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# Cationic and Neutral Diphenyldiazomethanerhodium(II) Complexes as Catalytically Active Species in the C–C Coupling Reaction of Olefins and Diphenyldiazomethane

Helmut Werner,<sup>\*[a]</sup> Michael E. Schneider,<sup>[a]</sup> Marco Bosch,<sup>[a]</sup> Justin Wolf,<sup>[a]</sup> Jan H. Teuben,<sup>[b]</sup> Auke Meetsma,<sup>[c]</sup> and Sergej I. Troyanov<sup>[d]</sup>

Dedicated to Professor Günter Wilke on the occasion of his 75th birthday

**Abstract:** Cationic rhodium(II) complexes *cis*-[Rh(acetone)<sub>2</sub>(L)(L')]<sup>+</sup> (**2**: L = L' = C<sub>8</sub>H<sub>14</sub>; **3**: L = C<sub>8</sub>H<sub>14</sub>; L' = PiPr<sub>3</sub>; **4**: L = L' = PiPr<sub>3</sub>), prepared from [RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub> and isolated as PF<sub>6</sub> salts, catalyze the C–C coupling reaction of diphenyldiazomethane with ethene, propene, and styrene. In most cases, a mixture of isomeric olefins and cyclopropanes were obtained which are formally built up by one equivalent of RCH=CH<sub>2</sub> (R = H, Me, Ph) and one equivalent of CPh<sub>2</sub>. The efficiency and selectivity of the catalyst depends significantly on the coordination sphere

around the rhodium(II) center. Treatment of **4** with Ph<sub>2</sub>CN<sub>2</sub> in the molar ratio of 1:1 and 1:2 gave the complexes *trans*-[Rh(PiPr<sub>3</sub>)<sub>2</sub>(acetone)(η<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)]PF<sub>6</sub> (**8**) and *trans*-[Rh(PiPr<sub>3</sub>)<sub>2</sub>(η<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub> (**9**), of which **8** was characterized by X-ray crystallography. Since **8** and **9** not only react with ethene but also catalyze the reaction of C<sub>2</sub>H<sub>4</sub> and free Ph<sub>2</sub>CN<sub>2</sub>, they can be regarded as intermediates

(possibly resting states) in the C–C coupling process. The lability of **8** and **9** is illustrated by the reactions with pyridine and NaX (X = Cl, Br, I, N<sub>3</sub>) which afford the mono(diphenyldiazomethane)rhodium(II) compounds *trans*-[Rh(PiPr<sub>3</sub>)<sub>2</sub>(py)(η<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)]PF<sub>6</sub> (**10**) and *trans*-[RhX(η<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] (**11**–**14**), respectively. The catalytic activity of the neutral complexes **11**–**14** is somewhat less than that of the cationic species **8**, **9** and decreases in the order Cl > Br > I > N<sub>3</sub>.

**Keywords:** acetone complexes · C–C coupling · N ligands · P ligands · rhodium

## Introduction

During studies directed to the synthesis of carbenerhodium(II) complexes of the general composition *trans*-[RhCl(=CR<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>], we observed that the dimer [RhCl(PiPr<sub>3</sub>)<sub>2</sub>]<sub>2</sub> as well

as the monomeric ethene derivative *trans*-[RhCl(C<sub>2</sub>H<sub>4</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] react with diphenyldiazomethane to afford the square-planar diazoalkane compound *trans*-[RhCl(N<sub>2</sub>CPh<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>].<sup>[1]</sup> Moreover, we discovered that various rhodium(II) complexes including [RhCl(PiPr<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and [RhCl(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> catalyze the reaction of ethene and diphenyldiazomethane to give almost selectively 1,1-diphenylprop-1-ene Ph<sub>2</sub>C=CHMe.<sup>[1, 2]</sup> The formation of this trisubstituted olefin can be formally understood as the coupling of two carbene fragments :CPh<sub>2</sub> and :CHMe, of which the latter is generated from the isomeric ethene. Besides Ph<sub>2</sub>C=CHMe, there were only traces of 1,1-diphenylcyclopropane detected which was surprising insofar as it was well known that dinuclear bis(carboxylato)rhodium(II) compounds such as [Rh<sub>2</sub>(μ-O<sub>2</sub>CMe)<sub>4</sub>] and derivatives thereof are effective catalysts for the synthesis of cyclopropanes from olefins and diazoalkanes.<sup>[3]</sup> In the context of these investigations we also found that, if the anionic ligand in the chlororhodium(II) complexes is substituted by acetate, benzoate, or acetylacetonate, the catalytic activity decreases and besides Ph<sub>2</sub>C=CHMe and *cyclo*-1,1-C<sub>3</sub>H<sub>4</sub>Ph<sub>2</sub>, a third isomer CH<sub>2</sub>=CHCHPh<sub>2</sub> is formed from C<sub>2</sub>H<sub>4</sub> and Ph<sub>2</sub>CN<sub>2</sub>.<sup>[4]</sup>

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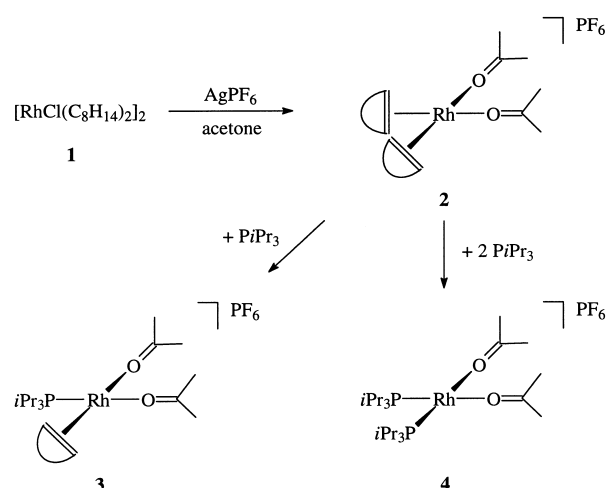
Because of this apparent influence of the anionic ligand on both the reactivity and the selectivity, we became interested to find out whether *cationic* rhodium(II) complexes also catalyze the reaction of olefins (not only ethene) and diphenyldiazomethane and what the products of these C–C coupling processes are. Here we report on the preparation of a series of compounds of the general composition *cis*-[Rh(acetone)<sub>2</sub>(L)(L')]PF<sub>6</sub>, on the synthesis of cationic as well as neutral rhodium(II) complexes containing Ph<sub>2</sub>CN<sub>2</sub> as a ligand, and on the catalytic activity of these species in C–C coupling reactions. Some preliminary results have already been communicated.<sup>[5]</sup>

## Results and Discussion

**Cationic bis(acetone)rhodium(II) complexes:** From earlier work it was already known that the dimeric diolefinrhodium(II) complexes [[RhCl(diolefin)]<sub>2</sub>] (diolefin = norbornadiene, cycloocta-1,5-diene) react with AgPF<sub>6</sub> in a coordinating solvent such as acetone or THF to give the compounds [Rh(S)<sub>2</sub>(diolefin)]PF<sub>6</sub> (S = acetone, THF).<sup>[6]</sup> The “silver-salt-method” had also been used in our laboratory for the preparation of the bis(cyclooctene) derivative **2** (Scheme 1) which contains four labile monodentate ligands. These are easily displaced by a bidentate donor such as *i*Pr<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OMe to produce [Rh( $\kappa^2$ -*O,P*-*i*Pr<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OMe)<sub>2</sub>]PF<sub>6</sub> in a good yield.<sup>[7]</sup>

In order to confirm the supposed stereochemistry of the cation of **2**, an X-ray crystal structure analysis was carried out

**Abstract in German:** Die kationischen Rhodium(II)-Komplexe *cis*-[Rh(acetone)<sub>2</sub>(L)(L')]PF<sub>6</sub> (**2**: L = L' = C<sub>8</sub>H<sub>14</sub>; **3**: L = C<sub>8</sub>H<sub>14</sub>; L' = PiPr<sub>3</sub>; **4**: L = L' = PiPr<sub>3</sub>), die aus [[RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub>] hergestellt und als PF<sub>6</sub>-Salze isoliert wurden, katalysieren die C-C-Kupplungsreaktion von Diphenyldiazomethan mit Ethen, Propen und Styrol. In den meisten Fällen wird ein Gemisch isomerer Olefine und Cyclopropane erhalten, die sich formal aus einem Äquivalent RCH=CH<sub>2</sub> (R = H, Me, Ph) und einem Äquivalent CPh<sub>2</sub> zusammensetzen. Die Effektivität und die Selektivität des Katalysators hängen entscheidend von der Koordinationssphäre des Rhodium(II)-Zentrums ab. Die Umsetzungen von **4** mit Ph<sub>2</sub>CN<sub>2</sub> im Molverhältnis 1:1 und 1:2 liefern die Komplexe *trans*-[Rh(PiPr<sub>3</sub>)<sub>2</sub>(acetone)( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)]PF<sub>6</sub> (**8**) und *trans*-[Rh(PiPr<sub>3</sub>)<sub>2</sub>( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)]PF<sub>6</sub> (**9**), von denen **8** durch eine Kristallstrukturanalyse charakterisiert wurde. Da die Verbindungen **8** und **9** nicht nur mit Ethen reagieren, sondern auch die Reaktion von C<sub>2</sub>H<sub>4</sub> mit freiem Ph<sub>2</sub>CN<sub>2</sub> katalysieren, können sie als Zwischenstufen (möglicherweise als „resting state“) in dem C-C-Kupplungsprozess angesehen werden. Die Labilität von **8** und **9** zeigt sich bei den Reaktionen mit Pyridin und NaX (X = Cl, Br, I, N<sub>3</sub>), die zu den Mono(diphenyldiazomethan)rhodium(II)-Verbindungen *trans*-[Rh(PiPr<sub>3</sub>)<sub>2</sub>(py)( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)]PF<sub>6</sub> (**10**) und *trans*-[RhX( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] (**11–14**) führen. Die katalytische Aktivität der Neutralkomplexen **11–14** ist etwas geringer als diejenige der kationischen Spezies **8, 9** und nimmt in der Reihenfolge Cl > Br > I > N<sub>3</sub> ab.



Scheme 1. Preparation of the cationic bis(acetone)rhodium(II) complexes **2–4** from the bis(cyclooctene) complex **1**.

(Figure 1) which reveals that the coordination sphere around the rhodium center is distorted square-planar. The cyclooctene as well as the acetone ligands are in *cis* disposition, the distances Rh(1)–O(1) and Rh(1)–O(2) (2.138(4) and 2.126(4) Å) being somewhat longer than the Rh–O distance

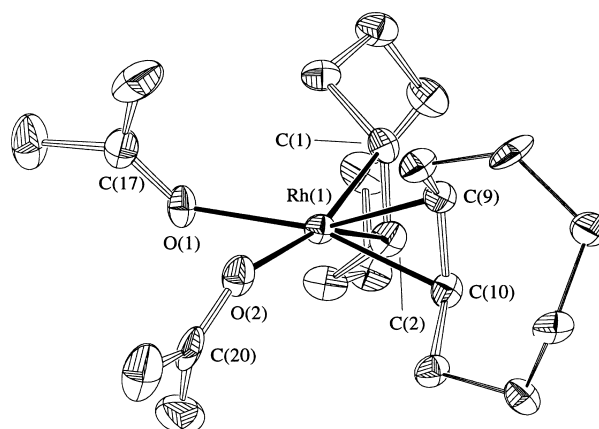
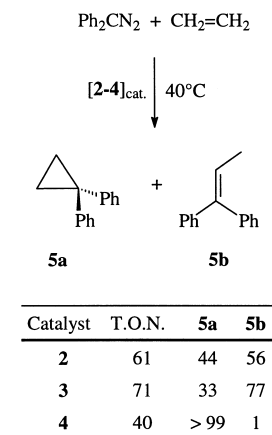


Figure 1. Molecular structure of **2** (anionic ligand omitted for clarity). Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh(1)–O(1) 2.138(4), Rh(1)–O(2) 2.126(4), Rh(1)–C(1) 2.126(5), Rh(1)–C(2) 2.122(5), Rh(1)–C(9) 2.113(5), Rh(1)–C(10) 2.148(5), C(1)–C(2) 1.394(7), C(9)–C(10) 1.393(7), O(1)–C(17) 1.232(7), O(2)–C(20) 1.240(7); O(1)–Rh(1)–O(2) 83.87(14), Rh(1)–O(1)–C(17) 126.8(4), Rh(1)–O(2)–C(20) 127.3(4).

(2.078(2) Å) in the cation *trans*-[Rh(=C=C=CPh<sub>2</sub>)(acetone)(PiPr<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.<sup>[8]</sup> The coordinated C–C bonds of the C<sub>8</sub>H<sub>14</sub> ligands are significantly elongated compared with the free olefin indicating a relative high degree of back bonding from the metal to the olefin. The bond angles Rh(1)–O(1)–C(17) and Rh(1)–O(2)–C(20) are 126.8(4)° and 127.3(4)°, respectively, which indicates that the acetone ligands are coordinated through one of the lone pairs of electrons on the oxygen atom.

Upon treatment of **2** with PiPr<sub>3</sub> in diethyl ether a replacement of one cyclooctene ligand occurs and the PF<sub>6</sub> salt of the cationic monophosphane complex **3** is formed. The composition of the yellow crystalline solid is supported both by the

elemental analysis and the spectroscopic data. The IR spectrum of **3** displays two C=O stretching frequencies at 1701 and 1658  $\text{cm}^{-1}$  in agreement with a *cis* disposition of the two acetone units. We note that the reaction of **2** with two equivalents of triisopropylphosphane generates the bis(phosphane) compound **4** which in contrast to **3** is a violet, quite air-sensitive solid.<sup>[8]</sup> The presence of 1:1 electrolytes has been confirmed for **3** as well as for **4** by conductivity measurements.



Scheme 2. Results of the catalytic reaction of ethene and  $\text{Ph}_2\text{CN}_2$  with compounds **2–4** as catalyst (T.O.N. = turnover number = [(mmol product)/(mmol catalyst)]); ratio of **5a** and **5b** in %).

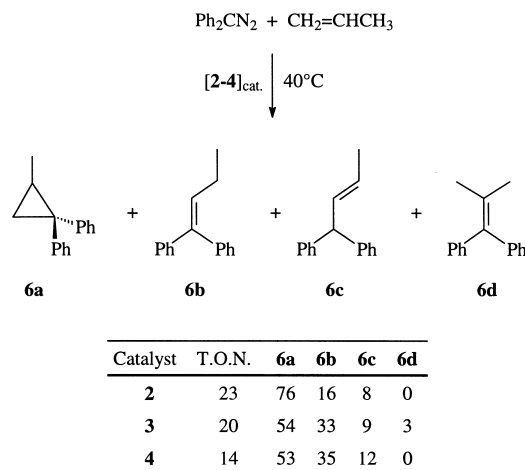
1-ene (**5b**) decreases. In contrast, substitution of *both* olefinic ligands by triisopropylphosphane leads to a significant decrease in activity but also to a tremendous increase in selectivity, the cyclopropanation product **5a** being almost exclusively formed.

The mechanism of the reaction of ethene and diphenyldiazomethane in the presence of **2**, **3**, or **4** as catalyst is not clear as yet. We assume that in the initial stage of the catalytic process both  $\text{C}_2\text{H}_4$  and  $\text{Ph}_2\text{CN}_2$  are coordinated to rhodium and that, after elimination of  $\text{N}_2$ , a four-membered  $\text{RhC}_3$  cycle is formed. The next step could be the opening of the metallacyclobutane ring to give a chainlike cationic intermediate  $\text{RhCH}_2\text{CH}_2\text{CPh}_2^+$  bearing the positive charge at the trisubstituted terminal carbon atom. Reductive elimination and ring closure should yield the cyclopropane **5a**. Regarding the formation of the olefinic isomer **5b**, it is conceivable that the postulated metallacyclobutane reacts by  $\beta$ -H shift to afford a  $\pi$ -allyl(hydrido)rhodium(III) intermediate  $[\text{L}_3\text{RhH}(\eta^3\text{-CH}_2\text{CHCPh}_2)]^+$  which, by reductive coupling of the hydrido ligand and the  $\text{CH}_2$  carbon atom of the allyl unit, generates  $\text{Ph}_2\text{C}=\text{CHMe}$  (**5b**).

Interestingly, no formation of  $\text{CH}_2=\text{CPh}_2$ , which would be the result of a *retro*-[2+2] cycloaddition of the postulated metallacyclobutane, is observed. This finding, however, does not exclude the possibility of a metallacyclic intermediate. Recent studies on the reactivity of ethene toward carbene titanium complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\kappa^2\text{-O},\text{P-OCH}_2\text{CH}_2\text{PPh}_2)(=\text{CHtBu})]^{[9]}$  and  $[(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NtBu-}\kappa\text{-N})\text{Ti}(=\text{CHtBu})(\text{PMe}_3)]^{[10]}$  have shown that a mixture of C–C coupling rather

than metathesis products is generated. Moreover, in the first case the metallacyclobutane complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{CH}_2\text{CH}_2\text{CHtBu})(\kappa^2\text{-O},\text{P-OCH}_2\text{CH}_2\text{PPh}_2)]$  could be isolated and characterized.

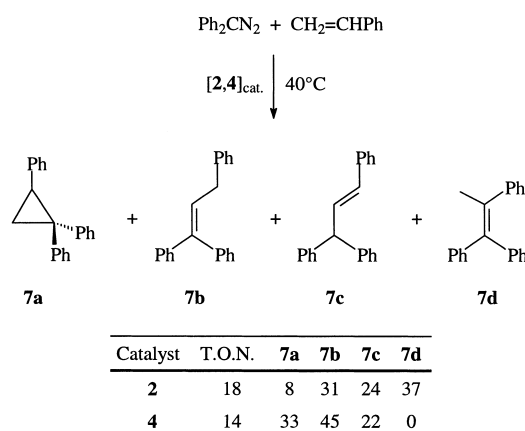
The cationic complexes not only catalyze the reaction of  $\text{Ph}_2\text{CN}_2$  with ethene but also that of diphenyldiazomethane with substituted olefins such as propene and styrene. With  $\text{CH}_2=\text{CHCH}_3$  and  $\text{Ph}_2\text{CN}_2$  as starting materials and catalytic amounts of **2–4** (in THF at 40 °C) a mixture of four isomers (**6a–6d**) is formed (Scheme 3). In each case the dominating



Scheme 3. Results of the catalytic reaction of propene and  $\text{Ph}_2\text{CN}_2$  with compounds **2–4** as catalyst (T.O.N. = turnover number = [(mmol product)/(mmol catalyst)]); ratio of **6a**, **6b**, **6c**, and **6d** in %).

species is the trisubstituted cyclopropane **6a**; the relative amount of this C–C coupling product decreases with the increasing number of phosphane ligands at the rhodium center. This result is in contrast to the  $\text{C}_2\text{H}_4/\text{Ph}_2\text{CN}_2$  system where the opposite trend is observed.

A decrease in selectivity is also observed for the rhodium-catalyzed reaction of diphenyldiazomethane with styrene. With the phosphane-free compound **2** as the catalyst, the isomeric olefins **7b–7d** are generated in nearly equal amounts; in this case (Scheme 4) the trisubstituted cyclo-



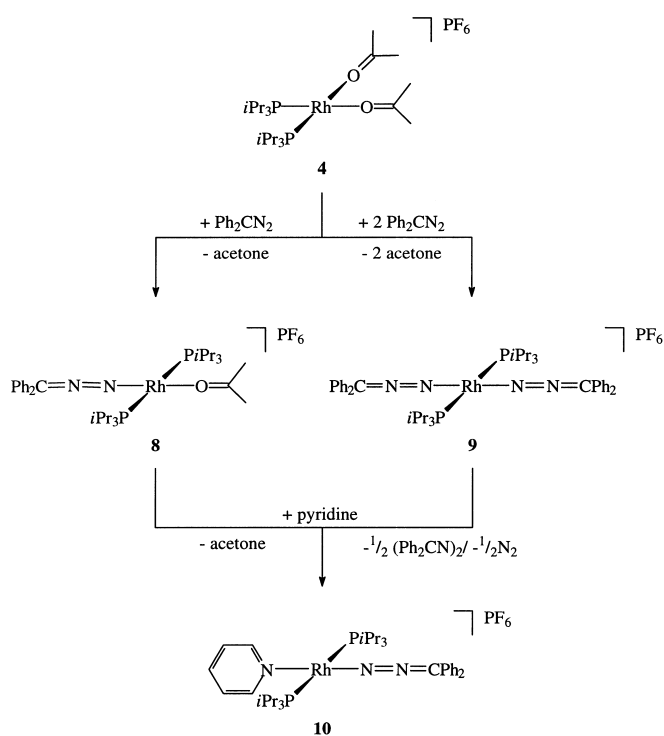
Scheme 4. Results of the catalytic reaction of styrene and  $\text{Ph}_2\text{CN}_2$  with compounds **2–4** as catalyst (T.O.N. = turnover number = [(mmol product)/(mmol catalyst)]); ratio of **7a**, **7b**, **7c**, and **7d** in %).

propane **7a** is the minor product. In contrast to **2**, the bis(phosphane) complex **4** is somewhat more selective and converts one third of the starting materials PhCH=CH<sub>2</sub> and Ph<sub>2</sub>CN<sub>2</sub> to 1,1,2-triphenylcyclopropane and two thirds to a 2:1 mixture of the olefins **7c** and **7d**. In our opinion, there is no rationale at the moment which could explain the influence of the coordination sphere around the metal center on the catalytic activity of the cationic species. Importantly, however, the selectivity of the C–C coupling process critically depends on the type of ligands bonded to rhodium(I); apparently the presence of the sterically demanding triisopropylphosphanes seems to disfavor a high degree of selectivity.

**Isolation of possible intermediates:** In order to prove whether the proposed catalytic cycles for the reactions of ethene and its derivatives with diphenyldiazomethane involve the formation of Rh(N<sub>2</sub>CPh<sub>2</sub>) species as intermediates, the reactivity of the cationic complexes toward Ph<sub>2</sub>CN<sub>2</sub> has been investigated. The bis(cyclooctene) compound **2** is rather inert toward the diazoalkane; after stirring a suspension of the starting materials in diethyl ether for 30 min no reaction was observed.

The monophosphane complex behaves differently. Addition of one equivalent of Ph<sub>2</sub>CN<sub>2</sub> to a suspension of **3** in ether leads, even at –78 °C, to a smooth change of color of the solution from red to off-white. While the remaining redbrown solid was shown by <sup>31</sup>P NMR spectroscopy to be the unchanged starting material **3**, the solution contained the ketazine Ph<sub>2</sub>C=N=N=CPh<sub>2</sub> (confirmed by GC/MS) which is probably generated by a metal-catalyzed conversion of Ph<sub>2</sub>CN<sub>2</sub>. We note that Lemenovskii and co-workers have already reported that the reactions of the trishydrides [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MH<sub>3</sub>] (M = Nb, Ta) with diaryldiazomethanes RR'CN<sub>2</sub> afford the corresponding ketazines RR'C=N=N=CRR', in this case probably via the monohydrido compounds [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MH(η<sup>1</sup>-N<sub>2</sub>CRR')] as intermediates.<sup>[11]</sup>

Stable cationic diphenyldiazomethanerhodium(I) complexes are formed from the bis(acetone)rhodium(I) derivative **4** as the starting material. Treatment of a suspension of **4** in ether with either one or two equivalents of Ph<sub>2</sub>CN<sub>2</sub> at –78 °C leads to a stepwise substitution of the ketonic ligands and gives the compounds **8** and **9** in about 80% yield (Scheme 5). Both **8** and **9** are dark green, moderately air-sensitive solids, the composition of which has been confirmed by elemental analyses and conductivity measurements. The <sup>31</sup>P NMR spectra of **8** and **9** display a doublet with a <sup>31</sup>P–<sup>103</sup>Rh coupling constant of 122.1 Hz (**8**) and 116.2 Hz (**9**) indicating that, in contrast to the starting material **4**, the two phosphane ligands are in *trans* disposition.<sup>[7, 8]</sup> In the <sup>13</sup>C NMR spectra of **8** and **9**, the resonance for the diazoalkane carbon atom Ph<sub>2</sub>CN<sub>2</sub> appears at δ = 84.5 (**8**) and δ = 83.3 (**9**) as a broad singlet, the broadening probably being due to the quadrupole moment of the nitrogen atoms. Regarding the stability of the mono-substitution product **8** it should be mentioned that in solution a partial disproportionation of **8** to **4** and **9** occurs. The <sup>31</sup>P NMR spectrum of **8** in [D<sub>6</sub>]acetone shows, besides the doublet at δ = 40.2, two other doublets at δ = 60.3 (for **4**) and δ = 46.5 (for **9**) with the intensity ratio of approximately 4:1:1.



Scheme 5. Preparation of the cationic diphenyldiazomethanerhodium(I) complexes **8**–**10** from the bis(acetone) complex **4**.

Despite the lability of **8** in solution, we were able to grow single crystals by slow diffusion of ether into a saturated solution of **8** in acetone. The result of the X-ray crystal structure analysis is shown in Figure 2. The coordination

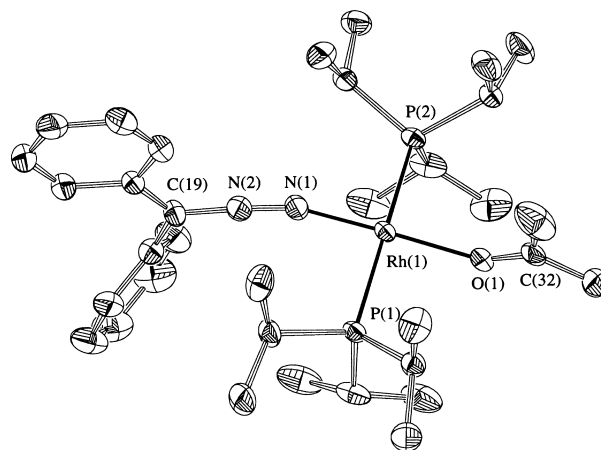


Figure 2. Molecular structure of **8** (anionic ligand omitted for clarity). Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh(1)–P(1) 2.3546(8), Rh(1)–P(2) 2.3693(8), Rh(1)–O(1) 2.039(2), Rh(1)–N(1) 1.869(3), N(1)–N(2) 1.157(4), N(2)–C(19) 1.312(4), O(1)–C(32) 1.237(4); P(1)–Rh(1)–P(2) 170.88(3), P(1)–Rh(1)–O(1) 90.36(6), P(1)–Rh(1)–N(1) 91.71(8), P(2)–Rh(1)–O(1) 89.47(6), P(2)–Rh(1)–N(1) 87.29(8), O(1)–Rh(1)–N(1) 172.21(10), Rh(1)–O(1)–C(32) 140.1(2), Rh(1)–N(1)–N(2) 161.0(2), N(1)–N(2)–C(19) 171.6(3).

geometry around the metal center is slightly distorted square-planar with bond angles P(1)–Rh(1)–P(2) and O(1)–Rh(1)–N(1) of 170.88(3)° and 172.21(10)°, respectively. The Rh(1)–N(1)–N(2) chain is considerably bent, the bond angle being

about  $10^\circ$  smaller than in the octahedral cationic tungsten compound  $[\text{WBr}(\text{N}_2\text{CMe}_2)(\text{dppe})_2]^+$  ( $\text{dppe} = 1,2\text{-C}_2\text{H}_4(\text{PPh}_2)_2$ ).<sup>[12]</sup> The more remarkable fact, however, is that the N(1)–N(2)–C(19) angle is nearly linear ( $171.6(3)^\circ$ ) which is unusual compared to other N-bonded diazoalkane metal complexes.<sup>[13]</sup> Since the size of the bond angle N–N–C in compounds  $[\text{L}_n\text{M}(\eta^1\text{-N}_2\text{CRR}') ]^{n+}$  should depend on the degree of  $d \rightarrow \pi^*$  metal-to-ligand back bonding, gaining a maximum at an N–N–C angle of  $120^\circ$ , we assume that in **8** the diphenyldiazomethane behaves predominantly as a  $\sigma$ -donor ligand. An analogous conclusion has been drawn in the case of *trans*- $[\text{RhCl}\{\eta^1\text{-N}_2\text{C}(\text{C}_6\text{H}_4)_2\text{CO}\}(\text{PiPr}_3)_2]$ <sup>[14]</sup> and some other  $[\text{M}(\eta^1\text{-N}_2\text{CR}_2)]$  complexes.<sup>[15, 16]</sup>

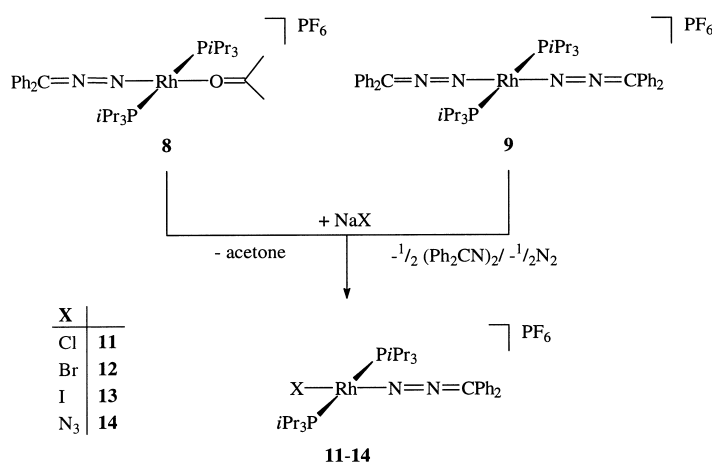
Regarding the distances in **8**, the N(1)–N(2) and N(2)–C(19) bond lengths are rather short (1.157(4) and 1.312(4) Å) and quite similar to those in free diazomethane (1.12 and 1.32 Å).<sup>[13]</sup> This similarity supports the proposal that the  $\sigma$ -donor character of the diphenyldiazomethane ligand in **8** dominates. The Rh(1)–N(1) distance (1.869(3) Å) is rather short and comparable to the Rh–N bond length in the square-planar dinitrogenrhodium(II) complex *trans*- $[\text{RhCl}(\text{N}_2)(\text{PiPr}_3)_2]$ .<sup>[17]</sup>

Both the cationic compounds **8** and **9** are quite labile and react smoothly with pyridine to give the monosubstituted product **10** (see Scheme 5). While in the reaction of **8** with pyridine the acetone ligand is replaced, treatment of **9** with pyridine leads to the formation of  $\text{N}_2$  and the ketazine  $\text{Ph}_2\text{C}=\text{N}=\text{N}=\text{CPh}_2$  as the by-products. Compound **10** is a green, moderately air-sensitive solid, the composition of which has been confirmed by analytical and spectroscopic data. The appearance of a doublet of virtual triplets for the  $\text{PCHCH}_3$  protons in the  $^1\text{H}$  NMR spectrum and of a sharp doublet with a  $^{31}\text{P} - ^{103}\text{Rh}$  coupling constant of 126.7 Hz in the  $^{31}\text{P}$  NMR spectrum are indicative for the *trans* disposition of the phosphane ligands. The structural proposal for **10** is somewhat reminiscent to that for the amine complexes  $[\text{Rh}(\text{PNP})(\text{HNR}_2)]\text{PF}_6$  [ $\text{PNP} = 2,6\text{-NC}_5\text{H}_3(\text{CH}_2\text{PPh}_2)_2$ ] which are formed upon treatment of the ethene derivative  $[\text{Rh}(\text{PNP})(\text{C}_2\text{H}_4)]\text{PF}_6$  with secondary amines.<sup>[18]</sup>

To find out whether the isolated compounds **8** and **9** could play a role in the above-mentioned catalytic process between  $\text{C}_2\text{H}_4$  and  $\text{Ph}_2\text{CN}_2$ , both diazoalkane complexes were treated with ethene. In THF at  $40^\circ\text{C}$ , the major organic product is the cyclopropane derivative **5a**. Whereas in the case of **8**, only traces of **5b** (< 1%) are formed, the reaction of **9** with  $\text{C}_2\text{H}_4$  yields a mixture of **5a** to **5b** in the ratio of about 9:1. Since almost identical results regarding the product distribution are obtained for the catalytic reaction of  $\text{C}_2\text{H}_4$  and free  $\text{Ph}_2\text{CN}_2$ , we conclude that **8** and **9** can be regarded as intermediates (possibly resting states) in the catalytic cycle. For **9**, the turnover number (in THF at  $40^\circ\text{C}$ ) for the formation of the C–C coupling product **5a** of 33 is very similar to that with **4** as the catalyst.

**Neutral diphenyldiazomethanerhodium(II) complexes:** The pronounced lability of the cations of **8** and **9** prompted us to study also the reactivity of these species toward halide and azide anions. Both compounds **8** and **9** react smoothly with  $\text{NaX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3$ ) in ether to afford the neutral

diazoalkane complexes **11–14** in good to excellent yield (Scheme 6). Similarly to the chloro derivative **11**, which was previously prepared from  $[\text{RhCl}(\text{PiPr}_3)_2]_2$  or *trans*- $[\text{RhCl}(\text{C}_2\text{H}_4)(\text{PiPr}_3)_2]$  and  $\text{Ph}_2\text{CN}_2$ ,<sup>[1, 2a]</sup> the related compounds **12–14** are also dark green solids which are quite stable and



Scheme 6. Preparation of the neutral diphenyldiazomethanerhodium(II) complexes **11–14** from the cationic compounds **8** or **9** as the precursors.

neither on heating nor photolysis eliminate  $\text{N}_2$  to give *trans*- $[\text{RhX}(\text{CPh}_2)(\text{PiPr}_3)_2]$ .<sup>[19]</sup> Characteristic spectroscopic features of **12–14** are the N–N stretching frequency for the diphenyldiazomethane ligand at  $1940\text{--}1955\text{ cm}^{-1}$  in the IR and the singlet resonance for the  $\text{Ph}_2\text{CN}_2$  carbon atom at  $\delta = 78.3\text{--}79.4$  in the  $^{13}\text{C}$  NMR spectrum. For **14**, the  $\nu(\text{N}_3)$  band appears at  $2038\text{ cm}^{-1}$ .

The catalytic activity of the neutral compounds **11–14** in the reaction of  $\text{C}_2\text{H}_4$  and  $\text{Ph}_2\text{CN}_2$  is somewhat less than that of the cationic species **8** and **9** (for details see Experimental Section). The turnover number (in methylcyclohexane at  $40^\circ\text{C}$ ) decreases in the order  $\text{Cl} > \text{Br} > \text{I} > \text{N}_3$ . A more noteworthy observation is that a significant difference exists in the selectivity between **11** on one side and **12–14** on the other. While upon treatment of ethene with diphenyldiazomethane in the presence of **11** as the catalyst almost exclusively the trisubstituted olefin **5b** is formed, the analogous reaction of  $\text{C}_2\text{H}_4$  and  $\text{Ph}_2\text{CN}_2$  with **12**, **13**, or **14** as the catalyst yield a mixture **5a** and **5b** in the ratio of 19:81 (**12**), 8:92 (**13**), and 39:61 (**14**), respectively. These data confirm (as mentioned above) that the ligands coordinated to rhodium(II) as the active center play a crucial role for the C–C coupling process, even minor differences in the electron density at rhodium are possibly responsible for the preference for one or the other route.

## Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The commercially available starting materials ethene, propene and styrene were used without purification.  $\text{PiPr}_3$  was a commercial product from Strem Chemicals. The complexes  $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$  (**1**)<sup>[20]</sup>, *cis*- $[\text{Rh}(\text{acetone})_2(\text{C}_8\text{H}_{14})_2]\text{PF}_6$  (**2**),<sup>[7, 8]</sup> and *cis*- $[\text{Rh}(\text{acetone})_2(\text{PiPr}_3)_2]\text{PF}_6$  (**4**)<sup>[8]</sup> were prepared as described in the literature. NMR spectra were recorded, unless stated otherwise, at room temperature on Bruker AC 200 and Bruker AMX 400 instruments. Abbreviations used: s, singlet; d, doublet; q,

quartet; sept, septet; m, multiplet; br, broadened signal; dvt, doublet of virtual triplets;  $N = {}^3J(\text{P}(\text{H})) + {}^3J(\text{P}(\text{H}))$  or  ${}^2J(\text{P}(\text{C})) + {}^3J(\text{P}(\text{C}))$ , respectively. Conductivity measurements were carried out in nitromethane with a Schott Konduktometer CG 851. Melting and decomposition points were measured by DTA. IR spectra were recorded on a Bruker IFS 25 FT/IR spectrometer, and GC/MS analyses were carried out on a Hewlett Packard G1800A GCD system equipped with a capillary column (HP5, 25 m) and HP-Chemstation software.

**cis-[Rh(acetone)<sub>2</sub>(C<sub>8</sub>H<sub>14</sub>)(PiPr<sub>3</sub>)<sub>2</sub>PF<sub>6</sub> (3):** A suspension of **2** (119 mg, 0.20 mmol) in diethyl ether (4 mL) was treated at  $-78^\circ\text{C}$  with PiPr<sub>3</sub> (39  $\mu\text{L}$ , 0.20 mmol) and stirred for 10 min. The solvent was removed, the residue was washed with diethyl ether ( $2 \times 10$  mL) and pentane ( $3 \times 10$  mL) and dried in vacuo. The resulting brown powder was recrystallized by slow diffusion of diethyl ether (10 mL) into a solution of acetone (1 mL) which afforded a yellow solid. The precipitation was completed by addition of pentane (10 mL). The solvent was decanted, and the yellow solid was washed with pentane (10 mL) and dried. Yield = 99 mg, 78%; m.p.  $61^\circ\text{C}$  (decomp); conductivity  $\Lambda = 125 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ ; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu} = 1701, 1658$  (C=O),  $1354 \text{ cm}^{-1}$  (C=C);  ${}^1\text{H}$  NMR (400 MHz, [D<sub>6</sub>]acetone):  $\delta = 2.21$  (m, 2H; CH of C<sub>8</sub>H<sub>14</sub>), 2.09 (s, 12H; CH<sub>3</sub> of acetone), 1.93 (m, 3H; PCHCH<sub>3</sub>), 1.60, 1.49, 1.36 (all m, 12H; CH<sub>2</sub> of C<sub>8</sub>H<sub>14</sub>), 1.38 (dd,  ${}^3J(\text{P}(\text{H})) = 13.6$  Hz,  ${}^3J(\text{H},\text{H}) = 7.2$  Hz, 18H; PCHCH<sub>3</sub>);  ${}^{13}\text{C}$  NMR (100.6 MHz, [D<sub>6</sub>]acetone):  $\delta = 206.6$  (s, C=O), 62.5 (dd,  ${}^1J(\text{Rh},\text{C}) = 16.2$  Hz,  ${}^2J(\text{P},\text{C}) = 1.6$  Hz; CH of C<sub>8</sub>H<sub>14</sub>), 30.6 (s, CH<sub>3</sub> of acetone), 30.2, 28.7, 26.9 (all s, CH<sub>2</sub> of C<sub>8</sub>H<sub>14</sub>), 23.2 (d,  ${}^1J(\text{P},\text{C}) = 25.2$  Hz; PCHCH<sub>3</sub>), 20.0 (s, PCHCH<sub>3</sub>);  ${}^{31}\text{P}$  NMR (162.0 MHz, [D<sub>6</sub>]acetone):  $\delta = 63.1$  (d,  ${}^1J(\text{Rh},\text{P}) = 188.1$  Hz),  $-144.2$  (sept,  ${}^1J(\text{F},\text{P}) = 707.4$  Hz); elemental analysis (%) for C<sub>23</sub>H<sub>47</sub>F<sub>6</sub>O<sub>2</sub>P<sub>2</sub>Rh (634.5): calcd: C 43.54, H 7.47; found: C 43.91, H 7.71.

**trans-[Rh(PiPr<sub>3</sub>)<sub>2</sub>(acetone)( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)PF<sub>6</sub> (8):** A solution of **4** (260 mg, 0.38 mmol) in acetone (5 mL) was treated at  $-78^\circ\text{C}$  with one equivalent of a 0.5 M solution of Ph<sub>2</sub>CN<sub>2</sub> (0.76 mL, 0.38 mmol) in methylcyclohexane. A change of color from violet to dark green occurred. After the reaction mixture was warmed to room temperature and stirred for 1 h, a dark green solid precipitated. The solvent was decanted, the dark green precipitate was washed with diethyl ether ( $3 \times 5$  mL) and pentane ( $2 \times 5$  mL), and dried. Yield = 284 mg, 91%; m.p.  $57^\circ\text{C}$  (decomp); conductivity  $\Lambda = 105 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ ; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu} = 1956$  (N=N)  $\text{cm}^{-1}$ ;  ${}^1\text{H}$  NMR (200 MHz, [D<sub>6</sub>]acetone):  $\delta = 7.53$  (m, 4H; *ortho* H of C<sub>6</sub>H<sub>5</sub>), 7.34 (m, 6H; *meta* and *para* H of C<sub>6</sub>H<sub>5</sub>), 2.06 (m, 6H; PCHCH<sub>3</sub>), 2.05 (s, 6H; CH<sub>3</sub> of acetone), 1.34 (dvt,  $N = 13.1$  Hz,  ${}^3J(\text{H},\text{H}) = 6.6$  Hz, 36H; PCHCH<sub>3</sub>);  ${}^{13}\text{C}$  NMR (50.3 MHz, [D<sub>6</sub>]acetone,  $-35^\circ\text{C}$ ):  $\delta = 206.6$  (s, C=O), 130.2, 127.6, 127.1, 126.3 (all s, C<sub>6</sub>H<sub>5</sub>), 84.5 (s, CN<sub>2</sub>), 30.6 (s, CH<sub>3</sub> of acetone), 23.5 (vt,  $N = 19.6$  Hz; PCHCH<sub>3</sub>), 19.5 (s, PCHCH<sub>3</sub>);  ${}^{31}\text{P}$  NMR (81.0 MHz, [D<sub>6</sub>]acetone):  $\delta = 40.2$  (d,  ${}^1J(\text{Rh},\text{P}) = 122.1$  Hz),  $-142.8$  (sept,  ${}^1J(\text{F},\text{P}) = 709.2$  Hz); elemental analysis (%) for C<sub>34</sub>H<sub>58</sub>F<sub>6</sub>N<sub>2</sub>O<sub>1</sub>P<sub>2</sub>Rh (820.5): calcd: C 49.76, H 7.12, N 3.41; found: C 49.50, H 6.80, N 3.29.

**trans-[Rh(PiPr<sub>3</sub>)<sub>2</sub>( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub> (9):** A solution of **4** (358 mg, 0.52 mmol) in acetone (5 mL) was treated at room temperature with a 1.0 M solution of Ph<sub>2</sub>CN<sub>2</sub> (1.31 mL, 1.31 mmol) in methylcyclohexane. The resulting dark green solution was stirred for 3 min, and then hexane (20 mL) was added. A dark green precipitate was formed, which was separated from the mother liquor, washed with hexane (portions of 20 mL) until the hexane solution was colorless. The residue was dried, then dissolved in acetone (0.5 mL) and the solution layered with diethyl ether (10 mL). The resulting dark green microcrystalline solid was separated, washed with pentane ( $2 \times 2$  mL) and dried in vacuo. Yield = 380 mg, 76%; m.p.  $62^\circ\text{C}$  (decomp); conductivity  $\Lambda = 102 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ ; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu} = 1948$  (N=N)  $\text{cm}^{-1}$ ;  ${}^1\text{H}$  NMR (200 MHz, [D<sub>6</sub>]acetone):  $\delta = 7.54$  (d,  ${}^3J(\text{H},\text{H}) = 7.7$  Hz, 8H; *ortho* H of C<sub>6</sub>H<sub>5</sub>), 7.37 (m, 12H; *meta* and *para* H of C<sub>6</sub>H<sub>5</sub>), 2.03 (m, 6H; PCHCH<sub>3</sub>), 1.26 (dvt,  $N = 14.3$  Hz,  ${}^3J(\text{H},\text{H}) = 6.9$  Hz, 36H; PCHCH<sub>3</sub>);  ${}^{13}\text{C}$  NMR (50.3 MHz, [D<sub>8</sub>]THF,  $-35^\circ\text{C}$ ):  $\delta = 130.5, 129.4, 128.0, 127.5$  (all s, C<sub>6</sub>H<sub>5</sub>), 83.3 (s, CN<sub>2</sub>), 24.8 (vt,  $N = 19.4$  Hz; PCHCH<sub>3</sub>), 19.6 (s, PCHCH<sub>3</sub>);  ${}^{31}\text{P}$  NMR (81.0 MHz, [D<sub>6</sub>]acetone):  $\delta = 46.5$  (d,  ${}^1J(\text{Rh},\text{P}) = 116.2$  Hz),  $-142.7$  (sept,  ${}^1J(\text{F},\text{P}) = 707.3$  Hz); elemental analysis (%) for C<sub>44</sub>H<sub>62</sub>F<sub>6</sub>N<sub>4</sub>P<sub>3</sub>Rh (956.8): calcd: C 55.23, H 6.53, N 5.86; found: C 55.19, H 6.60, N 5.54.

**trans-[Rh(PiPr<sub>3</sub>)<sub>2</sub>(py)( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)PF<sub>6</sub> (10):** A suspension of **8** (61 mg, 0.07 mmol) or **9** (67 mg, 0.07 mmol) in diethyl ether (10 mL) was treated at room temperature with an excess of pyridine (0.5 mL, 6.2 mmol). After the mixture was stirred for 15 min, a brownish-green suspension was formed. The solvent was decanted, the solid green residue washed with diethyl ether

( $2 \times 2$  mL) and pentane ( $3 \times 2$  mL) and dried in vacuo. Yield = 56 mg, 91%; m.p.  $64^\circ\text{C}$  (decomp); conductivity  $\Lambda = 87 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ . IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu} = 1984$  (N=N)  $\text{cm}^{-1}$ ;  ${}^1\text{H}$  NMR (200 MHz, [D<sub>6</sub>]acetone):  $\delta = 9.03$  (m, 2H; *ortho* H of NC<sub>5</sub>H<sub>3</sub>), 7.96 (m, 1H; *para* H of NC<sub>5</sub>H<sub>3</sub>), 7.63 (m, 2H; *meta* H of NC<sub>5</sub>H<sub>3</sub>), 7.47 (m, 4H; *ortho* H of C<sub>6</sub>H<sub>5</sub>), 7.27 (m, 6H; *para* and *meta* H of C<sub>6</sub>H<sub>5</sub>), 1.86 (m, 6H; PCHCH<sub>3</sub>), 1.28 (dvt,  $N = 13.4$  Hz,  ${}^3J(\text{H},\text{H}) = 7.3$  Hz, 36H; PCHCH<sub>3</sub>);  ${}^{13}\text{C}$  NMR (50.3 MHz, [D<sub>6</sub>]acetone,  $-35^\circ\text{C}$ ):  $\delta = 154.7$  (s, *ortho* C of NC<sub>5</sub>H<sub>3</sub>), 139.0 (s, *para* C of NC<sub>5</sub>H<sub>3</sub>), 129.9, 127.5, 127.2, 126.5 (all s, C<sub>6</sub>H<sub>5</sub>), 126.8 (s, *meta* C of NC<sub>5</sub>H<sub>3</sub>), 66.0 (s, CN<sub>2</sub>), 24.1 (vt,  $N = 19.0$  Hz; PCHCH<sub>3</sub>), 19.8 (s, PCHCH<sub>3</sub>);  ${}^{31}\text{P}$  NMR (81.0 MHz, [D<sub>6</sub>]acetone):  $\delta = 38.0$  (d,  ${}^1J(\text{Rh},\text{P}) = 126.7$  Hz),  $-142.7$  (sept,  ${}^1J(\text{F},\text{P}) = 707.0$  Hz); elemental analysis (%) for C<sub>36</sub>H<sub>57</sub>F<sub>6</sub>N<sub>3</sub>P<sub>3</sub>Rh (841.7): calcd: C 51.37, H 6.83, N 4.99; found: C 51.23, H 6.86, N 4.85.

**trans-[RhCl( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] (11):** A suspension of **8** (66 mg, 0.08 mmol) or **9** (77 mg, 0.08 mmol) in diethyl ether (10 mL) was treated with an excess of NaCl (50 mg, 0.86 mmol) and was stirred for 3 h at room temperature. The solvent was removed in vacuo and the residue extracted with hexane (20 mL). The extract was evaporated to dryness in vacuo to give a dark green solid which was washed with cold methanol ( $2 \times 1$  mL) and dried in vacuo. Yield = 29 mg, 68%. Compound **11** was characterized by comparison of the spectroscopic data with those of an authentic sample.<sup>[1], 2a]</sup>

**trans-[RhBr( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] (12):** This was prepared as described for **11**, using **8** (66 mg, 0.08 mmol) and NaBr (80 mg, 0.78 mmol) as starting materials. Dark green solid; yield = 33 mg, 71%; m.p.  $51^\circ\text{C}$  (decomp). IR (KBr):  $\tilde{\nu} = 1943$  (N=N)  $\text{cm}^{-1}$ ;  ${}^1\text{H}$  NMR (200 MHz, [D<sub>6</sub>]benzene):  $\delta = 7.41$  (m, 4H; *ortho* H of C<sub>6</sub>H<sub>5</sub>), 7.19 (m, 4H; *meta* H of C<sub>6</sub>H<sub>5</sub>), 6.89 (m, 2H; *para* H of C<sub>6</sub>H<sub>5</sub>), 2.42 (m, 6H; PCHCH<sub>3</sub>), 1.27 (dvt,  $N = 13.2$  Hz,  ${}^3J(\text{H},\text{H}) = 6.9$  Hz, 36H; PCHCH<sub>3</sub>);  ${}^{13}\text{C}$  NMR (50.3 MHz, [D<sub>6</sub>]benzene):  $\delta = 128.9, 128.3, 125.4, 124.5$  (all s, C<sub>6</sub>H<sub>5</sub>), 79.1 (s, CN<sub>2</sub>), 24.1 (vt,  $N = 18.5$  Hz; PCHCH<sub>3</sub>), 20.1 (s, PCHCH<sub>3</sub>);  ${}^{31}\text{P}$  NMR (81.0 MHz, [D<sub>6</sub>]benzene):  $\delta = 40.9$  (d,  ${}^1J(\text{Rh},\text{P}) = 119.1$  Hz); elemental analysis (%) for C<sub>31</sub>H<sub>52</sub>BrN<sub>2</sub>P<sub>2</sub>Rh (697.5): calcd: C 54.79, H 7.51, N 4.02; found: C 54.38, H 7.67, N 4.08.

**trans-[RhI( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] (13):** This was prepared as described for **11**, using **8** (66 mg, 0.08 mmol) and NaI (120 mg, 0.80 mmol) as starting materials. Dark green solid; yield = 43 mg, 87%; m.p.  $48^\circ\text{C}$  (decomp). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu} = 2032$  (N=N)  $\text{cm}^{-1}$ ;  ${}^1\text{H}$  NMR (200 MHz, [D<sub>6</sub>]benzene):  $\delta = 7.39$  (m, 4H; *ortho* H of C<sub>6</sub>H<sub>5</sub>), 7.17 (m, 4H; *meta* H of C<sub>6</sub>H<sub>5</sub>), 6.90 (m, 2H; *para* H of C<sub>6</sub>H<sub>5</sub>), 2.52 (m, 6H; PCHCH<sub>3</sub>), 1.26 (dvt,  $N = 13.2$  Hz,  ${}^3J(\text{H},\text{H}) = 6.9$  Hz, 36H; PCHCH<sub>3</sub>);  ${}^{13}\text{C}$  NMR (50.3 MHz, [D<sub>6</sub>]benzene):  $\delta = 129.0, 128.3, 125.3, 124.7$  (all s, C<sub>6</sub>H<sub>5</sub>), 79.4 (s, CN<sub>2</sub>), 25.2 (vt,  $N = 18.8$  Hz; PCHCH<sub>3</sub>), 20.4 (s, PCHCH<sub>3</sub>);  ${}^{31}\text{P}$  NMR (81.0 MHz, [D<sub>6</sub>]benzene):  $\delta = 40.8$  (d,  ${}^1J(\text{Rh},\text{P}) = 116.2$  Hz); elemental analysis (%) for C<sub>31</sub>H<sub>52</sub>I<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Rh (744.5): calcd: C 50.01, H 7.04, N 3.76; found: C 49.30, H 6.78, N 4.10.

**trans-[Rh(N<sub>3</sub>)( $\eta^1$ -N<sub>2</sub>CPh<sub>2</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] (14):** This was prepared as described for **11**, using **8** (66 mg, 0.08 mmol) and NaN<sub>3</sub> (52 mg, 0.80 mmol) as starting materials. Dark green solid; yield = 31 mg, 56%; m.p.  $58^\circ\text{C}$  (decomp). IR (hexane):  $\tilde{\nu} = 2038$  (N=N of N<sub>3</sub>), 1948 (N=N of N<sub>2</sub>CPh<sub>2</sub>)  $\text{cm}^{-1}$ ;  ${}^1\text{H}$  NMR (200 MHz, [D<sub>6</sub>]benzene):  $\delta = 7.34$  (m, 4H; *ortho* H of C<sub>6</sub>H<sub>5</sub>), 7.19 (m, 4H; *meta* H of C<sub>6</sub>H<sub>5</sub>), 6.87 (m, 2H; *para* H of C<sub>6</sub>H<sub>5</sub>), 2.12 (m, 6H; PCHCH<sub>3</sub>), 1.20 (dvt,  $N = 13.6$  Hz,  ${}^3J(\text{H},\text{H}) = 6.9$  Hz, 36H; PCHCH<sub>3</sub>);  ${}^{13}\text{C}$  NMR (50.3 MHz, [D<sub>6</sub>]benzene):  $\delta = 129.9, 129.0, 128.3, 129.1, 124.6$  (all s, C<sub>6</sub>H<sub>5</sub>), 78.3 (s, CN<sub>2</sub>), 24.0 (vt,  $N = 17.6$  Hz; PCHCH<sub>3</sub>), 19.7 (s, PCHCH<sub>3</sub>);  ${}^{31}\text{P}$  NMR (81.0 MHz, [D<sub>6</sub>]benzene):  $\delta = 44.3$  (d,  ${}^1J(\text{Rh},\text{P}) = 123.5$  Hz); elemental analysis (%) for C<sub>31</sub>H<sub>52</sub>N<sub>3</sub>P<sub>2</sub>Rh (659.7): calcd: C 56.44, H 7.95, N 10.62; found: C 56.21, H 8.07, N 10.06.

**Catalytic reactions of Ph<sub>2</sub>CN<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> with 2–4, 8, and 9 as catalyst:** In a typical experiment, a solution of the catalyst (10–20 mg, ca. 0.04 mmol) in THF (6 mL) was treated dropwise (ca. 10 mL h<sup>-1</sup>) at  $40^\circ\text{C}$  with a 0.1 M solution of diphenyldiazomethane in methylcyclohexane/THF (1:4). While adding the substrate, a slow stream of ethene was passed through the solution. The catalytic reaction was finished when the violet color of the diazoalkane solution did not disappear on further addition to the reaction mixture. The solvent was removed in vacuo, and the oily residue was dissolved in hexane (5 mL). In order to destroy excess Ph<sub>2</sub>CN<sub>2</sub> and separate the catalyst from the reaction products, the mixture was filtered through Al<sub>2</sub>O<sub>3</sub> (neutral, activity grade III, height of column 7 cm). After evaporation of the solvent, a colorless oil consisting of a mixture of **5a** and **5b** was isolated from the eluate. The ratio of the products, diphenylcyclopropane (**5a**) and 1,1-diphenylpropene (**5b**), was determined by integration of characteristic signals in the  ${}^1\text{H}$  NMR spectra and by GC/MS analysis. The

results with **2–4** as the catalyst are summarized in Scheme 2. With **8** and **9** as the catalyst, the ratio of **5a** to **5b** is >99:1 and the turnover numbers are 17 (with **8**) and 33 (with **9**).

**Catalytic reactions of Ph<sub>2</sub>CN<sub>2</sub> and propene with 2–4 as catalyst:** In an analogous manner to the catalytic reaction of Ph<sub>2</sub>CN<sub>2</sub> with ethene by using propene as the olefinic substrate. After evaporation of the solvent of the eluate, a colorless oil consisting of a mixture of **6a**, **6b**, *E/Z* **6c** and **6d** was isolated. The results are summarized in Scheme 3.

**Catalytic reactions of Ph<sub>2</sub>CN<sub>2</sub> and styrene with 2 or 4 as catalyst:** A solution of **2** or **4** (10–20 mg, ca. 0.04 mmol) and styrene (50 molar equivalents) in THF (6 mL) was treated dropwise (ca. 10 mL h<sup>-1</sup>) at 40 °C with a 0.1 M solution of diphenyldiazomethane in methylcyclohexane/THF (1:4). The catalytic reaction was finished when the violet color of the diazoalkane solution did not disappear on further addition to the reaction mixture. Workup of the reaction mixture was carried out as described for the catalytic reactions with ethene. After evaporation of the solvent of the eluate, a colorless oil consisting of a mixture of **7a**, **7b**, **7c**, and **7d** was isolated. The results are summarized in Scheme 4.

**Catalytic reactions of Ph<sub>2</sub>CN<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> with 12–14 as catalyst:** In an analogous manner to the reactions with **2–4** as catalyst, by using a solution of **12**, **13**, or **14** (10–20 mg, ca. 0.04 mmol) in methylcyclohexane (6 mL). A mixture of **5a** and **5b** was obtained in the ratio of 19:81 (for **12**), 8:92 (for **13**) and 39:61 (for **14**). The turnover numbers were 27 (for **12**), 18 (for **13**), and 17 (for **14**).

**X-ray structural analysis of the compounds 2 and 8:**<sup>[21]</sup> Single crystals of **2** and **8** were grown by slow diffusion of diethyl ether (10 mL) into a saturated solution of **2** or **8** in acetone (1 mL). The yellow/orange (**2**) and dark green (**8**) crystalline products were washed with pentane (2 × 1 mL) and dried under a stream of argon. Crystal data for the two structures are represented in Table 1. The data for **2** and **8** were collected from a glassfiber-mounted single crystal which was prepared under an inert atmosphere and transferred into a cold nitrogen stream of the low temperature unit<sup>[22]</sup> mounted on a ENRAF-Nonius CAD-4F diffractometer with monochromated MoK<sub>α</sub> radiation (λ = 0.71073 Å).<sup>[23]</sup> The structures were solved by Patterson methods and extension of the models were accomplished by direct methods applied to difference structure factors

Table 1. Crystal structure data for **2** and **8**.

Compound	<b>2</b> <sup>[d]</sup>	<b>8</b>
formula	C <sub>22</sub> H <sub>40</sub> F <sub>6</sub> O <sub>2</sub> RhP	C <sub>34</sub> H <sub>58</sub> F <sub>6</sub> N <sub>2</sub> OP <sub>3</sub> Rh
M <sub>r</sub>	584.43	820.66
T [K]	130	130
cryst. size [mm <sup>3</sup> ]	0.3 × 0.3 × 0.6	0.1 × 0.1 × 0.6
space group	P $\bar{1}$	P2 <sub>1</sub> /n (no. 14)
cell dimensions determination	24 rflns, 16.8 < θ < 17.7	24 rflns, 16.2 < θ < 17.9
a [pm]	1282.4(1)	1369.6(1)
b [pm]	1289.5(1)	1199.3(1)
c [pm]	3153.1(1)	2457.1(1)
α [°]	99.950(6)	–
β [°]	90.888(4)	102.41(1)
γ [°]	90.068(4)	–
V [nm <sup>3</sup> ]	5.1231(6)	3.9417(5)
Z	8	4
ρ <sub>calcd</sub> [Mg m <sup>-3</sup> ]	1.515	1.383
μ [mm <sup>-1</sup> ]	0.789	0.612
F(000)	2416	1712
2θ max [°]	52	54
no. meas. rflns.	18648	8707
no. unique rflns.	18633	8573
no. rflns. used	16207	7859
refined parameters	1245	665
R1 [I > 2σ(I)] <sup>[a]</sup>	0.0478	0.0368
wR2 (all data) <sup>[b]</sup>	0.1262	0.0880
g1; g2 <sup>[c]</sup>	0.0565; 15.2674	0.0484; 1.5161
resid. elec. ρ [10 <sup>-6</sup> e pm <sup>-3</sup> ]	0.96/–1.01	0.78/–0.65

[a]  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . [b]  $wR2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}$ . [c]  $w = 1 / [\sigma^2(F_o^2) + (g1 \times P)^2 + g2 \times P]$ ;  $P = (F_o^2 + 2F_c^2) / 3$ . [d] The asymmetric unit contains four independent molecules **2a–d**. In this table the formula and M<sub>r</sub> represent one molecule only.

using the program DIRDIF.<sup>[24]</sup> All structures were refined by full matrix least-squares procedures on F<sup>2</sup> with SHELX93.<sup>[25]</sup> The asymmetric unit of **2** contains four formula units, each consisting of two moieties; a cationic rhodium complex and a PF<sub>6</sub><sup>-</sup> counterion. For **2** a weak hydrogen bonding between the methyl groups of the coordinated actone and fluor atoms of the PF<sub>6</sub><sup>-</sup> anions is observed.<sup>[26]</sup> For **8** the positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all hydrogen atoms, of which the coordinates and the isotropic thermal displacement parameters were refined. The methyl hydrogen atoms of the acetone moiety were ultimately refined riding on their carrier atoms with their positions calculated by using sp<sup>3</sup> hybridization at the C atom as appropriate with U<sub>iso</sub> = 1.5 × U<sub>equiv</sub> of their parent atom, C(33) and C(34), respectively. The methyl groups in both **2** and **8** were refined as rigid groups, which were allowed to rotate free. The PF<sub>6</sub><sup>-</sup> ion in **8** is rotational disordered over the F(1)–P(3)–F(2) axis. The site occupancy factor of the major component was refined to a value of 0.69(2).

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