DALTON
FULL PAPER

Preparation, molecular structure and reactivity of mono- and di-nuclear sulfonato rhodium(I) complexes

Helmut Werner, Marco Bosch, Michael E. Schneider, Christine Hahn, Frank Kukla, Matthias Manger, Bettina Windmüller, Birgit Weberndörfer and Matthias Laubender

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: helmut.werner@mail.uni-wuerzburg.de

Received 28th July, Accepted 7th September 1998

The reaction of $[Rh(\eta^3\text{-}C_3H_5)(PPr^i_3)_2]$ **1** or $[Rh(\eta^3\text{-}CH_2Ph)(PPr^i_3)_2]$ **2** with an equimolar amount of RSO_3H (R = Me, *p*-tolyl, CF_3, F, Camph) led to the formation of the monomeric sulfonatorhodium(I) complexes $[Rh\{\eta^2\text{-}O_2S(O)R\}(PPr^i_3)_2]$ **3**–**7** in excellent yield. An alternative route for the preparation of **4** (R = *p*-tolyl) and **5** (R = CF_3) is based on the reaction of PPr^i_3 with the dinuclear compounds $[\{Rh(C_8H_{14})_2[\mu\text{-}O_2S(O)R]\}_2]$, which were obtained either from $[\{Rh(C_8H_{14})_2(\mu\text{-}Cl)\}_2]$ **8** or $[\{Rh(C_8H_{14})_2(\mu\text{-}OH)\}_2]$ **9** as starting materials. Compounds **3**–**7** react smoothly with hydrogen by oxidative addition to give the dihydridorhodium(III) complexes $[RhH_2\{\eta^2\text{-}O_2S(O)R\}(PPr^i_3)_2]$. Moreover, on treatment of **3**–**6** with CO and C_2H_4 the chelating bond of the sulfonate ligand is partially opened and the carbonyl and ethene complexes *trans*-$[Rh\{\eta^1\text{-}OS(O)_2R\}(L)(PPr^i_3)_2]$ (L = CO or C_2H_4) are formed. The bis(stibine)-rhodium(I) derivative *trans*-$[Rh\{\eta^1\text{-}OS(O)_2CF_3\}(C_2H_4)(SbPr^i_3)_2]$ was obtained from $[\{Rh(C_2H_4)_2[\mu\text{-}O_2S(O)CF_3]\}_2]$ and $SbPr^i_3$. Reaction of the compounds $[Rh\{\eta^2\text{-}O_2S(O)CF_3\}(olefin)(PPr^i_3)]$ (olefin = C_8H_{14} or C_2H_4) with benzene led to the displacement of the sulfonate ligand and to the formation of the half-sandwich-type complexes $[Rh\{\eta^6\text{-}C_6H_6\}(olefin)(PPr^i_3)][CF_3SO_3]$ containing a rather labile benzene–rhodium bond. The preparation of the vinylidene complex *trans*-$[Rh\{\eta^1\text{-}OS(O)C_6H_4Me\text{-}p\}(=C=CHPh)(PPr^i_3)_2]$ is also described and the crystal and molecular structures of three compounds have been determined. The four-co-ordinate sulfonato complexes **3**–**6** are active catalysts in the C–C coupling reaction of ethene and diphenyldiazomethane. Besides the three isomeric 1 : 1 adducts of C_2H_4 and CPh_2, quite unexpectedly also the 2 : 1 adduct 3,3-diphenylpent-1-ene is formed.

One of the most noteworthy discoveries, which we made in recent years, was that in the presence of catalytic amounts of chlororhodium(I) complexes such as $[\{RhCl(PPr^i_3)_2\}_2]$ or $[\{RhCl(C_2H_4)_2\}_2]$, ethene and diphenyldiazomethane react to give almost selectively 1,1-diphenylprop-1-ene $Ph_2C{=}CHMe$.[1] This trisubstituted olefin is *formally* built up by the coupling of two carbene fragments **:**CPh_2 and **:**CHMe, of which the latter is generated from the isomeric ethene. It was previously known that dinuclear rhodium(II) compounds such as $[Rh_2(\mu\text{-}O_2CMe)_4]$ and derivatives thereof are active catalysts for the synthesis of cyclopropanes from olefins and diazoalkanes,[2] but the formation of $Ph_2C{=}CHMe$ from Ph_2CN_2 and C_2H_4 was without precedent. Following our initial studies, we also found that, if the acetylacetonato complex $[Rh(acac)(C_2H_4)_2]$ was used instead of $[\{RhCl(C_2H_4)_2\}_2]$ as the catalyst, 1,1-diphenylcyclopropane and not the isomeric 1,1-diphenylprop-1-ene was formed from ethene and diphenyldiazomethane. In contrast, the hexafluoroacetylacetonato derivative $[Rh(acac\text{-}F_6)(C_2H_4)_2]$ behaves similarly to the chloro complex $[\{RhCl(C_2H_4)_2\}_2]$ and with C_2H_4–Ph_2CN_2 generates catalytically (although with low turnover numbers) 1,1-diphenylprop-1-ene.[3,4]

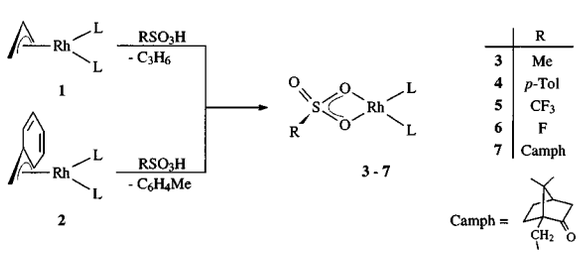
It was this apparent influence of the anionic ligand of the rhodium(I) complexes on both the reactivity and selectivity of the C–C coupling reaction that prompted us to prepare a series of compounds of the general composition $[Rh\{\eta^2\text{-}O_2S(O)R\}(PPr^i_3)_2]$. The main reason why we chose the sulfonate derivatives was that the low nucleophilicity of the RSO_3^- anions makes this ligand an excellent leaving group, and we assumed that this could be an important aspect for the catalytic activity. Moreover, the sulfonate ligand may adopt either a bridging, a η^1- or a η^2-bonding mode upon co-ordination to a metal centre as was recently reported for carboxylato rhodium(I) compounds of a similar type.[5,6]

The present paper describes the preparation of mono- and di-nuclear sulfonatorhodium(I) complexes, the reactivity of these species toward H_2, CO, C_2H_4, phenylacetylene and benzene, and the use of the bis(phosphine) complexes $[Rh\{\eta^2\text{-}O_2S(O)R\}(PPr^i_3)_2]$ as catalysts for the reaction of ethene and diphenyldiazomethane. Some preliminary results of these studies have been communicated.[7]

Results and discussion

Preparation of mono- and di-nuclear sulfonate complexes

The most convenient synthetic routes leading to the mononuclear sulfonatorhodium(I) compounds **3**–**7** are shown in Scheme 1. The reactions of the starting materials **1** and **2** with



Scheme 1 L = PPr^i_3.

sulfonic acids were carried out in diethyl ether at −78 °C and gave propene and toluene, respectively, as by-products. Similarly, Stuhl and Muetterties[8] prepared the sulfonatomanganese(I) derivative $[Mn\{\eta^2\text{-}O_2S(O)CF_3\}(CO)_2\{P(OPr^i)_3\}_2]$ by protonation of $[Mn(\eta^3\text{-}C_3H_5)(CO)_2\{P(OPr^i)_3\}_2]$ with CF_3SO_3H. The rhodium complexes **3**–**7** are red or violet air-sensitive solids which have been characterized by elemental analysis and spectroscopic techniques. While the IR spectra of

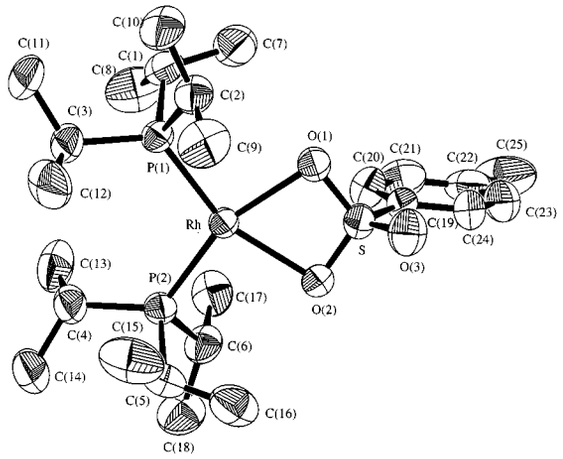


Fig. 1 An ORTEP plot of complex **4**.

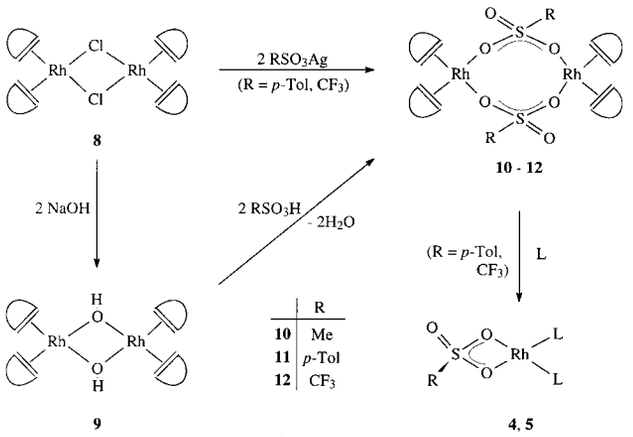
Table 1 Selected bond lengths (Å) and angles (°) for complex **4**

Rh–O(1)	2.217(2)	S–O(1)	1.476(2)
Rh–O(2)	2.227(2)	S–O(2)	1.475(2)
Rh–P(1)	2.206(1)	S–O(3)	1.429(2)
Rh–P(2)	2.218(1)	S–C(19)	1.761(3)
P(1)–Rh–P(2)	106.31(3)	Rh–O(2)–S	94.5(1)
P(1)–Rh–O(1)	93.85(6)	O(1)–S–O(2)	106.3(1)
P(1)–Rh–O(2)	157.86(6)	O(1)–S–O(3)	114.8(1)
P(2)–Rh–O(1)	159.79(6)	O(2)–S–O(3)	114.4(2)
P(2)–Rh–O(2)	95.70(6)	O(1)–S–C(19)	107.7(1)
O(1)–Rh–O(2)	64.21(7)	O(2)–S–C(19)	105.9(1)
Rh–O(1)–S	94.8(1)	O(3)–S–C(19)	107.2(2)

the related carboxylato compounds $[Rh(\eta^2\text{-}O_2CR)(PPr^i_3)_2]$ clearly support the chelate structure,[5,6] the IR data of **3**–**7** are less informative and do not distinguish between a η^1- and η^2-bonding mode of the sulfonato unit.[9] As far as compounds **3**–**6** are concerned, the *cis* disposition of the two phosphine ligands is indicated by the appearance of one signal for the CH_3 protons of the isopropyl groups in the ^{1}H NMR spectrum which due to P–H and H–H coupling is split into a doublet of doublets in the case of **3**, **5** and **6**. For **7**, which contains a chiral substituent at the sulfur atom, two doublets of doublets are observed. The ^{31}P NMR spectra of **3**–**7** display one doublet, the Rh–P coupling of which (210–220 Hz) is also consistent with a *cis* disposition of the PPr^i_3 ligands.[5,10]

To confirm the structural proposal for the complexes **3**–**7**, a single-crystal X-ray diffraction study of **4** was carried out. The ORTEP[11] plot (Fig. 1) reveals that the ligand sphere around the metal centre is distorted square planar with the two phosphorus and the two oxygen atoms O(1) and O(2) lying exactly in the same plane as rhodium. The symmetrical arrangement of the ligands is illustrated by almost identical Rh–P and Rh–O distances (see Table 1), the latter [Rh–O(1) and Rh–O(2)] being about 0.05 Å longer than in the analogous acetato compound $[Rh(\eta^2\text{-}O_2CMe)(PPr^i_3)_2]$. However, the bite angle O–Rh–O in **4** [64.21(7)°] and in $[Rh(\eta^2\text{-}O_2CMe)(PPr^i_3)_2]$ [60.2(1)°] is quite similar which could be due to the steric requirements of the bulky phosphine groups. The angle O(1)–S–O(2) [106.3(1)°] is only slightly smaller than would be anticipated for an ideal tetrahedral geometry.

An alternative synthetic pathway to compounds **4** and **5** is outlined in Scheme 2. Treatment of the well known cyclooctene complex **8** with 2 equivalents of RSO_3Ag (R = *p*-Tol or CF_3) in CH_2Cl_2 or CH_2Cl_2–Et_2O led to a displacement of the bridging chlorides by *p*-toluene- or trifluoromethane-sulfonates and gave compounds **11** and **12** as yellow solids in excellent yield. Instead of **8**, the corresponding dimeric μ-hydroxo complex **9** could also be used as starting material for the preparation

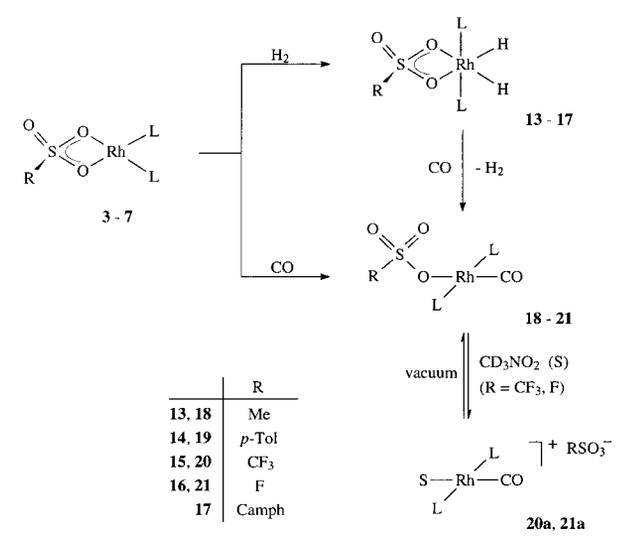


Scheme 2 $\bigcirc$ = C_8H_{14}, L = PPr^i_3.

of **10** and **11**. It reacted with 2 equivalents of $MeSO_3H$ or *p*-$MeC_6H_4SO_3H\cdot H_2O$ in CH_2Cl_2 to afford the μ-sulfonato derivatives almost quantitatively. Compound **9** was prepared by reaction of **8** with an excess of NaOH in a two-phase system of C_6H_6–water following the procedure described by Alper and coworkers[12] for the synthesis of $[\{Rh(PPh_3)_2(\mu\text{-}OH)\}_2]$. Along a similar route, the related triisopropylphosphine complex $[\{Rh(PPr^i_3)_2(\mu\text{-}OH)\}_2]$ was prepared in our laboratory and characterized by crystal structure analysis.[13] The μ-sulfonato compounds **10**–**12** are yellow or orange-yellow, only moderately air-sensitive solids which are soluble in CH_2Cl_2, thf or ether and in the case of **12** even in saturated hydrocarbons. The reactions of **11** and **12** with triisopropylphosphine in ether at −78 °C proceed rather quickly and afford **4** and **5** in 75–90% yield.

Addition reactions of η^2-sulfonato and μ-sulfonato rhodium(I) complexes

The chelate complexes **3**–**7** are quite labile and react smoothly at room temperature with H_2 as well as with CO and C_2H_4. On treatment with hydrogen, the dihydridorhodium(III) compounds **13**–**17** (Scheme 3) are obtained as white, nearly



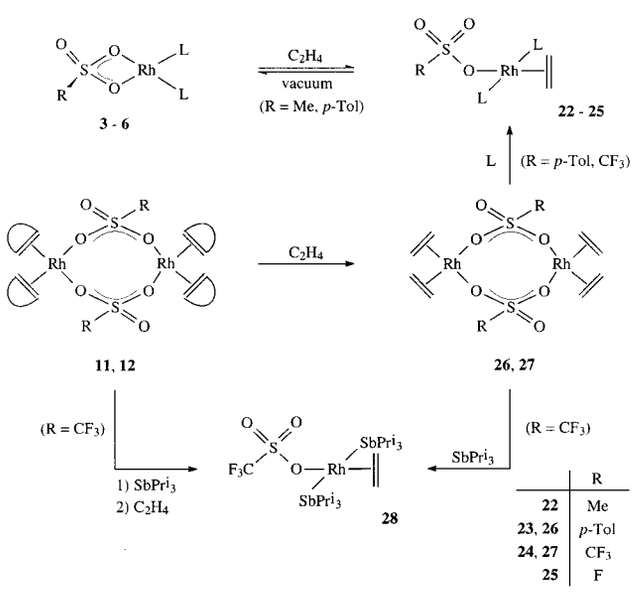
Scheme 3 L = PPr^i_3.

air-stable solids in excellent yield. The hydrido complexes are soluble in most organic solvents and can be stored under H_2 at −78 °C for weeks. *In vacuo* they slowly lose hydrogen and regenerate the starting materials **3**–**7**. The ^{31}P NMR spectra of **13**–**17** display at room temperature only one resonance (doublet in ^{31}P-{^{1}H} and doublet of triplets in off-resonance) with a ^{103}Rh–^{31}P coupling which is typical for *trans* disposed triisopropylphosphine ligands.[14] In the ^{1}H NMR spectra there

is also only one set of signals at δ −25.3 to −25.8 for the hydride ligands. Since for a rigid six-co-ordinate structure as shown in Scheme 3 two stereoisomers should exist, we assume that at 25 °C these isomers rapidly interconvert. If the ^{31}P NMR spectra are measured in CD_2Cl_2 at −90 °C or in [$^2H_8$]toluene at −80 °C, a slight broadening of the single resonance is observed indicating that even under these conditions the interconversion of the two isomers is very fast on the NMR timescale. The same seems to be true in the case of the four-co-ordinate complex **7** for which the NMR data equally suggest an effective C_2 symmetry. It should be mentioned that compound **4** catalyses the hydrogenation of phenylactylene to styrene and we assume that the dihydrido derivative **14** is involved in this process.[15]

Like **13**–**17**, the carbonyl complexes **18**–**21** are formed almost quantitatively by passing a slow stream of CO through a solution of **3**–**6** in hexane at room temperature. As far as the properties of **18**–**21** are concerned, a special feature is that while **18** and **19** are soluble in benzene or ether, the related species **20** and **21** are not. Conductivity measurements in nitromethane indicate that in this solvent the neutral compounds **20** and **21** are in equilibrium with the ionic species **20a** and **21a** (see Scheme 3). This can be understood by the general behaviour of $CF_3SO_3^-$ and FSO_3^- as good leaving groups. Owing to these results we assume that the NMR data measured for the carbonyl derivatives of the trifluoromethanesulfonato and the fluorosulfato rhodium complexes in nitromethane correspond to **20a** and **21a** and not to **20** and **21**, respectively.

Treatment of complexes **3**–**6** with C_2H_4 led to the formation of **22**–**25** the structure of which is probably quite similar to that of the carbonyl compounds **18**–**21** (see Scheme 4). Since the



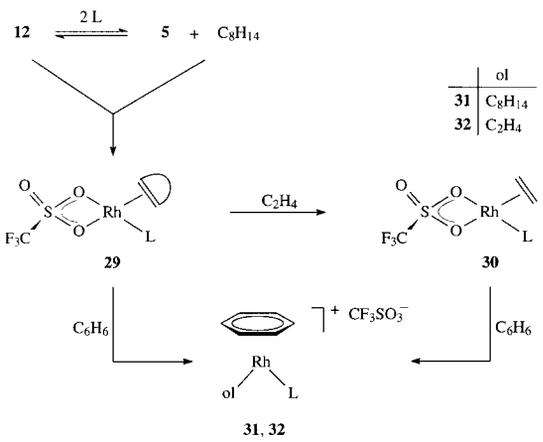
Scheme 4 L = PPr^i_3.

ethene complexes in analogy to the dihydrido derivatives are also unstable *in vacuo*, undergoing loss of C_2H_4, the NMR spectra of **22**–**25** were recorded in C_6D_6 which was saturated with ethene. The mass spectrum of **23** confirmed that the compound is monomeric in the solid state.

The ethene complexes **23** and **24** are not only formed from **4** and **5** but also from the sulfonato-bridged compounds **11** and **12** as starting materials. In the initial step the cyclooctene ligands of **11** and **12** are displaced by ethene to afford the corresponding dinuclear intermediates **26** and **27** both of which were isolated as yellow solids in excellent yield. While compound **26** is stable (and thus could be characterized by elemental analysis), the triflato derivative **27** is rather labile and decomposes rapidly in solution. We note that Aresta *et al.*[16] reported the preparation of monomeric [$Rh(O_3SCF_3)(C_2H_4)_2$] from [{$RhCl(C_2H_4)_2$}$_2$] and CF_3SO_3Ag which was found to be unstable under nitrogen and even under ethene. In contrast, the mass spectrum of **27** revealed that this compound (obtained from **12**) is a dimer and not a monomer in the solid state. Treatment of **26** and **27** with triisopropylphosphine led both to bridge cleavage and partial displacement of ethene to give the complexes **23** and **24** almost quantitatively.

The dinuclear triflato derivative **12** reacts with triisopropylstibine in pentane even at −40 °C yielding a labile species that presumably contains both $SbPr^i_3$ and cyclooctene as ligands.[17] Treatment of this intermediate with ethene affords compound **28** which was isolated as an analytically pure solid in 86% yield. The same product is also obtained from **27** and an equimolar amount of $SbPr^i_3$. We would like to point out that, recently, we described the synthesis of the corresponding chlorobis(stibine) complex *trans*-[$RhCl(C_2H_4)(SbPr^i_3)_2$] which is an excellent starting material for the preparation of a whole series of carbene rhodium(I) derivatives.[18,19]

The mixed cyclooctene–triisopropylphosphine rhodium(I) complex **29** containing a chelating triflate ligand is accessible from compound **12** and 2 equivalents of PPr^i_3 (Scheme 5).



Scheme 5 L = PPr^i_3.

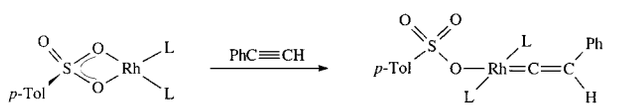
If this reaction is monitored at room temperature a change from orange to violet-brown initially occurs which is smoothly reversed after *ca.* 2 h. The ^{31}P NMR measurements revealed that in the first stage of the process the bis(phosphine) complex **5** is formed which in the presence of unchanged starting material **12** (and cyclooctene) affords the mixed olefin–phosphine derivative **29**. The same product is obtained from **12** and **5** in the molar ratio of 1:2 in pentane. Treatment of **29** with C_2H_4 led to the formation of the ethene–phosphine complex **30** which was isolated in *ca.* 70% yield as an analytically pure yellow solid. The ^{1}H NMR spectrum of **30** in CD_2Cl_2 at room temperature displays a broad singlet at δ 2.75 for the C_2H_4 protons indicating that under these conditions rotation of the olefinic ligand around the Rh–C_2H_4 bond is only slightly hindered. In the ^{13}C NMR spectrum of **30** the resonance for the C_2H_4 carbon atoms appears at δ 43.7 as a doublet with a ^{103}Rh–^{13}C coupling constant of 15.3 Hz.

The molecular structure of compound **29** was determined by X-ray crystallography. There are two independent molecules **A** and **B** in the unit cell, of which **A** is shown in Fig. 2. As the ORTEP plot reveals, the configuration around rhodium is slightly distorted square planar and therefore to some extent analogous to that of the tosylate complex **4**. However, the bond angle between phosphorus, rhodium and the centre of the C=C double bond for **29** (molecule **A**) is 97.15° (94.59° for **B**) and thus somewhat smaller than the bond angle P(1)–Rh–P(2) in compound **4**. The atoms S, O(1), O(2), Rh, P and the centre of the C=C bond lie almost in the same plane, the dihedral angle between the planes [O(1), S, O(2)] and [O(1), Rh, O(2)] for molecule **A** being 11.1(1)° and for molecule **B** 10.7(1)°. The corresponding dihedral angles between [O(1), Rh, O(2)] and (P,

Rh, centre of C=C) are 7.9(1)° for **A** and 8.0(1)° for **B**, respectively. While the Rh–O bond lengths in **4** are nearly identical, those in **29** are not (see Table 2); due to the different ligands (C_8H_{14} and PPr^i_3) in *trans* position they differ by *ca.* 0.13 Å. In contrast, the distances Rh–P(1) and Rh–P(2) in **4** and Rh–P in **29** are almost the same.

Dissolving either compound **29** or **30** in benzene leads to the displacement of the triflate ligand and to the formation of the cationic half-sandwich-type complexes **31** and **32** in virtually quantitative yield. Both **31** and **32** are yellow, only moderately air-sensitive solids which have been characterized by elemental analysis, IR, NMR and (in the case of **31**) FAB mass spectroscopy. In solution in the absence of benzene they are quite labile and regenerate the starting materials **29** and **30**, respectively. Despite this lability, a crystal structure analysis of **31** could be carried out, and the result of this study is summarized in Fig. 3 and Table 3. Similar to compound **29**, there are two independent molecules **A** and **B** in the unit cell which differ in the conformation of the cyclooctene ligand. The bond length Rh–P as well as the distances Rh–C(30) and Rh–C(31) are somewhat longer than in the square-planar complex **29** which could be due to the cationic nature and the closed-shell electron configuration of the half-sandwich-type molecule. The angle between P, Rh and the centre of the C=C bond in **31** is 92.69° for molecule **A** and 93.27° for molecule **B**, respectively. The distances between rhodium and the carbon atoms of the benzene ligand lie between 2.313(3) and 2.361(4) Å for **A** and between 2.296(4) and 2.365(4) Å for **B**, and this range is typical also for other arenerhodium(I) compounds.[20]

The reactivity of complex **4** as a representative of four-co-ordinate bis(triisopropylphosphine)rhodium(I) sulfonato compounds toward a terminal alkyne such as phenylacetylene is illustrated in Scheme 6. In toluene solution at room temperature a smooth reaction between **4** and PhC≡CH takes place which gives the vinylidene complex **33** as a violet crystalline solid in 91% isolated yield. The most typical spectroscopic



4 **33**

Scheme 6 L = PPr^i_3.

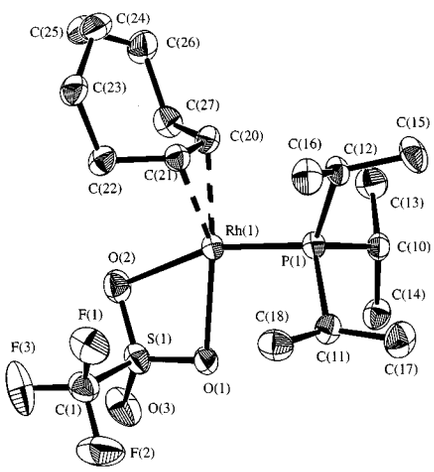


Fig. 2 An ORTEP plot of complex **29**.

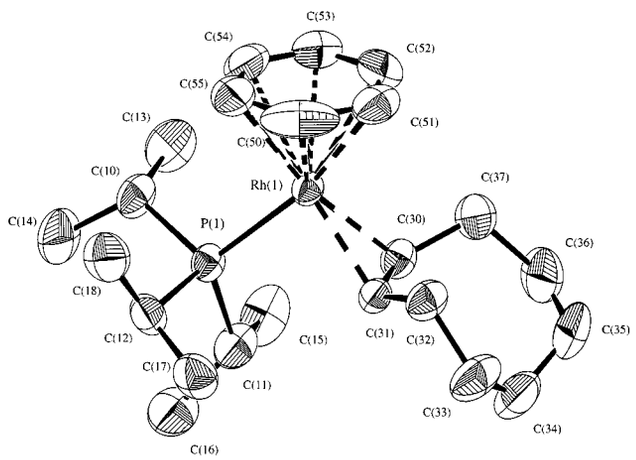


Fig. 3 An ORTEP plot of the cation of complex **31**.

Table 2 Selected bond lengths (Å) and angles (°) for complex **29** (there are two independent molecules **A** and **B** in the unit cell)

	A	**B**		**A**	**B**
Rh–P	2.192(1)	2.194(1)	C(20)–C(21)	1.413(5)	1.404(5)
Rh–O(1)	2.219(3)	2.205(3)	S–O(1)	1.477(3)	1.471(3)
Rh–O(2)	2.351(2)	2.339(2)	S–O(2)	1.458(3)	1.456(3)
Rh–C(20)	2.091(4)	2.091(4)	S–O(3)	1.422(3)	1.424(3)
Rh–C(21)	2.074(4)	2.073(4)	S–C(1)	1.820(5)	1.820(4)
P–Rh–O(1)	98.41(7)	97.64(7)	O(1)–Rh–O(2)	63.02(9)	63.00(9)
P–Rh–O(2)	160.55(7)	160.16(7)	O(1)–S–O(2)	109.1(2)	108.6(2)
P–Rh–C(20)	94.9(1)	95.3(1)	O(1)–S–O(3)	116.5(2)	116.5(2)
P–Rh–C(21)	96.9(1)	96.3(1)	O(2)–S–O(3)	117.3(2)	117.6(2)
Rh–O(1)–S	95.8(1)	96.2(1)	O(1)–S–C(1)	104.0(2)	103.9(2)
Rh–O(2)–S	90.9(1)	91.1(1)	O(2)–S–C(1)	103.6(2)	103.9(2)

Table 3 Selected bond lengths (Å) and angles (°) for cationic complex **31** (there are two independent molecules **A** and **B** in the unit cell)

	A	**B**		**A**	**B**
Rh–P	2.294(1)	2.290(1)	Rh–C(52)	2.338(4)	2.324(3)
Rh–C(30)	2.141(3)	2.141(3)	Rh–C(53)	2.361(4)	2.365(4)
Rh–C(31)	2.138(3)	2.143(3)	Rh–C(54)	2.320(3)	2.362(4)
Rh–C(50)	2.330(3)	2.332(4)	Rh–C(55)	2.328(3)	2.296(4)
Rh–C(51)	2.313(3)	2.346(4)	C(30)–C(31)	1.403(4)	1.396(5)
P–Rh–C(30)	94.43(9)	93.92(9)	Rh–C(31)–C(30)	71.0(2)	70.9(2)
P–Rh–C(31)	90.43(8)	91.35(9)	C(30)–C(31)–C(32)	122.8(3)	124.8(3)
Rh–C(30)–C(31)	70.7(2)	71.0(2)	C(31)–C(30)–C(37)	123.0(3)	122.6(3)

Table 4 Catalytic cycles and composition of the mixture of products obtained from ethene and diphenyldiazomethane in methylcyclohexane according to Scheme 7

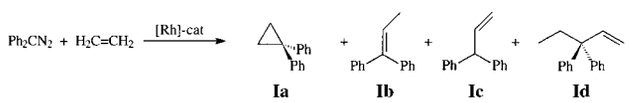
		Product (%)			
[Rh]-cat	Cycles[a]	**Ia**	**Ib**	**Ic**	**Id**
3	24	2	86	4	8
4	11	2	87	2	9
5[b]	47	7	37	1	55
6[b]	37	5	29	0	66

[a] Cycle = mmol product/mmol catalyst. [b] In toluene.

features of **33** are the doublet of triplets at δ 1.51 for the =C*H*Ph proton in the ^{1}H NMR and the low-field resonance (also a doublet of triplets) at δ 301.1 for the α-carbon atom of the vinylidene unit in the ^{13}C NMR spectrum. These data are in good agreement with those of the corresponding chloro and acetato derivatives *trans*-[RhX(=C=CHPh)(PPr^i_3)$_2$] (X = Cl or $MeCO_2$) which have recently been prepared in our laboratory.[5,14]

Catalytic studies

In the same way as the dimeric chloro derivative [{RhCl(PPr^i_3)$_2$}$_2$], the new *monomeric* sulfonatorhodium(I) complexes **3**–**6** are also active catalysts in the C–C coupling reaction of ethene and diphenyldiazomethane. The most noteworthy feature is that the selectivity depends significantly on the substituent R of the sulfonate ligand. While in the reaction with either **3** or **4** as catalyst 1,1-diphenylprop-1-ene **Ib** (Scheme 7)



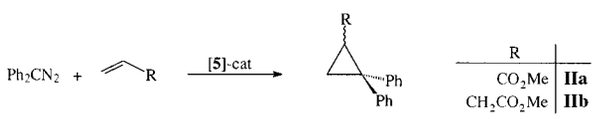
Scheme 7

is the major product, in the presence of **5** and **6** 3,3-diphenylpent-1-ene **Id** is the dominating species (see Table 4). This 2 : 1 adduct of C_2H_4 and Ph_2CN_2 is formed in only minor quantities if **3**, **4** or the chlororhodium(I) dimer [{RhCl(PPr^i_3)$_2$}$_2$] is used as catalyst. In all C–C coupling reactions of ethene and diphenyldiazomethane, which are catalysed by bis(triisopropylphosphine)rhodium(I) compounds of the general type [{RhX(PPr^i_3)$_2$}$_n$] (n = 1 or 2), only trace amounts of 3,3-diphenylprop-1-ene **Ic** (which is generated selectively in the stoichiometric reaction of *trans*-[{RhCl(=CPh_2)($SbPr^i_3$)$_2$}$_2$] with ethene)[19] are obtained.

The mechanism for the formation of compound **Id** is not clear as yet. We assume that in analogy to the reaction of ethene and diphenyldiazomethane with [{RhCl(PPr^i_3)$_2$}$_2$] as catalyst,[1] in the initial stage of the catalytic process both C_2H_4 and CPh_2 are co-ordinated to rhodium, and that subsequently a rhodacyclobutane is formed. The next step could be either an insertion of ethene into one of the Rh–C bonds of the metallacyclobutane to give a six-membered RhC_5 cycle or a β-H shift to generate a RhH(CH_2CHCPh_2) intermediate. Addition of C_2H_4 to this intermediate followed by the insertion of the olefin into the Rh–H bond could afford a Rh(C_2H_5)(CH_2CHCPh_2) species which by metal-mediated C–C coupling yields **Id**. If the catalytic cycle involves the above mentioned RhC_5 ring system, then upon a β-H shift a RhH($CH_2CH_2CPh_2CH$=CH_2) intermediate could be formed which by reductive elimination generates **Id**. Precedence for the postulated insertion of ethene into the metal–carbon bond of a metallacyclobutane can be found in the work of Binger and Schuchardt,[21] who argue that the palladium(0)-catalysed cycloaddition of methylenecyclopropane and olefins presumably proceeds through a PdC_5 intermediate. We cannot rule out that one of the initial steps in the formation of **Id** (following the co-ordination of ethene to the metal centre) is an intramolecular C–H activation to give a RhH(CH=CH_2) intermediate which could then react with a second molecule of C_2H_4 to afford a Rh(C_2H_5)(CH=CH_2) species. However, the reason why we consider this mechanistic route as less likely is that we failed to observe the generation of a hydrido(vinyl)rhodium(III) compound on photolysis of **24** or **25**, respectively.

With regard to the conversion of two ethene molecules into two σ-bonded ligands in the co-ordination sphere of a d^8 metal centre it should be pointed out that Carmona and co-workers[22] recently showed that the iridium complex [IrTp*(C_2H_4)$_2$] [Tp* = tris(3,5-dimethylpyrazol-1-yl)hydroborate] rearranges thermally or photochemically to the isomer [IrTp*(H)(CH=CH_2)(C_2H_4)]. On treatment with acetonitrile this compound yields the ethyl–vinyl derivative [IrTp*(CH=CH_2)(C_2H_5)-(NCMe)], which in the presence of catalytic amounts of water undergoes an intramolecular coupling of the vinyl and acetonitrile ligands to afford a five-membered iridapyrrole ring.[23] With [RhTp*(C_2H_4)$_2$] as the starting material a related conversion into [RhTp*(CH=CH_2)(C_2H_5)(L)] (L = NCMe or py) takes place.[24]

In order to find out whether olefins other than ethene would also react with diphenyldiazomethane by C–C coupling, the reaction of Ph_2CN_2 with methyl acrylate and CH_2=$CHCH_2$-CO_2Me in the presence of the triflato complex **5** as the catalyst was also investigated. As is shown in Scheme 8, only cyclo-



Scheme 8

propanation occurs and the corresponding esters **IIa** and **IIb** are formed. Whereas for **IIa** the number of cycles is 55, the yield of **IIb** is rather low and could not be increased by using an excess of the diazoalkane.

Current work in our laboratory is aimed at the further exploration of the use of the sulfonatorhodium(I) as well as the related carboxylatorhodium(I) complexes in other types of C–C coupling reactions among which the cyclooligomerization of butadiene is of particular interest.[7]

Experimental

All reactions were carried out under an atmosphere of argon by Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials **1**, **2**[5] and **8**[25] were prepared by published methods. The NMR spectra were recorded on Bruker AC 200 and AMX 400 instruments and the IR spectra on a Perkin-Elmer 1420 spectrometer. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; vt, virtual triplet; N = ^3J(PH) + ^5J(PH) or ^1J(PC) + ^3J(PC), respectively. Conductivity data (Λ) in nitromethane.

Preparations

[Rh{η^2-O_2S(O)Me}(PPr^i_3)$_2$] 3. (a) A solution of compound **1** (0.219 g, 0.47 mmol) in ether (15 cm^3) was treated dropwise with $MeSO_3H$ (0.031 cm^3, 0.48 mmol) at −78 °C. After the addition a white suspension was formed which was warmed to room temperature to give an orange-red solution. The solution was stirred for 1 h, the solvent removed *in vacuo* and the residue extracted twice with pentane (40 cm^3). The combined extracts were brought to dryness *in vacuo*, the remaining red solid was washed with small portions of pentane (−20 °C) and dried: yield 0.153 g (63%).

(b) A solution of compound **2** (0.241 g, 0.47 mmol) in ether (15 cm^3) was treated dropwise with $MeSO_3H$ (0.031 cm^3, 0.48 mmol) at −78 °C. A red solution formed which was warmed to

room temperature. After it was stirred for 30 min, the solvent was removed *in vacuo* and the residue washed twice with small portions of pentane (−20 °C) to give a red solid: yield 0.130 g (54%); mp 110 °C (decomp.) (Found: C, 43.71; H, 8.94; S, 5.88. $C_{19}H_{45}O_3P_2RhS$ requires C, 44.02; H, 8.75; S, 6.18%). IR (KBr): $\nu(O_3S)$ 1201, 1190 and 1049 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.68 (3 H, s, SCH_3), 1.80 (6 H, m, $CHCH_3$) and 1.23 [36 H, dd, J(PH) 13.0, J(HH) 7.1 Hz, $CHCH_3$]; δ_C (50.3 MHz) 40.0 (s, SCH_3), 25.5 (vt, N 21.3 Hz, $CHCH_3$) and 20.3 (s, $CHCH_3$); δ_P (81.0 MHz) 70.2 [d, J(RhP) 212.2 Hz].

[Rh{η²-$O_2S(O)C_6H_4Me$-*p*}(PPr^i_3)$_2$] 4. A solution of compound **1** (0.116 g, 0.25 mmol) in toluene (2 cm^3) was treated with *p*-$MeC_6H_4SO_3H$ (0.048 g, 0.25 mmol) and stirred for 1 h at room temperature. A change from yellow to red occurred. The solvent was removed *in vacuo*, the residue extracted with acetone (20 cm^3) and the extract concentrated to *ca.* 2 cm^3 *in vacuo*. Red crystals precipitated which were filtered off, washed twice with small portions of acetone (0 °C) and dried: yield 0.131 g (88%); mp 80 °C (decomp.) (Found: C, 50.62; H, 8.63. $C_{25}H_{49}O_3P_2RhS$ requires C, 50.50; H, 8.31%). NMR (C_6D_6): δ_H (200 MHz) 8.34, 6.86 (4 H, both m, C_6H_4), 1.90 (3 H, s, $C_6H_4CH_3$), 1.83 (6 H, m, $CHCH_3$) and 1.24 (36 H, m, $CHCH_3$); δ_C (50.3 MHz) 141.3 [d, J(RhC) 15.8 Hz, *ipso*-C of C_6H_4], 129.5, 129.0, 127.2 (all s, C_6H_4), 25.7 (vt, N 21.0 Hz, $CHCH_3$), 21.1 (s, $C_6H_4CH_3$) and 20.4 (s, $CHCH_3$); δ_P (81.0 MHz) 70.3 [d, J(RhP) 212.5 Hz].

Alternatively, compound **4** was prepared on treatment of a solution of **11** (0.040 g, 0.04 mmol) in ether (4 cm^3) with PPr^i_3 (0.031 cm^3, 0.16 mmol) at −78 °C. After the solution was stirred for 5 min the solvent was removed *in vacuo*. The oily residue was dissolved in pentane (1.5 cm^3) and the solution stored for 12 h at −78 °C to give a red solid: yield 0.066 g (72%).

[Rh{η²-$O_2S(O)CF_3$}(PPr^i_3)$_2$] 5. This compound was prepared as described for **3**, using either **1** (0.088 g, 0.19 mmol) and CF_3SO_3H (0.017 cm^3, 0.19 mmol) or **2** (0.160 g, 0.31 mmol) and CF_3SO_3H (0.028 cm^3, 0.32 mmol) as starting materials. Violet solid: yield 0.102 g (95%) from **1** and 0.103 g (58%) from **2**; mp 80 °C (decomp.) (Found: C, 39.60; H, 7.48; S, 5.36. $C_{19}H_{42}F_3O_3P_2RhS$ requires C, 39.87; H, 7.40; S, 5.60%). MS (70 eV): *m*/*z* 573 (M^+). IR (KBr): $\nu(O_3S)$ 1263 and 1030, $\nu(CF_3)$ 1253 and 1161 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 1.70 (6 H, m, $CHCH_3$) and 1.13 [36 H, dd, J(PH) 13.5, J(HH) 7.3 Hz, $CHCH_3$]; δ_C (50.3 MHz) 121.4 [q, J(FC) 316.9 Hz, CF_3], 25.7 (vt, N 23.1 Hz, $CHCH_3$) and 20.0 (s, $CHCH_3$); δ_F (188.2 MHz) −77.1 (s); δ_P (81.0 MHz) 69.9 [d, J(RhP) 219.5 Hz].

Alternatively, compound **5** was prepared on treatment of a solution of **12** (0.038 g, 0.04 mmol) in ether (4 cm^3) with PPr^i_3 (0.031 cm^3, 0.16 mmol) at −78 °C. After the solution was stirred for 5 min the solvent was removed *in vacuo*, the violet residue washed twice with 2 cm^3 portions of pentane (−40 °C) and dried: yield 0.041 g (89%).

[Rh{η²-$O_2S(O)F$}(PPr^i_3)$_2$] 6. This compound was prepared as described for **3**, using either **1** (0.154 g, 0.33 mmol) and FSO_3H (0.019 cm^3, 0.33 mmol) or **2** (0.251 g, 0.49 mmol) and FSO_3H (0.028 cm^3, 0.49 mmol) as starting materials. Violet solid: yield 0.152 g (88%) from **1** and 0.256 g (81%) from **2**; mp 64 °C (decomp.) (Found: C, 41.02; H, 8.02; S, 6.62. $C_{18}H_{42}FO_3P_2RhS$ requires C, 41.38; H, 8.10; S, 6.14%). MS (70 eV): *m*/*z* 522 (M^+). IR (KBr): $\nu(O_3S)$ 1312, 1240 and 1062, ν(SF) 775 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 1.69 (6 H, m, $CHCH_3$) and 1.14 [36 H, dd, J(PH) 13.4, J(HH) 7.2 Hz, $CHCH_3$]; δ_C (50.3 MHz) 25.8 (vt, N 22.2 Hz, $CHCH_3$) and 20.1 (s, $CHCH_3$); δ_F (188.2 MHz) 40.7 (s); δ_P (81.0 MHz) 70.5 [d, J(RhP) 220.1 Hz].

[Rh{η²-$O_2S(O)C_{10}H_{15}O$}(PPr^i_3)$_2$] 7. This compound was prepared as described for **4**, using **1** (0.116 g, 0.25 mmol) and (1*S*)-camphor-10-sulfonic acid (0.058 g, 0.25 mmol) as starting materials. Red solid: yield 0.134 g (82%); mp 45 °C (decomp.) (Found: C, 51.12; H, 8.67; S, 4.64. $C_{28}H_{57}O_4P_2RhS$ requires C, 51.37; H, 8.78; S, 4.90%). NMR (C_6D_6): δ_H (400 MHz) 4.14, 3.18 [2 H, both d, J(HH) 15.1, CH_2SO_3], 2.10–1.45 (7 H, br m, 7 H of $C_{10}H_{15}$), 1.85 (6 H, m, $CHCH_3$), 1.28 [18 H, dd, J(PH) 12.8, J(HH) 5.6, $CHCH_3$], 1.27 [18 H, dd, J(PH) 12.8, J(HH) 5.5 Hz, $CHCH_3$], 1.15, 0.59 (6 H, both s, CH_3 of $C_{10}H_{15}$); δ_P (162.0 MHz) 69.8 [d, J(RhP) 213.0 Hz].

[{Rh(C_8H_{14})$_2$}$_2$(μ-OH)$_2$] 9. A two phase system of complex **8** (0.315 g, 0.44 mmol) in C_6H_6 (15 cm^3), NaOH (0.12 g, 3.0 mmol) and [$PhCH_2NEt_3$]Cl (0.050 g) in water (10 cm^3) was stirred at room temperature for 4 h. The C_6H_6 layer was decanted and the aqueous phase extracted with 10 cm^3 of C_6H_6. The combined benzene fractions were dried over Na_2SO_4 and then filtered. From the filtrate the solvent was removed *in vacuo* to give a yellow solid. The solid was washed three times with 5 cm^3 portions of pentane and dried *in vacuo*. Pale yellow solid: yield 0.265 g (89%); mp 70 °C (decomp.) (Found: C, 56.66; H, 8.29. $C_{32}H_{58}O_2Rh_2$ requires C, 56.47; H, 8.58%). IR (KBr): ν(OH) 3676 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.44 (8 H, m, =CH of C_8H_{14}), 2.48–1.13 (48 H, br m, CH_2 of C_8H_{14}) and −1.23 (2 H, br s, OH); δ_C 72.49 (br m, =CH of C_8H_{14}), 30.24, 28.64, 28.59 (all s, CH_2 of C_8H_{14}).

[{Rh(C_8H_{14})$_2$}$_2${μ-$O_2S(O)Me$}$_2$] 10. A solution of complex **9** (0.455 g, 0.67 mmol) in CH_2Cl_2 (30 cm^3) was treated at room temperature with $MeSO_3H$ (0.087 cm^3, 1.34 mmol). The mixture was stirred for 2 h and then the solvent was removed *in vacuo*. The resulting yellow solid was washed three times with 5 cm^3 portions of Et_2O and dried: yield 0.416 g (74%); mp 124 °C (decomp.) (Found: C, 48.49; H, 7.27; S, 7.87. $C_{34}H_{62}O_6Rh_2S_2$ requires C, 48.80; H, 7.47; S, 7.66%). IR (KBr): $\nu(O_3S)$ 1276, 1207, 1070 and 1012, $\nu(CF_3)$ 1260 and 1170 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.47 (6 H, s, CH_3), 2.14 (16 H, m, =CH and CH_2 of C_8H_{14}), 1.78, 1.52, 1.38 (40 H, all br m, CH_2 of C_8H_{14}); δ_C (50.3 MHz) 73.6 [d, J(RhC) 15.7 Hz, =CH of C_8H_{14}], 39.4 (s, CH_3), 29.7, 28.2, 26.6 (all s, CH_2 of C_8H_{14}).

[{Rh(C_8H_{14})$_2$}$_2${μ-$O_2S(O)C_6H_4Me$-*p*}$_2$] 11. A suspension of compound **8** (0.520 g, 0.72 mmol) and *p*-$MeC_6H_4SO_3Ag$ (0.420 g, 1.45 mmol) in CH_2Cl_2 (35 cm^3) was stirred for 2 d at room temperature. A white solid precipitated and a change of the solution from orange-red to orange-yellow occurred. The solvent was removed *in vacuo*, the residue extracted with ether (40 cm^3) and the extract brought to dryness *in vacuo*. A yellow solid was isolated which was repeatedly washed with 5 cm^3 portions of pentane and dried: yield 0.570 g (80%); mp 168 °C (decomp.) (Found: C, 55.81; H, 6.95; Rh, 20.62; S, 6.54. $C_{46}H_{70}O_6Rh_2S_2$ requires C, 55.87; H, 7.13; Rh, 20.81; S, 6.48%). IR (CH_2Cl_2): $\nu(O_3S)$ 1190, 1115, 1068 and 1022 cm^{-1}. NMR ($CDCl_3$): δ_H (200 MHz) 8.03 (4 H, m, *ortho*-H of SC_6H_4), 7.27 (4 H, m, *meta*-H of SC_6H_4), 2.56 (8 H, m, =CH of C_8H_{14}), 2.39 (6 H, s, $C_6H_4CH_3$), 2.32–1.17 (48 H, br m, CH_2 of C_8H_{14}); δ_C (50.3 MHz) 142.6 (s, *ipso*-C of SC_6H_4), 137.4, 129.1, 126.4 (all s, C_6H_4), 73.9 [d, J(RhC) 15.7 Hz, =CH of C_8H_{14}], 29.2, 28.0, 26.1 (all s, CH_2 of C_8H_{14}) and 21.4 (s, $C_6H_4CH_3$).

Alternatively, compound **11** was prepared on treatment of a solution of **9** (0.352 g, 0.519 mmol) in CH_2Cl_2 (30 cm^3) with *p*-$MeC_6H_4SO_3H{\cdot}H_2O$ (0.247 g, 1.30 mmol). The mixture was stirred for 4 h at room temperature, the solvent removed *in vacuo* and the residue extracted twice with 15 cm^3 portions of C_6H_6. The benzene layers were dried over Na_2SO_4 and filtered. Removal of the solvent *in vacuo* afforded a yellow solid which was washed three times with 5 cm^3 portions of ether and dried: yield 0.375 g (72%).

[{Rh(C_8H_{14})$_2$}$_2${μ-$O_2S(O)CF_3$}$_2$] 12. A solution of compound **8** (0.340 g, 0.47 mmol) in CH_2Cl_2–ether (2:1, 25 cm^3) was treated with a solution of CF_3SO_3Ag (0.234 g, 0.91 mmol) in

ether (15 cm^3) and stirred for 2 h at room temperature. A white solid precipitated and a gradual change of the solution from orange-yellow to yellow occurred. The solvent was removed *in vacuo* and the residue extracted with hexane (40 cm^3). The extract was slowly concentrated *in vacuo* until an orange-yellow solid began to precipitate. The solution was then stored for 24 h at −78 °C, the precipitate separated from the mother-liquor, washed twice with 3 cm^3 portions of pentane (−40 °C) and dried: yield 0.318 g (71%); mp 73 °C (decomp.) (Found: C, 42.86; H, 5.95; S, 6.64. $C_{34}H_{56}F_6O_6Rh_2S_2$ requires C, 43.22; H, 5.97; S, 6.79%). IR (CH_2Cl_2): ν(CF) 1245, $\nu(O_3S)$ 1195, 1135, 1045 and 1005 cm^{-1}. NMR ($CDCl_3$ for ^1H and ^{13}C): δ_H (200 MHz) 2.63 (8 H, m, =CH of C_8H_{14}), 2.24–1.32 (48 H, br m, CH_2 of C_8H_{14}); δ_C (50.3 MHz) 119.3 [q, J(FC) 318.8 Hz, CF_3], 74.1 [d, J(RhC) 15.7 Hz, =CH of C_8H_{14}], 29.1, 27.4, 26.1 (all s, CH_2 of C_8H_{14}); δ_F (188.3 MHz, CD_2Cl_2) −77.1 (s).

[$RhH_2\{\eta^2$-$O_2S(O)Me\}(PPr^i_3)_2$] 13. A slow stream of hydrogen was passed for *ca.* 5 s through a solution of complex **3** (0.064 g, 0.12 mmol) in ether (8 cm^3). A rapid change from red to almost white occurred. After the solution was stirred for 15 min at room temperature the solvent was removed *in vacuo*. The remaining white solid was washed with small quantities of pentane (−78 °C) and quickly dried: yield 0.057 g (88%): mp 41 °C (decomp.) (Found: C, 43.60; H, 9.18; S, 5.99. $C_{19}H_{47}O_3P_2RhS$ requires C, 43.84; H, 9.10; S, 6.16%). IR (KBr): ν(RhH) 2165 and 2135, $\nu(O_3S)$ 1207, 1193 and 1043 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.60 (3 H, s, SMe), 2.18 (6 H, m, C*H*CH_3), 1.25 [36 H, dvt, N 14.3, J(HH) 7.1, CHC*H*$_3$] and −25.30 [2 H, dt, J(RhH) 29.1, J(PH) 14.8 Hz, RhH]; δ_C (100.6 MHz) 39.5 (s, SCH_3), 25.7 [vt, N 21.4 Hz, *C*HCH_3] and 20.4 (s, CH*C*H_3); δ_P (162.0 MHz) 60.9 [d, dt in off-resonance, J(RhP) 115.0 Hz].

[$RhH_2\{\eta^2$-$O_2S(O)C_6H_4Me$-*p*$\}(PPr^i_3)_2$] 14. This compound was prepared as described for **13**, using **4** (0.059 g, 0.10 mmol) in CH_2Cl_2 (5 cm^3) as starting material. After the white solid was washed with small quantities of pentane (−78 °C) it was dried *in vacuo* for not more than 5 min: yield 0.057 g (95%); mp 112 °C (decomp.) (Found: C, 49.90; H, 8.79; S, 5.30. $C_{25}H_{51}O_3P_2RhS$ requires C, 50.33; H, 8.62; S, 5.37%). NMR (C_6D_6): δ_H (200 MHz) 8.01–6.77 (4 H, m, C_6H_4), 2.14 (6 H, m, C*H*CH_3), 1.89 (3 H, s, $C_6H_4CH_3$), 1.18 [36 H, dvt, N 13.1, J(HH) 7.3, CHC*H*$_3$] and −25.26 [2 H, dt, J(RhH) 30.5, J(PH) 14.5 Hz, RhH]; δ_P (81.0 MHz) 61.8 [d, dt in off-resonance, J(RhP) 114.8 Hz].

[$RhH_2\{\eta^2$-$O_2S(O)CF_3\}(PPr^i_3)_2$] 15. A slow stream of hydrogen was passed for *ca.* 5 s through a solution of complex **5** (0.117 g, 0.21 mmol) in ether (5 cm^3). A rapid change from violet to pale yellow occurred. After the solution was stirred for 15 min at room temperature the solvent was removed *in vacuo*. The residue was extracted with pentane (30 cm^3), the extract filtered and the filtrate brought to dryness *in vacuo*. The remaining white solid was washed with small quantities of pentane (−78 °C) and quickly dried: yield 0.085 g (68%); mp 52 °C (decomp.) (Found: C, 39.84; H, 7.64; S, 5.17. $C_{19}H_{44}F_3O_3P_2RhS$ requires C, 39.71; H, 7.72; S, 5.57%). MS (70 eV): m/z 574.8 (M^+). IR (KBr): ν(RhH) 2194 and 2135, $\nu(CF_3)$ 1258 and 1171, $\nu(O_3S)$ 1270 and 1032 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.16 (6 H, m, C*H*CH_3), 1.08 [36 H, dvt, N 13.9, J(HH) 6.9, CHC*H*$_3$] and −25.80 [2 H, dt, J(RhH) 33.5, J(PH) 14.5 Hz, RhH]; δ_C (50.3 MHz) 121.0 [q, J(CF) 319.5 Hz, CF_3], 24.9 (vt, N 21.9 Hz, *C*HCH_3) and 20.2 (s, CH*C*H_3); δ_F (188.2 MHz) −77.3 (s); δ_P (81.0 MHz) 60.9 [d, dt in off-resonance, J(RhP) 114.1 Hz].

[$RhH_2\{\eta^2$-$O_2S(O)F\}(PPr^i_3)_2$] 16. This compound was prepared as described for **13**, using **6** (0.136 g, 0.26 mmol) in ether (3 cm^3) as starting material. White solid: yield 0.105 g (77%); mp 45 °C (decomp.) (Found: C, 40.98; H, 8.42; S, 6.11. $C_{18}H_{44}FO_3P_2RhS$ requires C, 41.22; H, 8.46; S, 6.11%). IR (KBr): ν(RhH) 2180 and 2158, $\nu(O_3S)$ 1285, 1252 and 1078, ν(SF) 740 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.07 (6 H, m, C*H*CH_3), 1.10 [36 H, dvt, N 13.7, J(HH) 6.7, CHC*H*$_3$] and −25.60 [2 H, dt, J(RhH) 33.0, J(PH) 14.8 Hz, RhH]; δ_C (50.3 MHz) 25.2 (vt, N 22.1 Hz, *C*HCH_3) and 20.2 (s, CH*C*H_3); δ_F (188.2 MHz) 41.6 (s, SF); δ_P (81.0 MHz) 60.6 [d, dt in off-resonance, J(RhP) 114.5 Hz].

[$RhH_2\{\eta^2$-$O_2S(O)C_{10}H_{15}O\}(PPr^i_3)_2$] 17. This compound was prepared as described for **13**, using **7** (0.059 g, 0.09 mmol) in CH_2Cl_2 (5 cm^3) as starting material. White solid: yield 0.054 g (92%); mp 42 °C (decomp.) (Found: C, 50.70; H, 9.05; S, 4.47. $C_{28}H_{59}O_3P_2RhS$ requires C, 51.21; H, 9.06; S, 4.88%). IR (KBr): ν(RhH) 2120 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 3.86, 3.04 [2 H, both d, J(HH) 16.0 Hz, CH_2SO_3], 2.32 (6 H, m, C*H*CH_3), 2.07–1.40 (7 H, m, 7 H of $C_{10}H_{15}$), 1.25 [36 H, dvt, N 13.1, J(HH) 5.8, CHC*H*$_3$], 1.21, 0.57 (6 H, both s, CH_3 of $C_{10}H_{15}$) and −25.31 [2 H, dt, J(RhH) 30.5, J(PH) 14.4 Hz, RhH]; δ_P (81.0 MHz) 61.4 [d, dt in off-resonance, J(RhP) 114.8 Hz].

***trans*-[$Rh\{\eta^1$-$OS(O)_2Me\}(CO)(PPr^i_3)_2$] 18.** A slow stream of CO was passed for *ca.* 5 s through a solution of complex **3** (0.067 g, 0.13 mmol) in hexane (2 cm^3). The resulting pale yellow suspension was stirred for 15 min at room temperature. After the solvent was removed *in vacuo*, the remaining white solid was washed three times with pentane (2 cm^3) and dried: yield 0.063 g (88%); mp 122 °C (decomp.) (Found: C, 43.69; H, 8.05; S, 5.90. $C_{20}H_{45}O_4P_2RhS$ requires C, 43.94; H, 8.30; S, 5.87%). MS (70 eV): m/z 546 (M^+). IR (KBr): ν(CO) 1964, $\nu(O_3S)$ 1265 and 1033 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.61 (3 H, s, SCH_3), 2.54 (6 H, m, C*H*CH_3) and 1.25 [36 H, dvt, N 14.1, J(HH) 7.2 Hz, CHC*H*$_3$]; δ_C (50.3 MHz) 191.1 [dt, J(RhC) 76.7, J(PC) 16.4 Hz, CO], 40.1 (s, SMe), 24.9 (vt, N 20.3 Hz, *C*HCH_3) and 20.3 (s, CH*C*H_3); δ_P (81.0 MHz) 51.4 [d, J(RhP) 119.2 Hz].

Alternatively, compound **18** was prepared on treatment of a solution of **13** (0.068 g, 0.13 mmol) in hexane (2 cm^3). The resulting suspension was worked up as described above. White solid: yield 0.060 g (85%).

***trans*-[$Rh\{\eta^1$-$OS(O)_2C_6H_4Me$-*p*$\}(CO)(PPr^i_3)_2$] 19.** This compound was prepared as described for **18**, using **4** (0.071 g, 0.12 mmol) as starting material. Light yellow solid: yield 0.066 g (89%); mp 117 °C (decomp.) (Found: C, 49.69; H, 8.00; S, 5.18. $C_{26}H_{49}O_4P_2RhS$ requires C, 50.16; H, 7.93; S, 5.15%). IR (KBr): ν(CO) 1945 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 7.99–6.83 (4 H, m, C_6H_4), 2.46 (6 H, m, C*H*CH_3), 1.95 (3 H, s, $C_6H_4CH_3$) and 1.23 [36 H, dvt, N 13.9, J(HH) 7.3 Hz, CHC*H*$_3$]; δ_P (81.0 MHz) 51.7 [d, J(RhP) 119.1 Hz].

***trans*-[$Rh\{\eta^1$-$OS(O)_2CF_3\}(CO)(PPr^i_3)_2$] 20.** This compound was prepared as described for **18**, using either **5** (0.089 g, 0.16 mmol) or **15** (0.090 g, 0.16 mmol) as starting material. Light yellow solid: yield 0.087 g (93%) from **5** or 0.083 g (90%) from **15**; mp 112 °C (decomp.) (Found: C, 39.69; H, 7.11; S, 5.39. $C_{20}H_{42}F_3O_4P_2RhS$ requires C, 40.01; H, 7.05; S, 5.34%). Λ 35 Ω^{-1} cm^2 mol^{-1}. MS (70 eV): m/z 600 (M^+). IR (KBr): ν(CO) 1964, $\nu(O_3S)$ 1273 and 1042, $\nu(CF_3)$ 1253 and 1171 cm^{-1}. NMR (CD_3NO_2): δ_H (400 MHz) 2.69 (6 H, m, C*H*CH_3) and 1.44 [36 H, dvt, N 15.6, J(HH) 7.2 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 191.6 [dt, J(RhC) 65.4, J(PC) 13.6, CO], 122.4 [q, J(CF) 320.9 Hz, CF_3], 28.7 (vt, N 24.8 Hz, *C*HCH_3) and 20.6 (s, CH*C*H_3); δ_F (376.4 MHz) −78.4 (s); δ_P (162.0 MHz) 57.4 [d, J(RhP) 100.4 Hz]. Since the NMR spectra were measured in CD_3NO_2 the signals probably correspond to the ionic species **20a** (see Scheme 3).

***trans*-[$Rh\{\eta^1$-$OS(O)_2F\}(CO)(PPr^i_3)_2$] 21.** This compound was prepared as described for **18**, using either **6** (0.108 g, 0.21 mmol)

or **16** (0.116 g, 0.21 mmol) as starting material. Pale yellow solid: yield 0.110 g (95%) from **6** or 0.105 g (91%) from **16**; mp 121 °C (decomp.) (Found: C, 41.21; H, 7.36; S, 5.91. $C_{19}H_{42}FO_4PRhS$ requires C, 41.46; H, 7.69; S, 5.82%). Λ 31 Ω^{-1} cm^2 mol^{-1}. MS (70 eV): *m*/*z* 550 (M^+). IR (KBr): ν(CO) 1946, $\nu(O_3S)$ 1286 and 1063, ν(SF) 700 cm^{-1}. NMR (CD_3NO_2): δ_H (400 MHz) 2.68 (6 H, m, C*H*CH_3) and 1.44 [36 H, dvt, *N* 15.2, *J*(HH) 7.2 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 191.6 [dt, *J*(RhC) 65.4, *J*(PC) 13.6 Hz, CO], 28.7 (vt, *N* 24.8 Hz, *C*HCH$_3$) and 20.5 (s, CH*C*H$_3$); δ_F (376.4 MHz) 36.5 (s); δ_P (162.0 MHz) 57.4 [d, *J*(RhP) 100.3 Hz]. Since the NMR spectra were measured in CD_3NO_2 the signals probably correspond to the ionic species **21a** (see Scheme 3).

***trans*-[Rh{η^1-OS(O)$_2$Me}(C$_2$H$_4$)(PPr$^i_3$)$_2$] 22.** A slow stream of ethene was passed through a suspension of complex **3** (0.102 g, 0.20 mmol) in pentane (5 cm^3). After the reaction mixture was stirred for 30 min at room temperature it was concentrated to *ca.* 1 cm^3 by passing a stream of ethene through the solution. After the solution was stored for 12 h at −78 °C a yellow microcrystalline solid precipitated which was separated from the mother-liquor, washed twice with small portions of pentane (−78 °C) and dried with a stream of ethene: yield 0.104 g (97%); mp 74 °C (decomp.) (Found: C, 45.71; H, 9.15; S, 5.56. $C_{21}H_{49}O_3P_2RhS$ requires C, 46.14; H, 9.04; S, 5.85%). IR (KBr): $\nu(O_3S)$ 1252, 1162 and 1039 cm^{-1}. NMR (C_6D_6, saturated with C_2H_4): δ_H (400 MHz) 2.70 (3 H, s, SCH_3), 2.47 (4 H, m, C_2H_4), 2.26 (6 H, m, C*H*CH$_3$) and 1.21 [36 H, *N* 13.2, *J*(HH) 6.4 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 40.2 (s, SCH_3), 33.3 [d, *J*(RhC) 16.5 Hz, C_2H_4], 22.8 (vt, *N* 16.3 Hz, *C*HCH$_3$) and 20.5 (s, CH*C*H$_3$); δ_P (162.0 MHz) 35.2 [d, *J*(RhP) 119.1 Hz].

***trans*-[Rh{η^1-OS(O)$_2$C$_6$H$_4$Me-*p*}(C$_2$H$_4$)(PPr$^i_3$)$_2$] 23.** This compound was prepared as described for **22**, using **4** (0.075 g, 0.13 mmol) as starting material. Yellow microcrystalline solid: yield 0.067 g (85%); mp 58 °C (decomp.) (Found: C, 52.14; H, 8.86; S, 5.16. $C_{27}H_{53}O_3P_2RhS$ requires C, 52.09; H, 8.58; S, 5.15%). MS (70 eV): *m*/*z* 622 (M^+). IR (KBr): $\nu(O_3S)$ 1259 and 1032 cm^{-1}. NMR (C_6D_6, saturated with C_2H_4): δ_H (200 MHz) 8.02, 6.85 (4 H, both m, C_6H_4), 2.51 (4 H, m, C_2H_4), 2.17 (6 H, m, C*H*CH$_3$), 1.99 (3 H, s, C$_6$H$_4$C*H*$_3$) and 1.20 [36 H, *N* 13.2, *J*(HH) 6.6 Hz, CHC*H*$_3$]; δ_C (50.3 MHz) 144.2 (s, *ipso*-C of SC_6H_4), 139.3, 128.3, 127.0 (all s, C_6H_4), 33.2 [d, *J*(RhC) 16.6 Hz, C_2H_4], 22.9 (vt, *N* 16.6 Hz, *C*HCH$_3$), 21.1 (s, C$_6$H$_4$*C*H$_3$) and 20.4 (s, CH*C*H$_3$); δ_P (162.0 MHz) 35.6 [d, *J*(RhP) 119.2 Hz].

Alternatively, compound **23** was prepared on treatment of a suspension of **26** (0.028 g, 0.04 mmol) in C_6D_6 (0.5 cm^3) with PPr$^i_3$ (0.030 cm^3, 0.16 mmol). The ^{1}H NMR spectrum displayed only the signals of **23** and of free ethene.

***trans*-[Rh{η^1-OS(O)$_2$CF$_3$}(C$_2$H$_4$)(PPr$^i_3$)$_2$] 24.** This compound was prepared as described for **22**, using **5** (0.077 g, 0.14 mmol) as starting material. Yellow microcrystalline solid: yield 0.065 g (80%); mp 76 °C (decomp.) (Found: C, 41.90; H, 7.53; S, 5.27. $C_{21}H_{46}F_3O_3P_2RhS$ requires C, 41.99; H, 7.72; S, 5.33%). IR (KBr): $\nu(O_3S)$ 1305 and 1026, $\nu(CF_3)$ 1230 and 1165 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.54 (4 H, m, C_2H_4), 2.13 (6 H, m, C*H*CH$_3$) and 1.15 [36 H, *N* 13.2, *J*(HH) 6.9 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 120.8 [q, *J*(FC) 321.0 Hz, CF_3], 33.7 (br s, C_2H_4), 22.9 (vt, *N* 17.3 Hz, *C*HCH$_3$) and 20.3 (s, CH*C*H$_3$); δ_F (188.2 MHz) −76.7 (s); δ_P (188.2 MHz) 34.6 [d, *J*(RhP) 117.5 Hz].

Alternatively, compound **23** was prepared on treatment of a suspension of **27** (0.040 g, 0.06 mmol) in C_4D_8O (0.5 cm^3) at −20 °C with PPr$^i_3$ (0.045 cm^3, 0.24 mmol). The ^{1}H NMR spectrum displayed only the signals of **24** and of free ethene.

***trans*-[Rh{η^1-OS(O)$_2$F}(C$_2$H$_4$)(PPr$^i_3$)$_2$] 25.** This compound was prepared as described for **22**, using **6** (0.098 g, 0.19 mmol) as starting material. Yellow microcrystalline solid: yield 0.102 g (98%); mp 52 °C (decomp.) (Found: C, 43.22; H, 8.23; S, 5.74. $C_{20}H_{46}FO_3P_2RhS$ requires C, 43.64; H, 8.42; S, 5.82%). MS (70 eV): *m*/*z* 550 (M^+). IR (KBr): $\nu(O_3S)$ 1332, 1231 and 1083, ν(SF) 739 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 2.38 [4 H, dd, *J*(RhH) 6.7, *J*(PH) 4.0, C_2H_4], 2.01 (6 H, m, C*H*CH$_3$) and 1.15 [36 H, *N* 13.1, *J*(HH) 6.8 Hz, CHC*H*$_3$]; δ_C (50.3 MHz) 34.8 [d, *J*(RhC) 17.7 Hz, C_2H_4], 21.6 (vt, *N* 17.6 Hz, *C*HCH$_3$) and 19.6 (s, CH*C*H$_3$); δ_F (188.2 MHz) 42.8 (s); δ_P (81.0 MHz) 35.8 [d, *J*(RhP) 117.3 Hz].

[{Rh(C$_2$H$_4$)$_2$}$_2${μ-O$_2$S(O)C$_6$H$_4$Me-*p*}$_2$] 26. A slow stream of ethene was passed through a suspension of complex **11** (0.110 g, 0.11 mmol) in hexane (4 cm^3) for 1 min at room temperature. After the reaction mixture was stirred for 5 min it was stored until the pale yellow solid and the solution were separated. The mother-liquor was decanted, the pale yellow solid repeatedly washed with 5 cm^3 portions of pentane and dried: yield 0.062 g (85%); mp 134 °C (decomp.) (Found: C, 39.75; H, 4.62; S, 9.28. $C_{22}H_{30}O_6Rh_2S_2$ requires C, 40.01; H, 4.58; S, 9.71%). IR (CH_2Cl_2): $\nu(O_3S)$ 1195, 1132, 1048 and 1015 cm^{-1}. NMR ($CDCl_3$, 60 °C): δ_H (200 MHz) 7.82 (4 H, m, *ortho*-H of SC_6H_4), 6.80 (4 H, m, *meta*-H of SC_6H_4), 3.00 (12 H, s, C_2H_4) and 1.93 (6 H, s, C$_6$H$_4$C*H*$_3$); δ_C (50.3 MHz) 141.5 (s, *ipso*-C of SC_6H_4), 140.7, 129.1, 126.7 (all s, C_6H_4), 60.6 (br m, C_2H_4) and 21.0 (s, C$_6$H$_4$*C*H$_3$).

[{Rh(C$_2$H$_4$)$_2$}$_2${μ-O$_2$S(O)CF$_3$}$_2$] 27. This compound was prepared as described for **26**, using **12** (0.080 g, 0.08 mmol) as starting material. Yellow solid: yield 0.040 g (76%); mp 131 °C (decomp.). MS (70 eV): *m*/*z* (%) 616 (0.4) [M^+], 5.88 (1.0) [$M^+ - C_2H_4$], 560 (2.3) [$M^+ - 2C_2H_4$], 532 (0.4) [$M^+ - 3C_2H_4$], 504 (2.8) [$M^+ - 4C_2H_4$], 252 (12.3) [$RhO_3SCF_3^+$] and 103 (33) [Rh^+].

***trans*-[Rh{η^1-OS(O)$_2$CF$_3$}(C$_2$H$_4$)(SbPr$^i_3$)$_2$] 28.** A suspension of complex **12** (0.122 g, 0.12 mmol) in pentane (5 cm^3) was treated at −40 °C with SbPr$^i_3$ (0.105 cm^3, 0.49 mmol). A red solution was formed which was stirred for 10 min at −40 °C. A slow stream of ethene was then passed through the solution (*ca.* 1 min) and a yellow solid precipitated. The mother-liquor was decanted, the solid washed three times with 2 cm^3 portions of pentane (−40 °C) and dried: yield 0.171 g (86%); mp 47 °C (decomp.) (Found: C, 40.35; H, 6.41; S, 3.98. $C_{27}H_{53}O_3RhSSb_2$ requires C, 40.33; H, 6.64; S, 3.99%). IR (C_6H_6): $\nu(O_3S)$ 1263, 1153 and 1105 cm^{-1}. NMR: δ_H (200 MHz, C_6D_6) 8.05, 6.88 (4 H, both m, C_6H_4), 3.59 (4 H, br s, C_2H_4), 2.11 (6 H, m, C*H*CH$_3$), 1.95 (3 H, s, C$_6$H$_4$C*H*$_3$) and 1.30 [36 H, d, *J*(HH) 7.0 Hz, CHC*H*$_3$]; δ_C (50.3 MHz, $CDCl_3$) 143.4 (br s, *ipso*-C of SC_6H_4), 139.6, 128.7, 126.8 (all s, C_6H_4), 29.5 (m, C_2H_4), 22.1 (s, CH*C*H$_3$) and 19.0 (br s, *C*HCH$_3$).

Alternatively, compound **28** was prepared on treatment of a suspension of **27** (0.098 g, 0.10 mmol) and SbPr$^i_3$ (0.098 cm^3, 0.40 mmol) in pentane (15 cm^3) at −40 °C. Yellow solid: yield 0.142 g (89%).

[Rh{η^2-O$_2$S(O)CF$_3$}(C$_8$H$_{14}$)(PPr$^i_3$)] 29. A solution of complex **12** (0.529 g, 0.56 mmol) in pentane (25 cm^3) was treated at 0 °C with PPr$^i_3$ (0.148 cm^3, 1.12 mmol) to give a violet-brown reaction mixture which was stirred for 2 h at room temperature. The resulting orange solution was concentrated to *ca.* 2 cm^2 *in vacuo* which led to the precipitation of an orange-red microcrystalline solid. The mother-liquor was decanted, the residue washed three times with 5 cm^3 portions of pentane (−78 °C) and dried *in vacuo*: yield 0.380 g (65%); mp 36 °C (decomp.) (Found: C, 41.78; H, 6.51; S, 6.01. $C_{18}H_{35}F_3O_3PRhS$ requires C, 41.38; H, 6.75; S, 6.14%). MS (70 eV): *m*/*z* 522 (M^+). IR (KBr): $\nu(O_3S)$ 1259, 1249 and 1021, $\nu(CF_3)$ 1244, 1179 and 1169 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 3.01 [2 H, m, *J*(HH) 9.8, =CH of C_8H_{14}], 2.13 [2 H, dd, *J*(HH) 12.3, 3.1, CH_2 of C_8H_{14}], 1.75

(3 H, m, C*H*CH_3), 1.55 (2 H, m, CH_2 of C_8H_{14}), 1.38 (8 H, br m, CH_2 of C_8H_{14}) and 1.23 [18 H, dd, *J*(PH) 13.9, *J*(HH) 7.2 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 120.0 [q, *J*(CF) 319.4, CF_3], 61.1 [d, *J*(RhC) 18.3, =CH of C_8H_{14}], 29.7, 28.5, 26.8 (all s, CH_2 of C_8H_{14}), 23.8 [d, *J*(PC) 26.4 Hz, *C*HCH$_3$] and 19.7 (s, CH*C*H$_3$); δ_F (376.4 MHz) −78.5 (s); δ_P (162 MHz) 78.7 [d, *J*(RhP) 212.8 Hz].

[Rh{η^2-O$_2$S(O)CF$_3$}(C$_2$H$_4$)(PPr$^i_3$)] 30. A solution of complex **29** (0.197 g, 0.38 mmol) in pentane (10 cm^3), prepared *in situ* from **12** (0.178 g, 0.19 mmol) and PPr$^i_3$ (0.074 cm^3, 0.38 mmol), was treated at room temperature for 10 s with a stream of ethene which afforded a yellow suspension. The solvent was decanted, the yellow microcrystalline residue washed three times with 5 cm^3 portions of pentane and dried *in vacuo*: yield 0.114 g (69%); mp 50 °C (decomp.) (Found: C, 32.54; H, 5.72; S, 7.05. $C_{12}H_{25}F_3O_3PRhS$ requires C, 32.74; H, 5.72; S, 7.28%). NMR (CD_2Cl_2): δ_H (400 MHz) 2.75 (4 H, br s, C_2H_4), 1.83 (3 H, m, C*H*CH$_3$) and 1.33 [18 H, *J*(PH) 13.8, *J*(HH) 7.0 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 119.0 [q, *J*(FC) 318.5, CF_3], 43.7 [d, *J*(RhC) 15.3, C_2H_4], 23.1 [d, *J*(PC) 25.8 Hz, *C*HCH$_3$] and 19.8 (s, CH*C*H$_3$); δ_F (376.4 MHz) −78.4 (s); δ_P (162 MHz) 69.5 [d, *J*(RhP) 189.7 Hz].

[Rh(η^6-C$_6$H$_6$)(C$_8$H$_{14}$)(PPr$^i_3$)][O$_3$SCF$_3$] 31. A solution of compound **29** (0.089 g, 0.17 mmol) in C_6H_6 (5 cm^3) was stirred for 12 h at room temperature. A yellow solution was formed, which was filtered and the filtrate concentrated to *ca.* 1 cm^3 *in vacuo*. Addition of pentane (5 cm^3) afforded a yellow suspension which was stored for 2 h. The solvent was then decanted, the yellow microcrystalline residue washed twice with 5 cm^3 portions of pentane and dried *in vacuo*: yield 0.093 g (92%); mp 67 °C (decomp.) (Found: C, 48.06; H, 6.90; Rh, 17.48; S, 5.15. $C_{24}H_{41}F_3O_3PRhS$ requires C, 47.99; H, 6.89; Rh, 17.15; S, 5.33%). MS-FAB: *m*/*z* (%) 451 (0.7) [M$^+$ − O_3SCF_3], 373 (1.0) [Rh(C_8H_{14})(PPr$^i_3$)]$^+$ and 263 (4.0) [Rh(PPr$^i_3$)]$^+$. IR (KBr): ν(O_3S) 1276 and 1059, ν(CF_3) 1183 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 6.70 (6 H, s, C_6H_6), 3.09 [2 H, d, *J*(RhH) 9.4, =CH of C_8H_{14}], 2.38 [2 H, dd, *J*(HH) 9.7, 3.0, CH_2 of C_8H_{14}], 1.87 (3 H, m, C*H*CH$_3$), 1.49 (2 H, m, CH_2 of C_8H_{14}), 1.39 (8 H, br m, CH_2 of C_8H_{14}) and 1.32 [18 H, dd, *J*(PH) 14.1, *J*(HH) 7.4 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 67.9 [d, *J*(RhC) 14.3 Hz, =CH of C_8H_{14}], 34.2, 32.4, 26.4 (all s, CH_2 of C_8H_{14}), 25.5 [d, *J*(PC) 23.8 Hz, *C*HCH$_3$] and 19.9 (s, CH*C*H$_3$); δ_F (376.4 MHz) −78.0 (s); δ_P (162 MHz) 63.7 [d, *J*(RhP) 182.4 Hz].

[Rh(η^6-C$_6$H$_6$)(C$_2$H$_4$)(PPr$^i_3$)][O$_3$SCF$_3$] 32. This compound was prepared as described for **31**, using **30** (0.264 g, 0.60 mmol) as starting material. Pale yellow solid: yield 0.281 g (90%); mp 82 °C (decomp.) (Found: C, 40.81; H, 5.85; S, 6.02. $C_{18}H_{31}F_3O_3PRhS$ requires C, 41.71; H, 6.03; S, 6.19%). IR (KBr): ν(O_3S) 1270 and 1028, ν(CF_3) 1156 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 6.77 (6 H, s, C_6H_6), 3.33, 2.23 (4 H, both m, C_2H_4), 1.84 (3 H, m, C*H*CH$_3$) and 1.20 [18 H, dd, *J*(PH) 14.1, *J*(HH) 7.0 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 121.2 [q, *J*(FC) 321.1 Hz, CF_3], 104.5 (br s, C_6H_6), 40.6 [d, *J*(RhC) 13.2, C_2H_4], 25.3 [d, *J*(PC) 24.4 Hz, *C*HCH$_3$] and 19.6 (s, CH*C*H$_3$); δ_F (376.4 MHz) −78.5 (s); δ_P (162 MHz) 65.8 [d, *J*(RhP) 176.3 Hz].

[Rh{η^1-OS(O$_2$)C$_6$H$_4$Me-*p*}(C=CHPh)(PPr$^i_3$)$_2$] 33. A solution of complex **4** (0.089 g, 0.15 mmol) in toluene (2 cm^3) was treated with phenylacetylene (0.017 cm^3, 0.15 mmol) and stirred for 6 h at room temperature. A smooth change from red to violet occurred. The solvent was removed, the residue extracted with ether (20 cm^3) and the extract brought to dryness *in vacuo*. The remaining solid was dissolved in acetone (2 cm^3) and the solution stored for 12 h at −78 °C. Violet crystals precipitated which were washed twice with 2 cm^3 portions of acetone (0 °C) and dried: yield 0.095 g (91%); mp 74 °C (decomp.) (Found: C, 56.61; H, 8.01; S, 4.53. $C_{33}H_{55}O_3P_2RhS$ requires C, 56.89; H, 7.96; S, 4.60%). MS (ES): *m*/*z* (%) 605 (2.7) [M$^+$ − $C_6H_4CH_3$]. NMR (C_6D_6): δ_H (200 MHz) 7.99–6.85 (9 H, m, C_6H_5 and C_6H_4), 2.61 (6 H, m, C*H*CH$_3$), 1.97 (3 H, s, $C_6H_4CH_3$), 1.51 [1 H, dt, *J*(RhH) 1.5, *J*(PH) 2.9, =C*H*Ph] and 1.24 [36 H, dvt, *N* 13.9, *J*(HH) 7.3 Hz, CHC*H*$_3$]; δ_C (100.6 MHz) 301.1 [dt, *J*(RhC) 61.0, *J*(PC) 17.3 Hz, Rh=C], 143.6, 139.7, 135.2, 128.6, 128.5, 126.7, 125.7, 125.5 (all s, C_6H_5 and C_6H_4), 112.2 [dt, *J*(RhC) 17.3, *J*(PC) 6.1, =*C*HPh], 24.1 [vt, *N* 19.6 Hz, *C*HCH$_3$], 21.1 (s, $C_6H_4CH_3$) and 20.3 (s, CH*C*H$_3$); δ_P (81.0 MHz) 44.8 [d, *J*(RhP) 136.6 Hz].

Catalytic studies

Reactions of Ph_2CN_2 and C_2H_4 with complexes 3–6 as catalysts. A solution of a complex (*ca.* 20 mg, *ca.* 0.04 mmol) in methylcyclohexane (6 cm^3) for **3**, **4** or toluene (6 cm^3) for **5**, **6** was treated dropwise at 40 °C with a 0.5 mol dm^{-3} solution of diphenyldiazomethane in methylcyclohexane while bubbling ethene through the solution. The catalytic reaction was finished when the violet colour of the diazoalkane solution did not disappear on further addition to the reaction mixture. The solvent was removed *in vacuo*, and the oily residue dissolved in 2–3 cm^3 of hexane. In order to destroy the excess of Ph_2CN_2 and separate the catalyst, the mixture was filtered through Al_2O_3 (neutral, activity grade III, height of column 3 cm). After evaporation of the solvent, an oil containing a mixture of **Ia**–**Id** was isolated from the eluate. The ratio of the products was determined by integration of characteristic signals in the ^{1}H NMR spectra and by GC-MS analysis. The results are summarized in Table 4.

Reaction of Ph_2CN_2 and methyl acrylate with complex 5 as catalyst. In an analogous manner to the catalytic reaction of Ph_2CN_2 and ethene, a solution of complex **5** (17 mg, 0.03 mmol) and methyl acrylate (2.6 cm^3, 3.0 mmol) in methylcyclohexane (6 cm^3) was treated dropwise at 40 °C with a 0.1 mol dm^{-3} solution of diphenyldiazomethane in toluene. After work-up, a clear oil was isolated and characterized by ^{1}H NMR data and GC-MS analysis as **IIa**: yield 390 mg (1.55 mmol). If instead of methyl acrylate the corresponding ester CH_2=$CHCH_2CO_2Me$ was used as the substrate, a small quantity (11 mg, 0.04 mmol) of an off-white oil was isolated. It was characterized by ^{1}H NMR data and GC-MS analysis as **IIb**.

Crystallography

Single crystals of complex **4** were grown from acetone (8 °C), those of **29** from pentane (20 °C) and those of **31** from benzene (20 °C). Crystal data collection parameters are summarized in Table 5. Intensity data were corrected for Lorentz-polarization effects. Data reduction were performed for **4** and **31** with SDP[26] and for **29** with Stoe IPDS software. The structures were solved by direct methods (SHELXS 86).[27] For **29** and **31** two independent molecules (**A** and **B**) were found in the asymmetric units with different conformations of the cyclooctene ligand. In Figs. 1 and 2 only molecule **A** of **29** and **31**, respectively, is shown. Table 5 contains the crystallographic data of each whole asymmetric unit (molecule **A** and **B**), the chemical formula and the formula weight, however, belong to one molecule only. Atomic coordinates and anisotropic displacement parameters of the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 (SHELXL 93).[28] The positions of the hydrogen atoms [except of H(20), H(21), H(40) and H(41) in **29** and C(30), H(31), H(40) and H(41) in **31**] were calculated according to ideal geometry using the riding method.

CCDC reference number 186/1157.

See http://www.rsc.org/suppdata/dt/1998/3549/ for crystallographic files in .cif format.

Table 5 Crystal data for complexes **4**, **29** and **31**

	4	**29**	**31** [a]
Formula	$C_{25}H_{49}O_3P_2RhS$	$C_{18}H_{35}F_3O_3PRhS$	$C_{24}H_{41}F_3O_3PRhS$
M	594.55	522.40	600.51
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	10.498(4)	14.177(3)	14.042(4)
b/Å	14.104(3)	17.626(6)	15.347(4)
c/Å	20.276(7)	19.038(6)	15.532(2)
α/°	—	—	63.12(2)
β/°	92.89(2)	103.61(3)	73.03(2)
γ/°	—	—	70.98(2)
U/Å^3	2998(2)	4624(2)	2781(1)
T/K	293	173	293
Z	4	8	4
D_c/g cm^{-3}	1.317	1.501	1.434
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	0.761	0.928	0.782
No. reflections measured	4422	36543	9104
No. unique reflections (R_{int})	4156 (0.0127)	8695 (0.0746)	8703 (0.0096)
$R1$ [b]	0.0266	0.0334	0.0294
$wR2$ [c]	0.0717	0.0683	0.0751

[a] For complex **31** an extinction parameter was refined to $(5.98 \pm 0.23) \times 10^{-3}$. [b] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o > 2\sigma(F_o)$] for the number of observed reflections [$I > 2\sigma(I)$], respectively. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0377P)^2 + 1.1100P]$ (**4**), $[\sigma^2(F_o^2) + (0.0289P)^2 + 0.0000P]$ (**29**), $[\sigma^2(F_o^2) + (0.0347P)^2 + 2.5370P]$ (**31**), where $P = (F_o^2 + 2F_c^2)/3$; for all data reflections, respectively.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie for financial support, the latter in particular for Ph.D. grants to M. E. S. and M. M. We are also grateful to Mrs R. Schedl and Mr C. P. Kneis (DTA measurements and elemental analyses), to Dr G. Lange and Dr M. Herderich (mass spectra), to Degussa AG and BASF AG (chemicals), and to Dr J. Wolf for numerous valuable discussions.

References

1 J. Wolf, L. Brandt, A. Fries and H. Werner, *Angew. Chem.*, 1990, **102**, 584; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 510; H. Werner, *J. Organomet. Chem.*, 1994, **475**, 45.
2 A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot and P. Teyssié, *J. Org. Chem.*, 1980, **45**, 695; M. P. Doyle, *Acc. Chem. Res.*, 1986, **19**, 348; M. P. Doyle, W. R. Winchester, J. A. A. Hoorn, V. Lynch, S. H. Simonsen and R. Ghosh, *J. Am. Chem. Soc.*, 1993, **115**, 9968.
3 L. Brandt, Ph.D. Thesis, Universität Würzburg, 1991.
4 L. Brandt, A. Fries, N. Mahr, H. Werner and J. Wolf, *Selective Reactions of Metal-Activated Molecules*, eds. H. Werner, A. G. Griesbeck, W. Adam, G. Bringmann and W. Kiefer, Vieweg Verlag, Braunschweig, 1992, p. 171.
5 M. Schäfer, J. Wolf, H. Werner, *J. Chem. Soc., Chem. Commun.*, 1991, 1341; H. Werner, M. Schäfer, O. Nürnberg and J. Wolf, *Chem. Ber.*, 1994, **127**, 27; M. Schäfer, J. Wolf and H. Werner, *J. Organomet. Chem.*, 1994, **476**, 85.
6 H. Werner, S. Poelsma, M. E. Schneider, B. Windmüller and D. Barth, *Chem. Ber.*, 1996, **129**, 647.
7 M. E. Schneider and H. Werner, 10. International Symposium on Homogeneous Catalysis, Princeton, 1996.
8 L. S. Stuhl and E. L. Muetterties, *Inorg. Chem.*, 1978, **17**, 2148.
9 G. A. Lawrance, *Chem. Rev.*, 1986, **86**, 17.
10 K. Wang, G. P. Rosini, S. P. Nolan and A. S. Goldman, *J. Am. Chem. Soc.*, 1995, **117**, 5082.
11 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
12 V. V. Grushin, V. F. Kuznetsov, C. Bensimon and H. Alper, *Organometallics*, 1995, **14**, 3927.
13 O. Gevert, J. Wolf and H. Werner, *Organometallics*, 1996, **15**, 2806.
14 H. Werner, F. J. Garcia Alonso, H. Otto and J. Wolf, *Z. Naturforsch., Teil B*, 1988, **43**, 722; H. Werner and U. Brekau, *Z. Naturforsch., Teil B*, 1989, **44**, 1438; T. Rappert, O. Nürnberg, N. Mahr, J. Wolf and H. Werner, *Organometallics*, 1992, **11**, 4156.
15 U. Möhring, M. Schäfer, F. Kukla, M. Schlaf and H. Werner, *J. Mol. Catal. A*, 1995, **99**, 55.
16 M. Aresta, E. Quaranta and A. Albinati, *Organometallics*, 1993, **12**, 2032.
17 For a recent review on stibine transition-metal complexes see N. R. Champness and W. Levason, *Coord. Chem. Rev.*, 1994, **133**, 115.
18 P. Schwab, N. Mahr, J. Wolf and H. Werner, *Angew. Chem.*, 1993, **105**, 1498; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1480; H. Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert and J. Wolf, *Chem. Eur. J.*, 1997, **3**, 1375.
19 H. Werner, *J. Organomet. Chem.*, 1995, **500**, 331.
20 J. Halpern, D. P. Riley, A. S. C. Chan and J. J. Pluth, *J. Am. Chem. Soc.*, 1977, **99**, 8055; E. T. Singewald, C. S. Slone, C. L. Stern, C. A. Mirkin, G. P. A. Yap, L. M. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.*, 1997, **119**, 3048; M. Manger, Ph.D. Thesis, Universität Würzburg, 1997.
21 P. Binger and U. Schuchardt, *Angew. Chem.*, 1977, **89**, 254; *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 249; *Chem. Ber.*, 1981, **114**, 3313.
22 Y. Alvarado, O. Boutry, E. Gutiérrez, A. Monge, C. M. Nicasio, M. L. Poveda, P. J. Pérez, C. Ruíz, C. Bianchini and E. Carmona, *Chem. Eur. J.*, 1997, **3**, 860; P. J. Perez, M. L. Poveda and E. Carmona, *J. Chem. Soc., Chem. Commun.*, 1992, 8.
23 Y. Alvarado, P. J. Daff, P. J. Perez, M. L. Poveda, R. Sanchez-Delgado and E. Carmona, *Organometallics*, 1996, **15**, 2192.
24 P. J. Perez, M. L. Poveda and E. Carmona, *Angew. Chem.*, 1995, **107**, 242; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 231.
25 A. van der Ent and A. L. Onderdelinden, *Inorg. Synth.*, 1973, **14**, 92.
26 B. A. Frenz, The Enraf-Nonius CAD4 SDP, a real time system for concurrent X-ray data collection and structure determination, in *Computing in Crystallography*, Delft University Press, Delft, 1978, p. 64.
27 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
28 G. M. Sheldrick, SHELXL 93, A program for crystal structure refinement, University of Göttingen, 1993.

Paper 8/05900D