Synthesis, Molecular Structure, and Reactivity of Rhodium(I) Complexes with Diazoalkanes and Related Substrates as Ligands

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A series of (diazoalkane)rhodium(I) compounds of the general composition *trans*-[RhCl(N$_2$CRR′)(P*i*Pr$_3$)$_2$] with R = R′ = Ph, *p*-C$_6$H$_4$Me, *p*-C$_6$H$_4$Cl and R = Ph, R′ = *p*-C$_6$H$_4$Me, *o*-C$_6$H$_4$Me, CH$_3$, CH$_2$Ph, CF$_3$ has been prepared from the dimer [RhCl(P*i*Pr$_3$)$_2$]$_2$ (**1**) and the diazoalkane. This preparative route has also been extended to complexes in which the N$_2$C unit(s) of 1,4-C$_6$H$_4${C(Ph)N$_2$}$_2$, 9-diazofluorene, 9,10-anthraquinone-9-diazide, and 3-methyl-1,4-naphthoquinone-1-diazide is (are) linked to a 14-electron [RhCl(P*i*Pr$_3$)$_2$] fragment. While C(CO$_2$Et)$_2$N$_2$ behaves as expected and affords upon treatment with **1** the complex *trans*-[RhCl{N$_2$C(CO$_2$Et)$_2$}(P*i*Pr$_3$)$_2$), CH(CO$_2$Et)N$_2$ reacts with the same starting material to give the dinitrogen derivative *trans*-[RhCl(N$_2$)(P*i*Pr$_3$)$_2$] (**12**). The reactions of *trans*-[RhCl(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (**2**) with both N$_2$CC$_4$Cl$_4$ and N$_2$CC$_4$Ph$_4$ afford *trans*-[RhCl(N$_2$CC$_4$X$_4$)(P*i*Pr$_3$)$_2$] (X = Cl, Ph), and the same type of ligand exchange takes place by treatment of *trans*-[RhCl(C$_2$H$_4$)(Sb*i*Pr$_3$)$_2$] with N$_2$CC$_4$Cl$_4$. The reactions of *trans*-[RhCl(N$_2$CRR′)(P*i*Pr$_3$)$_2$] (**3**−**7**, where R and R′ are aryl) with excess ethene give, instead of a disubstituted cyclopropane, exclusively the trisubstituted olefin CH$_3$CH=CRR′. The reaction of **1** with PhC(R)NNH$_2$ (R = Ph, Me) proceeds mainly by orthometalation to yield the six-coordinate rhodium(III) complexes [Rh(H)Cl{κ^2-*C*,*N*-C$_6$H$_4$C(NNH$_2$)R}(P*i*Pr$_3$)$_2$]; of these, that with R = Ph reacts with Al$_2$O$_3$ to give *trans*-[RhCl(N$_2$CPh$_2$)(P*i*Pr$_3$)$_2$] and **12**. The alkynylrhodium(I) derivatives *trans*-[Rh(C≡CX)(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (X = H, *t*Bu) behave similarly to **2** and afford upon treatment with Ph$_2$CN$_2$ and C$_{12}$H$_8$CN$_2$ the corresponding diazoalkane compounds *trans*-[Rh(C≡CX)(N$_2$CRR′)(P*i*Pr$_3$)$_2$] by ligand exchange. The reaction of **2** with the diazo ketones RC(O)C(Ph)N$_2$ (R = Ph, Me) leads to complexes of the general composition [RhCl{N$_2$C(Ph)C(O)Ph}(P*i*Pr$_3$)$_2$], in which the diazo ketone is probably coordinated in a chelating fashion to the metal center. The keto ester derivative (CH$_3$)$_2$CHCH$_2$CH$_2$C(O)C(CO$_2$Me)N$_2$ reacts with **2** to give a mixture of two isomers, one of which could be separated by fractional crystallization. The supposed chelating bonding mode of the diazo ligand in this compound via the terminal nitrogen and the keto oxygen could be confirmed by an X-ray crystal structure analysis.

Introduction

In the context of our studies on rhodium vinylidenes *trans*-[RhCl(=C=CRR′)(P*i*Pr$_3$)$_2$][1] and their homologues *trans*-[RhCl{=C(=C)$_n$RR′)(P*i*Pr$_3$)$_2$] (*n* = 2,[2] 4[3]), we also attempted to prepare the parent compounds of this series, having the general composition *trans*-[RhCl(=CRR′)(P*i*Pr$_3$)$_2$]. Since the obvious choice to generate the required carbene ligand :CRR′ was to use diazoalkanes RR′CN$_2$ as precursors, we treated the dimer [RhCl(P*i*Pr$_3$)$_2$]$_2$, which was previously employed as the starting material for the preparation of *trans*-[RhCl(=C=CRR′)(P*i*Pr$_3$)$_2$] and *trans*-[RhCl{=C(=C)$_n$RR′)(P*i*Pr$_3$)$_2$], with various diazoalkanes at ambient temperatures. After we failed to obtain the rhodium carbenes *trans*-[RhCl(=CRR′)(P*i*Pr$_3$)$_2$] by this route,[4] we found that it is more appropriate to prepare in the initial step the corresponding bis(stibine) derivatives *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$] and subsequently replace the two stibines for two phosphine ligands.[5] Both the bis(stibine) and the bis(phosphine) complexes could be converted to the η^5-cyclopentadienyl compounds [(η^5-C$_5$H$_5$)Rh(=CRR′)(E*i*Pr$_3$)] (E = P, Sb),[6] which, similarly to the square-planar counterparts, have a rich chemistry indeed.

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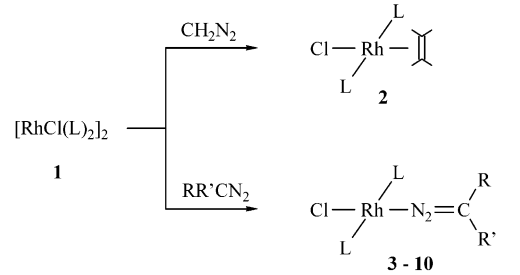
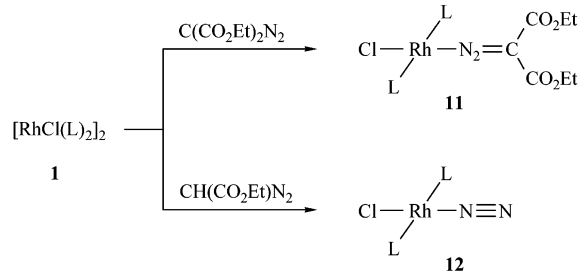
Scheme 1[a]



	R	R'		R	R'
3	Ph	Ph	**7**	*p*-C_6H_4Cl	*p*-C_6H_4Cl
4	*p*-Tol	*p*-Tol	**8**	Ph	CH_3
5	Ph	*p*-Tol	**9**	Ph	CH_2Ph
6	Ph	*o*-Tol	**10**	Ph	CF_3

[a] L = P*i*Pr$_3$.

Scheme 2[a]



[a] L = P*i*Pr$_3$.

The present paper describes the synthesis and molecular structure of the diazoalkane complexes *trans*-[RhCl(N_2CRR′)(P*i*Pr$_3$)$_2$], originally considered as useful precursors for the generation of four-coordinate rhodium carbenes, and the reactions of these compounds toward ethene. Moreover, we report the preparation of the series of alkynylrhodium(I) derivatives *trans*-[Rh(C≡CX)(N_2CRR′)(P*i*Pr$_3$)$_2$] and the isolation and structural characterization of an unusual rhodium complex with a coordinated diazo keto ester that behaves as a chelating ligand. Some preliminary results of this work have already been communicated.[4]

Results and Discussion

Preparation of Rhodium(I) Complexes with Coordinated Ph_2CN_2 and Derivatives Thereof. The peculiar dimer **1**[7] reacts with diazomethane in diethyl ether to give, instead of *trans*-[RhCl(=CH_2)(P*i*Pr$_3$)$_2$] or *trans*-[RhCl(N_2CH_2)(P*i*Pr$_3$)$_2$], exclusively the corresponding (ethene)rhodium compound **2** (Scheme 1), being also accessible from **1** and C_2H_4.[8] Since the reaction of **1** with CH_2N_2 is quite fast even at low temperature, we failed to find out whether the diazomethane and/or the carbene complex is formed as an intermediate.

Similarly to CH_2N_2, diphenyldiazomethane and derivatives thereof are also highly reactive toward compound **1** and afford either in diethyl ether or in toluene the diazoalkane complexes **3**−**10** in good to excellent yields. The addition of the RR′CN_2 ligand to the postulated 14-electron species [RhCl(P*i*Pr$_3$)$_2$], formed by dissociation of **1**,[9] is accompanied by a characteristic change of color from violet to green. The isolated products, with the exception of **10**, are air-sensitive but can be stored at room temperature under argon for days without decomposition. They were all characterized by elemental analysis and spectroscopic techniques. With respect to the bonding mode, the position of the ν(N_2C) stretching vibration at ca. 1935−1940 cm^{-1} in the IR spectra suggests an end-on coordination of the RR′CN_2 ligand.[10] The ^{1}H NMR spectra of **3**−**10** display one doublet of virtual triplets for the PCHCH_3 protons, indicating that, in contrast to the starting material **1**, the two phosphine units are in a trans disposition.[11,12] In the ^{13}C NMR spectra, the resonance for the diazoalkane carbon atom RR′CN_2 appears at δ 72.2−78.7 (**3**−**7**, **9**) or 65.9 (**10**) as a broad singlet, the broadening probably being due to the quadrupole moment of the nitrogen atoms. Regarding the stability of the products, it should be mentioned that complex **8**, formed from 1-phenyldiazoethane, in solution slowly decomposes to generate *trans*-[RhCl(N_2)(P*i*Pr$_3$)$_2$] (**12**).[8,13]

The dinitrogen compound **12** is also obtained from **1** and CH(CO_2Et)N_2 (see Scheme 2). In contrast, treatment of the starting material **1** with the diester C(CO_2Et)$_2N_2$ gives, under the same conditions as used for the preparation of **3**−**10**, the expected diazoalkane complex **11** in 80% isolated yield. The IR spectrum of the air-stable product shows the ν(C=O) stretching mode at 1730 cm^{-1}, thus almost the same position as for the free ligand. Therefore, a possible interaction of one of the C=O ester groups with the metal can be excluded. In this context we note that the reaction of **1** with PhC(O)CHN_2 leads to the formation of the unusual compound [RhCl(P*i*Pr$_3$){*i*Pr$_3$PCHC(O)Ph}], in which the functionalized ylide is coordinated like an η^3-allyl ligand via the ylidic carbon, the acyl carbon, and the oxygen to the rhodium center.[14]

The results covering the reactions of dimer **1** with 1,4-bis(α-diazophenyl)benzene, 9-diazofluorene, and the anthraquinone and naphthoquinone derivatives $N_2CC_{13}H_8O$ and $N_2CC_{10}H_8O$ are summarized in Scheme 3. In diethyl ether or toluene as solvent, the substrates react nearly spontaneously to give the dinuclear (**13**) or mononuclear (**14**−**16**) complexes as green or red-brown air-stable solids in 79−89% yield. One typical

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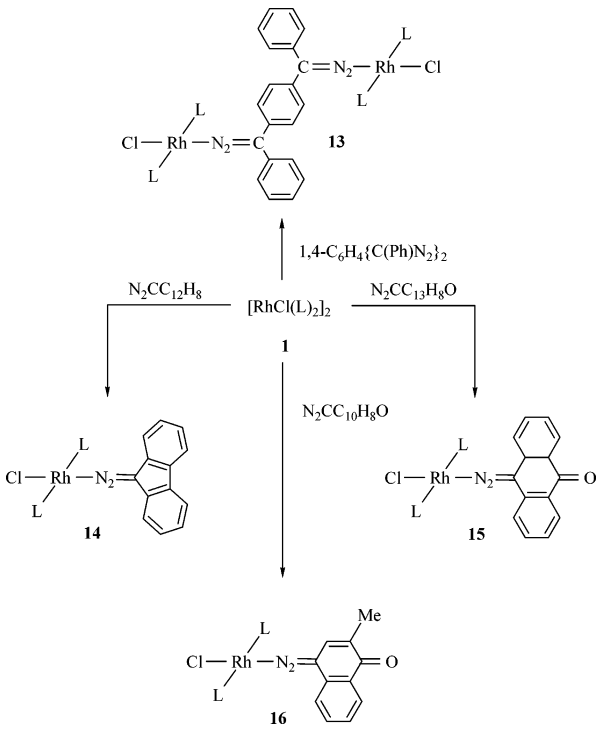
Scheme 3[a]



[a] L = P*i*Pr$_3$.

spectroscopic feature of **15** and **16** is the position of the $\nu(N_2C)$ vibration at 2083 cm^{-1} (for **15**) and 2088 cm^{-1} (for **16**), which appears at significantly higher wavenumbers than for **3**−**11**, **13**, and **14**. The ^{13}C NMR spectra of **15** and **16** display a sharp singlet at δ 178.9 (for **15**) and 178.8 (for **16**), being characteristic for a quinone-type C═O carbon atom. Attempts to link only one N_2C unit of 1,4-bis(α-diazophenyl)benzene to the 14-electron [RhCl(P*i*Pr$_3$)$_2$] fragment remained unsuccessful.

To confirm the proposed bonding mode of $N_2CC_{13}H_8O$, an X-ray crystal structure analysis of compound **15** was carried out. The ORTEP plot (Figure 1) reveals that the coordination sphere around the rhodium center is slightly distorted square planar. The two phosphine ligands are trans to each other, forming a P(1)−Rh−P(2) axis with a bond angle of 176.91(5)°. The diazoalkane unit is only coordinated via the terminal nitrogen atom with a Rh−N(1) distance of 1.836(5) Å, which is somewhat shorter than in the cation *trans*-[Rh(acetone)(N$_2$CPh$_2$)(P*i*Pr$_3$)$_2$]$^+$ (1.869(3) Å)[15] and in the dinitrogen complex **12** (1.885(4) Å).[13] In contrast to the Rh(N$_2$CC$_4$Cl$_4$) derivative **20** (see below), the Rh−N(1)−N(2) axis is not significantly bent, which could be a consequence of the steric requirements caused by the bulky triisopropylphosphine ligands and the $N_2CC_{13}H_8O$ unit. The plane [P(1),P(2),Cl,N(1)] is nearly perpendicular to the plane formed by the carbon atoms C(1), C(2), C(7), C(8), C(9), and C(14), the dihedral angle being 79.6°. The bond length N(1)−N(2) at 1.150(6) Å is almost identical with that in the cation [Rh(acetone)(N$_2$CPh$_2$)(P*i*Pr$_3$)$_2$]$^+$ (1.157(4) Å) and lies between those of an N═N double bond and an N≡N triple bond.[16] Regarding the bonding mode of the $N_2CC_{13}H_8O$ moiety, we note that in the related nickel complex [Ni(N$_2$CC$_{12}$H$_8$)(CN*t*Bu)$_2$] the 9-diazofluorene is coordinated side-on and thus both nitrogen atoms are linked to the metal center.[17]

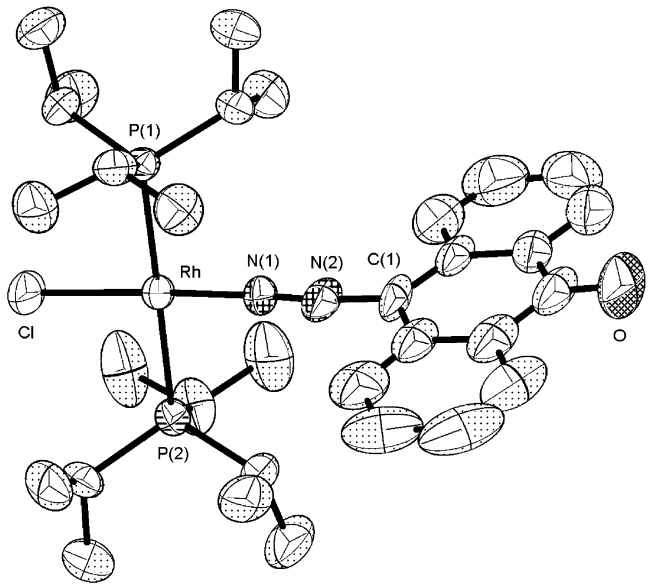
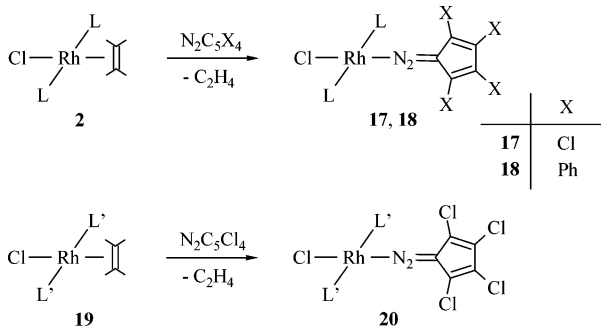


Figure 1. Molecular diagram of compound **15**. Selected bond distances (Å) and angles (deg): Rh−P(1) = 2.3539(15), Rh−P(2) = 2.3512(15), Rh−Cl = 2.3093(16), Rh−N(1) = 1.836(5), N(1)−N(2) = 1.150(6), N(2)−C(1) = 1.326(8); P(1)−Rh−P(2) = 176.91(5), Cl−Rh−N(1) = 175.84(16), P(1)−Rh−Cl = 89.72(5), P(1)−Rh−N(1) = 90.62(15), P(2)−Rh−Cl = 88.84(6), P(2)−Rh−N(1) = 91.01(15), Rh−N(1)−N(2) = 173.7(5), N(1)−N(2)−C(1) = 172.3(8).

Scheme 4[a]



[a] L = P*i*Pr$_3$, L′ = Sb*i*Pr$_3$.

Rhodium(I) Complexes with Coordinated N$_2$CC$_4$X$_4$ Units. After it had been shown that chlorometal compounds such as [RhCl(η^4-C$_8$H$_{12}$)]$_2$ react with the diazocyclopentadiene derivative N$_2$CC$_4$Cl$_4$ to afford half-sandwich-type complexes with C$_5$Cl$_5$ as a η^5-bonded ligand,[18] we were prompted to study also the reactivity of **2** (being more easily to handle than **1**) toward N$_2$CC$_4$Cl$_4$ and the tetraphenyl counterpart N$_2$CC$_4$Ph$_4$. However, instead of [(η^5-C$_5$R$_5$)Rh(P*i*Pr$_3$)$_2$] or [(η^5-C$_5$R$_5$)Rh(C$_2$H$_4$)(P*i*Pr$_3$)] (R = Cl, Ph) we isolated the (diazocyclopentadiene)rhodium(I) compounds **17** and **18** in almost quantitative yield (Scheme 4). The deep green (**17**) or brown-yellow (**18**) solids are air-stable and readily soluble in solvents such as benzene, chloroform, and dichloromethane. Even if they are stored in solution at room temperature for several days, no conversion to

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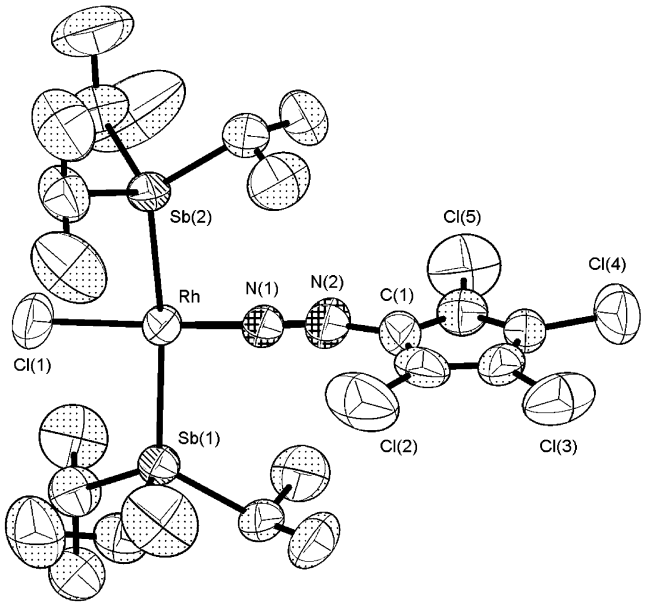
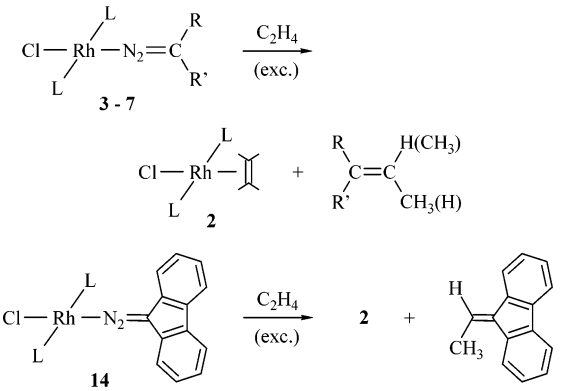


Figure 2. Molecular diagram of compound **20**. Selected bond distances (Å) and angles (deg): Rh−Sb(1) = 2.5912(8), Rh−Sb(2) = 2.6022(8), Rh−Cl = 2.291(2), Rh−N(1) = 1.788(6), N(1)−N(2) = 1.144(8), N(2)−C(1) = 1.37(1); Sb(1)−Rh−Sb(2) = 171.46(3), Cl−Rh−N(1) = 178.3(2), Rh−N(1)−N(2) = 170.1(8), N(1)−N(2)−C(1) = 154(1).

a [Rh(η^5-C_5R_5)] derivative, to a carbenerhodium(I) complex, or to **12** occurs. The chemical shift of the N_2C carbon resonance in the ^{13}C NMR spectra of **17** and **18** differs only slightly from that of **3** or **14** and **15**, and thus we assume that the diazocyclopentadiene units are bonded end-on to the metal center.

Taking into consideration that, in contrast to **1** or **2**, the bis(stibine) compound **19** reacts with Ph_2CN_2 and other diazoalkanes such as (*p*-Tol)$_2CN_2$, (*p*-Tol)C(Ph)N_2, and $CF_3C(Ph)N_2$ to give the corresponding carbene complexes *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$] by elimination of N_2,[5] we also investigated the reactivity of **19** toward $N_2CC_4Cl_4$. However, instead of obtaining *trans*-[RhCl(=CC_4Cl_4)(Sb*i*Pr$_3$)$_2$] we isolated the corresponding diazocyclopentadiene complex **20** as an olive green solid in excellent yield. The molecular structure of **20** has been determined crystallographically and is shown in Figure 2. Similarly to **15**, the coordination geometry is distorted square-planar with bond angles for the N(1)−Rh−Cl and Sb(1)−Rh−Sb(2) axes of, respectively, 178.3(2) and 171.46(3)°. The $N_2CC_4Cl_4$ unit possesses the "singly bent" configuration, as has also been found for the iridium compounds *trans*-[IrCl($N_2CC_4Cl_4$)(PPh_3)$_2$][19] and *trans*-[IrCl($N_2CC_4Cl_4$)(Sb*i*Pr$_3$)$_2$].[20] The nitrogen, carbon, and chlorine atoms of the coordinated diazocyclopentadiene derivative lie in one plane which is nearly perpendicular to the plane containing Rh, Cl, Sb(1), and Sb(2). The dihedral angle between the two planes is 85.5(2)°. In analogy to **15**, the distance N(1)−N(2) of 1.144(8) Å is halfway between those of a N=N double bond and a N≡N triple bond, being in agreement with the assumption that $N_2CC_4Cl_4$ is a moderate

Scheme 5[a]



[a] L = P*i*Pr$_3$.

π-acceptor ligand. It should be noted that in the complex [Ru(CO)$_2$(PPh_3)$_2$($N_2CC_4Cl_4$)] the diazocyclopentadiene unit is not end-on but side-on bonded via both nitrogen atoms to the ruthenium center.[21]

Reactions of the Diazoalkane Complexes with Ethene. Since it is known that dinuclear rhodium(II) compounds such as [$Rh_2(O_2CMe)_4$] and derivatives thereof catalyze the reactions of ethene and diaryldiazomethanes to give substituted cyclopropanes,[22] we also attempted to use the rhodium(I) complexes **3**−**7** for cyclopropanation reactions. By treating **3**−**7** in benzene at room temperature, only a very slow reaction occurs. After raising the temperature to 40 °C, an equilibrium between the diazoalkane complex and the corresponding ethene derivative **2** is reached, which under an ethene atmosphere lies mainly on the side of **2**. Most surprisingly, the product generated from the coordinated diazoalkane and ethene is not the expected 1,1-diarylcyclopropane but CH_3CH=CRR′ (Scheme 5). This olefin is formally built up by the linking of the :CRR′ fragment of the diazoalkane, with :$CHCH_3$ being an isomer of ethene. Within the accuracy of NMR measurements, the yield of CH_3CH=CRR′ is quantitative. To explain the mechanism of the unusual C−C coupling reaction, we assume that in the initial stage both C_2H_4 and RR′CN_2 are coordinated to rhodium and that, after elimination of N_2, a four-membered RhC_3 metallacycle is formed. The next step could be an H-shift from the β-CH_2 unit of the metallacyclobutane ring to afford a η^3-allyl(hydrido)rhodium intermediate, which by reductive coupling of the hydrido ligand with the CH_2 carbon atom of the η^3-CH_2CHCRR' moiety generates the olefin CH_3-CH=CRR′. Compound **14** behaves similarly to **3**−**7** and upon treatment with ethene gives **2** and the fulvene derivative CH_3CH=$CC_{12}H_8$.

Reactions of Dimer 1 with Phenylhydrazones. To find out whether diazoalkanerhodium(I) complexes such as **3** and **8** can be obtained without using RR′CN_2 as the precursors, the reactivity of **1** toward phenyl hydrazones has been investigated. There is ample evidence for the ability of phosphinerhodium(I) compounds of the general compositions [RhCl(PR_3)$_2$]$_2$ and

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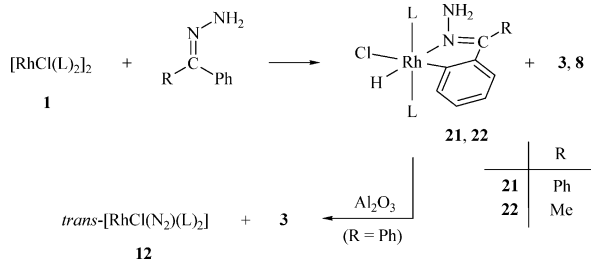
Scheme 6[a]



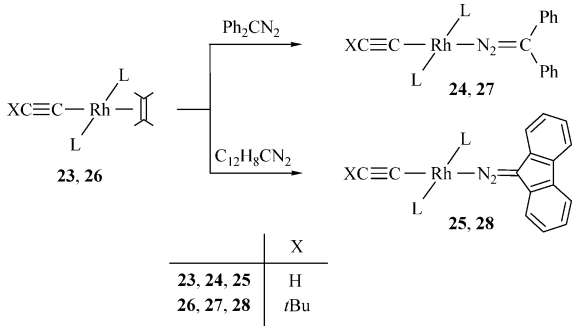
[a] L = P*i*Pr$_3$.

[RhCl(PR$_3$)$_3$] to react with hydrocarbons or other organic molecules by abstraction of hydrogen and formation of hydridorhodium complexes.[23]

Treatment of a solution of the starting material **1** with diphenyl hydrazone in toluene leads to a rapid change of color from violet to red-brown and gives, after extraction with and recrystallization from pentane, the ortho-metalated rhodium(II) compound **21** in 70% isolated yield. In the mother liquor, besides **21** the diazoalkane complex **3** could be detected in small quantities. Typical spectroscopic features of **21** are the hydride signal at δ −14.22 in the ^{1}H NMR spectrum, which is split into a doublet of triplets due to ^{1}H−^{103}Rh and ^{1}H−^{31}P couplings, the low-field resonance at δ 167.2 (also a doublet of triplets) in the ^{13}C NMR spectrum, assigned to the metal-bonded carbon atom of the six-membered ring, and the ν(NH) stretches at 3360 and 3248 cm^{-1} in the IR spectrum, indicating that the NNH$_2$ unit is still intact. The fact that the two phosphine ligands of **21** are stereochemically equivalent is confirmed by the appearance of only one signal (doublet) in the ^{31}P NMR spectrum. In the corresponding ^{1}H-decoupled ^{31}P NMR spectrum this doublet becomes a doublet of doublets due to additional coupling of the ^{31}P nuclei with the hydride. The reaction of **1** with CH$_3$C(Ph)═NNH$_2$ proceeds in a fashion analogous to that with Ph$_2$C═NNH$_2$, but in this case the main product **22** (see Scheme 6) could not be completely separated from the diazoalkane derivative **8** and small amounts of other byproducts. Therefore, compound **22** has been characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Regarding the mechanism of formation of **21** and **22**, we assume that in the initial step a hydrazonerhodium(I) intermediate, in which the hydrazone is probably coordinated via the C═N nitrogen atom, is generated. Subsequent oxidative addition of a C−H bond of the phenyl ring, being a well-known reaction also for diphenylimine derivatives,[24] would then afford the ortho-metalated rhodium(III) complex. The question whether the diazoalkane compound **3** or **8** is formed from the supposed intermediate *trans*-[RhCl{H$_2$NN═C(Ph)R}(P*i*Pr$_3$)$_2$] or from the rhodium(III) complexes **21** and **22** is open to speculation. When we attempted to generate **3** from **21** by using a chromatographic column filled with deactivated Al$_2$O$_3$, we obtained a mixture of **3** and the dinitrogen compound **12** in small quantities. Further attempts to form **3** by treatment of **21** with [RhCl(PPh$_3$)$_3$] or **1** remained unsuccessful.

Scheme 7[a]



[a] L = P*i*Pr$_3$.

Alkynylrhodium(I) Complexes with Diazoalkane Ligands. After we found that in iridium complexes *trans*-[IrX(N$_2$CRR′)(P*i*Pr$_3$)$_2$] the bond between iridium and the diazoalkane ligand could be stabilized if instead of chloride an alkyl or alkynyl group is linked to the metal center,[25] we also studied the reactivity of alkynylrhodium compounds *trans*-[Rh(C≡CX)(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] toward diazoalkanes. The hope, however, that with these starting materials it could be possible to even isolate a rhodium(I) complex with coordinated CH$_2$N$_2$ or PhCHN$_2$, was not fulfilled. While both **23** and **26** (see Scheme 7) react with Ph$_2$CN$_2$ and C$_{12}$H$_8$CN$_2$ in pentane to give the expected diazoalkane complexes **24**, **25**, **27**, and **28** in 79−95% yield, the reactions of **23** and **26** with CH$_2$N$_2$ or PhCHN$_2$ give mixtures of products which could not be separated by common techniques. If the reaction of **26** with PhCHN$_2$ in toluene-d_8 was monitored at −40 °C in an NMR tube, the ^{1}H NMR spectrum displayed a signal at δ 4.14, which could be tentatively assigned to the PhC*H* proton of the required compound *trans*-[Rh(C≡C*t*Bu)(N$_2$CHPh)(P*i*Pr$_3$)$_2$]. After the temperature was raised to 0 °C, this signal completely disappeared. At this stage, the IR spectrum of the solution showed an absorption at 2120 cm^{-1}, indicating that possibly the dinitrogen complex *trans*-[Rh(C≡C*t*Bu)(N$_2$)(P*i*Pr$_3$)$_2$] had been generated. In contrast to **12**, this molecule seems to be very labile, and thus all attempts to isolate it failed.

The isolated diazoalkane complexes **24**, **25**, **27**, and **28** are green, microcrystalline solids which are more stable in solution and toward oxygen than their chloro counterparts. In addition to the broadened ν(N$_2$C) mode at 1920 cm^{-1}, the IR spectra of **24** and **27** display intense bands at around 3240−3280 and 1935 cm^{-1}, which are assigned to the ≡CH and C≡C stretching vibrations. The ν(C≡C) stretches of **25** and **28** appear at 2070 and 2050 cm^{-1}, respectively. Typical features of the ^{13}C NMR spectra of **24**, **25**, **27**, and **28** are the signal for the N$_2$C carbon at δ 71−75 and the two low-field resonances for the ^{13}C nuclei of the alkynyl groups. The latter are split into doublets of triplets due to ^{13}C−^{103}Rh and ^{13}C−^{31}P couplings.

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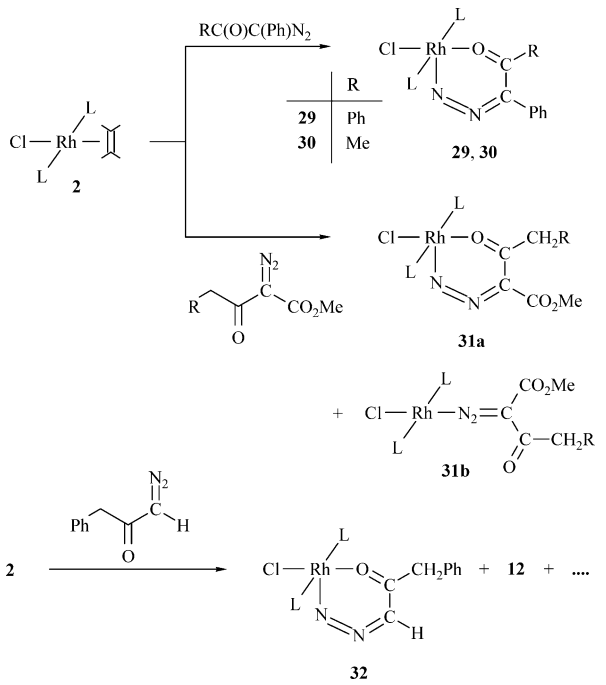
Scheme 8[a]



[a] L = P*i*Pr$_3$, R = $CH_2CH(CH_3)_2$.

Rhodium(I) Complexes with Diazo Ketones and Diazo Keto Esters as Ligands. Under the same conditions as used for the preparation of **17** and **18**, compound **2** also reacts with diazo ketones RC(O)C(Ph)-N_2 (R = Ph, Me) by ligand exchange and formation of the rhodium(I) complexes **29** and **30**, respectively (Scheme 8). The diazo keto ester $RCH_2C(O)C(CO_2Me)$-N_2 (R = $CH_2CH(CH_3)_2$) behaves similarly and, upon treatment with **2**, affords the corresponding rhodium-(I) derivative **31**. In each case the yield is good to excellent. However, while for **29** and **30** the NMR spectra confirm that only one product has been formed, the NMR spectra of **31** leave no doubt that two species (probably the isomers **31a** and **31b**) are present.

In attempting to separate the isomers by fractional crystallization from pentane, single crystals were isolated, which were investigated by an X-ray diffraction analysis. There were two independent molecules **A** and **B** in the unit cell, which differ in both the conformation of the isopentyl fragment and the arrangement of the isopropyl groups around the phosphorus atoms. The structure of molecule **A** is depicted in Figure 3. Most surprisingly, the rhodium center is not four- but five-coordinated, the polyhedron corresponding to a slightly distorted square pyramid. The basal plane of the pyramid is built up by the two phosphorus atoms, still in a trans disposition, and the chloride and the ketonic oxygen atom, which are also trans to each other. The apical position is occupied by the terminal nitrogen of the diazo unit. While the axis P(1)−Rh(1)−P(2) is somewhat bent, the bond angles around rhodium deviate only marginally from the ideal 90° value. The Rh(1)−N(2) distance of 1.990(4) Å is significantly lengthened compared with **15** (1.836(5) Å) and **20** (1.788(6) Å), probably being a consequence of the formation of the chelate ring. This chelate ring is perfectly planar and lies perpendicular to the plane containing Rh(1), Cl(1), P(1), P(2), and O(3). The dihedral angle between the two

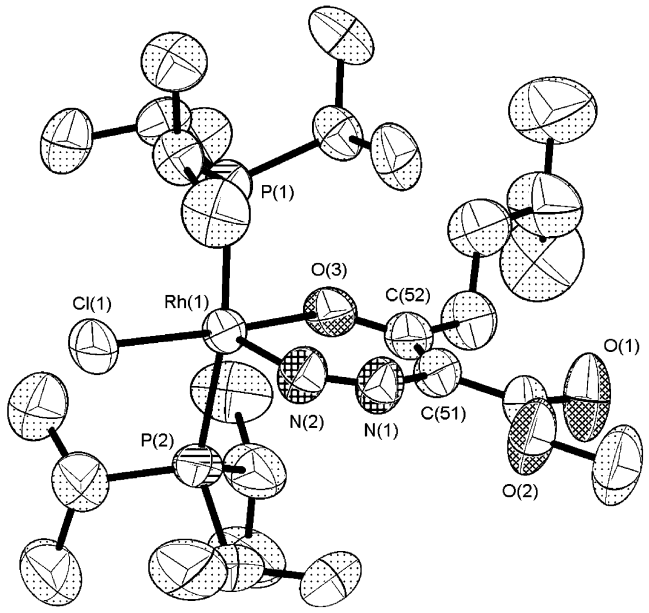


Figure 3. Molecular diagram of compound **31a** (for molecule **A** of the unit cell). Selected bond distances (Å) and angles (deg): Rh(1)−P(1) = 2.399(1), Rh(1)−P(2) = 2.372(1), Rh(1)−Cl(1) = 2.350(1), Rh(1)−O(3) = 2.043(3), Rh(1)−N(2) = 1.990(4), N(1)−N(2) = 1.212(5), N(1)−C(51) = 1.393(6), C(51)−C(52) = 1.400(7), C(52)−O(3) = 1.285-(6); P(1)−Rh(1)−P(2) = 165.32(5), Cl(1)−Rh(1)−O(3) = 173.7(1), P(1)−Rh(1)−Cl(1) = 90.13(5), P(2)−Rh(1)−Cl(1) = 88.89(4), P(1)−Rh(1)−O(3) = 89.28(9), P(2)−Rh(1)−O(3) = 90.10(9), O(3)−Rh(1)−N(2) = 89.4(1), Rh(1)−N(2)−N(1) = 123.6(3), N(2)−N(1)−C(51) = 134.3(4), N(1)−C(51)−C(52) = 120.3(4), C(51)−C(52)−O(3) = 124.7(4), C(52)−O(3)−Rh(1) = 127.1(3).

planes amounts to 89.30(8)°. Not only the Rh(1)−N(2) distance but also the N(1)−N(2) bond length (1.212(5) Å) is considerably longer than in **15** (1.150(6) Å) and **20** (1.144(8) Å), indicating that due to the bending Rh-(1)−N(2)−N(1) of 134.3(4)° the N−N bond strength has been reduced. Since the distances N(1)−C(51) and O(3)−C(52) are longer than a normal N=C or C=O double bond and the distance C(51)−C(52) shorter than a C−C single bond, we assume that the π-electrons of the chelate ring are mainly delocalized. It is conceivable that also the ester group is part of the delocalized system, because the atoms C(50), O(1), O(2), and C(58) lie in the same plane as the six-membered chelate ring.

The reasons to believe that the structure of the diazo ketone complexes **29** and **30** is similar to that of **31a** but different from that of **3**−**11** and **13**−**16** are as follows. (1) Compounds **29**, **30**, and **31a** are red, while all the other rhodium(I) complexes (apart from **11** and **14**) shown in Schemes 1−3 are green. (2) The chemical shifts of the ^{31}P NMR resonances for **29**, **30**, and **31a** (in C_6D_6 or $C_6D_5CD_3$) are δ 31.0−32.3, while those for **3**−**11** and **13**−**15** (in C_6D_6) are δ 38.5−42.5. (3) The ^{1}H NMR spectra of **3**−**11** and **13**−**16** show only one signal (doublet of virtual triplets) for the protons of the methyl groups of the isopropyl units, whereas the spectra of **29** and **30** show two. Accordingly, the ^{13}C NMR spectra of **29** and **30** display two singlets for the $PCHCH_3$ carbon atoms, whereas in the spectra of **3**−**11** and **13**−**16** there is only one signal for the ^{13}C nuclei of phosphine−CH_3 units. (4) The chemical shifts of the ^{13}C NMR signals for the N_2C carbon atoms of **29** and **30** (δ ca. 100−101)

differ by ca. 20−30 ppm from those of the related carbon atoms of the diazoalkane compounds **3**−**7**, **9**−**11**, and **13**−**15**. The positions at lower fields are consistent with an increased delocalization of the π-electrons in the postulated chelate ring.

The detection of the two species **31a** and **31b** in the product of the reaction of **2** with the diazo keto ester derivative $RCH_2C(O)C(CO_2Me)N_2$ deserves additional comment. The ^{1}H NMR spectrum of the product (in toluene-d_8) displays at 253 K two signals for the OCH_3 protons at δ 3.53 and 3.40 in the approximate ratio of 10:1. When the temperature is raised, the intensity changes and at 313 K approaches a ratio of 1:2. The situation in the ^{31}P NMR spectra is similar. At 253 K two doublets are observed at δ 42.6 and 31.0, the latter of which dominates. At higher temperatures, the intensity of the two signals changes, and above 303 K the dominating one is that at δ ca. 43.5. These changes in intensity observed with changes in temperature are reversible. Taking the data for the four-coordinated complexes **3**−**11** and **13**−**16** as well as those for the presumably five-coordinated compounds **29** and **30** into consideration, we conclude that the major species in solution at lower temperatures is **31a** and that at higher temperatures is **31b**. Since **31a** dominates at 253 K and below, it is not surprising that the single crystals, grown from pentane at 195 K, contain only this isomer. Although according to the NMR data there is no doubt that in solution an equilibrium between **31a** and **31b** exists, it was not possible, neither in the ^{1}H nor in the ^{31}P NMR spectra, to observe coalescence, since above 333 K both isomers decompose.

The diazo ketone $PhCH_2C(O)CHN_2$, which is somewhat similar in structure to the diazo keto ester derivative, reacts with the starting material **2** less selectively. In addition to the anticipated compound **32** (see Scheme 8), the dinitrogen complex **12** as well as small amounts of unidentified byproducts (ca. 10%) are formed, which could not be separated from **32**. The ratio of **32** to **12** was approximately 2:1. The ^{31}P NMR spectrum of **32** shows (in C_6D_6) only one set of signals for the phosphorus atoms, indicating that only one isomer is formed. The appearance of a multiplet instead of one doublet of virtual triplets for the phosphine−methyl protons and, even more, the chemical shift of δ 31.1 (**31a**: δ 31.6) for the ^{31}P NMR signal suggests that, as in the case of **29**, **30**, and **31a**, also in **32** the rhodium is five-coordinated and the diazo ketone is bonded as a chelating ligand.

Conclusions

The work presented in this paper has shown that a variety of diazoalkanes $RR'CN_2$, which upon treatment with *trans*-[RhCl(C_2H_4)(Sb*i*Pr$_3$)$_2$] (**19**) afford the corresponding rhodium(I) carbenes *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$],[5] react with either the dimer [RhCl(P*i*Pr$_3$)$_2$]$_2$ (**1**) or the ethene derivatives *trans*-[RhX(C_2H_4)(P*i*Pr$_3$)$_2$] (**2**, **23**, **26**) to give complexes such as **3**−**11**, **13**−**18**, **24**, **25**, **27**, and **28**, in which the intact diazoalkane is coordinated via the terminal nitrogen atom to the metal center. It thus appears that P*i*Pr$_3$, as the better σ-donor ligand compared with Sb*i*Pr$_3$, hinders the elimination of N_2 and stabilizes the Rh−N_2CRR′ bond. It is conceivable that also the smaller distance Rh−P compared with Rh−Sb, leading to a more crowded coordination sphere in the starting materials **1**, **2**, **23** and **26**, prevents a η^2-N,N or η^2-N,C coordination of the diazoalkane, which possibly is the prerequisite for the generation of a metal carbene.

Apart from the reactions of the diazoalkane complexes **3**−**7** and **14** toward ethene, which instead of disubstituted cyclopropanes give exclusively trisubstituted olefins $CH_3CH{=}CRR'$, the most unusual facet of our studies is the formation of five-coordinated rhodium(I) compounds with diazo ketones and a diazo keto ester derivative as chelating ligands. This result deserves particular attention insofar as (1) rhodium(I) strongly prefers the coordination number 4 with a square-planar geometry and (2) the donor capability of a ketonic oxygen atom is not very pronounced. The formation of a six-membered chelate ring in the complexes **29**, **30**, and **31a** seems to be the crucial driving force that obviously overcomes the assumed strain of the RhN_2C_2O system and thus leads to products with an 18-electron count.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**,[7a] **2**,[8a] **19**,[26] **23**,[27] and **26**[28] were prepared as described in the literature. NMR spectra were recorded on Bruker WH 90, Bruker AC 200, and Bruker AMX 400 instruments at room temperature, if not otherwise stated. IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrometer and mass spectra on a Finnigan 90 MAT instrument. Melting points were measured by DTA. Abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened signal. The term vt indicates a virtual triplet, and $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$.

Reaction of Compound 1 with CH_2N_2. A solution of **1** (110 mg, 0.12 mmol) in diethyl ether (10 mL) was treated dropwise with a 0.1 M solution of CH_2N_2 in diethyl ether (2.5 mL, 0.25 mmol) at room temperature. A rapid evolution of gas (N_2) occurred. The solvent was evaporated in vacuo, and the residue was recrystallized from toluene/pentane (1:10). A yellow microcrystalline solid was obtained, which was shown by comparison of the ^{1}H and ^{31}P NMR spectra with those of an authentic sample to be *trans*-[RhCl(C_2H_4)(P*i*Pr$_3$)$_2$] (**2**).[8a] Yield: 111 mg (94%).

Preparation of *trans*-[RhCl(N_2CPh_2)(P*i*Pr$_3$)$_2$] (3). A solution of **1** (335 mg, 0.37 mmol) in diethyl ether (20 mL) was treated at −50 °C with a solution of Ph_2CN_2 (142 mg, 0.73 mmol) in diethyl ether (5 mL). The solution was slowly warmed to room temperature, which led to a change of color from violet to green. After the solution was stirred at ca. 20 °C for 10 min, it was concentrated to ca. 5 mL and then layered with pentane (30 mL). The mixture was stored at −78 °C for 12 h, which led to the precipitation of green air-sensitive crystals. They were separated from the mother liquor, washed twice with small amounts of pentane (0 °C), and dried: yield 368 mg (77%); mp 94 °C dec. Anal. Calcd for $C_{31}H_{52}ClN_2P_2Rh$: C, 57.01; H, 8.03; N, 4.29. Found: C, 56.35; H, 8.26; N, 3.99. IR (KBr): $\nu(N_2C)$ 1940 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.20 (br m, 10 H, C_6H_5), 2.35 (m, 6 H, PC*H*CH$_3$), 1.26 (dvt, N = 13.3, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 129.5, 128.9, 125.1, 124.3 (all s, C_6H_5), 78.7 (br s,

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N_2C), 23.6 (vt, N = 18.2 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 38.5 (d, J(Rh,P) = 118.5 Hz).

Preparation of *trans*-[RhCl{N_2C(*p*-Tol)$_2$}(P*i*Pr$_3$)$_2$] (4). This compound was prepared as described for **3** from **1** (85 mg, 0.09 mmol) and (*p*-Tol)$_2CN_2$ (42 mg, 0.18 mmol) in diethyl ether (8 mL): dark green solid; yield 102 mg (83%); mp 86 °C dec. Anal. Calcd for $C_{33}H_{56}ClN_2P_2Rh$: C, 58.19; H, 8.29; N, 4.11. Found: C, 58.18; H, 8.43; N, 4.10. IR (KBr): ν(N_2C) 1941 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.34, 7.01 (both m, 4 H each, C_6H_4), 2.35 (m, 6 H, PC*H*CH$_3$), 2.13 (s, 6 H, C_6H_4C*H*$_3$), 1.26 (dvt, N = 13.3, J(H,H) = 6.9 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 133.7, 129.7, 126.4, 125.3 (all s, C_6H_4), 78.5 (br s, N_2C), 23.6 (vt, N = 17.6 Hz, P*C*HCH$_3$), 20.9 (s, C_6H_4*C*H$_3$), 20.1 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 41.7 (d, J(Rh,P) = 120.6 Hz).

Preparation of *trans*-[RhCl{N_2C(*p*-Tol)Ph}(P*i*Pr$_3$)$_2$] (5). This compound was prepared as described for **3** from **1** (155 mg, 0.17 mmol) and Ph(*p*-Tol)CN_2 (70 mg, 0.34 mmol) in diethyl ether (8 mL): dark green solid; yield 196 mg (87%); mp 91 °C dec. Anal. Calcd for $C_{32}H_{54}ClN_2P_2Rh$: C, 57.62; H, 8.16; N, 4.19. Found: C, 57.30; H, 8.43; N, 3.93. IR (KBr): ν(N_2C) 1937 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.90−7.08 (br m, 9 H, C_6H_5 and C_6H_4), 2.38 (m, 6 H, PC*H*CH$_3$), 2.12 (s, 3 H, C_6H_4C*H*$_3$), 1.25 (dvt, N = 14.4, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 140.1 (s, *ipso*-C of C_6H_4), 131.7, 130.3, 128.2, 125.5, 122.2, 121.0, 118.6 (all s, C_6H_5 and C_6H_4), 74.4 (br s, N_2C), 24.8 (vt, N = 19.5 Hz, P*C*HCH$_3$), 22.7 (s, C_6H_4*C*H$_3$), 20.2 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 41.8 (d, J(Rh,P) = 129.4 Hz).

Preparation of *trans*-[RhCl{N_2C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$] (6). This compound was prepared as described for **3** from **1** (150 mg, 0.16 mmol) and Ph(*o*-Tol)CN_2 (68 mg, 0.33 mmol) in diethyl ether (8 mL): dark green solid; yield 121 mg (55%); mp 101 °C dec. Anal. Calcd for $C_{32}H_{54}ClN_2P_2Rh$: C, 57.61; H, 8.16; N, 4.19. Found: C, 57.66; H, 8.24; N, 3.98. IR (KBr): ν(N_2C) 1936 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.43−6.83 (br m, 9 H, C_6H_5 and C_6H_4), 2.37 (m, 6 H, PC*H*CH$_3$), 2.15 (s, 3 H, C_6H_4C*H*$_3$), 1.27 (dvt, N = 13.1, J(H,H) = 6.9 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 150.6 (s, *ipso*-C of C_6H_4), 134.0, 130.7, 128.9, 128.3, 126.0, 125.6, 124.8, 124.1 (all s, C_6H_5 and C_6H_4), 78.5 (br s, N_2C), 23.6 (vt, N = 18.5 Hz, P*C*HCH$_3$), 20.9 (s, C_6H_4*C*H$_3$), 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 41.7 (d, J(Rh,P) = 122.2 Hz).

Preparation of *trans*-[RhCl{N_2C(*p*-C_6H_4Cl)$_2$}(P*i*Pr$_3$)$_2$] (7). This compound was prepared as described for **3** from **1** (92 mg, 0.10 mmol) and (*p*-C_6H_4Cl)$_2CN_2$ (53 mg, 0.20 mmol) in diethyl ether (7 mL): dark green solid; yield 114 mg (78%); mp 114 °C dec. Anal. Calcd for $C_{31}H_{50}Cl_3N_2P_2Rh$: C, 51.57; H, 6.98; N, 3.88. Found: C, 51.89; H, 7.17; N, 4.17. IR (KBr): ν(N_2C) 1934 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.32−6.89 (br m, 8 H, C_6H_4), 2.13 (m, 6 H, PC*H*CH$_3$), 1.07 (dvt, N = 13.5, J(H,H) = 6.9 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 129.4, 129.1, 127.7, 126.9 (all s, C_6H_4), 76.5 (br s, N_2C), 23.6 (vt, N = 18.5 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 42.1 (d, J(Rh,P) = 119.2 Hz).

Preparation of *trans*-[RhCl{N_2C(CH$_3$)Ph}(P*i*Pr$_3$)$_2$] (8). A solution of **1** (45 mg, 0.05 mmol) in diethyl ether (5 mL) was treated dropwise at −78 °C with a solution of $CH_3C(Ph)N_2$ (13 mg, 0.10 mmol) in diethyl ether (2 mL). The solution was slowly warmed to −30 °C, which led to a change of color from violet to green. After the solution was stirred for 5 min, it was concentrated to ca. 1 mL and then layered with pentane (5 mL). The mixture was then stored at −78 °C for 2 h, which led to the precipitation of light green air-sensitive crystals. They were separated from the mother liquor, washed twice with small amounts of pentane (−20 °C), and dried: yield 53 mg (89%); mp 42 °C dec. Anal. Calcd for $C_{26}H_{50}ClN_2P_2Rh$: C, 53.17; H, 8.81; N, 4.54. Found: C, 52.84; H, 8.52; N, 4.74. IR (KBr): ν(N_2C) 1935 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.30−6.94 (br m, 5 H, C_6H_5), 2.36 (m, 6 H, PC*H*CH$_3$), 2.15 (t, J(P,H) = 1.3 Hz, N_2CCH_3), 1.29 (dvt, N = 13.1, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 40.6 (d, J(Rh,P) = 123.0 Hz).

Preparation of *trans*-[RhCl{N_2C(CH$_2$Ph)Ph}(P*i*Pr$_3$)$_2$] (9). This compound was prepared as described for **3** from **1** (50 mg, 0.055 mmol) and $PhCH_2C(Ph)N_2$ (23 mg, 0.11 mmol) in diethyl ether (6 mL): dark green solid; yield 70 mg (95%); mp 64 °C dec. Anal. Calcd for $C_{32}H_{54}ClN_2P_2Rh$: C, 58.23; H, 8.33; N, 4.08. Found: C, 57.62; H, 8.16; N, 4.20. IR (KBr): ν(N_2C) 1940 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.14−6.93 (br m, 10 H, C_6H_5), 3.82 (br s, 2 H, C*H*$_2$Ph), 2.32 (m, 6 H, PC*H*CH$_3$), 1.25 (dvt, N = 13.9, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 140.8, 138.0 (both s, *ipso*-C of C_6H_5), 132.0, 128.7, 128.1, 126.6, 122.2, 121.5 (all s, C_6H_5), 72.2 (br s, N_2C), 28.5 (s, *C*H$_2$Ph), 23.4 (vt, N = 18.0 Hz, P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 40.5 (d, J(Rh,P) = 120.0 Hz).

Preparation of *trans*-[RhCl{N_2C(CF$_3$)Ph}(P*i*Pr$_3$)$_2$] (10). This compound was prepared as described for **3** from **1** (92 mg, 0.10 mmol) and $CF_3C(Ph)N_2$ (37 mg, 0.20 mmol) in diethyl ether (8 mL): green air-stable solid; yield 120 mg (93%); mp 83 °C. Anal. Calcd for $C_{26}H_{47}ClF_3N_2P_2Rh$: C, 47.91; H, 7.64; N, 4.47. Found: C, 48.42; H, 7.34; N, 4.34. IR (KBr): ν(N_2C) 1935 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.22−7.05 (br m, 5 H, C_6H_5), 2.32 (m, 6 H, PC*H*CH$_3$), 1.22 (dvt, N = 13.5, J(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 128.9, 125.1, 123.5, 121.7 (all s, C_6H_5), 121.7 (q, J(C,F) = 268.5 Hz, CF_3), 65.9 (br s, N_2C), 23.8 (vt, N = 19.1 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{19}F NMR (84.2 MHz, C_6D_6): δ −56.2 (s). ^{31}P NMR (81.0 MHz, C_6D_6): δ 40.8 (d, J(Rh,P) = 115.7 Hz).

Preparation of *trans*-[RhCl{N_2C(CO$_2$Et)$_2$}(P*i*Pr$_3$)$_2$] (11). This compound was prepared similarly as described for **3** from **1** (85 mg, 0.09 mmol) and $N_2C(CO_2Et)_2$ (34 mg, 0.18 mmol) in toluene (5 mL) at room temperature. After recrystallization from toluene/pentane (1:3) at −78 °C, red air-stable crystals were obtained: yield 95 mg (80%); mp 145 °C dec. Anal. Calcd for $C_{25}H_{52}ClN_2O_4P_2Rh$: C, 46.55; H, 8.12; N, 4.34. Found: C, 46.29; H, 7.86; N, 4.04. IR (KBr): ν(N_2C) 1945 (br), ν(C=O) 1730 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 4.16 (q, J(H,H) = 7.2 Hz, 2 H, C*H*$_2$CH$_3$), 2.37 (m, 6 H, PC*H*CH$_3$), 1.26 (dvt, N = 13.3, J(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$), 1.06 (t, J(H,H) = 7.2 Hz, CH$_2$C*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 159.8 (s, *C*O$_2$Et), 76.3 (br s, N_2C), 59.9 (s, *C*H$_2$CH$_3$), 23.8 (vt, N = 19.5 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$), 14.8 (s, CH$_2$*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 42.4 (d, J(Rh,P) = 114.6 Hz).

Formation of *trans*-[RhCl(N$_2$)(P*i*Pr$_3$)$_2$] (12). A solution of **1** (61 mg, 0.065 mmol) in diethyl ether (5 mL) was treated at −50 °C with $CH(CO_2Et)N_2$ (15 mg, 0.13 mmol). The solution was slowly warmed to room temperature, which led to a change of color from violet to brown. After the solution was stirred at ca. 20 °C for 10 min, it was concentrated to ca. 5 mL and then layered with pentane (15 mL). The mixture was stored at −78 °C for 12 h, which led to the precipitation of a pale brown microcrystalline solid. This was shown by comparison of the IR and ^{31}P NMR data to be **12**.[8a,13]

Preparation of *trans,trans*-[{RhCl(P*i*Pr$_3$)$_2$}$_2${μ-C_6H_4-(C(Ph)N$_2$)$_2$}] (13). This compound was prepared as described for **3** from **1** (53 mg, 0.06 mmol) and 1,4-C_6H_4{$C(Ph)N_2$}$_2$ (18 mg, 0.06 mmol) in diethyl ether (8 mL): olive green air-stable solid; yield 61 mg (86%); mp 82 °C. Anal. Calcd for $C_{56}H_{98}Cl_2N_4P_4Rh_2$: C, 55.24; H, 8.26; N, 4.58. Found: C, 54.77; H, 8.04; N, 4.56. IR (KBr): ν(N_2C) 1934 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.50−6.87 (br m, 14 H, C_6H_5 and C_6H_4), 2.39 (m, 6 H, PC*H*CH$_3$), 1.29 (dvt, N = 13.3, J(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 129.4, 128.9, 128.3, 125.6, 125.1, 124.3 (all s, C_6H_5 and C_6H_4), 78.8 (br s, N_2C), 23.6 (vt, N = 18.4 Hz, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 40.7 (d, J(Rh,P) = 122.6 Hz).

Preparation of *trans*-[RhCl(N$_2$CC$_{12}$H$_8$)(P*i*Pr$_3$)$_2$] (14). This compound was prepared as described for **3** from **1** (164 mg, 0.18 mmol) and 9-diazofluorene (68 mg, 0.36 mmol) in diethyl ether (8 mL): red-brown air-stable solid; yield 204 mg

(88%); mp 36 °C. Anal. Calcd for $C_{31}H_{50}ClN_2P_2Rh$: C, 57.19; H, 7.74; N, 4.30. Found: C, 57.53; H, 8.01; N, 4.30. IR (KBr): $\nu(N_2C)$ 1915 (br) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.86 (ddd, $J(H,H) = 7.8$, 1,1 and 0.7 Hz, 2 H, H^1 and H^8), 7.63 (br d, $J(H,H) = 7.8$ Hz, 2 H, H^4 and H^5), 7.35, 7.10 (both ddd, $J(H,H) = 7.8$, 7.6 and 1.1 Hz, 2 H each, H^2, H^7 and H^3, H^6), 2.30 (m, 6 H, PC*H*CH_3), 1.19 (dvt, $N = 13.7$, $J(H,H) = 7.1$ Hz, 36 H, PCHC*H*$_3$); the protons are numbered clockwise beginning at the ortho position next to the five-membered ring. ^{13}C NMR (50.3 MHz, C_6D_6): δ 131.2, 128.3, 125.5, 122.6, 121.0, 118.7 (all s, C_6H_4), 68.5 (br s, N_2C), 23.7 (vt, $N = 19.5$ Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 43.8 (d, $J(Rh,P) = 116.3$ Hz).

Preparation of *trans*-[RhCl($N_2CC_{13}H_8O$)(P*i*Pr$_3$)$_2$] (15). This compound was prepared similarly as described for **3** from **1** (85 mg, 0.09 mmol) and 9,10-anthraquinone-9-diazide (40 mg, 0.18 mmol) in toluene (5 mL) at room temperature: green air-stable solid; yield 112 mg (89%); mp 138 °C dec. Anal. Calcd for $C_{32}H_{50}ClN_2OP_2Rh$: C, 56.60; H, 7.42; N, 4.13. Found: C, 56.84; H, 7.26; N, 4.34. IR (KBr): $\nu(N_2C)$ 2083, $\nu(C{=}O)$ 1618 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 8.78, 7.54 (both m, 8 H, 2x C_6H_4), 2.73 (m, 6 H, PC*H*CH_3), 1.60 (dvt, $N = 13.8$, $J(H,H) = 7.2$ Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 178.9 (s, C=O), 133.7, 131.3, 130.3, 129.3, 128.6, 128.1, 127.9, 127.1, 124.7, 123.2, 121.7 (all s, 2 × C_6H_4), 75.7 (br s, N_2C), 24.1 (vt, $N = 19.4$ Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 42.5 (d, $J(Rh,P) = 114.3$ Hz).

Preparation of *trans*-[RhCl($N_2CC_{10}H_8O$)(P*i*Pr$_3$)$_2$] (16). This compound was prepared as described for **3** from **1** (85 mg, 0.09 mmol) and 3-methyl-1,4-naphthoquinone-1-diazide (33 mg, 0.18 mmol) in toluene (5 mL) at room temperature: green air-stable solid; yield 94 mg (79%); mp 127 °C dec. Anal. Calcd for $C_{29}H_{50}ClN_2OP_2Rh$: C, 54.17; H, 7.84; N, 4.36. Found: C, 54.43; H, 7.55; N, 4.40. IR (KBr): $\nu(N_2C)$ 2088, $\nu(C{=}O)$ 1635 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 8.33, 7.19 (both m, 5 H, C_6H_4 and CH), 2.37 (m, 6 H, PC*H*CH_3), 2.15 (s, 3 H, CH_3), 1.25 (dvt, $N = 13.9$, $J(H,H) = 7.1$ Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 178.8 (s, C=O), 131.4, 129.7, 129.1, 128.7, 128.1, 127.9, 124.2, 121.8 (all s, C_6H_4, CH and *C*CH_3), 106.9 (br s, N_2C), 23.9 (vt, $N = 19.6$ Hz, P*C*HCH$_3$), 18.9 (s, PCH*C*H$_3$), 17.6 (s, C*C*H$_3$). ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 42.9 (d, $J(Rh,P) = 112.8$ Hz).

Preparation of *trans*-[RhCl($N_2C_5Cl_4$)(P*i*Pr$_3$)$_2$] (17). A solution of **2** (90 mg, 0.18 mmol) in toluene (5 mL) was treated with tetrachlorodiazocyclopentadiene (41 mg, 0.18 mmol) and stirred for 3 h at room temperature. A change of color from yellow to deep green occurred. The solvent was evaporated in vacuo, and the residue was washed three times with pentane (5 mL each) and recrystallized from toluene/pentane (1:3). After the solution was stored at −78 °C, deep green air-stable crystals precipitated, which were separated from the mother liquor, washed twice with small amounts of pentane, and dried: yield 117 mg (92%); mp 172 °C dec. Anal. Calcd for $C_{23}H_{42}Cl_5N_2P_2Rh$: C, 40.11; H, 6.15; N, 4.07. Found: C, 40.23; H, 5.93; N, 4.25. IR (KBr): $\nu(N_2C)$ 1997 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 2.43 (m, 6 H, PC*H*CH_3), 1.28 (dvt, $N = 14.1$, $J(H,H) = 7.1$ Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 109.3, 102.1 (both s, C_4Cl_4), 83.7 (br s, N_2C), 23.8 (vt, $N = 20.1$ Hz, P*C*HCH$_3$), 19.5 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 43.9 (d, $J(Rh,P) = 109.9$ Hz).

Preparation of *trans*-[RhCl($N_2C_5Ph_4$)(P*i*Pr$_3$)$_2$] (18). This compound was prepared as described for **17** from **2** (90 mg, 0.18 mmol) and tetraphenyldiazocyclopentadiene (71 mg, 0.18 mmol) in toluene (5 mL): brown-yellow air-stable solid; yield 136 mg (86%); mp 154 °C. Anal. Calcd for $C_{47}H_{62}ClN_2P_2Rh$: C, 66.00; H, 7.31; N, 3.28. Found: C, 65.99; H, 7.09; N, 2.99. IR (KBr): $\nu(N_2C)$ 2058 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 7.37−6.93 (br m, 20 H, C_6H_5), 2.47 (m, 6 H, PC*H*CH_3), 1.31 (dvt, $N = 13.8$, $J(H,H) = 7.2$ Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 137.8, 137.3, 132.1, 130.2, 128.6, 127.9, 126.1, 125.6, 125.1 (all s, C_6H_5), 94.5 (br s, N_2C), 24.2 (vt, $N =$ 19.4 Hz, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 41.9 (d, $J(Rh,P) = 114.3$ Hz).

Preparation of *trans*-[RhCl($N_2C_5Cl_4$)(Sb*i*Pr$_3$)$_2$] (20). A solution of **19** (73 mg, 0.11 mmol) in pentane (10 mL) was cooled to −78 °C and treated with a solution of tetrachlorodiazocyclopentadiene (50 mg, 0.22 mmol) in diethyl ether (5 mL). A change of color from orange-brown to green occurred. After the solution was warmed to room temperarure, the solvent was evaporated in vacuo. The olive green residue was washed twice with methanol (3 mL each) and once with pentane (5 mL) and dried. From the combined washings 1 equiv of $N_2C_5Cl_4$ could be reisolated. Yield of **20**: 75 mg (79%). Mp: 104 °C dec. Anal. Calcd for $C_{23}H_{42}Cl_5N_2RhSb_2$: C, 31.74; H, 4.86; N, 3.22; Rh, 11.82. Found: C, 31.62; H, 5.07; N, 3.20; Rh, 11.87. IR (KBr): $\nu(N_2C)$ 1942 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 2.20 (sept, $J(H,H) = 7.3$ Hz, 6 H, SbC*H*CH_3), 1.27 (d, $J(H,H) = 7.3$ Hz, 36 H, SbCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 109.3, 102.5 (both s, C_4Cl_4), 77.0 (s, N_2C), 22.0 (s, SbCH*C*H$_3$), 20.2 (br s, Sb*C*HCH$_3$).

Reactions of Compounds 3−7 and 14 with Ethene. A slow stream of ethene was passed through a solution of the diazoalkane complex (ca. 0.04 mmol) in C_6D_6 for 30 s at room temperature. After the solution was warmed to 40 °C and stirred for 1 h, the composition of the reaction mixture was investigated by ^1H NMR spectroscopy. In addition to the resonances of compound **2**, only signals corresponding to the C−C coupling products $CH_3CH{=}CRR'$ (R = R′ = Ph; R = R′ = *p*-Tol; R = Ph, R′ = *p*-Tol; R = Ph, R′ = *o*-Tol; R = R′ = *p*-C_6H_4-Cl; R,R′ = $C_{12}H_8$) could be observed. For **11** and **15** as starting materials, no reaction with ethene could be detected.

Preparation of [Rh(H)Cl{κ^2-*C*,*N*-$C_6H_4C(NNH_2)Ph$}-(P*i*Pr$_3$)$_2$] (21). A solution of **1** (90 mg, 0.095 mmol) in toluene (5 mL) was treated with a solution of diphenyl hydrazone (39 mg, 0.19 mmol) in toluene (2 mL) and stirred for 30 min at room temperature. A change of color from violet to red-brown occurred. The solvent was evaporated in vacuo and the residue extracted with pentane (20 mL). The extract was concentrated to ca. 3 mL in vacuo and then stored for 12 h at −78 °C. A light brown microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with small amounts of pentane (0 °C), and dried. The mother liquor consisted mainly of **21** and the diazoalkane complex **3**. Yield of **21**: 90 mg (70%). Mp: 133 °C dec. Anal. Calcd for $C_{31}H_{54}ClN_2P_2Rh$: C, 56.84; H, 8.31; N, 4.28. Found: C, 57.37; H, 8.07; N, 4.64. MS (EI): *m*/*z* 458 [Rh(P*i*Pr$_3$)$_2$Cl$^+$], 195 [$NH_2NC(Ph)C_6H_4^+$]. IR (KBr): ν(NH) 3360, 3248 (both br), ν(RhH) 2104 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.72, 7.53 (both d, $J(H,H) = 7.3$ Hz, 1 H each, *o*-H of C_6H_4), 7.40 (m, 2 H, C_6H_5), 7.27−6.70 (br m, 5 H, C_6H_4 and C_6H_5), 5.12 (br s, 2 H, NH_2), 2.16 (m, 6 H, PC*H*CH_3), 1.30 (dvt, $N = 13.1$, $J(H,H) = 7.3$ Hz, 18 H, PCHC*H*$_3$), 1.10 (dvt, $N = 14.5$, $J(H,H) = 7.3$ Hz, 18 H, PCHC*H*$_3$), −14.22 (dt, $J(Rh,H) = 14.5$, $J(P,H) = 14.5$ Hz, 1 H, RhH). ^{13}C NMR (50.3 MHz, C_6D_6): δ 167.2 (dt, $J(Rh,C) = 31.8$, $J(P,C) = 8.9$ Hz, RhC), 155.9 (s, C=N), 146.6, 140.0, 133.3, 129.5, 129.1, 129.0, 128.3, 127.0, 126.7, 125.8, 120.8 (all s, C_6H_4 and C_6H_5), 24.9 (vt, $N = 21.6$ Hz, P*C*HCH$_3$), 19.6, 19.4 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 36.9 (d, $J(Rh,P) =$ 109.0 Hz; dd in off-resonance).

Preparation of [Rh(H)Cl{κ^2-*C*,*N*-$C_6H_4C(NNH_2)CH_3$}-(P*i*Pr$_3$)$_2$] (22). This compound was prepared as described for **21** from **1** (97 mg, 0.105 mmol) and $PhC(CH_3){=}NNH_2$ (28 mg, 0.21 mmol) in toluene (5 mL). After extraction of the residue with pentane, a brown oil was obtained, which contained in addition to **22** small amounts of byproducts. Attempts to separate the components failed. Spectroscopic data for **22** are as follows. IR (KBr): ν(NH) 3380, 3280 (both br), ν(RhH) 2090 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.75, 7.09 (both d, $J(H,H) = 7.3$ Hz, 2 H each, *o*-H and *m*-H of C_6H_4), 4.79 (br s, 2 H, NH_2), 2.40 (m, 6 H, PC*H*CH_3), 1.54 (s, 3 H, CCH_3), 1.35 (dvt, $N = 13.1$, $J(H,H) = 7.2$ Hz, 18 H, PCHC*H*$_3$), 0.96 (dvt, $N =$ 14.3, $J(H,H) = 7.2$ Hz, 18 H, PCHC*H*$_3$), −14.23 (dt, $J(Rh,H)$

= 14.6, J(P,H) = 13.0 Hz, 1 H, RhH). ^{13}C NMR (50.3 MHz, C_6D_6): δ 167.5 (dt, J(Rh,C) = 32.3, J(P,C) = 8.8 Hz, RhC), 156.2 (s, C═N), 145.9, 139.0, 127.1, 123.7, 125.8, 120.7 (all s, C_6H_4), 24.6 (vt, N = 20.3 Hz, P*C*HCH$_3$), 19.5, 19.1 (both s, PCH*C*H$_3$), 11.9 (s, C*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 37.3 (d, J(Rh,P) = 110.4 Hz; dd in off-resonance).

Attempted Conversion of Compound 21 to 3. A solution of **21** (106 mg, 0.16 mmol) in hexane (2 mL) was poured onto a column filled with Al_2O_3 (neutral, activity grade V, length of column 5 cm). With hexane, a green fraction was eluted which consisted of **3** and the dinitrogen complex **12**. Subsequent elution with toluene afforded a brownish fraction in which, besides small amounts of **21**, only unidentified products could be detected.

Preparation of *trans*-[Rh(C≡CH)(N$_2$CPh$_2$)(P*i*Pr$_3$)$_2$] (24). A solution of **23** (65 mg, 0.13 mmol) in pentane (5 mL) was treated at −30 °C with a solution of Ph_2CN_2 (26 mg, 0.13 mmol) in pentane (2 mL). The solution was slowly warmed to room temperature, which led to the precipitation of a finely divided green solid. After the solution was stirred at ca. 20 °C for 10 min, the solvent was evaporated in vacuo and the residue recrystallized from pentane (10 mL) at −78 °C. Green moderately air-sensitive crystals were formed, which were separated from the mother liquor, washed twice with small amounts of pentane (0 °C), and dried: yield 70 mg (80%); mp 35 °C dec. Anal. Calcd for $C_{33}H_{53}N_2P_2Rh$: C, 61.68; H, 8.31; N, 4.36. Found: C, 61.42; H, 8.30; N, 4.01. MS (EI): m/z 642 [M$^+$], 448 [M$^+$ − Ph_2CN_2]. IR (hexane): ν(≡CH) 3280, ν(C≡C) 1935, ν(N$_2$C) 1920 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.42−6.90 (br m, 10 H, C_6H_5), 3.02 (d, J(Rh,H) = 2.0 Hz, 1 H, ≡CH), 2.43 (m, 6 H, PC*H*CH$_3$), 1.29 (dvt, N = 13.3, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 129.9, 129.0, 124.9, 124.4 (all s, C_6H_5), 113.8 (dt, J(Rh,C) = 15.3, J(P,C) = 3.2 Hz, C≡*C*H), 109.2 (dt, J(Rh,C) = 51.3, J(P,C) = 20.8 Hz, *C*≡CH), 75.5 (br s, N$_2$C), 24.9 (vt, N = 18.5 Hz, P*C*HCH$_3$), 20.5 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 46.4 (d, J(Rh,P) = 132.2 Hz).

Preparation of *trans*-[Rh(C≡CH)(N$_2$CC$_{12}$H$_8$)(P*i*Pr$_3$)$_2$] (25). A solution of **23** (86 mg, 0.18 mmol) in pentane (8 mL) was treated at −30 °C with a solution of $C_{12}H_8CN_2$ (35 mg, 0.18 mmol) in pentane (4 mL). The solution was slowly warmed to room temperature, which led to a change of color from orange-red to olive green. After the solution was stirred at ca. 20 °C for 5 min, the solvent was evaporated in vacuo and the residue recrystallized from acetone (5 mL) at −30 °C. Olive green moderately air-sensitive crystals were formed, which were separated from the mother liquor, washed twice with small amounts of acetone (0 °C), and dried: yield 91 mg (79%); mp 89 °C. Anal. Calcd for $C_{33}H_{51}N_2P_2Rh$: C, 61.87; H, 8.03; N, 4.37. Found: C, 61.74; H, 8.23; N, 3.91. IR (KBr): ν(≡CH) 3240, ν(C≡C) 1935, ν(N$_2$C) 1920 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.86 (br d, J(H,H) = 7.9 Hz, 2 H, H^1 and H^8), 7.66 (br d, J(H,H) = 7.9 Hz, 2 H, H^4 and H^5), 7.32, 7.10 (both ddd, J(H,H) = 7.8, 7.5 and 1.1 Hz, 2 H each, H^2, H^7 and H^3, H^6), 3.12 (dt, J(Rh,H) = 2.0, J(P,H) = 1.8 Hz, C≡CH), 2.41 (m, 6 H, PC*H*CH$_3$), 1.25 (dvt, N = 13.5, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$); the protons are numbered clockwise beginning at the ortho position next to the five-membered ring. ^{13}C NMR (50.3 MHz, C_6D_6): δ 131.5, 130.5, 125.7, 122.7, 121.1, 118.6 (all s, C_6H_4), 116.3 (dt, J(Rh,C) = 14.3, J(P,C) = 3.7 Hz, C≡*C*H), 71.2 (br s, N$_2$C), 24.9 (vt, N = 18.5 Hz, P*C*HCH$_3$), 20.3 (s, PCH*C*H$_3$); signal for *C*≡CH probably covered by signal of solvent. ^{31}P NMR (81.0 MHz, C_6D_6): δ 48.1 (d, J(Rh,P) = 129.3 Hz).

Preparation of *trans*-[Rh(C≡C*t*Bu)(N$_2$CPh$_2$)(P*i*Pr$_3$)$_2$] (27). This compound was prepared as described for **24** from **26** (102 mg, 0.19 mmol) and Ph_2CN_2 (37 mg, 0.19 mmol) in pentane (8 mL). After recrystallization from pentane at −78 °C green, slightly air-sensitive crystals were obtained: yield 127 mg (95%); mp 94 °C dec. Anal. Calcd for $C_{37}H_{61}N_2P_2Rh$: C, 63.60; H, 8.80; N, 4.04. Found: C, 63.37; H, 8.96; N, 3.64. IR (hexane): ν(C≡C) 2070, ν(N$_2$C) 1930 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.44−6.81 (br m, 10 H, C_6H_5), 2.42 (m, 6 H, PC*H*CH$_3$), 1.28 (dvt, N = 15.2, J(H,H) = 6.9 Hz, 36 H, PCHC*H*$_3$), 1.26 (s, 9 H, CCH$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 136.8 (dt, J(Rh,C) = 14.4, J(P,C) = 3.2 Hz, C≡*C*t Bu), 130.3, 129.0, 124.7, 124.0 (all s, C_6H_5), 98.5 (dt, J(Rh,C) = 51.3, J(P,C) = 20.8 Hz, *C*≡C*t*Bu), 75.2 (br s, N$_2$C), 32.6 (s, *C*CH$_3$), 29.8 (s, C*C*H$_3$), 24.7 (vt, N = 18.5 Hz, P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 46.9 (d, J(Rh,P) = 132.2 Hz).

Preparation of *trans*-[Rh(C≡C*t*Bu)(N$_2$CC$_{12}$H$_8$)(P*i*Pr$_3$)$_2$] (28). This compound was prepared as described for **24** from **26** (97 mg, 0.18 mmol) and $C_{12}H_8CN_2$ (35 mg, 0.18 mmol) in pentane (8 mL). After recrystallization from acetone at −30 °C green, slightly air-sensitive crystals were obtained: yield 104 mg (82%); mp 109 °C dec. Anal. Calcd for $C_{37}H_{59}N_2P_2Rh$: C, 63.78; H, 8.89; N, 4.02. Found: C, 63.92; H, 8.80; N, 3.97. MS (EI): m/z 696 [M$^+$], 504 [M$^+$ − $C_{12}H_8CN_2$]. IR (C_6H_6): ν(C≡C) 2050, ν(N$_2$C) 1930 (br) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.88 (br d, J(H,H) = 7.7 Hz, 2 H, H^1 and H^8), 7.67 (br d, J(H,H) = 7.9 Hz, 2 H, H^4 and H^5), 7.34, 7.10 (both ddd, J(H,H) = 7.9, 7.7 and 1.1 Hz, 2 H each, H^2, H^7 and H^3, H^6), 2.42 (m, 6 H, PC*H*CH$_3$), 1.25 (dvt, N = 13.5, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$), 1.22 (s, 9 H, CCH$_3$); the protons are numbered clockwise beginning at the ortho position next to the five-membered ring. ^{13}C NMR (50.3 MHz, C_6D_6): δ 139.9 (dt, J(Rh,C) = 13.9, J(P,C) = 3.2 Hz, C≡*C*t Bu), 130.3, 129.4, 125.5, 122.2, 121.0, 118.5 (all s, C_6H_4), 98.0 (dt, J(Rh,C) = 51.8, J(P,C) = 21.3 Hz, *C*≡C*t*Bu), 74.4 (br s, N$_2$C), 32.4 (s, *C*CH$_3$), 29.7 (s, C*C*H$_3$), 24.8 (vt, N = 19.4 Hz, P*C*HCH$_3$), 20.3 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 48.2 (d, J(Rh,P) = 129.3 Hz).

Preparation of [RhCl{κ^2-*N*,*O*-N$_2$C(Ph)C(O)Ph}(P*i*Pr$_3$)$_2$] (29). A solution of **2** (90 mg, 0.18 mmol) in toluene (5 mL) was treated with PhC(O)C(Ph)N$_2$ (40 mg, 0.18 mmol) and stirred for 3 h at room temperature. A change of color from yellow to red occurred. The solvent was evaporated in vacuo, and the residue was washed three times with pentane (5 mL each) and recrystallized from toluene/pentane (1:3). After the solution was stored at −78 °C, orange-red, moderately air-stable crystals precipitated, which were separated from the mother liquor, washed twice with small amounts of pentane, and dried: yield 92 mg (73%); mp 94 °C dec. Anal. Calcd for $C_{32}H_{52}ClN_2OP_2Rh$: C, 56.42; H, 7.71; N, 4.11. Found: C, 56.14; H, 7.96; N, 3.78. IR (KBr): ν(N$_2$C) 1935 (br), ν(C═O) 1610 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.17, 7.07 (both m, 5 H each, C_6H_5), 2.62 (m, 6 H, PC*H*CH$_3$), 1.30, 1.26 (both dvt, N = 13.2, J(H,H) = 7.2 Hz, 18 H each, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 150.9 (s, C═O), 139.3, 138.6 (both s, *ipso*-C of C_6H_5), 130.2, 129.3, 128.6, 128.3, 127.2, 125.4 (all s, C_6H_5), 101.2 (br s, N$_2$C), 23.2 (vt, N = 17.2 Hz, P*C*HCH$_3$), 19.6, 19.5 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 31.1 (d, J(Rh,P) = 112.8 Hz).

Preparation of [RhCl{κ^2-*N*,*O*-N$_2$C(Ph)C(O)Me}(P*i*Pr$_3$)$_2$] (30). This compound was prepared as described for **29** from **2** (90 mg, 0.18 mmol) and CH$_3$C(O)C(Ph)N$_2$ (29 mg, 0.18 mmol) in toluene (5 mL): orange-red, moderately air-stable solid; yield 74 mg (65%); mp 108 °C dec. Anal. Calcd for $C_{27}H_{50}ClN_2OP_2Rh$: C, 52.39; H, 8.14; N, 4.53. Found: C, 51.90; H, 8.23; N, 4.11. IR (KBr): ν(N$_2$C) 1933 (br), ν(C═O) 1686 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 7.59−7.18 (br m, 5 H, C_6H_5), 2.63 (m, 6 H, PC*H*CH$_3$), 2.00 (s, 3 H, C(O)CH$_3$), 1.41, 1.30 (both dvt, N = 13.1, J(H,H) = 7.1 Hz, 18 H each, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 151.7 (s, C═O), 139.3 (s, *ipso*-C of C_6H_5), 130.0, 129.6, 129.3, 128.8, 125.8 (all s, C_6H_5), 100.3 (br s, N$_2$C), 23.5 (vt, N = 17.8 Hz, P*C*HCH$_3$), 20.9 (s, C(O)*C*H$_3$), 19.5, 19.2 (both s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 31.0 (d, J(Rh,P) = 114.3 Hz).

Preparation of [RhCl{N$_2$C(CO$_2$Me)C(O)CH$_2$CH$_2$CH(CH$_3$)$_2$}(P*i*Pr$_3$)$_2$] (31a,b). A solution of **2** (100 mg, 0.20 mmol) in toluene (10 mL) was cooled to −78 °C and then treated with the diazo derivative of the keto ester (CH$_3$)$_2$CHCH$_2$CH$_2$C(O)C(CO$_2$Me)N$_2$ (40 mg, 0.20 mmol). A change of color from

Table 1. Crystallographic Data for Compounds 15, 20, and 31[a]

	15	20	31a
formula	$C_{32}H_{50}ClN_2OP_2Rh$	$C_{23}H_{42}Cl_5N_2RhSb_2$	$C_{27}H_{56}ClN_2O_3P_2Rh$
M_r	679.04	870.25	657.04
cryst size, mm	0.2 × 0.2 × 0.2	0.70 × 0.45 × 0.20	0.75 × 0.38 × 0.32
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	10.820(2)	16.205(6)	11.2842(5)
b, Å	11.8560(10)	14.517(3)	18.0279(8)
c, Å	14.419(2)	14.779(6)	19.2465(9)
α, deg	70.810(10)	90	117.278(4)
β, deg	82.920(10)	101.24(2)	97.328(4)
γ, deg	72.370(10)	90	96.510(4)
V, Å^3	1664.3(4)	3410(2)	3385.3(3)
Z	2	4	2
d_{calcd}, g cm^{-3}	1.355	1.695	1.289
T, K	293(2)	293(2)	293(2)
μ, mm^{-1}	0.716	2.451	0.699
scan method	ω/θ	ω/θ	ω/θ
2θ(max), deg	43.96	46	46
total no. of rflns	4073	4483	9928
no. of unique rflns	4072 (R(int) = 0.0000)	4028 (R(int) = 0.0090)	9367 (R(int) = 0.0142)
no. of obsd rflns ($I > 2\sigma(I)$)	3188	3527	8003
no. of rflns used for refinement	4072	4028	9367
no. of params refined	364	311	679
final R indices ($I > 2\sigma(I)$)	R1 = 0.0308, wR2 = 0.0939[a]	R1 = 0.0336, wR2 = 0.0838[a]	R1 = 0.0453, wR2 = 0.1182[a]
R indices (all data)	R1 = 0.0597, wR2 = 0.1295[a]	R1 = 0.0395, wR2 = 0.0892[a]	R1 = 0.0534, wR2 = 0.1291[a]
resid electron density, e Å^{-3}	0.452/−0.469	1.285/−0.613	1.032/−0.656

[a] $w^{-1} = [\sigma^2F_o^2 + (0.0866P)^2 + 0.0000P]$ (**15**), $w^{-1} = [\sigma^2F_o^2 + (0.0406P)^2 + 11.0144P]$ (**20**), $w^{-1} = [\sigma^2F_o^2 + (0.0671P)^2 + 5.2986P]$ (**31a**), where $P = (F_o^2+2F_c^2)/3$.

yellow to dark red occurred. After the cooling bath was removed, the solution was stirred for 1 h. The solvent was evaporated in vacuo, and the oily residue was dissolved in pentane (8 mL). The solution was stored at −78 °C for 12 h, which led to the precipitation of red crystals. They were separated from the mother liquor, washed three times with small amounts of pentane (−30 °C), and dried: yield 113 mg (84%). Anal. Calcd for $C_{27}H_{56}ClN_2O_3P_2Rh$: C, 49.35; H, 8.59; N, 4.26. Found: C, 49.46; H, 8.85; N, 4.20. IR (KBr): $\nu(N_2C)$ 1950, 1900 (br), $\nu(CO_2Me)$ 1701, $\nu(C{=}O)$ 1653, 1634 cm^{-1}. ^{1}H NMR (200 MHz, $C_6D_5CD_3$, 291 K): δ 3.60, 3.47 (both s, OCH_3), 3.17 (m, $C(O)CH_2$), 2.35 (m, $PCHCH_3$), 1.60 (m, $(CH_3)_2CHCH_2$), 1.22, 1.05 (both m, $PCHCH_3$), 0.95, 0.88 (both d, J(H,H) = 7.2 Hz, $CH(CH_3)_2$). ^{1}H NMR (200 MHz, $C_6D_5CD_3$, 223 K): δ 3.54 (br s, OCH_3), 3.17 (m, $C(O)CH_2$), 2.19 (m, $PCHCH_3$), 1.56 (m, $(CH_3)_2CHCH_2$), 1.06, 0.91 (both br m, $PCHCH_3$ and $CH(CH_3)_2$). ^{1}H NMR (200 MHz, $C_6D_5CD_3$, 253 K): δ 3.53, 3.40 (both s, OCH_3), 3.11 (m, $C(O)CH_2$), 2.25 (m, $PCHCH_3$), 1.55 (m, $(CH_3)_2CHCH_2$), 1.09, 0.94 (both m, $PCHCH_3$), 0.91, 0.81 (both d, J(H,H) = 7.3 Hz, $CH(CH_3)_2$). ^{1}H NMR (200 MHz, $C_6D_5CD_3$, 313 K): δ 3.65, 3.54 (both s, OCH_3), 3.14 (m, $C(O)CH_2$), 2.44 (m, $PCHCH_3$), 1.67 (m, $(CH_3)_2CHCH_2$), 1.33, 1.14 (both m, $PCHCH_3$), 0.94 (br d, $CH(CH_3)_2$). ^{1}H NMR (200 MHz, $C_6D_5CD_3$, 333 K): δ 3.56 (br s, OCH_3), 3.11 (m, $C(O)CH_2$), 2.46 (m, $PCHCH_3$), 1.67 (m, $(CH_3)_2CHCH_2$), 1.31 (br m, $PCHCH_3$), 0.95 (br d, $CH(CH_3)_2$). ^{31}P NMR (81.0 MHz, $C_6D_5CD_3$, 291 K): δ 43.1 (d, J(Rh,P) = 113.4 Hz), 31.6 (d, J(Rh,P) = 111.9 Hz). ^{31}P NMR (81.0 MHz, $C_6D_5CD_3$, 223 K): δ 42.3 (d, J(Rh,P) = 114.5 Hz), 30.7 (d, J(Rh,P) = 112.6 Hz). ^{31}P NMR (81.0 MHz, $C_6D_5CD_3$, 333 K): δ 43.8 (d, J(Rh,P) = 111.8 Hz), 32.3 (d, J(Rh,P) = 110.5 Hz).

Reaction of Compound 2 with $PhCH_2C(O)CHN_2$. A solution of **2** (90 mg, 0.18 mmol) in toluene (8 mL) was treated at −78 °C with a solution of $PhCH_2C(O)CHN_2$ (29 mg, 0.18 mmol) in toluene (2 mL). After the cooling bath was removed, the solution was stirred for 1 h. The solvent was evaporated in vacuo, and the oily residue was dissolved in $C_6D_5CD_3$ (0.5 mL). The ^{1}H and ^{31}P NMR spectra revealed that, in addition to traces of unidentified byproducts, the compounds **32** and **12** were formed in the approximate ratio of 2:1. While attempts to separate these compounds by fractional crystallization failed, the attempted separation by column chromatography led mainly to decomposition. Data for **32** are as follows. ^{1}H NMR (200 MHz, C_6D_6): δ 7.05 (m, 5 H, C_6H_5), 6.59 (s, 1 H, N_2CH), 3.10 (s, 2 H, CH_2), 2.31 (m, 6 H, $PCHCH_3$), 1.20 (m, 36 H, $PCHCH_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 31.1 (d, J(Rh,P) = 114.2 Hz).

X-ray Structure Determination of Compounds 15, 20, and 31a. Single crystals of **15** were grown from toluene/hexane at room temperature, those of **20** from acetone at −30 °C, and those of **31a** from pentane at −20 °C. The data were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystal data collection parameters are summarized in Table 1. Intensity data were corrected by Lorentz and polarization effects, and empirical absorption corrections were applied (Ψ scan method, minimum transmission 93.00% for **15**, 56.28% for **20**, and 93.19% for **31a**). The structures were solved by direct methods (SHELXS-86).[29] Atomic coordinates and anisotropic displacement parameters were refined by full-matrix least squares against F_o^2 (SHELXL-93).[30] The asymmetric unit of **31a** contains two independent molecules, which differs both in the conformation of one isopropyl group and in the conformation of the phosphines.

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Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **15**, **20**, and **31a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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