assume that an intramolecular rearrangement occurs and that the migration of the phosphane from a bridging to a terminal position is accompanied by migration of an acac ligand from one metal center to the other.

Substitution reactions of the acetylacetonato ligands: After we found that the acac ligands of the stibane-bridged complex **4** can be replaced by acetate and trifluoroacetate without cleaving the Rh(μ-Sb*i*Pr$_3$)Rh bridge,[5] we were interested to find out whether a similar substitution can also take place with the phosphane counterpart **6**. Treatment of **6** with an equimolar amount of CF_3CO_2H in benzene at room temperature leads to replacement of one acac ligand and affords the mixed $Rh_2(acac)(O_2CCF_3)$ compound **19** as a red-brown solid in pratically quantitative yield (Scheme 5). Acetic acid behaves similarly to CF_3CO_2H toward **6** but gives a mixture of products, among which the desired complex **20** dominates (ca. 80%). Apart from the starting material (ca. 10%), the bis(acetate) derivative **22** could also be detected. Attempts to separate **20** from the by-products by fractional crystallization or column chromatography failed. Although the ^{31}P NMR spectra of the substitution products **19** and **20** show in both cases the expected doublet of doublets, the $^1J(Rh,P)$ coupling constants are quite different. For **20** the values of 117.0 and 106.8 Hz indicate that the PMe_3 ligand probably occupies a doubly bridging position, like in the precursor **6** ($^1J(Rh,P) = 110.6$ Hz), while the $^1J(Rh,P)$ values for **19** are 155.9 and 69.8 Hz. Comparing these values with those of the unsymmetrical compound **5** ($^1J(Rh,P) = 147.5$, 81.4 Hz) suggests that the phosphane in **19** is semibridging and the CF_3CO_2 unit behaves as a monodentate ligand. The IR spectrum of **19** displays a relatively broad band for the asymmetric ν(OCO) mode at 1654 cm^{-1}, which is consistent with the proposed structure.[12]

The reactions of **6** with an excess of CF_3CO_2H or CH_3CO_2H lead to the displacement of both acac ligands and give the symmetrical complexes **21** and **22** in excellent yields. The $Rh_2(O_2CCF_3)_2$ derivative contained traces of impurities which, owing to the high solubility of **21** in all common organic solvents, could not be completely separated. The bis(acetate) counterpart **22**, which was characterized by a correct elemental analysis, is a brown, moderately air stable solid, which is thermally more stable than its precursor **6**. Since the ^{31}P NMR spectra of both **21** and **22** display a sharp triplet with a $^1J(Rh,P)$ coupling constant which is very similar to that of **6**, there is no doubt that the PMe_3 ligand occupies a symmetrical bridging position.

Compound **6** reacts with a twofold excess of phenol to afford the monosubstitution product **23** (see Scheme 5). Neither by using an even higher concentration of PhOH nor by increasing the temperature could the second acac ligand be displaced. As expected, the ^{31}P NMR spectrum of **23** shows a doublet of doublets, with $^1J(Rh,P)$ coupling constants of



Scheme 5. Substitution reactions of **6**.

162.4 and 61.0 Hz. The similarity of these values to those of **19** equally supports the assumption that in the $Rh_2(acac)(O_2CCF_3)$ complex the trifluoroacetato ligand is κ^1-bonded.

Conclusion

The present investigations have shown that the members of the new family of dinuclear rhodium complexes of the general composition $[Rh_2X_2(\mu\text{-}CRR')_2(\mu\text{-}L)]$ exist not only for $L=SbR_3$ but also for $L=PR_3$. With regard to common knowledge,[3] we believe that this is a fundamental breakthrough. Moreover, apart from the accessibility of phosphane-bridged complexes such as **5**, **6**, **10**–**15**, and **19**–**23**, it is interesting that some of them are remarkably stable and, at least for the smaller phosphanes PMe_3, PEt_3, and PMe_2Ph, show no or only a minor tendency to form products with the phosphane in a terminal position. The unsymmetrical compounds **5**, **10**, and **12** have significantly higher thermal stability than their symmetrical counterparts **6**, **11**, and **14**, and this could be due to steric strain caused by the presence of two acac ligands and two bulky CPh_2 units in these molecules. We note that the total electron count for the dinuclear phosphane-bridged complexes **5**, **10**, **12**, and **13** is 28, while it is 30 for **6**, **11**, **14**, **15** and their congeners.

Regarding the unique role of tertiary phosphanes PR_3 in the symmetrical dinuclear compounds $[Rh_2X_2(\mu\text{-}CPh_2)_2(\mu\text{-}PR_3)]$, the question arises whether the five-coordinate phosphorus atom should be considered as P^{III} or P^{V}. Molecules of the general composition PR_3X_2 mostly have a trigonal-bipyramidal structure, but this is not found for complex **6**. The C-P-C angles of the bridging trimethylphosphane in this compound are 103.60(16), 101.84(15), and 97.36(15)°, and the average value of 100.93° is nearly the same as that of free PMe_3 (98.9°).[13] The other bond angles around phosphorus in **6** lie in the range between 62.61(2)° (Rh-P-Rh) and 150.25(12)° (Rh-P-C), and thus are not consistent with a trigonal-bipyramidal geometry. If we also take the P–C bond lengths into consideration, which are 1.808(3), 1.832(3) and 1.840(3) Å (av 1.827 Å) in **6** and 1.843 Å in uncoordinated PMe_3, the conclusion is that the bonding of PMe_3 to two transition-metal centers does not perturb its structure, and thus the phosphorus atom presumably remains P^{III}.

However, the novel phosphane-bridged dirhodium complexes are not only exceptional from a structural point of view but also in their reactivity. For example, the terminal acac ligands of **6** can be replaced stepwise by acetate or trifluoroacetate without changing the central $[Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)]$ part of the molecule. A similar reaction occurs between **6** and Me_3SiBr or Me_3SiI to give the PMe_3-bridged dibromo and diiodo counterparts of the parent stibane complex **2**.[14] The replacement of a larger phosphane such as $PnBu_3$ or PEt_3 by a smaller analogue such as PMe_3 or PMe_2Ph in the bridging position might equally by possible, but upon treatment of $[Rh_2(\kappa^2\text{-}acac)_2(\mu\text{-}CPh_2)_2(\mu\text{-}PR_3)]$ ($R=nBu$, Et) with PMe_2R' ($R'=Me$, Ph) the preferred pathway was rearrangement of the phosphane-bridged complexes to the mixed-valent Rh^0-Rh^{II} isomers. With regard to future studies, it would be interesting to determine whether dinuclear complexes with $[M(\mu\text{-}PR_3)M]$ cores could be also prepared for other transition-metals such as Ru, Pd, and Ir, and whether besides tertiary phosphanes related P-donor ligands such as PF_3, PCl_3, or PH_3 could be coordinated in a doubly-bridging mode. In this context we note that in attempting to obtain a dinuclear palladium compound with $Pd(\mu\text{-}PF_3)Pd$ as the building block, Balch et al. previously reported the preparation and structural characterization of a cationic Pd_3 complex in which a nearly equilateral triangle of palladium atoms is bridged at the edges by diphenylphosphinomethane ligands and capped by the triply bridging phosphorus atom of PF_3.[15] Moreover, the recent discovery by Reau et al. that substituted phospholes can bridge two palladium centers should encourage further work in this field.[16]

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **3**, **4**, **8**, and **9** were prepared as described in the literature.[6] NMR spectra were recorded at room temperature on Bruker AC 200, Bruker DRX 300, and Bruker AMX 400 instruments, and IR spectra on a Perkin-Elmer 1420 IR spectrophotometer. Melting points were measured by differential thermal analysis (DTA) with a Thermoanalyzer DuPont 9000.

$[Rh_2Cl(\kappa^2\text{-}acac)(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)]$ (5): A solution of **3** (77 mg, 0.08 mmol) in pentane/diethyl ether (2/1, 30 mL) was treated at −78 °C with PMe_3 (9 μL, 0.08 mmol) and warmed to room temperature over about 30 min. The color of the solution changed from dark red to yellow, and a red-brown solid precipitated. The solution was separated, the solid was washed with pentane/diethyl ether (3×5 mL) and dried; yield 51 mg (82 %); m.p. 204 °C (decomp); IR (KBr): $\tilde{\nu}=1580$, 1523 cm^{-1} (CO_{acac}); ^1H NMR (C_6D_6, 200 MHz): $\delta=8.46$, 8.33 (both m, 8H, *ortho*-H of C_6H_5), 7.03, 6.89, 6.62 (all m, 12H, *meta*- and *para*-H of C_6H_5), 5.45 (s, 1H, CH of acac), 1.89 (s, 6H, CH_3 of acac), 0.74 ppm (d, $J(P,H)=10.6$ Hz, 9H, PCH_3); ^{13}C NMR (CD_2Cl_2, 100.6 MHz): $\delta=189.3$ (s, CO of acac), 174.8 (ddd, $J(Rh,C)=30.5$ Hz, $J(Rh',C)=20.7$ Hz, $J(P,C)=3.6$ Hz, CPh_2), 153.6 (d, $J(P,C)=2.1$ Hz, *ipso*-C of C_6H_5), 153.5 (s, *ipso*-C of C_6H_5), 127.7, 127.1, 126.6, 125.7, 125.4, 124.5 (all s, C_6H_5), 100.9 (d, $J(Rh,C)=1.5$ Hz, CH of acac), 28.2 (s, CH_3 of acac), 22.4 ppm (d, $J(P,C)=40.7$ Hz, PCH_3); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta=-36.4$ ppm (dd, $J(Rh,P)=147.5$, $J(Rh',P)=81.4$ Hz); elemental analysis (%) for $C_{34}H_{36}ClO_2PRh_2$ (748.9): calcd: C 54.53, H 4.85; found: C 54.52, H 4.98.

$[Rh_2(\kappa^2\text{-}acac)_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)]$ (6): Method A: A solution of **5** (98 mg, 0.13 mmol) in acetone (20 mL) was treated with Na(acac) (64 mg, 0.52 mmol) and stirred for 4 h at room temperature. After the solvent was evaporated in vacuo, the residue was extracted with pentane/diethyl ether (2/1, 3×50 mL). The combined extracts were brought to dryness in vacuo, the pale brown residue was washed with pentane (3×3 mL, 0 °C) and dried; yield 104 mg (98 %). Method B: A solution of **4** (678 mg, 0.69 mmol) in benzene (30 mL) was treated dropwise with PMe_3 (78 μL, 0.76 mmol) and stirred for 2 h at room temperature. After the solvent was evaporated in vacuo, the pale brown residue was washed with diethyl ether (3×5 mL, 0 °C) and dried; yield 452 mg (81 %); m.p. 62 °C (decomp); IR (KBr): $\tilde{\nu}=1579$, 1518 cm^{-1} (CO_{acac}); ^1H NMR (300 MHz, C_6D_6): $\delta=8.19$, 7.40 (both m, 8H, *ortho*-H of C_6H_5), 7.08 (m, 4H, *meta*-H of C_6H_5), 6.96 (m, 2H, *para*-H of C_6H_5), 6.76 (m, 4H, *meta*-H of C_6H_5), 6.68 (m, 2H, *para*-H of C_6H_5), 5.54 (s, 2H, CH of acac), 1.96 (s, 12H, CH_3 of acac), 1.06 ppm (d, $J(P,H)=11.0$ Hz, 9H, PCH_3); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta=188.7$ (s, CO of acac), 170.7 (dt, $J(Rh,C)=24.7$, $J(P,C)=4.4$ Hz, CPh_2), 157.3 (d, $J(P,C)=3.3$ Hz, *ipso*-C of C_6H_5), 157.1 (s, *ipso*-C of C_6H_5), 126.9, 126.8, 126.5, 125.4, 125.2, 124.8 (all s, C_6H_5), 100.8 (s, CH of acac), 28.4 (s, CH_3 of acac), 22.1 ppm (d, $J(P,C)=39.6$ Hz, PCH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta=-30.4$ (t, $J(Rh,P)=110.6$ Hz); elemental analysis (%) for $C_{39}H_{43}O_4PRh_2$ (812.6): calcd: C 57.65, H 5.33; found: C 57.30, H 5.29.

[(κ^2-acac)Rh(μ-CPh$_2$)$_2$(μ-CO)Rh(κ^2-acac)(PMe$_3$)] (7): A slow stream of CO was passed for 5 s through a solution of **6** (57 mg, 0.07 mmol) in benzene (15 mL) at room temperature. A quick change of color from red-brown to light red occurred. After the solution was stirred for 5 min, the solvent was evaporated in vacuo, and the red solid was washed with pentane (2×3 mL) and dried; yield 56 mg (95%); m.p. 66°C (decomp); IR (KBr): $\tilde{\nu}$=1829 (CO), 1584, 1516 cm^{-1} (CO$_{acac}$); ^{1}H NMR (300 MHz, C$_6$D$_6$): δ=7.55, 7.08 (both m, 8H, *ortho*-H of C$_6$H$_5$), 6.98, 6.83 (both m, 12H, *meta*- and *para*-C of C$_6$H$_5$), 5.44, 5.36 (both s, 2H, CH of acac), 1.86 (s, 3H, CH$_3$ of acac), 1.76 (s, 6H, CH$_3$ of acac), 1.22 (s, 3H, CH$_3$ of acac), 0.70 ppm (dd, J(P,H)=9.5, J(RhH)=0.6 Hz, 9H, PCH$_3$); ^{13}C NMR (75.5 MHz, C$_6$D$_6$): δ=214.9 (ddd, J(Rh,C)=47.8, J(Rh′,C)=40.7, J(P,C)=2.0 Hz, μ-CO), 203.8 (ddd, J(P,C)=77.3, J(Rh,C)=21.4, J(Rh′,C)=12.2 Hz, *C*Ph$_2$), 189.8, 189.3, 186.5 (all s, CO of acac), 159.8 (t, J(Rh,C)=20.3 Hz, *C*Ph$_2$), 157.6 (d, J(P,C)=3.0 Hz, *ipso*-C of C$_6$H$_5$), 156.6, 156.5, 154.4 (all s, *ipso*-C of C$_6$H$_5$), 132.2, 131.4, 128.7, 127.9, 127.4, 127.3, 127.2, 127.1, 126.2, 126.1, 125.9, 125.7 (all s, C$_6$H$_5$), 100.8 (d, J(Rh,C)=2.9 Hz, CH of acac), 99.0 (s, CH of acac), 28.3, 28.1, 27.1 (all s, CH$_3$ of acac), 11.2 ppm (d, J(P,C)=20.3 Hz, PCH$_3$); ^{31}P NMR (81.0 MHz, C$_6$D$_6$): δ=−5.5 ppm (dd, J(Rh,P)=129.1, J(Rh′,P)=7.6 Hz); elemental analysis (%) for C$_{40}$H$_{43}$O$_5$PRh$_2$ (840.6): calcd: C 57.16, 5.16; found: C 57.59, H 5.55.

[Rh$_2$Cl(κ^2-acac-f$_3$)(μ-CPh$_2$)$_2$(μ-PMe$_3$)] (10): This compound was prepared as described for **5**, starting from **8** (154 mg, 0.16 mmol) and PMe$_3$ (16 μL, 0.16 mmol) in pentane/diethyl ether (2/1, 60 mL). Brown solid; yield 104 mg (82%); m.p. 150°C (decomp); IR (KBr): $\tilde{\nu}$=1614 cm^{-1} (CO$_{acac\text{-}f3}$); ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ=7.85 (m, 4H, *ortho*-H of C$_6$H$_5$), 7.22, 6.95, 6.73 (all m, 16H, C$_6$H$_5$), 6.18 (s, 1H, CH of acac-f$_3$), 2.39 (s, 3H, CH$_3$ of acac-f$_3$), 0.94 ppm (d, J(P,H)=10.9 Hz, 9H, PCH$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz): δ=197.5 (s, CO of acac-f$_3$), 178.1 (ddd, J(Rh,C)=29.5, J(Rh′,C)=21.4, J(P,C)=3.0 Hz, *C*Ph$_2$), 169.7 (q, J(F,C)=32.6 Hz, CO of acac-f$_3$), 153.1, 153.0 (both s, *ipso*-C of C$_6$H$_5$), 127.9, 127.2, 127.0, 126.1, 125.2, 124.3 (all s, C$_6$H$_5$), 119.1 (q, J(F,C)=285.8 Hz, CF$_3$), 96.4 (s, CH of acac-f$_3$), 29.6 (s, CH$_3$ of acac-f$_3$), 22.5 ppm (d, J(P,C)=40.7 Hz, PCH$_3$); ^{19}F NMR (CD$_2$Cl$_2$, 188.3 MHz): δ=−75.5 ppm (s); ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ=−36.8 ppm (dd, J(Rh,P)=144.1, J(Rh′,P)=86.5 Hz); elemental analysis (%) for C$_{34}$H$_{33}$ClF$_3$O$_2$PRh$_2$ (802.9): calcd: C 50.86, H 4.14; found: C 50.20, H 4.34.

[Rh$_2$(κ^2-acac-f$_3$)$_2$(μ-CPh$_2$)$_2$(μ-PMe$_3$)] (11): This compound was prepared as described for **6**, method B, starting from **9** (95 mg, 0.09 mmol) and PMe$_3$ (10 μL, 0.10 mmol) in benzene (30 mL). Red-brown solid; yield 62 mg (78%); m.p. 46°C (decomp); ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ=7.97, 7.21 (m, 8H, *ortho*-H of C$_6$H$_5$), 7.04, 6.70, 6.62 (all m, 12H, *meta*- and *para*-H of C$_6$H$_5$), 5.93 (s, 2H, CH of acac-f$_3$), 1.72 (s, 6H, CH$_3$ of acac-f$_3$), 0.85 ppm (d, J(P,H)=11.2 Hz, 9H, PCH$_3$); ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ=196.6 (s, CO of acac-f$_3$), 176.4 (dt, J(Rh,C)=24.8, J(P,C)=3.8 Hz, *C*Ph$_2$), 169.9 (q, J(F,C)=32.4 Hz, CO of acac-f$_3$), 155.9 (d, J(P,C)=2.9 Hz, *ipso*-C of C$_6$H$_5$), 155.6 (s, *ipso*-C of C$_6$H$_5$), 127.3, 127.2, 126.2, 126.1, 125.5, 124.6 (all s, C$_6$H$_5$), 119.8 (q, J(F,C)=285.1 Hz, CF$_3$), 96.2 (s, CH of acac-f$_3$), 29.3 (s, CH$_3$ of acac-f$_3$), 21.5 ppm (d, J(P,C)=39.1 Hz, PCH$_3$); ^{19}F NMR (C$_6$D$_6$, 188.3 MHz): δ=−75.0 ppm (s); ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ=−21.2 ppm (t, J(Rh,P)=110.2 Hz); elemental analysis (%) for C$_{39}$H$_{37}$F$_6$O$_4$PRh$_2$ (920.5): calcd: C 50.89, H 4.05; found: C 50.20, H 4.48.

[Rh$_2$Cl(κ^2-acac)(μ-CPh$_2$)$_2$(μ-PEt$_3$)] (12): This compound was prepared as described for **5**, starting from **3** (91 mg, 0.10 mmol) and PEt$_3$ (14 μL, 0.10 mmol). Dark brown solid; yield 63 mg (81%); m.p. 146°C (decomp); IR (KBr): $\tilde{\nu}$=1579, 1517 cm^{-1} (CO$_{acac}$); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ=8.30, 7.53 (both m, 8H, *ortho*-H of C$_6$H$_5$), 7.01, 6.87, 6.66 (all m, 12H, *meta*- and *para*-H of C$_6$H$_5$), 5.54 (s, 1H, CH of acac), 1.94 (s, 6H, CH$_3$ of acac), 1.13 (m, 6H, PCH$_2$), 0.69 ppm (m, 9H, PCH$_2$C*H*$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 75.5 MHz): δ=189.4 (s, CO of acac), 171.7 (ddd, J(Rh,C)=31.6 Hz, J(Rh′,C)=21.5 Hz, J(P,C)=4.0 Hz, *C*Ph$_2$), 154.1 (m, *ipso*-C of C$_6$H$_5$), 127.8, 127.2, 126.7, 125.8, 125.7, 124.7 (all s, C$_6$H$_5$), 101.2 (d, J(Rh,C)=1.8 Hz, CH of acac), 28.6 (d, J(Rh,C)=1.1 Hz, CH$_3$ of acac), 21.6 (d, J(P,C)=34.5 Hz, PCH$_2$), 8.5 ppm (d, J(P,C)=5.1 Hz, PCH$_2$C*H*$_3$); ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ=−2.7 ppm (dd, J(Rh,P)=144.9, J(Rh′,P)=68.7 Hz); elemental analysis (%) for C$_{37}$H$_{42}$ClO$_2$PRh$_2$ (791.0): calcd: C 56.18, H 5.35; found: C 55.77, H 5.58.

[Rh$_2$Cl(κ^2-acac)(μ-CPh$_2$)$_2$(μ-P*n*Bu$_3$)] (13): A solution of **3** (50 mg, 0.05 mmol) in a pentane/diethyl ether (2/1) was treated at −78°C with P*n*Bu$_3$ (13 μL, 0.05 mmol). The solution was warmed to room temperature over about 30 min, stirred for 10 min, and then the solvent was evaporated in vacuo. The ^{31}P NMR spectrum of the residue revealed a mixture of products with **13** as the dominant species. Attempts to separate **13** from the by-products by fractional crystallization failed. Data for **13**: ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ=−9.9 ppm (dd, J(Rh,P)=139.8, J(Rh′,P)=73.7 Hz).

[Rh$_2$(κ^2-acac)$_2$(μ-CPh$_2$)$_2$(μ-PEt$_3$)] (14): A solution of **4** (152 mg, 0.15 mmol) in diethyl ether (50 mL) was treated at −30°C with PEt$_3$ (67 μL, 0.46 mmol) and, after warming to 0°C, stirred for 4 h. A gradual change of color from brown to red-brown occurred. The solution was concentrated in vacuo to about 5 mL and then stored for 15 h at −60°C. Red-brown crystals precipitated, which were separated from the mother liquor, washed with pentane (2×3 mL), and dried; yield 80 mg (61%); m.p. 48°C (decomp); IR (KBr): $\tilde{\nu}$=1582, 1518 cm^{-1} (CO$_{acac}$); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ=8.22, 7.38 (both m, 8H, *ortho*-H of C$_6$H$_5$), 7.10, 6.75 (both m, 12H, *meta*- and *para*-H of C$_6$H$_5$), 5.58 (s, 2H, CH of acac), 1.98 (s, 12H, CH$_3$ of acac), 1.56 (m, 6H, PCH$_2$), 0.73 ppm (m, 9H, PCH$_2$C*H*$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz, 253 K): δ=187.7 (s, CO of acac), 174.0 (t, J(Rh,C)=24.8 Hz, *C*Ph$_2$), 156.3 (d, J(P,C)=1.9 Hz, *ipso*-C of C$_6$H$_5$), 156.0 (s, *ipso*-C of C$_6$H$_5$), 127.4, 126.2, 125.9, 124.9, 123.8, 123.7 (all s, C$_6$H$_5$), 99.4 (s, CH of acac), 28.2 (s, CH$_3$ of acac), 21.5 (d, J(P,C)=32.4 Hz, PCH$_2$), 8.7 ppm (d, J(P,C)=5.7 Hz, PCH$_2$CH$_3$); ^{31}P NMR (CD$_2$Cl$_2$, 162.0 MHz, 253 K): δ=23.7 ppm (t, J(Rh,P)=102.5 Hz); elemental analysis (%) for C$_{42}$H$_{49}$O$_4$PRh$_2$ (854.6): calcd: C 59.03, 5.78; found: C 59.14, H 6.04.

[Rh$_2$(κ^2-acac)$_2$(μ-CPh$_2$)$_2$(μ-PMe$_2$Ph)] (15): This compound was prepared as described for **6**, method B, starting from **4** (81 mg, 0.08 mmol) and PMe$_2$Ph (13 μL, 0.09 mmol) in benzene (10 mL). Red-brown solid; yield 51 mg (71%); m.p. 106°C (decomp); IR (KBr): $\tilde{\nu}$=1582, 1520 cm^{-1} (CO$_{acac}$); ^{1}H NMR (C$_6$D$_6$, 200 Hz): δ=8.06, 7.31 (both m, 8H, *ortho*-H of C$_6$H$_5$), 7.03, 6.91, 6.67 (all m, 17H, C$_6$H$_5$), 5.45 (s, 2H, CH of acac), 1.92 (s, 12H, CH$_3$ of acac), 1.58 ppm (d, J(P,H)=10.6 Hz, 6H, PCH$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz): δ=188.3 (s, CO of acac), 170.2 (dt, J(Rh,C)=24.8 Hz, J(P,C)=4.8 Hz, *C*Ph$_2$), 157.5 (s, *ipso*-C of CC$_6$H$_5$), 156.9 (d, J(P,C)=2.9 Hz, *ipso*-C of CC$_6$H$_5$), 140.3 (d, J(P,C)=52.4 Hz, *ipso*-C of PC$_6$H$_5$), 132.2 (d, J(P,C)=2.9 Hz, *para*-C of PC$_6$H$_5$), 130.6 (d, J(P,C)=9.5 Hz, *ortho*- or *meta*-C of PC$_6$H$_5$), 128.3 (d, J(P,C)=10.5 Hz, *ortho*- or *meta*-C of PC$_6$H$_5$), 127.1, 126.6, 125.8, 125.6, 125.4, 124.9 (all s, CC$_6$H$_5$), 100.6 (s, CH of acac), 28.1 (s, CH$_3$ of acac), 20.4 ppm (d, J(P,C)=42.9 Hz, PCH$_3$); ^{31}P NMR (CD$_2$Cl$_2$, 162.0 MHz): δ=−35.9 ppm (t, J(Rh,P)=109.0 Hz); elemental analysis (%) for C$_{44}$H$_{45}$O$_4$PRh$_2$ (874.6): calcd: C 60.42, H 5.19; found: C 59.94, H 5.26.

[(PEt$_3$)Rh(μ-CPh$_2$)$_2$Rh(κ^2-acac)$_2$] (16): Method A: A solution of **4** (469 mg, 0.47 mmol) in benzene (70 mL) was treated with PEt$_3$ (139 μL, 0.95 mmol) and stirred for two days at room temperature. The solvent was evaporated in vacuo, the residue was suspended in hexane (10 mL), and the suspension was subjected to chromatography on Al$_2$O$_3$ (neutral, activity grade V, height of column 10 cm). With hexane a colorless fraction was eluted which was withdrawn. Subsequently, with hexane/diethyl ether (5/1) a brownish-green fraction was eluted, which was concentrated in vacuo to about 20 mL. After the solution was stored for 15 h at −60°C, a brownish green solid precipitated, which was washed with hexane (2×5 mL; 0°C) and dried; yield 351 mg (86%). Method B: A solution of **14** (43 mg, 0.05 mmol) in benzene (50 mL) was stirred for 15 h at room temperature. After the solvent was evaporated in vacuo, the remaining solid was washed with pentane (2×2 mL; 0°C) and dried; yield 41 mg (95%); m.p. 41°C (decomp); IR (KBr): $\tilde{\nu}$=1582, 1516 cm^{-1} (CO$_{acac}$); ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ=8.04, 7.67 (both m, 8H, *ortho*-H of C$_6$H$_5$), 7.29 (m, 6H, *meta*- and *para*-H of C$_6$H$_5$), 6.96 (m, 2H, *para*-H of C$_6$H$_5$), 6.87 (m, 4H, *meta*-H of C$_6$H$_5$), 4.87 (s, 2H, CH of acac), 1.86, 1.44 (both s, 12H, CH$_3$ of acac), 1.24 (m, 6H, PCH$_2$), 0.63 ppm (m, 9H, PCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ=186.5, 184.0 (both s, CO of acac), 159.2 (ddd, J(Rh,C)=38.7, J(Rh′,C)=29.5, J(P,C)=11.2 Hz, *C*Ph$_2$), 148.5, 145.2 (both s, *ipso*-C of C$_6$H$_5$), 130.0, 129.9, 127.4, 126.7, 125.8, 125.5 (all s, C$_6$H$_5$), 98.8 (s, CH of acac), 27.9, 26.9 (both s, CH$_3$ of acac), 18.5 (dd, J(P,C)=21.4, J(Rh,C)=3.1 Hz, PCH$_2$), 8.3 ppm (s, PCH$_2$CH$_3$); ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ=17.3 ppm (dd, J(Rh,P)=264.9, J(Rh′,P)=4.8 Hz); elemental analysis (%) for C$_{42}$H$_{49}$O$_4$PRh$_2$ (854.6): C 59.03, H 5.78; found: C 59.17, H 6.01.

[(PMePh$_2$)Rh(μ-CPh$_2$)$_2$Rh(κ^2-acac)$_2$] (17): A solution of **4** (475 mg, 0.48 mmol) in benzene (30 mL) was treated with PMePh$_2$ (271 μL, 1.44 mmol) and stirred for 6 h at room temperature. The solvent was evaporated in vacuo, the remaining residue was suspended in hexane (20 mL), and the suspension was subjected to chromatography on Al_2O_3 (neutral, activity grade V, height of column 10 cm). With hexane a colorless fraction was eluted which was withdrawn. Subsequently, with hexane/diethyl ether (5/1) a brownish-green fraction was eluted, which was concentrated in vacuo to about 20 mL. After the solution was stored for 15 h at −60 °C, a brownish green solid precipitated, which was washed with hexane (2×5 mL, 0 °C) and dried; yield 387 mg (86 %); m.p. 79 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1587, 1577, 1516 cm^{-1} (CO$_{acac}$); ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 7.90, 7.54, 7.28, 7.13, 7.02, 6.93, 6.81 (all m, 30 H, C$_6$H$_5$), 4.87 (s, 2 H, CH of acac), 1.85, 1.43 (both s, 12 H, CH$_3$ of acac), 1.32 ppm (dd, J(P,H) = 7.3, J(RhH) = 1.8 Hz, 3 H, PCH$_3$); ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 186.6, 184.2 (both s, CO of acac), 160.6 (m, *C*Ph$_2$), 148.0, 145.1 (both s, *ipso*-C of CC$_6$H$_5$), 136.5 (dd, J(P,C) = 38.1, J(Rh,C) = 3.8 Hz, *ipso*-C of PC$_6$H$_5$), 132.8 (d, J(P,C) = 13.3 Hz, *ortho*- or *meta*-C of PC$_6$H$_5$), 132.4 (d, J(P,C) = 11.4 Hz, *ortho*- or *meta*-C of PC$_6$H$_5$), 129.7, 129.6, 127.7, 127.6, 126.8, 126.0, 125.7 (all s, *para*-C of PC$_6$H$_5$ and *ortho*-, *meta*- and *para*-C of CC$_6$H$_5$), 98.8 (s, CH of acac), 27.8, 26.9 (both s, CH$_3$ of acac), 14.4 ppm (dd, J(P,C) = 25.8, J(Rh,C) = 2.9 Hz, PCH$_3$); ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ = 16.5 ppm (dd, J(Rh,P) = 281.4, J(Rh′,P) = 5.1 Hz); elemental analysis (%) for C$_{49}$H$_{47}$O$_4$PRh$_2$ (936.7): calcd: C 62.83, H 5.06; found: C 62.45, H 5.08.

[(P*n*Bu$_3$)Rh(μ-CPh$_2$)$_2$Rh(κ^2-acac)$_2$] (18): This compound was prepared as described for **16**, method A, starting from **4** (146 mg, 0.15 mmol) and P*n*Bu$_3$ (73 μL, 0.30 mmol) in benzene (10 mL). Brown solid; yield 127 mg (91 %); m.p. 85 °C (decomp); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 8.10, 7.68 (both m, 8 H, *ortho*-H of C$_6$H$_5$), 7.33, 6.88, (m, 12 H, C$_6$H$_5$), 4.88 (s, 2 H, CH of acac), 1.88, 1.44 (both s, 12 H, CH$_3$ of acac), 1.33–1.20 (m, 18 H, CH$_2$ of P*n*Bu$_3$), 0.81 ppm (m, 9 H, CH$_3$ of P*n*Bu$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz, 253 K): δ = 185.8, 183.5 (both s, CO of acac), 156.7 (m, *C*Ph$_2$), 146.6, 144.1 (both s, *ipso*-C of C$_6$H$_5$), 128.8, 128.7, 127.4, 127.0, 126.1, 125.1 (all s, C$_6$H$_5$), 97.9 (s, CH of acac), 27.4, 26.2 (both s, CH$_3$ of acac), 25.1 (dd, J(P,C) = 21.0 Hz, J(Rh,C) = 1.9 Hz, P*C*H$_2$), 24.2 (d, J(P,C) = 2.8 Hz, CH$_2$ of P*n*Bu$_3$), 23.5 (d, J(P,C) = 3.8 Hz, CH$_2$ of P*n*Bu$_3$), 13.4 ppm (s, CH$_3$ of P*n*Bu$_3$); ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ = 10.4 ppm (dd, J(Rh,P) = 269.5, J(Rh′,P) = 5.1 Hz); elemental analysis (%) for C$_{48}$H$_{61}$O$_4$PRh$_2$ (938.8): calcd: C 61.41, H 6.55; found: C 61.04, H 6.13.

[Rh$_2$(κ^1-O$_2$CCF$_3$)(κ^2-acac)(μ-CPh$_2$)$_2$(μ-PMe$_3$)] (19): A solution of **6** (70 mg, 0.09 mmol) in benzene (5 mL) was treated with CF$_3$CO$_2$H (7 μL, 0.09 mmol) and stirred for 4 h at room temperature. The solvent was evaporated in vacuo, the remaining red-brown solid was washed with pentane (2×2 mL; 0 °C) and dried; yield 70 mg (98 %); m.p. 77 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1654 (OCO$_{asym}$), 1582, 1521 cm^{-1} (CO$_{acac}$); ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 8.06, 7.30 (both m, 8 H, *ortho*-H of C$_6$H$_5$), 7.05 (m, 4 H, *meta*-H of C$_6$H$_5$), 6.90 (m, 2 H, *para*-H of C$_6$H$_5$), 6.62 (m, 6 H, *meta*-H and *para*-H of C$_6$H$_5$), 5.44 (s, 1 H, CH of acac), 1.86 (s, 6 H, CH$_3$ of acac), 0.76 ppm (d, J(P,H) = 11.2 Hz, 9 H, PMe$_3$); ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 189.3 (s, CO of acac), 175.4 (ddd, J(Rh,C) = 31.5 Hz, J(Rh′,C) = 21.5 Hz, J(P,C) = 3.8 Hz, *C*Ph$_2$), 154.3 (s, *ipso*-C of C$_6$H$_5$), 128.1, 127.5, 127.1, 126.1, 124.9, 124.1 (all s, C$_6$H$_5$), 118.0 (q, J(F,C) = 288.9 Hz, *C*F$_3$), 101.2 (s, CH of acac), 28.1 (s, CH$_3$ of acac), 20.9 ppm (d, J(P,C) = 41.0 Hz, PMe$_3$), signal of *C*O$_2$CF$_3$ not exactly located; ^{19}F NMR (C$_6$D$_6$, 188.3 MHz): δ = −73.6 ppm (s); ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ = −23.9 ppm (dd, J(Rh,P) = 155.9, J(Rh′,P) = 69.8 Hz); elemental analysis (%) for C$_{36}$H$_{36}$F$_3$O$_4$PRh$_2$ (826.5): calcd: C 52.32, H 4.39; found: C 52.71, H 4.60.

[Rh$_2$(κ^2-O$_2$CCH$_3$)(κ^2-acac)(μ-CPh$_2$)$_2$(μ-PMe$_3$)] (20): A solution of **6** (62 mg (0.08 mmol) in toluene (10 mL) was treated at −78 °C with acetic acid (4 μL, 0.08 mmol) and, after its warming to room temperature, stirred for 2 h. The solvent was removed in vacuo to give a light brown solid. The ^{1}H and ^{31}P NMR spectra of the solid revealed that apart from compound **20** (ca. 80 %) both the starting material **6** (ca. 10 %) and the bis(acetate) complex **22** (ca. 10 %) were present. Since attempts to separate **20** from the by-products failed, the main component was characterized spectroscopically. Data for **20**: IR (KBr): $\tilde{\nu}$ = 1582, 1518 cm^{-1} (CO$_{acac}$); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 8.12, 7.45 (both m, 8 H, *ortho*-H of C$_6$H$_5$), 7.00, 6.70 (both m, 12 H, *meta*- and *para*-H of C$_6$H$_5$), 5.49 (s, 1 H, CH of acac), 2.24 (s, 3 H, CO$_2$CH$_3$), 1.93 (s, 6 H, CH$_3$ of acac), 1.00 ppm (d, J(P,H) = 11.0 Hz, 9 H, PMe$_3$); ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ = −43.6 ppm (dd, J(Rh,P) = 117.0, J(Rh′,P) = 106.8 Hz).

[Rh$_2$(κ^2-O$_2$CCF$_3$)$_2$(μ-CPh$_2$)$_2$(μ-PMe$_3$)] (21): A solution of **6** (123 mg, 0.15 mmol) in diethyl ether (5 mL) was treated with CF$_3$CO$_2$H (232 μL, 3.03 mmol) and stirred for 1 h at room temperature. The solvent was evaporated in vacuo to give a brownish yellow solid. The NMR spectra showed that apart from compound **21** some by-products (ca. 10 %) were formed, which due the excellent solubility of all components in common organic solvents, could not be separated. Data for **21**: IR (KBr): $\tilde{\nu}$ = 1657 ν(OCO$_{sym}$), 1443 cm^{-1} (OCO$_{asym}$); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 7.76, 7.25 (both m, 8 H, *ortho*-H of C$_6$H$_5$), 6.80, 6.53 (both m, 12 H, *meta*- and *para*-H of C$_6$H$_5$), 0.64 ppm (d, J(P,H) = 11.3 Hz, 9 H, PMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 100.6 MHz, 253 K): δ = 166.5 (m, *C*Ph$_2$), 152.3, 150.5 (both s, *ipso*-C of C$_6$H$_5$), 129.8, 128.7, 128.1, 127.6, 122.8, 122.4 (both s, C$_6$H$_5$), 116.0 (q, J(F,C) = 287.0 Hz, *C*F$_3$), 20.1 ppm (d, J(P,C) = 40.0 Hz, PMe$_3$), signal of *C*O$_2$CF$_3$ could not be exactly located; ^{19}F NMR (CD$_2$Cl$_2$, 188.3 MHz, 253 K): δ = −74.5 ppm (s); ^{31}P NMR (C$_6$D$_6$, 81.0 MHz): δ = −16.0 ppm (t, J(Rh,P) = 110.6 Hz).

[Rh$_2$(κ^2-O$_2$CCH$_3$)$_2$(μ-CPh$_2$)$_2$(μ-PMe$_3$)] (22): A solution of **6** (67 mg, 0.08 mmol) in benzene (10 mL) was treated with an excess of acetic acid (300 μL, 5.25 mmol) and stirred for 2 h at room temperature. The solvent was evaporated in vacuo, and the remaining brown solid was washed with diethyl ether (2×3 mL) and dried; yield 57 mg (94 %); m.p. 91 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1449 cm^{-1} (OCO$_{sym}$); ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 8.28, 7.46 (both m, 8 H, *ortho*-H of C$_6$H$_5$), 7.07 (m, 4 H, *meta*-H of C$_6$H$_5$), 6.84 (m, 2 H, *para*-H of C$_6$H$_5$), 6.67 (m, 4 H, *meta*-H of C$_6$H$_5$), 6.59 (m, 2 H, *para*-H of C$_6$H$_5$), 2.17 (s, 6 H, CO$_2$CH$_3$), 0.91 ppm (d, J(P,H) = 10.9 Hz, 9 H, PCH$_3$); ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 187.2 (s, *C*O$_2$CH$_3$), 182.7 (dt, J(Rh,C) = 25.0 Hz, J(P,C) = 4.3 Hz, *C*Ph$_2$), 155.8 (d, J(P,C) = 4.1 Hz, *ipso*-C of C$_6$H$_5$), 155.4 (s, *ipso*-C of C$_6$H$_5$), 128.1, 127.5, 126.7, 126.1, 124.4, 124.1 (all s, C$_6$H$_5$), 23.5 (s, CO$_2$CH$_3$), 22.6 ppm (d, J(P,C) = 39.7 Hz, PCH$_3$); ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ = −45.9 ppm (t, J(Rh,P) = 115.0 Hz); elemental analysis (%) for C$_{33}$H$_{35}$O$_4$PRh$_2$ (732.4): calcd: C 54.12, H 4.82; found: C 53.90, H 4.59.

[Rh$_2$(κ^1-OPh)(κ^2-acac)(μ-CPh$_2$)$_2$(μ-PMe$_3$)] (23): A solution of **6** (80 mg, 0.10 mmol) in benzene (10 mL) was treated with phenol (93 mg, 0.98 mmol) and stirred for three days at room temperature. The solvent and excess phenol were removed in vacuo, and the remaining brown solid was washed with pentane (3×5 mL) and dried; yield 76 mg (96 %); m.p. 55 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1580, 1519 cm^{-1} (CO$_{acac}$); ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 8.30, 7.21 (both m, 8 H, *ortho*-H of C$_6$H$_5$), 7.09, 6.96, 6.60 (all m, 17 H, C$_6$H$_5$), 5.42 (s, 1 H, CH of acac), 1.88 (s, 6 H, CH$_3$ of acac), 0.73 ppm (d, J(P,H) = 10.8 Hz, 9 H, PMe$_3$); ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 189.0 (s, CO of acac), 170.7 (ddd, J(Rh,C) = 29.6 Hz, J(Rh′,C) = 21.0 Hz, J(P,C) = 3.8 Hz, *C*Ph$_2$), 154.7 (d, J(P,C) = 2.9 Hz, *ipso*-C of C$_6$H$_5$), 154.6 (s, *ipso*-C of C$_6$H$_5$), 131.8, 129.8, 128.3, 127.9, 127.2, 126.8, 125.8, 125.5, 125.4 (all s, C$_6$H$_5$), 100.9 (s, CH of acac), 23.2 (s, CH$_3$ of acac), 22.0 ppm (d, J(P,C) = 40.7 Hz, PMe$_3$); signal of *ipso*-C carbon atom of OC$_6$H$_5$ could not be exactly located; ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ = −26.2 ppm (dd, J(Rh,P) = 162.4, J(Rh′,P) = 61.0 Hz); elemental analysis (%) for C$_{40}$H$_{41}$O$_3$PRh$_2$ (806.6): calcd: C 59.57, H 5.12; found: C 58.98, H 5.24.

X-ray structure determinations of compounds 5 and 6: Single crystals of **5** and **6** were grown from acetone at 5 °C (**5**) or at room temperature (**6**). Crystal data collection parameters for the two structures are presented in Table 1. Intensity data were corrected for Lorentzian and polarization effects, and a semiempirical absorption correction was applied. The structures were solved by direct methods with SHELXS-97.[17] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method on F^2 with SHELXL-97.[18] The positions of all hydrogen atoms were calculated according to ideal geometry (d(C–H) = 0.95 Å) and refined by using the riding method; they were used only in calculating structure factors.[19]

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Table 1. Crystal structure data of compounds **5** and **6**.

	5	**6**
formula	$C_{34}H_{36}ClO_2PRh_2$	$C_{39}H_{43}O_4PRh_2$
molecular mass	748.87	812.52
crystal size	$0.3\times0.2\times0.2$	$0.4\times0.4\times0.4$
crystal system	monoclinic	monoclinic
space group	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)
a [Å]	33.925(7)	10.436(2)
b [Å]	10.279(2)	21.5125(10)
c [Å]	18.109(4)	16.678(4)
β [°]	98.15(3)	107.843(10)
V [Å^3]	6251(2)	3564.2(11)
Z	8	4
ρ_{calcd} [g cm^{-3}]	1.591	1.514
diffractometer	Stoe IPDS	Enraf Nonius CAD4
radiation	$Mo_{K\alpha}$ (0.71073 Å)	$Mo_{K\alpha}$ (0.71073 Å)
T [K]	173(2)	193(2)
μ [mm^{-1}]	1.222	1.010
scan method	φ scans	ω/θ scans
2θ(max) [°]	50.00	53.92
total reflections	12940	9426
unique reflections	5450	7753
observed reflections [$I>2\sigma(I)$]	3183	6642
R_1	0.0354	0.0291
wR_2	0.0575	0.0662
GOF	0.780	1.072
reflection/parameter ratio	14.93	18.37
residual electron density [e Å^{-3}]	+0.537/− 1.091	+0.355/−0.856

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[19] CCDC-146302 (**5**) and CCDC-146303 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk)..

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