866 *Organometallics* **1997,** *16,* 866−870

A Series of Novel Binuclear Iron−Rhodium Complexes Prepared from Ethynylferrocene[†,1]

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Received September 26, 1996[⊗]

The chlororhodium(I) compound $[RhCl(P\mathit{i}Pr_3)_2]_2$ (**1**) reacts with ethynylferrocene (**2**) by oxidative addition to give the alkynyl(hydrido)rhodium(III) complex $[RhH(C{\equiv}CFc)Cl(P\mathit{i}Pr_3)_2]$ (**3**) almost quantitatively $[Fc = (\eta^5\text{-}C_5H_4-)Fe(\eta^5\text{-}C_5H_5)]$. Compound **3** is slowly converted in benzene at room temperature to the vinylidene isomer *trans*-$[RhCl(=C=CHFc)(P\mathit{i}Pr_3)_2]$ (**4**). Treatment of **4** with Grignard reagents RMgX affords the phenyl- and vinylrhodium(I) derivatives *trans*-$[Rh(R)(=C=CHFc)(P\mathit{i}Pr_3)_2]$ (**5**, **6**) of which the latter ($R = CH{=}CH_2$) rearranges to the isomeric η^3-2−4-butadienyl complex $[Rh(\eta^3\text{-}\mathit{trans}\text{-}CH_2CHC{=}CHFc)(P\mathit{i}Pr_3)_2]$ (**8**). The corresponding η^3-allyl compound $[Rh(\eta^3\text{-}\mathit{anti}\text{-}CH_2CH{=}CHFc)(P\mathit{i}Pr_3)_2]$ (**7**) is obtained from **4** and CH_3MgI, possibly via *trans*-$[Rh(CH_3)(=C=CHFc)(P\mathit{i}Pr_3)_2]$ as an intermediate. The X-ray crystal structure analysis of **7** confirms the *anti* position of the ferrocenyl group at the allylic ligand.

Introduction

We have previously shown that in the coordination sphere of rhodium(I) terminal alkynes $HC{\equiv}CR$ can be easily converted to the isomeric vinylidenes.[2,3] By using $[RhCl(P\mathit{i}Pr_3)_2]_2$ (**1**) as the starting material, the reaction with $HC{\equiv}CR$ occurs stepwise: the initially formed π-alkyne complex *trans*-$[RhCl(HC{\equiv}CR)(P\mathit{i}Pr_3)_2]$ affords first the alkynyl(hydrido)rhodium(III) derivative $[RhH(C{\equiv}CR)Cl(P\mathit{i}Pr_3)_2]$ which then rearranges to the final product *trans*-$[RhCl(=C=CHR)(P\mathit{i}Pr_3)_2]$. In the course of our investigations we found that the stability of the five-coordinate intermediate $[RhH(C{\equiv}CR)Cl(P\mathit{i}Pr_3)_2]$ significantly depends on the substituent R, compounds with sterically demanding moieties such as *t*Bu[2c] or CMe_2OH[2e] being more stable than those with H or simple alkyl groups. The phenylethynyl complex $[RhH(C{\equiv}CPh)Cl(P\mathit{i}Pr_3)_2]$ adopts an intermediary position: under carefully controlled conditions it can be isolated and spectroscopically characterized, but even at room temperature it reacts quite rapidly to give the vinylidene isomer.[2b]

Since not for steric but for electronic reasons the phenyl and ferrocenyl units are comparable, we decided also to study the reactivity of ethynylferrocene **2** toward **1**. We note that most recently Dixneuf et al. described the synthesis of heterobimetallic Fe−Ni and Fe−Pd oligomers which were obtained from a diynylferrocene derivative as a precursor.[4]

In this paper we report the preparation of the alkynyl and vinylidene complexes of composition $[RhH(C{\equiv}CFc)Cl(P\mathit{i}Pr_3)_2]$ and *trans*-$[RhCl(=C=CHFc)(P\mathit{i}Pr_3)_2]$ with $Fc = (\eta^5\text{-}C_5H_4-)Fe(\eta^5\text{-}C_5H_5)$, the nucleophilic substitution of the chloro ligand of the vinylidene compound by phenyl and vinyl groups, and the conversion of the postulated, in situ generated species *trans*-$[Rh(CH_3)(=C=CHFc)(P\mathit{i}Pr_3)_2]$ and of the isolated analogue *trans*-$[Rh(CH{=}CH_2)(=C=CHFc)(P\mathit{i}Pr_3)_2]$ to the isomeric η^3-allyl and η^3-butadienyl derivatives.

Results and Discussion

Reaction of the extremely air-sensitive chloro compound **1** with **2** in pentane at 10 °C results in a clean and quantitative formation of the alkynyl(hydrido)rhodium(III) complex **3** (Scheme 1). Even by monitoring the process in C_6D_6 by ^1H NMR spectroscopy, the supposed intermediate *trans*-$[RhCl(HC{\equiv}CFc)(P\mathit{i}Pr_3)_2]$ could not be observed. The five-coordinate compound **3** is an orange solid which is soluble in most organic solvents and decomposes at 105 °C. The most characteristic features of the spectroscopic data are the $C{\equiv}C$ stretching frequency of the alkynyl ligand at 2090 cm^{-1} in the IR spectrum and the high-field resonance of the hydridic hydrogen at δ −27.98 in the ^1H NMR spectrum. The latter is split into a doublet of triplets due to Rh−H and P−H coupling.

The isomerization of the alkynyl hydrido to the vinylidene complex **4** occurs rather slowly in benzene at room temperature and can be followed by a change of color from orange to green. Upon recrystallization from acetone, green, only moderately air-sensitive crystals are isolated in virtually quantitative yield. The generation of the vinylidene ligand is indicated by the appearance of two doublets of triplets in the low field region of the ^{13}C NMR as well as by the signal of the $C{=}C\mathit{H}R$ proton at δ 0.90 in the ^1H NMR spectrum. Compound **4** is less soluble in common organic solvents

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[†] Dedicated to Professor Walter Siebert on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

(1) Part 41 of the series Vinylidene Transition-Metal Complexes. For part 40, see: Braun, T.; Meuer, P.; Werner, H. *Organometallics* **1996**, *15*, 4075−4077.

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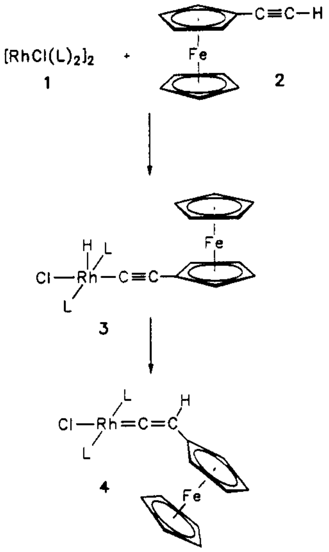
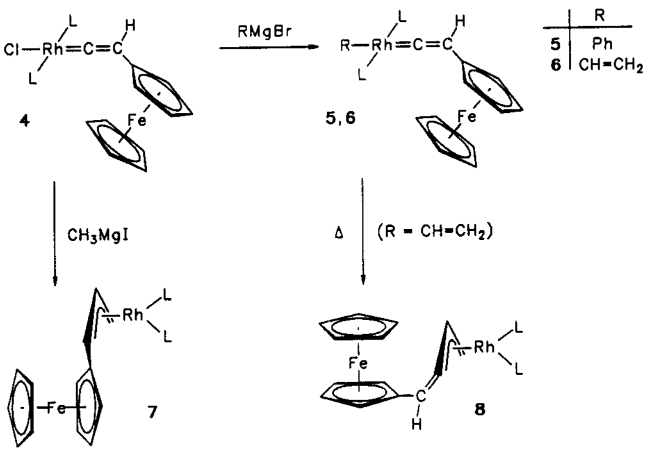
S0276-7333(96)00825-4 CCC: $14.00

Scheme 1[a]



[a] L = P*i*Pr$_3$.

Scheme 2[a]



[a] L = P*i*Pr$_3$.

than the analogous derivatives *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$] with R = alkyl or aryl which we attribute to the bulky and quite polar ferrocenyl group.

The chloro complex **4** reacts with phenyl and vinyl Grignard reagents in benzene–ether or benzene–THF to give the phenyl- and vinylrhodium(I) compounds **5** and **6** in 75–80% yield (Scheme 2). Since the IR and the NMR data for the Rh=C=CHFc unit of the starting material **4** and the products **5** and **6** are quite similar, we conclude that the attack of the nucleophile is exclusively directed to the Rh–Cl and not to the Rh–C bond. The ^{1}H NMR spectrum of **6** displays three distinct multiplets at δ 7.90, 6.30, and 5.27 for the vinyl protons which in off-resonance appear as doublets of doublets of doublets. As expected, the *trans* coupling $J(H^1H^2)$ is considerably larger than the *cis* coupling $J(H^1H^3)$ and both exceed by far the coupling between the protons of the CH$_2$ group. In the ^{31}P NMR spectra of **5** and **6** only one signal (doublet) with a similar chemical shift as that of **4** is observed, and thus, there is no doubt that the two phosphine ligands are *trans* disposed.

Like the vinylrhodium(I) derivatives *trans*-[Rh(CH=CH$_2$)(=C=CHR)(P*i*Pr$_3$)$_2$] (R = Ph, *t*Bu), which we prepared quite recently,[5] compound **6** also undergoes an isomerization reaction leading to the η^3-2–4-butadienyl complex **8**. The ^{1}H NMR spectrum of the orange, air-sensitive solid displays a rather complex pattern for the protons H^1–H^4 (for exact assignment see Experimental Section) which is due to Rh–H, P–H and H–H couplings. The resonance of the *syn* proton H^3 reveals a considerably smaller H–H coupling with the central proton H^2 than that of the *anti* proton H^4 which is in agreement with previous findings.[6,7] Since in the ^{13}C NMR spectrum of **8** a significant difference of the chemical shift (ca. 120 ppm) for the signals of the carbon atoms C^2 and C^4 is observed, we assume that the allylic fragment of the butadienyl unit is unsymmetrically coordinated to the metal center. This structural proposal is supported by the ^{31}P NMR spectrum of **8** which displays two separate doublets of doublets with distinctly different Rh–P coupling constants.

The (η^3-allyl)rhodium analogue of the η^3-butadienyl complex **8** has also been prepared although the expected precursor *trans*-[Rh(CH$_3$)(=C=CHFc)(P*i*Pr$_3$)$_2$] could not be isolated. Treatment of the chloro derivative **4** with CH$_3$MgI in benzene–ether at 5 °C leads to a smooth change of color from green to orange and gives, after removal of the solvent and recrystallization from acetone, orange crystals in 79% yield. Both the ^{1}H and ^{13}C NMR data indicate that the ferrocenyl-substituted η^3-allyl complex **7** has been obtained. With regard to the mechanism of this reaction, we assume that initially by nucleophilic substitution of the metal-bonded chloride the four-coordinate intermediate *trans*-[Rh(CH$_3$)(=C=CHFc)(P*i*Pr$_3$)$_2$] is generated which quickly rearranges by migratory insertion of the vinylidene ligand into the Rh–CH$_3$ bond to give **7**. It is conceivable that during the rearrangement a η^1-vinyl species [Rh{η^1-C(CH$_3$)=CHFc}(P*i*Pr$_3$)$_2$], analogous to [Rh(η^1-CH$_2$Ph)(P*i*Pr$_3$)$_2$],[7] is formed which by β-H shift reacts to give a four-coordinate (η^2-allene)hydridorhodium derivative.[8] The final product could then be formed by a hydride transfer from the metal to the central carbon atom of the allene unit. Support for the assumption that a vinyl ligand such as C(CH$_3$)=CHFc can rearrange to a 1-substituted allyl group stems from previous work by Schwartz et al., who found that the iridium compound *trans*-[Ir{*Z*-C(CH$_3$)=CHCH$_3$}(CO)(PPh$_3$)$_2$] reacts on warming in C$_6$D$_6$ to give the allyl isomer [Ir(η^3-*syn*-1-CH$_3$C$_3$H$_4$)(CO)(PPh$_3$)$_2$].[9] A similar process involving a *cationic* vinylrhodium(III) complex has been previously studied in our laboratory.[10]

The reason why the supposed intermediate *trans*-[Rh(CH$_3$)(=C=CHFc)(P*i*Pr$_3$)$_2$] is much more labile than the structurally related species **5** and **6** is not quite clear. The difference is also remarkable insofar as the analogous compounds *trans*-[Rh(CH$_3$)(=C=CHR)(P*i*Pr$_3$)$_2$] with R = H, Ph, and *t*Bu have been isolated and fully

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(7) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, *127*, 27–38.

(8) For the reverse process, the insertion of an allene into a Rh–H bond, see: Osakada, K.; Choi, J.-C.; Koizumi, T.; Yamaguchi, I.; Yamamoto, T. *Organometallics* **1995**, *14*, 4962–4965.

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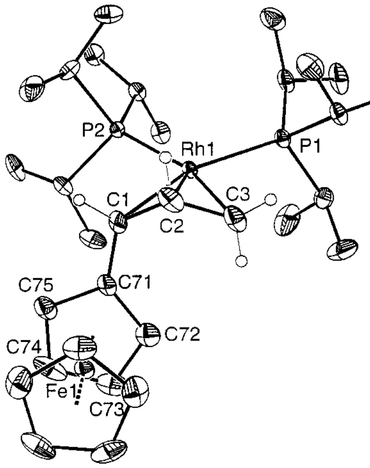

Figure 1. Solid state structure of **7**, with anisotropic uncertainty parameters depicting 50% probability. Hydrogen atoms other than those bonded to the allyl moiety have been omitted for clarity.

Table 1. Selected Bond Distances and Angles with Esd's for Compound 7

	Bond Distances (Å)		
Rh–C1	2.254(4)	C1–C71	1.467(6)
Rh–C2	2.114(4)	Fe–C71	2.086(4)
Rh–C3	2.198(4)	Fe–C72	2.050(4)
Rh–P1	2.306(1)	Fe–C73	2.041(4)
Rh–P2	2.304(1)	Fe–C74	2.037(4)
C1–C2	1.412(6)	Fe–C75	2.040(4)
C2–C3	1.403(6)		
	Bond Angles (deg)		
P1–Rh–P2	108.3(4)	Rh–C2–C3	74.3(2)
C1–Rh–C2	37.6(2)	Rh–C3–C2	67.8(2)
C1–Rh–C3	67.5(2)	C1–C2–C3	123.0(4)
C2–Rh–C3	37.9(2)	Rh–C1–C71	113.4(2)
Rh–C1–C2	65.9(2)	C2–C1–C71	127.9(4)
Rh–C2–C1	76.6(2)		

characterized by IR and NMR spectroscopy.[5] They isomerize in benzene at room temperature rather slowly (in ca. 12 h) to afford the η^3-allyl complexes [Rh(η^3-CH_2CHCHR)(P*i*Pr$_3$)$_2$] of which that with R = Ph is formed in the *syn* and that with R = *t*Bu in the *anti* configuration.[11] The metal-mediated C–C coupling of a methyl and a vinylidene ligand to give an allylic unit is not limited to rhodium and has recently also been observed in ruthenium chemistry.[1]

To confirm the stereochemical arrangement of complex **7**, an X-ray diffraction study was carried out. As shown in Figure 1, the substituted allylic ligand is η^3 bonded with the ferrocenyl unit in the *anti* position. The most notable feature is that the bond lengths between the metal and the terminal carbon atoms of the C_3 moiety are unequal and differ by ca. 0.06 Å. In spite of the slightly unsymmetrical coordination of the allylic ligand, the two Rh–P distances as well as the C1–C2 and the C2–C3 bond lengths are equal within their estimated standard deviations (Table 1). The C1–C71 distance of the terminal allylic carbon atom to the five-membered ring of the ferrocenyl fragment is 1.467(6) Å and thus nearly the same as in a Fc-substituted allylpalladium(II) complex in which the sandwich-type unit is bonded to the central carbon atom.[12] The bite angle P1–Rh–P2 of 108.3(4)°is virtually the same as in the η^3-benzylrhodium(I) derivative [Rh(η^3-$CH_2C_6H_4$-Me)(P*i*Pr$_3$)$_2$] [108.8(1)°].[7] This is noteworthy as in the latter the Rh–P distances differ by 0.09 Å probably due to the unsymmetrical coordination of the benzylic ligand. The plane containing the carbon atoms C1, C2, and C3 of compound **7** is not exactly perpendicular to the P1,Rh,P2 plane. The orthogonal of the first best plane intersects that of the latter at an angle of 77.8°.

Conclusion

The present investigations have shown that a remarkable difference exists in the reactivity of phenylacetylene HC≡CPh and ethynylferrocene (**2**) toward [RhCl(P*i*Pr$_3$)$_2$]$_2$ (**1**). While on treatment with **1** the former yields a stable π-alkyne complex with the [RhCl(P*i*Pr$_3$)$_2$] unit, the corresponding compound with **2** as ligand is extremely labile and quickly rearranges to the alkynyl(hydrido)rhodium(III) isomer **3**. This species as well as the short-lived analogue [RhH(C≡CPh)Cl(P*i*Pr$_3$)$_2$] are readily converted to the vinylidene complexes **4** and *trans*-[RhCl(=C=CHPh)(P*i*Pr$_3$)$_2$] which both undergo substitution reactions with methyl, vinyl, and phenyl Grignard reagents to give the σ-bonded derivatives *trans*-[Rh(R)(=C=CHFc)(P*i*Pr$_3$)$_2$] and *trans*-[Rh(R)(=C=CHPh)(P*i*Pr$_3$)$_2$], respectively. For R = CH_3, the kinetic stability of the two related vinylidenerhodium(I) compounds is strikingly different. Whereas the complex with C=CHPh as ligand can be isolated and stored at room temperature for some time,[5] the counterpart with Fc instead of Ph as substituent reacts instantaneously to afford the π-allyl complex **7**. The remarkable feature is that in **7** the ferrocenyl unit occupies the *anti* position at the allyl unit and thus behaves analogously to the *tert*-butyl group. From this we conclude that the steric and not the electronic effects of the Fc moiety mainly determine the course of the rearrangement of the supposed intermediate *trans*-[Rh(CH_3)(=C=CHFc)(P*i*Pr$_3$)$_2$] to give **7**.

The C–C coupling which occurs during the formation of **7** is not limited to methyl and vinylidene but also takes place between vinyl and vinylidene, in this case generating an η-2–4-butadienyl ligand. It should be emphasized that this C–C coupling process does not need the support of a Lewis base like CO[5] or acetonitrile[13] and occurs despite the fact that in the square-planar precursors the methyl or vinyl and the vinylidene ligands are *trans* to each other. We finally note that the formation of an η-2–4-butadienyl unit by a metal-assisted C–C coupling is not restricted to rhodium and has recently also been observed in C_5H_5Ru chemistry.[1]

Experimental Section

All reactions were carried out under an atmosphere of argon by use of Schlenk techniques. The starting materials [RhCl(P*i*Pr$_3$)$_2$]$_2$ (**1**)[14] and [(η^5-C_5H_5)Fe(η^5-$C_5H_4C{\equiv}CH$)] (**2**)[15] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a Perkin-Elmer 1420

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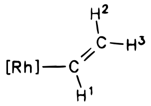
infrared spectrometer, and mass spectra on a Finnigan 90 MAT instrument. Melting points were determined by DTA.

Preparation of [RhH{(C≡C-η^5-C_5H_4)Fe(η^5-C_5H_5)}Cl-(P*i*Pr$_3$)$_2$] (3). A solution of **1** (260 mg, 0.28 mmol) in 5 mL of pentane was treated at 10 °C with **2** (120 mg, 0.57 mmol) which led to a change of color from red-violet to yellow. After the solution was stirred for 5 min, orange crystals began to precipitate. The solution was stored for 1 h at −78 °C, and the precipitate was separated from the mother liquor, washed three times with 3-mL portions of pentane (−20 °C), and dried: yield 349 mg (92%); mp 105 °C dec; IR (C_6H_6) ν(C≡C) 2090 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) δ 4.25 (m, 2H, C_5H_4R), 4.17 (s, 5H, C_5H_5), 3.98 (m, 2H, C_5H_4R), 2.87 (m, 6H, PC*H*CH$_3$), 1.33 [dvt, $N = 13.1$, J(HH) = 7.3 Hz, 18H, PCHC*H*$_3$], 1.30 [dvt, $N = 13.1$, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$], −27.98 [dt, J(RhH) = 39.6, J(PH) = 17.1 Hz, 1H, RhH]; ^{31}P NMR (C_6D_6, 81.0 MHz) δ 50.2 [d, J(RhP) = 99.0 Hz]. Anal. Calcd for $C_{30}H_{52}ClFeP_2Rh$: C, 53.87; H, 7.84. Found: C, 53.54; H, 7.89.

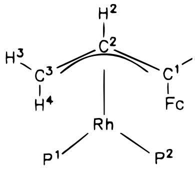
Preparation of *trans*-[RhCl{(=C=CH-η^5-C_5H_4)Fe(η^5-C_5H_5)}(P*i*Pr$_3$)$_2$] (4). A solution of **3** (230 mg, 0.34 mmol) in 5 mL of benzene was stirred for 10 h at room temperature. A smooth change of color from orange to green occurred. The solvent was removed in vacuo, the residue was dissolved in 15 mL of acetone, and the solution was stored for 24 h at −78 °C. Green crystals precipitated which were separated from the mother liquor, washed three times with 3 mL portions of acetone (−20 °C), and dried: yield 221 mg (96%); mp 143 °C; IR (C_6H_6) ν(C=C) 1620 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) δ 3.99 (s, 5H, C_5H_5), 3.94 (m, 4H, C_5H_4R), 2.75 (m, 6H, PC*H*CH$_3$), 1.31 [dvt, $N = 13.5$, J(HH) = 6.9 Hz, 36H, PCHC*H*$_3$], 0.90 [dt, J(RhH) = 0.7, J(PH) = 3.3 Hz, 1H, Rh=C=C*H*R]; ^{13}C NMR (C_6D_6, 50.3 MHz) δ 294.4 [dt, J(RhC) = 59.1, J(PC) = 16.5 Hz, Rh=*C*=CHR], 104.6 [dt, J(RhC) = 15.9, J(PC) = 6.4 Hz, Rh=C=*C*HR], 70.9 [t, J(PC) = 2.2 Hz, *i*-C_5H_4R], 69.0 (s, C_5H_5), 67.5, 66.3 (both s, C_5H_4R), 23.7 [dvt, J(RhC) = 1.3, $N = 20.0$ Hz, P*C*HCH$_3$], 20.4 (s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz) δ 43.3 [d, J(RhP) = 134.6 Hz]; MS (70 eV) *m/z* 668 (M$^+$), 458 [RhCl(P*i*Pr$_3$)$_2$$^+$], 210 (**2**$^+$). Anal. Calcd for $C_{30}H_{52}ClFeP_2Rh$ (668.9): C, 53.87; H, 7.84. Found: C, 53.57; H, 7.60.

Preparation of *trans*-[Rh(C_6H_5){(=C=CH-η^5-C_5H_4)Fe-(η^5-C_5H_5)}(P*i*Pr$_3$)$_2$] (5). A solution of **4** (175 mg, 0.26 mmol) in 3 mL of benzene was treated at 10 °C with 0.5 mL of a 1.0 M solution of C_6H_5MgBr in ether. After the reaction mixture was stirred for 2 h at room temperature, the solvent was removed in vacuo, and the residue was extracted with 30 mL of pentane. The extract was filtered, and the filtrate was concentrated to about 3 mL in vacuo and then stored for 15 h at −78 °C. Dark green crystals precipitated which were separated from the mother liquor, washed three times with 2 mL portions of acetone (−20 °C), and dried: yield 138 mg (74%); mp 67 °C dec; IR (C_6H_6) ν(C=C) 1605 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) δ 7.93 (m, 2H, *o*-C_6H_5), 7.43 (m, 2H, *m*-C_6H_5), 6.98 (m, 1H, *p*-C_6H_5), 4.09 (s, 5H, C_5H_5), 4.08, 4.00 (both m, 2H each, C_5H_4R), 2.35 (m, 6H, PC*H*CH$_3$), 1.57 [t, J(PH) = 4.2 Hz, 1H, Rh=C=C*H*R], 1.21 [dvt, $N = 13.2$, J(HH) = 6.9 Hz, 36H, PCHC*H*$_3$]; ^{31}P NMR (C_6D_6, 81.0 MHz) δ 40.9 [d, J(RhP) = 145.8 Hz]. Anal. Calcd for $C_{36}H_{57}FeP_2Rh$: C, 60.85; H, 8.09. Found: C, 60.28; H, 7.80.

Preparation of *trans*-[Rh(CH=CH$_2$){(=C=CH-η^5-C_5H_4)-Fe(η^5-C_5H_5)}(P*i*Pr$_3$)$_2$] (6). This was prepared as described for **5**, from **4** (220 mg, 0.33 mmol) and 0.50 mL of a 1.0 M solution of CH$_2$=CHMgBr in THF. Upon recrystallization from pentane (−78 °C) a violet microcrystalline solid was obtained: yield 172 mg (79%); mp 91 °C dec; IR (C_6H_6) ν(C=C) 1610 cm^{-1}; ^{1}H NMR (C_6D_6, 200 MHz) (assignments shown below) δ 7.90 [m, in ^{1}H{^{31}P} ddd, J(RhH^1) = 1.1, J(H^{1}H^2) = 19.8, J(H^{1}H^3) = 14.2 Hz, 1H, H^1], 6.30 [m, in ^{1}H{^{31}P} ddd, J(RhH^3) = 2.9, J(H^{1}H^3) = 14.2, J(H^{2}H^3) = 4.2 Hz, 1H, H^3], 5.27 [m, in ^{1}H{^{31}P} ddd, J(RhH^2) = 1.4, J(H^{1}H^2) = 19.8, J(H^{2}H^3) = 4.2 Hz, 1H, H^2], 4.07 (s, 5H, C_5H_5), 4.03, 3.99 (both m, 2H each, C_5H_4R), 2.63 (m, 6H, PC*H*CH$_3$), 1.27 [dvt, N = 13.1, J(HH) = 7.0 Hz, 36H, PCHC*H*$_3$]; signal of =C*H*R partly covered by signal of PCHC*H*$_3$; ^{13}C NMR (C_6D_6, 50.3 MHz) δ 301.0 [dt, J(RhC) = 47.0, J(PC) = 17.2 Hz, Rh=*C*=CHR], 175.0 [dt, J(RhC) = 26.1, J(PC) = 14.0 Hz, Rh−*C*H=CH$_2$], 120.4 [t, J(PC) = 3.8 Hz, Rh−CH=*C*H$_2$], 110.6 [dt, J(RhC) = 10.8, J(PC) = 5.4 Hz, Rh=C=*C*HR], 73.7 [t, J(PC) = 2.5 Hz, *i*-C_5H_4R], 68.9 (s, C_5H_5), 67.1, 65.6 (both s, C_5H_4R), 25.5 [dvt, J(RhC) = 1.3, N = 19.7 Hz, P*C*HCH$_3$], 20.5 (s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 81.0 MHz) δ 44.1 [d, J(RhP) = 145.6 Hz]. Anal. Calcd for $C_{32}H_{55}FeP_2Rh$: C, 58.19; H, 8.39. Found: C, 58.43; H, 8.45.

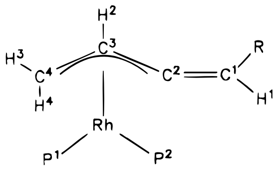


Preparation of [Rh{(η^3-*anti*-CH$_2$CHCH-η^5-C_5H_4)Fe(η^5-C_5H_5)}(P*i*Pr$_3$)$_2$] (7). A solution of **4** (134 mg, 0.20 mmol) in 5 mL of benzene was treated at 5 °C with 0.4 mL of a 1.0 M solution of CH$_3$MgI in ether and then stirred for 3 h at room temperature. A smooth change of color from green to orange occurred. The solvent was removed, the residue was extracted with 15 mL of pentane, and the extract was brought to dryness in vacuo. The residue was dissolved in 10 mL of acetone, and the solution was stored for 2 d at −78 °C. Orange crystals precipitated, which were separated from the mother liquor, washed three times with 2 mL portions of acetone (−20 °C), and dried: yield 103 mg (79%); mp 92 °C dec; ^{1}H NMR (C_6D_6, 400 MHz) (assignments shown below) δ 4.98 [m, in ^{1}H{^{31}P} dddd, J(RhH^2) = 1.7, J(H^{2}H^4) = 12.1, J(H^{1}H^2) = 7.9, J(H^{2}H^3) = 7.8 Hz, 1H, *H*^{2}], 4.46 [m, in ^{1}H{^{31}P} d, J(H^{1}H^2) = 7.9 Hz, 1H, *H*^{1}], 4.18 (s, 5H, C_5H_5), 4.15, 3.99, 3.91 (all m, 4H, C*H* of C_5H_4R), 2.86 [m, in ^{1}H{^{31}P} d, J(H^{2}H^3) = 7.8 Hz, 1H, *H*^{3}), 2.45 (dd, br, J(P^{2}H^4) = 7.2, J(H^{2}H^4) = 12.1 Hz, 1H, *H*^{4}), 2.21, 2.13 (both m, 3H each, PC*H*CH$_3$), 1.25 [dd, J(PH) = 12.8, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.21 [dd, J(PH) = 11.6, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.14 [dd, J(PH) = 11.2, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.05 [dd, J(PH) = 12.4, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 100.6 MHz) δ 94.2 [d, J(PC) = 5.7 Hz, *i*-C_5H_4R)], 90.8 (m, *C*^{2}), 70.0, 67.9, 67.8, 65.8 (all s, C_5H_4R), 69.7 (s, C_5H_5), 61.4 [ddd, J(RhC) = 22.9, J(P^{1}C) = 8.0, J(P^{2}C) = 4.1 Hz, *C*^{1}], 45.1 [ddd, J(RhC) = 28.5, J(P^{2}C) = 8.2, J(P^{1}C) = 5.5 Hz, *C*^{3}], 28.7 [d, br, J(PC) = 14.4 Hz, P*C*HCH$_3$], 28.6 [d, br, J(PC) = 13.2 Hz, P*C*HCH$_3$], 21.4, 21.2 [both d, J(PC) = 3.2 Hz, PCH*C*H$_3$], 20.5, 20.4 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz) δ 55.4 [dd, J(RhP) = 191.8, J(PP) = 20.2 Hz, P^1], 47.9 [dd, J(RhP) = 191.0, J(PP) = 20.2 Hz, P^2]. Anal. Calcd for $C_{31}H_{55}FeP_2Rh$: C, 57.42; H, 8.55. Found: C, 56.97; H, 8.49.



Preparation of [Rh{(η^3-*trans*-CH$_2$CHC=CH-η^5-C_5H_4)-Fe(η^5-C_5H_5)}(P*i*Pr$_3$)$_2$] (8). A solution of **6** (110 mg, 0.17 mmol) in 3 mL of benzene was stirred for 1 h at 50 °C which led to a change of color from green to orange. Upon cooling of the solution to room temperature, the solvent was removed, the residue was dissolved in 3 mL of acetone, and the solution was stored for 10 h at −78 °C. Orange crystals were formed which were isolated as described for **7**: yield 89 mg (81%); mp 99 °C dec; ^{1}H NMR (C_6D_6, 400 MHz) (assignments shown below) δ 5.93 [dd, J(P^{1}H) = 5.1, J(H^{1}H^2) = 2.1 Hz, 1H, H^1], 4.70, 4.62 (both m, 1H each, C_5H_4R), 4.59 (m, 1H, H^2), 4.14 (s, 5H, C_5H_5), 4.13 (m, 2H, C_5H_4R), 3.19 [m, in ^{1}H{^{31}P} d, J(H^{2}H^3) = 7.4 Hz, 1H, H^3], 2.37, 2.15 (both m, 3H each, PC*H*CH$_3$), 2.21 [dd, J(P^{2}H^4) = 6.2, J(H^{2}H^4) = 12.1 Hz, 1H, H^4], 1.30 [dd, J(PH) = 13.0, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.25 [dd, J(PH) = 12.1, J(HH) = 7.3 Hz, 9H, PCHC*H*$_3$], 1.17 [dd, J(PH) = 12.6, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.13 [dd, J(PH) = 12.1, J(HH) = 7.2

Hz, 9H, PCHCH_3]; ^{13}C NMR (C_6D_6, 100.6 MHz) δ 168.7 [ddd, J(RhC) = 39.2, J(P^{1}C) = 19.1, J(P^{2}C) = 9.1 Hz, C^2], 107.5 (s, C^1), 88.8 [d, J(PC) = 7.0 Hz, *i*-C_5H_4R], 79.1 [d, J(RhC) = 3.6 Hz, C^3], 69.2, 68.0, 66.8, 66.7 (all s, C_5H_5 and C_5H_4R), 49.2 [ddd, J(RhC) = 24.1, J(P^{2}C) = 6.2, J(P^{1}C) = 5.9 Hz, C^4], 28.4 [d, J(PC) = 12.2 Hz, P*C*HCH$_3$], 27.7 [d, J(PC) = 14.9 Hz, P*C*HCH$_3$], 21.4 [d, J(PC) = 2.9 Hz, PCH*C*H$_3$], 20.8 [d, J(PC) = 3.0 Hz, PCH*C*H$_3$], 20.7, 20.5 (both s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz) δ 53.8 [dd, J(RhP) = 198.3, J(PP) = 21.7 Hz, P^2], 47.3 [dd, J(RhP) = 160.5, J(PP) = 21.7 Hz, P^1]. Anal. Calcd for $C_{32}H_{55}FeP_2Rh$: C, 58.19; H, 8.39. Found: C, 57.88; H, 7.93.



X-ray Measurements of 7. Single crystals were grown from acetone at −20 °C. Crystal data for **7**: $C_{31}H_{55}FeP_2Rh$, $M = 648.45$, monoclinic, space group $P2_1/n$, $a = 9.895(1)$ Å, $b = 15.081(3)$ Å, $c = 21.683(3)$ Å, $\beta = 103.09(2)°$, $V = 3151.6(8)$ Å^3, $Z = 4$, $D_c = 1.367$ Mg m^{-3}, μ (Mo K$_\alpha$) = 1.103 mm^{-1}. Intensities of a 0.5 × 0.5 × 0.5 mm rapidly cooled crystal in an oil drop[16] were collected by the φ-scan method to $2\theta_{\max} = 50°$. Of a total of 5581 scanned reflections 5580 were independent and used to refine 341 parameters, with a largest difference peak and hole of 1.11 and −0.60 e Å^{-3}. $R1$ ($F > 4\sigma(F)$) = 0.046 and w$R2$ = 0.094 (all data) with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and w$R2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$. The data set was collected on a Stoe-Huber-Siemens diffractometer fitted with a Siemens CCD detector system at 153(2) K using Mo K$_\alpha$ radiation ($\lambda = 0.710\ 73$ pm). Semiempirical absorption correction was applied. The structure was solved by direct methods.[17] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions, except for those who are bonded to the C1−C3 allylic moiety, which were refined freely. The structure was refined against F^2 with a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$, where $P = (F_o^2 + 2F_c^2)/3$.[18]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Grant SFB 347), the Volkswagen-Stiftung, and the Fonds der Chemischen Industrie for financial support. We also gratefully acknowledge support by Mrs. I. Geiter (technical assistance), Mrs. R. Schedl and Mr. C. P. Kneis (elemental analysis and DTA), Mrs. M. L. Schäfer and Dr. W. Buchner (NMR measurements), Dr. G. Lange and Mr. F. Dadrich (mass spectra), and Degussa AG (chemicals).

Supporting Information Available: An ORTEP diagram and tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **7** (8 pages). Ordering information is given on any current masthead page.

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