C3-symmetry Mo3S4 aminophosphino clusters combining three sources of stereogenicity: stereocontrol directed by hydrogen bond interactions and ligand configuration

Carmina Alfonso,a Marta Feliz,b Vicent S. Safonta and Rosa Llusar*a

A diastereoselective synthesis of proline containing aminophosphino cubane-type Mo3S4 clusters, (P)-[Mo3S4Cl2(15R,2R)-PPro]Cl (P)-[Mo3S4Cl2((S,S)-(N,S)-Cl), has been achieved in high yields by reacting the corresponding enantiomerically pure PPro (S) and (S)-2-(diphenylphosphino)ethyl|pyrrolidine ligands with the Mo3S4Cl4(PPPh3)2H2O complex. Circular dichroism, nuclear magnetic resonance and X-ray techniques confirm that the (P)-[Mo3S4Cl2((1,R)-Cl and (P)-[Mo3S4Cl2((S,S)-(N,S)-Cl] Cl cluster cations are diastereoisomers which combine three sources of stereogenicity provided by the cluster framework, one carbon atom of the aminophosphine ligand and the nitrogen stereogenic center. The higher stability of the (P)-[Mo3S4Cl2] Cl cation is due to stabilizing vicinal Cl⋯-HN interactions as well as due to the cis-fused conformation of the bicyclic system formed upon coordination of the aminophosphine ligand.

Introduction

One of the most intriguing aspects in the chemistry of transition metal clusters concerns their potential as selective catalysts beautifully exemplified in the specificity of some enzymes.1,2 In general, enantioselectivities using cluster-based chiral catalysts are low in comparison with mononuclear catalysts although evidence exists on the strong chiral induction by extended to tungsten and selenium as well as to other optically pure diphosphines.9–11 All these complexes combine the cluster framework chirality with that of the diphosphine ligand. In addition, these trimetallic Mo3S4 compounds can act as metalloligands for a second transition metal to afford catalytically active chiral Mo3S4Cu clusters with moderate enantioselection in cyclopropanation reactions while preserving the absolute configuration of the cluster framework.8

Motivated by the important role of the NH group in catalysis, we decided to explore synthetic routes aimed to obtain optically pure aminophosphine derivatives of the Mo3S4 cluster core.12 For that, we have chosen commercially available chiral aminophosphines derived from (R) and (S)-proline, whose structures are depicted in Fig. 2. The reaction outcome

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References

invariably leads to \( \{P\} \)-diastereoisomers unlike the results obtained with diphosphines. To rationalize this unexpected result, theoretical calculations on the relative energies among different stereoisomers have been undertaken.

**Results and discussion**

**Synthesis and structure**

The molecular \( \text{Mo}_3\text{S}_4\text{Cl}_4(\text{PPh}_3)_3(\text{H}_2\text{O})_2 \) precursor has been successfully employed for the preparation of \([\text{Mo}_3\text{S}_4\text{Cl}_3(\text{diamino})_3]^{+}\) and \([\text{Mo}_3\text{S}_4\text{Cl}_3(\text{diphosphino})_3]^{+}\) cluster complexes.\(^5,13\) The reaction between \( \text{Mo}_3\text{S}_4\text{Cl}_4(\text{PPh}_3)_3(\text{H}_2\text{O})_2 \) with stoichiometric amounts of the aminophosphine ligand \((\text{R})\)-PPro or its enantiomer, \((\text{S})\)-PPro, leads to the enantiopure cluster complexes \([\text{Mo}_3\text{S}_4\text{Cl}_3((\text{1S},\text{2R})\text{-PPro})_3]\)Cl (m, 85% yields, according to eqn (1), where PPro is noted as its \((\text{R})\)- or \((\text{S})\)-enantiomer, indistinctively. Structural studies show that upon N-coordination, the nitrogen atom of the pyrrolidine ring becomes stereogenic and invariably adopts an S conformation, as discussed next.

\[
\text{Mo}_3\text{S}_4\text{Cl}_4(\text{PPh}_3)_3(\text{H}_2\text{O})_2 + 3\text{PPro} \rightarrow [\text{Mo}_3\text{S}_4\text{Cl}_3(\text{PPro})_3]\text{Cl} + 3\text{PPh}_3 + 2\text{H}_2\text{O} \tag{1}
\]

The reaction products with both \((\text{R})\)-PPro, and \((\text{S})\)-PPro show one peak centered at 1330 m/z associated with the \([\text{Mo}_3\text{S}_4\text{Cl}_3(\text{PPro})_3]^{+}\) cation on the basis of the \(m/z\) value and its characteristic isotopic pattern. However, there are small differences between the chemical shifts of the unique peak observed in the \(^{31}\text{P}\)(\(^1\text{H}\)) NMR spectra of the \([\text{Mo-}\{\text{S}_N,\text{R}_C\}]^{+}\) (32.3 ppm) and \([\text{Mo-}\{\text{S}_N,\text{S}_C\}]^{+}\) (32.1 ppm) complexes and those assigned to three equivalent phosphorus atoms. These differences indicate that these two cluster cations are not enantiomers, a conclusion that was supported by circular dichroism (CD) spectroscopy. Fig. 3 shows the CD spectra of sample solutions of the chlorido salts of the \([\text{Mo-}\{\text{S}_N,\text{R}_C\}]\)Cl (black line) and \([\text{Mo-}\{\text{S}_N,\text{S}_C\}]\)Cl (red line) complexes.

![Fig. 1] Absolute configurations of the \(\{P\}\) (left) and \(\{M\}\) (right) \(\text{Mo}_3\text{S}_4\) diastereomers. The \(\{P\}\) symbol refers to a clockwise sense of rotation of the chlorine ligands around the threefold axis with the capping sulphur pointing towards the viewer. The \(\{M\}\) symbol refers to the anticlockwise rotation.

![Fig. 2] Structure of \((\text{R})\)-2-\{(diphenylphosphino)methyl\}pyrrolidine \((\text{R})\)-PPro, left) and \((\text{S})\)-2-\{(diphenylphosphino)methyl\}pyrrolidine \((\text{S})\)-PPro, right).

![Fig. 3] CD spectra of \([\text{Mo-}\{\text{S}_N,\text{R}_C\}]\)Cl (black line) and \([\text{Mo-}\{\text{S}_N,\text{S}_C\}]\)Cl (red line) complexes.
around 255–260 nm shows a red shift with regard to that of the free aminophosphine ligand (220 nm) and opposite signs. The most intense bands registered for both complexes below 250 nm have the same sign and can be tentatively assigned to transitions between orbitals with a marked contribution from the $S$ nitrogen stereogenic center.\textsuperscript{14,15} The specific rotation is considerable for both analogues diphosphino complexes, which show values from approximately one order of magnitude lower than that of the free aminophosphine ligand (220 nm) and opposite signs. The most intense bands registered for both complexes below 250 nm have the same sign and can be tentatively assigned to transitions between orbitals with a marked contribution from the $S$ nitrogen stereogenic center.\textsuperscript{14,15} The specific rotation is considerably diminished for both analogues diphosphino complexes, which show values from approximately one order of magnitude lower than that of the free aminophosphine ligand (220 nm) and opposite signs.

The absolute configuration of the $[\text{Mo}(S,N,R,C)]^+$ and $[\text{Mo}(S,N,S,C)]^+$ cations was determined by X-ray crystallography from their tetrafluoroborate salts. Both structures are solved in the non-centrosymmetric $P2_13$ cubic group with Flack parameters close to zero, and the Mo$_3$S$_4$ cluster core located on a $C_1$ axis passing through the capping sulphur, the absolute configuration being $P$ for both $[\text{Mo}(S,N,R,C)]^+$ and $[\text{Mo}(S,N,S,C)]^+$ cations. An ORTEP representation of the two cations is depicted in Fig. 4. The stereochemistry of the PPro aminophosphine ligand as $R$ for $(P)$-$[\text{Mo}(S,N,R,C)]^+$ and $S$ for $(P)$-$[\text{Mo}(S,N,S,C)]^+$ could be established with no ambiguity. X-ray confirms that these $(P)$-$[\text{Mo}(S,N,R,C)]^+$ and $(P)$-$[\text{Mo}(S,N,S,C)]^+$ cluster cations are diastereoisomers that combine the chirality ($R$ or $S$) of the PPro aminophosphine ligand with that of the cluster framework. In addition, the pyrrolidine ring can adopt two conformations upon $N$-coordination that allow the stereogenic nitrogen atom to be $R$ or $S$ ($S$ in our case) and the concomitant introduction of a third source of stereogenicity.

Table 1 lists the most relevant bond distances for $(P)$-$[\text{Mo}(S,N,R,C)]^+$ and $(P)$-$[\text{Mo}(S,N,S,C)]^+$ together with those of a closely related aminophosphino complex. The interatomic Mo–Mo and Mo–$S$ distances follow the tendencies observed for other Mo$_3$S$_4$ cluster compounds.\textsuperscript{10,16,17} Each molybdenum atom in $(P)$-$[\text{Mo}(S,N,R,C)]^+$ and $(P)$-$[\text{Mo}(S,N,S,C)]^+$ is in a pseudo-octahedral environment defined by three sulphur atoms, one chlorine atom, and the nitrogen and phosphorus atoms of the aminophosphine ligand, where the phosphorus atom is located trans to the capping sulphur. Such preferential spatial disposition of the aminophosphine ligand when coordinated to cuboidal Mo$_3$S$_4$ cluster units is not unprecedented, and considerably diminishes the number of potential stereoisomers, 

<table>
<thead>
<tr>
<th>Distance$^a$ (Å)</th>
<th>$(P)$-$[\text{Mo}(S,N,R,C)]\text{BF}_4$</th>
<th>$(P)$-$[\text{Mo}(S,N,S,C)]\text{BF}_4$</th>
<th>$[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{edpp})] \text{BPh}_4$</th>
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<tr>
<td>Mo–Mo</td>
<td>2.752(1)</td>
<td>2.757(1)</td>
<td>2.746(3)</td>
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<td>Mo–($\mu_1$)–$S$</td>
<td>2.364(3)</td>
<td>2.353(3)</td>
<td>2.361(3)</td>
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<tr>
<td>Mo–($\mu$–$S$)$^+$</td>
<td>2.277(2)</td>
<td>2.293(2)</td>
<td>2.286(3)</td>
</tr>
<tr>
<td>Mo–$P$</td>
<td>2.297(2)</td>
<td>2.294(2)</td>
<td>2.296(3)</td>
</tr>
<tr>
<td>Mo–$R$</td>
<td>2.547(2)</td>
<td>2.550(2)</td>
<td>2.541(3)</td>
</tr>
<tr>
<td>Mo–$N$</td>
<td>2.300(7)</td>
<td>2.289(7)</td>
<td>2.273(3)</td>
</tr>
<tr>
<td>Mo–$Cl$</td>
<td>2.461(2)</td>
<td>2.484(2)</td>
<td>2.462(3)</td>
</tr>
<tr>
<td>Dihedral $C_1$–$N$–$C_2$–$C_4$</td>
<td>11.269$^c$</td>
<td>96.860$^c$</td>
<td></td>
</tr>
<tr>
<td>Dihedral $C_3$–$C_2$–$N$–Mo</td>
<td>179.416$^c$</td>
<td>14.402$^c$</td>
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</table>

$^a$ Standard deviations for averaged values are given in brackets. $^b$ Data taken from ref. 6. $^c$ Distance trans to the Mo–$N$ bond. $^d$ Distance trans to the Mo–Cl bond.
as also observed in W3S4 clusters. Coordination of the chiral PPro ligand to the metal results in the formation of a stereogenic nitrogen center incorporated into a [3.3.0] bicyclic system (see Fig. 4 and 5a). This bicyclic system adopts a cis-fused conformation in the \( \left[ \text{Mo}\left(\text{S}_{3}\text{N}_{2}\text{C}_{2}\right)\right]^{+} \) complex, which is known to be thermodynamically more stable than the trans-fused structure by analogy to bicyclooctanes. The calculated dihedral angles \( \text{C}_{5}-\text{N}-\text{C}_{2}-\text{C}_{1} \) and \( \text{C}_{1}-\text{C}_{2}-\text{N}-\text{Mo} \), see Table 1) confirm the cis conformation of the bicyclic system with values of 96.86° and 14.40° respectively. In the case of the \( \left[ \text{Mo}\left(\text{S}_{3}\text{N}_{2}\text{C}_{2}\right)\right]^{+} \) complex, both rings lie nearly in the same plane with dihedral angles of 11.269° and 179.416°. As a result, a selective formation of an \( S \) configuration at each stereogenic nitrogen center takes place for both \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) and \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) diastereoisomers. Note that once the stereochemistry of a nitrogen center is defined, that of the other two nitrogen atoms is equally fixed. The interatomic distances in both clusters are similar to those observed for \( \left[ \text{Mo}\text{S}_{3}\text{Cl}_{4}\text{PPro}\right]^{2+} \) \( \text{BPh}_{4}^{-} \) (edpp = (2-aminoethyl)diphenylphosphine), as can be seen in Table 1. The small deviations among \( \mu-S \) bond distances in the three complexes suggest a similar trans influence of the nitrogen vs. the chlorine atoms in these compounds in contrast with the differences found in the corresponding \( \left[ \text{Mo}\text{S}_{3}\text{Cl}_{4}(\text{diphosphine})\right]^{+} \) cluster cations.

The chlorine and nitrogen atoms in \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) and \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) are found on the same side of a trimetallic plane, as emphasized in Fig. 5b, allowing multiple Cl--HN interactions. Short Cl--HN interactions are observed in \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) between the chlorine atom coordinated to one metal and the hydrogen atom of the amino group coordinated to the adjacent metal, resulting in a vicinal Cl--HN bond length of 2.379 Å (see Fig. 5a) vs. the 2.941 Å found in \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \). Similar values, ranging from 2.436 to 2.995 Å, are reported for the aminophosphine \( \left[ \text{Mo}\text{S}_{3}\text{Cl}_{4}\text{PPro}\right]^{2+} \) cluster analogue. These vicinal Cl--HN interactions are expected to confer to the \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) cation an additional stability. On the other hand, the Cl--N distances associated with the geminal Cl--HN interactions, in which the NH and the Cl belong to the coordination sphere of the same metal center of the cluster unit, (3.055 Å for \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \), and 3.170 Å for \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) are slightly longer than the corresponding distance reported for the \( \left[ \text{Mo}\text{S}_{3}\text{Cl}_{4}\text{PPro}\right]^{2+} \) cation (3.021 Å). This confirms the similar chelating mode for both edpp and \( \text{P} \)- or \( \text{S} \)-PPro aminophosphines.

To summarize, the reaction between \( \text{Mo}\text{S}_{3}\text{Cl}_{4}\text{PPh}_{3}(\text{H}_{2}\text{O})_{3} \) and \( \text{P} \)-PPro or \( \text{S} \)-PPro is diastereoselective towards the \( \left( \text{P}\right)\text{Mo}\text{S}_{3}\text{Cl}_{4}(\text{PPh}_{3})e \) configuration with the preservation of the stereochemistry of the aminophosphine and formation of an \( S \) stereogenic nitrogen center. This result is unexpected based on our previous observations on diphosphino \( \text{Mo}\text{S}_{3}\text{Cl}_{4} \) clusters that showed the stereoselective formation of the \( \left( \text{P}\right)\text{M}_{3}\text{Q}_{4} \) \( \left( \text{M} = \text{Mo}, \text{W} \right) \) configuration upon coordination of the enantiomerically pure \( \left( \text{P}\right) \)-diphosphine, and the \( \left( \text{M}\right) \)-diphosphine configuration when the \( \left( \text{S},\text{S}\right) \)-ligand was reacted instead. In both cases, the chirality of the diphosphine was preserved. In order to explain the preferential diastereoselective formation of \( \left[ \text{Mo}\text{S}_{3}\text{Cl}_{4}(\text{PPro})_{3}\right]^{2+} \) complexes, DFT calculations were performed to study the differences between relative energies among the four possible isomers.

**Theoretical calculations**

Four diastereoisomers \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+}, \left[ \text{M}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+}, \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) and \( \left[ \text{M}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) have been taken as cluster models for the B3LYP calculations. The initial structural parameters of \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) and \( \left[ \text{P}\left(\text{Mo}\left(\text{S}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) cations have been extracted from crystallographic data, whereas the \( \left( \text{M}\right) \)-isomers have been built by changing the chlorine and aminophosphine orientation, but preserving the configuration of the stereogenic centers. The optimized bond

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Fig. 5 ORTEP representations of the \( \left[ \text{P}\left(\text{Mo}\left(\text{S}_{3}\text{N}_{2}\text{C}_{2}\right)\right)\right]^{+} \) complex. Phenyl groups are omitted. (a) Hydrogen atoms have been deleted for simplicity, except for those bonded to stereogenic centers. (b) Carbon and hydrogen atoms are omitted for clarity.
Table 2  Theoretically averaged bond distances, dihedral angles, and relative energies for compounds (P)[Mo–(S₅R₃)]⁺, (P)[Mo–(S₅S₅C)]⁺, (M)[Mo–(S₅R₃)]⁺ and (M)[Mo–(S₅S₅C)]⁺.

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>(P)[Mo–(S₅R₃)]⁺</th>
<th>(P)[Mo–(S₅S₅C)]⁺</th>
<th>(M)[Mo–(S₅R₃)]⁺</th>
<th>(M)[Mo–(S₅S₅C)]⁺</th>
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<tr>
<td>Mo–Mo</td>
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<td>2.805</td>
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<td>Mo–(μ₁−S)</td>
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<tr>
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<td>Mo–P</td>
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<td>2.633</td>
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<td>Mo–N</td>
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<td>Mo–Cl</td>
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<td>2.544</td>
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<tr>
<td>Dihedral C₃−N–C₂–C₁</td>
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<td>95.723°</td>
<td>24.866°</td>
<td>81.800°</td>
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<td>Energies (kcal mol⁻¹)</td>
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<td>0.0</td>
<td>20.2</td>
<td>20.0</td>
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</table>

a  Distance trans to the Mo–N bond. b  Distance trans to the Mo–Cl bond.

Conclusions

Two cluster complexes [Mo₅S₅Cl₃(PPro)₃]Cl have been prepared in high yields by reacting stoichiometric amounts of the (R)- and (S)-PPro ligands with the Mo₅S₅Cl₃[PPh₃]₃(H₂O)₂ complex. ³¹P{¹H} NMR and CD analyses suggest that both cluster compounds are diastereomeric. Single-crystal X-ray confirms the preferential disposition of the chiral PPro aminophosphine ligand once coordinated to the trinuclear backbone to allow two (P)-stereoisomers, namely (P)[Mo–(S₅R₃)]Cl and (P)[Mo–(S₅S₅C)]Cl, with the preservation of the stereochemistry of the aminophosphine and the selective formation of a stereogenic nitrogen center with S configuration. These results confirm the presence of three sources of stereogenicity integrated in each cluster compound. A short stabilizing Cl···H distance has been found in the (P)[Mo–(S₅R₃)]Cl complex from experimental and B3LYP methods. The calculated relative energies of the four possible (P)- and (M)[Mo₅S₅Cl₃(PPro)₃]⁺ stereoisomers support the thermodynamic preference of the formation of (P)-isomers. The cis-fused conformation of the molydbenum–PPro bicyclic system observed in (P)[Mo–(S₅S₅C)]⁺ confines some additional stabilization to the system, and the stabilizing effect of the Cl···H interaction has been supported by electronic population (NBO) and topological...
(ELF) analyses. These new aminophosphine trimetallic complexes which combine three sources of stereogenicity constitute an ideal “proof of concept” system to evidence metal cluster catalysis.

Experimental section

General remarks

Precursor Mo₅S₄Cl₄(PPh)₃(THF) was prepared according to literature methods.¹⁹,²⁰ ESI-MS spectra were recorded with a Quattro LC (quadrupole–hexapole–quadrupole) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, UK). The cone voltage was set at 20 V unless otherwise stated using CH₃CN as the mobile phase.

Preparation of (P)[Mo-(S₆R₆)]Cl₆

To a green suspension of [Mo₅S₄Cl₄(PPh)₃(solvent)] (57.0 mg, 0.0423 mmol) in ethanol (5 mL) were added 3.2 equivalents of enantiomerically pure aminophosphine (S)-2-[(diphenylphosphino)methyl]pyrrolidine, (S)-PPro, (36.5 mg, 0.1355 mmol) under a nitrogen atmosphere. After 3 hours, the green solution was concentrated under reduced pressure and the desired product was precipitated by adding hexane. Finally, the green solid was concentrated under reduced pressure and the desired product was precipitated by adding hexane. Finally, the green solid was washed with hexane to yield 46.7 mg (81%).

¹³¹P [¹H] NMR (121 MHz, CD₂Cl₂) δ (ppm): 32.3 (s, 3P). ESI-MS (20 V, CH₃CN) m/z: 1330 (M⁺).

Preparation of (P)[Mo-(S₆R₆)]Cl₆

This compound was prepared and purified following the procedure described for (P)[Mo-(S₆R₆)]Cl₆, but using the enantiomerically pure aminophosphine (S)-2-[(diphenylphosphino)methyl]pyrrolidine, (S)-PPro. A green solid was obtained (89%).

¹³¹P [¹H] NMR (121 MHz, CD₂Cl₂) δ (ppm): 32.1 (s, 3P). ESI-MS (20 V, CH₃CN) m/z: 1330 (M⁺).

X-ray data collection and structure refinement

Diffraction data for enantiomerically pure compounds (P)[Mo-(S₆R₆)]BF₄ and (P)[Mo-(S₆R₆)]BF₄ were collected on an Agilent Supernova diffractometer equipped with an Atlas CCD detector using Mo Kα radiation (λ = 0.71073 Å). Absorption corrections based on the multiscan method were applied.²¹,²² Structures were solved using direct methods in SHELXS-13 and refined with full matrix method based on F² using the OLEX software package.²³,²⁴ Suitable crystals for X-ray studies of (P)[Mo-(S₆R₆)]BF₄ and (P)[Mo-(S₆R₆)]BF₄ were grown by slow diffusion of toluene into a sample solution in CH₂Cl₂.

Anion exchange, Cl⁻ by BF₄⁻, was carried out by elution with a NaBF₄ solution in acetone after absorption of a CH₂Cl₂ solution of (P)[Mo-(S₆R₆)]BF₄ or (P)[Mo-(S₆R₆)]BF₄ in a silica gel column. Crystal data for (P)[Mo-(S₆R₆)]BF₄: C₁₁H₁₅BF₄Cl(P₉O₅S₄P₅)₃, M = 1417.15, cubic, space group P2₁₃ (no. 198), a = b = c = 19.0728 (2) Å, α = β = γ = 90.00°, V = 6938.1 (2) Å³, T = 200.00 (10) K, Z = 4, µ = 0.881 mm⁻¹. Reflections (collected/unique): 14 383/3964 (Rint = 0.0309). The final refinement converged with R₁ = 0.0484 and wR₂ = 0.1535 for all reflections, GOF = 1.158, max/min residual electron density 0.91/−0.45 e Å⁻³. Flack parameter: −0.07 (2). Anisotropic displacement parameters were refined for all non-H atoms. After reaching convergence large solvent voids appear in the structure. However, the absence of electron density in the voids makes any model meaningless.

Crystal data for (P)[Mo-(S₆R₆)]BF₄: C₁₁H₁₅BF₄Cl(P₉O₅S₄P₅)₃, M = 1509.27, cubic, space group P2₁₃ (no. 198), a = b = c = 19.5506 (3) Å, α = β = γ = 90.00°, V = 7472.7 (19) Å³, T = 200.00 (14) K, Z = 4, µ = 0.832 mm⁻¹. Reflections (collected/unique): 28 631/6384 (Rint = 0.0471). The final refinement converged with R₁ = 0.0694 and wR₂ = 0.1184 for all reflections, GOF = 1.164, max/min residual electron density 0.80/−0.53 e Å⁻³. Flack parameter: −0.03 (2). Anisotropic displacement parameters were refined for all non-H atoms.

Computational details

All geometry optimizations and NBO calculations were performed with the Gaussian09 program suite.²⁵ Density functional theory was applied with the Becke hybrid B3LYP functional.²⁶–²⁸ The double-ξ pseudo-orbital basis set LanL2DZ, in which all atoms are represented by the relativistic core LanL2 potential of Los Alamos, was used. The geometry optimizations have been performed in the gas phase without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum has been reached. The ELF analysis has been performed by means of the TopMod package,²⁹ considering a cubical grid a step size smaller than 0.05 Bohr, on the wavefunction obtained at the B3LYP/3-21G//B3LYP/LanL2DZ theoretical level.

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References


