Note

Insight into the mechanism of diazocompounds transformation catalyzed by hetero cuboidal clusters [Mo$_3$CuQ$_4$(MeBPE)$_3$X$_4$]$^+$, (Q = S, Se; X = Cl, Br): The catalytically active species

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In memory of Professor F. Albert Cotton who passed away on February 20, 2007 and in recognition of his valuable and enormous contributions to the chemical sciences.

Abstract

Two enantiomerically pure trinuclear compounds of formula (*P*)-[Mo$_3$S$_4${(*R,R*)-Me–BPE}$_3$Br$_3$]Br and (*P*)-[Mo$_3$Se$_4${(*R,R*)-Me–BPE}$_3$Cl$_3$]Cl, (*P*)-**1b.Br** and (*P*)-**1c.Cl**, respectively, have been synthesized in a good yield and a stereospecific manner by excision of polymeric [Mo$_3$Q$_7$X$_4$]$_n$ (Q = S or Se, X = Cl or Br) phases with (*R,R*)-Me–BPE{1,2-bis[(2*R*,5*R*)-2,5-(dimethylphospholan-1-yl)]ethane}. They have been transformed into chiral hetereo cuboidal compounds [Mo$_3$S$_4${(*R,R*)-Me–BPE}$_3$Br$_3$]PF$_6$, (*P*)-**2b.PF$_6$**, and [Mo$_3$Se$_4${(*R,R*)-Me–BPE}$_3$Cl$_3$]PF$_6$, (*P*)-**2c.PF$_6$**, by reaction with copper salts. All these compounds have been characterized by ^{31}P NMR, IR, UV–Vis, mass spectrometry, elemental analysis, and chiral dichroism. The catalytic potential of tetranuclear cuboidal compounds has been assessed in the paradigm intermolecular cyclopropanation reaction of styrene with ethyl diazoacetate. Results are compared with those obtained for the analogue [Mo$_3$S$_4${(*R,R*)-Me–BPE}$_3$Cl$_3$]PF$_6$, (*P*)-**2a.PF$_6$**. The catalytic data demonstrate that the Se derivative (*P*)-**2c.PF$_6$** is less reactive than the S analogues, but it leads to a similar product distribution as the sulfide analogue (*P*)-**2a.PF$_6$**. By contrast, exchange of chlorine by the bulky bromine gives rise to a catalyst which makes the carbene dimerization more competitive. These data agree with temporal breaking of one of the Cu–Q bonds to generate an active catalytic species.
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1. Introduction

The last decade has witnessed a great interest in the chemistry of heterodimetallic clusters with cubane-type structures, M$_3$M′Q$_4$ (where M = Mo, W; Q = S, Se and M′ is a transition metal) because of their numerous and significant potential applications [1] in various fields. F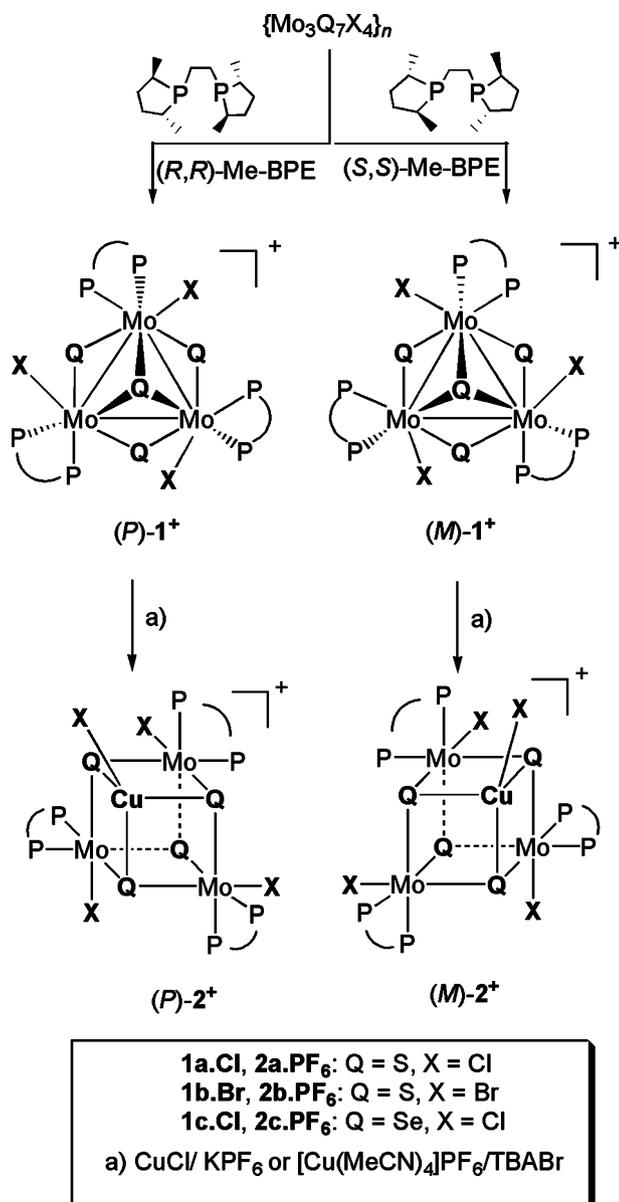or example, metal sulphur clusters are used as enzymatic models in bioinorganic issues [2]. Other important features of their chemistry relate to the potential of species such as Mo$_3$M′S$_4$ (M′ = Co, Ni) clusters as molecular models for the active sites of heterogeneous Co/MoS$_2$ or Ni/MoS$_2$ industrial catalysts [3]. In addition, [M$_3$CuQ$_4${(dmpe)$_3$X$_4$]$^+$ cluster cations (M = Mo, W; X = Cl, Br; dmpe = 1,2-bis(dimethylphosphine)ethane; Q = S, Se) have shown nonlinear properties as optical limiters [4].

Among the many non-aqueous routes to M$_3$M′Q$_4$ compounds, we have developed one which begins with cluster excision from polymeric {Mo$_3$Q$_7$X$_4$}$_n$ phases with diphosphanes [4,5]. The trinuclear [Mo$_3$Q$_4$(diphosphane)$_3$X$_3$]$^+$ cluster generated possesses C_3-symmetry, with the Mo$_3$Q$_4$

core having one phosphorus atom from the diphosphine ligand *trans* to the capping sulphur atom and the other one *trans* to the bridging sulphur atom. Such stereospecific rearrangement around the Mo_3S_4 core results in structures with backbone chirality, which has been recently exploited for the synthesis of enantiomerically pure (*P*)- and (*M*)-[$Mo_3S_4\{(R,R)$-Me–BPE$\}_3Cl_3$]Cl salts ((*R,R*)-Me–BPE = (+)-1,2-bis[(2R,5R)-2,5-(dimethylphospholan-1-yl)]ethane, **1a.Cl** in Scheme 1) by excision of the polymeric {Mo_3-$S_7Cl_4\}_n$ phase with (*R,R*)-Me–BPE and (*S,S*)-Me–BPE, respectively [6]. These two chiral compounds were employed as precursors for enantiomerically pure heterodimetallic salts of formula (*P*)-[$Mo_3CuS_4\{(R,R)$-Me–BPE$\}_3$- Cl_4]PF_6, (*P*)-**2a.PF$_6$**, and (*M*)-[$Mo_3S_4\{(S,S)$-Me–BPE$\}_3$- Cl_4]PF_6, (*M*)-**2a.PF$_6$**, as illustrated in Scheme 1.

The application of compounds containing the Mo_3M' Q_4 cuboidal cluster as catalysts for organic reactions is largely unexplored. Exceptions to these are the palladium- and nickel-based systems, which catalyse the addition of methanol or carboxylic acids to electron-deficient alkynes and the intramolecular hydroamination of aminoalkynes, as well as ruthenium clusters explored as effective catalysts for the N–N cleavage of hydrazines [7]. In this context, we have recently reported that (*P*)- and (*M*)-**2a.PF$_6$** are active catalysts for the intramolecular and intermolecular cyclopropanation reactions of diazocompounds, however their enantioselectivity was found to be low. The mechanism of the diazo transformation catalysed by **2a.PF$_6$** is still not clear. Although the cluster **2a$^+$** is recovered unchanged after completion of the catalytic process, there are reasonable doubts that it is a catalytic active species. In fact, it is difficult to explain how the diazocompound can coordinate to the copper without halogen or chalcogen decoordination.

The synthetic strategy for the preparation of chiral heterodimetallic compounds **2a.PF$_6$** is efficient and stereospecific, therefore, it could be extended to the synthesis of other analogues. To obtain further insight into the role of the cubane cluster in the transformation of diazocompounds, we carried out the synthesis of the bromine and selenium analogues of **2a**, such as **2b.PF$_6$** and **2c.PF$_6$** (Scheme 1) and used them in the classic reaction of cyclopropanation of styrene with ethyl diazoacetate. The catalytic results demonstrate that the presence of a bulkier chalcogen decreases the reactivity of the catalyst, but it leads to a similar product distribution to **2a.PF$_6$**. By contrast, the exchange of the halogen by the bulky bromine gives rise to a catalyst which makes the carbene dimerization more competitive. In all the cases, the cyclopropanes *E/Z* isomer ratio is close to 2.5/1.0 and the enantioselectivity is still low.

Scheme 1.

2. Experimental

2.1. General data

All reactions were carried out under nitrogen atmosphere using standard Schlenck techniques. The polymeric phases {$Mo_3S_7X_4\}_n$ (X = Cl, Br) [8] and the selenium analogue polymeric phase {$Mo_3Se_7Cl_4\}_n$ [8b] were prepared according to methods found in the literature. The chiral trinuclear and hetero cuboidal clusters (*P*)-**1a** and (*P*)-**2a** were prepared as described [6]. The remaining reactants were obtained from commercial sources and used as received. Solvents for synthesis were dried and degassed by standard methods before use.

^{31}P{^{1}H} NMR spectra were recorded on a Varian 300 MHz spectrometer, using CD_2Cl_2 as a solvent and are referenced to external 85% H_3PO_4. Electrospray mass spectra were recorded on a Micromass Quattro LC instrument using dichloromethane as solvent. Circular dichroism measurements were recorded on a JASCO J-810

spectropolarimeter. The sample solutions were prepared in a 1 cm path length quartz cuvette and measured at 25 °C. UV–Vis measurements were carried out in a Shimadzu UV-1603 instrument and the samples were prepared in a 1-cm path length quartz cuvette, and measured at room temperature. Column chromatography was carried out using silica gel (60 Å).

2.2. Preparation of (P)-[Mo₃S₄((R,R)-Me–BPE)₃Br₃](Br) (1b)

The molecular compound [TBA]$_2$[Mo$_3$S$_7$Br$_6$] (0.150 g, 0.102 mmol), where TBA = tetrabutylammonium was reacted with (R,R)-Me–BPE (0.118 g, 0.457 mmol) in CH$_3$CN (20 mL) under refluxing conditions for 24 h. The green solution was filtered to remove a small amount of undissolved material. The filtrate was concentrated and then ether was added to form a precipitate. The green solid was washed with 10 mL of benzene, followed by 30 mL of a mixture of toluene:acetone (95:5), and finally with ether to yield 0.107 g (70%) of 1b: ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.44 MHz) δ: 49.31 (dd, 3P), 62.62 (dd, 3P) (second order system AA′A″BB′B″). IR (cm^{-1}, KBr): 2926 (i), 2864 (i), 953 (i), 1452 (i), 1407 (m), 1067 (m), 921 (d), 694 (m), 626 (m), 459 (d). UV–Vis (nm, CH$_2$Cl$_2$): 632, 394, 343, 289. ESI-MS (CH$_3$CN, 80 V): m/z (%) = 1431 (100) [M$^+$]. Anal. Calc. Mo$_3$Br$_4$S$_4$C$_{42}$H$_{84}$P$_6$: C, 33.39; H, 5.62. Found: C, 33.15; H, 5.41%.

2.3. Preparation of (P)-[Mo₃CuS₄((R,R)-Me–BPE)₃Br₄]PF₆ (2b)

This cluster was prepared following a similar procedure to that of (P)-2a [6] but dissolving [Mo$_3$S$_4$((R,R)-Me–BPE)$_3$Br$_3$]Br (0.080 g, 0.060 mmol) and TBABr (0.030 g, 0.086 mmol) in the presence of an excess of [Cu-(MeCN)$_4$]PF$_6$ (0.112 g, 0.303 mmol) in 20 mL of THF under nitrogen. After refluxing the reaction for 24 h, unreacted solid [Cu(MeCN)$_4$]PF$_6$ was separated by filtration and the desired product was precipitated by addition of ether. The precipitated was filtered off, redisolved in CH$_2$Cl$_2$ and adsorbed in a silica gel column. The column was first washed with CH$_2$Cl$_2$ and then eluted with a 2 M KPF$_6$ solution in acetone, affording a red solution. The solution was taken to dryness, redissolved in 15 mL of CH$_2$Cl$_2$ and filtered in order to eliminate the insoluble KBr and KPF$_6$ inorganic salts. Remaining TBABr salt was removed by several washing with water (4 × 15 mL). The dichloromethane phase was dried over MgSO$_4$ and the resulting solution was taken to dryness to yield 0.050 g (73%) of 2b as a red solid: ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.44 MHz) δ: 30.15 (d, 3P), 87.3 (d, 3P). IR (cm^{-1}, KBr): 1419 (i), 940 (i), 840 (i, P–F), 558 (i, P–F), 441 (d), 420 (d), 358 (d). UV–Vis (nm, CH$_2$Cl$_2$): 603 (b), 441 (b), 331 (b), 285 (b). ESI-EM (CH$_2$Cl$_2$, 85 V) m/z: 1514 (M$^+$). Anal. Calc. Mo$_3$Br$_4$CuS$_4$P$_7$F$_6$C$_{42}$H$_{84}$: C, 30.50; H, 5.13. Found: C, 31.12; H, 5.34%.

2.4. Preparation of (P)-[Mo₃Se₄((R,R)-Me–BPE)₃Cl₃](Cl) (1c)

This compound was prepared by an excision reaction of the polymeric {Mo$_3$Se$_7$Cl$_4$}$_n$ phase (0.300 g, 0.306 mmol) with (R,R)-Me–BPE (0.355 g, 1.374 mmol) in CH$_3$CN (25 mL) under reflux. After 48 h, the reaction mixture was filtered to remove a small amount of the insoluble impurities. The resulting filtrate was dried under vacuum, and the solid was recrystallized from CH$_2$Cl$_2$/ether mixtures to yield 213 mg (46%) of 1c as a brown solid. ^{31}P{^{1}H} NMR (in CD$_2$Cl$_2$, 121.44 MHz) δ = 54.47 (dd, 3P), 72.91 (dd, 3P). IR (cm^{-1}, KBr): 2926 (i), 2864 (i), 953 (i), 1452 (i), 1407 (m), 1067 (m), 921 (d), 694 (m), 626 (m), 459 (d). UV–Vis (nm, CH$_2$Cl$_2$): λ(ε): 442 (6761.90), 245 (55809.52 mol^{-1} m^3 cm^{-1}). ESI-MS (CH$_2$Cl$_2$, 80 V) m/z: 1485 [M$^+$]. Anal. Calc. Mo$_3$Cl$_4$Se$_4$P$_6$C$_{18}$H$_{48}$: C, 30.94; H, 5.20. Found: C, 30.30; H, 4.90%.

2.5. Preparation of (P)-[Mo₃CuSe₄((R,R)-Me–BPE)₃Cl₄]PF₆ (2c)

Compound (P)-[Mo$_3$Se$_4$((R,R)-Me–BPE)$_3$Cl$_3$](Cl) (0.150 g, 0.099 mmol) 1c reacted with an excess of [Cu(MeCN)$_4$]PF$_6$ (0.050 g, 0.505 mmol) and TBACl (0.040 g, 0.140 mmol) in CH$_2$Cl$_2$ (15 mL) for 24 h at room temperature. The same procedure described for compound 2b was followed to obtain 0,131 g (82%) in yield of compound 2c, as red solid: ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.44 MHz) δ: 56.22 (d, 3P), 69.52 (d, 3P). IR (cm^{-1}, KBr): 2926.89 (i), 2853 (i), 1458 (i), 1260 (m), 1070 (i), 904 (i), 796 (m), 692 (i), 466 (d), 421 (d), 360 (d). UV–Vis (nm, CH$_2$Cl$_2$) λ(ε): 525 (2135.80), 467 (2216.05), 336 (8574.08). ESI-EM (CH$_2$Cl$_2$, 85 V) m/z: 1514 (M$^+$). Anal. Calc. Mo$_3$Cl$_4$CuS$_4$P$_7$F$_6$C$_{42}$H$_{84}$: C, 31.14; H, 5.24. Found: C, 31.64; H, 5.41%.

3. Results and discussion

3.1. Synthesis of trinuclear and tetranuclear compounds

As in the case of 1a.Cl, the reaction between the chiral phosphane (R,R)-Me–BPE and [TBA]$_2$[Mo$_3$S$_7$Br$_6$] in CH$_3$CN (20 mL) led to the formation of only one out of the four possible trinuclear complexes with formula [Mo$_3$S$_4$((R,R)-Me–BPE)$_3$Br$_3$](Br). Data from ^{31}P NMR (two doublets at 49.31 and 62.62 ppm, typical features of a second order AA′A″BB′B″ system) and IR spectroscopy, mass spectrometry, and elemental analysis for this compound were consistent with the structure of 1b.Br (Scheme 1). The stereochemistry of this compound was considered as (P) by comparison of its CD spectrum with that of (P)-1a.Cl [6]; each had a positive sign in its spectrum. On treatment of (P)-1b.Br with [Cu(MeCN)$_4$]PF$_6$/TBABr, the chiral hetereo cuboidal cluster (P)-[Mo$_3$CuS$_4$((R,R)-Me–BPE)$_3$Br$_4$]PF$_6$, (P)-2b.PF$_6$ (Scheme 1), was obtained in good yield [9]. This compound was characterized by ^{31}P

NMR (two doublets, at 30.15 and 87.3 ppm), mass spectrometry and elemental analysis.

The preparation of the selenium trinuclear salt, [Mo$_3$Se$_4$((R,R)-Me–BPE)$_3$Cl$_3$](Cl) was carried out in a similar manner as the sulphur analogues. Its structure was assigned as (P)-**1c.Cl** (Scheme 1) on the basis of ^{31}P NMR (two doublet of doublets at 54.47 and 72.91), IR and UV–Vis absorption as well as CD spectroscopy (positive sign), mass spectrometry and elemental analysis. The hetero dimetallic cuboidal compound (P)-**2c.PF$_6$** was also obtained in good yield by reacting (P)-**1c.Cl** with Cu(MeCN)$_4$PF$_6$/KPF$_6$. Unfortunately, attempts to obtain suitable crystals for X-ray diffraction analysis were unsuccessful for all these compounds.

3.2. Mechanistic studies

The intermolecular cyclopropanation reaction of styrene with ethyl diazoacetate has been used as model reaction. Studies have shown that the ligand structure of the metal complex can have a strong influence on the cyclopropanation yield and in the enantioselectivity of the process (when chiral complexes are used), but examples in which the Z/E diastereoselectivity is higher than 2.5 are exceptionally rare [10]. The catalytic results with (P)-**2b.PF$_6$** and (P)-**2c.PF$_6$** in dichloromethane at reflux are shown in Table 1. The substitution of chlorine in **2a.PF$_6$** by bromine led to a complex which produced a different product distribution in the diazocompound transformation. Thus, the cyclopropane products were obtained with a lower yield with (P)-**2b.PF$_6$** than with (P)-**2a.PF$_6$** (41% and 77%, respectively). The chiral seleno cuboidal (P)-**2c.PF$_6$** led only to slightly lower cyclopropanation yield (70%) than (P)-**2a.PF$_6$**, but it proved less reactive as needed 12 h for inducing complete diazo transformation.

Two hypotheses have been posed for the generation of the active catalytic species: (a) decoordination of the halide attached to the copper in the dimetallic cuboidal cluster **2$^+$**, and (b) temporal breaking of one of Cu–Q bonds (Scheme 2) [11].

On the one hand, in the case of decoordination of the halide, reaction of the resulting species (structure A in

Table 1
Catalytic results data[a]
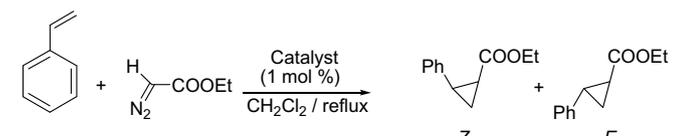
Entry	Catalyst	Time (h)	Yield (%)	E/Z
1	(P)-**2a.PF$_6$**	5	77	2.3
2	(P)-**2b.PF$_6$**	5	41	2.6
3	(P)-**2c.PF$_6$**	12	70	2.6

[a] The carbene dimerization was the side reaction. For a similar and general setup of the catalytic cyclopropanation reaction of styrene with ethyl diazoacetate, see Ref. [12].
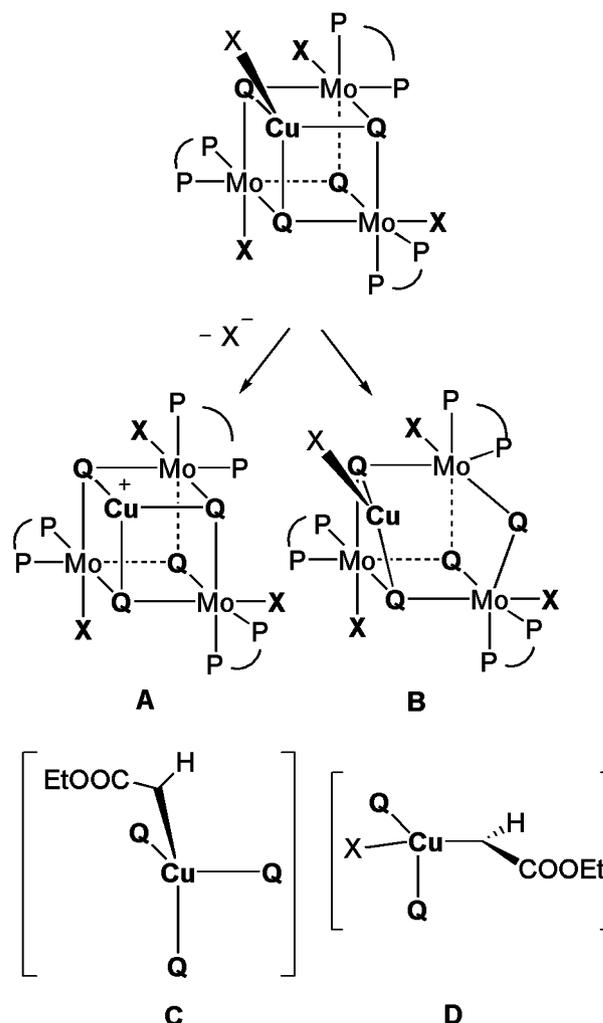
Scheme 2. Proposed active species involved in the Cu-catalyzed cyclopropanation of styrene with ethyl diazoacetate.

Scheme 2) with diazoacetate ester followed by loss of nitrogen would lead to the copper carbenoid schematically depicted as C (Scheme 2). An unimportant difference in the product distribution should be expected between **2a.PF$_6$** and **2b.PF$_6$**, since the remaining halogen atoms are coordinated to the molybdenum atoms, and they are far away from the active centre. In fact, this was not the case, and the cyclopropanation yield drastically decreased with **2b.PF$_6$**.

On the other hand, in the case of temporal breaking of one of the Cu–Q bonds (structure B in Scheme 2) the carbenoid would have a structure schematically depicted as D in Scheme 2. The metal–carbene intermediate could be less stable when it derives from **2b.PF$_6$** than when it arises from **2a.PF$_6$** and **2c.PF$_6$**, due to the higher steric hindrance provoked by the bromo atom than the chloro atom attached to the copper ion. In fact, the side reaction (dimerization of the free carbene) was more competitive in the case of using **2b.PF$_6$**.

All the **2.PF$_6$** complexes showed low enantioselectivity, which could be due to the long-distance between the Cu

active centre and the phosphine ligand, together with an insufficient bulkiness of the latter.

4. Summary

Our approach to build enantiopure chiral trinuclear clusters with $Mo_3S_4Cl_4$ core in a stereoselective manner, as well as enantiopure chiral hetero cuboidal clusters of the $Mo_3CuS_4Cl_4$ type, has been extended to the bromine derivative and selenium analogues, (*P*)-**1b.Br**, (*P*)-**1c.Cl**, (*P*)-**2b.PF**$_6$, and (*P*)-**2c.PF**$_6$. The application of the cubane type compounds (*P*)-**2b.PF**$_6$, and (*P*)-**2c.PF**$_6$ in the cyclopropanation reaction of styrene with ethyl diazoacetate has been successfully used to obtain insight into the nature of the active catalytic species. According with the experimental results, we suggest temporal breaking of one of the Cu–chalcogen bonds to generate the carbenoid intermediate.

Acknowledgement

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