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Diastereomeric metallatetrahedron complexes of the type $Re_2(AgPR_3)_2(\mu\text{-}PCy_2)(CO)_7Z$ (R = Et and Ph; Z = (−)- and (+)-camphanate): synthesis, structure and CD data

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Diastereomeric pairs of metallatetrahedron clusters of the type $Re_2(AgPR_3)_2(\mu\text{-}PCy_2)(CO)_7$(ax-(+)/(−)-camph) ((+)-auxiliary, R = Ph **4a**, **4b** or Et: **6a**, **6b** and (−)-auxiliary, R = Ph **5a**, **5b** or R = Et: **7a**, **7b**) were prepared from the η^1-carboxylate substituted dirhenium salt $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}\eta^1\text{-}(+)/(-)\text{-camph})]$ (camph = camphanate) and less than stoichiometric amounts of $[Ag(PR_3)BF_4]$ (R = Ph or Et) in solution at room temperature. The diastereomers were separated using PLC and identified by means of IR, ^1H and ^{31}P NMR, UV/VIS and CD spectroscopy. Using single crystal X-ray analysis the molecular structure of **4a/4b** in material **I** and **4a/5a** in **II** have been determined to assign the absolute configuration of the clockwise (*C*) and anticlockwise (*A*) configurated tetrahedral Re_2Ag_2 framework in a ligand sphere of C_1 symmetry. These are the first structures which show a chelate like co-ordination of the carboxylic group of the camphanate ligand in a heterometallic cluster complex. Based on their CD spectra the absolute configuration of other chiral carboxylate substituted metallatetrahedra of the type $Re_2(MPR_3)_2(\mu\text{-}PCy_2)(CO)_7$(ax-OC(O)R) (M = Au or Ag) can be assigned.

Introduction

Small heterometallic cluster complexes containing a polyhedral metal–metal framework with symmetry of C_1, C_2 or D_3 are chiral. Until now numerous chiral clusters of transition metals have been synthesized. However, only a few of them have been studied chiroptically.[1–8] The first chiral cluster complex which was prepared enatiomerically pure, analysed by CD and ORD spectroscopy and whose absolute configuration was established by single crystal structure analysis was $FeCoMo(C_5H_5)S(CO)_8$.[2] Except for some examples of tetrahedral cluster complexes with triangular metal arrangement capped by a phosphido,[5,6,9–11] sulfido,[2,3,5,12,13] selenido,[14] alkylidyne[4,5,11,15] or arsenido[13,16] group, enantiomerically pure cluster compounds of metallatetrahedron type with a four transition metal framework are so far unknown. They remain especially a preparative challenge because of an inherent trend to undergo racemization or epimerization. For example, $Re_2(AuPCy_3)_2(\mu\text{-}PMen_2)(\mu\text{-}C\text{-}(n\text{-}Bu)O)(CO)_6$ (Men = (−)-menthyl) dissolved in $CDCl_3$ shows a diastereomeric excess (de) of 43% in equilibrium state at room temperature (^{31}P NMR: δ 126.6 and 134.7 (s, 1P, μ-P)). After chromatographic separation one of the diastereomers (95% de) epimerizes with first order kinetics with k_1, k_{-1} and activation parameters $\Delta H^\ddagger$ kJ mol^{-1} 84(2), 81(2), $\Delta S^\ddagger$/J K^{-1} mol^{-1} −53(5), −55(5) and $\Delta G^\ddagger$ kJ mol^{-1} 99(2), 98(3) *via* an experimentally supported inversion of the acyl bridge.[17]

In our continued efforts to synthesize metallatetrahedron clusters which are more stable against isomerization in solution, we previously described the stepwise synthesis of functionalized clusters $Re_2(AuPPh_3)_2(\mu\text{-}PCy_2)(CO)_7$(ax-X) (X = Cl, Br, I[18] or η^1-OC(R^1)O, R^1 = H, Me, CF_3, Ph or 3,4-$(MeO)_2C_6H_3$[19]). These cluster formations always start with a selective nucleophilic addition reaction of equimolar amounts of LiPh and $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$ **1** to give the salt $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(C(Ph)O)(CO)_7]$ **2**. For X = halide, **2** is treated with two equivalents of $AuX(PPh_3)$. For X = η^1-OC(R^1)O **2** is treated with an excess of R^1CO_2H to form $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}\eta^1\text{-}OC(O)R^1)]$ with subsequent aggregation of the dirhenium complex with two equivalents of $[Au(PPh_3)]BF_4$.[19] In all cases of metallatetrahedron clusters studied so far the Re_2Au_2 core is embedded in a ligand sphere of C_1 symmetry; however, separation of the racemic products into enantiomers is not possible yet. One way to get separable diastereomers of this cluster type is the co-ordination of a chiral monocarboxylic acid. (The choice of appropriate dicarboxylic monoesters having a chiral alcoholic group for a final reesterification reaction should also open a preparative access to enantiomerically pure metallatetrahedron complexes.)

In this paper, the synthesis of the metallatetrahedron clusters $Re_2(AgPR_3)_2(\mu\text{-}PCy_2)(CO)_7$(ax-OC($R^1$)O) (R = Ph or Et; OC(O)$R^1$ = (+), (−)-camphanate), camph is reported based on the preparative approach outlined above. The four pairs of diastereomers which are also interconnected by enantiomeric relationships were studied by CD spectroscopy. Their absolute metallatetrahedron configuration (see Fig. 1) was determined by a single crystal X-ray analysis of *rac*-$Re_2(AgPPh_3)_2(\mu\text{-}PCy_2)(CO)_7$(ax-camph). These compounds allow one to study the interaction between electron rich metallatetrahedra and distinct enantiomerically pure ligands and how this affects the chiroptical properties.

Results and discussion

Preparation of the compounds

Equimolar amounts of compound **1** and LiPh react to form **2** which is converted with an 1.8 molar excess of (+)- and (−)-camphanic acid, respectively, at 60 °C to the η^1-carboxylate

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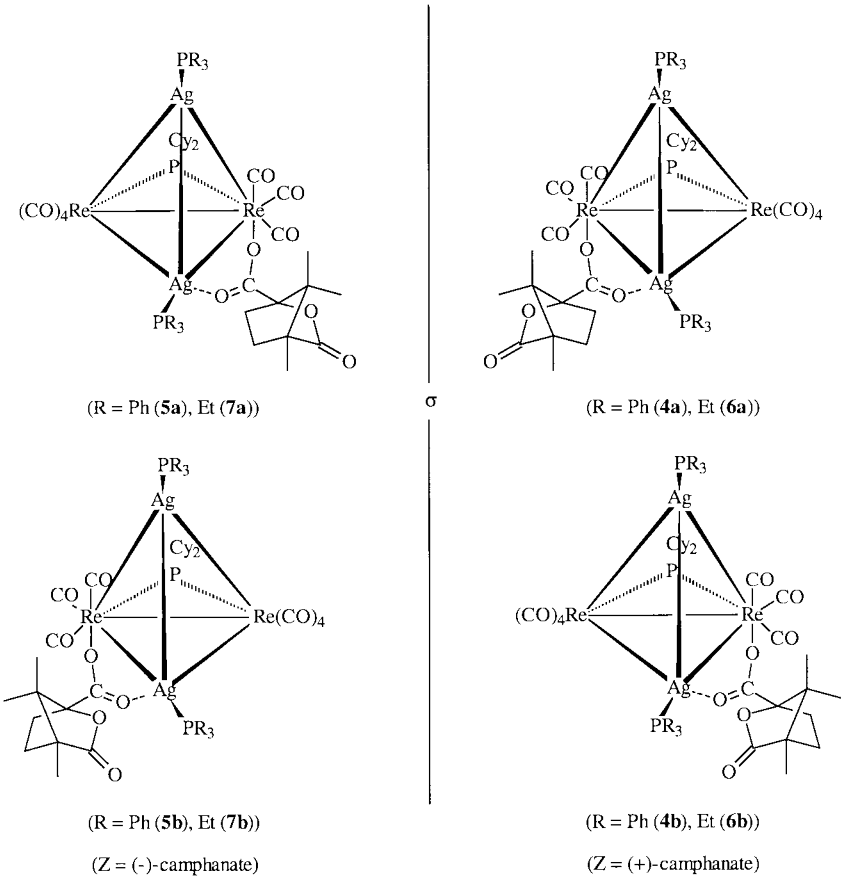


(R = Ph (5a), Et (7a))

(R = Ph (4a), Et (6a))

(R = Ph (5b), Et (7b))

(Z = (-)-camphanate)

(R = Ph (4b), Et (6b))

(Z = (+)-camphanate)

Fig. 1 All stereoisomers.

substituted dirhenium salt Li[$Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}\eta^1\text{-}(+),(-)\text{-camph})$] **3**. Each of the diastereomeric pairs present show singlets in the ^{31}P NMR spectra (THF, $CDCl_3$) at δ 74.2 and 73.2. The integrals of these signals in both cases indicate a de value of 17%. The subsequent reaction of the intermediate **3** with only 1.7 and 1.8 equivalents, respectively, of the silver complex [$Ag(PR_3)$]BF_4 (R = Ph or Et) at room temperature generates within 5 min yellow diastereomeric pairs of the type $Re_2(AgPR_3)_2(\mu\text{-}PCy_2)(CO)_7(ax\text{-}(+)/(-)\text{-camph})$ ((+)-auxiliary, R = Ph **4a**, **4b** or Et **6a**, **6b** and (−)-auxiliary, R = Ph **5a**, **5b** or Et **7a**, **7b**) in yields of 37 to 59%. The less than stoichiometric amount of the silver complex is necessary in order to avoid a decomposition of the final clusters which is triggered and accelerated by unseparable traces of $AgBF_4$ in the agent [$Ag(PR_3)$]BF_4 from the preparation process.[20,21] The reaction pathway is illustrated in Scheme 1. All final PLC procedures deliver two yellow main fractions each containing one diastereomer. In accordance with the decreasing R_f values the component of each head fraction is denoted with the additional label **a** and that one of each tail fraction with **b**. The identification of **4a**, **4b**–**7a**, **7b** was done by means of IR (ν CO, CO_2), UV/VIS, CD and ^1H and ^{31}P NMR measurements. The theoretically expected number of $\nu(CO, CO_2)$ absorption bands was confirmed with seven modes for the CO ligands, one for the lactone and the residual two (ν_{asym} and ν_{sym}) represent the co-ordinated carboxylate group in the camphanate ligand.[19,22] All the compounds exhibit in the ^{31}P NMR spectra in addition to the singlet of the phosphido bridge two double doublets in the range of δ 15 to 20 of one $AgPR_3$ fragment. The related coupling between the ^{31}P atom and the silver isotopes ^{107}Ag and ^{109}Ag ranging from 418 to 477 Hz is bigger for $^1J_{P^{109}Ag}$ than for $^1J_{P^{107}Ag}$.[23] The signal for the second coinage metal fragment mutates to a broad one or double triplet. The de values of **4a**, **4b**–**7a**, **7b**, selected IR and ^{31}P NMR data of the phosphorus bridge atoms and δ ^1H NMR data of the camphanic methyl groups are presented in Table 1. The stereoisomeric relationships between the synthesized cluster complexes are illustrated in Fig. 1. The cluster pairs **4a**/**4b**, **5a**/**5b**, **6a**/**6b** and **7a**/**7b** (and **4a**/**5b**, **4b**/**5a**, **6a**/**7b**, **6b**/**7a**) are diastereomers, while the pairs **4a**/**5a** and **4b**/**5b** (R = Ph) as well as those of **6a**/**7a** and **6b**/**7b** (R = Et) are enantiomers. Consequently, each pair of diastereomers is correlated with two different absolute configurations in the cluster framework with respect to the co-ordination of the two stereochemically different Re atoms by the (+)- or (−)-camphanate ligand. The de values of the phenyl derivatives are obtained from the ^1H NMR spectra by integrating the singlets of one methyl group in the camphanate ligand at δ 0.67 and 0.52, respectively. The diastereomers whose ^1H NMR signal is at δ 0.67 (**4a**, **5a**) can be isolated diastereomerically pure (100% de), whereas the diastereomers with the singlet at δ 0.52 (**4b**, **5b**) are only isolated with a de value of 95%. Unfortunately, the same procedure does not work for the ethyl derivatives because of signal overlaps of the camphanic methyl groups. Their de values, therefore, are estimated from the ^{31}P NMR spectra. The integration of the phosphido bridge singlets at δ 129.9 (**6a**, **7a**) and 128.3 (**6b**, **7b**) lead to de values of 100 (**6b**, **7b**), 96 (**6a**) and 85% (**7a**). As expected the mentioned enantiomeric pairs (Fig. 1) are confirmed by the same spectroscopic data (IR, ^1H and ^{31}P NMR) (Table 1) and mirror inverted features in the CD spectra (Figs. 2 and 3). In contrast, the respective pairs of diastereomers are characterized by different ^1H and ^{31}P NMR data but identical ν (CO, CO_2) IR absorption bands; only the asymmetric $\nu(CO_2)$ mode of the co-ordinated carboxylic function is found at different wavenumbers (Table 1). The CD spectra of the diastereomeric pairs are approximately mirror images, too (Figs. 2 and 3).

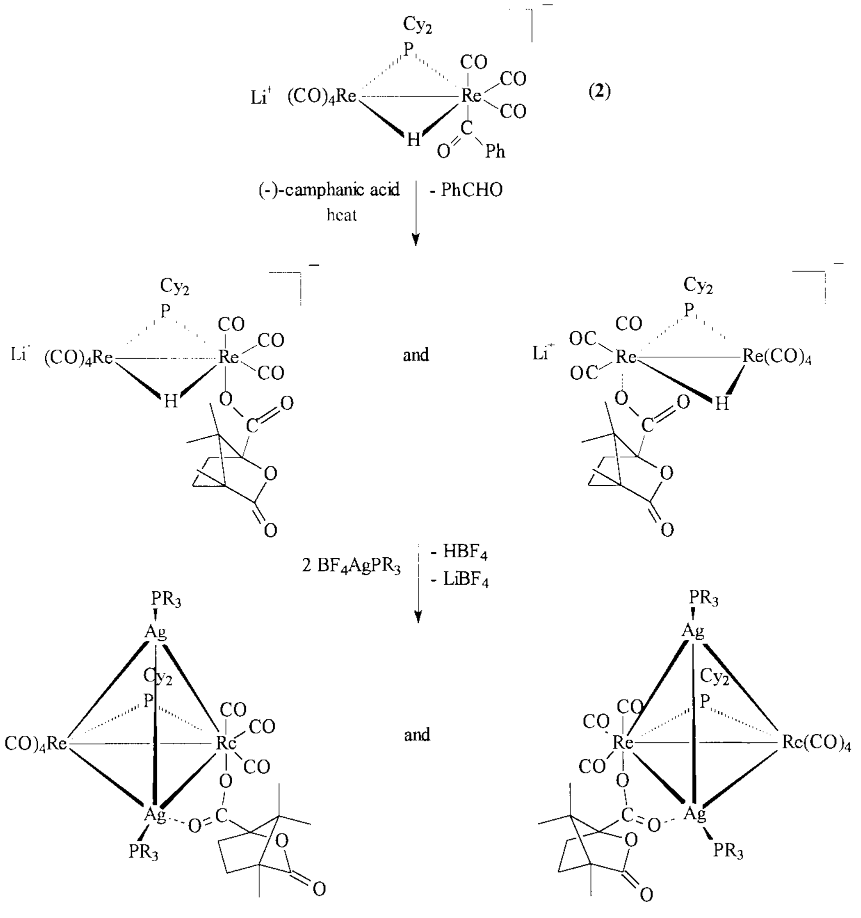
Crystallization of the diastereomeric pair 4a/4b (I) and the enantiomeric pair 4a/5a (II)

For all the prepared compounds, attempts to get diastereomerically pure single crystals using the vapor pressure

Table 1 Selected spectroscopic data of all stereoisomers prepared

Complex	de value (%)	^{31}P NMR (δ, J/Hz) (s, μ-P)[a]	^{1}H NMR (δ, J/Hz) (s, CH_3, camphanate)[a]	IR $\nu_{asym}(CO_2)$[b]/cm^{-1}	CD λ/nm ($\Delta\varepsilon$/L mol^{-1} cm^{-1})[c]	UV-vis λ_{max}/nm (ε/L mol^{-1} cm^{-1})[c]
4a	100	126.7	0.67, 0.84, 0.96	1593	202 (27.8), 223 (23.9), 251 (26.8), 270 (−12.7), 295 (−5.0), 313 (0.4), 335 (−4.6), 380 (4.8)	($c = 8.6 \times 10^{-5}$ mol L^{-1}) 197.5 (165000)
4b	95	126.3	0.52, 0.83, 0.97	1608	202 (−15.9), 213 (2.8), 224 (−13.8), 247 (−16.2), 272 (10.2), 297 (3.3), 312 (−3.2), 332 (1.2), 378 (−5.9)	($c = 5.1 \times 10^{-5}$ mol L^{-1}) 197 (143000)
5a	100	126.7	0.67, 0.84, 0.96	1593	202 (−25.5), 222 (−19.9), 248 (−22.4), 268 (8.4), 296 (2.5), 311 (−2.2), 332 (3.4), 374 (−5.1)	($c = 4.7 \times 10^{-5}$ mol L^{-1}) 197 (158000)
5b	95	126.3	0.52, 0.83, 0.97	1608	200 (21.8), 214 (−4.4), 226 (10.5), 244 (12.0), 270 (−11.7), 294 (−4.7), 315 (1.2), 331 (−2.9), 373 (3.8)	($c = 5.2 \times 10^{-5}$ mol L^{-1}) 197.5 (146000)
6a	96	129.9	0.86, 0.92, 1.01	1597	200 (15.8), 213 (−14.1), 231 (39.2), 261 (−13.7), 280 (sh, −5.3), 309 (1.3), 334 (−2.3), 380 (4.6)	($c = 1.39 \times 10^{-4}$ mol L^{-1}) 197.5 (46500)
6b	100	128.3	0.86, 1.02 (2 CH_3)	1614	200 (−27.4), 214 (23.8), 231 (−43.6), 262 (16.1), 283 (sh, +7.3), 311 (−0.9), 333 (2.9), 377 (−5.3)	($c = 1.41 \times 10^{-4}$ mol L^{-1}) 197 (59700)
7a	85	129.9	0.86, 0.92, 1.01	1597	200 (−12.1), 215 (12.9), 232 (−30.2), 264 (12.2), 283 (sh, +4.4), 307 (−0.7), 332 (2.6), 370 (−2.7)	($c = 1.21 \times 10^{-4}$ mol L^{-1}) 198 (54900)
7b	100	128.3	0.86, 1.02 (2 CH_3)	1614	200 (19.9), 212 (−24.1), 231 (45.8), 262 (−15.9), 284 (sh, −6.2), 309 (1.3), 337 (−2.1), 382 (6.0)	($c = 1.34 \times 10^{-4}$ mol L^{-1}) 197 (63500)

[a] In $CHCl_3$. [b] CaF_2 optics. [c] In C_2H_5OH.



(R = Ph (**5a**), Et (**7a**))   (R = Ph (**5b**), Et (**7b**))

Scheme 1 Formation of the diastereomers.

equilization method for crystal growth failed. At temperatures below 0 °C none of the diastereomers crystallizes, but at room temperature after an average period of two weeks crystallization takes place. Single crystals (**I**) obtained from crystallization of diastereomerically pure **4a** in toluene at 25 °C contained both diastereomers (**4a** and **4b**) in ratio 1 : 1, as could be shown

Table 2 Crystallographic data for **I** and **II**

Formula	$C_{65}H_{65}Ag_2O_{11}P_3Re_2 \cdot 1.5\ C_6H_5Me$	$C_{65}H_{65}Ag_2O_{11}P_3Re_2 \cdot CHCl_3$
M	1841.4	1822.6
Crystal system	Triclinic	Triclinic
Space group	$P1$ (no. 1)	$P\bar{1}$ (no. 2)
T/K	173(2)	293(2)
a/Å	14.374(1)	14.723(8)
b/Å	16.115(1)	16.244(4)
c/Å	16.641(1)	16.665(4)
α/°	98.12(1)	98.26(1)
β/°	98.35(1)	100.47(2)
γ/°	101.83(1)	101.69(2)
U/Å^3	3674.1(4)	3770(2)
Z	2	2
μ(Mo-Kα)/mm^{-1}	3.931	3.933
Data (measured/unique)	91833/53396	13788/13221
R_{int}	0.060	0.076
$R1/wR2$	0.047/0.100	0.078/0.291

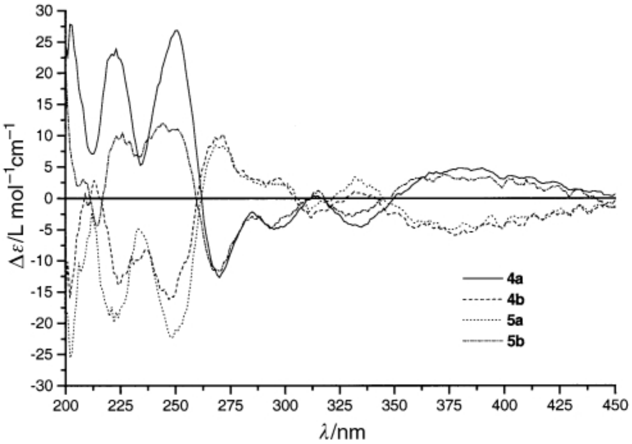


Fig. 2 CD spectra in EtOH of all stereoisomers of $Re_2(AgPPh_3)_2$-(μ-PCy_2)$(CO)_7$(camph).

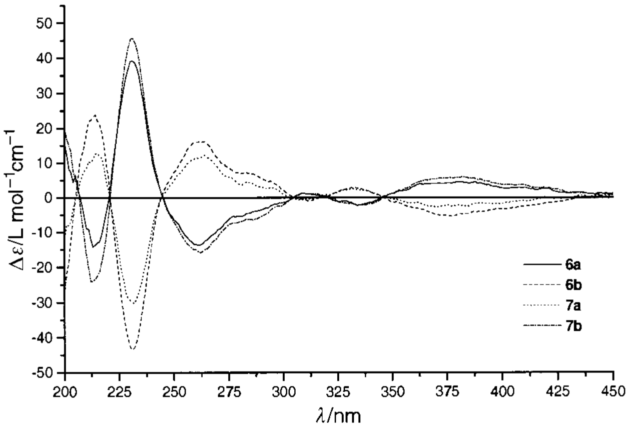


Fig. 3 CD spectra in EtOH of all stereoisomers of $Re_2(AgPEt_3)_2$-(μ-PCy_2)$(CO)_7$(camph).

by single crystal analysis as well as by ^1H and ^{31}P NMR data. This means that the considered camphanate substituted metallatetrahedra are able to epimerize as well as the diastereomers of the above mentioned tetrahedral cluster $Re_2(AuPCy_3)_2$-(μ-$PMen_2$)(μ-C(n-Bu)O)$(CO)_6$ (see Introduction). However, this latter process is doubtlessly faster. In order to grow crystals at all it was necessary to start from solutions containing molecules which, according to the absolute configuration of the Re_2Ag_2 framework, are mirror images. This is ensured with the diastereomeric pairs **4a**/**4b**, **5a**/**5b**, **6a**/**6b**, **7a**/**7b** and the enantiomeric ones **4a**/**5a**, **4b**/**5b**, **6a**/**7a** and **6b**/**7b**. For determination of the absolute configuration of the cluster framework single crystals (**II**) of **4a**/**5a** were grown from $CHCl_3$ solution at −20 °C.

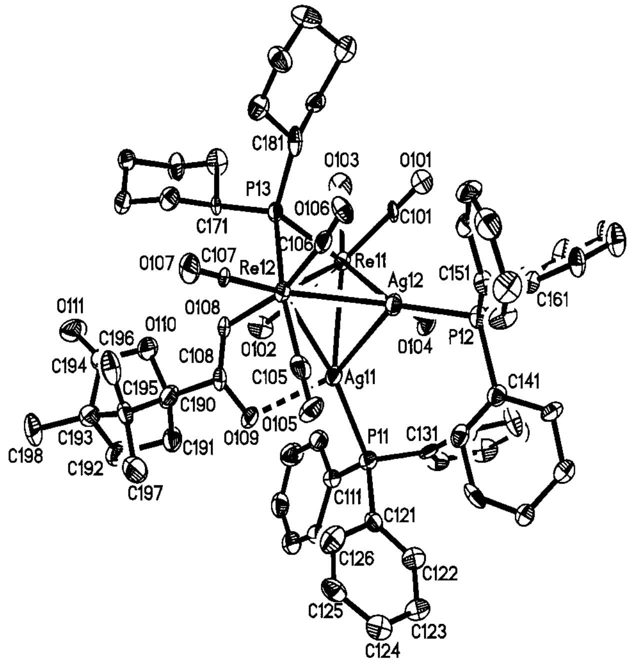


Fig. 4 Molecular structure of **I**, molecule **4a**, showing 50% probability ellipsoids. Hydrogen atoms omitted for clarity. Numbering schemes of phenyl and cyclohexyl groups follow that of C121–C126.

Molecular structures of I (4a/4b) and II (4a/5a)

The unit cell of **I** (non-centrosymmetric space group $P1$) contains two independent diastereomeric molecules **4a** and **4b** and three toluene solvent molecules. Molecules **4a** and **4b** are virtually mirror images, exhibiting the same metal framework and ligand co-ordination but both with the (+)-camphanate group attached (see Fig. 1; Tables 2, 3). The following description focuses on **4a** (Fig. 4) with atom numbering 1x; corresponding atoms for **4b** are numbered 2x, and where appropriate the geometric parameters for **4b** are given in brackets. The molecular core consists of a Re_2Ag_2 tetrahedron with a μ-PCy_2 group that bridges the Re–Re bond of 3.2315(5) Å [3.2350(5)]. The basic geometries of related Re_2Au_2 metallatetrahedra have been described.[18,24] The Re11 atom is co-ordinated by four terminal carbonyl ligands and Re12 by three CO ligands and the (+)-camphanate group with a Re12–O108 bond length of 2.178(4) Å [2.202(4)]. These non-metal ligands show ecliptic arrangement at both metal centres; the related torsion angles range from 0.1 to 7.4° [0.3 to 8.8]. Each Ag atom is connected to one Ag and two Re atoms and a terminal PPh_3 ligand, but Ag11 additionally shows another co-ordinative interaction from O109 of the camphanate ligand with a Ag11–O109 distance of 2.461(4) Å [2.425(4)]. Accordingly, the co-ordination of Ag11

Table 3 Selected bond distances (Å) and angles (°) for isomers **4a** and **4b**

For **4a**					
Re11–Re12	3.2315(5)	Re11–P13	2.466(1)	Re12–P13	2.426(2)
Re11–Ag11	2.9381(6)	Re11–Ag12	2.9543(6)	Re12–Ag11	2.9616(5)
Re12–Ag12	2.9075(5)	Re12–O108	2.178(4)	Ag11–Ag12	2.7168(7)
Ag11–P11	2.436(2)	Ag12–P12	2.417(2)	O108–C108	1.282(7)
C108–O109	1.229(7)	C108–C190	1.577(8)		
Ag11–Re11–Ag12	54.91(2)	Ag11–Re11–Re12	57.14(1)	Ag12–Re11–Re12	55.86(1)
Ag12–Re12–Ag11	55.14(1)	Ag12–Re12–Re11	57.24(1)	Ag11–Re12–Re11	56.44(1)
Ag12–Ag11–Re11	62.85(2)	Ag12–Ag11–Re12	61.42(1)	Re11–Ag11–Re12	66.42(1)
Ag11–Ag12–Re12	63.44(1)	Ag11–Ag12–Re11	62.24(2)	Re12–Ag12–Re11	66.90(1)
P11–Ag11–Ag12	119.97(4)	P11–Ag11–Re11	131.65(4)	P11–Ag11–Re12	161.61(4)
P12–Ag12–Ag11	133.18(4)	P12–Ag12–Re12	144.24(4)	P12–Ag12–Re11	146.26(4)
Re11–P13–Re12	82.67(5)	Re12–O108–C108	126.4(3)	O108–C108–C109	127.9(5)
For **4b**					
Re21–Re22	3.2350(5)	Re21–P23	2.478(1)	Re22–P23	2.425(2)
Re21–Ag21	2.9430(6)	Re21–Ag22	2.9501(6)	Re22–Ag21	2.9522(6)
Re22–Ag22	2.9048(5)	Re22–0208	2.202(4)	Ag21–Ag22	2.7332(7)
Ag21–P21	2.434(2)	Ag22–P22	2.418(2)	0208–C208	1.239(7)
C208–0209	1.281(7)	C208–C290	1.490(8)		
Ag21–Re21–Ag22	55.26(2)	Ag21–Re21–Re22	56.85(1)	Ag22–Re21–Re22	55.79(1)
Ag22–Re22–Ag21	55.63(1)	Ag22–Re22–Re21	57.13(1)	Ag21–Re22–Re21	56.58(1)
Ag22–Ag21–Re21	62.50(2)	Ag22–Ag21–Re22	61.31(1)	Re21–Ag21–Re22	66.56(1)
Ag21–Ag22–Re22	63.06(1)	Ag21–Ag22–Re21	62.23(2)	Re22–Ag22–Re21	67.07(1)
P21–Ag21–Ag22	118.23(4)	P21–Ag21–Re21	130.68(4)	P21–Ag21–Re22	161.90(4)
P22–Ag22–Ag21	134.50(4)	P22–Ag22–Re22	141.74(4)	P22–Ag22–Re21	148.00(4)
Re21–P23–Re22	82.56(5)	Re22–0208–C208	128.0(4)	0208–C208–0209	124.4(6)

atom is strongly distorted (P11–Ag11–Ag12 119.97(4), P11–Ag11–Re11 131.65(4), P11–Ag11–Re12 161.61(4)°) compared to that of Ag12 (P12–Ag12–Ag11 133.18(4), P12–Ag12–Re11 146.26(4), P12–Ag12–Re12 144.24(4)°). Thus the camphanate group acts as a bidentate ligand bridging the 2.9616(5) Å [2.9522(6)] long heteronuclear Re12–Ag11 edge; the remaining Re–Ag bond lengths are 2.9075(5) to 2.9543(5) Å [2.9048(5) to 2.9501(6)]. This is the first crystallographically determined example of any bidentate carboxylate ligand for a heteronuclear Re–M moiety where M is a transition metal. For camphanate as bidentate ligand only two homonuclear structures are known: a dicopper complex[25] and a dirhodium complex.[26] In these the respective metal–oxygen bonds are of nearly equal length and differ only by about 0.03 Å. No other crystal structures of compounds with camphanate as a single co-ordinating ligand are known either. Incidentally, the report on the rhodium complex is rather inconsistent because the reported centrosymmetric complex, nevertheless assigned as being chiral, would require racemization of the camphanate.

In order correctly to assign the CD spectra to the corresponding diastereomers it was necessary to determine the structure of the enantiomeric pair **4a**/**5a**. It crystallizes as **II** with one $CHCl_3$ solvent molecule per asymmetric unit in centrosymmetric space group $P\bar{1}$, **4a** with the (+)-camphanate and **5a** with the (−)-camphanate as ligand. The co-ordination geometries are the same as described for structure **I** and need not to be discussed any further.

Assignment of the absolute configuration

The axially substituted metallatetrahedra with Re_2Ag_2 core are of C_1 symmetry. They show planar chirality[27] because a chiral plane runs through both Re atoms and the bridging phosphorus ligand. The novelty of the prepared chiral tetrahedra derivatives required a definition in terms of *C* and *A* nomenclature for assigning the absolute configuration.[28] Accordingly, the molecule is oriented in such a way that the ligand of the highest priority is in front of the chiral plane facing the observer (see Fig. 5). In this case this is the camphanate ligand. Then the priority sequence of the three atoms in the chiral plane is determined (Re1 $\longrightarrow$ Re2 $\longrightarrow$ P3). If the sequence is clockwise the absolute configuration is C, if it is counterclockwise the molecule is *A*-configurated. The absolute configuration of the cluster framework of **4a** as *A* and **5a** as *C* was established by X-ray crystallographic analysis of **II.** On this basis, the assignment of the CD spectra to absolute tetrahedral configuration is possible.

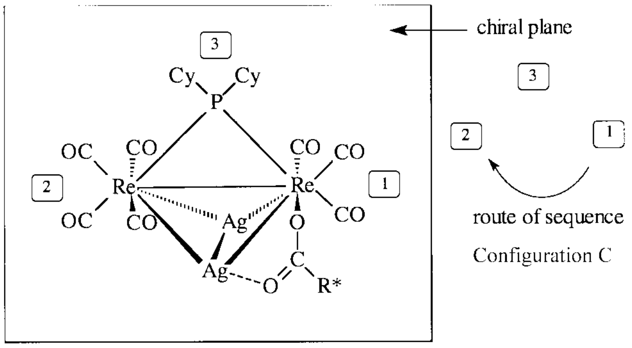


Fig. 5 Assignment of the absolute configuration.

Chiroptical properties

The UV/VIS spectra of the carboxylate substituted metallatetrahedra (Table 1) are not very informative. Maximum extinction is observed at the limit of the experimentally accessible wavelength range at 197 nm. The absorption coefficient ε nearly triples when the phosphorus co-ordinated ethyl groups (about 55000 L mol^{-1} cm^{-1}) are replaced by phenyl groups (about 150000 L mol^{-1} cm^{-1}). The spectral features at longer wavelengths are insignificant. Even with derivative spectroscopy it was not possible to identify distinct bands including the lowest energy absorption which is responsible for the yellow colour of these clusters. The related HOMO for the electron transition might be of the type π $[Re_2(\mu\text{-}PCy_2)]$.[29] In contrast, several absorptions are observed in the CD spectra indicating different electronic transitions. Generally, the $\Delta\varepsilon$ values of the diastereomerically pure compounds **4a**, **5a**, **6b**, **7b** are higher than those with lower de. The CD curves of the respective pairs of diastereomers in the range 200–450 nm are approximately mirror images (especially the ethyl derivatives). Since in the CD spectrum camphanic acid only absorbs below 240 nm with small $\Delta\varepsilon$ values ((+)-camphanic acid $\lambda = 213$ nm, $\Delta\varepsilon = 1.2$ L mol^{-1} cm^{-1}; (−)-camphanic acid $\lambda = 214$, $\Delta\varepsilon = -1.4$ L mol^{-1} cm^{-1}), essentially all observed Cotton effects of the diastereomerically pure compounds are due to cluster-based dissymmetry, *i.e.* of the chirality of the tetrahedral Re_2Ag_2 framework with a ligand sphere of C_1 symmetry. Thirty years ago it was postulated that chiroptical properties of organometallic complexes are dominated by metal chromophores.[30] Hence diastereomers with a ligand of the same absolute configuration but with different cluster framework should have mirror-inverted CD and ORD spectra. This was established, for example, for NiNi′CC′ tetrahedra,[1] tetrahedra with an EMM′M″ core (SFeCoM (M = Cr, Mo, W),[3] CCoNiMo,[4,5] PFeCoW[6]) and chiral triosmium carbonyl clusters with heteronuclear diatomic bridges (C=O and C=N).[7] Thus, we find two sets of spectra. In one which is comprised of the diastereomeric pairs **4a/5b** and **6a/7b** the longest wavelength absorption around 375 nm is positive, followed (in **4a** and **5b**) by negative bands at 335, 295 and 270 nm and positive bands at 250 and 225 nm. (For the ethyl derivatives **6a** and **7b**, the corresponding bands are increasingly blue-shifted; in addition the 213 nm band is negative.) The spectra of the other set belong to the corresponding enantiomers and have an approximately inverted shape. Following the successful determination of the absolute configuration of **4a** as *C* and **5a** as *A* we are able to assign the absolute configuration of the metal framework on the basis of the corresponding CD spectra. Thus, **5b**, **6a**, and **7b** are *C*-configurated, while **4b**, **6b**, and **7a** have the *A* configuration, as drawn in Fig. 1. Also, the absolute configurations of the other known chiral carboxylate substituted metallatetrahedra $Re_2(MPR_3)_2(\mu\text{-}PCy_2)(CO)_7Z$ (M = Au, R = Ph, Z = (+)-, (−)-camphanates, (+)- and (−)-prolinate; M = Ag, R = Ph, Z = (+)-2-(6-methoxy-2-naphthyl)propionate)[31] can now be assigned depending on which set of spectra they belong to.

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 and phosphorus-31 NMR spectra 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).

Starting materials

The dirhenium compound $Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8$[32] and the coinage metal complex $[AgCl(PPh_3)]$[33] were prepared according to the synthetic routes cited. The *in situ* preparations of $[Ag(PPh_3)]BF_4$,[21] $[Ag(PEt_3)]BF_4$[20] and $Li[Re_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(ax\text{-}C(Ph)O)]$[18] were performed according to literature methods. (+)-Camphanic acid, (−)-camphanic acid and LiPh ($c = 1.6$ 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 $Re_2(AgPR_3)_2(\mu\text{-}PCy_2)(CO)_7((+)\text{-camph})$ (R = Ph 4a, 4b or Et 6a, 6b) and of (−)-camphanate (R = Ph 5a, 5b or Et 7a, 7b)

A solution of complex **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 with 56 mg (0.34 mmol) (+)- and (−)-camphanic acid, respectively, and stirred at 60 °C for 5h. After cooling to room temperature each of the diastereomeric intermediates $Li[Re_2(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_7(ax\text{-}(+)/(-)\text{-camph})]$ **3** was identified by the following spectroscopic data. IR [cm^{-1}] ν(CO, CO_2) (THF) : 2079s, 2004vs, 1984s, 1967m, 1932s, 1903vs, 1876vs, 1786s and 1630s. ^{31}P NMR (THF–$CDCl_3$): δ 74.2 (s, P, µ-P) and 73.2 (s, P, µ-P). The integrated singlets showed a ratio of 1.4 : 1 (17% de) for both diastereomeric pairs of **3**. Afterwards 146 mg (0.32 mmol) $[Ag(PPh_3)]BF_4$ and 106.4 mg (0.34 mmol) $[Ag(PEt_3)]BF_4$, respectively, dissolved in 10 mL dichloromethane were added dropwise to **3**. After stirring the deep yellow solution for 5 min the solvent was removed under reduced pressure.

Separation of the diastereomers 4a, 4b, 5a, 5b

The dark yellow residue was seperated by PLC using n-hexane–acetone (4 : 1) as eluent. The resulting yellow main fraction contains both diastereomers (yield **4** 192 (59), **5** 137 mg (42%)). The separation of the diastereomers was achieved by a second PLC procedure with n-hexane–dichlormethane (1 : 2) as eluent.

Separation of the diastereomers 6a, 6b, 7a, 7b

The residue was seperated by PLC with n-hexane–acetone (4 : 1) as eluent giving one yellow main fraction (yield: **6** 152 mg (57%), **7** 127 mg (48%)) At $R_f = 0.5$ the eluent was changed to n-hexane–dichloromethane (1 : 3). In order of decreasing R_f values the diastereomers **6a**, **7a** and **6b**, **7b** were obtained (yield **6a** 41 (15), **6b** 70 (26), **7a** 37 (14), **7b** 61 mg (23%)).

4a, **5a** : IR [cm^{-1}], ν(CO, CO_2) (CH_2Cl_2) 2046m, 1988vs, 1965vs, 1943vs, 1927vs, 1905s, 1863s, 1776m, 1593m and 1329w. ^{31}P NMR ($CDCl_3$): δ 19.6 (m, 1P, $AgPPh_3$), 20.0 (2dd, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 416$, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 458$, $^2J_{\mathrm{P}^{107/109}\mathrm{Ag}} = 31$ Hz, 1P, $AgPPh_3$) and 126.7 (s, 1P, µ-P). ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 3 H, Me), 0.84 (s, 3 H, Me), 0.96 (s, 3 H, Me), 0.88–2.4 (m, 26 H, camphanate, Cy) and 7.1–7.4 (m, 30 H, Ph).

4b, **5b** : IR [cm^{-1}], ν(CO, CO_2) (CH_2Cl_2) 2046m, 1988vs, 1967vs, 1944vs, 1927vs, 1903s, 1863s, 1776m, 1608w and 1329w. ^{31}P NMR ($CDCl_3$): δ 19.8 (2d, broad, 1P, $AgPPh_3$), 20.2 (2dd, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 416$, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 458$, $^2J_{\mathrm{P}^{107/109}\mathrm{Ag}} = 31$ Hz, 1P, $AgPPh_3$) and 126.3 (s, 1P, µ-P). ^{1}H NMR ($CDCl_3$): δ 0.52 (s, 3 H, Me), 0.83 (s, 3 H, Me), 0.97 (s, 3 H, Me), 0.85–2.4 (m, 26 H, camphanate, Cy) and 7.2–7.4 (m, 30 H, Ph). Calc. for $C_{65}H_{65}Ag_2O_{11}P_3Re_2$: C, 45.84; H, 3.85. Found: **4a** C, 45.82; H, 3.75. **4b** C, 45.45; H, 3.62. **5a** C, 46.02; H, 3.76. **5b** C, 45.49; H, 3.69%.

6a, **7a** : IR [cm^{-1}], ν(CO, CO_2) (CH_2Cl_2) 2044m, 1984vs, 1961vs, 1942vs, 1921s, 1901s, 1855m, 1774m, 1597w and 1329vw. ^{31}P NMR ($CDCl_3$): δ 15.2 (2dd, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 428$, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 477$, $^2J_{\mathrm{P}^{107/109}\mathrm{Ag}} = 33$ Hz, 1P, $AgPPh_3$), 16.6 (2dt, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 391$, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 452$, $^2J_{\mathrm{P}^{107/109}\mathrm{Ag}} = 31$ Hz, 1P, $AgPPh_3$) and 129.9 (s, 1P, µ-P). ^{1}H NMR ($CDCl_3$): δ 0.86 (s, 3 H, Me), 0.92 (s, 3 H, Me), 1.01 (s, 3 H, Me) and 1.1–2.4 (m, 68 H, camphanate, Cy, Et).

6b, **7b** : IR [cm^{-1}], ν(CO, CO_2) (CH_2Cl_2) 2044m, 1984vs, 1961vs, 1942vs, 1923vs, 1901s, 1855m, 1774m, 1614w and 1329vw. ^{31}P NMR ($CDCl_3$): δ 15.1 (2dd, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 429$, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 478$, $^2J_{\mathrm{P}^{107/109}\mathrm{Ag}} = 32$ Hz, 1P, $AgPPh_3$), 16.7 (2dt, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 397$, $^1J_{\mathrm{P}^{107}\mathrm{Ag}} = 458$, $^2J_{\mathrm{P}^{107/109}\mathrm{Ag}} = 31$ Hz, 1P, $AgPPh_3$) and 128.3 (s, 1P, μ-P). ^{1}H NMR (CDCl$_3$): δ 0.86 (s, 3 H, Me), 1.02 (s, 6 H, 2 Me) and 1.1–2.4 (m, 68 H, camphanate, Cy, Et). Calc. for $C_{41}H_{65}Ag_2O_{11}P_3Re_2$: C, 35.05; H, 4.66. Found: **6a** C, 35.57; H, 4.46. **6b** C, 35.13; H, 4.60. **7a** C, 35.8; H, 4.45. **7b** C, 35.7; H, 4.48%.

Crystal structure determinations

Pertinent crystallographic data for structures **I** (**4a**/**4b**) and **II** (**4a**/**5a**) are summarized in Table 2. Data set **I** was collected on a Nonius KappaCCD diffractometer with Mo-Kα radiation. Lorentz polarization correction, no absorption correction. Data for **II** were collected on a Bruker AXS P4 diffractometer with Mo-Kα radiation. Three standard reflections monitored after every 400 showed a decrease of 15% in intensities. Lorentz polarization and gaussian absorption corrections were applied. The structures were solved by direct and conventional Fourier methods. Full-matrix least-squares refinement based on F^2 anisotropically; geometrically placed hydrogen atoms were refined with a riding model.

First attempts to solve and refine **I** in space group *P*1 were not successful. Apart from the configuration of the camphanate ligand the two independent molecules in the unit cell are almost inversion related. So with a centrosymmetric $P\bar{1}$ model solution refinement proceeded smoothly resulting in then disordered camphanate ligands which differ only in the positions of one O *vs*. CH$_2$ and one C=O *vs*. CH$_2$ group (see Fig. 1). At this stage a complete second set of inversion related atomic co-ordinates was included and the structure then refined in the correct space group *P*1. The absolute structure was determined by refining the absolute structure parameter (0.008(5)) in full agreement with the known (+)-camphanate configuration. Program used for calculations: SHELX 97.[34]

CCDC reference number 186/2054.

See http://www.rsc.org/suppdata/dt/b0/b003013i/ crystallographic files in .cif format.

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