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


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

Abstract: Cationic rhodium(Ι) complexes cis-[Rh(acetone)(L)(L')] (2: L = L' = C6H5CH2; 3: L = C6H5; L' = PrPr3; 4: L = L' = PrPr3), prepared from [[RhCl(C6H5)2]3] 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 CPH3. The efficiency and selectivity of the catalyst depends significantly on the coordination sphere around the rhodium(Ι) center. Treatment of 4 with Ph3CN2 in the molar ratio of 1:1 and 1:2 gave the complexes trans-[Rh(PPr3)3(acetone)(η5-N2CPH3)]PF6 (8) and trans-[Rh(PPr3)3(acetone)(η5-N2CPH3)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 C6H5 and free Ph3CN2, 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(Ι) compounds trans-[Rh(PPr3)3(py)(η5-N2CPH3)]PF6 (10) and trans-[RhX(η5-N2CPH3)(PPr3)3] (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(Ι) complexes of the general composition trans-[RhCl(=CR3)-(PPr3)3], we observed that the dimer [[RhCl(PPr3)3]2] as well as the monomeric ethene derivative trans-[RhCl(C6H5)-(PPr3)3] react with diphenyldiazomethane to afford the square-planar diazoalkane compound trans-[RhCl(N2CPH3)-(PPr3)3].[1] Moreover, we discovered that various rhodium(Ι) complexes including [[RhCl(PPr3)3]2] and [[RhCl(C6H5)3]] catalyze the reaction of ethene and diphenyldiazomethane to give almost selectively 1,1-diphenylprop-1-ene Ph3C=CHMe.[2] The formation of this trisubstituted olefin can be formally understood as the coupling of two carbene fragments ≡CPh3 and ≡CHMe, of which the latter is generated from the isomeric ethene. Besides Ph3C=CHMe, there were only traces of 1,1-diphenylcyclopropane detected which was surprising insofar as it was well known that dinuclear bis(carboxylato)rhodium(Ι) compounds such as [Rh2(μ-O2CMe)2] 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(Ι) complexes is substituted by acetate, benzoate, or acetylacetonate, the catalytic activity decreases and besides Ph3C=CHMe and cyclo-1,1-C6H5Ph2, a third isomer CH2=CHCOPh2 is formed from C6H5 and Ph3CN2.[4]
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(0) complexes also catalyze the reaction of olefins (not only ethene) and diphenylazido-methane 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-[RhCl(acetone)(L)-(L′)]PF₆, on the synthesis of cationic as well as neutral rhodium(0) 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.¹⁵

Results and Discussion

Cationic bis(acetone)rhodium(0) complexes: From earlier work it was already known that the dimeric diolefinrhodium(0) complexes [[RhCl₂(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(S₅)₂(diolefin)]PF₆ (S = acetone, THF).¹⁶ 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 iPr₂PCH₂CH₂OMe to produce [Rh(k²-O,P,iPr₂PCH₂CH₂OMe)]PF₆ in a good yield.¹⁷

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(0)-Komplexe cis-[Rh(acetone)₂(L)(L')]⁺ (2: L = L' = C₃H₆; 3: L = C₆H₆; L' = PtPr₃; 4: L = L' = PtPr₃), die aus [[RhCl₂(C₃H₆)₂]₂] hergestellt und als PF₆-Salze isoliert wurden, katalysieren die C-C-Kupplungsreaktion von Diphenylazido-methan mit Ethen, Propen und Styrol. In den meisten Fällen wird ein Gemisch isomerer Olefine und Cyclopropane erhalten, die sich formal aus einem Äquivalent RCH₂(R = H, Me, Ph) und einem Äquivalent C₆H₆ zusammensetzen. Die Effektivität und die Selektivität des Katalysators hängen entscheidend von der Koordinationssphäre des Rhodium(0)-Zentrums ab. Die Umsetzungen von 4 mit Ph₂CN₂ im Molverhältnis 1:1 und 1:2 liefern die Komplexe trans-[Rh(PiPr₃)₂(acetone)(N₂-C₆H₆)]PF₆ (8) und trans-[Rh(PiPr₃)₂(N₂-C₆H₆)]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 C₆H₆ 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[diphenylazido-methan]rhodium(0)-Verbindungen trans-[Rh(PiPr₃)₂(py)(N₂-C₆H₆)]PF₆ (10) und trans-[RhX(N₂-C₆H₆)(PiPr₃)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(0) complexes 2–4 from the bis(cyclooctene) complex 1.](image)

(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 (2.078(2) Å) in the cation trans-[Rh(C=O)₂(C₆H₆)(acetone)·(PiPr₃)]⁺.¹⁸ The coordinated C–C bonds of the C₆H₆ 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 PtPr₃ 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 trisopropylphosphine generates the bis(phosphane) compound 4 which in contrast to 3 is a violet, quite air-sensitive solid.[9] The presence of 1:1 electrolytes has been confirmed for 3 as well as for 4 by conductivity measurements.

**Catalytic activity of compounds 2–4:** As has been described for the neutral complexes trans-[Rhl(C₅H₅)(P(Pr)₃)]. [Rh(η²-O₂CR)(P(Pr)₃)], [Rh(acac)-(P(Pr)₃)], and [RhCl(C₅H₅)]₂, the cationic compounds 2–4 also catalyze the C–C coupling reaction of ethene and diphenylazidomethane. The most noteworthy feature is that both the activity and the selectivity significantly depend on the coordination sphere around the rhodium(II) center (see Scheme 2). If one cyclcopropene ligand in 2 is displaced by P(PPh3), the activity increases while the amount of 1,1-diphenycyclopropane 5a compared to 1,1-diphenylethylene (5b) decreases. In contrast, substitution of both olefinic ligands by trisopropylphosphine 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 Ph₃CN, are coordinated to rhodium and that, after elimination of N₂, a four-membered RhC₄ cycle is formed. The next step could be the opening of the metallocyclobutenene ring to give a chiral cationic intermediate RhCH₂CH₂CP₃⁺ 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 metallocyclobutene reacts by β-H shift to afford a π-allyl(hydrodorhodium(III) intermediate [L₂RhPh₂(CH₂CH₂P₃)]⁺ which, by reductive coupling of the diyad ligand and the CH₄ carbon atom of the allyl unit, generates Ph₃C=CHMe (5b).

Interestingly, no formation of CH₂=CHPh₂, which would be the result of a retro-[2+2] cycloaddition of the postulated metallaolivaneene, is observed. This finding, which does not exclude the possibility of a metalla-a-cyclic intermediate. Recent studies on the reactivity of ethene toward carbene titanium complexes [(η²-C₂H₄)Ti(κ²-O,P-OC₃H₇)CH(CH₂)₃P(Ph)]⁻ (4) [10] and [(η²-C₂H₄(CH₂)₃NiBu₃-κ³,N)Ti(κ²CHBu)₂(PMe₅)]⁻[11] have shown that a mixture of C–C coupling rather than metathesis products is generated. Moreover, in the first case the metallaolivaneene complex [(η²-C₂H₄)-

\[\text{Ph}_3\text{CN}_2 + \text{CH}_2=\text{CH}_2 \rightarrow \text{[2-4]}_{\text{cat}} \rightarrow 40^\circ \text{C} \]

**Scheme 2.** Results of the catalytic reaction of ethene and Ph₃CN, with compounds 2–4 as catalyst (T.O.N. = turnover number = [mmol product]/(mmol catalyst)) ratio of 5a and 5b in %.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T.O.N.</th>
<th>5a</th>
<th>5b</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>61</td>
<td>44</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>71</td>
<td>33</td>
<td>77</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>&gt;99</td>
<td>1</td>
</tr>
</tbody>
</table>

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/Ph₃CN, system where the opposite trend is observed.

A decrease in selectivity is also observed for the rhodium-catalyzed reaction of diphenylazidomethane 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-

\[\text{Ph}_3\text{CN}_2 + \text{CH}_2=\text{CH}_2 \rightarrow \text{[2-4]}_{\text{cat}} \rightarrow 40^\circ \text{C} \]

**Scheme 4.** Results of the catalytic reaction of styrene and Ph₃CN, with compounds 2–4 as catalyst (T.O.N. = turnover number = [mmol product]/(mmol catalyst)) ratio of 7a, 7b, 7c, and 7d in %.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T.O.N.</th>
<th>7a</th>
<th>7b</th>
<th>7c</th>
<th>7d</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>18</td>
<td>8</td>
<td>31</td>
<td>24</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>14</td>
<td>33</td>
<td>45</td>
<td>22</td>
<td>0</td>
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</tbody>
</table>
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=CH2 and Ph3SeCN 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(II); apparently the presence of the sterically demanding triisopropylphosphines 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(N2PPh2) species as intermediates, the reactivity of the cationic complexes toward Ph3SeCN 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 Ph3SeCN 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 31P NMR spectroscopy to be the unchanged starting material 3, the solution contained the ketazine Ph3Se–N–Se–Ph3, (confirmed by GC/MS) which is probably generated by a metal-catalyzed conversion of Ph3SeCN. We note that Lemenovskii and co-workers have already reported that the reactions of the trishydrides [(C6H5)2M]2 (M=Nb, Ta) with diaryldiazomethanes RR'CN=N–Se–RR'', afford the corresponding ketazines RR'''C=N–N=RR'', in this case probably via the monohydrido compounds [(C6H5)2M(p,N–N=CR)] 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 one or two equivalents of Ph3SeCN 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 31P NMR spectra of 8 and 9 display a doublet with a 31P–103Rh coupling constant of 122.1 Hz (8) and 116.2 Hz (9) indicating that, in contrast to the starting material 4, the two phosphate ligands are in *trans* disposition.[7,8] In the 13C NMR spectra of 8 and 9, the resonance for the diazoalkane carbon atom Ph3SeCN appears at δ = 84.5 (8) and δ = 83.3 (9) as a broad singlet, the broadening probably being due to the quadrupolar 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 31P NMR spectrum of 8 in [D6]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.](image)

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 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° smaller than in the octahedral cationic tungsten compound [WBr5(N2C2Me2)3(dppe)]+ (dppe = 1,2-C2H4(PPh2)2)[13] The more remarkable fact, however, is that the N(1)-N(2)-
C(19) angle is nearly linear (171.6(3)°) which is unusual compared to other N-bonded diazoolkane metal complexes.[13] Since the size of the bond angle N-N-C in compounds [L,M{η9-N2-C(NR3)}]+ should depend on the degree of ππ-
metal-to-ligand back bonding, gaining a maximum at an N-N-
C angle of 120°, we assume that in 8 the diphenyldiazoo-
methane behaves predominantly as a σ-donor ligand. An analogous conclusion has been drawn in the case of trans-
[RhCl{η2-N2C(C6H11)2}CO][Pr(Pr3)2][14] and some other [M{η9-
N2-C(NR3)}] 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 diazoo-
methane (1.12 and 1.32 Å).[13] This similarity supports the proposal that the σ-donor character of the diphenyldiazoo-
methane 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(0) complex trans-[RhCl(N=C-
H2)2(Pr(Pr3)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 acetoxy ligand is replaced, treatment of 9 with pyridine leads to the formation of N2 and the ketazine
Ph2C=O-N=N-Ph2 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 PCHCH2 protons in the 1H NMR spectrum and of a sharp doublet with a 1P–Rh coupling constant of 126.7 Hz in the
31P 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
[Rh(PNP)(HNR2)]PF6 [PNP = 2-NC6H4(CH3)2PPh2] which are formed upon treatment of the ethene derivative
[Rh(PNP)(CH2)2H]PF6 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
C2H4 and Ph2CN2, both diazoolkane 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 C2H4 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 C2H4 and free Ph2CN2, 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 diphenyldiazooantherumhodium(0) 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 (X = Cl, Br, I, N3) in ether to afford the neutral
diazoolkane complexes 11–14 in good to excellent yield (Scheme 6). Similarly to the chloro derivative 11, which was previously prepared from [RhCl(Pr(Pr3)2)], or trans-[RhCl-
(C4H9)2(Pr(Pr3)2)] and Ph3CN2,[1,2] the related compounds 12–
14 are also dark green solids which are quite stable and
neither on heating nor photolysis eliminate N2 to give trans-
[RhX(=CPh2)(Pr(Pr3)2)].[19] Characteristic spectroscopic features of 12–14 are the N–N stretching frequency for the diphenyldiazooantherum-
ligand at 1940–1955 cm–1 in the IR and the singlet resonance for the Ph3CN2 carbon atom at δ = 78.3–79.4 in the 13C NMR spectrum. For 14, the ν(N3) band appears at 2038 cm–1.

The catalytic activity of the neutral compounds 11–14 in the reaction of C2H4 and Ph3CN2 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 Cl > Br > I > N3. A more note-
worthy 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 diphenyldiazooantherum in the presence of 11 as the catalyst almost exclusively the trisubstituted olefin 5b is formed, the analogous reaction of
C2H4 and Ph3CN2 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(0) 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 styrane were used without purification. Pr(Pr3)2 was a commercial product from Strem Chemicals. The complexes [RhCl(C2H4)2], [1] cis-
[Rh(acetone)(C2H4)2]PF6, [2] and cis-[Rh(acetone)(C2H4)2]PF6 [4] 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,
trans-[RhCl(η4=Cp2)2(CO)(PR3)] (10): 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 NaCN (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 × 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.24,25

trans-[RhBr(η4=Cp2)2(CO)(PR3)] (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): ν = 1943 (N=N cm⁻¹); 1H NMR (200 MHz, [D6]benzene): δ = 7.41 (m, 4H; ortho H of C6H4), 7.19 (m, 4H; meta H of C6H4), 6.98 (m, 2H; para H of C6H4), 2.24 (m, 6H; 4,4'-methylenediphenoxy-2,2'-propane, 2.72 (d, J = 13.2 Hz, 2H); 3.27 (d, J = 6.9 Hz, 3H; PCH3); 31P NMR (50.3 MHz, [D6]benzene): δ = 128.9, 128.3, 125.4, 124.5 (all s, CH3); 79.1 (s, CN), 24.1 (t, J = 18.5 Hz; PCH3), 20.1 (s; PCH3); 31P NMR (81.0 MHz, [D6]benzene): δ = 40.9 (d, J = 119.1 Hz); elemental analysis (%) for C32H33BrN2P2Rh (975.1): Calculated: C 54.79, H 7.51, N 4.02; found: C 54.38, H 7.67, N 4.08.

trans-[RhCl(η4=Cp2)2(CO)(PR3)] (13): This was prepared as described for 11, using 8 (66 mg, 0.08 mmol) and NaCl (120 mg, 0.80 mmol) as starting materials. Dark green solid: yield = 43 mg, 87%; m.p. 48 °C (decomp). IR (CHCl3): ν = 2032 (N=N cm⁻¹); 1H NMR (200 MHz, [D6]benzene): δ = 7.39 (m, 4H; ortho H of C6H4), 7.17 (m, 4H; meta H of C6H4), 6.90 (m, 2H; para H of C6H4), 2.52 (m, 6H; 4,4'-methylenediphenoxy-2,2'-propane, 2.72 (d, J = 13.2 Hz, 2H); 3.17 (d, J = 6.9 Hz, 3H; PCH3); 31P NMR (50.3 MHz, [D6]benzene): δ = 129.0, 128.3, 125.4, 124.7 (all s, CH3); 79.4 (s, CN), 25.2 (t, J = 18.8 Hz; PCH3), 20.4 (s; PCH3); 31P NMR (81.0 MHz, [D6]benzene): δ = 40.8 (d, J = 116.2 Hz); elemental analysis (%) for C32H33BrN2P2Rh (744.5): calculated: C 50.01, H 7.04, N 3.76; found: C 49.30, H 6.78, N 4.10.

trans-[RhCl(η4=Cp2)2(CO)(PR3)] (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): ν = 2038 (N=N cm⁻¹); 1H NMR (200 MHz, [D6]benzene): δ = 7.39 (m, 4H; ortho H of C6H4), 7.17 (m, 4H; meta H of C6H4), 6.90 (m, 2H; para H of C6H4), 2.52 (m, 6H; 4,4'-methylenediphenoxy-2,2'-propane, 2.72 (d, J = 13.2 Hz, 2H); 3.17 (d, J = 6.9 Hz, 3H; PCH3); 31P NMR (50.3 MHz, [D6]benzene): δ = 129.0, 128.3, 125.4, 124.7 (all s, CH3); 78.3 (s, CN), 24.0 (t, J = 17.6 Hz; PCH3), 19.7 (s; PCH3); 31P NMR (81.0 MHz, [D6]benzene): δ = 44.3 (d, J = 123.5 Hz); elemental analysis (%) for C32H33N2P2Rh (659.7): calculated: C 56.44, H 7.95, N 10.62; found: C 56.21, H 8.07, N 10.06.

Catalytic reactions of Ph2CN and CH2 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) at 40 °C with a 0.1M solution of diphenyldiazomethane in methylethylenechylene/THF (1:4). After adding the substrate, a slow stream of ethene was passed through the solution. The catalytic reaction was finished when the 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 Ph2CN; and separate the catalyst from the reaction products, the mixture was filtered through Al2O3 (neutral, activated grade, III height, column of 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, diphenylecylopropene (5a) and 1,1-diphenylethylene (5b), was determined by integration of characteristic signals in the 1H 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 Ph₂CN and propene with 2 - 4 as catalyst: In an analogous manner to the catalytic reaction of Ph₂CN with ethene by using promoted porphyrinic olefin 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 Ph₂CN 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 diphenylazoniobenzene in methylene chloride/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 Ph₂CN and C₆H₄ 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 methylene chloride (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) in 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 x 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 a ENRAF-Nomius CAD-4F diffracтомeter with monochromated MoKα 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 using the program DIRDIF.[24] All structures were refined by full matrix least-squares procedures on F² with SHELX93.[25] The asymmetric unit of 2 contains four formula units, each consisting of two moieties: a cationic rhodium complex and a P₂E₄ counterion. For a 2 weak hydrogen bonding between the methyl groups of the coordinated acryne and fluor atoms of the P₂E₄ 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 sp² hybridization at the C atom as appropriate with Uiso = 1.5 x Ueq 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 P₂E₄ ion in 8 is rotational disordered over the F(1)-(F(3)·F(2)) axis. The site occupancy factor of the major component was refined to a value of 0.69(2).

Acknowledgement

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Table 1. Crystal structure data for 2 and 8.

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<th>Compound</th>
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<tr>
<td>formula</td>
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<td>C₆H₄F₄N₄OP,Rh</td>
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<tr>
<td>M_r</td>
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<td>T [K]</td>
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<td>0.78 - 0.65</td>
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</table>

[a] R₁ = Σ||F₁| - |F₂||/Σ|F₁|. [b] wR₂ = Σ[w(F²₁ - F²₂)]/Σ[w(F²₁)] [c] w₁ = [w(F²₁) + (g₁ + 1)P²]/2 [d] P = (F₂ + 2F₁)/3. [e] The asymmetric unit consists of four independent molecules 2a - d. In this table the formula and M_r represent one molecule only.

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[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).

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