Transition Metal Complexes with Sulfur Ligands, 110[1]

Chirotopic and Stereogenic Metal Centers in [M(L)(L')('RS_4')] Complexes with Chiral Thioether-Thiolate Ligands 'RS_4'-H_2 ['MeS_4'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)propanato(2−), '$CH_3(CH_2)_2S_4$'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)pentanato(2−), '$HO(CH_2)_9S_4$'$^{2-}$ = 10,11-bis(2-mercaptophenylthio)-1-undecanolato(2−), '$PhCH_2S_4$'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)-3-phenylpropanato(2−)]

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In order to investigate the stereochemistry of substitution reactions of chiral pseudo-octahedral complexes the chiral thioether-thiolate ligands 'RS_4'-H_2 (= $HSC_6H_4SCHRCH_2SC_6H_4SH$) with R = CH_3− (**5**), $CH_3(CH_2)_2$− (**6**), $HO(CH_2)_9$− (**7**), and $PhCH_2$− (**8**) were synthesized by template alkylation of Na_2[Ni('S_2')$_2$] ['S_2'$^{2-}$ = 1,2-benzenedithiolate(2−)] with 1,2-dibromoalkanes $BrCHRCH_2Br$ (R = CH_3−, **1**; R = $CH_3(CH_2)_2$−, **2**; R = $HO(CH_2)_9$−, **3**; R = $PhCH_2$−, **4**) and isolated after hydrolyses. Reactions of 'RS_4'-H_2 with [$RuCl_2(PPh_3)_3$] or [$Mo(O)_2(acac)_2$] yielded [$Ru(PPh_3)_2$('RS_4')] (R = CH_3−, **9**; R = $HO(CH_2)_9$−, **10**; R = $PhCH_2$−, **11**) and [$Mo(O)_2$('MeS_4')] (**12**). [$Ru(PPh_3)_2$('MeS_4')] · 2 CH_2Cl_2 (**9** · 2 CH_2Cl_2) and [$Mo(O)_2$('MeS_4')] (**12**) were characterized by X-ray structure determination. In both complexes, the metal centers are surrounded pseudo-octahedrally by four sulfur donors of the 'MeS_4' ligand and two cis coligands. The methyl substituent at the stereogenic C* atom of the C_2 bridge of the 'MeS_4' ligands assumes an equatorial position. In addition, the metal centers of these complexes are chirotopic and prostereogenic. Crystal data of **9** · 2 CH_2Cl_2 in comparison with [$Ru(PBu_3)_2$('S_4')] and those of **12** in comparison with [$Mo(O)_2$('S_4')] show that distances and angles of the coordination cores are not influenced by the substituents on the C_2 bridge. Reactions of the [$Ru(PPh_3)_2$('RS_4')] complexes (**9**−**11**) with the achiral substrates CO and PMe_3, however, yielded diastereomers of [$Ru(PPh_3)$(L)('RS_4')] (L = CO, R = CH_3−, **13**; L = CO, R = $HO(CH_2)_9$−, **14**; L = CO, R = $PhCH_2$−, **15**; L = PMe_3, R = CH_3−, **16**; L = PMe_3, R = $HO(CH_2)_9$−, **17**; L = PMe_3, R = $PhCH_2$−, **18**) in diastereomeric excesses between 60 and 82%. The diastereomer of [$Ru(PPh_3)$(CO)('MeS_4')] (**13**) which could be characterized by X-ray structure determination exhibits the CO ligand in trans position to the thioether donor which is bound to the stereogenic C* atom of the C_2 bridge. Reaction of **9** · 2 CH_2Cl_2 with the optically pure bidentate diphosphine (+)-(*S*,*S*)-DIOP [= (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] yielded 1:1 mixtures of two diastereomers of [Ru(DIOP)('MeS_4')] (**19**) one of which was separated in pure form by HPLC.

Introduction

Chiral metal complexes render possible numerous stoichiometric or catalytic asymmetric syntheses[2]. If in these syntheses bonds to the metal center are generated or cleaved, the question arises, whether exactly definable stereochemical properties of the metal center will influence the recognition of chiral substrates and their asymmetric conversion. In short terms: Does the metal center itself influence the transfer of chiral information in metal centered asymmetric reactions? The term 'chiral metal center' implicates such an influence[3].

This term is still commonly used[4], although Mislow and Siegel demonstrated in 1984 that the term 'chiral center' is misleading and should better be replaced by the terms 'stereogenic and/or chirotopic center'[5,6]. Such a differentiation is indispensable for metal complexes with coordination numbers higher than four. Furthermore, such metal complexes can be chiral without having 'centers, planes or axes of chirality'[7]. For instance, chirality can also be observed for the polynuclear active centers of numerous metal enzymes. The surrounding chiral protein causes these centers to become chiral (or more correctly: chirotopic) such that the individual metal centers are stereochemically inequivalent even if the metal atoms are part of chiral symmetrical subunits, e.g., the iron atoms of $[Fe_4S_4(RS_4)]^{n-}$ (n = 3, 2, 1) clusters in ferredoxins[8].

In order to elucidate the question in which way stereochemical properties of metal centers influence the course of metal centered reactions, we started by investigating mononuclear complexes.

Recently we have shown that the metal centers in complexes of type **I**, **II**, and **III** can precisely be differentiated

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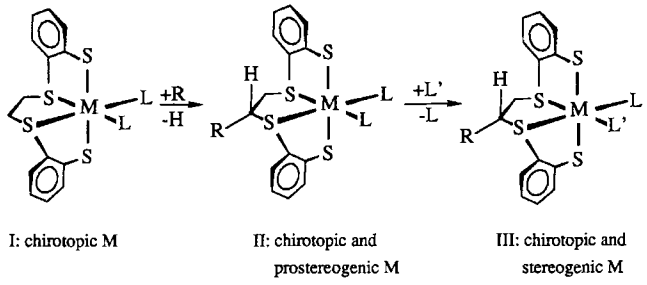
with regard to their chirotopicity and stereogenicity[6] (Scheme 1). All three complexes are chiral, but only **III** contains a stereogenic metal center[5].

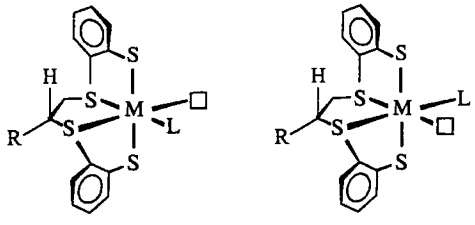
Scheme 1. Stereochemical properties of the metal center M in octahedral [M('S_4')] complexes



I: chirotopic M | II: chirotopic and prostereogenic M | III: chirotopic and stereogenic M

In the C_2 symmetrical complex [M(L)$_2$('S_4')] **I** ['S_4'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2−)] the metal center is chirotopic, but not stereogenic. Introduction of a substituent R into the C_2H_4 bridge of the 'S_4'$^{2-}$ ligand results in a C_1 symmetrical [M(L)$_2$('RS_4')] complex **II** and causes the metal center to become prostereogenic with respect to an exchange L/L'. Only such a L/L' exchange or – more generally – any further desymmetrization yields a chirotopic and stereogenic metal center, because now, for example, the permutation of the ligands L and L' in [M(L)(L')('RS_4')] **III** yields distinguishable stereoisomers.

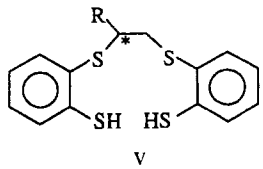
Correspondingly, removal of one of the two ligands L in **II** leads to the coordinatively unsaturated complexes **IVa** and **IVb** which have stereogenic metal centers, too.



IVa IVb

Hence the question arises whether introduction of a substituent R into the C_2 bridge of the [M('S_4')] fragments leads to stereoselectivity in substitution reactions of [M(L)$_2$('RS_4')] complexes. Here, this question was investigated for the easiest case in which achiral ligands L are exchanged for achiral ligands L'.

This required the synthesis of 'RS_4'-H_2 ligands of type **V** carrying various substituents R at the stereogenic C* atom and of suitable [M(L)$_2$('RS_4')] complexes.

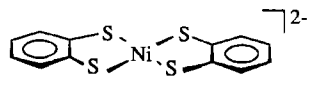


V

Results

Synthesis of Chiral Thioether-Thiolate Ligands 'RS_4'-H_2

The required 'RS_4'$^{2-}$ ligands **5**–**8** are formed in template alkylations of [Ni('S_2')$_2$]$^{2-}$ ['S_2'$^{2-}$ = 1,2-benzenedithiolate(2−)] with vicinal dibromides *rac*-RCHBr-CH_2Br according to the general eq. (1):



+ rac-RCHBr-CH_2Br

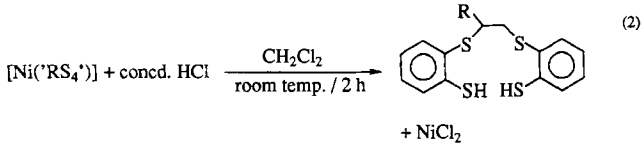
MeOH, 20 °C - 50 °C / 24 h - 2 d → [Ni('RS_4')] + 2 Br$^-$ (1)

R = CH_3-, **1**; R = $CH_3(CH_2)_2$-, **2**

R = $HO(CH_2)_9$-, **3**; R = $PhCH_2$-, **4**

The [Ni('RS_4')] complexes **1**–**4** were isolated as brown to dark brown powders. They are sparingly soluble only in DMSO or CH_2Cl_2 in which, however, they rapidly decompose. This prevented their recrystallization and allowed their characterization only by elemental analysis, FD mass, and IR spectroscopy. Their IR spectra (KBr pellets), however, do not exhibit any characteristic bands in addition to the typical bands of the 'RS_4'$^{2-}$ ligands.

While the structure of the resulting [Ni('RS_4')] complexes remained unsettled, the 'RS_4'-H_2 ligands could unambiguously be identified. Hydrolysis of the [Ni('RS_4')] complexes with concentrated hydrochloric acid yielded the free thiols 'RS_4'-H_2 as colorless to yellow brown oils according to eq. (2).



[Ni('RS_4')] + concd. HCl → (CH_2Cl_2, room temp. / 2 h) → + $NiCl_2$ (2)

R = CH_3-, **1**

R = $CH_3(CH_2)_2$-, **2**

R = $HO(CH_2)_9$-, **3**

R = $PhCH_2$-, **4**

R = CH_3-, **5**

R = $CH_3(CH_2)_2$-, **6**

R = $HO(CH_2)_9$-, **7**

R = $PhCH_2$-, **8**

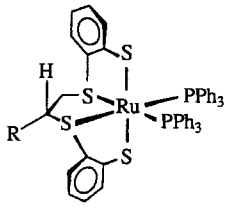
Due to their C_1 symmetry the thiols **5**–**8** exhibit two characteristic SH singlets at δ = 4–5 in their ^{1}H-NMR spectra. The ^{1}H-NMR spectrum of **5** additionally shows a characteristic pattern at δ = 2.9–3.8 for the C_2H_3R protons and a CH_3 doublet at 1.41 ppm which results from coupling with the methine proton of the C_2H_3R bridge. The ^{13}C-NMR spectra show the number of ^{13}C signals to be expected for C_1 symmetrical compounds. In the IR spectra of **5**–**8** only one ν(SH) band in the range between 2510–2520 cm^{-1} can be observed, the IR spectrum of **7** additionally exhibits a broad ν(OH) band at 3362 cm^{-1}.

Syntheses of [Ru(PPh$_3$)$_2$('MeS$_4$')] (9), [Ru(PPh$_3$)$_2$('HO(CH$_2$)$_9$S$_4$')] (10), [Ru(PPh$_3$)$_2$('PhCH$_2$S$_4$')] (11), and [Mo(O)$_2$('MeS$_4$')] (12)

In order to obtain complexes with chirotopic and prostereogenic metal centers the chiral ligands 'RS$_4$'-H$_2$ **5**, **7**, and **8** were coordinated to [Ru(PPh$_3$)$_2$] and [Mo(O)$_2$] fragments. Compounds **9** and **11** were obtained by the reaction according to eq. (3a). In order to facilitate work-up and separation from unreacted starting material, the synthesis of **10** was carried out in boiling MeOH by using the sodium salt of the ligand according to eq. (3b). **12** formed in the reaction according to eq. (4).

$$[RuCl_2(PPh_3)_3] + \text{'}RS_4\text{'}\text{-}H_2 \xrightarrow[-\,2\,HCl\,/\,-\,PPh_3]{THF\,/\,5\,h\,/\,reflux} \quad (3a)$$

R = CH$_3$-, **5**; R = PhCH$_2$-, **8**



R = CH$_3$-, **9**; R = PhCH$_2$-, **11**

$$[RuCl_2(PPh_3)_3] + \text{'}HO(CH_2)_9S_4\text{'}\text{-}Na_2 \xrightarrow[-\,2\,NaCl\,/\,-\,PPh_3]{MeOH\,/\,5\,h\,/\,reflux} \quad (3b)$$

[Ru(PPh$_3$)$_2$('HO(CH$_2$)$_9$S$_4$')]

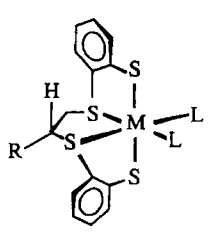
10

$$[Mo(O)_2(acac)_2] + \mathbf{5} \xrightarrow[-\,2\,acac\text{-}H]{THF\,/\,room\,Temp.\,/\,2\,h} [Mo(O)_2(\text{'}MeS_4\text{'})] \quad (4)$$

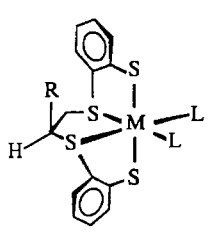
12

The [Ru(PPh$_3$)$_2$('RS$_4$')] complexes **9**–**11** were obtained as yellow to yellow green powders, **12** was isolated as red brown powder. Compounds **9**, **10**, **11**, and **12** are considerably better soluble than the parent [Ru(PPh$_3$)$_2$('S$_4$')] in common organic solvents such as toluene, CHCl$_3$ or CH$_3$CN. The molecular structures of **9** · 2 CH$_2$Cl$_2$ and **12** were elucidated by X-ray structural analysis. In both complexes, the CH$_3$ substituents assume equatorial positions as has been found previously in [Mo(NO)$_2$('MeS$_4$')]. [Mo(NO)$_2$('MeS$_4$')] is formed in a diastereoselective reaction when racemic [Mo(NO)$_2$('S$_2$')$_2$]$^{2-}$ is alkylated with *rac*-1,2-BrCH(CH$_3$)CH$_2$Br[6].

When the chiral 'RS$_4$'$^{2-}$ ligands coordinate to metal centers to yield pseudo-octahedral [M(L)$_2$('RS$_4$')] complexes, theoretically two diastereomeric pairs of enantiomers can form, which differ with respect to the equatorial (**IIa**) and axial (**IIb**) position of R.



IIa



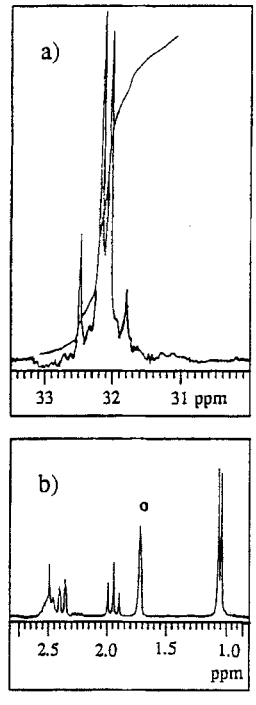
IIb

In the ^{1}H- and ^{31}P-NMR spectra of the raw products obtained according to eqs. (3) and (4), only one of the two possible pairs of enantiomers can be detected. Hence, the 'RS$_4$'$^{2-}$ ligands coordinate to the [M(L)$_2$] fragments in diastereospecific way, and the reactions represent special cases of so-called 'ligand stereospecificity'[9].

Due to the C_1 symmetry of **9**, **10**, and **11**, the two PPh$_3$ ligands are magnetically no longer equivalent and give rise to typical AB patterns with $^2J(^{31}P^{31}P)$ coupling constants of 30–40 Hz in the ^{31}P-NMR spectra[10] (Figure 1a).

In the ^{1}H-NMR spectra, the 'RS$_4$' protons of the free thiols and coordinated thiolates show slightly different chemical shifts, but nearly identical splitting patterns. A particularly suitable NMR probe is the characteristic CH$_3$ doublet of 'CH$_3$S$_4$' which appears at δ = 1.07 in **9** (Figure 1b) and at δ = 1.30 in **12**.

Figure 1. a) ^{31}P-NMR spectrum (109.4 MHz) and b) ^{1}H-NMR spectrum (270 MHz) of [Ru(PPh$_3$)$_2$('MeS$_4$')] (**9**) in [D$_8$]THF (○ = THF)



The oxo complex **12** shows two intensive and characteristic ν(M=O) bands at 919 and 886 cm^{-1} in its IR spectrum (KBr pellet).

X-ray Structure Determinations of [Ru(PPh$_3$)$_2$('MeS$_4$')] · 2 CH$_2$Cl$_2$ (9 · 2 CH$_2$Cl$_2$), [Mo(O)$_2$('MeS$_4$')] (12), and [Ru(PPh$_3$)(CO)('MeS$_4$')] (13)

The synthesis of [Ru(PPh$_3$)(CO)('MeS$_4$')] (**13**) will be described below, but its X-ray structure determination is included here for the sake of conciseness.

Figure 2 shows the molecular structures of **9** · 2 CH$_2$Cl$_2$ and **12**, selected distances and angles are listed in Table 1.

In both complexes, the metal centers are pseudo-octahedrally surrounded by four sulfur atoms and two coligands. The thiolate donors occupy trans positions, the

PPh_3 and oxo ligands cis positions. The CH_3 substituents of the C_2 bridge in the five membered MS_2C_2 rings (M = Ru, Mo) assume equatorial or exo positions as previously observed in $[Mo(NO)_2('MeS_4')]$[6] indicating that this configuration is sterically preferred.

Figure 2. Molecular structures of a) $[Ru(PPh_3)_2('MeS_4')]$ (**9**) and b) $[Mo(O)_2('MeS_4')]$ (**12**) (H atoms omitted)

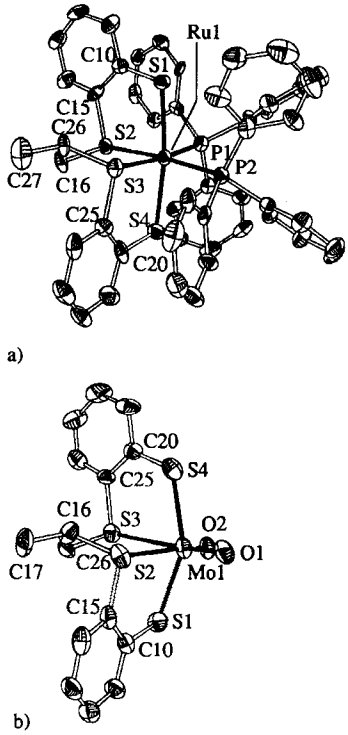


Table 1. Selected distances [pm] and angles (deg) of a) $[Ru(PPh_3)_2('MeS_4')] \cdot 2\ CH_2Cl_2$ (**9** · 2 CH_2Cl_2) and b) $[Mo(O)_2('MeS_4')]$ (**12**)

a) $[Ru(PPh_3)_2('MeS_4')] \cdot 2\ CH_2Cl_2$			
Ru(1)-S(1)	240.2(4)	S(1)-Ru(1)-P(1)	88.3(1)
Ru(1)-S(2)	235.4(3)	S(4)-Ru(1)-P(2)	88.3(1)
Ru(1)-S(3)	237.8(4)	S(4)-Ru(1)-P(1)	96.1(1)
Ru(1)-S(4)	240.9(4)	S(1)-Ru(1)-P(2)	97.6(2)
Ru(1)-P(1)	237.0(4)	S(2)-Ru(1)-S(1)	85.8(1)
Ru(1)-P(2)	237.5(5)	S(3)-Ru(1)-P(2)	86.0(1)
C(16)-C(26)	150.7(17)	S(3)-Ru(1)-P(1)	172.0(1)
S(3)-C(26)	184.9(11)	S(2)-Ru(1)-P(2)	171.8(1)
S(3)-C(25)	181.0(13)	P(1)-Ru(1)-P(2)	101.8(1)
S(4)-C(20)	175.0(14)	C(16)-C(26)-C(27)	111.4(9)
b) $[Mo(O)_2('MeS_4')]$			
Mo(1)-S(1)	240.9(4)	S(1)-Mo(1)-O(1)	106.2(3)
Mo(1)-S(2)	269.3(5)	S(4)-Mo(1)-O(2)	104.4(3)
Mo(1)-S(3)	266.3(3)	S(2)-Mo(1)-O(1)	86.5(2)
Mo(1)-S(4)	241.4(4)	S(3)-Mo(1)-O(2)	86.7(2)
Mo(1)-O(1)	169.0(7)	S(4)-Mo(1)-O(1)	90.7(3)
Mo(1)-O(2)	169.3(5)	S(1)-Mo(1)-O(2)	90.1(3)
C(16)-C(26)	150.0(15)	S(2)-Mo(1)-O(2)	163.0(2)
S(2)-C(26)	184.3(11)	S(3)-Mo(1)-O(1)	163.0(2)
S(2)-C(15)	175.5(13)	O(1)-Mo(1)-O(2)	109.3(3)
S(1)-C(10)	176.8(10)	C(26)-C(16)-C(17)	110.9(9)

The angles C(16)−C(26)−C(27) in **9** · 2 CH_2Cl_2 and C(26)−C(16)−C(17) in **12** are in the range common for a tetrahedron angle, and no significant distortion of these angles due to the methyl substituent can be recognized. The M−S(thioether) distances of the two compounds differ slightly; the M−S(thioether) distance of the thioether bound to the stereogenic C* atom is somewhat longer than that of the thioether bound to the non-stereogenic center [2.4(4) pm in **9** and 3.0(5) pm in **12**]. Similar and even greater differences, however, are also found in $[Ru(PR_3)_2('S_4')]$ complexes of the parent 'S_4'$^{2-}$ ligand (see below). Therefore, they cannot be traced back to the R substituent of the 'RS_4'$^{2-}$ ligands. In addition, the Ru−P or Mo−O distances in trans position to these M−S(thioether) bonds are identical within standard deviation. The same holds for the two M−S(thiolate) distances. In conclusion, no significant distortion of the $[M(L)_2('RS_4')]$ skeletons being due to the R substituents can be recognized.

Relatively long M−S(thioether) distances such as in **12** are certainly caused by the strong trans influence of the oxo ligands and have previously been observed in related complexes[11−13].

Trans influence of coligands such as CO appears to affect also the molecular structure of $[Ru(PPh_3)(CO)('MeS_4')]$ (**13**). Figure 3 shows the molecular structure of **13**, Table 2 lists selected distances and angles.

Figure 3. Molecular structure of $[Ru(PPh_3)(CO)('MeS_4')]$ (**13**) (H atoms omitted)

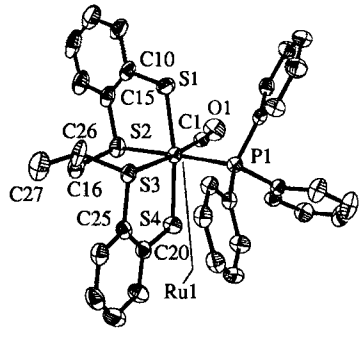


Table 2. Selected distances [pm] and angles (deg) of $[Ru(PPh_3)(CO)('MeS_4')]$ (**13**)

Ru(1)-S(1)	238.1(2)	S(1)-Ru(1)-C(1)	90.8(1)
Ru(1)-S(2)	237.2(1)	S(4)-Ru(1)-P(1)	90.8(1)
Ru(1)-S(3)	243.0(1)	S(4)-Ru(1)-C(1)	96.8(1)
Ru(1)-S(4)	240.2(1)	S(1)-Ru(1)-P(1)	94.2(1)
Ru(1)-C(1)	185.0(4)	S(2)-Ru(1)-S(1)	87.0(1)
Ru(1)-P(1)	233.0(1)	S(3)-Ru(1)-P(1)	92.9(1)
C(16)-C(26)	152.0(6)	C(1)-Ru(1)-S(3)	173.4(1)
S(3)-C(26)	185.0(4)	S(2)-Ru(1)-P(1)	178.8(1)
S(3)-C(25)	177.9(5)	C(1)-Ru(1)-P(1)	93.2(1)
S(4)-C(20)	175.0(4)	C(16)-C(26)-C(27)	112.7(4)
C(1)-O(1)	114.7(5)	Ru(1)-C(1)-O(1)	175.0(4)

Complex **13** exhibits basically the same $[Ru('RS_4')]$ core structure as $[Ru(PPh_3)_2('MeS_4')]$. The CO ligand occupies the position which is trans to the thioether atom carrying the stereogenic C* atom. Due to the trans effect, the Ru−S(thioether) distance trans to the CO group [Ru(1)−S(3) = 243.0(1) pm] is slightly longer than the cis counterpart [Ru(1)−S(2) = 237.2(1) pm]. Because of the smaller CO group, the angle PRuC in **13** decreases to 93.2(1)° in comparison with the angle PRuP in **9** [101.8(1)°],

Table 3. Comparison of distances [pm] and angles (deg) of $[Ru(PPh_3)_2('MeS_4')]$ (**9**) $[Ru(PR_3)_2('S_4')]$, and $[Ru(PPh_3)(CO)('MeS_4')]$ (**13**)

distances (pm)			
Ru(1)-S(1)	240.2(4)	240.2(6)	238.1(2)
Ru(1)-S(2)	235.4(3)	236.2(6)	237.2(1)
Ru(1)-S(3)	237.8(4)	239.9(6)	243.0(1)
Ru(1)-S(4)	240.9(4)	240.8(6)	240.2(1)
Ru(1)-P(1)	237.0(4)	237.1(6)	233.0(1)
Ru(1)-P(2)	237.5(5)	233.2(6)	—
Ru(1)-C(1)	—	—	114.7(5)
angles (deg)			
P(1)-Ru(1)-P(2)	101.8(1)	94.6(2)	—
C(1)-Ru(1)-P(2)	—	—	93.2(1)
S(3)-Ru(1)-P(2)	86.0(1)	88.5(2)	92.9(1)
S(2)-Ru(1)-P(1)	85.8(1)	89.8(2)	—
S(2)-Ru(1)-C(1)	—	—	86.6(1)
S(3)-Ru(1)-P(1)	172.0(1)	175.4(2)	—
S(3)-Ru(1)-C(1)	—	—	173.4(1)
S(1)-Ru(1)-S(4)	171.9(1)	170.4(2)	170.7(1)
S(2)-Ru(1)-S(3)	86.6(1)	87.2(2)	87.3(1)

the $[RuS_4]$ framework, however, does not significantly change.

With regard to substitution reactions, a comparison of distances and angles in **9** and **12** and the parent $[M(L)_2('S_4')]$ complexes was of particular importance. In the case of the Ru complexes, because the molecular structure of $[Ru(PPh_3)_2('S_4')]$ could not yet be determined by X-ray structural analysis, the molecular parameters of $[Ru(P\mathit{n}Bu_3)_2('S_4')]$[14] had to be used for this purpose. Tables 3 and 4 list relevant molecular parameters.

Table 4. Comparison of distances [pm] and angles (deg) of $[Mo(O)_2('MeS_4')]$ (**12**) and $[Mo(O)_2('S_4')]$

distances (pm)		
Mo(1)-S(1)	240.9(4)	239.3(7)
Mo(1)-S(2)	269.3(2)	269.0(6)
Mo(1)-S(3)	266.3(3)	268.4(7)
Mo(1)-S(4)	241.4(4)	241.1(7)
Mo(1)-O(1)	169.0(7)	171.0(2)
Mo(1)-O(2)	169.3(5)	172.0(2)
angles (deg)		
O(1)-Mo(1)-O(2)	109.3(3)	111.1(1)
S(2)-Mo(1)-O(1)	86.5(2)	87.1(5)
S(3)-Mo(1)-O(2)	86.7(2)	85.1(3)
S(3)-Mo(1)-O(1)	163.0(2)	161.1(1)
S(3)-Mo(1)-S(2)	78.3(1)	78.1(2)
S(4)-Mo(1)-S(1)	152.8(1)	156.2(3)

Table 3 shows that distances and angles within the $[Ru('RS_4')]$ skeletons (R = H, CH_3) of all three Ru complexes are nearly identical and do not show any tendency which could be due to either the CH_3 substituent on the C_2 bridge or the different size of the PR_3 ligands. The PR_3 ligands only influence the PRuP angle which in **9** [101.8(1)°] is distinctly larger than in $[Ru(PBu_3)_2('S_4')]$ [94.6(2)°]. The SRuS angles, however, demonstrate that even the very different sterical demand of the PR_3 ligands on one hand and of the combination CO/PPh_3 on the other hand does not lead to a significant change of the $[Ru('S_4')]$ or $[Ru('RS_4')]$ skeletal geometry.

Likewise, also the molecular parameters of **12** and $[Mo(O)_2('S_4')]$[11,13] in Table 4 do not show any structural change which could be caused by the CH_3 substituent on the C_2 bridge of **12**.

Reactions of $[Ru(PPh_3)_2('MeS_4')]$ (9), $[Ru(PPh_3)_2('HO(CH_2)_9S_4')]$ (10), and $[Ru(PPh_3)_2('PhCH_2S_4')]$ (11) with CO and PMe_3

In order to clarify the question raised at the beginning as to whether stereogenic metal centers influence the transfer of chiral information, substitution reactions of $[Ru(PPh_3)_2('RS_4')]$ (**9**, **10**, and **11**) with CO and PMe_3 were investigated. The stereoisomers which can potentially result from these reactions are depicted in Scheme 2.

As mentioned above, $[Ru(PPh_3)_2('RS_4')]$ complexes theoretically can exist in two diastereomeric forms, but the complexes investigated here contained only one diastereomer (as pair of enantiomers). In the case of **9**, this diastereomer proved to have equatorial R substituents. Only this diastereomer was considered in Scheme 2, and the stereoisomers resulting from substitution reactions can be classified as follows:

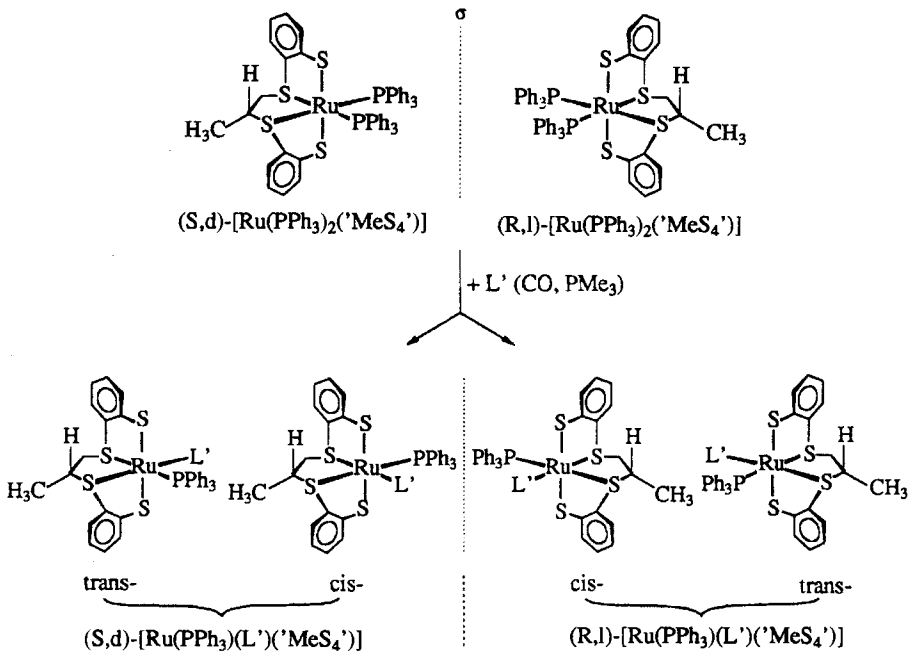
R/S and *d/l* designate the configurations of metal center and stereogenic C* atom, *trans* and *cis* the position of the entering ligand L′ which can be either trans or cis to the thioether donor which is bound to the stereogenic C* atom carrying the R substituent.

When the $[Ru(PPh_3)_2('RS_4')]$ complexes **9**, **10**, and **11** were treated with CO or PMe_3, one PPh_3 ligand was exchanged according to eq. (5).

The reactions with CO were monitored by IR spectroscopy. After two hours, the intensity of the resulting ν(CO) IR bands no longer increased, but in order to secure the completeness of the reactions the solutions were saturated with CO for two more hours. In all cases, reaction mixtures and subsequently isolated products showed only one ν(CO) IR band, which appeared in KBr at 1960–1963 cm^{-1}.

In order to determine the ratios of diastereomers, the reaction mixtures were evaporated to dryness, and the resulting raw products were examined by NMR spectroscopy, preferably by ^{31}P-NMR spectroscopy. Figure 4 shows the ^{31}P-NMR spectrum of the raw product of $[Ru(PPh_3)(CO)('MeS_4')]$ (**13**). It demonstrates that the raw product contains only two diastereomers (as pairs of enantiomers) each exhibiting one ^{31}P-NMR signal.

Scheme 2. Stereoisomers resulting from substitution reactions of $[Ru(PPh_3)_2('MeS_4')]$ (**9**) with achiral L' = CO, PMe_3



$$[Ru(PPh_3)_2('RS_4')] + L' \xrightarrow[-PPh_3]{THF\,/\,20\,^\circ C\,/\,5\,h} [Ru(PPh_3)(L')('RS_4')] \quad (5)$$

R = CH_3-, **9**

R = $HO(CH_2)_9$-, **10**

R = $PhCH_2$-, **11**

R = CH_3-, L' = CO, **13**

L' = PMe_3, **16**

R = $HO(CH_2)_9$, L' = CO, **14**

L' = PMe_3, **17**

R = $PhCH_2$-, L' = CO, **15**

L' = PMe_3, **18**

The ^{1}H-NMR spectra of the $[Ru(PPh_3)(L')('RS_4')]$ complexes **14**–**18** usually exhibit superimposed multiplets resulting from the H atoms at the benzene rings and the C_2H_3R entities, for $[Ru(PPh_3)(CO)('MeS_4')]$ (**13**), however, the ratio of diastereomers could also be determined from the intensity of the CH_3 doublets of the "MeS_4" ligand. The results are summarized in Table 5.

Figure 4. ^{31}P-NMR spectrum of the raw product of $[Ru(PPh_3)(CO)('MeS_4')]$ (**13**) (109.4 MHz, CD_2Cl_2)

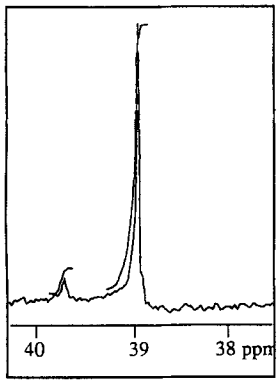


Table 5. ^{31}P-NMR data, ratio of diastereomers, and diastereomeric excesses (d.e.) of $[Ru(PPh_3)(L')('RS_4')]$ complexes with R = CH_3, $HO[CH_2]_9$, $PhCH_2$ und L' = CO, PMe_3 (**13**–**18**)

Complex	$^{31}P\{^1H\}$ NMR data (δ values)	Ratio of diastereomers (diastereomeric excesses d.e.)
$[Ru(PPh_3)(CO)('MeS_4')]$ (**13**)	38.8/ 39.6[a]	1:9.8 ± 0.5 81% d.e.
$[Ru(PPh_3)(PMe_3)('MeS_4')]$ (**16**)	35.2; −3.15/ 36.8; −3.95[b]	1:10 ± 0.5 82% d.e.
$[Ru(PPh_3)(CO)('HO(CH_2)_9S_4')]$ (**14**)	37.9/ 39.0[b]	1:5 ± 1 67% d.e.
$[Ru(PPh_3)(PMe_3)('HO(CH_2)_9S_4')]$ (**17**)	34.9; −3.15 37.95; −3.70[b]	1:5.2 ± 0.4 68% d.e.
$[Ru(PPh_3)(CO)('PhCH_2S_4')]$ (**15**)	38.0/ 39.2[b]	1:4.5 ± 0.9 63% d.e.
$[Ru(PPh_3)(PMe_3)('PhCH_2S_4')]$ (**18**)	34.2; −2.6 38.7; −4.2[b]	1:4.1 ± 0.9 60% d.e.

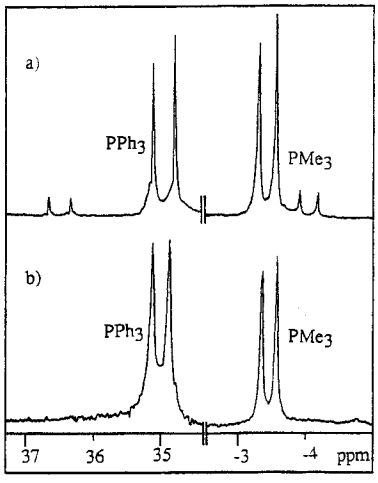
[a] In CD_2Cl_2, rel. ext. H_3PO_4. – [b] In $CDCl_3$, rel. ext. H_3PO_4.

Table 5 shows that in all cases those two diastereomers formed which could theoretically be expected. However, one diastereomer formed in excess. The diastereomeric excesses amounted to about 60–68% for **14**/**17** and **15**/**18** and increased to approximately 82% in **13**/**16**. Moreover, a comparison of the respective CO and PMe_3 complexes shows that not the entering CO or PMe_3 but the substituent R influences the diastereomeric excesses, and that the excesses are considerably larger in the case of the "MeS_4" complexes than in the case of the complexes exhibiting bulkier R substituents.

The complexes **13** and **16** were isolated as yellow powders after recrystallization from THF. Through fractional crystallization from toluene at −30 °C, one diastereomer of **16**

separated in pure form, such that assignment of ^{1}H- and ^{31}P-NMR signals became possible (Figure 5). The doublet splitting of the PPh_3 and the PMe_3 signals through $^2J(^{31}P^{31}P)$ coupling is characteristic of all [Ru(PPh_3)(PMe_3)('RS_4')] complexes.

Figure 5. ^{31}P-NMR spectra of a) the raw product and b) the isolated diastereomer of [Ru(PPh_3)(PMe_3)('MeS_4')] (**16**) (109.4 MHz, $CDCl_3$)



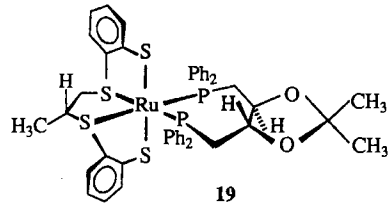
Reaction of [Ru(PPh_3)$_2$('MeS_4')] with (+)-(*S,S*)-DIOP

In a further experiment, racemic [Ru(PPh_3)$_2$('MeS_4')] was allowed to react with the optically pure (+)-(*S,S*)-DIOP ((+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane). Here, several alternatives had to be considered. *1)* Only one enantiomer of [Ru(PPh_3)$_2$('MeS_4')] reacts with DIOP functioning as chelate ligand and the other enantiomer is left unaltered. In a couple of cases, this type of reaction has been observed with racemates leading to high enantioselectivities[15]. *2)* DIOP reacts with both enantiomers of [Ru(PPh_3)$_2$('MeS_4')], but to a different extent. *3)* DIOP functions as bridging ligand between homochiral or heterochiral [Ru(PPh_3)$_2$('MeS_4')] fragments.

In the reaction according to eq. (6), both diastereomers of [Ru(DIOP)('MeS_4')] which are theoretically possible are formed in equal amounts.

rac-[Ru(PPh_3)$_2$('MeS_4')] + (+)-(S,S)-DIOP $\xrightarrow[-\,2\ PPh_3]{THF\,/\,5\ h\,/\,reflux}$ (6)

(S,d)-(S,S)-



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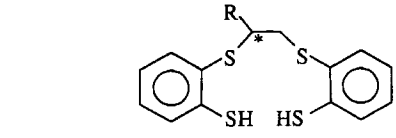
+ (R,l)-(S,S)-[Ru(DIOP)('MeS_4')]

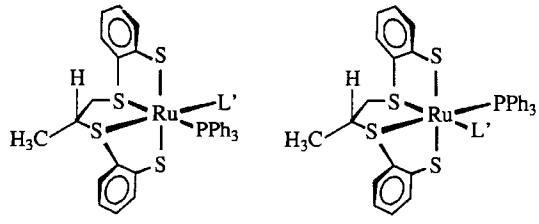
It was not possible to change the ratio of diastereomers by reducing the amount of applied DIOP to 0.5 equivalent. In this case, again both diastereomers of [Ru(DIOP)('MeS_4')] were formed in a ratio 1:1, and approximately one half of the starting [Ru(PPh_3)$_2$('MeS_4')] remained unreacted. Binuclear complexes could not be observed.

Preparative HPLC allowed us to separate both diastereomers such that, at least, in principle metal complexes could now be isolated in enantiomerically pure form which exhibit chirotopic and prostereogenic metal centers.

Discussion and Summary

Template alkylation of $[Ni('S_2')_2]^{2-}$ ions with suitable vicinal dibromides and hydrolysis of the resulting [Ni('RS_4')] complexes with aqueous HCl provided the chiral 'RS_4'-H_2 thiols in free state for the first time.





This enabled the synthesis of chiral [M(L)(L')('RS_4')] complexes containing not only chirotopic but also stereogenic metal centers[6].

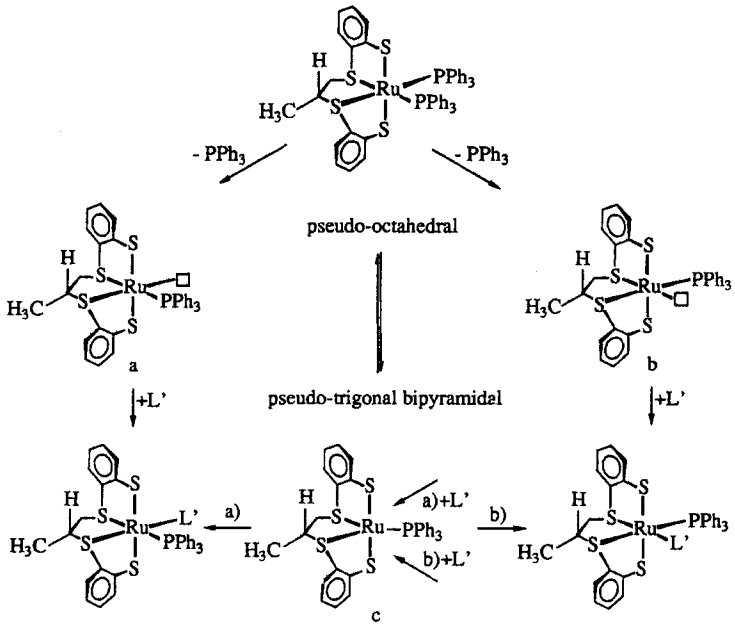
Reaction of [$RuCl_2(PPh_3)_3$] or [$Mo(O)_2(acac)_2$] with these 'RS_4'-H_2 thiols yielded the corresponding [Ru(PPh_3)$_2$('RS_4')] and [$Mo(O)_2$('RS_4')] complexes of which [Ru(PPh_3)$_2$('MeS_4')] · 2 CH_2Cl_2 (**9** · 2 CH_2Cl_2) and [$Mo(O)_2$('MeS_4')] (**12**) could be characterized by X-ray structure determination. In both complexes, the Me substituents occupy equatorial positions in the five membered [MS_2C_2] rings. Comparison of **9** and **12** with [Ru($PnBu_3$)$_2$('S_4')] and [$Mo(O)_2$('S_4')] carrying the parent "S_4" ligand showed that the introduction of the R substituent into the 'S_4' ligand and the resulting stereogenic C* atom do not significantly influence the molecular parameters of the corresponding [M('S_4')] cores. While the symmetry is reduced from C_2 to C_1, distances and angles remain nearly identical. For example, [M(L)$_2$('RS_4')] complexes (L = PPh_3, $PnBu_3$; R = H, CH_3) exhibit different PRuP angles depending on the size of the PR_3 ligands[16], but practically invariant [Ru('RS_4')] skeletons.

On account of this, it could be expected that substitution of PPh_3 by the achiral ligands CO or PMe_3 in [Ru(PPh_3)$_2$('RS_4')] would lead to approximately equal amounts of the two diastereomers which are theoretically possible.

However, in the case of [Ru(PPh_3)(L')('MeS_4]')] (L' = CO, **13**; L' = PMe_3, **16**) diastereomeric excesses of about 80% were observed indicating a remarkably high diastereoselectivity.

If the reaction mechanism of the substitution is dissociative and formation of the coordinatively unsaturated frag-

Scheme 3. Two alternative pathways leading to diastereomers of [Ru(PPh$_3$](L')('RS$_4$')]



ments [Ru(PPh$_3$)('RS$_4$')] represents the rate-determining step, two different reaction pathways leading to diastereoselectivity can be discussed (Scheme 3).

1) One of the two PPh_3 ligands is split off preferentially, even if the X-ray structural parameters do not indicate unequally strong Ru–P bonds. As a consequence, the resulting pseudo-octahedral and diastereomeric fragments [Ru(PPh$_3$)('RS$_4$')] **a** and **b** form in unequal amounts yielding [Ru(PPh$_3$)(L')('RS$_4$')] upon reaction with L' in the observed diastereomeric excesses.

2) Both diastereomeric fragments [Ru(PPh$_3$)('RS$_4$')] **a** and **b** form in equal amounts but are, like other five-coordinate complexes, stereochemically non-rigid and instantaneously isomerize to the trigonal-bipyramidal fragment **c**. Then, entrance of L' along either way a) or way b) has to be preferred in order to explain the observed diastereoselectivity.

Which one of these two alternatives applies cannot yet be decided and is possibly of secondary interest only. More important appears to be the result that the stereogenicity of the metal centers in [Ru(PPh$_3$)('RS$_4$')] fragments induces diastereoselectivity even in reactions with achiral 'substrates'. This result could become of interest for metal centered asymmetric reactions aiming at high stereoselectivity.

The reaction of racemic [Ru(PPh$_3$)$_2$('MeS$_4$')] with the bidentate (+)-(*S,S*)-DIOP yielded the two possible diastereomers of [Ru(DIOP)('MeS$_4$')] in a 1:1 ratio with DIOP functioning as chelate ligand. This ratio could not be changed by varying the amount of applied DIOP, however, the two diastereomers could be separated such that optically pure complexes were obtained which possess chirotopic and prostereogenic metal centers.

Support of these investigations by the *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental

General Methods: Unless noted otherwise, all reactions were carried out under nitrogen at room temperature by using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR spectroscopy. – IR spectra of solutions were recorded in CaF_2 cuvettes with compensation of solvent bands; liquids were measured with NaCl disks and solids as KBr pellets. IR: Perkin Elmer 1620 FT IR. – NMR: Jeol JNM-GX 270 and EX 270 FT-NMR. – MS: Varian MAT 212. – HPLC: Knauer HPLC pump 64 preparative, Spherisorb ODS 2 (250 × 8 mm, 5 μm, Knauer), CH_3CN/H_2O = 5:1 (v/v) (detection with Knauer UV/Vis photometer at λ = 220 nm).

1,2-Benzenedithiol[17], Na_2[Ni('S$_2$')$_2$][18] ['S$_2$'$^{2-}$ = 1,2-benzenedithiolate(2–)], 1,2-dibromopentane[19], 10,11-dibromo-1-undecanol[19], 2,3-dibromo-1-phenylpropane[19], [$RuCl_2(PPh_3)_3$][20], PMe_3[21], [$Mo(O)_2(acac)_2$][22] were prepared by literature methods. (+)-(S,S)-DIOP [(+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] was purchased from Aldrich Chemical Co.

Synthesis of [Ni('RS$_4$')] Complexes. – General Procedure: In a typical experiment, a solution of about 15–30 mmol of Na_2[Ni('S$_2$')$_2$] in MeOH (50–100 ml) was combined with an equimolar quantity of the corresponding vicinal dibromo compound and stirred for 1–2 d at temperatures between 20°C and 50°C. The resulting brown to dark brown precipitates were isolated, washed with H_2O (40 ml) and MeOH (30 ml) and dried in vacuo (12 h).

[Ni('MeS$_4$')] (**1**): 11.5 g (30 mmol) of Na_2[Ni('S$_2$')$_2$], 3.1 ml (30 mmol) of 1,2-dibromopropane, 100 ml of MeOH, 50°C, 24 h. Yield: 6.6 g brown [Ni('MeS$_4$')] (57%). – $C_{15}H_{14}NiS_4$ (381.21): calcd. C 47.26, H 3.70; found C 46.98, H 3.51. – FD MS (CH_2Cl_2), *m/z*: 381 [Ni('MeS$_4$')]$^+$.

[Ni('CH$_3$(CH$_2$)$_2$S$_4$')] (**2**): 5.8 g (15 mmol) of Na_2[Ni('S$_2$')$_2$], 2.25 ml (15 mmol) of 1,2-dibromopentane, 50 ml of MeOH, 20°C, 48 h. Yield: 4.4 g brown [Ni('$CH_3(CH_2)_2S_4$')] (71%). – $C_{17}H_{18}NiS_4$ (409.26): calcd. C 49.89, H 4.43, S 31.33; found C 48.40, H 4.38, S 28.70. – FD MS (CH_2Cl_2), *m/z*: 409 [Ni('$CH_3(CH_2)_2S_4$')]$^+$.

[Ni('HO(CH$_2$)$_9$S$_4$')] (**3**): 11.5 g (30 mmol) of Na_2[Ni('S$_2$')$_2$], 7.5 ml (30 mmol) of 10,11-dibromo-1-undecanol, 100 ml of MeOH, 20°C, 48 h. Yield: 7.7 g dark brown [Ni('HO(CH$_2$)$_9$S$_4$')] (50%). – $C_{23}H_{30}NiOS_4$ (509.42): calcd. C 54.22, H 5.94, S 25.17; found C 52.19, H 5.50, S 23.14. – FD MS (CH_2Cl_2), *m/z*: 509 [Ni('HO(CH$_2$)$_9$S$_4$')]$^+$.

[Ni('PhCH$_2$S$_4$')] (**4**): 5.8 g (15 mmol) of Na_2[Ni('S$_2$')$_2$], 2.8 ml (15 mmol) of 1,2-dibromo-3-phenylpropane, 80 ml of MeOH, 20°C, 24 h. Yield: 4.4 g brown [Ni('PhCH$_2$S$_4$')] (63%). – $C_{21}H_{18}NiS_4$ (457.31): calcd. C 55.15, H 3.97; found C 54.50, H 4.27. – FD MS (CH_2Cl_2), *m/z*: 457 [Ni('PhCH$_2$S$_4$')]$^+$.

Synthesis of 'RS$_4$'-H$_2$. – General Procedure for Hydrolysis of [Ni('RS$_4$')] with Concentrated Hydrochloric Acid [R = CH_3-, (**1**); R = $CH_3(CH_2)_2$-, (**2**); R = $HO(CH_2)_9$-, (**3**); R = $PhCH_2$-, (**4**)]: A suspension of [Ni('RS$_4$')] (5 mmol) in 50 ml of CH_2Cl_2 was combined with 30 ml of concentrated HCl_{aq} and vigorously stirred for 2 h, in the course of which a green aqueous and a colourless organic phase formed. The CH_2Cl_2 phase was separated and the aqueous phase was extracted with 30 ml of CH_2Cl_2. The CH_2Cl_2 phases were combined, CH_2Cl_2 was evaporated in vacuo, the resulting residue was redissolved in 20 ml of CCl_4 and the CCl_4 solution was filtered over SiO_2 (about 5 g). The SiO_2 was washed with additional 30 ml of CCl_4, and the combined filtrates were concentrated in vacuo. The remaining thiols 'RS$_4$'-H$_2$ were colourless to yellow-brown oils. Yield: 70–88%.

'MeS$_4$'-H$_2$ (**5**): 1.91 g (5 mmol) of [Ni('MeS$_4$')]; Yield: 1.3 g 'MeS$_4$'-H$_2$ (80%). – $C_{15}H_{16}S_4$ (324.52): calcd. C 55.51, H 4.97, S 39.52; found C 55.03, H 4.88, S 39.29. – IR (CCl_4): $\tilde{\nu}$ = 2511 cm^{-1} (SH). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.41 (d, 3H, CH_3), 2.82–2.90 (m, 1H, CH_2), 3.20–3.27 (m, 1H, CH_2), 3.29–3.37 (m, 1H, CH), 4.19 (s, 1H, SH), 4.40 (s, 1H, SH), 6.96–7.34 (m, 8H, C_6H_4). – ^{13}C{^{1}H} NMR (67.70 MHz, $CDCl_3$): δ = 19.38, 40.90, 42.59, (C_{alkyl}); 125.58, 125.86, 127.61, 128.32, 128.46, 128.74, 130.72, 132.03, 132.56, 134.92, 135.81, 138.37 (C_{Aryl}). – FD MS (THF), *m/z*: 325 ['MeS$_4$'-H$_2^+$].

'CH$_3$(CH$_2$)$_2$S$_4$'-H$_2$ (**6**): 1.8 g (4.4 mmol) of [Ni('CH$_3$(CH$_2$)$_2$S$_4$')]; Yield: 1.1 g 'CH$_3$(CH$_2$)$_2$S$_4$'-H$_2$ (72%). – $C_{17}H_{20}S_4$ (352.57): calcd. C 57.91, H 5.72, S 36.37; found C 57.04, H 5.64, S 35.59. – IR (CCl_4): $\tilde{\nu}$ = 2511 cm^{-1} (SH). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.95 (t, 3H, CH_3), 1.45–1.70, 1.95–2.10 (m, 4H, CH_2), 2.90–3.00 (m, 1H, CH_2), 3.20–3.27 (m, 2H, CH_2, CH), 4.15 (s, 1H, SH), 4.40 (s, 1H, SH), 6.90–7.35 (m, 8H, C_6H_4). – ^{13}C{^{1}H} NMR (67.70 MHz, $CDCl_3$): δ = 14.7, 21.0, 35.7, 40.5, 44.0 (C_{alkyl}); 126.25, 126.6, 128.2, 128.6, 129.1, 129.7, 131.8, 132.8, 133.4, 135.5, 136.7, 138.9 (C_{aryl}). – FD MS (THF), *m/z*: 352 ['CH$_3$(CH$_2$)$_2$S$_4$'-H$_2^+$].

'HO(CH$_2$)$_9$S$_4$'-H$_2$ (**7**): 2.3 g (4.5 mmol) of [Ni('HO(CH$_2$)$_9$S$_4$')]; Yield: 1.6 g 'HO(CH$_2$)$_9$S$_4$'-H$_2$ (70%). – $C_{23}H_{32}OS_4$ (452.73): calcd. C 61.02, H 7.12, S 28.32; found: C 59.10, H 7.17, S 26.10. – IR (CCl_4): $\tilde{\nu}$ = 3361 cm^{-1} (OH), 2510 cm^{-1} (SH). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.32 (m, 16H, CH_3, CH_2), 2.85–3.67 (m, 5H, CH_2, CH), 4.22 (s, 1H, SH), 4.40 (s, 1H, SH), 6.94–7.41 (m, 8H, C_6H_4). – ^{13}C{^{1}H} NMR (67.70 MHz, $CDCl_3$) δ = 26.3, 27.4, 29.4, 29.8, 30.2, 33.4, 35.5, 40.5, 49.0, 54.2, 63.6, (C_{alkyl}); 126.3, 126.6, 128.3, 129.1, 129.6, 129.8, 131.8, 132.8, 133.5, 135.7, 136.6, 138.8 (C_{aryl}). – FD MS (THF), *m/z*: 453 ['OH(CH$_2$)$_9$S$_4$'-H$_2^+$].

'PhCH$_2$S$_4$'-H$_2$ (**8**): 2.3 g (5 mmol) of [Ni('PhCH$_2$S$_4$')]; Yield: 1.5 g 'PhCH$_2$S$_4$'-H$_2$ (75%). – $C_{21}H_{20}S_4$ (400.62): calcd. C 62.96, H 5.03; found C 63.10, H 5.31. – IR (CCl_4): $\tilde{\nu}$ = 2515 cm^{-1} (SH). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.75–3.35 (m, 5H, CH_2 with CH), 4.10 (s, 1H, SH), 4.25 (s, 1H, SH), 6.85–7.35 (m, 13H, C_6H_4, C_6H_5). – ^{13}C{^{1}H} NMR (67.70 MHz, $CDCl_3$): δ = 38.78, 39.14, 49.73 (C_{alkyl}), 125.50, 125.93, 126.32, 127.62, 127.98, 128.40, 128.79, 129.26, 129.44, 131.20, 131.96, 133.20, 135.47, 136.15, 138.17, 138.9 (C_{aryl}). – FD MS (THF), *m/z*: 400 ['PhCH$_2$S$_4$'-H$_2^+$].

Synthesis of [Ru(PPh$_3$)$_2$('MeS$_4$')] · 2 CH$_2$Cl$_2$ (**9** · 2 CH_2Cl_2): A suspension of [$RuCl_2(PPh_3)_3$] (2.9 g, 3.0 mmol) in 60 ml of THF was combined with **5** (0.5 ml, 3.0 mmol) and heated at reflux for 5 h. The solvent was removed in vacuo and the resulting residue was redissolved in CH_2Cl_2 (20 ml). At room temperature, yellow crystals precipitated, which were separated after 2 d, washed with Et_2O (30 ml) and dried in vacuo (6 h). Yield: 1.31 g (39%). – $C_{53}H_{48}Cl_4P_2RuS_4$ (1118.03): calcd. C 56.94, H 4.33, S 11.47; found C 57.26, H 4.39, S 11.67. – ^{1}H NMR (270 MHz, [D$_8$]THF): δ = 1.07 (d, 3H, CH_3), 1.95 (m, 1H, CH_2), 2.47 (m, 1H, CH_2), 2.50 (m, 1H, CH), 6.37–7.45 (m, 38H, C_6H_4, C_6H_5). – ^{13}C{^{1}H} NMR (67.70 MHz, $CDCl_3$): 17.5, 48.02 [$^3J(^{13}C^{31}P)$ = 4.2 Hz], 48.08 [$^3J(^{13}C^{31}P)$ = 4.7 Hz] (C_{alkyl}); 120.0–160.5 (C_{aryl}). – ^{31}P{^{1}H} NMR (109.4 MHz, [D$_8$]THF): δ = 31.86 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 31.7 Hz], 32.26 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 31.7 Hz]. – FD MS (^{102}Ru, CH_2Cl_2), *m/z*: 949 [Ru(PPh_3)$_2$('MeS$_4$')]$^+$.

Synthesis of [Ru(PPh$_3$)$_2$('HO(CH$_2$)$_9$S$_4$')] (**10**): A solution of 'HO(CH$_2$)$_9$S$_4$'-Na$_2$ (1.0 g, 2.0 mmol) in 50 ml of MeOH was combined with [$RuCl_2(PPh_3)_3$] (1.92 g, 2.0 mmol) and heated at reflux for 4 h. The resulting yellow brown suspension was filtered while hot, the volume of the filtrate was reduced to about 25 ml and cooled to –30°C. A yellow precipitate formed which was separated after 24 h, washed with MeOH (25 ml) and dried in vacuo (5 h). Yield: 600 mg (31%). – $C_{59}H_{60}OP_2RuS_4$ (1076.38): calcd. C 65.83, H 5.62, S 11.91; found C 66.05, H 5.64, S 10.32. – ^{1}H NMR (270 MHz, C_6D_6): δ = 0.64–1.46 (m, 16H, CH_2), 2.20 (m, 2H, CH_2), 2.51 (m, 1H, CH), 3.40 (t, 2H, CH_2), 6.35–7.70 (m, 23H, C_6H_4, C_6H_5). – ^{31}P{^{1}H} NMR (109.4 MHz, C_6D_6): δ = 30.75 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 38.3 Hz], 30.85 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 38.3 Hz]. – FD MS (^{102}Ru, $CHCl_3$), *m/z*: 1076 [Ru(PPh_3)$_2$('HO(CH$_2$)$_9$S$_4$')]$^+$.

Synthesis of [Ru(PPh$_3$)$_2$('PhCH$_2$S$_4$')] (**11**): A suspension of [$RuCl_2(PPh_3)_3$] (1.85 g, 1.9 mmol) in 40 ml of THF was combined with **8** (763 mg, 1.9 mmol) and heated at reflux for 5 h. The solvent was removed in vacuo, the resulting residue was stirred with Et_2O (40 ml) for 2 h, separated, washed with Et_2O (30 ml) and dried in vacuo (6 h). Yield: 1.14 g (58%). – $C_{57}H_{48}P_2RuS_4$ (1024.27): calcd. C 66.84, H 4.72; found C 65.50, H 4.33. – ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 1.88 (m, 1H, CH_2), 2.20 (m, 1H, CH_2), 2.40 (m, 1H, CH_2), 2.82 (m, 1H, CH), 3.17 (m, 1H, CH_2), 6.45–7.50 (m, 13H, C_6H_4, C_6H_5). – ^{31}P{^{1}H} NMR (109.4 MHz, CD_2Cl_2): δ = 30.26 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 31.7 Hz], 29.82 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 31.7 Hz]. – FD MS (^{102}Ru, $CHCl_3$), *m/z*: 1025 [Ru(PPh_3)$_2$('PhCH$_2$S$_4$')]$^+$.

Synthesis of [Mo(O)$_2$('MeS$_4$')] (**12**): A solution of [$Mo(O)_2(acac)_2$] (1.0 g, 3.05 mmol) in 30 ml of THF was combined with **5** (0.46 ml, 3.05 mmol) and stirred for 2 h. The volume of the resulting dark red solution was reduced to 10 ml. Upon addition of MeOH (40 ml) a red-brown precipitate formed which was separated, washed with MeOH (20 ml) and dried in vacuo. Yield: 685 mg (50%). – $C_{15}H_{14}MoO_2S_4$ (450.44): calcd. C 39.99, H 3.13, S 28.47; found C 40.18, H 2.98, S 28.52. – IR (KBr): $\tilde{\nu}$ = 919, 886 cm^{-1} (M=O). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.30 (d, 3H, CH_3), 2.90 (m, 1H, CH_2), 3.20 (m, 1H, CH_2), 3.35 (m, 1H, CH), 7.10–7.50 (m, 8H, C_6H_4). – ^{13}C{^{1}H} NMR (67.70 MHz, $CDCl_3$): δ = 20.05, 48.00, 48.45 (C_{alkyl}), 124.7, 126.0, 127.3, 128.8, 131.3, 131.6, 131.8, 132.1, 134.2, 137.0, 151.5, 152.5 (C_{aryl}). – FD MS (^{98}Mo, THF), *m/z*: 453 [Mo(O)$_2$('MeS$_4$')]$^+$.

Substitution Reactions of [Ru(PPh$_3$)$_2$('RS$_4$')] with CO and PMe$_3$ and Determination of Diastereomeric Excesses (d.e.). – General Procedure: After completion of the respective reactions the reaction mixtures were evaporated to dryness, and the diastereomeric excesses in the resulting residues were directly determined by NMR spectroscopy before carrying out procedures of purification. In the case of [Ru(PPh$_3$)(L')('HO(CH$_2$)$_9$S$_4$')] and [Ru(PPh$_3$)(L')-('PhCH$_2$S$_4$')] (L' = CO, PMe$_3$), attempts to obtain analytically pure samples by recrystallizations failed; the raw products, however, allowed an unambiguous determination of diastereomeric excesses.

[Ru(PPh$_3$)(CO)('MeS$_4$')] (**13**): CO was bubbled through a solution of **9** (1.81 g, 1.62 mmol) in 80 ml of THF for 5 h. Recrystallization from THF yielded a yellow powder. Yield: 950 mg (82%). – $C_{34}H_{29}OPRuS_4$ (713.85): calcd. C 57.20, H 4.09; found 57.19, H 4.22. – IR (THF): $\tilde{\nu}$ = 1963 cm^{-1} (CO). – NMR data for both diastereomers: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.17, 1.32 (d, 3H, CH_3), 2.10–3.95 (m, 3H, CH_2, CH), 6.55–7.70 (m, 23H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 38.75 (s, PPh_3), 39.6 (s, PPh_3). – FD MS (^{102}Ru, THF), *m/z*: 714 [Ru(PPh$_3$)(CO)('MeS$_4$')]$^+$.

[Ru(PPh$_3$)(CO)('HO(CH$_2$)$_9$S$_4$')] (**14**): CO was bubbled through a solution of **10** (1.54 g, 1.43 mmol) in 80 ml of THF for 5 h. The solution was evaporated to dryness. – IR (THF): $\tilde{\nu}$ = 1963 cm^{-1} (CO). – NMR data for both diastereomers: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.75–1.65 (m, 16H, CH_2), 1.9–3.95 (m, 3H, CH_2, CH), 3.25–3.60 (m, 2H, CH_2), 6.40–7.60 (m, 23H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 37.9 (s, PPh_3), 39.0 (s, PPh_3). – FD MS (^{102}Ru, THF), *m/z*: 843 [Ru(PPh$_3$)(CO)('HO(CH$_2$)$_9$S$_4$')]$^+$.

[Ru(PPh$_3$)(CO)('PhCH$_2$S$_4$')] (**15**): CO was bubbled through a solution of **11** (1.54 g, 1.50 mmol) in 80 ml of THF for 5 h. The solution was evaporated to dryness. – IR (THF): $\tilde{\nu}$ = 1963 cm^{-1} (CO). – NMR data for both diastereomers: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.95–3.85 (m, 5H, CH_2, CH), 6.45–7.70 (m, 28H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 38.0 (s, PPh_3), 39.2 (s, PPh_3). – FD MS (^{102}Ru, THF), *m/z*: 791 [Ru(PPh$_3$)(CO)('Ph(CH$_2$)S$_4$')]$^+$.

[Ru(PPh$_3$)(PMe$_3$)('MeS$_4$')] (**16**): A solution of **9** (640 mg, 0.57 mmol) in 60 ml of THF was combined with PMe_3 (1 ml, 10.0 mmol) and stirred for 5 h. The solution was evaporated to dryness. Stirring of the resulting residue with Et_2O (20 ml) for 2 h yielded a yellow powder which was separated. Recrystallization of the yellow powder from toluene (+20°C → −30°C) yielded orange crystals of one diastereomer. Yield: 400 mg (98.1%). – $C_{36}H_{38}P_2RuS_4$ (761.91): calcd. C 56.75, H 5.03, S 16.83; found C 56.93, H 5.32, S 16.87. – NMR data for both diastereomers: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.10–1.35 (m, 12H, PCH_3, CH_3), 1.50–2.65 (m, 3H, CH_2, CH), 6.45–7.75 (m, 23H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 35.2 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 35 Hz], 36.8 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 35 Hz], −3.95 [d, PMe_3, $^2J(^{31}P^{31}P)$ = 35 Hz], −3.15 [d, PMe_3, $^2J(^{31}P^{31}P)$ = 35 Hz]. – FD MS (^{102}Ru, THF), *m/z*: 762 [Ru(PPh$_3$)(PMe$_3$)('MeS$_4$')]$^+$. – NMR data for the separated diastereomer: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.12 [d, 9H, PCH_3, $^2J(^{31}P^1H)$ = 7.9 Hz], 1.75 (d, 3H, CH_3), 2.10–2.22 (m, 1H, CH_2), 2.40–2.55 (m, 1H, CH), 2.57–2.65 (m, 1H, CH_2), 6.45–7.75 (m, 23H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 35.2 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 35 Hz], −3.15 [d, PMe_3, $^2J(^{31}P^{31}P)$ = 35 Hz].

[Ru(PPh$_3$)(PMe$_3$)('HO(CH$_2$)$_9$S$_4$')] (**17**): A solution of **10** (220 mg, 0.20 mmol) in 60 ml of THF was combined with PMe_3 (1 ml, 10.0 mmol) and stirred for 5 h. The solution was evaporated to dryness. – NMR data for both diastereomers: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.9–1.6 (m, 27H, CH_3, CH_2), 2.05 (m, 1H, CH_2), 2.17 (m, 1H, CH), 2.60 (m, 1H, CH_2), 6.45–7.75 (m, 23H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 34.9 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 38 Hz], 37.95 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 38 Hz], −3.15 [d, PMe_3, $^2J(^{31}P^{31}P)$ = 35 Hz], −3.70 [d, PMe_3, $^2J(^{31}P^{31}P)$ = 35 Hz]. – FD MS (^{102}Ru, THF), *m/z*: 891 [Ru(PPh$_3$)(PMe$_3$)-('HO(CH$_2$)$_9$S$_4$')]$^+$.

[Ru(PPh$_3$)(PMe$_3$)('PhCH$_2$S$_4$')] (**18**): A solution of **11** (220 mg, 0.21 mmol) in 60 ml of THF was combined with PMe_3 (1 ml, 10.0 mmol) and stirred for 5 h. The solution was evaporated to dryness. – NMR data for both diastereomers: ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.0–1.15 (m, 9H, PCH_3), 1.25–3.30 (m, 5H, CH_2, CH), 6.40–7.70 (m, 28H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$): δ = 34.2 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 38 Hz], 38.7 [d, PPh_3, $^2J(^{31}P^{31}P)$ = 38 Hz], −2.6 [d, PMe_3, $^2J(^{31}P^{31}P)$ = 38.5 Hz], −4.2 [d, PMe_3, $^2J(^{31}P^{31}P)$ = 38.5 Hz]. – FD MS (^{102}Ru, THF): *m/z*: 838 [Ru(PPh$_3$)(PMe$_3$)('PhCH$_2$S$_4$')]$^+$.

[Ru(DIOP)('MeS$_4$')] (**19**): A solution of 671 mg (0.6 mmol) of **9** · 2 CH_2Cl_2 and 300 mg (0.6 mmol) of (+)-(*S,S*)-DIOP in THF (30 ml) was stirred at reflux for 5 h. The solvent was evaporated in vacuo. After determination of the diastereomeric ratio the raw product was purified by column chromatography (diameter: 3 cm, length: 40 cm, Al_2O_3 N Act. I, hexane/THF 5/3). The solvent was evaporated from the filtrate, and the residue was dried in vacuo (24 h). Recrystallization from THF (+20°C → −78°C) yielded orange microcrystals of [Ru(DIOP)('MeS$_4$')]. Yield: 200 mg (45%). – $C_{46}H_{46}O_2P_2RuS_4$ (922.08): calcd. C 59.91, H 5.03, S 13.91; found C 59.65, H 5.39, S 13.77. – NMR data for both diastereomers (raw product): ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 1.13 (d, 3H, CH_3), 1.21 (d, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.95–5.15 (m, 18H, CH_2, CH), 6.45–7.95 (m, 56H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, CD_2Cl_2): δ = 14.75, 17.70 (d, PPh_2R), 25.2, 26.70 (d, PPh_2R).

Separation of (S,d)-(S,S)-[Ru(DIOP)('MeS$_4$')] and (R,l)-(S,S)-[Ru(DIOP)('MeS$_4$')]: A solution of 135 mg (0.15 mmol) of diastereomeric [Ru(DIOP)('MeS$_4$')] in 2 ml of CH_3CN was injected into the HPLC column and eluted with acetonitrile/H_2O (5:1).

Diastereomer I (Retention time: 27.58 min): ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 1.17 (d, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.96 (m, 1H, CH_2), 2.46 (m, 1H, CH_2), 2.52–2.78 (m, 3H, CH), 3.17 (m, 1H, CH_2), 3.58 (m, 1H, CH_2), 3.88 (m, 1H, CH_2), 4.04 (m, 1H, CH_2), 6.65–7.90 (m, 28H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, CD_2Cl_2): δ = 25.05 [d, PPh_2R, $^2J(^{31}P^{31}P)$ = 38.9 Hz], 26.58 [d, PPh_2R, $^2J(^{31}P^{31}P)$ = 38.9 Hz].

Diastereomer II (Retention time: 31.40 min): ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 1.10 (d, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.88 (m, 1H, CH_2), 2.33 (m, 1H, CH_2), 2.55 (m, 1H, CH), 2.69 (m, 1H, CH_2), 2.88 (m, 1H, CH_2), 2.96–3.14 (m, 2H, CH_2), 4.28 (m, 1H, CH), 5.08 (m, 1H, CH), 6.36–7.66 (m, 28H, C_6H_5, C_6H_4). – ^{31}P{^{1}H} NMR (109.4 MHz, CD_2Cl_2): δ = 14.64 [d, PPh_2R, $^2J(^{31}P^{31}P)$ = 43.8 Hz], 17.68 (d, PPh_2R, $^2J(^{31}P^{31}P)$ = 43.8 Hz].

*X-ray Structure Determination of [Ru(PPh$_3$)$_3$('MeS$_4$')] · 2 CH_2Cl_2 (**9** · 2 CH_2Cl_2), [Mo(O)$_2$('MeS$_4$')] (**12**), and [Ru(PPh$_3$)$_2$-('MeS$_4$')]* (**13**): Single crystals of **9** · 2 CH_2Cl_2 and **13** were obtained from saturated CH_2Cl_2 and $CHCl_3$ solutions which were kept at room temperature in Schlenk tubes plugged with a rubber stopper in order to allow slow evaporation of the solvent by diffusion. Single crystals of **12** were grown from a saturated THF solution which was layered with Et_2O at room temperature. – Suit-

Table 6. Selected crystallographic data for $[Ru(PPh_3)_2('MeS_4')] \cdot 2\ CH_2Cl_2$ (**9** · 2 CH_2Cl_2), $[Mo(O)_2('MeS_4')]$ (**12**), and $[Ru(PPh_3)(CO)('MeS_4')]$ (**13**)

compound	**9** • 2 CH_2Cl_2	**12**	**13**
Formula	$C_{53}H_{48}Cl_4P_2RuS_4$	$C_{15}H_{14}MoO_2S_4$	$C_{34}H_{29}OPRuS_4$
M_r [g/mol]	1118.1	450.4	713.9
Habit	light brown prisms	orange coloured blocks	yellow blocks
Crystal size [nm^3]	0.4 x 0.4 x 0.4	0.4 x 0.3 x 0.3	0.5 x 0.4 x 0.4
F(000)	2272	904	1456
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a[Å]	20.824(4)	7.654(2)	9.290(3)
b[Å]	11.528(7)	30.180(15)	20.631(6)
c[Å]	22.290(5)	7.654(2)	16.252(4)
β[°]	113.39(2)	106.69(2)	96.94(2)
Cell volume [$Å^3$]	4910(3)	1693(1)	3092(1)
Z	4	4	4
$D_{calcd.}$ [g/cm^3]	1.51	1.77	1.53
μ [cm^{-1}]	8.1	12.7	8.6
Temperature [K]	200	200	200
Radiation [pm]	$Mo_{K\alpha}$ (71.073)	$Mo_{K\alpha}$ (71.073)	$Mo_{K\alpha}$ (71.073)
Scan technique	ω-scan	ω-scan	ω-scan
2Θ - range [°]	3-54	3-54	3-54
Scan speed [°/min]	3-29 °/min	3-29 °/min	3-29 °/min
Measured reflections	12193	7948	6057
Independent reflections	10795	3724	4878
Observed reflections	4010	2002	3530
Absorption correction	none	none	none
Program [23]	SHELXTL-PLUS	SHELXTL-PLUS	SHELXTL-PLUS
Weighting scheme	$1/\sigma^2$	$1/\sigma^2$	$1/\sigma^2$
σ-Criterion	$F > 4\ \sigma(F)$	$F > 4\ \sigma(F)$	$F > 4\ \sigma(F)$
Refined parameters	577	199	370
R / R_W [%]	6.2 / 5.1	6.0 / 5.3	2.8 / 2.6

able single crystals were sealed in glass capillaries, and mounted on the diffractometer (Siemens P4). Structures were solved by direct methods (SHELXTL-PLUS)[23]. Non-hydrogen atoms were refined anisotropically, H atoms were taken from difference Fourier syntheses and fixed on these positions with common isotropic temperature factors. Selected crystallographic data are listed in Table 6[24].

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[23] *SHELXTL-PLUS for Siemens Crystallographic Research Systems*, Release 4 21/V, Copyright **1990** by Siemens Analytical X-Ray Instruments Inc., Madison, WI.

[24] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401489 ($[Ru(PPh_3)_2('MeS_4')] \cdot 2\ CH_2Cl_2$), CSD-401488 ($[Mo(O)_2('MeS_4')]$), CSD-401480 ($[Ru(PPh_3)(CO)('MeS_4')]$), the names of the authors and the journal citation. [95015]