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C–C coupling reactions in the coordination sphere of rhodium(I) and rhodium(III): New routes for the di- and trimerization of terminal alkynes†

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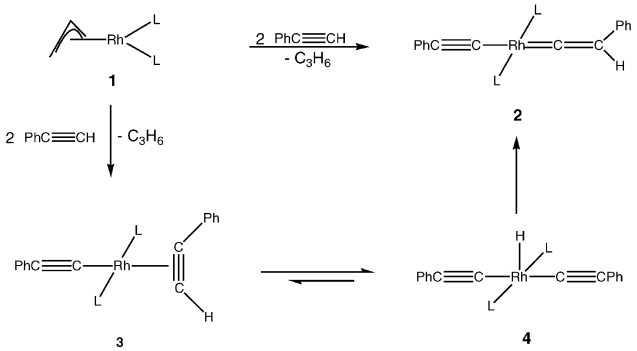
The alkynyl(vinylidene)rhodium(I) complexes *trans*-[Rh(C≡CR)(=C=CHR)(P*i*Pr$_3$)$_2$] **2, 5, 6** react with CO by migratory insertion to give stereoselectively the butenynyl compounds *trans*-[Rh{η^1-(*Z*)-C(=CHR)C≡CR}-(CO)(P*i*Pr$_3$)$_2$] (*Z*)-**7–9**, of which (*Z*)-**7** (R = Ph) and (*Z*)-**8** (R = *t*Bu) rearrange upon heating or UV irradiation to the (*E*) isomers. Similarly, *trans*-[Rh{η^1-C(=CH$_2$)C≡CPh}(CO)(P*i*Pr$_3$)$_2$] **12** and *trans*-[Rh{η^1-(*Z*)-C(=CHCO$_2$Me)C≡CR}(CO)(P*i*Pr$_3$)$_2$] (*Z*)-**15**, (*Z*)-**16** have been prepared. At room temperature, the corresponding "non-substituted" derivative *trans*-[Rh{η^1-C(=CH$_2$)C≡CH}(CO)(P*i*Pr$_3$)$_2$] **18** is in equilibrium with the butatrienyl isomer *trans*-[Rh(η^1-CH=C=C=CH$_2$)(CO)(P*i*Pr$_3$)$_2$] **19** that rearranges photochemically to the alkynyl complex *trans*-[Rh(C≡CCH=CH$_2$)(CO)(P*i*Pr$_3$)$_2$] **20**. Reactions of (*Z*)-**7**, (*E*)-**7**, (*Z*)-**8** and (*E*)-**8** with carboxylic acids R′CO$_2$H (R′ = CH$_3$, CF$_3$) yield either the butenyne (*Z*)- and/or (*E*)-RC≡CCH=CHR or a mixture of the butenyne and the isomeric butatriene, the ratio of which depends on both R and R′. Treatment of **2** (R = Ph) with HCl at −40 °C affords five-coordinate [RhCl(C≡CPh){(*Z*)-CH=CHPh}(P*i*Pr$_3$)$_2$] **23**, which at room temperature reacts by C–C coupling to give *trans*-[RhCl{η^2-(*Z*)-PhC≡CCH=CHPh}(P*i*Pr$_3$)$_2$] (*Z*)-**21**. The related compound *trans*-[RhCl(η^2-HC≡CCH=CH$_2$)(P*i*Pr$_3$)$_2$] **27**, prepared from *trans*-[Rh(C≡CH)(=C=CH$_2$)(P*i*Pr$_3$)$_2$] **17** and HCl, rearranges to the vinylvinylidene isomer *trans*-[RhCl(=C=CHCH=CH$_2$)(P*i*Pr$_3$)$_2$] **28**. While stepwise reaction of **2** with CF$_3$CO$_2$H yields, *via* alkynyl(vinyl)rhodium(III) intermediates (*Z*)-**29** and (*E*)-**29**, the alkyne complexes *trans*-[Rh(κ^1-O$_2$CCF$_3$)(η^2-PhC≡CCH=CHPh)(P*i*Pr$_3$)$_2$] (*Z*)-**30** and (*E*)-**30**, from **2** and CH$_3$CO$_2$H the acetato derivative [Rh(κ^2-O$_2$CCH$_3$)(P*i*Pr$_3$)$_2$] **33** and (*Z*)-PhC≡CCH=CHPh are obtained. From **6** (R = CO$_2$Me) and HCl or HC≡CCO$_2$Me the chelate complexes [RhX(C≡CCO$_2$Me){κ^2(*C*,*O*)-CH=CHC(OMe)=O}(P*i*Pr$_3$)$_2$] **34** (X = Cl) and **35** (X = C≡CCO$_2$Me) have been prepared. In contrast to the reactions of [Rh(κ^2-O$_2$CCH$_3$)(C≡CE)-(CH=CHE)(P*i*Pr$_3$)$_2$] **37** (E = CO$_2$Me) with chloride sources which give, *via* intramolecular C–C coupling, four-coordinate *trans*-[RhCl{η^2-(*E*)-EC≡CCH=CHE}(P*i*Pr$_3$)$_2$] (*E*)-**36**, treatment of **37** with HC≡CE affords, *via* insertion of the alkyne into the rhodium–vinyl bond, six-coordinate [Rh(κ^2-O$_2$CCH$_3$)(C≡CE){η^1-(*E*,*E*)-C(=CHE)CH=CHE}(P*i*Pr$_3$)$_2$] **38**. The latter reacts with MgCl$_2$ to yield *trans*-[RhCl{η^2-(*E*,*E*)-EC≡CC(=CHE)-CH=CHE}(P*i*Pr$_3$)$_2$] **39**, which, in the presence of CO, generates the substituted hexadienyne (*E*,*E*)-EC≡CC(=CHE)CH=CHE **40**.

Introduction

The catalytic dimerization of terminal alkynes has been intensively studied in recent years.[1] With electron-rich transition-metal compounds as catalysts, it is generally assumed that the C–C bond-forming reaction occurs either by alkynyl–vinyl or alkynyl–vinylidene coupling.[2] Although it has been observed that occasionally the dimerization of RC≡CH can lead to butatriene derivatives (*E*)/(*Z*)-RCH=C=C=CHR,[3–7] in most cases a mixture of 1,3- and 1,4-disubstituted butenynes, RC≡CC(R)=CH$_2$ and (*E*)/(*Z*)-RC≡CCH=CHR, is formed.[8]

In the context of our investigations on the chemistry of vinylidenerhodium(I) complexes,[9] we found that the chloro derivatives *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$] react with organolithium compounds or Grignard reagents to give the substitution products *trans*-[Rh(R′)(=C=CHR)(P*i*Pr$_3$)$_2$] (R′ = alkyl, aryl, vinyl, alkynyl) in high yields.[10] An alternative route to obtain the complexes with R′ = C≡CR consists of the reaction of the η^3-allyl compound [Rh(η^3-C$_3$H$_5$)(P*i*Pr$_3$)$_2$] **1** with terminal alkynes in the molar ratio of 1 : 2 in pentane or pentane/NEt$_3$ as the solvent.[11] As illustrated with phenylacetylene as the substrate (see Scheme 1), the alkynyl(vinylidene) complex **2** is formed *via* the alkynerhodium(I) and alkynyl(hydrido)rhodium(III) intermediates **3** and **4**, the first of which could be isolated in analytically pure form.



Scheme 1 (L = P*i*Pr$_3$).

The present work is an extension of our studies on the rhodium-assisted coupling of an alkyl, aryl or vinyl group with a vinylidene ligand.[10] We report the synthesis of a series of four-coordinate enynylrhodium(I) complexes, their reactions with acidic substrates to give either enynes and/or butatrienes, different routes to prepare enynerhodium(I) compounds by intramolecular C–C coupling, and a new mechanistic pathway for the trimerization of a terminal alkyne that does not lead to a

† Dedicated to Professor Wolfgang Kläui, with the best of good wishes, on the occasion of his 60th birthday.

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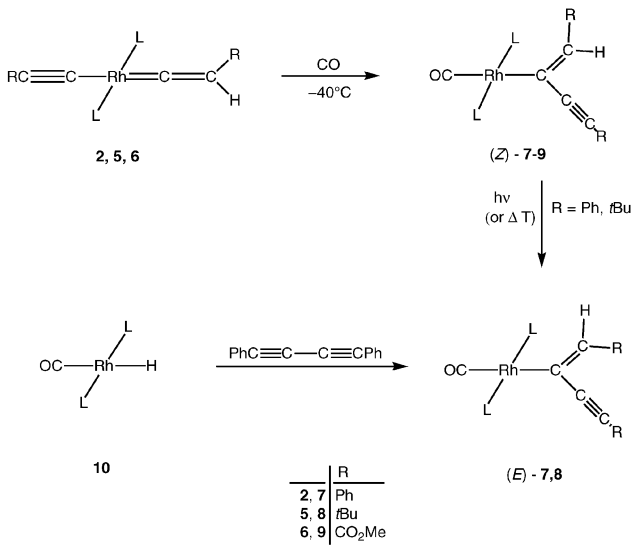
benzene but selectively to a hexadienyne derivative. Part of the results have already been communicated.[12,13]

Results and discussion

CO-induced coupling of alkynyl and vinylidene units

The alkynyl(vinylidene) complexes **2, 5** and **6**, prepared from **1** and two equivalents of RC≡CH,[11,14] are highly reactive toward carbon monoxide. Passing a slow stream of CO through a solution of **2, 5** or **6** in pentane at −40 °C leads to a change of colour from blue-green to yellow and, after low-temperature crystallization from pentane, gave yellow crystalline solids of composition (*Z*)-**7–9** in about 80% yield (Scheme 2). The IR spectra of the moderately air-sensitive products show two characteristic bands at, respectively, 1930–1955 cm^{-1} and 2155–2160 cm^{-1}, which are assigned to the CO and C≡C stretching frequencies. Since in the ^1H NMR spectra of (*Z*)-**7–9** the chemical shift of the signal of the vinylic =CH proton, which appears as a doublet-of-triplets due to ^1H–^{103}Rh and ^1H–^{31}P couplings, is quite similar to that found for the enyl complexes *trans*-[Rh(CR=CHR′)(CO)(P*i*Pr$_3$)$_2$] (R = Me, Ph, *p*-Tol, CH=CH$_2$; R′ = *t*Bu, Ph),[10] we assume that the (*Z*) isomers, having the substituents R and C≡CR in a *trans* orientation at the C=C bond, are exclusively formed. The stereochemical course of the reaction is noteworthy insofar as Wakatsuki *et al.* reported the exclusive formation of the thermodynamically favoured (*E*) isomer of the enynylruthenium compound [RuCl{C(=CH*t*Bu)C≡C*t*Bu}(CO)(PPh$_3$)$_2$] after stepwise treatment of [RuCl$_2$(=C=CH*t*Bu)(PPh$_3$)$_2$] with LiC≡C*t*Bu and CO.[3]



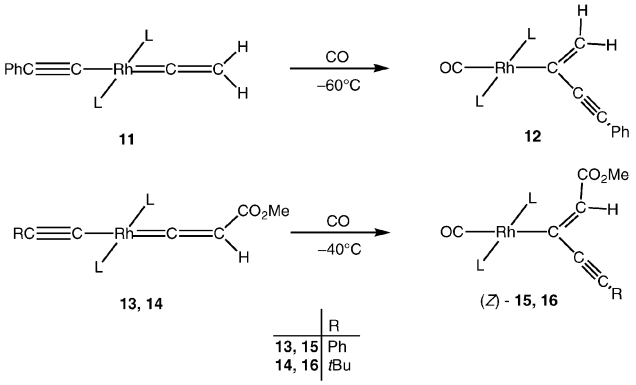
Scheme 2 (L = P*i*Pr$_3$).

The proposed stereochemistry of the four-coordinate rhodium complexes obtained from the starting materials **2, 5, 6** and CO has been confirmed by an X-ray crystal structure analysis of (*Z*)-**9**.[12] The most important result is that the enynyl unit lies perpendicular to the coordination plane around rhodium and that there is no additional interaction between the triple bond or the ester unit and the metal centre.

In benzene solution, the *t*Bu-substituted complex (*Z*)-**8** is slightly labile and, after stirring the solution for 6 h at 40 °C, rearranges nearly quantitatively to the isomer (*E*)-**8**. This compound, being a yellow solid similar to (*Z*)-**8**, is equally formed by UV-irradiation of a solution of the (*Z*) isomer in benzene for 2 h at 15 °C. In this case the yield is 74%. While the photochemical route can also be applied for the isomerization of (*Z*)-**7** to (*E*)-**7**, attempts to generate the isomer (*E*)-**9** from (*Z*)-**9** failed. Regarding the ^1H NMR spectra of (*E*)-**7** and (*E*)-**8**, there is a characteristic difference to those of the (*Z*) isomers insofar as the resonance for the vinyl =CH proton appears at δ 6.91 and 5.44 and is thus shifted by more than 1.1 ppm to higher fields. The ^{13}C NMR spectra of (*Z*)-**7**, (*Z*)-**8** and (*E*)-**7**, (*E*)-**8** display four signals for the carbon atoms of the C$_4$ enynyl unit in the range of δ 85 to 160 and there are only minor differences in the chemical shifts between the (*Z*) and the (*E*) isomers.

An alternative method to obtain (*E*)-**7** consists of the reaction of the hydrido compound **10** with the diyne PhC≡CC≡CPh affording the product in 75% yield (see Scheme 2). We note that there is precedent for the preparation of enynyl transition-metal complexes from hydrido–metal precursors and diynes which in all cases led to the formation of the corresponding (*E*) isomers.[15]

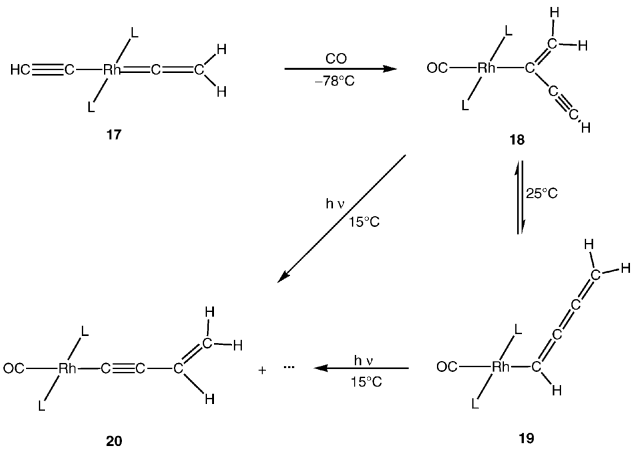
In the presence of CO, the alkynyl(vinylidene) complexes **11, 13** and **14**, having different substituents at the β-carbon atoms of the alkynyl and the vinylidene ligands, behave analogously to their more symmetrical counterparts **2, 5** and **6**. Under similar conditions as applied for the preparation of (*Z*)-**7–9**, the enynylrhodium(I) compounds **12** and (*Z*)-**15**, (*Z*)-**16** were formed in high yields (Scheme 3). Since the reactions of **13** and **14** with CO afford exclusively the complexes with the CO$_2$Me group linked to β-carbon atom of the vinylic moiety, we assume that the mechanism of formation of (*Z*)-**15**, (*Z*)-**16** is best described as the CO-induced migration of the alkynyl ligand to the α-carbon atom of the vinylidene unit. If the rearrangement proceeded *via* an intermediate hexa-coordinate [RhH(C≡CR)(C≡CCO$_2$Me)(CO)(P*i*Pr$_3$)$_2$] species, presumably a mixture of (*Z*)-**15** or (*Z*)-**16** and the corresponding isomer *trans*-[Rh{C(=CHR)C≡CCO$_2$Me}(CO)(P*i*Pr$_3$)$_2$] would be formed. The importance of steric factors probably explains why not only for (*Z*)-**7–9** but also in the case of (*Z*)-**15** and (*Z*)-**16** the attack of the alkynyl residue takes place exclusively at that side of the molecule which is opposite to the CO$_2$Me group.



Scheme 3 (L = P*i*Pr$_3$).

Treatment of the "non-substituted" alkynyl(vinylidene) complex **17** with CO led to a remarkable rearrangement of the carbon-bonded ligands. As expected, in the initial step the enynyl compound **18** is formed and isolated as a yellow microcrystalline solid in 84% yield (Scheme 4). Typical spectroscopic features of **18** are the signals for the three protons of the enynyl ligand in the ^1H NMR spectrum which appear for the =CH$_2$ protons at δ 6.66 and 5.52 as doublets-of-doublets-of-triplets and for the ≡CH proton at δ 3.41 as a singlet.

When a solution of **18** in toluene-d_8 was slowly warmed to room temperature, NMR spectra indicated the formation of a new compound of proposed formulation **19**. The ratio of **18 : 19** is about 65 : 35, which does not change after the solution has been stirred for 2 h. The ^1H NMR spectrum of **19** displays the three resonances for the butatrienyl protons at δ 7.93 (RhCH) and δ 5.45 and 5.23 (=CH$_2$), all of them are split into doublets-of-doublets-of-doublets-of-triplets. Similar chemical shifts (as well as ^1H–^1H and ^1H–^{31}P coupling constants) were found for the octahedral iridium complex [IrCl(OTf)(CH=C=C=CHMe)(CO)(PPh$_3$)$_2$] (Tf = triflate), which was prepared by Stang *et al.* from



Scheme 4 (L = P*i*Pr$_3$).

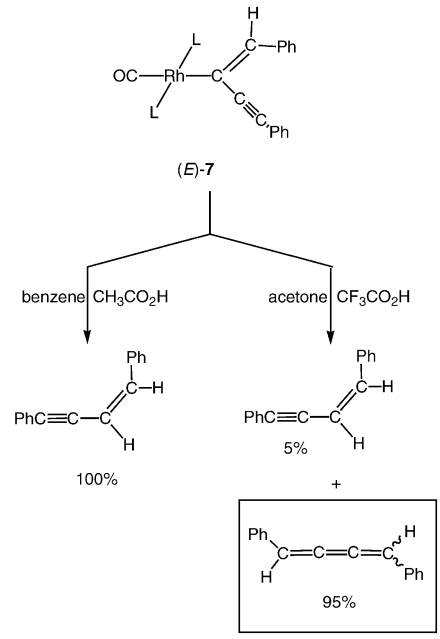
trans-[IrCl(CO)(PPh$_3$)$_2$] and HC≡CC(OTf)=CHMe.[16] In contrast to **18**, the ^{1}H and ^{13}C NMR spectra of **19** illustrate that the two triisopropylphosphine ligands are equivalent, thus indicating that the rotation of the C$_4$ ligand around the Ir–C axis is fast on the NMR timescale.

When we attempted to enrich the mixture of **18** and **19** in the butatrienyl complex **19** by UV irradiation, we observed that under the chosen conditions (C$_6$D$_6$, 15 °C) both compounds are labile and rearrange to a third isomer assumed to be the substituted alkynyl complex **20**. In addition, some unidentified decomposition products were formed which could not be separated from **20** by fractional crystallization or column chromatography. The ^{1}H NMR spectrum of **20** shows for the protons of the vinyl group three doublets-of-doublets-of-triplets with chemical shifts that are similar to those of the CH=CH$_2$ protons of the vinylvinylidene compound *trans*-[RhCl(=C=CHCH=CH$_2$)(P*i*Pr$_3$)$_2$].[17] When we attempted to elucidate the mechanism of formation of **20** by monitoring the isomerization reaction in an NMR tube, we were unable to detect any intermediate. The most plausible path to give **20** appears to be a 1,3-shift of the enynyl ligand of **18** along the C–C≡CH axis, followed by the migration of the alkynyl proton to the γ-carbon atom. If instead of **18** the butatrienyl derivative **19** would be the precursor, the generation of a short-lived five-coordinate hydridorhodium(I) compound [RhH(=C=C=C=CH$_2$)(CO)(P*i*Pr$_3$)$_2$] is conceivable which *via* a 1,3-hydride shift from the metal to the γ-carbon atom of the cumulated C$_4$ unit would give the product. It should be mentioned that while we succeeded in preparing an iridium(I) complex with an Ir=C=C=C=CR$_2$ chain,[18] we failed to generate the rhodium(I) counterpart.

Acid-induced formation of butenynes and butatrienes

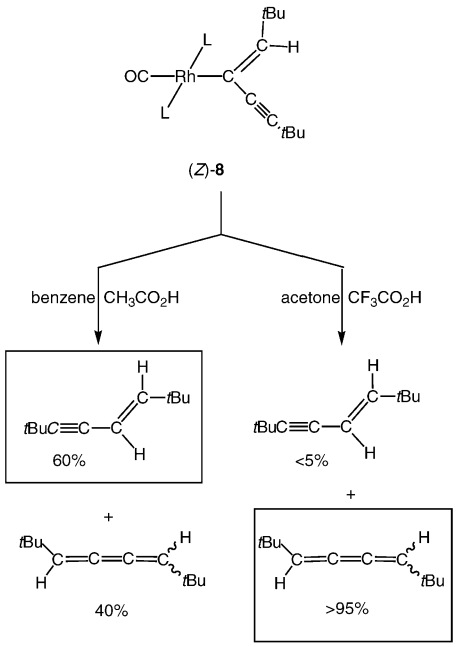
The cleavage of the enynyl–metal bond in (*E*)-**7** by acetic acid in benzene affords, besides the carboxylato complex *trans*-[Rh(κ^1-O$_2$CCH$_3$)(CO)(P*i*Pr$_3$)$_2$],[19] exclusively the expected butenyne (*Z*)-PhC≡CCH=CHPh (Scheme 5). If the reaction of (*E*)-**7** is carried out with CF$_3$CO$_2$H instead of acetic acid and in acetone instead of benzene as solvent, besides *trans*-[Rh(κ^1-O$_2$CCF$_3$)(CO)(P*i*Pr$_3$)$_2$][19] surprisingly a mixture of (*E*)/(*Z*)-PhCH=C=C=CHPh (*ca.* 95%) and (*Z*)-PhC≡CCH=CHPh (*ca.* 5%) is formed. The ratio of the (*E*) and (*Z*) isomers of 1,4-diphenylbutatriene is 9 : 1.

In contrast to (*E*)-**7**, the corresponding (*Z*) isomer is inert toward CH$_3$CO$_2$H. If (*Z*)-**7** is treated with CF$_3$CO$_2$H, the composition of the organic products, obtained by cleavage of the enynyl–rhodium bond, depends on the solvent used. While in benzene at 40 °C as well as in acetone at room temperature the dominating products are the 1,4-diphenylbutatrienes (*E*)/(*Z*)-PhCH=C=C=CHPh, the minor product formed in benzene is (*E*)-PhC≡CCH=CHPh but in acetone it is the (*Z*) isomer.



Scheme 5 (L = P*i*Pr$_3$).

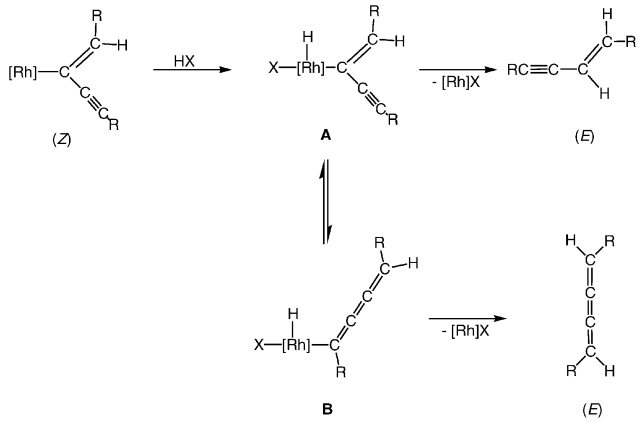
The reaction of (*E*)-**8** with both acetic acid (in benzene) and trifluoroacetic acid (in benzene or acetone) always leads to a mixture of the butatrienes (*E*)/(*Z*)-*t*BuCH=C=C=CH*t*Bu and the butenyne (*Z*)-*t*BuC≡CCH=CH*t*Bu, with either the former or the latter as the dominating products. The isomer (*Z*)-**8** reacts with CF$_3$CO$_2$H in benzene or acetone to give mainly a mixture of (*E*)- and (*Z*)-*t*BuCH=C=C=CH*t*Bu, whereas with CH$_3$CO$_2$H in benzene besides the butatrienes (*E*)/(*Z*)-*t*BuCH=C=C=CH*t*Bu (*ca.* 40%) also the butenyne (*E*)-*t*BuC≡CCH=CH*t*Bu (*ca.* 60%) is formed (Scheme 6). In all cases, the organic products were known and identified by comparison of the NMR data with those reported in the literature.[5,7,20–25]



Scheme 6 (L = P*i*Pr$_3$).

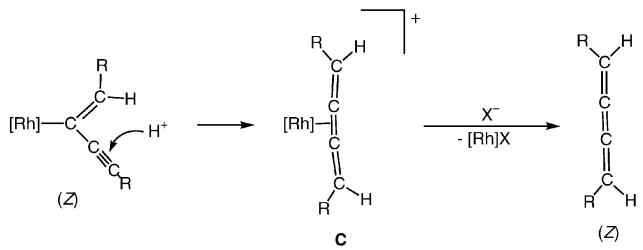
To summarize the results about the reactivity of the enynyl complexes (*E*)/(*Z*)-**7** and (*E*)/(*Z*)-**8** toward CH$_3$CO$_2$H and CF$_3$CO$_2$H, the first conclusion is that independent of the strength of the acid and the type of the solvent the (*E*)-isomers (*E*)-**7** and (*E*)-**8** afford (either as the major or the minor

product) the corresponding (*Z*)-butenyne and the (*Z*)-isomers (*Z*)-**7** and (*Z*)-**8** afford the corresponding (*E*)-butenyne. This is in agreement with work in the literature.[26] Mechanistically we assume that the formation of the butenynes proceeds *via* a hexa-coordinate intermediate **A** (see Scheme 7, shown for the (*Z*)-enynyl complexes as the precursors), which is generated from the four-coordinate starting material by oxidative addition of the acid HX at the metal centre. Reductive elimination from **A** would give (*E*)-RC≡CCH=CHR and *trans*-[RhX(CO)(P*i*Pr$_3$)$_2$]. To explain the formation of the butatrienes, it is conceivable that in solution intermediate **A** is in equilibrium with intermediate **B** (see the generation of **19** from **18**, shown in Scheme 4), which analogously to **A** reacts by reductive elimination to produce the cumulene.



Scheme 7 ([Rh] = Rh(CO)(P*i*Pr$_3$)$_2$).

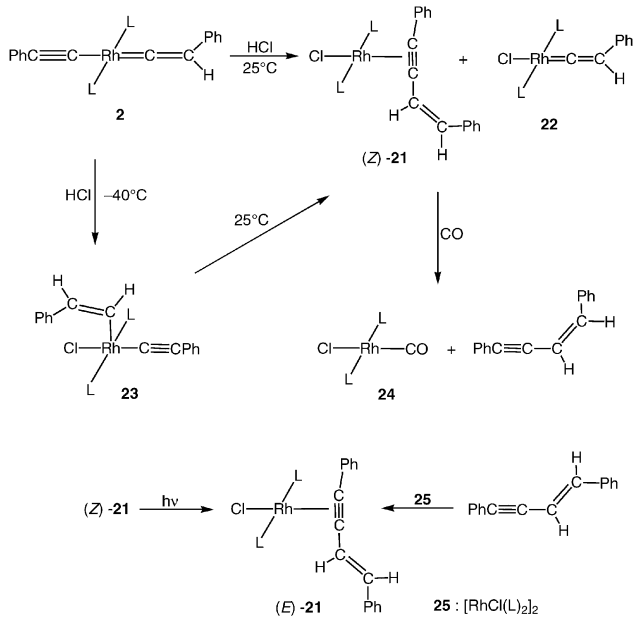
However, since the reductive elimination of intermediate **B** can only lead to the (*E*)-isomer of the corresponding butatriene and since at least for the reactions of (*Z*)-**7** with CF_3CO_2H in benzene and of (*Z*)-**8** with CF_3CO_2H in acetone the (*Z*)-configured butatriene is the dominant isomer, a second mechanism shown in Scheme 8 has also to be taken into consideration. We assume that in particular for the stronger acid CF_3CO_2H the attack of the proton can not only occur at the metal centre but also at the C≡C triple bond.[27] The generated cationic butatriene complex **C** could subsequently react with the carboxylate anion to give *trans*-[RhX(CO)(P*i*Pr$_3$)$_2$] and (*Z*)-RCH=C=C=CHR. We note that the molecular structure of (*Z*)-**9** reveals,[12] that the proton attack at the C≡C triple bond is favoured from the side opposite to the metal, which could explain why compounds (*Z*)-**7** and (*Z*)-**8**, in the presence of CF_3CO_2H, predominantly afford the (*Z*)- and not the (*E*)-configured butatriene. Moreover, if we take results obtained for cleavage reactions of vinyl transition-metal compounds into account,[28] we can not completely exclude that in the enynyl complexes **7** and **8** or in intermediates such as **A** or **B** an acid-induced isomerization of the metal-bound C_4 unit occurs. However, under the reaction conditions (ratio of starting material to acid = 1 : 1) this possibility is less likely.



Scheme 8 ([Rh] = Rh(CO)(P*i*Pr$_3$)$_2$).

Acid-induced C–C coupling reactions

The observation, that the vinylidene complexes *trans*-[IrCl(=C=CHR)(P*i*Pr$_3$)$_2$] (R = H, Me, Ph) react with HBF_4 to give initially the hydridoiridium(III) cations [IrH(Cl)(=C=CHR)(P*i*Pr$_3$)$_2$]$^+$ which rearrange to the carbyne–metal isomers [IrCl(≡CCH$_2$R)(P*i*Pr$_3$)$_2$]$^+$,[29] prompted us to investigate also the reactivity of the rhodium vinylidenes **2, 6** and **17** toward Brønsted acids. Treating a solution of **2** in benzene with an equimolar amount of HCl at room temperature leads to a smooth change of colour from blue-green to orange and, as indicated by the ^{31}P NMR spectrum, affords a mixture of the alkyne complex (*Z*)-**21** and the chlororhodium(I) compound **22** (Scheme 9). After evaporation of the solvent and extraction of the residue with pentane, the major product (*Z*)-**21** was isolated as an orange-red solid in 49% yield.



Scheme 9 (L = P*i*Pr$_3$).

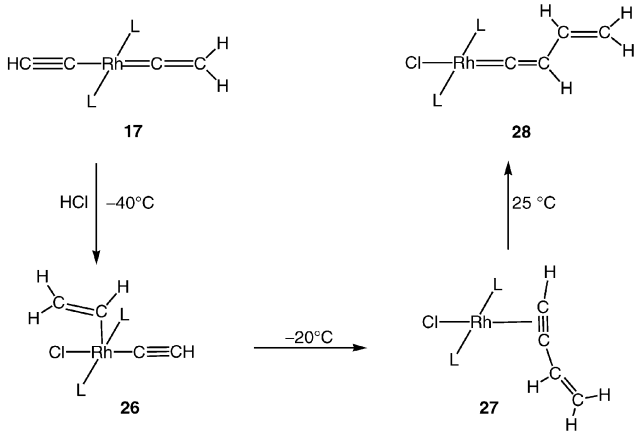
However, if the reaction of **2** with HCl was carried out in diethyl ether at −40 °C, instead of the alkynerhodium(I) complex (*Z*)-**21** the five-coordinate alkynyl(vinyl)rhodium(III) compound **23** was generated. It was isolated as a red, only moderately air-sensitive solid that is quite labile and rearranges in benzene at room temperature to give the isomer (*Z*)-**21** in nearly quantitative yield. In contrast to the ^{1}H NMR spectrum of (*Z*)-**21**, which displays the signals for the protons of the vinyl group at δ 6.75 (C*H*=CHPh) and 6.45 (CH=C*H*Ph), the ^{1}H NMR spectrum of **23** shows the resonances for the vinyl protons at δ 8.09 (C*H*=CHPh) and 5.76 (CH=C*H*Ph), respectively. Both spectra display two doublets-of-virtual triplets for the methyl protons of the isopropyl units thus indicating that the phosphine ligands are *trans*-disposed. Although for **23** a trigonal-bipyramidal structure can not be excluded, we assume that in analogy to five-coordinate [Rh(C≡CMe)$_2${C(Me)=CH$_2$}(P*i*Pr$_3$)$_2$] a square-pyramidal configuration is preferred.[14]

Regarding the mechanism of formation of the alkynyl(vinyl) complex, the initial step probably consists of an attack of the proton at the metal centre of **2** to give the six-coordinate intermediate [RhH(Cl)(C≡CPh)(=C=CHPh)(P*i*Pr$_3$)$_2$], which reacts by migratory insertion of the vinylidene ligand into the Rh–H bond to produce **23**. The observed (*Z*)-selectivity would be in agreement with the stereochemistry found for (*Z*)-**7** (see Scheme 2). The subsequent C–C coupling reaction of **23** to give (*Z*)-**21** obviously has a low energy of activation since it proceeds also in the absence of solvent and, under these conditions, is completed at 60 °C in *ca.* 90 min. To explain the formation of **22** as a by-product in the reaction of **2** with HCl at room temperature, it is likely that at room temperature the supposed intermediate [RhH(Cl)(C≡CPh)(=C=CHPh)(P*i*Pr$_3$)$_2$] can eliminate phenylacetylene and thus gives the four-coordinate species.

We finally note that treatment of (*Z*)-**21** with CO rapidly leads to a displacement of the enyne ligand and gives the carbonyl complex **24** and (*Z*)-PhC≡CCH=CHPh.

Under UV-irradiation, compound (*Z*)-**21** is also labile and rearranges (benzene, 15 °C, 30 min) quantitatively to the (*E*)-isomer (see Scheme 9). An alternative route to prepare (*E*)-**21** consists of the reaction of the dimeric rhodium(I) complex **25** with (*E*)-PhC≡CCH=CHPh that affords the product in almost quantitative yield. Typical spectroscopic features of (*E*)-**21** are the CH=C*H*Ph proton resonance in the ^{1}H NMR spectrum, which appears at lower field than the signal for the C*H*=CHPh proton, and the size of the corresponding ^{3}J(H,H) coupling constant that is significantly smaller than for (*Z*)-**21**. Similarly to (*Z*)-**7** and (*E*)-**7**, the ^{13}C NMR spectra of (*Z*)-**21** and (*E*)-**21** reveal only minor differences in the chemical shifts and coupling constants for the resonances of the carbon atoms of the C_4 unit.

The "non-substituted" alkynyl(vinylidene) complex **17** reacts with HCl under the same conditions as applied for the preparation of **23** to afford the alkynyl(vinyl)rhodium(III) compound **26** in virtually quantitative yield (Scheme 10). The isolated orange solid is only slightly air-sensitive and readily soluble in most organic solvents. Diagnostic for the presence of the vinyl ligand are the three resonances in the ^{1}H NMR spectrum at δ 7.29 (RhCH), 5.47 and 4.50 (both =CH_2) which appear as doublets-of-doublets-of-doublets-of triplets due to ^{1}H–^{1}H (twice), ^{1}H–^{103}Rh and ^{1}H–^{31}P couplings.

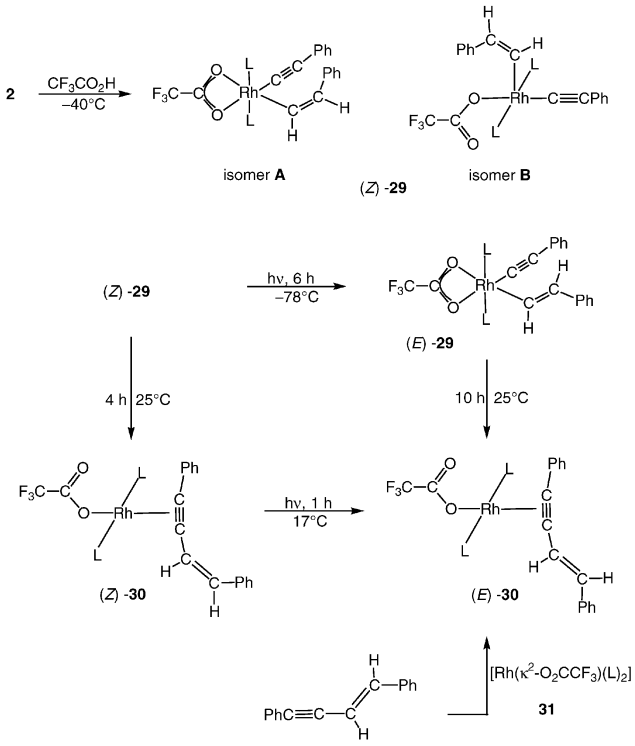


Scheme 10 (L = P*i*Pr$_3$).

Similarly to compound **23**, the five-coordinate complex **26** is exceedingly labile and rearranges in benzene at room temperature to give the rhodium vinylidene **28** in 89% yield. However, if a solution of **26** in toluene-d_8 is slowly warmed from −60 °C to −20 °C, the formation of intermediate **27** could be detected. After increasing the temperature, it reacts to form isomer **28**. Both **27** and **28** had already been described in the literature and were prepared from **25** and vinylacetylene.[17] The stepwise conversion of **26** to **27** and finally to **28** also occurs in a KBr matrix between −40 °C and 0 °C and can easily be monitored by IR spectroscopy.

The starting material **2** reacts not only with HCl but also with CF_3CO_2H in diethyl ether at −40 °C to generate the alkynyl(vinyl) complex (*Z*)-**29** (Scheme 11). This product is a yellow, practically air-stable solid for which a correct elemental analysis has been obtained. The IR-spectrum of (*Z*)-**29** shows for the asymmetric OCO-stretching mode of the CF_3CO_2 unit a characteristic absorption at 1640 cm^{-1} indicating that the carboxylate is coordinated to rhodium in a chelating fashion.[30]

In contrast to the IR spectrum, the ^{1}H NMR spectrum of (*Z*)-**29** reveals that in solution two isomeric forms **A** and **B** exist, one of which contains the carboxylate as a monodentate ligand. In toluene-d_8 at 233 K, the ratio of **A : B** is approximately 1 : 1. Typical features for the hexa-coordinate isomer **A** in the ^{1}H NMR spectrum are a doublet-of-triplets at δ 7.79 for the



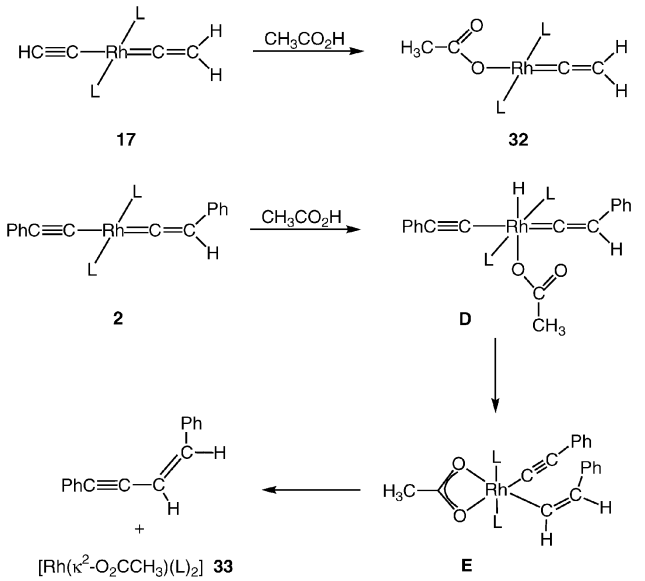
Scheme 11 (L = P*i*Pr$_3$).

vinylic proton in α position and a multiplet (doublet-of-doublets after ^{31}P-decoupling) at δ 6.60 for the CH=C*H*Ph proton in β position. For isomer **B**, the corresponding resonances appear at δ 7.60 as a doublet-of-doublets-of-triplets and at δ 6.32 as a multiplet (doublet-of-doublets after ^{31}P-decoupling). Since the signal at lower field for the C*H*=CHPh proton shows a relatively large ^{2}J(Rh,H) coupling constant, we assume that, similarly to **26**, the structure of **B** corresponds to a square-pyramid.

If a solution of (*Z*)-**29** in toluene-d_8, containing both isomers **A** and **B**, is irradiated at low temperature, a quantitative isomerization to (*E*)-**29** occurs. After evaporation of the solvent *in vacuo*, the product was isolated as a light yellow, slightly air-sensitive solid in 94% yield. The ^{1}H and ^{31}P NMR spectra of (*E*)-**29** reveal that only one isomer is formed, probably containing the carboxylate as a chelating ligand. Diagnostic for the *trans*-disposition of rhodium and the phenyl group at the C=C double bond in (*E*)-**29** is the size of the ^{1}H–^{1}H coupling constant for the signals of the vinylic protons which is larger by 3 Hz compared to isomer **A** of (*Z*)-**29**.

In the solid state, both compounds (*Z*)-**29** and (*E*)-**29** are relatively stable and rearrange very slowly at room temperature (in 5 to 7 days) to the enyne complexes (*Z*)-**30** and (*E*)-**30**. However, in solution the (*Z*)-isomer (*Z*)-**29** is significantly more labile and reacts in benzene at 25 °C in 4 h quantitatively to (*Z*)-**30**. Under the same conditions, the rearrangement of (*E*)-**29** to (*E*)-**30** is much slower and is only completed after 10 h. Isomer (*E*)-**30** is also accessible either by UV-irradiation of (*Z*)-**30** in benzene or upon treatment of the chelate complex **31** with (*E*)-PhC≡CCH=CHPh (see Scheme 11). The ^{1}H and ^{13}C NMR data for the enyne ligands in (*Z*)-**30** and (*E*)-**30** are very similar to those of the chloro compounds (*Z*)-**21** and (*E*)-**21** and thus deserve no forther comment.

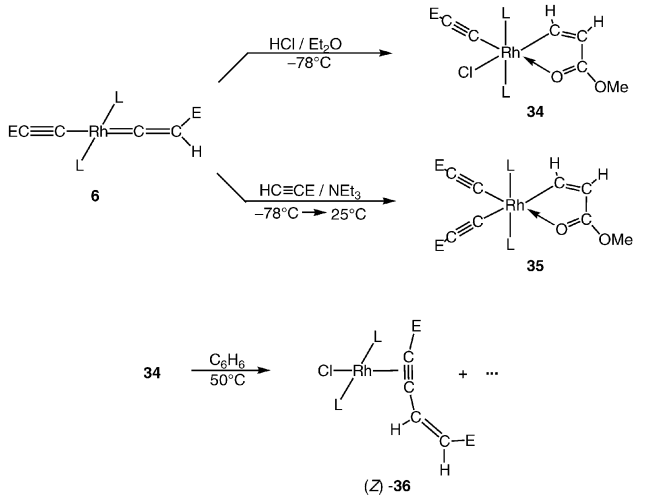
The reactions of the alkynyl(vinylidene) complexes **2** and **17** with acetic acid in benzene at room temperature proceed differently. While the "non-substituted" derivative **17** affords by protolytic cleavage of the Rh–C≡CH bond the four-coordinate rhodium vinylidene **32**, the phenyl-substituted compound **2** gives, under the same conditions, the chelate complex **33** and the (*Z*)-configurated enyne (*Z*)-PhC≡CCH=CHPh (Scheme 12). We assume that in the initial step an oxidative addition of the



Scheme 12 (L = P*i*Pr$_3$).

acid to the metal centre of **2** occurs followed by rearrangement of intermediate **D** to isomer **E**. In contrast to (*Z*)-**29**, this hexa-coordinate species is very labile at room temperature and generates *via* intramolecular C–C coupling and elimination of the enyne the acetate complex **33**. We note that the four-coordinate compound *trans*-[Rh(κ^1-O$_2$CMe)(=C=CHPh)(P*i*Pr$_3$)$_2$], previously prepared from [RhH(C≡CPh)(κ^2-O$_2$CMe)(P*i*Pr$_3$)$_2$][31] but not isolated in the reaction of **2** with acetic acid, also reacts with phenylacetylene to give **33** and (*Z*)-PhC≡CCH=CHPh.

The reaction of the CO$_2$Me-substituted alkynyl(vinylidene)-rhodium(I) compound **6** with HCl in diethyl ether at low temperature leads to the formation of complex **34**, in which the substituted vinyl unit acts as a chelating ligand (Scheme 13). In contrast to the products obtained from **2** or **17** and HCl (which are orange or red), compound **34** is a white solid, the colour being typical for hexa-coordinate rhodium(III) derivatives.

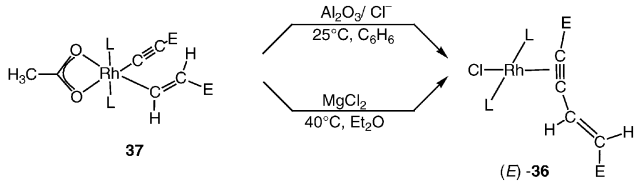


Scheme 13 (L = P*i*Pr$_3$; E = CO$_2$Me).

Under similar conditions, the starting material **6** also reacts with HC≡CCO$_2$Me in neat NEt$_3$ as solvent to afford the rhodium(III) complex **35** with the fragment *cis*-Rh(C≡CCO$_2$Me)$_2$ as a molecular building block. Diagnostic for the presence of a five-membered MCH=CHC(OMe)=O chelate ring in both **34** and **35** is the position of the C=O stretching mode in the IR spectrum,[32] which appears at 1580 cm^{-1}. In the ^{1}H and ^{13}C NMR spectra of **34** and **35**, the resonance for the RhCH proton (δ 10.14 and 10.45) as well as the signal for the corresponding carbon atom (δ 204.7 and 218.2) is observed at rather low field which is in agreement with data reported for the related iridium compound [IrH(Cl){κ^2(*C*,*O*)-CH=CHC(OMe)=O}(P*i*Pr$_3$)$_2$].[33] We note that a variety of transition-metal complexes of general composition [M{κ^2(*C*,*O*)-CR=CHC(R′)=O}(L)$_n$] are known and have been prepared either from low-valent transition-metal precursors and Michael systems RCH=CHC(O)R′ by C–H activation[33,34] or from hydridometal compounds and RC≡CC(O)R′ by insertion of the activated alkyne into the M–H bond.[32,35]

The alkynyl(vinyl)rhodium(III) derivatives **34** and **35** are relatively inert and in benzene at 50 °C react rather slowly. While in the case of **35** only decomposition occurs, the reaction of **34** leads to a mixture of products with the alkyne complex (*Z*)-**36** as the dominating species (see Scheme 13). Attempts to separate the by-products (which could not be identified) by fractional crystallization or column chromatography failed. Typical spectroscopic features of (*Z*)-**36** are the ν(C≡C) absorption in the IR spectrum at 1860 cm^{-1} and the resonances for the vinylic protons in the ^{1}H NMR spectrum at δ 6.52 and 5.77, respectively. The size of the ^3J(H,H) coupling constant of these signals (11.8 Hz) indicates that the vinylic protons are *cis*-disposed.

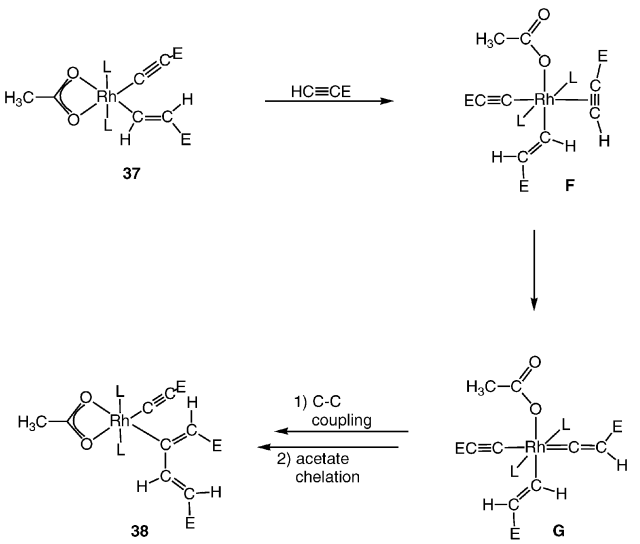
In contrast to **34** and **35**, the acetatorhodium(III) compound **37**, being previously prepared either from **6** or [RhH(C≡CCO$_2$-Me)(κ^2-O$_2$CMe)(P*i*Pr$_3$)$_2$] as the precursor,[31] is more labile. It not only reacts with CO to give *trans*-[Rh(κ^1-O$_2$CMe)(CO)(P*i*Pr$_3$)$_2$] and (*E*)-EC≡CCH=CHE (E = CO$_2$Me),[13] but also affords, in the presence of chloride ions, the four-coordinate alkyne complex (*E*)-**36** *via* intramolecular C–C coupling. By using MgCl$_2$ as the chloride source and diethyl ether as the solvent, the yield of (*E*)-**36**, isolated as a red air-stable solid, is 72%. We assume that in the initial step of the reactions shown in Scheme 14 a displacement of the acetato ligand by chloride occurs and that the intermediate [RhCl(C≡CE)(CH=CHE)(P*i*Pr$_3$)$_2$] (E = CO$_2$Me), analogously to compounds **23** and **26** (see Schemes 9 and 10), rapidly rearranges to the coupling product.



Scheme 14 (L = P*i*Pr$_3$, E = CO$_2$Me).

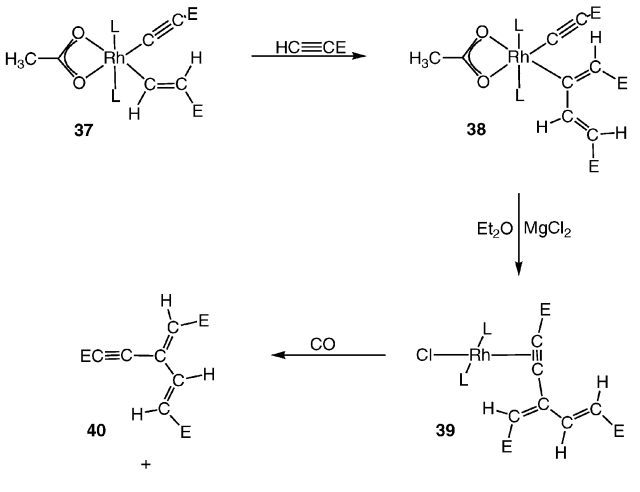
Quite surprisingly, the hexa-coordinate alkynyl(vinyl) complex **37** reacts, even at room temperature, also with methyl propiolate. In contrast to the reaction with CO,[13] a white solid analyzing as **38** is formed instead of the butenyne (*E*)-EC≡CCH=CHE (E = CO$_2$Me). As the X-ray crystal structure analysis of **38** revealed,[13] the metal centre is octahedrally coordinated with the two phosphines in *trans* position. Noteworthy is the unsymmetrical coordination of the acetato ligand (distances Rh–O = 2.151(5) and 2.260(6) Å), which is probably due to the different *trans* influence of the alkynyl and the butadienyl group. It is also worth mentioning, that the C$_4$ unit has the thermodynamically more favoured (*E*) configuration at both C=C double bonds. In agreement with the structure found in the crystal, the ^{13}C NMR spectrum of **38** displays for the carbon atoms of the butadienyl ligand four resonances at δ 163.6, 148.0, 126.9 and 118.3, which were assigned on the basis of the splitting patterns and DEPT measurements. Regarding the mechanism of formation of **38**, we assume that initially by partial opening of the acetate–metal bond one molecule of methyl propiolate is added to the rhodium centre to generate intermediate **F**. This step is followed by a rearrangement of the coordinated terminal alkyne to the isomeric vinylidene to afford **G** (Scheme 15). Subsequent migration of the vinyl unit to the α-carbon atom of the vinylidene and chelation of the acetate ligand would finally

yield the product. It should be mentioned that upon treatment of *trans*-[Rh(CH=CH$_2$)(=C=CHPh)(P*i*Pr$_3$)$_2$] with CO a similar migratory insertion occurs to give a carbonylrhodium(I) complex with σ-bonded C(=CHPh)CH=CH$_2$ as a ligand.[10]



Scheme 15 (L = P*i*Pr$_3$, E = CO$_2$Me).

In the absence of a further substrate, compound **38** is thermally stable and even on heating to 60 °C does not react by C–C coupling. However, the coupling of the alkynyl and butadienyl ligands at rhodium can be achieved if a solution of **38** in diethyl ether is treated with an excess of MgCl$_2$·6H$_2$O and Na$_2$CO$_3$ and then stirred for 4 h at 40 °C. From the crude reaction product, a deep-red air-stable solid analyzing as **39** has been isolated in 79% yield (Scheme 16). Owing to the X-ray crystal structure analysis of **39**,[13] the metal centre is coordinated in a distorted square-planar fashion with the phosphorus, chlorine, rhodium atoms and the alkyne carbon atom carrying the CO$_2$Me group lying in the same plane. The second alkyne carbon atom is located significantly above this plane. However, despite the unsymmetrical coordination of the RC≡CR′ moiety to the metal centre, the two Rh–C distances are nearly identical. The butadienyl substituent at the C≡C bond still has the (*E*,*E*) configuration which illustrates that during the C–C coupling process no (*E*)/(*Z*) isomerization takes place. In the ^{1}H NMR spectrum of **39**, the resonances of the protons of the C$_4$ substituent are observed at δ 9.10 (doublet), 8.00 (singlet) and 7.40 (doublet) and are thus shifted to lower field, compared to precursor **38**.



Scheme 16 (L = P*i*Pr$_3$, E = CO$_2$Me).

Similarly to the butenyne complex (*Z*)-**21** (see Scheme 9), compound **39** reacts with CO in benzene readily at room temperature. A rapid ligand substitution occurs which is indicated by an instantaneous change of colour from deep-red to light yellow. Equimolar amounts of both the carbonylrhodium(I) derivative **24** and the hexadienyne **40** are formed in virtually quantitative yield. The composition of **40** has been substantiated by GC/MS and ^{1}H NMR spectroscopy. We note that, in contrast to the reaction of [Ni(CO)$_2$(PPh$_3$)$_2$] with methyl propiolate,[36] in the stepwise rhodium-assisted trimerization of HC≡CCO$_2$Me no cyclic C$_6$H$_3$(C≡CCO$_2$Me)$_3$ isomer can be detected. As far as we know, only in the oligomerization of ferrocenylethyne, catalyzed by [Ni(CO)$_2$(PPh$_3$)$_2$], a branched trimer (*E*,*E*)-FcC≡C–C(=CHFc)CH=CHFc [Fc = (η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)], structurally related to **40**, is formed apart from the corresponding butenyne and benzene derivatives.[37]

Conclusion

The results reported in this paper illustrate that the coupling of the two carbon-bonded ligands in four-coordinate alkynyl(vinylidene)rhodium(I) complexes can be achieved by two different routes. While treatment of *trans*-[Rh(C≡CR)(=C=CHR′)(P*i*Pr$_3$)$_2$] with CO yields the butenynylrhodium(I) derivatives *trans*-[Rh{η^1-(*Z*)-C(=CHR′)C≡CR}(CO)(P*i*Pr$_3$)$_2$] by migratory insertion of the vinylidene unit into the alkynyl–metal bond, the same starting materials react with HCl, at low temperature, to give five-coordinate alkynyl(vinyl)rhodium(III) compounds which rearrange upon warming to give the alkyne complexes *trans*-[RhCl{η^2-(*Z*)-RC≡CCH=CHR′}(P*i*Pr$_3$)$_2$]. The reactions of *trans*-[Rh(C≡CPh)(=C=CHPh)(P*i*Pr$_3$)$_2$] with carboxylic acids R′CO$_2$H (R′ = CF$_3$, CH$_3$) proceed similarly and afford either the four-coordinate butenynerhodium(I) complex *trans*-[Rh(κ^1-O$_2$CCF$_3$){η^2-(*Z*)-PhC≡CCH=CHPh}(P*i*Pr$_3$)$_2$] or [Rh(κ^2-O$_2$CCH$_3$)(P*i*Pr$_3$)$_2$] and free butenyne (*Z*)-PhC≡C-CH=CHPh. An interesting aspect of the reactivity of the compounds *trans*-[Rh{η^1-(*Z*)-C(=CHR)C≡CR}(CO)(P*i*Pr$_3$)$_2$] and *trans*-[Rh{η^1-(*E*)-C(=CHR)C≡CR}(CO)(P*i*Pr$_3$)$_2$] (R = Ph, *t*Bu) is that upon treatment with carboxylic acids R′CO$_2$H either the butenyne (*Z*)/(*E*)-RC≡CCH=CHR or a mixture of the butenyne and the isomeric butatriene is formed, the ratio depending on both R and R′. Another noteworthy result of this work is that the hexa-coordinate alkynyl(vinyl) complex [Rh(κ^2-O$_2$CCH$_3$)(C≡CE)(CH=CHE)(P*i*Pr$_3$)$_2$] (E = CO$_2$Me) reacts with HC≡CE by insertion of the alkyne into the vinyl–rhodium bond to give the butadienyl–metal derivative [Rh(κ^2-O$_2$CMe)(C≡CE){η^1-(*E*,*E*)-C(=CHE)CH=CHE}(P*i*Pr$_3$)$_2$], which in the presence of MgCl$_2$ undergoes an intramolecular C–C coupling to yield four-coordinate *trans*-[RhCl{η^2-(*E*,*E*)-EC≡CC(=CHE)CH=CHE}(P*i*Pr$_3$)$_2$]. The reaction of this compound with CO generates the formerly unknown branched trisubstituted hexadienyne (*E*,*E*)-EC≡CC(=CHE)CH=CHE, formally built up by three alkyne molecules HC≡CE.

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **2, 5, 6**,[14] **10**,[38] **11, 13, 14, 17**,[14] **25**[39] and **31**[40] were prepared as described in the literature. NMR spectra were recorded at room temperature (if not otherwise stated) on Jeol FX 90 Q, Bruker AC 200 and Bruker AMX 400 instruments. IR spectra were recorded on a IFS 25 FT-IR infrared spectrometer, and mass spectra on a Finnigan 90 MAT instrument. Melting points were measured by differential thermal analysis (DTA) with a Thermoanalyzer Du Pont 900. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; vt, virtual triplet; m, multiplet; br, broadened signal; coupling constants *J* and *N* in Hz; *N* = ^3J(PH) + ^5J(PH) or ^2J(PC) + ^4J(PC).

Preparations

***trans*-[Rh{η¹-(*Z*)-C(=CHPh)C≡CPh}(CO)(P*i*Pr$_3$)$_2$] (*Z*)-7.** A slow stream of CO was passed through a solution of **2** (123 mg, 0.20 mmol) in pentane (10 cm^3) at −40 °C. A smooth change of colour from blue-green to yellow occurred. After the solution was stirred for 5 min, it was concentrated *in vacuo* to *ca.* 2 cm^3 and then stored at −78 °C for 5 days. A pale yellow solid precipitated, which was separated from the mother liquor, washed twice with 0.5 cm^3 portions of pentane (−20 °C) and dried: yield 100 mg (78%); mp 138 °C (decomp.) (Found: C, 64.35; H, 8.62. $C_{35}H_{53}OP_2Rh$ requires C, 64.21; H, 8.16%). IR (hexane): (C≡C) 2155, (CO) 1945 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 8.61, 7.53 (2 H each, both m, *ortho*-H of C_6H_5), 8.02 [1 H, dt, J(Rh,H) = 2.4, J(P,H) = 2.3 Hz, =C*H*Ph], 7.31 − 6.93 (6 H, br m, *meta*- and *para*-H of C_6H_5), 2.37 (6 H, m, PC*H*CH$_3$), 1.33 [18 H, dvt, N = 13.9, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.08 [18 H, dvt, N = 13.2, J(H,H) = 7.0 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 195.8 [dt, J(Rh,C) = 55.8, J(P,C) = 15.5 Hz, RhCO], 159.7 [dt, J(Rh,C) = 28.4, J(P,C) = 14.2 Hz, Rh*C*=C], 146.4 [t, J(P,C) = 4.3 Hz, =*C*HPh], 143.8 [d, J(Rh,C) = 1.9 Hz, *ipso*-C of CHPh], 131.1, 129.3, 128.5, 127.8, 127.5, 126.5, 125.9 (all s, C_6H_5), 102.6 [t, J(P,C) = 1.9 Hz, *C*≡CPh], 97.5 (s, C≡*C*Ph), 26.4 (vt, N = 20.3 Hz, P*C*HCH$_3$), 20.8, 19.8 (both s, PCH*C*H$_3$); δ_P (36.2 MHz) 43.1 [d, J(Rh,P) = 139.2 Hz].

***trans*-[Rh{η¹-(*Z*)-C(=CH*t*Bu)C≡C*t*Bu}(CO)(P*i*Pr$_3$)$_2$] (*Z*)-8.** This compound was prepared as described for (*Z*)-**7**, from **5** (120 mg, 0.20 mmol) and CO in diethyl ether (5 cm^3). Yellow microcrystalline solid: yield 102 mg (81%); mp 94 °C (decomp.) (Found: C, 60.54; H, 10.26. $C_{31}H_{61}OP_2Rh$ requires C, 60.58; H, 10.00%). IR (KBr): (C≡C) 2160, (CO) 1930 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 6.81 [1 H, dt, J(Rh,H) = 2.3, J(P,H) = 2.2 Hz, =C*H*t*Bu*], 2.46 (6 H, m, PC*H*CH$_3$), 1.33 [18 H, dvt, N = 13.1, J(H,H) = 7.0 Hz, PCHC*H*$_3$], 1.32 [18 H, dvt, N = 13.4, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.29, 1.28 (9 H each, both s, CCH$_3$); δ_C (50.3 MHz) 196.2 [dt, J(Rh,C) = 55.6, J(P,C) = 16.5 Hz, RhCO], 155.2 [t, J(P,C) = 4.5 Hz, =*C*H*t*Bu], 143.2 [dt, J(Rh,C) = 27.4, J(P,C) = 13.7 Hz, Rh*C*=C], 100.6 (s, C≡*C*t*Bu*), 90.2 [td, J(P,C) = 1.8, J(Rh,C) = 1.3 Hz, *C*≡C*t*Bu], 34.3 [td, J(P,C) = 1.3, J(Rh,C) = 1.0 Hz, =CH*C*CH$_3$], 32.0 (s, ≡CC*C*H$_3$), 31.2 [t, J(P,C) = 1.8 Hz, =CHC*C*H$_3$], 28.8 (s, ≡*C*CH$_3$), 26.4 [dvt, N = 18.9, J(Rh,C) = 1.0 Hz, P*C*HCH$_3$], 20.9, 20.3 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 40.8 [d, J(Rh,P) = 143.7 Hz].

***trans*-[Rh{η¹-(*Z*)-C(=CHCO$_2$Me)C≡CCO$_2$Me}(CO)(P*i*Pr$_3$)$_2$] (*Z*)-9.** This compound was prepared as described for (*Z*)-**7**, from **6** (98 mg, 0.17 mmol) and CO in pentane (10 cm^3). Light yellow, air-stable crystals: yield 84 mg (82%); mp 85 °C (decomp.) (Found: C, 52.46; H, 7.91. $C_{27}H_{49}O_5P_2Rh$ requires C, 52.43; H, 7.98%). IR (hexane): (C≡C) 2155, (CO) 1955 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 7.21 [1 H, td, J(P,H) = 2.7, J(Rh,H) = 2.6 Hz, =C*H*CO$_2$Me], 3.51 (3 H, s, =CHCO$_2$C*H*$_3$), 3.34 (3 H, s, ≡CCO$_2$C*H*$_3$), 2.23 (6 H, m, PC*H*CH$_3$), 1.35 [18 H, dvt, N = 14.0, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.13 [18 H, dvt, N = 13.3, J(H,H) = 7.0 Hz, PCHC*H*$_3$]; δ_C (50.3 MHz) 196.3 [dt, J(Rh,C) = 57.8, J(P,C) = 15.6 Hz, RhCO], 186.6 [dt, J(Rh,C) = 27.8, J(P,C) = 13.9 Hz, Rh*C*=C], 169.7 [dt, J(Rh,C) = 1.9, J(P,C) = 1.4 Hz, =CH*C*O$_2$CH$_3$], 155.6 (s, ≡C*C*O$_2$CH$_3$), 135.1 [td, J(P,C) = 3.9, J(Rh,C) = 1.9 Hz, =*C*HCO$_2$CH$_3$], 100.4 (s, C≡*C*CO$_2$CH$_3$), 96.6 [t, J(P,C) = 1.6 Hz, *C*≡CO$_2$CH$_3$], 51.5 (s, C≡CO$_2$*C*H$_3$), 50.7 (br s, =CHCO$_2$*C*H$_3$), 26.4 [dvt, N = 20.4, J(Rh,C) = 1.4 Hz, P*C*HCH$_3$], 20.5, 19.5 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 44.1 [d, J(Rh,P) = 136.3 Hz].

***trans*-[Rh{η¹-(*E*)-C(=CHPh)C≡CPh}(CO)(P*i*Pr$_3$)$_2$] (*E*)-7.** *Method a.* A solution of (*Z*)-**7** (80 mg, 0.12 mmol) in C_6D_6 (0.5 cm^3) was irradiated at 15 °C with a UV lamp (Osram 500 W, water filter, λ = 300 nm) for 5 h. A change of colour from light yellow to orange-brown occurred. After the solvent was evaporated *in vacuo*, the oily residue was dissolved in hexane (1 cm^3) and the solution was chromatographed on Al_2O_3 (basic, activity grade V, height of column 5 cm). With hexane/toluene (5 : 1) an orange fraction was eluted which was brought to dryness *in vacuo*. The residue was recrystallized from pentane to give orange, air-stable crystals: yield 47 mg (59%).

Method b. A solution of **10** (141 mg, 0.32 mmol) in benzene (5 cm^3) was treated with PhC≡CC≡CPh (38 mg, 0.19 mmol) and stirred for 4 h at room temperature. The solvent was evaporated *in vacuo*, and the residue was extracted with pentane (25 cm^3). The extract was brought to dryness *in vacuo*, the remaining orange residue was washed three times with 2 cm^3 portions of pentane and dried: yield 155 mg (75%); mp 108 °C (Found: C, 64.42; H, 8.45. $C_{35}H_{53}OP_2Rh$ requires C, 64.21; H, 8.16%). IR (hexane): (C≡C) 2120, (CO) 1945 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 8.12, 7.57 (2 H each, both m, *ortho*-H of C_6H_5), 7.28, 7.12, 7.03 (2 H each, all m, *meta*- and *para*-H of C_6H_5), 6.91 [1 H, dt, J(Rh,H) = 1.8, J(P,H) = 1.8 Hz, =C*H*Ph], 2.38 (6 H, m, PC*H*CH$_3$), 1.31 [18 H, dvt, N = 13.3, J(H,H) = 6.8 Hz, PCHC*H*$_3$], 1.27 [18 H, dvt, N = 13.5, J(H,H) = 6.8 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 196.5 [dt, J(Rh,C) = 57.2, J(P,C) = 14.8 Hz, RhCO], 152.1 [dt, J(Rh,C) = 26.9, J(P,C) = 14.3 Hz, Rh*C*=C], 144.4 [t, J(P,C) = 5.0 Hz, =*C*HPh], 141.1 [br d, J(Rh,C) = 2.4 Hz, *ipso*-C of CHPh], 130.8, 128.7, 128.6, 128.5, 127.4, 126.7, 125.6 (all s, C_6H_5), 106.0 (s, *C*≡CPh), 98.0 (s, C≡*C*Ph), 26.2 (vt, N = 19.6 Hz, P*C*HCH$_3$), 20.5, 20.4 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 45.1 [d, J(Rh,P) = 140.7 Hz].

***trans*-[Rh{η¹-(*E*)-C(=CH*t*Bu)C≡C*t*Bu}(CO)(P*i*Pr$_3$)$_2$] (*E*)-8.**

Method a. Analogously as described for (*E*)-**7**, method a), from (*Z*)-**8** (60 mg, 0.10 mmol) in C_6D_6 (0.5 cm^3); time of irradiation 2 h. Yellow microcrystalline solid: yield 45 mg (74%).

Method b. A solution of (*Z*)-**8** (60 mg, 0.10 mmol) in benzene (2 cm^3) was stirred for 6 h at 40 °C. After the solution was cooled to room temperature, the solvent was evaporated *in vacuo*. The residue was dissolved in pentane (1 cm^3) and the solution was stored for 12 h at −78 °C. Yellow air-stable crystals precipitated, which were separated from the mother liquor, washed twice with 0.5 cm^3 portions of pentane (−20 °C) and dried; yield 52 mg (86%); mp 88 °C (Found: C, 60.24; H, 10.20. $C_{31}H_{61}OP_2Rh$ requires C, 60.58; H, 10.00%). IR (KBr): (C≡C) 2175, (CO) 1930 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 5.44 [1 H, dt, J(Rh,H) = 1.9, J(P,H) = 1.9 Hz, =C*H*t*Bu*], 2.44 (6 H, m, PC*H*CH$_3$), 1.36 (9 H, s, =CHCC*H*$_3$), 1.33 [18 H, dvt, N = 13.5, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.31 [18 H, dvt, N = 12.8, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.28 (9 H, s, ≡CCCH$_3$); δ_C (100.6 MHz) 196.4 [dt, J(Rh,C) = 56.4, J(P,C) = 15.1 Hz, RhCO], 150.7 [t, J(P,C) = 5.0 Hz, =*C*H*t*Bu], 145.9 [dt, J(Rh,C) = 26.2, J(P,C) = 13.9 Hz, Rh*C*=C], 112.3 (s, C≡*C*t*Bu*), 85.6 [td, J(P,C) = 1.9, J(Rh,C) = 1.0 Hz, *C*≡C*t*Bu], 36.1 [dt, J(Rh,C) = 1.1, J(P,C) = 1.0 Hz, =CH*C*CH$_3$], 31.4 (s, ≡CC*C*H$_3$), 30.7 [t, J(P,C) = 1.2 Hz, =CHC*C*H$_3$], 29.2 (s, ≡*C*CH$_3$), 25.8 [dvt, N = 19.5, J(Rh,C) = 1.4 Hz, P*C*HCH$_3$], 20.8, 20.4 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 44.5 [d, J(Rh,P) = 145.9 Hz].

***trans*-[Rh{η¹-C(=CH$_2$)C≡CPh}(CO)(P*i*Pr$_3$)$_2$] 12.** This compound was prepared as described for (*Z*)-**7**, from **11** (97 mg, 0.18 mmol) and CO in pentane (5 cm^3). Pale yellow, air-stable crystals: yield 84 mg (82%); mp 93 °C (decomp.) (Found: C, 60.54; H, 8.49. $C_{29}H_{49}OP_2Rh$ requires C, 60.20; H, 8.54%). MS (70 eV): *m*/*z* 578 (M^+). IR (hexane): (C≡C) 2150, (CO) 1940 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.53 (2 H, m, *ortho*-H of C_6H_5), 7.09 (2 H, m, *meta*-H of C_6H_5), 6.97 (1 H, m, *para*-H of C_6H_5), 6.69 [1 H, ddt, J(H,H) = 4.9, J(Rh,H) = 2.8, J(P,H) = 2.6 Hz, one H of =CH$_2$ *trans* to Rh], 5.57 [1 H, dtd, J(H,H) = 4.9, J(P,H) = 2.1, J(Rh,H) = 1.5 Hz, one H of =CH$_2$ *cis* to Rh], 2.42 (6 H, m, PC*H*CH$_3$), 1.33 [18 H, dvt, N = 13.1, J(H,H) = 6.8 Hz, PCHC*H*$_3$], 1.30 [18 H, dvt, N = 13.3, J(H,H) = 6.9 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 196.7 [dt, J(Rh,C) = 56.7, J(P,C) = 14.7 Hz, RhCO], 159.9 [dt, J(Rh,C) = 27.6, J(P,C) = 14.6 Hz, Rh*C*=C], 130.3 [t, J(P,C) = 4.8 Hz, =CH$_2$], 131.0, 128.5, 127.5, 126.4 (all s, C_6H_5), 100.8 [t, J(P,C) = 1.8 Hz, *C*≡CPh], 95.8

(s, C≡*C*Ph), 26.1 (vt, $N = 20.0$ Hz, P*C*HCH$_3$), 20.6, 20.3 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 46.5 [d, J(Rh,P) = 140.4 Hz].

***trans*-[Rh{η¹-(*Z*)-C(=CHCO$_2$Me)C≡CPh}(CO)(P*i*Pr$_3$)$_2$] (*Z*)-15.** This compound was prepared as described for (*Z*)-**7**, from **13** (192 mg, 0.33 mmol) and CO in pentane (10 cm^3) at −40 °C. Yellow air-stable crystals: yield 159 mg (75%); mp 126 °C (Found: C, 58.78; H, 8.21. $C_{31}H_{51}O_3P_2Rh$ requires C, 58.49; H, 8.07%). IR (KBr): (C≡C) 2150, (CO) 1935 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.43 (2 H, m, *ortho*-H of C_6H_5), 7.35 [1 H, dt, J(Rh,H) = 2.4, J(P,H) = 2.4 Hz, =C*H*CO$_2$Me], 7.06 (2 H, m, *meta*-H of C_6H_5), 6.97 (1 H, m, *para*-H of C_6H_5), 3.59 (3 H, s, CO$_2$CH$_3$), 2.31 (6 H, m, PC*H*CH$_3$), 1.38 [18 H, dvt, $N = 13.8$, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.20 [18 H, dvt, $N = 13.2$, J(H,H) = 7.0 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 196.9 [dt, J(Rh,C) = 56.7, J(P,C) = 15.6 Hz, RhCO], 191.6 [dt, J(Rh,C) = 28.4, J(P,C) = 14.0 Hz, Rh*C*=C], 170.4 [dt, J(Rh,C) = 1.4, J(P,C) = 1.4 Hz, *C*O$_2$CH$_3$], 134.0 [td, J(P,C) = 3.7, J(Rh,C) = 1.0 Hz, =*C*HCO$_2$CH$_3$], 131.3, 128.6, 127.5, 126.3 (all s, C_6H_5), 106.3 (s, C≡*C*Ph), 99.4 [t, J(P,C) = 1.6 Hz, *C*≡CPh], 50.5 (s, CO$_2$*C*H$_3$), 26.4 [dvt, $N = 20.0$, J(Rh,C) = 1.3 Hz, P*C*HCH$_3$], 20.7, 19.7 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 43.9 [d, J(Rh,P) = 140.0 Hz].

***trans*-[Rh{η¹-(*Z*)-C(=CHCO$_2$Me)C≡C*t*Bu}(CO)(P*i*Pr$_3$)$_2$] (*Z*)-16.** This compound was prepared as described for (*Z*)-**7**, from **14** (117 mg, 0.22 mmol) and CO in pentane (10 cm^3) at −40 °C. Yellow air-stable crystals: yield 104 mg (85%); mp 121 °C (Found: C, 56.58; H, 9.11. $C_{29}H_{55}O_3P_2Rh$ requires C, 56.49; H, 8.99%). IR (hexane): (CO) 1940 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.25 [1 H, dt, J(Rh,H) = 2.4, J(P,H) = 2.4 Hz, =C*H*CO$_2$Me], 3.56 (3 H, s, CO$_2$CH$_3$), 2.31 (6 H, m, PC*H*CH$_3$), 1.40 [18 H, dvt, $N = 13.8$, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.23 (9 H, s, CCH$_3$), 1.22 [18 H, dvt, $N = 13.1$, J(H,H) = 7.0 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 197.0 [dt, J(Rh,C) = 56.2, J(P,C) = 15.8 Hz, RhCO], 194.1 [dt, J(Rh,C) = 28.7, J(P,C) = 14.3 Hz, Rh*C*=C], 170.5 [dt, J(Rh,C) = 1.4, J(P,C) = 1.4 Hz, *C*O$_2$CH$_3$], 133.6 [td, J(P,C) = 3.8, J(Rh,C) = 1.0 Hz, =*C*HCO$_2$CH$_3$], 113.6 (s, C≡*C*t*Bu*), 89.4 [t, J(P,C) = 1.6 Hz, *C*≡C*t*Bu], 50.3 (s, CO$_2$*C*H$_3$), 31.3 (s, C*C*H$_3$), 29.0 (s, *C*CH$_3$), 26.4 [dvt, $N = 19.9$, J(Rh,C) = 1.4 Hz, P*C*HCH$_3$], 20.8, 19.8 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 43.9 [d, J(Rh,P) = 141.6 Hz].

***trans*-[Rh{η¹-C(=CH$_2$)C≡CH}(CO)(P*i*Pr$_3$)$_2$] 18.** This compound was prepared as described for (*Z*)-**7**, from **17** (80 mg, 0.17 mmol) and CO in pentane (4 cm^3) at −78 °C. Yellow, moderately air-stable crystals: yield 71 mg (84%); mp 90 °C (decomp.) (Found: C, 55.35; H, 9.28. $C_{23}H_{45}OP_2Rh$ requires C, 54.98; H, 9.03%). IR (KBr): ν(≡CH) 3305, ν(C≡C) 2055, (CO) 1935 cm^{-1}. NMR (toluene-d_8, −20 °C): δ_H (400 MHz) 6.66 [1 H, ddt, J(H,H) = 5.0, J(Rh,H) = 2.8, J(P,H) = 2.1 Hz, one H of =CH$_2$ *trans* to Rh], 5.52 [1 H, ddt, J(H,H) = 5.0, J(Rh,H) = 2.2, J(P,H) = 2.1 Hz, one H of =CH$_2$ *cis* to Rh], 3.41 (s, C≡CH), 2.24 (6 H, m, PC*H*CH$_3$), 1.31 [18 H, dvt, $N = 13.3$, J(H,H) = 7.0 Hz, PCHC*H*$_3$], 1.28 [18 H, dvt, $N = 13.8$, J(H,H) = 7.2 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 196.6 [dt, J(Rh,C) = 56.3, J(P,C) = 14.8 Hz, RhCO], 159.7 [dt, J(Rh,C) = 27.6, J(P,C) = 15.0 Hz, Rh*C*=C], 132.2 [t, J(P,C) = 4.7 Hz, =CH$_2$], 94.6 [t, J(P,C) = 1.8 Hz, *C*≡CH], 82.2 (s, C≡*C*H), 26.1 [vt, $N = 20.0$ Hz, P*C*HCH$_3$], 20.6, 20.4 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 46.9 [d, J(Rh,P) = 139.8 Hz]. *Note*: The NMR spectra measured at room temperature display also some signals assigned to **19**.

Isomerization of 18 to *trans*-[Rh(η¹-CH=C=C=CH$_2$)(CO)(P*i*Pr$_3$)$_2$] 19. A solution of **18**, generated from **17** (51 mg, 0.11 mmol) and CO in toluene-d_8 (0.5 cm^3) at −78 °C, was slowly warmed to room temperature. The NMR spectra indicate that a mixture of **18** and **19** in the ratio 65 : 35 is formed. Data for **19**: NMR (toluene-d_8): δ_H (400 MHz) 7.93 [1 H, dddt, J(Rh,H) = 3.8, J(P,H) = 4.2, J(H,H) = 10.5 and 10.7 Hz, RhCH], 5.45 [1 H, dddt, J(H,H) = 10.7 and 5.2, J(P,H) = 1.9, J(Rh,H) = 1.2 Hz, one H of =CH$_2$], 5.23 [1 H, dddt, J(H,H) = 10.5 and 5.2, J(P,H) = 2.1, J(Rh,H) = 1.5 Hz, one H of =CH$_2$], 2.24 (6 H, m, PC*H*CH$_3$), 1.22 [36 H, dvt, $N = 13.8$, J(H,H) = 7.0 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 196.9 [dt, J(Rh,C) = 58.1, J(P,C) = 13.8 Hz, RhCO], 185.9 [td, J(P,C) = 3.9, J(Rh,C) = 1.9 Hz, RhCH=*C*], 162.6 [t, J(P,C) = 4.8 Hz, RhCH=C=*C*], 154.3 [dt, J(Rh,C) = 27.7, J(P,C) = 17.2 Hz, RhCH], 84.8 [t, J(P,C) = 3.3 Hz, =CH$_2$], 25.8 [vt, $N = 20.7$ Hz, P*C*HCH$_3$], 20.2 (s, PCH*C*H$_3$); δ_P (162.0 MHz) 50.3 [d, J(Rh,P) = 136.6 Hz].

Generation of *trans*-[Rh(C≡CCH=CH$_2$)(CO)(P*i*Pr$_3$)$_2$] 20. A solution containing a mixture of **18** and **19** (51 mg, 0.10 mmol) in C_6D_6 (0.5 cm^3) was irradiated at 15 °C with a UV lamp (Osram 500 W, water filter, $\lambda > 300$ nm) for 45 min. The NMR spectra indicate that besides some unidentified by-products compound **20** was formed as the dominant species: yield *ca.* 70%. Data for **20**: NMR (C_6D_6): δ_H (400 MHz) 6.08 [1 H, ddt, J(H,H) = 17.3 and 10.7, J(P,H) = 1.9 Hz, C*H*=CH$_2$], 5.35 [1 H, ddt, J(H,H) = 17.3 and 3.0, J(P,H) = 1.0 Hz, one H of =CH$_2$], 4.99 [1 H, ddt, J(H,H) = 10.7 and 3.0, J(P,H) = 0.7 Hz, one H of =CH$_2$], 2.46 (6 H, m, PC*H*CH$_3$), 1.31 [36 H, dvt, $N = 13.8$, J(H,H) = 7.1 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 196.5 [dt, J(Rh,C) = 58.4, J(P,C) = 13.6 Hz, RhCO], 126.3 [dt, J(Rh,C) = 41.3, J(P,C) = 22.7 Hz, Rh*C*≡C], 121.9 (br s, *C*H=CH$_2$), 119.3 [dt, J(Rh,C) = 12.6, J(P,C) = 3.2 Hz, RhC≡*C*], 117.8 [t, J(P,C) = 2.6 Hz, =CH$_2$], 26.3 [vt, $N = 22.3$ Hz, P*C*HCH$_3$], 20.5 (s, PCH*C*H$_3$); δ_P (162.0 MHz) 54.0 [d, J(Rh,P) = 127.5 Hz].

Reaction of (*E*)-7 with carboxylic acids.

Method a. A solution of (*E*)-**7** (39 mg, 0.06 mmol) in C_6D_6 (0.5 cm^3) was treated with acetic acid (0.0034 cm^3, 0.06 mmol) and stirred for 10 min at room temperature. The NMR spectra revealed that besides *trans*-[Rh(κ¹-O$_2$CCH$_3$)(CO)(P*i*Pr$_3$)$_2$][19] the butenyne (*Z*)-PhC≡CCH=CHPh was exclusively formed. It was characterized by comparison of the NMR data with those reported in the literature.[5,20]

Method b. A solution of (*E*)-**7** (39 mg, 0.06 mmol) in acetone-d_6 (0.5 cm^3) was treated with CF$_3$CO$_2$H (0.0047 cm^3, 0.06 mmol) and stirred for 10 min at room temperature. The NMR spectra revealed that besides *trans*-[Rh(κ¹-O$_2$CCF$_3$)(CO)(P*i*Pr$_3$)$_2$][19] a mixture of (*E*)/(*Z*)-PhCH=C=C=CHPh (*ca.* 95%, ratio of (*E*)/(*Z*) = 9 : 1) and (*Z*)-PhC≡CCH=CHPh (*ca.* 5%) was formed. The isomeric butatrienes were characterized by comparison of the NMR data with those reported in the literature.[7]

Reaction of (*Z*)-7 with CF$_3$CO$_2$H.

Method a. A solution of (*Z*)-**7** (39 mg, 0.06 mmol) in C_6D_6 (0.5 cm^3) was treated with CF$_3$CO$_2$H (0.0047 cm^3, 0.06 mmol) and stirred for 30 min at 40 °C. The NMR spectra revealed that besides *trans*-[Rh(κ¹-O$_2$CCF$_3$)(CO)(P*i*Pr$_3$)$_2$][19] a mixture of (*E*)/(*Z*)-PhCH=C=C=CHPh (*ca.* 90%, ratio of (*E*)/(*Z*) = 1 : 4) and (*E*)-PhC≡CCH=CHPh (*ca.* 10%) was formed. The organic products were characterized by comparison of the NMR data with those reported in the literature.[5,20,21]

Method b. A solution of (*Z*)-**7** (39 mg, 0.06 mmol) in acetone-d_6 (0.5 cm^3) was treated with CF$_3$CO$_2$H (0.0047 cm^3, 0.06 mmol) and stirred for 20 min at room temperature. The NMR spectra revealed that besides *trans*-[Rh(κ¹-O$_2$CCF$_3$)(CO)(P*i*Pr$_3$)$_2$][19] a mixture of (*E*)/(*Z*)-PhCH=C=C=CHPh (*ca.* 95%, ratio of (*E*)/(*Z*) = 45 : 55) and (*Z*)-PhC≡CCH=CHPh (*ca.* 5%) was formed. The organic products were characterized by comparison of the NMR data with those reported in the literature.[5,7,20,21]

Reaction of (*E*)-8 with carboxylic acids.

Method a. A solution of (*E*)-**8** (37 mg, 0.06 mmol) in C_6D_6 (0.5 cm^3) was treated with acetic acid (0.0034 cm^3, 0.06 mmol) and stirred for 2 h at 40 °C. The NMR spectra revealed that besides *trans*-[Rh(κ¹-O$_2$CCH$_3$)(CO)(P*i*Pr$_3$)$_2$][19] a mixture of (*E*)/(*Z*)-*t*BuCH=C=C=CH*t*Bu (*ca.* 65%, ratio of (*E*)/(*Z*) = 15 : 85) and (*Z*)-*t*BuC≡CCH=CH*t*Bu (*ca.* 35%) was formed. The butenyne[5,22,23] and the isomeric butatrienes[24,25]

were characterized by comparison of the NMR data with those reported in the literature.

Method b. A solution of (*E*)-**8** (37 mg, 0.06 mmol) in C_6D_6 (0.5 cm^3) was treated with CF_3CO_2H (0.0047 cm^3, 0.06 mmol) and stirred for 5 min at room temperature. The NMR spectra revealed that besides *trans*-[Rh(κ^1-O_2CCF_3)(CO)($PiPr_3$)$_2$][19] a mixture of (*E*)/(*Z*)-*t*BuCH=C=C=CH*t*Bu (*ca.* 20%, ratio of (*E*)/(*Z*) = 7 : 3) and (*Z*)-*t*BuC≡CCH=CH*t*Bu (*ca.* 80%) was formed. The butenyne[5,22,23] and the isomeric butatrienes[24,25] were characterized by comparison of the NMR data with those reported in the literature.

Method c. A solution of (*E*)-**8** (37 mg, 0.06 mmol) in acetone-d_6 (0.5 cm^3) was treated with CF_3CO_2H (0.0047 cm^3, 0.06 mmol) and stirred for 5 min at room temperature. The NMR spectra revealed that besides *trans*-[Rh(κ^1-O_2CCF_3)(CO)($PiPr_3$)$_2$][19] a mixture of (*E*)/(*Z*)-*t*BuCH=C=C=CH*t*Bu (*ca.* 65%, ratio of (*E*)/(*Z*) = 85 : 15) and (*Z*)-*t*BuC≡CCH=CH*t*Bu (*ca.* 35%) was formed. The butenyne[5,22,23] and the isomeric butatrienes[24,25] were characterized by comparison of the NMR data with those reported in the literature.

Reaction of (*Z*)-8 with carboxylic acids.

Method a. A solution of (*Z*)-**8** (37 mg, 0.06 mmol) in C_6D_6 (0.5 cm^3) was treated with acetic acid (0.0034 cm^3, 0.06 mmol) and stirred for 2 h at 40 °C. The NMR spectra revealed that besides *trans*-[Rh(κ^1-O_2CCH_3)(CO)($PiPr_3$)$_2$][19] a mixture of (*E*)/(*Z*)-*t*BuCH=C=C=CH*t*Bu (*ca.* 40%, ratio of (*E*)/(*Z*) = 4 : 1) and (*E*)-*t*BuC≡CCH=CH*t*Bu (*ca.* 60%) was formed. The butenyne[5,22,23] and the isomeric butatrienes[24] were characterized by comparison of the NMR data with those reported in the literature.

Method b. A solution of (*Z*)-**8** (37 mg, 0.06 mmol) in C_6D_6 (0.5 cm^3) was treated with CF_3CO_2H (0.0047 cm^3, 0.06 mmol) and stirred for 5 min at room temperature. The NMR spectra revealed that besides *trans*-[Rh(κ^1-O_2CCF_3)(CO)($PiPr_3$)$_2$][19] a mixture of (*E*)/(*Z*)-*t*BuCH=C=C=CH*t*Bu (*ca.* 75%, ratio of (*E*)/(*Z*) = 55 : 45) and (*E*)-*t*BuC≡CCH=CH*t*Bu (*ca.* 25%) was formed. The butenyne[5,22,23] and the isomeric butatrienes[24] were characterized by comparison of the NMR data with those reported in the literature.

Method c. A suspension of (*Z*)-**8** (37 mg, 0.06 mmol) in acetone-d_6 (0.5 cm^3) was treated with CF_3CO_2H (0.0047 cm^3, 0.06 mmol) and stirred for 2 h at room temperature. The NMR spectra revealed that besides *trans*-[Rh(κ^1-O_2CCF_3)(CO)($PiPr_3$)$_2$][19] a mixture of (*E*)/(*Z*)-*t*BuCH=C=C=CH*t*Bu (> 95%, ratio of (*E*)/(*Z*) = 3 : 7) and (*E*)-*t*BuC≡CCH=CH*t*Bu (< 5%) was formed. The butenyne[5,22,23] and the isomeric butatrienes[24] were characterized by comparison of the NMR data with those reported in the literature.

***trans*-[RhCl{η^2-(*Z*)-PhC≡CCH=CHPh}($PiPr_3$)$_2$] (*Z*)-21.**

Method a. A solution of **2** (102 mg, 0.16 mmol) in benzene (2 cm^3) was treated dropwise with a 0.35 M solution of HCl in benzene (0.46 cm^3, 0.16 mmol), and the mixture was stirred for 3 h at room temperature. The ^{31}P NMR spectrum indicated that besides some decomposition products a mixture of (*Z*)-**21** (*ca.* 70%) and *trans*-[RhCl(=C=CHPh)($PiPr_3$)$_2$] **22** (*ca.* 15–20%) was generated. The solvent was evaporated *in vacuo* and the residue was extracted with pentane (30 cm^3). The extract was concentrated to *ca.* 3 cm^3 *in vacuo* and then stored for 12 h at −78 °C. An orange-red microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with small amounts of pentane (−20 °C) and dried: yield 53 mg (49%).

Method b. A solution of **23** (90 mg, 0.14 mmol) in benzene (2 cm^3) was stirred for 3 h at room temperature and then worked-up as described for a). Orange-red crystals: yield 77 mg (85%); mp 119 °C (decomp.) (Found: C, 61.25; H, 8.31. $C_{34}H_{54}ClP_2Rh$ requires C, 61.58; H, 8.21%). IR (KBr): (C≡C) 1850 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 8.04, 7.51 (2 H each, m, *ortho*-H of C_6H_5), 7.20 − 6.84 (6 H, br m, *meta*- and *para*-H of C_6H_5), 6.75 [1 H, dd, J(H,H) = 12.4, J(P,H) = 1.5 Hz, C*H*=CHPh], 6.45 [1 H, d, J(H,H) = 12.4 Hz, CH=C*H*Ph], 2.37 (6 H, m, PC*H*CH_3), 1.31 [18 H, dvt, N = 13.3, J(H,H) = 6.8 Hz, PCHC*H*$_3$], 1.17 [18 H, dvt, N = 12.6, J(H,H) = 7.0 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 137.7 (s, *ipso*-C of C_6H_5), 133.7 (s, CH=*C*HPh), 130.7, 129.6, 129.4, 128.5, 127.6, 127.4, 126.9 (all s, C_6H_5), 119.5 [d, J(Rh,C) = 1.9 Hz, *C*H=CHPh], 91.7 [dt, J(Rh,C) = 17.1, J(P,C) = 3.0 Hz, Ph*C*≡C], 78.5 [d, J(Rh,C) = 12.8 Hz, PhC≡*C*], 23.3 (vt, N = 17.3 Hz, P*C*HCH$_3$), 20.8, 19.9 (both s, PCH*C*H$_3$); δ_P (36.2 MHz) 32.0 [d, J(Rh,P) = 118.7 Hz].

***trans*-[RhCl{η^2-(*E*)-PhC≡CCH=CHPh}($PiPr_3$)$_2$] (*E*)-21.**

Method a. A solution of (*Z*)-**21** (77 mg, 0.12 mmol) in benzene (2 cm^3) was irradiated with a UV lamp (Osram 500 W, water filter, λ > 300 nm) at 17 °C. The ^{31}P NMR spectrum revealed that after 30 min a quantitative isomerization had taken place. The solvent was evaporated *in vacuo* and the residue was recrystallized from pentane at −78 °C to give an orange-red microcrystalline solid: yield 62 mg (87%).

Method b. A solution of **25** (73 mg, 0.08 mmol) in diethyl ether (4 cm^3) was treated with (*E*)-PhC≡CCH=CHPh (32.5 mg, 0.16 mmol) and stirred for 5 min at room temperature. A quick change of colour from deep violet to orange-red occurred. The solution was worked-up as described for a). Orange-red solid: yield 94 mg (89%); mp 147 °C (decomp.) (Found: C, 61.35; H, 8.59. $C_{34}H_{54}ClP_2Rh$ requires C, 61.58; H, 8.21%). IR (KBr): (C≡C) 1830 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 8.15, 7.47 (2 H each, m, *ortho*-H of C_6H_5), 7.54 [1 H, d, J(H,H) = 15.6 Hz, CH=C*H*Ph], 7.21 − 7.04 (6 H, br m, *meta*- and *para*-H of C_6H_5), 6.99 [1 H, dd, J(H,H) = 15.6, J(Rh,H) = 1.7 Hz, C*H*=CHPh], 2.32 (6 H, m, PC*H*CH_3), 1.28 [18 H, dvt, N = 13.4, J(H,H) = 6.8 Hz, PCHC*H*$_3$], 1.22 [18 H, dvt, N = 13.2, J(H,H) = 6.7 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 138.3 (s, *ipso*-C of C_6H_5), 135.2 (s, CH=*C*HPh), 131.0, 130.8, 129.2, 128.1, 127.7, 126.8, 126.3 (all s, C_6H_5), 117.1 (s, *C*H=CHPh), 89.5 [dt, J(Rh,C) = 17.2, J(P,C) = 3.7 Hz, Ph*C*≡C], 82.4 [dt, J(Rh,C) = 16.1, J(P,C) = 2.1 Hz, PhC≡*C*], 24.1 (vt, N = 17.6 Hz, P*C*HCH$_3$), 20.9, 20.4 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 33.4 [d, J(Rh,P) = 116.0 Hz].

[RhCl(C≡CPh){(*Z*)-CH=CHPh}($PiPr_3$)$_2$] 23. A slow stream of gaseous HCl was passed over the solution of **2** (140 mg, 0.22 mmol) in diethyl ether (5 cm^3) at −40 °C. As soon as the colour of the solution changed from blue-green to bright red, the volatiles were evaporated *in vacuo*. The remaining red solid was washed twice with 2 cm^3 portions of pentane (−20 °C) and dried; yield 130 mg (88%); converting temperature to (*Z*)-**21** 65 °C (Found: C, 61.90; H, 7.89. $C_{34}H_{54}ClP_2Rh$ requires C, 61.58; H, 8.21%). IR (KBr): (C≡C) 2075 cm^{-1}. NMR (toluene-d_8, 233 K): δ_H (400 MHz) 8.19, 7.47 (2 H each, both m, *ortho*-H of C_6H_5), 8.09 [1 H, m, dd in $^1H\{^{31}P\}$, J(H,H) = 4.8, J(Rh,H) = 4.6 Hz, C*H*=CHPh], 7.19 − 6.93 (6 H, br m, *meta*- and *para*-H of C_6H_5), 5.76 [1 H, m, dd in $^1H\{^{31}P\}$, J(Rh,H) = 4.8, J(H,H) = 4.8 Hz, CH=C*H*Ph], 2.95 (6 H, m, PC*H*CH_3), 1.13 [18 H, dvt, N = 13.5, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.09 [18 H, dvt, N = 13.6, J(H,H) = 7.0 Hz, PCHC*H*$_3$]; δ_P (36.2 MHz) 30.5 [d, J(Rh,P) = 98.2 Hz].

Reaction of (*Z*)-21 with CO. A slow stream of CO was passed through a solution of (*Z*)-**21** (66 mg, 0.10 mmol) in C_6D_6 (0.5 cm^3) for 30 s at room temperature. The ^1H and ^{31}P NMR spectra revealed that besides *trans*-[RhCl(CO)($PiPr_3$)$_2$][41] (*E*)-PhC≡CCH=CHPh was exclusively formed. It was characterized by comparison of the NMR data with those reported in the literature.[5,20]

[RhCl(C≡CH)(CH=CH$_2$)($PiPr_3$)$_2$] 26. This compound was prepared as described for **23**, from **17** (67 mg, 0.14 mmol) and HCl in diethyl ether (10 cm^3) at −40 °C. Orange-yellow microcrystalline solid: yield 66 mg (91%); converting temperature to **27** 62 °C (Found: C, 51.64; H, 8.88. $C_{22}H_{46}ClP_2Rh$ requires C, 51.72; H, 8.68%). IR (KBr): (≡CH) 3285, (C≡C) 1960 cm^{-1}. NMR (toluene-d_8, 243 K): δ_H (90 MHz) 7.29 [1 H, ddtd, J(H,H) = 13.1

and 4.8, J(P,H) = 1.8, J(Rh,H) = 1.6 Hz, RhCH], 5.47 [1 H, dddt, J(H,H) = 13.1, J(Rh,H) = 2.4, J(P,H) = 2.3, J(H,H) = 2.2 Hz, one H of =CH_2 *cis* to Rh], 4.50 [1 H, dddt, J(Rh,H) = 4.8, J(H,H) = 4.8 and 2.2, J(P,H) = 2.1 Hz, one H of =CH_2 *trans* to Rh], 3.05 (6 H, m, PC*H*CH_3), 2.35 [1 H, dt, J(Rh,H) = 2.6, J(P,H) = 1.5 Hz, C≡CH], 1.21, 1.19 [18 H each, both dvt, N = 13.8, J(H,H) = 6.8 Hz, PCHC*H*$_3$]; δ_P (36.2 MHz) 27.2 [d, J(Rh,P) = 99.6 Hz].

Generation of *trans*-[RhCl(HC≡CCH=CH_2)(P*i*Pr_3)$_2$] 27. A solution of **26** (48 mg, 0.09 mmol) in toluene-d_8 (0.5 cm^3) was slowly warmed from −60 °C to −20 °C. The ^{31}P NMR spectrum indicated that the starting material was converted to isomer **27**: δ_P (36.2 MHz) 33.3 [d, J(Rh,P) = 117.2 Hz]. The conversion of **26** to **27** also occurred in a KBr matrix by warming from −40 °C to 0 °C; in this case the generated isomer was identified by comparison of the IR data with those reported in the literature.[17]

Conversion of 26 to *trans*-[RhCl(=C=CHCH=CH_2)(P*i*Pr_3)$_2$] 28. A solution of **26** (77 mg, 0.15 mmol) in benzene (2 cm^3) was stirred for 20 min at room temperature. The solvent was evaporated *in vacuo* and the residue recrystallized from pentane at −78 °C to give a dark green microcrystalline solid: yield 67 mg (89%). The product was characterized by comparison of the ^{1}H and ^{13}C NMR data with those reported in the literature.[17]

[Rh(κ$^{1(2)}$-O_2CCF_3)(C≡CPh){(*Z*)-CH=CHPh}(P*i*Pr_3)$_2$] (*Z*)-29. A solution of **2** (163 mg, 0.26 mmol) in diethyl ether (5 cm^3) was treated dropwise with a 0.4 M solution of CF_3CO_2H in diethyl ether (0.7 cm^3) at −40 °C. A change of colour from blue-green to yellow occurred. The solvent was evaporated *in vacuo*, the remaining light yellow solid was washed twice with 2 cm^3 portions of pentane (−20 °C) and dried; yield 141 mg (73%); converting temperature to (*Z*)-**29** 75 °C (Found: C, 58.32; H, 7.56. $C_{36}H_{54}F_3O_2P_2Rh$ requires C, 58.38; H, 7.35%). IR (KBr): (C≡C) 2105, (OCO_{as}) 1640 cm^{-1}. The NMR spectra (toluene-d_8, 233 K) revealed that in solution a mixture of two isomers **A** and **B** (see Scheme 11) in the ratio of *ca.* 1 : 1 are present: δ_H (400 MHz) 8.27, 7.73, 7.56, 7.45 (2 H each, all m, *ortho*-H of C_6H_5), 7.79 [1 H, dt, J(H,H) = 10.5, J(P,H) = 3.7 Hz, C*H*=CHPh of isomer **A**], 7.60 [1 H, ddt, J(H,H) = 7.5, J(Rh,H) = 5.2, J(P,H) = 1.7 Hz, C*H*=CHPh of isomer **B**], 7.26 − 6.94 (12 H, br m, *meta*- and *para*-H of C_6H_5), 6.60 [1 H, m, dd in ^{1}H{^{31}P}, J(H,H) = 10.5, J(Rh,H) = 1.6 Hz, CH=C*H*Ph of isomer **A**], 6.32 [1 H, m, dd in ^{1}H{^{31}P}, J(H,H) = 7.5, J(Rh,H) = 2.3 Hz, CH=C*H*Ph of isomer **B**], 2.53, 2.47 (6 H each, both m, PC*H*CH_3), 1.25 [18 H, dvt, N = 13.7, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 1.19 [18 H, dvt, N = 13.6, J(H,H) = 7.2 Hz, PCHC*H*$_3$], 1.03 [18 H, dvt, N = 13.2, J(H,H) = 7.1 Hz, PCHC*H*$_3$], 0.96 [18 H, dvt, N = 13.2, J(H,H) = 7.2 Hz, PCHC*H*$_3$]; δ_P (36.2 MHz) 27.3, 26.8 [both d, J(Rh,P) = 96.7 Hz].

[Rh(κ^2-O_2CCF_3)(C≡CPh){(*E*)-CH=CHPh}(P*i*Pr_3)$_2$] (*E*)-29. A solution of (*Z*)-**29** (63 mg, 0.09 mmol) in toluene-d_8 (1 cm^3) was irradiated at −78 °C with a UV lamp (Osram 500 W, water filter, λ > 300 nm). The ^{31}P NMR spectrum revealed that after 6 h a quantitative isomerization had taken place. After the solution was warmed to −20 °C, the solvent was evaporated *in vacuo*, the remaining light yellow solid was washed twice with 2 cm^3 portions of pentane (−20 °C) and dried; yield 58 mg (94%); converting temperature to (*E*)-**30** 89 °C (Found: C, 57.83; H, 6.99. $C_{36}H_{54}F_3O_2P_2Rh$ requires C, 58.38; H, 7.35%). IR (KBr): (C≡C) 2100, (OCO_{as}) 1630 cm^{-1}. NMR: δ_H (400 MHz, CD_2Cl_2, 295 K) 7.97 [1 H, ddt, J(H,H) = 13.4, J(Rh,H) = 2.6, J(P,H) = 2.6 Hz, C*H*=CHPh], 7.24, 7.13, 7.09 (10 H, all m, C_6H_5), 6.52 [1 H, dtd, J(H,H) = 13.4, J(P,H) = 2.1, J(Rh,H) = 1.9 Hz, CH=C*H*Ph], 2.75 (6 H, m, PC*H*CH_3), 1.38 [18 H, dvt, N = 13.8, J(H,H) = 7.0 Hz, PCHC*H*$_3$], 1.31 [18 H, dvt, N = 13.6, J(H,H) = 7.0 Hz, PCHC*H*$_3$]; δ_P (36.2 MHz, toluene-d_8, 223 K) 25.9 [d, J(Rh,P) = 98.2 Hz].

***trans*-[Rh(κ^1-O_2CCF_3){η^2-(*Z*)-PhC≡CCH=CHPh}(P*i*Pr_3)$_2$] (*Z*)-30.**

Method a. A solution of **2** (107 mg, 0.17 mmol) in benzene (2 cm^3) was treated with CF_3CO_2H (0.0134 cm^3, 0.17 mmol) and stirred for 5 h at room temperature. The ^{31}P NMR spectrum indicated that besides some decomposition products a mixture of (*Z*)-**30** (*ca.* 85%) and *trans*-[Rh(κ^1-O_2CCF_3)(=C=CHPh)(P*i*Pr_3)$_2$][31] (*ca.* 5%) was formed. The solvent was evaporated *in vacuo* and the residue was extracted with pentane (30 cm^3). The extract was concentrated to *ca.* 3 cm^3 *in vacuo* and then stored for 12 h at −78 °C. An orange-red microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with small amounts of pentane (−20 °C) and dried: yield 85 mg (67%).

Method b. A solution of (*Z*)-**29** (113 mg, 0.15 mmol) in benzene (2 cm^3) was stirred for 4 h at room temperature and then worked-up as described for a). Orange-red crystals: yield 98 mg (87%); mp 104 °C (decomp.) (Found: C, 58.48; H, 7.50. $C_{36}H_{54}F_3O_2P_2Rh$ requires C, 58.38; H, 7.35%). IR (KBr): (C≡C) 1860, ν(OCO_{as}) 1680 cm^{-1}. NMR (C_6D_6): δ_H (90 MHz) 8.37, 7.46 (2 H each, m, *ortho*-H of C_6H_5), 7.21 − 6.92 (6 H, br m, *meta*- and *para*-H of C_6H_5), 6.65 [1 H, dd, J(H,H) = 12.4, J(Rh,H) = 1.4 Hz, C*H*=CHPh], 6.45 [1 H, d, J(H,H) = 12.4 Hz, CH=C*H*Ph], 1.96 (6 H, m, PC*H*CH_3), 1.29 [18 H, dvt, N = 13.5, J(H,H) = 6.9 Hz, PCHC*H*$_3$], 1.00 [18 H, dvt, N = 12.7, J(H,H) = 6.9 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 160.4 [q, J(F,C) = 35.1 Hz, CF_3CO_2], 137.4 (s, *ipso*-C of C_6H_5), 134.1 (s, CH=*C*HPh), 131.0, 129.9, 129.6, 128.6, 127.9, 127.8, 127.6 (all s, C_6H_5), 118.3 (s, *C*H=CHPh], 116.9 [q, J(F,C) = 292.8 Hz, CF_3CO_2], 87.8 [dt, J(Rh,C) = 17.8, J(P,C) = 2.3 Hz, Ph*C*≡C], 72.4 [d, J(Rh,C) = 13.4 Hz, PhC≡*C*], 23.0 (vt, N = 16.8 Hz, P*C*HCH$_3$), 20.6, 19.3 (both s, PCH*C*H$_3$); δ_P (36.2 MHz) 30.0 [d, J(Rh,P) = 121.6 Hz].

***trans*-[Rh(κ^1-O_2CCF_3){η^2-(*E*)-PhC≡CCH=CHPh}(P*i*Pr_3)$_2$] (*E*)-30.**

Method a. A solution of (*E*)-**29** (97 mg, 0.13 mmol) in benzene (2 cm^3) was stirred for 10 h at room temperature. A change of colour from yellow to orange-red occurred. The solvent was evaporated *in vacuo* and the residue was recrystallized from pentane at −78 °C. Orange-red microcrystalline solid: yield 85 mg (88%).

Method b. A solution of (*Z*)-**30** (73 mg, 0.10 mmol) in benzene (1 cm^3) was irradiated with a UV lamp (Osram 500 W, water filter, λ > 300 nm) at 17 °C. The ^{31}P NMR spectrum revealed that after 1 h a quantitative isomerization had taken place. The solution was worked-up as described for a). Orange-red solid: yield 98 mg (87%).

Method c. A solution of **31** (69 mg, 0.13 mmol) in diethyl ether (4 cm^3) was treated with (*E*)-PhC≡CCH=CHPh (26.2 mg, 0.13 mmol) and stirred for 3 min at room temperature. The solution was worked-up as described for a). Orange-red solid: yield 85 mg (89%); mp 98 °C (decomp.) (Found: C, 58.60; H, 7.39. $C_{36}H_{54}F_3O_2P_2Rh$ requires C, 58.38; H, 7.35%). IR (KBr): (C≡C) 1840, ν(OCO_{as}) 1690 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 8.35, 7.50 (2 H each, m, *ortho*-H of C_6H_5), 7.79 [1 H, d, J(H,H) = 15.7 Hz, CH=C*H*Ph], 7.23 − 7.04 (6 H, br m, *meta*- and *para*-H of C_6H_5), 6.93 [1 H, dd, J(H,H) = 15.7, J(Rh,H) = 1.5 Hz, C*H*=CHPh], 1.96 (6 H, m, PC*H*CH_3), 1.22 [18 H, dvt, N = 13.4, J(H,H) = 6.8 Hz, PCHC*H*$_3$], 1.10 [18 H, dvt, N = 13.2, J(H,H) = 6.8 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 160.4 [q, J(F,C) = 35.2 Hz, CF_3CO_2], 137.8 (s, *ipso*-C of C_6H_5), 136.3 (s, CH=*C*HPh), 130.9, 130.1, 129.3, 128.3, 128.0, 127.3, 126.4 (all s, C_6H_5), 117.0 [q, J(F,C) = 292.8 Hz, *C*F_3CO_2], 115.9 (s, *C*H=CHPh], 84.7 [dt, J(Rh,C) = 18.2, J(P,C) = 3.3 Hz, Ph*C*≡C], 77.4 [dt, J(Rh,C) = 16.4, J(P,C) = 2.2 Hz, PhC≡*C*], 23.6 (vt, N = 17.0 Hz, P*C*HCH$_3$), 20.4, 19.8 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 33.4 [d, J(Rh,P) = 116.0 Hz].

***trans*-[Rh(κ^1-O_2CCH_3)(=C=CH_2)(P*i*Pr_3)$_2$] 32.** A solution of **17** (81 mg, 0.17 mmol) in benzene (1 cm^3) was treated

with acetic acid (0.01 cm^3, 0.17 mmol) and stirred for 1 h at room temperature. The solvent was evaporated *in vacuo* and the residue was extracted with pentane (20 cm^3). The extract was concentrated to *ca.* 5 cm^3 *in vacuo* and the solution was stored for 12 h at −78 °C. Violet crystals precipitated which were identified by comparison of the IR and NMR data with those of an authentic sample:[31] 60 mg (69%).

Reaction of 2 with acetic acid. A solution of **2** (75 mg, 0.12 mmol) in toluene-d_8 (1 cm^3) was treated with acetic acid (0.007 cm^3, 0.12 mmol) and stirred for 2 h at room temperature. The ^1H and ^{31}P NMR spectra revealed that a mixture of **33**[40] and (*Z*)-PhC≡CCH=CHPh was formed. If the reaction was monitored by ^{31}P NMR spectroscopy, an intermediate could be detected [δ_P (36.2 MHz) 26.6 (d, *J*(Rh,P) = 98.2 Hz)] which was tentatively assigned as [Rh(κ²-O_2CCH_3)(C≡CPh){(*Z*)-CH=CHPh}($PiPr_3$)$_2$] **E** (see Scheme 12).

[RhCl(C≡CCO_2Me){κ²(*C*,*O*)-CH=CHC(OMe)=O}($PiPr_3$)$_2$] 34. A slow stream of HCl was passed under stirring through a solution of **6** (183 mg, 0.31 mmol) in diethyl ether (4 cm^3) at −78 °C. A change of colour from blue-green to yellow occurred and a white solid precipitated. After removal of excess HCl *in vacuo*, the precipitate was separated from the mother liquor, washed twice with 2 cm^3 portions of pentane (−20 °C) and dried. The mother liquor was brought to dryness *in vacuo*, the residue was washed with small amounts of pentane (−20 °C) and, after it was dried, combined with the white precipitate: yield 175 mg (91%); mp 101 °C (decomp.) (Found: C, 49.88; H, 7.97. $C_{26}H_{50}ClO_4P_2Rh$ requires C, 49.81; H, 8.04%). IR (CH_2Cl_2): (C≡C) 2110, (C=$O_{uncoord}$) 1680, (C=O_{coord}) 1580 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 10.14 [1 H, ddt, *J*(H,H) = 7.3, *J*(Rh,H) = 1.8, *J*(P,H) = 1.7 Hz, RhCH], 5.91 [1 H, dtd, *J*(H,H) = 7.3, *J*(P,H) = 1.7, *J*(Rh,H) = 1.5 Hz, RhCH=C*H*], 3.46, 3.43 (3 H each, both s, OCH_3), 2.63 (6 H, m, PC*H*CH_3), 1.44, 1.13 [18 H each, both dvt, *N* = 13.0, *J*(H,H) = 6.8 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 204.7 [dt, *J*(Rh,C) = 26.0, *J*(P,C) = 7.8 Hz, RhCH], 178.9 [d, *J*(Rh,C) = 3.0 Hz, =CH*C*O_2Me], 153.6 [dt, *J*(Rh,C) = 2.0, *J*(P,C) = 2.0 Hz, ≡C*C*O_2Me], 121.0 [td, *J*(P,C) = 2.5, *J*(Rh,C) = 2.1 Hz, RhCH=*C*H], 103.8 [dt, *J*(Rh,C) = 53.2, *J*(P,C) = 17.2 Hz, Rh*C*≡C], 102.4 [dt, *J*(Rh,C) = 9.1, *J*(P,C) = 2.8 Hz, RhC≡*C*], 53.0, 51.0 (both s, CO_2CH_3), 23.9 (vt, *N* = 20.4 Hz, P*C*HCH_3), 20.6, 20.0 (both s, PCH*C*H_3); δ_P (162.0 MHz) 27.0 [d, *J*(Rh,P) = 89.9 Hz].

[Rh(C≡CCO_2Me)$_2${κ²(*C*,*O*)-CH=CHC(OMe)=O}($PiPr_3$)$_2$] 35. A solution of **6** (107 mg, 0.18 mmol) in NEt_3 (4 cm^3) was treated with HC≡CCO_2Me (0.0017 cm^3, 0.19 mmol) at −78 °C and, while it was stirred, in 1 h warmed to room temperature. A change of colour from blue-green to yellow occurred. The solvent was evaporated *in vacuo*, the residue was dissolved in benzene (1 cm^3) and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With benzene a pale yellow fraction was eluted, which was brought to dryness *in vacuo*. The remaining off-white solid was washed twice with 2 cm^3 portions of pentane (−20 °C) and dried: yield 78 mg (64%) (Found: C, 53.47; H, 7.74. $C_{30}H_{53}O_6P_2Rh$ requires C, 53.41; H, 7.92%). IR (CH_2Cl_2): (C≡C) 2105, 2085, (C=$O_{uncoord}$) 1670, (C=O_{coord}) 1580 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 10.45 [1 H, m, dd in $^1H\{^{31}P\}$, *J*(H,H) = 8.9, *J*(Rh,H) = 1.8 Hz, RhCH], 6.26 [1 H, m, d in $^1H\{^{31}P\}$, *J*(H,H) = 8.9 Hz, RhCH=C*H*], 3.45, 3.43, 3.36 (3 H each, all s, OCH_3), 2.56 (6 H, m, PC*H*CH_3), 1.36 [18 H, dvt, *N* = 13.8, *J*(H,H) = 7.0 Hz, PCHC*H*$_3$], 1.22 [18 H, dvt, *N* = 13.4, *J*(H,H) = 6.9 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 218.2 [dt, *J*(Rh,C) = 20.9, *J*(P,C) = 8.6 Hz, RhCH], 180.8 [d, *J*(Rh,C) = 1.9 Hz, =CH*C*O_2Me], 154.3 (br s, ≡C*C*O_2Me), 153.4 [d, *J*(Rh,C) = 1.8 Hz, ≡C*C*O_2Me], 124.6 [dt, *J*(Rh,C) = 33.7, *J*(P,C) = 16.8 Hz, C–Rh–*C*≡C], 123.0 (br s, RhCH=*C*H), 106.9 [d, *J*(Rh,C) = 5.0 Hz, C–Rh–C≡*C*], 103.8 [dt, *J*(Rh,C) = 53.2, *J*(P,C) = 17.2 Hz, O–Rh–*C*≡C], 99.5 [dt, *J*(Rh,C) = 10.9, *J*(P,C) = 2.0 Hz, O–Rh–C≡*C*], 52.9, 51.0, 50.9 (all s, CO_2CH_3), 25.0 (vt, *N* = 21.5 Hz, P*C*HCH_3), 20.6, 20.2 (both s, PCH*C*H_3); δ_P (36.2 MHz) 31.5 [d, *J*(Rh,P) = 86.5 Hz].

***trans*-[RhCl{η²-(*Z*)-MeO_2CC≡CCH=CHCO_2Me}($PiPr_3$)$_2$] (*Z*)-36.** A solution of **34** (70 mg, 0.11 mmol) in benzene (1 cm^3) was stirred for 36 h at 50 °C. A change of colour from yellow to red occurred. After the solvent was evaporated *in vacuo*, an oily red residue was obtained. The ^1H and ^{31}P NMR spectra indicate that a mixture of products was formed with (*Z*)-**36** as the main component (*ca.* 75%). Attempts to separate (*Z*)-**36** from the by-products either by fractional crystallization or chromatographic techniques failed. Data for (*Z*)-**36**: IR (C_6H_6): (C≡C) 1860, (C=O) 1715, 1690 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 6.52 [1 H, dd, *J*(H,H) = 11.8, *J*(Rh,H) = 1.3 Hz, C*H*=CHCO_2Me], 5.77 [1 H, d, *J*(H,H) = 11.8 Hz, =C*H*CO_2Me], 3.53, 3.41 (3 H each, both s, CO_2CH_3), 2.48 (6 H, m, PC*H*CH_3), 1.30 [18 H, dvt, *N* = 13.3, *J*(H,H) = 7.0 Hz, PCHC*H*$_3$], 1.23 [18 H, dvt, *N* = 13.6, *J*(H,H) = 7.1 Hz, PCHC*H*$_3$]; δ_P (81.0 MHz) 34.3 [d, *J*(Rh,P) = 111.9 Hz].

***trans*-[RhCl{η²-(*E*)-MeO_2CC≡CCH=CHCO_2Me}($PiPr_3$)$_2$] (*E*)-36.**

Method a. A solution of **37** (104 mg, 0.16 mmol) in benzene (2 cm^3) was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 15 cm). With benzene as the eluant, the colour of the mobile phase changed from yellow to red. The red fraction was brought to dryness *in vacuo*. After the residue was recrystallized from pentane at −78 °C, a red microcrystalline solid was obtained: yield 53 mg (53%).

Method b. A solution of **37** (97 mg, 0.15 mmol) in diethyl ether (5 cm^3) was treated with an excess of both $MgCl_2·6H_2O$ (*ca.* 250 mg) and Na_2CO_3 (*ca.* 250 mg) and stirred for 2 h at 40 °C. A change of colour from yellow to red occurred. After the solution was cooled to room temperature, the solvent was evaporated *in vacuo* and the residue was extracted with pentane (20 cm^3). The extract was brought to dryness *in vacuo* and the residue was recrystallized from pentane at −78 °C to give a red microcrystalline solid: yield 66 mg (72%); mp 125 °C (decomp.) (Found: C, 50.04; H, 8.08. $C_{26}H_{50}ClO_4P_2Rh$ requires C, 49.81; H, 8.04%). IR (KBr): (C≡C) 1830, (C=O) 1705, 1675 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.51 [1 H, dd, *J*(H,H) = 15.3, *J*(Rh,H) = 1.7 Hz, C*H*=CHCO_2Me], 7.13 [1 H, d, *J*(H,H) = 15.3 Hz, =C*H*CO_2Me], 3.49, 3.39 (3 H each, both s, CO_2CH_3), 2.30 (6 H, m, PC*H*CH_3), 1.25 [18 H, dvt, *N* = 13.6, *J*(H,H) = 6.9 Hz, PCHC*H*$_3$], 1.19 [18 H, dvt, *N* = 13.3, *J*(H,H) = 6.8 Hz, PCHC*H*$_3$]; δ_C (100.6 MHz) 166.8 (s, =CH*C*O_2Me), 156.6 (br s, ≡C*C*O_2Me), 130.9 (s, =*C*HCO_2Me), 126.8 [d, *J*(Rh,C) = 1.0 Hz, *C*H=CHCO_2Me], 95.0 [dt, *J*(Rh,C) = 17.2, *J*(P,C) = 2.9 Hz, *C*≡C], 89.9 [dt, *J*(Rh,C) = 18.1, *J*(P,C) = 4.1 Hz, C≡*C*], 51.5, 51.4 (both s, CO_2CH_3), 23.8 (vt, *N* = 18.5 Hz, P*C*HCH_3), 20.4, 20.0 (both s, PCH*C*H_3); δ_P (162.0 MHz) 35.4 [d, *J*(Rh,P) = 110.8 Hz].

[Rh(κ²-O_2CCH_3)(C≡CCO_2Me){η¹-(*E*,*E*)-C(=CHCO_2Me)-CH=CHCO_2Me}($PiPr_3$)$_2$] 38. A solution of **37** (98 mg, 0.15 mmol) in benzene (1 cm^3) was treated with HC≡CCO_2Me (0.0013 cm^3, 0.15 mmol) and stirred for 1 h at room temperature. The solvent was evaporated *in vacuo* and the residue was extracted with hexane/diethyl ether (1 : 1, 15 cm^3). The extract was brought to dryness *in vacuo* and the residue recrystallized from pentane at −78 °C. The precipitated white solid was washed with 2 cm^3 portions of pentane (−20 °C) and dried: yield 84 mg (76%); mp 110 °C (decomp.) (Found: C, 52.15; H, 7.79. $C_{32}H_{57}O_8P_2Rh$ requires C, 52.32; H, 7.82%). IR (C_6H_6): (C≡C) 2100, (C=O) 1710, 1685 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 8.36 [1 H, d, *J*(H,H) = 15.8 Hz, C*H*=CHCO_2Me], 6.72 [1 H, m, d in $^1H\{^{31}P\}$, *J*(Rh,H) = 2.4 Hz, RhC=C*H*CO_2Me], 6.34 [1 H, d, *J*(H,H) = 15.8 Hz, CH=C*H*CO_2Me], 3.44, 3.38, 3.37 (3 H each, all s, OCH_3), 2.67 (6 H, m, PC*H*CH_3), 1.68 (3 H, s, CH_3CO_2Rh), 1.40 [18 H, dvt, *N* = 14.0, *J*(H,H) = 7.1 Hz,

PCHCH_3], 1.12 [18 H, dvt, N = 13.1, J(H,H) = 6.8 Hz, PCHCH_3]; δ_C (100.6 MHz) 184.3 [dt, J(Rh,C) = 1.2, J(P,C) = 1.2 Hz, RhO_2CCH_3], 167.0 (s, CH=CHCO_2Me), 163.9 [dt, J(Rh,C) = 3.5, J(P,C) = 1.0 Hz, RhC=CHCO_2Me], 163.6 [dt, J(Rh,C) = 30.6, J(P,C) = 7.8 Hz, RhC=CHCO_2Me], 153.7 [br d, J(Rh,C) = 1.4 Hz, ≡CCO_2Me], 153.4 [d, J(Rh,C) = 1.8 Hz, ≡CCO_2Me], 148.0 (br s, CH=CHCO_2Me), 126.9 [br t, J(P,C) = 2.5 Hz, RhC=CHCO_2Me], 118.3 (s, CH=CHCO_2Me), 111.8 [dt, J(Rh,C) = 51.4, J(P,C) = 16.8 Hz, RhC≡C], 100.5 [dt, J(Rh,C) = 10.1, J(P,C) = 2.0 Hz, RhC≡C], 51.2, 51.1, 50.6 (all s, CO_2CH_3), 24.8 (s, RhO_2CCH_3), 24.1 (vt, N = 20.0 Hz, PCHCH$_3$), 20.1, 19.7 (both s, PCHCH_3); δ_P (162.0 MHz) 26.3 [d, J(Rh,P) = 93.2 Hz].

***trans*-[RhCl{η²-(*E*,*E*)-MeO$_2$CC≡CC(=CHCO$_2$Me)CH=CHCO$_2$Me}(P*i*Pr$_3$)$_2$] 39.** A solution of **38** (125 mg, 0.17 mmol) in diethyl ether (10 cm^3) was treated with an excess of both $MgCl_2 \cdot 6H_2O$ (*ca.* 250 mg) and Na_2CO_3 (*ca.* 250 mg) and stirred for 4 h at 40 °C. A change of colour from yellow to cherry-red occurred. After the solution was cooled to room temperature, the solvent was evaporated *in vacuo* and residue was extracted with pentane (30 cm^3). The extract was brought to dryness *in vacuo* and the residue was recrystallized from pentane at −78 °C to give a deep-red microcrystalline solid: yield 96 mg (79%); mp 128 °C (decomp.) (Found: C, 51.15; H, 7.87. $C_{30}H_{54}ClO_6P_2Rh$ requires C, 50.68; H, 7.65%). IR (hexane): (C≡C) 1845, (C=O) 1725, 1715, 1700 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 9.11 [1 H, d, J(H,H) = 16.0 Hz, CH=CHCO$_2$Me], 8.00 (1 H, s, C≡CC=CHCO$_2$Me), 7.40 [br d, J(H,H) = 16.0 Hz, CH=CHCO$_2$Me], 3.49, 3.37, 3.35 (3 H each, all s, OCH_3), 2.35 (6 H, m, PCHCH$_3$), 1.28 [18 H, dvt, N = 13.8, J(H,H) = 7.0 Hz, PCHCH_3], 1.11 [18 H, dvt, N = 13.1, J(H,H) = 6.7 Hz, PCHCH_3]; δ_C (100.6 MHz) 166.7, 166.5 (both s, =CHCO_2Me), 158.8 (br s, ≡CCO_2Me], 138.6 (s, C≡CC=CH), 137.0 (s, C≡CCCH=CH), 130.7 (s, C≡CC=CHCO$_2$Me), 128.0 (s, CH=CHCO$_2$Me), 93.1 [dt, J(Rh,C) = 17.9, J(P,C) = 2.6 Hz, C≡CCO$_2$Me], 88.2 [br d, J(Rh,C) = 16.5 Hz, C≡CCO$_2$Me], 51.7, 51.5, 51.3 (all s, CO_2CH_3), 23.5 (vt, N = 18.4 Hz, PCHCH$_3$), 20.6, 19.6 (both s, PCHCH_3); δ_P (162.0 MHz) 33.6 [d, J(Rh,P) = 110.6 Hz].

Reaction of 39 with CO. A slow stream of CO was passed through a solution of **39** (59 mg, 0.08 mmol) in C_6D_6 (0.5 cm^3) for 15 s at room temperature. A quick change of colour from red to yellow occurred. The ^{1}H and ^{31}P NMR spectra revealed that besides **24**[41] an equimolar amount of (*E*,*E*)-MeO$_2$CC≡CC(=CHCO$_2$Me)CH=CHCO$_2$Me **40** was formed. Data for **40**: NMR (C_6D_6): δ_H (200 MHz) 8.78 [1 H, d, J(H,H) = 15.9 Hz, CH=CHCO$_2$Me], 6.66 [d, J(H,H) = 15.9 Hz, CH=CHCO$_2$Me], 5.95 (1 H, s, C≡CC=CHCO$_2$Me), 3.28, 3.20, 3.15 (3 H each, all s, OCH_3).

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