A New Family of Mixed-Valence Dinuclear Rhodium Complexes Containing the Two Metal Centers in Different Stereochemical Environments

Ulrich Herber, Thomas Pechmann, Birgit Weberndörfer, Kerstin Ilg, and Helmut Werner*[a]

Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

Abstract: A series of dinuclear chelate complexes of the general composition $[Rh_2(\kappa^2\text{-}L)_2(\mu\text{-}CR_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (R = Ph, *p*-Tol; L = $CF_3CO_2^-$, acac$^-$, acac-f_3^-) and $[Rh_2Cl(\kappa^2\text{-}L)(\mu\text{-}CR_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (R = Ph, *p*-Tol; L = acac$^-$, acac-f_3^-) has been prepared by replacement of the chloro ligands in the precursors $[Rh_2Cl_2(\mu\text{-}CR_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ by anionic chelates. The lability of the $Sb\textit{i}Pr_3$ bridge in the rhodium dimers is illustrated by the reactions of $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CR_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (**7**, **8**) with Lewis bases such as CO, CN*t*Bu, and $SbEt_3$ which lead to the formation of the substitution products $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CR_2)_2(\mu\text{-}L')]$ (**13**–**16**) in excellent yields. Treatment of **7** and **8** with sterically demanding tertiary phosphanes PR_3 ($R_3 = \textit{i}Pr_3$, $\textit{i}Pr_2Ph$, $\textit{i}PrPh_2$, Ph_3) affords the mixed-valence Rh^0–Rh^{II} complexes $[(\kappa^2\text{-acac})_2Rh(\mu\text{-}CPh_2)_2Rh(PR_3)]$ (**21**–**24**) and $[(\kappa^2\text{-acac})_2Rh\{\mu\text{-}C(p\text{-}Tol)_2\}_2Rh(P\textit{i}Pr_3)]$ (**25**) for which there is no precedence. The terminal $P\textit{i}Pr_3$ ligand of **21** is easily displaced by alkynes, CN*t*Bu, and CO to give, by preserving the $\{(\kappa^2\text{-acac})_2Rh(\mu\text{-}CPh_2)_2Rh\}$ molecular core, the related dinuclear compounds **26**–**31** in which the coordination number of the Rh^0 center is 3, 4, or 5. The molecular structures of $[Rh_2Cl(\kappa^2\text{-acac})(\mu\text{-}CPh_2)_2(\mu\text{-}Sb\textit{i}Pr_3)]$ (**5**), $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CPh_2)_2(\mu\text{-CO})]$ (**13**), $[(\kappa^2\text{-acac})_2Rh(\mu\text{-}CPh_2)_2Rh(P\textit{i}Pr_3)]$ (**21**), and $[(\kappa^2\text{-acac})_2Rh(\mu\text{-}CPh_2)_2Rh(CN\textit{t}Bu)_2]$ (**30**) have been determined crystallographically.

Keywords: acetylacetonato complexes · antimony · carbene ligands · mixed-valent compounds · rhodium

Introduction

In the course of investigations concerned with the reactivity of square-planar carbene complexes *trans*-$[RhCl(=CRR')(Sb\textit{i}Pr_3)_2]$, which were prepared from *trans*-$[RhCl(C_2H_4)(Sb\textit{i}Pr_3)_2]$ and diazoalkanes $RR'CN_2$, we recently discovered that these compounds are thermally quite labile and react upon heating in benzene at 60 °C by partial elimination of $Sb\textit{i}Pr_3$ to afford the rhodium complexes **1a**–**c** in excellent yields.[1] Taking into consideration that the bridging coordination mode of trialkylstibanes was not only new but also unexpected,[2] we were rather surprised that these dinuclear molecules with rhodium(I) in a tetrahedral geometry are remarkably stable, in most cases decomposing at temperatures around 190 °C or even above. Nevertheless, the stibane-bridged compounds **1a**–**c** are fairly reactive and, as shown in Scheme 1, upon treatment of **1a** with CN*t*Bu or less bulky trialkylstibanes the dirhodium complexes **2** and **3** are formed by bridge–ligand exchange.

Based on the results shown in Scheme 1,[1] we were interested to know whether the dinuclear structure with the core molecular fragment $\{Rh(\mu\text{-}Sb\textit{i}Pr_3)(\mu\text{-}CRR')_2Rh\}$ would be maintained if the axial chloro ligands are replaced by chelating anions. The outcome of this substitution would be not only an increase in the cooordination number of rhodium, but also a change of the coordination geometry around the two metal centers. We have already found that the reaction of **1a** with NaC_5H_5 affords the dinuclear complex $[Rh_2(C_5H_5)_2(\mu\text{-}CPh_2)_2]$, which no longer contains a bridging stibane unit.[1]

In this paper we report that by using trifluoroacetate or acetylacetonates as anionic substrates, the chloro ligands can indeed be replaced *without* changing the triply-bridged Rh_2 moiety. However, the more noteworthy result of this study is that the bis(acetylacetonato)dirhodium complexes obtained by this route open the gate to the synthesis of a new family of mixed-valence Rh^0–Rh^{II} compounds in which the coordination number of the zerovalent metal center can be 3, 4, or 5. A short communication about the first steps of this investigation has already appeared.[3]

[a] Prof. Dr. H. Werner, Dr. U. Herber, Dipl.-Chem. T. Pechmann, Dr. B. Weberndörfer, Dr. K. Ilg
Institut für Anorganische Chemie der Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: helmut.werner@mail.uni-wuerzburg.de

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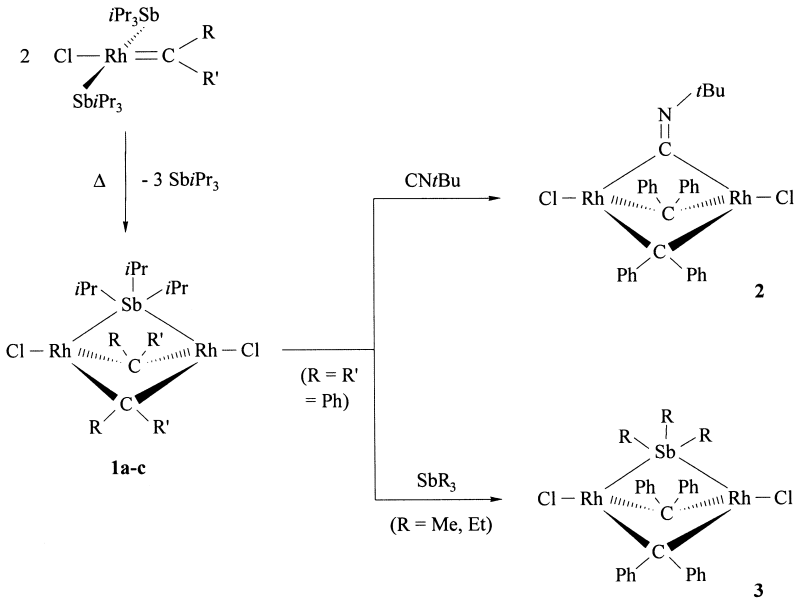

Scheme 1. Preparation of complexes **2** and **3** (**1a**: R = R′ = Ph; **1b**: R = R′ = *p*-Tol; **1c**: R = Ph, R′ = *p*-Tol).

Results and Discussion

Replacement of the axial chlorides of the dirhodium complexes by chelating ligands: In contrast to the reactivity of **1a** toward NaC_5H_5, treatment of the same starting material with 2.5 equivalents of CF_3CO_2Tl in acetone at room temperature leads to the formation of the disubstituted product **4**, which has been isolated in 86% yield (Scheme 2). The dark red microcrystalline compound, the composition of which has been confirmed by elemental analysis, is considerably more soluble than **1a** in diethyl ether and pentane; this makes separation of the byproduct TlCl easy. Attempts to perform the separation by column chromatography with deactivated (i.e., chloride containing) Al_2O_3 led to the regeneration of **1a** illustrating the lability of the Rh–O_2CCF_3 bond.

With Tl(acac) instead of CF_3CO_2Tl a stepwise replacement of the axial chloro ligands of **1a** by acetylacetonate has been achieved. The reaction of **1a** with an equimolar amount of Tl(acac) in acetone affords, after chromatographic workup and recrystallization of the product from acetone/diethyl ether, the monosubstituted compound **5** as brown, moderately air-sensitive crystals in 73% yield. The bis(di-*p*-tolylcarbene)dirhodium complex **6** is accessible by the same route (Scheme 3). Owing to the different coordination numbers at the two metal centers, the resonance for the ^{13}C nuclei of the carbene carbon atoms appears in the ^{13}C NMR spectra of **5** and **6** as a multiplet instead of a triplet as found for the dichloro precursors **1a** and **1b**.

The fact that the replacement of one chloride in **1a** by acetylacetonate is not accompanied by the cleavage of the stibane bridge has been confirmed by the X-ray crystal structure analysis of **5** (see Figure 1). Due to the asymmetry of the dinuclear molecule, the stibane and one of the diphenylcarbene ligands are linked to the two rhodium atoms in an unsymmetrical fashion. The bond lengths Sb–Rh1 and Sb–Rh2 differ by about 0.35 Å and those between the carbene carbon atom C2 and Rh1 and Rh2, respectively, by approximately the same value. Relative to the bonds in the starting material **1a**, the Sb–Rh1 bond is about 0.19 Å shorter and that of Sb–Rh2 about 0.18 Å longer; this is probably due to the different (mono- vs. bidentate) nature of the anionic ligands. It is also worth noting that the acetylacetonate is coordinated in an unsymmetrical mode (Rh1–O1 2.064(3), Rh1–O2 2.274(4) Å), thereby the shorter Rh1–O1 bond being opposite to the shorter Rh1–C1 bond. The molecular fragment (O1,O2,Rh1,Rh2) is almost planar, whereas the Rh1-Rh2-Cl axis is slightly more bent (171.55(3)°) than in **1a** (175.45(4)°).[1] The rhodium–rhodium distance in **5** is about 0.15 Å longer than in the precursor **1a**, but still lies in the range of other rhodium(I) complexes with a metal–metal bond.[4]

The reactions of **1a** and **1b** with Tl(acac) in the molar ratio of 1:2.4 lead to the formation of the symmetrical dinuclear compounds **7** and **8** (see Scheme 3). These compounds like the monosubstituted products **5** and **6** have been isolated, after recrystallization from pentane, as brown solids in excellent

Abstract in German: *Die Darstellung einer Reihe zweikerniger Chelatkomplexe der allgemeinen Zusammensetzung $[Rh_2(\kappa^2\text{-}L)_2(\mu\text{-}CR_2)_2(\mu\text{-}SbiPr_3)]$ (R = Ph, p-Tol; L = $CF_3CO_2^-$, acac$^-$, acac-f_3^-) und $[Rh_2Cl(\kappa^2\text{-}L)(\mu\text{-}CR_2)_2(\mu\text{-}SbiPr_3)]$ (R = Ph, p-Tol; L = acac$^-$, acac-f_3^-) gelingt durch Austausch der Chloroliganden in den Ausgangsverbindungen $[Rh_2Cl_2(\mu\text{-}CR_2)_2(\mu\text{-}SbiPr_3)]$ durch anionische Chelatbildner. Die Labilität der $SbiPr_3$-Brücke in den Chelatkomplexen $[Rh_2(\kappa^2\text{-}acac)_2(\mu\text{-}CR_2)_2(\mu\text{-}SbiPr_3)]$ (**7**, **8**) belegen deren Reaktionen mit Lewis-Basen wie CO, CNtBu und $SbEt_3$, die zu den Substitutionsprodukten $[Rh_2(\kappa^2\text{-}acac)_2(\mu\text{-}CR_2)_2(\mu\text{-}L')]$ (**13**–**16**) in sehr guten Ausbeuten führen. Bei Zugabe sterisch anspruchsvoller tertiärer Phosphane PR_3 ($R_3 = iPr_3$, iPr_2Ph, $iPrPh_2$, Ph_3) zu Lösungen von **7** und **8** entstehen die neuartigen gemischt-valenten Rh^0-Rh^{II}-Komplexe $[(\kappa^2\text{-}acac)_2Rh(\mu\text{-}CPh_2)_2Rh(PR_3)]$ (**21**–**24**) und $[(\kappa^2\text{-}acac)_2Rh\{\mu\text{-}C(p\text{-}Tol)_2\}_2Rh(PiPr_3)]$ (**25**), in denen (für R = iPr) der terminale Phosphanligand leicht durch Alkine, CNtBu und CO ersetzt werden kann. Dabei bilden sich unter Erhalt der $\{(\kappa^2\text{-}acac)_2Rh(\mu\text{-}CPh_2)_2Rh\}$-Moleküleinheit die entsprechenden zweikernigen Komplexe **26**–**31**, in denen die Koordinationszahl am Rh^0-Zentrum 3, 4 oder 5 ist. Die Molekülstruktur der Verbindungen $[Rh_2Cl(\kappa^2\text{-}acac)(\mu\text{-}CPh_2)_2(\mu\text{-}SbiPr_3)]$ (**5**), $[Rh_2(\kappa^2\text{-}acac)_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$ (**13**), $[(\kappa^2\text{-}acac)_2Rh(\mu\text{-}CPh_2)_2Rh(PiPr_3)]$ (**21**) und $[(\kappa^2\text{-}acac)_2Rh(\mu\text{-}CPh_2)_2Rh(CNtBu)_2]$ (**30**) wurde auf kristallographischem Wege bestimmt.*

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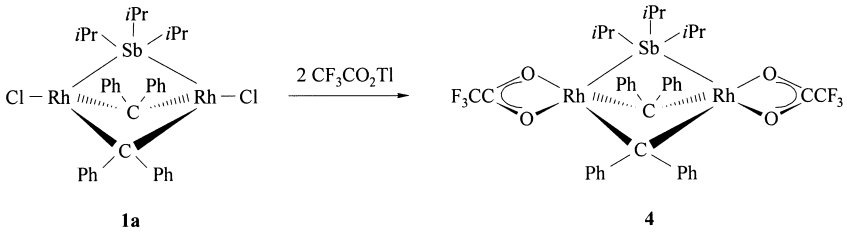
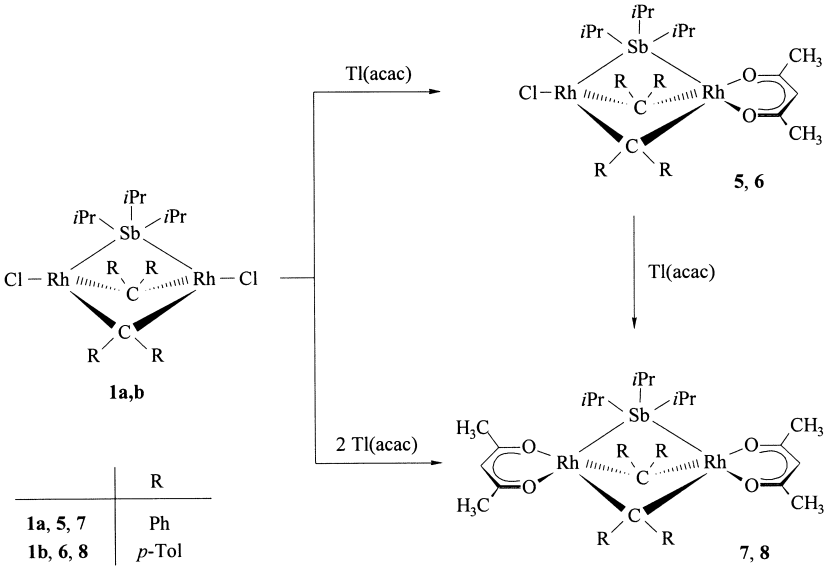
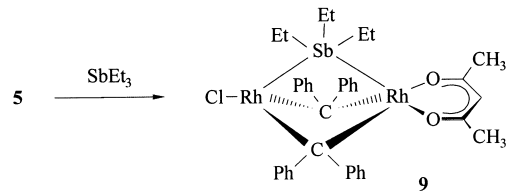


1a 4

Scheme 2. Preparation of complex **4**.





Scheme 3. Preparation of complexes **5**–**9**.

yields. Both **7** and **8** can also be obtained upon treatment of **5** or **6** with a slight excess of Tl(acac). Quite remarkably, the dinuclear bis(acetylacetonato) complexes **7** and **8** are thermally significantly less stable than the unsymmetrical acetylacetonato(chloro) counterparts and decompose at 55 °C and 62 °C, respectively. Regarding the spectroscopic data of **7**, we note that the resonance for the carbene carbon atoms appears in the ^{13}C NMR spectrum at $\delta = 176.8$, which is approximately 9 ppm upfield relative to that observed in **1a**. A similar upfield shift (by ca. 5 ppm) has been observed for the corresponding signal of the μ-*C*Ph$_2$ carbon atoms of the triethylstibane-bridged complex **9**, which like the analogue [Rh$_2$Cl$_2$(μ-CPh$_2$)$_2$(μ-SbEt$_3$)] (see Scheme 1) is accessible in 94% yield by bridge–ligand exchange from **5** and SbEt$_3$ in benzene.

The dinuclear compounds **10** and **11**, structurally related to **6** and **7**, with one or two trifluorinated acetylacetonato ligands have been prepared from **1b** or **1a** and one or two equivalents of Tl(acac-f$_3$) (Scheme 4). In analogy to what we found for the [Rh$_2$Cl(acac)] and [Rh$_2$(acac)$_2$] complexes, the symmetrical molecule **11** decomposes at rather low temperature (47 °C), while the less symmetrical species is thermally stable up to 176 °C. Attempts to obtain dirhodium compounds with a {Rh(μ-CR$_2$)$_2$(μ-Sb*i*Pr$_3$)Rh} framework and one or two chelating *hexafluorinated* acetylacetonates failed. A possible explanation is that owing to the presence of two CF$_3$ units the Lewis basicity of the anionic substrate is considerably reduced, and thus a substitution of the chloro ligands in the starting materials by acac-f$_6^-$ does not take place.

Reactions of the dinuclear chelate complexes with CO and tertiary phosphines: The lability of the {Rh(μ-Sb*i*Pr$_3$)Rh} bridge, already illustrated by the substitution reactions of **1a** and **1b** with CN*t*Bu und SbR$_3$ shown in Scheme 1, is also found for the bis(acetylacetonato)dirhodium compounds **7** and **8**. However, while the dichloro derivative **1a** reacts with carbon monoxide to give the presumably polymeric product **12**,[1, 5] upon treatment of **7** or **8** with CO in benzene at room temperature the triply-bridged dinuclear complexes **13** and **14** are exclusively formed (Scheme 5). The reactions of **7** with CN*t*Bu and SbEt$_3$ also lead to the replacement of the bridging Sb*i*Pr$_3$ unit and afford the dinuclear complexes **15** and **16** in nearly quantitative yields. In all cases (i.e., in the formation of **13**–**16**), the exchange of the stibane ligand occurs without any further rearrangement of the molecular core. Typical spectroscopic data of **13** and **14** are the CO stretching modes at 1842 and 1849 cm^{-1}, respectively, in the IR spectra and the signal for the μ-CO carbon atom at $\delta = 182.8$ (for both **13** and **14**) in the ^{13}C NMR spectra.

The result of the X-ray crystal structure analysis of **13** is shown in Figure 2. The asymmetric unit contains one half of the molecule, the second half being generated by C_2 symmetry. The axis of rotation passes through the atoms C19 and O3. The coordination geometry around the rhodium center Rh1 can be described as distorted square-pyramidal with the carbon atom C6 in the apical position. The deviation of the atoms C6A, C19, O1, O2, and Rh1 from the best plane is

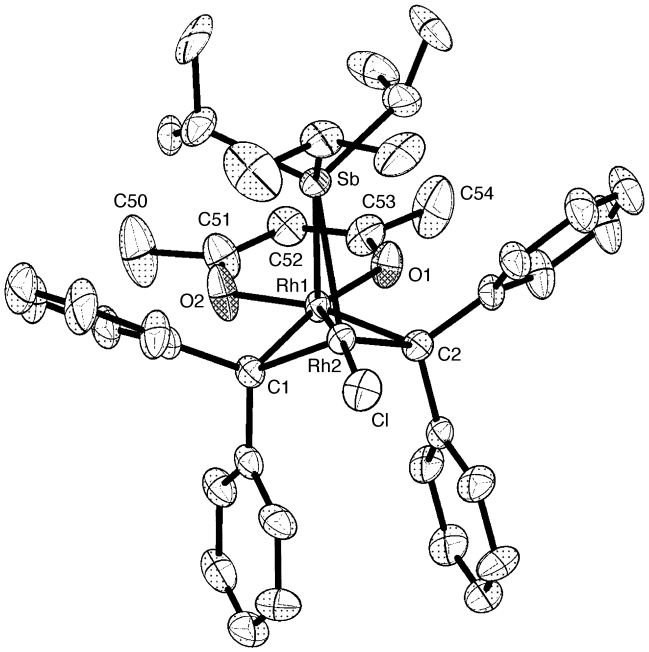
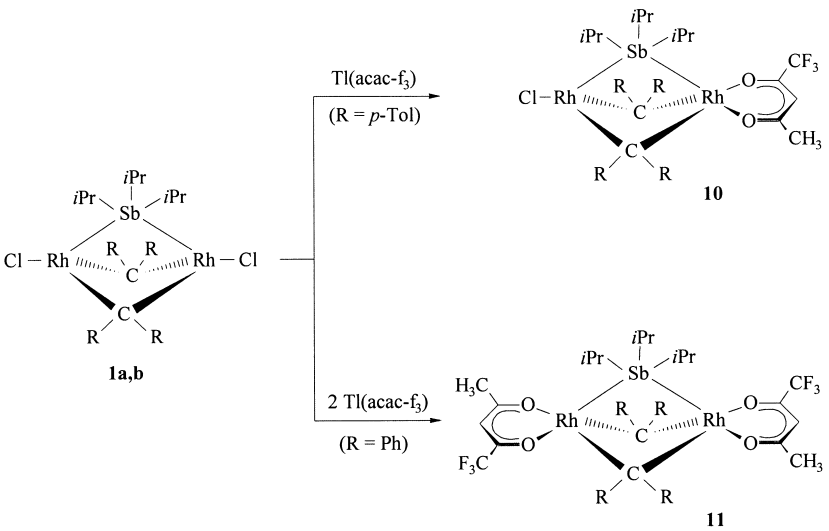


Figure 1. Molecular structure of **5**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh1–Rh2 2.6796(6), Rh1–Sb 2.498(1), Rh2–Sb 2.846(1), Rh1–C1 2.030(4), Rh1–C2 2.187(4), Rh2–C1 2.053(4), Rh2–C2 1.825(4), Rh1–O1 2.064(3), Rh1–O2 2.274(4), Rh2–Cl 2.483(1); Rh1-Sb-Rh2 59.77(2), Sb-Rh1-Rh2 66.57(2), Sb-Rh2-Rh1 53.66(2), Rh1-Rh2-Cl 171.55(3), Rh1-C1-Rh2 82.0(2), Rh1-C2-Rh2 83.3(2), C1-Rh1-C2 83.2(2), C1-Rh2-C2 92.3(2), C1-Rh1-O1 167.0(1), C2-Rh1-O2 165.9(1), O1-Rh1-O2 78.5(1).

−0.205(1) Å for C19, 0.100(1) Å for C6A, −0.188(1) Å for O2, 0.099(1) Å for O1, and 0.194(1) Å for Rh1. The molecule is highly symmetric and, in contrast to **5** (see Figure 1), also the two acetylacetonato ligands are symmetrically linked to the rhodium centers. The distance Rh1–Rh1A is quite short (2.4933(9) Å) and comparable both to that in **1a** (2.5349(5) Å)[1] and to that in the bis(diphenylcarbene) complexes $[Rh_2Cl_2(py)_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$ (2.51 Å)[4a] and $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$ (2.54 Å).[4b] The bond length Rh1–C19 in **13** is slightly shorter than the bond lengths between rhodium and the carbene carbon atoms C6 and C6A; this is in agreement with the data for the above-mentioned $\{Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)\}$ compounds.[4a,b]

The difference in the reactivity of **1a** and **7** toward bulky trialkylphosphanes is even more striking than toward CO. We already reported that treatment of **1a** with P*i*Pr$_3$, P*i*Pr$_2$Ph, P*i*PrPh$_2$, and PPh$_3$ led to to the stable mononuclear carbene complexes **17**–**20** by displacement of the stibane and cleavage of the bridging bonds.[1] An analogous behavior is observed for the bis(trifluoroacetato) derivative **4**, which reacts with four equivalents of P*i*Pr$_3$ to give *trans*-[Rh(κ^1-O_2CCF_3)(=CPh_2)(P*i*Pr$_3$)$_2$]. This square-planar rhodium(I) compound was recently prepared from **17** and CF_3CO_2Tl.[6] The reaction of the bis(acetylacetonate) **7** with an excess of P*i*Pr$_3$ is much more slow than that of **1a** with the same phosphane and affords, after four hours at 60 °C in benzene, the novel dinuclear complex **21** in 68% isolated yield (Scheme 6). P*i*Pr$_2$Ph, P*i*PrPh$_2$, and PPh$_3$ behave similarly toward **7** and gave, after reaction times of 8, 24, and 48 hours, respectively, the related compounds **22**–**24** in equally good yields. Following the same methodology, the bis(di-*p*-tolylcarbene) complex **25** is obtained from **8** and excess P*i*Pr$_3$. Compounds **21**–**25** are brown modestly air-sensitive solids, which are soluble in most common organic solvents and which have been characterized by elemental analysis and mass spectrometry.

The ^{1}H and ^{13}C NMR spectra of **21**–**25** display two sets of signals for the protons and carbon atoms of the OC(CH$_3$) moieties of the coordinated acetylacetonates pointing to an unsymmetrical environment around the central $\{Rh(\mu\text{-}CR_2)_2Rh\}$ core. This proposal has been confirmed by the X-ray crystal structure analysis of **21** (Figure 3). One of the chelating ligands has migrated from one metal center to the other and its former position is occupied by the triisopropylphosphane. The stibane ligand has been replaced, while the bridging diphenylcarbene units are maintained. The distances between the less-coordinated metal center Rh1 and the carbene carbon atoms C1 and C2 are 0.17 Å shorter than those between Rh2 and C1 and C2, and they differ only slightly to the Rh–C bond lengths in **1a** (2.003(1) and 2.007(3) Å). The distance Rh1–Rh2 of **21** is nearly the same as that in compound **5** (see Figure 1). In analogy to **5**, the acetylacetonato ligands are not coordinated in a symmetrical fashion and, therefore, in both six-membered chelate rings the Rh–O bond lengths differ by 0.08 to 0.10 Å. The bond axis Rh2-Rh1-P is not exactly linear; this is probably a consequence of the steric repulsion between the phenyl and the isopropyl groups of the carbene and phosphane ligands. We assume that the unsymmetrical structure of **21** is also maintained in solution, since



Scheme 4. Preparation of complexes **10** and **11**.

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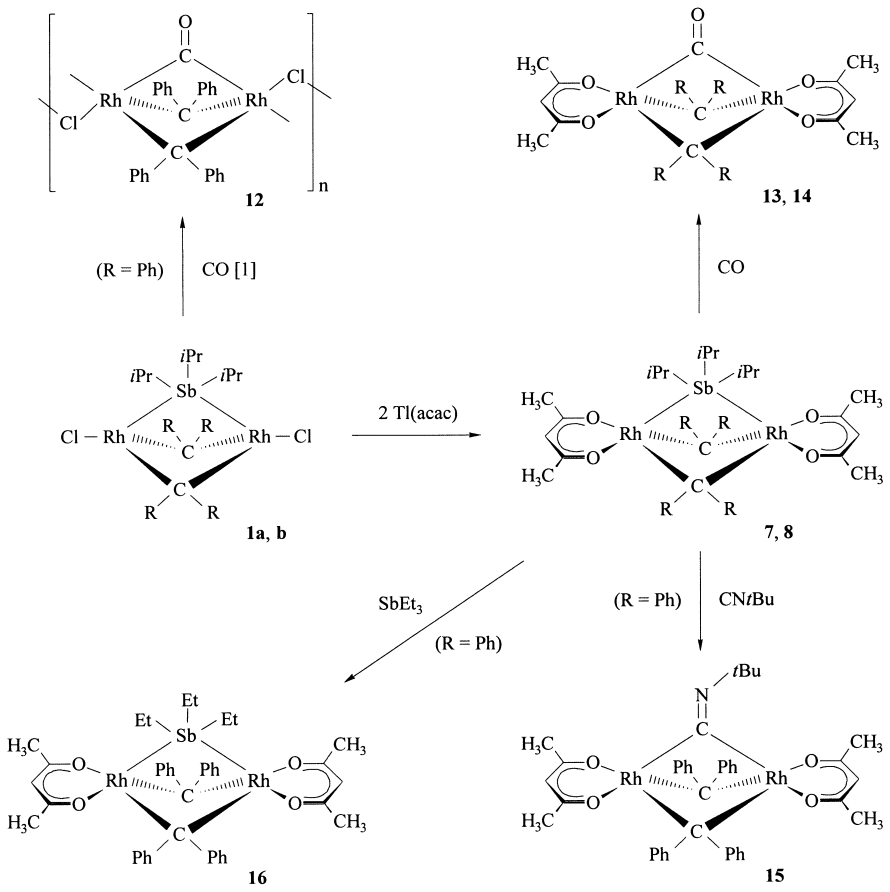


Scheme 5. Preparation of complexes **12**–**16** (**13**: R = Ph; **14**: R = *p*-Tol).

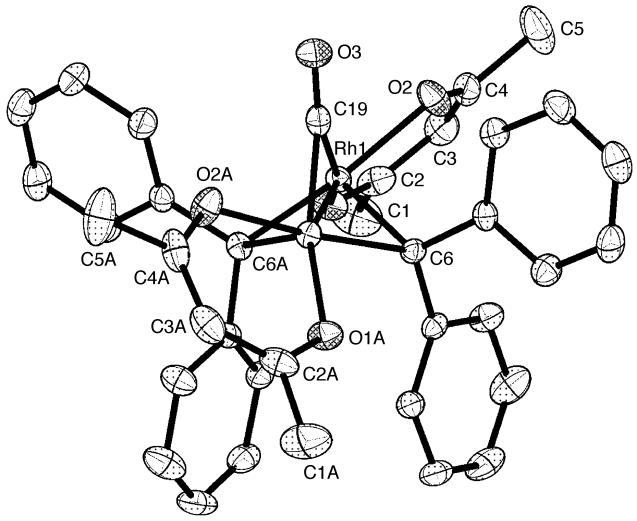
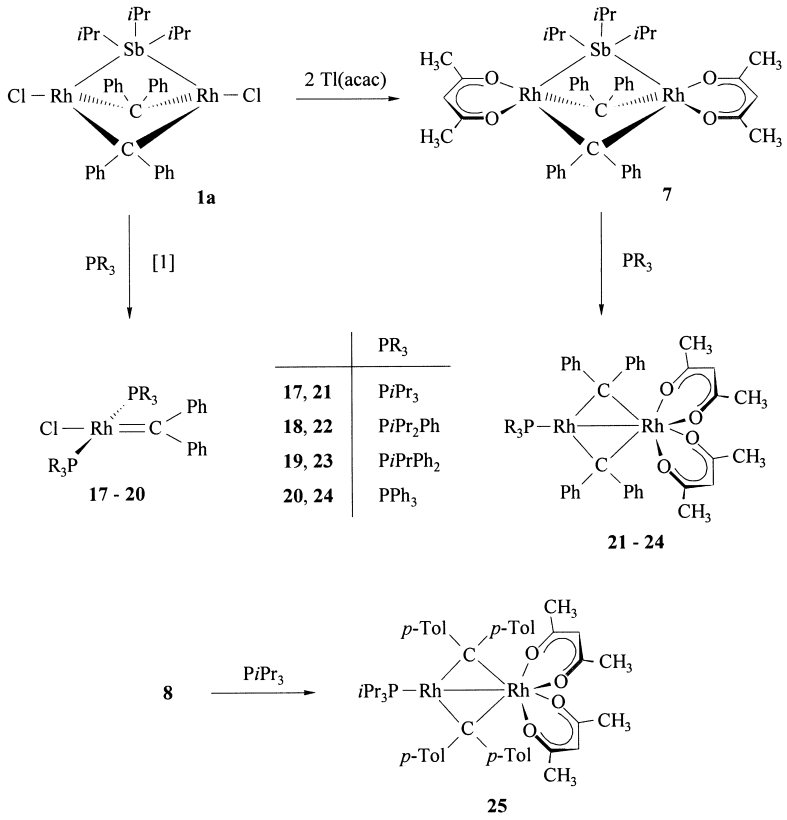


Figure 2. Molecular structure of **13**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh1–Rh1A 2.4933(9), Rh–C6 2.078(3), Rh–C6A 2.037(2), Rh–C19 1.956(3), Rh–O1 2.066(2), Rh–O2 2.109(2); Rh-C6-Rh1A 74.58(8), Rh-C19-Rh1A 79.2(2), C6-Rh-Rh1A 51.95(7), C6-Rh-C6A 90.7(1), C6-Rh-C19 83.06(9), C19-Rh-Rh1A 50.40(8), C6-Rh-O1 119.37(9), C6-Rh-O2 93.43(9), O1-Rh-O2 86.19(8).

the ^{31}P NMR spectrum displays a sharp doublet of doublets at $\delta = 40.5$ with a large ^{1}J(P,Rh) and a small ^{2}J(P,Rh) coupling constant of 257.7 and 5.9 Hz, respectively. An almost identical pattern is observed in the ^{31}P NMR spectra of **22**–**24** as well as in the spectrum of the bis(di-*p*-tolylcarbene) derivative **25**.

Mixed-valence dinuclear rhodium complexes with different σ-donor/π-acceptor ligands: The dirhodium compound **21**, which is thermally stable up to 75 °C, reacts smoothly at room temperature with a variety of Lewis bases. With an excess of terminal alkynes HC≡CR (R = CH_2OCH_3, Me, Ph) or $CH_3C{\equiv}CCO_2Et$ the triisopropylphosphane is displaced by one alkyne ligand and, after chromatographic workup and recrystallization from diethyl ether/hexane, the substitution products **26**–**29** are isolated as orange solids in good to excellent yields (Scheme 7). Similarly to the phosphane complexes **21**–**24**, the ^{1}H and ^{13}C NMR spectra of **26**–**29** also display two sets of resonances for the protons and carbon atoms of the chelated acetylacetonato groups indicating an unsymmetrical coordination environment around the {Rh(μ-CPh_2)$_2$Rh} core. This has been confirmed by the X-ray crystal structure analysis of **26**.[7] The Rh–Rh distance in **26** is approximately 0.03 Å shorter than in **21**, whereas both the Rh–C_{Ph} and Rh–O bond lengths differ only slightly to those of the phosphane derivative. The axis of the alkyne carbon atoms lies perpendicular to the RhC_2Rh plane with the CH_2OMe fragment bent away from the nearby rhodium center. We note that all attempts to rearrange the alkyne to an isomeric vinylidene ligand either by heating or photolyzing solutions of **26** or **27** in benzene failed.

The reaction of **21** with CN*t*Bu leads to the replacement of the phosphane ligand by *two* isocyanide molecules and affords the bis(isocyanide) compound **30** in 89 % yield. The red air-sensitive solid is readily soluble in dichloromethane and benzene, almost insoluble in pentane, and thermally stable up to 122 °C. The molecular structure of **30** has been determined crystallographically. As Figure 4 shows, the low-valent rhodium center Rh1 is coordinated in a considerably distorted square-planar fashion with a bond angle C70-Rh1-C80 of 91.41(18)° and bond angles C2-Rh1-C1, C70-Rh1-C2, and C1-Rh1-C80 that deviate significantly from the ideal 90° value. The distances between Rh1 and C1 and C2 are shorter than those between Rh2 and the carbene carbon atoms although the difference in the bond lengths in **30** is smaller than in the triisopropylphosphane derivative **21**. The coordination geometry around the higher-valent metal center Rh2 is distorted octahedral and quite similar to that found in **21**. Both



Scheme 6. Preparation of complexes **21** and **35**.

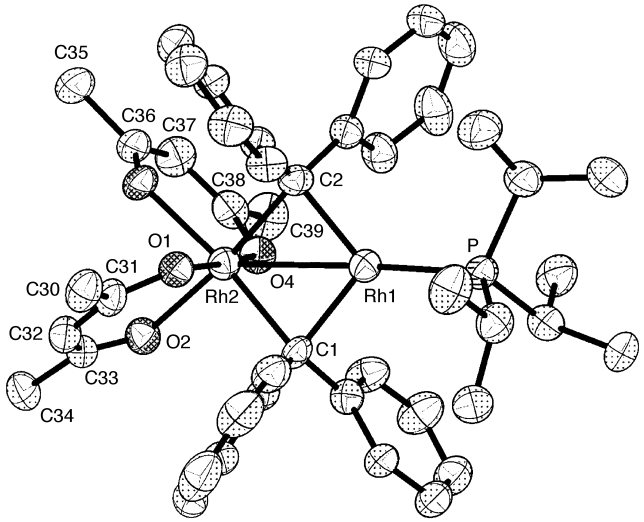


Figure 3. Molecular structure of **21**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh1–Rh2 2.6317(7), Rh1–P 2.332(2), Rh1–C1 1.982(6), Rh1–C2 1.982(5), Rh2–C1 2.158(5), Rh2–C2 2.153(6), Rh2–O1 2.008(4), Rh2–O2 2.114(4), Rh2–O3 2.115(4), Rh2–O4 2.037(4); Rh2-Rh1-P 169.91(4), Rh1-C1-Rh2 78.8(2), Rh1-C2-Rh2 78.9(2), P-Rh1-C1 122.4(2), P-Rh1-C2 125.3(2), C1-Rh1-C2 103.7(2), C1-Rh2-C2 92.6(2), O1-Rh2-O4 170.0(2), O2-Rh2-C2 173.1(2), O3-Rh2-C1 169.8(2).

acetylacetonates of **30** are coordinated unsymmetrically to Rh2, the difference in the Rh–O bond lengths being approximately 0.10 Å for each chelating ligand. The distance Rh1–Rh2 is 2.6082(8) Å and thus slightly shorter than in **5** and **21**.

An increase in the coordination number of the low-valent rhodium center also occurs if the phosphane ligand of the precursor molecule **21** is displaced by carbon monoxide. Upon passing a slow stream of CO through a solution of **21** in pentane, the dinuclear complex **31** (see Scheme 7) is formed in excellent yield. The presence of *three* carbonyl ligands (instead of *two* isocyanides in **30**) is confirmed by the elemental analysis and the mass spectrum. Moreover, the IR spectrum of **31** displays three CO stretching modes at 2056, 2016, and 1965 cm^{-1} in agreement with the proposed structure. In contrast to CO, the related ligand PF_3 reacts with **21** in pentane to give a mixture of products which could not be separated either by fractional crystallization or chromatographic techniques.

Conclusion

The present investigations have shown that the family of dinuclear rhodium complexes with bridging trialkylstibanes can be extended by replacing the terminal chlorides in the starting materials $[Rh_2Cl_2(\mu\text{-}CR_2)_2(\mu\text{-}SbiPr_3)]$ for chelating ligands such as trifluoroacetate or acetylacetonates. The new compounds **4**–**11** and **16** deserve particular interest not only insofar as they contain the still very unusual $\{Rh(\mu\text{-}SbR_3)Rh\}$ moiety as a building block, but, even more, as they are the precursors for a series of mixed-valence Rh^0–Rh^{II} complexes for which there is no precedence. These complexes generated by treatment of the stibane-bridged molecules with sterically demanding tertiary phosphanes or by subsequent reaction of the phosphane derivatives with alkynes, *tert*-butylisocyanide, and CO still contain two bridging diarylcarbene ligands, which probably stabilize the unsymmetrical coordination sphere around the two metal centers. It should be pointed out that dinuclear rhodium compounds with $\{Rh(\mu\text{-}CR_2)_2Rh\}$ as a molecular core were already known,[4, 5, 8, 9] but in none of these species the two rhodium atoms have a different oxidation state.

The mixed-valence complexes **21**–**31** with a d^9 (Rh^0) and a d^7 (Rh^{II}) metal center are diamagnetic and, therefore, it is reasonable to assume that these molecules contain a metal–metal single bond. The Rh–Rh distances found in **21** (2.6317(7) Å) and **30** (2.6082(8) Å) would be in agreement with this proposal. However, the surprising result is that these distances are not much different from those in **1a** (2.5349(5) Å),[1] **5** (2.6796(6) Å), **13** (2.4933(9) Å), and

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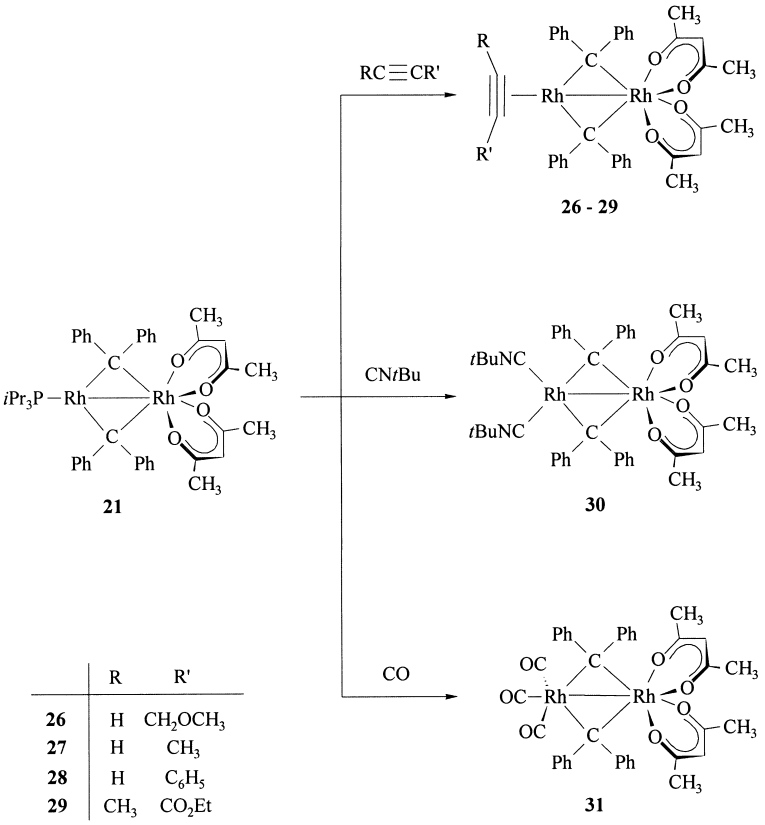

	R	R'
26	H	CH_2OCH_3
27	H	CH_3
28	H	C_6H_5
29	CH_3	CO_2Et

Scheme 7. Preparation of complexes **26** and **31**.

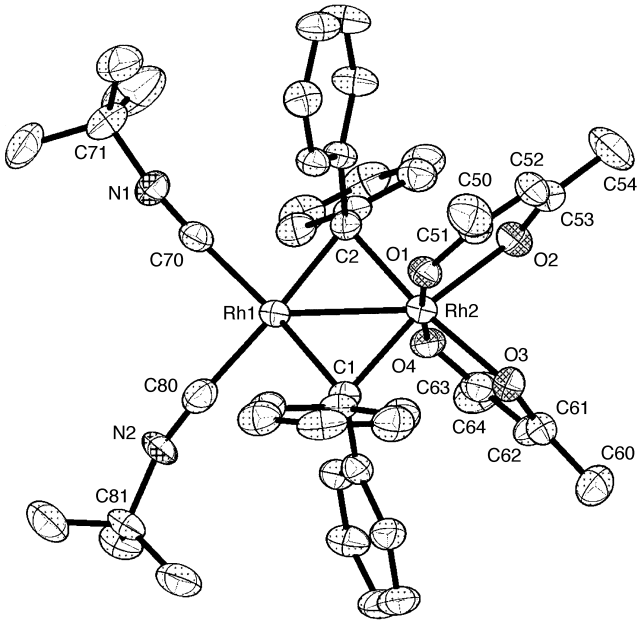

Figure 4. Molecular structure of **30**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh1–Rh2 2.6082(8), Rh1–C1 2.046(4), Rh1–C2 2.070(4), Rh2–C1 2.125(5), Rh2–C2 2.108(4), Rh1–C70 1.964(5), Rh1–C80 1.964(5), Rh2–O1 2.012(3), Rh2–O2 2.113(3), Rh2–O3 2.105(3), Rh2–O4 1.998(3); Rh1-C1-Rh2 77.39(14), Rh1-C2-Rh2 77.26(14), C1-Rh1-C2 104.63(17), C1-Rh2-C2 100.55(16), C1-Rh1-C70 166.67(17), C2-Rh1-C70 82.59(17), C1-Rh1-C80 84.33(18), C2-Rh1-C80 163.8(2), C70-Rh1-C80 91.41(18), C1-Rh2-O2 169.10(16), C2-Rh2-O3 172.53(13), O1-Rh2-O2 91.02(13), O1-Rh2-O4 174.78(12), O2-Rh2-O3 82.29(13), O2-Rh2-O4 84.07(13), O3-Rh2-O4 91.94(13).

$[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$ (2.54 Å),[4b] and in each of these complexes there are two d^8 (Rh^I) metal centers. Therefore, we conclude that the Rh–Rh distance determined in all the above-mentioned compounds is mainly dictated by the relative rigidity of the $\{Rh(\mu\text{-}CPh_2)_2Rh\}$ molecular core, independently whether this unit is tilted as in **1a**, **5**, **13**, and $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$ or planar as in **21** and **30**. In the mixed-valence Rh^0–Rh^{II} complexes $[(CO)Rh\{(PhO)_2PN(Et)\text{-}P(OPh)_2\}_2RhCl_2]$ and $[Rh_2(dfpma)_3X_2(L)]$ (dfpma = $CH_3N(PF_2)_2$; X = Cl, Br; L = dfpma, PF_3, PPh_3) reported by Haines[10] and Nocera,[11] the Rh–Rh distance is significantly longer than in **21** and **30**; this is probably due to the range of the bridging diphosphazane ligands.

However, the novel mixed-valence compounds described here are not only interesting from a structural point of view, but also with respect to their reactivity toward Lewis bases. With the P*i*Pr$_3$ derivative **21** as the starting material, the corresponding dinuclear monoalkyne, bis(isocyanide) and tricarbonyl complexes **26**–**31** have been obtained by ligand exchange. The composition of these compounds illustrates that the coordination sphere around the low-valent rhodium center can change and, depending on the size of the ligands, it is quite flexible. Current work in our group is primarily aimed to elucidate the electrochemistry of the Rh^0–Rh^{II} dimers with the hope to use these species both as electron reservoirs and as starting materials for oxidative addition reactions.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1a**, **1b**,[1] Tl(acac), and Tl(acac-f_3)[12] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC200, Bruker AMX400 and Bruker DSX400 instruments, IR spectra on a Bruker IFS25 FT-IR infrared spectrometer, and mass spectra on a Finnigan 90MAT instrument. Melting points were measured by differential thermal analysis (DTA) with a Thermoanalyzer Du Pont 9000. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broadened signal.

$[Rh_2(\kappa^2\text{-}O_2CCF_3)_2(\mu\text{-}CPh_2)_2(\mu\text{-}SbiPr_3)]$ (4): A solution of **1a** (95 mg, 0.11 mmol) in acetone (15 mL) was treated with CF_3CO_2Tl (89 mg, 0.28 mmol) and stirred for 1 h at room temperature. The solvent was removed in vacuo, and the residue was extracted three times with pentane (10 mL each). The combined extracts were concentrated to about 5 mL and then stored at 5 °C for 3 d. Dark red crystals precipitated, which were separated from the mother liquor, washed with small quantities of pentane (0 °C), and dried in vacuo. Yield 96 mg (86 %); m.p. 109 °C (decomp); IR (C_6H_6): $\tilde{\nu}$ = 1615 $(OCO)_{sym}$, 1440 cm^{-1} $(OCO)_{asym}$; ^1H NMR (400 MHz,

C_6D_6): $\delta = 8.01$ (m, 4H; *ortho*-H of C_6H_5), 7.35 (m, 4H; *ortho*-H of C_6H_5), 6.86–6.52 (m, 12H; *meta*- and *para*-H of C_6H_5), 1.25 (sept, J(H,H) = 6.8 Hz, 3H; SbC*H*CH_3), 0.98 (d, J(H,H) = 6.8 Hz, 18H; SbCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 188.2$ (t, J(Rh,C) = 25.4 Hz; *C*Ph_2), 168.2 (q, J(C,F) = 38.7 Hz; CF_3CO_2), 155.6, 153.8 (both s; *ipso*-C of C_6H_5), 128.4, 127.9, 127.5, 124.2, 123.4, 123.2 (all s; C_6H_5), 25.3 (s; SbC*H*CH_3), 21.7 (s; SbCH*C*H$_3$); ^{19}F NMR (376.4 MHz, C_6D_6,): $\delta = -74.3$ (s); elemental analysis calcd (%) for $C_{39}H_{41}F_6O_4Rh_2Sb$ (1015.3): C 46.14, H 4.07; found: C 46.29, H 4.05.

[Rh$_2$Cl(κ^2-acac)(μ-CPh$_2$)$_2$(μ-Sb*i*Pr$_3$)] (5): A solution of **1a** (78 mg, 0.09 mmol) in acetone (15 mL) was treated at 0 °C with Tl(acac) (27 mg, 0.09 mmol) and after warming to room temperature stirred for 30 min. The solvent was removed in vacuo, and the residue was extracted three times with pentane (10 mL each). The combined extracts were concentrated to about 2 mL, and the solution was subjected to chromatography on Al_2O_3 (neutral, activity grade V). With pentane, an off-white fraction was eluted which was withdrawn. Subsequent elution with benzene afforded a brown-red fraction, which was brought to dryness in vacuo. After recrystallization of the residue from acetone/diethyl ether (1:1; 10 mL) at −20 °C brown crystals were isolated, which were washed with small quantities of pentane (0 °C) and dried in vacuo. Yield 61 mg (73%); m.p. 144 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1584$, 1519 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.29$, 7.45 (both m, 4H each; *ortho*-H of C_6H_5), 7.00 (m, 4H; *meta*-H of C_6H_5), 6.82 (m, 2H; *para*-H of C_6H_5), 6.63 (m, 4H; *meta*-H of C_6H_5), 6.57 (m, 2H; *para*-H of C_6H_5), 5.57 (s, 1H; CH of acac), 1.99 (s, 6H; CH_3 of acac), 1.63 (sept, J(H,H) = 7.4 Hz, 3H; SbC*H*CH_3), 0.99 (d, J(H,H) = 7.4 Hz, 18H; SbCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 188.7$ (s; CO of acac), 177.3 (m; *C*Ph_2), 156.5, 155.0 (both s; *ipso*-C of C_6H_5), 127.5, 127.2, 126.7, 126.1, 125.2, 125.0 (all s; C_6H_5), 101.3 (s; CH of acac), 28.3 (s; CH_3 of acac), 24.8 (s; Sb*C*HCH$_3$), 21.4 (s; SbCH*C*H$_3$); elemental analysis calcd (%) for $C_{40}H_{48}ClO_2Rh_2Sb$ (923.8): C 52.00, H 5.24; found: C 51.83, H 5.07.

[Rh$_2$Cl(κ^2-acac){μ-C(*p*-Tol)$_2$}$_2$(μ-Sb*i*Pr$_3$)] (6): This compound was prepared as described for **5**, with **1b** (74 mg, 0.08 mmol) and Tl(acac) (25 mg, 0.08 mmol) as starting materials. Brown solid; yield 70 mg (89%); m.p. 130 °C; IR (C_6H_6): $\tilde{\nu} = 1583$, 1520 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, C_6D_6,): $\delta = 8.21$, 7.29 (both d, J(H,H) = 7.9 Hz, 4H each; *ortho*-H of *p*-Tol), 6.82, 6.42 (both d, J(H,H) = 7.9 Hz, 4H each; *meta*-H of *p*-Tol), 5.62 (s, 1H; CH of acac), 2.09 (s, 6H; CH_3 of *p*-Tol), 2.00 (s, 6H; CH_3 of acac) 1.86 (s, 6H; CH_3 of *p*-Tol), 1.72 (sept, J(H,H) = 7.3 Hz, 3H; SbC*H*CH_3), 1.04 (d, J(H,H) = 7.3 Hz, 18H; SbCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 188.6$ (s; CO of acac), 177.7 (m; *C*Ph_2), 153.9, 152.6 (both s; *ipso*-C of *p*-Tol), 137.2, 135.1 (both s; *para*-C of *p*-Tol), 129.0, 126.7, 125.3, 123.8 (all s; *ortho*- and *meta*-C of *p*-Tol), 101.2 (s; CH of acac), 28.4 (s; CH_3 of acac), 24.5 (s; Sb*C*HCH$_3$), 21.5 (s; CH_3 of *p*-Tol), 21.1 (s; SbCH*C*H$_3$); elemental analysis calcd (%) for $C_{44}H_{56}ClO_2Rh_2Sb$ (979.9): C 53.93, H 5.76; found: C 54.33, H 5.53.

[Rh$_2$(κ^2-acac)$_2$(μ-CPh$_2$)$_2$(μ-Sb*i*Pr$_3$)] (7): A solution of **1a** (84 mg, 0.10 mmol) in acetone (15 mL) was treated with Tl(acac) (73 mg, 0.24 mmol) and stirred for 2 h at room temperature. The solvent was removed in vacuo, and the residue was extracted three times with pentane (10 mL each). The combined extracts were concentrated to ca. 3 mL, and the solution was subjected to chromatography on Al_2O_3 (neutral, activity grade V). With pentane, an off-white fraction was eluted which was withdrawn. Elution with benzene afforded a brown-red fraction, which was brought to dryness in vacuo. The residue was dissolved in pentane (8 mL), and the solution stored at −78 °C for 24 h. Brown crystals precipitated, which were washed with small quantities of pentane (0 °C) and dried in vacuo. Yield 85 mg (86%); m.p. 55 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1583$, 1515 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.34$, 7.68 (both m, 8H; *ortho*-H of C_6H_5), 7.35–6.97 (m, 8H; *meta*-H of C_6H_5), 6.72–6.58 (m, 4H; *para*-H of C_6H_5), 5.58 (s, 2H; CH of acac), 2.00 (s, 12H; CH_3 of acac), 1.91 (sept, J(H,H) = 7.4 Hz, 3H; SbC*H*CH_3), 0.96 (d, J(H,H) = 7.4 Hz, 18H; SbCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 188.4$ (s; CO of acac), 176.8 (t, J(Rh,C) = 20.8 Hz; *C*Ph_2), 160.5, 156.0 (both s; *ipso*-C of C_6H_5), 138.8, 129.7, 129.1, 126.8, 126.1, 126.0 (all s; C_6H_5), 100.6 (s; CH of acac), 28.6 (s; CH_3 of acac), 25.6 (s; Sb*C*HCH$_3$), 21.3 (s; SbCH*C*H$_3$); elemental analysis calcd (%) for $C_{45}H_{55}O_4Rh_2Sb$ (987.5): C 54.73, H 5.61, Rh 20.84; found: C 54.63, H 5.50, Rh 19.96.

[Rh$_2$(κ^2-acac)$_2${μ-C(*p*-Tol)$_2$}$_2$(μ-Sb*i*Pr$_3$)] (8): This compound was prepared as described for **7**, with **1b** (74 mg, 0.08 mmol) and Tl(acac) (49 mg, 0.16 mmol) as starting materials. Brown solid; yield 68 mg (84%); m.p. 62 °C (decomp); IR (KBr): $\tilde{\nu} = 1583$, 1518 cm^{-1} (CO_{acac}); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 8.28$ (d, J(H,H) = 8.0 Hz, 4H; *ortho*-H of *p*-Tol), 7.25 (m, 8H; *ortho*- and *meta*-H of *p*-Tol), 6.48 (d, J(H,H) = 8.0 Hz, 4H; *meta*-H of *p*-Tol), 5.61 (s, 2H; CH of acac), 2.11 (s, 6H; CH_3 of *p*-Tol), 2.04 (s, 12H; CH_3 of acac), 1.95 (s, 6H; CH_3 of *p*-Tol), 1.94 (sept, J(H,H) = 7.3 Hz, 3H; SbC*H*CH_3), 1.15 (d, J(H,H) = 7.3 Hz, 18H; SbCHC*H*$_3$); elemental analysis calcd (%) for $C_{49}H_{63}O_4Rh_2Sb$ (1043.6): C 56.39, H 6.09; found: C 55.96, H 5.89.

[Rh$_2$Cl(κ^2-acac)(μ-CPh$_2$)$_2$(μ-SbEt$_3$)] (9): A solution of **5** (100 mg, 0.11 mmol) in benzene (10 mL) was treated with $SbEt_3$ (26 μL, 0.16 mmol) and stirred for 1 h at room temperature. The solvent was removed in vacuo, and the remaining pale-brown solid was washed twice with small quantities of pentane (0 °C) and dried in vacuo. Yield 90 mg (94%); m.p. 176 °C (decomp); IR (KBr): $\tilde{\nu} = 1578$, 1517 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.23$, 7.46 (both m, 4H each; *ortho*-H of C_6H_5), 7.01 (m, 4H; *meta*-H of C_6H_5), 6.88 (m, 2H; *para*-H of C_6H_5), 6.63 (m, 6H; *meta*-H and *para*-H of C_6H_5), 5.44 (s, 1H; CH of acac), 1.92 (s, 6H; CH_3 of acac), 1.09 (q, J(H,H) = 7.9 Hz, 6H; SbCH_2CH$_3$), 0.74 (t, J(H,H) = 7.9 Hz, 9H; SbCH$_2$C*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 188.8$ (s; CO of acac), 178.4 (dd, J(Rh,C) = 25.4, 19.6 Hz; *C*Ph_2), 156.5, 153.9 (both s; *ipso*-C of C_6H_5), 127.6, 127.2, 126.6, 126.5, 126.2, 124.8 (all s; C_6H_5), 101.0 (d, J(Rh,C) = 1.5 Hz; CH of acac), 28.1 (s; CH_3 of acac), 10.8 (s; Sb*C*H$_2$CH$_3$), 10.2 (s; SbCH$_2$*C*H$_3$); elemental analysis calcd (%) for $C_{37}H_{42}ClO_2Rh_2Sb$ (881.8): C 50.40, H 4.80; found: C 50.15, H 4.89.

[Rh$_2$Cl(κ^2-acac-f$_3$){μ-C(*p*-Tol)$_2$}$_2$(μ-Sb*i*Pr$_3$)] (10): A solution of **1b** (125 mg, 0.15 mmol) in acetone (15 mL) was treated at 0 °C with Tl(acac-f$_3$) (41 mg, 0.15 mmol) and, after warming to room temperature, was stirred for 30 min. The solvent was removed in vacuo, and the residue was extracted three times with pentane (10 mL each). The combined extracts were concentrated to about 15 mL, and the solution was stored at −78 °C for 12 h. Brown crystals precipitated, which were washed with small quantities of pentane (0 °C) and dried in vacuo. Yield 104 mg (67%); m.p. 176 °C (decomp); IR (C_6H_6): $\tilde{\nu} = 1615$ cm^{-1} ($CO_{acac\text{-}f3}$); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 8.13$, 7.23 (both d, J(H,H) = 8.0 Hz, 4H each; *ortho*-H of *p*-Tol), 6.80, 6.39 (both d, J(H,H) = 8.0 Hz, 4H each; *meta*-H of *p*-Tol), 5.05 (s, 1H; CH of acac-f$_3$), 1.93 (s, 6H; CH_3 of *p*-Tol), 1.86 (s, 3H; CH_3 of acac-f$_3$), 1.82 (s, 6H; CH_3 of *p*-Tol), 1.73 (sept, J(H,H) = 6.9 Hz, 3H; SbC*H*CH_3), 1.05 (d, J(H,H) = 6.9 Hz, 18H; SbCHC*H*$_3$); ^{19}F NMR (188.3 MHz, C_6D_6,): $\delta = -75.2$ (s); elemental analysis calcd (%) for $C_{44}H_{53}ClF_3O_2Rh_2Sb$ (1033.9): C 51.11, H 5.17; found: C 50.83, H 4.76.

[Rh$_2$(κ^2-acac-f$_3$)$_2$(μ-CPh$_2$)$_2$(μ-Sb*i*Pr$_3$)] (11): This compound was prepared as described for **10**, with **1a** (80 mg, 0.09 mmol) and Tl(acac-f$_3$) (71 mg, 0.23 mmol) as starting materials. The reaction was carried out at room temperature; reaction time 2 h. Brown solid; yield: 76 mg (77%); m.p. 47 °C (decomp); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 8.18$ (m, 4H; *ortho*-H of C_6H_5), 7.13–6.99 (m, 8H; *ortho*- and *meta*-H of C_6H_5), 6.69–6.55 (m, 8H; *meta*- and *para*-H of C_6H_5), 6.00 (s, 2H; CH of acac-f$_3$), 1.87 (sept, J(H,H) = 7.3 Hz, 3H; SbC*H*CH_3), 1.79 (s, 6H; CH_3 of acac), 0.99 (d, J(H,H) = 7.3 Hz, 18H; SbCHC*H*$_3$); ^{19}F NMR (188.3 MHz, C_6D_6): $\delta = -75.0$ (s); elemental analysis calcd (%) for $C_{45}H_{49}F_6O_4Rh_2Sb$ (1095.4): C 49.34, H 4.51; found: C 49.79, H 4.26.

[Rh$_2$(κ^2-acac)$_2${μ-CPh$_2$}$_2$(μ-CO)] (13): A slow stream of CO was passed through a solution of **7** (85 mg, 0.10 mmol) in benzene (10 mL) for 15 s at room temperature. After the solution was stirred for 30 min, the solvent was removed in vacuo and the residue recrystallized from dichloromethane/pentane (1:10; 15 mL) at 5 °C. Red crystals precipitated which were separated from the mother liquor, washed with small quantities of pentane (0 °C), and dried. Yield 59 mg (89%); m.p. 48 °C (decomp); IR (KBr): $\tilde{\nu} = 1842$ (CO), 1583, 1521 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.60$, 7.12 (both m, 4H each; *ortho*-H of C_6H_5), 7.00, 6.77 (both m, 12H; *meta*-H and *para*-H of C_6H_5), 5.36 (s, 2H; CH of acac), 1.76 (s, 12H; CH_3 of acac); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 189.5$ (s; CO of acac), 182.8 (m; μ-CO), 154.4, 154.3 (both s; *ipso*-C of C_6H_5), 129.9, 128.5, 127.6, 127.1, 126.1, 126.0 (all s; C_6H_5), 101.5 (s; CH of acac), 27.9 (s; CH_3 of acac), signal for *C*Ph_2 could not be exactly located; elemental analysis calcd (%) for $C_{37}H_{34}O_5Rh_2$ (764.5): C 58.13, H 4.48; found: C 57.87, H 4.45.

[Rh$_2$(κ^2-acac)$_2${μ-C(*p*-Tol)$_2$}$_2$(μ-CO)] (14): This compound was prepared as described for **13**, with **8** (70 mg, 0.08 mmol) and CO as starting materials. Red solid; yield 55 mg (86%); m.p. 58 °C (decomp); IR (KBr): $\tilde{\nu} = 1849$ (CO), 1579, 1522 cm^{-1} (CO_{acac}); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.62$, 7.07

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(both d, J(H,H) = 8.1 Hz, 4H each; *ortho*-H of *p*-Tol), 6.86, 6.58 (both d, J(H,H) = 8.1 Hz, 4H each; *meta*-H of *p*-Tol), 5.38 (s, 2H; CH of acac), 2.05, 1.94 (both s, 6H each; CH_3 of *p*-Tol), 1.79 (s, 12H; CH_3 of acac); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 189.4 (s; CO of acac), 182.8 (t, J(Rh,C) = 19.3 Hz; μ-CO), 152.1, 151.9 (both s; *ipso*-C of *p*-Tol), 137.8, 135.4 (both s; *para*-C of *p*-Tol), 129.1, 128.7, 128.4, 125.9 (all s; *p*-Tol), 101.3 (s; CH of acac), 28.0 (s; CH_3 of acac), 21.2 (s; CH_3 of *p*-Tol), signal for $C(p\text{-Tol})_2$ could not be exactly located; elemental analysis calcd (%) for $C_{41}H_{42}O_5Rh_2$ (820.6): C 60.01, H 5.16; found: C 59.73, H 4.87.

[Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-CN*t*Bu)] (15): A solution of **7** (83 mg, 0.08 mmol) in pentane (40 mL) was treated dropwise with CN*t*Bu (10 µL, 0.08 mmol) at −50 °C. After warming to room temperature, the solution was stirred for 45 min. The solvent was removed in vacuo, and the residue recrystallized from pentane (5 mL) at −78 °C. Red crystals precipitated, which were separated from the mother liquor and dried in vacuo. Yield 61 mg (89 %); m.p. 166 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.70, 7.17 (both m, 8H; *ortho*-H of C_6H_5), 7.07, 6.78 (both m, 12H; *meta*- and *para*-H of C_6H_5), 5.42 (s, 2H; CH of acac), 1.79 (s, 12H; CH_3 of acac), 1.16 (s, 9H; CH_3 of CN*t*Bu); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 188.9 (s; CO of acac), 177.1 (t, J(Rh,C) = 20.9 Hz; CPh_2), 150.0, 149.9 (both s; *ipso*-C of C_6H_5), 129.8, 126.9, 126.8, 126.7, 126.2, 125.6 (all s; C_6H_5), 101.0 (s; CH of acac), 60.8 (s; $C(CH_3)_3$), 30.8 (s; $C(CH_3)_3$), 28.1 (s; CH_3 of acac), signal for *C*N*t*Bu could not be exactly located; elemental analysis calcd (%) for $C_{41}H_{43}NO_4Rh_2$ (819.6): C 60.08, H 5.29, N 1.71; found: C 60.37, H 5.16, N 1.80.

[Rh_2(κ^2-acac)$_2$(μ-CPh_2)$_2$(μ-$SbEt_3$)] (16): This compound was prepared as described for **9**, with **7** (165 mg, 0.17 mmol) and $SbEt_3$ (40 µL, 0.25 mmol) as starting materials: Pale brown solid; yield 157 mg (99 %); m.p. 116 °C (decomp); MS (FAB, 2-nitrophenyloctylether): *m*/*z*: 944 $[M]^+$, 736 $[M - SbEt_3]^+$, 637 $[M - SbEt_3 - acac]^+$; IR (C_6H_6): $\tilde{\nu}$ = 1580, 1520 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, C_6D_6): δ = 8.25, 7.25 (both m, 8H; *ortho*-H of C_6H_5), 7.18 (m, 4H; *meta*-H of C_6H_5), 7.06 (m, 2H; *para*-H of C_6H_5), 6.72 (m, 4H; *meta*-H of C_6H_5), 6.64 (m, 2H; *para*-H of C_6H_5), 5.43 (s, 2H; CH of acac), 1.95 (s, 12H; CH_3 of acac), 1.24 (q, J(H,H) = 7.9 Hz, 6H; $SbCH_2CH_3$), 0.71 (t, J(H,H) = 7.9 Hz, 9H; $SbCH_2CH_3$); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 188.4 (s; CO of acac), 177.6 (t, J(Rh,C) = 20.0 Hz; CPh_2), 156.3, 156.2 (both s; *ipso*-C of C_6H_5), 129.3, 126.8, 126.3, 126.2, 125.7, 125.4 (all s; C_6H_5), 100.2 (s; CH of acac), 28.3 (s; CH_3 of acac), 12.3 (s; $SbCH_2CH_3$), 10.4 (s; $SbCH_2CH_3$); elemental analysis calcd (%) for $C_{42}H_{49}O_4Rh_2Sb$ (945.4): C 53.36, H 5.22; found: C 53.32, H 5.24.

[(κ^2-acac)$_2$Rh(μ-CPh_2)$_2$Rh(P*i*Pr$_3$)] (21): A solution of **7** (105 mg, 0.11 mmol) in benzene (20 mL) was treated with P*i*Pr$_3$ (105 µL, 0.55 mmol) and stirred for 4 h at 60 °C. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolved in pentane (3 mL), and the solution was subjected to chromatography on Al_2O_3 (neutral, activity grade V). With pentane, an off-white fraction was eluted which was withdrawn. Elution with benzene afforded a brown fraction, which was brought to dryness in vacuo. Recrystallization of the residue from pentane (15 mL) at 5 °C gave brown crystals, which were separated from the mother liquor and dried in vacuo. Yield 67 mg (68 %); m.p. 75 °C (decomp); MS (FAB, 2-nitrophenyloctylether): *m*/*z*: 896 $[M]^+$, 797 $[M - acac]^+$, 637 $[M - PiPr_3 - acac]^+$; ^{1}H NMR (400 MHz, C_6D_6): δ = 8.32, 7.86–7.76, 7.35–7.24, 6.87 (all m, 20H; C_6H_5), 4.86 (s, 2H; CH of acac), 1.90 (m, 3H; PC*H*CH_3), 1.84, 1.42 (both s, 6H each; CH_3 of acac), 0.88–0.78 (m, 18H; PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6,): δ = 186.4, 183.8 (both s; CO of acac), 160.5 (m; CPh_2), 151.1, 148.1 (both s; *ipso*-C of C_6H_5), 132.0, 129.5, 129.1, 128.7, 127.1, 126.5, 125.8, 125.4 (all s; C_6H_5), 98.7 (s; CH of acac), 27.7, 26.7 (both s; CH_3 of acac), 25.4 (m; P*C*HCH_3), 22.5 (m; PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): δ = 40.5 (dd, ^1J(P,Rh) = 257.7, ^2J(P,Rh) = 5.9 Hz); elemental analysis calcd (%) for $C_{45}H_{55}O_4PRh_2$ (896.7): C 60.28, H 6.18, Rh 22.95; found: C 60.51, H 5.73, Rh 23.68.

[(κ^2-acac)$_2$Rh(μ-CPh_2)$_2$Rh(P*i*Pr$_2$Ph)] (22): A solution of **7** (100 mg, 0.11 mmol) in benzene (20 mL) was treated with P*i*Pr$_2$Ph (106 µL, 0.55 mmol) and stirred for 8 h at 60 °C. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolved in diethyl ether/pentane (1:5; 10 mL) and the solution was subjected to chromatography on Al_2O_3 (neutral, activity grade V). With pentane, an off-white fraction was eluted which was withdrawn. Elution with benzene afforded a brown fraction, which was brought to dryness in vacuo. Recrystallization of the residue from diethyl ether/pentane (1:5; 10 mL) at 5 °C led to the formation of brown crystals, which were separated from the mother liquor and dried in vacuo. Yield 82 mg (79 %); m.p. 52 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): δ = 8.16, 7.78, 7.69, 7.34, 7.23–6.97, 6.84 (all m, 25H; C_6H_5), 4.86 (s, 2H; CH of acac), 2.16 (m, 2H; PC*H*CH_3), 1.84, 1.42 (both s, 6H each; CH_3 of acac), 1.14, 0.92, 0.73, 0.46 (all dd, J(P,H) = 15.8, J(H,H) = 7.1 Hz, 3H each; PCHC*H*$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): δ = 37.7 (dd, ^1J(P,Rh) = 267.1, ^2J(P,Rh) = 5.9 Hz); elemental analysis calcd (%) for $C_{48}H_{53}O_4PRh_2$ (930.7): C 61.94, H 5.74; found: C 62.32, H 6.03.

[(κ^2-acac)$_2$Rh(μ-CPh_2)$_2$Rh(P*i*PrPh$_2$)] (23): A solution of **7** (98 mg, 0.10 mmol) in benzene (20 mL) was treated with P*i*PrPh$_2$ (114 mg, 0.50 mmol) and stirred for 24 h at 60 °C. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolved in diethyl ether/pentane (1:3; 10 mL), and the solution was worked up as described for **22**. Brown solid; yield 72 mg (76 %); m.p. 100 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): δ = 8.03, 7.79, 7.52, 7.34, 7.23–6.94, 6.76 (all m, 30H; C_6H_5), 4.86 (s, 2H; CH of acac), 2.13 (m, 1H; PC*H*CH_3), 1.82, 1.40 (both s, 6H each; CH_3 of acac), 0.66, 0.24 (both dd, J(P,H) = 14.6, J(H,H) = 7.0 Hz, 3H each; PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 186.5, 184.0 (both s; CO of acac), 149.6, 146.5 (both s; *ipso*-C of C_6H_5), 135.0 (d, J(P,C) = 12.2 Hz; *ipso*-C of PC_6H_5), 133.9 (d, J(P,C) = 10.2 Hz; *ortho*-C of PC_6H_5), 130.3 (d, J(P,C) = 3.1 Hz; *meta*-C of PC_6H_5), 129.6, 129.2, 128.9, 127.4, 126.8, 126.0, 125.5 (all s; *para*-C of PC_6H_5 and *ortho*-, *meta*- and *para*-C of C_6H_5), 98.9 (s; CH of acac), 27.7, 26.7 (both s; CH_3 of acac), 29.3 (m; P*C*HCH$_3$), 18.5 (s; PCH*C*H$_3$), signal for *C*Ph$_2$ could not be exactly located; ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.3 (dd, ^1J(P,Rh) = 272.1, ^2J(P,Rh) = 5.4 Hz); elemental analysis calcd (%) for $C_{51}H_{51}O_4PRh_2$ (964.6): C 63.49, H 5.33; found: C 64.39, H 5.03.

[(κ^2-acac)$_2$Rh(μ-CPh_2)$_2$Rh(PPh_3)] (24): A solution of **7** (119 mg, 0.12 mmol) in benzene (20 mL) was treated with PPh_3 (157 mg, 0.60 mmol) and stirred for 48 h at 60 °C. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolved in diethyl ether/pentane (2:1; 10 mL) and the solution was worked up as described for **22**. Brown solid; yield 72 mg (76 %); m.p. 98 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): δ = 8.03, 7.79 (both m, 4H each; *ortho*-H of C_6H_5), 7.26, 7.04–6.87, 6.71 (all m, 27H; PC_6H_5 and *meta*- and *para*-H of C_6H_5), 4.83 (s, 2H; CH of acac), 1.86, 1.42 (both s, 6H each; CH_3 of acac); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 186.4, 184.1 (both s; CO of acac), 148.5, 146.3 (both s; *ipso*-C of C_6H_5), 134.1 (d, J(C,P) = 12.2 Hz; *ipso*-C of PC_6H_5), 131.1 (d, J(C,P) = 3.1 Hz; *meta*-C of PC_6H_5), 128.3 (d, J(PC) = 4.1 Hz; *ortho*-C of PC_6H_5), 127.0, 126.6, 126.2, 125.3 (all s; *para*-C of PC_6H_5 and *ortho*-, *meta*- and *para*-C of C_6H_5), 98.6 (s; CH of acac), 27.8, 27.0 (both s; CH_3 of acac), signal for *C*Ph$_2$ could not be exactly located; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 33.9 (dd, ^1J(P,Rh) = 274.7, ^2J(P,Rh) = 6.8 Hz); elemental analysis calcd (%) for $C_{54}H_{49}O_4PRh_2$ (998.7): C 64.94, H 4.95; found: C 64.49, H 5.36.

[(κ^2-acac)$_2$Rh{μ-C(*p*-Tol)$_2$}Rh(P*i*Pr$_3$)] (25): This compound was prepared as described for **21**, with **8** (104 mg, 0.10 mmol) and P*i*Pr$_3$ (95 µL, 0.50 mmol) as starting materials. Brown solid; yield 70 mg (74 %); m.p. 64 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): δ = 8.24, 7.81 (both d, J(H,H) = 8.2 Hz, 4H each; *ortho*-H of *p*-Tol), 7.12, 6.75 (both d, J(H,H) = 8.2 Hz, 4H each; *meta*-H of *p*-Tol), 4.89 (s, 2H; CH of acac), 2.20 (s, 6H; CH_3 of *p*-Tol), 1.93 (m, 3H; PC*H*CH_3), 1.89 (s, 6H; CH_3 of *p*-Tol), 1.87, 1.48 (both s, 6H each; CH_3 of acac), 0.92–0.83 (m, 18H; PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 186.2, 183.6 (both s; CO of acac), 148.0, 145.3 (both s; *ipso*-C of *p*-Tol), 135.0, 134.7 (both s; *para*-C of *p*-Tol), 131.4, 129.6, 128.8, 127.3 (all s; *p*-Tol), 98.7 (s; CH of acac), 27.8, 26.7 (both s; CH_3 of acac), 25.4 (m; P*C*HCH$_3$), 21.5, 21.4 (both s; CH_3 of *p*-Tol), 20.5 (m; PCH*C*H$_3$), signal for *C*Ph$_2$ could not be exactly located; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 42.3 (dd, ^1J(P,Rh) = 259.4, ^2J(P,Rh) = 6.8 Hz); elemental analysis calcd (%) for $C_{49}H_{63}O_4PRh_2$ (952.8): C 61.77, H 6.66; found: C 62.13, H 6.45.

[(κ^2-acac)$_2$Rh(μ-CPh_2)$_2$Rh(η^2-HC≡CCH_2OCH_3)] (26): A solution of **21** (312 mg, 0.28 mmol) in diethyl ether (20 mL) was treated with HC≡CCH_2OCH_3 (240 µL, 2.80 mmol) and stirred for 10 h at room temperature. A gradual change of color from dark red to red-orange occurred. The solvent was removed in vacuo, and the residue was extracted with methanol (20 mL). The extract was brought to dryness in vacuo, the remaining residue was suspended in hexane (5 mL), and the suspension was subjected to chromatography on Al_2O_3 (neutral, activity grade V). With hexane, an off-white fraction was eluted which was withdrawn. Elution with hexane/diethyl ether (5:1) afforded a red fraction, of which the solvent was removed. The residue was washed twice with pentane (3 mL each; −30 °C)

and recrystallized from acetone/pentane (1:5; 10 mL) at −78 °C. After the solution was stored for 2 d, orange crystals precipitated, which were separated from the mother liquor and dried in vacuo. Yield 151 mg (67 %); m.p. 93 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1943 (C≡C), 1585, 1577, 1516 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.45, 7.35, 7.17, 7.00, 6.87 (all m, 21 H; C_6H_5 and ≡CH), 4.69, 4.68 (both s, 1 H each; CH of acac), 4.66 (br s, 2 H; CH_2OCH_3), 3.43 (s, 3 H; CH_2OCH_3), 1.93, 1.92, 1.34, 1.28 (all s, 3 H each; CH_3 of acac); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 186.1, 186.0, 184.6, 184.5 (all s; CO of acac), 183.0 (m; CPh_2), 153.8, 153.6, 150.9, 150.6 (all s; *ipso*-C of C_6H_5), 134.1 (d, J(Rh,C) = 24.0 Hz; ≡CCH_2OCH_3), 130.4, 130.3, 130.1, 126.4, 126.2, 125.9, 125.7, 125.5, 125.4, 125.3 (all s; C_6H_5), 121.9 (d, J(Rh,C) = 22.5 Hz; ≡CH), 98.1, 98.0 (both s; CH of acac), 66.1 (s; CH_2OCH_3), 57.8 (s; CH_2OCH_3), 27.7, 27.6, 26.8, 26.7 (all s; CH_3 of acac); elemental analysis calcd (%) for $C_{40}H_{40}O_5Rh_2$ (806.6): C 59.57, H 5.00; found: C 59.29, H 4.71.

[(κ^2-acac)$_2$Rh(μ-CPh$_2$)$_2$Rh(η^2-HC≡CCH$_3$)] (27): A solution of **21** (138 mg, 0.16 mmol) in acetone (20 mL) was stirred under a propyne atmosphere for 10 h at room temperature. A gradual change of color from dark red to red-orange occurred. The solvent was removed in vacuo, the residue was suspended in hexane (5 mL), and the solution was then worked up as described for **23**. After recrystallization from acetone/pentane (1:10; 10 mL) orange crystals were obtained. Yield 90 mg (83 %); m.p. 150 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1579, 1517 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.47, 7.35, 7.16, 6.98, 6.87 (all m, 20 H; C_6H_5), 6.91 (m, 1 H; ≡CH), 4.68, 4.67 (both s, 1 H each; CH of acac), 2.50 (m, 3 H; ≡CCH_3), 1.93, 1.92, 1.33, 1.27 (all s, 3 H each; CH_3 of acac); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 186.0, 185.9, 184.6, 184.5 (all s; CO of acac), 180.6 (m; CPh_2), 153.9, 153.8, 151.4, 150.8 (all s; *ipso*-C of C_6H_5), 135.7 (d, J(Rh,C) = 23.6 Hz; ≡CCH_3), 130.4, 130.2, 129.6, 126.4, 126.1, 125.8, 125.4, 125.3, 125.2, 125.0 (all s; C_6H_5), 119.5 (d, J(Rh,C) = 20.8 Hz; ≡CH), 98.1, 97.9 (both s; CH of acac), 27.7, 27.6, 26.8, 26.7 (all s; CH_3 of acac), 12.6 (s; ≡CCH_3); elemental analysis calcd (%) for $C_{39}H_{38}O_4Rh_2$ (776.5): C 60.32, H 4.93; found: C 60.09, H 4.83.

[(κ^2-acac)$_2$Rh(μ-CPh$_2$)$_2$Rh(η^2-HC≡CPh)] (28): This compound was prepared as described for **26**, with **21** (140 mg, 0.16 mmol) and phenylacetylene (175 μL, 1.60 mmol) as starting materials; time of reaction 4 h. Recrystallization from diethyl ether/hexane (1:10; 10 mL) gave orange crystals. Yield 67 mg (50 %); m.p. 140 °C (decomp); IR (KBr): $\tilde{\nu}$ (CO_{acac}) = 1585, 1577, 1515 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.76 (d, J(Rh,H) = 4.1 Hz, 1 H; ≡CH), 7.64, 7.42, 7.25, 7.04, 6.89, 6.67 (all m, 25 H; C_6H_5), 4.75, 4.73 (both s, 1 H each; CH of acac), 1.99, 1.95, 1.50, 1.23 (all s, 3 H each; CH_3 of acac); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 186.4, 185.8, 184.8, 184.5 (all s; CO of acac), 184.4, 181.9 (both dd, J(Rh,C) = 32.5, 28.5 Hz; CPh_2), 164.5, 153.5, 151.0, 150.4 (all s; *ipso*-C of C(C_6H_5)$_2$), 137.5 (d, J(Rh,C) = 23.4 Hz; ≡CPh), 131.8, 131.7, 130.5, 130.4, 129.9, 129.6, 129.5, 128.2, 126.3, 126.2, 126.1, 125.9, 125.5, 125.4, 125.3, 124.9 (all s; C_6H_5), 124.8 (d, J(Rh,C) = 23.4 Hz, ≡CH), 98.1, 98.0 (both s; CH of acac), 27.9, 27.6, 26.9, 26.4 (all s; CH_3 of acac), signal of the *ipso*-C atoms of ≡CC_6H_5 could not be exactly located; elemental analysis calcd (%) for $C_{44}H_{40}O_4Rh_2$ (838.6): C 63.02, H 4.81; found: C 63.04, H 5.11.

[(κ^2-acac)$_2$Rh(μ-CPh$_2$)$_2$Rh(η^2-CH$_3$C≡CCO$_2$Et)] (29): A solution of **21** (130 mg, 0.15 mmol) in diethyl ether (15 mL) was treated with CH_3C≡CCO_2Et (175 μL, 1.50 mmol) and stirred for 5 d at room temperature. The solvent was removed in vacuo, the residue was suspended in hexane, and the suspension was subjected to chromatography on Al_2O_3 (neutral, activity grade V). With hexane, an off-white fraction was eluted which was withdrawn. Extraction with hexane/diethyl ether (10:1) afforded a red fraction, which was concentrated to about 5 mL in vacuo. After the solution was stored at −78 °C for 1 d, orange crystals precipitated, which were separated from the mother liquor, washed twice with pentane (3 mL each; −20 °C), and dried in vacuo. Yield 93 mg (73 %); m.p. 180 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1869 (C≡C), 1705 (C=O), 1585, 1579, 1518 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.56, 7.41, 7.28, 7.18, 7.03, 6.89 (all m, 20 H; C_6H_5), 4.73, 4.68 (both s, 1 H each; CH of acac), 4.31 (q, J(H,H) = 7.0 Hz, 2 H; $CO_2CH_2CH_3$), 2.36 (d, J(Rh,H) = 2.6 Hz, 3 H; ≡CCH_3), 1.94, 1.93, 1.43, 1.23 (all s, 3 H each; CH_3 of acac), 1.31 (t, J(H,H) = 7.0 Hz, 3 H; $CO_2CH_2CH_3$); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 186.1, 185.9, 184.6 (all s; CO of acac), 185.4 (dd, J(Rh,C) = 31.5, 28.5 Hz; CPh_2), 184.9 (dd, J(Rh,C) = 32.6, 28.5 Hz; CPh_2), 157.9 (d, J(Rh,C) = 2.0 Hz; CO_2Et), 153.8, 153.4, 151.5, 149.6 (all s; *ipso*-C of C_6H_5), 138.1 (d, J(Rh,C) = 26.4 Hz; ≡CCH_3), 130.4, 130.2, 130.1, 129.8, 126.5, 126.3, 126.1, 126.0, 125.9, 125.7, 125.6, 125.4 (all s; C_6H_5), 121.6 (d, J(Rh,C) = 22.4 Hz; ≡CCO_2Et), 98.1, 98.0 (both s; CH of acac), 61.8 (s; $CO_2CH_2CH_3$), 27.6, 27.0, 26.5, 26.4 (all s; CH_3 of acac), 14.2, 13.2 (both s; ≡CCH_3 and $CO_2CH_2CH_3$); elemental analysis calcd (%) for $C_{42}H_{42}O_6Rh_2$ (848.6): C 59.45, H 4.99; found: C 59.15, H 4.93.

Table 1. Crystal structure data of compounds **5**, **13**, **21**, and **30**.

	5	**13**	**21**	**30**
formula	$C_{40}H_{48}ClO_2Rh_2Sb$	$C_{37}H_{34}O_5Rh_2$	$C_{45}H_{55}O_4PRh_2$	$C_{46}H_{52}N_2O_4Rh_2$
M_r	923.80	764.46	896.68	902.72
T [K]	173(2)	173(2)	173(2)	173(2)
crystal size [mm^3]	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.2 × 0.2 × 0.1
space group	$P2_1/c$ (no. 14)	$I2/a$ (no. 15)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
cell-dimension determination	5000 reflns	5000 reflns	5000 reflns	5000 reflns
	$2.05 < \theta <$ 30.52	$2.40 < \theta <$ 29.23	$2.22 < \theta <$ 28.21	$2.33 < \theta <$ 27.06
a [pm]	1166.4(3)	1723.2(5)	1059.2(1)	1067.46(13)
b [pm]	1899.3(4)	1007.0(3)	1809.0(2)	1302.40(15)
c [pm]	1697.8(5)	1939.3(6)	2156.7(2)	1735.80(19)
α [°]	90.0	90.0	90.0	96.828(13)
β [°]	89.57(3)	113.63(3)	99.88(1)	105.071(13)
γ [°]	90.0	90.0	90.0	110.578(13)
V [nm^3]	3.761(2)	3.083(2)	4.0712(7)	2.1217(4)
Z	4	4	4	2
ρ_{calcd} [Mg m^{-3}]	1.631	1.647	1.463	1.413
μ [mm^{-1}]	1.679	1.101	0.891	0.821
F(000)	1848	1544	1848	928
$2\theta_{max}$ [°]	61.04	58.46	56.42	50.7
measured reflections	40486	21011	42944	23219
unique reflections	8126	4160	9945	7324
reflection used	8126	4160	9945	7324
parameters	454	201	479	498
$R1$ [$I > 2\sigma(I)$][a]	0.0337	0.0310	0.0598	0.0385
$wR2$ (all data)	0.0763	0.0598	0.1624	0.1007
$g1$:$g2$	0.041:0.00	0.0269:0.00	0.1017:0.00	0.0591:0.00
residual electron density ρ [10^{-6} e pm^{-3}]	0.809/−1.19	0.895/−1.242	0.884/−2.087	1.254/−1.183

[a] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$.

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[(κ^2-acac)$_2$Rh(μ-CPh$_2$)$_2$Rh(CN*t*Bu)$_2$] (30): A solution of **21** (120 mg, 0.13 mmol) in pentane (20 mL) was treated with CN*t*Bu (73 μL, 0.65 mmol) at room temperature. A red solid precipitated. After stirring the reaction mixture for 1 h, the solution was decanted. The residue was washed three times with pentane (5 mL each) and then recrystallized from diethyl ether/pentane (1:1; 15 mL) at 5 °C. Red crystals were obtained, which were separated from the mother liquor and dried in vacuo. Yield 104 mg (89 %); m.p. 122 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.26$, 7.45 (both m, 8H; *ortho*-H of C_6H_5), 7.42, 7.26, 6.90 (all m, 12H; *meta*- and *para*-H of C_6H_5), 4.65 (s, 2H; CH of acac), 1.86, 1.31 (both s, 6H each; CH_3 of acac), 0.76 (s, 18H; CH_3 of CN*t*Bu); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 185.0$, 184.6 (both s; CO of acac), 157.2, 155.6 (both s; *ipso*-C of C_6H_5), 132.1, 131.1, 125.8, 125.7, 124.6, 124.3 (all s; C_6H_5), 98.1 (s; CH of acac), 56.2 (s; $C(CH_3)_3$), 29.8 (s; $C(CH_3)_3$), 27.9, 26.6 (both s; CH_3 of acac), signals for CN*t*Bu and CPh_2 could not be exactly located; elemental analysis calcd (%) for $C_{46}H_{52}N_2O_4Rh_2$ (902.7): C 61.21, H 5.81, N 3.10; found: C 60.93, H 5.64, N 2.74.

[(κ^2-acac)$_2$Rh(μ-CPh$_2$)$_2$Rh(CO)$_3$] (31): A slow stream of carbon monoxide was passed through a solution of **21** (110 mg, 0.12 mmol) in pentane (20 mL) for 10 s at room temperature. After the solution was stirred for 10 min, the solvent was removed in vacuo and the residue was recrystallized from diethyl ether/pentane (1:1; 10 mL) at −20 °C. Red crystals were obtained which were separated from the mother liquor and dried in vacuo. Yield 90 mg (89 %); m.p. 111 °C (decomp); MS (DCI): *m*/*z*: 821 $[M+1]^+$, 765 $[M+1-2\,CO]^+$, 736 $[M+1-3\,CO]^+$; IR (C_6H_6): $\tilde{\nu} = 2056$, 2016, 1965 (CO), 1588, 1576, 1518 cm^{-1} (CO_{acac}); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 8.26$, 7.45 (both m, 4H each; *ortho*-H of C_6H_5), 7.47–6.75 (m, 12H; *meta*- and *para*-H of C_6H_5), 4.55 (s, 2H; CH of acac), 1.72, 1.22 (both s, 6H each; CH_3 of acac); elemental analysis calcd (%) for $C_{39}H_{34}O_7Rh_2$ (820.5): C 57.09, H 4.18; found: C 56.85, H 3.99.

X-ray crystal structure determination of compounds 5, 13, 21, and 30: Single crystals of **5** were grown from a saturated solution of **5** in acetone/diethyl ether (1:1) at −20 °C. Crystals of **13** were obtained from a solution of CH_2Cl_2/pentane (1:5) at 5 °C. Crystals of **21** and **30** were grown from a saturated solutions of **21** and **30** in diethyl ether/pentane (1:1) at 5 °C, respectively. Crystal data for the four structures are presented in Table 1. The data for **5**, **13**, **21**, and **30** were collected at low temperature from an oil-coated, shock-cooled crystal[13] on a Stoe IPDS instrument with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by Patterson or Direct methods with SHELXS-86 for **5** and **13**, and with SHELXS-97 for **21** and **30**.[14] All structures were refined by full matrix least-squares procedures on F^2 with SHELXL-86 (**5**, **13**) or SHELXL-97 (**21**, **30**).[15] Two isopropyl groups of **5** were disordered and were found in two positions with an occupancy factor of 0.57:0.43 and 0.67:0.33; they were refined anisotropically with restraints. The asymmetric unit of **13** contains only half of the molecule with the CO ligand on the crystallographic axis. The second half was generated by the symmetry operation $-x+1/2, y, -z$. For the structure of **30** the extinction parameter was refined to 0.0095(6).

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