Cationic Ruthenium-Sulfine Complexes: Synthesis and Dynamic Behaviour [1]

Nikolai Kuhnert[a], Nicolai Burzlaff[b], Eberhard Dombrowski, and Wolfdieter A. Schenk

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany
[a] Current address: Department of Chemistry, University of Surrey, Guildford GU2 5XH, UK
[b] Current address: Fachbereich Chemie, Universität Konstanz,
Universitätsstraße 10, D-78457 Konstanz, Germany

Reprint requests to Prof. Dr. W. A. Schenk. Fax: +49-(0)931-8884605.
E-mail: wolfdieter.schenk@mail.uni-wuerzburg.de

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Ruthenium Complexes, Thioaldehyde Complexes, Sulfine Complexes

Cationic ruthenium sulfine complexes $[CpRu(PR'_3)_2(O=S=CHR)]PF_6$ have been obtained by a variety of methods. Oxidation of the thioaldehyde complexes $[CpRu(PR'_3)_2(S=CHR)]PF_6$ with either 2-tosyl-3-phenyl-oxaziridine ($PR'_3 = PMe_3$) or magnesium-monoperoxyphthalate ($PR'_3 = {}^1/_2$ dppm) gave complexes of arylsulfines (R = Ph, 3-C_6H_4F, 4-C_6H_4Cl, 4-C_6H_4OMe) selectively in their thermodynamically less stable *E* form. Siloxane elimination from the sulfinato complexes $[CpRu(PMe_3)_2(SO_2CHRSiMe_3)]$ yielded complexes of aliphatic sulfines, $[CpRu(PMe_3)_2(O=S=CHR)]PF_6$ (R = H, Me). Treatment of $[CpRu(dppm)(SO_2CH_2R)]$ with acetyl chloride led to an oxygen redistribution giving complexes of thioaldehydes $[CpRu(dppm)(\eta^2\text{-}S=CH_2)]PF_6$ and $[CpRu(dppm)(\eta^1\text{-}S=CHR)]PF_6$ (R = Ph, 4-C_6H_4Cl). The structure of the latter was determined by X-ray crystallography. The loss of oxygen can be suppressed by performing the acylation-elimination sequence in the presence of poly-(4-vinylpyridine). This provided a selective access to complexes of *Z*-sulfines, $[CpRu(PMe_3)_2(O=S=CHR)]PF_6$ (R = Ph, 4-C_6H_4Cl) and $[CpRu(dppm)(O=S=CHR)]PF_6$ (R = Ph, 4-C_6H_4Cl, COOEt, Cl). Complexes of the parent sulfine $O=S=CH_2$ were also obtained by SO transfer to the methylene complex $[CpRu(PMe_3)_2(CH_2)]PF_6$ and methylene transfer to the sulfur monoxide complex $[Cp^*Ru(PMe_3)_2(SO)]PF_6$. Most of the new sulfine complexes exhibit dynamic behaviour in solution, *i. e.* ligand rotation, ligand inversion, and η^2 / η^1 hapticity change. *O*-Alkylation provided the dicationic complex $[CpRu(PMe_3)_2(EtO\text{-}S=CHMe)](PF_6)_2$, and S-oxidation gave the sulfene complexes $[(C_5R_5)Ru(PMe_3)_2(O_2S=CH_2)]PF_6$ (R = H, Me).

Introduction

The chemistry of sulfines (thiocarbonyl-S-oxides) RR'C=S=O has developed rapidly during the past twenty years [2, 3]. While derivatives with RR' ≠ H are reasonably stable, isolable compounds, the thioaldehyde-S-oxides RHC=S=O have only a fleeting existence unless they are kinetically stabilized by bulky substituents R [4]. Sulfines undergo a multitude of interesting and synthetically useful reactions such as nucleophilic additions at carbon or sulfur, cycloadditions, and rearrangements [2 - 4]. In this context, thioaldehyde-S-oxides are in general used only as transient intermediates. Despite their low stability, the chemistry of thioaldehyde-S-oxides has received notable attention due to the fact that this class of organosulfur compounds is playing a considerable role in *allium* plants. For example, the lachrimatory factor of the onion *allium cepa* has been identified as *Z*-ethylsulfine [5].

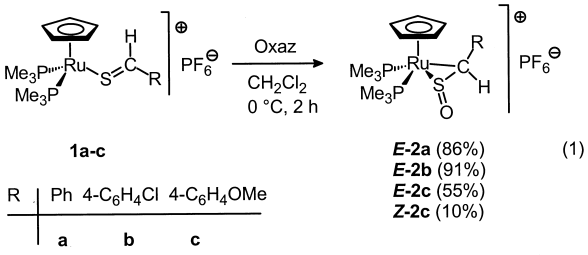
Unstable organic molecules can often be stabilised by coordination to transition metal complexes. Typical examples are carbenes [6 - 8] or thioaldehydes [9] whose metal complexes have found widespread use as reagents in organic synthesis. Sulfine complexes have mostly been prepared from isolable sulfines [10 - 14]. An osmium complex of the parent sulfine, $[OsCl(NO)(PPh_3)_2(\eta^2\text{-}H_2C=S=O)]$, has been synthesised by oxidation of the corresponding thioformaldehyde complex [15, 16], and a platinum fluorenylsulfine complex has been obtained by reaction of the correspond-

ing SO_2 complex with a silylated organolithium reagent [10]. In a few instances dynamic equilibria have been found to exist between different isomers [14]. Structure and bonding of sulfine complexes are now well understood [17], their reactions however remain an open field. In this contribution we report some new syntheses of sulfine complexes by oxidation of thioaldehyde complexes, 1,2-elimination of suitable sulfinato complexes, SO transfer to a carbene complex, as well as methylene transfer to a complex of sulfur monoxide. Furthermore, the dynamic behaviour and linkage isomerism of these compounds as well as some aspects of their reactivity will be reported. Preliminary accounts of this work have been communicated [18, 19].

Synthesis of Sulfine Complexes by Oxygen Transfer

As a first approach to cationic ruthenium sulfine complexes we investigated the oxidation of thioaldehyde complexes which, in turn, are readily obtainable from the corresponding ruthenium thiolates [20]. Indeed, electrophilic oxygen transfer to **1a-c** (eq. (1)) or **3a-c** (eq. (2)) gave the desired sulfine complexes in quite satisfactory yields.

The new compounds are yellow crystalline materials which, due to their ionic nature, are soluble only in polar organic media such as dichloromethane or acetone. The presence of a sulfine ligand can easily be diagnosed from a strong

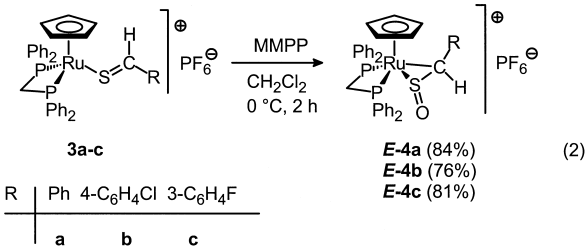


1a-c

R	Ph	4-C_6H_4Cl	4-C_6H_4OMe
	a	**b**	**c**

***E*-2a** (86%)
***E*-2b** (91%)
***E*-2c** (55%)
***Z*-2c** (10%) (1)

Oxaz = 2-tosyl-3-phenyl-oxaziridine



3a-c

R	Ph	4-C_6H_4Cl	3-C_6H_4F
	a	**b**	**c**

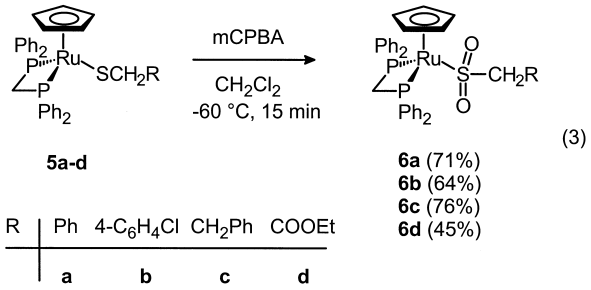
***E*-4a** (84%)
***E*-4b** (76%)
***E*-4c** (81%) (2)

MMPP = magnesium-monoperoxyphthalate

ν(SO) absorption near 1030 cm^{-1} in the infrared spectra. The ^{31}P NMR spectra consist of AB systems indicating the side-on η^2(C,S) coordination mode of the sulfine ligand. The resonance of the sulfine carbon atom appeares as a doublet at around 70 (**2a-c**) or 80 (**4a-c**) ppm, respectively. Coupling to only one of the two nonequivalent phosphorus nuclei is another diagnostic feature of the η^2 (C,S) coordination. The proton bound to the sulfine carbon atom finally gives rise to a doublet resonance at 5 ppm; strong coupling with one of the phosphorus nuclei indicates that this proton is positioned *anti* to the Cp ring [21] as shown in equations (1) and (2). The highly selective formation of the sulfine ligand in its thermodynamically less favored *E* form is quite remarkable and will be discussed below (In order to avoid confusion the descriptors *E* and *Z* will henceforth be used to denote the stereochemistry of the *isolated* sulfine ligand, neglecting the presence of the ruthenium complex fragment). Only **2c** was obtaind as a 5:1 mixture of *E* and *Z* isomers which could be separated by column chromatography. While ***E*-2c** has spectroscopic properties very similar to those of the other compounds of this series, ***Z*-2c** is unique: A singlet at ambient temperature in the ^{31}P NMR and a broad singlet of the sulfine proton in the ^1H NMR spectrum are indicative of the η^1(S) bonding mode. The carbon atom of the sulfine ligand gives rise to a low-field signal at 201 ppm, in a range typical for uncoordinated sulfines [22], which also can be taken as diagnostic of the η^1(S) bonding mode. The *Z* geometry of the RHC=S=O group finally is inferred *inter alia* from the low-field shift of the aromatic ortho protons [2].

Synthesis of Sulfine Complexes by 1,2-Elimination Reactions

Several synthetic routes are available for the synthesis of the required sulfinato complexes **6a-d** and **8a-d**: Oxidation of the corresponding thiolate complexes (eq. (3)) [23, 24], SO_2 insertion into the ruthenium-carbon bond (eq. (4)) [24], and Grignard addition to a sulfur dioxide complex (eq. (5)) [25]. The chloromethylsulfinato complex [CpRu(dppm)(SO_2CH_2Cl)] (**6e**) finally was obtained from [CpRu(dppm)(SO_2)]Cl and diazomethane [21]. The products are pale yellow air-stable crystalline materials whose spectroscopic data are very similar to those of their known analogues [23 - 25].



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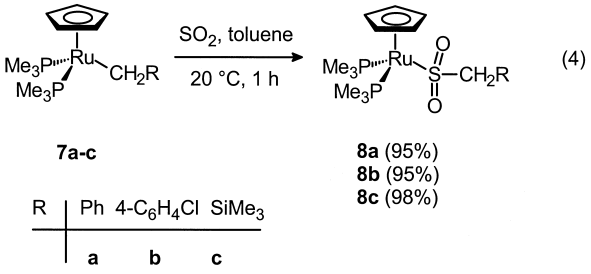

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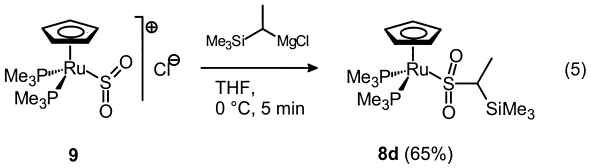

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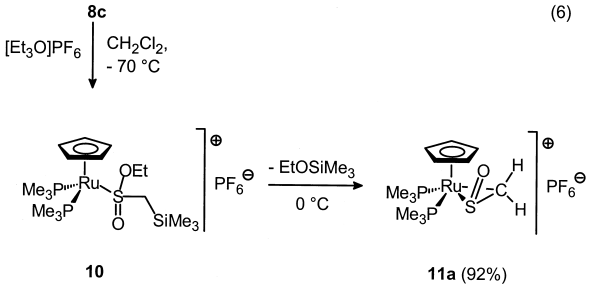
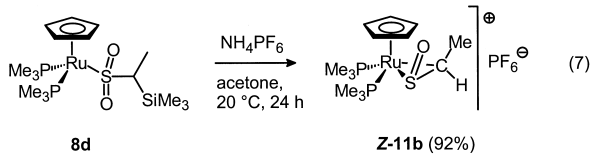


(6)

Componds **8c** and **8d** lend themselves to siloxane eliminations reminiscent of the Peterson olefination [26, 27]. Towards that end, **8c** was alkylated with triethyloxonium hexafluorophosphate (eq. (6)).

An intermediate, **10**, could be isolated at low temperature and spectroscopically identified. This compound is very similar to the other known half-sandwich ruthenium complexes of sulfinic acid esters [24]: Diastereotopic methylene protons of the ethoxy group and nonequivalent phosphorus nuclei indicate the formation of a center of asymmetry. Upon warming to room temperature, **10** eliminates $EtOSiMe_3$ to give **11a**. This, to the best of our knowledge, is only the second complex of the parent sulfine, after the osmium complex mentioned in the Introduction.

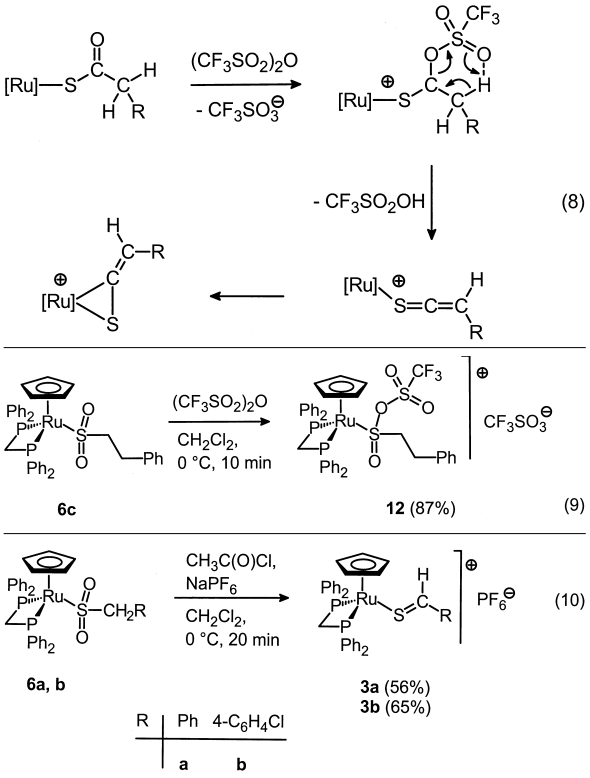


(7)

When **8d** was treated with ammonium hexafluorophosphate at room temperature, an apparently similar elimination of $HOSiMe_3$ occurred leading to the *Z*-methylsulfine complex **11b** (eq. (7)).

11a, b are colorless crystalline compounds the properties of which are similar to those of **2a-c**. While **11b** has a static structure, the broad NMR signals of **11a** indicate some dynamic behaviour in solution which will be further discussed below. At –70 °C the ^{31}P NMR spectrum of **11a** consists of an AB system, and the ^{13}C resonance of the sulfine carbon atom appeares as a doublet at 60 ppm confirming the side-on (η^2) bonding mode also for the parent compound. The methylene protons give rise to two doublets of doublets. The one resonating at higher field is split by strong coupling to one of the phosphorus nuclei and must therefore be assigned to the proton *anti* to the Cp ring. The *syn* proton which resonates 0.8 ppm further downfield is only weakly coupled to the phosphorus nuclei. A similar situation was observed for the closely analogous sulfene complex $[Cp^*Ru(PMe_3)_2(H_2C{=}SO_2)]^+$ [21]. For isomeric *Z* and *E* sulfines it is generally observed that a proton *cis* to a sulfine function resonates between 1.2 and 1.7 ppm downfield from the *trans* proton in the corresponding *Z* sulfine [22]. On this basis we have to conclude that the S=O function in **11a** is positioned *syn* to the Cp ring (eq. (6)). The geometry of **11b** was further corroborated by NOE and lanthanide shift experiments. A strong NOE was observed between the Cp and CH_3 groups demonstrating their mutual proximity. Addition of 2.5 and 5.0 μmol of $Eu(thd)_3$ to a CD_2Cl_2 solution of 50 μmol **11b** produced sizeable downfield shifts of both the Cp and CH_3 signals while the signal of the unique proton was only slightly affected. Assuming as usual that the europium shift reagent associates with the most polar group in the molecule, this confirms that also in **11b** the S=O group is positioned *syn* to the Cp ring as shown in eq. (7).

We have recently presented a new method to produce metal-coordinated thioketenes under mild con-

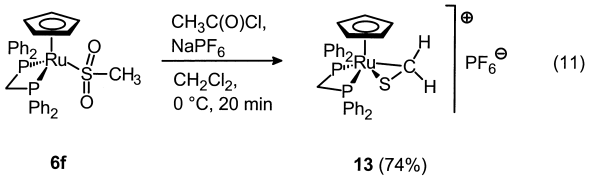


ditions and in high yields [28]. It consists of an acylation of a coordinated thiocarboxylate followed by an intramolecular 1,2-elimination of the corresponding acid (eq. (8)).

In a similar attempt the sulfinate complex **6c** was treated with triflic anhydride. A dark blue oil resulted which could not be fully purified. Nevertheless, we have sufficient spectroscopic evidence that this material is **12**, a ruthenium complex of a mixed anhydride of trifluoromethanesulfonic and 2-phenylethanesulfinic acids (eq. (9)).

The introduction of a positive charge into the complex leads to a considerable downfield shift of the Cp and SCH_2 protons. The two phosphorus nuclei have become nonequivalent due to the creation of an asymmetric stereocenter at sulfur, and two separate ^{19}F NMR signals are observed for the anhydride group and the triflate anion. **12** does not undergo the desired elimination, certainly because of lacking acidity of the SCH_2 group.

Similar treatment of the benzylsulfinato complexes with acetyl chloride gave purple reaction mixtures from which, surprisingly, the known thioaldehyde complexes **3a, b** [20] could be isolated in fair to good yields (eq. (10)).

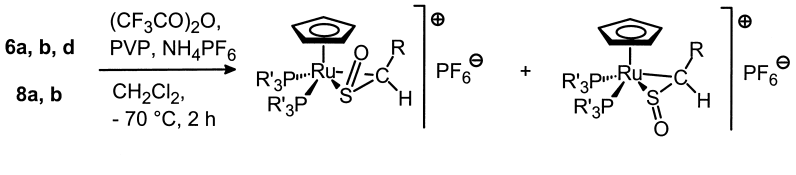


The corresponding uncoordinated aldehydes RCHO and the sulfur dioxide complex $[CpRu(dppm)(SO_2)]PF_6$ [29] were detected as side products of this reaction. **3a, b** were identified by comparison of their NMR spectra with those of authentic samples [20], and **3b** was further characterized by an X-ray structure determination. While the mechanism of this oxygen redistribution remains obscure we seized the opportunity to prepare a ruthenium complex of thioformaldehyde (**13**) from methanesulfinate complex **6f** [24, 25] (eq. (11)).

13 was isolated as a beige, air-stable microcrystalline powder. The side-on coordination of the thioformaldehyde molecule is apparent from the high-field shift of its ^{13}C NMR signal, the two nonequivalent CH_2 protons, only one of which is strongly coupled to one of the P nuclei, and the AB system in the ^{31}P NMR spectrum.

Control experiments have subsequently shown that the oxygen transfer can be avoided by slow, stepwise addition of the acylating reagent and by adding poly(4-vinylpyridine) to the reaction mixture. Under these conditions, treatment of the sulfinato complexes **6a**, **b, d** and **8a**, **b** with trifluoroacetic acid anhydride at -70 °C gives the desired sulfine complexes **2a**, **b** and **4a, b, d**, predominantly as their *Z* diastereoisomers (eq. (12)).

The *Z*/*E* selectivity is temperature-dependent: When the synthesis of compounds **4a, b** was carried out at 0 °C an equimolar mixture of both isomers was obtained. The *Z* isomers produced in this reaction are very similar in appearence to the *E* isomers described before. NMR spectroscopy reveals that both isomers of **4d** are static but the *Z* isomers of **4a, b**, unlike their *E* congeners, are dynamic at room temperature. At –70 °C static spectra were also observed for ***Z*-4a** and ***Z*-4b**: Nonequivalent P nuclei again prove the side-on coordination of the sulfine ligand. Strong coupling of the unique proton to one of the phosphorus nuclei indicates that this proton is situated *anti* to the Cp ring and, consequently, both the oxygen atom and the group R are *syn* to the Cp ring as shown in equation (12).

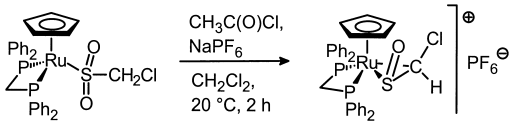


Z *E*

(12)

$(R'_3P)_2$ \ R	Ph	4-C_6H_4Cl	COOEt
$(Me_3P)_2$	**2a**	**2b**	
(dppm)	**4a**	**4b**	**4d**

***Z*-2a** (24%)
***Z*-2b** (21%)
4a (84%) (*Z* : *E* = 5 : 1)
4b (87%) (*Z* : *E* = 5 : 1)
4d (81%) (*Z* : *E* = 2 : 1)



6e **14** (51%) (13)

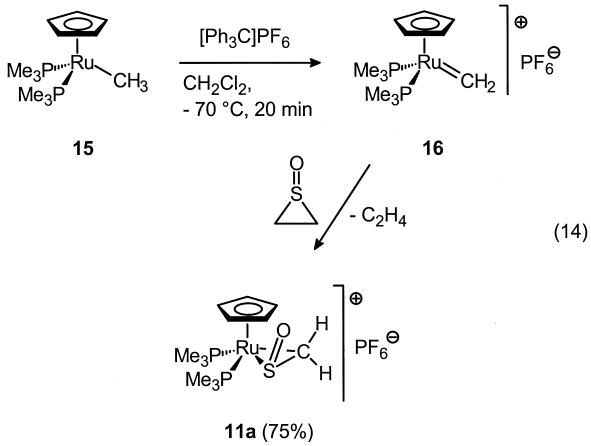
The chlorosulfine complex **14** finally was obtained by reacting **6e** with acetyl chloride (eq. 13)).

The spectroscopic properties of **14** are similar to those of the other *Z*-sulfine complexes. In particular, the strong coupling of the sulfine proton with one of the P nuclei of the dppm ligand indicates that this proton is positioned *anti* to the Cp ring. There is no unambiguous spectroscopic proof of the *Z* geometry of **14**, however, since all 1,2-elimination reactions produced predominantly or exclusively the *Z* isomers it is not unreasonable to assume the same to hold in this case.

Synthesis of Sulfine Complexes from Sulfur Monoxide and Methylene Units

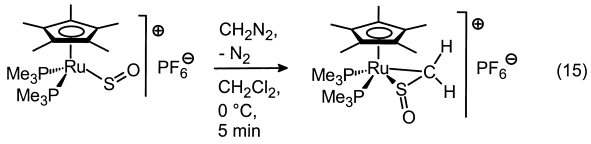
A further quite effective synthesis of the sulfine complex **11a** is provided by the addition of sulfur monoxide to the methylene complex **16** which in turn is readily accessed via hydride abstraction [30] from the corresponding methyl complex **15** [24]. As an SO transfer reagent we used thiirane-1-oxide [31] (eq. (14)).

The intermediate **16** was detected by its downfield proton NMR signal at 16.3 ppm, a range typical of cationic methylene complexes [30]. Taken together this reaction sequence is analogous to the synthesis of sulfene complexes from methylene complexes and SO_2 [32, 33]. The inverted synthesis of a sulfine complex by methylene addition to a sulfur monoxide complex is also possible as shown in eq. (15).



15 **16**

11a (75%) (14)



17 **18** (84%) (15)

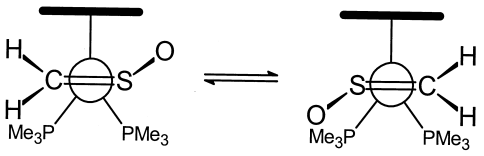
Addition of diazomethane to the deep green SO complex **17** [34] was accompanied by rapid discoloration and gas evolution. From the mixture the sulfine complex **18** was isolated as an off-white microcrystalline powder. A strong absorption in the IR spectrum at 1036 cm^{-1} is diagnostic of the sulfine ligand. Two nonequivalent P nuclei in the ^{31}P NMR spectrum and a high-field signal for the sulfine carbon atom in the ^{13}C NMR spectrum indicate that in this compound the CH_2=S=O ligand is side-on coordinated as it is in the analogous Cp complex **11a**. The ^1H NMR spectrum, however, reveals an important difference. In **18**, the methylene proton *anti* to the Cp ring resonates downfield from the *syn* proton. This is convincing evidence that also the S=O group is in the *anti* position. We tried to corroborate

this finding by an X-ray structure determination. Unfortunately, **18** crystallized in the cumbersome space group $Pb2_1a$. Although a good data set was obtained the structure could not be fully refined – a problem not unknown for this space group [35]. Nevertheless the position of the S=O group *anti* to the Cp* ring was clearly revealed.

Dynamic Behaviour of the Sulfine Complexes

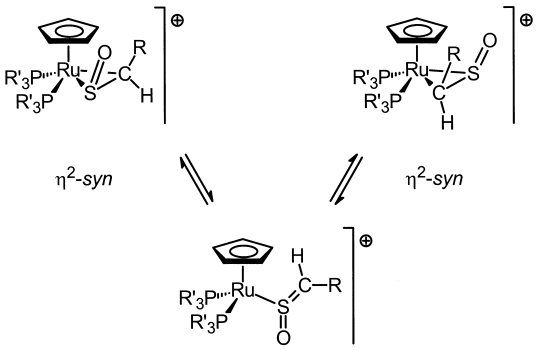
Three types of dynamic phenomena should be expected for sulfine complexes of the type $[Cp(R'_3P)_2Ru(O=S=CHR)]^+$: (a) ligand rotation, (b) ligand inversion, and (c) hapticity (η^2 / η^1) change. The latter two are intimately connected.

A clear case of ligand rotation without ligand inversion is represented by **11a**. At –70 °C the ^{31}P NMR spectrum consists of an AB system with resonances at 13.9 and 11.9 ppm, $^2J(P,P)$ = 45 Hz. An additional small doublet at 13.0 ppm is due to the presence of the second (*anti*) rotamer whose other doublet apparently overlaps with the 11.9 ppm signal of the *syn* rotamer. Upon warming all signals broaden and coalesce into a broad hump at 25 °C. At 50 °C one broad AB system with resonances at 9.9 and 8.9 ppm, $^2J(P,P)$ = 44 Hz reappears. The fact that the two phosphorus nuclei remain nonequivalent in the fast-excange spectra indicates that a hapticity change with concomitant inversion at sulfur is not involved in this process (eq. (16)).



(16)

syn-**11a** *anti*-**11a**



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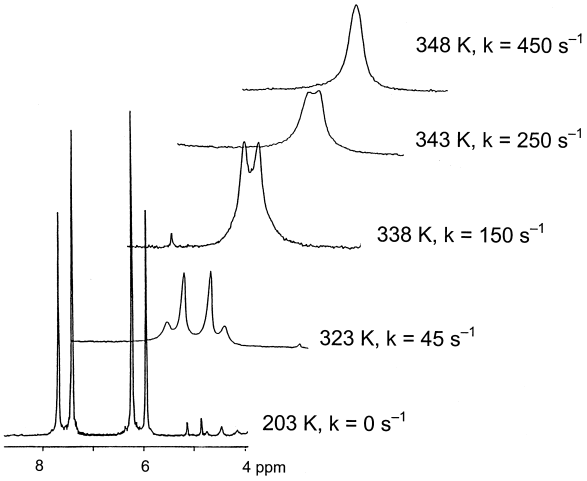


Fig. 1. Temperature dependence of the ^{31}P NMR spectrum of $[CpRu(PMe_3)_2(\eta^2\text{-}Z\text{-}O=S=CHMe)]PF_6$ (***Z*-11b**).

The dynamic behaviour of the methylsulfine complex ***Z*-11b** is in sharp contrast to that of **11a**. The room temperature ^{31}P NMR spectrum consists of a single AB system indicating the presence of only one species with nonequivalent phosphorus nuclei. Upon warming the AB system coalesces into a broad singlet as the P nuclei become equivalent. The complete preservation of the symmetry of the spectra (Fig. 1) indicates that under these conditions the intermediate η^1 isomer (eq. (17)) is present only in negligible amount. A complete lineshape analysis using the program DNMR 5 [36] yielded an activation barrier for this process of $\Delta G^{\neq}$ = 69 kJ/mol.

A similar behaviour was found for ***Z*-4a**. In this case the activation barrier is appreciably lower ($\Delta G^{\neq}$ = 55 kJ/mol), and a slight asymmetry in the ^{31}P NMR spectra at intermediate exchange rates indicates the appearance of the η^1 isomer in the equilibrium.

Clear examples of hapticity change are provided by both isomers of **2c**. As mentioned previously, ***Z*-2c** is actually present at room temperature in its η^1 form. Upon cooling the broad singlet of the sulfine proton at 6.45 ppm disappears and reappears at –70 °C as a doublet at 4.24 ppm, $J(P,H)$ = 14.2 Hz. The activation barrier as determined from the ^{31}P NMR spectra is quite low ($\Delta G^{\neq}$ = 48 kJ/mol). ***E*-2c** undergoes a corresponding transition between +30 and +70 °C with a much higher activation barrier ($\Delta G^{\neq}$ = 63 kJ/mol). The shift of the hapticity equilibrium can be followed by the disappearance of the doublet signal of the sulfine proton at 5.26 ppm and

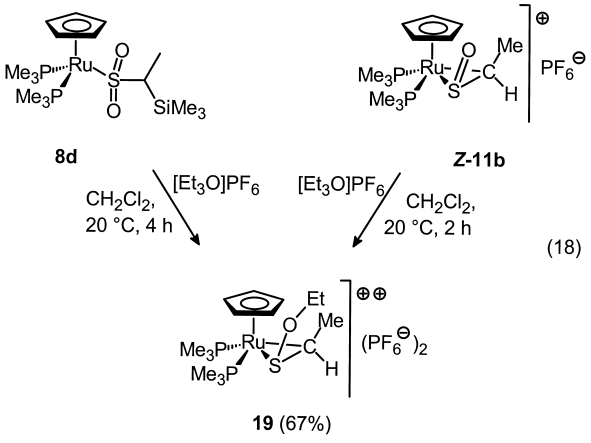
its reappearance as a singlet at 5.85 ppm upon warming. Thus the η^2 / η^1 equilibrium can in these cases be completely shifted to either side by a change of temperature.

Reactions of the Sulfine Complexes

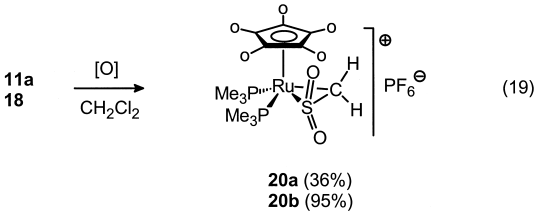
Although the sulfine complexes of this study are positively charged they can still be alkylated at the S=O function. Thus ***Z*-11b** reacts with triethyloxonium hexafluorophosphate to give the dicationic complex **19** in quantitative yield. **19** can even more conveniently be obtained directly from the sulfinate precursor **8d** (eq. (18)).

19 is a colorless crystalline, moderately stable compound. The introduction of a second positive charge into the complex leads to 0.7 ppm downfield shifts of the Cp and sulfine CH signals. Changes of the P,P and P,C coupling constants indicate subtle alterations of the bonding within the three-membered Ru-S-C ring. A strong NOE between the Cp, Me and EtO groups verifies the stereochemistry depicted in eq. (18).

The complexes of the parent sulfine, **11a** and **18**, can readily be oxidized to the corresponding sulfene complexes **20a, b** (eq. (19)).



(18)



(19)

11a, 20a: o— = H, [O] = $(PhIO)_x$
18, 20b: o— = Me, [O] = dimethyldioxirane

20a, b are colorless crystalline compounds. **20b** was identified by comparison with an authentic sample [21]. **20a** has very similar properties. In particular, the extreme high-field shift of the methylene carbon atom (–22.3 ppm) is diagnostic for the side-on coordinated sulfene ligand. From the sharp ^{31}P NMR spectra it is immediately obvious that both sulfene complexes are static on the NMR timescale. The introduction of a second oxygen atom into the ligand sphere causes an additional high-field shift of 1.75 ppm for the proton *syn* to the Cp ring and of 2.75 ppm for the *anti* proton.

Structure Determination of the Thioaldehyde Complex

[CpRu(dppm){S=CH(4-C_6H_4Cl)}]PF_6 (**3b**)

A crystal of **3b•acetone** was subjected to an X-ray structure determination. The structure of the cation is shown in Fig. 2, important bond distances and angles are given in Table 1.

The geometry of the $[CpRu(dppm)]^+$ part is very similar to that in other complexes containing this fragment, *e. g.* $[CpRu(dppm)(SO_2Et)]$ [25] or $[CpRu(dppm)\{SC(O)CH_2Ph\}]$ [28]. The entire thiobenzaldehyde ligand and the ruthenium atom lie in a perfect plane which coincides with the approximate mirror plane of the cation. The two large substituents at the C=S double bond occupy trans positions. This is generally observed for thioaldehyde complexes [9] including the closely related compound $[CpRu(dppe)\{S=CH(4\text{-}C_6H_4OMe)\}]PF_6$ [20]. The C=S bond of the latter complex is 1.7 pm longer than that in **3b** as a result of the +M effect of the methoxy group. A notable difference of the two structures concerns the rotational arrangement of the Ru-S bond. In the sterically more encumbered dppe complex the CH group of the thioaldehyde ligand is positioned *syn* to the Cp ring and tilted sideways to avoid a too close contact with the protons of the Cp ring. In the dppm complex **3b** the P-Ru-P angle is 13° smaller. As a result, the CH group can well be accommodated between the phenyl groups of the chelate phosphine ligand.

Discussion

With this work we present a number of different reactions leading to cationic ruthenium com-

Table 1. Important bond distances (pm) and angles (°) within the cation of [CpRu(dppm){S=CH(4-C_6H_4Cl)}]PF_6 (**3b**).

Ru-P(1)	228.3(3)	P(1)-Ru-P(2)	71.37(9)
Ru-P(2)	228.9(2)	P(1)-Ru-S	95.97(9)
Ru-S	225.2(2)	P(2)-Ru-S	95.35(8)
Ru-Cp[a]	214.6	Ru-S-C(71)	122.4(3)
S-C(71)	161.5(9)	S-C(71)-C(72)	125.5(7)
C(71)-C(72)	143.0(12)		

[a] Cp denotes the midpoint of the C_5H_5 ring. The average of the Ru-C(ring) distances is 219 pm.

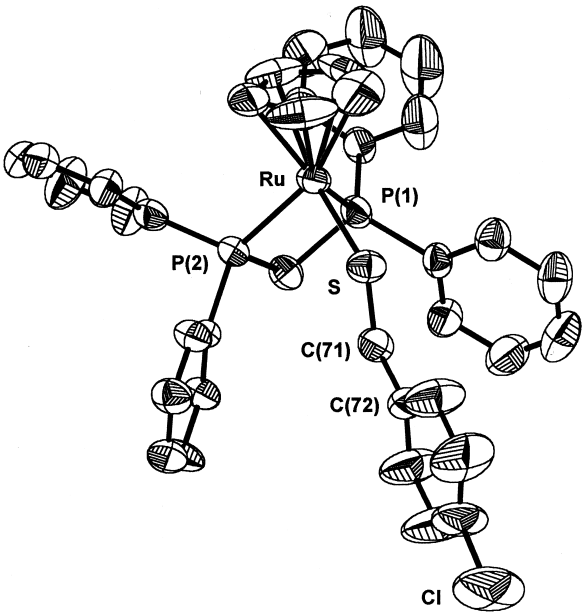
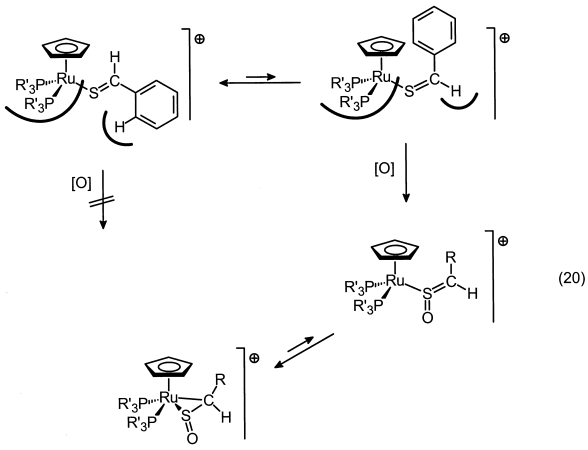
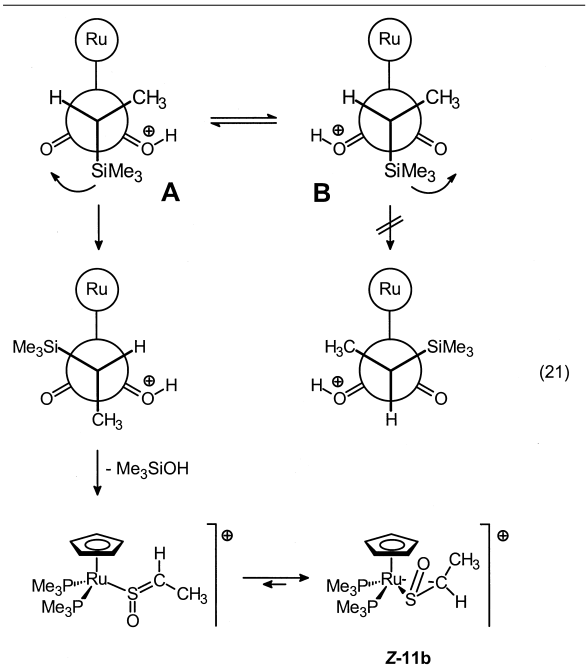


Fig. 2. View of the cation of [CpRu(dppm){S=CH(4-C_6H_4Cl)}]PF_6 (**3b**). Hydrogen atoms omitted for clarity.



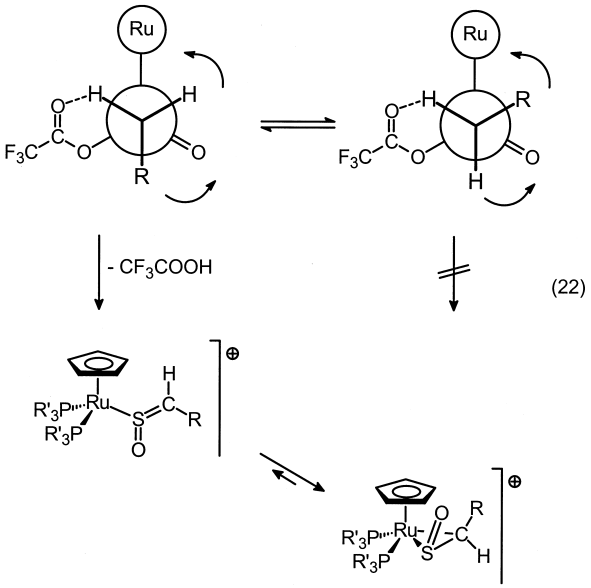


plexes of sulfines. The oxidation of thioaldehyde complexes as described by eqs (1) and (2) is unusual insofar as it produces the sulfine ligands in their thermodynamically less favored *E* form. At first sight this result is unexpected since the starting thioaldehyde complexes are present as their *E* isomers [9, 20] which upon electrophilic oxygen transfer should give complexes of *Z*-sulfines. *E* and *Z* isomers, however, are in a rapid equilibrium even at low temperature [9]. For the *E* isomer, access of the bulky oxidant is sterically inhibited (eq. (20). Thus oxidation of the less abundant but more reactive *Z* isomer prevails, producing the coordinated sulfine in its *E* form in high selectivity.

The C=S double bond of the sulfine ligand can also be generated by suitable 1,2-elimination reactions starting from readily available sulfinato complexes. The siloxane elimination route as described by eqs (6) and (7) is a close parallel of the Peterson olefination [26, 27]. In our case the reaction is initiated by electrophilic attack at one of the sulfinato oxygen atoms. From earlier observations we know that this step is reversible [24] and not diastereoselective [37]. In the case of ***Z*-11b** (eq. (7)) the observed stereoselectivity may be explained as follows: Protonation of the ground state rotamer of **8d** can give two diastereoisomeric sulfinic acid complexes **A** and **B** (eq. (21)) which are in a rapid

equilibrium. Even if diastereoisomer **A** were disfavored for steric reasons, the rotation about the S-C bond would require distinctly less energy. The usual *anti* elimination [27] then produces the η^1 isomer of ***Z*-11b** which subsequently equilibrates to the η^2 form.

The acylation-elimination route as described by eqs (12) and (13) is reminiscent of the synthesis of ketenes by pyrolysis of anhydrides [38]. The first step, formation of the mixed anhydride complex (eq. (9)), is facilitated by the strongly electron-donating properties of the $[Cp(R'_3P)_2Ru]^+$ complex [24]. The following intramolecular elimination of acid is the rate-determining step as evidenced by a small but distinct kinetic isotope effect: When a mixture of $[CpRu(dppm)(SO_2CH_2Ph)]$ (**4a**) and $[CpRu(dppm)(SO_2CD_2Ph)]$ (**4a-D$_2$**) was treated with a substoichiometric amount of $(CF_3CO)_2O$, the undeuterated complex reacted faster by a factor of 1.2. Such a small KIE is indicative of a non-linear cyclic transition state. Proton abstraction by an external base would lead to a more or less linear transition state with a KIE much larger than 2 [39, 40]. The observed selectivity for the *Z* product arises from the *trans*-staggered arrangement of the sulfinato ligand in the starting material as shown by an X-ray structure determination of the closely related complex $[CpRu(dppm)(SO_2Et)]$ [25]. Formation of the sulfine ligand in its *E* form would require a 180° rotation of the S-C bond leading to an unfavourable eclipsed conformation (eq. (22)).



The decomposition of the sulfine complexes in the reaction with acylating agents is not well understood. In a control experiment **4b** was treated with CF_3COOH. Only a slow unspecific decomposition was observed. This indicates that the sulfine complexes of this study are less acid sensitive than uncoordinated sulfines [2]. On the other hand, treatment of **4b** with $(CF_3CO)_2O$ gave the corresponding thioaldehyde complex **3b** in good yield. Thus the beneficial effect of poly(4-vinylpyridine) in the reaction according to eq. (12) seems to stem from a suppression of the buildup of a local excess of anhydride rather than from the scavenging of acid. The formation of the sulfur dioxide complex and uncoordinated aldehyde in this reaction may have some precedence in a) the exhaustive oxidation of sulfines to SO_2 and the corresponding carbonyl compounds [2, 3], and b) the strongly oxidizing properties of mixtures of sulfoxides and acetic acid anhydride or oxalyl chloride [41, 42].

The remaining two syntheses of sulfine complexes (eqs (14), (15)) make use of the pronounced electrophilicity of methylene complex **16** and sulfur monoxide complex **17**, respectively. The close analogy with the preparation of the isostructural sulfene complexes $[(C_5R_5)Ru(PR'_3)_2(\eta^2\text{-}H_2C{=}SO_2)]PF_6$ [33] is immediately obvious. It should be mentioned here that a limited number of arylsulfines have been obtained from diazo compounds and *in situ* prepared sulfur monoxide [2, 3].

The rotation of a π-bonding ligand such as an alkene or carbene on a $[CpML_2]$ complex fragment is a fairly facile process [43]. This is mainly due to the small energy gap between the two orthogonal frontier orbitals HOMO (a") and HOMO-1 (a') [44 - 46]. The complex of the parent sulfine, **11a**, is a further example of this behaviour. The rapid exchange between the major (*syn*) and minor (*anti*) isomer can easily be observed by dynamic NMR. That the analogous pentamethylcyclopentadienyl complex **18** appears rigid on the NMR timescale might simply be due to the fact that the minor (now the *syn*) isomer is present in too small an amount to make the process observable by DNMR. The analogous sulfene complex $[Cp^*Ru(PMe_3)_2(H_2C{=}SO_2)]^+$ is indeed static [21], while the closely related sulfur trioxide complex $[Cp^*Ru(PMe_3)_2(O{=}SO_2)]^+$ is again dynamic [47]. These subtle differences point to different π-backbonding

abilities of these three ligands, which seem to be largest for sulfene.

A different type of ligand dynamics is observed for the methylsulfine complex ***Z*-11b**. The site exchange of the two phosphorus nuclei can only be explained by a formal inversion at both sulfur and carbon which must occur *via* the corresponding η^1 isomer (eq. (17)). That this isomer becomes thermally accessible is certainly due to the +I effect of the methyl group which raises the energies of both the lone pair at sulfur and the π^* level of the sulfine ligand. Hence the η^1 isomer is stabilized while at the same time the η^2 isomer is destabilized. Comparison of the isomeric pairs ***E/Z*-2c** and ***E/Z*-4a** finally points to the importance of steric effects. For the *Z* isomers the η^1-coordination mode is further stabilized due to the complete relief of steric interactions between the group R and the bulky metal complex. As a result, complexes of *Z*-sulfines undergo hapticity changes more readily than their *E* counterparts.

Conclusions

A number of convenient routes to cationic ruthenium complexes of sulfines have been developed. Both *E* and *Z* forms of the coordinated sulfines can be accessed stereoselectively. The complexes exhibit a variety of dynamic phenomena such as ligand rotation, ligand inversion, and (η^2/η^1) hapticity change. Exploratory experiments have so far identified electrophilic attack at oxygen and oxygen transfer to sulfur as perhaps typical reactions. In further work we plan to investigate the propensity of these complexes to undergo cycloadditios which may be expected to parallel those of the analogous thioaldehyde complexes [20].

Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of dry nitrogen using suitably purified solvents. [$CpRu(PPh_3)_2Cl$] [48], [$CpRu(PMe_3)_2Cl$] [49], the thiobenzaldehyde complexes **1a-c** and **3a-c** [20], the thiolate complexes **5a-c** [20, 24], the sulfinate complexes **6a, c, e, f** [21, 24, 25], the alkyl complexes **7a, 15** [24], the sulfur monoxide complex **17** [29], 2-tosyl-3-phenyl-oxaziridine [50], thiirane-1-oxide [51], iodosylbenzene [52], and dimethyldioxirane [53] were obtained as described in the literature. 3-Chloroperoxybenzoic acid (mCPBA) was dried under vacuum at 80 °C and titrated iodometrically. Magnesium-monoperoxyphthalate hexahydrate (MMPP) and all other reagents were used as purchased. For chromatographic separations a silica (Merck, grain size 0.063 - 0.200 mm) column (2 cm diameter, 30 cm long) was used.

The following analytical instruments were used: IR: Perkin-Elmer 283, Bruker IFS 25; NMR: Bruker AMX 400 (^{1}H, 400 MHz, TMS; ^{13}C, 100 MHz, TMS; ^{31}P, 162 MHz, H_3PO_4). Chemical shifts δ in [ppm], coupling constants *J* or N = |*J* + *J*'| in [Hz]. Signals of aryl groups and signals of the CH_2 group of the dppm ligand are uncharacteristic and have been omitted from the lists of spectral data. All PF_6^- salts exhibit a septet at $\delta = -144.0$ ppm (J = 710 Hz) in their ^{31}P NMR spectra. Melting or decomposition points were determined by differential scanning calorimetry (DSC) using a TA-Instruments model TA 3000 thermal analyzer.

*[$CpRu(PMe_3)_2(O{=}S{=}CHR)]PF_6$ (**2a-c**)*

To a cooled (0 °C) solution of the thioaldehyde complex (0.50 mmol) in dichloromethane (15 ml) 2-tosyl-3-phenyl-oxaziridine (0.13 g, 0.50 mmol) was added. The mixture was kept 2 h at this temperature, and a gradual color change from dark red to light brown was observed. After evaporation to dryness the residue was extracted twice with toluene (10 ml) to remove the imine byproduct. Recrystallization from dichloromethane / diethylether gave the sulfine complexes as beige or yellow crystalline solids.

***E*-2a:/** Yield 0.26 g (86%), yellow crystalline powder, m.p. 109 °C (dec). $C_{18}H_{29}F_6OP_3RuS$ (601.5): calcd. C 35.94, H 4.86; found C 35.97, H 4.57.

IR (Nujol): 1020 cm^{-1} (SO). – ^{1}H NMR (acetone-d_6): 5.55 (s, 5H, Cp), 5.25 (dd, J = 11.8 Hz, J' = 1.2 Hz, 1H, OSCH), 1.86 (d, J = 10.0 Hz, 9H, PMe_3), 1.76 (d, J = 10.4 Hz, 9H, PMe_3). – ^{13}C NMR (acetone-d_6): 93.6 (s, Cp), 71.9 (d, J = 9 Hz, OSC), 21.3 (dd, J = 35 Hz, J' = 2 Hz, PMe_3), 19.1 (dd, J = 35 Hz, J' = 2 Hz, PMe_3). – ^{31}P NMR (acetone-d_6): 9.7, 8.8 (AB system, J = 45 Hz).

***E*-2b:** Yield 0.29 g (91%), yellow crystalline powder, m. p. 92 °C (dec). $C_{18}H_{28}ClF_6OP_3RuS$ (635.9): calcd. C 34.00, H 4.44; found C 34.30, H 4.37.

IR (Nujol): 1036 cm^{-1} (SO). – ^{1}H NMR (acetone-d_6): 5.14 (s, 5H, Cp), 5.02 (dd, J = 12.8 Hz, J' = 1.0 Hz, 1H, OSCH), 1.73 (d, J = 9.6 Hz, 9H, PMe_3), 1.68 (d, J = 9.9 Hz, 9H, PMe_3). – ^{13}C NMR (acetone-d_6): 92.9 (s, Cp), 70.8 (d, J = 7 Hz, OSC), 21.8 (d, J = 28 Hz, PMe_3), 19.6 (d, J = 29 Hz, PMe_3). – ^{31}P NMR (acetone-d_6): 8.4, 8.2 (AB system, J = 45 Hz).

2c: The crude product which was obtained as described above was chromatographed over silica. With dichloromethane a red band was eluted which was discarded. With dichloromethane / acetone 5:1 a yellow band containing ***E*-2c** was obtained, and finally after elution

with dichloromethane / acetone 2:1 a greenish yellow band containing ***Z*-2c** followed.

***E*-2c:** Yield 0.17 g (55%), yellow crystalline powder, m. p. 82 °C (dec). $C_{19}H_{31}F_6OP_3RuS$ (631.5): calcd. C 36.14, H 4.95; found C 35.70, H 4.75.

IR (Nujol): 1028 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.52 (s, 5H, Cp), 5.26 (d, J = 10.2 Hz, 1H, OSCH), 3.77 (s, 3H, OMe), 1.86 (d, J = 9.6 Hz, 9H, PMe_3), 1.75 (d, J = 9.9 Hz, 9H, PMe_3). – ^{13}C NMR (acetone-d_6): 93.4 (s, Cp), 72.1 (d, J = 7 Hz, OSC), 55.5 (s, OMe), 21.7 (d, J = 29 Hz, PMe_3), 19.8 (d, J = 28 Hz, PMe_3). – ^{31}P NMR (acetone-d_6): 9.6, 9.1 (AB system, J = 46 Hz).

***Z*-2c:** Yield 0.03 g (10%), yellow crystalline powder, m. p. 79 °C (dec). $C_{19}H_{31}F_6OP_3RuS$ (631.5): calcd. C 36.14, H 4.95; found C 36.86, H 5.25.

IR (Nujol): 1028 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 6.45 (s, br, 1H, OSCH), 5.47 (s, 5H, Cp), 3.82 (s, 3H, OMe), 1.77 (vt, N = 9.9 Hz, 18H, PMe_3). – ^{13}C NMR (acetone-d_6): 201.1 (s, OSC), 90.7 (s, Cp), 55.6 (s, OMe), 20.8 (ABX system, N = 31 Hz, PMe_3). - ^{31}P NMR (acetone-d_6): 6.4 (s). – ^{31}P NMR (acetone-d_6, –70 °C): 9.5, 8.8 (AB system, J = 43 Hz).

[CpRu(dppm)(O=S=CHR)]PF_6 (**4a-c**)

To a cooled (0 °C) solution of the thioaldehyde complex (0.50 mmol) in acetone (15 ml) were added magnesium-monoperoxyphthalate (0.25 g, 0.50 mmol) and ethanol (10 ml). The mixture was kept 30 min at this temperature, and a gradual color change from dark red to light brown was observed. After evaporation to dryness the residue was chromatographed over silica. With dichloromethane / acetone 2:1 a yellow band was eluted. The products were obtained after recrystallization from dichloromethane / diethylether as beige or light brown crystalline solids.

***E*-4a:** Yield 0.35 g (84%), light brown crystalline powder, m. p. 88 °C (dec). – $C_{37}H_{33}F_6OP_3RuS$ (833.7): calcd. C 53.30, H 3.99; found C 53.76, H 4.07.

IR (Nujol): 1035 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.32 (s, 5H, Cp), 5.05 (d, J = 16.0 Hz, 1H, OSCH). – ^{13}C NMR (acetone-d_6): 93.5 (s, Cp), 80.4 (d, J = 7 Hz, OSC). – ^{31}P NMR (acetone-d_6): 4.6, –3.4 (AB system, J = 93 Hz).

***E*-4b:** Yield 0.33 g (76%), light brown crystalline powder. – $C_{37}H_{32}ClF_6OP_3RuS$ (868.2): calcd. C 51.19, H 3.72; found C 52.05, H 4.21.

IR (Nujol): 1033 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.24 (s, 5H, Cp), 5.15 (d, J = 15.8 Hz, 1H, OSCH). – ^{13}C NMR (acetone-d_6): 92.9 (s, Cp), 81.2 (d, J = 8 Hz, OSC). – ^{31}P NMR (acetone-d_6): 4.4, –3.3 (AB system, J = 93 Hz).

***E*-4c:** Yield 0.35 g (81%), beige crystalline powder. $C_{37}H_{32}F_7OP_3RuS$ (851.7): calcd. C 52.18, H 3.79; found C 52.70, H 3.79.

IR (Nujol): 1033 cm^{-1} (SO). – ^1H NMR (acetone-d_6): 5.34 (s, 5H, Cp), 4.99 (d, J = 15.6 Hz, 1H, OSCH). – ^{13}C NMR (acetone-d_6): 93.1 (s, Cp), 77.1 (s, OSC). – ^{31}P NMR (acetone-d_6): 4.8, –3.6 (AB system, J = 96 Hz).

[CpRu(dppm)(SCH_2COOEt)] (**5d**)

[CpRu(PPh_3)$_2$Cl] (0.73 g, 1.00 mmol) and $NaSCH_2$-COOEt (0.17 g, 1.20 mmol) were dissolved in a mixture of THF (20 ml) and ethanol (15 ml) and heated under reflux for 2 h. The mixture was evaporated and the residue chromatographed over a short (10 cm) silica column using THF / diethylether 1:2 as eluent. The broad orange band was collected and the product recrystallized from toluene / hexane.

5d: Yield 0.54 g (81%), yellow crystalline powder, m. p. 151 °C (dec). $C_{34}H_{34}O_2P_2RuS$ (699.7): calcd. C 60.98, H 5.12; found C 60.46, H 5.12.

^1H NMR (C_6D_6): 5.04 (s, 5H, Cp), 4.30 (s, 2H, SCH_2), 3.93 (q, J = 6.8 Hz, 2H, OCH_2), 0.92 (t, J = 6.8 Hz, 3H, CH_3). – ^{13}C NMR (C_6D_6): 174.5 (s, C=O), 80.6 (s, Cp), 59.7 (s, OCH_2), 36.7 (t, J = 7 Hz, SCH_2), 14.2 (s, CH_3). – ^{31}P NMR (C_6D_6): 15.6 (s).

[CpRu(dppm)(SO_2CH_2R)] (**6b, d**)

These compounds were obtained by oxidation of the corresponding thiolates **5b, d** (0.20 mmol) with an excess of 3-chloroperoxybenzoic acid (0.42 mmol) as described in ref. [24].

6b: Yield 95 mg (64%), yellow crystalline powder, m. p. 221 °C (dec). – $C_{37}H_{33}ClO_2P_2RuS$ (740.2): calcd. C 60.04, H 4.49; found C 59.08, H 4.42.

IR (Nujol): 1155, 1028 cm^{-1} (SO). – ^1H NMR ($CDCl_3$): 4.82 (s, 5H, Cp), 3.36 (s, 2H, SCH_2). – ^{13}C NMR ($CDCl_3$): 82.6 (s, Cp), 74.1 (s, SCH_2). – ^{31}P NMR ($CDCl_3$): 13.4 (s). **6d:** Yield 65 mg (45%), yellow crystalline powder, m. p. 202 °C (dec). – $C_{34}H_{34}O_4P_2RuS$ (701.7): calcd. C 58.20, H 4.88; found C 58.67, H 4.98.

IR (Nujol): 1701 cm^{-1} (CO), 1152, 1021 cm^{-1} (SO). – ^1H NMR ($CDCl_3$): 4.99 (s, 5H, Cp), 4.03 (q, J = 7.2 Hz, 2H, OCH_2), 3.13 (s, 2H, SCH_2), 1.18 (t, J = 7.2 Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): 165.5 (s, CO), 82.8 (s, Cp), 74.8 (s, SCH_2), 59.9 (s, OCH_2), 13.9 (s, CH_3). – ^{31}P NMR ($CDCl_3$): 12.8 (s).

[CpRu(PMe_3)$_2$(CH_2R)] (**7b, c**)

The alkyl complexes were obtained by reacting [CpRu(PMe_3)$_2$Cl] (2.00 mmol) with a stoichiometric amount of the corresponding Grignard reagent as described in ref [24].

7b: Yield 0.82 g (92%), yellow oil. – ^1H NMR (C_6D_6): 4.21 (s, 5H, Cp), 2.28 (t, J = 7.0 Hz, 2H, $RuCH_2$), 1.04 (vt, N = 8.2 Hz, 18H, PMe_3). – ^{31}P NMR (C_6D_6): 12.4 (s).

7c: Yield 0.67 g (82%), yellow oil. – ^{1}H NMR (C_6D_6): 4.42 (s, 5H, Cp), 1.05 (vt, N = 8.0 Hz, 18H, PMe_3), 0.31 (s, 9H, $SiMe_3$), –0.90 (t, *J* = 7.6 Hz, 2H, $RuCH_2$). – ^{31}P NMR (C_6D_6): 12.4 (s).

*[CpRu(PMe$_3$)$_2$(SO$_2$CH$_2$R)] (**8a - c**)*

Sulfur dioxide was bubbled briefly through a solution of the alkyl complex (1.00 mmol) in toluene (50 ml). The mixture was then evaporated to 5 ml and the product precipitated by adding hexane.

8a: Yield 0.43 g (95%), yellow crystalline powder, m. p. 181 °C (dec).

IR (Nujol): 1156, 1028 cm^{-1} (SO). – ^{1}H NMR ($CDCl_3$): 4.64 (s, 5H, Cp), 4.06 (s, 2H, SCH_2), 1.49 (vt, N = 9.3 Hz, 18H, PMe_3). – ^{13}C NMR ($CDCl_3$): 82.7 (s, Cp), 78.9 (s, SCH_2), 22.8 (ABX system, N = 32 Hz, PMe_3). – ^{31}P NMR ($CDCl_3$): 10.5 (s).

8b: Yield 0.48 g (95%), yellow crystalline powder, m. p. 151 °C (dec).

IR (Nujol): 1156, 1026 cm^{-1} (SO). – ^{1}H NMR ($CDCl_3$): 4.64 (s, 5H, Cp), 3.96 (s, 2H, SCH_2), 1.46 (vt, N = 9.3 Hz, 18H, PMe_3). – ^{13}C NMR ($CDCl_3$): 82.7 (s, Cp), 78.9 (s, SCH_2), 22.8 (ABX system, N = 32 Hz, PMe_3). – ^{31}P NMR ($CDCl_3$): 10.6 (s).

8c: Yield 0.46 g (98%), colorless crystalline powder, m. p. 173 °C (dec).

IR (Nujol): 1148, 1028 cm^{-1} (SO). – ^{1}H NMR ($CDCl_3$): 4.58 (s, 5H, Cp), 2.82 (s, 2H, SCH_2), 1.39 (vt, N = 9.3 Hz, 18H, PMe_3), –0.04 (s, 9H, $SiMe_3$). – ^{13}C NMR ($CDCl_3$): 83.3 (s, Cp), 69.9 (s, SCH_2), 22.7 (ABX system, N = 32 Hz, PMe_3), 0.3 (s, $SiMe_3$). – ^{31}P NMR ($CDCl_3$): 11.2 (s).

*[CpRu(PMe$_3$)$_2$(SO$_2$CHMeSiMe$_3$)] (**8d**)*

To a suspension of **9** (0.41 g, 1.00 mmol) in THF (10 ml) was added at 0 °C a solution of 1-(trimethylsilyl)-ethylmagnesium chloride in THF (1.20 mmol). After a few minutes all the solids dissolved whereupon methanol (0.50 ml) was added to quench any excess Grignard reagent. The mixture was evaporated to dryness and the residue chromatographed over silica with acetone as eluent followed by recrystallization from toluene / hexane.

8d: Yield 0.31 g (65%), colorless crystalline powder, m. p. 156 °C (dec).

IR (Nujol): 1149, 1023 cm^{-1} (SO). – ^{1}H NMR ($CDCl_3$): 4.67 (s, 5H, Cp), 2.41 (q, *J* = 7.6 Hz, 1H, SCH), 1.56 (d, *J* = 9.2 Hz, 9H, PMe_3), 1.54 (d, *J* = 9.2 Hz, 9H, PMe_3), 1.25 (d, *J* = 7.6 Hz, 3H, Me), 0.13 (s, 9H, $SiMe_3$). – ^{13}C NMR ($CDCl_3$): 82.5 (s, Cp), 68.7 (s, SCH_2), 23.0 (d, *J* = 29 Hz, PMe_3), 22.8 (d, *J* = 30 Hz, PMe_3), 13.5 (s, Me), 1.4 (s, $SiMe_3$). – ^{31}P NMR ($CDCl_3$): 11.9, 10.3 (AB system, *J* = 46 Hz).

*[CpRu(PMe$_3$)$_2$(SO$_2$)]Cl (**9**)*

Sulfur dioxide was bubbled briefly through a solution of [CpRu(PMe_3)$_2$Cl] (0.70 g, 2.00 mmol) in dichloromethane (50 ml), causing color changes from orange *via* black and red to yellow. The mixture was then evaporated to dryness and the product washed with diethylether.

9: Yield 0.82 g (98%), yellow crystalline powder. – ^{1}H NMR (acetone-d_6): 5.72 (s, 5H, Cp), 1.83 (vt, N = 9.2 Hz, 18H, PMe_3). – ^{13}C NMR (acetone-d_6): 92.0 (s, Cp), 21.5 (ABX system, N = 32 Hz, PMe_3). – ^{31}P NMR (acetone-d_6): 4.9 (s).

*[CpRu(PMe$_3$)$_2${S(O)(OEt)CH$_2$SiMe$_3$}]PF$_6$ (**10**)*

To a cooled (–70 °C) solution of **8c** (47 mg, 0.10 mmol) in dichloromethane (5 ml) triethyloxonium hexafluorophosphate (25 mg, 0.10 mmol) was added. The mixture was briefly warmed to room temperature and evaporated to dryness. The residue was washed with benzene and recrystallized from dichloromethane / diethylether. The product was contaminated with 15% (by NMR) of **11a** which could not be removed.

10: Yield 57 mg (89%), colorless crystalline powder. – ^{1}H NMR (acetone-d_6): 5.27 (s, 5H, Cp), 4.10 (m, 2H, OCH_2), 3.88, 3.53 (AB system, *J* = 13.4 Hz, 2H, SCH_2), 1.75 (d, *J* = 9.6 Hz, 9H, PMe_3), 1.70 (d, *J* = 9.7 Hz, 9H, PMe_3), 1.39 (t, *J* = 7.1 Hz, 3H, CH_3), 0.22 (s, 9H, $SiMe_3$). – ^{31}P NMR (acetone-d_6): 6.1, 4.9 (AB system, *J* = 42 Hz).

*[CpRu(PMe$_3$)$_2$ (O=S=CH$_2$)]PF$_6$ (**11a**)*

To a cooled (–40 °C) solution of **8c** (0.47 g, 1.00 mmol) in dichloromethane (25 ml) triethyloxonium hexafluorophosphate (0.25 g, 1.00 mmol) was added. The mixture was warmed to room temperature and stirred for 2 h. After evaporation to dryness the residue was washed with diethylether and recrystallized from dichloromethane / diethylether.

11a: Yield 0.48 g (92%), colorless crystalline powder, m. p. 91 - 94 °C (dec). – $C_{12}H_{25}F_6OP_3RuS$ (525.4): calcd. C 27.43, H 4.80; found C 27.67, H 4.57.

IR (Nujol): 1040 cm^{-1} (SO). – ^{1}H NMR (acetone-d_6, –70 °C): 5.56 (s, 5H, Cp), 4.23 (dd, *J* = 5.2 Hz, *J′* = 1.4 Hz, 1H, OSCH), 3.45 (dd, *J* = 15.4 Hz, *J′* = 5.2 Hz, 1H, OSCH), 1.86 (d, *J* = 10.0 Hz, 9H, PMe_3), 1.67 (d, *J* = 10.2 Hz, 9H, PMe_3). – ^{13}C NMR (acetone-d_6, –70 °C): 92.4 (s, Cp), 60.2 (d, *J* = 13 Hz, OSC), 21.8 (m, PMe_3). – ^{31}P NMR (acetone-d_6, –70 °C): 13.9, 11.9 (AB system, *J* = 45 Hz). – ^{31}P NMR (acetone-d_6, 20 °C): 9.8 (s, br). – ^{31}P NMR (acetone-d_6, 50 °C): 9.9, 8.8 (AB system, *J* = 44 Hz).

*[CpRu(PMe$_3$)$_2$(O=S=CHMe)]PF$_6$ (**Z-11b**)*

NH_4PF_6 (0.18 g, 1.10 mmol) was added to a solution of **8d** (0.48 g, 1.00 mmol) in acetone (50 ml). The mixture was stirred for 24 h and any liberated ammonia removed by repeated evacuation. The mixture was then evaporated to dryness, the residue dissolved in dichloromethane (10 ml) and filtered over celite, the solvent evaporated and the product recrystallized from dichloromethane / diethylether.

***Z*-11b:** Yield 0.50 g (92%), greenish-yellow crystalline powder, m. p. 112 °C (dec). $C_{13}H_{27}F_6OP_3RuS$ (539.4): calcd. C 28.95, H 5.05; found C 29.01, H 5.06.

IR (Nujol): 1022 cm^{-1} (SO). – ^{1}H NMR (acetone-d$_6$): 5.45 (s, 5H, Cp), 3.51 (ddq, J = 18.6 Hz, J' = 6.2 Hz, J'' = 1.0 Hz, 1H, OSCH), 2.12 (d, J = 6.2 Hz, 3H, CH_3), 1.73 (t, J = 10.3 Hz, 18H, PMe_3). - ^{13}C NMR (acetone-d$_6$): 94.3 (s, Cp), 64.1 (d, J = 12 Hz, OSC), 22.4 (d, J = 27 Hz, PMe_3), 19.9 (d, J = 29 Hz, PMe_3), 16.1 (s, CH_3). - ^{31}P NMR (acetone-d$_6$): 7.3, 6.4 (AB system, J = 46 Hz).

*[CpRu(dppm){SO(OTf)CH$_2$CH$_2$Ph}]OTf (**12**)*

Triflic anhydride (32 μl, 0.18 mmol) was added to a cooled (0 °C) solution of **6c** (120 mg, 0.17 mmol) in dichloromethane (5 ml), resulting in a rapid color change to dark blue. The solvent was removed under vacuum and the remaining dark blue oil washed repeatedly with 5 ml portions of benzene and diethylether.

12: Yield 145 mg (87%), dark blue oil. – ^{1}H NMR ($CDCl_3$): 5.51 (s, 5H, Cp), 3.73 (m, 2H, SCH_2), 3.55 (m, 2H, CH_2Ph). – ^{13}C NMR ($CDCl_3$): 96.5 (s, Cp), 75.0 (s, SCH_2), 30.9 (s, CH_2Ph), CF_3 signals not detected. – ^{19}F NMR ($CDCl_3$): –83.1 (s, SOTf), –77.9 (s, OTf^-). – ^{31}P NMR ($CDCl_3$): -8.8, –16.9 (AB system, J = 87 Hz).

*[CpRu(dppm)(S=CHR)]PF$_6$ (**3a, b, 13**), from sulfinate complexes **6a, b, f***

Acetyl chloride (1.50 ml, 21 mmol) and sodium hexafluorophosphate (0.34 g, 2.00 mmol) were added to a solution of the respective sulfinate complex (2.00 mmol) in dichloromethane (50 ml), resulting in a color change to purple. After 2 h the mixture was evaporated to dryness. The crude product was found by NMR (^{1}H, ^{31}P) to contain 70% thioaldehyde complex, 30% [CpRu(dppm)(SO_2)]PF_6 [29], and a corresponding amount of free benzaldehyde. The mixture was chromatographed over silica. With dichloromethane a yellow band was eluted first, followed by a broad purple band which was eluted with dichloromethane / acetone 2:1. This was collected, evaporated, and recrystallized from dichloromethane / diethyl ether.

3a: Yield 0.95 g (56%), purple crystalline powder, identical by m. p. and NMR with an authentic sample [20].

3b: Yield 1.11 g (65%), purple crystalline powder, identical by m. p. and NMR with an authentic sample [20].

13: Yield 1.10 g (74%), beige crystalline powder, m. p. 238 °C (dec). – $C_{31}H_{29}F_6P_3RuS$ (741.6): calcd. C 50.21, H 3.94; found C 48.81, H 4.11. – ^{1}H NMR ($CDCl_3$): 5.86 (s, 5H, Cp), 5.27 (s, br, 1H, SCH), 2.79 (d, J = 13.8 Hz, 1H, SCH). – ^{13}C NMR ($CDCl_3$): 91.2 (s, Cp), 35.4 (s, SCH_2). – ^{31}P NMR ($CDCl_3$): 4.1, -1.5 (AB system, J = 96 Hz).

*[CpRu(PMe$_3$)$_2$(O=S=CHR)]PF$_6$ (**Z-2a, b**, from sulfinate complexes **8a, b***

To a cooled (–70 °C) solution of the sulfinate complex (1.00 mmol) and poly(vinylpyridine) (0.50 g) in dichloromethane (50 ml) trifluoroacetic acid anhydride (0.13 g, 0.50 mmol) was added in three portions over a course of 2 h. After a further 1 h at this temperature, NH_4PF_6 (0.20 g, 1.20 mmol) was added. The mixture was evaporated to dryness and the residue chromatographed over silica. A brown band was eluted first with dichloromethane / acetone 10:1 followed by a brownish-red band which was eluted with dichloromethane / acetone 4:1. Recrystallization from dichloromethane / diethylether gave the sulfine complexes as beige or brownish crystalline solids.

***Z*-2a:** Yield 0.14 g (24%), brownish crystalline, slightly impure (by NMR) powder. – ^{1}H NMR (acetone-d$_6$): 6.10 (s, br, 1H, OSCH), 5.47 (s, 5H, Cp), 1.81 (m, 18H, PMe_3). – ^{31}P NMR (acetone-d$_6$): 6.3 (s).

***Z*-2b:** Yield 0.13 g (21%), beige crystalline powder, m. p. 92 °C (dec). – $C_{18}H_{28}ClF_6OP_3RuS$ (635.9): calcd. C 34.00, H 4.44; found C 33.84, H 4.36. – ^{1}H NMR (acetone-d$_6$): 6.30 (s, br, 1H, OSCH), 5.49 (s, 5H, Cp). – ^{31}P NMR (acetone-d$_6$): 6.3 (s).

*[CpRu(dppm)(O=S=CHR)]PF$_6$ (**4a-c**), from sulfinate complexes **6a-d***

To a cooled (–70 °C) solution of the sulfinate complex (1.00 mmol) and poly(vinylpyridine) (0.50 g) in dichloromethane (50 ml) trifluoroacetic acid anhydride (0.13 g, 0.50 mmol) was added in three portions over a course of 2 h. After a further 1 h at this temperature, NH_4PF_6 (0.20 g, 1.20 mmol) was added. The mixture was evaporated to 10 ml and filtered over celite. The filtrate was taken to dryness and the residue washed with diethylether (30 ml) and toluene (30 ml). Recrystallization from dichloromethane / diethylether gave the sulfine complexes as 5:1 (**4a, b**) or 2:1 (**4d**) mixtures (by NMR) of *Z* and *E* isomers.

4a: Yield 0.70 g (84%), brownish red crystalline powder, m. p. 88 °C (dec). – $C_{37}H_{33}F_6OP_3RuS$ (833.7): calcd. C 53.30, H 3.99; found C 53.76, H 4.07. – IR (Nujol): 1035 cm^{-1} (SO).

***Z*-4a:** ^{1}H NMR (acetone-d_6, –70 °C): 5.07 (s, 5H, Cp), 4.01 (d, J = 17.2 Hz, 1H, OSCH). – ^{13}C NMR (acetone-d_6): 91.2 (s, Cp). – ^{31}P NMR (acetone-d_6, –70 °C): 1.7, 1.2 (AB system, J = 96 Hz).

***E*-4a:** See data given above.

4b: Yield 0.75 g (87%), brownish red crystalline powder. – $C_{37}H_{32}ClF_6OP_3RuS$ (868.2): calcd. C 51.19, H 3.72; found C 52.05, H 4.21. – IR (Nujol): 1033 cm^{-1} (SO).

***Z*-4b:** ^{1}H NMR (acetone-d_6, –70 °C): 5.31 (s, 5H, Cp), 4.08 (vt, N = 19.2 Hz, 1H, OSCH). – ^{13}C NMR (acetone-d_6): 90.0 (s, Cp). – ^{31}P NMR (acetone-d_6, -70 °C): 0.2, 0.1 (AB system, J = 96 Hz).

***E*-4b:** See data given above.

4d: Yield 0.67 g (81%), beige crystalline powder, m. p. 103 °C (dec). – $C_{34}H_{33}F_6O_3P_3RuS$ (829.7): calcd. C 49.22, H 4.01. found C 49.53, H 3.97. – IR (Nujol): 1717, 1704 cm^{-1} (CO), 1026 cm^{-1} (SO).

***Z*-4d:** ^{1}H NMR ($CDCl_3$): 5.47 (s, 5H, Cp), 3.51 (dq, J = 10.6 Hz, J' = 7.1 Hz, 1H, OCH_2), 2.55 (dq, J = 10.6 Hz, J' = 7.1 Hz, 1H, OCH_2), 0.84 (t, J = 7.1 Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): 165.2 (s, CO), 94.4 (s, Cp), 68.1 (s, OCH_2), 62.9 (d, J = 14 Hz, OSC), 13.0 (s, CH_3). – ^{31}P NMR ($CDCl_3$): –2.3, –11.4 (AB system, J = 102 Hz).

***E*-4d:** ^{1}H NMR ($CDCl_3$): 5.47 (s, 5H, Cp), 4.18 (m, br, 1H, OCH_2), 3.95 (m, br, 1H, OCH_2), 0.91 (t, J = 7.4 Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): Signals obscured by the major isomer. – ^{31}P NMR ($CDCl_3$): –6.0, –12.5 (AB system, J = 96 Hz).

[CpRu(dppm)(O=S=CHCl)]PF_6 (**14**)

Acetyl chloride (0.50 ml, 7.0 mmol) and sodium hexafluorophosphate (0.07 g, 0.41 mmol) were added to a solution of **6e** (0.24 g, 0.40 mmol) in dichloromethane (10 ml). After 2 h the mixture was evaporated to dryness and the residue washed with diethylether. The crude product was chromatographed over a short (7 cm) silica column. With dichloromethane / acetone 20:1 a yellow band was eluted which was collected, evaporated, and recrystallized from dichloromethane / diethyl ether.

14: Yield 0.16 g (51%), yellow crystalline powder, m. p. 125 °C (dec). – $C_{31}H_{28}ClF_6OP_3RuS$ (792.1): calcd. C 47.01, H 3.56. found C 47.03, H 3.85.

IR (Nujol): 1028 cm^{-1} (SO). – ^{1}H NMR ($CDCl_6$): 5.21 (s, 5H, Cp), 5.05 (dd, J = 18.9 Hz, J' = 2.1 Hz, 1H, OSCH). – ^{13}C NMR ($CDCl_6$): 97.3 (s, Cp). – ^{31}P NMR ($CDCl_6$): 9.5, –10.1 (AB system, J = 92 Hz).

[CpRu(PMe_3)$_2$ (O=S=CH_2)]PF_6 (**11a**)*, from [CpRu(PMe_3)$_2$(CH_3)]* (**15**)

To a cooled (–70 °C) solution of **15** (0.33 g, 1.00 mmol) in dichloromethane (20 ml) triphenylcarbenium hexafluorophosphate (0.39 g, 1.00 mmol) was added. Within 20 min at this temperature the color of the mixture turned red. Thiirane-1-oxide (80 μl, 1.16 mmol) was added causing a gradual color change to greenish yellow. The mixture was warmed to room temperature and stirred for 1 h. After evaporation to 2 ml the product was precipitated by adding diethylether (30 ml).

11a: Yield 0.39 g (75%), colorless crystalline powder, identical by m. p. and NMR with an authentic sample.

The formation of the carbene complex [CpRu(PMe_3)$_2$(CH_2)]PF_6 (**16**) in this reaction was demonstrated by an NMR tube experiment: Addition of Ph_3CPF_6 to a solution of **15** in CD_2Cl_2 at –70 °C produced new ^{1}H signals at δ = 16.30 (t, J = 4.2 Hz, 2H, $RuCH_2$), 4.99 (s, 5H, Cp), 1.84 (vt, N = 8.9 Hz, 18H, PMe_3).

*[Cp*Ru(PMe_3)$_2$(O=S=CH_2)]PF_6* (**18**)

To a cooled (0 °C) dark green solution of **17** (110 mg, 0.19 mmol) in dichloromethane (15 ml) a solution of diazomethane in diethylether (0.19 mmol) was added. Gas evolution and an immediate color change to greenish yellow was observed. The mixture was evaporated to 0.5 ml and the product precipitated by adding diethylether. The supernatant was syringed off and the residue washed twice with diethylether.

18: Yield 93 mg (84%), off-white crystalline powder, m. p. 177 °C (dec). – $C_{17}H_{35}F_6OP_3RuS$ (595.5): calcd. C 34.29, H 5.92; found C 33.99, H 5.94.

IR (Nujol): 1036 cm^{-1} (SO). – ^{1}H NMR (CD_2Cl_2): 3.41 (dd, J = 16.4 Hz, J' = 5.4 Hz, 1H, OSCH), 2.74 (d, J = 5.4 Hz, 1H, OSCH), 1.66 (t, J = 1.2 Hz, 15H, Cp*), 1.65 (d, J = 9.4 Hz, 9H, PMe_3), 1.51 (d, J = 9.4 Hz, 9H, PMe_3). – ^{13}C NMR (CD_2Cl_2): 101.74 (s, Cp*), 52.9 (d, J = 13 Hz, OSC), 20.5 (d, J = 34 Hz, PMe_3), 18.2 (d, J = 34 Hz, PMe_3), 10.0 (s, Cp*). – ^{31}P NMR (CD_2Cl_2): 6.1, 3.5 (AB system, J = 52 Hz).

[CpRu(PMe_3)$_2$(EtOS=CHMe)](PF_6)$_2$ (**19**)

Triethyloxonium hexafluorophosphate (125 mg, 0.50 mmol) was added to a solution of **8d** (120 mg, 0.25 mmol) in dichloromethane (10 ml). The mixture was stirred at room temperature for 4 h and then evaporated to dryness. The residue was recrystallized from dichloromethane / acetone.

19: Yield 120 mg (67%), colorless crystalline powder, m. p. 67 °C (dec). – $C_{15}H_{32}F_{12}OP_4RuS$ (713.4): calcd. C 25.25, H 4.52; found C 25.21, H 4.57. – ^{1}H NMR (acetone-d_6): 6.21 (s, 5H, Cp), 4.52 (m, 2H, OCH_2), 4.18 (ddq, J = 20.5 Hz, J' = 6.5 Hz, J'' = 1.0 Hz, 1H, SCH), 2.39 (dd, J = 6.5 Hz, J' = 2.0 Hz, 3H, CH_3), 2.10 (d, J = 10.9 Hz, 9H, PMe_3), 1.84 (d, J = 11.3 Hz, 9H, PMe_3), 1.43 (t, J = 7.0 Hz, 3H, CH_3). – ^{13}C NMR (acetone-d_6): 96.9 (s, Cp),

76.8 (s, OCH_2), 54.6 (dd, J = 7 Hz, J' = 2 Hz, OSC), 21.5 (d, J = 38 Hz, PMe_3), 20.4 (d, J = 37 Hz, PMe_3), 16.3 (s, CH_3), 15.6 (s, CH_3). – ^{31}P NMR (acetone-d_6): 6.7, 5.2 (AB system, J = 37 Hz).

*[CpRu(PMe$_3$)$_2$(O$_2$S=CH$_2$)]PF$_6$ (**20a**)*

To a cooled (0 °C) solution of **11a** (0.26 g, 0.50 mmol) in dichloromethane (4 ml) freshly prepared iodosylbenzene (0.20 g, 0.90 mmol) was added. The mixture was stirred for 4 h. The yellow precipitate was collected by filtration, washed with diethylether, and recrystallized from dichloromethane / diethylether.

20a: Yield 97 mg (36%), yellow crystalline powder, m. p. 109 °C (dec). – $C_{12}H_{25}F_6O_2P_3RuS$ (541.4): calcd. C 26.62, H 4.65; found C 27.95, H 4.72.

IR (Nujol): 1220, 1104 cm^{-1} (SO). – ^{1}H NMR (acetone-d_6): 5.91 (s, 5H, Cp), 2.57 (d, J = 3.3 Hz, 1H, SCH_2), 1.99 (d, J = 11.0 Hz, 9H, PMe_3), 1.85 (d, J = 11.6 Hz, 9H, PMe_3). 0.70 (dd, J = 17.6 Hz, J' = 3.3 Hz, 1H, SCH_2). – ^{13}C NMR (acetone-d_6): 96.0 (s, Cp), 20.6 (d, J = 35 Hz, PMe_3), 19.8 (d, J = 36 Hz, PMe_3), –22.3 (d, J = 5 Hz, SCH_2). – ^{31}P NMR (acetone-d_6): 9.7, 7.7 (AB system, J = 42 Hz).

*[Cp*Ru(PMe$_3$)$_2$(O$_2$S=CH$_2$)]PF$_6$ (**20b**)*

To a cooled (–70 °C) solution of **18** (24 mg, 0.04 mmol) in dichloromethane (10 ml) a solution of dimethyldioxirane in acetone (0.05 mmol) was added. The mixture was stirred for 5 min and then evaporated to dryness. The residue was dissolved in dichloromethane (0.5 ml) and the product precipitated by adding diethylether.

20b: Yield 23 mg (95%), beige crystalline powder, identical by m. p. and NMR with an authentic sample [21].

*X-ray structure determination of [CpRu(dppm){S=CH(4-C$_6$H$_4$Cl)}]PF$_6$ (**3b**)*

Deep red crystals suitable for structure determination were obtained from acetone / hexane solutions. 25 centered reflections from a crystal of the dimensions given in Table 2 gave a monoclinic unit cell. Data were collected from one fourth of the reflection sphere in the range $2° < \theta < 23.5°$ (Enraf-Nonius CAD 4 diffractometer, Mo-K_α radiation, graphite monochromator, filter factor 16.4). An empirical absorption correction based on the counts of 9 reflections was applied. The structure was solved by Patterson methods (program SHELXS 86) [54] in the space group $P2_1/n$ (Nr. 14). In the asymmetric unit one molecule of acetone was found which was refined anisotropically. H atoms were included in idealized positions, coupled to their respective carbon atoms. Least-squares cycles using the SHELXL 93 program package [55] led to the R values given in Table 2. The 5 highest maxima of the final difference Fourier map were all below 0.480 e Å^{-3}. Further details of the structure determination may be obtained from Cambridge Crystallographic Data Centre on quoting the deposition number CCDC 175701.

Table 2. Details of the structure determination of [CpRu(dppm){S=CH(4-C_6H_4Cl)}]PF_6 · acetone (**3b** · acetone).

Formula	$C_{37}H_{32}ClF_6P_3RuS \cdot C_3H_6O$
F. wt.	910.2
Color	deep red
Crystal size (mm)	0.2×0.2×0.05
Temperature (K)	293(2)
λ (Å)	0.70930
Space group	$P\,2_1/n$ (No. 14)
a (Å)	11.312(6)
b (Å)	19.795(6)
c (Å)	18.838(11)
β (°)	93.96(3)
V (Å^3)	4208(4)
Z	4
ρ (calcd) (mg mm^{-3})	1.437
μ (Mo-K_α) (cm^{-1})	2.49
θ Range (°)	2.0 - 23.4
Index range h	0, 12
k	0, 22
l	–21, 21
Measured reflections	6568
Independent reflections	6214
Parameters	478
R^a	0.0618
$wR_2{}^a$	0.1316

[a] $I_0 > 2\,\sigma(I_0)$.

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