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Stereoselective addition reactions of ruthenium thioaldehyde complexes☆

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Dedicated to Professor Helmut Werner on the occasion of his (formal) retirement and in recognition of his outstanding contributions to organometallic chemistry

Abstract

Halfsandwich-ruthenium complexes of thiobenzaldehydes and thiocinnamaldehydes can be prepared either by hydride abstraction from benzylthiolate complexes or by condensation of a Ru–SH complex with the corresponding benzaldehyde or cinnamaldehyde. The former reaction is closely analogous to the key step of the biosynthesis of penicillin. The thiobenzaldehyde complexes add a variety of anionic carbon nucleophiles to give complexes of secondary thiolates. Furthermore, they undergo [2+4]-cycloadditions with 1,3-dienes forming complexes of 3,6-dihydro-2*H*-thiopyranes. The thiocinnamaldehyde complexes add electron-rich and -poor dienophiles to give complexes of 3,4-dihydro-2*H*-thiopyranes and 4*H*-thiopyranes, respectively. The reaction with diazomethane results in a formal [4+1]-cycloaddition giving metal-coordinated 2,3-dihydrothiophenes. These reactions are easily modified into diastereoselective addition reactions by the use of the enantiomerically pure complex fragment [CpRu{(*S*,*S*)-CHIRAPHOS}]$^+$ as a chiral auxiliary. The organic part can be cleaved from the metal under mild conditions, and the metal complex is recovered in a form suitable to reenter the synthetic cycle.

Keywords: Chiral complexes; Ruthenium complexes; Thioaldehydes; Nucleophilic addition; Cycloaddition reactions; Thiopyranes

1. Introduction

Short-lived and highly reactive molecules can often be stabilized by incorporation into a transition metal complex [2]. In an ideal case, the species under consideration is not only stabilized but sufficiently modified such that it can undergo novel stoichiometric and perhaps even catalytic reactions. Thioaldehydes are typical examples of the so-called 'double bond rule': the fairly weak π type overlap between a 3p orbital of sulfur and a 2p orbital at carbon encourages oligomerization reactions to such an extent that thioaldehydes R(H)C=S can only be isolated as monomers if stabilized by bulky substituents R [3,4] or by coordination to transition metals [5].

The use of chiral transition metal complexes as diastereo-directing auxiliaries in stoichiometric reactions is a topic of long-standing interest [6,7]. In the majority of work, cyclopentadienyl complexes of the types [CpMo(CO)$_2$(L–L*)] [8], [CpM(NO)(PPh$_3$)L] (M = Mn [6], Re [9]), [CpFe(CO)(PPh$_3$)L] [10] and [CpRu(L–L*)L] [11] (L–L* = chiral bidentate ligand) were employed. Halfsandwich-ruthenium complexes of the latter type turned out to be quite effective chiral auxiliaries in the atroposelective ring opening of biaryl thionolactones [12–14], in C–C coupling reactions involving coordinated sulfene [15], and in particular in the diastereoselective oxidation of thioether ligands [16–20]. Here we review our work on the synthesis and reactions of corresponding ruthenium thioaldehyde complexes [CpRu(L–L)(S=CHR)]PF$_6$ (where the coligand L–L may be either achiral or chiral) with particular emphasis on diastereoselective additions.

☆ See Ref. [1].

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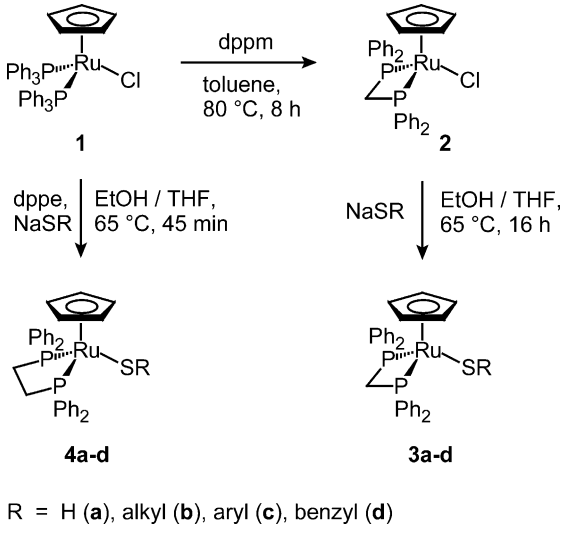
2. Synthesis of ruthenium thioaldehyde complexes [CpRu(L–L){S=C(H)R}]PF_6

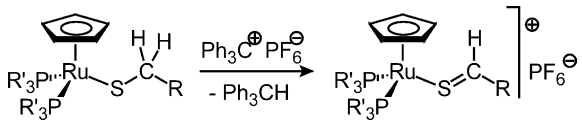
In order to be useful in a general application, the required starting materials should be readily accessible and reasonably stable such that they can be handled without the need for special equipment or techniques. This is certainly the case for the halfsandwich-ruthenium complexes described here. The starting material **1** is synthesized in one step from hydrated ruthenium(III) chloride, cyclopentadiene and triphenylphosphine [21]. Exchange of the monodentate phosphine ligand for bis(diphenylphosphino)methane (dppm) gives **2** [22], which reacts with NaSH or almost any organic thiolate NaSR in a polar solvent mixture to give the desired thiolate complexes **3** [23–26]. The synthesis of the corresponding 1,2-bis(diphenylphosphino)ethane (dppe) complexes **4** can even be carried out as a one-pot reaction (Scheme 1) [27].

Compounds **3** and **4** are readily transformed into thioaldehyde complexes by two principally different routes. The first one consists of a (formal) hydride abstraction from the benzylic position (Scheme 2) [28,29]. This reaction was later extended to the synthesis of chiral rhenium complexes [CpRe(NO)(PR'_3)(S=CHR)]BF_4 [30,31].

The hydride abstraction from organotransition metal complexes is commonly initiated by a single electron transfer (SET) which is followed by the transfer of a H atom [32,33]. Under favorable circumstances the initially formed radical cation may be detected spectroscopically [34] or even isolated [35]. Treichel et al. have been able to obtain stable, deep blue 17-electron complexes [CpRu$(L)_2$(SPh)]PF_6 (L = PMe_3, $P(OMe)_3$, 1/2 dppe) from the oxidation of the corresponding neutral complexes with $AgPF_6$ [26]. Indeed, if the



Scheme 1. Synthesis of halfsandwich-ruthenium thiolate complexes **3** and **4**.

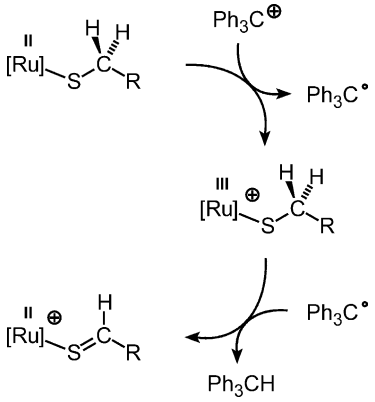


Scheme 2. Synthesis of ruthenium thiobenzaldehyde complexes via hydride abstraction from the benzylic position.

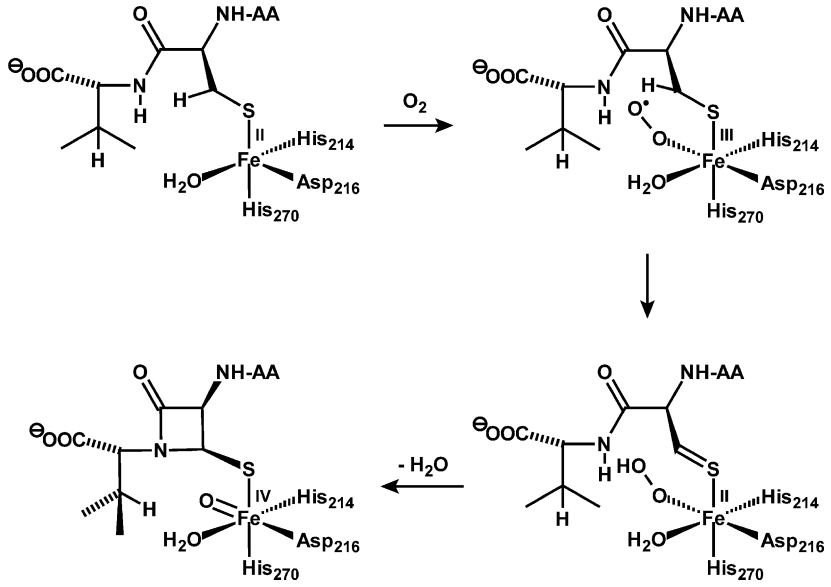
reactions of Scheme 2 are carried out at −70 °C a transient deep blue color can be observed. The reaction of the deuterated benzylthiolate complex [CpRu(dppm)(SCD_2Ph)] with Ph_3CPF_6 revealed that practically all the abstracted deuterium ended up as Ph_3CD, and the mono-deuterated complex [CpRu(dppm)(SCHDPh)] reacted with a kinetic isotope effect of $k_H/k_D = 5.6$ [29], indicating that the H-transfer step has a linear transition state [36,37]. Taken together, this evidence points to the two-step mechanism outlined in Scheme 3. Two facts are apparently important for the success of this reaction. Firstly, low-valent thiolate complexes have a HOMO at high energy which is M–S antibonding and to which metal d and sulfur p orbitals contribute about equally [38,39]. This explains how an oxidation of the metal atom can lead to an activation of a relatively remote C–H bond. Secondly, the fairly large reactant molecules are held together in a solvent cage long enough to suppress possible side reactions.

Thus the synthesis of thioaldehyde complexes by hydride abstraction has a striking similarity to the key steps of the biosynthesis of penicillin (Scheme 4) [40,41]. Here, O_2 is the reagent which oxidizes iron(II) to iron(III) and at the same time creates a radical center perfectly positioned to abstract a hydrogen atom from the CH_2 group of the coordinated cystein. The thioaldehyde thus formed is stabilized by coordination to iron. The hydroperoxide ligand deprotonates the adjacent amide function which then attacks the thioaldehyde carbon to close the β-lactam ring [42]. As will be shown below, nucleophilic attack at carbon is one of the principal reaction modes of thioaldehyde complexes.

A second and equally versatile synthesis of thioaldehyde complexes is based on the condensation of a metal-



Scheme 3. Proposed mechanism of the two-step hydride abstraction.



Scheme 4. The key steps of the penicillin biosynthesis [40,41].

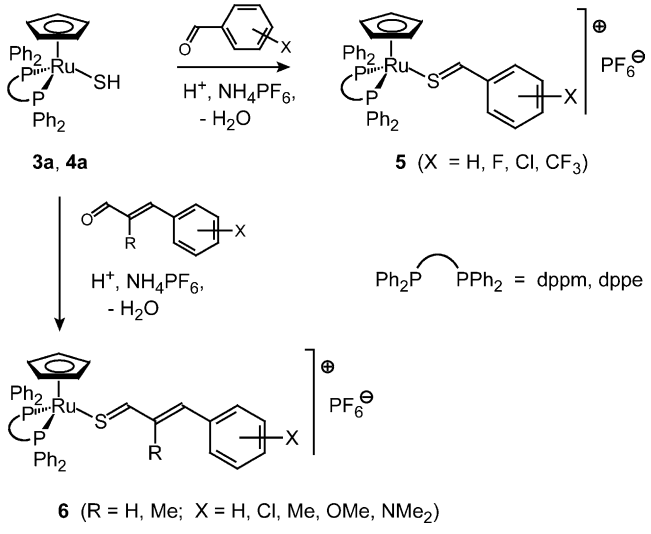
bound SH group with aldehydes. Such a reaction had been used by Angelici in one of the early syntheses of tungsten complexes $[W(CO)_5(S{=}CHR)]$, but it was found to be limited to aryl groups R bearing electron-releasing substituents [43]. In our case, this reaction could be successfully employed for the synthesis of a wide range of thiobenzaldehyde and thiocinnamaldehyde complexes (Scheme 5) [27,44,45].

3. Properties and structure

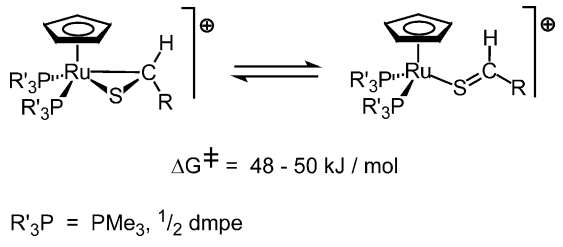
The thioaldehyde complexes described herein are highly colored (burgundy red, purple, or blue) crystalline materials. The terminal η^1(S) coordination of the thiocarbonyl function was unambiguously deduced from ^{1}H- and ^{13}C-NMR data as well as X-ray structure determinations (see below). However, when the chelating aryl phosphine ligand is replaced by the strongly electron-releasing PMe_3 or 1,2-bis(dimethylphosphino)ethane (dmpe), then η^1(S) and η^2(C,S) isomers are found to be present in a temperature-dependent dynamic equilibrium (Scheme 6) [29]. In addition to a high electron density at the metal, electron-withdrawing substituents at the phenyl group as well as low temperature favor the side-on coordination mode.

The structures of three representative thioaldehyde complexes are shown in Figs. 1–3.

η^1(S)-Coordinated thioaldehyde complexes always assume the thermodynamically favored *E* configuration [5], and this was also found for the halfsandwich-ruthenium complexes [28,29] including the two examples shown in Figs. 1 and 2. The C–S distance in the coordinated 4-chlorothiobenzaldehyde is only marginally longer than in the sterically protected monomer 2,4,6-tri(*tert*-butyl)thiobenzaldehyde (160.2(5) pm [48]). This indicates an electronically unperturbed C=S double bond in the complex. A slightly longer C–S bond was found in the thiocinnamaldehyde complex shown in Fig.



Scheme 5. Synthesis of thioaldehyde complexes via condensation reactions.



Scheme 6. Dynamic equilibrium between isomeric η^1 and η^2 thioaldehyde complexes.

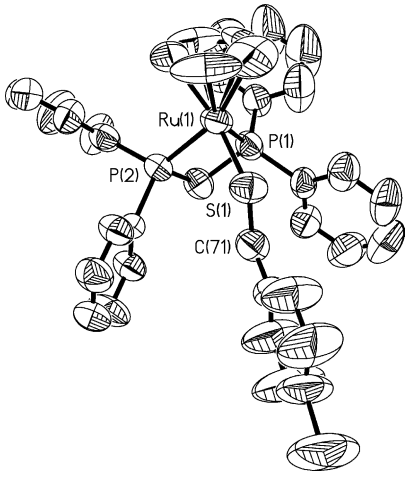


Fig. 1. Structure of the cation of [CpRu(dppm){S=C(H)(4-C_6H_4Cl)}]PF_6 [46], hydrogen atoms omitted for clarity. Bond distances: Ru–P(1), 228.3(3); Ru–P(2), 228.9(2); Ru–S, 225.2(2); S–C, 161.5(9) pm.

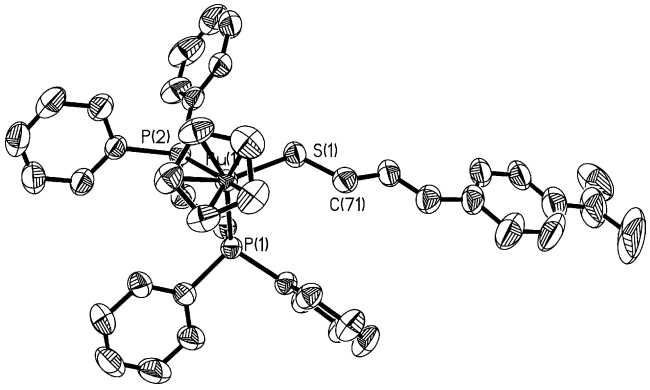


Fig. 2. Structure of the cation of [CpRu(dppe){S=C(H)–C(H)=C(H)(4-$C_6H_4NMe_2$)}]PF_6 [27], hydrogen atoms omitted for clarity. Bond distances: Ru–P(1), 228.47(13); Ru–P(2), 229.26(12); Ru–S, 232.00(13); S–C, 165.5(5) pm.

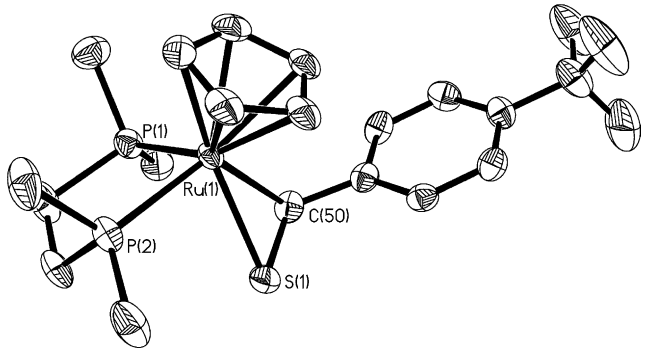
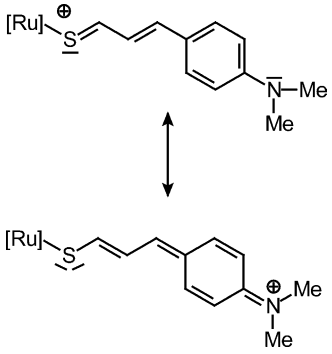


Fig. 3. Structure of the cation of [CpRu(dmpe){S=C(H)(4-$C_6H_4CF_3$)}]BPh_4 [47], hydrogen atoms omitted for clarity. Bond distances: Ru–P(1), 230.44(8), Ru–P(2), 231.39(8); Ru–S, 238.70(8); Ru–C, 224.0(3); S–C 171.1(3) pm.

2. Additional remarkable features of that structure are an also quite long Ru–S bond and a planar dimethylamino substituent, pointing at a significant contribution of an enethiolate resonance form (Scheme 7).



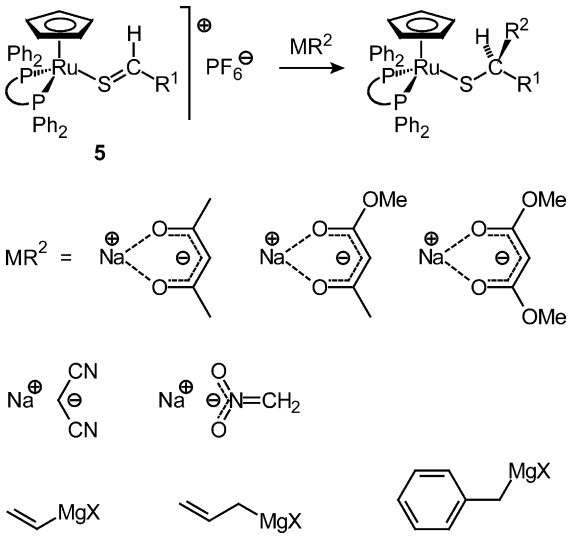
Scheme 7. Two resonance forms of the thiocinnamaldehyde complex [CpRu(dppe){S=C(H)C(H)=C(H)(4-$C_6H_4NMe_2$)}]PF_6.

As expected, the C–S bond in the side-on coordinated thiobenzaldehyde complex (Fig. 3) is much longer. Almost equal bond lengths were found for the isoelectronic complexes $[W(CO)_3(dmpe)(\eta^2\text{-}S{=}CH_2)]$ [1], $[CpRe(NO)(PPh_3)(\eta^2\text{-}S{=}CH_2)]^+$ [49], $[CpRe(NO)(PPh_3)\{\eta^2\text{-}S{=}C(H)Ph\}]^+$ [30], and many others [5]. A bond length in this range corresponds to a reduction of the C–S bond order to 1.3 as the result of an extensive charge transfer into the π* level of the thiocarbonyl group [1]. One might therefore expect that η^2-thioaldehyde complexes are largely unreactive towards nucleophiles or dienes. However, the η^1 isomer present in the equilibrium according to Scheme 6 will always provide a pathway for further transformations. Indeed, orange crystals of [CpRu(dmpe){η^2-S=C(H)(4-$C_6H_4CF_3$)}]BPh_4, redissolved in CD_2Cl_2, give a purple solution which contains almost exclusively the η^1 isomer [47].

4. Addition of nucleophiles

Nucleophilic addition is one of the principal reaction modes of thioaldehyde complexes [5]. Early in our study we had found that the ruthenium complexes readily add hydride, alkoxide, thiolate, or PMe_3 [29]. The attempted addition of organolithium or Grignard reagents led to extensive decomposition, probably due to competing electron transfer [50]. However, anionic carbon nucleophiles with less negative oxidation potentials such as deprotonated β-diketones, β-ketoesters, diesters, malodinitrile, nitromethane, and even vinyl, allyl or benzyl Grignard reagents add cleanly to give neutral ruthenium complexes of secondary thiolates (Scheme 8).

Thiocarbonyl compounds (thioketones, thioesters) normally add carbon nucleophiles at sulfur (thiophilic addition [51,52]). In the present case, however, the sulfur atom is blocked by the transition metal which directs the nucleophile to the adjacent carbon atom. Structures of



Scheme 8. Addition of anionic nucleophiles to the thiocarbonyl group.

two representative examples of the secondary thiolate complexes thus formed are shown in Figs. 4 and 5.

The addition of a nucleophile reduces the bond order between carbon and sulfur to one, as can be seen from a 24 pm increase of the bond distance. The Ru–S distance increases as well due to the rehybridization to sp^3 at sulfur and the buildup of the antibonding π interaction mentioned above [38,39].

5. Cycloaddition reactions

Free thioaldehydes, which may be generated in situ by a variety of methods, are highly reactive dienophiles [53–55]. This type of reactivity is certainly attenuated by coordination to transition metal complexes, but it is by no means fully suppressed. This has been demonstrated primarily through the work of Fischer et al. who had been able to add a variety of 1,3-dienes to thiobenzaldehyde complexes of the type $[W(CO)_5\{S{=}C(H)R\}]$ [5].

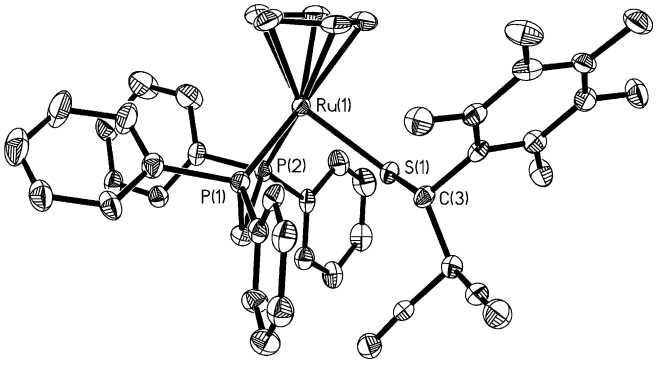


Fig. 4. Structure of the malodinitrile adduct $[CpRu(dppm)\{SC(H)(C_6F_5)C(H)(CN)_2\}]$ [47], hydrogen atoms omitted for clarity. Bond distances: Ru–P(1), 226.62(15); Ru–P(2), 227.54(15); Ru–S, 238.53(12); S–C, 182.8(5) pm.

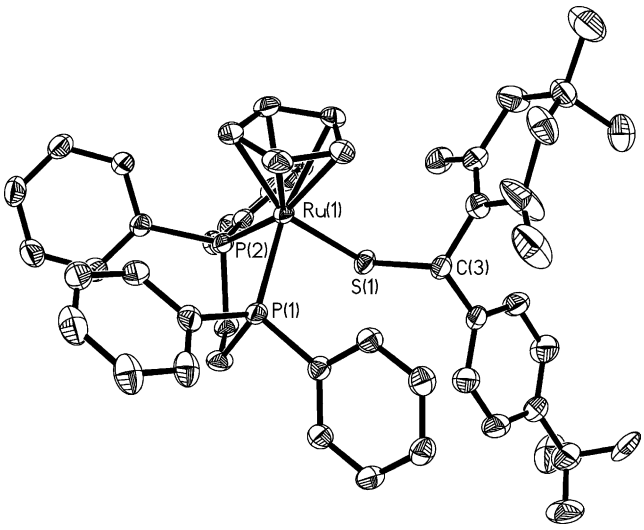
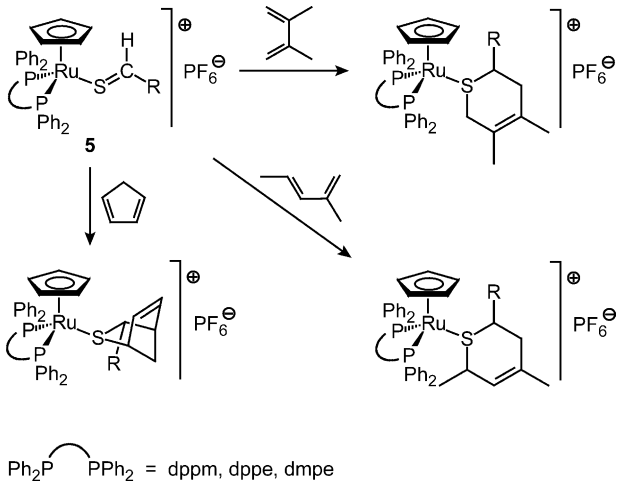


Fig. 5. Structure of the dimedone adduct $[CpRu(dppe)\{SC(H)(4\text{-}C_6H_4CF_3)C_8H_{11}O_2\}]$ [47], hydrogen atoms omitted for clarity. Bond distances: Ru–P(1), 226.99(9); Ru–P(2), 227.63(9); Ru–S, 241.37(9); S–C, 185.4(4) pm.

In our case, the thiocarbonyl function is situated in a sterically still more congested environment. Nevertheless, the addition of cyclopentadiene or open-chain 1,3-dienes proceeds readily to the expected 3,6-dihydro-2*H*-thiopyranes (Scheme 9) [29].

The addition of cyclopentadiene is remarkable insofar as it leads with high stereoselectivity to the *exo*-aryl product [29] since this allows the sterically more demanding complex fragment to enter the less encumbered *endo* position. It should be noted here that the tungsten pentacarbonyl complexes mentioned above behave similarly [56,57].

After having established the reactivity of the ruthenium thiobenzaldehyde complexes towards 1,3-dienes, it seemed quite likely that analogous complexes of thiocinnamaldehydes would readily add dienophiles. Indeed,



Scheme 9. [2+4]-Cycloaddition reactions of ruthenium thiobenzaldehyde complexes.

electron-rich alkenes (e.g. vinyl ethers) as well as electron-poor ones (styrenes, acrolein, acrylic ester, methyl vinyl ketone), and also propiolic acid ester react smoothly to give complexes of 3,4-dihydro-2*H*-thiopyranes and 4*H*-thiopyranes, respectively (Scheme 10).

The addition proceeds with high regioselectivity and generally good diastereoselectivity [27]. In all cases studied so far *endo*-addition was favored, which is in line with previous observations concerning Diels–Alder additions of α,β-unsaturated thioamides [58] and dithioesters [59].

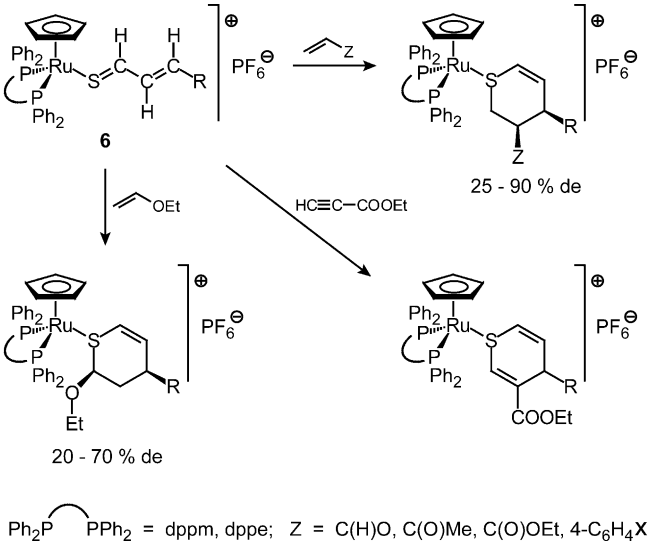
The ruthenium thiocinnamaldehyde complexes also react with diazomethane in a formal [4+1]-cycloaddition to give 2,3-dihydrothiophenes (Scheme 11).

We have not yet investigated the mechanism of this reaction. However, there is an analogy to a similar addition of diphenyldiazomethane to $[W(CO)_5\{S{=}C(H)Ph\}]$ which gives a complex of triphenylthiirane via a 1,3,4-thiadiazolidine intermediate [60].

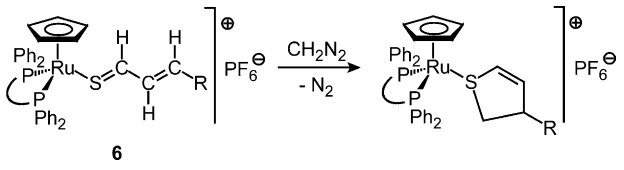
6. Chiral, enantiomerically pure ruthenium thioaldehyde complexes

The reactions outlined in Schemes 1, 2 and 5 are easily adapted to the synthesis of chiral, enantiomerically pure ruthenium thioaldehyde complexes. To this end, the known [CpRu{(*S*,*S*)-CHIRAPHOS}Cl] [61] was first converted to the SH complex **7**, from which the thiobenzaldehyde complexes **8** and the thiocinnamaldehyde complexes **9** are easily accessible (Scheme 12).

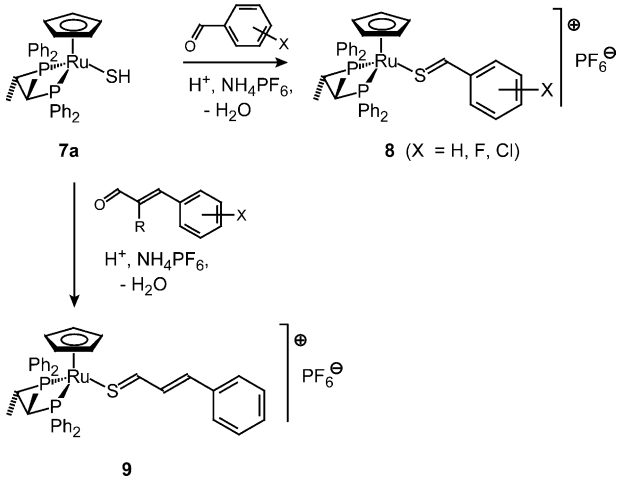
In order to get a first impression of the suitability of the complex fragment $[CpRu\{(S,S)\text{-CHIRAPHOS}\}]^+$ as a chiral auxiliary, we tested the addition of 1,3-butadiene and three of its derivatives to *m*- and *p*-



Scheme 10. [4+2]-Cycloaddition reactions of ruthenium thiocinnamaldehyde complexes.



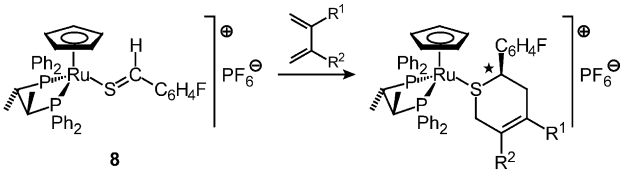
Scheme 11. [4+1]-Cycloaddition reaction of ruthenium thiocinnamaldehyde complexes.



Scheme 12. Synthesis of chiral, enantiomerically pure ruthenium thioaldehyde complexes.

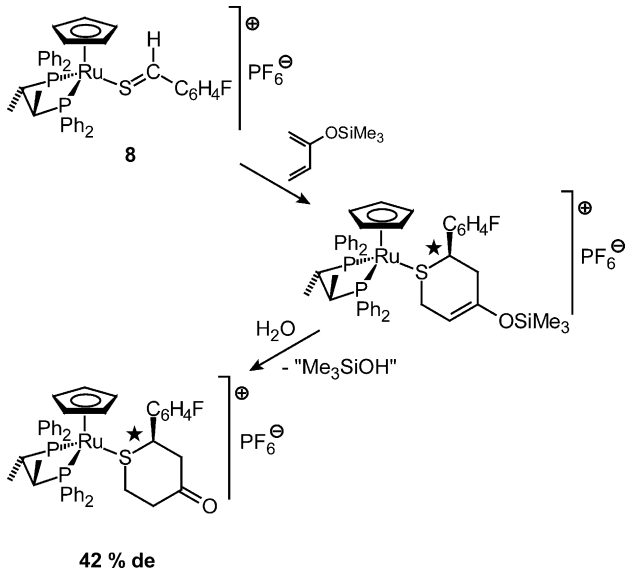
fluoro-substituted thiobenzaldehyde complexes (Scheme 13). Moderate to good diastereoselectivities (in favor of the (*R*)-configuration at the newly created stereocenter) were obtained [62] which might be further improved by the use of other, sterically more demanding chiral diphosphine ligands.

The reaction shown in Scheme 14 demonstrates that ruthenium complexes of this type easily survive the hydrolysis of a silyl-enolether function. This, of course, is not surprising as we have in the past used such complexes under quite harsh conditions without noticeable decomposition [16–19]. An X-ray structure deter-



C_6H_4F	R^1	R^2	de (%)
p	H	H	78
p	H	Me	42
p	Me	Me	50
m	Me	Me	50
p	OMe	OMe	24
m	OMe	OMe	36

Scheme 13. Diastereoselective Diels–Alder reactions of chiral, enantiomerically pure ruthenium thiobenzaldehyde complexes.



Scheme 14. Hydrolysis of a silyl-enolether product.

mination of the major diastereoisomer of the hydrolysis product shows that this, too, has (*R*)-configuration at the newly created stereocenter (Fig. 6).

In the course of our work, we have developed methods to detach ligands which have been assembled in the protecting coordination sphere of halfsandwich-ruthenium complexes [13,15–19,63–65]. The cyclic thioether ligands presented here are in general only weakly bound and can be easily cleaved from the metal by reaction with acetonitrile at room temperature (Scheme 15).

The organic product is separated by extracting the mixture with an unpolar solvent such as hexane or toluene in which the ionic acetonitrile complex is totally insoluble. The latter can be recovered by recrystallization from acetonitrile/diethylether and reused in the synthesis of the starting thiolate complexes **3**, **4** and **7**.

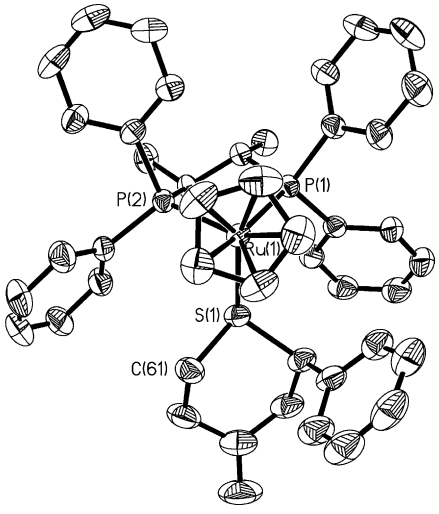
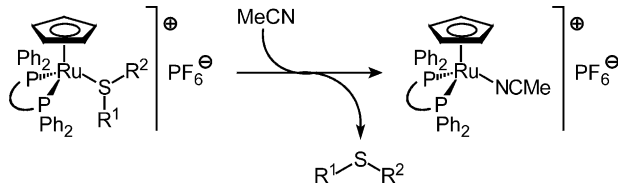


Fig. 6. Structure of the cation of [CpRu{(*S*,*S*)-CHIRAPHOS}{$SC_5H_7O(C_6H_4F)$}]PF_6 [62], hydrogen atoms omitted for clarity. Bond distances: Ru–P(1), 231.59(10); Ru–P(2), 227.45(10); Ru–S, 234.60(10) pm.



Scheme 15. Detachment of cycloaddition products.

7. Conclusions and outlook

The work summarized here demonstrates that half-sandwich-ruthenium complexes of the type [CpRu(L–L)L]$^+$ are ideally suited to stabilize thioaldehyde ligands while still allowing for a variety of addition reactions of the C=S function. These reactions proceed with moderate to good diastereoselectivity if chiral diphosphines are used as supporting ligands (L–L). The organic component is easily detached and separated from the metal complex which is recovered in a form suitable for reuse in the synthetic cycle. Future work will have to concentrate on the optimization of the diastereoselectivity by the use of C_2-symmetric diphosphines which have been particularly designed for that purpose.

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