CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200500907

Unprecedented Stereoselective Synthesis of Catalytically Active Chiral Mo_3CuS_4 Clusters

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Abstract: Cluster excision of polymeric $\{Mo_3S_7Cl_4\}_n$ phases with chiral phosphane (+)-1,2-bis[(2*R*,5*R*)-2,5-(dimethylphospholan-1-yl)]ethane ((*R*,*R*)-Me-BPE) or with its enantiomer ((*S*,*S*)-Me-BPE) yields the stereoselective formation of the trinuclear cluster complexes $[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]^+$ ([(*P*)-**1**]$^+$) and $[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]^+$ ([(*M*)-**1**]$^+$), respectively. These complexes posses an incomplete cuboidal structure with the metal atoms defining an equilateral triangle and one capping and three bridging sulfur atoms. The *P* and *M* symbols refer to the rotation of the chlorine atoms around the C_3 axis, with the capping sulphur atom pointing towards the viewer. Incorporation of copper into these trinuclear complexes affords heterodimetallic cubane-type compounds of formula $[Mo_3CuS_4\{(R,R)\text{-Me-BPE}\}_3Cl_4]^+$ ([(*P*)-**2**]$^+$) or $[Mo_3CuS_4\{(S,S)\text{-Me-BPE}\}_3Cl_4]^+$ ([(*M*)-**2**]$^+$), respectively, for which the chirality of the trinuclear precursor is preserved in the final product. Cationic complexes [(*P*)-**1**]$^+$, [(*M*)-**1**]$^+$, [(*P*)-**2**]$^+$, and [(*M*)-**2**]$^+$ combine the chirality of the metal cluster framework with that of the optically active diphosphane ligands. The known racemic $[Mo_3CuS_4(dmpe)_3Cl_4]^+$ cluster (dmpe = 1,2-bis(dimethylphosphanyl)ethane) as well as the new enantiomerically pure Mo_3CuS_4 [(*P*)-**2**]$^+$ and [(*M*)-**2**]$^+$ complexes are efficient catalysts for the intramolecular cyclopropanation of 1-diazo-5-hexen-2-one (**3**) and for the intermolecular cyclopropanation of alkenes, such as styrene and 2-phenylpropene, with ethyl diazoacetate. In all cases, the cyclopropanation products were obtained in high yields. The diastereoselectivity in the intermolecular cyclopropanation of the alkenes and the enantioselectivity in the inter- or intramolecular processes are only moderate.

Keywords: asymmetric catalysis · chirality · cluster compounds · molybdenum · phosphane ligands

Introduction

Transition-metal chalcogenide clusters with cubane-type structures, in which the metal and the chalcogen atoms occupy adjacent vertices in a cube, have been used as simple models for metalloenzymes and industrial hydrodesulfurization processes.[1–3] Despite their relevance as enzymatic models, the application of these $Mo_3M'S_4$ (M′ = transition metal) cuboidal clusters as catalysts for organic reactions is largely unexplored; exceptions being the palladium- and nickel-based systems that catalyze the addition of methanol or carboxylic acids to electron-deficient alkynes[4–6] and the Mo_3RuS_4 clusters that are effective for the N−N bond cleavage of hydrazines.[7]

The development of transition-metal cluster chemistry is closely related to the existence of rational methods for their synthesis. In the past twenty years, several efficient approaches have evolved, namely excision from solid-state polymers and building-block processes from lower nuclearity synthons. In particular, cluster excision from polymeric $\{M_3Q_7X_4\}_n$ phases with diphosphanes has been used to prepare a series of complexes of the general formula $[M_3Q_4(\text{diphosphane})_3X_3]^+$ (M = Mo, W; Q = S, Se; X = Cl, Br).[8] Such synthetic strategies have been illustrated in the preparation of the trinuclear $[Mo_3S_4(dmpe)_3Cl_3]^+$ sulfido cluster (dmpe = 1,2-bis(dimethylphosphino)ethane), recently reported by us.[9] The specific coordination of the diphosphane ligand, with one phosphorus atom *trans* to the capping

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sulfur atom and the other *trans* to the bridging sulfur atom, results in cubane-type sulfido clusters with backbone chirality. This trinuclear complex is obtained as a racemic mixture of the *P* and *M* enantiomers.[10] Once the chirality of one metal center is defined, that of the other two metallic centers is equally fixed.

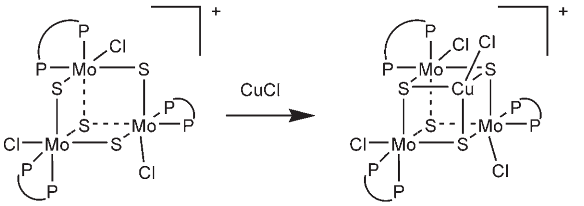
These complexes react with a second metal to build up chiral heterodimetallic cubane-type clusters of formula $[M_3M'Q_4(\text{diphosphane})_3X_3L]^+$ (M′ = Co, Ni, Cu, and Pd; L = ligand coordinated to the heterometal) as racemic mixtures.[8] However, no studies concerning their resolution or a strategy for their diastereoselective synthesis have been reported. So far, the catalytic performance of cuboidal Mo_3CuS_4 species has never been studied.

Here we report a straightforward preparation of two enantiomerically pure cuboidal Mo_3CuS_4 clusters, namely $[(P)\text{-}\mathbf{2}]^+$ or $[(M)\text{-}\mathbf{2}]^+$, based on the diastereoselective and efficient construction of their trinuclear Mo_3S_4 precursors, $[(P)\text{-}\mathbf{1}]^+$ or $[(M)\text{-}\mathbf{1}]^+$, respectively, by using either (+)-1,2-bis[(2*R*,5*R*)-2,5-(dimethylphospholan-1-yl)]ethane ((*R*,*R*)-Me-BPE) or its enantiomer ((*S*,*S*)-Me-BPE). We also present the capability of the racemic cluster of formula $[Mo_3CuS_4(dmpe)_3Cl_4]^+$ as an efficient catalyst for the transformation of diazo compounds, as well as preliminary studies on the catalytic performance of the chiral cubane-type cluster in enantioselective carbene transfer reactions, in both intra- and intermolecular processes.

Abstract in Spanish: *La reacción de escisión de la fase polimérica* $\{Mo_3S_7Cl_4\}_n$ *con la fosfina quiral (+)-1,2-bis-[(2R,5R)-2,5-(dimetilfosfolan-1-il)]etano, (R,R)-Me-BPE, o con su enantiómero, (S,S)-Me-BPE, conduce a la formación estereoselectiva de los complejos clúster trinucleares* $[Mo_3S_4(\text{R,R-Me-BPE})_3Cl_3]^+$ *(*$[(\text{P})\text{-}\mathbf{1}]^+$*) y* $[Mo_3S_4(\text{S,S-Me-BPE})_3Cl_3]^+$ *(*$[(\text{M})\text{-}\mathbf{1}]^+$*), respectivamente. Estos complejos poseen una estructura de cubo incompleto, dónde los átomos metálicos definen un triángulo equilátero, con un azufre unido a tres átomos de molibdeno y tres azufres puente. Los símbolos P y M hacen referencia a la rotación de los átomos de cloro alrededor del eje* C_3*, con el azufre apuntado dirigido hacia el observador. La incorporación de cobre a estos complejos trinucleares conduce a compuestos heterodimetálicos con estructura tipo cubano de fórmula* $[Mo_3CuS_4(\text{R,R-Me-BPE})_3Cl_4]^+$ *(*$[(\text{P})\text{-}\mathbf{2}]^+$*) y* $[Mo_3CuS_4(\text{S,S-Me-BPE})_3Cl_4]^+$ *(*$[(\text{M})\text{-}\mathbf{2}]^+$*) donde la quiralidad del precursor trinuclear se mantiene en el producto final. Los complejos catiónicos* $[(\text{P})\text{-}\mathbf{1}]^+$*,* $[(\text{M})\text{-}\mathbf{1}]^+$*,* $[(\text{P})\text{-}\mathbf{2}]^+$ *y* $[(\text{M})\text{-}\mathbf{2}]^+$ *combinan la quiralidad del esqueleto clúster con la de los ligandos difosfina. El clúster racémico* $[Mo_3CuS_4(dmpe)_3Cl_4]^+$ *(dmpe=1,2-bis(dimetilfosfino)etano), así como los complejos* Mo_3CuS_4 *enantioméricamente puros* $[(\text{P})\text{-}\mathbf{2}]^+$ *o* $[(\text{M})\text{-}\mathbf{2}]^+$ *son catalizadores eficaces para la reacción de ciclopropanación intramolecular de 1-diazo-5-hexen-2-ona (**3**) y para la ciclopropanación intermolecular de alquenos, estireno y 2-fenilpropeno, con etil diazoacetato. En todos los casos los productos de ciclopropanación se obtienen con rendimientos elevados. La diastereoselectividad en la ciclopropanación intermolecular de alquenos y la enantioselectividad en los procesos tanto inter- como intramoleculares son únicamente moderadas.*

Results and Discussion

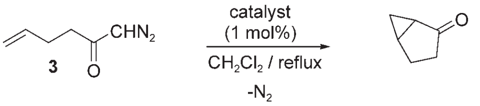
The effectiveness of copper(I) compounds for diazo transformations is well documented.[11] This fact prompted us to investigate the catalytic activity of the racemic $[Mo_3CuS_4(dmpe)_3Cl_4]^+$ copper cluster in the intramolecular cyclopropanation of 1-diazo-5-hexen-2-one (**3**), as well as in the intermolecular cyclopropanation of alkenes with ethyl diazoacetate. Cuboidal complex $[Mo_3CuS_4(dmpe)_3Cl_4]^+$ was prepared readily as a racemic mixture from the reaction of the $[Mo_3S_4(dmpe)_3Cl_3]^+$ complex with CuCl or $[Cu(CH_3CN)_4]PF_6$ in THF at room temperature, as represented in Scheme 1.[12,13]



Scheme 1. General synthetic procedure for $[Mo_3Cu(\text{diphosphane})_3Cl_4]^+$ clusters.

The α-diazoketone was added to a solution of the copper-containing cluster in dichloromethane under reflux and the mixture was stirred for 24 hours. The cyclopropanation product, formulated as [3.1.0]pentan-2-one (**4**), was obtained in a 95 % yield, as shown in Table 1.[14] The UV-visible and ESI mass spectra of the resulting solution after the complete transformation of the diazo precursor indicated that the Mo_3CuS_4 cluster remained intact. Besides, no traces of free phosphane in the solution were detected, as confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopic analysis. In addition, the racemic cuboidal complex $[Mo_3CuS_4(dmpe)_3Cl_4]^+$ was efficient for cyclopropanation of styrene with ethyl diazoacetate (ca. 80 % yield; *E*/*Z* = 2.4, see Table 2).

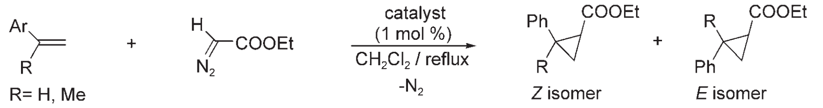
Table 1. Intramolecular cyclopropanation of α-diazoketone (**3**) catalyzed by *rac*-$[Mo_3CuS_4(dmpe)_3Cl_4]^+$ or $[(P)\text{-}\mathbf{2}]^+$.[a]



Catalyst	Yield of cyclopropane[c] [%]	*ee* [%]
rac-$[Mo_3CuS_4(dmpe)_3Cl_4]^{+[b]}$	95	–
$[(P)\text{-}\mathbf{2}]^+$	84	25

[a] Reactions were carried out under a nitrogen atmosphere. [b] *rac* = racemic. [c] Isolated yields.

Table 2. Catalytic cyclopropanation of styrenes with ethyl diazoacetate using catalysts *rac*-$[Mo_3CuS_4(dmpe)_3Cl_4]^+$ or $[(P)\text{-}\mathbf{2}]^+$.[a]



Alkene	Catalyst	Yield of cyclopropane[b] [%]	*E*/*Z*[c]	*Z* isomer[d] *ee* [%]	*E* isomer[d] *ee* [%]
styrene	*rac*-$[Mo_3CuS_4(dmpe)_3Cl_4]^+$	80	2.4	–	–
styrene	$[(P)\text{-}\mathbf{2}]^+$	88	2.6	21	20
2-phenylpropene	$[(P)\text{-}\mathbf{2}]^+$	84	2.6	12	16

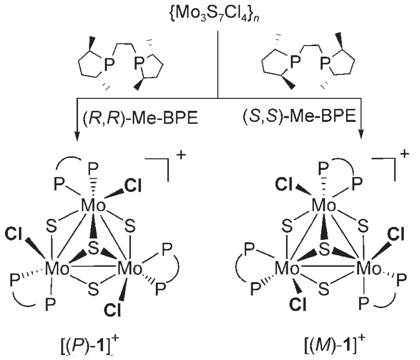
[a] All reactions were carried out under a nitrogen atmosphere. [b] Isolated yields. [c] Determined by ^1H NMR spectroscopy. [d] Determined by GC analysis using a 2,3-di-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl) β-CDX column.

Furthermore, a control experiment was performed to ascertain that the trinuclear $[Mo_3S_4(dmpe)_3Cl_3]Cl$ compound was catalytically inactive in the α-diazoketone transformation.

Motivated by the catalytic behavior of this racemic tetranuclear cluster, we decided to investigate the stereoselective synthesis of a closely related compound. Vahreckamp et al. have prepared optically active organometallic clusters with framework chirality based on the presence of four different elements within the tetrahedron cluster unit.[15] A different strategy to obtain enantiomerically pure transition-metal complexes consists of their transformation into diastereoisomers by the use of chiral ligands, and their subsequent separation by means of crystallization or chromatographic methods, which is always a time-consuming task. Indeed, the use of chiral phosphanes in the synthesis of mononuclear catalysts for enantioselective reactions is prevalent. In this context, asymmetric induction of mononuclear transition-metal complexes containing chiral phosphane ligands, such as (*R*,*R*)-Me-BPE and its respective enantiomer (*S*,*S*)-Me-BPE, are well known.[16,17] However, relatively few examples concerning the preparation of chiral cluster compounds and cluster-based catalysts with chiral phosphanes as ligands have been reported.[18] It should also be noted that the synthesis of chiral phosphane ligands containing clusters is very promising, as the resulting compounds might combine two sources of chirality, one arising from the chiral phosphane ligands (designated as *R*,*R* and *S*,*S*), and another coming from the polynuclear cluster framework (designated as *P* and *M*).

Reaction of the chiral diphosphane (*R*,*R*)-Me-BPE with the polymeric $\{Mo_3S_7Cl_4\}_n$ phase showed a unique efficiency and stereoselectivity in the formation of only one out of the four possible trinuclear $[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]^+$ diastereoisomers, $[(P)\text{-}\mathbf{1}]^+$, as represented in Scheme 2.

The circular dichroism (CD) spectrum of $[(P)\text{-}\mathbf{1}]^+$ shows two signals at $\lambda_{max}=265$ and 416 nm for +450 and +136 mdeg, respectively (Figure 1). On the other hand, the reaction of (*S*,*S*)-Me-BPE with the $\{Mo_3S_7Cl_4\}_n$ phase (Scheme 2) led to the selective formation of a unique diastereoisomer $[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]^+$ ($[(M)\text{-}\mathbf{1}]^+$) also displaying two signals at $\lambda_{max}=265$ and 413 nm with similar intensities, but opposite signs to those produced by the (*R*,*R*)-Me-BPE complex. These observations indicate that these compounds are enantiomers, taking into account that both CD spectra were recorded at concentrations with equal absorbance intensities in the UV-visible region. Further evidence is provided by the fact that these compounds have the same $^{31}P\{^1H\}$ NMR spectrum, with two doublets of doublets at $\delta=53.79$ (three P atoms) and 64.77 ppm (three P atoms), typical features for a (AA′A″BB′B″) system.



Scheme 2. Synthesis of chiral trinuclear clusters.

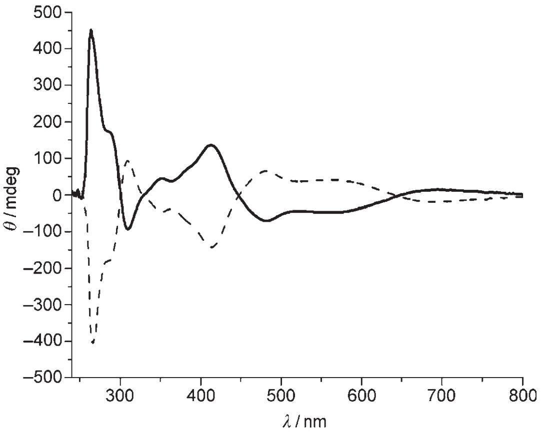


Figure 1. Circular dichroism spectra of $[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]^+$, ($[(P)\text{-}\mathbf{1}]^+$, ——) and $[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]^+$ ($[(M)\text{-}\mathbf{1}]^+$, - - -) in dichloromethane at 25 °C at 1.53×10^{-4} M.

The absolute configuration for $[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]^+$ and $[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]^+$ were determined by X-ray crystallography as *P* and *M*, respectively. An ORTEP representation of these two enantiomers is given in Figure 2. Both “paddlewheel” structures were

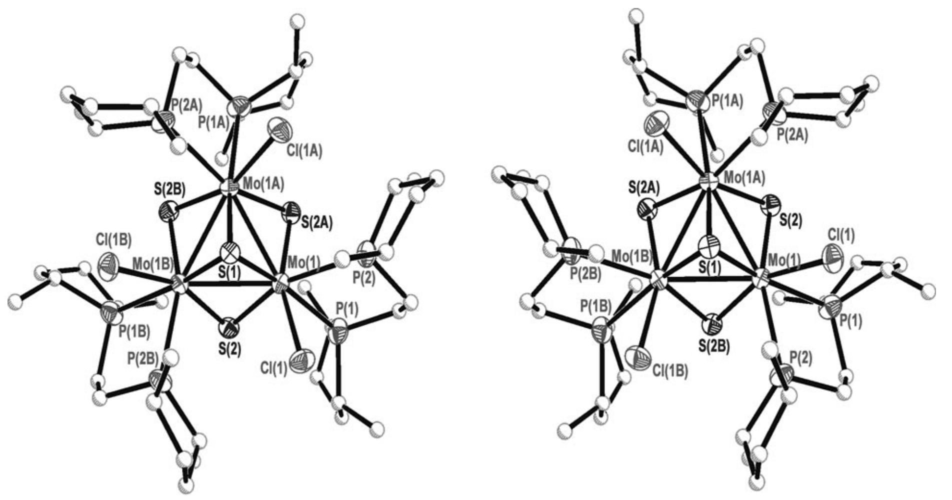


Figure 2. ORTEP plot of $[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]PF_6$ ($[(P)\text{-}\mathbf{1}]PF_6$, left) and $[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]PF_6$ ($[(M)\text{-}\mathbf{1}]PF_6$, right) with the atom-numbering scheme (50 % probability ellipsoids). Carbon atoms are drawn as spheres for clarity. Selected bond lengths [Å]: $[(P)\text{-}\mathbf{1}]PF_6$: Mo–Mo 2.8011(8), Mo(1)–(μ_3-S(1)) 2.360(2), Mo(1)–(μ-S(2)) 2.327(2), Mo(1)–(μ-S(2 A)) 2.283(2), Mo(1)–P(1) 2.568(2), Mo(1)–P(2) 2.641(2), Mo–Cl 2.487(2); $[(M)\text{-}\mathbf{1}]PF_6$: Mo–Mo 2.7975(9), Mo(1)–(μ_3-S(1)) 2.362(2), Mo(1)–(μ-S(2)) 2.322(2), Mo(1)–(μ-S(2A)) 2.282(2), Mo(1)–P(1) 2.558(2), Mo(1)–P(2) 2.633(2), Mo–Cl 2.485(2).

solved in the noncentrosymmetric space group *R*3 with the Mo_3S_4 core located on a three-fold axis. Deviations from the ideal C_{3v} symmetry are attributable to the specific arrangement of the two phosphorous and one chlorine atoms in the external sites on each Mo atom. In each case, the uniform stereochemistry of the diphosphane ligands was observed with no ambiguity. The refined values of the Flack parameters equal zero for the two absolute structures reported, *P* for $[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]^+$ and *M* for $[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]^+$. Steric interactions upon ligand coordination are thought to be responsible for this unprecedented stereoselectivity in the preparation of compounds of the Mo_3S_4 core type.

The X-ray analysis performed on racemic $[Mo_3CuS_4(dmpe)_3Cl_4]^+$ samples revealed that there was no significant structural rearrangement on going from the trinuclear to the tetranuclear complex.[12] Therefore, one would expect that reaction of cluster $[(P)\text{-}\mathbf{1}]^+$ or $[(M)\text{-}\mathbf{1}]^+$ with CuCl would produce the enantiomerically pure heterodimetallic cuboidal cluster $[(P)\text{-}\mathbf{2}]^+$ or $[(M)\text{-}\mathbf{2}]^+$, respectively.

Subsequent reaction of $[(P)\text{-}\mathbf{1}]^+$ or $[(M)\text{-}\mathbf{1}]^+$ with CuCl proceeded in a similar way to the copper incorporation into the dmpe-containing trinuclear complex to afford only the heterodimetallic cubane-type cluster without changes in the chirality of the trinuclear precursors [Eq. (1) and (2)]:

$$\begin{aligned}&(P)\text{-}[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]^+ + CuCl \rightarrow\\&(P)\text{-}[Mo_3CuS_4\{(R,R)\text{-Me-BPE}\}_3Cl_4]^+\end{aligned}\qquad(1)$$

$$\begin{aligned}&(M)\text{-}[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]^+ + CuCl \rightarrow\\&(M)\text{-}[Mo_3CuS_4\{(S,S)\text{-Me-BPE}\}_3Cl_4]^+\end{aligned}\qquad(2)$$

In the case of $(M)\text{-}[Mo_3CuS_4\{(S,S)\text{-Me-BPE}\}_3Cl_4]^+$ ($[(M)\text{-}\mathbf{2}]^+$), the absolute configuration was determined by X-ray analysis on single crystals and confirmed by CD measurements, as previously detailed for its trinuclear $[(M)\text{-}\mathbf{1}]^+$ precursor (Figure 3). The Cu–Cl distance in $[(M)\text{-}\mathbf{2}]^+$ of 2.18 Å is similar to that found for *rac*-$[Mo_3S_4Cu(dmpe)_3Cl_4]^+$ but significantly longer than that found in other Cu^I halide complexes. The CD spectra of $[(P)\text{-}\mathbf{2}]^+$ and $[(M)\text{-}\mathbf{2}]^+$ are represented in Figure 4, supporting without ambiguity the fact that both cubanes are enantiomers.

The same sequence in the signs of the CD bands, as illustrated in Figures 1 and 4, obtained either for compounds $[(P)\text{-}\mathbf{1}]^+$ and $[(P)\text{-}\mathbf{2}]^+$ or $[(M)\text{-}\mathbf{1}]^+$ and $[(M)\text{-}\mathbf{2}]^+$, can be considered characteristic of the cluster asymmetry, as the chiral diphosphane does not display electronic transitions in the $\lambda = 240$–800 nm interval.

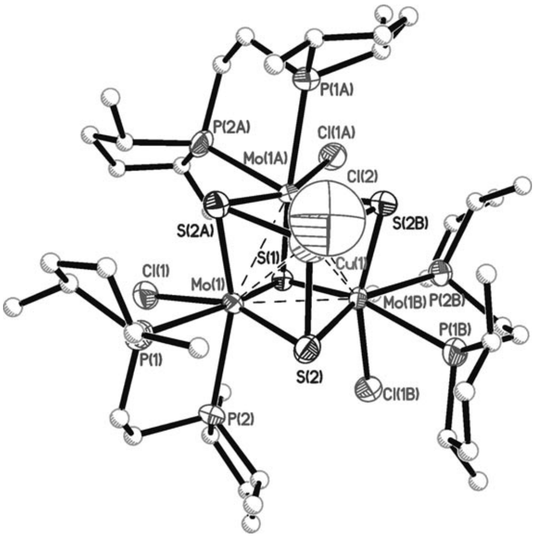


Figure 3. ORTEP plot of $[Mo_3CuS_4\{(S,S)\text{-Me-BPE}\}_3Cl_4]CuCl_2$ ($[(M)\text{-}\mathbf{2}]CuCl_2$) with the atom-numbering scheme (50 % probability ellipsoids). Carbon atoms are drawn as spheres for clarity. Selected bond lengths [Å]: Mo–Mo 2.804(2), Mo(1)–(μ_3-S(1)) 2.352(6), Mo(1)–(μ_3-S(2)) 2.311(5), Mo(1)–(μ_3-S(2A)) 2.368(5), Mo(1)–P(1) 2.590(5), Mo(1)–P(2) 2.632(5), Mo(1)–Cl 2.458(5), Mo(1)–Cu(1) 2.843(3), Cu(1)–(μ_3-S(2)) 2.312(5), Cu(1)–Cl 2.18(1).

With these enantiomerically pure cubane-type clusters in hand, we performed preliminary studies on the activity and selectivity of the enantiomerically pure cubane $[(P)\text{-}\mathbf{2}]^+$ using the intramolecular cyclization of α-diazoketone **3**, as well as the intermolecular cyclopropanation of alkenes (i.e., styrene and 2-phenylpropene) with ethyl diazoacetate, as model catalytic reactions (Tables 1 and 2).[14] In all cases, the

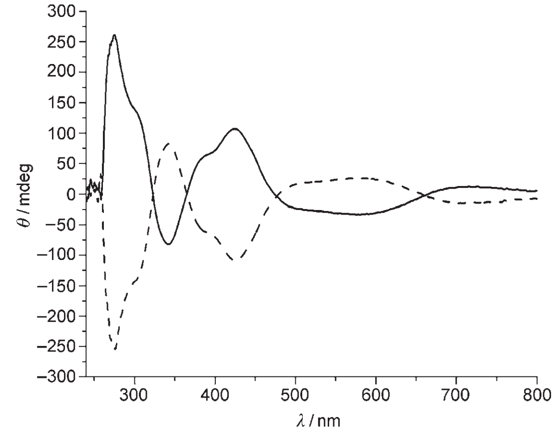


Figure 4. Circular dichroism spectra of $[Mo_3CuS_4\{(R,R)\text{-Me-BPE}\}_3Cl_4]CuCl_2$ ($[(P)\text{-}\mathbf{2}]CuCl_2$, ——) and $[Mo_3CuS_4\{(S,S)\text{-Me-BPE}\}_3Cl_4]CuCl_2$ ($[(M)\text{-}\mathbf{2}]CuCl_2$, – – –) in dichloromethane (1.33×10^{-4} and 1.35×10^{-4} M, respectively) at 25 °C.

cyclopropanation products were obtained in high yields. The diastereoselectivity in the intermolecular cyclopropanation of the alkenes and the enantioselectivity in the inter- and intramolecular processes are not very high. The lower enantioselectivities observed for the cyclopropanation products of the chiral-cluster-catalyzed reactions, in comparison with those produced by copper(I)-containing chiral N-donor ligands, could be due to an inherent disadvantage of the copper-containing cuboidal cluster catalysts.[19] The formation of the presumably electrophilic copper carbene and the preferred approach of the incoming alkene to the copper carbene could mean a reaction can occur when there is not enough steric hindrance between the substituents at the carbene and those at the chiral phosphane, the latter not being coordinated to the copper ion.[20] At this very early point in our studies, we can only speculate that the degree of induction could be raised by a gradual increase of the steric hindrance in the chiral pocket constructed by the chiral diphosphane in the coordination sphere of the catalytically active copper center.

To ascertain that the integrity of the cubane clusters remains after catalysis, the corresponding $^{31}P\{^1H\}$ NMR spectra of $[(P)\text{-}\mathbf{2}]^+$, before and after its involvement in the catalytic cyclopropanation of styrene with ethyl diazoacetate, were recorded. The similarity in signal shifts and intensities, as well as the absence of new signals, provide evidence that the cubane structure remains intact after catalysis. It should also be noted that a systematic UV-visible analysis of compound $[(P)\text{-}\mathbf{2}]^+$, before and after cyclopropanation of styrene, was carried out. In fact, this experiment was extremely useful to quantify the concentration of the catalyst after the ethyl diazoacetate transformation. UV-visible spectra monitored at $\lambda_{max}=474$ and 529 nm did not show any degradation of the cubane complex.

Conclusion

Enantiomerically pure cuboidal complexes, namely (P)-$[Mo_3CuS_4\{(R,R)\text{-Me-BPE}\}_3Cl_4]^+$ ($[(P)\text{-}\mathbf{2}]^+$) or (M)-$[Mo_3CuS_4\{(S,S)\text{-Me-BPE}\}_3Cl_4]^+$ ($[(M)\text{-}\mathbf{2}]^+$) can be readily and diastereoselectively prepared by using the right chiral diphosphanes and the adequate polymeric $\{M_3Q_7X_4\}_n$ phase. Enantiomerically pure clusters containing chiral phosphane ligands and catalytically active centers of the general formula $[M_3M'Q_4(\text{diphosphane})_3X_3L]^+$ could be lead structures for a new series of chiral catalysts. Ongoing studies are being directed at developing more efficient cubane-type catalysts by extending this strategy to other chalcogens or/and catalytically active transition metals, as well as by using them for other catalytic organic transformations.

Experimental Section

General: $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian 300 MHz spectrometer using CD_2Cl_2 as the solvent and are referenced to external 85 % H_3PO_4. Electrospray ionization (ESI) mass spectra were recorded on a Micromass Quattro LC instrument using dichloromethane as the solvent. Circular dichroism measurements were recorded on a JASCO J-810 spectropolarimeter. The sample solutions were prepared in a quartz cuvette of 1 cm path length and measured at 25 °C. UV/Vis measurements were carried out by using a Shimadzu UV-1603 instrument and the samples were prepared in a quartz cuvette of 1 cm path length, and measured at room temperature. The *ee* values for the cyclopropane products were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl) β-cyclodextrin (CDX) column.

All reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. The polymeric $\{Mo_3S_7Cl_4\}_n$ phase and the heterodimetallic $[Mo_3CuS_4(\text{dmpe})_3Cl_4]^+$ complex were prepared according to literature methods.[21,12] The remaining reactants were obtained from commercial sources and used as received. Solvents for use in syntheses were dried and degassed by standard methods before use. Chromatographic work was performed by using silica gel (60 Å).

$[Mo_3S_4\{(R,R)\text{-Me-BPE}\}_3Cl_3]Cl$, $[(P)\text{-}\mathbf{1}]Cl$: This compound was prepared by an excision reaction of the polymeric $\{Mo_3S_7Cl_4\}$ phase (150 mg, 0.229 mmol) with (R,R)-Me-BPE (267 mg, 1.034 mmol) in acetonitrile (20 mL) under reflux. After 48 h, the reaction mixture was filtered, the solvent was removed under vacuum, and the solid was dissolved in dichloromethane. Addition of ether (30 mL) caused the complete precipitation of a green solid (280 mg, 92 %). $^{31}P\{^1H\}$ NMR (121.47 MHz, CD_2Cl_2, 25 °C): $\delta=53.79$ (dd, 3P), 64.77 ppm (dd, 3P) (AA′A″BB′B″ system); UV/Vis (CH_2Cl_2): λ_{max} (ε)=408 (5993.20), 299 nm (12 401.36 $mol^{-1}m^3cm^{-1}$); ESI-MS (30 V): *m*/*z* (%): 1299 (100) $[M]^+$; elemental analysis calcd (%) for $Mo_3S_4Cl_4C_{42}H_{84}P_6$: C 37.85, H 6.36; found: C 37.81, H 6.38.

$[Mo_3S_4\{(S,S)\text{-Me-BPE}\}_3Cl_3]Cl$, $[(M)\text{-}\mathbf{1}]Cl$: This complex was prepared following the procedure described for $[(P)\text{-}\mathbf{1}]Cl$ but using the enantiomerically pure (S,S)-Me-BPE phosphane. Yield: 91 %; $^{31}P\{^1H\}$ NMR (121.47 MHz, CD_2Cl_2, 25 °C): $\delta=53.80$ (dd, 3P), 64.81 ppm (dd, 3P) (AA′A″BB′B″ system); UV/Vis (CH_2Cl_2): λ_{max} (ε)=408 (6827.60), 299 nm (14 165.52 $mol^{-1}m^3cm^{-1}$); ESI-MS (30 V): *m*/*z* (%): 1299 (100) $[M]^+$; elemental analysis calcd (%) for $Mo_3S_4Cl_4C_{42}H_{84}$: C 37.85, H 6.36; found: C 37.84, H 6.47.

$[Mo_3CuS_4\{(R,R)\text{-Me-BPE}\}_3Cl_4]CuCl_2$, $[(P)\text{-}\mathbf{2}]CuCl_2$: Compound $[(P)\text{-}\mathbf{1}]Cl$ (80 mg, 0.060 mmol) and an excess of CuCl (36 mg, 0.364 mmol) were dissolved in dichloromethane (10 mL). The reaction mixture turned red in 5 min and was stirred for 4 h at room temperature. Then, the resulting solution was filtered under an inert atmosphere and evaporated to dryness to yield the desired dark red product (76 mg, 88.5 %). $[\alpha]_D^{20}=$

−8 ($c=0.5$ in $CHCl_3$); $^{31}P\{^1H\}$ NMR (121.47 MHz, CD_2Cl_2, 25 °C): $\delta=61.36$ (d, 3P), 68.40 ppm (d, 3P); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 508 (2044), 311 nm (11207 $mol^{-1}m^3cm^{-1}$); ESI-MS (30 V): *m*/*z* (%): 1396 (100) $[M]^+$; elemental analysis calcd (%) for $Mo_3Cu_2S_4Cl_6C_{42}H_{84}P_6$: C 32.93, H 5.54, S 8.37; found: C 32.96, H 5.56, S 8.19.

$[Mo_3CuS_4\{(S,S)\text{-Me-BPE}\}_3Cl_4]CuCl_2$, $[(M)\text{-}\mathbf{2}]CuCl_2$: This compound was prepared following the procedure described for complex $[(P)\text{-}\mathbf{2}]CuCl_2$ but using $[(M)\text{-}\mathbf{1}]Cl$ as the starting material. Yield: 73 mg (85%). Suitable crystals for X-ray determination for compound $[(M)\text{-}\mathbf{2}]CuCl_2$ were grown by slow diffusion of ether into sample solutions in dichloromethane. $[\alpha]_D^{20}=+8$ ($c=0.5$ in $CHCl_3$); $^{31}P\{^1H\}$ NMR (121.47 MHz, CD_2Cl_2, 25 °C): $\delta=61.32$ (d, 3P), 68.35 ppm (d, 3P); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 508 (2192), 311 nm (11821 $mol^{-1}m^3cm^{-1}$); ESI-MS (30 V): *m*/*z* (%): 1396 (100) $[M]^+$; elemental analysis calcd (%) for $Mo_3Cu_2S_4Cl_6C_{42}H_{84}P_6$: C 32.93, H 5.54, S 8.37; found: C 32.94, H 5.52, S 8.15.

Table 3. Crystallographic data for $[(P)\text{-}\mathbf{1}]PF_6$, $[(M)\text{-}\mathbf{1}]PF_6$, and $[(M)\text{-}\mathbf{2}]CuCl_2$.

	$[(P)\text{-}\mathbf{1}]PF_6$	$[(M)\text{-}\mathbf{1}]PF_6$	$[(M)\text{-}\mathbf{2}]CuCl_2$
empirical formula	$C_{42}H_{84}Mo_3P_7S_4Cl_3F_6$	$C_{42}H_{84}Mo_3P_7S_4Cl_3F_6$	$C_{42}H_{84}Mo_3P_7S_4Cl_6F_6Cu_2$
formula weight	1442.29	1442.29	1530.75
crystal system	trigonal	trigonal	trigonal
a [Å]	15.404(2)	15.3572(4)	14.5248(8)
b [Å]	15.404(2)	15.3572(4)	14.5248(8)
c [Å]	23.058(7)	23.0235(13)	25.103(3)
V [$Å^3$]	4738.4(18)	4702.5(3)	4586.4 (6)
T [K]	293(2)	293(2)	293(2)
space group	*R*3	*R*3	*R*3
Z	3	3	3
$\mu(Mo_{K\alpha})$ [mm^{-1}]	1.068	1.528	1.868
reflections collected	12712	11373	6545
θ range for data collection	1.76 to 29.99°	1.77 to 28.28°	2.29 to 21.98°
unique reflections	5883 ($R_{int}=0.0367$)	4061 ($R_{int}=0.0532$)	2519 ($R_{int}=0.0994$)
goodness-of-fit on F^2	1.063	1.056	1.263
$R1^{[a]}/wR2^{[b]}$	0.0470/0.1230	0.0474/0.1193	0.0710/0.1163
$R1^{[a]}/wR2^{[b]}$ (all data)	0.0596/0.1310	0.0657/0.1277	0.1117/0.1250
residual ρ [$e\,A^{-3}$]	1.570 and −0.512	0.720 and −0.874	0.447 and −0.298

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma F_o$. [b] $wR2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

X-ray data collection and structure refinement: Suitable crystals for X-ray diffraction for compounds $[(P)\text{-}\mathbf{1}]PF_6$ and $[(M)\text{-}\mathbf{1}]PF_6$ were grown by slow diffusion of toluene into a sample solution of the PF_6^- salt in dichloromethane. Replacement of the Cl^- anion in clusters $[(P)\text{-}\mathbf{1}]Cl$ and $[(M)\text{-}\mathbf{1}]Cl$ were carried out by using silica gel chromatography, eluting the product with a saturated solution of KPF_6 in acetone. In the case of complex $[(M)\text{-}\mathbf{2}]CuCl_2$, crystals were grown under nitrogen in a dry box. The data collection was performed on a Bruker Smart CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) in an essentially routine manner. The diffraction frames were integrated by using the SAINT package and corrected for absorption with SADABS.[22,23] The crystal parameters and basic information relating to data collection and structure refinement for the three compounds are summarized in Table 3.

In all three compounds, the positions of the heavy atoms were determined by using direct methods and successive-difference electron-density maps using the SHELXTL 5.10 software package.[24] Difference Fourier maps were carried out to locate the remaining atoms. Refinement was performed by means of the full-matrix least-squares method based on F^2. All atoms were refined anisotropically except for the fluorine atoms in compounds $[(P)\text{-}\mathbf{1}]PF_6$ and $[(M)\text{-}\mathbf{1}]PF_6$ and carbon atoms in compound $[(M)\text{-}\mathbf{2}]CuCl_2$. The positions of all hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms.

CCDC-270138 ($[(P)\text{-}\mathbf{1}]PF_6$), CCDC-270139 ($[(M)\text{-}\mathbf{1}]PF_6$), and CCDC-270140 ($[(M)\text{-}\mathbf{2}]CuCl_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank Generalitat Valenciana (Grants IIARCO/2004/163 and IIARCO/2004/158) and the "Ministerio de Ciencia y Tecnología" (Grant BQU2002-00313) for financial support of this work. The European Cooperation in the Field of Scientific and Technical Research (COST) Action D24 (WG-0008-02) is also gratefully acknowledged.

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Received: July 28, 2005