

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

Helmut Werner,^{*,[a]} Michael E. Schneider,^[a] Marco Bosch,^[a] Justin Wolf,^[a] Jan H. Teuben,^[b] Auke Meetsma,^[c] and Sergei I. Troyanov^[d]

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

Abstract: Cationic rhodium(II) complexes *cis*-[Rh(acetone)₂(L)(L')]⁺ (**2**: L = L' = C₈H₁₄; **3**: L = C₈H₁₄; L' = PiPr₃; **4**: L = L' = PiPr₃), prepared from [RhCl(C₈H₁₄)₂]₂ and isolated as PF₆ 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=CH₂ (R = H, Me, Ph) and one equivalent of CPh₂. The efficiency and selectivity of the catalyst depends significantly on the coordination sphere

around the rhodium(II) center. Treatment of **4** with Ph₂CN₂ in the molar ratio of 1:1 and 1:2 gave the complexes *trans*-[Rh(PiPr₃)₂(acetone)(η¹-N₂CPh₂)]PF₆ (**8**) and *trans*-[Rh(PiPr₃)₂(η¹-N₂CPh₂)₂]⁺PF₆[−] (**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 C₂H₄ and free Ph₂CN₂, 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, N₃) which afford the mono(diphenyldiazomethane)rhodium(II) compounds *trans*-[Rh(PiPr₃)₂(py)(η¹-N₂CPh₂)]PF₆ (**10**) and *trans*-[RhX(η¹-N₂CPh₂)(PiPr₃)₂] (**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 > N₃.

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(=CR₂)(PiPr₃)₂], we observed that the dimer [RhCl(PiPr₃)₂]₂ as well

as the monomeric ethene derivative *trans*-[RhCl(C₂H₄)(PiPr₃)₂] react with diphenyldiazomethane to afford the square-planar diazoalkane compound *trans*-[RhCl(N₂CPh₂)(PiPr₃)₂].^[1] Moreover, we discovered that various rhodium(II) complexes including [RhCl(PiPr₃)₂]₂ and [RhCl(C₂H₄)₂]₂ catalyze the reaction of ethene and diphenyldiazomethane to give almost selectively 1,1-diphenylprop-1-ene Ph₂C=CHMe.^[1, 2] The formation of this trisubstituted olefin can be formally understood as the coupling of two carbene fragments :CPh₂ and :CHMe, of which the latter is generated from the isomeric ethene. Besides Ph₂C=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 [Rh₂(μ-O₂CMe)₄] and derivatives thereof are effective catalysts for the synthesis of cyclopropanes from olefins and diazoalkanes.^[3] 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 Ph₂C=CHMe and *cyclo*-1,1-C₃H₄Ph₂, a third isomer CH₂=CHCHPh₂ is formed from C₂H₄ and Ph₂CN₂.^[4]

[a] Prof. Dr. H. Werner, Dr. M. E. Schneider, Dipl.-Chem. M. Bosch, Dr. J. Wolf
Institut für Anorganische Chemie der Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4605
E-mail: helmut.werner@mail.uni-wuerzburg.de

[b] Prof. Dr. J. H. Teuben
Groningen Center for Catalysis and Synthesis
Department of Chemistry of the University of Groningen
Nijenborgh 4, 9747 AG Groningen (The Netherlands)
E-mail: teuben@chem.rug.nl

[c] Drs. A. Meetsma
Department of Chemical Physics of the University of Groningen
Nijenborgh 4, 9747 AG Groningen (The Netherlands)
E-mail: a.meetsma@fwn.rug.nl

[d] Dr. S. I. Troyanov
Institut für Chemie der Humboldt Universität Berlin
Hessische Strasse 1-2, 10115 Berlin (Germany)
E-mail: sergej = troyanov@rz.hu-berlin.de

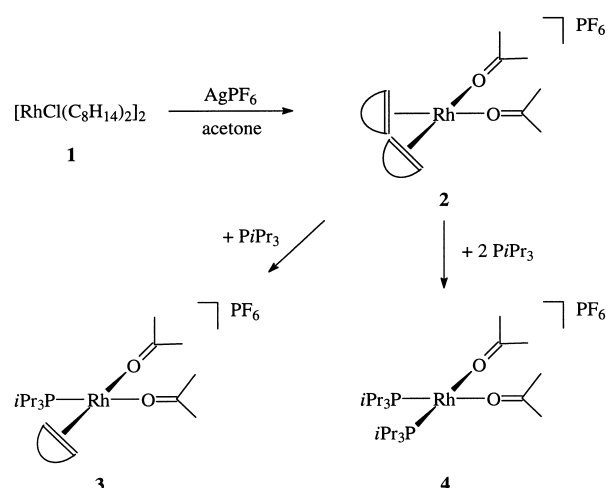
Because of this apparent influence of the anionic ligand on both the reactivity and the selectivity, we became interested to find out whether *cationic* rhodium(I) complexes also catalyze the reaction of olefins (not only ethene) and diphenyldiazomethane and what the products of these C–C coupling processes are. Here we report on the preparation of a series of compounds of the general composition *cis*-[Rh(acetone)₂(L)(L')]PF₆, on the synthesis of cationic as well as neutral rhodium(I) complexes containing Ph₂CN₂ as a ligand, and on the catalytic activity of these species in C–C coupling reactions. Some preliminary results have already been communicated.^[5]

Results and Discussion

Cationic bis(acetone)rhodium(I) complexes: From earlier work it was already known that the dimeric diolefinrhodium(I) complexes [RhCl(diolefin)]₂ (diolefin = norbornadiene, cycloocta-1,5-diene) react with AgPF₆ in a coordinating solvent such as acetone or THF to give the compounds [Rh(S)₂(diolefin)]PF₆ (S = acetone, THF).^[6] 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*Pr₂PCH₂CH₂OMe to produce [Rh(κ²-O,*P*-*i*Pr₂PCH₂CH₂OMe)₂](PF₆) in a good yield.^[7]

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(I)-Komplexe *cis*-[Rh(acetone)₂(L)(L')]PF₆ (**2**: L = L' = C₈H₁₄; **3**: L = C₈H₁₄; L' = *Pi*Pr₃; **4**: L = L' = *Pi*Pr₃), die aus [[RhCl(C₈H₁₄)₂]] hergestellt und als PF₆-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=CH₂ (R = H, Me, Ph) und einem Äquivalent CPh₂ zusammensetzen. Die Effektivität und die Selektivität des Katalysators hängen entscheidend von der Koordinationssphäre des Rhodium(I)-Zentrums ab. Die Umsetzungen von **4** mit Ph₂CN₂ im Molverhältnis 1:1 und 1:2 liefern die Komplexe *trans*-[Rh(*Pi*Pr₃)₂(acetone)(η¹-N₂CPh₂)]PF₆ (**8**) und *trans*-[Rh(*Pi*Pr₃)₂(η¹-N₂CPh₂)₂](PF₆) (**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 C₂H₄ mit freiem Ph₂CN₂ 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, N₃), die zu den Mono(diphenyldiazomethan)rhodium(I)-Verbindungen *trans*-[Rh(*Pi*Pr₃)₂(py)(η¹-N₂CPh₂)]PF₆ (**10**) und *trans*-[RhX(η¹-N₂CPh₂)(*Pi*Pr₃)₂] (**11**–**14**) führen. Die katalytische Aktivität der Neutralkomplexe **11**–**14** ist etwas geringer als diejenige der kationischen Spezies **8**, **9** und nimmt in der Reihenfolge Cl > Br > I > N₃ ab.



Scheme 1. Preparation of the cationic bis(acetone)rhodium(I) 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

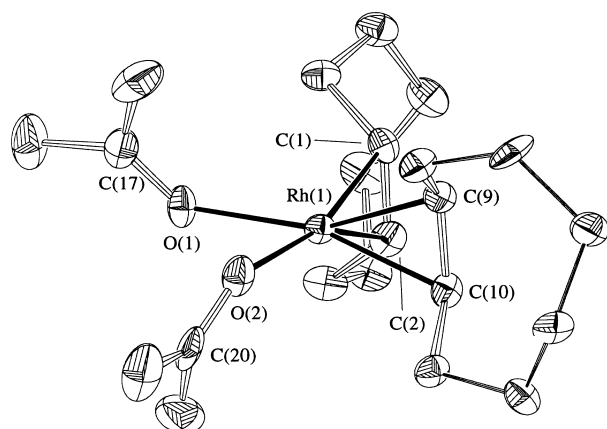
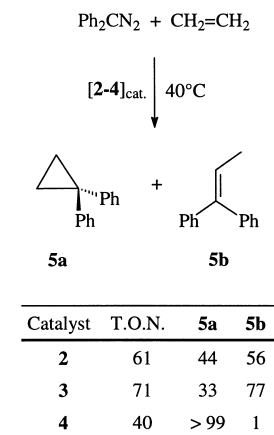


Figure 1. Molecular structure of **2** (anionic ligand omitted for clarity). Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh(1)–O(1) 2.138(4), Rh(1)–O(2) 2.126(4), Rh(1)–C(1) 2.126(5), Rh(1)–C(2) 2.122(5), Rh(1)–C(9) 2.113(5), Rh(1)–C(10) 2.148(5), C(1)–C(2) 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=CPh₂)(acetone)(*Pi*Pr₃)₂]⁺.^[8] The coordinated C–C bonds of the C₈H₁₄ 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 *Pi*Pr₃ in diethyl ether a replacement of one cyclooctene ligand occurs and the PF₆ 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 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.^[8] 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 Ph₂CN₂ with compounds **2–4** as catalyst (T.O.N. = turnover number = [(mmol product)/(mmol catalyst)]); ratio of **5a** and **5b** in %).

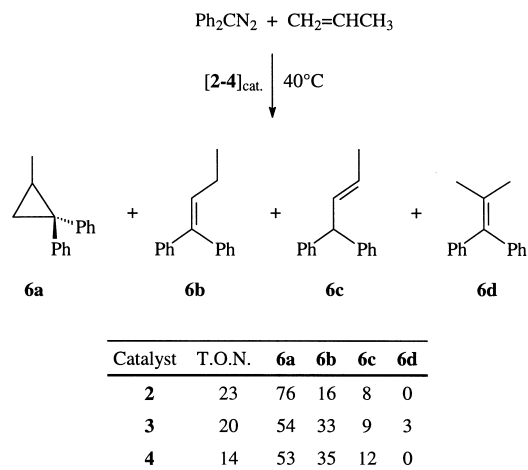
1-ene (**5b**) decreases. In contrast, substitution of *both* olefinic ligands by triisopropylphosphane leads to a significant decrease in activity but also to a tremendous increase in selectivity, the cyclopropanation product **5a** being almost exclusively formed.

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 C₂H₄ and Ph₂CN₂ are coordinated to rhodium and that, after elimination of N₂, a four-membered RhC₃ cycle is formed. The next step could be the opening of the metallacyclobutane ring to give a chainlike cationic intermediate RhCH₂CH₂CPh₂⁺ 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 β-H shift to afford a π-allyl(hydrido)rhodium(III) intermediate [L₃RhH-(η³-CH₂CHCPh₂)]⁺ which, by reductive coupling of the hydrido ligand and the CH₂ carbon atom of the allyl unit, generates Ph₂C=CHMe (**5b**).

Interestingly, no formation of CH₂=CPh₂, 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 [(η⁵-C₅H₅)Ti(κ²-O,*P*-OCH₂CH₂PPh₂)(=CH*t*Bu)]^[9] and [(η⁵-C₅H₄(CH₂)₂N*t*Bu-κ-*N*)Ti(=CH*t*Bu)(PMe₃)]^[10] have shown that a mixture of C–C coupling rather

than metathesis products is generated. Moreover, in the first case the metallacyclobutane complex [(η⁵-C₅H₅)-Ti(CH₂CH₂CH*t*Bu)(κ²-O,*P*-OCH₂CH₂PPh₂)] could be isolated and characterized.

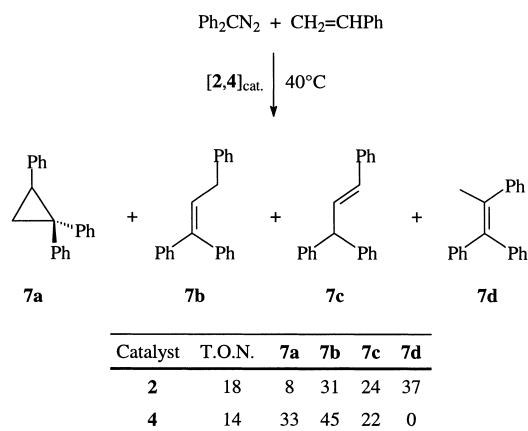
The cationic complexes not only catalyze the reaction of Ph₂CN₂ with ethene but also that of diphenyldiazomethane with substituted olefins such as propene and styrene. With CH₂=CHCH₃ and Ph₂CN₂ as starting materials and catalytic amounts of **2–4** (in THF at 40 °C) a mixture of four isomers (**6a–6d**) is formed (Scheme 3). In each case the dominating



Scheme 3. Results of the catalytic reaction of propene and Ph₂CN₂ 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 C₂H₄/Ph₂CN₂ 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-



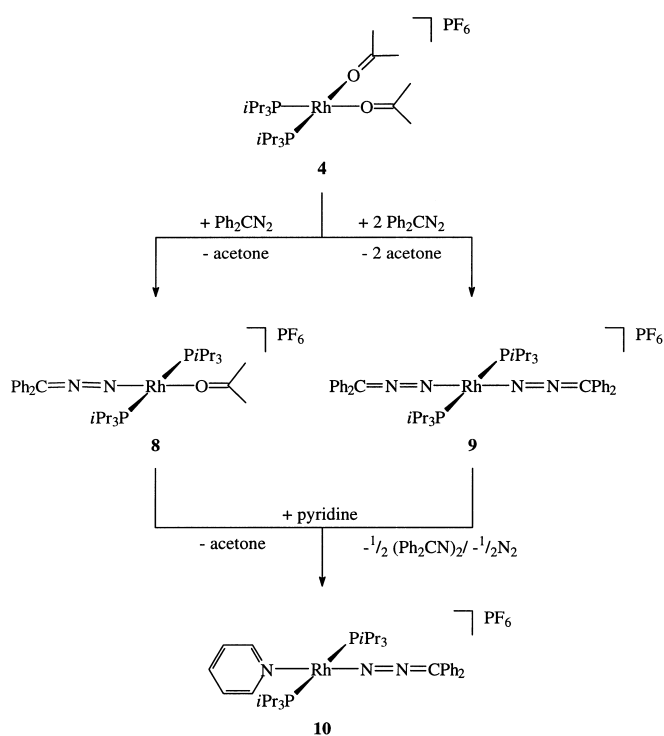
Scheme 4. Results of the catalytic reaction of styrene and Ph₂CN₂ with compounds **2–4** as catalyst (T.O.N. = turnover number = [(mmol product)/(mmol catalyst)]); ratio of **7a**, **7b**, **7c**, and **7d** in %).

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_2 and Ph_2CN_2 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 $\text{Rh}(\text{N}_2\text{CPh}_2)$ species as intermediates, the reactivity of the cationic complexes toward Ph_2CN_2 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_2CN_2 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 ^{31}P NMR spectroscopy to be the unchanged starting material **3**, the solution contained the ketazine $\text{Ph}_2\text{C=N=N=CPh}_2$ (confirmed by GC/MS) which is probably generated by a metal-catalyzed conversion of Ph_2CN_2 . We note that Lemenovskii and co-workers have already reported that the reactions of the trishydrides $[(\text{C}_5\text{H}_5)_2\text{MH}_3]$ ($\text{M}=\text{Nb}, \text{Ta}$) with diaryldiazomethanes $\text{RR}'\text{CN}_2$ afford the corresponding ketazines $\text{RR}'\text{C=N=N=CRR}'$, in this case probably via the monohydrido compounds $[(\text{C}_5\text{H}_5)_2\text{MH}(\eta^1\text{-N}_2\text{CRR}')] as intermediates.$ ^[11]

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_2CN_2 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 ^{31}P NMR spectra of **8** and **9** display a doublet with a $^{31}\text{P} - ^{103}\text{Rh}$ 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.^[7, 8] In the ^{13}C NMR spectra of **8** and **9**, the resonance for the diazoalkane carbon atom Ph_2CN_2 appears at $\delta = 84.5$ (**8**) and $\delta = 83.3$ (**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 ^{31}P NMR spectrum of **8** in $[\text{D}_6]\text{acetone}$ shows, besides the doublet at $\delta = 40.2$, two other doublets at $\delta = 60.3$ (for **4**) and $\delta = 46.5$ (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

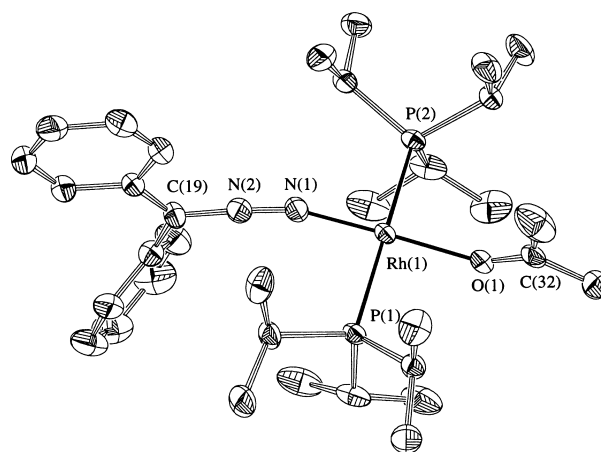


Figure 2. Molecular structure of **8** (anionic ligand omitted for clarity). Principal bond lengths [Å] and angles [$^\circ$] with estimated standard deviations in parentheses: Rh(1)–P(1) 2.3546(8), Rh(1)–P(2) 2.3693(8), Rh(1)–O(1) 2.039(2), Rh(1)–N(1) 1.869(3), N(1)–N(2) 1.157(4), N(2)–C(19) 1.312(4), 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 $170.88(3)^\circ$ and $172.21(10)^\circ$, respectively. The Rh(1)–N(1)–N(2) chain is considerably bent, the bond angle being

about 10° smaller than in the octahedral cationic tungsten compound $[\text{WBr}(\text{N}_2\text{CMe}_2)(\text{dppe})_2]^+$ ($\text{dppe} = 1,2\text{-C}_2\text{H}_4(\text{PPh}_2)_2$).^[12] 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.^[13] 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° , we assume that in **8** the diphenyldiazomethane behaves predominantly as a σ -donor ligand. An analogous conclusion has been drawn in the case of *trans*- $[\text{RhCl}\{\eta^1\text{-N}_2\text{C}(\text{C}_6\text{H}_4)_2\text{CO}\}(\text{PiPr}_3)_2]$ ^[14] and some other $[\text{M}(\eta^1\text{-N}_2\text{CR}_2)]$ complexes.^[15, 16]

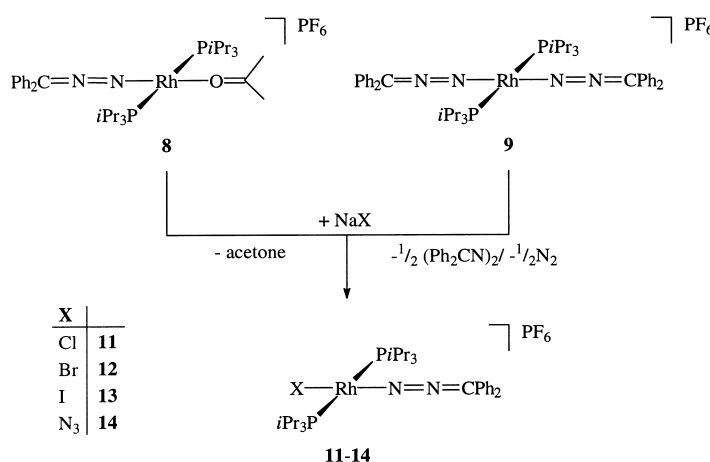
Regarding the distances in **8**, the N(1)–N(2) and N(2)–C(19) bond lengths are rather short (1.157(4) and 1.312(4) Å) and quite similar to those in free diazomethane (1.12 and 1.32 Å).^[13] This similarity supports the proposal that the σ -donor character of the diphenyldiazomethane ligand in **8** 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*- $[\text{RhCl}(\text{N}_2)(\text{PiPr}_3)_2]$.^[17]

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 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 PCHCH_3 protons in the ^1H NMR spectrum and of a sharp doublet with a ^{31}P – ^{103}Rh coupling constant of 126.7 Hz in the ^{31}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.^[18]

To find out whether the isolated compounds **8** and **9** could play a role in the above-mentioned catalytic process between C_2H_4 and Ph_2CN_2 , both diazoalkane complexes were treated with ethene. In THF at 40°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 C_2H_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 C_2H_4 and free Ph_2CN_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°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 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 Ph_2CN_2 ,^[1, 2a] 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 N_2 to give *trans*- $[\text{RhX}(\text{CPh}_2)(\text{PiPr}_3)_2]$.^[19] 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 Ph_2CN_2 carbon atom at $\delta = 78.3\text{--}79.4$ in the ^{13}C NMR spectrum. For **14**, the $\nu(\text{N}_3)$ band appears at 2038 cm^{-1} .

The catalytic activity of the neutral compounds **11–14** in the reaction of C_2H_4 and Ph_2CN_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°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 C_2H_4 and Ph_2CN_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. PiPr_3 was a commercial product from Strem Chemicals. The complexes $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ (**1**)^[20], *cis*- $[\text{Rh}(\text{acetone})_2(\text{C}_8\text{H}_{14})_2]\text{PF}_6$ (**2**)^[7, 8] and *cis*- $[\text{Rh}(\text{acetone})_2(\text{PiPr}_3)_2]\text{PF}_6$ (**4**)^[8] 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; $N = {}^3J(\text{P(H)}) + {}^3J(\text{P(H)})$ or ${}^2J(\text{P(C)}) + {}^2J(\text{P(C)})$, 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)₂(C₈H₁₄)(PiPr₃)₂PF₆ (3): A suspension of **2** (119 mg, 0.20 mmol) in diethyl ether (4 mL) was treated at -78°C with PiPr₃ (39 μL , 0.20 mmol) and stirred for 10 min. The solvent was removed, the residue was washed with diethyl ether ($2 \times 10\text{ mL}$) and pentane ($3 \times 10\text{ mL}$) 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°C (decomp); conductivity $\Lambda = 125\text{ cm}^2\Omega^{-1}\text{ mol}^{-1}$; IR (CH₂Cl₂): $\bar{\nu} = 1701, 1658$ (C=O), 1354 cm^{-1} (C=C); ${}^1\text{H}$ NMR (400 MHz, [D₆]acetone): $\delta = 2.21$ (m, 2H; CH of C₈H₁₄), 2.09 (s, 12H; CH₃ of acetone), 1.93 (m, 3H; PCHCH₃), 1.60, 1.49, 1.36 (all m, 12H; CH₂ of C₈H₁₄), 1.38 (dd, ${}^3J(\text{P(H)}) = 13.6\text{ Hz}$, ${}^3J(\text{H(H)}) = 7.2\text{ Hz}$, 18H; PCHCH₃); ${}^{13}\text{C}$ NMR (100.6 MHz, [D₆]acetone): $\delta = 206.6$ (s, C=O), 62.5 (dd, ${}^1J(\text{Rh,C}) = 16.2\text{ Hz}$, ${}^2J(\text{P,C}) = 1.6\text{ Hz}$; CH of C₈H₁₄), 30.6 (s, CH₃ of acetone), 30.2, 28.7, 26.9 (all s, CH₂ of C₈H₁₄), 23.2 (d, ${}^1J(\text{P,C}) = 25.2\text{ Hz}$; PCHCH₃), 20.0 (s, PCHCH₃); ${}^{31}\text{P}$ NMR (162.0 MHz, [D₆]acetone): $\delta = 63.1$ (d, ${}^1J(\text{Rh,P}) = 188.1\text{ Hz}$), -144.2 (sept, ${}^1J(\text{F,P}) = 707.4\text{ Hz}$); elemental analysis (%) for C₂₃H₄₇F₆O₂P₂Rh (634.5): calcd: C 43.54, H 7.47; found: C 43.91, H 7.71.

trans-[Rh(PiPr₃)₂(acetone)(η^1 -N₂CPh₂)]PF₆ (8): A solution of **4** (260 mg, 0.38 mmol) in acetone (5 mL) was treated at -78°C with one equivalent of a 0.5 M solution of Ph₂CN₂ (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 ($3 \times 5\text{ mL}$) and pentane ($2 \times 5\text{ mL}$), and dried. Yield = 284 mg, 91%; m.p. 57°C (decomp); conductivity $\Lambda = 105\text{ cm}^2\Omega^{-1}\text{ mol}^{-1}$; IR (CH₂Cl₂): $\bar{\nu} = 1956$ (N=N) cm^{-1} ; ${}^1\text{H}$ NMR (200 MHz, [D₆]acetone): $\delta = 7.53$ (m, 4H; *ortho* H of C₆H₅), 7.34 (m, 6H; *meta* and *para* H of C₆H₅), 2.06 (m, 6H; PCHCH₃), 2.05 (s, 6H; CH₃ of acetone), 1.34 (dvt, $N = 13.1\text{ Hz}$, ${}^3J(\text{H,H}) = 6.6\text{ Hz}$, 36H; PCHCH₃); ${}^{13}\text{C}$ NMR (50.3 MHz, [D₆]acetone, -35°C): $\delta = 206.6$ (s, C=O), 130.2, 127.6, 127.1, 126.3 (all s, C₆H₅), 84.5 (s, CN₂), 30.6 (s, CH₃ of acetone), 23.5 (vt, $N = 19.6\text{ Hz}$; PCHCH₃), 19.5 (s, PCHCH₃); ${}^{31}\text{P}$ NMR (81.0 MHz, [D₆]acetone): $\delta = 40.2$ (d, ${}^1J(\text{Rh,P}) = 122.1\text{ Hz}$), -142.8 (sept, ${}^1J(\text{F,P}) = 709.2\text{ Hz}$); elemental analysis (%) for C₃₄H₃₈F₆N₂O₂P₂Rh (820.5): calcd: C 49.76, H 7.12, N 3.41; found: C 49.50, H 6.80, N 3.29.

trans-[Rh(PiPr₃)₂(η^1 -N₂CPh₂)₂]PF₆ (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 Ph₂CN₂ (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 ($2 \times 2\text{ mL}$) and dried in vacuo. Yield = 380 mg, 76%; m.p. 62°C (decomp); conductivity $\Lambda = 102\text{ cm}^2\Omega^{-1}\text{ mol}^{-1}$; IR (CH₂Cl₂): $\bar{\nu} = 1948$ (N=N) cm^{-1} ; ${}^1\text{H}$ NMR (200 MHz, [D₆]acetone): $\delta = 7.54$ (d, ${}^3J(\text{H,H}) = 7.7\text{ Hz}$, 8H; *ortho* H of C₆H₅), 7.37 (m, 12H; *meta* and *para* H of C₆H₅), 2.03 (m, 6H; PCHCH₃), 1.26 (dvt, $N = 14.3\text{ Hz}$, ${}^3J(\text{H,H}) = 6.9\text{ Hz}$, 36H; PCHCH₃); ${}^{13}\text{C}$ NMR (50.3 MHz, [D₈]THF, -35°C): $\delta = 130.5, 129.4, 128.0, 127.5$ (all s, C₆H₅), 83.3 (s, CN₂), 24.8 (vt, $N = 19.4\text{ Hz}$; PCHCH₃), 19.6 (s, PCHCH₃); ${}^{31}\text{P}$ NMR (81.0 MHz, [D₆]acetone): $\delta = 46.5$ (d, ${}^1J(\text{Rh,P}) = 116.2\text{ Hz}$), -142.7 (sept, ${}^1J(\text{F,P}) = 707.3\text{ Hz}$); elemental analysis (%) for C₄₄H₆₆F₆N₄P₂Rh (956.8): calcd: C 55.23, H 6.53, N 5.86; found: C 55.19, H 6.60, N 5.54.

trans-[Rh(PiPr₃)₂(py)(η^1 -N₂CPh₂)]PF₆ (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

($2 \times 2\text{ mL}$) and pentane ($3 \times 2\text{ mL}$) and dried in vacuo. Yield = 56 mg, 91%; m.p. 64°C (decomp); conductivity $\Lambda = 87\text{ cm}^2\Omega^{-1}\text{ mol}^{-1}$; IR (CH₂Cl₂): $\bar{\nu} = 1984$ (N=N) cm^{-1} ; ${}^1\text{H}$ NMR (200 MHz, [D₆]acetone): $\delta = 9.03$ (m, 2H; *ortho* H of NC₅H₃), 7.96 (m, 1H; *para* H of NC₅H₃), 7.63 (m, 2H; *meta* H of NC₅H₃), 7.47 (m, 4H; *ortho* H of C₆H₅), 7.27 (m, 6H; *para* and *meta* H of C₆H₅), 1.86 (m, 6H; PCHCH₃), 1.28 (dvt, $N = 13.4\text{ Hz}$, ${}^3J(\text{H,H}) = 7.3\text{ Hz}$, 36H; PCHCH₃); ${}^{13}\text{C}$ NMR (50.3 MHz, [D₆]acetone, -35°C): $\delta = 154.7$ (s, *ortho* C of NC₅H₃), 139.0 (s, *para* C of NC₅H₃), 129.9, 127.5, 127.2, 126.5 (all s, C₆H₅), 126.8 (s, *meta* C of NC₅H₃), 66.0 (s, CN₂), 24.1 (vt, $N = 19.0\text{ Hz}$; PCHCH₃), 19.8 (s, PCHCH₃); ${}^{31}\text{P}$ NMR (81.0 MHz, [D₆]acetone): $\delta = 38.0$ (d, ${}^1J(\text{Rh,P}) = 126.7\text{ Hz}$), -142.7 (sept, ${}^1J(\text{F,P}) = 707.0\text{ Hz}$); elemental analysis (%) for C₃₆H₅₇F₆N₃P₃Rh (841.7): calcd: C 51.37, H 6.83, N 4.99; found: C 51.23, H 6.86, N 4.85.

trans-[RhCl(η^1 -N₂CPh₂)(PiPr₃)₂] (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 ($2 \times 1\text{ mL}$) and dried in vacuo. Yield = 29 mg, 68%. Compound **11** was characterized by comparison of the spectroscopic data with those of an authentic sample.^[1, 2a]

trans-[RhBr(η^1 -N₂CPh₂)(PiPr₃)₂] (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°C (decomp). IR (KBr): $\bar{\nu} = 1943$ (N=N) cm^{-1} ; ${}^1\text{H}$ NMR (200 MHz, [D₆]benzene): $\delta = 7.41$ (m, 4H; *ortho* H of C₆H₅), 7.19 (m, 4H; *meta* H of C₆H₅), 6.89 (m, 2H; *para* H of C₆H₅), 2.42 (m, 6H; PCHCH₃), 1.27 (dvt, $N = 13.2\text{ Hz}$, ${}^3J(\text{H,H}) = 6.9\text{ Hz}$, 36H; PCHCH₃); ${}^{13}\text{C}$ NMR (50.3 MHz, [D₆]benzene): $\delta = 128.9, 128.3, 125.4, 124.5$ (all s, C₆H₅), 79.1 (s, CN₂), 24.1 (vt, $N = 18.5\text{ Hz}$; PCHCH₃), 20.1 (s, PCHCH₃); ${}^{31}\text{P}$ NMR (81.0 MHz, [D₆]benzene): $\delta = 40.9$ (d, ${}^1J(\text{Rh,P}) = 119.1\text{ Hz}$); elemental analysis (%) for C₃₁H₃₂BrN₂P₂Rh (697.5): calcd: C 54.79, H 7.51, N 4.02; found: C 54.38, H 7.67, N 4.08.

trans-[RhI(η^1 -N₂CPh₂)(PiPr₃)₂] (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°C (decomp); IR (CH₂Cl₂): $\bar{\nu} = 2032$ (N=N) cm^{-1} ; ${}^1\text{H}$ NMR (200 MHz, [D₆]benzene): $\delta = 7.39$ (m, 4H; *ortho* H of C₆H₅), 7.17 (m, 4H; *meta* H of C₆H₅), 6.90 (m, 2H; *para* H of C₆H₅), 2.52 (m, 6H; PCHCH₃), 1.26 (dvt, $N = 13.2\text{ Hz}$, ${}^3J(\text{H,H}) = 6.9\text{ Hz}$, 36H; PCHCH₃); ${}^{13}\text{C}$ NMR (50.3 MHz, [D₆]benzene): $\delta = 129.0, 128.3, 125.3, 124.7$ (all s, C₆H₅), 79.4 (s, CN₂), 25.2 (vt, $N = 18.8\text{ Hz}$; PCHCH₃), 20.4 (s, PCHCH₃); ${}^{31}\text{P}$ NMR (81.0 MHz, [D₆]benzene): $\delta = 40.8$ (d, ${}^1J(\text{Rh,P}) = 116.2\text{ Hz}$); elemental analysis (%) for C₃₁H₃₂IN₂P₂Rh (744.5): calcd: C 50.01, H 7.04, N 3.76; found: C 49.30, H 6.78, N 4.10.

trans-[Rh(N₃)(η^1 -N₂CPh₂)(PiPr₃)₂] (14): This was prepared as described for **11**, using **8** (66 mg, 0.08 mmol) and NaN₃ (52 mg, 0.80 mmol) as starting materials. Dark green solid; yield = 31 mg, 56%; m.p. 58°C (decomp); IR (hexane): $\bar{\nu} = 2038$ (N=N of N₃), 1948 (N=N of N₂CPh₂) cm^{-1} ; ${}^1\text{H}$ NMR (200 MHz, [D₆]benzene): $\delta = 7.34$ (m, 4H; *ortho* H of C₆H₅), 7.19 (m, 4H; *meta* H of C₆H₅), 6.87 (m, 2H; *para* H of C₆H₅), 2.12 (m, 6H; PCHCH₃), 1.20 (dvt, $N = 13.6\text{ Hz}$, ${}^3J(\text{H,H}) = 6.9\text{ Hz}$, 36H; PCHCH₃); ${}^{13}\text{C}$ NMR (50.3 MHz, [D₆]benzene): $\delta = 129.9, 129.0, 128.3, 125.1, 124.6$ (all s, C₆H₅), 78.3 (s, CN₂), 24.0 (vt, $N = 17.6\text{ Hz}$; PCHCH₃), 19.7 (s, PCHCH₃); ${}^{31}\text{P}$ NMR (81.0 MHz, [D₆]benzene): $\delta = 44.3$ (d, ${}^1J(\text{Rh,P}) = 123.5\text{ Hz}$); elemental analysis (%) for C₃₁H₃₂N₅P₂Rh (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 Ph₂CN₂ and C₂H₄ 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^{-1}) at 40°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 Ph₂CN₂ and separate the catalyst from the reaction products, the mixture was filtered through Al₂O₃ (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 Ph₂CN₂ and propene with 2–4 as catalyst: In an analogous manner to the catalytic reaction of Ph₂CN₂ 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 Ph₂CN₂ 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^{−1}) 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 Ph₂CN₂ and C₂H₄ 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:^[21] 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^[22] mounted on an ENRAF-Nonius CAD-4F diffractometer with monochromated MoK_α radiation (λ = 0.71073 Å).^[23] 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	2 ^[d]	8
formula	C ₂₂ H ₄₀ F ₆ O ₂ RhP	C ₃₄ H ₅₈ F ₆ N ₂ OP ₃ Rh
<i>M_r</i>	584.43	820.66
<i>T</i> [K]	130	130
cryst. size [mm ³]	0.3 × 0.3 × 0.6	0.1 × 0.1 × 0.6
space group	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>n</i> (no. 14)
cell dimensions determination	24 rflns, 16.8 < θ < 17.7	24 rflns, 16.2 < θ < 17.9
<i>a</i> [pm]	1282.4(1)	1369.6(1)
<i>b</i> [pm]	1289.5(1)	1199.3(1)
<i>c</i> [pm]	3153.1(1)	2457.1(1)
α [°]	99.950(6)	–
β [°]	90.888(4)	102.41(1)
γ [°]	90.068(4)	–
<i>V</i> [nm ³]	5.1231(6)	3.9417(5)
<i>Z</i>	8	4
ρ _{calcd} [Mg m ^{−3}]	1.515	1.383
μ [mm ^{−1}]	0.789	0.612
<i>F</i> (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
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0478	0.0368
<i>wR</i> 2 (all data) ^[b]	0.1262	0.0880
<i>g</i> 1; <i>g</i> 2 ^[c]	0.0565; 15.2674	0.0484; 1.5161
resid. elec. ρ [10 ^{−6} e pm ^{−3}]	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_r* represent one molecule only.

using the program DIRDIF.^[24] All structures were refined by full matrix least-squares procedures on *F*² with SHELX93.^[25] The asymmetric unit of **2** contains four formula units, each consisting of two moieties; a cationic rhodium complex and a PF₆[−] counterion. For **2** a weak hydrogen bonding between the methyl groups of the coordinated acetone and fluor atoms of the PF₆[−] anions is observed.^[26] 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 sp³ hybridization at the C atom as appropriate with *U*_{iso} = 1.5 × *U*_{equiv} 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 PF₆[−] 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).

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie for financial support, the latter in particular for a Ph.D. grant to M. E. S. We are also grateful to Mrs. R. Schedl and Mr. C. P. Kneis (DTA and elemental analysis), Mrs. M.-L. Schäfer and Dr. W. Buchner (NMR spectra), and BASF AG for various gifts of chemicals. M. B. gratefully acknowledges support from the European Union (SOK-RATES program).

- [1] J. Wolf, L. Brandt, A. Fries, H. Werner, *Angew. Chem.* **1990**, *102*, 584–586; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 510–512.
- [2] a) L. Brandt, Dissertation, Universität Würzburg, **1991**; b) A. Fries, Dissertation, Universität Würzburg, **1993**; c) E. Bleuel, Dissertation, Universität Würzburg, submitted.
- [3] a) A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot, P. Teyssie, *J. Org. Chem.* **1980**, *45*, 695–702; b) M. P. Doyle, *Acc. Chem. Res.* **1986**, *19*, 348–356; c) M. P. Doyle, W. R. Winchester, J. A. A. Hoorn, V. Lynch, S. H. Simonsen, R. Ghosh, *J. Am. Chem. Soc.* **1993**, *115*, 9968–9978.
- [4] L. Brandt, A. Fries, N. Mahr, H. Werner, J. Wolf in *Selective Reactions of Metal-Activated Molecules* (Eds.: H. Werner, A. G. Griesbeck, W. Adam, G. Bringmann, W. Kiefer), Vieweg, Braunschweig, **1992**, p. 171–174.
- [5] M. E. Schneider, H. Werner, *X. International Symposium on Homogeneous Catalysis*, Princeton, **1996**.
- [6] a) J. R. Shapley, R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1969**, *91*, 2816–2817; b) R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 2397–2407.
- [7] B. Windmüller, J. Wolf, H. Werner, *J. Organomet. Chem.* **1995**, *502*, 147–161.
- [8] B. Windmüller, O. Nürnberg, J. Wolf, H. Werner, *Eur. J. Inorg. Chem.* **1999**, 613–619.
- [9] J. A. van Doorn, H. van der Heijden, A. G. Orpen, *Organometallics* **1995**, *14*, 1278–1283.
- [10] a) P. J. Sinnema, L. Veen, A. L. Spek, N. Veldman, J. H. Teuben, *Organometallics* **1997**, *16*, 4245–4247; b) P. J. Sinnema, Dissertation, Rijksuniversiteit Groningen, **1999**.

- [11] D. A. Lemenovski, M. Putala, G. I. Nikonov, N. B. Kazennova, D. S. Yufit, Yu. T. Truchkov, *J. Organomet. Chem.* **1993**, 454, 123–131.
- [12] J. Chatt, R. A. Head, P. B. Hitchcock, W. Hussain, G. J. Leigh, *J. Organomet. Chem.* **1977**, 133, C1–C4.
- [13] a) D. Sellmann, *Angew. Chem.* **1974**, 86, 692–702; *Angew. Chem. Int. Ed. Engl.* **1974**, 13, 639–649; b) M. Putala, D. A. Lemenovskii, *Russ. Chem. Rev.* **1994**, 63, 197–216.
- [14] N. Mahr, Dissertation, Universität Würzburg, **1994**.
- [15] a) W. A. Herrmann, *Angew. Chem.* **1978**, 90, 855–868; *Angew. Chem. Int. Ed. Engl.* **1978**, 17, 800–813; b) W. A. Herrmann, G. Kriechbaum, M. L. Ziegler, P. Wülknitz, *Chem. Ber.* **1981**, 114, 276–284.
- [16] a) K. D. Schramm, J. A. Ibers, *Inorg. Chem.* **1980**, 19, 1231–1236; b) M. J. Menu, G. Crocco, M. Dartiguenave, Y. Dartiguenave, G. Bertrand, *J. Chem. Soc. Chem. Commun.* **1988**, 1598–1599.
- [17] D. L. Thorn, T. H. Tulip, J. A. Ibers, *J. Chem. Soc. Dalton Trans.* **1979**, 2022–2025.
- [18] C. Hahn, J. Sieler, R. Taube, *Chem. Ber./Recueil* **1997**, 130, 939–945.
- [19] a) P. Schwab, N. Mahr, J. Wolf, H. Werner *Angew. Chem.* **1993**, 105, 1498–1500; *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1480–1482; b) H. Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert, J. Wolf, *Chem. Eur. J.* **1997**, 3, 1375–1384.
- [20] A. van der Ent, A. L. Onderdelinden, *Inorg. Synth.* **1973**, 14, 92–95.
- [21] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publications no. CCDC-139831 (**2**) and CCDC-139830 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EK, UK (Fax(+44)1223–336–033; e-mail: deposit@ccdc.cam.ac.uk).
- [22] F. van Bolhuis, *J. Appl. Crystallogr.* **1971**, 4, 263–264.
- [23] ENRAF-Nonius CAD4/PC Version 1.5c of May 1995. ENRAF-Nonius Delft, Scientific Instruments Division, Delft, The Netherlands.
- [24] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israël, J. M. M. Smits, The DIRDIF program system, *Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, **1994**.
- [25] G. M. Sheldrick, Program for Crystal Structure Refinement, University of Göttingen, **1996**.
- [26] a) Z. Berkovitch-Yellin, L. Leiserowitz, *Acta Cryst.* **1984**, B40, 159–165; b) A. Bondi, *J. Phys. Chem.* **1964**, 68, 441–451.

Received: February 2, 2000 [F2275]