A Series of (Butadiene)rhodium(I) Complexes with an Open-Sandwich- or Half-Sandwich-Type Structure

Marco Bosch, Matthias Laubender, Birgit Weberndörfer, and Helmut Werner*[a]

Dedicated to Professor Hubert Schmidbaur on the occasion of his 65th birthday

Abstract: A series of mono(diene)- and bis(diene)rhodium(I) compounds (diene = butadiene, 2-methylbutadiene (isoprene), and 2,3-dimethylbutadiene) was prepared from the triflato-bridged dimer [Rh{μ-$O_2S(O)CF_3$}(C_8H_{14})$_2$]$_2$ (**1**). Reaction of **1** with excess diene affords the monomeric complexes [Rh{η^1-OS(O)$_2$CF$_3$}(η^4-diene)$_2$] (**2**–**4**) which, as established by X-ray crystal structure analysis of the isoprene derivative **3**, possess a sandwich-type structure with the open site of the two parallel diene units directed towards the monodentate triflato ligand. Treatment of compounds **2**–**4** with an equimolar amount of P*i*Pr$_3$ gives the ionic compounds [Rh(η^4-diene)$_2$(P*i*Pr$_3$)]O$_3$SCF$_3$ (**5**–**7**), which can also be prepared from [Rh{η^2-O$_2$S(O)CF$_3$}(P*i*Pr$_3$)(C_8H_{14})] (**9**) and excess diene. The arrangement of the two diolefin ligands in the cations of **5**–**7** is quite similar to that in **2**–**4**, as shown by an X-ray diffraction study of the butadiene derivative **5**. The reaction of **9** with *one* equivalent of 2,3-dimethylbutadiene affords the mono(diene) complex [Rh{η^1-OS(O)$_2$CF$_3$}(η^4-C_6H_{10})(P*i*Pr$_3$)] (**8**). X-ray crystal structure analysis of this complex reveals that the plane containing the rhodium, the metal-bound oxygen, and the phosphorus atoms does not lie exactly perpendicular to the plane of the diene. Treatment of **2** and **3** with P*i*Pr$_3$ (molar ratio = 1:3) leads to ligand displacement and nucleophilic attack of a phosphane on one diene ligand to form the π-allylphosphonium complexes [Rh{η^3-*anti*-(*i*Pr$_3$PCH$_2$)*C*H*C*R*C*H$_2$}(P*i*Pr$_3$)$_2$]O$_3$SCF$_3$ (**10**, **11**). The structure of the PF_6^- salt of the corresponding cation with R = CH$_3$ has been determined by X-ray crystallography.

Keywords: diene complexes • phosphanes • rhodium • triflato complexes • X-ray diffraction studies

Introduction

Recent work in our group has shown that the four-coordinate bis(phosphane)sulfonatorhodium(I) compounds [Rh{η^2-O$_2$S(O)R}(P*i*Pr$_3$)$_2$] (R = Me, *p*-Tol, CF$_3$, F) are active catalysts in the C–C coupling reaction of ethene and diphenyldiazomethane. Depending on the substituent R on the sulfonato ligand, it was found that besides the three isomeric 1:1 adducts of C_2H_4 and CPh_2 (1,1-diphenylprop-1-ene, 3,3-diphenylprop-1-ene, and 1,1-diphenylcyclopropane), quite unexpectedly, the 2:1 adduct 3,3-diphenylpent-1-ene was also formed.[1] Studies to elucidate the mechanism of this unusual C–C coupling reaction revealed that, in the absence of diphenyldiazomethane, a rhodium(I)-catalyzed di- or oligomerization of ethene occurred.[2] Moreover, if butadiene was used instead of ethene as the olefinic substrate with the fluorosulfonato- or trifluoromethylsulfonatorhodium(I) complex as the catalyst, then a rapid polymerization of butadiene to *trans*-1,4-polybutadiene took place.[3] A remarkable side-product of this reaction was found (by GC/MS) to be all-*trans*-1,5,9,13-cyclohexadecatetraene; however, this was obtained in less than 5% yield.[2b]

The formation of this cyclotetramer is interesting for two reasons. First, the all-*trans* isomer of $C_{16}H_{24}$ is a convenient starting material for the synthesis of 4,8,12-cyclohexadecatriene-1-one, which is a synthetic substitute for muscone (3-methylcyclopentadecanone).[4] Secondly, the process resembles the cyclotrimerization of butadiene catalyzed by 'naked nickel' as described by Wilke et al.[5, 6] Studies concerning the mechanism of this cyclotrimerization reaction revealed that the butadiene coordinates initially to the nickel(0) center followed by the addition of a second molecule of C_4H_6 to generate a bis(allyl)nickel(II) species. This relatively stable intermediate reacts with a third molecule of butadiene to give a well-characterized C_{12}-bis(allyl)nickel(II) complex that affords all-*trans*-1,5,9-cyclododecatriene after ring closure. Taking these results into consideration, we assumed that the mechanism of the rhodium(I)-catalyzed cyclooligomerization of butadiene, discovered in our laboratory, could be similar to that for the formation of all-*trans*-$C_{12}H_{18}$, and that as yet

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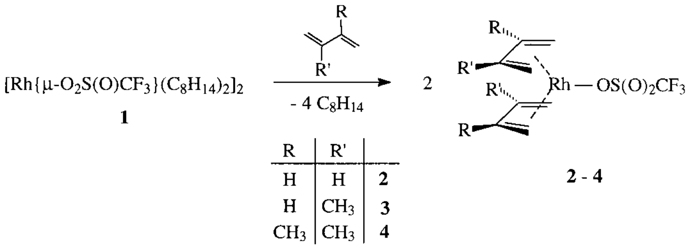
unknown mono- and bis(butadiene)rhodium derivatives might be involved as intermediates.

In this paper we describe the isolation and structural characterization of a series of (diene)rhodium(I) complexes in which the metal center has either a 16- or an 18-electron configuration. These complexes are presently used as starting materials for a more efficient, but still highly selective, cyclotetra- or cyclooligomerization reaction of butadiene, the mechanism of which will be discussed at a later date.

Results and Discussion

The first step in the synthesis of the new diolefin rhodium(I) compounds involves the replacement of the cyclooctene ligands in the dimeric starting material [Rh{μ-$O_2S(O)CF_3$}$(C_8H_{14})_2$]$_2$ (**1**). Treatment of an orange solution of **1** in pentane with an excess of butadiene (C_4H_6), isoprene (2-methylbutadiene; C_5H_8), or 2,3-dimethylbutadiene (C_6H_{10}) immediately gave a white suspension from which, after separation of the two phases, the monomeric complexes [Rh{η^1-OS(O)$_2$CF$_3$}(η^4-diene)$_2$] (**2**–**4**) were isolated in virtually quantitative yield (Scheme 1). Compounds **2**–**4** are light yellow solids that are only moderately soluble in aromatic hydrocarbons, but readily soluble in polar organic solvents such as THF, CH_2Cl_2, or acetone. They can be stored under argon at −10 °C for several days without decomposition.

Abstract in German: *Eine Reihe von Mono(dien)- und Bis(dien)rhodium(I)-Verbindungen mit den Dienen Butadien, 2-Methylbutadien (Isopren) und 2,3-Dimethylbutadien wurde ausgehend von dem Triflat-verbrückten Dimer [Rh{μ-$O_2S(O)CF_3$}$(C_8H_{14})_2$]$_2$ (**1**) hergestellt. Die Reaktion von **1** mit einem Überschuss des Diens liefert die monomeren Komplexe [Rh{η^1-OS(O)$_2$CF$_3$}(η^4-diene)$_2$] (**2**–**4**), welche nach dem Ergebnis der Kristallstrukturanalyse des Isoprenderivats **3** eine Sandwich-ähnliche Struktur besitzen. Die offene Seite der zwei parallelen Dien-Einheiten zeigt dabei in Richtung des einzähnigen Triflatliganden. Umsetzung von **2**–**4** mit einer äquimolaren Menge PiPr$_3$ ergibt die ionischen Verbindungen [Rh(η^4-diene)$_2$(PiPr$_3$)]O$_3$SCF$_3$ (**5**–**7**), die auch ausgehend von [Rh{η^2-$O_2S(O)CF_3$}(PiPr$_3$)(C_8H_{14})] (**9**) und überschüssigem Dien erhältlich sind. Die Anordnung der zwei diolefinischen Liganden in den Kationen von **5**–**7** ist sehr ähnlich wie in **2**–**4**, was durch die Röntgenbeugungsuntersuchung der Butadienverbindung **5** belegt ist. Bei der Reaktion von **9** mit einem Äquivalent 2,3-Dimethylbutadien entsteht der Mono(dien)-Komplex [Rh{η^1-OS(O)$_2$CF$_3$}(η^4-C_6H_{10})(PiPr$_3$)] (**8**), in dem laut Kristallstrukturanalyse die Ebene mit dem Rhodium-, dem metallgebundenen Sauerstoff- und dem Phosphoratom nicht exakt senkrecht auf der Dien-Ebene steht. Durch Umsetzung von **2** und **3** mit PiPr$_3$ im Molverhältnis 1:3 bilden sich durch Ligandenverdrängung und nucleophilen Angriff eines Phosphans auf einen Dienligand die π-Allylphosphonium-Komplexe [Rh{η^3-anti-(iPr$_3$PCH$_2$)CHCRCH$_2$}(PiPr$_3$)$_2$]O$_3$SCF$_3$ (**10**, **11**). Die Struktur des [PF$_6$]$^-$-Salzes des Kations mit R = CH$_3$ wurde röntgenographisch bestimmt.*



R	R'	
H	H	2
H	CH3	3
CH3	CH3	4

Scheme 1. Synthesis of the bis(diene) complexes **2**–**4** from the cyclooctene complex **1**.

In solution at room temperature, the sulfonato complexes **2**–**4** are fluxional on the NMR timescale as indicated by the broad signals for the diene moieties in the ^1H and ^{13}C NMR spectra. Even at −80 °C, the ^1H NMR spectrum of **2** in [D$_6$]acetone shows a complicated set of signals; these can be assigned to the presence of two butadiene ligands. At 40 °C only one set of signals is observed, typical of a η^4-coordinated C_4H_6 system.[7, 8] We assume that the fluxionality of complexes **2**–**4** is because of an interconversion between an η^4- and an η^2-coordination mode for one of the diene units; this could be assisted by the ability of the triflate to act as both a mono- and a bidentate ligand. The work by Nelson et al. is in agreement with this interpretation.[7b]

Compound **2** decomposes in [D$_6$]acetone as well as in CD_2Cl_2, and therefore no ^{13}C NMR spectroscopic data could be obtained. In contrast, solutions of **3** and **4** in either [D$_6$]acetone or CD_2Cl_2 are stable for several days at room temperature. In the ^{13}C NMR spectra of these complexes the resonances for the diene carbon atoms are shifted upfield by approximately 40 ppm relative to the corresponding free diene. The IR spectra of **2**–**4** in CH_2Cl_2 display a $\tilde{\nu}(OSO_{asymm})$ stretching frequency at 1308 (**2**) or 1305 cm^{-1} (**3** and **4**) that is characteristic of a η^1-coordinated sulfonato ligand.[9] From these data, we conclude that compounds **2**–**4** are monomeric, and this is supported by the EI-mass spectrum of **2** (m/z = 360, [M^+]).

In order to confirm the proposed structure, an X-ray diffraction analysis of the isoprene derivative was carried out. Yellow crystals of **3** were obtained by slow diffusion of ether into a solution of **3** in acetone at room temperature. The result of the crystallographic study is summarized in Figure 1.

As Figure 1 shows, the pentacoordinate rhodium(I) complex **3** has a distorted square-pyramidal geometry with the CH_2 groups of the isoprene ligands forming the base of the pyramid. The apical position is occupied by the oxygen atom of the sulfonato ligand. It is interesting to note that the isoprene ligands in **3** adopt a staggered conformation with respect to the methyl substituents. The Rh–C bond lengths of 2.151(2)–2.206(2) Å are in good agreement with those found in [RhCl(C_4H_6)$_2$][10] and other (butadiene)rhodium(I) complexes.[8, 11] The distances C(1)–C(2), C(3)–C(4), C(6)–C(7), and C(8)–C(9) of about 1.40 Å are clearly shorter than those for C(2)–C(3) and C(7)–C(8) [1.441(2) and 1.443(2) Å] and suggest an η^4-coordination of the diene ligand to the metal center. Moreover, the sum of the bond angles C(1)-C(2)-C(3) [117.7(2)°], C(1)-C(2)-C(5) [121.7(2)°], and C(5)-C(2)-C(3) [120.3(2)°] equals 359.7(6)°, thus supporting an sp^2-config-

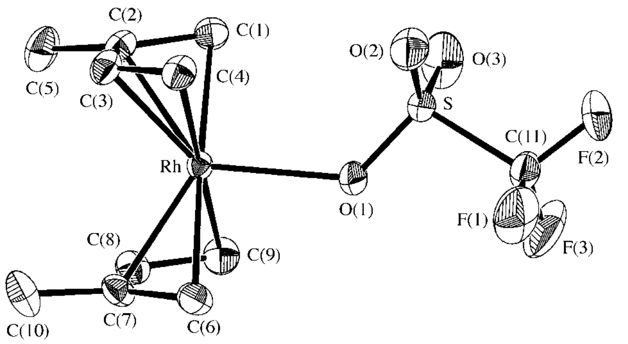
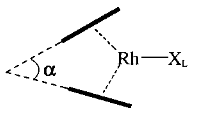


Figure 1. Molecular structure of **3**. Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh–C(1) 2.187(2), Rh–C(2) 2.170(2), Rh–C(3) 2.151(2), Rh–C(4) 2.206(2), Rh–C(6) 2.202(2), Rh–C(7) 2.189(2), Rh–C(8) 2.162(2), Rh–C(9) 2.201(2), Rh–O(1) 2.289(1), S–O(1) 1.456(1), C(1)–C(2) 1.406(2), C(2)–C(3) 1.441(2), C(3)–C(4) 1.395(2), C(2)–C(5) 1.498(3), C(6)–C(7) 1.397(2), C(7)–C(8) 1.443(2), C(8)–C(9) 1.396(3), C(7)–C(10) 1.503(3); C(1)-C(2)-C(3) 117.7(2), C(1)-C(2)-C(5) 121.7(2), C(3)-C(2)-C(5) 120.3(2), C(4)-C(3)-C(2) 121.2(2), C(6)-C(7)-C(8) 118.3(2), C(6)-C(7)-C(10) 121.0(2), C(8)-C(7)-C(10) 120.3(2), C(9)-C(8)-C(7) 120.9(2).

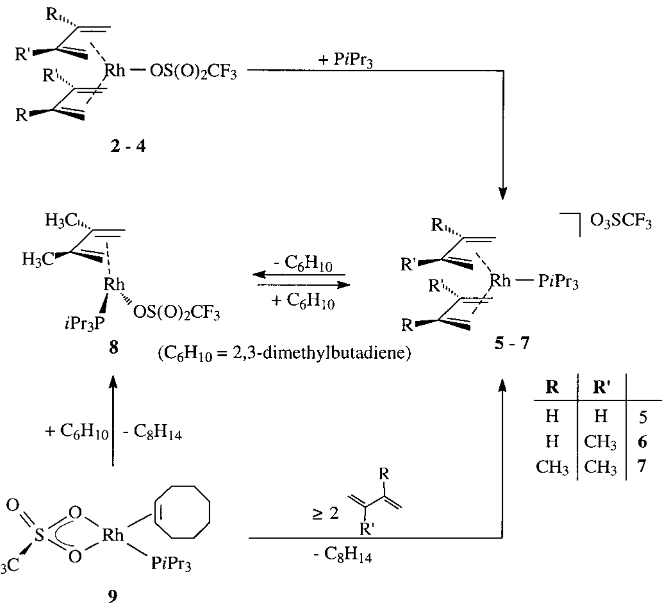
uration on C(2). The same applies for C(3), C(7), and C(8). The two isoprene ligands lie parallel to each other as indicated by the angle between the planes C(1)-C(2)-C(3)-C(4) and C(6)-C(7)-C(8)-C(9) of 2.7(2)° (Figure 2). The Rh–O(1) distance of 2.289(1) Å in **3** is significantly longer than in the related tosylato complex [Rh(η^4-C_8H_{12})(H_2O){η^1-OS(O)$_2$-*p*-Tol}] [2.102(3) Å];[12] this could be due to the higher coordination number of rhodium(I) in the isoprene derivative **3**. It should be mentioned that the diene ligation in **3** (and also in **5** and **8**, see below) is in accordance with a general rule proposed by Yasuda and Nakamura about the configuration of metal-diene units in electron-poor and electron-rich transition metal complexes.[11e]



X_L	α
O_3SCF_3	2.7(2)°
P*i*Pr_3	16.6(8)°

Figure 2. Schematic drawing for the arrangement of the diene ligands in compounds **3** and **5**. The angle α increases with the steric bulk of the ligand X_L attached to the rhodium center.

The triflato ligand in the five-coordinate compounds **2**–**4** is only weakly bound to the metal center and is therefore easily displaced by better donor groups such as trialkylphosphanes. Treatment of a solution of **2**, **3**, or **4** in acetone with P*i*Pr_3 (1.0 equiv) at room temperature leads to a change of color from yellow to orange, which, after work-up, gives the ionic complexes [Rh(η^4-diene)$_2$(P*i*Pr_3)]O_3SCF_3 (**5**–**7**) in good-to-excellent yield (Scheme 2). Compounds **5**–**7** can also be prepared by treating the cyclooctene derivative [Rh{η^2-$O_2S(O)CF_3$}(P*i*Pr_3)(C_8H_{14})] (**9**)[1] with excess diene in pentane. Like the sulfonato complexes **2**–**4**, the phosphane-substituted derivatives **5**–**7** are insoluble in nonpolar organic solvents, but soluble in acetone and dichloromethane. We note that a counterpart of the bis(butadiene) complex **5** with the composition [Rh(η^4-C_4H_6)$_2$(PPh_3)]ClO_4 (prepared from [Rh(NBD)(PPh_3)$_2$]ClO_4 (NBD = norbornadiene) and excess butadiene) had already been reported by Schrock and Osborn in 1971.[13] However, the disadvantage of the synthesis of [Rh(η^4-C_4H_6)$_2$(PPh_3)]ClO_4 is that one equivalent of PPh_3 is formed as a by-product. Therefore the yield of the bis(butadiene) metal derivative could only be increased to about 50% if the reaction mixture was treated with small amounts of aqueous H_2O_2.



R	R'	
H	H	**5**
H	CH$_3$	**6**
CH$_3$	CH$_3$	**7**

Scheme 2. Two routes to the bis(diene)phosphane complexes **5**–**7**.

The phosphane-substituted rhodium(I) complexes **5**–**7** are moderately air-sensitive, white solids that can be stored under argon at room temperature for days without decomposition. The ^1H NMR spectra of compounds **5**–**7** in CD_2Cl_2 confirm that the diolefin and P*i*Pr_3 ligands are present in the ratio of 2:1. In addition, the ^{13}C NMR spectra of the cations display only one set of signals for the two diene groups, indicating a symmetric orientation of these ligands around the metal center. In the ^{31}P NMR spectra of **5**–**7** one doublet is observed at $\delta \approx 45$ with a ^1J(Rh,P) coupling of 144–160 Hz. The absence of a $\tilde{\nu}$(OSO_{asymm}) stretch at around 1300 cm^{-1} in the IR spectra of **5**–**7** suggests that the triflato unit acts as a noncoordinating anion.[9] In contrast to **5** and **6**, compound **7** undergoes a ligand-distribution process in solution and is in equilibrium with free 2,3-dimethylbutadiene and the mono(diene) complex **8** (see Scheme 2).

The molecular structure of the butadiene-phosphane derivative **5** was determined by X-ray crystallography. There are two independent molecules, **5a** and **5b**, in the unit cell; **5a** is shown in Figure 3. The coordination geometry around the rhodium center is square-pyramidal, with the CH_2 groups of the butadiene ligands at the base of the pyramid. The apical position of the cationic species is occupied by the phosphorus atom of the triisopropylphosphane ligand. As in compound **3**, the C–C bond lengths of the C_4H_6 units together with the bond angles C(1)-C(2)-C(3), C(4)-C(3)-C(2), C(5)-C(6)-C(7), and C(8)-C(7)-C(6) (all ≈ 120°) indicate a η^4-coordination

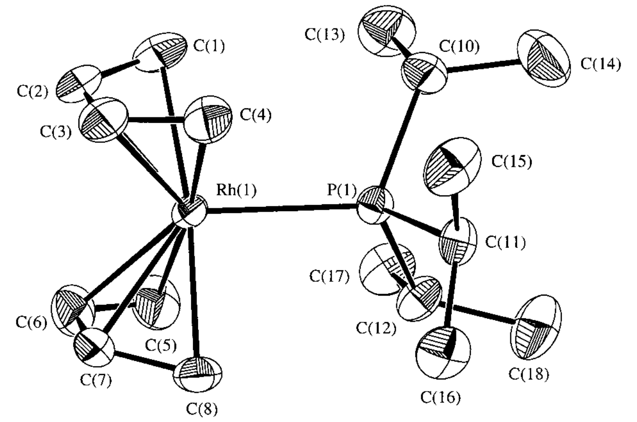


Figure 3. Molecular structure of **5a** (anionic ligand omitted for clarity). Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh(1) – C(1) 2.227(8), Rh(1) – C(2) 2.157(8), Rh(1) – C(3) 2.169(8), Rh(1) – C(4) 2.202(8), Rh(1) – C(5) 2.21(8), Rh(1) – C(6) 2.163(8), Rh(1) – C(7) 2.161(8), Rh(1) – C(8) 2.223(8), Rh(1) – P(1) 2.411(2), C(1) – C(2) 1.406(13), C(2) – C(3) 1.431(14), C(3) – C(4) 1.385(13), C(5) – C(6) 1.405(12), C(6) – C(7) 1.424(13), C(7) – C(8) 1.398(13); C(1)-C(2)-C(3) 119.8(9), C(4)-C(3)-C(2) 119.1(9), C(5)-C(6)-C(7) 118.5(8), C(8)-C(7)-C(6) 119.1(8).

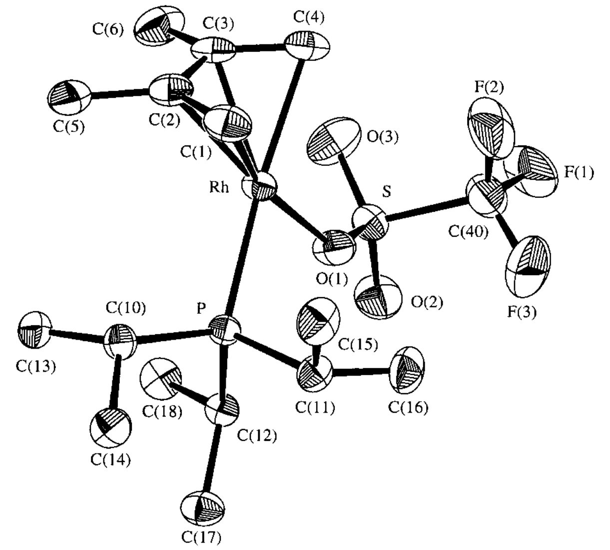


Figure 4. Molecular structure of **8**. Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh – C(1) 2.103(5), Rh – C(2) 2.106(5), Rh – C(3) 2.162(4), Rh – C(4) 2.233(5), Rh – O(1) 2.136(3), Rh – P 2.329(1), S – O(1) 1.454(3), C(1) – C(2) 1.407(7), C(2) – C(3) 1.451(6), C(3) – C(4) 1.391(7), C(2) – C(5) 1.504(7), C(3) – C(6) 1.499(6); O(1)-Rh-P 86.77(8), S-O(1)-Rh 137.2(2), C(1)-C(2)-C(3) 117.3(5), C(1)-C(2)-C(5) 121.5(5), C(3)-C(2)-C(5) 121.2(5), C(4)-C(3)-C(2) 118.7(5), C(4)-C(3)-C(6) 119.8(5), C(6)-C(3)-C(2) 120.8(5).

mode for both butadiene ligands. The Rh(1) – P(1) distance in **5a** of 2.411(2) Å is rather long, possibly due to steric repulsion between the bulky phosphane ligand and the diene systems. As a result, the planes of the C_4H_6 ligands are not parallel to each other but tilted by 16.6(8)° (Figure 2).

After we had found that the chelate compound [Rh{η^2-$OS(O)_2CF_3$}(P*i*Pr_3)(C_8H_{14})] (**9**) reacted with an excess of diene to give the bis(diolefin) complexes **5** – **7**, analogous reactions of **9** with *one* equivalent of diene per rhodium were also carried out. Unfortunately, all attempts to prepare the mono(butadiene)- and mono(isoprene)rhodium derivatives [Rh{η^1-$OS(O)_2CF_3$}(P*i*Pr_3)(η^4-diene)] failed either by the above mentioned method or by the reaction of [Rh{η^2-$O_2S(O)CF_3$}(P*i*Pr_3)$_2$][1] and **2** or **3** (1.0 equiv). In contrast, the reaction of **9** with an equimolar amount of 2,3-dimethylbutadiene gave the mono(diene) complex [Rh{η^1-$OS(O)_2CF_3$}(P*i*Pr_3)(η^4-C_6H_{10})] (**8**) as a red, moderately air-stable solid in 77% yield (Scheme 2). The η^1-coordination of the sulfonato ligand is indicated by the appearance of a $\tilde{\nu}(OSO_{asymm})$ stretching frequency at 1318 cm^{-1} in the IR spectrum.[9] The ^1H NMR spectrum of **8** (in CD_2Cl_2) displays the expected set of resonances for the protons of the diene and P*i*Pr_3 ligands in a ratio of 1:1. In contrast to the asymmetric molecular structure found in the crystal, both the ^1H and the ^{13}C NMR spectra of **8** indicate C_s symmetry, and so this compound, like the bis(diene) complexes **2** – **4**, is fluxional in solution. Attempts to freeze out the intramolecular rearrangement upon cooling failed.

The X-ray crystal structure of **8** is shown in Figure 4 and can be described as an open half-sandwich with the two monodentate P*i*Pr_3 and O_3SCF_3 ligands coordinated *cis* to the metal center. The C–C bond lengths of the diene unit differ in the same way as was found for the bis(diolefin) complexes **3** and **5**. An interesting aspect is that the Rh–C bonds *trans* to the triflato ligand [Rh – C(1) and Rh – C(2)] in **8** are significantly shorter than the Rh – C distances found in **3** and **5** as well as in other (butadiene)rhodium compounds.[8, 11] The angle between the planes [C(1),C(2),C(3),C(4)] and [O(1),Rh,P] of 75.7(2)° deviates somewhat from the ideal value of 90° for a perpendicular arrangement; this is possibly due to the steric demands of the three different ligands. The Rh – P distance of 2.329(1) Å is almost the same as in other four-coordinate (triisopropylphosphane)rhodium(I) compounds.[1, 14] Furthermore, the Rh – O(1) distance of 2.136(3) Å in **8** is in good agreement with the Rh – O bond length of 2.102(3) Å found in the structurally related complex [Rh{η^1-$OS(O)_2$-*p*-Tol}(COD)(H_2O)].[12]

As an extension of our studies on the reactivity of the bis(diolefin) complexes (outlined in Scheme 2), the sulfonato derivatives **2** and **3** were also treated with P*i*Pr_3 (2.0 equiv) in acetone. A rapid change of color from orange to red occurred and, as the ^1H and ^{31}P NMR spectra revealed, a mixture of two compounds was formed. While it could be shown by comparison of the spectroscopic data that one of the two components is the bis(diene)phosphane complex **5** or **6**, the composition of the other remained unknown. However, if a third equivalent of P*i*Pr_3 was added to the reaction mixture, a yellow solution was generated, the NMR spectra of which contained peaks from only the unknown product and the free diene. After the solutions were concentrated in vacuo and pentane was added, small yellow crystals of **10** and **11**, respectively, were precipitated. In each case, the isolated yield of the very air-sensitive solids was about 70%. In contrast, the reaction of the bis(2,3-dimethylbutadiene) complex **4** with either two or three equivalents of P*i*Pr_3 gave a complicated mixture of products from which no well-defined compounds could be isolated.

For the complexes **10** and **11**, both the elemental analyses and the NMR spectral data support the assumption that

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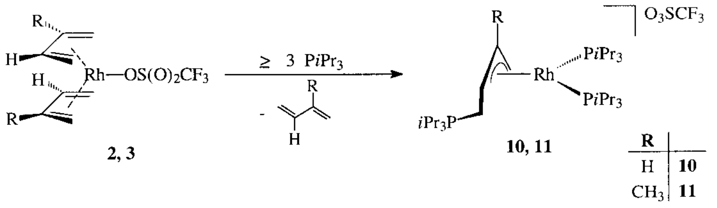
the π-allylphosphonium complexes [Rh{η^3-*anti*-(iPr$_3$PCH$_2$)-*C*H*C*R*C*H$_2$}(PiPr$_3$)$_2$]O$_3$SCF$_3$ (Scheme 3) were obtained from the starting materials **2** or **3** and three molecules of PiPr$_3$. The ^{31}P NMR spectra of **10** and **11** (in CD$_2$Cl$_2$) display three sets of signals, which seems to be a typical feature of these types of complexes. The doublet-of-doublets-of-doublets at $\delta \approx 52.3$ and the doublet-of-doublets at $\delta = 48.7$ (**10**) or 50.0 (**11**) are assigned to the two phosphanes P$_c$ and P$_b$ (for notation see Figure 7 in the Experimental Section) bound *cis* to the metal center. This assignment is supported by the large rhodium–phosphorus coupling constants of 178 to 187 Hz and the phosphorus–phosphorus coupling constants of approximately 22 Hz. The third signal for the phosphorus atom P$_a$ of the phosphonium moiety appears at higher field ($\delta = 32.4$ for **10** and 32.7 for **11**) and shows a much smaller ^{31}P–^{31}P coupling. Both the coupling constants and the ^{31}P–^{31}P correlation spectrum of **10** confirm that the three phosphanes with the nuclei P$_a$, P$_b$, and P$_c$ are part of the same molecule.



Scheme 3. Formation of the π-allylphosphonium complexes **10** and **11**.

The allyl protons of compounds **10** and **11** give rise to a complicated spin system and therefore the corresponding resonances in the ^{1}H NMR spectra appear as multiplets owing to coupling with different ^{1}H, ^{31}P, and ^{103}Rh nuclei. The chemical shifts of these signals are in agreement with those of substituted π-allylrhodium(I) complexes.[15] The CH$_2$ protons in α-position to P$_a$ (H$_a$ and H$_{a'}$) are diastereotopic and their signals are split into two sets of multiplets at $\delta = 2.33$, 1.64 (**10**) and 2.45, 1.67 (**11**), respectively.

The ^{13}C NMR signals of the allylic carbon atoms of **10** and **11** were assigned from ^{135}DEPT and ^{90}DEPT experiments, as well as from ^{1}H-^{13}C correlation spectra. The signals for C^2 and C^4 are found at $\delta \approx 45$ and appear as multiplets which simplify to doublets-of-doublets-of-doublets by selective ^{13}C{^{31}P$_a$} decoupling. A characteristic feature of the allylphosphonium ligand is the large upfield shift for the resonance of C^1 to $\delta = 16.5$ (**10**) and 18.0 (**11**), with the carbon–phosphorus coupling constant ^1J(P,C) ≈ 20.0 Hz. The signal of the CH carbon atom of the triisopropylphosphonium group in **10** and **11** is also shifted upfield by about 8 ppm relative to the metal-bound triisopropylphosphanes. Finally, we note that the *anti* position of the CH$_2$PiPr$_3$ substituent at the allylic unit was unambiguously established by NOE experiments. For **10**, irradiation of the signal at $\delta = 4.59$ (H$_c$) gave an NOE effect on the resonances at $\delta = 3.29$ (H$_b$) and 2.74 (H$_c$), while irradiation of the signal at $\delta = 2.33$ (H$_{a/a'}$) produced a corresponding NOE effect on the resonances at $\delta = 3.29$ (H$_b$) and 1.64 (H$_{a/a'}$). Likewise in the case of **11**, irradiation of the signal at $\delta = 1.72$ (CH$_3$ on C^3) resulted in an NOE effect on the signals at $\delta = 2.98$ (H$_b$) and 2.60 (H$_c$), and irradiation of the signal at $\delta = 2.45$ (H$_{a/a'}$) affected the resonances at $\delta = 2.98$ (H$_b$) and 1.67 (H$_{a/a'}$). Therefore we conclude that the arrangement of the CH$_2$PiPr$_3$ fragment at the π-allyl ligand is analogous to that found in **13**.

After attempts to grow single crystals of either **10** or **11** failed, the PF$_6^-$ salt of the π-allylphosphonium complex was prepared for the isoprene derivative **3**. The synthesis was carried out by a one-pot reaction of *cis*-[Rh(C$_8$H$_{14}$)$_2${O=C(CH$_3$)$_2$}$_2$]PF$_6$ (**12**),[16] excess isoprene, and PiPr$_3$ (3.5 equiv) in CH$_2$Cl$_2$. The product [Rh{η^3-*anti*-(iPr$_3$PCH$_2$)*C*H*C*(CH$_3$)*C*H$_2$}(PiPr$_3$)$_2$]PF$_6$ (**13**) was obtained in 77% yield. Slow diffusion of pentane into a solution of **13** in acetone afforded orange, needle-shaped crystals suitable for X-ray diffraction. As revealed in Figure 5 the rhodium has a distorted square-planar coordination sphere with the substituted π-allyl ligand occupying two coordination sites. The bulky CH$_2$PiPr$_3$ unit points away from the metal center as indicated by the Rh–C(5) distance of 2.972(3) Å and the Rh-C(4)-C(5) angle of 105.1(2)°. The Rh–C(1), Rh–C(2), and Rh–C(3) bond lengths are between 2.122(3) and 2.194(3) Å, and are thus in good agreement with those of other substituted π-allylrhodium(I) complexes.[15] The positive charge on the phosphorus atom P(3) causes a decrease in the P–C bond lengths of about 0.06 Å relative to the neutral PiPr$_3$ ligands. The Rh–P(1) and Rh–P(2) bond lengths of approximately 2.32 Å, as well as the bond angle P(1)-Rh-P(2) of 107.17(3)°, are quite similar to those of related *cis*-disposed bis(triisopropylphosphane)rhodium(I) derivatives.[1, 15]

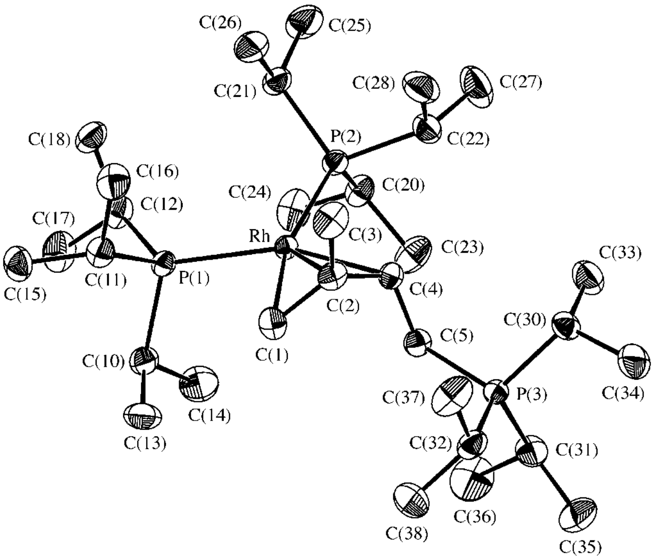


Figure 5. Molecular structure of **13** (anionic ligand omitted for clarity). Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh–C(1) 2.175(3), Rh–C(2) 2.122(3), Rh–C(4) 2.194(3), Rh–P(1) 2.3264(8), Rh–P(2) 2.3176(8), C(1)–C(2) 1.404(5), C(2)–C(4) 1.419(4), C(2)–C(3) 1.506(5), C(4)–C(5) 1.512(5), P(3)–C(5) 1.823(3), P(3)–C(30) 1.815(3), P(3)–C(31) 1.823(4), P(3)–C(32) 1.819; C(1)-Rh-C(4) 67.58(12), C(1)-Rh-P(1) 90.21(9), C(4)-Rh-P(2) 95.50(8), P(2)-Rh-P(1) 107.17(3), C(5)-C(4)-Rh 105.1(2), C(1)-C(2)-C(3) 121.0(3), C(1)-C(2)-C(4) 118.8(3), C(4)-C(2)-C(3) 119.9(3), C(2)-C(4)-C(5) 124.2(3), C(4)-C(5)-P(3) 117.9(2).

With regard to the mechanism of formation of the π-allylphosphonium complexes **10** and **11**, there is no doubt that in the initial step the substitution products **5** and **6** are formed, which then possibly react with a second equivalent of $\mathrm{P}i\mathrm{Pr_3}$ to give the cationic species $[\mathrm{Rh(dien)(P}i\mathrm{Pr_3)_2}]^+$. It could be for steric reasons that treatment of these intermediates with a third molecule of the bulky triisopropylphosphane does not lead to the displacement of the diolefin ligand, but instead affords the allylphosphonium unit by attack of the phosphane on one of the terminal carbon atoms of the diene. We note that a counterpart of the aforementioned cationic species with the composition $[\mathrm{Rh}(\eta^4\text{-}\mathrm{C_4H_6})(\mathrm{PPh_3})_2]\mathrm{ClO_4}$ is known,[13] and that this reacts with triphenylphosphane (which is less bulky than $\mathrm{P}i\mathrm{Pr_3}$) by displacement of the butadiene ligand to give the cation $[\mathrm{Rh(PPh_3)_3(S)}]^+$ (S = solvent molecule).

Conclusion

The present investigation has shown that treatment of the binuclear starting material **1** with excess butadiene, isoprene, or 2,3-dimethylbutadiene results in the smooth replacement of the cyclooctene ligands to form the bis(diene) complexes **2**–**4** with an open-sandwich-type structure. The substitution of the monoolefins is accompanied by a change in the coordination mode of the triflato ligand from μ_2 to η^1. In agreement with Pearson's HSAB concept,[17] the bonding between rhodium and oxygen in the mononuclear bis(diene) compounds **2**–**4** is rather weak and therefore these complexes react rapidly with one equivalent of $\mathrm{P}i\mathrm{Pr_3}$ to afford the ionic derivatives **5**–**7**. In the course of this substitution process, the structure of the bis(diene)-metal framework remains almost unchanged. In contrast to the neutral sulfonatorhodium(I) compounds **2**–**4**, one of the rhodium–diene bonds is easily cleaved in the related cationic species $[\mathrm{Rh(dien)_2(P}i\mathrm{Pr_3)}]^+$ and, for diene = butadiene and isoprene, the π-allylphosphonium complexes **10** and **11** are generated in the presence of three equivalents of triisopropylphosphane. To the best of our knowledge there is only one report in the literature in which a similar nucleophilic attack of a tertiary phosphane on an open diene ligand has been described. Most recently, Poli and co-workers found that treatment of the cation $[\mathrm{C_5H_5Mo}(s\text{-}cis\text{-}supine\text{-}\mathrm{C_4H_6})(s\text{-}trans\text{-}\mathrm{C_4H_6})]^+$ with $\mathrm{PMe_3}$ forms the corresponding 1:1 adduct $[\mathrm{C_5H_5Mo}(s\text{-}cis\text{-}supine\text{-}\mathrm{C_4H_6})\{syn\text{-}prone\text{-}(\mathrm{Me_3PCH_2})\mathit{CHCHCH}_2\}]^+$.[18] This is similar to the reactions of **2** and **3** with $\mathrm{P}i\mathrm{Pr_3}$ in which the stereoselective attack of the phosphane on the butadiene ligand gives exclusively the *anti* instead of the *syn* isomer of the substituted π-allylic ligand. With regard to $\mathrm{P}i\mathrm{Pr_3}$ as a P donor, it should be mentioned that both we[19] and others[20] have observed that this phosphane is a particularly good substrate for nucleophilic additions at unsaturated carbon-bonded ligands. Precedence for the activation of butadiene by a rhodium(I) complex with sterically demanding phosphine ligands comes from the work by Fryzuk and co-workers who found that the reaction of $[\mathrm{Rh(dippp)}(\mu\text{-H})]_2$ [dippp = bis(diisopropylphosphino)propane] with excess butadiene yielded the binuclear rhodium(I) complex $[\{\mathrm{Rh(dippp)}\}_2(\mu\text{-}\eta^3,\eta^3\text{-}\mathrm{C_4H_6})]$ with a bridging bis(allyl)-type ligand.[21]

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The commercially avail able starting materials butadiene, isoprene, and 2,3-dimethylbutadiene were used without further purification. $\mathrm{P}i\mathrm{Pr_3}$ was a commercial product bought from Strem Chemicals. The rhodium(I) complexes $[\mathrm{Rh}\{\mu\text{-}\mathrm{O_2S(O)CF_3}\}(\mathrm{C_8H_{14}})_2]_2$ (**1**),[1] $[\mathrm{Rh}\{\eta^2\text{-}\mathrm{O_2S(O)CF_3}\}(\mathrm{P}i\mathrm{Pr_3})(\mathrm{C_8H_{14}})]$ (**9**),[1] and *cis*-$[\mathrm{Rh(C_8H_{14})_2\{O{=}C(CH_3)_2\}_2]PF_6}$ (**12**)[16] were prepared as described in the literature. NMR spectra were recorded at RT unless stated otherwise on Bruker AC200 and Bruker AMX400 instruments. Abbreviations used: s, singlet; d, doublet; q, quartet; sept, septet; m, multiplet; br, broadened signal. Melting points were measured by DTA. IR spectra were recorded on a Bruker IFS25 FT/IR spectrometer and mass spectra on a 8200 Finnigan MAT instrument.

$[\mathrm{Rh}\{\eta^1\text{-}\mathrm{OS(O)_2CF_3}\}(\eta^4\text{-}\mathrm{C_4H_6})_2]$ (2): A stream of butadiene was passed for 10 s through an orange solution of **1** (181 mg, 0.19 mmol) in pentane (10 mL) at RT. An instantaneous reaction took place to afford a white precipitate. The solvent was decanted, and the residue was washed with pentane (3 × 5 mL) and dried in vacuo. Yield = 132 mg, 96 %; m.p. 56 °C (decomp); IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ = 1308, 1231, 1213 ($\mathrm{OSO_{asymm}}$), 1181 ($\mathrm{CF_{asymm}}$), 1031 cm^{-1} ($\mathrm{OSO_{symm}}$); ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 5.84 (br m, 4H; H$_c$), 4.11 (br m, 4H; H$_b$), 2.80 (br m, 4H; H$_a$); ^{1}H NMR (400 MHz, [D$_6$]acetone, 40 °C): δ = 5.75 (m, 4H; H$_c$), 3.97 (d, 4H, ^3J(H,H) = 6.9 Hz; H$_b$), 2.61 (d, 4H, ^3J(H,H) = 10.6 Hz; H$_a$), for assignment of diene protons see Figure 6; ^{19}F NMR (376.4 MHz, [D$_6$]acetone): δ = –78.6 (s, CF$_3$); MS (70 eV, EI): *m*/*z* (%): = 360 (0.7) [M^+], 306 0.2 [$M^+ - \mathrm{C_4H_6}$], 210 (2.4) [$M^+ - \mathrm{O_3SCF_3}$], 157 (0.8) [$\mathrm{RhC_4H_6}^+$]), 103 (1.2) [$^{103}\mathrm{Rh}^+$]; $\mathrm{C_9H_{12}F_3O_3RhS}$ (360.2): calcd S 8.90; found S 8.46.

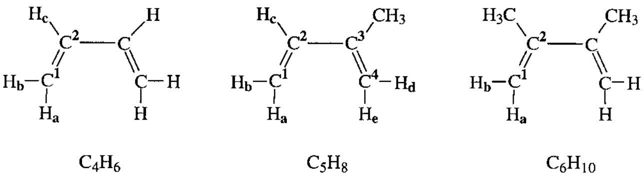


Figure 6. Assignment of the diene protons and carbon atoms in compounds **2**–**8**.

$[\mathrm{Rh}\{\eta^1\text{-}\mathrm{OS(O)_2CF_3}\}(\eta^4\text{-}\mathrm{C_5H_8})_2]$ (3): This was prepared as described above for compound **2** by reaction of **1** (54 mg, 0.06 mmol) with isoprene (0.1 mL, 68 mg, 1.0 mmol) in pentane (5 mL). Yellow solid; yield = 41 mg, 93 %; m.p. 114 °C (decomp); IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ = 1305, 1233, 1213 ($\mathrm{OSO_{asymm}}$), 1172 ($\mathrm{CF_{asymm}}$), 1025 cm^{-1} ($\mathrm{OSO_{symm}}$); ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 5.35 (m, 2H; H$_c$), 4.05, 3.97 (both br m, 4H; H$_e$ and H$_b$), 2.53, 2.44 (both br m, 4H; H$_d$ and H$_a$), 1.92 (s, 6H; CH$_3$); ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 121.6 (q, ^1J(F,C) = 321.2 Hz; CF$_3$), 117.2 (br, C^3), 104.2 (br, C^2), 61.2 (br, C^4), 60.3 (br, C^1), 22.0 (br s, CH$_3$), for assignment of diene protons and carbon atoms see Figure 6; ^{19}F NMR (376.4 MHz, [D$_6$]acetone): δ = –78.3 (s, CF$_3$); $\mathrm{C_{11}H_{16}F_3O_3RhS}$ (388.2): calcd C 34.03, H 4.15, S 8.26; found C 33.89, H 4.04, S 8.23.

$[\mathrm{Rh}\{\eta^1\text{-}\mathrm{OS(O)_2CF_3}\}(\eta^4\text{-}\mathrm{C_6H_{10}})_2]$ (4): This was prepared as described above for compound **2** by reaction of **1** (66 mg, 0.07 mmol) with 2,3-dimethylbutadiene (0.1 mL, 0.98 mmol) in pentane (5 mL). Pale yellow solid; yield = 53 mg, 91 %; m.p. 88 °C (decomp); IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ = 1301, 1232, 1216 ($\mathrm{OSO_{asymm}}$), 1172 ($\mathrm{CF_{asymm}}$), 1022 cm^{-1} ($\mathrm{OSO_{symm}}$); ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 4.07 (br m, 4H; H$_b$), 2.53 (br m, 4H; H$_a$), 1.80 (s, 12H; CH$_3$); ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 121.3 (q, ^1J(C,F) = 321.8 Hz; CF$_3$), 115.9 (s, C^2), 63.1 (s, C^1), 18.2 (s, CH$_3$), for assignment of diene protons and carbon atoms see Figure 6; ^{19}F NMR (376.4 MHz, [D$_6$]acetone): δ = –78.5 (s, CF$_3$); $\mathrm{C_{13}H_{20}F_3O_3RhS}$ (416.3): calcd C 37.51, H 4.84, S 7.70; found C 37.59, H 4.80, S 7.58.

$[\mathrm{Rh}(\eta^4\text{-}\mathrm{C_4H_6})_2(\mathrm{P}i\mathrm{Pr_3})]\mathrm{O_3SCF_3}$ (5): a) A solution of **9** was generated in situ from **1** (104 mg, 0.11 mmol) and $\mathrm{P}i\mathrm{Pr_3}$ (42 µL, 0.22 mmol) in pentane (10 mL). The reaction mixture was stirred for 30 min at RT, after which a stream of butadiene was passed through the solution for 10 s. A white solid was precipitated from the orange solution. The solvent was decanted, and the remaining white solid was washed with pentane (3 × 5 mL) and then dried in vacuo. Yield = 109 mg, 96 %.

b) A solution of **2** (46 mg, 0.13 mmol) in acetone (10 mL) was treated with P*i*Pr$_3$ (25 μL, 0.13 mmol) and stirred for 5 min at RT. A change in color from yellow to orange occurred. The solution was concentrated in vacuo (2 mL) and after addition of pentane (10 mL) a white solid was precipitated. This was worked up as described in a) above. Yield = 56 mg, 85 %; m.p. 84 °C (decomp); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1270–1260 (OSO$_{asymm}$), 1256 (CF$_{symm}$), 1172 (CF$_{asymm}$), 1031 cm^{-1} (OSO$_{symm}$); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 5.92 (m, 4H; H$_c$), 3.20 (br m, 4H; H$_b$), 2.56 (m, 3H; PC*H*CH$_3$), 1.40 (dd, ^3J(P,H) = 13.6 Hz, ^3J(H,H) = 7.2 Hz, 18H; PCHC*H*$_3$), 1.32 (br m, 4H; H$_a$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 90.8 (br s, C^2), 52.4 (br s, C^1), 28.0 (d, ^1J(P,C) = 20.3 Hz; P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$), for assignment of diene protons and carbon atoms see Figure 6; ^{19}F NMR (376.4 MHz, CD$_2$Cl$_2$): δ = −78.7 (s, CF$_3$); ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 47.7 (d, ^1J(Rh,P) = 159.5 Hz); C$_{18}$H$_{33}$F$_3$O$_3$PRhS (520.4): calcd C 41.55, H 6.39, S 6.16; found C 41.37, H 6.31, S 6.46.

[Rh(η^4-C$_5$H$_8$)$_2$(P*i*Pr$_3$)]O$_3$SCF$_3$ (6): This was prepared as described above for complex **5** by reaction of either a) compound **1** (105 mg, 0.11 mmol), P*i*Pr$_3$ (43 μL, 0.22 mmol), and isoprene (1 mL, 0.68 g, 10 mmol) in pentane (10 mL), or b) compound **3** (41 mg, 0.11 mmol) and P*i*Pr$_3$ (21 μL, 0.11 mmol) in acetone (10 mL). White solid; yield = 93 mg, 76 % (a), or 52 mg, 83 % (b); m.p. 104 °C (decomp); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1270–1260 (OSO$_{asymm}$, CF$_{symm}$), 1172 (CF$_{asymm}$), 1031 cm^{-1} (OSO$_{symm}$); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 5.00 (m, 2H; H$_c$), 3.25 (d, ^3J(H,H) = 7.2 Hz, 2H; H$_b$), 3.02 (s, 2H; H$_e$), 2.52 (m, 3H; PC*H*CH$_3$), 2.26 (d, ^4J(P,H) = 2.8 Hz, 6H; CH$_3$), 1.38, 1.37 (both dd, ^3J(P,H) = 13.4 Hz, ^3J(H,H) = 7.2 Hz, 18H; PCHC*H*$_3$), 1.22 (dd, ^3J(P,H) = 10.8 Hz, ^3J(H,H) = 10.8 Hz, 2H; H$_a$), 1.05 (d, ^3J(P,H) = 11.6 Hz, 2H; H$_d$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 121.2 (q, ^1J(F,C) = 321.6 Hz; CF$_3$), 111.4 (d, ^1J(Rh,C) = 2.0 Hz; C^3), 99.0 (d, ^1J(Rh,C) = 2.0 Hz; C^2), 50.8 (dd, ^1J(Rh,C) = 9.1 Hz, ^2J(P,C) = 3.5 Hz; C^4), 49.1 (dd, ^1J(Rh,C) = 9.0 Hz, ^2J(P,C) = 3.9 Hz; C^1), 27.3 (d, ^1J(P,C) = 18.4 Hz; P*C*HCH$_3$), 22.1 (s, C*C*H$_3$), 20.3 (s, PCH*C*H$_3$), for assignment of diene protons and carbon atoms see Figure 6; ^{19}F NMR (376.4 MHz, CD$_2$Cl$_2$): δ = −78.6 (s, CF$_3$); ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 46.1 (d, ^1J(Rh,P) = 152.4 Hz); C$_{20}$H$_{37}$F$_3$O$_3$PRhS (548.5): calcd C 43.80, H 6.80, S 5.85; found C 43.61, H 6.72, S 5.52.

[Rh(η^4-C$_6$H$_{10}$)$_2$(P*i*Pr$_3$)]O$_3$SCF$_3$ (7): This was prepared as described above for complex **5** by reaction of either a) compound **1** (180 mg, 0.19 mmol), P*i*Pr$_3$ (75 μL, 0.38 mmol) and 2,3-dimethylbutadiene (1 mL, 0.68 g, 10 mmol) in pentane (10 mL), or b) compound **3** (70 mg, 0.17 mmol) and P*i*Pr$_3$ (32 μL, 0.17 mmol) in CH$_2$Cl$_2$ (10 mL). White solid; yield = 176 mg, 82 % (a) or 82 mg, 77 % (b); m.p. 107 °C (decomp); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1270–1260, 1224 (OSO$_{asymm}$, CF$_{symm}$), 1147 (CF$_{asymm}$), 1029 cm^{-1} (OSO$_{symm}$); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 3.01 (s, 4H; H$_b$), 2.51 (m, 3H; PC*H*CH$_3$), 1.91 (d, ^4J(P,H) = 2.9 Hz, 12H; CH$_3$), 1.39 (dd, ^3J(P,H) = 13.1 Hz, ^3J(H,H) = 7.2 Hz, 18H; PCHC*H*$_3$), 1.02 (d, ^3J(P,H) = 15.0 Hz, 2H; H$_a$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 121.1 (q, ^1J(F,C) = 320.4 Hz; CF$_3$), 108.8 (dd, ^1J(Rh,C) = 2.0 Hz, ^2J(P,C) = 3.0 Hz; C^2), 51.1 (dd, ^1J(Rh,C) = 9.7 Hz, ^2J(P,C) = 4.6 Hz; C^1), 26.7 (d, ^1J(P,C) = 17.3 Hz; P*C*HCH$_3$), 20.5 (s, PCH*C*H$_3$), 17.8 (s, C*C*H$_3$), for assignment of diene protons and carbon atoms see Figure 6; ^{19}F NMR (376.4 MHz, CD$_2$Cl$_2$): δ = −78.6 (s, CF$_3$); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$): δ = 44.5 (d, ^1J(Rh,P) = 143.9 Hz); C$_{22}$H$_{41}$F$_3$O$_3$PRhS (576.5): calcd C 45.84, H 7.17, S 5.56; found C 45.53, H 6.78, S 5.55.

[Rh{η^1-OS(O)$_2$CF$_3$}(η^4-C$_6$H$_{10}$)(P*i*Pr$_3$)] (8): A solution of **9** was generated in situ by addition of P*i*Pr$_3$ (49 μL, 0.26 mmol) to a solution of **1** (121 mg, 0.13 mmol) in pentane (20 mL). This solution was treated with 2,3-dimethylbutadiene (29 μL, 0.26 mmol) and stirred for 30 min at RT. A red suspension was formed, from which the solvent was removed in vacuo. The remaining residue was dissolved in ether (5 mL), and the resulting solution was stored overnight at −78 °C. A red microcrystalline solid was precipitated, which was then separated from the mother liquor, washed with pentane, and dried under a stream of argon. Yield = 98 mg, 77 %; m.p. 52 °C (decomp); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1318, 1232, 1203 (OSO$_{asymm}$), 1177 (CF$_{asymm}$), 1014 cm^{-1} (OSO$_{symm}$); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 3.18 (s, 2H; H$_b$), 2.21 (m, 3H; PC*H*CH$_3$), 2.04 (s, 6H; CH$_3$), 1.47 (m, 2H; H$_a$), 1.28 (dd, ^3J(P,H) = 13.8 Hz, ^3J(H,H) = 7.1 Hz, 18H; PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 119.2 (q, ^1J(C,F) = 319.0 Hz; CF$_3$), 101.6 (d, ^1J(Rh,C) = 7.6 Hz; C^2), 50.0 (dd, ^1J(Rh,C) = 11.8 Hz, ^2J(P,C) = 5.5 Hz; C^1), 23.8 (d, ^1J(P,C) = 19.4 Hz; P*C*HCH$_3$), 19.3 (s, PCH*C*H$_3$), 19.0 (s, C*C*H$_3$), for assignment of diene protons and carbon atoms see Figure 6; ^{19}F NMR (376.4 MHz, CD$_2$Cl$_2$): δ = −78.2 (s, CF$_3$); ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 46.0 (d, ^1J(Rh,P) = 174.4 Hz]; MS (70 eV, EI): *m*/*z* (%): = 494 (5.0) [M^+], 410 (1.7) [M^+ − C$_6$H$_{10}$], 345 (1.9) [M^+ − O$_3$SCF$_3$], 334 (1.3) [M^+ − P*i*Pr$_3$], 262 (2.9) [RhP*i*Pr$_3^+$], 185 (2.9) [RhC$_6$H$_{10}^+$], 160 (100) [P*i*Pr$_3^+$], 103 (7.1) [^{103}Rh$^+$]; C$_{16}$H$_{31}$F$_3$O$_3$PRhS (494.4): calcd C 38.87, H 6.32; found C 38.52, H 6.45.

***anti,cis*-[Rh{η^3-(*i*Pr$_3$PCH$_2$)*C*H*C*H*C*H$_2$}(P*i*Pr$_3$)$_2$]O$_3$SCF$_3$ (10)**: A solution of **2** (75 mg, 0.21 mmol) in acetone (10 mL) was treated with P*i*Pr$_3$ (131 μL, 0.67 mmol) and stirred for 10 min at RT. A change in color from red to yellow occurred. The solution was concentrated in vacuo (ca. 2 mL) and pentane (30 mL) was then added. A yellow solid was precipitated, which was separated from the mother liquor, washed with pentane (3 × 5 mL) and then dried in vacuo. Yield = 112 mg, 68 %; m.p. 134 °C (decomp); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 4.59 (m, 1H; H$_e$), 3.29 (m, 1H; H$_b$), 2.74 (m, 1H; H$_c$), 2.70 (dsept, ^2J(P,H) = 12.4 Hz, ^3J(H,H) = 7.2 Hz, 3H; P$_a$C*H*CH$_3$), 2.33 (m, 1H; H$_{a/a'}$), 2.27, 2.23 (both m, 6H; P$_{b/c}$C*H*CH$_3$), 1.71 (m, 1H; H$_d$), 1.64 (m, 1H; H$_{a/a'}$), 1.41 (dd, ^3J(P,H) = 15.6 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.40 (dd, ^3J(P,H) = 15.2 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.28 (dd, ^3J(P,H) = 12.8 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.26 (dd, ^3J(P,H) = 13.6 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.22 (dd, ^3J(P,H) = 9.2 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.21 (dd, ^3J(P,H) = 6.8 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 121.4 (q, ^1J(F,C) = 321.9 Hz; CF$_3$), 93.4 (d, ^1J(Rh,C) = 6.0 Hz; C^3), 44.4 (m; in ^{13}C{^{31}P$_a$} ddd, ^2J(P,C) = 23.9, 4.5 Hz, ^1J(Rh,C) = 10.1 Hz; C^2), 43.1 (m; in ^{13}C{^{31}P$_a$} ddd, ^2J(P,C) = 21.8, 4.4 Hz, ^1J(Rh,C) = 8.2 Hz; C^4), 29.0 (d, ^1J(P,C) = 14.0 Hz; P$_{b/c}$*C*HCH$_3$), 28.5 (d, ^1J(P,C) = 15.0 Hz; P$_{b/c}$*C*HCH$_3$), 21.5 (d, ^2J(P,C) = 3.0 Hz; P$_{b/c}$CH*C*H$_3$), 21.1 (d, ^2J(P,C) = 2.8 Hz; P$_{b/c}$CH*C*H$_3$), 20.7 (d, ^1J(P,C) = 39.7 Hz; P$_a$*C*HCH$_3$), 20.6, 20.5, (both s, P$_{b/c}$CH*C*H$_3$), 17.1 (d, ^2J(P,C) = 3.5 Hz; P$_a$CH*C*H$_3$), 16.5 (br d, ^1J(P,C) = 20.0 Hz; C^1); ^{19}F NMR (376.4 MHz, CD$_2$Cl$_2$): δ = −78.7 (s, CF$_3$); ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 52.4 (ddd, ^1J(Rh,P) = 182.2 Hz, ^2J(P,P) = 22.0 Hz, ^4J(P,P) = 12.0 Hz; P$_c$), 48.7 (dd, ^1J(Rh,P) = 187.0 Hz, ^2J(P,P) = 22.0 Hz; P$_b$), 32.4 (d, ^4J(P,P) = 12.0 Hz; P$_a$), for assignment of protons, and carbon and phosphorus atoms see Figure 7; C$_{32}$H$_{69}$F$_3$O$_3$P$_3$RhS (786.8): calcd C 48.85, H 8.84, S 4.08; found C 48.65, H 9.00, S 4.09.

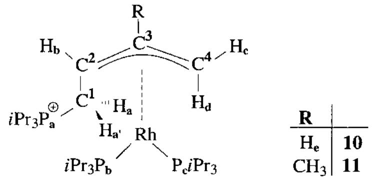


Figure 7. Assignment of the protons, carbon, and phosphorus atoms in compounds **10** and **11**.

***anti,cis*-[Rh{η^3-(*i*Pr$_3$PCH$_2$)*C*H*C*(CH$_3$)*C*H$_2$}(P*i*Pr$_3$)$_2$]O$_3$SCF$_3$ (11)**: This was prepared as described above for **10** by reaction of compound **3** (34 mg, 0.09 mmol) with P*i*Pr$_3$ (54 μL, 0.28 mmol) in acetone (10 mL). Yellow solid; yield = 49 mg, 71 %; m.p. 124 °C (decomp); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.98 (m, 1H; H$_b$), 2.62 (dsept, ^1J(P,H) = 14.0 Hz, ^3J(H,H) = 7.3 Hz, 3H; P$_a$C*H*CH$_3$), 2.60 (m, 1H; H$_c$), 2.45 (m, 1H; H$_{a/a'}$), 2.28, 2.06 (both m, 6H; P$_{b/c}$C*H*CH$_3$), 1.83, (m, 1H; H$_d$), 1.72 (s, 3H; CC*H*$_3$), 1.67 (m, 1H; H$_{a/a'}$), 1.40 (dd, ^3J(P,H) = 15.6 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.39 (dd, ^3J(P,H) = 15.2 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.28 (dd, ^3J(P,H) = 14.4 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.27 (dd, ^2J(P,H) = 16.8 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.21 (dd, ^3J(P,H) = 11.6 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$), 1.20 (dd, ^3J(P,H) = 8.6 Hz, ^3J(H,H) = 7.2 Hz, 9H; PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$): δ = 121.4 (q, ^1J(F,C) = 321.3 Hz; CF$_3$), 104.9 (d, ^1J(Rh,C) = 8.1 Hz; C^3), 46.1 (m; in ^{13}C{^{31}P$_a$} ddd, ^2J(P,C) = 27.1, 6.0 Hz, ^1J(Rh,C) = 7.8 Hz; C^4), 45.1 (m; in ^{13}C{^{31}P$_a$} ^2J(P,C) = 28.5, 5.7 Hz, ^1J(Rh,C) = 10.6 Hz; C^2), 28.7 (d, ^1J(P,C) = 15.4 Hz; P$_{b/c}$*C*HCH$_3$), 28.6 (d, ^1J(P,C) = 16.3 Hz; P$_{b/c}$*C*HCH$_3$), 25.7 (s, C*C*H$_3$), 21.6 (d, ^2J(P,C) = 3.3 Hz; P$_{b/c}$CH*C*H$_3$), 21.3 (d, ^2J(P,C) = 2.8 Hz; P$_{b/c}$CH*C*H$_3$), 20.7 (d, ^1J(P,C) = 39.6 Hz; P$_a$*C*HCH$_3$), 20.6, 20.4 (both s, P$_{b/c}$CH*C*H$_3$), 18.0 (br d, ^1J(P,C) = 20.5 Hz; C^1), 17.1, 17.0 (both d, ^2J(P,C) = 3.3 Hz; P$_a$CH*C*H$_3$); ^{19}F NMR (376.4 MHz, CD$_2$Cl$_2$): δ = −78.7 (s, CF$_3$); ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$): δ = 52.3 (ddd, ^1J(Rh,P) = 177.8 Hz, ^2J(P,P) = 21.6 Hz, ^4J(P,P) =

13.7 Hz; P$_c$), 50.0 (dd, ^1J(Rh,P) = 185.1 Hz, ^2J(P,P) = 21.6 Hz; P$_b$), 32.7 (dd ^3J(Rh,P) = 4.4 Hz, ^4J(P,P) = 13.7 Hz; P$_a$), for assignment of protons, and carbon and phosphorus atoms see Figure 7; $C_{33}H_{71}F_3O_3P_3RhS$ (800.8): calcd C 49.50, H 8.94, S 4.00; found C 49.27, H 8.85, S 4.16.

***anti,cis*-[Rh{η^3-(*i*Pr$_3$PCH$_2$)*CHC*(CH$_3$)*CH*$_2$}(P*i*Pr$_3$)$_2$]PF$_6$ (13)**: A solution of **12** (206 mg, 0.38 mmol) in CH_2Cl_2 (10 mL) was treated with isoprene (0.1 mL, 68 mg, 1.0 mmol) at RT. After addition of P*i*Pr$_3$ (220 µL, 1.13 mmol) to the light yellow solution, a color change to red occurred. The solution was stirred for 30 min and then concentrated in vacuo (ca. 2 mL). Addition of pentane (15 mL) afforded a red oily precipitate. The mother liquor was decanted and the oily residue washed with pentane (5 × 5 mL). A very air-sensitive, yellow solid was obtained which was dried in vacuo. Yield = 232 mg, 77 %; m.p. 148 °C (decomp); ^{19}F NMR (376.4 MHz, CD_2Cl_2): $\delta = -73.2$ (d, ^1J(P,F) = 710.6 Hz; PF$_6$); ^{31}P NMR (162.0 MHz, CD_2Cl_2): -144.4 (sept, ^1J(F,P) = 710.6 Hz; PF$_6$); the ^{1}H, ^{13}C, and ^{31}P NMR data for the protons, carbon, and phosphorus atoms of the ligands on the cation are virtually identical to those in compound **11**; $C_{32}H_{71}F_6P_4Rh$ (796.7): calcd C 48.24, H 8.98, F 14.31, P 15.55; found C 48.06, H 9.04, F 14.09, P 15.30.

X-ray structural analysis of the compounds 3, 5, 8, and 13:[22] Single crystals of **3** were grown by slow diffusion of ether into a solution of **3** in acetone. Crystals of **5** were grown from a saturated solution of **5** in methanol. Crystals of **8** were obtained from a saturated solution of **8** in ether at −78 °C, and crystals of **13** were grown by slow diffusion of pentane into a solution of **13** in acetone. Crystal data for the four structures are presented in Table 1. The data for **3**, **5**, **8**, and **13** were collected at low temperature from an oil-coated, shock-cooled crystal[23] on a ENRAF-Nonius CAD4 instrument with monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) for **3**, **5**, and **8**, and on a Stoe IPDS for **13**. Semiempirical absorption corrections were applied for **3**, **5**, and **8**.[24] The structures were solved by Patterson or direct methods with SHELXS-86 for **3** and **8**, and with SHELXS-97 for **5** and **13**.[25] All structures were refined by full matrix least-squares procedures on F^2 with SHELXL-93 (**3**, **8**) or SHELXL-97 (**5**, **13**).[26] For the structure of **3** the extinction parameter was refined to 0.00321(9). For compound **5**, two independent molecules were found in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen-atom positions. All hydrogen atoms of **3** and H1a, H1b, H4a, and H4b of **8** were found in a final Fourier synthesis and refined isotropically without restraints. The hydrogen atoms H1a, H1b, H4a, H4b, H5a, H5b, H8a, H8b, H31a, H31b, H34a, H34b, H35a, H35b, H38a, and H38b of **5** were found in a final Fourier synthesis and refined isotropically with restraints on the bond distance and with *U*(eq) 1.2 times larger than the appended C atoms. The hydrogen atoms H1a, H1b, H4, H5a, and H5b of **13** were found in a final Fourier synthesis and refined isotropically with *U*(eq) 1.2 times larger than the appended C atoms. The PF$_6^-$ counterion of **13** is disordered and was found in two positions with an occupancy of 0.73:0.27; it was refined anisotropically with restraints.

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Table 1. Crystal structure data for **3**, **5**, **8**, and **13**.

	3	**5**[d]	**8**	**13**
formula	$C_{11}H_{16}F_3O_3RhS$	$C_{18}H_{33}F_3O_3PRhS$	$C_{16}H_{31}F_3O_3PRhS$	$C_{32}H_{71}F_6P_4Rh$
M_r	388.21	520.38	494.35	796.68
T [K]	173(2)	173(2)	173(2)	173(2)
crystal size [mm^3]	0.5 × 0.3 × 0.2	0.6 × 0.4 × 0.2	0.2 × 0.2 × 0.1	0.1 × 0.1 × 0.1
space group	*C*2/*c* (no. 15)	*P*2$_1$/*n* (no. 14)	*P*2$_1$/*c* (no. 14)	*P*2$_1$/*c* (no. 14)
cell dimension determination	25 reflns, $10 < \theta < 15$	25 reflns, $10 < \theta < 15$	25 reflns, $10 < \theta < 15$	5000 reflns, $2.26 < \theta < 27.06$
a [pm]	2035.8(6)	2055.9(5)	1436.3(2)	1935.6(2)
b [pm]	865.59(9)	917.3(2)	949.5(1)	880.83(7)
c [pm]	1572.2(4)	2441.9(5)	1656.0(3)	2479.0(3)
β [°]	91.76(1)	105.62(1)	111.363(7)	111.48(1)
V [nm^3]	2.769(1)	4.435(2)	2.1032(6)	3.9331(7)
Z	8	8	4	4
ρ_c [Mg m^{-3}]	1.862	1.559	1.561	1.345
μ [mm^{-1}]	1.404	0.967	1.015	0.641
F(000)	1552	2144	1016	1688
2θ max [°]	62	50	50	54
measured reflections	4554	10144	3912	36463
unique reflections	4401	7806	3689	8560
reflections used	4400	7803	3689	8560
refined parameters	237	499	250	425
$R1$ [$I > 2\sigma(I)$][a]	0.0213	0.0679	0.0375	0.0387
$wR2$ (all data)[b]	0.0527	0.1877	0.0831	0.0958
$g1$; $g2$[c]	0.0228; 4.3854	0.0855; 25.5699	0.0229; 3.1413	0.0558; 0.00
residual electron density ρ [10^{-6} e pm^{-3}]	0.439/ − 0.678	3.858/ − 0.958	0.452/ − 0.404	0.791/ − 0.970

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (g1 \times P)^2 + g2 \times P]$; $P = (F_o^2 + 2F_c^2)/3$. [d] The asymmetric unit contains two independent molecules **5a** and **5b**. In this table the formula and M_r represent one molecule only.

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[22] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-112323 (**3**), 112324 (**5**), 112325 (**8**), and 112326 (**13**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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