Sulfur(IV) Compounds as Ligands, 23[◇]

C−C Coupling Reactions of (Sulfene)ruthenium Complexes with Enolates

Wolfdieter A. Schenk* and Jürgen Bezler

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany
Fax: (internat.) + 49(0)931/888-4605
E-mail: wolfdieter.schenk@mail.uni-wuerzburg.de

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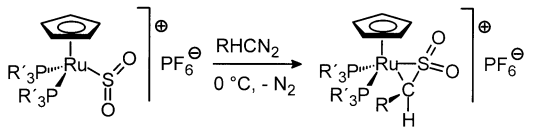
Sulfene complexes $[CpRu(PR'_3)_2(RHC{=}SO_2)]PF_6$ (**2a**−**d**) are obtained from the corresponding sulfur dioxide complexes **1a**−**c** and diazomethane or -ethane. Reaction of $[CpRu(dppm)(SO_2)]Cl$ (**1d**) and phenyldiazomethane gives the chlorobenzylsulfinato complex $[CpRu(dppm)(SO_2CHPhCl)]$ (**3**). Alternatively, **2a** may be synthesized by sulfur dioxide addition to the carbene complex $[CpRu(dppm)(CH_2)]PF_6$ (**5**) which, in turn, is obtained from the corresponding methyl complex $[CpRu(dppm)(CH_3)]$ and $[Ph_3C]PF_6$. Treatment of **2a**−**d** or **3** with the enolates of cyclic 2-methyl-1,3-diketones, methyl malonates, open-chain cyano or β-oxo esters, and cyclic β-oxo esters gives the C−C coupling products **6a**, **b**, **7a**−**e**, **8a**−**c**, **9a**−**c** in high yields and, in one case, with high diastereoselectivity as well. The functionalized sulfinate ligands thus formed may be alkylated and subsequently removed from the metal center by ligand substitution with acetonitrile. After $MeCN/SO_2$ exchange, the ruthenium complex can be recycled.

Highly reactive and unstable molecules can often be stabilized by coordination to a transition metal − this principle is certainly one of the most fascinating aspects of organic transition-metal chemistry.[1] In an ideal case, the species under consideration is not only "tamed", but is sufficiently modified such that it undergoes novel types of reactions. Sulfenes $R^1R^2C{=}SO_2$ are short-lived intermediates that may be generated for example by 1,2-elimination or [2 + 4]-cycloreversion reactions.[2] Their typical transformations include 1,2-additions across the C=S double bond, nucleophilic addition at sulfur, and cycloadditions.[2][3][4][5][6][7] Recently, we have synthesized $\eta^2(C,S)$-sulfene complexes of the type $[CpRu(PR_3)_2(CH_2{=}SO_2)]^+$ by methylene addition to the corresponding sulfur dioxide complexes.[8][9] In these species, the formal polarity of the sulfene is reversed. Nucleophiles such as halide or pseudohalide ions, amines and phosphanes are added at the carbon atom. With enamines, C−C coupling occurs with high yield and chemoselectivity.[9] We now report on the addition of enolates to sulfene complexes.



1a - c **2a - d** (1)

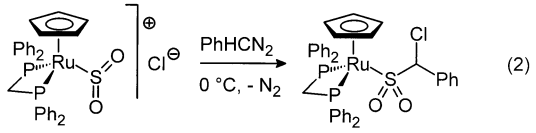
R′3P	dppm	dppe	(Me3P)2	dppm
R	H	H	H	Me
	1a	**1b**	**1c**	
	2a	**2b**	**2c**	**2d**

Results

Synthesis of Sulfene Complexes

The reaction of the sulfur dioxide complex **1a** with diazomethane or -ethane to give the sulfene complexes **2a**,**d** has been described previously.[9] Similarly, **1b**, **c** give the sulfene complexes **2b**, **c** (eq. 1).

Attempts to perform analogous reactions of **1a** with phenyldiazomethane, diphenyldiazomethane, or diazoacetic acid esters were unsuccessful. However, when we treated the chloride salt **1d** with phenyldiazomethane, we obtained the chlorobenzylsulfinate complex **3** in high yield (eq. 2). Complex **3** represents a synthetic equivalent for the corresponding phenylsulfene complex (see below).



1d **3** (2)

An alternative synthetic access to sulfene complexes is provided by the addition of SO_2 to carbene complexes.[10][11] Thus, when the methyl complex **4** is treated at low temperature with triphenylmethyl hexafluorophosphate, a red solution of the carbene complex **5** is obtained,[12] which, upon addition of SO_2, undergoes immediate discoloration to yield **2a** (eq. 3). However, in spite of

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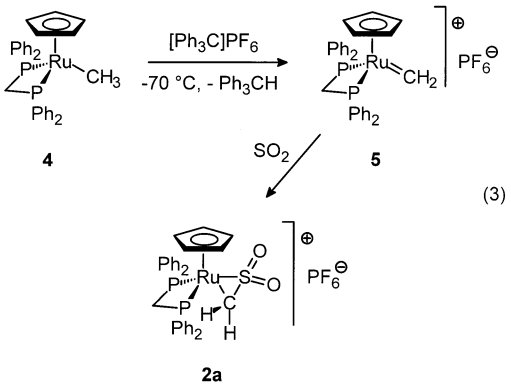
numerous attempts, we have not been able to extend this reaction to complexes of substituted sulfenes.



(3)

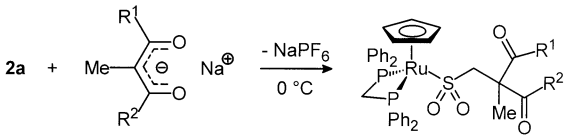
2b, **c** are slightly yellow crystalline compounds which, even at −20°C, decompose within a few days. **2c** has spectroscopic properties very similar to those of **2a** and the crystallographically characterized complex $[Cp^*Ru(PMe_3)_2(\eta^2\text{-}CH_2{=}SO_2)]PF_6$.[9] **2b**, on the other hand, is unusual in that it is fluxional on the NMR timescale due to a rapid rotation of the sulfene ligand. Standard treatment[13] of the temperature-dependent ^{31}P-NMR spectra using a two-site exchange model[14] yields an activation barrier of $\Delta G^{\neq} = 60$ kJ mol^{-1}. A similar ligand rotation has been found for the analogous sulfur trioxide complex $[Cp^*Ru(PMe_3)_2(\eta^2\text{-}O{=}SO_2)]PF_6$.[15] In the ^{1}H-NMR spectra, the two non-equivalent protons of the methylene groups give rise to two widely separated signals with the typical geminal coupling of ca. 4 Hz. The high-field signals show additional splitting due to strong coupling with one of the two phosphorus atoms. The ^{13}C resonance of the sulfene carbon atom appears as a doublet at $\delta = -20$. Finally, two fairly strong absorptions in the infrared spectrum at $\tilde{\nu} \approx 1230$ and 1100 cm^{-1} are typical for the $\eta^2(C,S)$-coordinated sulfene ligand.[9]

The chlorobenzylsulfinato complex **3** is a yellow, crystalline, air-stable compound. The two diastereotopic phosphorus atoms give rise to a narrow AB system in the ^{31}P-NMR spectrum, while the resonance of the α-carbon nucleus at the sulfur atom is split into a narrow doublet of doublets due to coupling with the two non-equivalent phosphorus nuclei. Here, the ν(SO) absorptions fall in the typical range of *S*-sulfinato complexes.[16]

Reactions with Enolates

Reactions of **2a** in THF with the sodium enolates of 2-methylcyclopentane-1,3-dione and 2,5,5-trimethylcyclohexane-1,3-dione gave the expected addition compounds **6a**, **b** in good yields (eq. 4).

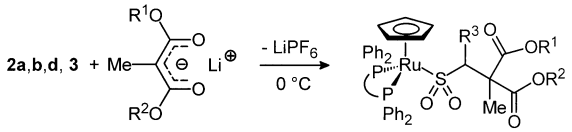
Similarly, treatment of **2a**, **b** and **d** with the lithium enolates of the diethyl or isopropylidene esters of methylmalonic acid yielded the C−C coupling products **7a**−**d**, while



R^1, R^2	$-CH_2CH_2-$	$-CH_2CMe_2CH_2-$
	6a	**6b**

(4)

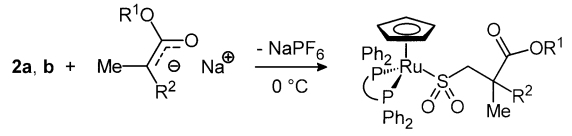
the analogous phenyl derivative **7e** was obtained from the chlorobenzylsulfinate complex **3** (eq. 5).



R^1, R^2	Et, Et	$-CMe_2-$	Et, Et	Et, Et	Et, Et
R^3	H	H	H	Me	Ph
$Ph_2P\frown PPh_2$	dppm	dppm	dppe	dppm	dppm
	7a	**7b**	**7c**	**7d**	**7e**

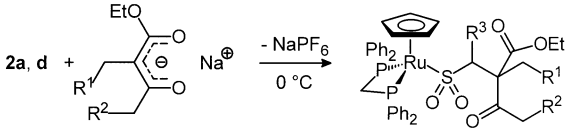
(5)

Products **6** and **7** were obtained as light-yellow crystalline solids. Due to their symmetrical structure they have fairly simple NMR spectra, which are in full accord with the constitutions shown in eqs. 4 and 5. Of note is the significant downfield shift (> 90 ppm) of the resonance of the former sulfene carbon atom that accompanies its release from the ruthenium atom. In similar experiments, the sulfene complexes **2a**, **b** were treated with the ester enolates of 2-methyl-3-oxobutyric acid and 2-cyanopropionic acid (eq. 6), while **2a**, **d** were allowed to react with the deprotonated esters of 2-oxocyclopentane- and 2-oxocyclohexane-1-carboxylic acids (eq. 7).



R^1	Et	Et	*t*-Bu
R^2	C(O)Me	CN	C(O)Me
$Ph_2P\frown PPh_2$	dppm	dppm	dppe
	8a	**8b**	**8c**

(6)



R^1, R^2	$-CH_2-$	$-CH_2CH_2-$	$-CH_2-$
R^3	H	H	Me
	9a	**9b**	**9c**

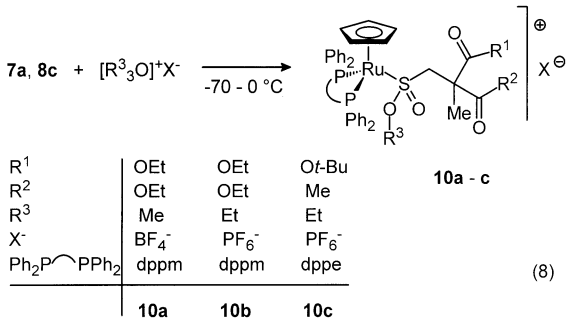
(7)

Again, the expected coupling products were obtained in good yields as light-yellow, air-stable, crystalline materials.

Since a stereocenter adjacent to the sulfene carbon atom is formed in this reaction, the methylene protons as well as the phosphorus nuclei become diastereotopic. **9c** was isolated in 71% yield as a single diastereoisomer. NMR-spectroscopic analysis of the crude reaction mixture revealed an almost quantitative formation of **9c** and none of the opposite diastereomer. Unfortunately, this compound crystallized only as stacks of very thin platelets, which were unsuitable for X-ray structure determination.

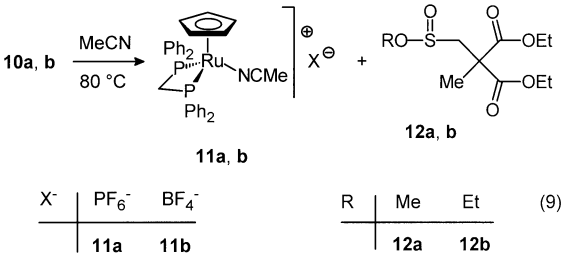
Release of the Sulfinate Ligands

The reactions of **7a** and **8c** with oxonium salts in dichloromethane (eq. 8) gave the expected *O*-alkylation[17] products **10a−c**, which were isolated in almost quantitative yield as yellow, crystalline, highly moisture-sensitive materials. Alkylation of one of the S=O functions introduces a new stereocenter at the sulfur atom and renders the methylene protons as well as the phosphorus nuclei diastereotopic. Only negligible diastereoselectivity (2%) is observed in the formation of **10c**.



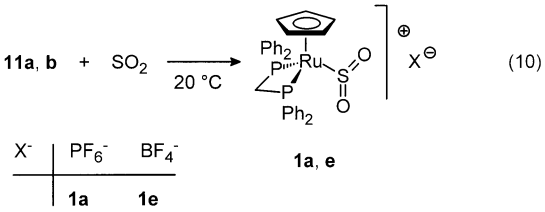
(8)

The role of sulfinic acid esters as ligands in coordination compounds has received very little attention.[17][18] Compared to sulfoxides, they are expected to be quite weak donors. Indeed, when **10a**, **b** are heated in acetonitrile a slow ligand substitution takes place yielding the known acetonitrile complex **11**[19] along with the free esters **12a**, **b** (eq. 9).



(9)

Despite the long reaction time, we observed no rearrangement[20] to the corresponding sulfones. The mixtures could be readily separated by extraction with diethyl ether, leaving **12a**, **b** in quantitative yields as colorless oils. **11** may be converted back into the starting SO_2 complex **1a** or its BF_4^- salt **1e** simply by dissolving it in liquid sulfur dioxide and allowing it to react for a few days at 20°C (eq. 10).



(10)

Discussion

The methylene transfer outlined in eq. 1 is initiated by nucleophilic attack of the diazo compound on the coordinated sulfur dioxide.[9] This explains why less nucleophilic diazo compounds do not react − phenyldiazomethane seems to represent the limiting case. The expected phenylsulfene complex was too unstable to be isolated but, due to its high electrophilicity,[9] could be trapped by the addition of chloride ions. The "inverse synthesis" of the sulfene complex **2a** as outlined in eq. 3 indicates that low-valent cationic carbene complexes such as **5**, which are normally seen as role models of electrophilic carbenes,[21] may also exhibit some nucleophilic character. A further extension of this synthesis to complexes of substituted sulfenes, however, was thwarted by the inaccessibility of the corresponding carbene complexes.

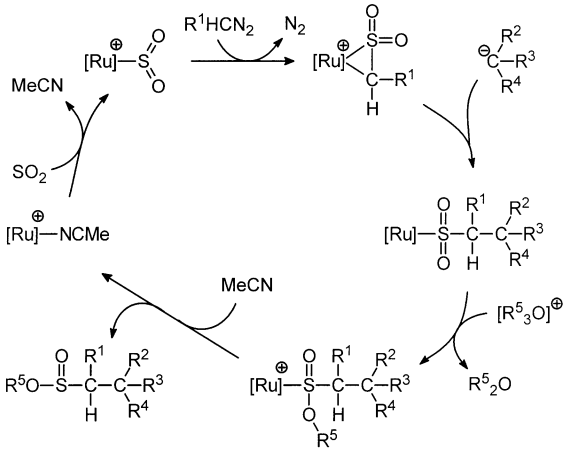
The rapid rotation of the sulfene ligand in **2b** deserves some comment. On the basis of steric considerations alone, it might be tempting to assume that the sulfene ligand can rotate more freely in the less congested dppm complex **2a**. The rotational barrier of a single-faced π-acceptor ligand, however, depends to a large extent on the spatial extension and energy difference of the occupied a′ and a″ frontier orbitals of the [$CpML_2$] fragment.[22] The antisymmetric a″ is the HOMO which is also M−L antibonding. With increasing pyramidalization of the [$CpML_2$] fragment, that is with decreasing L−M−L angle, the energy of this orbital is increased,[23] leading to a stronger fixation of the π-acceptor ligand perpendicular to the symmetry plane of the [$CpML_2$] complex.

Even in the early stages of this project, it soon became apparent that cationic sulfene complexes are highly reactive electrophiles.[8] Compared to uncoordinated sulfene, which adds nucleophiles at the sulfur atom,[2][3] the sulfene complexes studied here exhibit a reversed polarity;[9] only hard nucleophiles such as alkoxides are added at the sulfur atom.[8] Initial attempts to treat **2a** with Na[acac] gave intractable product mixtures, the spectral analyses of which indeed indicated competing C−C and C−O coupling, as well as further reactions initiated by deprotonation of the products. All these problems could readily be overcome by employing salts of tertiary C−H acidic compounds. In these cases, the reactions are clean and give the desired addition products in high yields. Particularly noteworthy is the high diastereoselectivity of the formation of **9c** (eq. 7). This is certainly a result of the rigid fixation of the methylsulfene

ligand in a sterically congested environment, which allows the prochiral enolate to approach in one orientation only.

The alkylation of the sulfinate function to give complexes of sulfinic acid esters provides a means of removing the metal complex from the organic moiety under mild conditions. Furthermore, the ionic acetonitrile complex thus obtained is easily separated from the organic component and can be converted back to the sulfur dioxide complex. A closed cycle is thus created, which allows the assembly of chain-extended sulfinic acid esters from sulfur dioxide, diazomethane or -ethane, and enolates (Scheme 1). Pertinent literature reports sulfinic acid esters to be prone to rearrangement to the corresponding sulfones.[20] Under our conditions, no such rearrangement could be detected, but we have at present no clear explanation as to the unexpected stability of **12a**, **b**.

Scheme 1



Esters of sulfinic acids have a number of important applications in organic synthesis.[24] Most pertinent work has been carried out on arenesulfinic acid esters, which seem to be much more readily accessible than their alkane counterparts. It is thus particularly gratifying that the reaction sequence outlined here not only provides esters of aliphatic sulfinic acids, but also tolerates a number of different functional groups.

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Experimental Section

All experiments were carried out in Schlenk tubes under nitrogen using suitably purified solvents. The crystallization of oily products was often conveniently induced by immersing the Schlenk tube in a small ultrasonic cleaning bath. − IR: Perkin-Elmer 283, Bruker IFS 25. − ^{1}H NMR: Bruker AMX 400, δ values relative to TMS; diastereotopic methylene protons of ethoxy groups invariably gave well-resolved ABX_3 spectra with ^2J(H,H) = 10.5 Hz and ^3J(H,H) = 7.1 Hz; for the sake of simplicity they are denoted in the following as "res. m" (resolved multiplet). − ^{13}C NMR: Bruker AMX 400, δ values relative to TMS; assignments were routinely checked by DEPT; in some cases the ^{13}C-NMR signals of quaternary carbon atoms were too weak to be detected. − ^{31}P NMR: Bruker AMX 400, δ values relative to 85% H_3PO_4. The ^{1}H- and ^{13}C-NMR signals of the phosphane ligands and the ^{31}P-NMR signals of the PF_6^- ion are very similar for all compounds and have therefore been omitted from the lists of spectral data. − Elemental analyses: Analytical Laboratory of the Institut für Anorganische Chemie. − The following starting materials were obtained as described in the literature: $[CpRu(PR_3)_2(SO_2)]X$ (**1a−d**),[25] [CpRu(dppm)Cl],[19] $[CpRu(dppm)(RHC{=}SO_2)]PF_6$ (**2a**, **d**),[9] diazomethane, diazoethane,[26] phenyldiazomethane.[27] Enolates were obtained from the corresponding 1,3-dicarbonyl compounds by deprotonation using lithium diisopropylamide or sodium bis(trimethylsilyl)amide. All other reagents were used as purchased.

[CpRu(dppe)(H$_2$C=SO$_2$)]PF$_6$ (**2b**): To a solution of **1b** (177 mg, 0.23 mmol) in dichloromethane (20 ml) a solution of diazomethane in diethyl ether (1 ml, 0.30 mmol) was added at −70°C. Gas evolution and a rapid color change to light-yellow were observed. The mixture was allowed to warm to 0°C, and all volatiles were removed in vacuo. After recrystallization from dichloromethane/pentane, a tan-colored microcrystalline powder was obtained. Yield 160 mg (89%), m.p. 156°C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2, −70°C): δ = 0.02 [dd, ^2J(H,H) = 4.4 Hz, ^3J(P,H) = 16.8 Hz, 1 H, HC=SO_2], 3.30 (br. m, 1 H, HC=SO_2), 5.68 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, −70°C): δ = −20.2 [d, ^2J(P,C) = 6 Hz, $H_2C{=}SO_2$], 85.6 (s, C_5H_5). − ^{31}P NMR (162 MHz, CD_2Cl_2, −70°C): δ = 73.8 [d, ^2J(P,P) = 20 Hz], 78.7 [d, ^2J(P,P) = 20 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1236, 1093 cm^{-1} (S=O). − $C_{32}H_{31}F_6O_2P_3RuS$ (787.6): calcd. C 48.80, H 3.97, S 4.07; found C 48.88, H 4.14, S 4.01.

[CpRu(PMe$_3$)$_2$(H$_2$C=SO$_2$)]PF$_6$ (**2c**): This compound was prepared analogously from **1c** (120 mg, 0.23 mmol) and diazomethane (0.45 mmol). Yield 109 mg (89%), m.p. 91°C (dec.). − ^{1}H NMR (400 MHz, [D_6]acetone, 20°C): δ = 0.71 [dd, ^2J(H,H) = 3.9 Hz, ^3J(P,H) = 17.6 Hz, 1 H, HC=SO_2], 2.57 (br. m, 1 H, HC=SO_2), 5.92 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D_6]acetone, 20°C): δ = −22.3 [d, ^2J(P,C) = 5 Hz, $H_2C{=}SO_2$], 96.0 (s, C_5H_5). − ^{31}P NMR (162 MHz, [D_6]acetone, 20°C): δ = 7.7 [d, ^2J(P,P) = 43 Hz], 9.7 [d, ^2J(P,P) = 43 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1220, 1104 cm^{-1} (S=O). − $C_{12}H_{25}F_6O_2P_3RuS$ (541.4): calcd. C 26.62, H 4.65; found C 26.95, H 4.72.

[CpRu(dppm)(SO$_2$CHClPh)] (**3**): This compound was prepared analogously from **1d** (85 mg, 0.13 mmol) and phenyldiazomethane (0.25 mmol). The crude product was purified by chromatography on a short silica gel column using acetone/dichloromethane (2:1) as eluent. Yield 68 mg (71%), m.p. 171°C (dec.). − ^{1}H NMR (400 MHz, C_6D_6, 20°C): δ = 4.50 (s, 1 H, CHClPh), 4.89 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, C_6D_6, 20°C): δ = 83.2 [t, ^2J(P,C) = 2 Hz, C_5H_5], 83.3 [dd, ^2J(P,C) = 2 Hz, ^2J(P,C) = 1 Hz, CHClPh]. − ^{31}P NMR (162 MHz, C_6D_6, 20°C): δ = 11.0 [d, ^2J(P,P) = 90 Hz], 12.2 [d, ^2J(P,P) = 90 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1184, 1032 cm^{-1} (S=O). − $C_{37}H_{33}ClO_2P_2RuS$ (740.2): calcd. C 60.04, H 4.49; found C 60.65, H 4.57.

[CpRu(dppm)(CH$_3$)] (**4**): A solution of [CpRu(dppm)Cl] (300 mg, 0.51 mmol) in toluene (10 ml) was treated at 20°C with methylmagnesium chloride in THF (1.54 mmol). After 20 h, the excess Grignard reagent was quenched by adding methanol (5 ml). All volatile material was then removed in vacuo and the solid residue was redissolved in toluene (20 ml). The resulting solution was filtered through Celite, and the filtrate was concentrated to a volume of 2 ml. Addition of pentane resulted in the deposition of the product as yellow crystals. Yield 185 mg (64%), m.p. 176°C (dec.). − ^{1}H NMR (400 MHz, C_6D_6, 20°C): δ = 0.20 [t, ^3J(P,H) = 7.1 Hz, 3 H, $RuCH_3$], 4.87 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, C_6D_6,

20°C): δ = −23.1 [t, ^2J(P,C) = 13 Hz, $RuCH_3$], 80.3 [t, ^2J(P,C) = 2 Hz, C_5H_5]. − ^{31}P NMR (162 MHz, C_6D_6, 20°C): δ = 22.8 (s). − $C_{31}H_{30}P_2Ru$ (565.6): calcd. C 65.83, H 5.35; found C 65.52, H 5.42.

[CpRu(dppm)(H$_2$C=SO$_2$)]PF$_6$ (**2a**). − *From* **4**: To a solution of **4** (185 mg, 0.33 mmol) in dichloromethane (20 ml), a solution of $[Ph_3C]PF_6$ (130 mg, 0.34 mmol) in the same solvent (2 ml) was added at −70°C. Sulfur dioxide was then introduced into the deep-red solution, and the mixture allowed to warm to 0°C. After concentration to a volume of 2 ml, the product was precipitated by adding pentane. Yield 218 mg (86%), colorless crystalline powder, identical (NMR, IR) with the known **2a**.[9]

Addition of Enolates: To a solution of Li[N(*i*Pr)$_2$] (25 mg, 0.22 mmol) or Na[N(SiMe$_3$)$_2$] (40 mg, 0.22 mmol) in THF (5 ml), an equimolar amount of the respective C−H acidic compound was added at −70°C. The resulting slurry was then added to a solution of 0.20 mmol of the sulfene complex in THF (10 ml). The mixture was allowed to warm to 20°C and stirred for 2 h. The solvent was then removed in vacuo, the oily residue was taken up in dichloromethane and chromatographed (neutral alumina, activity grade I, acetone/dichloromethane, 2:1). A broad, light-yellow band containing the product was collected. The solvent was evaporated and the product was recrystallized from benzene/pentane.

6a: Yield 76 mg (51%), m.p. 232°C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 0.58 (s, 3 H, CH_3), 2.34−2.48, 2.87−2.92 (m, 4 H, CH_2CH_2), 2.89 (s, 2 H, SO_2CH_2), 4.95 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20°C): δ = 20.2 (s, CH_3), 35.2 (s, CH_2CH_2), 52.9 (s, C_{quat}), 82.3 (s, CH_2SO_2), 84.0 [t, ^2J(P,C) = 2 Hz, C_5H_5], 216.2 (s, CO). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 12.9 (s). − IR (Nujol): $\tilde{\nu}$ = 1715 (C=O), 1144, 1024 cm^{-1} (S=O). − $C_{37}H_{36}O_4P_2RuS$ (739.8): calcd. C 60.07, H 4.91; found C 60.54, H 5.30.

6b: Yield 124 mg (79%), m.p. 221°C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 0.64 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3), 2.07 [d, ^2J(H,H) = 14.3 Hz, 2 H, CH_2], 2.82 [d, ^2J(H,H) = 14.3 Hz, 2 H, CH_2], 2.78 (s, 2 H, SO_2CH_2), 4.97 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20°C): δ = 19.1 (s, CH_3), 27.1 (s, CH_3), 30.6 (s, CH_3), 30.9 (s, CMe_2), 52.4(s, CH_2), 62.4 (s, C_{quat}), 78.2 (s, CH_2SO_2), 83.8 (s, C_5H_5), 209.0 (s, CO). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 13.5 (s). − IR (Nujol): $\tilde{\nu}$ = 1716, 1688 (C=O), 1144, 1032 cm^{-1} (S=O). − $C_{40}H_{42}O_4P_2RuS$ (781.9): calcd. C 61.44, H 5.41; found C 60.96, H 5.26.

7a: Yield 125 mg (78%), m.p. 183°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.19 [t, ^3J(H,H) = 7.1 Hz, 6 H, CH_3], 1.36 (s, 3 H, CH_3), 2.86 (s, 2 H, SO_2CH_2), 4.10 (res. m, 4 H, OCH_2), 4.93 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.0 (s, CH_3), 19.4 (s, CH_3), 53.2 (s, C_{quat}), 61.0 (s, OCH_2), 73.3 (s, CH_2SO_2), 83.6 (s, C_5H_5), 171.5 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 12.6 (s). − IR (Nujol): $\tilde{\nu}$ = 1740, 1712 (C=O), 1152, 1028 cm^{-1} (S=O). − $C_{39}H_{42}O_6P_2RuS$ (801.8): calcd. C 58.42, H 5.28; found C 57.96, H 5.59.

7b: Yield 129 mg (82%), m.p. 207°C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 1.48 (s, 3 H, CH_3), 1.56 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 2.94 (s, 2 H, SO_2CH_2), 4.95 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 27.0 (s, CH_3), 27.6 (s, CH_3), 30.2 (s, CH_3), 43.4 (s, C_{quat}), 75.3 (s, CH_2SO_2), 83.6 (s, C_5H_5), 106.5 (s, O_2CMe_2), 168.5 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 13.1 (s). − IR (Nujol): $\tilde{\nu}$ = 1744, 1732 (C=O), 1160, 1028 cm^{-1} (S=O). − $C_{38}H_{38}O_6P_2RuS$ (785.8): calcd. C 58.08, H 4.87; found C 58.17, H 4.87.

7c: Yield 124 mg (76%), m.p. 209°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.18 [t, ^3J(H,H) = 7.1 Hz, 6 H, CH_3], 1.36 (s, 3 H, CH_3), 2.57 (s, 2 H, SO_2CH_2), 4.07 (res. m, 4 H, OCH_2), 4.85 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.0 (s, CH_3), 19.2 (s, CH_3), 53.2 (s, C_{quat}), 61.0 (s, OCH_2), 72.3 (s, CH_2SO_2), 85.6 (s, C_5H_5), 171.4 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 83.0 (s). − IR (Nujol): $\tilde{\nu}$ = 1741, 1725 (C=O), 1142, 1024 cm^{-1} (S=O). − $C_{40}H_{44}O_6P_2RuS$ (815.9): calcd. C 58.89, H 5.44; found C 58.18, H 5.22.

7d: Yield 117 mg (72%), m.p. 207°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 0.41 [t, ^3J(H,H) = 7.3 Hz, 3 H, CH_3], 1.15 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.21 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.43 (s, 3 H, CH_3), 3.66 [q, ^3J(H,H) = 7.3 Hz, 1 H, SO_2CHMe], 4.02 (res. m, 2 H, OCH_2), 4.17 (res. m, 2 H, OCH_2), 5.02 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 11.2 (s, CH_3), 14.2 (s, CH_3), 15.6 (s, CH_3), 57,5 (s, C_{quat}), 61.0 (s, OCH_2), 61.1 (s, OCH_2), 74.5 (s, SO_2CHMe), 82.7 (s, C_5H_5), 171.3 (s, CO), 171.4 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 8.8 [d, ^2J(P,P) = 86 Hz], 11.1 [d, ^2J(P,P) = 86 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1744, 1704 (C=O), 1156, 1024 cm^{-1} (S=O). − $C_{40}H_{44}O_6P_2RuS$ (815.9): calcd. C 58.89, H 5.44; found C 57.99, H 5.07.

7e: This compound was obtained from **3**. To ensure complete reaction the mixture was refluxed for 2 h. Yield 142 mg (81%), m.p. 156°C (dec.). − ^{1}H NMR (400 MHz, C_6D_6, 20°C): δ = 0.75 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 0.94 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 2.33 (s, 3 H, CH_3), 3.64 (res. m, 2 H, OCH_2), 3.95 (res. m, 1 H, OCH_2), 4.13 (res. m, 1 H, OCH_2), 4.35 (s, 5 H, C_5H_5), 4.55 (s, 1 H, SO_2CHPh). − ^{13}C NMR (100 MHz, C_6D_6, 20°C): δ = 13.8 (s, CH_3), 14.0 (s, CH_3), 18.2 (s, CH_3), 58,4 (s, C_{quat}), 60.5 (s, OCH_2), 60.8 (s, OCH_2), 78.4 (s, $CHPhSO_2$), 82.6 (s, C_5H_5), 170.3 (s, CO), 170.5 (s, CO). − ^{31}P NMR (162 MHz, C_6D_6, 20°C): δ = 9.9 [d, ^2J(P,P) = 90 Hz], 14.0 [d, ^2J(P,P) = 90 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1725, 1713 (C=O), 1141, 1022 cm^{-1} (S=O). − $C_{45}H_{46}O_6P_2RuS$ (877.9): calcd. C 61.56, H 5.28; found C 61.72, H 5.19.

8a: Yield 114 mg (74%), m.p. 221°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.19 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.37 (s, 3 H, CH_3), 1.98 [s, 3 H, $C(O)CH_3$], 2.85 [d, ^2J(H,H) = 13.7 Hz, 1 H, SO_2CH_2], 2.94 [d, ^2J(H,H) = 13.7 Hz, 1 H, SO_2CH_2], 4.10 [q, ^3J(H,H) = 7.1 Hz, 2 H, OCH_2], 4.94 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.0 (s, CH_3), 19.3 (s, CH_3), 26.3 (s, CH_3), 58.8 (s, C_{quat}), 61.0 (s, OCH_2), 74.2 (s, CH_2SO_2), 83.7 (s, C_5H_5), 172.2 (s, CO), 205.8 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 12.6 [d, ^2J(P,P) = 90 Hz], 12.9 [d, ^2J(P,P) = 90 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1728, 1708 (C=O), 1148, 1036 cm^{-1} (S=O). − $C_{38}H_{40}O_5P_2RuS$ (771.8): calcd. C 59.14, H 5.22; found C 58.90, H 5.08.

8b: Yield 47 mg (31%), m.p. 211°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.28 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.37 (s, 3 H, CH_3), 2.51 [d, ^2J(H,H) = 13.2 Hz, 1 H, SO_2CH_2], 2.75 [d, ^2J(H,H) = 13.2 Hz, 1 H, SO_2CH_2], 4.22 (res. m, 1 H, OCH_2), 4.23 (res. m, 1 H, OCH_2), 4.95 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (s, CH_3), 22.2 (s, CH_3), 40.6 (s, C_{quat}), 62.5 (s, OCH_2), 73.0 (s, CH_2SO_2), 83.6 (s, C_5H_5), 119.7 (s, CN), 168.6 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 12.5 [d, ^2J(P,P) = 90 Hz], 13.0 [d, ^2J(P,P) = 90 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1744 (C=O), 1168, 1032 cm^{-1} (S=O). − $C_{37}H_{37}NO_4P_2RuS$ (754.8): calcd. C 58.88, H 4.94, N 1.86; found C 59.09, H 4.45, N 1.23.

8c: Yield 127 mg (78%), m.p. 216°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.35 (s, 12 H, *t*Bu and CH_3), 2.04 [s, 3 H, $C(O)CH_3$], 2.32 [d, ^2J(H,H) = 14.0 Hz, 1 H, SO_2CH_2], 2.87 [d, ^2J(H,H) = 14.0 Hz, 1 H, SO_2CH_2], 4.84 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 19.5 (s, CH_3), 26.9 (s, CH_3),

27,7 (s, *t*Bu), 59.1 (s, C_{quat}), 73.5 (s, CH_2SO_2), 80.7 (s, CMe_3), 85.6 (s, C_5H_5), 170.7 (s, CO), 206.1 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 82.1 [d, ^2J(P,P) = 19 Hz], 84.2 [d, ^2J(P,P) = 19 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1725, 1702 (C=O), 1140, 1022 cm^{-1} (S=O). − $C_{41}H_{46}O_5P_2RuS$ (813.9): calcd. C 60.51, H 5.70; found C 60.39, H 5.92.

9a: Yield 111 mg (71%), m.p. 190°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.12 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.56 (m, 2 H, CH_2), 1.99 (m, 2 H, CH_2), 2.22 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 2.50 (m, 2 H, CH_2), 2.95 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 4.02 (res. m, 1 H, OCH_2), 4.03 (res. m, 1 H, OCH_2), 4.87 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.1 (s, CH_3), 19.4 (s, CH_2), 30.4 (s, CH_2), 37.4 (s, CH_2), 59.6 (s, C_{quat}), 61.1 (s, OCH_2), 71.1 (s, CH_2SO_2), 83.8 (s, C_5H_5), 170.1 (s, CO), 214.6 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 12.4 [d, ^2J(P,P) = 90 Hz], 13.1 [d, ^2J(P,P) = 90 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1745, 1716 (C=O), 1149, 1022 cm^{-1} (S=O). − $C_{39}H_{40}O_5P_2RuS$ (783.8): calcd. C 59.76, H 5.14; found C 58.47, H 5.02.

9b: Yield 123 mg (77%), m.p. 172°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.14 [t, ^3J(H,H) = 7.0 Hz, 3 H, CH_3], 1.28−1.54 (m, 4 H, CH_2), 2.05 (m, 4 H, CH_2), 2.79 [d, ^2J(H,H) = 13.0 Hz, 1 H, SO_2CH_2], 2.90 [d, ^2J(H,H) = 13.0 Hz, 1 H, SO_2CH_2], 4.06 [q, ^3J(H,H) = 7.0 Hz, 2 H, OCH_2], 4.88 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.1 (s, CH_3), 21.2 (s, CH_2), 26.4 (s, CH_2), 32.4 (s, CH_2), 39.6 (s, CH_2), 60.9 (s, C_{quat}), 60.9 (s, OCH_2), 72.0 (s, CH_2SO_2), 83.7 (s, C_5H_5), 171.1 (s, CO), 207.7 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 12.6 [d, ^2J(P,P) = 90 Hz], 12.8 [d, ^2J(P,P) = 90 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1731, 1701 (C=O), 1153, 1028 cm^{-1} (S=O). − $C_{40}H_{42}O_5P_2RuS$ (797.9): calcd. C 60.22, H 5.31; found C 59.92, H 5.37.

9c: Yield 113 mg (71%), m.p. 191°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 0.79 [t, ^3J(H,H) = 6.3 Hz, 3 H, CH_3], 1.26 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.66−1.91 (m, 2 H, CH_2), 2.08 (m, 1 H, CH_2), 2.43 (m, 1 H, CH_2), 2.52 (m, 2 H, CH_2), 3.72 [q, ^3J(H,H) = 6.3 Hz, 1 H, SO_2CH], 4.15 (res. m, 1 H, OCH_2), 4.16 (res. m, 1 H, OCH_2), 5.07 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.7 (s, CH_3), 14.6 (s, CH_3), 19.1 (s, CH_2), 29.3 (s, CH_2), 32.1 (s, CH_2), 59.3 (s, OCH_2), 82.4 (s, C_5H_5), 98.6 (s, $CHSO_2$), 165.3 (s, CO), signals of C_{quat} and CO (ketone) not detected due to low intensity. − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 11.9 [d, ^2J(P,P) = 88 Hz], 10.0 [d, ^2J(P,P) = 88 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1672, 1613 (C=O), 1153, 1028 cm^{-1} (S=O). − $C_{40}H_{42}O_5P_2RuS$ (797.9): calcd. C 60.22, H 5.31; found C 59.99, H 5.12.

O-Alkylation of the Sulfinato Complexes: To a solution of the sulfinato complex (0.1 mmol) in dichloromethane (10 ml), a solution of the oxonium salt in the same solvent was added at −70°C. After being allowed to warm to 20°C, the mixture was concentrated to a volume of 1 ml and the product was precipitated by the addition of pentane. In some instances, **10a** separated as an oil. In this event, it was found that crystallization could be induced by ultrasound treatment under pentane.

10a: Yield 85 mg (94%), m.p. 88°C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 1.10 (s, 3 H, CH_3), 1.20 [t, ^3J(H,H) = 7.2 Hz, 6 H, CH_3], 2.82 (s, 3 H, $SOCH_3$), 3.07 [d, ^2J(H,H) = 15.0 Hz, 1 H, SO_2CH_2], 3.63 [d, ^2J(H,H) = 15.0 Hz, 1 H, SO_2CH_2], 4.15 (res. m, 4 H, OCH_2), 5.31 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20°C): δ = 14.1 (s, CH_3), 14.2 (s, CH_3), 19.3 (s, CH_3), 52.0 (s, $SOCH_3$), 55.7 (s, C_{quat}), 62.2 (s, OCH_2), 62.6 (s, OCH_2), 74.4 (s, CH_2SO_2), 84.6 (s, C_5H_5), 169.7 (s, CO), 169.9 (s, CO). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 2.6 [d, ^2J(P,P) = 86 Hz], 5.8 [d, ^2J(P,P) = 86 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1726 (C=O) cm^{-1}. − $C_{40}H_{45}BF_4O_6P_2RuS$ (903.7): calcd. C 53.16, H 5.02; found C 52.69, H 5.35.

10b: Yield 91 mg (93%), m.p. 135°C (dec.). − ^{1}H NMR (400 MHz, [D_6]acetone, 20°C): δ = 1.10 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.16 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.21 [t, ^3J(H,H) = 7.1 Hz, 3 H, $SOCH_3$], 1.22 (s, 3 H, CH_3), 2.95 [dq, ^3J(H,H) = 7.1 Hz, ^2J(H,H) = 9.6 Hz, 1 H, OCH_2], 3.07 [d, ^2J(H,H) = 15.1 Hz, 1 H, SO_2CH_2], 3.62 [dq, ^3J(H,H) = 7.1 Hz, ^2J(H,H) = 9.6 Hz, 1 H, OCH_2], 3.88 [d, ^2J(H,H) = 15.1 Hz, 1 H, SO_2CH_2], 4.10 (res. m, 4 H, OCH_2), 5.55 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D_6]acetone, 20°C): δ = 13.9 (s, CH_3), 14.0 (s, CH_3), 14.1 (s, CH_3), 19.2 (s, CH_3), 54.1 (s, C_{quat}), 61.9 (s, OCH_2), 62.4 (s, OCH_2), 63.1 (s, OCH_2), 73.6 (s, CH_2SO_2), 85.6 (s, C_5H_5), 169.7 (s, CO), 170.0 (s, CO). − ^{31}P NMR (162 MHz, [D_6]acetone, 20°C): δ = 2.6 [d, ^2J(P,P) = 85 Hz], 5.5 [d, ^2J(P,P) = 85 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1733 (C=O), 1150 (S=O) cm^{-1}. − $C_{41}H_{47}F_6O_6P_3RuS$ (975.9): calcd. C 50.46, H 4.85; found C 50.82, H 4.99.

10c: Yield 90 mg (91%), m.p. 118°C (dec.). − ^{1}H NMR (400 MHz, [D_6]acetone, 20°C) (assignment to the two different diastereomers was not possible): δ = 0.75 [t, ^3J(H,H) = 7.0 Hz, 3 H, CH_3], 1.20 (s, 3 H, CH_3), 1.40 (s, 9 H, *t*Bu), 1.93, 2.04 [s, 3 H, C(O)CH_3], 2.71, 2.86, 3.30, 3.32 [d, ^2J(H,H) = 15.2 Hz, 2 H, SO_2CH_2], 2.95 (m, 2 H, $SOCH_2$), 5.41, 5.42 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D_6]acetone, 20°C): δ = 13.8, 14.6 (s, CH_3), 18.9, 19.4 (s, CH_3), 25.6, 26.2 (s, CH_3), 27.6, 27.7 (s, *t*Bu), 60.6, 60.7 (s, C_{quat}), 62.4, 62.6 (s, $SOCH_2$), 73.9, 74.2 (s, CH_2SO_2), 83.0, 83.1 (s, CMe_3), 87.4, 87.5 (s, C_5H_5), 169.6, 169.7 (s, CO), 202.3, 202.7 (s, CO). − ^{31}P NMR (162 MHz, [D_6]acetone, 20°C), major (51%) diastereomer: δ = 69.2 [d, ^2J(P,P) = 21 Hz], 73.3 [d, ^2J(P,P) = 21 Hz], minor (49%) diastereomer: δ = 66.2 [d, ^2J(P,P) = 21 Hz], 72.8 [d, ^2J(P,P) = 21 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1716 (C=O), 1150 cm^{-1} (S=O). − $C_{43}H_{51}F_6O_5P_3RuS$ (987.9): calcd. C 52.28, H 5.20, S 3.25; found C 51.99, H 5.33, S 3.15.

Liberation of the Sulfinic Acid Esters: The respective ester complexes **10a**, **b** (0.2 mmol) were dissolved in acetonitrile (10 ml) and heated under reflux (15 h). Thereafter, the mixtures were concentrated to dryness and the resulting residues were suspended in diethyl ether. The acetonitrile complexes **11a**, **b** separated as yellow powders upon ultrasound treatment. In each case, the supernatant was concentrated to dryness, leaving the esters **12a**, **b** as colorless, spectroscopically pure oils in almost quantitative yields.

12a: ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.24 [t, ^3J(H,H) = 7.1 Hz, 6 H, CH_3], 1.58 (s, 3 H, CH_3), 3.16 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.34 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.72 (s, 3 H, $SOCH_3$), 4.19 [q, ^3J(H,H) = 7.1 Hz, 4 H, OCH_2]. − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (s, CH_3), 20.5 (s, CH_3), 51.4 (s, C_{quat}), 62.0 (s, OCH_2), 62.1 (s, OCH_2), 63.0 (s, CH_2SO_2), 170.1 (s, CO).

12b: ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.25 [t, ^3J(H,H) = 7.1 Hz, 6 H, CH_3], 1.32 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.58 (s, 3 H, CH_3), 3.19 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.36 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 4.06 (res. m, 2 H, $SOCH_2$), 4.19 (res. m, 2 H, OCH_2), 4.20 (res. m, 2 H, OCH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (s, CH_3), 15.8 (s, CH_3), 20.4 (s, CH_3), 51.5 (s, C_{quat}), 62.0 (s, OCH_2), 62.1 (s, OCH_2), 63.2 (s, $SOCH_2$), 65.0 (s, CH_2SO_2), 170.1 (s, CO), 170.2 (s, CO).

Acetonitrile/SO_2 Exchange: In a small pressure tube, equipped with a Teflon needle valve, liquid sulfur dioxide (5 ml) was condensed onto the acetonitrile complex **11a**, **b** (0.1 mmol). After 7 d at 20°C, the tube was vented and the yellow residue was recrystallized from dichloromethane/pentane.

1a: Yield 72 mg (95%), spectroscopically identical to authentic material.[19]

1e: Yield 67 mg (96%) m.p. 158°C. – ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = −3.2 (s). – IR (Nujol): $\tilde{\nu}$ = 1279, 1115 (S=O) cm^{-1}. – $C_{30}H_{27}BF_4O_2P_2RuS$ (701.4): calcd. C 51.37, H 3.88, S 4.57; found C 50.94, H 3.88, S 4.50.

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