Carbenerhodium Complexes of the Half-Sandwich-Type: Synthesis, Substitution, and Addition Reactions

Helmut Werner,* Peter Schwab, Elke Bleuel, Norbert Mahr, Bettina Windmüller, and Justin Wolf[a]

Dedicated to Professor Dieter Sellmann on the occasion of his 60th birthday

Abstract: A series of carbenerhodium(I) complexes of the general composition $[(\eta^5\text{-}C_5H_5)Rh(=CRR')(L)]$ (**2a–2i**) with $R = R' =$ aryl and $L = Sb\textit{i}Pr_3$ or PR_3 has been prepared from the square-planar precursors *trans*-$[RhCl(=CRR')(L)_2]$ and NaC_5H_5 in excellent yields. Reaction of the *triisopropylstibane* derivative **2a**, which contains a rather labile Rh–Sb bond, with CO, PMe_3, and CNR (R = Me, CH_2Ph, *t*Bu) leads to the displacement of the $Sb\textit{i}Pr_3$ ligand and affords the substitution products $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(L)]$ (**3–7**). In contrast, treatment of the *triisopropylphosphane* compound **2c** with CO and CN*t*Bu leads to the cleavage of the $Rh=CPh_2$ bond and gives besides $[(\eta^5\text{-}C_5H_5)Rh(P\textit{i}Pr_3)(L)]$ (**10**, **12**) by metal-assisted C–C coupling diphenylketene $Ph_2C=C=O$ (**11**) or the corresponding imine $Ph_2C=C=N\textit{t}Bu$ (**13**). While the reaction of **2a**, **c** with C_2H_4 yields $[(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(L)]$ (**14**, **15**) and the trisubstituted olefin $Ph_2C=CHCH_3$ (**16**), treatment of **2a**, **c** with RN_3 leads to the cleavage of *both* the $Rh-E\textit{i}Pr_3$ and $Rh=CPh_2$ bonds and gives the chelate complexes $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}RNNNR)]$ (**19**, **20**). The substitution products **3** (L = CO) and **4** ($L = PMe_3$) react with an equimolar amount of sulfur or selenium by addition of the chalcogen to the $Rh=CPh_2$ bond to generate the complexes $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}ECPh_2)(L)]$ (**21–24**) with thio- or selenobenzophenone as ligand. Similarly, treatment of **3** with CuCl affords the unusual 1:2 adduct $[(\eta^5\text{-}C_5H_5)(CO)Rh(\mu\text{-}CPh_2)(CuCl)_2]$ (**25**), which reacts with NaC_5H_5 to form $[(\eta^5\text{-}C_5H_5)(CO)Rh(\mu\text{-}CPh_2)Cu(\eta^5\text{-}C_5H_5)]$ (**26**). The molecular structures of **3** and **22** have been determined by X-ray crystallography.

Keywords: carbene complexes · carbonyl complexes · cyclopentadienyl complexes · C–C coupling · rhodium

Introduction

In the context of our investigations on the reactivity of the fascinating dimer $[\{RhCl(P\textit{i}Pr_3)_2\}_2]$,[1] which led inter alia to a series of organometallic cumulenes *trans*-$[RhCl\{=C(=C)_n\text{-}RR'\}(P\textit{i}Pr_3)_2]$ ($n = 1$,[2] 2,[3] and 4[4]), we recently developed also a convenient synthetic route to related rhodium carbenes *trans*-$[RhCl(=CRR')(P\textit{i}Pr_3)_2]$. However in order to obtain these stable 16-electron species, the dimer $[\{RhCl(P\textit{i}Pr_3)_2\}_2]$ could not be used as starting material. The method of choice was to treat the bis(stibane)rhodium(I) compound *trans*-$[RhCl(C_2H_4)(Sb\textit{i}Pr_3)_2]$ in the initial step with diazoalkanes $R'RCN_2$ to form *trans*-$[RhCl(=CRR')(Sb\textit{i}Pr_3)_2]$ by displacement of ethene and elimination of N_2, and then substitute the two rather weakly bound stibanes for phosphanes. Besides $P\textit{i}Pr_3$ also $P\textit{i}Pr_2Ph$, $P\textit{i}PrPh_2$, PPh_3, and PPh_2Me could be applied as displacing substrates and thus a manifold of carbenerhodium(I) complexes of the general composition *trans*-$[RhCl(=CRR')(PR''_3)_2]$ was prepared.[5] An important observation of the original studies about the reactivity of *trans*-$[RhCl(=CRR')(Sb\textit{i}Pr_3)_2]$ was that not only the stibanes but also the chloro *and* the carbene ligand could be replaced by nucleophiles. If C_2H_4 or CO were used, for $R = R' =$ Ph the carbene did not yield a dimer or oligomer but gave the C–C coupling products shown in Scheme 1 in almost quantitative yield.[5c]

The unusual and interesting behavior of the square-planar compounds *trans*-$[RhCl(=CRR')(L)_2]$ with $L = Sb\textit{i}Pr_3$ and PR_3 prompted us to also study in more detail the reactivity of the corresponding half-sandwich-type complexes $[(\eta^5\text{-}C_5H_5)Rh(=CRR')(L)]$, of which for $L = P\textit{i}Pr_3$ the vinylidene and allenylidene analogues $[(\eta^5\text{-}C_5H_5)Rh(=C=CHR)(L)]$[6] and $[(\eta^5\text{-}C_5H_5)Rh(=C=C=CPh_2)(L)]$ were known.[7] Herein, we describe the preparation of a family of these η^5-cyclopentadienylrhodium carbene derivatives, their reactions with nucleophiles, and illustrate with some examples also the

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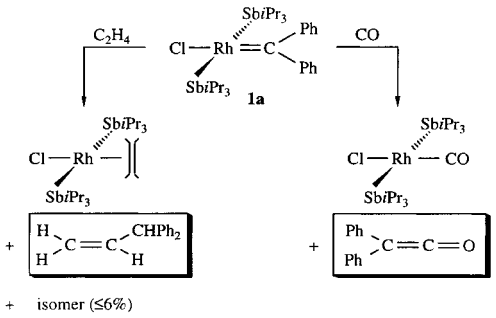
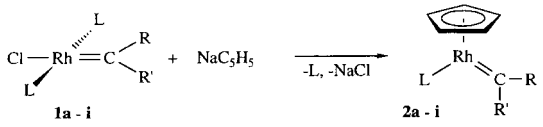


Scheme 1.

possibility of adding electron-deficient species such as sulfur, selenium, or CuCl to the Rh–C double bond.

Results and Discussion

Preparation of η^5-cyclopentadienylrhodium(I) complexes with diarylcarbenes as ligands: In contrast to the rhodium vinylidenes *trans*-[RhCl(=C=CHR)($P i Pr_3$)$_2$], which are rather inert toward lithium or sodium cyclopentadienyl, the square-planar compounds **1a–i** react with NaC_5H_5 in THF at room temperature to give the η^5-cyclopentadienyl complexes **2a–i** (Scheme 2) in good to excellent yield. After chromatographic

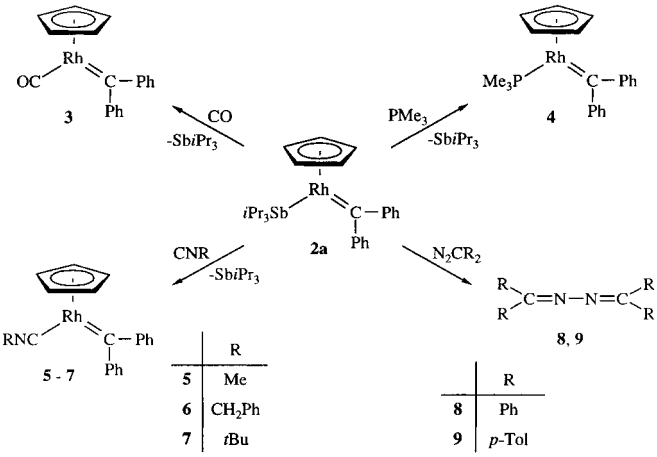


	L	R	R'
1a, 2a	Sb*i*Pr$_3$	Ph	Ph
1b, 2b	Sb*i*Pr$_3$	Ph	*o*-Tol
1c, 2c	P*i*Pr$_3$	Ph	Ph
1d, 2d	P*i*Pr$_3$	Ph	*p*-Tol
1e, 2e	P*i*Pr$_3$	*p*-Tol	*p*-Tol
1f, 2f	P*i*Pr$_2$Ph	Ph	Ph
1g, 2g	P*i*PrPh$_2$	Ph	Ph
1h, 2h	PPh$_3$	Ph	Ph
1i, 2i	PMePh$_2$	Ph	Ph

Scheme 2.

workup, the analytically pure products were isolated as deeply colored solids which are only moderately air-sensitive and readily soluble in most common organic solvents (with the exception of methanol). The ^{13}C NMR spectra of **2a**, **b** and **2d–i** display (similarly to **2c**[5c]) a resonance for the carbene carbon atom in the low-field region at $\delta \approx 250-270$, which compared with the 16-electron precursors **1a–i** is shifted upfield by about 45–75 ppm. Like the signal for the cyclopentadienyl carbon atoms, also the Rh=C resonance is split into a doublet of doublets due to $^{13}C-^{31}P$ and $^{13}C-^{103}Rh$ coupling. The ^{1}H NMR spectra of **2a**, **b** and **2d**, **e** exhibit only one set of resonances for the protons of the diastereotopic methyl groups of the isopropyl substituents, indicating that on the NMR time scale (in solution at room temperature) the rotation around the metal–carbene bond is not significantly hindered. It should be mentioned that various attempts to prepare the pentamethylcyclopentadienylrhodium(I) derivatives [(η^5-C_5Me_5)Rh(=CPh$_2$)(L)] (L = Sb*i*Pr$_3$, P*i*Pr$_3$) from **1a** or **1c** and LiC_5Me_5 or NaC_5Me_5 failed.

Ligand substitution reactions of the carbenerhodium(I) complexes 2a and 2c: Similarly to the square-planar compound **1a**,[5] also the related half-sandwich-type complex **2a** contains a labile Rh–Sb bond and therefore the stibane ligand can easily be displaced by CO, PMe_3, and isocyanides (Scheme 3).



Scheme 3.

In pentane at room temperature, the reactions of **2a** with these Lewis bases proceed quite smoothly and afford the corresponding η^5-cyclopentadienyl derivatives **3**, **4**, and **5–7** in 83–89% yield. In contrast to PMe_3, the more bulky triisopropylphosphane appears to be unable to substitute the stibane moiety and therefore after stirring a solution of **2a** and P*i*Pr$_3$ in pentane for 6 h the starting material **2a** was reisolated. Typical spectroscopic features of **3** are the strong ν(CO) absorption at 1982 cm^{-1} in the IR spectrum and the two low-field signals (both doublets) at $\delta = 286.7$ and 192.7 for the ^{13}C nuclei of the carbene and the CO ligand in the ^{13}C NMR spectrum. The resonance for the carbene-carbon atoms *C*Ph$_2$ appears in the ^{13}C NMR spectra of **5–7** at around $\delta = 268-269$ and is thus shifted somewhat up-field compared with that of **3**, which is in agreement with the stronger σ-donor character of the isocyanides.

The molecular structure of compound **3** is shown in Figure 1. The molecule possesses the expected two-legged piano-stool configuration with a Rh–CO distance (1.844(4) Å) that is about 0.04 Å longer than in related carbonylrhodium(I) complexes with a heteroatom-stabilized carbene ligand of the Fischer type.[8] On the other hand, the Rh–$C_{carbene}$ bond length of **3** (1.906(3) Å) is somewhat shorter than in these compounds (1.925(3)–1.994(7) Å),[8] which is in accord with the general bonding scheme.[9] Compared with the data of **1a** and **1c**,[5] the Rh–C1 distance in **3** is slightly longer, which could be due to the presence of two strong donating stibane or phosphane ligands in the square-planar precursors.

The reaction of **2a** with diphenyl- and bis(*p*-tolyl)diazomethane, which was undertaken to find out whether a C–C

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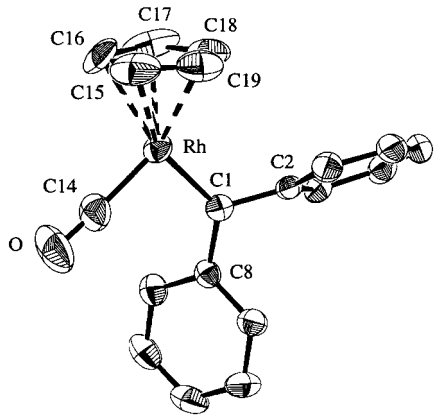
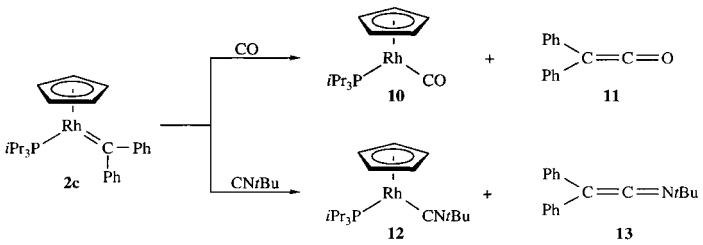


Figure 1. Molecular structure of **3**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh–C1 1.906(3), Rh–C14 1.844(4), C1–C2 1.485(4), C1–C8 1.482(4), C14–O 1.137(4), Rh–C15 2.264(4), Rh–C16 2.260(4), Rh–C17 2.253(4), Rh–C18 2.235(4), Rh–C19 2.269(4); C1-Rh-C14 92.53(14), C2-C1-C8 112.4(2), Rh-C1-C2 119.34(19), Rh-C1-C8 128.3(2).

coupling between the carbene ligand and the CR_2 fragment of the substrate occurs, followed an unexpected pathway. Instead of an olefin $Ph_2C{=}CR_2$ or a bis(carbene) complex $[(\eta^5\text{-}C_5H_5)Rh(CPh_2)(CR_2)]$, obtained by substitution of Sb*i*Pr$_3$ for CR_2, the respective diazine **8** or **9** was formed. After column chromatography of the crude product, besides the diazine most of the starting compound **2a** was re-isolated. With regard to the mechanism of the reaction of **2a** with R_2CN_2, we assume that in the initial step a highly labile 1:1 adduct of the 18-electron half-sandwich-type complex **2a** and CR_2 is generated, which reacts with a second molecule of R_2CN_2 to give the C–N coupling product.

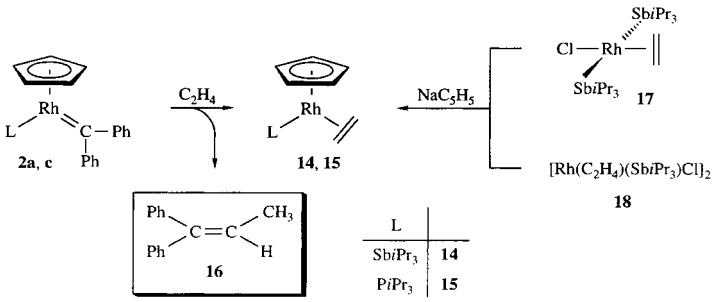
The reaction of the triisopropylphosphane compound **2c** with CO and CN*t*Bu did not lead to the displacement of P*i*Pr$_3$ but took a different course. Instead of **3** and **7** (see Scheme 3), the carbonyl and isocyanide derivatives **10**[10] and **12** were formed (Scheme 4). As the organic products, diphenylketene



Scheme 4.

11 and *N-tert*-butylketenimine **13** were obtained. They were separated from the metal-containing compounds by column chromatography and identified by their IR and ^{13}C NMR spectra. It is quite noteworthy that despite the difference in the electronic configuration between **1a**, **c** on one hand and **2a**, **c** on the other, the compounds **1c** and **2c** behave completely analogously toward CO and CN*t*Bu. Since tetraphenylethene, which is produced from CPh_2 generated in situ,[11] could not be detected as a by-product in the reactions of **2c** with CO and CN*t*Bu, we assume that both the ketene **11** and the ketenimine **13** are formed by C–C coupling in the coordination sphere of rhodium.

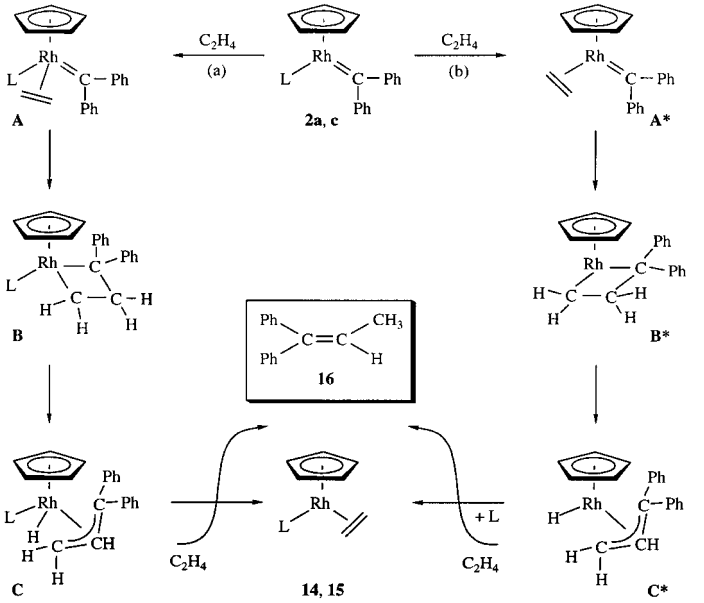
The diphenylcarbene complexes **2a** and **2c** also react even at room temperature with ethene. In this case, instead of the stibane or phosphane ligand the carbene unit is displaced and besides the ethene half-sandwich-type complex **14** or **15**, respectively, the trisubstituted olefin **16** is generated (Scheme 5). This olefin is formally built up by two carbene



Scheme 5.

fragments, one originating from the CPh_2 unit of **2a**, **c** and the other from ethene. There is, however, a difference between the square-planar precursors **1a**, **c** and the cyclopentadienyl compounds **2a**, **c** in the behavior toward C_2H_4 insofar, as **1c** reacts with ethene to give **16**, while treatment of **1a** with C_2H_4 affords the isomer $CH_2{=}CHCHPh_2$ as the main product.[5] We note that in neither case, with **1a**, **c** or with **2a**, **c** and C_2H_4 as starting materials, another isomer of **16**, namely 1.1-diphenylcyclopropane, is formed. In addition it should be mentioned that the ethene complex **14** is accessible not only from **2a** and excess C_2H_4 but also from the precursors **17** or **18** and NaC_5H_5 (see Scheme 5).

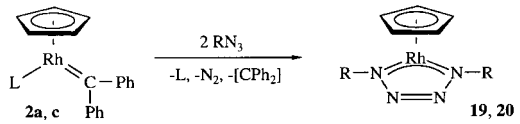
A mechanistic proposal for the formation of **16** from **2a**, **c** and C_2H_4 is outlined in Scheme 6. In agreement with earlier results,[5] we assume that in the initial stage of the reaction



Scheme 6.

both the carbene CPh_2 and ethene are coordinated to rhodium. Although the proposed intermediate **A** is a 20-electron species, we prefer not to exclude route (a) since it is known that ligand substitution reactions of half-sandwich-type rhodium(I) complexes follow an associative mechanism.[12] The next step either on path (a) or (b) could be the formation of a metallacyclobutane (**B** or **B***), which, via a β-H shift, should afford a (η^3-allyl)hydridorhodium(III) intermediate. Either **C** or **C*** could then react by reductive coupling of the hydrido ligand and the less shielded CH_2 carbon atom of the allylic moiety to generate **16**. We note that this mechanistic scheme is in line with the original hypothesis for the rhodium-catalyzed formation of the trisubstituted olefin **16** from ethene and free diphenyldiazomethane which involves a labile Rh(=CPh_2) compound as an intermediate.[13]

Attempts to connect a carbene and a nitrene fragment in the coordination sphere of rhodium and generate a ketimine $Ph_2C{=}NR$ by C–N coupling led to an unexpected result. If the starting materials **2a** or **2c** are treated with phenyl- or *p*-tolylazide in pentane, instead of an addition of the azide or the corresponding nitrene to the Rh–C double bond the displacement of *both* the carbene and the stibane or phosphane ligands takes place. After chromatographic workup, the products **19** and **20** (see Scheme 7) are obtained as red,

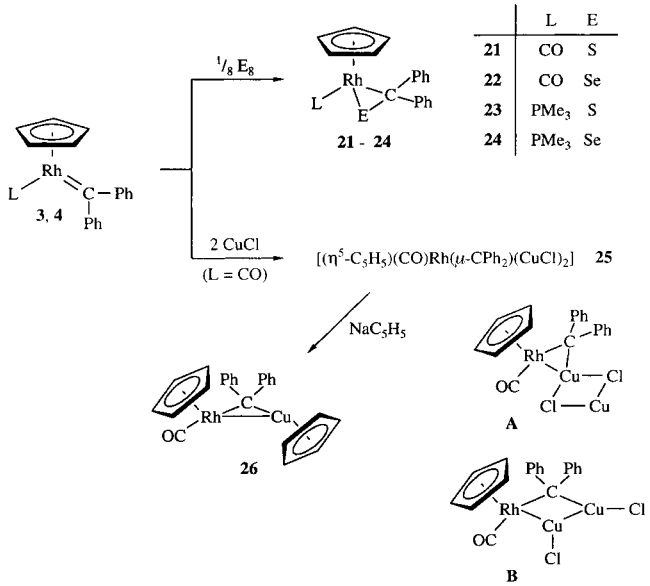


	R
19	Ph
20	*p*-Tol

Scheme 7.

moderately air-stable solids in about 70% yield. The elemental analyses, the mass spectra, and also the NMR spectroscopic data confirm that besides the cyclopentadienyl ring only the fragment N_4R_2 (R = Ph, *p*-Tol) is coordinated to rhodium. There is precedence for the formation of tetraazadiene complexes of the general composition [(η^5-C_5R_5)M(κ^2-R′*N*N*N*R′)] from half-sandwich-type precursors [(η^5-C_5R_5)M(L)$_2$] and R′N_3 insofar as both Nakamura and Otsuka[14] and Trogler and co-workers[15] found that [(η^5-C_5H_5)Co(CO)$_2$] reacts with organic azides R′N_3 to afford the compounds [(η^5-C_5H_5)Co(κ^2-R′*N*N*N*R′)] by displacement of the two CO ligands. Moreover, we observed that also the bis(trimethylphosphane)cobalt derivative [(η^5-C_5Me_5)-Co(PMe_3)$_2$] upon treatment with PhN_3 gives [(η^5-C_5Me_5)-Co(κ^2-Ph*N*N*N*Ph)].[16] The general experience is that tetraazadienes possess relatively strong π-acceptor properties and are thus able to stabilize electron-rich molecular fragments such as [(η^5-C_5R_5)Co], [(η^5-C_5H_5)Rh], etc.[17]

Addition reactions of the carbenerhodium(I) complexes 3 and 4: Similarly to the vinylidene compounds [(η^5-C_5H_5)Rh(=C=CHR)(P*i*Pr$_3$)], which were shown to undergo addition reactions with electrophilic substrates,[2c, 18] the carbene complexes **3** and **4** equally react with sulfur and selenium by attack of the chalcogen at the Rh–C double bond. After stirring a solution of **3** or **4** with an equimolar amount of sulfur or selenium in benzene, followed by column chromatography of the reaction mixture, the compounds **21**–**24** are obtained as light yellow (**21**), light brown (**22**), or orange-yellow (**23**, **24**) solids in 65–95% yield (Scheme 8). Both the elemental



	L	E
21	CO	S
22	CO	Se
23	PMe_3	S
24	PMe_3	Se

Scheme 8.

analyses and the mass spectra of **21**–**24** indicate that half-sandwich-type rhodium complexes with thio- or selenobenzophenone as ligands were formed. The ^{13}C NMR spectra of **21**–**24** display a resonance for the E*C*Ph_2 carbon atom at $\delta \approx$ 79–96 which is significantly shifted upfield (by 175–195 ppm) compared with the signal of the *C*Ph_2 carbon atom of the carbene precursor. Since there is also a dramatic difference in the chemical shift for the signal of the ^{13}C nuclei of S*C*Ph_2 in **21** ($\delta = 93.3$) and **23** ($\delta = 79.1$) on one hand and of free thiobenzophenone ($\delta = 240.1$)[19] on the other, we assume that the bonding between rhodium and E*C*Ph_2 is best represented by a three-membered ring structure as shown in Scheme 8. This proposal is supported not only by the NMR data but also by the mass spectra of **21**–**24** in which the peak for the fragment ion [(C_5H_5)Rh(E*C*Ph_2)]$^+$ appears with relative high intensity. In this context we note that to the best of our knowledge only one other type of transition metal complexes with S*C*Ph_2 as ligand, namely [M(κ^2-S*C*Ph_2)(CO)$_5$] (M = Cr, W) is known and has been prepared from the corresponding metal diphenylcarbenes and phenylisoselenocyanate.[20] Moreover, it should be mentioned that analogously to **4** the triisopropylphosphane counterpart **2c** also reacts with an equimolar amount of sulfur to afford the corresponding thiobenzophenonerhodium complex [(η^5-C_5H_5)Rh(S*C*Ph_2)-(P*i*Pr$_3$)] which however is rather labile and rapidly decomposes in solution or during chromatographic workup.

The X-ray crystal structure analysis of **22** (Figure 2) confirms the linkage of selenobenzophenone through selenium *and* carbon to the metal center. The coordination

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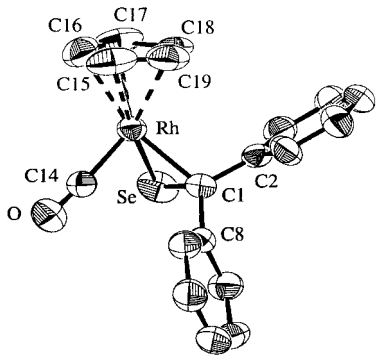

Figure 2. Molecular structure of **22**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): Rh–Se 2.4421(10), Rh–C1 2.152(5), Rh–C14 1.865(8), Rh–C15 2.193(8), Rh–C16 2.229(8), Rh–C17 2.267(8), Rh–C18 2.222(9), Rh–C19 2.230(8), Se–C1 1.908(5), O–C14 1.128(10), C1–C2 1.506(10), C1–C8 1.510(8); Se-Rh-C1 48.58(14), Rh-Se-C1 57.75(16), Rh-C1-Se 73.67(18), Se-Rh-C14 89.6(2), Rh-C14-O 176.0(7), C1-Rh-C14 93.7(3), Se-C1-C2 118.4(4), Se-C1-C8 115.8(4), C2-C1-C8 113.0(5), Rh-C1-C2 110.9(4), Rh-C1-C8 119.9(4).

geometry around the rhodium center can be described as pseudo-trigonal planar with the carbon atom C14, the midpoint of the cyclopentadienyl ring, and the centroid of the Se–C1 bond at the corners. The two planes (Rh,Se,C1) and (C14,Rh,Se) lie nearly perpendicular to the plane formed by the three carbon atoms C1, C2, and C8. The bond length Se–C1 (1.908(5) Å) is almost identical to that in the related selenoaldehyde complex $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}SeCHMe)(P\mathit{i}Pr_3)]$ (1.917(5) Å)[21] and only slightly longer than that in the tungsten compound $[W(CO)_5(\kappa^2\text{-}SeCHPh)]$ (1.86(2) and 1.88(2) Å)[22]. Compared with $Se(CH_3)_2$ (1.98(1) Å)[23] and both $Se{=}CH_2$ and Se=CHMe (1.758(1) Å),[24] the distance Se–C1 in **22** corresponds more to that of a carbon–selenium single bond which is in agreement with the proposed selenometallacyclopropane structure. Besides the Se–C1 bond length, also the distances Rh–Se and Rh–C1 as well as the bond angles Rh-Se-C1, Rh-C1-Se, and Se-Rh-C1 are quite similar to that in $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}SeCHMe)(P\mathit{i}Pr_3)]$.[21] The bond lengths Rh–C14 and C14–O in **22** are virtually the same as in the carbene complex **3** which means that the addition of the selenium to the Rh–C double bond has nearly no influence on the bonding between rhodium and CO.

Following earlier attempts to generate mixed-metal rhodium–copper compounds with bridging vinylidene ligands,[18b] we also investigated the reactivity of the carbene complex **3** toward CuCl. Treatment of a solution of **3** in benzene with *one* equivalent of CuCl gave, after stirring for 2 h at room temperature, a reaction mixture which still contained considerable amounts of the starting material **3**. Addition of a second equivalent of CuCl led to the formation of a clear solution from which after column chromatography a deep red, moderately air-stable solid was isolated in 87% yield. Both the elemental analysis and the mass spectrum confirmed that instead of the expected 1:1 the corresponding 1:2 adduct **25** of **3** and CuCl was obtained (see Scheme 8). The ^{13}C NMR spectrum of **25** displays in the low-field region two resonances (both doublets) at $\delta = 217.0$ and 189.9 which show a rather large $^{13}C-^{103}Rh$ coupling and are assigned to the ^{13}C nuclei of the carbene and the carbonyl ligand, respectively. Since the signal of the $C\mathrm{Ph}_2$ carbon atom is shifted upfield by about 70 ppm compared to that of **3**, we assume that the carbene occupies a bridging position and thus for **25** a structure like **A** or **B** seems to be possible.

The reaction of **25** with excess NaC_5H_5 in THF affords the substitution product **26** which, according to the analytical data, contains rhodium and copper not in the ratio of 1:2 but 1:1. In agreement with the structural proposal, which is shown in Scheme 8, both the ^1H and ^{13}C NMR spectra of **26** display *two* signals for the protons and the carbon nuclei of the cyclopentadienyl ligands of which in either case only *one* is split into a doublet. Therefore, this signal (in the ^1H NMR spectrum at $\delta = 4.97$ and in the ^{13}C NMR spectrum at $\delta = 90.3$) can be assigned to the C,H atoms of the five-membered ring bonded to rhodium. An analogous compound in which the unsaturated carbene $C{=}CH_2$ bridges a $(\eta^5\text{-}C_5H_5)Rh(P\mathit{i}Pr_3)$ and a $(\eta^5\text{-}C_5H_5)Cu$ unit has been obtained from the respective precursor $[(\eta^5\text{-}C_5H_5)(P\mathit{i}Pr_3)Rh(\mu\text{-}C{=}CH_2)CuCl]$ and NaC_5H_5.[18b]

Conclusion

The work presented herein has shown that half-sandwich-type complexes of the general composition $[(\eta^5\text{-}C_5H_5)Rh(=CRR')(L)]$, where R and R′ is aryl and L a two-electron donor ligand, are easily accessible and offer a rich chemistry. While the compound with R = R′ = Ph and L = Sb*i*Pr$_3$ reacts smoothly with CO, PMe_3, and isocyanides by substitution of the stibane ligand, the Rh–L bond in the corresponding complex with L = P*i*Pr$_3$ is quite stable. Therefore, treatment of $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(P\mathit{i}Pr_3)]$ with CO and CN*t*Bu does not lead to $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(CX)]$ (X = O, N*t*Bu) but instead gives $[(\eta^5\text{-}C_5H_5)Rh(CX)(P\mathit{i}Pr_3)]$ and, by metal-assisted C–C coupling, diphenylketene $Ph_2C{=}C{=}O$ and the related ketenimine $Ph_2C{=}C{=}N\mathit{t}Bu$. Most remarkably, the reactions of ethene with both $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(Sb\mathit{i}Pr_3)]$ and $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(P\mathit{i}Pr_3)]$ also occur by cleavage of the $Rh{=}CPh_2$ bond and yield besides the ethene compounds $[(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(L)]$ (L = Sb*i*Pr$_3$, P*i*Pr$_3$) the trisubstituted olefin $Ph_2C{=}CHCH_3$. In contrast to CO, CN*t*Bu, and C_2H_4, aryl azides RN_3 react with the carbenerhodium precursors by displacement of the carbene *and* the stibane or phosphane ligand to give the chelate complexes $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}RNNN\mathit{N}R)]$ in excellent yields.

The $Rh{=}CPh_2$ unit can also be used as building block for the generation of molecules such as $SCPh_2$ or $SeCPh_2$ which is illustrated by the formation of $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}ECPh_2)(CO)]$ and $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}ECPh_2)(PMe_3)]$ (E = S, Se) from $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(CO)]$ or $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(PMe_3)]$ and equimolar amounts of sulfur or selenium, respectively. Moreover, CuCl also adds to the $Rh{=}CPh_2$ bond of the carbonyl(carbene)rhodium complex and yields a heterobimetallic compound with the carbene in a bridging position. Finally, we note that PF_3 behaves completely differently toward $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(P\mathit{i}Pr_3)]$ than CO and gives by migratory insertion of the carbene ligand into a C–H bond the ring-substituted product $[(\eta^5\text{-}C_5H_4CHPh_2)Rh(PF_3)(P\mathit{i}Pr_3)]$. [25]

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1a–d**, **1f–i**,[5c] **2c**,[5c] **17**,[26] and **18**[26] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, and IR spectra on a Perkin-Elmer 1420 or an IFS 25 FT-IR infrared spectrometer. Melting points were measured by differential thermal analysis (DTA). Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; sept, septet; m, multiplet; br, broadened signal; $N = {}^3J(P,H)+{}^5J(P,H)$ or ${}^1J(P,C)+{}^3J(P,C)$.

***trans*-[RhCl{=C(*p*-Tol)$_2$}(P*i*Pr$_3$)$_2$] (1e)**: A solution of *trans*-[RhCl{=C(*p*-Tol)$_2$}(Sb*i*Pr$_3$)$_2$][5c] (149 mg, 0.18 mmol) in pentane (10 mL) was treated with P*i*Pr$_3$ (68 μL, 0.36 mmol) and stirred for 30 min at room temperature. The reaction mixture was concentrated to about 2 mL in vacuo, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With pentane, a green fraction was eluted, which was concentrated to about 5 mL in vacuo and then stored for two days at −78 °C. Green crystals precipitated, which were separated from the mother liquor and dried; yield 112 mg (96 %); m.p. 69 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 8.00$ (m, 4H; *ortho*-H of $C_6H_4CH_3$), 6.85 (m, 4H; *meta*-H of $C_6H_4CH_3$), 2.38 (m, 6H; PC*H*CH$_3$), 1.80 (s, 6H; $C_6H_4CH_3$), 1.22 (dvt, $N = 13.2$, $J(H,H) = 6.7$ Hz, 36H; PCHC*H*$_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 317.0$ (dt, $J(Rh,C) = 38.1$, $J(P,C) = 8.3$ Hz; Rh=C), 160.0 (s; *ipso*-C of $C_6H_4CH_3$), 158.3 (s; *para*-C of $C_6H_4CH_3$), 131.0, 130.1, 129.3, 129.0, 128.8, 128.6, 128.3, 126.9 (all s; *ortho*- and *meta*-C of $C_6H_4CH_3$), 25.3 (vt, $N =$ 17.8 Hz; P*C*HCH$_3$), 22.6 (s; $C_6H_4CH_3$), 20.7 (s; PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 23.3$ (d, $J(Rh,P) = 171.2$ Hz); elemental analysis for $C_{33}H_{56}ClP_2Rh$ (653.1): calcd: C 60.69, H 8.64; found: C 61.00, H 8.48.

[(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(Sb*i*Pr$_3$)] (2a): A solution of **1a** (83 mg, 0.10 mmol) in THF (10 mL) was treated with NaC_5H_5 (44 mg, 0.50 mmol) at room temperature. A spontaneous change of color from green to deep blue occurred. After the reaction mixture was stirred for 30 min, the solvent was removed in vacuo. The oily residue was extracted with pentane (10 mL), and the extract concentrated to 1 mL in vacuo. The solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, a blue fraction was eluted, which after removal of the solvent gave a blue solid. This was washed twice with small portions of methanol and recrystallized from pentane at −30 °C. After 18 h, blue crystals precipitated which were separated from the mother liquor, washed with a small quantity of pentane and dried; yield 47 mg (78 %); m.p. 30 °C (decomp); MS (70 eV): *m*/*z* (I$_r$): 585 (0.3; [M^+]), 334 (2.7; [M^+ − Sb*i*Pr$_3$]), 269 (0.6; [Rh=CPh$_2$]$^+$), 251 (55; [Sb*i*Pr$_3$]$^+$), 168 (15; [RhC$_5$H$_5$]$^+$); ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.69$ (m, 4H; *ortho*-H of C_6H_5), 7.13–6.98 (m, 6H; *meta*- and *para*-H of C_6H_5), 5.00 (d, $J(Rh,H) = 0.9$ Hz, 5H; C_5H_5), 1.35 (sept, $J(H,H) = 7.0$ Hz, 3H; SbC*H*CH$_3$), 1.10 (d, $J(H,H) = 7.0$ Hz, 18H; SbCHC*H*$_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 261.0$ (d, $J(Rh,C) = 46.9$ Hz, Rh=C), 166.7, 160.0 (both s; *ipso*-C of C_6H_5), 132.1, 129.8, 129.7, 129.1, 128.3, 128.1 (all s; *ortho*-, *meta*-, and *para*-C of C_6H_5), 82.8 (d, $J(Rh,C) = 3.8$ Hz; C_5H_5), 21.6 (s; SbCH*C*H$_3$), 18.3 (d, $J(Rh,C) = 3.2$ Hz; Sb*C*HCH$_3$); elemental analysis for $C_{27}H_{36}RhSb$ (585.2): calcd: C 55.41, H 6.20, Rh 17.58; found: C 55.39, H 6.34, Rh 17.61.

[(η^5-C$_5$H$_5$)Rh{=C(*o*-Tol)Ph}(Sb*i*Pr$_3$)] (2b) was prepared as described for **2a**, from **1b** (82 mg, 0.10 mmol) and NaC_5H_5 (44 mg, 0.50 mmol) in THF (10 mL); yield 44 mg (73 %). Blue-violet oil; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.57$ (m, 3H; *ortho*-H of C_6H_5 and $C_6H_4CH_3$), 7.33–6.83 (m, 6H; *meta*- and *para*-H of C_6H_5 and $C_6H_4CH_3$), 4.63 (br s, 5H; C_5H_5), 2.04 (s, 3H; $C_6H_4CH_3$), 1.74 (sept, $J(H,H) = 7.1$ Hz, 3H; SbC*H*CH$_3$), 1.29 (d, $J(H,H) =$ 7.1 Hz, 18H; SbCHC*H*$_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 253.7$ (d, $J(Rh,C) = 46.6$ Hz; Rh=C), 155.7, 154.6 (both s; *ipso*-C of C_6H_5 and $C_6H_4CH_3$), 130.1, 129.3, 128.3, 127.2, 124.6, 124.5, 122.8, 122.4 (all s; *ortho*-, *meta*-, and *para*-C of C_6H_5 and $C_6H_4CH_3$), 88.3 (d, $J(Rh,C) = 3.8$ Hz; C_5H_5), 22.7 (s; $C_6H_4CH_3$), 21.4 (s; SbCH*C*H$_3$), 18.3 (s; Sb*C*HCH$_3$); elemental analysis for $C_{28}H_{38}RhSb$ (599.3): calcd: C 56.12, H 6.39; found: C 56.49, H 6.05.

[(η^5-C$_5$H$_5$)Rh{=C(*p*-Tol)Ph}(P*i*Pr$_3$)] (2d): A solution of **1d** (89 mg, 0.14 mmol) in THF (10 mL) was treated with NaC_5H_5 (61 mg, 0.70 mmol) and stirred for 30 min at room temperature. A change of color from green to deep blue occurred. The reaction mixture was concentrated to 2 mL in vacuo, and MeI (1.0 mL, 16 mmol) was added. After the suspension was stirred for 15 min at room temperature, the volatile components were removed in vacuo. The oily residue was extracted with pentane (20 mL), and the extract concentrated to 2 mL in vacuo. The solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 2.5 cm). With pentane, a blue fraction was eluted, which after removal of the solvent gave a blue solid. Recrystallization from methanol/pentane (2/1.5 mL) at −20 °C gave blue crystals, which were separated from the mother liquor and dried; yield 57 mg (80 %); m.p. 85 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.73$, 7.69 (both m, 2H each; *ortho*-H of C_6H_5 and $C_6H_4CH_3$), 7.18–6.76 (m, 5H; *meta*- and *para*-H of C_6H_5 and *meta*-H of $C_6H_4CH_3$), 5.00 (br s, 5H; C_5H_5), 2.02 (s, 3H; $C_6H_4CH_3$), 1.51 (br sept, $J(H,H) = 7.2$ Hz, 3H; PC*H*CH$_3$), 0.99 (dd, $J(P,H) = 13.1$, $J(H,H) = 7.2$ Hz, 18H; PCHC*H*$_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 261.4$ (dd, $J(Rh,C) =$ 51.5, $J(P,C) = 17.2$ Hz; Rh=C), 145.9, 144.7 (both s; *ipso*-C of C_6H_5 and $C_6H_4CH_3$), 135.6 (s; *para*-C of $C_6H_4CH_3$), 131.9, 130.4, 130.1, 129.1, 128.3 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5 and *ortho*- and *meta*-C of $C_6H_4CH_3$), 86.1 (dd, $J(Rh,C) = J(P,C) = 3.2$ Hz; C_5H_5), 26.7 (d, $J(P,C) =$ 19.1 Hz; P*C*HCH$_3$), 21.7 (s; $C_6H_4CH_3$), 20.4 (s; PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 58.0$ (d, $J(Rh,P) = 244.1$ Hz); elemental analysis for $C_{28}H_{38}PRh$ (508.5): calcd: C 66.14, H 7.53; found: C 66.02, H 7.39.

[(η^5-C$_5$H$_5$)Rh{=C(*p*-Tol)$_2$}(P*i*Pr$_3$)] (2e): Compound **2e** was prepared as described for **2d**, from **1e** (74 mg, 0.11 mmol) and NaC_5H_5 (50 mg, 0.56 mmol) in THF (10 mL); yield 50 mg (84 %). Deep blue crystals; m.p. 36 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.76–6.79$ (m, 8H; *ortho*- and *meta*-H of $C_6H_4CH_3$), 5.05 (dd, $J(Rh,H) = J(P,H) =$ 0.9 Hz, 5H; C_5H_5), 1.92 (s, 6H; $C_6H_4CH_3$), 1.54 (br sept, $J(H,H) = 7.2$ Hz, 3H; PC*H*CH$_3$), 1.00 (dd, $J(P,H) = 13.0$, $J(H,H) =$ 7.2 Hz, 18H; PCHC*H*$_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 262.0$ (dd, $J(Rh,C) = 50.2$, $J(P,C) = 17.2$ Hz; Rh=C), 142.0 (s; *ipso*-C of $C_6H_4CH_3$), 136.0 (s; *para*-C of $C_6H_4CH_3$), 131.9, 128.9, 128.3, 127.7 (all s; *ortho*- and *meta*-C of $C_6H_4CH_3$), 86.2 (dd, $J(Rh,C) = J(P,C) =$ 2.5 Hz; C_5H_5), 26.8 (d, $J(P,C) = 20.3$ Hz; P*C*HCH$_3$), 21.6 (s; $C_6H_4CH_3$), 20.5 (s; PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 58.5$ (d, $J(Rh,P) =$ 245.8 Hz); elemental analysis for $C_{29}H_{40}PRh$ (522.5): calcd: C 66.66, H 7.72; found: C 66.25, H 7.58.

[(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(P*i*Pr$_2$Ph)] (2f): Compound **2f** was prepared as described for **2d**, from **1f** (84 mg, 0.12 mmol) and NaC_5H_5 (53 mg, 0.60 mmol) in THF (10 mL); yield 53 mg (84 %). Deep blue crystals; m.p. 45 °C (decomp.); ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.61–7.51$ (m, 6H; *ortho*-H of C_6H_5P and C_6H_5), 7.06–6.99 (m, 9H; *meta*- and *para*-H of C_6H_5P and C_6H_5), 4.91 (dd, $J(Rh,H) = J(P,H) = 0.8$ Hz, 5H; C_5H_5), 1.53 (m, 2H; PC*H*CH$_3$), 0.82 (dd, $J(P,H) = 15.2$, $J(H,H) = 6.9$ Hz, 6H; PCHC*H*$_3$), 0.76 (dd, $J(P,H) = 13.6$, $J(H,H) = 6.8$ Hz, 6H; PCHC*H*$_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 265.1$ (dd, $J(Rh,C) = 50.4$, $J(P,C) = 18.0$ Hz; Rh=C), 135.7, 135.3 (both s; *ipso*-C of C_6H_5), 135.2 (d, $J(P,C) = 31.1$ Hz; *ipso*-C of C_6H_5P), 134.9 (d, $J(P,C) = 18.9$ Hz; *meta*-C of C_6H_5P), 134.3 (d, $J(P,C) = 9.8$ Hz; *ortho*-C of C_6H_5P), 129.0, 128.3, 128.2, 127.5, 126.8, 125.2 (all s; *para*-C of C_6H_5P and *ortho*-, *meta*-, and *para*-C of C_6H_5), 86.9 (dd, $J(Rh,C) = J(P,C) =$ 2.5 Hz; C_5H_5), 20.0 (d, $J(P,C) = 18.9$ Hz; P*C*HCH$_3$), 18.1 (s; PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 53.5$ (d, $J(Rh,P) = 248.0$ Hz); elemental analysis for $C_{30}H_{34}PRh$ (528.5): calcd: C 68.18, H 6.48; found: C 68.19, H 6.79.

[(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(P*i*PrPh$_2$)] (2g): A solution of **1g** (89 mg, 0.12 mmol) in THF (10 mL) was treated with NaC_5H_5 (51 mg, 0.58 mmol) and stirred for 30 min at room temperature. The solvent was removed in vacuo, and the bluish-black residue was extracted with pentane (15 mL). The extract was concentrated to about 2 mL in vacuo, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 2.5 cm). With hexane, a blue-violet fraction was eluted, from which after removal of the solvent a deep blue solid was obtained; yield 53 mg (79 %); m.p. 44 °C (decomp); ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.61–7.46$ (m, 8H; *ortho*-H of C_6H_5P and C_6H_5), 7.10–7.01 (m, 12H; *meta*- and *para*-H of C_6H_5P and C_6H_5), 4.88 (dd, $J(Rh,H) = J(P,H) = 0.8$ Hz, 5H; C_5H_5), 1.28 (m, 1H; PC*H*CH$_3$), 1.02 (dd, $J(P,H) = 16.0$, $J(H,H) = 7.0$ Hz, 3H; PCHC*H*$_3$), 0.70 (dd, $J(P,H) = 15.1$, $J(H,H) = 6.9$ Hz, 3H; PCHC*H*$_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 264.2$ (dd, $J(Rh,C) = 49.8$, $J(P,C) = 17.6$ Hz; Rh=C), 138.4 (d, $J(P,C) = 35.2$ Hz; *ipso*-C of C_6H_5P), 134.1 (d, $J(P,C) = 10.1$ Hz; *ortho*-C of C_6H_5P), 131.3 (d, $J(P,C) = 10.6$ Hz; *meta*-C of C_6H_5P), 131.0, 130.2 (both s; *ipso*-C of C_6H_5), 128.8, 128.7, 128.5, 128.1, 127.9, 127.5, 127.4 (all s; *para*-C of C_6H_5P and *ortho*-, *meta*-, and *para*-C of C_6H_5), 87.9 (dd, $J(Rh,C) =$ $J(P,C) = 2.9$ Hz; C_5H_5), 22.0 (d, $J(P,C) = 21.8$ Hz; P*C*HCH$_3$), 19.1 (s; PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 51.9$ (d, $J(Rh,P) =$

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250.7 Hz); elemental analysis for $C_{33}H_{32}PRh$ (562.5): calcd: C 70.46, H 5.73; found: C 69.97, H 5.79.

[(η^5-C_5H_5)Rh(=CPh_2)(PPh_3)] (2h): Compound **2h** was prepared as described for **2g**, from **1h** (99 mg, 0.12 mmol) and NaC_5H_5 (53 mg, 0.60 mmol) in THF (10 mL); yield 47 mg (66 %). Blue-violet solid; m.p. 56 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.60$ (m, 10H; *ortho*-H of C_6H_5P and C_6H_5), 6.96 (m, 15H; *meta*- and *para*-H of C_6H_5P and C_6H_5), 4.86 (dd, $J(Rh,H) = J(P,H) = 0.8$ Hz, 5H; C_5H_5); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 269.1$ (dd, $J(Rh,C) = 49.8$, $J(P,C) = 16.1$ Hz; Rh=C), 138.6 (d, $J(P,C) = 41.3$ Hz; *ipso*-C of C_6H_5P), 134.5 (d, $J(P,C) = 13.1$ Hz; *meta*-C of C_6H_5P), 134.2, 134.1 (both s; *ipso*-C of C_6H_5), 128.8, 128.1, 127.9, 126.8, 124.9 (all s; *para*-C of C_6H_5P and *ortho*-, *meta*-, and *para*-C of C_6H_5), 127.6 (d, $J(P,C) = 9.1$ Hz; *ortho*-C of C_6H_5P), 88.3 (dd, $J(Rh,C) = J(P,C) = 3.0$ Hz; C_5H_5); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 47.7$ (d, $J(Rh,P) = 258.7$ Hz); elemental analysis for $C_{36}H_{30}PRh$ (596.5): calcd: C 72.49, H 5.07; found: C 72.67, H 5.10.

[(η^5-C_5H_5)Rh(=CPh_2)($PMePh_2$)] (2i): Compound **2i** was prepared as described for **2g**, from **1i** (92 mg, 0.13 mmol) and NaC_5H_5 (57 mg, 0.65 mmol) in THF (10 mL); yield 43 mg (62 %). Red-violet solid; m.p. 32 °C (decomp); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.71 - 7.44$ (m, 8H; *ortho*-H of C_6H_5P and C_6H_5), 7.05 (m, 12H; *meta*- and *para*-H of C_6H_5P and C_6H_5), 4.80 (br s, 5H; C_5H_5), 1.04 (dd, $J(P,H) = 8.4$, $J(Rh,H) = 1.6$ Hz, 3H; PCH_3); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 265.7$ (dd, $J(Rh,C) = 50.8$, $J(P,C) = 17.6$ Hz; Rh=C), 142.4 (d, $J(P,C) = 40.2$ Hz; *ipso*-C of C_6H_5P), 132.5 (d, $J(P,C) = 13.1$ Hz; *meta*-C of C_6H_5P), 132.0 (d, $J(P,C) = 11.1$ Hz; *ortho*-C of C_6H_5P), 130.2 (s; *ipso*-C of C_6H_5), 128.8, 127.9, 124.7, 124.3 (all s; *para*-C of C_6H_5P and *ortho*-, *meta*-, and *para*-C of C_6H_5), 87.8 (dd, $J(Rh,C) = J(P,C) = 3.0$ Hz; C_5H_5), 15.7 (dd, $J(P,C) = 26.2$, $J(Rh,C) = 2.8$ Hz; PCH_3); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 24.5$ (d, $J(Rh,P) = 257.2$ Hz); elemental analysis for $C_{31}H_{28}PRh$ (534.4): calcd: C 69.67, H 5.28; found: C 70.05, H 5.14.

[(η^5-C_5H_5)Rh(=CPh_2)(CO)] (3): A slow stream of CO was passed through a solution of **2a** (70 mg, 0.12 mmol) in pentane (10 mL) for 30 s at room temperature. While the solution was stirred for 1 h, a change of color from blue to violet and finally to deep red occurred. The solvent was removed, the residue was dissolved in hexane (2 mL), and the solution was chromatographed on Al_2O_3 (neutral, activity grade III, height of column 3.0 cm). With hexane, a red fraction was eluted, from which after removal of the solvent a red solid was obtained. The solid was washed twice with small quantities of methanol (−20 °C) and recrystallized from pentane (3 mL). Upon storing at −78 °C for 3 h, red needles were formed, which were separated from the mother liquor, washed with small quantities of pentane (−20 °C), and dried; yield 38 mg (87 %); m.p. 49 °C (decomp); MS (70 eV): *m*/*z* (I_r): 362 (13; [M^+]), 334 (100; [$M^+ - CO$]), 297 (5.4; [$M^+ - C_5H_5$]), 269 (3.3; [$Rh{=}CPh_2]^+$), 196 (0.3; [$M^+ - CPh_2$]), 168 (55; [$RhC_5H_5]^+$); IR (KBr): $\tilde{\nu} = 1982$ cm^{-1} (CO); ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.43$ (m, 4H; *ortho*-H of C_6H_5), 7.14–6.91 (m, 6H; *meta*- and *para*-H of C_6H_5), 4.92 (d, $J(Rh,H) = 0.7$ Hz, 5H; C_5H_5); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 286.7$ (d, $J(Rh,C) = 48.0$ Hz; Rh=C), 192.7 (d, $J(Rh,C) = 101.7$ Hz; Rh−CO), 164.1, 161.6 (both s; *ipso*-C of C_6H_5), 128.8, 128.3, 127.7, 127.0, 126.8, 125.2 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5), 89.7 (d, $J(Rh,C) = 3.5$ Hz; C_5H_5); elemental analysis for $C_{19}H_{15}ORh$ (362.2): calcd: C 63.00, H 4.17; found: C 63.08, H 4.12.

[(η^5-C_5H_5)Rh(=CPh_2)(PMe_3)] (4): A solution of **2a** (59 mg, 0.10 mmol) in pentane (10 mL) was treated with a solution of PMe_3 (10 μL, 0.10 mmol) in pentane (3 mL) and stirred for 1 h at room temperature. A gradual change of color from blue to violet occurred. The solvent was removed in vacuo, and the violet residue was washed with small quantities of methanol (−20 °C). The solid was recrystallized from pentane (5 mL). Upon storing at −78 °C for 1 h, violet crystals were formed, which were separated from the mother liquor, washed with small quantities of pentane (−20 °C), and dried; yield 34 mg (83 %); m.p. 113 °C (decomp); MS (70 eV): *m*/*z* (I_r): 410 (49; [M^+]), 345 (0.7; [$M^+ - C_5H_5$]), 334 (66; [$M^+ - PMe_3$]), 332 (100; [$C_2Ph_4]^+$), 244 (1.4; [$M^+ - CPh_2$]), 242 (10; [$Ph_2CPMe_3]^+$), 168 (38; [$RhC_5H_5]^+$); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.30 - 7.16$ (m, 4H; *ortho*-H of C_6H_5), 7.11–7.00 (m, 6H; *meta*- and *para*-H of C_6H_5), 4.95 (dd, $J(Rh,H) = J(P,H) = 0.8$ Hz, 5H; C_5H_5), 1.11 (dd, $J(P,H) = 8.9$ Hz, $J(Rh,H) = 1.4$ Hz, 9H; PCH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 263.2$ (dd, $J(Rh,C) = 50.9$, $J(P,C) = 16.5$ Hz; Rh=C), 166.0, 164.0 (both s; *ipso*-C of C_6H_5), 127.0, 126.5, 125.5, 125.0, 124.2, 123.7 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5), 85.9 (dd, $J(Rh,C) = J(P,C) = 3.0$ Hz; C_5H_5), 22.5 (d, $J(P,C) = 26.3$ Hz; PCH_3); ^{31}P NMR ($CDCl_3$, 81.0 MHz): $\delta = -10.0$ (d, $J(Rh,P) = 248.5$ Hz); elemental analysis for $C_{21}H_{24}PRh$ (410.3): calcd: C 61.47, H 5.90; found: C 61.42, H 6.09.

[(η^5-C_5H_5)Rh(=CPh_2)(CNMe)] (5): A solution of **2a** (159 mg, 0.27 mmol) in pentane (15 mL) was treated with MeNC (15 μL, 0.27 mmol) and stirred for 1 h at room temperature. A change of color from blue to red-violet occurred. The solvent was removed in vacuo, the residue was dissolved in diethyl ether (1 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity grade III, height of column 3.0 cm). With benzene, a red-violet fraction was eluted which was brought to dryness in vacuo. The residue was recrystallized from pentane (5 mL). Upon storing the solution at −78 °C for 2 d, red-violet crystals precipitated, which were separated from the mother liquor, washed twice with small quantities of pentane (−20 °C) and dried; yield 84 mg (83 %); m.p. 94 °C (decomp); MS (70 eV): *m*/*z* (I_r): 375 (5.2; [M^+]), 334 (11; [$M^+ - CNMe$]), 209 (0.7; [$M^+ - CPh_2$]), 168 (11; [$RhC_5H_5]^+$); IR (KBr): $\tilde{\nu} = 2129$ cm^{-1} (C≡N); ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.68$ (m, 4H; *ortho*-H of C_6H_5), 7.10–6.97 (m, 6H; *meta*- and *para*-H of C_6H_5), 5.12 (d, $J(Rh,H) = 0.6$ Hz, 5H; C_5H_5), 2.00 (d, $J(Rh,H) = 0.9$ Hz, 3H; $CNCH_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 268.4$ (d, $J(Rh,C) = 51.3$ Hz; Rh=C), 165.4, 163.2 (both s; *ipso*-C of C_6H_5), 150.4 (d, $J(Rh,C) = 96.7$ Hz; RhCN), 138.8, 136.4, 132.0, 130.8, 125.9, 122.8 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5), 86.8 (d, $J(Rh,C) = 3.4$ Hz; C_5H_5), 28.2 (s; $CNCH_3$); elemental analysis for $C_{20}H_{18}NRh$ (375.3): calcd: C 64.01, H 4.83, N 3.73; found: C 63.93, H 4.64, N 3.92.

[(η^5-C_5H_5)Rh(=CPh_2)($CNCH_2Ph$)] (6): Compound **6** was prepared as described for **5**, from **2a** (139 mg, 0.24 mmol) and $PhCH_2NC$ (29 μL, 0.24 mmol) in pentane (15 mL); yield 91 mg (84 %). Red-violet crystals; m.p. 97 °C (decomp); MS (70 eV): *m*/*z* (I_r): 451 (1.3; [M^+]), 334 (1.9; [$M^+ - CNCH_2Ph$]), 285 (28; [$M^+ - CPh_2$]), 168 (35; [$RhC_5H_5]^+$); IR (KBr): $\tilde{\nu} = 2122$ cm^{-1} (C≡N); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.69$ (m, 2H; *ortho*-H of $CH_2C_6H_5$), 7.50–7.44 (m, 4H; *ortho*-H of C_6H_5), 7.13–6.91 (m, 9H; *meta*- and *para*-H of C_6H_5 and $CH_2C_6H_5$), 5.13 (d, $J(Rh,H) = 0.5$ Hz, 5H; C_5H_5), 3.85 (br s, 2H; $CH_2C_6H_5$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 269.9$ (d, $J(Rh,C) = 50.8$ Hz; Rh=C), 165.5, 163.2, 160.1 (all s; *ipso*-C of C_6H_5 and $CH_2C_6H_5$), 153.2 (d, $J(Rh,C) = 98.6$ Hz; RhCN), 130.7, 128.8, 127.0, 126.2, 125.7, 125.0, 124.5, 124.4, 123.6 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5 and $CH_2C_6H_5$), 87.1 (d, $J(Rh,C) = 3.1$ Hz; C_5H_5), 47.4 (s; $CH_2C_6H_5$); elemental analysis for $C_{26}H_{22}NRh$ (451.4): calcd: C 69.19, H 4.92, N 3.11; found: C 68.89, H 4.93, N 2.99.

[(η^5-C_5H_5)Rh(=CPh_2)(CN*t*Bu)] (7): Compound **7** was prepared as described for **5**, from **2a** (84 mg, 0.14 mmol) and CN*t*Bu (17 μL, 0.14 mmol) in pentane (15 mL); yield 53 mg (89 %). Red-violet needles; m.p. 88 °C (decomp); MS (70 eV): *m*/*z* (I_r): 417 (42; [M^+]), 334 (100; [$M^+ -$ CN*t*Bu]), 269 (5.0; [$Rh{=}CPh_2]^+$), 251 (0.4; [$M^+ - CPh_2$]), 168 (61; [$RhC_5H_5^+$]); IR (KBr): $\tilde{\nu} = 2118$ cm^{-1} (C≡N); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.55 - 7.45$ (m, 4H; *ortho*-H of C_6H_5), 7.11 (m, 2H; *para*-H of C_6H_5), 7.01 (m, 4H; *meta*-H of C_6H_5), 5.14 (d, $J(Rh,H) = 0.4$ Hz, 5H; C_5H_5), 0.78 (s, 9H; $C(CH_3)_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 267.9$ (d, $J(Rh,C) = 50.3$ Hz; Rh=C), 165.6, 163.9 (both s; *ipso*-C of C_6H_5), 148.2 (d, $J(Rh,C) = 98.3$ Hz; RhCN), 127.5, 127.0, 126.3, 125.6, 125.4, 125.0 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5), 86.7 (d, $J(Rh,C) = 3.9$ Hz; C_5H_5), 55.9 (s; $C(CH_3)_3$), 30.1 (s; $C(CH_3)_3$); elemental analysis for $C_{23}H_{24}NRh$ (417.4): calcd: C 66.19, H 5.80, N 3.36; found: C 66.50, H 6.04, N 3.23.

Reaction of compound 2a with R_2CN_2 (R = Ph, *p*-Tol): A solution of **2a** (59 mg, 0.10 mmol) in pentane (10 mL) was treated at −78 °C with a solution of Ph_2CN_2 (19 mg, 0.10 mmol) in pentane (2 mL). On warming the mixture to room temperature, a change of color from blue to brown occurred. After the solvent was removed in vacuo, an oily residue was obtained, which was identified by ^{1}H and ^{13}C NMR spectroscopy as a mixture of the starting material **2a** and $Ph_2C{=}N{-}N{=}CPh_2$ (**8**). If an excess of Ph_2CN_2 was used, **8** was formed in quantitative yield while a partial decomposition of **2a** took place. Column chromatography on Al_2O_3 afforded a pure sample of **8**, which was identified by elemental analysis. The reaction of **2a** with $(p\text{-Tol})_2CN_2$ proceeded analogously and gave $(p\text{-Tol})_2C{=}N{-}N{=}C(p\text{-Tol})_2$ (**9**) in 95 % yield.

Reaction of compound 2c with CO: A slow stream of CO was passed through a solution of **2c** (49 mg, 0.10 mmol) in pentane (10 mL) for 30 s at room temperature. While the solution was stirred for 5 h, a change of color from blue to red-violet occurred. The solvent was removed in vacuo, the oily residue was dissolved in hexane (1 mL), and the solution was

chromatographed on Al_2O_3 (neutral, activity grade III, height of column 6.0 cm). With hexane, a orange-yellow fraction was eluted, from which after removal of the solvent an orange oil was obtained. This was identified by IR, ^1H, and ^{13}C NMR spectroscopy as [(η^5-C_5H_5)Rh(CO)(P*i*Pr$_3$)] (**10**).[10] With hexane/benzene (1:1), a red fraction was eluted, which contained diphenylketene (**11**), identified by IR and ^{13}C NMR spectroscopy;[27] yield 105 mg (55 %).

Reaction of compound 2c with CN*t*Bu: A solution of **2c** (49 mg, 0.10 mmol) in pentane (10 mL) was treated with CN*t*Bu (110 μL, 1.00 mmol) at room temperature. After the reaction mixture was stirred for 5 h, it was worked up analogously as described for the solution obtained from **2c** and CO. The products were identified by IR, ^1H, and ^{13}C NMR spectroscopy as [(η^5-C_5H_5)Rh(CN*t*Bu)(P*i*Pr$_3$)] (**12**) and $Ph_2C=C=N$*t*Bu (**13**);[28] yield (of **13**) 136 mg (55 %). Data for **12**: IR (C_6H_6): $\tilde{\nu}$ = 2143, 2032 cm^{-1} (C≡N); ^1H NMR (C_6D_6, 200 MHz): δ = 5.18 (br s, 5H; C_5H_5), 1.36 (dsept, J(P,H) = 13.1, J(H,H) = 7.2 Hz, 3H; PC*H*CH$_3$), 1.09 (dd, J(P,H) = 13.1, J(H,H) = 7.2 Hz, 18H; PCHC*H*$_3$), 0.92 (s, 9H; C(CH$_3$)$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 83.1 (d, J(Rh,P) = 206.3 Hz).

[(η^5-C_5H_5)Rh(C_2H_4)(Sb*i*Pr$_3$)) (14): a) A solution of **17** (67 mg, 0.10 mmol) in THF (10 mL) was treated with NaC_5H_5 (44 mg, 0.50 mmol) and stirred for 45 min at room temperature. A change of color from orange-brown to orange-yellow occurred. The solvent was removed in vacuo, the orange-yellow oily residue extracted with pentane (10 mL), and the extract concentrated to 0.5 mL. The solution was then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5.0 cm). With hexane, an orange-yellow fraction was eluted, from which after removal of the solvent an orange-yellow oil was obtained. This was dried at 10^{-3} mbar for 3 h; yield 29 mg (65 %).

b) A solution of **18** (83 mg, 0.10 mmol) in THF (10 mL) was treated with NaC_5H_5 (88 mg, 1.00 mmol) and stirred for 30 min at room temperature. The solvent was removed in vacuo and the residue was worked up as described for a); yield 77 mg (86 %).

c) A slow stream of ethene was passed through a solution of **2a** (57 mg, 0.10 mmol) in pentane (10 mL) for 20 s at room temperature. While the solution was stirred for 1 h, a change of color from deep blue to orange occurred. The solvent was removed in vacuo and the residue was worked up as described for a). The ^1H NMR spectrum confirmed that 1.1-diphenyl-1-propene (**16**)[29] was formed as the organic by-product; yield (of **14**) 34 mg (77 %). Data for **14**: Orange-yellow oil; ^1H NMR (C_6D_6, 200 MHz): δ = 5.12 (d, J(Rh,H) = 0.6 Hz, 5H; C_5H_5), 2.77 – 2.58, 2.24 – 2.08 (both m, 2H each; C_2H_4), 1.68 (sept, J(H,H) = 7.3 Hz, 3H; SbC*H*CH$_3$), 1.10 (d, J(H,H) = 7.3 Hz, 18H; SbCHC*H*$_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 82.0 (d, J(Rh,C) = 4.2 Hz; C_5H_5), 36.5 (d, J(Rh,C) = 13.6 Hz; C_2H_4), 21.4 (s; SbCH*C*H$_3$), 17.0 (d, J(Rh,C) = 2.5 Hz; SbC*H*CH$_3$); elemental analysis for $C_{16}H_{30}RhSb$ (447.1): calcd: C 42.99, H 6.76; found: C 43.12, H 6.62.

Reaction of compound 2c with ethene: In an NMR tube, a slow stream of ethene was passed through a solution of **2c** (25 mg, 0.05 mmol) in C_6D_6 (0.5 mL) for 10 s at room temperature. During 2 h, a change of color from deep blue to orange-yellow occurred. The ^1H NMR spectrum confirmed that both **15**[30] and 1.1-diphenyl-1-propene (**16**)[29] were formed; yield virtually quantitative.

[(η^5-C_5H_5)Rh(κ^2-Ph*N*NN*N*Ph)] (19): a) A solution of **2a** (68 mg, 0.12 mmol) in pentane (10 mL) was treated at −78 °C with PhN_3 (56 μL, 0.48 mmol). After the reaction mixture was warmed to room temperature, it was stirred for 45 min. A change of color from blue to red-brown, accompanied by the precipitation of a solid, occurred. The solvent was removed in vacuo, the residue was dissolved in a small quantity of diethyl ether, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5.0 cm). With diethyl ether, a red fraction was eluted, from which after removal of the solvent a red solid was obtained. This was washed three times with small quantities of pentane and dried; yield 30 mg (68 %).

b) A solution of **2c** (59 mg, 0.12 mmol) in pentane (10 mL) was treated at −78 °C with PhN_3 (56 μL, 0.48 mmol). After warming to room temperature, the reaction mixture was worked up as described for a); yield 30 mg (68 %); m.p. 224 °C (decomp); MS (70 eV): m/z (I$_r$): 378 (30; [M^+]), 350 (26; [$M^+ - N_2$]), 259 (100; [$C_5H_5RhNPh]^+$), 168 (91; [$RhC_5H_5]^+$); ^1H NMR (C_6D_6, 200 MHz): δ = 8.04 (m, 4H; *ortho*-H of C_6H_5), 7.65 – 7.45 (m, 6H; *meta*- and *para*-H of C_6H_5), 5.41 (d, J(Rh,H) = 0.7 Hz, 5H; C_5H_5); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 157.3 (s; *ipso*-C of C_6H_5), 128.9, 124.8, 121.3 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5), 81.6 (d, J(Rh,C) = 6.4 Hz; C_5H_5); elemental analysis for $C_{17}H_{15}N_4Rh$ (378.2): calcd: C 53.98, H 4.00, N 14.81; found: C 53.76, H 3.74, N 14.91.

[(η^5-C_5H_5)Rh{κ^2-(*p*-Tol)*N*NN*N*(*p*-Tol)}] (20): Compound **20** was prepared as described for **19**, from **2a** (71 mg, 0.12 mmol) or **2c** (59 mg, 0.12 mmol) and (*p*-Tol)N_3 (72 μL, 0.48 mmol) in pentane (10 mL); yield 35 mg (71 %). Red solid; m.p. 172 °C (decomp); MS (70 eV): m/z (I$_r$): 406 (29; [M^+]), 378 (24; [$M^+ - N_2$]), 273 (100; [C_5H_5RhN(*p*-Tol)]$^+$), 168 (92; [$RhC_5H_5]^+$), 133 (4; [(*p*-Tol)$N_3]^+$); ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.59 (m, 4H; *ortho*-H of $C_6H_4CH_3$), 7.05 (m, 4H; *meta*-H of $C_6H_4CH_3$), 5.00 (d, J(Rh,H) = 0.7 Hz, 5H; C_5H_5), 2.23 (s, 6H; $C_6H_4CH_3$); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 154.1 (d, J(Rh,C) = 3.8 Hz; *ipso*-C of $C_6H_4CH_3$), 136.1, 129.3, 123.8 (all s; *para*-, *ortho*- and *meta*-C of $C_6H_4CH_3$), 81.9 (d, J(Rh,C) = 6.1 Hz; C_5H_5), 21.1 (s; $C_6H_4CH_3$); elemental analysis for $C_{19}H_{19}N_4Rh$ (406.3): calcd: C 56.16, H 4.71, N 13.79; found: C 55.80, H 4.81, N 13.89.

[(η^5-C_5H_5)Rh(κ^2-SCPh$_2$)(CO)] (21): A solution of **3** (57 mg, 0.16 mmol) in benzene (10 mL) was treated with small portions of sulfur (5.0 mg, 0.16 mmol) and stirred for 1 h at room temperature. A gradual change of color from red to brown occurred. The solvent was removed in vacuo, the residue was dissolved in hexane (10 mL), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5.0 cm). With hexane, a first red-brown fraction was eluted, which was thrown away. With diethyl ether, a second yellow fraction was eluted, which after removal of the solvent gave a light yellow solid. This was washed with small quantities of pentane (−20 °C) and recrystallized from pentane (5 mL) at −78 °C. Upon storing the solution for 3 d, a light yellow microcrystalline solid precipitated, which was separated from the mother liquor, washed with small quantities of pentane (−20 °C) and dried; yield 40 mg (65 %); m.p. 146 °C (decomp); MS (70 eV): m/z (I$_r$): 394 (8.6; [M^+]), 366 (100; [M^+ − CO]), 362 (1.1; [$M^+ - S$]), 334 (1.7; [$C_5H_5RhCPh_2]^+$), 329 (14; [$M^+ - C_5H_5$]), 301 (26; [Rh(S)$CPh_2]^+$), 200 (2.2; [$C_5H_5RhS]^+$), 198 (41; [$SCPh_2]^+$), 196 (23; [$C_5H_5RhCO]^+$), 168 (14; [$RhC_5H_5]^+$); IR (KBr): $\tilde{\nu}$ = 2000 cm^{-1} (CO); ^1H NMR (C_6D_6, 400 MHz): δ = 7.83, 7.75 (both m, 2H each; *ortho*-H of C_6H_5), 7.11, 6.96 (both m, 2H each; *meta*-H of C_6H_5), 7.03, 6.86 (both m, 1H each; *para*-H of C_6H_5), 4.57 (d, J(Rh,H) = 0.5 Hz, 5H; C_5H_5); ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 186.4 (d, J(Rh,C) = 83.2 Hz; RhCO), 151.3, 150.6 (both s; *ipso*-C of C_6H_5), 132.1, 127.8, 127.3, 127.2, 126.5, 125.9 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5), 93.3 (d, J(Rh,C) = 16.6 Hz; Rh*C*Ph$_2$), 92.2 (d, J(Rh,C) = 4.2 Hz; C_5H_5); elemental analysis for $C_{19}H_{15}ORhS$ (394.3): calcd: C 57.88, H 3.83; found: C 58.12, H 3.93.

[(η^5-C_5H_5)Rh(κ^2-SeCPh$_2$)(CO)] (22): A solution of **3** (63 mg, 0.17 mmol) in benzene (10 mL) was treated with small portions of red selenium (13.7 mg, 0.17 mmol) and stirred for 1 h at room temperature. The solvent was removed in vacuo, the residue was dissolved in hexane (10 mL), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3.0 cm). With hexane/diethyl ether, an orange fraction was eluted, which after removal of the solvent gave an orange-yellow solid. This was recrystallized from pentane (10 mL) at −78 °C. Upon storing the solution for 5 h, an orange-yellow microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with 2 mL portions of pentane (−20 °C) and dried; yield 63 mg (82 %); m.p. 111 °C (decomp); MS (70 eV): m/z (I$_r$): 441 (8.8; [M^+]), 413 (68; [M^+ − CO), 362 (0.2; [$M^+ - Se$]), 348 (26; [$RhSeCPh_2]^+$), 334 (3.9; [$C_5H_5RhCPh_2]^+$), 247 (4.8; [$C_5H_5RhSe]^+$), 245 (11; [$SeCPh_2]^+$), 196 (4.5; [$C_5H_5RhCO]^+$), 168 (19; [$RhC_5H_5]^+$); IR (KBr): $\tilde{\nu}$ = 2001 cm^{-1} (CO); ^1H NMR (C_6D_6, 200 MHz): δ = 7.78 – 7.64 (m, 4H; *ortho*-H of C_6H_5), 7.14 – 6.84 (m, 6H; *meta*- and *para*-H of C_6H_5), 4.58 (d, J(Rh,H) = 0.7 Hz, 5H; C_5H_5); ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 187.0 (d, J(Rh,C) = 82.2 Hz; RhCO), 154.1, 153.6 (both s; *ipso*-C of C_6H_5), 132.7, 127.9, 127.7, 127.2, 126.5, 125.6 (all s; *ortho*-, *meta*- and *para*-C of C_6H_5), 96.3 (d, J(Rh,C) = 19.2 Hz; Rh*C*Ph$_2$), 92.3 (d, J(Rh,C) = 3.9 Hz; C_5H_5); elemental analysis for $C_{19}H_{15}ORhSe$ (441.2): calcd: C 51.73, H 3.43, Rh 23.32; found: C 52.01, H 3.35, Rh 23.35.

[(η^5-C_5H_5)Rh(κ^2-SCPh$_2$)(PMe$_3$)] (23): A solution of **4** (63 mg, 0.15 mmol) in benzene (5 mL) was treated with small portions of sulfur (4.9 mg, 0.15 mmol) and stirred for 15 min at room temperature. A gradual change of color from violet to brown occurred. The solvent was removed in vacuo, and the residue was washed several times with small quantities of pentane (−40 °C). The remaining light brown solid was dried in vacuo; yield 63 mg (95 %); m.p. 77 °C (decomp); MS (70 eV): m/z (I$_r$): 442 (53; [M^+]), 410 (16; [$M^+ - S$]), 366 (84; [$M^+ - PMe_3$]), 334 (3.7; [$C_5H_5RhCPh_2]^+$), 301 (28; [$RhSCPh_2]^+$), 269 (3.0; [$RhCPh_2]^+$), 198 (20; [$SCPh_2]^+$), 168 (24;

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$[RhC_5H_5]^+$); ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.99$ (m, 4H; *ortho*-H of C_6H_5), 7.09 (m, 2H; *para*-H of C_6H_5), 6.96 (m, 4H; *meta*-H of C_6H_5), 4.65 (dd, $J(Rh,H) = J(P,H) = 0.7$ Hz, 5H; C_5H_5), 0.54 (dd, $J(P,H) = 10.0$, $J(Rh,H) = 0.9$ Hz, 9H; PCH_3); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 154.0$, 152.1 (both s; *ipso*-C of C_6H_5), 133.6, 130.2, 127.5, 126.9, 125.4, 124.2 (all s; *ortho*-, *meta*-, and *para*-C of C_6H_5), 89.6 (dd, $J(Rh,C) = J(P,C) = 3.5$ Hz; C_5H_5), 79.1 (dd, $J(Rh,C) = 20.8$, $J(P,C) = 3.7$ Hz; Rh*C*Ph_2), 18.8 (d, $J(P,C) = 30.8$ Hz; PCH_3); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 1.0$ (d, $J(Rh,P) = 183.1$ Hz); elemental analysis for $C_{21}H_{24}PRhS$ (442.4): calcd: C 57.02, H 5.47; found: C 57.23, H 5.63.

[(η^5-C_5H_5)Rh(κ^2-SeCPh$_2$)(PMe$_3$)] (24): Compound **24** was prepared as described for **22**, from **4** (61 mg, 0.15 mmol) and red selenium (11.7 mg, 0.15 mmol) in benzene (10 mL); yield 61 mg (83%). Orange-yellow solid; m.p. 65 °C (decomp); MS (70 eV): *m*/*z* (I_r): 489 (58; $[M^+]$), 413 (90; $[M^+ - PMe_3]$), 410 (20; $[M^+ - Se]$), 348 (25; $[RhSeCPh_2]^+$), 334 (4.6; $[C_5H_5RhCPh_2]^+$), 269 (2.7; $[RhCPh_2]^+$), 245 (21; $[SeCPh_2]^+$), 168 (20; $[RhC_5H_5]^+$); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.95$ (m, 4H; *ortho*-H of C_6H_5), 7.01 (m, 2H; *para*-H of C_6H_5), 6.86 (m, 4H; *meta*-H of C_6H_5), 4.65 (dd, $J(Rh,H) = J(P,H) = 0.9$ Hz, 5H; C_5H_5), 0.59 (dd, $J(P,H) = 10.0$, $J(Rh,H) = 0.7$ Hz, 9H; PCH_3); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 156.5$, 154.6 (both s; *ipso*-C of C_6H_5), 134.0, 128.0, 127.8, 127.7, 125.5, 124.0 (all s; *ortho*-, *meta*-, and *para*-C of C_6H_5), 89.6 (dd, $J(Rh,C) = J(P,C) = 3.8$ Hz; C_5H_5), 85.1 (dd, $J(Rh,C) = 22.3$, $J(P,C) = 4.1$ Hz; Rh*C*Ph_2), 19.4 (d, $J(P,C) = 31.7$ Hz; PCH_3); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 0.6$ (d, $J(Rh,P) = 179.9$ Hz); elemental analysis for $C_{21}H_{24}PRhSe$ (489.3): calcd: C 51.55, H 4.94; found: C 51.73, H 5.09.

[(η^5-C_5H_5)(CO)Rh(μ-CPh$_2$)(CuCl)$_2$] (25): A solution of **3** (51 mg, 0.14 mmol) in benzene (10 mL) was treated with small portions of CuCl (27.0 mg, 0.28 mmol) and stirred for 2 h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated to about 1 mL in vacuo. The solution was then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With benzene, a red fraction was eluted, from which after removal of the solvent a deep red solid was obtained. This was washed several times with 5 mL portions of pentane and dried; yield 69 mg (87%); m.p. 126 °C (decomp); MS (70 eV): *m*/*z* (I_r): 560 (6.4; $[M^+]$), 532 (0.3; $[M^+ - CO]$), 433 (0.3; $[M^+ - CO - CuCl]$), 334 (100; $[C_5H_5RhCPh_2]^+$), 196 (5.7; $[C_5H_5RhCO]^+$), 168 (51; $[RhC_5H_5]^+$); IR (KBr): $\tilde{\nu} = 1989$ cm^{-1} (CO); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.43$ (m, 4H; *ortho*-H of C_6H_5), 7.27–7.17 (m, 4H; *meta*-H of C_6H_5), 7.11 (m, 2H; *para*-H of C_6H_5), 5.18 (br s, 5H; C_5H_5); ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 217.0$ (d, $J(Rh,C) = 45.8$ Hz; Rh*C*Ph_2), 189.9 (d, $J(Rh,C) = 86.7$ Hz; RhCO), 162.9, 157.4 (both s; *ipso*-C of C_6H_5), 129.7, 128.0, 127.6, 127.4, 127.1, 127.0 (all s; *ortho*-, *meta*-, and *para*-C of C_6H_5), 91.0 (d, $J(Rh,C) = 3.6$ Hz; C_5H_5); elemental analysis for $C_{19}H_{15}Cl_2Cu_2ORh$ (560.2): calcd: C 40.74, H 2.70, Rh 18.37; found: C 40.57, H 2.40, Rh 18.33.

[(η^5-C_5H_5)(CO)Rh(μ-CPh$_2$)Cu(η^5-C_5H_5)] (26): A solution of **25** (71 mg, 0.13 mmol) in THF (10 mL) was treated with a suspension of NaC_5H_5 (57.0 mg, 0.65 mmol) in THF (5 mL) and stirred for 30 min at room temperature. A gradual change of color from deep red to violet occurred. The solvent was removed in vacuo, the oily residue was extracted with benzene (10 mL), and the extract was concentrated to about 1 mL in vacuo. The solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4.0 cm). With benzene, a violet fraction was eluted, from which after removal of the solvent a red-violet solid was obtained. This was washed several times with small quantities of pentane (−20 °C) and dried; yield 48 mg (78%); m.p. 110 °C (decomp); MS (70 eV): *m*/*z* (I_r): 491 (1.2; $[M^+]$), 168 (16; $[RhC_5H_5]^+$), 128 (4.5; $[CuC_5H_5]^+$); IR (KBr): $\tilde{\nu} = 1974$ cm^{-1} (CO); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.17$ (m, 4H; *ortho*-H of C_6H_5), 7.02 (m, 2H; *para*-H of C_6H_5), 6.92 (m, 4H; *meta*-H of C_6H_5), 5.76 (s, 5H; CuC_5H_5) 4.97 (d, $J(Rh,H) = 0.5$ Hz, 5H; RhC_5H_5); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 206.3$ (d, $J(Rh,C) = 36.7$ Hz; Rh*C*Ph_2), 190.0 (d, $J(Rh,C) = 86.2$ Hz; RhCO), 163.4, 159.6 (both s; *ipso*-C of C_6H_5), 130.5, 127.8, 126.7, 126.6, 126.4, 126.2 (all s; *ortho*-, *meta*-, and *para*-C of C_6H_5), 99.7 (s; CuC_5H_5), 90.3 (d, $J(Rh,C) = 3.7$ Hz; RhC_5H_5); elemental analysis for $C_{24}H_{20}CuORh$ (490.9): calcd: C 58.72, H 4.11; found: C 59.06, H 3.79.

X-ray structure determination of compounds 3 and 22: Single crystals of **3** were grown from a saturated solution in hexane (60 °C), which was cooled to room temperature under an atmosphere of CO, and those of **22** from a saturated solution in hexane/toluene (4/1, 60 °C). Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied (ψ scans). The structures were solved by direct methods (SHELXS-97).[31] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method (SHELXL-97).[32] The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H = 0.95 Å) and used only in structure factor calculation.[33]

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Table 1. Crystal structure data of compounds **3** and **22**.

	3	**22**
formula	$C_{19}H_{15}ORh$	$C_{19}H_{15}ORhSe$
mol. mass	362.22	441.18
cryst. size [mm]	0.3 × 0.3 × 0.2	0.38 × 0.33 × 0.25
cryst. system	monoclinic	orthorhombic
space group	$P2_1/n$ (no. 14)	$Pca2_1$ (no. 29)
a [Å]	8.678(8)	15.289(2)
b [Å]	11.136(1)	6.551(2)
c [Å]	16.00(1)	16.496(4)
α [°]	90.0	90.0
β [°]	97.57(4)	90.0
γ [°]	90.0	90.0
V [Å^3]	1532.7(14)	1652.2(7)
Z	4	4
ρ_{calcd} [g cm^{-1}]	1.570	1.774
diffractometer	Enraf-Nonius CAD 4	Enraf-Nonius CAD 4
radiation (graphite-monochromated)	$Mo_{K\alpha}$ (0.71073 Å)	$Mo_{K\alpha}$ (0.71073 Å)
T [K]	223(2)	293(2)
μ [mm^{-1}]	1.109	3.235
transmission min. [%]	80.72	74.27
scan method	ω/θ	ω/θ
2θ (max) [°]	47.96	61.90
total reflections	2401	2949
unique reflections	2400	2948
observed reflections	1907	1979
	$[I > 2\sigma(I)]$	$[I > 2\sigma(I)]$
parameters refined	190	199
R_1	0.0236	0.0384
wR_2	0.0646	0.0914
GOF	1.041	1.067
reflection/parameter ratio	12.63	14.81
residual electron density [e Å^{-3}]	+0.464/−0.380	+0.605/−0.441

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[33] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-146602 and CCDC-146603. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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