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Diastereomeric metallatetrahedron complexes of the type $Re_2(MPPh_3)(M'PPh_3)(\mu\text{-}PCy_2)(CO)_7(-)$-thiocamphanate ($M = Ag, Au, M' = Cu, Ag, Au$): synthesis, structure and CD data

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Four pairs of diastereomeric metallatetrahedron complexes of the type $Re_2(MPPh_3)(M'PPh_3)$ $(\mu\text{-}PCy_2)(CO)_7(-)$-thiocamphanate have been synthesized, with identical ($M = M' = Au$ (**5a**, **5b**) and Ag (**6a**, **6b**)) and with mixed coinage metals ($M = Au$, $M' = Ag$ (**8a**, **8b**) and Cu (**9a**, **9b**)). After separation, the absolute configuration was determined by single crystal X-ray crystallography for **6a**, **8a** and **9a**. In agreement with solution (^{31}P and ^{1}H NMR) spectral data, the thiocamphanate acts as a μ-S bridging bidentate ligand along the Re-coinage metal edge; in the mixed coinage metal complexes coordination involves the lower homologue of the coinage metals. Signs of the long wavelength absorption bands in the CD spectra were found to correlate with the counter (*A*) or clockwise (*C*) configuration of the chiral transition metal core.

Introduction

We have described recently the synthesis of the functionalized metallatetrahedron complex $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7Cl$.[1] Formation of this cluster starts with the reaction between $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$ (**1**) and LiPh to give the salt $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}C(Ph)O)]$ (**2**). Treating **2** with $ClAuPPh_3$ yields the precursor $Li[Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}Cl)]$ (**3**)[1] which in a final so-called cluster-expansion reaction is combined with $ClMPPh_3$ (M = Ag, Cu) to give the racemic trimetallic tetrahedron complex $Re_2(AuPPh_3)(MPPh_3)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}Cl)$.[2] Separation of the racemate into enantiomers has not been achieved yet.

As described in this paper, a transformation of **3** by a ligand exchange with chiral (−)-potassium thiocamphanate to the diastereomeric intermediate $K[Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}(-)\text{-thiocamphanate})]$ (**K7**) opens a new preparative route to obtain separable diastereomeric metallatetrahedra with three different metal atoms in the framework. To date, neither a preparation of enantiomerically nor of diastereomerically pure metallatetrahedra with three different metals in the metal framework has been described. Present knowledge comprises only some examples of tetrahedral cluster complexes with a triangular metal arrangement capped by a phosphido, sulfido, selenido, alkylidyne or arsenido group (see references within ref. 3).

In a previous paper, we reported the synthesis of diastereomerically pure metallatetrahedron clusters of the type $Re_2(AgPR_3)_2(\mu\text{-}PCy_2)(CO)_7(ax\text{-}OC(O)R^1)$ (R = Ph, Et; $OC(O)R^1$ = (+)-, (−)-camphanate).[3] The CD spectra of these compounds were correlated with the absolute configuration of the metallatetrahedral framework (clockwise (*C*) and counterclockwise (*A*)), which was determined by single crystal X-ray analysis of the *C*-diastereomer of $Re_2(AgPPh_3)_2(\mu\text{-}PCy_2)(CO)_7$-(+)-camphanate and the *A*-diastereomer of $Re_2(AgPPh_3)_2(\mu\text{-}PCy_2)(CO)_7(-)$-camphanate.

In continuation of our earlier efforts, diastereomers of $Re_2(M'PPh_3)(M'PPh_3)(\mu\text{-}PCy_2)(CO)_7(-)$-thiocamphanate, with M, M′ = Au (**5a**, **5b**); M, M′ = Ag (**6a**, **6b**); M = Au, M′ = Ag (**8a**, **8b**); and M = Au, M′ = Cu (**9a**, **9b**), have been prepared and characterized spectroscopically. The absolute configuration of **6a**, **8a** and **9a** has been determined by single crystal X-ray analysis. The successful diastereomerically pure separation of such cluster complexes enables us to study factors—like different metal atoms in the framework and the type of chiral ligand—of influence on the CD effect. The CD-spectra of the new metallatetrahedron clusters have also been analysed to elucidate the correlation between the absolute configuration and chiroptical properties.

Results and discussion

Preparation of the compounds

Equimolar amounts of **1** and trimethyl nitrogen oxide (TMNO) in THF solution (Scheme 1) give $Re_2(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_7(ax\text{-}THF)$ and $Re_2(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_7(ax\text{-}N(CH_3)_3)$.[4] The mixture is quantitatively converted with an excess of (−)-potassium thiocamphanate at 60 °C to give the dirhenium salt $K[Re_2(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_7(ax\text{-}(-)\text{-thiocamphanate})]$ (**4**). The product shows two singlets in the ^{31}P NMR spectrum at 59.3 and 59.4 ppm corresponding to the two diastereomers which have been formed. These shifts are about 15 ppm upfield of the corresponding camphanate substituted derivatives.[3,5] The integrals do not indicate any diastereomeric excess. The subsequent reaction of **4** with two equivalents of $ClAuPPh_3$ or BF_4AgPPh_3, generates diastereomeric pairs of the metallatetrahedron complexes $Re_2(MPPh_3)_2(\mu\text{-}PCy_2)(CO)_7$-

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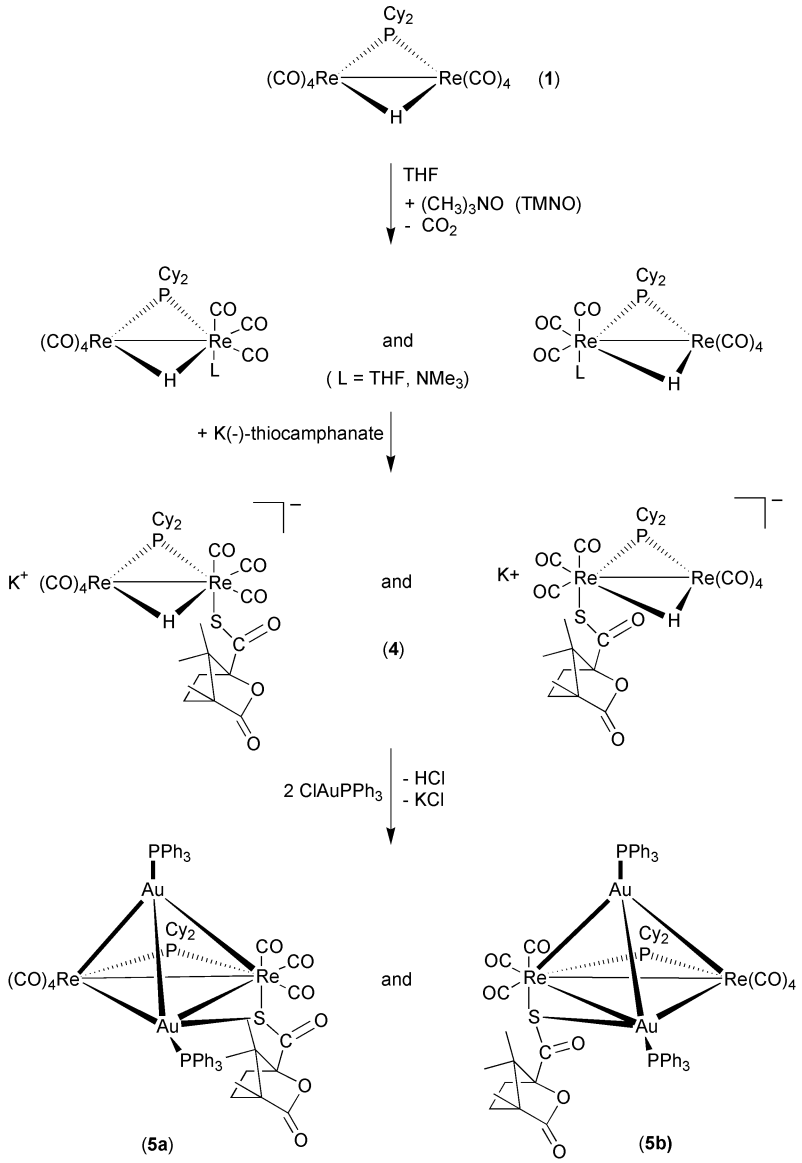


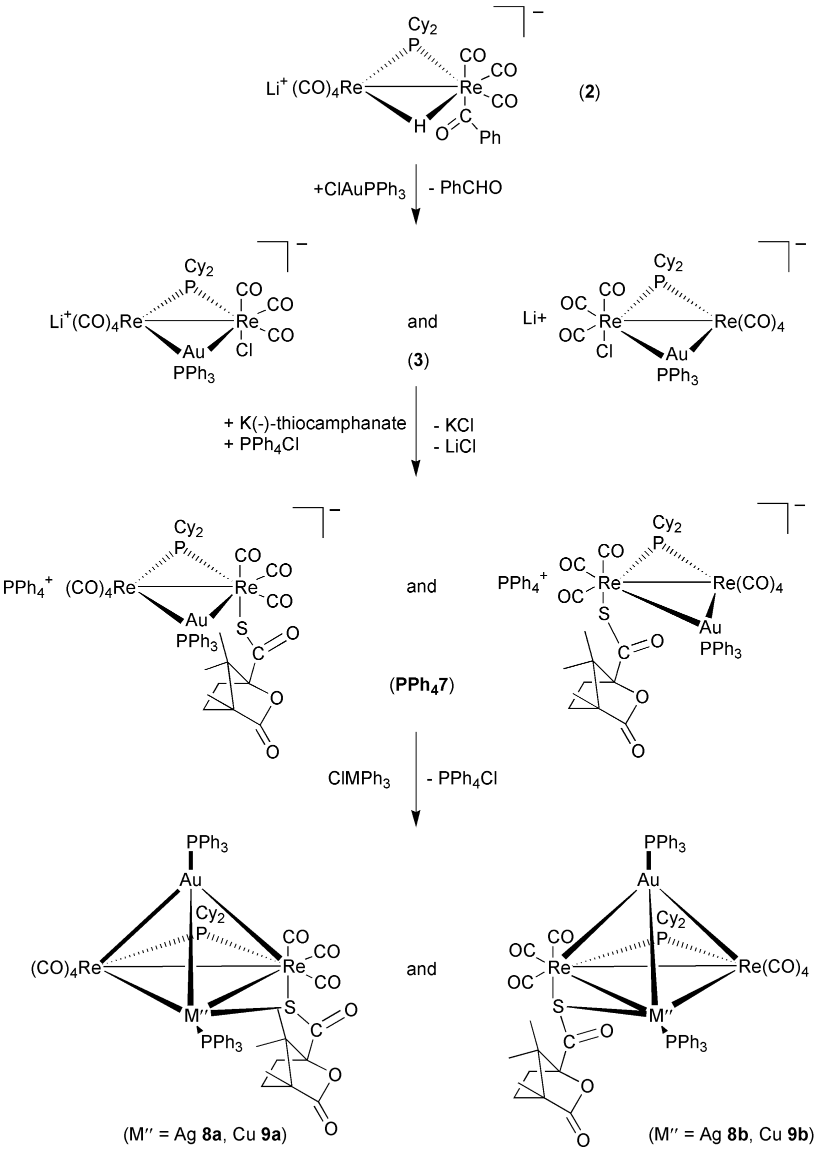
Scheme 1 Formation of the diastereomers **5a** and **5b**.

(−)-thiocamphanate, with M = Au: **5a**, **5b**, and M = Ag: **6a**, **6b**, in yields of 71 and 61%, respectively.

For complexes containing mixed coinage metals this synthetic route had to be changed. As shown in Scheme 2, the reaction starts with the dirhenium salt **2**, which is obtained from **1** and LiPh in THF. In the subsequent step **2** is reacted with $ClAuPPh_3$ to give the triangular precursor complex **3** which is converted through a nucleophilic ligand exchange reaction with an excess of (−)-potassium thiocamphanate to the diastereomeric $K[Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7$(ax-(−)-thiocamphanate)] (**K7**). Cation exchange against PPh_4^+ gives, in 75% yield, solid $PPh_4[Re_2(\mu\text{-}AuPPh_3)(\mu\text{-}PCy_2)(CO)_7$(ax-(−)-thiocamphanate)] (**PPh$_4$7**). In the ^{31}P NMR spectrum, each diastereomer shows three singlets: one (147.0/147.6 ppm) corresponding to the phosphido bridge, one (82.5/82.6) to the gold co-ordinated phosphorus and one (23.7) to the cationic PPh_4^+. The integrals of the phosphido bridge singlets indicate a diastereomeric excess (de) of 40% which is only observed after the ion exchange reaction with PPh_4Cl; there is no diastereomeric excess observed in the solution of **K7**. In the last step **PPh$_4$7** is reacted with $ClAgPPh_3$ or $ClCuPPh_3$ to give the diastereomeric pairs $Re_2(MPPh_3)(M'PPh_3)(\mu\text{-}PCy_2)(CO)_7$(−)-thiocamphanate, M = Au, M′ = Ag (**8a**, **8b**) and M = Au, M′ = Cu (**9a**, **9b**). Final separation was effected by PLC (preparative layer chromatography), which gave two yellow coloured main fractions containing one diastereomer each. Corresponding to decreasing R_f values the component of each head fraction is denoted with the additional label **a**, and that of each tail fraction with **b**.

The fractions were diastereomerically pure (100% de), which was confirmed by ^1H NMR (thiocamphanic methyl group signals) and ^{31}P NMR spectra. Further spectroscopic characterization of **5a**, **5b**, **6a**, **6b**, **8a**, **8b**, **9a** and **9b** was performed by IR, UV/VIS, CD and ^1H and ^{31}P NMR spectroscopy. The IR spectra agree with the theoretically expected number of carbonyl absorption bands (seven modes for the CO ligands, one for the lacton and the residual two (ν_{as} and ν_s) for the thiocarboxylate ligand[6,7]). In the ^{31}P NMR spectra the digold complexes **5a** and **5b** show, next to the singlet of the phosphido bridge, two double doublets in the range of 59 and 66 ppm, each in agreement with one $AuPPh_3$ fragment.[1,6] In the corresponding disilver compounds **6a** and **6b** there are, in addition to the singlet of the phosphido bridge, two double doublets at 20 ppm originating from one $AgPPh_3$ fragment. The coupling between the ^{31}P atom and the silver isotopes ^{107}Ag and ^{109}Ag ranging from 435 to 467 Hz is larger for $^1J_{P^{109}Ag}$ than for $^1J_{P^{107}Ag}$.[3,8] The signal for the second coin metal fragment degenerates into a double triplet.

The corresponding data of the mixed coinage metal clusters **8a**, **8b**, **9a** and **9b** are one signal of the phosphido bridge and one doublet in the region of 76 to 79 ppm which belongs to the $AuPPh_3$ fragment. In addition, the silver fragment $AgPPh_3$



Scheme 2 Formation of the diastereomers **8a**, **8b**, **9a** and **9b**.

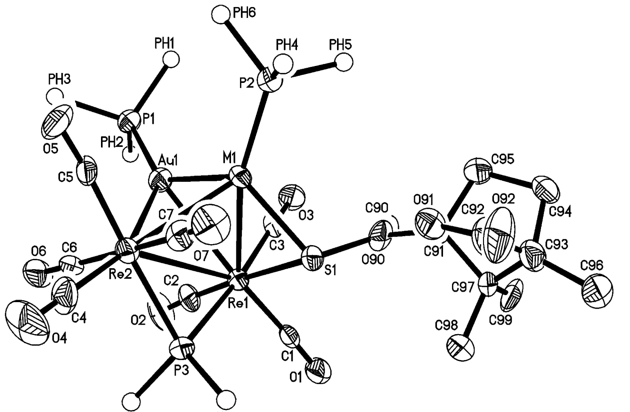


Fig. 1 Structure of $Re_2(AuPPh_3)(MPPh_3)(\mu\text{-}PCy_2)(CO)_7(-)$-thiocamphanate (M = Cu, Ag, Au) (PH = phenyl, CY = cyclohexyl groups).

of **8a** and **8b** is the origin of two doublets at 18 ppm, with coupling constants between ^{31}P atom and the silver isotopes ^{107}Ag and ^{109}Ag ranging from 459 to 532 Hz and being larger for $^1J_{P^{109}Ag}$ than for $^1J_{P^{107}Ag}$, as expected.[2,3,8] The ratios of $^1J_{P^{109}Ag}/^1J_{P^{107}Ag}$ for all of the complexes are in good agreement with the theoretical ratio of 1.15 of the two magnetic isotopes of silver (^{107}Ag, ^{109}Ag).[9] The copper containing metallatetrahedra **9a** and **9b** shows an additional singlet at *ca.* 9 ppm for the $CuPPh_3$ fragment. The spectroscopic data of the title compounds including the de values and selected IR and ^{31}P NMR data of the phosphorus bridge atoms and ^{1}H NMR data of the thiocamphanic methyl groups are summarized in Table 1.

With respect to the C_1 symmetry of the tetrahedral compounds two isomers regarding the constitution of the mixed coinage fragments $MPPh_3$ and $M'PPh_3$ in the tetrahedral metal core are possible. However, all prepared compounds are isolated isomerically pure. The lower homologues of the coinage metal fragments $M'PPh_3$ always occupy the position which is pseudo-*cis* to the thiocarboxylic ligand in order to establish for the sulfur donor atom a bridging bond pattern with this neighboring fragment (see Fig. 1).

Assignment of the absolute configuration

The symmetry of the axially substituted metallatetrahedra with an Re_2MM' core is C_1. They show planar chirality because a chiral plane runs through both Re atoms and the bridging phosphorus ligand. The definition of a clockwise (*C*) and an anticlockwise (*A*) configuration was made according to metallatetrahedra of the type $Re_2(AgPR_3)_2(\mu\text{-}PCy_2)(CO)_7$-(ax-$OC(O)R^1$) (R = Ph, Et; $OC(O)R^1$ = (+)-, (−)-camphanate).[3]

Molecular structures of 5a/5b, 6a, 8a and 9a

Diastereomeric pure single crystals of **6a**, **8a** and **9a** were

Table 1 Selected spectroscopic data of all title stereoisomers

	de value (%)	^{31}P NMR (δ, J/Hz) (s, μ-P)[a]	^{1}H NMR (δ, J/Hz) (s, CH$_3$, camphanate)[a]	IR ν_{as}(CO$_2$)[b]/cm^{-1}	CD λ ($\Delta\varepsilon$)/nm (L mol^{-1} cm^{-1})[c]	UV-VIS λ_{max} (ε)/nm (L mol^{-1} cm^{-1})[c]
5a	100	114.4	0.90, 0.91, 0.98	1608	207 (−7.0), 229 (−43.2), 247 (14.8), 269 (−10.7), 288 (−11.6), 321 (27.3), sh, 383 (−16.2), 459 (−5.0)	(c = 4.54 × 10^{-5} mol L^{-1}) 197/142.800
5b	100	114.7	0.44, 0.91, 0.95	1626	203 (18.3), 227 (21.2), 247 (−7.4), 267 (10.5), sh, 319 (−12.2), 339 (−8.0), 382 (9.3), 455 (2.7)	(c = 4.52 × 10^{-5} mol L^{-1}) 197/106.800
6a	100	106.8	0.89 (2 CH$_3$), 0.97	1616	205 (−14.5), 225 (−16.9), 236 (6.3), 251 (−41.0), 269 (28.4), 304 (29.1), 358 (−20.3), 421 (−8.2)	(c = 5.35 × 10^{-5} mol L^{-1}) 197/168.400
6b	100	106.6	0.48, 0.91, 0.95	1630	203 (32.6), 235 (−14.9), 252 (28.4), 271 (−17.3), 309 (−17.4), 358 (14.7), 430 (4.1)	(c = 5.23 × 10^{-5} mol L^{-1}) 197/167.300
8a	100	115.7	0.89 (2 CH$_3$), 0.96	1620	203 (−7.4), 215 (12.0), 228 (−19.9), 261 (−4.7), 280 (1.7), 287 (1.0), 319 (20.7), 373 (−14.5), 424 (−6.5)	(c = 5.64 × 10^{-5} mol L^{-1}) 196.5/119.500
8b	100	115.2	0.51, 0.92, 0.96	1631	201 (43.9), 217 (−8.5), 228 (12.6), 241 (−2.1), 259 (17.5), 279 (0), 288 (1.7), 318 (−20.0), 370 (16.6), 433 (6.5)	(c = 5.45 × 10^{-5} mol L^{-1}) 195.5/139.000
9a	100	118.5	0.89, 0.94, 0.98	1632	215 (13.9), 234 (−25.7), 254 (4.5), 272 (−17.1), 319 (25.3), 378 (−14.7), 446 (−5.2)	(c = 5.48 × 10^{-5} mol L^{-1}) 196/149.000
9b	100	118.3	0.25, 0.91, 0.97	1643	217 (−14.7), 235 (27.9), 254 (2.5), 272 (18.8), 318 (−22.3), 384 (18.2), 450 (6.6)	(c = 5.34 × 10^{-4} mol L^{-1}) 196/156.200

[a] In CDCl$_3$. [b] CaF$_2$ optics. [c] In C$_2$H$_5$OH. For the concentration, see the corresponding UV/VIS spectra.

obtained using the vapor pressure equalization method with CHCl$_3$ solution in the presence of *n*-pentane. Furthermore, single crystals of the diastereomeric pair of **5a** and **5b** were isolated from a toluene–*n*-pentane solution. The absolute configuration of **6a**, **8a** and **9a** must be assigned as *A* (see Fig. 1).

The basic features of this class of metallatetrahedra including the positions of carbonyl and phosphine ligands have already been described for Re$_2$Ag$_2$ cluster compounds with camphanate ligands[3] and need not be discussed in detail here. The camphanate with its carboxylate function acts as a bidentate ligand bridging one Re–Ag edge of the metal tetrahedron. The new structures reported are the first ones to exhibit μ-S bridging patterns of the (−)-thiocamphanate ligand along the Re–Au, –Ag or –Cu edges. Fig. 1 shows the structure of these isomolecular compounds. **5a** and **5b** contain the same (−)-thiocamphanate group and differ only in the ligand arrangement at the Re atoms as shown in Scheme 1. In both the Re$_2$AuAg (**8a**) and Re$_2$AuCu (**9a**) compounds the μ-S bridge involves the lower coinage metal homologue, *i.e.* Ag and Cu, respectively. Bond lengths (in Å) and angles (in °) for the Re1–S1, M1–S1, Re1–M1, S1–C90, and Re1–S1–M1 fragments are 2.500(3), 2.728(3), 2.9323(6), 1.750(11) and 68.08(6) for **5a/b** (average); 2.549(4), 2.650(4), 2.9295(12), 1.714(13) and 68.56(9) for **6a**; 2.535(6), 2.609(6), 2.8958(13), 1.70(2) and 69.72(14) for **8a**; and 2.533(4), 2.357(5), 2.804(2), 1.757(18) and 69.86(12) for **9a** (see Table 2). Other compounds with somewhat related Re(μ-S–R)M structural elements (but M = Cr, Mn, Rh; R = organic residue) show Re–S bond lengths from 2.384 to 2.508 Å, and S–C bond lengths between 1.789 and 1.849 Å.[10] Thiocamphanate moieties without M–S interactions have S–C bond lengths ranging from 1.72 to 1.78 Å.[11] The μ-S atom lies entirely in the heterometallic Re–M–Au(Ag) plane, the dihedral angles μ-SReM/MReAu(Ag) are 1.6 (**5a**), 1.3 (**6a**), 0.1 (**8a**) and 1.2° (**9a**).

Chiroptical properties

The UV/VIS spectra of the yellow and orange coloured title compounds with (−)-thiocamphanate as chiral auxiliary are not very informative. They show maximum absorptivity at the limit of the experimentally accessible wavelength range at 196/197 nm (Table 1), similar to the cluster complexes Re$_2$(AgPR$_3$)$_2$-(μ-PCy$_2$)(CO)$_7$(ax-OC(O)R^1) (R = Ph, Et; OC(O)R^1 = (+)-, (−)-camphanate) described earlier.[3] Also, the spectral features at longer wavelengths are insignificant in both types of cluster complexes. Even with derivative spectroscopic methods it was not possible to identify distinct bands including the lowest energy absorption, which is responsible for the colour of these clusters.

In contrast, all complexes show several distinct absorption bands in the CD spectra, which moreover adhere to a distinct pattern. As an example, consider the spectra of both diastereomers of the silver complexes **6** shown in Fig. 2. The almost mirror-image appearance of the two spectra, especially the close correspondence of the crossing points, attests not only to the successful separation of the diastereomers, but also to the pseudo-enantiomeric nature of their chromophores. Deviations from perfect mirror symmetry could be due to the chiral auxiliary, the perturbation of the chromophore by the chiral auxiliary or incomplete separation of the diastereomers.

The spectra are dominated, in the long wavelength region between 450 and 300 nm, by three broad bands with increasing intensities, of which the two with extrema around 440 and 360 nm have the same sign, which is negative in **6a**, positive in **6b**. There is then a cross-over to the most intense band at 310 nm, which is positive in **6a** and negative in **6b**. The appearance and the signs of these three bands correlate very strongly with the absolute configuration of the cluster framework. This fact is evident from a comparison of the CD-spectra with the remaining six complexes, shown in Figs. 3 and 4. In all compounds in

Table 2 Selected bond lengths (Å) and angles (°)

For **5a/b** (average values from both diastereomers):					
Re1–Re2	3.2537(6)	Re1–Au1	2.9323(6)	Re1–Au2	2.8966(6)
Re1–S1	2.500(3)	Re1–P3	2.431(3)	Re2–Au1	3.0181(7)
Re2–Au2	2.9085(7)	Re2–P3	2.466(3)	Au1–Au2	2.7118(7)
Au1–S1	2.728(3)	S1–C90	1.750(11)	C90–O90	1.193(14)
Re1–S1–Au1	68.08(6)	Re1–P3–Re2	83.28(10)	S1–C90–O90	126.2(9)
For **6a**:					
Re1–Re2	3.2707(8)	Re1–Ag1	2.9295(12)	Re1–Ag2	2.9067(14)
Re1–S1	2.549(4)	Re1–P3	2.432(4)	Re2–Ag1	3.0047(13)
Re2–Ag2	2.9371(15)	Re2–P3	2.477(4)	Ag1–Ag2	2.7284(15)
Ag1–S1	2.650(4)	S1–C90	1.714(13)	C90–O90	1.212(15)
Re1–S1–Ag1	68.56(9)	Re1–P3–Re2	83.54(13)	S1–C90–O90	125.6(11)
For **8a**:					
Re1–Re2	3.2767(12)	Re1–Au1	2.8958(13)	Re1–Ag1	2.9407(18)
Re1–S1	2.535(6)	Re1–P3	2.425(6)	Re2–Au1	2.8855(14)
Re2–Ag1	3.0105(18)	Re2–P3	2.463(6)	Au1–Ag1	2.7026(18)
Ag1–S1	2.609(6)	S1–C90	1.70(2)	C90–O90	1.26(2)
Re1–S1–Ag1	69.72(14)	Re1–P3–Re2	84.2(2)	S1–C90–O90	124.5(17)
For **9a**:					
Re1–Re2	3.253(1)	Re1–Au1	2.8873(11)	Re1–Cu1	2.804(2)
Re1–S1	2.533(4)	Re1–P3	2.427(5)	Re2–Au1	2.8842(11)
Re2–Cu1	2.918(2)	Re2–P3	2.485(5)	Au1–Cu1	2.584(2)
Cu1–S1	2.357(5)	S1–C90	1.757(18)	C90–O90	1.18(2)
Re1–S1–Cu1	69.86(12)	Re1–P3–Re2	82.95(15)	S1–C90–O90	124.1(15)

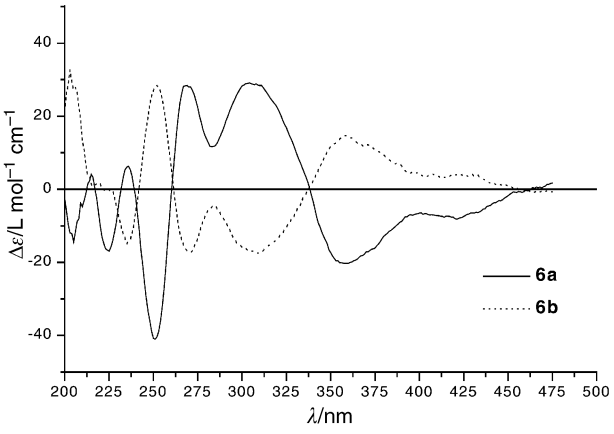


Fig. 2 CD spectra of **6a** and **6b**. For solvent and concentration, see Table 1.

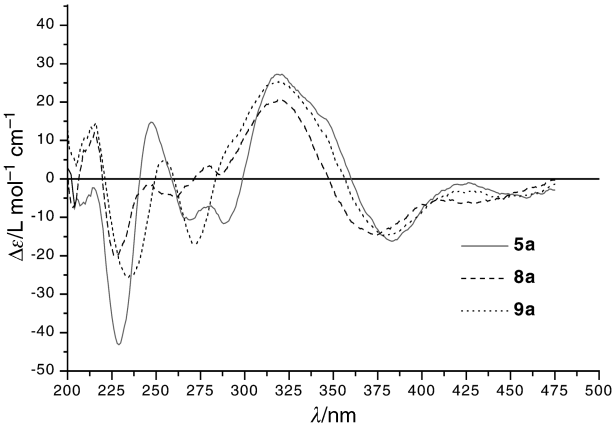


Fig. 3 CD spectra of *A*-configurated stereoisomers **5a**, **8a** and **9a**.

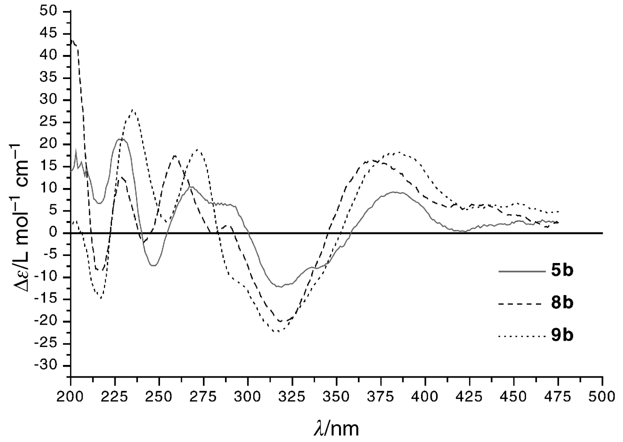


Fig. 4 CD spectra of *C*-configurated stereoisomers **5b**, **8b** and **9b**.

which the sequence of the relevant cluster atoms is counterclockwise or *A*, as in **6a**, the sign pattern is minus, minus, plus; in the ones in which the sequence is clockwise, or *C*, the pattern is plus, plus, minus. The nomenclature for assigning the absolute configuration as *A* or *C* has been described in detail elsewhere.[3] There are slight variations in the intensities and positions of the absorption maxima as a function of the metal substitution, but there is no exception to this correlation. This series of three bands is followed, toward higher energy, by several narrow bands with alternating signs in a more or less regular pattern. Thus, in **6a** there is a prominent plus, minus pair at 270 and 250 nm, which appears to correspond with a similar pair in the digold complex **5a**. This couple in **5a** is shifted in comparison with that of the disilver complex toward higher energy (hypsochromically). On the other hand, all bands of the long wavelength triple corresponding to **5** are shifted bathochromically relative to **6**. In the mixed coinage metal complexes **8** and **9**, this couple is not as prominent (like in **9**, where the extrema appear at 255 and 235 nm) or not developed at all (as in **8**). However, the correlation of these latter bands is on much less secure ground than the long wavelength triple.

The influence of the chiral auxiliary on the CD-spectra can be estimated from Fig. 5, in which the CD-spectrum of the thiocamphanate complex **6a** is shown together with the corresponding camphanate complex. While the λ_{max} values of the high-energy bands are essentially unchanged in the thio complex **6** relative to the oxo complex, their intensity is much higher. This enhancing effect of the thio group is even more

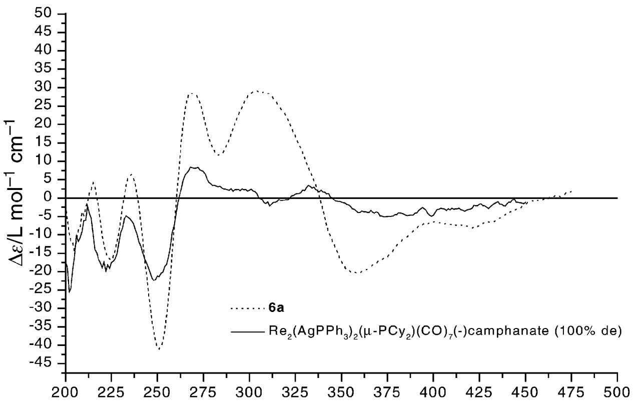


Fig. 5 CD spectra of **6a** and the corresponding camphanate derivative.[3]

evident in the long wavelength region: we have already pointed out the diagnostic value of the triple band in this region; in contrast, the oxo complex has very low absorption in this region, and only by comparison with other complexes with this ligand[3] does the sign pattern—which is the same as in the thio complexes—become evident. This observation must be a consequence of the different coordination pattern of the chiral auxiliaries (see molecular structures).

We conclude that the chiral discrimination exerted by the camphanate and the thiocamphanate groups and which affects the separation of the diastereomers in the PLC experiments does not include the chiroptical properties of the complexes—despite the fact that both chiral auxiliaries contain chromophores. To find an explanation for these observations, especially the nature of the different CD absorptions and how their sequence depends on the different coinage metal fragments, a computational treatment is warranted.

Experimental

General conditions

All reactions were performed with standard Schlenk techniques in solvents free of oxygen, which were dried according to literature methods, distilled and stored under an argon atmosphere. PLC (preparative layer chromatography) was carried out on glass plates (20 × 20 cm) coated with a mixture of gypsum and silica gel (Merck 60 PF_{254}, 1 mm thick).

Instrumentation

Infrared spectra were recorded on a Nicolet P510 FT IR spectrometer. Proton NMR and phosphorus-31 NMR spectra were recorded on a Bruker AMX 300 multinuclear pulsed Fourier transform spectrometer at 300 and 121.5 MHz, respectively, using internal tetramethylsilane and external 85% phosphoric acid, respectively, as a reference. Chemical shifts δ are given in ppm downfield from the reference. CD spectra were recorded on an Aviv 624 DS CD spectrometer and afterwards smoothed by Microcal Origin 5.0 with the Adjacent Averaging (5 points) function. UV/VIS spectra were measured using a Perkin-Elmer Lambda 5 UV spectrometer. For CD and UV/VIS measurements the same solution of the diastereomer was used (for concentration see Table 1). Elemental analyses were performed using a Perkin-Elmer 2400 CHN Elemental Analyzer.

Starting materials

The dirhenium compound $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$[12] and the coinage metal complexes $ClAuPPh_3$,[13] $ClAgPPh_3$[14] and $ClCuPPh_3$[15] were prepared according to literature methods. BF_4AgPPh_3[16] and $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}C(Ph)O)]$[1] were prepared *in-situ*. (−)-Thiocamphanate[17] was prepared according to the literature and deprotonated with K_2CO_3 in methanol. TMNO free of water was synthesized by sublimation of TMNO·2H_2O. TMNO·2H_2O, (−)-camphanic acid chloride and LiPh (1.6 M in THF) were purchased from Fluka, $Re_2(CO)_{10}$ from Acros and $AgBF_4$ from Strem Chemicals. All chemicals were laboratory grade and used as received.

Preparation of the diastereomers $Re_2(MPPh_3)_2(\mu\text{-}PCy_2)(CO)_7$-(−)-thiocamphanate (M = Au 5a, 5b, M = Ag 6a, 6b)

A solution of 150 mg (0.19 mmol) **1** (Re_2HP) in 10 mL THF was combined with 16 mg (0.21 mmol) TMNO at 0 °C to form a pale yellow mixture of $Re_2(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_7(ax\text{-}THF)$ and $Re_2(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_7(ax\text{-}N(CH_3)_3)$ which was characterized by the following spectroscopic data. IR [cm^{-1}] ν(CO) (THF): 2085 m, 2013 vs, 1992 s, 1946 m, 1915 s, 1898 s, 1878 s (sh). ^{31}P NMR (THF–$CDCl_3$): δ 77.3 (s, P, μ-P), 77.4 (s, P, μ-P). This solution was combined with 70 mg (0.29 mmol) (−)-potassium thiocamphanate and stirred at 60 °C for 12 h. After cooling to room temperature the diastereomeric intermediate $K[Re_2(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_7$(ax-(−)-thiocamphanate)] (**4**) was identified by the following spectroscopic data. IR [cm^{-1}] ν(CO, CO_2) (THF): 2079 s, 2002 vs, 1986 s (sh), 1928 s, 1901 s, 1878 vs, 1871 s (sh), 1782 s, 1595 m, 1327 w. ^{31}P NMR (THF–$CDCl_3$): δ 59.3 (s, P, μ-P), 59.4 (s, P, μ-P). These integrated singlets showed no diastereomeric excess. Afterwards, 188 mg (0.38 mmol) $ClAuPPh_3$ and 174 mg (0.38 mmol) BF_4AgPPh_3, respectively, dissolved in 10 mL CH_2Cl_2 were added dropwise into a solution of the intermediate **4**. After stirring the deep yellow solution for 5 min the solvent was removed under reduced pressure. The dark yellow residue was separated by PLC using *n*-hexane–dichloromethane (1 : 4) as eluent. Two yellow fractions were isolated. In order of decreasing R_f values the diastereomers **5a**, **6a** (head fractions) and **5b**, **6b** (tail fractions) were isolated (yield **5a** 105 (29), **5b** 150 (42), **6a** 83 (26) and **6b** 112 mg (35%)).

5a: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2056 m, 1994 vs, 1971 s (sh), 1961 vs, 1932 vs, 1886 m, 1774 m, 1608 w, 1331 vw. ^{31}P NMR ($CDCl_3$): δ 59.7 (dd, 1P, $AuPPh_3$, $^{3}J_{PP}$ = 3.0 Hz, $^{3}J_{PP}$ = 12.2 Hz), 66.4 (dd, $^{3}J_{PP}$ = 4.5 Hz, $^{3}J_{PP}$ = 12.1 Hz), 114.4 (s, 1P, μ-P). ^{1}H NMR ($CDCl_3$): δ 0.90 (s, 3H, Me), 0.91 (s, 3H, Me), 0.98 (s, 3H, Me), 1.1–2.4 (m, 26H, thiocamphanate, Cy), 7.2–7.65 (m, 30H, Ph).

5b: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2054 m, 1996 vs, 1971 s (sh), 1959 vs, 1934 vs, 1886 m, 1776 m, 1626 w, 1331 vw. ^{31}P NMR ($CDCl_3$): δ 59.6 (d, 1P, $AuPPh_3$, $^{3}J_{PP}$ = 11.2 Hz), 65.7 (d, 1P, $AuPPh_3$, $^{3}J_{PP}$ = 11.6 Hz), 114.7 (s, 1P, μ-P). ^{1}H NMR ($CDCl_3$): δ 0.44 (s, 3H, Me), 0.91 (s, 3H, Me), 0.95 (s, 3H, Me), 1.0–2.4 (m, 26H, thiocamphanate, Cy), 7.2–7.6 (m, 30H, Ph).

Anal. calc. for $C_{65}H_{65}Au_2O_{10}P_3Re_2S$ (1897.5 g mol^{-1}): C, 41.14; H, 3.45. Found: **5a** C, 41.84; H, 3.24. **5b** C, 41.30; H, 3.22%.

6a: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2046 s, 1988 vs, 1963 s (sh), 1950 vs, 1927 s, 1909 s (sh), 1876 m, 1776 m, 1616 w, 1331 vw. ^{31}P NMR ($CDCl_3$): δ 20.2 (2dd, $^{1}J_{P^{107}Ag}$ = 440 Hz, $^{1}J_{P^{109}Ag}$ = 467 Hz, $^{2}J_{P^{107/109}Ag}$ = 32 Hz, 1P, $AgPPh_3$), 22.1 (2 dt, 1P, $AgPPh_3$, $^{1}J_{P^{107}Ag}$ = 383 Hz, $^{1}J_{P^{109}Ag}$ = 436 Hz, $^{2}J_{P^{107/109}Ag}$ = 28 Hz), 106.8 (s, 1P, μ-P). ^{1}H NMR ($CDCl_3$): δ 0.89 (s, 6H, 2 Me), 0.97 (s, 3H, Me), 1.0–2.3 (m, 26H, thiocamphanate, Cy), 7.2–7.4 (m, 30H, Ph).

6b: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2046 s, 1990 vs, 1963 s (sh), 1948 vs, 1928 s, 1909 s (sh), 1878 m, 1776 m, 1630 w, 1331 vw. ^{31}P NMR ($CDCl_3$): δ 19.8 (2dd, $^{1}J_{P^{107}Ag}$ = 435 Hz, $^{1}J_{P^{109}Ag}$ = 465 Hz, $^{2}J_{P^{107/109}Ag}$ = 31 Hz, 1P, $AgPPh_3$), 21.7 (2 dt, 1P, $AgPPh_3$, $^{1}J_{P^{107}Ag}$ = 387 Hz, $^{1}J_{P^{109}Ag}$ = 440 Hz, $^{2}J_{P^{107/109}Ag}$ = 24 Hz), 106.6 (s, 1P, μ-P). ^{1}H NMR ($CDCl_3$): δ 0.48 (s, 3H, Me), 0.91 (s, 3H, Me), 0.95 (s, 3H, Me), 0.8–2.4 (m, 26H, thiocamphanate, Cy), 7.2–7.4 (m, 30H, Ph).

Anal. calc. for $C_{65}H_{65}Ag_2O_{10}P_3Re_2S$ (1719.3 g mol^{-1}): C, 45.40; H, 3.81. Found: **6a** C, 46.55; H, 3.97. **6b** C, 46.4; H, 3.59%.

Table 3 Crystallographic data for **5a/b**, **6a**, **8a** and **9a**

Structure	**5a/b**	**6a**	**8a**	**9a**
Formula	$C_{65}H_{65}Au_2O_{10}P_3Re_2S$	$C_{65}H_{65}Ag_2O_{10}P_3Re_2S\cdot Solv$ (see text)	$C_{65}H_{65}AgAuO_{10}P_3Re_2S\cdot 0.5\ CHCl_3$ (see text)	$C_{65}H_{65}AuCuO_{10}P_3Re_2S\cdot CHCl_3$ (see text)
M_r	1897.5	1719.3	1868.1	1883.4
Crystal size/mm	0.04 × 0.03 × 0.01	0.38 × 0.15 × 0.10	0.10 × 0.08 × 0.03	0.44 × 0.40 × 0.06
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Cell constants/Å,°				
a/°	15.459(1)	13.288(1)	13.1117(2)	13.227(2)
b/°	21.969(1)	18.737(3)	18.5856(3)	18.697(3)
c/°	18.712(1)	30.220(8)	29.2893(7)	29.532(5)
β	91.15(1)			
V/Å^3	6353.7(6)	7524(2)	7137.5(2)	7303(2)
Z	4	4	4	4
D_x/g cm^{-3}	1.984	1.518	1.738	1.713
T/K	203(2)	203(2)	203(2)	203(2)
2θ range/°	3.2–66.4	4.4–55.0	3.4–45.4	4.5–55.0
Intensities measured	67050	18811	9436	10878
independent (R_{int})	40482 (0.075)	16896 (0.052)	9436	10579 (0.036)
Structure solution	Direct and conventional Fourier methods			
Refinement	Full-matrix, least-squares, based on F^2, all non-hydrogen atoms anisotropic, H-atoms at calculated positions with riding model.			
$R1(I > 2\sigma(I))$; $wR2$(all)	0.061/0.153	0.068/0151	0.071/0.148	0.064/0.151
min/max ΔF (e Å^{-3})	−1.14/1.21	−0.91/0.87	−0.77/0.92	−1.38/0.97
S = Goof	1.024	0.881	0.954	0.927

Preparation of the diastereomeric precursor complex $PPh_4[Re_2(\mu\text{-}PCy_2)(\mu\text{-}AuPPh_3)(CO)_7$(ax-(−)-thiocamphanate)] ($PPh_4$7)

A solution of **2** (0.19 mmol) prepared from 150 mg (0.19 mmol) **1** and 116 µL (0.19 mmol) LiPh in 8 mL THF was combined dropwise with 94 mg (0.19 mmol) $ClAuPPh_3$ dissolved in 10 mL THF under vigorous stirring to generate $Li[Re_2(\mu\text{-}PCy_2)(\mu\text{-}AuPPh_3)(CO)_7$(ax-Cl)]. After stirring for 30 min 70 mg (0.29 mmol) (−)-potassium thiocamphanate was added and this solution was stirred for a further 3 h to form the diastereomeric cluster complex $K[Re_2(\mu\text{-}PCy_2)(\mu\text{-}AuPPh_3)(CO)_7$(ax-(−)-thiocamphanate)] (**K7**). The intermediate **K7** was identified by the subsequent spectroscopic data. IR [cm^{-1}], ν(CO, COS) (THF): 2046 m, 1973 m, 1954 s, 1938 vs, 1901 vs, 1874 vs, 1861 vs, 1776 s, 1585/1525 w (belonging to each diastereomer). ^{31}P NMR (THF–$CDCl_3$): δ 83.3(s, 1 P, $AuPPh_3$), 149.0 (s, P, µ-P), 151.5 (s, P, µ-P). 71 mg (0.19 mmol) PPh_4Cl was added to **K7** and the solvent was removed under reduced pressure. The residue was dissolved in methanol and the salt **PPh$_4$7** was precipitated by adding deoxygenated water dropwise, sucked off, washed three times each with water and *n*-hexane and dried *in vacuo* (40% de, yield: 253 mg, 75%).

PPh$_4$7: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2044 m, 1971 vs, 1954 vs, 1932 s (sh), 1894 s, 1854 s (sh), 1766 m, 1598/1587 w (belonging to each diastereomer), 1331 vw. ^{31}P NMR ($CDCl_3$): δ 23.7 (s, 1P, PPh_4), 82.6 (s, 1 P, $AuPPh_3$, major excess diastereomer), 82.5 (s, 1 P, $AuPPh_3$, minor excess diastereomer), 147.0 (s, 1P, µ-P, $^3J_{PP}$ = 12.4 Hz, major), 147.6 (s, 1P, µ-P, $^3J_{PP}$ = 12.5 Hz, minor), ^{1}H NMR ($CDCl_3$): δ 0.65 (s, 3H, Me, minor), 0.77 (s, 3H, Me, major), 0.82 (s, 3H, Me, minor), 0.93 (s, 3H, Me, minor), 0.96 (s, 6H, 2 Me, major), 1.0–2.6 (m, 26H, thiocamphanate, Cy), 7.2–7.9 (m, 45H, Ph).

Preparation of the diastereomers $Re_2(MPPh_3)(M'PPh_3)(\mu\text{-}PCy_2)(CO)_7$(−)-thiocamphanate (M = Au, M′ = Ag **8a**, **8b**, M′ = Cu **9a**, **9b**)

A solution of 150 mg (0.084 mmol) **PPh$_4$7** in 10 mL CH_2Cl_2 was combined with 34 mg (0.084 mmol) $ClAgPPh_3$ and 30.3 mg (0.084 mmol) $ClCuPPh_3$, respectively, and stirred for 15 min. The solvent was removed under reduced pressure. The yellow residue was separated into its diastereomers by PLC using CH_2Cl_2–*n*-hexane (3 : 1) as an eluent. In both experiments two yellow fractions were isolated. In order of decreasing R_f values the diastereomers **8a**, **9a** and **8b**, **9b** were isolated (yield **8a** 34 (22), **8b** 80 (53), **9a** 20 (13) and **9b** 55 mg (35%)).

8a: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2052 m, 1990 vs, 1969 s, 1954 vs, 1930 s, 1913 s (sh), 1886 m, 1776 m, 1620 w, 1330 vw. ^{31}P NMR ($CDCl_3$): δ 18.5 (2 d, 1P, $AgPPh_3$, $^1J_{P^{107}Ag}$ = 461 Hz, $^1J_{P^{109}Ag}$ = 532 Hz), 77.0 (d, 1P, $AuPPh_3$, $^2J_{P^{107/109}Ag}$ = 42.8 Hz), 115.7 (s, 1P, µ-P). ^{1}H NMR ($CDCl_3$): δ 0.89 (s, 6H, 2 Me), 0.96 (s, 3H, Me), 1.0–2.3 (m, 26H, thiocamphanate, Cy), 7.2–7.4 (m, 30H, Ph).

8b: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2050 m, 1992 vs, 1969 s, 1950 vs, 1932 s, 1919 s (sh), 1886 m, 1774 m, 1631 w, 1331 vw. ^{31}P NMR ($CDCl_3$): δ 18.2 (2 d, 1P, $AgPPh_3$, $^1J_{P^{107}Ag}$ = 459 Hz, $^1J_{P^{109}Ag}$ = 530 Hz), 76.4 (d, 1P, $AuPPh_3$, $^2J_{P^{107/109}Ag}$ = 39.1 Hz), 115.2 (s, 1P, µ-P). ^{1}H NMR ($CDCl_3$): δ 0.51 (s, 3H, Me), 0.92 (s, 3H, Me) 0.96 (s, 3H, Me), 1.0–2.4 (m, 26H, thiocamphanate, Cy), 7.2–7.4 (m, 30H, Ph).

Anal. calc. for $C_{65}H_{65}AgAuO_{10}P_3Re_2S$ (1808.4 g mol^{-1}): C, 43.17; H, 3.62. Found: **8a** C, 43.71; H, 3.42. **8b** C, 43.92; H, 3.46%.

9a: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2052 m, 1990 vs, 1973 s, 1948 s, 1934 s, 1913 s (sh), 1890 m, 1778 m, 1632 w, 1331 vw. ^{31}P NMR ($CDCl_3$): δ 9.1 (s, 1P, $CuPPh_3$), 78.6 (d, 1P, $AuPPh_3$, $^3J_{pp}$ = 6.7 Hz), 118.5 (d, 1P, µ-P, $^3J_{pp}$ = 5.7 Hz). ^{1}H NMR ($CDCl_3$): δ 0.89 (s, 3H, Me), 0.94 (s, 3H, Me), 0.98 (s, 3H, Me), 1.1–2.3 (m, 26H, thiocamphanate, Cy), 7.2–7.5 (m, 30H, Ph).

9b: IR [cm^{-1}], ν(CO, COS) (CH_2Cl_2): 2052 m, 1992 vs, 1973 s, 1950 s, 1936 s, 1915 s (sh), 1890 m, 1778 m, 1643 w, 1331 vw. ^{31}P NMR ($CDCl_3$): δ 9.6 (s, 1P, $CuPPh_3$), 78.6 (d, 1P, $AuPPh_3$, $^3J_{pp}$ = 6.3 Hz), 118.3 (d, 1P, µ-P, $^3J_{pp}$ = 6.0 Hz). ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 3H, Me), 0.91 (s, 3H, Me), 0.97 (s, 3H, Me), 1.2–2.4 (m, 26H, thiocamphanate, Cy), 7.2–7.5 (m, 30H, Ph).

Anal. calc. for $C_{65}H_{65}AuCuO_{10}P_3Re_2S$ (1764.1 g mol^{-1}): C, 44.25; H, 3.71. Found: **9a** C, 45.07; H, 3.88. **9b** C, 44.63; H, 3.65%.

Crystal structure determinations

Pertinent crystallographic data for **5a/b** **6a**, **8a** and **9a** are summarized in Table 3, selected geometric data are given in Table 2. Data for **5a/b** and **8a** were collected on a Nonius KappaCCD with Mo-Kα radiation at 203(2) K. Lorentz polarization correction, absorption correction *via* ψ-scans. Data for **6a** and **9a** were collected on a Bruker AXS P4 diffractometer with

Mo-Kα radiation at 203(2) K. Lorentz polarization and absorption corrections (ψ-scans) were applied. The structures were solved by direct and conventional Fourier methods. Full-matrix least-squares refinement based on F^2, non-hydrogen atoms anisotropically; hydrogen atoms were placed at idealized positions and refined with a riding model.[18]

5a/b contains per asymmetric unit two independent molecules which represent a pair of diastereomers. In **6a** two different regions per asymmetric unit with severely disordered chloroform and *n*-pentane solvent molecules could not be successfully modelled, leaving various diffuse electron density peaks in the ΔF map. After running the SQUEEZE routine of the PLATON package[19] the structure could be smoothly refined. The atomic positions of **6a** were used as starting parameters for the refinement of the isotypic **8a**. One $CHCl_3$ solvent molecule with occupation factor 0.5 per asymmetric unit. Additional regions of diffuse electron density (*n*-pentane solvent) were treated with SQUEEZE. **9a** contains one $CHCl_3$ solvent molecule per asymmetric unit, remaining regions of diffuse electron density were treated with SQUEEZE again. All structure refinements (Flack parameters) are consistent with the known (−)-configuration of the thiocamphanate ligand.

CCDC reference numbers 165357–165360.

See http://www.rsc.org/suppdata/dt/b1/b104999m/ for crystallographic data in CIF or other electronic format.

References

1 H. J. Haupt, M. Schwefer, H. Egold and U. Flörke, *Inorg. Chem.*, 1997, **36**, 184.

2 M. Schwefer, PhD Thesis, University of Paderborn, Germany, 1997.

3 H. J. Haupt, O. Seewald, U. Flörke, V. Buß and T. Weyhermüller, *J. Chem. Soc., Dalton Trans.*, 2000, 2837.

4 U. Koelle, *J. Organomet. Chem.*, 1977, **133**, 53; U. Koelle, *J. Organomet. Chem.*, 1978, **155**, 53; T. S. A. Hor, H. S. O. Chan, Y. P. Leong and M. M. Tan, *J. Organomet. Chem.*, 1989, **373**, 221; T. S. A. Hor, H. S. O. Chan and Y. P. Leong, *Thermochim. Acta*, 1989, **145**, 179; T. S. A. Hor and S. M. Chee, *J. Organomet. Chem.*, 1987, **331**, 23.

5 H. Egold, PhD Thesis, University of Paderborn, Germany, 1997.

6 H. J. Haupt, H. Egold, R. Siefert and U. Flörke, *Z. Anorg. Allg. Chem.*, 1997, **624**, 1863.

7 G. La Monica, S. Cenini, E. Forni, M. Manassero and V. G. Albano, *J. Organomet. Chem.*, 1976, **112**, 297; K. Raab and W. Beck, *Chem. Ber.*, 1985, **118**, 3830.

8 M. J. Freeman, M. Green, A. G. Orpen, I. D. Salter and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 1332; I. D. Salter and F. G. A. Stone, *J. Organomet. Chem.*, 1984, **260**, C71.

9 L. J. Baker, G. A. Bowmaker, D. Camp, Effendy, P. C. Healy, H. Schmidbaur, O. Steigelmann and A. White, *Inorg. Chem.*, 1992, **31**, 3656.

10 D. M. Antonelli and M. Cowie, *Inorg. Chem.*, 1990, **29**, 3339; I. L. Eremenko, H. Berke, B. I. Kolobkov and V. M. Novotortsev, *Organometallics*, 1994, **13**, 244; J.-J. Peng, S.-M. Peng, G.-H. Lee and Y. Chi, *Organometallics*, 1995, **14**, 626; I. L. Eremenko, S. Nefedov, H. Berke, B. I. Kolobkov and V. M. Novotortsev, *Organometallics*, 1995, **14**, 1132.

11 R. B. Woodward, *J. Am. Chem. Soc.*, 1981, **103**, 3210; M. Kiefer, R. Vogel and G. Helmchen, *Tetrahedron*, 1994, **50**, 7109.

12 H. J. Haupt, A. Merla and U. Flörke, *Z. Anorg. Allg. Chem.*, 1994, **620**, 999.

13 G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, ed. F. Enke, Verlag, Stuttgart 1981, vol. 3, p. 2091.

14 F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, 1965, **95**, 201.

15 F. Glocking and K. A. Hooton, *J. Chem. Soc.*, 1962, 2658.

16 A. Albinati, H. Lehner, L. M. Venanzi and M. Wolfer, *Inorg. Chem.*, 1987, **26**, 3933.

17 T. Toru, T. Kanefusa, E. Maekawa, Y. Ueno, K. Kondo and S. Eguchi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2675.

18 G. M. Sheldrick, SHELX 97, A Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1998.

19 A. L. Spek, PLATON, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.