Enantioselective Organic Syntheses With Chiral Transition Metal Complexes, 11[+]

Chiral Ruthenium–Sulfene Complexes – Synthesis and C–C Coupling Reactions

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Reaction of the chiral racemic complex [CpRu(mppe)-(SO_2)]PF_6 (**1**, mppe = $Me_2PC_2H_4PPh_2$) with diazomethane or -ethane gave the sulfene complexes [CpRu(mppe)(RHC=SO_2)]PF_6 (R = H, **2a**; R = Me, **2b**). Treatment of **2a** with prochiral enamines or deprotonated β-oxo esters yielded C–C coupling products with 32–60% de. An analog of **2a**, [NmcpRu(mppe)(H_2C=SO_2)]PF_6 (**8**, Nmcp = neomenthylcyclopentadienyl) was prepared in a four-step synthesis starting from LiNmcp and [$RuCl_2(PPh_3)_3$]. Repeated crystallization of the intermediate [NmcpRu(mppe)Cl] (**6**) provided diastereomerically pure **6′** which added methylene stereospecifically to give diastereomerically pure **8′**. Compound **8** turned out to be much less reactive towards nucleophiles than **2a**, but still added deprotonated ethyl 2-methyl-3-oxobutanoate with 44% de. The chiral, enantiomerically pure sulfur dioxide complex [CpRu(chir)(SO_2)]PF_6 [**10**, chir = (*S*,*S*)-$Ph_2PCHMeCHMePPh_2$] was synthesized from [CpRu(chir)Cl] and SO_2 and was characterized by X-ray crystallography. Reaction of **10** with diazomethane gave the enantiomerically pure sulfene complex [CpRu(chir)(H_2C=SO_2)]PF_6 (**11**). Addition reactions of **11** with *N*-(1-cyclopentenyl)morpholine, as well as with various enolates derived from β-oxo esters or 1,3-diesters proceeded with high yields and 20–90% de. The structure of a diastereomerically pure addition product, [CpRu(chir)(SO_2CH_2C(Me){C(O)Me}{C(O)O*t*Bu}] (**13d′**), was determined crystallographically and was shown to have (*R*) configuration at the quaternary carbon atom. After alkylation of one of the S=O functions, the sulfinate ligand was cleaved from the metal center by ligand substitution with acetonitrile, and the resulting acetonitrile complex **15** was converted back into **10** by treatment with SO_2.

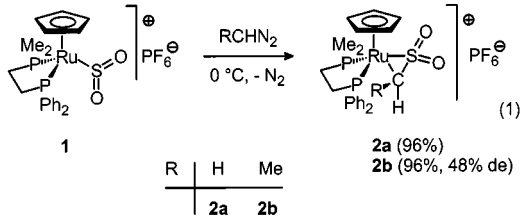
In previous publications we described the synthesis of ionic sulfene complexes of the type [$Cp(R_3'P)_2Ru(RHC$=SO_2)]PF_6 (R = H, Me) by methylene addition to sulfur dioxide complexes.[1–3] Through the coordination to a transition metal atom, the sulfene molecule experiences considerable stabilization as well as umpolung. The latter was demonstrated by addition reactions with a number of heteroatom and carbon nucleophiles, which occurred exclusively at carbon.[2][3]

The use of chiral transition metal complexes as diastereodirecting auxiliaries in stoichiometric reactions is a topic of long-standing interest.[4][5] In the majority of the work, complexes of the types [$CpMo(CO)_2(L-L^*)$],[6] [$CpM(NO)(PPh_3)L$] (M = Mn,[4] Re[7]), [$CpFe(CO)(PPh_3)L$][8][9] and [$CpRu(L-L^*)L$][10] (L–L* = chiral bidentate ligand) were employed. If L is a coordinated alkene, such complexes may undergo nucleophilic additions with remarkable diastereoselectivity.[5,7,11] In this context it seemed promising to carry out C–C coupling reactions with chirally modified sulfene complexes.

Results

Complexes with Metal-Centered Chirality

Reaction of the chiral racemic sulfur dioxide complex **1**[12] with diazomethane or -ethane gave the sulfene complexes **2a** and **2b** as colorless, crystalline, and thermally quite sensitive materials (Equation 1).



Compound **2a** was obtained as a single isomer with the CH_2 group *cis* to the PPh_2 group of the $Me_2PC_2H_4PPh_2$ (mppe) ligand. A strong NOE upon irradiation of the Cp resonance allowed the identification of the *exo*-H of the sulfene as well as the *exo*-CH_3 of the diphosphane ligand. Due to the small dihedral angle H–C–Ru–P,[2] the *endo*-H is strongly coupled to the *cis*-phosphorus atom,[13] which was shown by selective ^{31}P decoupling to be that of the PPh_2 group. Four different rotamers/diastereoisomers are possible for **2b**, of which only two were observed in a 74:26

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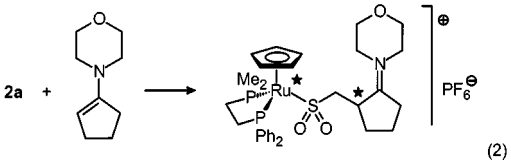
ratio. The major isomer **2b′** has the structure shown in Equation 1, as evidenced again by the large coupling of the *endo*-H with the PPh_2 group. The relative configurations of the two stereocenters are thus $R_{Ru},R_C/S_{Ru},S_C$. Unfortunately, the resonance of the sulfene-H of the minor isomer **2b″** could not be detected due to extensive signal overlap. In view of the fairly low diastereoselectivity of the addition reaction described below, it is reasonable to assume that **2b″** is the ($R_{Ru},S_C/S_{Ru},R_C$) diastereomer but we have no way of distinguishing between the two possible rotamers.

Cationic sulfene complexes readily undergo C−C coupling reactions with enamines.[3] Thus, treatment of **2a** with *N*-(1-cyclopentenyl)morpholine gave the immonium salt **3** in 76% yield and 60% de (Equation 2).

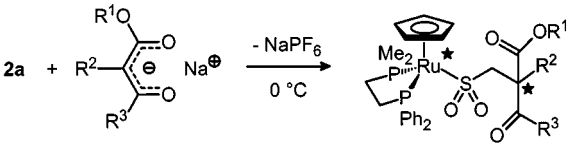


(2)

3 (76%, 60% de)

Immonium salt **3** is a colorless crystalline compound whose constitution was readily inferred from its spectroscopic data. Particularly characteristic is the AB system of the methylene group at sulfur and the downfield signal of the immonium carbon at $\delta = 203.4$. The shift differences in the NMR spectra of the two diastereoisomers are rather small due to the large spatial separation of the two stereocenters.

Reaction of **2a** with deprotonated β-oxo esters gave the neutral addition products **4a**−**c** in fair yields and diastereoselectivities (Equation 3).



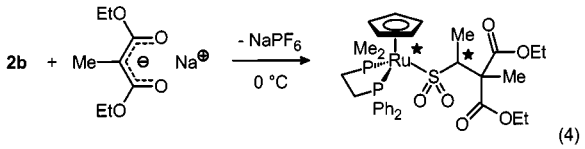
(3)

R^1	Et	*t*-Bu	Et
R^2, R^3	Me, Me	Me, Me	$-CH_2CH_2CH_2-$
	4a	**4b**	**4c**

4a (54%, 42% de)
4b (60%, 48% de)
4c (63%, 32% de)

Through chromatography and crystallization the major diastereoisomers could be enriched. The stereochemical course of enolate reactions is strongly influenced by the nature of the counter cation.[14] Therefore, the reaction of **2a** with deprotonated ethyl 2-oxocyclopentanecarboxylate was carried out on a small scale in the presence of various salts. Upon addition of $LiClO_4$, $MgBr_2$, or $ZnCl_2$ to the reaction mixture, the diastereoselectivity disappeared almost completely. However, the coupling product **4c** was formed with 81% de when the sodium enolate was first converted into a titanium enolate and then added to **2a**. Unfortunately, we were unable in this case to separate **4c** without its decomposition from the titanium-containing side products. Nevertheless, it appears that, with the choice of suitable reagents, highly stereoselective addition reactions can be performed.

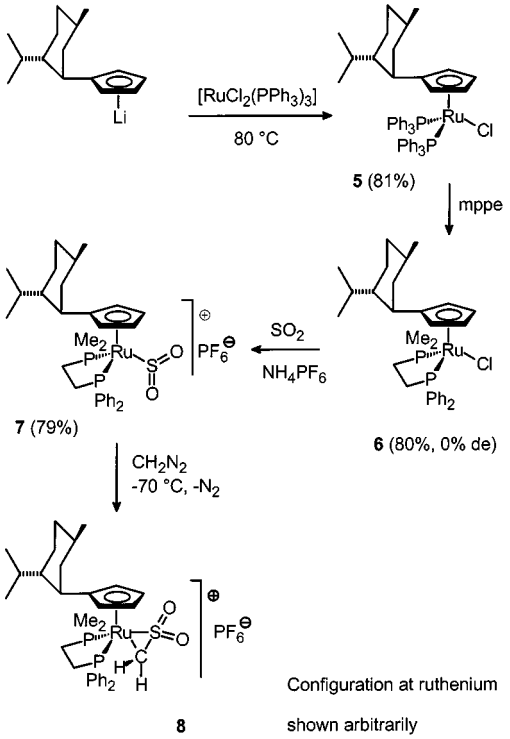
Nucleophilic additions on **2b** should be stereospecific with respect to the configuration at the sulfene carbon atom. Still, the addition of the sodium enolate of diethyl methylmalonate produced **4d** in somewhat lower de than expected (Equation 4). This is certainly due to competing decomposition which may affect both diastereoisomers of the thermolabile starting material **2b** at slightly different rates.



(4)

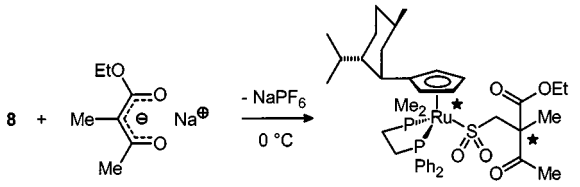
4d (71%, 26% de)

Although the results obtained so far were not overly promising we set out to synthesize enantiomerically pure analogs of **1** and **2a** (Scheme 1). Reaction of neomenthylcyclopentadienyllithium with $[RuCl_2(PPh_3)_3]$ gave **5** in high yield as a yellow crystalline compound which, unlike its C_5H_5 analog, is readily soluble even in aliphatic hydrocarbons. Notable spectroscopic features are four separated NMR signals of the protons on the cyclopentadienyl ring, and a narrow AB system in the ^{31}P NMR spectrum. Phosphane exchange with mppe gave **6** in high yield as a 50:50 mixture of diastereoisomers. Through repeated crystallizations a small amount of diastereomerically pure **6′** was obtained as orange-yellow crystals. Treatment of **6** with sulfur dioxide at room temperature gave the SO_2 complex **7** in high isolated yield as a yellow crystalline material. Similarly, **6′** gave **7′** as a single diastereoisomer, which to our knowledge is the first chiral, enantiomerically pure complex of sulfur dioxide.



Scheme 1. Synthesis of diastereoisomeric neomenthylcyclopentadienyl ruthenium complexes

The reaction of **7** or **7′** with diazomethane produced the expected sulfene complex either as the 50:50 mixture **8** or in its diastereomerically pure form **8′** (Scheme 1), both of which are brownish-white semisolid materials. Disappointingly, **8** and **8′** turned out to be even more labile than **2a**, to preclude the isolation of analytically pure samples and to hamper their use in further reactions considerably. In the next experiments, **8** was therefore generated in situ. The reaction with *N*-(1-cyclopentenyl)morpholine resulted only in complete decomposition of the sulfene complex. Enolate addition, however, gave the expected product **9**, after workup in 47% yield, as a 72:28 mixture of two diastereoisomers (Equation 5).

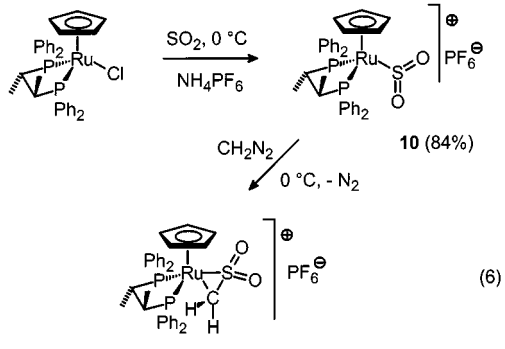


9 (47%, 44% de) (5)

Since this reaction is not expected to proceed with significantly higher diastereoselectivity than that described in Equation 3, we have to assume that the two remaining stereoisomers were lost during workup. Although **9** is a stable compound, neomenthylcyclopentadienyl complexes do not tend to crystallize well, therefore making it impossible to obtain analytically pure samples or achieve any further diastereoisomer enrichment.

Complexes with Ligand-Centered Chirality

We recently found that ligand-centered reactions of [CpRu(chir)L] complexes [chir = (*S*,*S*)-2,3-bis(diphenylphosphanyl)butane] proceed with remarkably high diastereoselectivity.[15−19] For example, the oxidation of coordinated thioethers routinely gave de values greater than 80% and up to 98%.[16−18] Thus, besides avoiding the tedious diastereoisomer separation step, we also expected improved selectivities for the C−C coupling reactions of sulfene complexes containing this chiral diphosphane ligand. The enantiomerically pure sulfur dioxide complex **10** was obtained as a yellow solid in high yield from [CpRu(chir)Cl] and SO_2 (Equation 6).



(6)

Diffusion of hexane into a dichloromethane solution gave crystals of **10**·$2CH_2Cl_2$ suitable for X-ray structure determination. Figure 1 shows a view of the cation. The structure may be described as distorted octahedral, in which the C_5H_5 ligand occupies three sites. As expected,[20][21] the SO_2 ligand aligns itself in the pseudo mirror plane of the $CpRu(PR_3)_2$ complex fragment. The two P−Ru−S angles differ by 5.3° as a result of the asymmetric nature of the chiral diphosphane ligand. The geometry around sulfur is perfectly planar, with the sum of the bond angles being 359.9°.

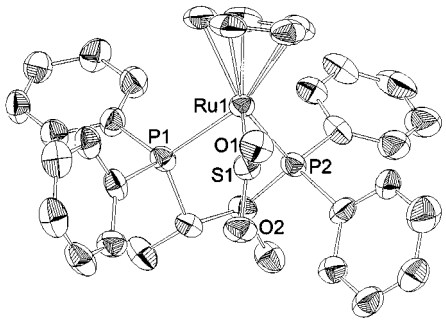
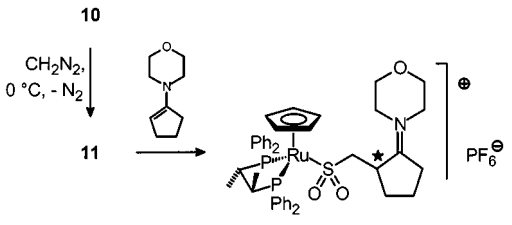


Figure 1. Molecular structure of [CpRu(chir)(SO_2)]PF_6·2 CH_2Cl_2 (**10**·$2CH_2Cl_2$) (hydrogen atoms, anion, and solvent molecules omitted); selected distances [pm] and angles [°] (standard deviations in parentheses): Ru(1)−P(1) 232.9(2), Ru(1)−P(2) 232.2(2), Ru(1)−S(1) 212.8(2), S(1)−O(1) 143.2(6), S(1)−O(2) 145.8(6), S(1)−Ru(1)−P(1) 88.48(8), S(1)−Ru(1)−P(2) 93.81(9), P(1)−Ru(1)−P(2) 83.41(8), Ru(1)−S(1)−O(1) 120.9(3), Ru(1)−S(1)−O(2) 125.1(3), O(1)−S(1)−O(2) 113.9(4)

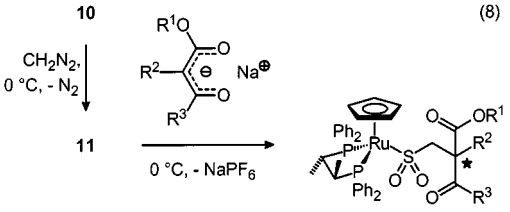
The reaction of **10** with diazomethane at −70°C gave the enantiomerically pure sulfene complex **11** in almost quantitative yield (Equation 6). Sulfene complex **11** is a colorless, crystalline compound which decomposes in solution at 20°C. NMR spectra taken at −60 °C revealed that **11** exists as a single rotamer. The two sulfene protons give signals at δ = 0.85 and 2.31, the latter of which was shown by NOE to arise from the proton *syn* to the Cp ligand.

In the following experiments the sulfene complex **11** was produced in situ and was treated with carbon nucleophiles. Thus, treatment of the solution with *N*-(1-cyclopentenyl)-morpholine gave **12** in 81% yield and 64% de (Equation 7). Apparently, the chir ligand does not introduce excessive steric hindrance that would inhibit the nucleophilic addition at the sulfene ligand. Furthermore, the diastereoselectivity achieved here represents some improvement over the analogous reaction of the racemic mppe complex **2a** (Equation 2).



12 (81%, 64% de) (7)

Reactions of **11** with deprotonated diethyl methylmalonate or deprotonated β-oxo esters gave the expected addition products **13a**−**e** in good yields (Equation 8). Complexes **13b** and **13d** were formed with considerably higher diastereoselectivity than their mppe analogs **4a** and **4b**.



(8)

R^1	Et	Et	Et	*t*-Bu	Et
R^2, R^3	Me, OEt	Me, Me	Me, Ph	Me, Me	-$CH_2CH_2CH_2$-
	13a	**13b**	**13c**	**13d**	**13e**
Yield (%)	79	84	76	81	76
de (%)	-	62	36	90	20

After recrystallization, the major diastereoisomer of **13d** was obtained pure and was subjected to an X-ray structure determination. A view of the molecule is shown in Figure 2.The geometry around ruthenium is very similar to that of **10**. The addition of an organic group to the SO_2 ligand results in a slight decrease of the Ru−P bond lengths and a sizeable increase of the Ru−S distance by 17.4 pm. The latter is due to the combined effects of raising the coordination number at sulfur from three to four and occupying the vacant b_2 orbital at sulfur, which is responsible for the carbene-type π-backbonding in η^1-planar SO_2 complexes.[20] Nevertheless, the Ru−S bond is still shorter than expected for a single bond, but this is commonly observed for electron-rich sulfinato complexes.[22] The difference of the P−Ru−S angles has increased to 8.8° as a result of the repulsions encountered between the organic groups of the sulfinate ligand and the chiral chelate phosphane. The configuration at the former enolate carbon atom C72 is (*R*).

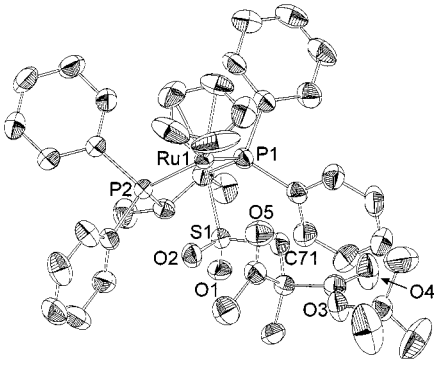
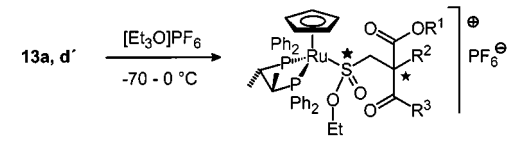


Figure 2. Molecular structure of [CpRu(chir){SO_2CH_2C(Me){C(O)Me}[C(O)O*t*Bu}}] (**13d′**) (hydrogen atoms omitted); selected distances [pm] and angles [°] (standard deviations in parentheses): Ru(1)−P(1) 228.0(2), Ru(1)−P(2) 228.3(2), Ru(1)−S(1) 230.2(2), S(1)−O(1) 146.7(3), S(1)−O(2) 146.8(4), S(1)−C(71) 182.7(5), S(1)−Ru(1)−P(1) 94.10(5), S(1)−Ru(1)−P(2) 85.28(5), P(1)−Ru(1)−P(2) 84.95(5), Ru(1)−S(1)−O(1) 115.3(2), Ru(1)−S(1)−O(2) 109.7(2), O(1)−S(1)−O(2) 113.4(2), Ru(1)−S(1)−C(71) 110.7(2)

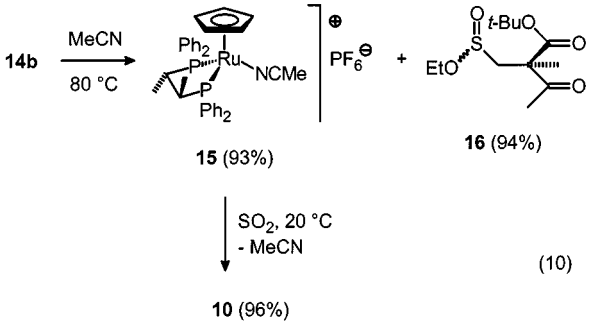
Electron-rich sulfinato complexes may be readily alkylated at one of the S=O functions.[3][23] Thus, reaction of **13a** or diastereomerically pure **13d′** with triethyloxonium hexafluorophosphate gave the sulfinic acid ester complexes **14a**, **b** in almost quantitative yields and, in the case of **14a**, good diastereoselectivity (Equation 9).



R^1	Et	*t*-Bu	**14a** (92%, 62% de)
R^2, R^3	Me, OEt	Me, Me	**14b** (94%, 6% de)
	14a	**14b**	

(9)

Sulfinic acid esters are weak donors which may readily be released from the metal.[3] Thus, heating **14b** in acetonitrile under reflux gave the acetonitrile complex **15** along with the diastereomeric ester **16**. Compound **15** may be converted back into the SO_2 complex **10** by treatment with sulfur dioxide (Equation 10).



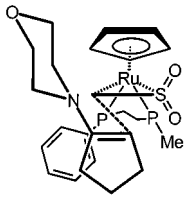
(10)

Discussion

In the symmetrical complex [CpRu(dppe)(CH_2=SO_2)]PF_6, the sulfene ligand rotates rapidly on the NMR timescale.[3] Therefore, we have to assume that in the similar sulfene complexes **2a**, **2b**, and **11**, the different rotamers are in thermodynamic equilibrium, dictated solely by steric requirements. Thus, for **2a** only one rotamer is found, in which the small CH_2 group is positioned *cis* to the large PPh_2 end of the chelate diphosphane. In **2b** the major (R_{Ru},R_C/S_{Ru},S_C) diastereoisomer has an analogous geometry with the methyl group in an *exo* position. The second isomer is most likely to be the opposite diastereomer. Both may even be in a slow equilibrium via an η^2-(S=O) bonded intermediate similar to the recently characterized sulfur trioxide complex [Cp*Ru(PMe_3)$_2$(η^2-O=SO_2)]-PF_6.[24]

Of the nucleophilic additions of **2a**, the reaction with the enamine (Equation 2) stands out for its fairly large diastereoselectivity. In this case, a prediction of the stereochemical course may be warranted. Simple molecular models suggest that the approach of (*R*)-**2a** on the *re* side of the enamine is favored, since this avoids any close contact

between the morpholino substituent and the *P*-phenyl group protruding into the space around the sulfene ligand (Scheme 2).



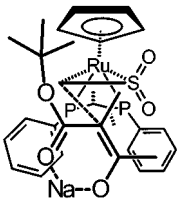
Scheme 2. Diastereoselective approach of *N*-(1-cyclopentenyl)morpholine to sulfene complex **2a**

The main product of the reaction (Equation 2) should thus be the (R_{Ru},R_C/S_{Ru},S_C) diastereoisomer. A remarkable gain in the diastereoselectivity of formation of **4c** was achieved when a titanium enolate was used. Such effects are often observed[14] but are difficult to interpret, since Ti^{IV} complexes of β-dicarbonyl compounds in solution invariably exist as mixtures of different monomers and dimers.[25] Precoordination of titanium to one of the sulfene oxygens may also have an influence.

Knowing that reactions at [NmcpRu(CO)$_2$X] proceed with rather low diastereoselectivity,[26][27] we had expected that the reactivity of the neomenthylcyclopentadienyl sulfene complex **8** would be quite similar to that of its C_5H_5 analog **2a**. Indeed, the de values of the formation of **4a** (Equation 3) and **9** (Equation 5) are almost the same. Nevertheless, the neomenthyl substituent does introduce considerable steric hindrance, as is seen in the lack of any reactions of **8** with enamines. An inspection of the molecular structures of [NmcpRu(CO)(PPh$_3$)I],[26] [NmcpRu(dppe)IEt]OTf,[27] and [NmcpRu(dppe)Cl][28] shows that the substituents at phosphorus force the Nmcp ligand into a rotational arrangement which places the neomenthyl group in close proximity to the site of the sulfene ligand and thus impedes nucleophilic additions. In view of the combined difficulties − low reactivity of the sulfene complex, unsatisfactory diastereoselectivity, and inefficient diastereoisomer separation − we finally abandoned the concept of chirality-at-the-metal.

The synthesis of the chiral, enantiomerically pure sulfene complex **11** posed no challenge at all. At low temperature, **11** is present as a single rotamer with the sulfene ligand oriented in such a way that the SO_2 group is placed into the largest void of the [CpRu(chir)] complex fragment.[17] The stereochemical course of the enamine addition (Equation 7) should therefore be again as outlined by Scheme 2, that is, the major diastereomer of **12** is expected to have (*R*) configuration at the newly created stereocenter. Unfortunately, we were unable to grow crystals of **12** suitable for an X-ray structure determination.

In the case of the enolate addition product **13d**, the (*R*) configuration at carbon was corroborated crystallographically. The outcome of the reaction would thus suggest a transition state as shown in Scheme 3, in which the large *tert*-butoxy group of the β-oxo ester is placed in the vicinity of the Cp ligand, which is less bulky than the PPh_2 groups of the chelate diphosphane. The solvated Na^+ cation is too far removed to interfere with the ruthenium complex.



Scheme 3. Diastereoselective approach of deprotonated β-oxo ester to sulfene complex **11**

Enantiomerically pure esters of sulfinic acids are important starting materials for the stereoselective synthesis of chiral sulfoxides.[29] It was, therefore, quite gratifying that the alkylation of **13a** (Equation 9) proceeded with good stereoselectivity. Inspection of the molecular structure of **13d′** or the closely related achiral sulfinate complex [CpRu(dppm)(SO_2Et)][22] shows that the SO_2R ligand in halfsandwich complexes is always oriented so that one of the two S=O groups is nested between the phenyl groups of the chelate diphosphane while the other one is accessible from the direction of the Cp ligand. For a chiral sulfinate complex with a fixed rotational arrangement of the SO_2R ligand such as **13a**, this means that the formation of the (R_S) ester complex will be favored. In the alkylation of **13d′**, the low de is then probably the result of a mismatch situation caused by the stereocenter at the quaternary carbon atom.

Conclusions

Chiral ruthenium halfsandwich complexes combine two interesting and potentially quite useful properties, the stabilization of otherwise short-lived unsaturated species, and the asymmetric induction in ligand-based reactions. The enantiomerically pure fragment $[CpRu(chir)]^+$ in particular stands out for its ready accessibility and excellent crystallization of almost all of its complexes. A promising potential in synthetic applications can thus be easily foreseen

Experimental Section

General Remarks: All experiments were carried out in Schlenk tubes under nitrogen in 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 in most cases gave well-resolved ABX_3 spectra with ^2J(H,H) = 9−11 Hz and ^3J(H,H) = 7.2 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 signal 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 Insti-

tut für Anorganische Chemie. − The following starting materials were obtained as described in the literature: [CpRu(mppe)(-SO_2)]PF_6 (**1**),[12] diazomethane, diazoethane,[30] neomenthylcyclopentadiene,[31] $[RuCl_2(PPh_3)_3]$,[32] [CpRu(chir)Cl].[33] Enolates were obtained from the corresponding 1,3-dicarbonyl compounds by deprotonation with sodium bis(trimethylsilyl)amide. All other reagents were used as purchased.

[CpRu(mppe)(CH_2=SO_2)]PF_6 (2a): To a solution of **1** (89 mg, 0.14 mmol) in dichloromethane (15 mL), a solution of diazomethane in diethyl ether (0.6 mL, 0.2 mmol) was added at −70 °C. Gas evolution and a rapid color change to pale yellow were observed. The mixture was allowed to warm to 0 °C, and was concentrated rapidly to 2 mL. Hexane (15 mL) was added to precipitate the tan-colored microcrystalline product. Yield 87 mg (96%), m.p. 98 °C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 0.20 [dd, ^2J(H,H) = 4.4 Hz, ^3J(P,H) = 16.1 Hz, 1 H, SO_2=CH_2], 2.41 [d, ^2J(H,H) = 4.4 Hz, SO_2=CH_2], 5.68 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = −19.1 [d, ^2J(P,C) = 6 Hz, SO_2=CH_2], 95.1 (s, C_5H_5). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 66.4 [d, J(P,P) = 18 Hz, PMe_2], 78.3 [d, J(P,P) = 18 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1236, 1104 cm^{-1} (S=O). − $C_{22}H_{27}F_6O_2P_3RuS$ (663.5): calcd. C 39.83, H 4.10; found C 39.97, H 4.00.

[CpRu(mppe)(CHMe=SO_2)]PF_6 (2b): This compound was prepared from **1** (146 mg, 0.22 mmol) and diazoethane (0.25 mmol) as described above except that the product was isolated at −30 °C by addition of precooled hexane. Yield 146 mg (96%), m.p. 129 °C (dec.). − Major diastereoisomer (74%): ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 0.68 [dq, ^3J(H,H) = 6.4 Hz, ^3J(P,H) = 16.4 Hz, 1 H, SO_2=CH], 1.50 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 5.61 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 2.1 [d, ^2J(P,C) = 5 Hz, CH=SO_2], 18.6 (s, CH_3), 95.9 (s, C_5H_5). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 67.6 [d, J(P,P) = 19 Hz, PMe_2], 77.6 [d, J(P,P) = 19 Hz, PPh_2]. − Minor diastereoisomer (26%): ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 1.74 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 5.46 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 91.4 (s, C_5H_5). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 64.6 [d, J(P,P) = 15 Hz, PMe_2], 85.8 [d, J(P,P) = 15 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1220, 1117 cm^{-1} (S=O). − $C_{23}H_{29}F_6O_2P_3RuS$ (677.5): calcd. C 40.77, H 4.31, S 4.73; found C 41.08, H 4.51, S 4.45.

[CpRu(mppe)$SO_2CH_2(C_9H_{15}NO)$]PF_6 (3): To a solution of **2a** (73 mg, 0.11 mmol) in dichloromethane (10 mL), a solution of *N*-(1-cyclopentenyl)morpholine in diethyl ether (0.5 mL, 0.12 mmol) was added at −70 °C. The solution was allowed to warm to 20 °C and stirred for an additional hour at this temperature. The mixture was then concentrated to 2 mL and the colorless product was precipitated by adding diethyl ether. Yield 68 mg (76%), m.p. 127 °C (dec.). − Major diastereoisomer (80%): ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 1.61−2.19 (m, 4 H, 2 × CH_2), 2.31 [dd, ^2J(H,H) = 13.6 Hz, ^3J(H,H) = 7.2 Hz, 1 H, SO_2CH], 2.44 [dd, ^2J(H,H) = 13.6 Hz, ^3J(H,H) = 7.2 Hz, 1 H, SO_2CH], 2.77−2.96 (m, 4 H, 2 × OCH_2), 3.72−3.99 (m, 4 H, 2 × NCH_2), 4.97 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 21.0 (s, C-4), 31.7 (s, C-3), 35.6 (s, C-5), 43.2 (s, C-2), 58.9 (s, NCH_2), 61.9 (s, NCH_2), 64.3 (s, OCH_2), 66.0 (s, OCH_2), 70.5 (s, SO_2CH_2), 84.0 (s, C_5H_5), 203.4 (s, C=N). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 51.7 [d, J(P,P) = 28 Hz, PMe_2], 85.2 [d, J(P,P) = 28 Hz, PPh_2]. − Minor diastereoisomer (20%): ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 1.61−2.19 (m, 4 H, 2 × CH_2), 2.77−2.96 (m, 4 H, 2 × OCH_2), 3.72−3.99 (m, 4 H, 2 × NCH_2), 4.92 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20 °C): δ = 22.3 (s, C-4), 32.4 (s, C-3), 35.1 (s, C-5), 39.7 (s, C-2), 65.6 (s, OCH_2), 67.0 (s, OCH_2), 74.1 (s, SO_2CH_2), 84.1 (s, C_5H_5). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20 °C): δ = 51.8 [d, J(P,P) = 26 Hz, PMe_2], 85.3 [d, J(P,P) = 26 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1678 cm^{-1} (C=N), 1132, 1017 cm^{-1} (S=O). − $C_{31}H_{42}F_6NO_3P_3RuS$ (816.7): calcd. C 45.59, H 5.18, N 1.72; found C 44.95, H 5.08, N 1.57.

Addition of Enolates to 2a: To a solution of 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 **2a** (135 mg, 0.20 mmol) in THF (20 mL). The mixture was allowed to warm to 20 °C and stirred for 2 h. The solvent was removed under vacuum, the oily residue was taken up in dichloromethane and chromatographed (neutral alumina, activity grade I, acetone/dichloromethane, 5:1). A broad, pale-yellow band containing the product was collected. The solvent was evaporated and the colorless product was recrystallized from benzene/hexanes.

4a: Yield 72 mg (54%), m.p. 115 °C (dec.). − Major diastereoisomer (71%): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.13 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.49 (s, 3 H, CH_3), 2.18 [d, ^2J(H,H) = 13.5 Hz, 1 H, SO_2CH_2], 2.26 (s, 3 H, CH_3), 3.46 [d, ^2J(H,H) = 13.5 Hz, 1 H, SO_2CH_2], 3.98 (res. m, OCH_2), 4.89 (s, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.9 (s, CH_3), 20.3 (s, CH_3), 27.8 (s, CH_3), 57.8 (s, C_{quat}), 60.9 (s, OCH_2), 74.7 (s, SO_2CH_2), 84.3 (s, C_5H_5), 171.9 (s, CO), 207.1 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 53.3 [d, J(P,P) = 28 Hz, PMe_2], 87.0 [d, J(P,P) = 28 Hz, PPh_2]. − Minor diastereoisomer (29%): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.22 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.37 (s, 3 H, CH_3), 1.81 (s, 3 H, CH_3), 2.19 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.21 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 4.17 (res. m, OCH_2), 4.92 (s, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 14.0 (s, CH_3), 18.5 (s, CH_3), 24.8 (s, CH_3), 59.3 (s, C_{quat}), 61.1 (s, OCH_2), 71.6 (s, SO_2CH_2), 84.1 (s, C_5H_5), 172.0 (s, CO), 204.4 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 53.5 [d, J(P,P) = 27 Hz, PMe_2], 86.8 [d, J(P,P) = 27 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1738, 1706 cm^{-1} (CO), 1187, 1150, 1000 cm^{-1} (S=O). − $C_{29}H_{38}O_5P_2RuS$ (661.7): calcd. C 52.64, H 5.79, S 4.85; found C 51.82, H 5.76, S 4.89.

4b: Yield 83 mg (60%), m.p. 160 °C (dec.). − Major diastereoisomer (74%): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.30 (s, 9 H, *t*Bu), 1.42 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.10 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.45 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 4.89 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 20.7 (s, CH_3), 27.5 (s, CH_3), 27.7 (s, *t*Bu), 31.7 (s, CH_3), 58.6 (s, C_{quat}), 74.5 (s, SO_2CH_2), 80.9 (s, C_{quat}), 84.2 (s, C_5H_5), 170.6 (s, CO), 206.7 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 53.3 [d, J(P,P) = 28 Hz, PMe_2], 87.0 [d, J(P,P) = 28 Hz, PPh_2]. − Minor diastereoisomer (26%): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.23 (s, 9 H, *t*Bu), 1.41 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 2.40 [d, ^2J(H,H) = 13.7 Hz, 1 H, SO_2CH_2], 3.07 [d, ^2J(H,H) = 13.7 Hz, 1 H, SO_2CH_2], 4.91 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 18.8 (s, CH_3), 27.8 (s, CH_3), 29.3 (s, *t*Bu), 59.9 (s, C_{quat}), 71.8 (s, SO_2CH_2), 83.7 (s, C_{quat}), 84.1 (s, C_5H_5), 170.9 (s, CO), 204.7 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20 °C): δ = 53.5 [d, J(P,P) = 28 Hz, PMe_2], 86.9 [d, J(P,P) = 28 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1727, 1700 cm^{-1} (CO), 1139, 1025 cm^{-1} (S=O). − $C_{31}H_{42}O_5P_2RuS$ (689.8): calcd. C 53.98, H 6.14; found C 53.28, H 6.38.

4c: Yield 85 mg (63%), m.p. 177 °C (dec.). − Major diastereoisomer (66%): ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.14 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 2.34 [d, ^2J(H,H) = 13.8 Hz, 1 H, SO_2CH_2], 3.31 [d, ^2J(H,H) = 13.8 Hz, 1 H, SO_2CH_2], 3.96 (res. m, 2 H, OCH_2), 4.90 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ =

14.0 (s, CH_3), 19.8 (s, CH_2), 30.8 (s, CH_2), 37.5 (CH_2), 58.6 (s, C_{quat}), 60.9 (s, OCH_2), 72.5 (s, SO_2CH_2), 84.5 (s, C_5H_5), 170.8 (s, CO), 215.5 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 53.3 [d, J(P,P) = 28 Hz, PMe_2], 86.9 [d, J(P,P) = 28 Hz, PPh_2]. − Minor diastereoisomer (34%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.21 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.63 [d, ^2J(H,H) = 13.5 Hz, 1 H, SO_2CH_2], 3.15 [d, ^2J(H,H) = 13.5 Hz, 1 H, SO_2CH_2], 4.13 [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 = 19.1 (s, CH_2), 19.5 (s, CH_3), 30.4 (s, CH_2), 37.0 (s, CH_2), 59.8 (s, C_{quat}), 61.2 (s, OCH_2), 69.0 (s, CH_2SO_2), 84.2 (s, C_5H_5), 169.2 (s, CO), 213.7 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 53.4 [d, J(P,P) = 28 Hz, PMe_2], 86.7 [d, J(P,P) = 28 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1742, 1721 cm^{-1} (CO), 1150, 1121, 1024, 1011 cm^{-1} (S=O). − $C_{30}H_{38}O_5P_2RuS$ (673.7): calcd. C 53.48, H 5.69; found C 52.62, H 5.44.

4c by Titanium Enolate Addition: Ethyl 2-oxocyclopentanecarboxylate (35 mg, 0.22 mmol) was deprotonated as described above and then treated at −30°C with $TiCl(OiPr)_3$. After addition of **2a** (135 mg, 0.20 mmol), the mixture was allowed to warm to 20°C and was stirred for 2 h. The solvent was removed under vacuum, and the oily residue was taken up in CD_2Cl_2 and analysed by ^{1}H and ^{31}P NMR, which indicated the formation of **4c** with 81% de. Attempted workup by hydrolysis and chromatography, however, resulted in an intractable mixture from which **4c** could not be separated in pure form.

[CpRu(mppe){$SO_2CH(Me)(C_8H_{13}O_4)$}] (4d): To a solution of $Na[N(SiMe_3)_2]$ (103 mg, 0.56 mmol) in THF (20 mL), diethyl methylmalonate (87 mg, 0.50 mmol) was added at −70°C. In a separate reaction, a solution of **1** (325 mg, 0.50 mmol) in dichloromethane (25 mL) was treated with a solution of diazoethane in diethyl ether (2.0 mL, 0.51 mmol) at −70°C and stirred at this temperature for 5 min. The two solutions were combined at −70 °C, and the resulting mixture was allowed to warm to 20 °C and was stirred for an additional hour. The solvent was then removed under vacuum and the oily residue was taken up in dichloromethane and chromatographed (neutral alumina, activity grade I, acetone/dichloromethane, 2:1). A broad, pale-yellow band containing the product was collected. The solvent was evaporated and the product was recrystallized from benzene/hexanes. Yield 251 mg (71%), m.p. 106°C (dec.). − Major diastereoisomer (63%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 0.19 [d, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.14 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.17−1.26 (m, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 3.45 [q, ^3J(H,H) = 7.2 Hz, 1 H, SO_2CH], 3.98−4.28 (m, 4 H, 2 × OCH_2], 4.84 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 9.7 (s, CH_3), 14.0 (s, CH_3), 14.1 (s, CH_3), 14.5 (s, CH_3), 58.0 (s, C_{quat}), 60.8 (s, OCH_2), 61.0 (s, OCH_2), 74.2 (s, SO_2CH), 83.5 (s, C_5H_5), 171.1 (s, CO), 171.2 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 61.0 [d, J(P,P) = 16 Hz, PMe_2], 85.9 [d, J(P,P) = 16 Hz, PPh_2]. − Minor diastereoisomer (37%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.16 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.17−1.26 (m, 3 H, CH_3), 1.24 [d, ^3J(H,H) = 8.0 Hz, 3 H, CH_3], 1.45 (s, 3 H, CH_3), 3.70 [q, ^3J(H,H) = 8.0 Hz, 1 H, SO_2CH], 3.98−4.28 (m, 4 H, 2 × OCH_2], 5.00 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 12.5 (s, CH_3), 14.0 (s, CH_3), 15.1 (s, CH_3), 29.4 (s, CH_3), 56.9 (s, C_{quat}), 61.0 (s, OCH_2), 61.2 (s, OCH_2), 71.7 (s, SO_2CH), 83.3 (s, C_5H_5), 171.1 (s, CO), 171.2 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 51.6 [d, J(P,P) = 29 Hz, PMe_2], 81.5 [d, J(P,P) = 29 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1731 cm^{-1} (CO), 1165, 1051 cm^{-1} (S=O). − $C_{31}H_{42}O_6P_2RuS$ (705.8): calcd. C 52.76, H 6.00, S 4.54; found C 53.01, H 6.01, S 4.54.

[NmCpRu(PPh_3)$_2$Cl] (5): To a solution of (+)-neomenthylcyclopentadiene (1.94 g, 9.49 mmol) in diethyl ether (50 mL) was added, at 0°C, a solution of methyllithium in diethyl ether (6.25 mL, 10.0 mmol). The mixture was allowed to warm to room temperature and was stirred overnight. A white precipitate was formed, which was washed thoroughly with diethyl ether; the resulting solution was dried under vacuum. The lithium neomenthylcyclopentadienide (84 mg, 0.40 mmol) was added to a solution of [$RuCl_2(PPh_3)_3$] (336 mg, 0.35 mmol) in benzene (30 mL). The mixture was heated under reflux for 1 h, causing a color change to orange. The solvent was removed under vacuum and the residue was chromatographed (silica gel, acetone/dichloromethane, 10:1). A broad orange band containing the product was collected and concentrated to dryness. The residue was taken up in hexane and treated with ultrasound whereupon the product separated out as an orange crystalline powder. Yield 212 mg (70%), m.p. 125°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 0.74 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 0.89 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 0.91 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 1.01−1.77 (m, 7 H, Nm), 2.43−2.51 (m, 2 H, Nm), 2.88−2.96 (m, 1 H, Nm), 3.05, 3.62, 3.91, 4.02 (4 × s, 4 × 1 H, C_5H_4Nm). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 21.3 (s, CH_3), 22.4 (s, CH_3), 22.7 (s, CH_3), 24.9 (s, CH_2), 28.0 (s, CH), 28.6 (s, CH), 34.3 (s, CH), 35.4 (s, CH_2), 38.1 (s, CH_2), 50.2 (s, CH), 73.5, 76.1 (2 × s, 2 × C_5H_4), 78.7, 80.4 [2 × d, ^2J(P,C) = 9 Hz, 2 × C_5H_4], 115.9 [d, ^2J(P,C) = 5 Hz, C_5H_4]. − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 39.9 [d, ^2J(P,P) = 41 Hz], 40.8 [d, ^2J(P,P) = 41 Hz]. − $C_{51}H_{53}ClP_2Ru$ (864.5): calcd. C 70.86, H 6.18; found C 70.81, H 6.19.

[NmCpRu(mppe)Cl] (6): A solution of **5** (425 mg, 0.49 mmol) and mppe (137 mg, 0.50 mmol) in benzene (100 mL) was heated under reflux for 20 h. The solvent was evaporated and the red oily residue was taken up in dichloromethane and chromatographed (silica gel, dichloromethane/acetone, 1:10). A broad, orange band containing the product was collected and the orange crystalline product was isolated as described above for **5**. Yield 242 mg (80%), m.p. 144°C (dec.). − Diastereoisomer **6′** (50%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 0.75 [d, ^3J(H,H) = 6.6 Hz, 3 H, CH_3], 0.82 [d, ^3J(H,H) = 6.2 Hz, 3 H, CH_3], 0.93 [d, ^3J(H,H) = 6.6 Hz, 3 H, CH_3], 0.95−1.95 (m, 7 H, Nm), 2.10−2.25 (m, 2 H, Nm), 2.80−2.88 (m, 1 H, Nm), 3.33, 3.97, 4.73, 5.07 (4 × s, 4 × 1 H, C_5H_4). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 20.6 (s, CH_3), 22.4 (s, CH_3), 23.1 (s, CH_3), 24.4 (s, CH_2), 28.6 (s, CH), 29.6 (s, CH), 35.2 (s, CH), 35.9 (s, CH_2), 40.6 (s, CH_2), 48.5 (s, CH), 63.9, 77.4 (2 × s, 2 × C_5H_4), 81.5 [d, ^2J(C,P) = 8 Hz, C_5H_4], 85.4 [d, ^2J(C,P) = 8 Hz, C_5H_4], 106.6 [d, ^2J(C,P) = 8 Hz, C_5H_4]. − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 51.8 [d, J(P,P) = 30 Hz, PMe_2], 84.3 [d, J(P,P) = 30 Hz, PPh_2]. − Diastereoisomer **6′′** (50%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 0.96 [d, ^3J(H,H) = 6.6 Hz, 3 H, CH_3], 0.92−1.95 (m, 13 H, Nm), 2.10−2.25 (m, 2 H, Nm), 2.93−2.99 (m, 1 H, Nm), 3.48, 3.95, 4.45, 4.98 (4 × s, 4 × 1 H, C_5H_4Nm). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 20.5 (s, CH_3), 22.3 (s, CH_3), 22.8 (s, CH_3), 24.3 (s, CH_2), 27.1 (s, CH), 29.4 (s, CH), 35.1 (s, CH), 35.7 (s, CH_2), 40.5 (s, CH_2), 48.4 (s, CH), 71.3 [d, ^2J(P,C) = 11 Hz, C_5H_4], 73.1 (s, C_5H_4), 77.5 [d, ^2J(P,C) = 8 Hz, C_5H_4], 87.8 [d, ^2J(P,C) = 6 Hz, C_5H_4], 106.5 [d, ^2J(P,C) = 6 Hz, C_5H_4]. − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 51.8 [d, J(P,P) = 29 Hz, PMe_2], 81.7 [d, J(P,P) = 29 Hz, PPh_2]. − $C_{31}H_{43}ClP_2Ru$ (614.2): calcd. C 60.62, H 7.06; found C 60.84, H 7.39. − A sample of diastereomerically pure **6′** was obtained from **6** (5.00 g) by four cycles of slow crystallization from toluene/hexane. Yield 0.45 g (18%).

[NmCpRu(mppe)(SO_2)]PF_6 (7): A pressure tube equipped with a teflon needle valve was charged with **6** (210 mg, 0.34 mmol), NH_4PF_6 (73 mg, 0.45 mmol), and dichloromethane (20 mL). After this solution was cooled to −70°C, an excess of sulfur dioxide (ca

1 mL) was condensed into it. The mixture was stirred at 20°C for 15 h, during which a color change to yellow occurred. The excess SO_2 was removed under vacuum and the solution was filtered through Celite. After this solution was concentrated to dryness, the residue was recrystallized from dichloromethane/pentane to obtain a yellow crystalline powder. Yield 212 mg (79%), m.p. 153°C (dec.). − Diastereoisomer **7′** (50%): ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 0.76 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 0.93 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 0.99 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 1.05−2.05 (m, 7 H, Nm), 2.50−2.68 (m, 2 H, Nm), 2.88−3.02 (m, 1 H, Nm), 4.62, 5.12, 5.32, 5.89 (4 × s, 4 × 1 H, C_5H_4). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 20.5 (s, CH_3), 22.4 (s, CH_3), 23.1 (s, CH_3), 24.4 (s, CH_2), 28.6 (s, CH), 29.6 (s, CH), 35.8 (s, CH), 36.0 (s, CH_2), 45.9 (s, CH_2), 49.2 (s, CH), 79.2 (s, C_5H_4), 95.1 [d, ^2J(C,P) = 4 Hz, C_5H_4], 96.4 [d, ^2J(C,P) = 6 Hz, C_5H_4], 122.76 (s, C_5H_4). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 55.7 [d, J(P,P) = 20 Hz, PMe_2], 77.9 [d, J(P,P) = 20 Hz, PPh_2]. − Diastereoisomer **7′′** (50%): ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 0.80 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 0.81 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 1.01 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 1.05−2.05 (m, 7 H, Nm), 2.50−2.68 (m, 2 H, Nm), 3.16−3.28 (m, 1 H, Nm), 5.12, 5.27, 5.84, 6.29 (4 × s, 4 × 1 H, C_5H_4). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 20.8 (s, CH_3), 22.5 (s, CH_3), 22.8 (s, CH_3), 24.7 (s, CH_2), 28.8 (s, CH), 30.4 (s, CH), 35.6 (s, CH), 35.9 (s, CH_2), 43.7 (s, CH_2), 48.2 (s, CH), 83.2, 87.9 (2 × s, 2 × C_5H_4), 94.4 [d, ^2J(C,P) = 2 Hz, C_5H_4], 95.0 [d, ^2J(C,P) = 4 Hz, C_5H_4], 122.81 (s, C_5H_4). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 55.5 [d, J(P,P) = 21 Hz, PMe_2], 74.8 [d, J(P,P) = 21 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1282, 1016 cm^{-1} (S=O). − $C_{31}H_{43}F_6O_2P_3RuS$ (787.7): calcd. C 47.27, H 5.50; found C 48.64, H 5.79. − From the same procedure, diastereomerically pure **7′** was obtained from pure **6′**.

[NmCpRu(mppe)(CH_2=SO_2)]PF_6 (8′): This compound was prepared from diastereomerically pure **7′** and diazomethane as described above for **2a**. Attempted crystallization at 0°C yielded only a pale-brown semi-solid product which was identified spectroscopically. − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 0.39 [dd, ^2J(H,H) = 4.4 Hz, ^3J(P,H) = 16.8 Hz, 1 H, SO_2=CH_2], 0.91 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 0.94 [d, ^3J(H,H) = 6.1 Hz, 3 H, CH_3], 1.04 [d, ^3J(H,H) = 6.3 Hz, 3 H, CH_3], 4.81, 5.31, 5.61, 5.98 (4 × s, 4 ×1 H, C_5H_4); due to sample decomposition, the remaining signals could not be assigned with certainty. − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 67.6 [d, J(P,P) = 16 Hz, PMe_2], 80.0 [d, J(P,P) = 16 Hz, PPh_2].

[NmCpRu(mppe){$SO_2CH_2(C_7H_{11}O_3)$}] (9): A solution of **7** (0.24 g, 0.30 mmol) in dichloromethane (20 mL) was treated consecutively with diazomethane and the sodium enolate of ethyl 2-methyl-3-oxobutanoate, as described above for the synthesis of **4d**. Chromatographic workup gave a yellow oil which could not be induced to crystallize. Yield 112 mg (47%) − Major diastereoisomer (72%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 0.71 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 0.82 [d, ^3J(H,H) = 6.0 Hz, 3 H, CH_3], 0.97 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 1.12 [t, ^3J(H,H) = 7.0 Hz, 3 H, CH_3], 1.54 (s, 3 H, CH_3), 2.11 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 2.45 (s, 3 H, CH_3), 2.92−2.95 (m, 1 H, CH), 3.44 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.87−4.01 (m, 2 H, OCH_2), 4.33, 4.78, 5.15, 5.40 (4 × s, 4 × 1 H, C_5H_4). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (s, CH_3), 27.8 (s, CH), 29.5 (s, CH), 36.0 (s, CH_2), 36.5 (s, CH), 42.3 (s, CH_2), 48.8 (s, CH), 57.7 (s, C_{quat}), 60.8 (s, OCH_2), 74.6 (s, SO_2CH_2), 75.1, 77.7, 88.0 (3 × s, 3 × C_5H_4), 98.6 [d, ^2J(P,C) = 4 Hz, C_5H_4], 106.8 [d, ^2J(P,C) = 10 Hz, C_5H_4], 172.0 (s, CO), 207.6 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 48.8 [d, J(P,P) = 28 Hz, PMe_2], 88.3 [d, J(P,P) = 28 Hz, PPh_2]. − Minor diastereoisomer (28%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 0.10 [d, ^3J(H,H) = 6.4 Hz, 3 H, CH_3], 0.88 [d, ^3J(H,H) = 6.0 Hz, 3 H, CH_3], 1.11 [t, ^3J(H,H) = 7.0 Hz, 3 H, CH_3], 1.51 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.29 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 2.96−3.01 (m, 1 H, CH), 3.42 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.87−4.01 (m, 2 H, OCH_2), 4.15, 5.03, 5.05, 5.14 (4 × s, 4 × 1 H, C_5H_4). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (s, CH_3), 34.5 (s, CH), 36.0 (s, CH_2), 41.8 (s, CH_2), 48.8 (s, CH), 57.8 (s, C_{quat}), 60.8 (s, OCH_2), 74.6, (s, SO_2CH_2), 75.2, 78.1, 87.9 (3 × s, 3 × C_5H_4), 94.3 [d, ^2J(P,C) = 4 Hz, C_5H_4], 105.9 [d, ^2J(P,C) = 10 Hz, C_5H_4], 171.9 (s, CO), 206.9 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 52.4 [d, J(P,P) = 26 Hz, PMe_2], 86.3 [d, J(P,P) = 26 Hz, PPh_2]. − IR (Nujol): $\tilde{\nu}$ = 1732, 1712 cm^{-1} (CO), 1136, 1025 cm^{-1} (S=O).

[CpRu(chir)(SO_2)]PF_6 (10): This compound was prepared from [CpRu(chir)Cl] (0.26 g, 0.42 mmol), NH_4PF_6 (88 mg, 0.54 mmol) and SO_2 as described above for **7**. Yield 0.28 g (84%), m.p. 160°C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 5.36 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20°C): δ = 92.2 (s, C_5H_5). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 69.3 [d, J(P,P) = 34 Hz], 74.2 [d, J(P,P) = 34 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1296, 1118 cm^{-1} (S=O). − $C_{33}H_{33}F_6O_2P_3RuS$ (801.7): calcd. C 49.44, H 4.15, S 4.00; found C 49.34, H 4.17, S 3.94.

[CpRu(chir)(SO_2=CH_2)]PF_6 (11): This compound was prepared from **10** (80 mg, 0.10 mmol) and diazomethane as described above for **2a**. Yield 78 mg (96%), m.p. 157°C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 0.85 [dd, ^2J(H,H) = 4.3 Hz, ^3J(H,P) = 16.7 Hz, 1 H, SO_2CH_2], 2.31 [dt, ^2J(H,H) = 4.3 Hz, ^3J(H,P) = 1.6 Hz, 1 H, SO_2CH_2], 5.21 (s, 5 H,C_5H_5). − ^{13}C NMR (100 MHz, CD_2Cl_2, 20°C): δ = −17.7 [d, ^2J(P,C) = 3 Hz, SO_2CH_2], 97.9 (s, C_5H_5). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 62.0 [d, J(P,P) = 42 Hz], 77.4 [d, J(P,P) = 42 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1245, 1104 cm^{-1} (S=O). − $C_{34}H_{35}F_6O_2P_3RuS$ (815.7): calcd. C 50.06, H 4.33, S 3.93; found C 50.25, H 4.56, S 4.08.

{CpRu(chir)[SO_2=$CH_2(C_9H_{15}NO)$]}PF_6 (12): A solution of **10** (88 mg, 0.11 mmol) in dichloromethane (10 mL) was treated consecutively with diazomethane and *N*-(1-cyclopentenyl)morpholine as described above for the synthesis of **3**. Yield 86 mg (81%), m.p. 141°C (dec.). − Major diastereoisomer (82%): ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 4.62 (s, 5 H, C_5H_5); due to extensive signal overlap the remaining resonances could not be assigned with certainty. − ^{13}C NMR (100 MHz, CD_2Cl_2, 20°C): δ = 21.0 (s, CH_2), 32.0 (s, CH_2), 35.6 (s, CH_2), 43.2 (s, CH), 54.7 (s, NCH_2), 65.3 (s, OCH_2), 66.6 (s, OCH_2), 68.5 (s, SO_2CH_2), 86.3 (s, C_5H_5), 202.9 (s, CN). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 67.3 [d, J(P,P) = 35 Hz], 85.4 [d, J(P,P) = 35 Hz]. − Minor diastereoisomer (18%): ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 4.61 (s, 5 H, C_5H_5); due to extensive signal overlap the remaining resonances could not be assigned with certainty. − ^{13}C NMR (100 MHz, CD_2Cl_2, 20°C): δ = 21.9 (s, CH_2), 31.3 (s, CH_2), 34.5 (s, CH_2), 44.0 (s, CH), 52.5 (s, NCH_2), 64.7 (s, OCH_2), 65.6 (s, OCH_2), 69.8 (s, SO_2CH_2), 86.5 (s, C_5H_5), 201.7 (s, CN). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 65.4 [d, J(P,P) = 36 Hz], 86.0 [d, J(P,P) = 36 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1666 cm^{-1} (CN), 1087, 995 cm^{-1} (S=O). − $C_{43}H_{50}F_6NO_3P_3RuS$ (968.9): calcd. C 53.30, H 5.20, N 1.45; found C 53.04, H 5.55, N 1.45.

Addition of Enolates to 11: A solution of **10** (0.16 g, 0.20 mmol) in dichloromethane (15 mL) was treated at −70°C with diazomethane and a suspension of the respective sodium enolate as described above for **4a−c**.

13a: Yield 133 mg (79%), m.p. 130°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.15 [t, ^3J(H,H) = 7.1 Hz, 3 H,

CH_3], 1.18 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.23 (s, 3 H, CH_3), 1.90 [d, ^2J(H,H) = 12.0 Hz, 1 H, SO_2CH_2], 3.07 [d, ^2J(H,H) = 12.0 Hz, 1 H, SO_2CH_2], 3.93−4.19 (m, 4 H, 2 × OCH_2), 4.53 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (s, 2 × CH_3), 19.4 (s, CH_3), 53.1 (s, C_{quat}), 60.9 (s, 2 × OCH_2), 69.8 (s, SO_2CH_2), 86.4 (s, C_5H_5), 171.2 (s, CO), 171.5 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 65.0 [d, J(P,P) = 34 Hz], 86.5 [d, J(P,P) = 34 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1734 cm^{-1} (CO), 1148, 1025 cm^{-1} (S=O). − $C_{42}H_{48}O_6P_2RuS$ (843.9): calcd. C 59.78, H 5.73; found C 59.50, H 5.99.

13b: Yield 137 mg (84%), m.p. 220°C (dec.). − Major diastereoisomer (81%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.19 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.49 (s, 3 H, CH_3), 1.89 (s, 3 H, CH_3), 1.88 [d, ^2J(H,H) = 13.4 Hz, 1 H, SO_2CH_2], 3.00 [d, ^2J(H,H) = 13.4 Hz, 1 H, SO_2CH2], 4.13 (res. m, 2 H, OCH_2), 4.65 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (s, CH_3), 18.6 (s, CH_3), 25.2 (s, CH_3), 59.3 (s, C_{quat}), 61.1 (s, OCH_2), 69.9 (s, SO_2CH_2), 86.5 (s, C_5H_5), 172.0 (s, CO), 204.8 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 65.3 [d, J(P,P) = 35 Hz], 86.4 [d, J(P,P) = 35 Hz]. − Minor diastereoisomer (19%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.14 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.61 (s, 3 H, CH_3), 1.81 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 2.24 (s, 3 H, CH_3), 3.28 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.97 (res. m, 2 H, OCH_2) 4.53 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.9 (s, CH_3), 20.4 (s, CH_3), 27.6 (s, CH_3), 57.8 (s, C_{quat}), 60.9 (s, OCH_2), 72.6 (s, SO_2CH_2), 86.6 (s, C_5H_5), 171.9 (s, CO), 207.3 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 65.2 [d, J(P,P) = 36 Hz], 86.6 [d, J(P,P) = 36 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1712 cm^{-1} (CO), 1144, 1022 cm^{-1} (S=O). − $C_{41}H_{46}O_5P_2RuS$ (813.9): calcd. C 60.51, H 5.70; found C 60.33, H 5.72.

13c: Yield 133 mg (76%), m.p. 121°C (dec.). − Major diastereoisomer (68%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.04 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.23 (s, 3 H, CH_3), 2.07 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.16 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.96−4.15 (m, 2 H, OCH_2), 4.50 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.7 (s, CH_3), 20.5 (s, CH_3), 57.4 (s, C_{quat}), 61.2 (s, OCH_2), 71.0 (s, SO_2CH_2), 86.3 (s, C_5H_5), 172.4 (s, CO), 198.0 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 65.2 [d, J(P,P) = 36 Hz], 86.6 [d, J(P,P) = 36 Hz]. − Minor diastereoisomer (32%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.07 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.22 (s, 3 H, CH_3), 2.10 [d, ^2J(H,H) = 13.4 Hz, 1 H, SO_2CH_2], 3.35 [d, ^2J(H,H) = 13.4 Hz, 1 H, SO_2CH_2], 3.96−4.15 (m, 2 H, OCH_2), 4.25 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 13.8 (s, CH_3), 21.2 (s, CH_3), 56.9 (s, C_{quat}), 61.1 (s, OCH_2), 71.7 (s, SO_2CH_2), 86.2 (s, C_5H_5), 172.5 (s, CO), 199.2 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 65.0 [d, J(P,P) = 36 Hz], 86.3 [d, J(P,P) = 36 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1680 cm^{-1} (CO), 1143, 1020 cm^{-1} (S=O). − $C_{46}H_{48}O_5P_2RuS$ (876.0): calcd. C 63.07, H 5.52; found C 62.94, H 5.84.

13d: Yield 136 mg (81%), m.p. 164°C (dec.). − Major diastereoisomer (95%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.38 (s, 9 H, *t*Bu), 1.47 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 2.21 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 2.88 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 4.56 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 19.0 (s, CH_3), 25.8 (s, CH_3), 27.8 (s, *t*Bu), 59.8 (s, C_{quat}), 70.9 (s, SO_2CH_2), 80.8 (s, C_{quat}), 86.5 (s, C_5H_5), 170.8 (s, CO), 205.4 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 66.8 [d, J(P,P) = 35 Hz], 86.6 [d, J(P,P) = 35 Hz]. − Minor diastereoisomer (5%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.86 (s, 3 H, CH_3), 2.33 [d, ^2J(H,H) = 13.4 Hz, 1 H, SO_2CH_2], 4.89 (s, 5 H, C_5H_5); remaining signals obscured by major diastereoisomer. − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 65.0 [d, J(P,P) = 36 Hz]; second doublet obscured by major diastereoisomer. − IR (Nujol): $\tilde{\nu}$ = 1732, 1701 cm^{-1} (CO), 1145, 1025 cm^{-1} (S=O). − $C_{43}H_{50}O_5P_2RuS$ (842.0): calcd. C 61.34, H 5.99; found C 61.85, H 6.26. − Recrystallization from benzene/hexane gave the major diastereoisomer **13d′** in pure form.

13e: Yield 125 mg (76%), m.p. 150°C (dec.). − Major diastereoisomer (60%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.18 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.70−2.22 (m, 4 H, CH_2CH_2), 1.99 [d, ^2J(H,H) = 13.3 Hz, 1 H, SO_2CH_2], 3.07 [d, ^2J(H,H) = 13.3 Hz, 1 H, SO_2CH_2], 3.38−3.57 (m, 2 H, CH_2), 4.10 (res. m, 2 H, OCH_2), 4.56 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.0 (s, CH_3), 19.5 (s, CH_2), 30.8 (s, CH_2), 37.2 (s, CH_2), 59.7 (s, C_{quat}), 61.2 (s, OCH_2), 67.8 (s, SO_2CH_2), 86.6 (s, C_5H_5), 169.4 (s, CO), 214.1 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 65.8 [d, J(P,P) = 35 Hz], 86.3 [d, J(P,P) = 35 Hz]. − Minor diastereoisomer (40%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.14 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.39 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 1.70−2.22 (m, 4 H, CH_2CH_2), 2.99 [d, ^2J(H,H) = 13.6 Hz, 1 H, SO_2CH_2], 3.38−3.57 (m, 2 H, CH_2), 3.97 (res. m, 2 H, OCH_2), 4.53 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 14.0 (s, CH_3), 20.0 (s, CH_2), 29.7 (s, CH_2), 37.6 (s, CH_2), 58.6 (s, C_{quat}), 60.9 (s, OCH_2), 70.2 (s, SO_2CH_2), 86.7 (s, C_5H_5), 170.9 (s, CO), 215.2 (s, CO). − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 66.0 [d, J(P,P) = 35 Hz], 86.5 [d, J(P,P) = 35 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1793, 1714 cm^{-1} (CO), 1146, 1021 cm^{-1} (S=O). − $C_{42}H_{46}O_5P_2RuS$ (825.9): calcd. C 61.08, H 5.61; found C 60.83, H 5.95.

***O*-Alkylation of the Sulfinato Complexes:** To a solution of the sulfinato complex (0.1 mmol) in dichloromethane (10 mL), a solution of triethyloxonium hexafluorophosphate (25 mg, 0.1 mmol) in the same solvent was added at −70°C. After being allowed to warm to room temperature, the mixture was concentrated to a volume of 1 mL and the product was precipitated by the addition of pentane.

14a: Yield 92 mg (92%), m.p. 121°C (dec.). − Major diastereoisomer (81%): ^{1}H NMR (400 MHz, [D_6]acetone, 20°C): δ = 0.81 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.11 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.19 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.36 (s, 3 H, CH_3), 2.65 [dq, ^2J(H,H) = 9.7 Hz, ^3J(H,H) = 7.2 Hz, S(O)OCH], 2.87 [dq, ^2J(H,H) = 9.7 Hz, ^3J(H,H) = 7.2 Hz, S(O)OCH_2], 3.10 [d, ^2J(H,H) = 16.0 Hz, 1 H, SO_2CH_2], 3.68 [d, ^2J(H,H) = 16.0 Hz, 1 H, SO_2CH_2], 3.91−4.21 (m, 4 H, 2 × OCH_2), 4.98 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D_6]acetone, 20°C): δ = 14.0 (s, CH_3), 14.1 (s, CH_3), 14.3 (s, CH_3), 19.0 (s, CH_3), 54.4 (s, C_{quat}), 60.9 (s, OCH_2), 62.0 (s, OCH_2), 62.4 (s, OCH_2), 72.6 (s, SO_2CH_2), 88.9 (s, C_5H_5), 170.0 (s, CO), 170.1 (s, CO). − ^{31}P NMR (162 MHz, [D_6]acetone, 20°C): δ = 55.7 [d, J(P,P) = 38 Hz], 76.2 [d, J(P,P) = 38 Hz]. − Minor diastereoisomer (19%): ^{1}H NMR (400 MHz, [D_6]acetone, 20°C): δ = 3.46 [d, ^2J(H,H) = 14.7 Hz, 1 H, SO_2CH_2], 4.98 (s, 5 H, C_5H_5); remaining signals obscured by major diastereoisomer. − ^{13}C NMR (100 MHz, [D_6]acetone, 20°C): δ = 19.0 (s, CH_3), 54.5 (s, C_{quat}), 60.9 (s, OCH_2), 62.1 (s, OCH_2), 62.6 (s, OCH_2), 70.9 (s, SO_2CH_2), 88.7 (s, C_5H_5). − ^{31}P NMR (162 MHz, [D_6]acetone, 20°C): δ = 55.8 [d, J(P,P) = 37 Hz,], 77.4 [d, J(P,P) = 37 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1735 cm^{-1} (CO), 1155 cm^{-1} (S=O). − $C_{44}H_{53}F_6O_6P_3RuS$ (1017.9): calcd. C 51.92, H 5.25, S 3.15; found C 52.19, H 5.05, S 3.06.

14b: Yield 95 mg (95%), m.p. 137°C (dec.). − Major diastereoisomer (53%): ^{1}H NMR (400 MHz, [D_6]acetone, 20°C): δ = 0.81 [t, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 1.27 (s, 3 H, CH_3), 1.32 (s, 9 H, *t*Bu), 1.95 (s, 3 H, CH_3), 2.55 [d, ^2J(H,H) = 15.2 Hz, 1 H, SO_2CH_2],

2.89 (res. m, 1 H, OCH_2), 3.70 (res. m, 1 H, OCH_2), 3.42 [d, ^2J(H,H) = 15.2 Hz, 1 H, SO_2CH_2], 4.98 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 14.0 (s, CH_3), 18.5 (s, CH_3), 26.5 (s, CH_3), 27.8 (s, *t*Bu), 60.9 (s, OCH_2), 61.1 (s, C_{quat}), 71.2 (s, SO_2CH_2), 82.8 (s, C_{quat}), 88.8 (s, C_5H_5), 169.2 (s, CO), 201.9 (s, CO). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 55.6 [d, *J*(P,P) = 37 Hz], 77.1 [d, *J*(P,P) = 37 Hz]. − Minor diastereoisomer (47%): ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 0.74 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.41 (s, 3 H, CH_3), 1.42 (s, 9 H, *t*Bu), 2.11 (s, 3 H, CH_3), 2.62 (res. m, 1 H, OCH_2), 2.99 [d, ^2J(H,H) = 15.2 Hz, 1 H, SO_2CH_2], 3.48 (res. m, 1 H, OCH_2), 3.73 [d, ^2J(H,H) = 15.2 Hz, 1 H, SO_2CH_2], 4.99 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 14.8 (s, CH_3), 19.1 (s, CH_3), 25.2 (s, CH_3), 27.5 (s, *t*Bu), 60.6 (s, OCH_2), 65.8 (s, C_{quat}), 72.6 (s, SO_2CH_2), 83.2 (s, C_{quat}), 88.7 (s, C_5H_5), 170.0 (s, CO), 203.0 (s, CO). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 55.9 [d, *J*(P,P) = 37 Hz], 76.2 [d, *J*(P,P) = 37 Hz]. − IR (Nujol): $\tilde{\nu}$ = 1715 cm^{-1} (CO), 1148 cm^{-1} (S=O). − $C_{45}H_{55}F_6O_5P_3RuS$ (1016.0): calcd. C 53.20, H 5.46; found C 53.43, H 5.75.

Liberation of the Sulfinic Acid Ester 16: 14b (0.22 g, 0.22 mmol) was dissolved in acetonitrile (10 mL) and heated under reflux for 15 h. Thereafter, the mixture was concentrated to dryness, and the resulting residue was suspended in diethyl ether. Upon ultrasonic treatment, complex **15** separated as a yellow powder, which was filtered off, washed with diethyl ether, and dried. The filtrate was concentrated to dryness, leaving the ester **16** as a colorless, spectroscopically pure oil.

15: Yield 0.16 g (93%), m.p. 113°C (dec.). − ^{1}H NMR (400 MHz, [D$_6$]acetone, 20°C): δ = 1.78 (s, 3 H, CH_3), 4.70 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, [D$_6$]acetone, 20°C): δ = 3.2 (s, CH_3), 83.2 [t, ^2J(P,C) = 2 Hz, C_5H_5], 127.5 (s, CN). − ^{31}P NMR (162 MHz, [D$_6$]acetone, 20°C): δ = 75.7 [d, *J*(P,P) = 40 Hz], 85.4 [d, *J*(P,P) = 40 Hz]. − $C_{35}H_{36}F_6NP_3Ru$ (778.7): calcd. C 53.99, H 4.66, N 1.80; found C 53.70, H 4.90, N 2.08.

16: Yield 58 mg (94%). − Major diastereoisomer (53%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.32 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.46 (s, 9 H, *t*Bu), 1.50 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 3.13 [d, ^2J(H,H) = 13.8 Hz, 1 H, SO_2CH_2], 3.28 [d, ^2J(H,H) = 13.8 Hz, 1 H, SO_2CH_2], 3.97−4.13 (m, 2 H, OCH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 15.8 (s, CH_3), 19.6 (s, CH_3), 22.5 (s, CH_3), 27.7 (s, *t*Bu), 58.0 (s, C_{quat}), 62.7 (s, CH_2), 65.1 (s, SO_2CH_2), 83.3 (s, C_{quat}), 169.7 (s, CO), 203.2 (s, CO). − Minor diastereoisomer (47%): ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 1.33 [t, ^3J(H,H) = 7.1 Hz, 3 H, CH_3], 1.45 (s, 9 H, *t*Bu), 1.50 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 3.16 [d, ^2J(H,H) = 13.8 Hz, 1 H, SO_2CH_2], 3.30 [d, ^2J(H,H) = 13.8 Hz, 1 H, SO_2CH_2], 3.97−4.13 (m, 2 H, OCH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 15.7 (s, CH_3), 19.7 (s, CH_3), 25.8 (s, CH_3), 27.7 (s, *t*Bu), 58.1 (s, C_{quat}), 62.7 (s, CH_2), 64.9 (s, SO_2CH_2), 83.2 (s, C_{quat}), 169.8 (s, CO), 203.3 (s, CO).

X-ray Structure Determination of [CpRu(chir)(SO$_2$)]PF$_6$·2CH$_2$Cl$_2$ (10·2CH$_2$Cl$_2$): $C_{33}H_{33}F_6O_2P_3RuS{\cdot}2CH_2Cl_2$: molecular mass 971.49, crystal size 0.6 × 0.4 × 0.35 mm, obtained by diffusion of pentane into a concentrated dichloromethane solution; orthorhombic crystal system, space group $P2_12_12_1$ (No. 19), a = 12.6062(13), b = 16.025(2), c = 19.614(3) Å; V = 3962.3(9) Å^3, Z = 4, $d_{calcd.}$ = 1.629 g cm^{-3}; μ(Mo-K_α) = 9.00 cm^{-1}. Data were collected at 193 K in the range 2° < Θ < 25° from slightly more than one-eighth of the reflection sphere (index range $0 \le h \le 14$, $-3 \le k \le 19$, $-3 \le l \le 23$, Enraf−Nonius CAD4 diffractometer, graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å). Of the 5595 measured reflections, 5128 were symmetry-independent and 4117 were classified as observed [$I_0 > 2\sigma(I_0)$]. An empirical absorption correction based on Ψ-scans was applied (average transmission 89.3%). The structure was solved by Direct Methods using the program package SHELXS-93[34] with hydrogen atoms included in their calculated positions. Refinement with the program package SHELXL-96[35] gave R_1 = 0.0545, wR_2 = 0.1214. The five highest maxima of a final difference Fourier map were below 0.78 e/Å^3. Further details of the structure determination may be obtained from the Cambridge Crystallographic Data Centre on quoting the depository number CCDC-132910.

X-ray Structure Determination of [CpRu(chir){SO$_2$CH$_2$C(Me)-{C(O)Me}[C(O)O*t*Bu]}] (13d′): $C_{43}H_{50}O_5P_2RuS$: molecular mass 841.90, crystal size 0.4 × 0.3 × 0.25 mm, obtained by diffusion of heptane into a concentrated benzene solution; tetragonal crystal system, space group $P4_32_12$ (No. 96), a = 16.389(2), b = 16.389(2), c = 29.607(5) Å; V = 7952(2) Å^3, Z = 8, $d_{calcd.}$ = 1.406 g cm^{-3}; μ(Mo-K_α) = 2.07 cm^{-1}. Data were collected at 293 K in the range 2° < Θ < 27° from one-eighth of the reflection sphere (index range $0 \le h \le 20$, $0 \le k \le 20$, $0 \le l \le 37$, Enraf−Nonius CAD4 diffractometer, graphite monochromator, Mo-K_α radiation, λ = 0.70930 Å). Of the 9400 measured reflections, 8646 were symmetry-independent and 5906 were classified as observed [$I_0 > 2\sigma(I_0)$]. An empirical absorption correction based on the counts of nine reflections was applied. The structure was solved by the Patterson method, with the program package SHELXS-86,[36] with hydrogen atoms included in their calculated positions. Refinement with the program package SHELXL-93[37] gave R_1 = 0.0444, wR_2 = 0.07128. The five highest maxima of a final difference Fourier map were below 0.30 e/Å^3. Further details of the structure determination may be obtained from the Cambridge Crystallographic Data Centre on quoting the depository number CCDC-132859.

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