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Acetylacetonato, pentachlorophenolato and carboxylato rhodium(I) complexes and their reactivity in the C–C coupling reaction of olefins and diazoalkanes

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Dedicated to Professor Malcolm Green, in honour of his numerous inspiring contributions to Organometallic Chemistry

Abstract

The acetylacetonato complexes [Rh(κ^2-O-O)(C_2H_4)(P*i*Pr$_3$)] (O-O = acac **5**, acac-f$_3$ **6**, acac-f$_6$ **7**) and [Rh(κ^2-O-O)(P*i*Pr$_3$)$_2$] (O-O = acac **10**, acac-f$_6$ **11**) were prepared from either [Rh(κ^2-O-O)(C_2H_4)$_2$] (**2–4**), [Rh(η^3-C_3H_5)(P*i*Pr$_3$)$_2$] (**8**) or [RhCl(P*i*Pr$_3$)$_2$]$_2$ (**9**) as the starting materials. While attempts to obtain the diazoalkane derivatives [Rh(κ^2-O-O)(N_2CR_2)(P*i*Pr$_3$)] (R = Ph, *p*-Tol) failed, treatment of **5–7** with $N_2CC_4Cl_4$ gave the corresponding substitution products [Rh(κ^2-O-O)($N_2CC_4Cl_4$)(P*i*Pr$_3$)] (**12–14**) in good yields. The reaction of **8** with C_6Cl_5OH afforded the square-planar complex [Rh(κ^2-OC_6Cl_5)(P*i*Pr$_3$)$_2$] (**15**), in which the pentachlorophenolato ligand is coordinated in a chelating fashion. From **15** and C_2H_4, O_2 and N_2CPh_2 the 1:1 adducts *trans*-[Rh(κ^1-OC_6Cl_5)(L)(P*i*Pr$_3$)$_2$] (**16–18**) were prepared. Compound **15** catalyzes the reaction of ethene with diaryldiazomethanes to give, instead of 1,1-diarylcyclopropanes, the isomeric olefins $R_2C{=}CHCH_3$ (R = C_6H_5 **1b**, *p*-C_6H_4Me **19**, *p*-C_6H_4Cl **20**) as the main products. The carboxylato complexes [Rh(κ^2-O_2CMe)(P*i*Pr$_3$)$_2$] (**21**) and [Rh(κ^2-O_2CCF_3)(P*i*Pr$_3$)$_2$] (**25**) react with N_2CRR' (R = R′ = C_4Cl_4; R = R′ = Ph; R = H, Ph, R′ = C(O)Ph) by opening the chelate bond to give the four-coordinate 1:1 adducts *trans*-[Rh(κ^1-O_2CMe)(N_2CRR')(P*i*Pr$_3$)$_2$] (**22–24**) and *trans*-[Rh(κ^1-O_2CCF_3)(N_2CRR')(P*i*Pr$_3$)$_2$](**26–28**), respectively. Treatment of **25** with $PhCHN_2$ produced the dinitrogen complex *trans*-[Rh(κ^1-O_2CCF_3)(N_2)(P*i*Pr$_3$)$_2$] (**29**). In contrast to the trifluoracetato compound **25**, which catalyzes the reaction of ethene and diaryldiazomethanes N_2CRR' to give mainly the trisubstituted olefins $R'RC{=}CHCH_3$, the corresponding reaction of C_2H_4 and N_2CRR' with acetato complex **21** as the catalyst affords the isomeric ethene derivatives $CH_2{=}CHCHRR'$ as the major products. A mechanism for this unexpected C–C coupling reaction is discussed.

Keywords: Rhodium; Acetylacetonato complexes; Pentachlorophenolato complexes; Carboxylato complexes; Diazoalkane complexes; C–C coupling reactions

1. Introduction

In the context of our studies on the preparation and reactivity of carbenerhodium(I) complexes of the general composition *trans*-[RhCl(=CRR′)(L)$_2$] with L = PR_3, AsR_3 and SbR_3 [1], we observed that upon treatment of [RhCl(C_2H_4)$_2$]$_2$, [Rh(κ^2-acac-f$_6$)(C_2H_4)$_2$] or [RhCl-(P*i*Pr$_3$)$_2$]$_2$ with an excess of ethene and diphenyldiazomethane a catalytic reaction occurred and the trisubstituted olefin 1,1-diphenylpropene (**1b**) was generated as the dominating product [2,3]. The formation of this olefin can be considered, in a formal sense, as the coupling of two carbene fragments :CPh_2 and :CHMe, of which the

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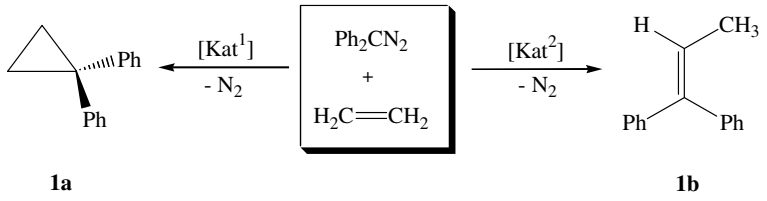


1a **1b**

[Kat^1] : [$Rh_2(O_2CCH_3)_4$], [$Rh_6(CO)_{16}$], [Rh(κ^2-acac)$(C_2H_4)_2$]

[Kat^2] : [$RhCl(C_2H_4)_2]_2$, [$RhCl(PiPr_3)_2]_2$, [Rh(κ^2-acac-f_6)$(C_2H_4)_2$]

Scheme 1.

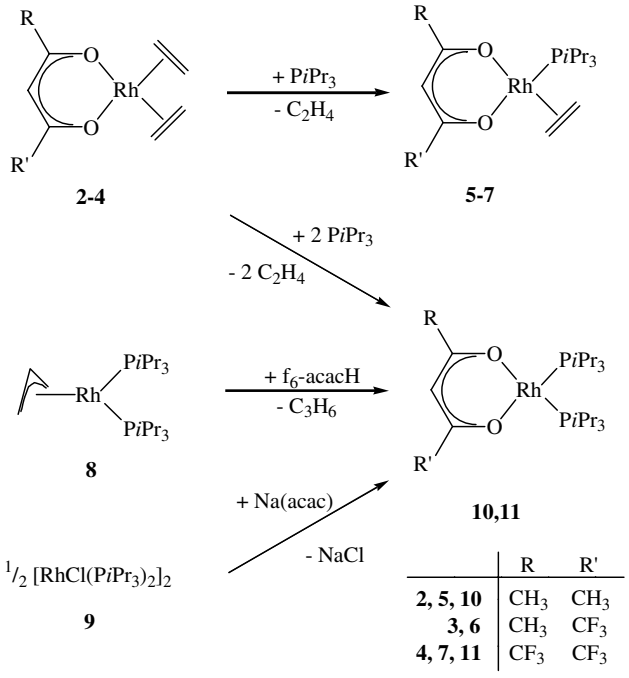
latter derives from the isomeric ethene. Besides **1b**, only traces of the isomeric disubstituted cyclopropane **1a** could be detected which was surprising insofar as it was well known that dinuclear bis(carboxylato)rhodium(II) compounds such as $[Rh_2(O_2CMe)_4]$ and derivatives thereof [4], some carbonylrhodium(0) clusters [5] and the chelated rhodium(I) complex [Rh(κ^2-acac)$(C_2H_4)_2$] [6] are effective catalysts for the synthesis of cyclopropanes from olefins and diazoalkanes (Scheme 1).

By taking the difference in reactivity of [Rh(κ^2-acac)$(C_2H_4)_2$] on one hand and of $[RhCl(C_2H_4)_2]_2$ and [Rh(κ^2-acac-f_6)$(C_2H_4)_2$] on the other into consideration, it became quite obvious that the anionic ligand of the corresponding rhodium complex has a significant influence on the course of the reaction of ethene and diphenyldiazomethane. Therefore, we set out to prepare some relatives of the above-mentioned chelated rhodium(I) compounds and to study their reactivity, in particular the directing role of the ligands in the C–C coupling reaction. For comparison, we also included in our investigations the mononuclear carboxylato derivatives [Rh(κ^2-O_2CR)$(PiPr_3)_2$] (R = CH_3, CF_3, *p*-C_6H_4OMe, *p*-$C_6H_4NO_2$), the preparation of which was recently reported by our group [7]. Some preliminary results of the present work have already been communicated [8].

2. Results and discussion

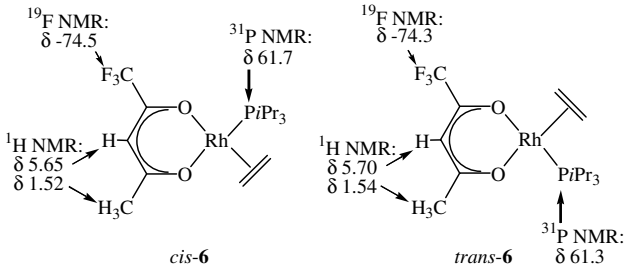
The synthetic routes leading to the mono(phosphine) and bis(phosphine) acetylacetonato complexes **5**–**7** and **10**, **11** are outlined in Scheme 2. The preparation of **5** and **7** by ligand exchange from **2** and **4** with an equimolar amount of $PiPr_3$ has previously been described and the spectroscopic data have been reported [9]. Compound **6** with acac-f_3 as an unsymmetrical chelating ligand, was isolated as a mixture of two isomers showing slightly different NMR signals (see Scheme 3). Since the isomers are formed in a ratio of *cis*-**6**:*trans*-**6** = 15:1, the corresponding signals can be easily assigned. The bis(phosphine) compound **11** was initially prepared from **4** and two equivalents of $PiPr_3$ in a modest yield [9]. The preferred pathway is the reaction of **8** with hexafluoroacetylacetone, which gives **11** in 76% yield by elimination of propene.

Quite surprisingly, the acac complex **10** is not accessible either from **2** and excess $PiPr_3$ or from **8** and acacH. However, it can be obtained by salt metathesis



	R	R'
2, 5, 10	CH_3	CH_3
3, 6	CH_3	CF_3
4, 7, 11	CF_3	CF_3

Scheme 2.



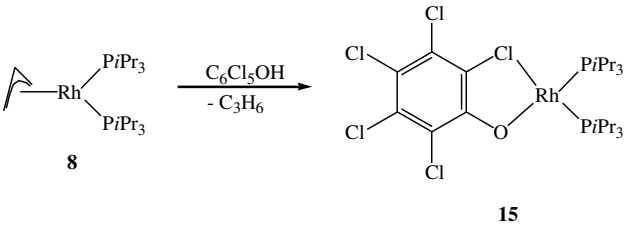
Scheme 3.

from **9** and Na(acac) in a slurry of diethylether. Both **10** and **11** are moderately air-sensitive solids, which are readily soluble in aromatic and chlorinated solvents but almost insoluble in pentane and diethylether. The IR as well as the ^{1}H and ^{13}C NMR data of **10** are similar to those of the bis(tricyclohexylphosphine) compound $[Rh(\kappa^2\text{-acac})(PCy_3)_2]$, the molecular structure of which was determined by X-ray crystallography [10].

While the ethene ligand in the chlororhodium(I) complex *trans*-$[RhCl(C_2H_4)(PiPr_3)_2]$ can be smoothly displaced by diphenyldiazomethane [2], attempts to substitute the olefin in compounds **5**–**7** by N_2CPh_2 failed. Although the formation of a 2:3 mixture of **1a** and **1b** could be detected by GC–MS, the composition of the organometallic product remained obscure.

However, the starting materials **5**–**7** react with $N_2CC_4Cl_4$ in pentane at low temperatures to afford the diazocyclopentadiene complexes **12**–**14** in 58–79% yields (Scheme 4). The greenish air-stable solids were characterized by elemental analysis and mass spectra. Even if they were stored in solution at 20 °C for several days, no conversion to a corresponding carbene derivative occurred by elimination of N_2. The IR spectra of **12**–**14** display the N–N stretching mode at around 1950 cm^{-1}, which is shifted by ca. 150 cm^{-1} to lower frequency compared with uncoordinated $N_2CC_4Cl_4$. Since the signals for the N_2C carbon atom appear in the ^{13}C NMR spectra of **12**–**14** at about the same chemical shift as that of *trans*-$[RhCl(N_2CC_4Cl_4)(SbiPr_3)_2]$ (which was characterized crystallographically) [11], we assume that the $N_2CC_4Cl_4$ ligands in **12**–**14** are bonded end-on to the metal center. In the presence of ethene, compounds **12**–**14** are inert and even upon heating do not undergo a C–C coupling reaction.

The preferred preparative route to obtain the pentachlorophenolato complex **15** is similar to that used for the related compound **11**. Treatment of **8** with an equimolar amount of C_6Cl_5OH in toluene gave **15** (Scheme 5) as a red microcrystalline solid, which is exceedingly air-sensitive and slowly decomposes in solution. The ^{1}H NMR spectrum of **15** shows at room temperature a single resonance for the methyl protons of the isopropyl groups indicating that under these conditions the two



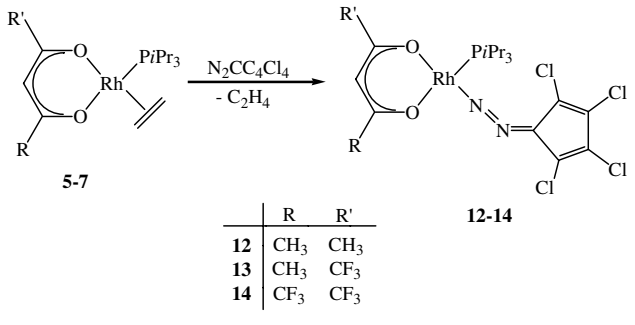
8 **15**

Scheme 5.

$PiPr_3$ ligands are equivalent on the NMR timescale. Accordingly, the ^{31}P NMR spectrum of **15** displays at 295 K one doublet at δ 61.2, which at 213 K splits into two doublets of doublets at δ 60.4 and 59.2. On the basis of these observations, we assume that at room temperature compound **15** is fluxional in solution and that the two identical chelates are transformed into each other via a three-coordinate species as an intermediate (Scheme 6). From the coalescence temperature (228 K in toluene-d_8) and the difference in the chemical shift of the two signals at 213 K in the ^{31}P NMR spectrum, a $\Delta G^{\neq}$ value of 37 kJ/mol can be calculated. We note that the chelating capability of the pentachlorophenolate anion is not unexpected and has also been illustrated in gold(I) [12,13] as well as in ruthenium(II) and osmium(II) chemistry [14].

In agreement with the rather weak interaction between Rh and Cl, compound **15** reacts readily at room temperature with ethene in pentane to give the non-chelate complex **16** in good yield (Scheme 7). The olefinic ligand is only weakly coordinated and thus, during attempts to dry **16** in vacuo, the starting material **15** was regenerated. Under argon at 295 K, or in solution at 223 K in the presence of excess ethene, **16** can be stored without decomposition. The ^{31}P NMR spectrum of **16** in toluene-d_8 shows at 223 K a doublet resonance with a ^{31}P–^{103}Rh coupling constant of 125.0 Hz, which is typical for a *trans*-disposed $PiPr_3$–Rh–$PiPr_3$ moiety [11,15].

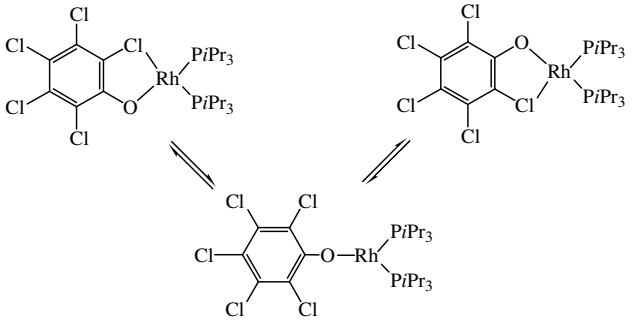
More readily than with ethene, compound **15** reacts with O_2 in pentane to form the 1:1 adduct **17**. The brownish compound, the composition of which has been substantiated by elemental analysis, is moderately air-sensitive and decomposes slowly both in solution and



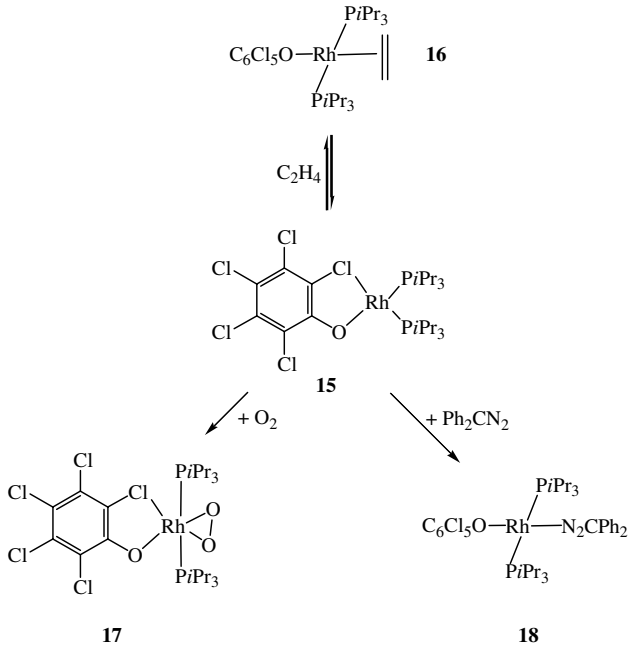
5-7 **12-14**

	R	R'
12	CH_3	CH_3
13	CH_3	CF_3
14	CF_3	CF_3

Scheme 4.



Scheme 6. Dynamics of compound **15** in solution.



Scheme 7.

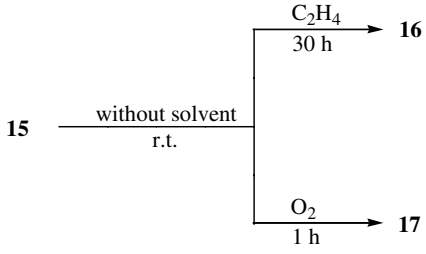
as a solid. Among the decomposition products, $OPiPr_3$ could be detected. The increased reactivity of **15** towards O_2 compared with C_2H_4 is illustrated by the fact that the solid–gas reaction with oxygen to give **17** is finished after 1 h at room temperature whereas the analogous reaction with ethene to afford **16** takes 30 h under the same conditions (Scheme 8). In either case, the product is formed in quantitative yield.

Treatment of **15** with diphenyldiazomethane also leads to partial opening of the chelate bond and to the formation of compound **18** (see Scheme 7). Similarly to the chlororhodium(I) derivative *trans*-[RhCl(N_2CPh_2)($PiPr_3$)$_2$], the phenolato complex **18** is a green air-sensitive solid that has been characterized by elemental analysis and spectroscopic techniques. With respect to the bonding mode, the position of the N–N stretching vibration at 2024 cm^{-1} in the IR spectrum suggests an end-on coordination of the N_2CPh_2 unit [16]. In the ^{13}C NMR spectrum, the resonance for the N_2C carbon atom appears at δ 87.1 as a broad singlet, the broadening probably being due to the quadrupole moment of the nitrogen atoms. The ^1H NMR spectrum of **18** displays one doublet of virtual triplets for the PCHCH_3 protons, which indicates that the two phosphine ligands are in a *trans* disposition [15,17].

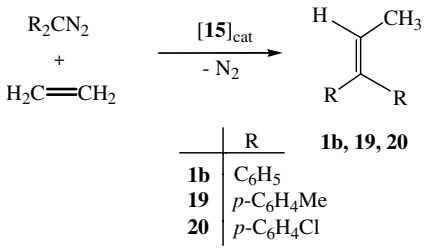
Although the diazoalkane complex **18** reacts with a saturated solution of ethene in benzene at 40 °C rather slowly to give the olefin **1b**, the precursor **15** catalyzes not only the reaction of C_2H_4 with N_2CPh_2 but also that of ethene with $N_2C(C_6H_4Me\text{-}p)_2$ and $N_2C(C_6H_4Cl\text{-}p)$, respectively (Scheme 9). By monitoring the corresponding reactions by NMR, the exclusive formation of the C–C coupling products **1b**, **19** and **20** has been observed. The turnover number (TON) is ca. 10 and thus is much lower than with [RhCl($PiPr_3$)$_2$]$_2$ or [RhCl(C_2H_4)$_2$]$_2$ as the catalyst [2,3].

To compare the reactivity of **15** with that of the related bis(triisopropylphosphine) analogues [Rh(κ^2-O_2CR)($PiPr_3$)$_2$], the reactions of the previously prepared carboxylato complexes **21** and **25** with various diazoalkanes have been investigated. The results are summarized in Schemes 10 and 11. While the acetato complex **21** reacts with $N_2CC_4Cl_4$ almost instantaneously to give the 1:1 adduct **22** in nearly quantitative yield, the corresponding reactions of **21** with N_2CPh_2 and $N_2C(Ph)C(O)Ph$ lead to equilibria between the starting material and compounds **23**, **24** which could not be completely shifted to the side of the products. Since attempts to separate **21** from **23** or **24** by fractional crystallization or column chromatography failed, the diazoalkane complexes **23** and **24** could only be characterized by IR and NMR spectroscopy. In contrast, the diazocyclopentadiene derivative **22** was isolated as a pale-green solid for which a correct elemental analysis was obtained. The spectroscopic data of **22**–**24** are in agreement with a square-planar arrangement of the four monodentate ligands around the rhodium(I) center and deserve no further comments.

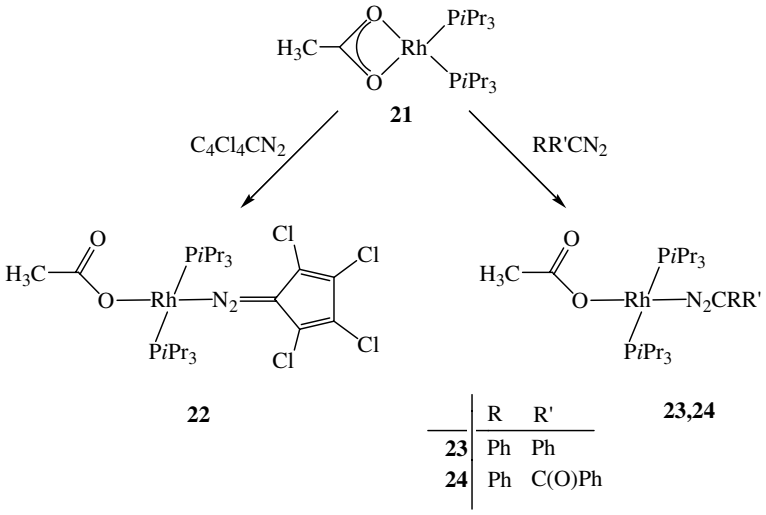
The trifluoracetato compound **25** is significantly more reactive toward diazoalkanes than the counterpart **21** and upon treatment with N_2CPh_2, $N_2CC_4Cl_4$ and $N_2CHC(O)Ph$ in pentane affords the expected 1:1 adducts **26**–**28** in good to excellent yields (Scheme 11). The IR spectra of the green (**26**, **27**) or yellow (**28**) solids display a band for the asymmetric OCO stretching mode



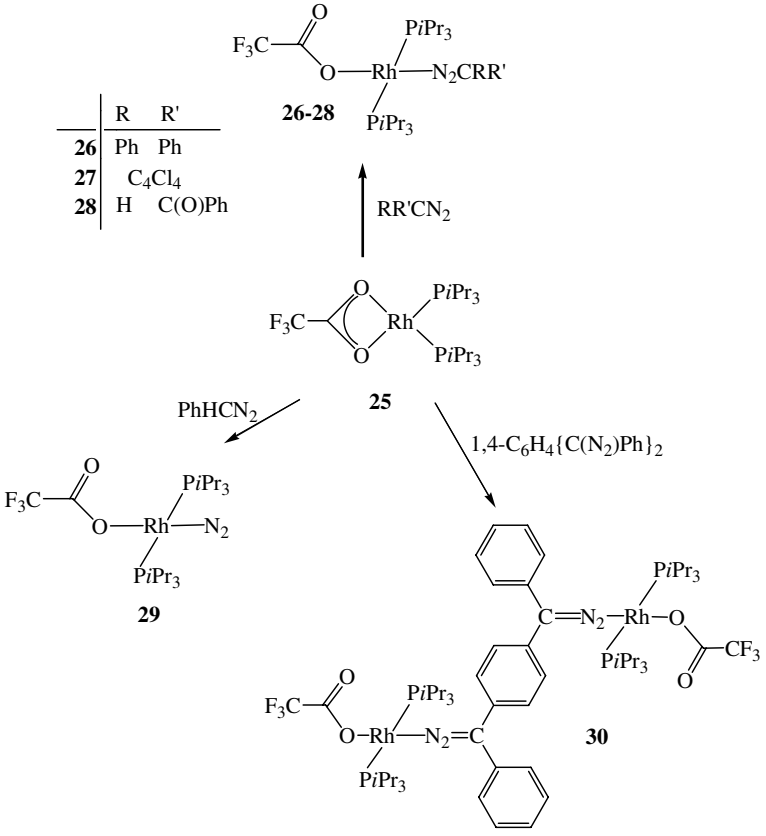
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

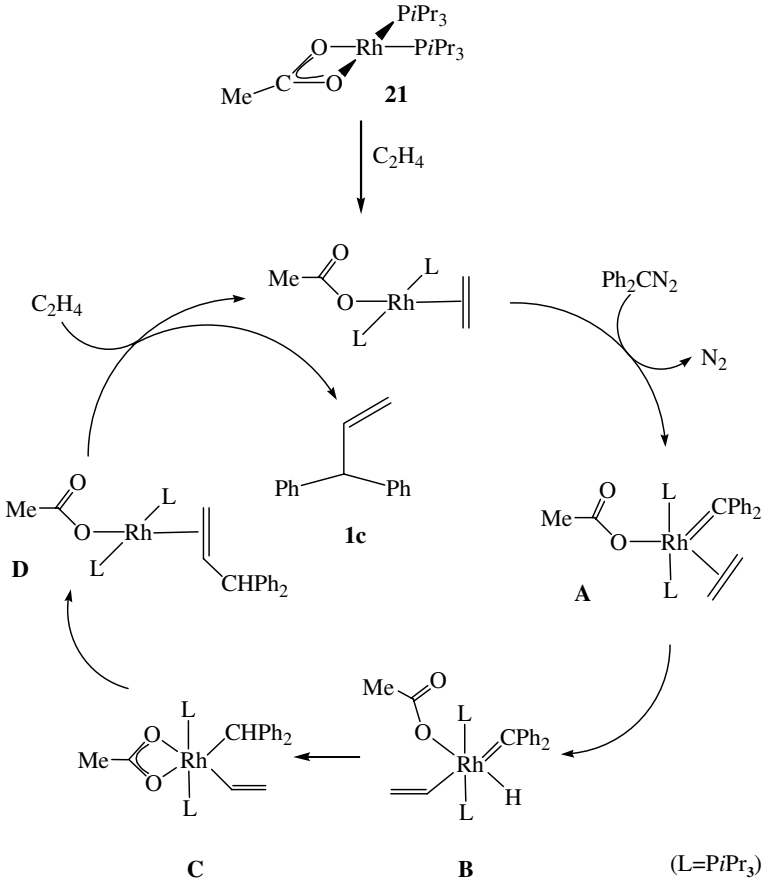
at around 1640–1700 cm^{-1}, which is consistent with the monodentate coordination of the trifluoracetato ligand [18]. The bis(diazoalkane) derivative 1,4-C_6H_4-$\{C(N_2)Ph\}_2$ behaves similarly to N_2CPh_2 and reacts with the starting material **25** in diethylether to give the dinuclear complex **30**. The ^{31}P NMR spectrum of **30** shows a doublet at δ 41.9, the chemical shift and the ^{31}P–^{103}Rh coupling constant of which are nearly identical to those of the corresponding signal for **26**.

In contrast to N_2CPh_2, phenyldiazomethane reacts with **25** in pentane to give, instead of *trans*-[Rh(κ^1-O_2CCF_3)(N_2CHPh)($PiPr_3$)$_2$], the dinitrogen complex **29** in 59% yield. Thus, the trifluoracetato compound behaves similarly to [RhCl($PiPr_3$)$_2$]$_2$ which upon treatment

Table 1
Data on the catalytic activity and composition of the product in the reaction of ethene and diaryldiazomethanes N_2CRR' (for details see Section 3)

Catalyst	TON[a]	R,R′	Product[b]
21	10	Ph_2	$CH_2{=}CHCHPh_2$ (**1c**)
21	13	Ph,*p*-C_6H_4Me	$CH_2{=}CHC(Ph)C_6H_4Me$-*p* (**31**)
21	11	Ph,*o*-C_6H_4Me	$CH_2{=}CHC(Ph)C_6H_4Me$-*o* (**32**)
21	10	(*p*-$C_6H_4Me)_2$	$CH_2{=}CHCH(C_6H_4Me$-*p*$)_2$ (**33**)
21	6	(*p*-$C_6H_4OMe)_2$	$CH_2{=}CHCH(C_6H_4OMe$-*p*$)_2$ (**34**)
21	7	(*p*-$C_6H_4Cl)_2$	$CH_2{=}CHCH(C_6H_4Cl$-*p*$)_2$ (**35**)
25	33	Ph_2	$CH_3CH{=}CPh_2$ (**1b**)
25	18	(*p*-$C_6H_4Me)_2$	$CH_3CH{=}C(C_6H_4Me$-*p*$)_2$ (**19**)
25	12	(*p*-$C_6H_4Cl)_2$	$CH_3CH{=}C(C_6H_4Cl$-*p*$)_2$ (**20**)

[a] TON = turnover number = mol product/mol catalyst.
[b] Dominating product, relative amount >94%.



Scheme 12.

with N_2CHPh affords *trans*-[RhCl(N_2)(P*i*Pr$_3$)$_2$] [19,20]. Diagnostic for the coordination of the N_2 ligand in **29** is the $\nu(N_2)$ stretch at 2098 cm^{-1} in the IR spectrum, which is shifted by ca. 160 cm^{-1} to higher frequency compared with the N_2CPh_2 derivative **26**. In solution, compound **29** is less stable than the counterparts **26** and **28** and decomposes slowly to give **25** as the dominating species.

Both the acetato and the trifluoracetato complexes **21** and **25** are also catalysts for the C–C coupling reaction of ethene and diaryldiazomethanes. However, while the catalytic activity is comparable to that of the pentachlorophenolato analogue **15** (see Scheme 9), the substituent of the carboxylato unit has a significant influence on the composition of the coupling product. With **25** as the catalyst, the reaction of C_2H_4 with $N_2C(C_6H_4X)_2$ (X = H, *p*-Me, *p*-Cl) leads almost exclusively to the formation of the trisubstituted olefins **1b**, **19** and **20** with turnover numbers (in toluene at 40 °C) of 33 (X = H), 18 (X = *p*-Me) and 12 (X = *p*-Cl), respectively. At the beginning

of the catalytic processes, the formation of the diazoalkane complexes *trans*-[Rh(κ^1-O_2CCF_3)(N_2CR_2)(P*i*Pr$_3$)$_2$] could be detected by ^{1}H and ^{31}P NMR spectroscopy.

With catalytic amounts of the acetate **21**, the reaction of ethene and diaryldiazomethanes N_2CRR' takes a different course. In this case, the coupling product is neither the disubstituted cyclopropane nor the trisubstituted olefin $CH_3CH{=}CRR'$ but, quite remarkably, the isomeric monosubstituted ethene derivative $CH_2{=}CHCHRR'$. Thus, formally an insertion of the carbene :CRR′ into one of the C—H bonds of ethene occurs. The TON values lie between 6 and 13 (see Table 1) and depend only slightly on the substituents R and R′. If instead of ethene, propene is treated with N_2CPh_2 in the presence of **21** as the catalyst, no reaction occurs under the same conditions. The coupling products $CH_2{=}CHCHRR'$, of which as far as we know those with R = Ph, R′ = *o*-C_6H_4Me, *p*-C_6H_4Me and R = R′ = *p*-C_6H_4(OMe), *p*-C_6H_4Cl have not been described in the literature, were characterized by GC–MS and ^{1}H NMR spectroscopy.

The mechanism of the reaction of ethene and diaryldiazomethanes with **21** as the catalyst to give predominantly the monosubstituted ethene derivative is not clear as yet. As shown in Scheme 12 with N_2CPh_2 as the substrate, we assume that in the initial step, in the presence of a large excess of ethene, the intermediate *trans*-[Rh(κ^1-O_2CCH_3)(C_2H_4)(P*i*Pr$_3$)$_2$] is formed and reacts with diphenyldiazomethane to generate the five-coordinate carbene(olefin) compound **A**. While we have postulated that on this stage, for chloride instead of acetate as the anionic ligand, ring closure occurs to give a metallacyclobutane, alternatively an intramolecular C—H activation could take place to afford the six-coordinate intermediate **B**. Migration of the hydride ligand from the metal to the carbene moiety with concomitant formation of a chelate ring would then give the alkyl(vinyl)rhodium(III) derivative **C**, that rearranges via intramolecular C–C coupling to generate **D**. With excess C_2H_4, the olefinic ligand of **D** could be replaced to produce **1c** (the isomer of **1a** and **1b**) and the ethene compound *trans*-[Rh(κ^1-O_2CCH_3)(C_2H_4)(P*i*Pr$_3$)$_2$], which can start a new catalytic cycle. To explain the rather low TON value for **1c** and the analogous C–C coupling products, we assume that in the course of the reaction either the initially formed ethene complex or one of the postulated intermediates decomposes to give free P*i*Pr$_3$ which reacts with the diazoalkane to form the corresponding phosphorus yield. With regard to the C—H activation step from **A** to **B**, it is worth mentioning that we recently observed, in the presence of L (pyridine or P*i*Pr$_3$), the formation of the hydrido(vinyl)iridium(III) complexes [IrH($CH{=}CH_2$)(κ^2-acac)(L)(P*i*Pr$_3$)] from the etheneiridium(I) precursor [Ir(κ^2-acac)(C_2H_4)(P*i*Pr$_3$)] under either photochemical or thermal conditions [21]. Moreover, in a control experiment we found that upon irradiation of a solution of **21** in C_6D_6, saturated with ethene, a hydridorhodium(III) intermediate is generated that displays in the ^{1}H NMR spectrum a high-field resonance at δ – 20.6, i.e., at a similar chemical shift as for [RhH(κ^1-O_2CCF_3)(κ^2-O_2CCF_3)(P*i*Pr$_3$)$_2$] (δ – 19.0) [22].

In summarizing, the present work extended the series of chelate rhodium(I) complexes with Rh(P*i*Pr$_3$)$_2$ as the core unit. These complexes not only react with ethene but also with diazoalkanes, in particular with N_2CPh_2 and $N_2CC_4Cl_4$, by opening of the chelate bond and formation of four-coordinate rhodium(I) derivatives with the two phosphine ligands in a *trans* disposition. In the presence of excess C_2H_4, compounds such as **15**, **21** and **25** catalyze the reaction of ethene and diaryldiazomethanes N_2CRR' to give, instead of the anticipated 1,1-disubstituted cyclopropane, either $CH_3CH{=}CRR'$ or the isomer $CH_2{=}CHCHRR'$ as the main product. The postulated mechanism for the formation of the terminal olefin, with the acetato complex **21** as the catalyst, involves a stepwise opening and closing of the chelating Rh(κ^2-O_2CCH_3) bond that allows the metal to maintain the preferred coordination number of four for rhodium(I) and six for rhodium(III). The question whether instead of compounds such as **15** and **25** the isolated carbene complexes *trans*-[Rh(OPh)($=CPh_2$)(P*i*Pr$_3$)$_2$] [16] and *trans*-[Rh(κ^1-O_2CCF_3)($=CPh_2$)(P*i*Pr$_3$)$_2$] [23] equally catalyze the reaction of ethene with diphenyldiazomethane to give either **1a**, **1b** or **1c** is currently being investigated in our laboratory.

3. Experimental

3.1. General considerations

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were purified and degassed by standard procedures. The starting materials **2**–**4** [24], **8** [7], **9** [25], **21** and **25** [7] were prepared as described in the literature. P*i*Pr$_3$ was a commercial product from Strem. IR spectra were recorded on a Perkin–Elmer 1420 infrared spectrometer and NMR spectra were recorded (if not otherwise mentioned) at room temperature (r.t.) on Bruker WH 90, Bruker AC 200 and Bruker AMX 400 instruments. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened signal; vt, virtual triplet; $N = {}^3J(PH) + {}^5J(PH)$ or $^1J(PC) + {}^3J(PC)$. Melting points were determined by Differential Thermal Analysis (DTA). The mass spectra were measured on a Finnigan 90 MAT instrument.

3.2. Preparation of [Rh(κ^2-acac)(C_2H_4)(P*i*Pr$_3$)] (5)

A solution of **2** (60 mg, 0.23 mmol) in 4 ml of pentane was treated with P*i*Pr$_3$ (42 μl, 0.23 mmol) and stirred for

15 min at r.t. The solvent was evaporated in vacuo and the orange residue was recrystallized from 1 ml of acetone at −78 °C: yield 70 mg (81%). The product was characterized spectroscopically by comparison with reference data [9].

3.3. Preparation of [Rh(κ²-acac-f_3)(C_2H_4)($PiPr_3$)] (*cis*- and *trans*-**6**)

This compound was prepared as described for **5**, with 100 mg (0.32 mmol) of **3** and 62 μl (0.32 mmol) of P*i*Pr_3 as starting materials. Orange solid, yield 130 mg (91%), m.p. 86 °C. *Anal*. Calc. for $C_{16}H_{29}F_3O_2PRh$: C, 43.23; H, 6.58. Found: C, 42.89; H, 6.71%. Spectroscopic data for *cis*-**6**: ^{1}H NMR (C_6D_6, 200 MHz): δ 5.65 [s, 1H, CHC(O)], 3.34, 2.76 (both br s, 4H, CH_2), 1.77 (m, 3H, PC*H* CH_3), 1.52 [s, 3H, $CH_3C(O)$], 1.08 [dd, ^3J(PH) = 13.0, ^3J(HH) = 7.2, 18H, PCHC*H*$_3$]. ^{19}F NMR (C_6D_6, 188.2 MHz): δ −74.5 (s, CF_3). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 61.7 [d, ^1J(RhP) = 179.8]. Spectroscopic data for *trans*-**6**: ^{1}H NMR (C_6D_6, 200 MHz): δ 5.70 [s, 1H, CHC(O)], 3.34, 2.76 (both br s, 4H, CH_2), 1.77 (m, 3H, PC*H*CH_3), 1.54 [s, 3H, $CH_3C(O)$], 1.08 [dd, ^3J(PH) = 13.0, ^3J(HH) = 7.2, 18H, PCHC*H*$_3$]. ^{19}F NMR (C_6D_6, 188.2 MHz): δ −74.3 (s, CF_3). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 61.3 [d, ^1J(RhP) = 180.9]. Ratio of *cis*-**6**:*trans*-**6** = 15:1.

3.4. Preparation of [Rh(κ²-acac-f_6)(C_2H_4)($PiPr_3$)] (**7**)

This compound was prepared as described for **5**, with 100 mg (0.27 mmol) of **4** and 64 μl (0.33 mmol) of P*i*Pr_3 as starting materials. Orange solid, yield 118 mg (91%). The product was characterized spectroscopically by comparison with reference data [9].

3.5. Preparation of [Rh(κ²-acac)($PiPr_3$)$_2$] (**10**)

A solution of **9** (241 mg, 0.26 mmol) in 10 ml of diethylether was treated with Na(acac) (150 mg, 1.23 mmol) and stirred for 2 h at r.t. After 30 ml of diethylether were added, the suspension was filtered and the filtrate was brought to dryness in vacuo. The residue was dissolved in 3 ml of boiling acetone and the solution was slowly cooled at −78 °C. Yellow crystals precipitated which were separated from the mother liquor and washed twice with small amounts of pentane: yield 192 mg (70%), m.p. 77 °C (dec.). *Anal*. Calc. for $C_{23}H_{49}O_2P_2Rh$: C, 52.85; H, 9.46; Rh, 19.71. Found: C, 52.39; H, 9.12; Rh, 19.36%. MS (70 eV): *m*/*z* 522 (M^+). IR (KBr): *ν*(N_2) 1958, *ν*(CO) 1579, 1510 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 5.35 [s, 1H, CHC(O)], 2.18 (m, 6H, PC*H*CH_3), 1.74 [s, 6H, $CH_3C(O)$], 1.36 [dd, ^3J(PH) = 12.0, ^3J(HH) = 7.3, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 183.3 (s, CO), 99.8 [s, *C*HC(O)], 27.1 [s, *C*$H_3C(O)$], 24.6 (vt, *N* = 19.1 Hz, P*C*HCH_3), 20.7 (s, PCH*C*H_3). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 59.4 [d, ^1J(RhP) = 192.1].

3.6. Preparation of [Rh(κ²-acac-f_6)($PiPr_3$)$_2$] (**11**)

A solution of **8** (74 mg, 0.16 mmol) in 10 ml of diethylether was treated with hexafluoroacetylacetone (23 μl, 0.16 mmol) and stirred for 20 min at r.t. The solvent was evaporated in vacuo and the residue was dissolved in 4 ml of acetone. After the solution was slowly cooled at −78 °C, orange crystals precipitated which were separated from the mother liquor and washed twice with small amounts of pentane: yield 77 mg (76%), m.p. 88 °C (dec.). *Anal*. Calc. for $C_{23}H_{43}F_6O_2P_2Rh$: C, 43.82; H, 6.87; Rh, 16.32. Found: C, 43.55; H, 6.69; Rh, 15.31%. MS (70 eV): *m*/*z* 630 (M^+). IR (hexane): *ν*(CO) 1541, 1508 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.27 [s, 1H, CHC(O)], 2.04 (m, 6H, PC*H*CH_3), 1.22 [dd, ^3J(PH) = 12.8, ^3J(HH) = 7.3, 36H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 170.0 [q, ^2J(FC) = 33.2, CO], 119.8 [q, ^1J(FC) = 280.1, CF_3], 91.8 [s, *C*HC(O)], 24.6 (vt, *N* = 21.1 Hz, P*C*HCH_3), 20.3 (s, PCH*C*H_3). ^{19}F NMR (C_6D_6, 188.2 MHz): δ −75.3 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 55.7 [d, ^1J(RhP) = 191.8].

3.7. Preparation of [Rh(κ²-acac)($N_2CC_4Cl_4$)($PiPr_3$)] (**12**)

A solution of **5** (86 mg, 0.22 mmol) in 15 ml of pentane was treated at −78 °C with $N_2CC_4Cl_4$ (101 mg, 0.44 mmol). After the solution was slowly warmed to 0 °C, it was stirred for 10 min. The solvent was evaporated in vacuo, the greenish residue was washed three times with 10 ml portions of pentane (−78 °C) and dried: yield 87 mg (67%), m.p. 61 °C (dec.). *Anal*. Calc. for $C_{19}H_{28}Cl_4N_2O_2PRh$: C, 38.54; H, 4.77; N, 4.73. Found: C, 38.26; H, 4.75; N, 4.47%. IR (hexane): *ν*(N_2) 1958, *ν*(CO) 1579, 1510 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 5.15 [s, 1H, CHC(O)], 2.55 (m, 3H, PC*H*CH_3), 1.92, 1.54 [both s, 3H each, $CH_3C(O)$], 1.20 [dd, ^3J(PH) = 14.2, ^3J(HH) = 7.2, 18H, PCHC*H*$_3$]. ^{13}C NMR ($C_6D_5CD_3$, 50.3 MHz, 233 K): δ 192.0, 182.5 (both s, CO), 109.8, 104.4 (both s, C_4Cl_4), 101.7 [s, *C*HC(O)], 81.7 (br s, N_2C), 27.9, 26.8 [both s, *C*$H_3C(O)$], 23.9 [d, ^1J(PC) = 24.6 Hz, P*C*HCH_3], 19.7 (s, PCH*C*H_3). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 64.0 [d, ^1J(RhP) = 164.7].

3.8. Preparation of [Rh(κ²-acac-f_3)($N_2CC_4Cl_4$)($PiPr_3$)] (*cis*- and *trans*-**13**)

This compound was prepared as described for **12**, with **6** (42 mg, 0.09 mmol) and $N_2CC_4Cl_4$ (43 mg, 0.19 mmol) in 5 ml of pentane as starting materials. Greenish solid; yield 48 mg (79%), m.p. 61 °C (dec.). *Anal*. Calc. for $C_{19}H_{25}Cl_4F_3N_2O_2PRh$: C, 35.32; H, 3.90; N, 4.34. Found: C, 35.25; H, 3.99; N, 4.19%. IR (diethylether):

$\nu(N_2)$ 1950 cm^{-1}. Spectroscopic data for *cis*-**13**: ^1H NMR ($C_6D_5CD_3$, 200 MHz): δ 5.79 [s, 1H, CHC(O)], 2.12 (m, 3H, PC*H*CH_3), 1.87 [s, 3H, $CH_3C(O)$], 1.15 [dd, $^3J(PH) = 14.2$, $^3J(HH) = 6.9$, 18H, PCHC*H*$_3$]. ^{13}C NMR ($C_6D_5CD_3$, 50.3 MHz, 223 K): δ 197.3 [s, $CH_3C(O)$], 162.8 [q, $^2J(FC) = 33.3$, $CF_3C(O)$], 118.1 [q, $^1J(FC) = 283.1$, CF_3], 110.4, 104.6 (both s, C_4Cl_4), 97.7 [s, *C*HC(O)], 84.6 (br s, N_2C), 28.8 [s, *C*$H_3C(O)$], 23.4 [d, $^1J(PC) = 25.0$ Hz, P*C*HCH$_3$], 19.6 (s, PCH*C*H$_3$). ^{31}P NMR ($C_6D_5CD_3$, 81.0 MHz): δ 66.6 [d, $^1J(RhP) = 164.3$]. Selected spectroscopic data for *trans*-**13**: ^1H NMR ($C_6D_5CD_3$, 200 MHz): δ 5.83 [s, 1H, CHC(O)]. ^{31}P NMR ($C_6D_5CD_3$, 81.0 MHz): δ 65.8 [d, $^1J(RhP) = 165.2$].

3.9. Preparation of [Rh(κ^2-acac-f_6)($N_2CC_4Cl_4$)(*PiPr*$_3$)] (**14**)

This compound was prepared as described for **12**, with **7** (144 mg, 0.29 mmol) and $N_2CC_4Cl_4$ (133 mg, 0.58 mmol) in 15 ml of pentane as starting materials. Greenish solid; yield 118 mg (58%), m.p. 67 °C (dec.). *Anal*. Calc. for $C_{19}H_{22}Cl_4F_6N_2O_2PRh$: C, 32.00; H, 3.17; N, 4.00. Found: C, 31.82; H, 3.06; N, 4.03%. MS (70 eV): *m*/*z* 700 (M^+). IR (KBr): $\nu(N_2)$ 1955 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 6.15 [s, 1H, CHC(O)], 1.77 (m, 3H, PC*H*CH_3), 0.91 [dd, $^3J(PH) = 14.7$, $^3J(HH) = 7.2$, 18H, PCHC*H*$_3$]. ^{13}C NMR ($C_6D_5CD_3$, 100.6 MHz, 223 K): δ 176.5 [q, $^2J(FC) = 35.2$, $CF_3C(O)$], 117.7 [q, $^1J(FC) = 273.6$, CF_3], 111.7, 105.5 (both s, C_4Cl_4), 91.7 [s, *C*HC(O)], 87.6 (br s, N_2C), 23.1 [d, $^1J(PC) = 25.7$, P*C*HCH$_3$], 19.0 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 68.0 [d, $^1J(RhP) = 164.6$].

3.10. Preparation of [Rh(κ^2-OC_6Cl_5)(*PiPr*$_3$)$_2$] (**15**)

A solution of **8** (166 mg, 0.36 mmol) in 10 ml of toluene was treated with a solution of pentachlorophenol (95 mg, 0.36 mmol) in 5 ml of toluene and stirred for 30 min at r.t. The solvent was evaporated in vacuo and the residue was extracted with 20 ml of pentane. The extract was brought to dryness in vacuo and the residue was recrystallized from acetone at −78 °C to give a red microcrystalline solid: yield 179 mg (73%), m.p. 124 °C (dec.). *Anal*. Calc. for $C_{24}H_{42}Cl_5OP_2Rh$: C, 41.85; H, 6.15. Found: C, 42.35; H, 6.80%. ^1H NMR (C_6D_6, 200 MHz): δ 2.02 (m, 6H, PC*H*CH_3), 1.22 [dd, $^3J(PH) = 12.8$, $^3J(HH) = 6.9$, 36 H, PCHC*H*$_3$]. ^{13}C *NMR* (C_6D_6, *50.3 MHz*): δ 161.8 (s, CO), 129.6, 121.9, 114.2 (all s, C_5Cl_5), 26.2 (vt, $N = 20.3$, P*C*HCH$_3$), 20.6 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz, 295 K): δ 61.2 [d, $^1J(RhP) = 203.4$]. ^{31}P NMR ($C_6D_5CD_3$, 162.0 MHz, 213 K): δ 60.4 [dd, $^1J(RhP) = 162.8$, $^2J(PP) = 47.0$, P*i*Pr$_3$ *cis* to Cl], 59.2 [dd, $^1J(Rh\ P) = 114.7$, $^2J(PP) = 47.0$, P*i*Pr$_3$ *trans* to Cl].

3.11. Preparation of trans-[Rh(κ^1-OC_6Cl_5)(C_2H_4)(*PiPr*$_3$)$_2$] (**16**)

A slow stream of ethene was passed for 1 min through a solution of **15** (98 mg, 0.14 mmol) in 5 ml of pentane at r.t. A change of colour from red to yellow occurred. After the solution was cooled at −78 °C, light yellow crystals precipitated which were separated from the mother liquor, washed twice with small amounts of pentane (−78 °C) and dried in a stream of argon: yield 72 mg (71%), m.p. 38 °C (dec.). *Anal*. Calc. for $C_{26}H_{46}Cl_5OP_2Rh$: C, 43.57; H, 6.47. Found: C, 43.46; H, 6.39%. ^1H NMR (C_6D_6, 200 MHz, 295 K): δ 2.34 (br s, 4H, C_2H_4), 1.71 (m, 6H, PC*H*CH_3), 1.07 [d, $^3J(HH) = 7.3$, 36H, PCHC*H*$_3$]. ^1H NMR ($C_6D_5CD_3$, 400 MHz, 223 K): δ 2.50 (br s, 4H, C_2H_4), 2.11 (br s, 6H, PC*H*CH_3), 1.25 (br s, 36H, PCHC*H*$_3$). ^{13}C NMR ($C_6D_5CD_3$, 100.6 MHz, 223 K): δ 160.4 (s, CO), 131.7, 123.2, 114.6 (all s, C_5Cl_5), 23.3 (vt, $N = 15.3$, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$), signal for C_2H_4 not exactly located. ^{31}P NMR ($C_6D_5CD_3$, 162.0 MHz, 223 K): δ 24.9 [d, $^1J(RhP) = 125.0$]. Compound **16** had alternatively been prepared by storing the starting material **15** in a Schlenk tube under an atmosphere of ethene for 30 h at r.t.; the yield was quantitative.

3.12. Preparation of [Rh(κ^2-OC_6Cl_5)(O_2)(*PiPr*$_3$)$_2$] (**17**)

A slow stream of O_2 was passed for 1 min through a solution of **15** (72 mg, 0.10 mmol) in 6 ml of pentane at r.t. The solution was concentrated to ca. 3 ml in vacuo and then stored at −78 °C for 12 h. A dark brown microcrystalline solid precipitated which was separated from the mother liquor, washed twice with small amounts of pentane (−20 °C) and dried: yield 59 mg (82%), m.p. 48 °C (dec.). *Anal*. Calc. for $C_{24}H_{42}Cl_5O_3P_2Rh$: C, 40.00; H, 5.87. Found: C, 39.73; H, 6.02%. IR (CH_2Cl_2): $\nu(O_2)$ 890 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 2.50 (m, 6H, PC*H*CH_3), 1.21 [dvt, $N = 13.1$, $^3J(HH) = 7.3$, 18H, PCHC*H*$_3$], 1.13 [dvt, $N = 14.2$, $^3J(HH) = 6.9$, 18H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 162.9 (s, CO), 133.5, 131.7, 131.1, 128.3, 123.0 (all s, C_5Cl_5), 22.3 (vt, $N = 19.4$, P*C*HCH$_3$), 19.6, 19.3 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 32.9 [d, $^1J(RhP) = 98.8$]. Compound **16** had alternatively been prepared by storing the starting material **15** in a Schlenk tube under an atmosphere of oxygen for 1 h at r.t.; the yield was quantitative.

3.13. Preparation of trans-[Rh(κ^1-OC_6Cl_5)(N_2CPh_2)(*PiPr*$_3$)$_2$] (**18**)

A solution of **15** (76 mg, 0.11 mmol) in 10 ml of pentane was treated dropwise at −78 °C with a solution of

diphenyldiazomethane (22 mg, 0.11 mmol) in 2 ml of pentane. While the solution was warmed to r.t., a change of colour first from red to dark brown and then to green occurred. The solution was stirred for 5 min at r.t. and then concentrated to ca. 2 ml in vacuo. After it was stored at −78 °C for 12 h, dark green crystals precipitated which were separated from the mother liquor, washed twice with small amounts of pentane (−20 °C) and dried: yield 70 mg (72%), m.p. 43 °C (dec.). *Anal.* Calc. for $C_{37}H_{52}Cl_5N_2OP_2Rh$: C, 50.33; H, 5.94; N, 3.17. Found: C, 49.97; H, 5.90; N, 2.82.%. IR (hexane): $\nu(N_2)$ 2043 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 7.30 (m, 4H, C_6H_5), 7.14–6.97 (br m, 6H, C_6H_5), 1.97 (m, 6H, PC*H*CH_3), 1.18 [dvt, $N = 13.2$, $^3J(HH) = 6.2$, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 161.8 (s, CO), 139.8, 132.0, 130.2, 129.7, 129.1, 128.9, 126.7 (all s, C_6H_5 and C_5Cl_5), 87.1 (br s, N_2C), 23.3 (vt, $N = 17.6$, P*C*HCH$_3$), 19.4 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 37.8 [d, $^1J(RhP) = 130.8$].

3.14. Catalytic reaction of ethene with diaryldiazomethanes with compound **15** as a catalyst

In an NMR tube, a slow stream of ethene was passed for 30 s through a solution of **15** (25 mg, 0.03 mmol) and N_2CR_2 (0.10 mmol) (R = Ph, *p*-C_6H_4Me, *p*-C_6H_4Cl) in 0.5 ml of C_6D_6 at r.t. After the solution was warmed to 40 °C, the formation of the olefins **1b** [26], **19** [27], **20** [28] was detected by ^1H NMR spectroscopy. After 30 min, the catalyst decomposed and no Rh-containing product could be characterized.

3.15. Preparation of *trans*-[Rh(κ^1-O_2CCH_3)(N_2C-C_4Cl_4)($PiPr_3$)$_2$] (**22**)

A solution of **21** (38 mg, 0.08 mmol) in 10 ml of pentane was treated at −78 °C with $N_2CC_4Cl_4$ (18 mg, 0.08 mmol). After the solution was slowly warmed to r.t., it was stirred for 10 min. The solvent was evaporated in vacuo and the greenish residue was recrystallized from pentane at −78 °C: yield 45 mg (80%), m.p. 85 °C (dec.). *Anal.* Calc. for $C_{25}H_{45}Cl_4N_2O_2P_2Rh$: C, 47.16; H, 6.37; N, 3.93. Found: C, 48.02; H, 6.67; N, 3.27%. IR (KBr): $\nu(N_2)$ 1930, $\nu(CO_2)$ 1625 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 2.00 (m, 6H, PC*H*CH_3), 1.73 (s, 3H, CH_3CO_2), 1.13 [dvt, $N = 13.9$, $^3J(HH) = 7.1$, 36H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 174.4 (s, CO_2), 102.0, 109.3 (both s, C_4Cl_4), 85.1 (br s, N_2C), 24.4 (vt, $N = 19.0$ Hz, P*C*HCH$_3$), 22.7 (s, *C*H_3CO_2), 19.7 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 46.0 [d, $^1J(RhP) = 117.7$].

3.16. Generation of *trans*-[Rh(κ^1-O_2CCH_3)(N_2CPh_2)-($PiPr_3$)$_2$] (**23**)

A solution of **21** (80 mg, 0.18 mmol) in 30 ml of diethylether was treated at −30 °C with a solution of diphenyldiazomethane (71 mg, 0.36 mmol) in 4 ml of diethylether. A change of colour from red to green occurred. The solution was warmed to r.t., stirred for 10 min, and the solvent was evaporated in vacuo. The residue was dissolved in 10 ml of pentane and the solution was stored at −78 °C for 6 h. A greenish-brown solid precipitated which was separated from the mother liquor, washed with small amounts of pentane (0 °C) and dried. The NMR spectra revealed that a mixture of **21** and **23** in the ratio of 1:2 was isolated. Attempts to separate the two compounds by fractional crystallization or chromatographic techniques failed. If the reaction was repeated by using a 10-fold excess of N_2CPh_2, a mixture of **21** and **23** in the approximate ratio of 1:3 was isolated. Spectroscopic data for **23**: IR (KBr): (N_2) 1950, $\nu(CO_2)$ 1635, 1495 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 7.40–6.83 (br m, 10H, C_6H_5), 2.06 (m, 6H, PC*H*CH_3), 2.00 (s, 3H, CH_3CO_2), 1.28 [dvt, $N = 13.5$, $^3J(HH) = 6.6$, 36H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 174.1 (s, CO_2), 79.4 (br s, N_2C), 24.0 (vt, $N = 17.3$ Hz, P*C*HCH$_3$), 20.6 (s, *C*H_3CO_2), 20.0 (s, PCH*C*H$_3$), signals for phenyl protons were partly covered by the solvent signal. ^{31}P NMR (C_6D_6, 81.0 MHz): δ 42.5 [d, $^1J(RhP) = 130.8$].

3.17. Generation of *trans*-[Rh(κ^1-O_2CCH_3){$N_2C(Ph)$-$C(O)Ph$}($PiPr_3$)$_2$] (**24**)

The reaction of **21** (63 mg, 0.13 mmol) with $N_2C(Ph)C(O)Ph$ (29 mg, 0.13 mmol) in diethylether was carried out as described above with N_2CPh_2 as the substrate. No change of colour occurred. A red solid was isolated which, owing to the NMR spectra, consisted of a mixture of **21** and **24** in the ratio of 1:4. Attempts to separate the two compounds failed. Spectroscopic data for **24**: IR (KBr): $\nu(N_2)$ 1920 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 7.96, 7.86 (both m, 2H each, C_6H_5), 7.20–6.77 (br m, 6H, C_6H_5), 2.43 (m, 6H, PC*H*CH_3), 1.67 (s, 3H, CH_3CO_2), 1.28, 1.27 [both dvt, $N = 13.4$, $^3J(HH) = 7.0$, 18H each, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 181.4 (s, CO_2), 158.1 (s, C═O), 108.8 (br s, N_2C), 23.4 (vt, $N = 17.3$ Hz, P*C*HCH$_3$), 20.5 (s, *C*H_3CO_2), 19.9, 19.8 (both s, PCH*C*H$_3$), signals for phenyl protons were partly covered by the solvent signal. ^{31}P NMR (C_6D_6, 162.0 MHz): δ 29.9 [d, $^1J(RhP) = 113.4$].

3.18. Preparation of *trans*-[Rh(κ^1-O_2CCF_3)(N_2CPh_2)-($PiPr_3$)$_2$] (**26**)

A solution of **25** (44 mg, 0.08 mmol) in 10 ml of pentane was treated at −78 °C with a solution of diphenyldiazomethane (18 mg, 0.08 mmol) in 2 ml of pentane. A change of colour from red to green occurred. The solution was warmed to r.t., stirred for 10 min, and the solvent was evaporated in vacuo. The

residue was recrystallized from pentane at −78 °C to give a green microcrystalline solid. This was separated from the mother liquor, washed with small amounts of pentane (−20 °C) and dried: yield 44 mg (73%), m.p. 52 °C (dec.). *Anal*. Calc. for $C_{33}H_{52}F_3N_2O_2P_2Rh$: C, 54.25; H, 7.17; N, 3.83. Found: C, 53.94; H, 7.09; N, 3.50%. IR (KBr): $\nu(N_2)$ 1936, $\nu(CO_2)$ 1640 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 7.70–6.84 (br m, 10H, C_6H_5), 1.97 (m, 6H, PC*H*CH_3), 1.20 [dvt, $N = 13.5$, $^3J(HH) = 6.9$, 36H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 160.6 [q, $^2J(CF) = 35.6$, CO_2], 129.0, 128.8, 125.4, 125.1 (all s, C_6H_5), 120.4 [q, $^1J(CF) = 277.2$, CF_3], 81.0 (br s, N_2C), 23.7 (vt, $N = 17.6$, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$). ^{19}F NMR (C_6D_6, 188.3 MHz): δ −74.6 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 42.2 [d, $^1J(RhP) = 126.4$].

3.19. Preparation of trans-[Rh(κ¹-O₂CCF₃)(N₂CC₄Cl₄)(PiPr₃)₂] (27)

This compound was prepared as described for **26**, with **25** (64 mg, 0.12 mmol) and $N_2CC_4Cl_4$ (27 mg, 0.12 mmol) as starting materials. Greenish microcrystalline solid; yield 83 mg (92%), m.p. 111 °C (dec.). *Anal*. Calc. for $C_{25}H_{42}Cl_4F_3N_2O_2P_2Rh$: C, 39.18; H, 5.52; N, 3.65. Found: C, 38.87; H, 5.36; N, 3.38%. IR (KBr): $\nu(N_2)$ 1940, $\nu(CO_2)$ 1700 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 1.93 (m, 6H, PC*H*CH_3), 1.10 [dvt, $N = 14.1$, $^3J(HH) = 7.1$, 36H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 159.6 [q, $^2J(FC) = 36.1$, CO_2], 119.5 [q, $^1J(FC) = 278.3$, CF_3], 110.2, 102.8 (both s, C_4Cl_4), 86.6 (br s, N_2C), 24.1 (vt, $N = 19.4$, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$). ^{19}F NMR (C_6D_6, 188.3 MHz): δ −74.4 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 46.5 [d, $^1J(RhP) = 114.8$].

3.20. Preparation of trans-[Rh(κ¹-O₂CCF₃){N₂CH-C(O)Ph}(PiPr₃)₂] (28)

This compound was prepared as described for **26**, with **25** (54 mg, 0.10 mmol) and $N_2CC_4Cl_4$ (27 mg, 0.12 mmol) as starting materials. Yellow microcrystalline solid; yield 62 mg (90%), m.p. 56 °C (dec.). *Anal*. Calc. for $C_{28}H_{50}F_3N_2O_3P_2Rh$: C, 49.27; H, 7.09; N, 4.10. Found: C, 49.48; H, 7.31; N, 3.87%. IR (KBr): $\nu(N_2)$ 1940, ν (CO_2) 1685, ν(C═O) 1625 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 8.28–7.14 (br m, 5H, C_6H_5), 2.20 (m, 6H, PC*H*CH_3), 1.42 (s, 1H, N_2CH), 1.20 [dvt, $N = 14.6$, $^3J(HH) = 7.6$, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 163.2 [q, $^2J(FC) = 34.7$, CO_2], 150.1 (s, C═O), 136.1, 128.8, 128.1, 126.6 (all s, C_6H_5), 122.6 [q, $^1J(FC) = 287.8$, CF_3], 83.5 (br s, N_2C), 24.0 (vt, $N = 17.8$, P*C*HCH$_3$), 19.6, 19.4 (both s, PCH*C*H$_3$). ^{19}F NMR (C_6D_6, 188.3 MHz): δ −74.1 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 31.5 [d, $^1J(RhP) = 117.1$].

3.21. Preparation of trans-[Rh(κ¹-O₂CCF₃)(N₂)(PiPr₃)₂] (29)

A solution of **25** (59 mg, 0.12 mmol) in 5 ml of pentane was treated at −50 °C with a solution of phenyldiazomethane (13 mg, 0.12 mmol) in 1 ml of pentane. While the solution was warmed to r.t., a brown solid precipitated. The suspension was stirred for 5 min, concentrated to ca. 2 ml in vacuo and then stored for 6 h at −78 °C. A brown microcrystalline solid was obtained, which was separated from the mother liquor, washed with small amounts of pentane (−20 °C) and dried: yield 40 mg (59%), m.p. 91 °C (dec.). *Anal*. Calc. for $C_{20}H_{42}F_3N_2O_2P_2Rh$: C, 42.56; H, 7.50; N, 4.96. Found: C, 43.02; H, 7.21; N, 5.36%. IR (KBr): $\nu(N_2)$ 2098, $\nu(CO_2)$ 1650 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 2.03 (m, 6H, PC*H*CH_3), 1.22 [dvt, $N = 13.5$, $^3J(HH) = 7.3$, 36 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 159.7 [q, $^2J(CF) = 35.7$, CO_2], 116.5 [q, $^1J(CF) = 255.1$, CF_3], 23.3 (vt, $N = 19.1$, P*C*HCH$_3$), 19.7 (s, PCH*C*H$_3$). ^{19}F NMR (C_6D_6, 188.3 MHz): δ −74.6 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 43.3 [d, $^1J(RhP) = 126.3$].

3.22. Preparation of trans,trans-[{Rh(κ¹-O₂CCF₃)(PiPr₃)₂}{μ-1.4-C₆H₄(C(Ph)N₂)₂}] (30)

A solution of **25** (74 mg, 0.14 mmol) in 5 ml of diethylether was treated dropwise at −78 °C with a solution of 1.4-$C_6H_4(C(Ph)N_2)_2$ (26 mg, 0.08 mmol) in 3 ml of diethylether. A change of colour from red to green occurred. The work-up procedure was the same as described for **26**. A dark green microcrystalline solid was obtained: yield 65 mg (68%), m.p. 46 °C (dec.). *Anal*. Calc. for $C_{60}H_{92}F_6N_4O_4P_4Rh_2$: C, 52.10; H, 7.14; N, 4.05. Found: C, 52.67; H, 7.41; N, 3.91%. IR (KBr): $\nu(N_2)$ 1930, $\nu(CO_2)$ 1630 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 7.88–6.89 (br m, 14H, C_6H_4 and C_6H_5), 2.00 (m, 12H, PC*H*CH_3), 1.24 [dvt, $N = 13.6$, $^3J(HH) = 6.8$, 72 H, PCHC*H*$_3$]. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 160.3 [q, $^2J(CF) = 35.1$, CO_2], 129.1, 127.9, 125.6, 125.5, 125.3, 124.5 (all s, C_6H_4 and C_6H_5), 122.4 [q, $^1J(CF) = 262.6$, CF_3], 81.2 (br s, N_2C), 23.8 (vt, $N = 17.5$, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{19}F NMR (C_6D_6, 376.5 MHz): δ −74.8 (s). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 42.21.9 [d, $^1J(RhP) = 126.3$].

3.23. Catalytic reaction of ethene with diaryldiazomethanes with compound 21 or 25 as a catalyst

In a typical experiment, a solution of the catalyst (20–30 mg, ca. 0.05 mmol) in 6 ml of toluene was treated dropwise (ca. 10 ml/h) at 40 °C with a 0.1 M solution of N_2CRR' in toluene. While adding the substrate, a slow stream of ethene was passed through the solution. The catalytic reaction was finished when the violet colour of the diazoalkane solution did not disappear on further

addition to the reaction mixture. The solvent was evaporated in vacuo and the oily residue was dissolved in 3 ml of hexane. In order to destroy the excess of N_2CRR' and separate the catalyst, the mixture was filtered through Al_2O_3 (neutral, activity grade III, height of column 4 cm). After removal of the solvent, a colorless oil was isolated from the eluate. The product was analyzed by GC–MS and the dominating olefin (see Table 1) characterized by ^1H NMR spectroscopy. The data for **1b** [26], **1c** [29], **19** [27], **20** [28] and **33** [30] were already reported. ^1H NMR data for N_2CRR' (C_6D_6, 200 MHz): **31**: δ 7.83, 7.77 [both d, $^3J(HH) = 8.2$, 2 H each, C_6H_4], 7.62–7.12 (br m, 5H, C_6H_5), 6.31 [ddd, $^3J(HH)_{trans} = 17.2$, $^3J(HH)_{cis} = 10.2$, $^3J(HH) = 7.3$, 1 H, C*H*=CH_2], 5.22 [ddd, $^3J(HH)_{cis} = 10.2$, $^2J(HH) = 1.5$, $^4J(HH) = 1.1$, 1 H, one H of =CH_2 *trans* to CH], 5.01 [ddd, $^3J(HH)_{trans} = 17.2$, $^2J(HH) = 1.5$, $^4J(HH) = 1.8$, 1 H, one H of =CH_2 *cis* to CH], 4.72 [br d, $^3J(HH) = 7.3$, 1H, C*H*RR′], 2.39 (s, 3H, $C_6H_4CH_3$). **32**: δ 7.31–6.82 (br m, 9H, C_6H_4 and C_6H_5), 6.18 [ddd, $^3J(HH)_{trans} = 16.8$, $^3J(HH)_{cis} = 10.2$, $^3J(HH) = 6.6$, 1H, C*H*=CH_2], 5.12 [ddd, $^3J(HH)_{cis} = 10.2$, $^2J(HH) = 1.5$, $^4J(HH) = 1.5$, 1H, one H of =CH_2 *trans* to CH], 4.81 [br d, $^3J(HH) = 6.6$, 1H, C*H*RR′], 4.75 [ddd, $^3J(HH)_{trans} = 17.2$, $^2J(HH) = 1.5$, $^4J(HH) = 1.8$, 1H, one H of =CH_2 *cis* to CH], 2.18 (s, 3H, $C_6H_4CH_3$). **34**: δ 7.28 [d, $^3J(HH) = 8.4$, 4H, C_6H_4], 7.02 [d, $^3J(HH) = 8.8$, 4H, C_6H_4], 6.44 [ddd, $^3J(HH)_{trans} = 17.2$, $^3J(HH)_{cis} = 10.2$, $^3J(HH) = 6.5$, 1H, C*H*=CH_2], 5.36 [br d, $^3J(HH)_{cis} = 10.2$, 1H, one H of =CH_2 *trans* to CH], 5.14 [ddd, $^3J(HH)_{trans} = 17.2$, $^2J(HH) = 1.5$, $^4J(HH) = 1.4$, 1H, one H of =CH_2 *cis* to CH], 4.82 [br d, $^3J(HH) = 7.3$, 1H, C*H*RR′], 2.94 (s, 3H, OCH_3). **35**: δ 7.90 [d, $^3J(HH) = 8.4$, 4H, C_6H_4], 7.40 (m, 4H, C_6H_4), 6.38 [ddd, $^3J(HH)_{trans} = 17.2$, $^3J(HH)_{cis} = 10.2$, $^3J(HH) = 6.9$, 1H, C*H*=CH_2], 5.42 [ddd, $^3J(HH)_{cis} = 10.2$, $^2J(HH) = 1.5$, $^4J(HH) = 1.2$, 1H, one H of =CH_2 *trans* to CH], 5.14 [ddd, $^3J(HH)_{trans} = 17.2$, $^2J(HH) = 1.5$, $^4J(HH) = 1.2$, 1H, one H of =CH_2 *cis* to CH], 4.85 [br d, $^3J(HH) = 7.3$, 1H, C*H*RR′].

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