5646 *Organometallics* **2010,** *29,* 5646–5660
DOI: 10.1021/om100554d

ORGANOMETALLICS
Article

Synthesis and Reactivity of Rhodium Mono- and Bis(diolefin) Complexes. Characterization of Intermediates in the Rhodium-Catalyzed Cyclotetramerization of Butadiene†

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Received June 4, 2010

Rhodium bis(diolefin) complexes of the general composition [Rh(η^4-diene)$_2$(L)]X (diene = butadiene, isoprene, 2,3-dimethylbutadiene; L = P*i*Pr$_3$, PCy$_3$, P*t*Bu$_2$Me, As*i*Pr$_3$, Sb*i*Pr$_3$, CO, CN*t*Bu, CN-2,6-C$_6$H$_3$*i*Pr$_2$; X = CF_3SO_3, B(Ar$_f$)$_4$) were prepared from the nonionic compounds [Rh{μ-O$_2$S(O)CF$_3$}(η^2-C$_8$H$_{14}$)$_2$]$_2$ (**1**) and [Rh{κ^1-OS(O)$_2$CF$_3$}(η^4-diene)$_2$] (**2**−**4**) as precursors. The reaction of **1** with 1,3-cyclohexadiene led to the formation of [(η^6-C$_6$H$_6$)Rh(η^4-C$_6$H$_8$)]CF_3SO_3, whereas from **1** and 6,6′-dimethylfulvene the unsymmetrical sandwich compound [{η^5-C$_5$H$_4$CH(CH$_3$)$_2$}Rh{η^5-C$_5$H$_4$C(=CH$_2$)CH$_3$}]CF_3SO_3 was obtained. From [Rh{κ^2-O$_2$S(O)CF$_3$}(P*i*Pr$_3$)$_2$] and 1,3-cyclohexadiene or 6,6′-dimethylfulvene the four-coordinated diene complexes [Rh(η^4-diene)(P*i*Pr$_3$)$_2$]CF_3SO_3 were prepared, the cyclohexadiene derivative of which slowly rearranged at room temperature to *cis*,*cis*,*trans*-[Rh{κ^2-O$_2$S(O)CF$_3$}(H)$_2$(P*i*Pr$_3$)$_2$] and benzene. Similarly, [Rh(η^4-C$_6$H$_8$){κ^2-*i*Pr$_2$P(CH$_2$)$_3$P*i*Pr$_2$}]CF_3SO_3, obtained from [Rh(η^4-C$_4$H$_6$){κ^2-*i*Pr$_2$P(CH$_2$)$_3$P*i*Pr$_2$}]CF_3SO_3 and 1,3-cyclohexadiene, rearranged at 50 °C to [(η^6-C$_6$H$_6$)Rh{κ^2-*i*Pr$_2$P(CH$_2$)$_3$P*i*Pr$_2$}]CF_3SO_3. The bis(butadiene) complexes [Rh(η^4-C$_4$H$_6$)$_2$(PR$_3$)]CF_3SO_3 (R = *i*Pr, Cy) reacted in CH_2Cl_2 at ambient temperature to afford the neutral C−C coupling products [Rh(η^3:η^3-C$_8$H$_{12}$){κ^1-OS(O)$_2$CF$_3$}(PR$_3$)], which upon treatment with NaB(Ar$_f$)$_4$ gave the ionic compounds [Rh(η^3:η^3-C$_8$H$_{12}$)(PR$_3$)]B(Ar$_f$)$_4$. The two isomers [Rh(η^4-C$_4$H$_6$)$_2$(PR$_3$)]CF_3SO_3 and [Rh(η^3:η^3-C$_8$H$_{12}$){κ^1-OS(O)$_2$CF$_3$}(PR$_3$)] are likely intermediates in the (cyclo)oligo- and polymerization of butadiene catalyzed by **1**/PR$_3$. While the oligomeric fraction predominantly consists of C$_{12}$ and C$_{16}$ olefinic hydrocarbons, the main component among the C$_{16}$ tetramers is *cis*,*cis*,*trans*,*trans*-1,5,9,13-cyclohexadecatetraene.

Introduction

Despite the plethora of studies about the transition-metal-catalyzed oligo- and polymerization of butadiene,[1−4] cyclotetramerization has received little attention in the literature. The obvious reason is that in contrast to the cyclotrimerization, which was intensively investigated by Wilke and others,[5,6] to the best of our knowledge no efficient and selective catalyst for the formation of the cyclotetramer has been discovered. Several attempts, mainly undertaken by research groups in the perfume and fragrance industry,[7] to develop an appropriate catalytic system remained unsuccessful.

In the context of our work on the use of rhodium(I) sulfonato compounds to catalyze C−C coupling reactions of olefins with diphenyldiazomethane,[8a] we recently reported that the four-coordinated rhodium(I) triflate [Rh{κ^2-O$_2$S(O)CF$_3$}(P*i*Pr$_3$)$_2$] catalyzes not only the di- and oligomerization of ethene but also the polymerization of butadiene.[8b,c] An unexpected side product of this process was 1,5,9,13-cyclohexadecatetraene. Although in the initial studies the yield of this cyclotetramer was rather low, we

†Part of the Dietmar Seyferth Festschrift. Dedicated to Professor Dietmar Seyferth in recognition of his scientific achievements and his prominent role as chief editor of Organometallics.

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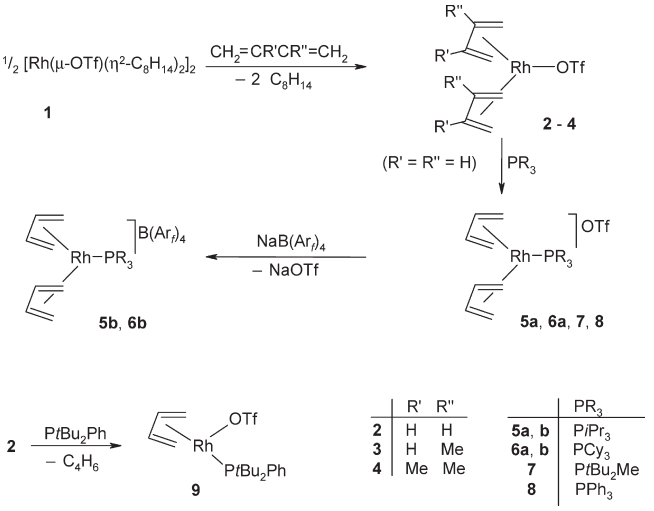
Scheme 1



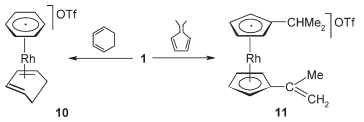
attempted to find out whether there could be a relationship regarding the mechanism of the rhodium-catalyzed cyclotetramerization and the nickel-catalyzed cyclotrimerization and polymerization of butadiene, the latter being quite well understood.[1,2,4−6,9]

In this article we disclose the preparation of a series of rhodium bis(diolefin) complexes of the general composition $[Rh(\eta^4\text{-diene})_2(L)]X$ (diene = butadiene, isoprene, 2,3-dimethylbutadiene; L = PR_3, As*i*Pr$_3$, Sb*i*Pr$_3$, CO, CNR; X = CF_3SO_3, $B(Ar_f)_4$) and, for diene = butadiene and PR_3 = P*i*Pr$_3$, PCy_3, its C−C coupling products $[Rh\{\eta^3{:}\eta^3\text{-}C_8H_{12}\}(PR_3)]X$. Several rhodium(I) mono(butadiene) and mono(cyclohexadiene) as well as some benzene, cyclopentadienyl, and π-allyl compounds were also prepared. Finally, the role of the bis(butadiene) complexes and the $\eta^3{:}\eta^3\text{-}C_8H_{12}$ C−C coupling products as intermediates in the cyclotetramerization reaction will be discussed. Some preliminary results have already been communicated.[10]

Results and Discussion

1. Preparation of Rhodium(I) Mono- and Bis(diolefin) Complexes from $[Rh\{\mu\text{-}O_2S(O)CF_3\}(\eta^2\text{-}C_8H_{14})_2]_2$ and $[Rh\{\kappa^1\text{-}OS(O)_2CF_3\}(s\text{-}cis\text{-}\eta^4\text{-}C_4H_6)_2]$ as the Precursors. In the context of our studies to elucidate the structure of supposed intermediates in the rhodium-catalyzed oligo- and polymerization of butadiene, we recently reacted the dimeric triflate-bridged cyclooctene rhodium(I) complex **1** with excess butadiene and isolated the five-coordinated product **2** (Scheme 1). The structure of the corresponding isoprene derivative **3** (prepared under the same conditions as **2** and **4**) was determined by X-ray crystallography.[11] Taking into account that the addition of 1 equiv of tricyclohexylphosphine to the nickel(0) compound $[Ni(s\text{-}cis\text{-}\eta^4\text{-}C_4H_4Me_2)_2]$ induces the coupling of the two ligated 2,3-dimethylbutadiene ligands, we similarly treated compound **2** with PCy_3, P*i*Pr$_3$, and P*t*Bu$_2$Me. In acetone or dichloromethane at room temperature,

Scheme 2



the ionic complexes **5a**, **6a**, and **7** were obtained and isolated as colorless solids in almost quantitative yield. Salt metathesis of **5a** and **6a** with $NaB(Ar_f)_4$ gave the corresponding tetraaryloborates **5b** and **6b**, which in solution are somewhat less labile than the triflate counterparts. The ^{1}H and ^{13}C NMR spectra of **5a**,**b**, **6a**,**b**, and **7** display only one set of signals for the proton and carbon atoms of the two butadiene units, which indicates a symmetric orientation of these ligands around the metal. In the case of **5a**, the s-cis disposition of the dienes was confirmed by an X-ray structure analysis.[11]

The reaction of **2** with 1 equiv of PPh_3 led to the formation of **8**, which was characterized by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy. The data are almost identical with those of the perchlorate $[Rh(s\text{-}cis\text{-}\eta^4\text{-}C_4H_6)_2(PPh_3)]ClO_4$, previously prepared by Schrock and Osborn from $[Rh(\eta^4\text{-}nor\text{-}C_7H_8)(PPh_3)_2]ClO_4$ and butadiene.[12] The reaction of **2** with PMe_3 in the ratio of 1:1 in dichloromethane afforded a mixture of products among which, apart from the starting material, the cations $[Rh(\eta^4\text{-}C_4H_6)_2(PMe_3)]^+$ and $[Rh(\eta^4\text{-}C_4H_6)(PMe_3)_3]^+$ could be identified by spectroscopic means.[13] The more bulky phosphine P*t*Bu$_2$Ph, which according to Tolman has the same cone angle as PCy_3,[14] reacted with **2** to give the uncharged complex **9**, isolated as an orange, slightly air-sensitive solid in 94% yield. In the ^{1}H NMR spectrum of **9** only three resonances for the butadiene protons appear, which is noteworthy insofar as, owing to the C_s symmetry of the molecule, six signals would be expected. As the ^{13}C NMR spectrum of **9** also shows only two resonances for the C_4H_6 carbon atoms, we assume that in solution the butadiene ligand rotates around the diene−rhodium axis, the rotation being fast on the NMR time scale.

The starting material **1** reacts not only with butadiene and its relatives but also with 1,3-cyclohexadiene. The product of this reaction, however, is not an analogue of **2** but the benzene rhodium(I) complex **10** (Scheme 2). It is a red-brown solid, the molar conductivity of which in nitromethane corresponds to that of an 1:1 electrolyte. The ^{1}H and ^{13}C NMR spectra of **10** display the same set of signals for the benzene and diene protons as was found for the uncharged complexes $[(\eta^6\text{-}C_6H_6)Fe(\eta^4\text{-}C_6H_8)]$ and $[(\eta^6\text{-}C_6H_6)Ru(\eta^4\text{-}C_6H_8)]$, respectively.[15] Regarding the formation of **10**, we assume that initially either the uncharged compound $[Rh\{\kappa^1\text{-}OS(O)_2CF_3\})(\eta^4\text{-}C_6H_8)_2]$ or the triflate of the 16-electron species $[Rh(\eta^4\text{-}C_6H_8)_2]^+$ is formed, which in several steps rearranges, possibly via $[(\eta^5\text{-}C_6H_7)RhH(\eta^4\text{-}C_6H_8)]^+$ and $[(\eta^6\text{-}C_6H_6)RhH(\eta^3\text{-}C_6H_9)]^+$, to the product. The loss of H_2 seems to be supported by the presence of free diene, which is

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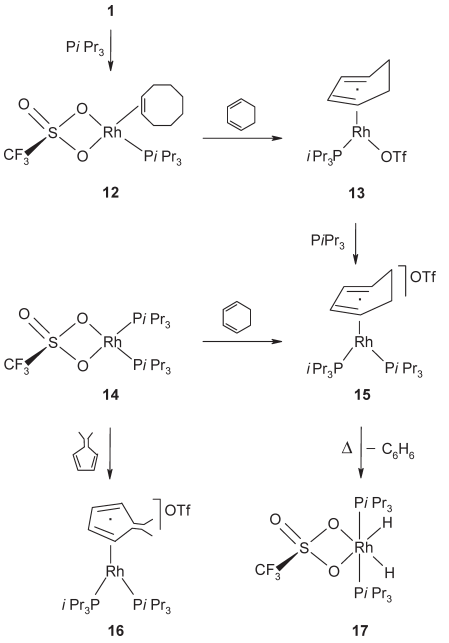
consistent with the observation that by using only 2 equiv of 1,3-C_6H_8 the yield of **10** is less than 50%. With excess diene, the yield of the isolated complex was 78%. Previously, it was mentioned that the reaction of $[Rh(\mu\text{-}Cl)(\eta^4\text{-}C_6H_8)]_2$ with $AgBF_4$ in the presence of 1,3-cyclohexadiene gave $[(\eta^6\text{-}C_6H_6)Rh(\eta^4\text{-}C_6H_8)]BF_4$,[16] but no analytical or spectroscopical data for this compound were given.

Under the same conditions as used for the preparation of **10**, the cyclooctene derivative **1** also reacted with 6,6-dimethylfulvene, affording exclusively the unsymmetrical sandwich complex **11**. It is a colorless air-stable solid, the properties of which resemble those of the rhodocenium salts $[Rh(\eta^5\text{-}C_5H_5)_2]X$.[17] Characteristic features in the ^1H NMR spectrum of **11** are two signals for the exocyclic methylene protons at δ 5.58 and 5.30 and a resonance for the $C(=CH_2)CH_3$ methyl protons at δ 2.00. The ^{13}C NMR spectrum of **11** displays six signals for the cyclopentadienyl carbon atoms, which are split into doublets with a $^{103}Rh,^{13}C$ coupling constant of 7.1 Hz. The two methylene carbon atoms resonate at δ 133.5 and 119.2 Hz, and the $C(=CH_2)CH_3$ carbon atom resonates at δ 21.1 Hz. These data perfectly agree with those of the uncharged complex $[\{\eta^5\text{-}C_5H_4C(=CH_2)CH_3\}Rh(\eta^4\text{-}nor\text{-}C_7H_8)]$.[18] Since the reaction of **1** with 6,6-dimethylfulvene does not lead to the symmetrical sandwich complex $[Rh\{\eta^5\text{-}C_5H_4CH(CH_3)_2\}_2]CF_3SO_3$, which would be expected if the exocyclic $C(CH_3)_2$ fragment of the fulvene is converted to the $CH(CH_3)_2$ unit by hydrogen abstraction from the solvent,[19] we assume that an intramolecular hydrogen transfer from one methyl group of an initially coordinated $\eta^4\text{-}C_5H_4\text{-}C(CH_3)_2$ ligand to a second dimethylfulvene moiety occurs. The 16-electron cation $[Rh\{\eta^4\text{-}C_5H_4C(CH_3)_2\}_2]^+$ could be an intermediate in this process.

With the aim to prepare the rhodium(I) complex $[Rh(\eta^4\text{-}C_6H_8)_2(PiPr_3)]CF_3SO_3$ as an analogue of **5a** with 1,3-cyclohexadiene as diene ligands, we treated the four-coordinated precursor **12**, generated in situ from **1** and $PiPr_3$,[8a] with excess 1,3-C_6H_8 but isolated the uncharged mono(diene) compound **13** in virtually quantitative yield (Scheme 3). The IR spectrum of the orange, only moderately air-sensitive solid shows for the asymmetric OSO stretching mode an absorption at 1317 cm^{-1}, which is consistent with the presence of a monodentate triflate ligand.[20] In analogy to **9**, the ^1H NMR spectrum of **13** displays only four resonances for the C_6H_8 protons at δ 5.11, 4.38, 1.88,and 0.94, whereas due to the C_s symmetry of the molecule eight signals would be expected. Assuming that a fast rotation of the 1,3-C_6H_8 ligand around the diene−rhodium axis occurs at room temperature, we measured the ^1H NMR spectrum of **13** in CD_2Cl_2 in a lower temperature range. At 183 K, each resonance of the olefinic protons is split into two slightly broadened singlets at δ 5.66 and 4.37 and δ 5.04 and 3.39, respectively. This is in agreement with our assumption. We note that even with a 10-fold excess of 1,3-cyclohexadiene compound **13** could not be converted into the coordinatively saturated 18-electron cation $[Rh(\eta^4\text{-}C_6H_8)_2(PiPr_3)]^+$.

Scheme 3



The reactions of either **13** with 1 equiv of $PiPr_3$ or of **14** (prepared from $[Rh(\eta^3\text{-}C_3H_5)(PiPr_3)_2]$ and CF_3SO_3H)[8a] with excess 1,3-cyclohexadiene afforded the four-coordinated bis(phosphine) complex **15** as a red, slightly air-sensitive solid in 80−85% yield. As for **13**, the ^1H NMR spectrum of **15** displays four resonances for the diene protons at δ 5.29, 4.98, 1.76, and 1.10, and the ^{31}P NMR spectrum shows a doublet at δ 41.2 with the rather large $^{103}Rh,^{31}P$ coupling constant of 170.3 Hz. Solutions of **15** in CH_2Cl_2 or CD_2Cl_2 are somewhat labile, and if they are stored at room temperature, a smooth change of color from red to yellow occurs. After 24 h, the ^1H NMR signals of **15** disappear and those of the rhodium(III) dihydrido compound **17** and free benzene are observed. The intensities of the signals of **17** and C_6H_6 correspond to a ratio of 1:1. The rhodium(III) dihydrido compound **17** was previously prepared in our laboratory from **14** and H_2.[8a]

The uncharged chelate complex **14** also reacts in dichloromethane with 6,6-dimethylfulvene to yield the ionic compound **16**. The ^{13}C NMR spectrum of the cation displays four resonances at δ 130.5, 130.4, 91.9, and 77.3 for the fulvene sp^2 carbon atoms, of which only that for the $C(CH_3)_2$ carbon does not show a $^{103}Rh,^{13}C$ coupling.[21] Therefore, it seems that the exocyclic C=C bond is not, or is only slightly, involved in the coordination to the metal and that a η^5- or η^6-bonding mode of the $C_5H_4C(CH_3)_2$ unit is of minor importance. In solutions of acetone or CH_2Cl_2 compound **16** is unstable, but in contrast to **15** it does not rearrange to a definite product; it produces a rhodium mirror instead.

The bis(butadiene) complex **2** (which with 1 equiv of $PiPr_3$ affords **5a**) reacts with $PiPr_3$ in the ratio of 1:3 to give the crystallographically characterized rhodium(I) compound $[Rh\{\eta^3\text{-}anti\text{-}(iPr_3PCH_2)CHCHCH_2\}(PiPr_3)_2]CF_3SO_3$.[11]

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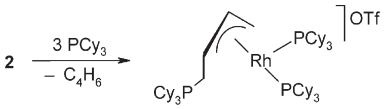
(21) (a) The other NMR data for the fulvene ligand of **15** correspond to those of the related complex $[Rh(\eta^4\text{-}C_5H_4CPh_2)\{P(OPh)_3\}_2]ClO_4$.[21b] (b) Jeffery, J.; Mawby, R. J.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1982**, 1411–1412.

Scheme 4



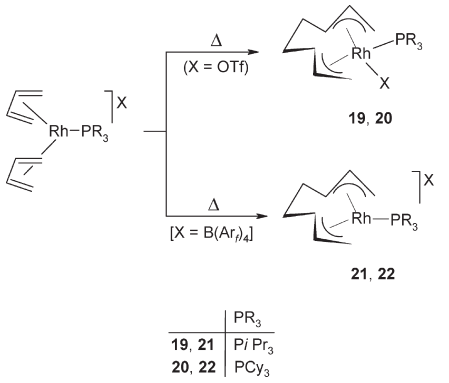
18

Under similar conditions, the reaction of **2** with PCy_3 in acetone results in the formation of the corresponding η^3-allylphosphonium derivative **18**. The proposed structure (see Scheme 4) is supported in particular by the ^{31}P NMR spectrum, which displays a doublet of doublet of doublets at δ 41.5 for the metal-bound phosphine in a position cis to the substituted η^3-allyl carbon atom and a doublet of doublets at δ 37.0 for the second metal-bound phosphine. Both signals exhibit a large $^{103}Rh,^{31}P$ coupling constant of, respectively, 181.7 and 186.1 Hz. The resonance for the carbon-linked ^{31}P nuclei appears as a doublet at δ 20.9 and shows a rather small $^{31}P,^{31}P$ coupling constant of 11.5 Hz. The ^1H and ^{13}C NMR data for the allylphosphonium ligand of **18** correspond to those of the triisopropylphosphine analogue. In contrast to PCy_3, triphenylphosphine reacts with **2** to yield not an analogue of **18** but rather the mono(diene) complex $[Rh(\eta^4\text{-}C_4H_6)(PPh_3)_2]CF_3SO_3$.[12b] Treatment of this compound with excess PPh_3 led to $[Rh(PPh_3)_3]CF_3SO_3$, which is also well-known.[22]

2. Thermally Induced C−C Coupling Reactions of the Phosphine Derivatives [Rh(*s-cis*-η^4-C_4H_6)$_2$(PR_3)]X. As mentioned above, solutions of **5a** and **6a** are not stable for longer periods of time and undergo a smooth change of color from orange to deep red. Monitoring the change by ^1H NMR spectroscopy reveals a decrease in the intensity of the signals for the butadiene protons and the appearance of six new resonances between δ 5.23 and 1.53 in CD_2Cl_2. If the solutions of **5a** are stored for 3 days or those of **6a** for 1 day at room temperature, the signals of the starting materials disappear. The rearrangement of **5a** and **6a** can be facilitated by heating and in dichloromethane under reflux is completed in 12 h for **5a** and in 6 h for **6a**. After removal of the solvent and recrystallization of the residue from CH_2Cl_2/pentane, the red, moderately air-stable solids **19** and **20** were isolated in ca. 75% yield. They can be stored without decomposition under argon at 0 °C for several days. The elemental analyses of **19** and **20** confirm that they have the same composition as the precursors **5a** and **6a**. An intramolecular C−C coupling of the two butadiene units has obviously occurred, and an η^3:η^3-octa-2,6-diene-1,8-diyl ligand is formed (Scheme 5).

For **19**, the presence of this ligand as well as the coordination of the triflate anion to rhodium has been substantiated by an X-ray structure analysis.[10] Apart from the fact that one terminal C_3 fragment of the C_8 chain is slightly distorted in comparison to the other, the noteworthy structural feature is that the Rh−O bond length of **19** is significantly longer (ca. 0.18 Å) than in the bis(butadiene) complex **2**. This could explain the fact that solutions of both **19** and **20** in nitromethane reveal a molar conductivity of ca. 70−75 $cm^2\ \Omega^{-1}\ mol^{-1}$, corresponding to a 1:1 electrolyte. Moreover, the IR spectra of **19** and **20** in CH_2Cl_2 show no absorptions in the range of 1310−1300 cm^{-1}, where an asymmetric OSO stretching mode for a coordinated triflate would be expected. The ^1H and ^{13}C NMR data for the C_8H_{12} ligand of **19** and **20** are quite similar to those of other transition-metal η^3:η^3-octa-2,6-diene-1,8-diyl and η^3:η^3-2,7-dimethylocta-2,6-diene-1,8-diyl complexes, such as $[(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{:}\eta^3\text{-}C_8H_{12})(L)]BF_4$ (L = CH_3CN, PMe_3),[23] $[Ni(\eta^3\text{:}\eta^3\text{-}C_8H_{12})(PPh_3)]$,[24] $[Ru(\eta^3\text{:}\eta^3\text{-}C_8H_{10}Me_2)Cl(\mu\text{-}Cl)]_2$,[25] and $[Ru(\eta^3\text{:}\eta^3\text{-}C_8H_{10}Me_2)(PiPr_3)Cl_2]$.[26] The NMR data of **19** and **20** confirm that only one stereoisomer is formed, despite the fact that, in principle, due to the syn and anti arrangement of the C_2H_4 bridge and the exo and endo orientation of the η^3-$CHCHCH_2$ units of the octadienediyl ligand, four diastereoisomers could be anticipated. The syn-exo,endo structure, found in the crystal for **19**, exists also in solution and thus seems to be the thermodynamically preferred species. The ^1H NMR spectra of **19** and **20** remain unchanged between −90 and 50 °C, indicating that no isomerization occurs in this range of temperature.

Scheme 5



Not only **5a** and **6a** but also **5b** and **6b** react on heating to afford the isomers **21** and **22** in good yields. The tetraaryolborates were also obtained from **19** and **20** and $NaB(Ar_f)_4$ in dichloromethane. In comparison to **5a** and **6a**, the phosphine complexes **7** and **8** behave differently, and when solutions of these compounds in CH_2Cl_2 or acetone were stirred at room temperature or elevated temperatures, a mixture of products was formed. An analogue of **19** or **20** could not be detected by NMR spectroscopy. The bis(isoprene) and bis(2,3-dimethylbutadiene) complexes $[Rh(s\text{-}cis\text{-}\eta^4\text{-}C_4H_5Me)_2(PiPr_3)]O_3SCF_3$ and $[Rh(s\text{-}cis\text{-}\eta^4\text{-}C_4H_4Me_2)_2(PiPr_3)]O_3SCF_3$,[11] structurally related to **5a**, undergo no isomerization when stirred in nitromethane for 6 h at 40 °C and were recovered unchanged.

The kinetics for the conversion of **5a**,**b** to **19** and **21** and of **6a**,**b** to **20** and **22** were determined in CD_3NO_2 using ^1H NMR spectroscopy. In each case, the reactions follow a first-order rate law. At 325 K, the tricyclohexylphosphine derivatives **6a**,**b** react slightly more quickly than the triisopropylphosphine counterparts **5a**,**b**; the difference in the free energy of activation $\Delta G^{\ddagger}$ is 1.1(5) kJ mol^{-1}. The anions $CF_3SO_3^-$ and $B(Ar_f)_4^-$ have nearly no influence; i.e., in the limit of errors the rate constants and the $\Delta G^{\ddagger}$ values for the

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Table 1. Activation Parameters for the Rearrangement of 5a to 19 and of 6a to 20

	$\Delta G^{\ddagger}$ (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
5a → **19**	99.9(5)	100.4(5)	1(2)
6a → **20**	98.8(5)	99.3(5)	2(2)

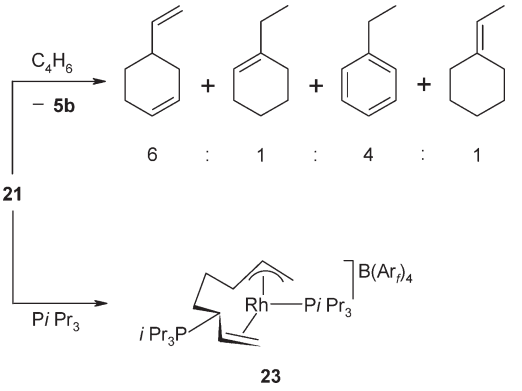
reactions of **5a**,**b** to **19** and **21** and of **6a**,**b** to **20** and **22** are the same.

The data for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, determined from the rate constants for the rearrangement of **5a** to **19** between 314.9 and 343.4 K and for the rearrangement of **6a** to **20** between 317.5 and 333.2 K in nitromethane, are summarized in Table 1. The values for $\Delta S^{\ddagger}$ are almost zero, indicating that the C−C coupling of the two butadiene ligands to generate the octadienediyl unit occurs intramolecularly. Since there is nearly no difference in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reactions of the P*i*Pr$_3$ complexes on one side and of the PCy$_3$ analogues on the other, one might assume that the initial step of the reactions consists of the dissociation of the phosphine ligand. While this could explain why the rate constants and the activation parameters for the C−C coupling processes to give **19** and **20** are nearly identical, a detailed theoretical investigation of alternative mechanistic paths for the formation of **19** led to a different result.[27] Using a gradient-corrected DFT method, it is most likely that the favorable route for the oxidative addition via C−C coupling starts from the prevalent 18-electron species [Rh(*s-cis*-η^4-C$_4$H$_6$)$_2$(P*i*Pr$_3$)]$^+$, which under kinetic control initially affords the η^3:η^3-anti isomer of the octadienediyl complex. The anti isomer consecutively transforms into the η^3:η^3-syn isomer **19**, which is the thermodynamically preferred species. It is worth noting that the computationally predicted energy profile is in complete agreement with the experimentally determined kinetic data.

Solutions of **21** and **22** in nitromethane are stable for weeks at room temperature. When the solutions are heated to 75 °C, mixtures of products are formed. In the case of **21**, the ^{1}H NMR spectrum showed after a short period of time a doublet of triplets at δ −23.7, indicating the formation of a rhodium(III) dihydrido species similar to **17** (see Scheme 3). Continuous heating led to the disappearance of this signal and the resonances of **21** as well. After removal of the solvent, a GC analysis of the oily residue revealed the presence of ethylbenzene and vinylcyclohexane as the main organic components. If a solution of **21** in CD_3NO_2 was stirred under a butadiene atmosphere for 3 h at 30 °C, apart from the bis(butadiene) complex **5b**, a mixture of 4-vinylcyclohexene, 1-ethylcyclohexene, ethylbenzene, and ethylidenecyclohexane in the ratio of 6:1:4:1 was formed. We note that 4-vinylcyclohexene is also the main product in the nickel(0)-catalyzed dimerization of butadiene, which proceeds via a nickel(II) η^3:η^3-octadienediyl intermediate.[24] With regard to the reaction of **21** with butadiene, we assume that the other organic products (1-ethylcyclohexene, ethylbenzene, and ethylidenecyclohexane) result from consecutive, rhodium-catalyzed reactions of initially generated 4-vinylcyclohexene. A rhodium(III) dihydrido species such as [RhH$_2$(P*i*Pr$_3$)$_2$(CH$_3$NO$_2$)$_2$]$^+$ could play a crucial role.

The addition of 1 equiv of P*i*Pr$_3$ to a solution of **21** in diethyl ether at 0 °C led to the formation of **23** by nucleophilic attack of the phosphine at one of the internal allylic carbon atoms (Scheme 6). The orange-yellow solid is rather air-sensitive and soluble in CH_2Cl_2, acetone, and diethyl ether. It can be stored under argon at −10 °C for several days. Each of the 12 protons and the 8 carbon atoms give rise to distinct resonances in the ^{1}H and ^{13}C NMR spectra of **23**, and each of these resonances is split due to couplings with ^{1}H, ^{13}C, ^{31}P, or ^{103}Rh nuclei. The designation of the signals for the protons of the phosphoniumoctadienyl moiety occurred on the basis of COSY and ^{1}H{^{31}P} NMR spectra. The chemical shifts of the allylic protons are in good agreement with those of [Rh{*anti*-η^3-(*i*Pr$_3$PCH$_2$)*C*H*C*H*C*H$_2$}(P*i*Pr$_3$)$_2$]CF$_3$SO$_3$ and other square-planar rhodium(I) η^3-allyl compounds.[11,28] A phosphoniumoctadienyl ligand similar to that found in **23** was recently generated at ruthenium by treatment of [RuCl$_2$(η^3:η^3-C$_8$H$_{10}$Me$_2$)(PF$_3$)] with PCy$_3$.[26]

Scheme 6



Similar to the reaction of **5a** to **19**, the addition of excess NaCl or KBr to solutions of **5a** in acetone at room temperature resulted in a change of color from orange to red. However, instead of the octadienediyl derivatives [Rh(η^3:η^3-C$_8$H$_{12}$)(P*i*Pr$_3$)X] (X = Cl, Br) the mono(butadiene) complexes **24** and **25** were formed (Scheme 7). They are analogues of **9** and **13** with the halide instead of the triflate coordinated to rhodium(I). The ^{1}H and ^{13}C NMR spectra of **24** and **25** show in CD_2Cl_2, even at 243 K, broadened signals which in analogy to **9** probably originate from a fast rotation of the diene ligand around the butadiene−rhodium axis. The X-ray structure analysis of **25** revealed a distorted-square-planar coordination sphere with a Br−Rh−P bond angle of 93.4°.[29] As in the case of [Rh{κ^1-OS(O)$_2$CF$_3$}(η^4-2,3-C$_4$H$_4$Me$_2$)(P*i*Pr$_3$)],[11] the diene ligand is linked unsymmetrically to the metal, and the Rh−C distances trans to bromide are significantly shorter than those trans to phosphorus. This illustrates the different trans influences of bromide on one side and P*i*Pr$_3$ on the other. The trans influence could also explain why the C−C bond lengths of the two terminal CH=CH$_2$ fragments of the butadiene ligand in **25** differ by ca. 0.11 Å, which is somewhat more than in [Rh{κ^1-OS(O)$_2$CF$_3$}(η^4-2,3-C$_4$H$_4$Me$_2$)(P*i*Pr$_3$)]. The Rh−Br and Rh−P distances in **25** of, respectively, 2.471(1) and 2.306(1) Å, agree quite well with those in related square-planar rhodium(I) bromo and rhodium(I) triisopropylphosphine compounds.[30,31]

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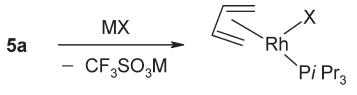
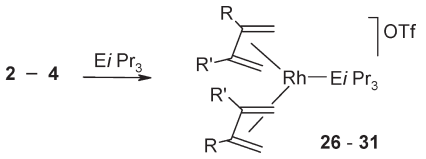
Scheme 7



24, **25**

	X
24	Cl
25	Br

Scheme 8



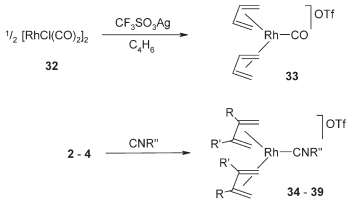
26 - 31

E = As	R	R'	E = Sb
26	H	H	**29**
27	Me	H	**30**
28	Me	Me	**31**

3. Rhodium(I) Mono- and Bis(diolefin) Complexes Containing Ligands Other Than P*i*Pr$_3$ and PCy$_3$. In attempting to find out whether the replacement of P*i*Pr$_3$ by ligands that are different in size and σ-donor/π-acceptor properties affects the C−C coupling of the two butadiene ligands, a series of compounds of the general composition [Rh(*cis*-η^4-C_4H_6)$_2$(L)]O_3SCF_3 was prepared. As for **5a**, the triisopropylarsine and triisopropylstibine derivatives **26** and **29** (Scheme 8) were obtained from **2** and equivalent amounts of As*i*Pr$_3$ and Sb*i*Pr$_3$. **26** and **29** are colorless solids, which are soluble in polar solvents and for short periods of time can be handled in air. Heating solutions of **26** and **29** in nitromethane at 60 °C for several hours did not result in the formation of the η^3:η^3-octadienediyl isomers; instead, the starting materials were recovered unchanged. The arsine complex **26** proved also to be inert toward an excess of As*i*Pr$_3$ and did not afford a rhodium η^3-allyl derivative with a CH_2As*i*Pr$_3$ functionality. It is worth noting that the reaction of **26** with Sb*i*Pr$_3$ in a 1:1 ratio gave the stibine derivative **29** and As*i*Pr$_3$, while on treatment of **29** with an equivalent amount of As*i*Pr$_3$ no ligand exchange occurred. Since the bond distances increase in the order Rh−P < Rh−As < Rh−Sb, it seems that not only the different σ-donor properties of the E*i*Pr$_3$ ligands but also steric requirements determine the stability of the five-coordinated bis(butadiene) complexes [Rh(*cis*-η^4-C_4H_6)$_2$(E*i*Pr$_3$)]O_3SCF_3.

The reactions of the bis(isoprene) and bis(2,3-dimethylbutadiene) compounds **3** and **4** (Scheme 1) with As*i*Pr$_3$ and Sb*i*Pr$_3$, carried out under the same conditions used for the preparation of **26**, gave the substitution products **27** and **28** and **30** and **31**, which owing to their ^{1}H and ^{13}C spectra are structurally related to the triisopropylphosphine counterparts [Rh(*cis*-η^4-C_4H_5Me)$_2$(P*i*Pr$_3$)]O_3SCF_3 and [Rh(*cis*-η^4-$C_4H_4Me_2$)$_2$(P*i*Pr$_3$)]O_3SCF_3.[11] Similar to the case for **26** and **29**, the isoprene and 2,3-dimethylbutadiene analogues are rather inert, and neither undergo a C−C coupling of the two diene ligands nor react with excess As*i*Pr$_3$ or Sb*i*Pr$_3$ by nucleophilic attack at the C_4 moiety. In contrast to the ^{1}H and ^{13}C NMR spectra of [Rh(*cis*-η^4-C_4H_5Me)$_2$(P*i*Pr$_3$)]-O_3SCF_3, those of **27** and **30** indicate that not only the anti isomer but mixtures of the anti and the syn isomers were formed.[32] For **27** the ratio of anti to syn was 91:9, and that for **30** was 86:14.

Scheme 9



R'' = *t* Bu	R	R'	R'' = Ar
34	H	H	**37**
35	Me	H	**38**
36	Me	Me	**39**

Passing a slow stream of CO through a solution of **2** in acetone led, after evaporation of ca. 80% of the solvent and addition of pentane, to the precipitation of a colorless solid which by drying in vacuo transforms into a yellow oil. The IR spectrum of the oil shows several CO stretching modes between 2030 and 2160 cm^{-1}, indicating that a mixture of rhodium carbonyl compounds is present. This is supported by the ^{1}H NMR spectrum of the oily substance, in which three sets of signals for the butadiene units appear. We assume that initially the wanted product **33** (see Scheme 9) is formed, which in vacuo loses the diene ligands in a stepwise fashion and decomposes to species such as [Rh(η^4-C_4H_6)-(CO)(OTf)], [Rh(μ-OTf)$(CO)_2$], etc.

To obtain the carbonyl complex **33** in analytically pure form, dimeric [Rh(μ-Cl)$(CO)_2$]$_2$ (**32**) was first treated with CF_3SO_3Ag and, after AgCl was filtered, subsequently with butadiene. The colorless solid, dried for only a short period of time at 0 °C in vacuo, is slightly air-sensitive and readily soluble in acetone and dichloromethane. The IR spectrum of **33** displays a ν(CO) band at 2096 cm^{-1}, which in comparison with the uncharged analogues [M(η^4-diene)$_2$(CO)] (M = Fe, Ru)[33] is shifted by ca. 100−120 cm^{-1} to higher wavenumbers. In comparison with **26** and **29**, the ^{1}H NMR signals for the butadiene protons of **33** are shifted by 0.4−1.4 ppm to lower fields, which is consistent with the stronger π-acceptor capability of CO in relation to As*i*Pr$_3$ and Sb*i*Pr$_3$. The isocyanide complexes **34**−**39** were prepared by the same route as their tertiary phosphine, arsine, and stibine counterparts and were completely characterized by analytical and spectroscopic means. In the case of the isoprene derivatives, the ratio of anti to syn stereoisomers was 78:22 for **35** and 76:24 for **38**. On heating, neither **34** nor **37** undergoes a C−C coupling reaction to furnish a product with a ligated η^3:η^3-C_8H_{12} unit.

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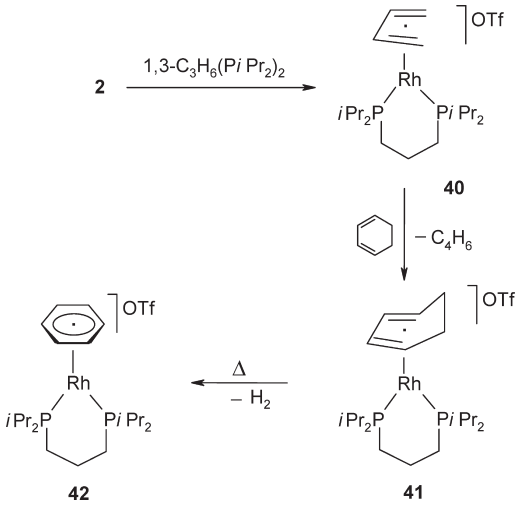
(32) In the anti isomers the methyl substituents of the two isoprene ligands are on opposite sides and in the syn isomers they are on the same side of the parallel C_4 planes.

(33) (a) Koerner von Gustorf, E.; Buchkremer, J.; Pfajfer, Z.; Grevels, F.-W. *Angew. Chem.* **1971**, *83*, 249−250; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 260−261. (b) Minniti, D.; Timms, P. L. *J. Organomet. Chem.* **1983**, *258*, C12–C14. (c) Noda, I.; Yasuda, H.; Nakamura, A. *Organometallics* **1983**, *2*, 1207–1214. (d) Cox, D. N.; Roulet, R. *Helv. Chim. Acta* **1984**, *67*, 1365–1367.

Scheme 10

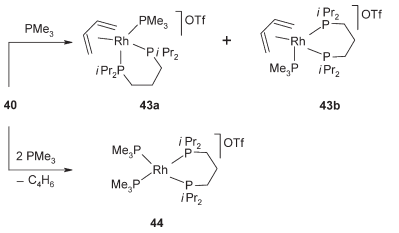


The reaction of **2** with 1 equiv of bidentate 1,3-C_3H_6-($PiPr_2$)$_2$ led to the formation of **40** by substitution of the triflate and one butadiene ligand (Scheme 10). The red air-stable product is not only inert in the solid state but also in acetone or dichloromethane solution and does not rearrange to a η^3-allylphosphonium species, as observed for the labile bis(triisopropylphosphine) analogue [Rh(η^4-C_4H_6)($PiPr_3$)$_2$]-CF_3SO_3.[11] A crystallographic study of **40** confirmed the square-planar coordination sphere around the rhodium atom with Rh−P distances of 2.297(3) Å,[29] which agree quite well with those in [Rh{*anti*-η^3-(*i*Pr_3PCH_2)*CHCHCH*$_2$)($PiPr_3$)$_2$]-PF_6 (2.3264(8) and 2.3176(8) Å).[11] The bite angle P−Rh−P of 94.76(12)° is similar to that in [Rh(η^3-$CH_2C_6H_5$){κ^2-*i*Pr_2P-$(CH_2)_3$P*i*Pr_2}] (96.99(4)°)[34] and [Rh_2H_2(μ-H)$_2$(μ-O_2ClO_2){κ^2-*i*Pr_2P$(CH_2)_3$P*i*Pr_2}$_2$] (94.9(1)°),[35] respectively.

The butadiene complex **40** reacted in dichloromethane with excess 1,3-C_6H_8 at room temperature to furnish the cyclohexadiene counterpart **41** as an orange-red, slightly air-sensitive solid. The properties as well as the ^{1}H and ^{31}P NMR data of **41** are in accord with those of the structurally related bis(triisopropylphosphine) derivative **15**. When a solution of **41** in CD_2Cl_2 was heated at 50 °C, a gradual change of color from red to light red occurred. After 3 h, the ^{1}H and ^{31}P NMR signals of **41** had disappeared and a new set of signals assigned to the rhodium(I) benzene complex **42** could be observed. Typical data for **42** are the singlet at δ 7.35, corresponding to six protons, in the ^{1}H NMR and the doublet at δ 47.9 in the ^{31}P NMR spectrum. The chemical shifts and the ^1J(Rh,P) coupling constant of the phosphorus resonance are in good agreement with the data for [(η^6-C_6H_6)Rh-(PEt_3)$_2$]BF_4[36] and [{η^6-C_6H_5(CH_2)$_3$P*i*Pr_2-κP}Rh{κ-*i*Pr_2P-$(CH_2)_3C_6H_5$}]PF_6,[37] respectively.

The reaction of **40** with 1 equiv of PMe_3 in dichloromethane at −30 °C resulted in the formation of the 1:1 adduct **43**, which was isolated as a yellow solid in excellent yield (Scheme 11). The anticipated attack of the phosphine at the butadiene ligand (as takes place in the case of **18**) did not occur. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **43** reveal that the five-coordinated cation consists of a ca. 7:1 mixture of two isomers, which differ in the steric arrangement of the bis-phosphinopropane and trimethylphosphine ligands. In the major (called *basal*) isomer **43a**, PMe_3 and one of the P*i*Pr_2 units occupy two of the basal positions of the square pyramid, while in the minor (called *apical*) isomer **43b** both P*i*Pr_2 units are in the base. This structural proposal is most clearly supported by the ^{31}P NMR spectrum of the mixture of the two isomers, which shows for **43a** one doublet of doublets of doublets for one and a doublet of doublets for the other P*i*Pr_2 moiety.[38] For **43b**, one doublet of doublets is observed for both P*i*Pr_2 units.

Scheme 11



The reaction of **40** with 2 equiv of PMe_3 afforded, under the same conditions as used for **43**, the four-coordinated complex **44** by displacement of the butadiene ligand. The product is quite stable and can be stored under an inert atmosphere for days at room temperature. The ^{31}P NMR spectrum of **44** is consistent with the presence of an AA′BB′X spin system, which was confirmed by simulation using the WIN-DAISY program of Bruker. The data were in excellent agreement with those of [$RuCl_2$\{κ^2-Ph_2P$(CH_2)_3$PPh_2\}(PMe-Ph_2)$_2$][39,40] and [Rh(η^3-$CH_2C_6H_5$){κ^2-*i*Pr_2P$(CH_2)_3$P*i*Pr_2}].[34]

4. Rhodium-Catalyzed Cyclotetramerization of Butadiene. Mechanistic studies on the nickel-catalyzed cyclotrimerization of butadiene, carried out in particular by Wilke and his group, unveiled that a nickel(II) complex of the composition [Ni(η^3:η^2:η^3-$C_{12}H_{18}$)] with a chain-like α,ω-bis(η^3-allyl)ene ligand is a key intermediate in this process.[1b,5] This species is presumably generated via the labile bis(butadiene) nickel(0) [Ni(η^4-C_4H_6)$_2$], which could undergo an oxidative C−C coupling of the butadiene ligands to give an isomeric [Ni-(C_8H_{12})] compound with the noncyclic C_8H_{12} ligand either in a η^3:η^3 or η^1:η^3 bonding mode. Subsequent addition of a third molecule of butadiene leads to the isolated and structurally characterized α,ω-bis(η^3-allyl)ene complex [Ni(η^3:η^2:η^3-$C_{12}H_{18}$)], which in the presence of excess butadiene affords 1,5,9-cyclododecatriene by ring closure. The postulated intermediate [Ni(η^4-C_4H_6)$_2$] is then re-formed, and the catalytic cycle can start again.

If the nickel catalysts used for the formation of cyclo-1,5,9-$C_{12}H_{18}$ were modified by adding a tertiary phosphine or

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(35) Tani, K.; Yamagata, T.; Tatsuno, Y.; Saito, T.; Yamagata, Y.; Yasuoka, N. *J. Chem. Soc., Chem. Commun.* **1986**, 494–495.
(36) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1988**, *7*, 1588–1596.
(37) Werner, H.; Canepa, G.; Ilg, K.; Wolf, J. *Organometallics* **2000**, *19*, 4756–4766.

(38) The assignment is based on the difference in the ^{103}Rh,^{31}P coupling constants, which for the apical P*i*Pr_2 phosphorus atom is 152.0 Hz, in comparison with ^1J(Rh,P) = 159.5 Hz for **3a**. The ^{103}Rh,^{31}P coupling constant for the basal P*i*Pr_2 phosphorus atom is 109.0 Hz, similar to ^1J(Rh,P) = 114.5 Hz for the PMe_3 phosphorus atom, which also occupies a basal position.
(39) (a) Baacke, M.; Hietkamp, S.; Morton, S.; Stelzer, O. *Chem. Ber.* **1982**, *115*, 1389–1398. (b) Baker, M. V.; Field, L. D. *Inorg. Chem.* **1987**, *26*, 2010–2011.
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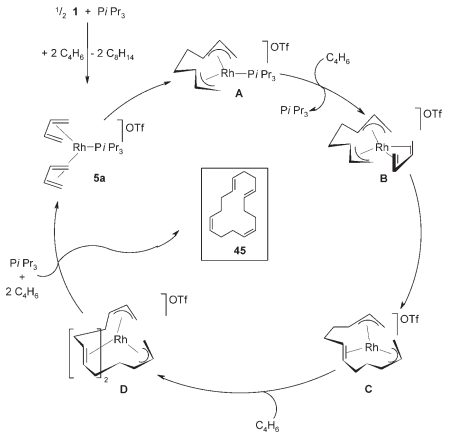
phosphite, dimerization of butadiene occurred. In general, a mixture of dimers is formed with 1,5-cyclooctadiene (COD) and 4-vinylcyclohexene (VCH) as the main components. With PCy_3, the ratio of COD and VCH is ca. 1:1.[1b] Wilke et al. assumed that in one of the initial stages of the reaction the nickel(II) octadienediyl compound [Ni(η^3:η^3-C_8H_{12})(PR_3)] is generated, which undergoes two stepwise η^3 to η^1 haptotropic shifts to give, apart from transient [Ni(PR_3)], COD and VCH plus minor amounts of other butadiene dimers.

Taking these results into consideration, some common aspects between the nickel-catalyzed dimerization and the rhodium-catalyzed tetramerization of butadiene are perceptible. The first is that the reactions of [Rh{κ^1-$OS(O)_2CF_3$}(η^4-C_4H_6)$_2$] (**2**), containing a labile triflate ligand, and (the postulated) [Ni(η^4-C_4H_6)$_2$] with PCy_3 occur via oxidative C−C coupling of the butadiene ligands to yield compounds with a η^3:η^3-cyclooctadienediyl ligand. Moreover, the nickel complexes [Ni(η^3:η^3-C_8H_{12})(PR_3)] as well as the corresponding rhodium derivatives [Rh(η^3:η^3-C_8H_{12})(PR_3)]X (such as **21**) react under mild conditions with butadiene to yield a mixture of C_8 hydrocarbons with VCH as one of the main components.

However, in the absence of free PR_3 the bis(butadiene) nickel compound [Ni(η^4-C_4H_6)$_2$] behaves differently from the bis(butadiene)phosphine rhodium derivatives **5a** and **6a**. While the first reacts with excess butadiene to yield cyclo-1,5,9-$C_{12}H_{18}$ almost exclusively, the rhodium complexes **5a** and **6a** give (in nitromethane at 75 °C) mixtures of (cyclo)-oligomers and polymers. As already mentioned,[10] the oligomeric fraction consists predominantly (ca. 90%) of a mixture of C_{12} and C_{16} hydrocarbons. Among the tetramers, a high selectivity for the cis,cis,trans,trans isomer of 1,5,9,13-cyclohexadecatetraene was observed. Raising the temperature to 95 °C resulted in a higher percentage of the tetramers in the oligomeric fraction but also in a significant increase of the amount of polymers.

To elucidate the influence of the solvent, the type of phosphine ligand, and the ratio Rh:PR_3, a series of experiments was carried out.[41] The dimeric rhodium(I) derivative **1** was used as the catalyst precursor. Under standard conditions (10 mL of solvent, 3 mL of butadiene, T = 90 °C, t = 5 h, Rh:C_4H_6 = 1:300), the highest amounts of (cyclo)oligomers of butadiene were formed if 2 mol of PR_3 (R = *i*Pr, Cy) was used per mole of **1**. In the absence of phosphine, only traces of (cyclo)oligomers were formed. The same result is obtained with the ratio of **1**:PR_3 = 1:4, probably because in this case a deactivation of the catalyst occurs. Regarding the influence of the solvent, the catalytic activity increases significantly in the order $CH_3CN \cong$ THF < acetone < methanol ≅ nitromethane. Similarly, the selectivity for 1,5,9,13-$C_{16}H_{24}$ compared with C_8, C_{12}, and other C_{16} (cyclo)oligomers[42] increases along CH_3CN < THF < acetone ≅ methanol < nitromethane. In methanol and nitromethane, the system **1**/PCy_3 is slightly more active than the counterpart **1**/P*i*Pr$_3$. A surprising result is that N*i*Pr$_3$, which in contrast to P*i*Pr$_3$ does not react with **2** to yield [Rh(*s*-*cis*-η^4-C_4H_6)$_2$(N*i*Pr$_3$)]O_3SCF_3, proved to be a good cocatalyst and favors the formation of 1,5,9,13-$C_{16}H_{24}$. In the first 10 min of the reaction (under standard conditions with the ratio **1**:N*i*Pr$_3$ = 1:2) only 1,5,9,13-$C_{16}H_{24}$ is generated and no other C_8, C_{12}, or C_{16} (cyclo)oligomers can be detected by GC/MS. The system **1**/N*i*Pr$_3$, however, is not stable for a longer period of time, and after ca. 1 h a distinct decrease in the catalytic activity (and the selectivity for 1,5,9,13-$C_{16}H_{24}$ as well) is observed. In contrast to the case for **5a**, which for the catalytic studies was prepared in situ from **2** and an equimolar amount of P*i*Pr$_3$, the arsine and stibine analogues **26** and **29** were catalytically inactive in the presence of butadiene.

Scheme 12



To summarize these results, it is not clear as yet what the final steps of the catalytic cycle for the tetramerization of butadiene to *cis*,*cis*,*trans*,*trans*-1,5,9,13-cyclohexatetraene **45** are. With Wilke's results as a given, we assume that the ionic intermediate **A** (which, as mentioned above, is in equilibrium with the isolated compound **19** in polar solvents such as nitromethane) reacts in the presence of excess butadiene by replacing the phosphine ligand to yield the butadiene adduct **B** (Scheme 12). This undergoes a 2-fold C−C coupling reaction to generate **C** and subsequently **D**. In the final step, and in the presence of butadiene and P*i*Pr$_3$, the 16-membered cyclotetraene **45** is formed and the precursor **5a** is regenerated. We assume that the byproducts of the catalytic reaction (*all-trans*-1,3,6,10-dodecatetraene, *cis*,*trans*,*trans*-1,3,6,10-dodecatetraene, *trans*-1,4-polybutadiene, etc.)[42] probably originate from the labile chain-like α,ω-bis(η^3-allyl)diene species **D**. Similarly, Wilke et al. proposed that the linear dodecatrienes, observed as byproducts in the nickel-catalyzed trimerization of butadiene to cyclo-1,5,9-$C_{12}H_{18}$, are generated from the open-chain [Ni(η^3:η^2:η^3-$C_{12}H_{18}$)] intermediate.[1b,5]

The unanswered question remains why [Ni(η^3:η^2:η^3-$C_{12}H_{18}$)] undergoes a reductive C−C coupling to furnish cyclo-1,5,9-$C_{12}H_{18}$ and the related intermediate **C** preferentially reacts with another molecule of butadiene to give **D** and finally **45**. One reason could be that [Ni(η^3:η^2:η^3-$C_{12}H_{18}$)] is a 18-electron and **C** a 16-electron species. The latter not only is electronically unsaturated but also has an open coordination site to which a butadiene molecule can be bound. We assume that this process is favored in comparison with the addition of P*i*Pr$_3$, possibly for steric reasons. Although the configuration of **D** is unknown, a simple model suggests that the coordination of the α,ω-bis(η^3-allyl)diene ligand to rhodium(III)

(41) For further details of the catalytic studies see: Bosch, M. Dissertation, Universität Würzburg, 2001, Chapter 7 and pp 346-356.

(42) GC/MS analyses confirmed that the C_{12} fraction consists mainly of a 2:1 mixture of *all-trans*-1,3,6,10-dodecatetraene and *cis*,*trans*,*trans*-1,3,6,10-dodecatetraene, in addition to small amounts of *all-trans*-1,5,9-cyclododecatriene and *cis*,*trans*,*trans*-1,5,9-cyclododecatriene. The linear tetraenes, cyclic trienes, and *trans*-1,4-polybutadiene were identified by ^{1}H and ^{13}C NMR spectroscopy.

in **D** causes a significant ring strain and thus facilitates the reductive elimination of **45**. A theoretical study in prospect should provide more insight into the energetic aspects and mechanism of the process.[27]

Conclusions

The present investigation has shown that the well-known rhodium(I) cyclooctene dimer **1** is a suitable starting material for the preparation of a series of rhodium(I) mono- and bis(diolefin) complexes. The most noteworthy representatives of this series are the bis(butadiene) compounds [Rh(*s-cis*-η^4-$C_4H_6)_2(PR_3)$]X (**5a**,**b** and **6a**,**b**), which catalyze the (cyclo)oligomerization of butadiene. The first and rate-determining step of this reaction consists of the C−C coupling of the butadiene ligands of **5a**,**b** or **6a**,**b** to afford the rhodium(III) octadienediyl isomers **19**−**22**, which with excess C_4H_6 undergo further C−C coupling reactions leading to C_{12}, C_{16}, and traces of higher oligomers and to *trans*-1,4-polybutadiene. Among these C−C coupling products, the tetramer **45** deserves particular attention because, in contrast to the transition-metal-catalyzed cyclotrimerization, almost nothing is known about the analogous cyclotetramerization of C_4H_6. In 1954, Reed reported that in the nickel-catalyzed oligomerization of butadiene with nickel carbonyl phosphine and phosphite compounds as catalysts, apart from 1,5-cyclooctadiene as the main product (yield 30−40%), a small amount of a configurationally uncharacterized cyclic tetramer was obtained.[43] Somewhat later, Dzhemilev et al.[44] and Miyake et al.[45] generated two catalytic systems from $TiCl_4/Et_2AlCl$/2-vinylfuran and from nickel η^3-allyl compounds, both of which convert butadiene to a mixture of linear and cyclic oligo- and polyenes. With the titanium system, which was previously used by Wilke for the polymerization and cyclotrimerization of butadiene,[46] a mixture of mainly all-trans cyclotrimers and all-trans cyclotetramers in a ratio of 7:3 was formed. With the nickel η^3-allyl compounds, a variety of C_8, C_{12}, C_{16}, C_{20}, and C_{24} (cyclo)oligomers were obtained. Among the cyclotetramers, **45** has not been identified.[45] In contrast to these results, the rhodium(I) bis(butadiene) and rhodium(III) cyclooctadienediyl complexes **5a**,**b**, **6a**,**b**, and **19**−**22** provide a rather narrow product distribution of butadiene oligomers and polymers and a relatively high selectivity for **45** in the oligomeric fraction.

To increase the amount of **45** and of other C_{16} isomers, which could be suitable for the preparation of muscone,[47] further variations of the ligand L in the rhodium(I) precursor [Rh(*s-cis*-η^4-$C_4H_6)_2$(L)]X might be successful. Our work, as well as that of Wilke and his group,[1,5,24] indicates that for both the rhodium- and the nickel-catalyzed (cyclo)oligomerization of butadiene sterically demanding phosphines or related phosphites seem to be promising tools. Recent theoretical investigations support this assumption.[48]

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(44) (a) Dzhemilev, U. M.; Gubaidullin, L. Y. *Zh. Org. Khim.* **1976**, *12*, 44-46; *Chem. Abstr.* **1976**, *84*, 121244. (b) Tolstikov, G. A.; Dzhemilev, U. M.; Gubaidullin, L. Y. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, *2*, 487; *Chem. Abstr.* **1975**, *82*, 139467.
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Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. $NaB(Ar_f)_4$[49] and the rhodium complexes **1**,[8a] **2**−**4**, **5a**,[11] **12**, **14**,[8a] and **32**[50] were prepared as described in the literature. P*i*Pr$_3$, PCy$_3$, P*t*Bu$_2$Me, and P*t*Bu$_2$Ph were commercial products from Strem Chemicals. As*i*Pr$_3$ and Sb*i*Pr$_3$ were gifts from members of our research group. The commercially available olefins were used without further purification. NMR spectra were recorded on Bruker AC 200, Bruker Avance 300, and Bruker AMX 400 instruments at room temperature, if not stated otherwise. IR spectra were recorded on Perkin-Elmer 1420 and Bruker IFS FT-IR spectrometers. Mass spectra were recorded on 8200 Finnigan MAT and Varian CH7MAT instruments. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broadened signal. The term vt indicates a virtual triplet, and $N = {}^3J(P,H) + {}^5J(P,H)$, ${}^1J(P,C) + {}^3J(P,C)$, or ${}^2J(P,C) + {}^4J(P,C)$. The coupling constants are given in hertz. The molar conductivity Λ_M was determined in nitromethane using a Schott CG 851 conductometer equipped with an LF 1050 cell. Kinetic measurements were carried out in NMR tubes using a Bruker Avance 300 spectrometer equipped with a variable-temperature unit. The solvent was CD_3NO_2. The signals of $B(Ar_f)_4^-$ were used as internal standards for the determination of the concentration of **19** and **20**, respectively. A general procedure for the catalytic reactions leading to (cyclo)oligomers and polymers of butadiene and for the separation and the analytical and spectroscopic data for **45** was already given.[10]

Preparation of [Rh(*s-cis*-η^4-$C_4H_6)_2$(P*i*Pr$_3$)]B(Ar$_f$)$_4$ (5b). A solution of **5a** (320 mg, 0.61 mmol) in dichloromethane (20 mL) was treated at 0 °C with $NaB(Ar_f)_4$ (541 mg, 0.61 mmol). After it was warmed to room temperature, the solution was stirred for 30 min. An off-white solid precipitated. The solution was filtered, and the filtrate was concentrated to ca. 2 mL in vacuo. After the argon atmosphere was replaced by butadiene and pentane (30 mL) was added, a colorless solid was formed. It was decanted from the solution, washed three times with pentane (5 mL each), and dried in vacuo: yield 591 mg (83%). Anal. Calcd for $C_{49}H_{45}BF_{24}PRh$: C, 47.67; H, 3.67. Found: C, 47.32; H, 3.54. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.76 (m, 8 H, *o*-H of Ar$_f$), 7.60 (br s, 4 H, *p*-H of Ar$_f$), 5.55 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.21 (br d, ^3J(H,H) = 6.9 Hz, 4 H, H of CH_2 *cis* to =CH), 2.54 (m, 3 H, PC*H*CH$_3$), 1.37 (dd, ^3J(P,H) = 13.7, ^3J(H,H) = 7.1 Hz, 18 H, PCHC*H*$_3$), 1.30 (br d, ^3J(H,H) = 10.2 Hz, 4 H, H of CH_2 *trans* to =CH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 162.2 (q, ^1J(B,C) = 49.9 Hz, *ipso*-C of Ar$_f$), 135.2 (br s, *o*-C of Ar$_f$), 129.3 (qq, ^2J(F,C) = 31.6, ^4J(F,C) = 2.8 Hz, *m*-C of Ar$_f$), 125.0 (q, ^1J(F,C) = 272.3 Hz, CF_3), 117.9 (sept, ^3J(F,C) = 3.9 Hz, *p*-C of Ar$_f$), 89.9 (d, ^1J(Rh,C) = 3.3 Hz, CH_2=*C*H*C*H=CH_2), 52.4 (dd, ^2J(Rh,C) = 8.5, ^1J(P,C) = 3.4 Hz, *C*H_2=CHCH=*C*H_2), 28.1 (d, ^1J(P,C) = 19.4 Hz, P*C*HCH$_3$), 20.3 (s, PCH*C*H$_3$). ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −63.1 (s). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 47.8 (d, ^1J(Rh,P) = 157.8 Hz).

Preparation of [Rh(*s-cis*-η^4-$C_4H_6)_2$(PCy$_3$)]CF$_3$SO$_3$ (6a). A solution of **2** (542 mg, 1.40 mmol) in dichloromethane (50 mL) was treated with PCy$_3$ (391 mg, 1.40 mmol) and stirred for 30 min at room temperature. After the solution was concentrated to ca. 2 mL in vacuo, the argon atmosphere was replaced by butadiene and pentane (30 mL) was added. A colorless solid was formed. It was decanted from the solution, washed three times with pentane (5 mL each), and dried in vacuo: yield 842 mg (94%); mp 77 °C dec. Λ_M = 72 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{27}H_{45}F_3O_3PRhS$: C, 50.62; H, 7.08; S, 5.01. Found: C, 50.86; H, 6.80; S, 4.68. IR (CH_2Cl_2): ν(OSO$_{asym}$) 1265, ν(CF$_{asym}$) 1161,

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$\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.91 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.21 (m, 4 H, H of CH_2 *cis* to =CH), 2.2−1.1 (br m, 37 H, C_6H_{11} and H of CH_2 *trans* to =CH). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 120.9 (q, ^1J(F,C) = 322.5 Hz, CF_3), 90.8 (br s, CH_2=*C*H*C*H=CH_2), 52.7 (br s, *C*H_2=CHCH=*C*H_2), 38.2 (br s, CH of C_6H_{11}), 31.0 (br s, γ-CH_2 of C_6H_{11}), 28.1 (d, ^2J(P,C) = 9.2 Hz, α-CH_2 of C_6H_{11}), 26.8 (s, β-CH_2 of C_6H_{11}). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.5 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 34.2 (d, ^1J(Rh,P) = 159.4 Hz).

Preparation of [Rh(*s-cis*-η^4-C_4H_6)$_2$(PCy_3)]$B(Ar_f)_4$ (6b). This compound was prepared as described for **5b** from **6a** (286 mg, 0.45 mmol) and $NaB(Ar_f)_4$ (399 mg, 0.45 mmol). A colorless solid was obtained: yield 500 mg (86%); mp 73 °C dec. Anal. Calcd for $C_{58}H_{57}BF_{24}PRh$: C, 51.42; H, 4.24. Found: C, 50.93; H, 4.24. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.75 (m, 8 H, *o*-H of Ar_f), 7.59 (br s, 4 H, *p*-H of Ar_f), 5.55 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.14 (d, ^3J(H,H) = 6.2 Hz, 4 H, H of CH_2 *cis* to =CH), 2.4−1.1 (br m, 37 H, C_6H_{11} and H of CH_2 *trans* to =CH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 162.2 (q, ^1J(B,C) = 49.6 Hz, *ipso*-C of Ar_f), 135.2 (br s, *o*-C of Ar_f), 129.3 (qq, ^2J(F,C) = 31.3, ^4J(F,C) = 2.6 Hz, *m*-C of Ar_f), 125.0 (q, ^1J(F,C) = 272.5 Hz, CF_3), 117.9 (sept, ^3J(F,C) = 3.3 Hz, *p*-C of Ar_f), 89.9 (d, ^1J(Rh,C) = 4.2 Hz, CH_2=*C*H*C*H=CH_2), 52.8 (dd, ^2J(Rh,C) = 8.3, ^1J(P,C) = 3.7 Hz, *C*H_2=CHCH=*C*H_2), 38.4 (d, ^1J(P,C) = 18.5 Hz, CH of C_6H_{11}), 31.1 (br s, γ-CH_2 of C_6H_{11}), 28.1 (d, ^2J(P,C) = 9.0 Hz, α-CH_2 of C_6H_{11}), 26.8 (s, β-CH_2 of C_6H_{11}). ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −63.1 (s). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 34.4 (d, ^1J(Rh,P) = 157.6 Hz).

Preparation of [Rh(*s-cis*-η^4-C_4H_6)$_2$($PtBu_2Me$)]CF_3SO_3 (7). This compound was prepared as described for **6a** from **2** (108 mg, 0.28 mmol) and $PtBu_2Me$ (56 μL, 0.28 mmol). A colorless solid was obtained: yield 146 mg (98%); mp 64 °C dec. Λ_M = 71 $cm^2\,\Omega^{-1}\,mol^{-1}$. Anal. Calcd for $C_{18}H_{33}F_3O_3PRhS$: C, 41.55; H, 6.39; S, 6.16. Found: C, 41.19; H, 6.35; S, 6.10. IR (CH_2Cl_2): $\nu(OSO_{asym})$ 1279, $\nu(CF_{sym})$ 1250, $\nu(CF_{asym})$ 1161, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 5.91 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.16 (m, 4 H, H of CH_2 *cis* to =CH), 1.53 (d, ^2J(P,H) = 6.7 Hz, 3 H, PCH_3), 1.12 (d, ^3J(P,H) = 13.6 Hz, 18 H, $PCCH_3$), signal of H of CH_2 *trans* to =CH not exactly located. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 90.9 (br s, CH_2=*C*H*C*H=CH_2), 54.5 (br s, *C*H_2=CHCH=*C*H_2), 38.0 (d, ^1J(P,C) = 12.8 Hz, P*C*CH_3), 30.4 (d, ^2J(P,C) = 4.1 Hz, PC*C*H_3), 6.8 (d, ^1J(P,C) = 20.6 Hz, PCH_3), signal of CF_3 not exactly located. ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −79.0 (s). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 45.2 (d, ^1J(Rh,P) = 159.4 Hz).

Preparation of [Rh(*s-cis*-η^4-C_4H_6)$_2$(PPh_3)]CF_3SO_3 (8). This compound was prepared as described for **6a** from **2** (178 mg, 0.46 mmol) and PPh_3 (121 mg, 0.46 mmol). A colorless solid was obtained: yield 267 mg (93%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.63 (m, 6 H, *o*-H of C_6H_5), 7.53 (m, 9 H, *m*-H and *p*-H of C_6H_5), 6.03 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.38 (d, 4 H, ^3J(H,H) = 6.3 Hz, H of CH_2 *cis* to =CH), 0.73 (dd, ^3J(P,H) = 11.1, ^3J(H,H) = 10.2 Hz, H of CH_2 *trans* to =CH). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 134.1 (d, ^2J(P,C) = 10.4 Hz, *o*-C of C_6H_5), 132.7 (d, ^1J(P,C) = 44.4 Hz, *ipso*-C of C_6H_5), 131.3 (d, ^4J(P,C) = 2.3 Hz, *p*-C of C_6H_5), 129.2 (d, ^3J(P,C) = 10.2 Hz, *m*-C of C_6H_5), 93.0 (d, ^1J(Rh,C) = 2.5 Hz, CH_2=*C*H*C*H=CH_2), 58.4 (dd, ^1J(Rh,C) = 8.6, ^2J(P,C) = 2.1 Hz, *C*H_2=CHCH=*C*H_2), signal of CF_3 not exactly located. ^{19}F NMR (282.3 MHz, CD_2Cl_2): δ −78.8 (s). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 45.6 (d, ^1J(Rh,P) = 164.8 Hz).

Preparation of [Rh{κ^1-$OS(O)_2CF_3$}(η^4-C_4H_6)($PtBu_2Ph$)] (9). A solution of **2** (70 mg, 0.18 mmol) in dichloromethane (5 mL) was treated with $PtBu_2Ph$ (46 μL, 0.18 mmol) and stirred for 30 min at room temperature. After the solution was concentrated to ca. 2 mL in vacuo, pentane (10 mL) was added. A red solid was formed. The mixture was cooled to −30 °C, and then the solution was decanted from the solid. The solid was washed three times with pentane (3 mL each) and dried in vacuo: yield 88 mg (94%); mp 69 °C dec. Anal. Calcd for $C_{19}H_{29}F_3O_3PRhS$: C, 43.19; H, 5.53; S, 6.07. Found: C, 42.95; H, 5.46; S, 6.02. MS (EI): *m*/*z* 528 (M^+), 474 ($M^+ - C_4H_6$), 324 ($M^+ - C_4H_6 - CF_3SO_3$), 306 ($M^+ - PtBu_2Ph$). IR (CH_2Cl_2): $\nu(OSO_{asym})$ 1273, $\nu(CF_{sym})$ 1254, $\nu(CF_{asym})$ 1173, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.69 (m, 2 H, *o*-H of C_6H_5), 7.46 (m, 3 H, *m*-H and *p*-H of C_6H_5), 5.31 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.22 (br d, ^3J(H,H) = 5.0 Hz, 2 H, H of CH_2 *cis* to =CH), 1.58 (br d, ^3J(H,H) = 12.0 Hz, 2 H, H of CH_2 *trans* to =CH), 1.41 (d, ^3J(P,H) = 13.8 Hz, 18 H, $PCCH_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 134.6 (d, ^2J(P,C) = 10.2 Hz, *o*-C of C_6H_5), 131.0 (dd, ^1J(P,C) = 31.5, ^2J(Rh,C) = 2.0 Hz, *ipso*-C of C_6H_5), 130.6 (d, ^4J(P,C) = 2.0 Hz, *p*-C of C_6H_5), 128.2 (d, ^3J(P,C) = 9.2 Hz, *m*-C of C_6H_5), 89.4 (br s, CH_2=*C*H*C*H=CH_2), 51.8 (br s, *C*H_2=CHCH=*C*H_2), 36.9 (d, ^1J(P,C) = 13.2 Hz, P*C*CH_3), 30.5 (d, ^2J(P,C) = 5.1 Hz, PC*C*H_3), signal of CF_3 not exactly located. ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.1 (s). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 59.8 (d, ^1J(Rh,P) = 180.2 Hz).

Preparation of [(η^6-C_6H_6)Rh(η^4-C_6H_8)]CF_3SO_3 (10). A solution of **1** (270 mg, 0.29 mmol) in diethyl ether/pentane (1:2, 20 mL) was treated with 1,3-cyclohexadiene (500 μL, 5.2 mmol) and irradiated for 1 h in an ultrasound bath. After the reaction mixture was stored for 30 min, a red-brown solid precipitated. The solution was decanted, and the remaining solid residue was washed three times with pentane (5 mL each) and dried in vacuo: yield 184 mg (78%); mp 102 °C dec. Λ_M = 62 $cm^2\,\Omega^{-1}\,mol^{-1}$. Anal. Calcd for $C_{13}H_{14}F_3O_3RhS$: C, 38.06; H, 3.44; S, 7.82. Found: C, 37.77; H, 3.42; S, 7.88. IR (CH_2Cl_2): $\nu(OSO_{asym})$ 1278, $\nu(CF_{sym})$ 1250, $\nu(CF_{asym})$ 1170, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 6.90 (s, 6 H, C_6H_6), 5.65 (m, 2 H, C*H*=CHCH$_2$), 4.64 (m, 2 H, CH=C*H*CH_2), 1.70 (br d, ^3J(H,H) = 12.7 Hz, 2 H of =CHC*H*$_2$), 1.28 (br d, ^3J(H,H) = 11.7 Hz, 2 H of =CHC*H*$_2$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 121.4 (q, ^1J(F,C) = 321.4 Hz, CF_3), 102.6 (d, ^1J(Rh,C) = 3.3 Hz, C_6H_6), 86.0 (d, ^1J(Rh,C) = 7.5 Hz, *C*H=CHCH$_2$), 71.9 (d, ^1J(Rh,C) = 14.0 Hz, CH=*C*HCH$_2$), 25.3 (s, CH_2). ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −79.0 (s).

Preparation of [{η^5-$C_5H_4CH(CH_3)_2$}Rh{η^5-$C_5H_4C(=CH_2)$-CH_3}]CF_3SO_3 (11). This compound was prepared as described for **10** from **1** (217 mg, 0.23 mmol) and 6,6′-dimethylfulvene (500 μL, 4.1 mmol). A colorless solid was obtained: yield 183 mg (86%); mp 78 °C dec. Λ_M = 105 $cm^2\,\Omega^{-1}\,mol^{-1}$. Anal. Calcd for $C_{17}H_{20}F_3O_3RhS$: C, 43.98; H, 4.34; S, 6.91. Found: C, 43.52; H, 4.17; S, 6.87. IR (CH_2Cl_2): $\nu(OSO_{asym})$ 1270, $\nu(CF_{sym})$ 1250, $\nu(CF_{asym})$ 1160, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 6.05, 5.89, 5.77 (all br s, 8 H, CH of five-membered rings), 5.58, 5.30 (both br s, 2 H, C=CH_2), 2.59 (sept, ^3J(H,H) = 6.9 Hz, 1 H, C*H*CH_3), 2.00 (s, 3 H, CH_3), 1.16 (d, ^3J(H,H) = 6.9 Hz, 6 H, CHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 133.5 (s, =*C*CH_3), 121.4 (q, ^1J(F,C) = 321.4 Hz, CF_3), 119.2 (s, CH_2), 119.9, 109.6 (both d, ^1J(Rh,C) = 7.1 Hz, *C*−R of five-membered rings), 87.1, 86.7, 85.6, 83.7 (all d, ^1J(Rh,C) = 7.1 Hz, CH of five-membered rings), 26.6 (s, *C*HCH_3), 23.2 (s, CH*C*H_3), 21.1 (s, =C*C*H_3). ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −78.6 (s).

Preparation of [Rh{κ^1-$OS(O)_2CF_3$}(η^4-C_6H_8)($PiPr_3$)] (13). A solution of **12** was generated in situ from **1** (145 mg, 0.15 mmol) and $PiPr_3$ (60 μL, 0.31 mmol) in pentane (10 mL) and then treated with 1,3-cyclohexadiene (1.0 mL, 10.5 mmol). The solution was stirred for 15 min at room temperature and, after it was concentrated to ca. 2 mL in vacuo, an orange solid precipitated. The mixture was cooled to −30 °C, and then the solution was decanted from the precipitate. The solid was washed three times with pentane (−30 °C, 2 mL each) and dried in vacuo: yield 147 mg (97%); mp 87 °C dec. Anal. Calcd for $C_{16}H_{29}F_3O_3PRhS$: C, 39.03; H, 5.94; S, 6.51. Found: C, 38.72; H, 5.57; S, 6.19. IR (CH_2Cl_2): $\nu(OSO_{asym})$ 1317, $\nu(CF_{sym})$ 1252, $\nu(CF_{asym})$ 1178, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.11 (br s, 2 H, C*H*=CHCH$_2$), 4.38 (br s, 2 H, CH=C*H*CH_2), 2.18 (m, 3 H, PC*H*CH_3), 1.88 (br d, ^3J(H,H) = 11.7 Hz, 2 H of CH$_2$CH_2), 1.26 (dd, ^3J(P,H) = 13.9, ^3J(H,H) = 7.2 Hz, 18 H, PCHC*H*$_3$), 0.94 (br d, ^3J(H,H) = 11.7 Hz, 2 H of CH$_2$CH_2). ^{13}C NMR

(100.6 MHz, CD_2Cl_2): δ 119.9 (q, ^1J(F,C) = 319.0 Hz, CF_3), 83.1 (br s, *C*H=CHCH$_2$), 71.7 (br s, CH=*C*HCH$_2$), 24.4 (d, ^1J(P,C) = 20.4 Hz, P*C*HCH$_3$), 21.3 (s, CH_2), 19.8 (s, PCH*C*H$_3$). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.1 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 50.6 (d, ^1J(Rh,P) = 181.4 Hz).

Preparation of [Rh(η^4-C_6H_8)(P*i*Pr$_3$)$_2$]CF_3SO_3 (15). (a) A solution of **14** was generated in situ from **1** (126 mg, 0.13 mmol) and P*i*Pr$_3$ (104 μL, 0.52 mmol) in dichloromethane (10 mL) at 0 °C and then treated with 1,3-cyclohexadiene (0.5 mL, 5.2 mmol). A change of color from violet to red occurred. After it was warmed to room temperature, the solution was concentrated to ca. 2 mL in vacuo. Addition of pentane (30 mL) led to the precipitation of a red solid, which was filtered, washed three times with pentane (0 °C, 5 mL each), and dried in vacuo: yield 139 mg (82%).

(b) A solution of **11** (137 mg, 0.28 mmol) in dichloromethane (10 mL) was treated at 0 °C with P*i*Pr$_3$ (55 μL, 0.28 mmol) and stirred for 15 min at 0 °C. After it was warmed to room temperature, the reaction mixture was worked up as described for (a): yield 155 mg (85%); mp 53 °C dec. Λ_M = 84 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{25}H_{50}F_3O_3P_2RhS$: C, 46.01; H, 7.72; S, 4.91. Found: C, 45.49; H, 7.60; S, 4.98. IR (CH_2Cl_2): ν(OSO_{asym}) 1270, ν(CF_{asym}) 1159, ν(OSO_{sym}) 1032 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.29 (br s, 2 H, C*H*=CHCH$_2$), 4.98 (br s, 2 H, CH=C*H*CH$_2$), 2.42 (m, 6 H, PC*H*CH$_3$), 1.76 (br d, ^3J(H,H) = 12.4 Hz, 2 H of CH_2CH_2), 1.37 (dvt, N = 10.1, ^3J(H,H) = 6.7 Hz, 36 H, PCHC*H*$_3$), 1.10 (br d, ^3J(H,H) = 12.4 Hz, 2 H of CH_2CH_2). ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −78.6 (s). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 41.2 (d, ^1J(Rh,P) = 170.3 Hz).

Preparation of [Rh{η^4-$C_5H_4C(CH_3)_2$}(P*i*Pr$_3$)$_2$]CF_3SO_3 (16). A solution of **14** was generated in situ from **1** (215 mg, 0.23 mmol) and P*i*Pr$_3$ (180 μL, 0.92 mmol) in dichloromethane (20 mL) at room temperature. Addition of 6,6′-dimethylfulvene (0.5 mL, 4.1 mmol) led to a change of color from violet to deep green. The solution was stirred for 15 min and then concentrated to ca. 2 mL in vacuo. After pentane (30 mL) was added, a deep green solid precipitated. It was separated from the solution, washed three times with pentane (0 °C, 5 mL each), and dried in vacuo: yield 278 mg (89%); mp 118 °C dec. Λ_M = 102 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{27}H_{52}F_3O_3P_2RhS$: C, 47.79; H, 7.72; S, 4.73. Found: C, 47.29; H, 7.26; S, 4.65. IR (CH_2Cl_2): ν(OSO_{asym}) 1277, ν(CF_{sym}) 1252, ν(CF_{asym}) 1157, ν(OSO_{sym}) 1031 cm^{-1}. ^{1}H NMR (200 MHz, CD_3NO_2): δ 5.86 (br s, 2 H, =C*H*C*H*= of five-membered ring), 5.54 (br s, 2 H, CH=C*H*C of five-membered ring), 2.40 (m, 6 H, PC*H*CH$_3$), 1.38 (dd, ^3J(P,H) = 14.1, ^3J(H,H) = 7.0 Hz, 18 H, PCHC*H*$_3$), 1.36 (dd, ^3J(P,H) = 14.1, ^3J(H,H) = 7.0 Hz, 18 H, PCHC*H*$_3$), 1.19 (br s, 6 H, =CCH$_3$). ^{13}C NMR (50.3 MHz, CD_3NO_2): δ 130.5 (s, =*C*CH$_3$), 130.4 (m, −C− of five-membered ring), 122.5 (q, ^1J(F,C) = 321.4 Hz, CF_3), 91.9 (d, ^1J(Rh,C) = 7.1 Hz, =*C*HC*H*= of five-membered ring), 77.3 (dt, ^1J(Rh,C) = ^1J(P,C) = 4.1 Hz, CH=*C*HC of five-membered ring), 29.7 (vt, N = 19.4 Hz, P*C*HCH$_3$), 24.8 (s, =C*C*H$_3$), 21.5, 20.7 (both s, PCH*C*H$_3$). ^{19}F NMR (188.2 MHz, CD_3NO_2): δ −78.6 (s). ^{31}P NMR (81.0 MHz, CD_3NO_2): δ 52.4.2 (d, ^1J(Rh,P) = 188.2 Hz).

Generation of *cis*,*cis*,*trans*-[Rh{κ^2-$O_2S(O)CF_3$}(H)$_2$(P*i*Pr$_3$)$_2$] (17). A solution of **15** (23 mg, 0.04 mmol) in CD_2Cl_2 (0.5 mL) was stored in an NMR tube for 12 h at room temperature. A slow change of color from red to orange and finally to pale yellow occurred. After the ^{1}H NMR signals of **15** had disappeared, only those of **17** and free benzene could be detected. For analytical and spectroscopic data of **17** see ref 8a.

Preparation of [Rh{*anti*-η^3-(Cy$_3$PCH$_2$)*C*H*C*H*C*H$_2$}(PCy$_3$)$_2$]CF_3SO_3 (18). A solution of **2** (45 mg, 0.12 mmol) in acetone (10 mL) was treated with PCy$_3$ (118 mg, 0.42 mmol) and stirred for 15 min at room temperature. After the solution was concentrated to ca. 2 mL in vacuo, pentane (30 mL) was added. A yellow air-sensitive solid was formed, which was filtered, washed three times with pentane (5 mL each), and dried in vacuo: yield 110 mg (80%); mp 132 °C dec. Anal. Calcd for $C_{59}H_{105}F_3O_3P_3RhS$: C, 61.76; H, 9.22; S, 2.80. Found: C, 61.50; H, 9.17; S, 2.87. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.63 (br m, 1 H, H of allylic CH_2 in *cis* position to central allylic CH), 3.11 (m, 1 H, PCH$_2$C*H*), 2.67 (br m, 1 H, H of central allylic CH), 2.33 (m, 6 H, CH of RhPC$_6$H$_{11}$), 2.27 (m, 1 H, one H of PCH$_2$), 2.05−1.20 (br m, 95 H, CH_2 of C$_6$H$_{11}$, CH of CPC$_6$H$_{11}$, PCH_2, and H of CH_2 in *trans* position to central allylic CH). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 121.4 (q, ^1J(F,C) = 321.9 Hz, CF_3), 92.8 (d, ^1J(Rh,C) = 5.5 Hz, central allylic CH), 45.1 (br m, PCH$_2$*C*H), 42.5 (br m, allylic CH_2), 39.7, 38.5 (both d, ^1J(P,C) = 26.2 Hz, CH of RhPC$_6$H$_{11}$), 31.7 (s, γ-CH_2 of CPC$_6$H$_{11}$), 31.4 (d, ^1J(P,C) = 37.4 Hz, CH of CPC$_6$H$_{11}$), 30.9, 30.4 (both s, γ-CH_2 of RhPC$_6$H$_{11}$), 28.5, 28.4, 28.3, 28.2 (all s, β-CH_2 of C$_6$H$_{11}$), 27.5, 27.4 (both d, ^2J(P,C) = 13.5 Hz, α-CH_2 of RhPC$_6$H$_{11}$), 27.2 (d, ^3J(P,C) = 19.5 Hz, β-CH_2 of CPC$_6$H$_{11}$), 27.0, 26.9 (both d, ^2J(P,C) = 11.0 Hz, α-CH_2 of RhPC$_6$H$_{11}$), 25.8 (s, α-CH_2 of CPC$_6$H$_{11}$), 16.7 (d, ^1J(P,C) = 17.6 Hz, PCH_2). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.8 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 41.5 (ddd, ^1J(Rh,P) = 181.7, ^2J(P,P) = 20.8, ^4J(P,P) = 11.5 Hz, RhP), 37.0 (dd, ^1J(Rh,P) = 186.1, ^2J(P,P) = 20.8 Hz, RhP), 20.9 (d, ^4J(P,P) = 11.5 Hz, CP).

Preparation of [Rh(η^3:η^3-C_8H_{12}){κ^1-$OS(O)_2CF_3$}(P*i*Pr$_3$)] (19). A solution of **5a** (175 mg, 0.34 mmol) in dichloromethane (10 mL) was heated under reflux for 6 h. A change of color from orange to deep red occurred. After the reaction mixture was cooled to room temperature, the solvent was removed in vacuo. The oily residue was washed three times with pentane (5 mL each) and the resulting red solid recrystallized from dichloromethane/pentane (1:5): yield 131 mg (75%); mp 104 °C dec. Λ_M = 73 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{18}H_{33}F_3O_3PRhS$: C, 41.55; H, 6.39; S, 6.16. Found: C, 41.37; H, 6.16; S, 6.01. IR (CH_2Cl_2): ν(OSO_{asym}) 1260 br, ν(CF_{sym}) 1239, ν(CF_{asym}) 1162, ν(OSO_{sym}) 1031 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.23 (ddd, ^3J(H,H) = 11.6, ^3J(H,H) = 10.6, ^3J(H,H) = 7.0 Hz, 2 H, CHC*H*CH$_2$ of allylic system), 4.88 (dd, ^3J(H,H) = 7.0, ^4J(H,H) = 1.8 Hz, 2 H, *cis*-disposed H of allylic CH_2), 4.21 (ddd, ^3J(H,H) = 10.6, ^3J(H,H) = 3.5, ^4J(H,H) = 1.8 Hz, 2 H, C*H*CHCH$_2$ of allylic system), 3.07 (dd, ^3J(H,H) = 11.6, ^3J(P,H) = 6.3 Hz, 2 H, *trans*-disposed H of allylic CH_2), 2.63 (m, 3 H, PC*H*CH$_3$), 2.28, 1.53 (both m, 2 H each, CH_2 next to the allylic system), 1.28 (dd, ^3J(P,H) = 14.3, ^3J(H,H) = 7.0 Hz, 9 H, PCHC*H*$_3$), 1.15 (dd, ^3J(P,H) = 13.8, ^3J(H,H) = 7.3 Hz, 9 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 120.7 (q, ^1J(F,C) = 320.5 Hz, CF_3), 97.0 (d, ^1J(Rh,C) = 5.3 Hz, CH*C*HCH$_2$ of allylic system), 91.1 (dd, ^1J(Rh,C) = 8.4, ^2J(P,C) = 6.4 Hz, *C*HCHCH$_2$ of allylic system), 69.9 (dd, ^1J(Rh,C) = 6.1, ^2J(P,C) = 3.8 Hz, CHCH*C*H$_2$ of allylic system), 29.2 (s, CH_2 next to the allylic system), 27.1 (d, ^1J(P,C) = 18.3 Hz, P*C*HCH$_3$), 19.8, 19.6 (both s, PCH*C*H$_3$). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.8 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 40.1 (d, ^1J(Rh,P) = 170.4 Hz).

Preparation of [Rh(η^3:η^3-C_8H_{12}){κ^1-$OS(O)_2CF_3$}(PCy$_3$)] (20). This compound was prepared as described for **19** from **6a** (493 mg, 0.77 mmol) in dichloromethane (10 mL). Time of reaction: 3 h. A red solid was obtained: yield 365 mg (74%); mp 123 °C dec. Λ_M = 71 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{27}H_{45}F_3O_3PRhS$: C, 50.62; H, 7.08; S, 5.00. Found: C, 49.94; H, 6.98; S, 4.87. IR (CH_2Cl_2): ν(OSO_{asym}) 1260 br, ν(CF_{sym}) 1253, ν(CF_{asym}) 1161, ν(OSO_{sym}) 1031 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.25 (ddd, ^3J(H,H) = 11.3, ^3J(H,H) = 10.6, ^3J(H,H) = 7.0 Hz, 2 H, CHC*H*CH$_2$ of allylic system), 4.82 (dd, ^3J(H,H) = 7.0, ^4J(H,H) = 1.4 Hz, 2 H, *cis*-disposed H of allylic CH_2), 4.21 (dd, ^3J(H,H) = 10.6, ^3J(H,H) = 3.2 Hz, 2 H, C*H*CHCH$_2$ of allylic system), 2.99 (dd, ^3J(H,H) = 11.3, ^3J(P,H) = 6.3 Hz, 2 H, *trans*-disposed H of allylic CH_2), 2.32 (m, 5 H, CH of C$_6$H$_{11}$ and one H of CH_2 next to the allylic system), 2.0−1.1 (br m, 32 H, CH_2 of C$_6$H$_{11}$ and one H of CH_2 next to the allylic system). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 120.8 (q, ^1J(F,C) = 321.5 Hz, CF_3), 97.4 (d, ^1J(Rh,C) = 5.1 Hz, CH*C*HCH$_2$ of allylic system), 92.7 (dd, ^1J(Rh,C) = 9.1, ^2J(P,C) = 7.1 Hz, *C*HCHCH$_2$ of allylic system), 70.1 (dd, ^1J(Rh,C) = 6.6, ^2J(P,C) = 3.6 Hz, CHCH*C*H$_2$ of allylic system), 37.0 (d, ^1J(P,C) = 17.3 Hz, CH of C$_6$H$_{11}$), 30.5 (d,

^3J(P,C) = 2.0 Hz, β-CH_2 of C_6H_{11}), 29.3 (s, CH_2 next to the allylic system), 28.1 (d, ^2J(P,C) = 9.2 Hz, α-CH_2 of C_6H_{11}), 28.0 (d, ^2J(P,C) = 8.1 Hz, α-CH_2 of C_6H_{11}), 26.5 (s, γ-CH_2 of C_6H_{11}). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 28.1 (d, ^1J(Rh,P) = 167.8 Hz).

Preparation of [Rh(η^3:η^3-C_8H_{12})(P*i*Pr$_3$)]B(Ar$_f$)$_4$ (21). (a) A solution of **5b** (242 mg, 0.20 mmol) in dichloromethane (10 mL) was heated under reflux for 12 h. A change of color from orange to deep red occurred. After the reaction mixture was cooled to room temperature, the solvent was removed in vacuo. The oily residue was washed three times with pentane (5 mL each) and the resulting red solid recrystallized from ether/pentane (1:5): yield 167 mg (69%).

(b) A solution of **19** (100 mg, 0.19 mmol) in dichloromethane (20 mL) was treated at 0 °C with NaB(Ar$_f$)$_4$ (170 mg, 0.19 mmol). After it was warmed to room temperature, the solution was stirred for 1 h. An off-white solid precipitated. The solution was decanted from the precipitate and then concentrated to ca. 2 mL in vacuo. Addition of pentane (30 mL) led to the formation of a red solid, which was filtered, washed three times with pentane (5 mL each), and dried in vacuo: yield 213 mg (90%); mp 110 °C dec. Λ_M = 63 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{49}H_{45}BF_{24}PRh$: C, 47.67; H, 3.67. Found: C, 47.78; H, 3.46. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.76 (m, 8 H, *o*-H of Ar$_f$), 7.60 (br s, 4 H, *p*-H of Ar$_f$), 5.23 (ddd, ^3J(H,H) = 11.5, ^3J(H,H) = 10.8, ^3J(H,H) = 6.9 Hz, 2 H, CHC*H*CH_2 of allylic system), 4.88 (d, ^3J(H,H) = 6.9 Hz, 2 H, *cis*-disposed H of allylic CH_2), 4.23 (dd, ^3J(H,H) = 10.8, ^3J(H,H) = 3.5 Hz, 2 H, C*H*$CHCH_2$ of allylic system), 2.97 (dd, ^3J(H,H) = 11.6, ^3J(P,H) = 6.4 Hz, 2 H, *trans*-disposed H of allylic CH_2), 2.62 (m, 3 H, PC*H*CH_3), 2.36, 1.63 (both m, 2 H each, CH_2 next to the allylic system), 1.27 (dd, ^3J(P,H) = 14.8, ^3J(H,H) = 7.1 Hz, 9 H, PCHC*H*$_3$), 1.13 (dd, ^3J(P,H) = 14.4, ^3J(H,H) = 7.1 Hz, 9 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 162.2 (q, ^1J(B,C) = 49.9 Hz, *ipso*-C of Ar$_f$), 135.3 (br s, *o*-C of Ar$_f$), 129.3 (qq, ^2J(F,C) = 31.4, ^4J(F,C) = 2.8 Hz, *m*-C of Ar$_f$), 125.0 (q, ^1J(F,C) = 272.5 Hz, CF_3), 117.9 (m, *p*-C of Ar$_f$), 98.4 (d, ^1J(Rh,C) = 4.6 Hz, CH*C*HCH_2 of allylic system), 98.3 (dd, ^1J(Rh,C) = 8.3, ^2J(P,C) = 5.5 Hz, *C*HCHCH_2 of allylic system), 69.6 (dd, ^1J(Rh,C) = 6.0, ^2J(P,C) = 4.2 Hz, CH_2 of allylic system), 29.6 (s, CH_2 next to the allylic system), 27.4 (d, ^1J(P,C) = 19.4 Hz, P*C*HCH_3), 20.0, 20.1 (both s, PCH*C*H_3). ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −63.1 (s). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 42.0 (d, ^1J(Rh,P) = 165.3 Hz).

Preparation of [Rh(η^3:η^3-C_8H_{12})(PCy$_3$)]B(Ar$_f$)$_4$ (22). This compound was prepared as described for **21**, either following method a from **6b** (360 mg, 0.27 mmol; time of reaction 3 h) or following method b from **20** (78 mg, 0.12 mmol) and NaB(Ar$_f$)$_4$ (108 mg, 0.12 mmol). A red solid was obtained: yield 284 mg (69%) from method a and 145 mg (88%) from method b; mp 115 °C dec. Λ_M = 48 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{58}H_{57}BF_{24}O_3PRh$: C, 51.42; H, 4.24. Found: C, 51.62; H, 4.34. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.76 (m, 8 H, *o*-H of Ar$_f$), 7.60 (s, 4 H, *p*-H of Ar$_f$), 5.24 (ddd, ^3J(H,H) = 11.5, ^3J(H,H) = 10.9, ^3J(H,H) = 7.0 Hz, 2 H, CHC*H*CH_2 of allylic system), 4.84 (dd, ^3J(H,H) = 7.0, ^4J(H,H) = 1.3 Hz, 2 H, *cis*-disposed H of allylic CH_2), 4.21 (dd, ^3J(H,H) = 10.9, ^3J(H,H) = 3.5 Hz, 2 H, C*H*$CHCH_2$ of allylic system), 2.95 (dd, ^3J(H,H) = 11.5, ^3J(P,H) = 6.3 Hz, 2 H, *trans*-disposed H of allylic CH_2), 2.35 (m, 5 H, CH of C_6H_{11} and one H of CH_2 next to the allylic system), 2.1−1.1 (br m, 32 H, CH_2 of C_6H_{11} and one H of CH_2 next to the allylic system). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 162.2 (q, ^1J(B,C) = 49.8 Hz, *ipso*-C of Ar$_f$), 135.2 (br s, *o*-C of Ar$_f$), 129.3 (qq, ^2J(F,C) = 31.5, ^4J(F,C) = 2.8 Hz, *m*-C of Ar$_f$), 125.0 (q, ^1J(F,C) = 272.6 Hz, CF_3), 117.9 (sept, ^3J(F,C) = 3.9 Hz, *p*-C of Ar$_f$), 98.4 (d, ^1J(Rh,C) = 5.3 Hz, CH*C*HCH_2 of allylic system), 97.8 (dd, ^1J(Rh,C) = 8.7, ^2J(P,C) = 6.0 Hz, *C*HCHCH_2 of allylic system), 70.0 (dd, ^1J(Rh,C) = 6.3, ^2J(P,C) = 4.2 Hz, CH_2 of allylic system), 37.3 (d, ^1J(P,C) = 18.4 Hz, CH of C_6H_{11}), 31.1, 31.0 (both s, β-CH_2 of C_6H_{11}), 29.5 (s, CH_2 next to the allylic system), 28.0 (d, ^2J(P,C) = 11.0 Hz, α-CH_2 of C_6H_{11}), 27.9 (d, ^2J(P,C) = 10.5 Hz, α-CH_2 of C_6H_{11}), 26.5, 26.4 (both s, γ-CH_2 of C_6H_{11}). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ 28.8 (d, ^1J(Rh,P) = 164.0 Hz).

Preparation of [Rh{η^2:η^3-*C*H$_2$=*C*HCH(P*i*Pr$_3$)(CH$_2$)$_2$*C*H*C*H*C*H$_2$}(P*i*Pr$_3$)]B(Ar$_f$)$_4$ (23). A solution of **21** (274 mg, 0.22 mmol) in diethyl ether (10 mL) was treated at 0 °C with P*i*Pr$_3$ (43 μL, 0.22 mmol). After it was warmed to room temperature, the solution was stirred for 15 min. A change of color from red to orange occurred. The solvent was reduced in vacuo, and the oily residue was washed twice with pentane (5 mL each). After the residue was stored for 12 h at 0 °C, an orange-yellow, air-sensitive solid was obtained: yield 305 mg (98%); mp 35 °C dec. Anal. Calcd for $C_{58}H_{66}BF_{24}P_2Rh$: C, 49.95; H, 4.77; F, 32.69; P, 4.44. Found: C, 49.70; H, 4.79; F, 32.46; P, 4.30. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.75 (m, 8 H, *o*-H of Ar$_f$), 7.59 (s, 4 H, *p*-H of Ar$_f$), 4.40 (m, 1 H, CHC*H*CH_2 of allylic system), 3.53 (dd, ^3J(H,H) = ^3J(P,H) = 7.2 Hz, 1 H, *cis*-disposed H of allylic CH_2), 3.02 (m, 1 H, C*H*=CH_2 of vinyl unit), 2.97 (dsept, ^2J(P,H) = 13.5, ^3J(H,H) = 7.0 Hz, 3 H, PC*H*CH_3 of P*i*Pr$_3$ bound to C), 2.88 (m, 1 H, C*H*$CHCH_2$ of allylic system), 2.85 (m, 1 H, *cis*-disposed H of vinylic CH_2), 2.49 (m, 3 H, PC*H*CH_3 of P*i*Pr$_3$ bound to Rh), 2.36, 2.16 (both m, 1 H each, CH_2CHPiPr$_3$), 2.15 (d, ^3J(H,H) = 11.4 Hz, 1 H, *trans*-disposed H of allylic CH_2), 2.01 (d, ^3J(H,H) = 12.3 Hz, 1 H, *trans*-disposed H of vinylic CH_2), 1.76 (dd, ^2J(P,H) = 12.4, ^3J(H,H) = 11.3 Hz, 1 H, C*H*P*i*Pr$_3$), 2.36, 1.63 (both m, 2 H each, CH_2 next to the allylic system), 1.45, 1.40 (both dd, ^3J(P,H) = 15.0, ^3J(H,H) = 7.3 Hz, 9 H each, PCHC*H*$_3$ of P*i*Pr$_3$ bound to C), 1.34, 1.22 (both m, 1 H each, CH_2 next to the allylic system), 1.18, 1.15 (both dd, ^3J(P,H) = 12.9, ^3J(H,H) = 7.2 Hz, 9 H each, PCHC*H*$_3$ of P*i*Pr$_3$ bound to Rh). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 162.2 (q, ^1J(B,C) = 49.9 Hz, *ipso*-C of Ar$_f$), 135.2 (br s, *o*-C of Ar$_f$), 129.3 (qq, ^2J(F,C) = 31.5, ^4J(F,C) = 2.9 Hz, *m*-C of Ar$_f$), 125.0 (q, ^1J(F,C) = 272.4 Hz, CF_3), 117.9 (sept, ^3J(F,C) = 3.8 Hz, *p*-C of Ar$_f$), 100.1 (dd, ^1J(Rh,C) = 4.6, ^2J(P,C) = 1.5 Hz, CH*C*HCH_2 of allylic system), 68.4 (ddd, ^1J(Rh,C) = 15.6, ^2J(P,C) = 6.1, ^2J(P′,C) = 1.4 Hz, *C*H=CH_2 of vinyl unit), 55.6 (ddd, ^1J(Rh,C) = 11.1, ^2J(P,C) = 4.4, ^2J(P′,C) = 2.3 Hz, *C*HCHCH_2 of allylic system), 45.8 (ddd, ^1J(Rh,C) = 8.3, ^2J(P,C) = ^2J(P′,C) = 2.9 Hz, CH_2 of allylic system), 36.4 (d, ^1J(P,C) = 27.6 Hz, *C*HP*i*Pr$_3$), 33.3 (d, ^3J(P,C) = 4.4 Hz, CH_2 next to the allylic system), 31.6 (dd, ^1J(Rh,C) = 11.6, ^2J(P,C) = 1.4 Hz, CH_2 of vinyl unit), 26.6 (d, ^1J(P,C) = 17.4 Hz, P*C*HCH_3 of P*i*Pr$_3$ bound to Rh), 21.8 (d, ^1J(P,C) = 39.2 Hz, P*C*HCH_3 of P*i*Pr$_3$ bound to C), 20.2, 19.8 (both s, P*C*HCH_3 of P*i*Pr$_3$ bound to Rh), 17.5, 17.4 (both d, ^2J(P,C) = 3.6 Hz, P*C*HCH_3 of P*i*Pr$_3$ bound to C), 16.7 (d, ^2J(P,C) = 2.9 Hz, *C*H2CHP*i*Pr$_3$). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −62.7 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 51.8 (dd, ^1J(Rh,P) = 168.7, ^4J(P,P) = 9.3 Hz, RhP*i*Pr$_3$), 39.2 (dd, ^3J(Rh,P) = 7.6, ^4J(P,P) = 9.3 Hz, CP*i*Pr$_3$).

Preparation of [RhCl(η^4-C_4H_6)(P*i*Pr$_3$)] (24). A solution of **5a** (134 mg, 0.26 mmol) in acetone (10 mL) was treated with NaCl (100 mg, 1.71 mmol) and stirred for 2 h at room temperature. An off-white solid precipitated, which was filtered, and the filtrate was brought to dryness in vacuo. The oily residue was recrystallized from diethyl ether at −20 °C to give a microcrystalline red solid: yield 72 mg (79%); mp 74 °C dec. Anal. Calcd for $C_{13}H_{27}ClPRh$: C, 44.27; H, 7.72. Found: C, 44.03; H, 7.56. MS (EI): *m*/*z* 353 (M^+), 316 (M^+ − Cl), 299 (M^+ − C_4H_6), 263 (M^+ − Cl − C_4H_6). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.10 (br s, 2 H, CH_2=C*H*C*H*=CH_2), 3.21 (br s, 2 H, H of CH_2 *cis* to =CH), 2.39 (m, 3 H, PC*H*CH_3), 1.83 (br s, 2 H, H of CH_2 *trans* to =CH), 1.27 (dd, ^3J(P,H) = 13.6, ^3J(H,H) = 7.2 Hz, 18 H, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 48.5 (d, ^1J(Rh,P) = 172.9 Hz).

Preparation of [RhBr(η^4-C_4H_6)(P*i*Pr$_3$)] (25). This compound was prepared as described for **24** from **5a** (201 mg, 0.39 mmol) and NaBr (250 mg, 2.10 mmol) in acetone (10 mL). A red solid was obtained: yield 118 mg (76%); mp 70 °C dec. Anal. Calcd for $C_{13}H_{27}BrPRh$: C, 39.32; H, 6.85. Found: C, 39.00; H, 6.79. ^{1}H

NMR (400 MHz, CD_2Cl_2): δ 5.10 (br s, 2 H, CH_2=C*H*C*H*=CH_2), 3.35 (br d, ^3J(H,H) = 5.0 Hz, 2 H, H of CH_2 *cis* to =CH), 2.44 (m, 3 H, PC*H*CH_3), 1.82 (br d, ^3J(H,H) = 10.0 Hz, 2 H, H of CH_2 *trans* to =CH), 1.27 (dd, ^3J(P,H) = 13.5, ^3J(H,H) = 7.3 Hz, 18 H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 90.0 (br s, CH_2=*C*H*C*H=CH_2), 54.0 (br s, *C*H_2=CHCH=*C*H_2), 25.3 (d, ^1J(P,C) = 21.0 Hz, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 48.7 (d, ^1J(Rh,P) = 173.0 Hz).

Preparation of [Rh(*s-cis*-η^4-C_4H_6)$_2$(As*i*Pr$_3$)]CF_3SO_3 (26). A solution of **2** (128 mg, 0.33 mmol) in acetone (10 mL) was treated with As*i*Pr$_3$ (65 μL, 0.33 mmol). After the solution was stirred for 15 min at room temperature, it was concentrated to ca. 3 mL in vacuo. Addition of pentane (20 mL) led to the formation of a colorless solid, from which the solution was decanted. The solid residue was washed four times with pentane (5 mL each) and dried in vacuo: yield 166 mg (88%); mp 125 °C dec. Anal. Calcd for $C_{18}H_{33}AsF_3O_3RhS$: C, 38.31; H, 5.89; S, 5.68. Found: C, 38.09; H, 5.75; S, 5.78. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1260 br, ν(CF_{asym}) 1152, ν(OSO_{sym}) 1033 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.86 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.16 (br d, ^3J(H,H) = 7.5 Hz, 4 H, H of CH_2 *cis* to =CH), 2.69 (sept, ^3J(H, H) = 7.2 Hz, 3 H, AsC*H*CH_3), 1.47 (br d, ^3J(H,H) = 9.7 Hz, 4 H, H of CH_2 *trans* to =CH), 1.44 (d, ^3J(H,H) = 7.2 Hz, 18 H, AsCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 121.3 (q, ^1J(F, C) = 321.1 Hz, CF_3), 90.0 (d, ^1J(Rh,C) = 3.6 Hz, CH_2=*C*H*C*H=CH_2), 49.9 (d, ^1J(Rh,C) = 8.0 Hz, *C*H_2=CHCH=*C*H_2), 28.7 (d, ^2J(P,C) = 2.2 Hz, As*C*HCH$_3$), 20.8 (s, AsCH*C*H$_3$). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s).

Preparation of [Rh(*s-cis*-η^4-C_4H_5Me)$_2$(As*i*Pr$_3$)]CF_3SO_3 (27). This compound was prepared as described for **26** from **3** (101 mg, 0.26 mmol) and As*i*Pr$_3$ (51 μL, 0.26 mmol). A colorless solid was obtained, which according to the ^{1}H and ^{13}C NMR spectra consists of a 9:1 mixture of the anti and syn isomers: yield 140 mg (89%); mp 132 °C dec. Anal. Calcd for $C_{20}H_{37}AsF_3O_3RhS$: C, 40.55; H, 6.30; S, 5.41. Found: C, 40.13; H, 6.31; S, 5.56. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1260 br, ν(CF_{asym}) 1151, ν(OSO_{sym}) 1031 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): anti isomer, δ 4.89 (dd, ^3J(H,H) = 10.6 and 7.3 Hz, 2 H, CH_2=C*H*CCH$_3$), 3.22 (dd, ^3J(H,H) = 7.3, ^2J(H,H) = 1.4 Hz, 2 H, H of CH_2 *cis* to =CH), 3.01 (s, 2 H, H of CH_2 *cis* to =CCH$_3$), 2.65 (sept, ^3J(H,H) = 7.2 Hz, 3 H, AsC*H*CH$_3$), 2.26 (s, 6 H, =CCH$_3$), 1.43, 1.42 (both d, ^3J(H,H) = 7.2 Hz, 9 H each, AsCHC*H*$_3$), 1.38 (br d, ^3J(H,H) = 10.6 Hz, 2 H, H of CH_2 *trans* to =CH), 1.21 (s, 2 H, H of CH_2 *trans* to =CCH$_3$); syn isomer, δ 5.51 (m, 2 H, CH_2=C*H*CCH$_3$), 3.11 (s, 2 H, H of CH_2 *cis* to =CCH$_3$), 3.02 (br d, ^3J(H,H) = 7.2 Hz, 2 H, H of CH_2 *cis* to =CH), other signals of syn isomer not exactly located. ^{13}C NMR (100.6 MHz, CD_2Cl_2): anti isomer, δ 121.3 (q, ^1J(F,C) = 321.4 Hz, CF_3), 110.3 (d, ^1J(Rh,C) = 3.6 Hz, *C*HCH$_3$), 98.0 (d, ^1J(Rh,C) = 4.4 Hz, *C*H=CH_2), 48.6 (d, ^1J(Rh,C) = 8.7 Hz, *C*H_2=CCH$_3$), 46.9 (d, ^1J(Rh,C) = 8.0 Hz, *C*H_2=CH), 28.2 (d, ^2J(P,C) = 1.4 Hz, As*C*HCH$_3$), 22.1 (s, =C*C*H$_3$), 20.8 (s, AsCH*C*H$_3$); syn isomer, δ 112.7 (d, ^1J(Rh,C) = 3.6 Hz, *C*HCH$_3$), 87.8 (d, ^1J(Rh,C) = 4.4 Hz, *C*H=CH_2), 49.8 (d, ^1J(Rh,C) = 8.7 Hz, *C*H_2=CCH$_3$), 47.3 (d, ^1J(Rh,C) = 8.7 Hz, *C*H_2=CH), 28.1 (d, ^2J(P,C) = 1.5 Hz, As*C*HCH$_3$), other signals of syn isomer not exactly located. ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s).

Preparation of [Rh(*s-cis*-η^4-$C_4H_4Me_2$)$_2$(As*i*Pr$_3$)]CF_3SO_3 (28). This compound was prepared as described for **26** from **4** (183 mg, 0.44 mmol) and As*i*Pr$_3$ (87 μL, 0.44 mmol). A colorless solid was obtained: yield 228 mg (84%); mp 148 °C dec. Anal. Calcd for $C_{22}H_{41}AsF_3O_3RhS$: C, 42.59; H, 6.66; S, 5.17. Found: C, 42.24; H, 6.36; S, 5.19. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1260 br, ν(CF_{asym}) 1154, ν(OSO_{sym}) 1032 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.99 (d, ^2J(H,H) = 1.5 Hz, 4 H, H of CH_2 *cis* to =CCH$_3$), 2.65 (sept, ^3J(H,H) = 7.3 Hz, 3 H, AsC*H*CH$_3$), 1.90 (s, 12 H, =CCH$_3$), 1.43 (d, ^3J(H,H) = 7.3 Hz, 18 H, AsCHC*H*$_3$), 1.21 (br s, 4 H, H of CH_2 *trans* to =CCH$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 121.3 (q, ^1J(F,C) = 321.3 Hz, CF_3), 107.5 (d, ^1J(Rh,C) = 3.8 Hz, *C*HCH$_3$), 48.7 (d, ^1J(Rh,C) = 9.5 Hz, CH_2), 27.6 (d, ^2J(Rh,C) = 2.0 Hz, As*C*HCH$_3$), 20.9 (s, AsCH*C*H$_3$), 17.7 (s, =C*C*H$_3$). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s).

Preparation of [Rh(*s-cis*-η^4-C_4H_6)$_2$(Sb*i*Pr$_3$)]CF_3SO_3 (29). This compound was prepared as described for **26** from **2** (78 mg, 0.08 mmol) and Sb*i*Pr$_3$ (17 μL, 0.08 mmol). A colorless solid was obtained: yield 92 mg (91%); mp 137 °C dec. Anal. Calcd for $C_{18}H_{33}F_3O_3RhSSb$: C, 35.37; H, 5.44; S, 5.25. Found: C, 35.37; H, 5.33; S, 5.34. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1260 br, ν(CF_{asym}) 1151, ν(OSO_{sym}) 1031 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 5.83 (m, 4 H, CH_2=C*H*C*H*=CH_2), 2.97 (br d, ^3J(H, H) = 6.9 Hz, 4 H, H of CH_2 *cis* to =CH), 2.73 (sept, ^3J(H,H) = 7.4 Hz, 3 H, SbC*H*CH_3), 1.51 (d, ^3J(H,H) = 7.4 Hz, 18 H, SbCHC*H*$_3$), 1.49 (br d, ^3J(H,H) = 9.9 Hz, 4 H, 4 H, H of CH_2 *trans* to =CH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 121.2 (q, ^1J(F, C) = 320.8 Hz, CF_3), 87.9 (d, ^1J(Rh,C) = 4.6 Hz, CH_2=*C*H*C*-H=CH_2), 45.4 (d, ^1J(Rh,C) = 8.3 Hz, *C*H_2=CHCH=*C*H_2), 21.8 (s, SbCH*C*H$_3$), 21.0 (d, ^2J(Rh,C) = 2.8 Hz, Sb*C*HCH$_3$). ^{19}F NMR (188.2 MHz, CD_2Cl_2): δ −79.1 (s).

Preparation of [Rh(*s-cis*-η^4-C_4H_5Me)$_2$(Sb*i*Pr$_3$)]CF_3SO_3 (30). This compound was prepared as described for **26** from **3** (96 mg, 0.25 mmol) and Sb*i*Pr$_3$ (53 μL, 0.25 mmol). A colorless solid was obtained, which according to the ^{1}H and ^{13}C NMR spectra consists of a 6:1 mixture of the anti and syn isomers: yield 154 mg (97%); mp 132 °C dec. Anal. Calcd for $C_{20}H_{37}F_3O_3RhSSb$: C, 37.58; H, 5.83; S, 5.02. Found: C, 37.35; H, 5.76; S, 5.06. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1260 br, ν(CF_{asym}) 1154, ν(OSO_{sym}) 1031 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): anti isomer, δ 4.96 (dd, ^3J(H,H) = 9.4 and 7.6 Hz, 2 H, CH_2=C*H*-CCH$_3$), 3.06 (dd, ^3J(H,H) = 7.6, ^2J(H,H) = 1.5 Hz, 2 H, H of CH_2 *cis* to =CH), 2.85 (br s, 2 H, H of CH_2 *cis* to =CCH$_3$), 2.70 (sept, ^3J(H,H) = 7.4 Hz, 3 H, SbC*H*CH$_3$), 2.29 (s, 6 H, =CCH$_3$), 1.51, 1.50 (both d, ^3J(H,H) = 7.4 Hz, 9 H each, SbCHC*H*$_3$), 1.41 (br d, ^3J(H,H) = 9.4 Hz, 2 H, H of CH_2 *trans* to =CH), 1.23 (s, 2 H, H of CH_2 *trans* to =CCH$_3$); syn isomer, δ 5.52 (m, 2 H, CH_2=C*H*CCH$_3$), 2.92 (s, 2 H, H of CH_2 *cis* to =CCH$_3$), 2.81 (dd, ^3J(H,H) = 7.2, ^2J(H,H) = 1.4 Hz, 2 H, H of CH_2 *cis* to =CH), other signals of *syn* isomer not exactly located. ^{13}C NMR (100.6 MHz, CD_2Cl_2): anti isomer, δ 121.3 (q, ^1J(F,C) = 321.5 Hz, CF_3), 107.8 (d, ^1J(Rh,C) = 4.1 Hz, *C*HCH$_3$), 96.0 (d, ^1J(Rh, C) = 4.7 Hz, *C*H=CH_2), 44.3 (d, ^1J(Rh,C) = 8.1 Hz, *C*H_2=CCH$_3$), 42.4 (d, ^1J(Rh,C) = 8.1 Hz, *C*H_2=CH), 21.9 (s, =C*C*H$_3$), 21.8 (s, SbCH*C*H$_3$), 20.9 (d, ^2J(P,C) = 2.0 Hz, Sb*C*HCH$_3$]; syn isomer, δ 109.5 (d, ^1J(Rh,C) = 3.5 Hz, *C*HCH$_3$), 85.9 (d, ^1J(Rh, C) = 4.5 Hz, *C*H=CH_2), 44.8 (d, ^1J(Rh,C) = 8.1 Hz, *C*H_2=CCH$_3$), 43.0 (d, ^1J(Rh,C) = 9.1 Hz, *C*H_2=CH), 22.6 (s, =C*C*H$_3$), other signals of syn isomer not exactly located. ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.6 (s).

Preparation of [Rh(*s-cis*-η^4-$C_4H_4Me_2$)$_2$(Sb*i*Pr$_3$)]CF_3SO_3 (31). This compound was prepared as described for **26** from **4** (50 mg, 0.12 mmol) and Sb*i*Pr$_3$ (25 μL, 0.12 mmol). A colorless solid was obtained: yield 76 mg (95%); mp 146 °C dec. Anal. Calcd for $C_{22}H_{41}F_3O_3RhSSb$: C, 39.60; H, 6.19; S, 4.81. Found: C, 39.33; H, 6.34; S, 4.72. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1260 br, ν(CF_{asym}) 1154, ν(OSO_{sym}) 1031 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.79 (d, ^2J(H,H) = 1.5 Hz, 4 H, H of CH_2 *cis* to =CCH$_3$), 2.70 (sept, ^3J(H,H) = 7.4 Hz, 3 H, SbC*H*CH$_3$), 1.93 (s, 12 H, =CCH$_3$), 1.51 (d, ^3J(H,H) = 7.4 Hz, 18 H, SbCHC*H*$_3$), 1.21 (br s, 4 H, H of CH_2 *trans* to =CCH$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 121.3 (q, ^1J(F,C) = 321.3 Hz, CF_3), 104.3 (d, ^1J(Rh,C) = 3.7 Hz, *C*HCH$_3$), 43.7 (d, ^1J(Rh,C) = 9.2 Hz, CH_2), 21.8 (s, SbCH*C*H$_3$), 20.9 (d, ^2J(Rh,C) = 1.9 Hz, Sb*C*HCH$_3$), 17.4 (s, =C*C*H$_3$). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −79.2 (s).

Preparation of [Rh(*s-cis*-η^4-C_4H_6)$_2$(CO)]CF_3SO_3 (33). A solution of **32** (320 mg, 0.82 mmol) in dichloromethane (30 mL) was treated with a solution of CF_3SO_3Ag (423 mg, 1.64 mmol) in diethyl ether (10 mL) and stirred for 1 h at room temperature. The precipitate was filtered, and a stream of butadiene was passed through the orange-red filtrate for 10 s. A change of color from

orange-red to off-white occurred. The solution was concentrated to ca. 5 mL in vacuo, and pentane (30 mL) was added. A colorless solid precipitated, from which the solution was decanted. The solid residue was washed three times with pentane (5 mL each) and dried in vacuo for 15 min at 0 °C: yield 465 mg (73%); mp 83 °C dec. Anal. Calcd for $C_{10}H_{12}F_3O_4RhS$: C, 30.94; H, 3.12; S, 8.26. Found: C, 30.61; H, 3.00; S, 8.06. IR (CH_2Cl_2): ν(CO) 2096, $\nu(OSO_{asym})$ 1260, $\nu(CF_{sym})$ 1250, $\nu(CF_{asym})$ 1163, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ 6.27 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.63 (d, ^3J(H,H) = 7.0 Hz, 4 H, H of CH_2 *cis* to =CH), 2.80 (d, ^3J(H,H) = 10.0 Hz, 4 H, H of CH_2 *trans* to =CH). ^{13}C NMR (100.6 MHz, acetone-d_6): δ 197.1 (d, ^1J(Rh,C) = 77.6 Hz, CO), 121.5 (q, ^1J(F,C) = 328.0 Hz, CF_3), 96.1 (d, ^1J(Rh,C) = 3.8 Hz, CH_2=*C*H*C*H=CH_2), 56.3 (d, ^1J(Rh,C) = 7.6 Hz, *C*H_2=CHCH=*C*H_2). ^{19}F NMR (376.4 MHz, acetone-d_6): δ −78.4 (s).

Preparation of (Rh(*s-cis*-η^4-C_4H_6)$_2$(CN*t*Bu)]CF_3SO_3 (34). This compound was prepared as described for **26** from **2** (44 mg, 0.12 mmol) and CN*t*Bu (14 μL, 0.12 mmol). A colorless solid was obtained: yield 53 mg (98%); mp 67 °C dec. Anal. Calcd for $C_{14}H_{21}F_3NO_3RhS$: C, 37.93; H, 4.77; N, 3.16; S, 7.23. Found: C, 37.54; H, 4.47; N, 3.47; S, 6.80. IR (CH_2Cl_2): ν(CN) 2196, $\nu(OSO_{asym})$ 1275, $\nu(CF_{sym})$ 1255, $\nu(CF_{asym})$ 1170, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.85 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.22 (d, ^3J(H,H) = 6.5 Hz, 4 H, H of CH_2 *cis* to =CH), 1.90 (d, ^3J(H,H) = 9.7 Hz, 4 H, H of CH_2 *trans* to =CH), 1.68 (s, CCH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 139.9 (dt, ^1J(Rh,C) = 75.3, $^1J(^{14}N,C)$ = 17.8 Hz, CN), 121.3 (q, ^1J(F,C) = 321.4 Hz, CF_3), 91.7 (d, ^1J(Rh,C) = 4.1 Hz, CH_2=*C*H*C*H=CH_2), 60.3 (t, $^1J(^{14}N,C)$ = 4.6 Hz, *C*CH_3), 52.4 (d, ^1J(Rh,C) = 7.1 Hz, *C*H_2=CHCH=*C*H_2), 30.6 (s, C*C*H_3). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s).

Preparation of [Rh(*s-cis*-η^4-C_4H_5Me)$_2$(CN*t*Bu)]CF_3SO_3 (35). This compound was prepared as described for **26** from **3** (85 mg, 0.22 mmol) and CN*t*Bu (25 μL, 0.22 mmol). A colorless solid was obtained, which according to the ^1H and ^{13}C NMR spectra consists of a 4:1 mixture of the anti and syn isomers: yield 95 mg (92%); mp 101 °C dec. Anal. Calcd for $C_{16}H_{25}F_3NO_3RhS$: C, 40.77; H, 5.34; N, 2.97; S, 6.80. Found: C, 40.46; H, 4.97; N, 3.24; S, 6.43. IR (CH_2Cl_2): ν(CN) 2195, $\nu(OSO_{asym})$ 1275, $\nu(CF_{sym})$ 1254, $\nu(CF_{asym})$ 1171, $\nu(OSO_{sym})$ 1032 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): anti isomer, δ 5.04 (dd, ^3J(H,H) = 10.6 and 7.4 Hz, 2 H, CH_2=C*H*CCH$_3$), 3.27 (dd, ^3J(H,H) = 7.4, ^2J(H,H) = 2.0 Hz, 2 H, H of CH_2 *cis* to =CH), 3.09 (s, 2 H, H of CH_2 *trans* to =CCH_3), 2.19 (s, 6 H, =CCH_3), 1.82 (d, ^3J(H,H) = 10.6 Hz, 2 H, H of CH_2 *trans* to =CH), 1.65 (br s, 11 H, $NCCH_3$ and H of CH_2 *cis* to =CCH_3); syn isomer, δ 5.57 (m, 2 H, CH_2=C*H*CCH$_3$), 3.16 (s, 2 H, H of CH_2 *trans* to =CCH_3), 3.05 (br d, ^3J(H,H) = 7.2 Hz, 2 H, H of CH_2 *cis* to =CH), 1.95 (s, 6 H, CCH_3), 1.67 (br d, ^3J(H,H) = 10.6 Hz, 2 H, H of CH_2 *trans* to =CH), 1.51 (br s, 9 H, $NCCH_3$), 1.47 (s, 2 H, H of CH_2 *cis* to =CCH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): anti isomer, δ 139.8 (dt, ^1J(Rh,C) = 73.2, $^1J(^{14}N,C)$ = 17.0 Hz, CN), 121.4 (q, ^1J(F, C) = 321.5 Hz, CF_3), 111.8 (d, ^1J(Rh,C) = 4.1 Hz, *C*HCH_3), 98.9 (d, ^1J(Rh,C) = 5.1 Hz, *C*H=CH_2), 60.2 (t, $^1J(^{14}N,C)$ = 4.6 Hz, N*C*CH_3), 51.4 (d, ^1J(Rh,C) = 8.1 Hz, *C*H_2=CCH_3), 49.5 (d, ^1J(Rh,C) = 8.1 Hz, *C*H_2=CH), 30.6 (s, NC*C*H_3), 21.9 (s, =C*C*H_3); syn isomer, δ 113.0 (d, ^1J(Rh,C) = 3.9 Hz, *C*HCH_3), 90.1 (d, ^1J(Rh,C) = 4.8 Hz, *C*H=CH_2), 58.5 (t, $^1J(^{14}N,C)$ = 5.0 Hz, N*C*CH_3), 52.0 (d, ^1J(Rh,C) = 8.5 Hz, *C*H_2=CCH_3), 50.1 (d, ^1J(Rh,C) = 9.1 Hz, *C*H_2=CH), 30.4 (s, NC*C*H_3), 20.3 (s, =C*C*H_3), other signals of syn isomer not exactly located. ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s).

Preparation of [Rh(*s-cis*-η^4-$C_4H_4Me_2$)$_2$(CN*t*Bu)]CF_3SO_3 (36). This compound was prepared as described for **26** from **4** (142 mg, 0.34 mmol) and CN*t*Bu (42 μL, 0.35 mmol). A colorless solid was obtained: yield 138 mg (81%); mp 130 °C dec. Anal. Calcd for $C_{18}H_{29}F_3NO_3RhS$: C, 43.29; H, 5.85; N, 2.80; S, 6.42. Found: C, 42.90; H, 5.42; N, 2.82; S, 6.25. IR (CH_2Cl_2): ν(CN) 2190, $\nu(OSO_{asym})$ 1275, $\nu(CF_{sym})$ 1250, $\nu(CF_{asym})$ 1171, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 3.03 (d, ^2J(H,H) = 1.7 Hz, 4 H, H of CH_2 *cis* to =CCH_3), 1.85 (s, 12 H, =CCH_3), 1.68 (d, ^2J(H,H) = 1.7 Hz, 4 H, H of CH_2 *trans* to =CCH_3), 1.63 (br s, 9 H, $NCCH_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 141.6 (dt, ^1J(Rh,C) = 71.7, $^1J(^{14}N,C)$ = 17.1 Hz, CN), 121.2 (q, ^1J(F,C) = 320.9 Hz, CF_3), 108.5 (d, ^1J(Rh,C) = 4.1 Hz, *C*HCH_3), 60.1 (t, $^1J(^{14}N,C)$ = 4.6 Hz, N*C*CH_3), 51.4 (d, ^1J(Rh,C) = 9.2 Hz, *C*H_2=CCH_3), 30.8 (s, NC*C*H_3), 17.6 (s, =C*C*H_3). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.6 (s).

Preparation of [Rh(*s-cis*-η^4-C_4H_6)$_2$(CN-2,6-C_6H_3iPr$_2$)]CF_3SO_3 (37). This compound was prepared as described for **26** from **2** (57 mg, 0.15 mmol) and CN-2-C_6H_3iPr$_2$ (40 μL, 0.16 mmol). A colorless solid was obtained: yield 82 mg (95%); mp 69 °C dec. Anal. Calcd for $C_{22}H_{29}F_3NO_3RhS$: C, 48.27; H, 5.33; N, 2.55; S, 5.85. Found: C, 47.98; H, 5.02; N, 2.46; S, 5.99. IR (CH_2Cl_2): ν(CN) 2172, $\nu(OSO_{asym})$ 1275, $\nu(CF_{sym})$ 1253, $\nu(CF_{asym})$ 1172, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.50 (m, 1 H, *p*-H of C_6H_3), 7.33 (m, 2 H, *m*-H of C_6H_5), 6.06 (m, 4 H, CH_2=C*H*C*H*=CH_2), 3.38 (d, ^3J(H,H) = 7.1 Hz, 4 H, H of CH_2 *cis* to =CH), 3.37 (sept, ^3J(H,H) = 6.9 Hz, 2 H, C*H*CH_3), 2.05 (d, ^3J(H,H) = 9.9 Hz, 4 H, H of CH_2 *trans* to =CH), 1.37 (d, ^3J(H,H) = 6.9 Hz, 6 H, CHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): 145.8 (s, *o*-C of C_6H_3), 131.4 (s, *p*-C of C_6H_5), 124.3 (s, *m*-C of C_6H_5), 121.4 (q, ^1J(F,C) = 321.5 Hz, CF_3), 92.4 (d, ^1J(Rh,C) = 3.5 Hz, CH_2=*C*H*C*H=CH_2), 52.4 (d, ^1J(Rh,C) = 7.7 Hz, *C*H_2=CHCH=*C*H_2), 30.8 (s, *C*HCH_3), 22.6 (s, CH*C*H_3); signals of *ipso*-C of C_6H_3 and CN not exactly located. ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s).

Preparation of [Rh(*s-cis*-η^4-C_4H_5Me)$_2$(CN-2,6-C_6H_3iPr$_2$)]CF_3SO_3 (38). This compound was prepared as described for **26** from **3** (85 mg, 0.22 mmol) and CN*t*Bu (25 μL, 0.22 mmol). A colorless solid was obtained, which according to the ^1H and ^{13}C NMR spectra consists of a 4:1 mixture of the anti and syn isomers: yield 95 mg (92%); mp 101 °C dec. Anal. Calcd for $C_{16}H_{25}F_3NO_3RhS$: C, 40.77; H, 5.34; N, 2.97; S, 6.80. Found: C, 40.46; H, 4.97; N, 3.24; S, 6.43. IR (CH_2Cl_2): ν(CN) 2195, $\nu(OSO_{asym})$ 1275, $\nu(CF_{sym})$ 1254, $\nu(CF_{asym})$ 1171, $\nu(OSO_{sym})$ 1032 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): anti isomer, δ 5.04 (dd, ^3J(H,H) = 10.6 and 7.4 Hz, 2 H, CH_2=C*H*CCH$_3$), 3.27 (dd, ^3J(H,H) = 7.4, ^2J(H,H) = 2.0 Hz, 2 H, H of CH_2 *cis* to =CH), 3.09 (s, 2 H, H of CH_2 *trans* to =CCH_3), 2.19 (s, 6 H, =CCH_3), 1.82 (d, ^3J(H,H) = 10.6 Hz, 2 H, H of CH_2 *trans* to =CH), 1.65 (br s, 11 H, $NCCH_3$ and H of CH_2 *cis* to =CCH_3); syn isomer, δ 5.57 (m, 2 H, CH_2=C*H*CCH$_3$), 3.16 (s, 2 H, H of CH_2 *trans* to =CCH_3), 3.05 (br d, ^3J(H,H) = 7.2 Hz, 2 H, H of CH_2 *cis* to =CH), 1.95 (s, 6 H, CCH_3), 1.67 (br d, ^3J(H,H) = 10.6 Hz, 2 H, H of CH_2 *trans* to =CH), 1.51 (br s, 9 H, $NCCH_3$), 1.47 (s, 2 H, H of CH_2 *cis* to =CCH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): anti isomer, δ 139.8 (dt, ^1J(Rh,C) = 73.2, $^1J(^{14}N,C)$ = 17.0 Hz, CN), 121.4 (q, ^1J(F,C) = 321.5 Hz, CF_3), 111.8 (d, ^1J(Rh,C) = 4.1 Hz, *C*HCH_3), 98.9 (d, ^1J(Rh,C) = 5.1 Hz, *C*H=CH_2), 60.2 (t, $^1J(^{14}N,C)$ = 4.6 Hz, N*C*CH_3), 51.4 (d, ^1J(Rh,C) = 8.1 Hz, *C*H_2=CCH_3), 49.5 (d, ^1J(Rh,C) = 8.1 Hz, *C*H_2=CH), 30.6 (s, NC*C*H_3), 21.9 (s, =C*C*H_3); syn isomer, δ 113.0 (d, ^1J(Rh, C) = 3.9 Hz, *C*HCH_3), 90.1 (d, ^1J(Rh,C) = 4.8 Hz, *C*H=CH_2), 58.5 (t, $^1J(^{14}N,C)$ = 5.0 Hz, N*C*CH_3), 52.0 (d, ^1J(Rh,C) = 8.5 Hz, *C*H_2=CCH_3), 50.1 (d, ^1J(Rh,C) = 9.1 Hz, *C*H_2=CH), 30.4 (s, NC*C*H_3), 20.3 (s, =C*C*H_3), other signals of syn isomer not exactly located. ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s).

Preparation of [Rh(*s-cis*-η^4-$C_4H_4Me_2$)$_2$(CN-2,6-C_6H_3iPr$_2$)]CF_3SO_3 (39). This compound was prepared as described for **26** from **4** (76 mg, 0.18 mmol) and CN-2,6-C_6H_3iPr$_2$ (42 μL, 0.18 mmol). A colorless solid was obtained: yield 108 mg (98%); mp 120 °C dec. Anal. Calcd for $C_{26}H_{35}F_3NO_3RhS$: C, 51.91; H, 5.86; N, 2.32; S, 5.33. Found: C, 51.57; H, 5.68; N, 2.45; S, 5.12. IR (CH_2Cl_2): ν(CN) 2163, $\nu(OSO_{asym})$ 1278, $\nu(CF_{sym})$ 1253, $\nu(CF_{asym})$ 1170, $\nu(OSO_{sym})$ 1031 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.48 (m, 1 H, *p*-H of C_6H_3), 7.31 (m, 2 H, *m*-H of C_6H_5), 3.31 (sept, ^3J(H,H) = 7.0 Hz, 2 H, C*H*CH_3), 3.21 (d, ^2J(H,H) = 1.4 Hz, 4 H, H of CH_2 *cis* to =CCH_3), 1.94 (s, 12 H, =CCH_3), 1.84 (s, 4 H, H of CH_2 *trans* to =CCH_3), 1.35 (d,

^3J(H,H) = 7.0 Hz, 12 H, CHCH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): 145.7 (s, *o*-C of C_6H_3), 131.3 (s, *p*-C of C_6H_5), 124.3 (s, *m*-C of C_6H_5), 121.3 (q, ^1J(F,C) = 321.4 Hz, CF_3), 109.3 (d, ^1J(Rh,C) = 3.0 Hz, =*C*CH$_3$), 51.0 (d, ^1J(Rh,C) = 9.1 Hz, *C*H$_2$=C), 30.7 (s, *C*HCH$_3$), 22.6 (s, CH*C*H$_3$), 17.4 (s, =C*C*H$_3$); signals of *ipso*-C of C_6H_3 and CN not exactly located. ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −79.1 (s).

Preparation of [Rh(η^4-C_4H_6){κ^2-*i*Pr_2P(CH_2)$_3$P*i*Pr_2}]CF_3SO_3 (40). A solution of **2** (210 mg, 0.54 mmol) in dichloromethane (20 mL) was treated with 1,3-C_3H_6(P*i*Pr_2)$_2$ (168 μL, 0.54 mmol) at −10 °C. After the solution was warmed to room temperature, it was stirred for 30 min. A change of color from light orange to red occurred. The reaction mixture was concentrated to ca. 3 mL in vacuo, and pentane (15 mL) was added. A red solid precipitated, from which the solution was decanted. The solid residue was washed three times with pentane (5 mL each) and dried in vacuo: yield 299 mg (95%); mp 104 °C dec. Anal. Calcd for $C_{20}H_{40}F_3O_3P_2RhS$: C, 41.24; H, 6.92; S, 5.50. Found: C, 40.95; H, 6.58; S, 5.43. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1270−1250 br, ν(CF_{asym}) 1154, ν(OSO_{sym}) 1030 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.50 (m, 2 H, CH_2=C*H*C*H*=CH_2), 4.34 (m, 2 H, H of CH_2 *cis* to =CH), 2.75 (d, ^3J(H,H) = 13.5 Hz, 2 H, H of CH_2 *trans* to =CH), 2.43 (m, 2 H, PC*H*CH$_3$), 2.06 (br m, 4 H PC*H*CH$_3$ and PCH_2CH_2), 1.66 (m, 4 H, PCH_2CH_2), 1.32 (dd, ^3J(P,H) = 17.4, ^3J(H,H) = 7.2 Hz, 6 H, PCHCH_3), 1.22 (dd, ^3J(P,H) = 12.9, ^3J(H,H) = 7.0 Hz, 6 H, PCHCH_3), 1.08 (dd, ^3J(P,H) = 15.9, ^3J(H,H) = 7.2 Hz, 6 H, PCHCH_3), 1.07 (dd, ^3J(P,H) = 15.3, ^3J(H,H) = 6.9 Hz, 6 H, PCHCH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 121.3 (q, ^1J(F,C) = 321.8 Hz, CF_3), 99.9 (d, ^1J(Rh,C) = 5.5 Hz, CH_2=*C*H*C*H=CH_2), 63.6 (dt, ^1J(Rh,C) = 6.2, ^2J(P,C) = 4.9 Hz, *C*H_2=CHCH=*C*H_2), 30.9 (vt, *N* = 26.4 Hz, P*C*HCH$_3$), 28.2 (vt, *N* = 26.4 Hz, P*C*HCH$_3$), 22.8 (vt, *N* = 3.5 Hz, PCH_2CH_2), 21.4 (vt, *N* = 4.8 Hz, PCH*C*H$_3$), 19.4, 19.3, 17.8 (all s, PCH*C*H$_3$), 17.7 (vt, *N* = 31.4 Hz, P*C*H_2CH_2). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 30.0 (d, ^1J(Rh,P) = 165.1 Hz).

Preparation of [Rh(η^4-C_6H_8){κ^2-*i*Pr_2P(CH_2)$_3$P*i*Pr_2}]CF_3SO_3 (41). A solution of **40** (192 mg, 0.33 mmol) in dichloromethane (20 mL) was treated with 1,3-cyclohexadiene (200 μL, 2.10 mmol) and stirred for 6 h at room temperature. The reaction mixture was concentrated to ca. 3 mL in vacuo, and pentane (15 mL) was added. An orange-red solid precipitated, from which the solution was decanted. The solid residue was washed three times with pentane (5 mL each) and dried in vacuo: yield 161 mg (80%); mp 87 °C dec. Anal. Calcd for $C_{22}H_{42}F_3O_3P_2RhS$: C, 43.43; H, 6.96; S, 5.27. Found: C, 43.23; H, 6.66; S, 5.20. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1270−1250 br, ν(CF_{asym}) 1151, ν(OSO_{sym}) 1032 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.37, 5.18 (br s, 2 H, C*H*=CHCH$_2$), 5.18 (br s, 2 H, CH=C*H*CH$_2$), 2.45 (m, 2 H, PC*H*CH$_3$), 2.05 (br m, 4 H, PC*H*CH$_3$ and PCH_2CH_2), 1.88 (br d, ^3J(H,H) = 11.7 Hz, 2 H of =CHCH_2), 1.66 (m, 4 H, PCH_2CH_2), 1.55 (br d, ^3J(H,H) = 11.7 Hz, 2 H of =CHCH_2), 1.34 (dd, ^3J(P,H) = 16.7, ^3J(H,H) = 7.4 Hz, 6 H, PCHCH_3), 1.23 (dd, ^3J(P,H) = 12.7, ^3J(H, H) = 6.9 Hz, 6 H, PCHCH_3), 1.08 (dd, ^3J(P,H) = 15.5, ^3J(H,H) = 7.0 Hz, 6 H, PCHCH_3), 1.06 (dd, ^3J(P,H) = 15.6, ^3J(H,H) = 6.7 Hz, 6 H, PCHCH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 121.4 (q, ^1J(F,C) = 321.4 Hz, CF_3), 92.8 (d, ^1J(Rh,C) = 5.1 Hz, *C*H=CH-CH_2), 81.5 (dt, ^1J(Rh,C) = 6.1, ^1J(P,C) = 5.1 Hz, CH=*C*HCH$_2$), 30.4 (vt, *N* = 24.4 Hz, P*C*HCH$_3$), 27.7 (vt, *N* = 24.4 Hz, P*C*HCH$_3$), 23.2 (vt, *N* = 3.0 Hz, PCH_2CH_2), 21.2 (vt, *N* = 4.0 Hz, PCH*C*H$_3$), 21.1 (s, =CH*C*H$_2$), 19.3, 19.0, 17.7 (all s, PCH*C*H$_3$), 18.0 (vt, *N* = 30.6 Hz, P*C*H_2CH_2). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.8 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 29.5 (d, ^1J(Rh,P) = 166.9 Hz).

Generation of [(η^6-C_6H_6)Rh{κ^2-*i*Pr_2P(CH_2)$_3$P*i*Pr_2}]CF_3SO_3 (42). A solution of **41** (63 mg, 0.10 mmol) in CD_2Cl_2 (0.5 mL) was heated at 50 °C in an oil bath. Following the course of the reaction by ^{1}H and ^{31}P NMR spectroscopy revealed a continuous decrease in intensity of the signals of **41** and a continuous increase in intensity of the signals of **42**. After 3 h, the signals of **41** had disappeared. Data for **42** are as follows. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.35 (s, 6 H, C_6H_6), 2.00 (m, 4 H, PC*H*CH$_3$), 1.72 (m, 2 H, PCH_2CH_2), 1.61 (m, 4 H, PCH_2CH_2), 1.2 (br m, 24 H PCHCH_3). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 47.9 (d, ^1J(Rh,P) = 189.9 Hz).

Preparation of [Rh(η^4-C_4H_6){κ^2-*i*Pr_2P(CH_2)$_3$P*i*Pr_2}(PMe_3)]-CF_3SO_3 (43a,b). A solution of **40** (105 mg, 0.18 mmol) in dichloromethane (20 mL) was treated with PMe_3 (18 μL, 0.18 mmol) at −30 °C. A quick change of color from red to orange occurred. After the solution was warmed to room temperature, it was stirred for 30 min. The reaction mixture was concentrated to ca. 3 mL in vacuo, and pentane (15 mL) was added. A yellow suspension was formed; after it was stored for 30 min, a yellow solid precipitated. The solution was decanted, and the solid residue was washed three times with pentane (5 mL each) and dried in vacuo. According to the NMR spectra it consists of a ca. 7:1 mixture of the basal and apical isomers **43a**,**b**: yield 102 mg (86%); mp 76 °C dec. Anal. Calcd for $C_{23}H_{49}F_3O_3P_3RhS$: C, 41.95; H, 7.50; S, 4.87. Found: C, 41.69; H, 7.30; S, 4.64. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1270−1250 br, ν(CF_{asym}) 1155, ν(OSO_{sym}) 1030 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2); **43a**, δ 5.78, 5.14 (both br s, 1 H each, =C*H*C*H*=), 2.60 (m, 2 H, one H of =CHCH_2 *cis* to =CH and one H of PC*H*CH$_3$), 2.50, 2.37 (both m, 2 H, PC*H*CH$_3$), 2.28 (br s, 1 H, one H of =CHCH_2 *cis* to =CH), 2.21 (m, 3 H, PC*H*CH$_3$ and PCH_2CH_2), 2.01, 1.61 (both m, 4 H, PCH_2CH_2), 1.40 (d, ^2J(P,H) = 7.9 Hz, 9 H, PCH_3), 1.36−1.15 (br m, 24 H, PCHCH_3), 1.06, 0.71 (both m, 1 H each, H of =CHCH_2 *trans* to =CH); **43b**, δ 5.84 (m, 2 H, =C*H*C*H*=), 1.62 (d, ^2J(P,H) = 7.9 Hz, 9 H, PCH_3), 0.37 (m, 2 H, H of =CHCH_2 *trans* to =CH), other signals not exactly located. ^{13}C NMR (100.6 MHz, CD_2Cl_2): **43a**, δ 120.9 (q, ^1J(F,C) = 321.0 Hz, CF_3), 86.5, 86.0 (both br s, =*C*H*C*H=), 39.5 (ddd, ^1J(Rh,C) = 6.2, ^2J(P,C) = 37.4 and 7.6 Hz, CH=*C*H_2), 37.7 (ddd, ^1J(Rh,C) = 6.2, ^2J(P,C) = 41.0 and 9.0 Hz, CH=*C*H_2), 32.3, 32.1 (both m, P*C*HCH$_3$), 31.7 (dd, ^1J(P,C) = 19.1, ^3J(P,C) = 3.5 Hz, P*C*HCH$_3$), 28.8 (d, ^1J(P,C) = 18.1 Hz, P*C*HCH$_3$), 25.1 (d, ^1J(P, C) = 18.1 Hz, P*C*H_2CH_2), 22.8 (dd, ^1J(P,C) = 23.2, ^3J(P,C) = 3.5 Hz, P*C*H_2CH_2), 20.8 (d, ^1J(P,C) = 24.8 Hz, PCH_3), 21.4, 21.3, 20.1, 20.0, 19.9, 19.8, 19.2, 18.5 (all s, PCH*C*H$_3$), 19.7 (s, PCH_2*C*H$_2$); **43b**, 87.9 (s, =*C*H*C*H=), 41.4 (dd, ^1J(Rh,C) = 7.3, ^2J(P,C) = 15.0 Hz, CH=*C*H_2), 29.6 (m, P*C*HCH$_3$), 29.3 (vt, *N* = 21.8 Hz, P*C*HCH$_3$), other signals not exactly located. ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.9 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): **43a**, δ 21.6 (ddd, ^1J(Rh,P) = 152.0, ^2J(P,P) = 18.5 and 5.4 Hz, PCHCH$_3$), 17.9 (dt, ^1J(Rh,P) = 109.0, ^2J(P,P) = 18.5 Hz, PCHCH$_3$), −21.1 (ddd, ^1J(Rh,P) = 114.2, ^2J(P,P) = 18.5 and 5.4 Hz, PCH_3); **43b**, δ 15.9 (dt, ^1J(Rh,P) = 113.3, ^2J(P,P) = 8.7 Hz, PCHCH$_3$), −20.0 (dt, ^1J(Rh,P) = 160.2, ^2J(P,P) = 8.7 Hz, PCH_3).

Preparation of [Rh{κ^2-*i*Pr_2P(CH_2)$_3$P*i*Pr_2}(PMe_3)$_2$]CF_3SO_3 (44). This compound was prepared as described for **43** from **40** (123 mg, 0.21 mmol) and PMe_3 (54 μL, 0.52 mmol). A yellow solid was obtained: yield 133 mg (91%); mp 56 °C dec. Anal. Calcd for $C_{22}H_{52}F_3O_3P_4RhS$: C, 38.83; H, 7.70; S, 4.71. Found: C, 38.51; H, 7.57; S, 4.59. IR (CH_2Cl_2): ν(OSO_{asym}) and ν(CF_{sym}) 1270−1250 br, ν(CF_{asym}) 1152, ν(OSO_{sym}) 1033 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.14 (dq, ^3J(P,H) = 14.7, ^3J(H,H) = 7.2 Hz, 2 H, PCH_2CH_2), 2.01 (m, 4 H, PC*H*CH$_3$), 1.77 (m, 4 H, PCH_2CH_2), 1.47 (d, ^2J(P,H) = 5.8 Hz, 18 H, PCH_3), 1.36−1.15 (br m, 24 H, PCHCH_3), 1.26 (dd, ^3J(P,H) = 12.1, ^3J(H,H) = 7.2 Hz, 12 H, PCHCH_3), 1.24 (dd, ^3J(P,H) = 16.0, ^3J(H,H) = 7.2 Hz, 12 H, PCHCH_3). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 121.3 (q, ^1J(F,C) = 321.4 Hz, CF_3), 28.6 (both m, P*C*HCH$_3$), 21.8 (br s, PCH*C*H$_3$), 21.1 (m, PCH_3), 19.5 (s, PCH_2*C*H$_2$), 18.7 (s, PCH*C*H$_3$), 17.5 (vt, *N* = 20.3 Hz, P*C*H_2CH_2). ^{19}F NMR (376.4 MHz, CD_2Cl_2): δ −78.7 (s). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 30.5 (AA′ part of an AA′BB′X spin system,, ^1J(Rh,P) = −131.0, ^2J(P,P) = 270.5, −43.1, and −46.4 Hz, PCHCH$_3$), −19.3 (BB′ part of an AA′BB′X spin system, ^1J(Rh,P) = −132.0, ^2J(P,P) = 270.5, −43.1, and −46.4 Hz, PCH_3).