

## Mixed-Metal Assemblies Based on Cyanide-Bridged Cubane-Type $\text{Mo}_3\text{CuS}_4/\text{Mo}_3\text{S}_4$ Clusters and Molybdenum Carbonyls

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The substitutional lability of Mo–Cl and Cu–Cl bonds in cubane-type  $\text{Mo}_3\text{CuS}_4$  and incomplete cubane-type  $\text{Mo}_3\text{S}_4$  clusters is exploited in an attempt to prepare cyanide-terminated complexes, namely  $[\text{Mo}_3\text{S}_4(\text{CuCN})(\text{dmpe})_3\text{Cl}_3]\text{PF}_6$  ( $[\mathbf{2}]\text{PF}_6$ ) and  $[\text{Mo}_3\text{S}_4(\text{dmpe})_3(\text{CN})_3]\text{PF}_6$  ( $[\mathbf{5}]\text{PF}_6$ ), and to subsequently use them as precursors in low-dimensional linking reactions. Mixed-metal assemblies formulated as  $[\text{Mo}_3\text{S}_4(\text{Cu}-\mu\text{CN})\cdots\text{Mo}(\text{CO})_5](\text{dmpe})_3\text{Cl}_3]^+$  ( $[\mathbf{3}]^+$ ) and  $[\text{Mo}_3\text{S}_4(\text{dmpe})_3(\mu\text{CN})\cdots\text{Mo}(\text{CO})_5]^+$  ( $[\mathbf{6}]^+$ ) are obtained by reaction of tetrahydrofuran solutions of  $[\mathbf{2}]\text{BPh}_4$  and  $[\mathbf{5}]\text{BPh}_4$  with the complex  $(\text{THF})\text{Mo}(\text{CO})_5$ . The intrinsic stability of the  $(\text{M}'-\mu\text{CN})\cdots\text{Mo}(\text{CO})_5$  linkages ( $\text{M}' = \text{Cu}$  in  $\mathbf{3}^+$  and  $\text{Mo}$  in  $\mathbf{6}^+$ ) in solution and in the gas phase is investigated through a combination of variable-temperature  $^{31}\text{P}$  NMR, IR, UV–vis spectroscopies, and electrospray ionization tandem mass spectrometry. The spectroscopic and electrochemical consequences of CN coordination as well as  $\text{Mo}(\text{CO})_5$  ligation either at the Cu or the Mo site in  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  clusters are reported. Replacement of Cl by CN or  $\text{CN}\cdots\text{Mo}(\text{CO})_5$  at the Cu site does not affect the redox potentials, whereas analogous substitution at Mo sites exerts a profound anodic shift of 220 and 500 mV upon Cl to CN and Cl to  $\text{CN}\cdots\text{Mo}(\text{CO})_5$  replacement, respectively.

### Introduction

Cyanide-coordinated metal complexes have been extensively used as building blocks of mixed-metal assemblies,<sup>1,2</sup> because of the ability of the CN ligand to act as an efficient charge transfer mediator,<sup>3</sup> or to allow magnetic exchange interactions.<sup>4</sup> The simplest way of constructing such aggregates is the attachment of metalocyanides to metal centers of mono- or polynuclear entities in an attempt to combine the physicochemical properties of both components. This idea of using high nuclearity compounds as central units was pioneered by Shriver, who demonstrated that several mononuclear cyanomanganese units can be

attached to the  $\text{Mo}_6\text{Cl}_8$  and  $\text{Ta}_6\text{Cl}_{12}$  clusters acting as central metal ions.<sup>5</sup> Other examples include the linkage of mononuclear Mn or Cr metalocyanides to metal–carbonyl clusters,<sup>6</sup>  $\text{Mo}_2$ ,<sup>7</sup>  $\text{Re}_2$ ,<sup>8</sup>  $\text{Ru}_2$ ,  $\text{Co}_3$ ,  $\text{Ni}_5$ ,<sup>9</sup> or  $\text{Fe}_4\text{S}_4$  entities.<sup>10</sup> Inspired by the success of using mononuclear metalocyanides as building units to construct functional solids, several groups are currently exploring the use of their expanded CN-coordinated cluster analogues on the basis of the rationale that their large size combined with structural and electronic diversity of these multinuclear species may lead to novel structural and physicochemical properties. This is illustrated with the use of octahedral face-capped

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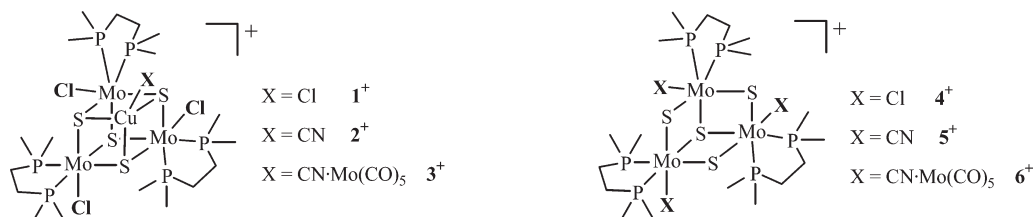
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**Figure 1.** Schematic representation with designations of  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  clusters.

$[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$  ( $\text{Q} = \text{S}, \text{Se}, \text{Te}$ )<sup>11,12</sup> and  $[\text{W}_6\text{S}_8(\text{CN})_6]^{6-13}$  or edge-bridged  $[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]^{4-14}$  cluster units in linking reactions with transition metals. CN-coordinated cubane-type clusters, namely  $[\text{M}_4\text{Te}_4(\text{CN})_{12}]^{n-}$  ( $\text{M} = \text{W},^{15} \text{Re}^{12,16}$ ) have also proved to be versatile building blocks in the preparation of larger discrete or extended solids.

A challenge remaining in this direction is that insoluble products are typically formed whose intimate structure is difficult to anticipate, mainly because of the large number of potential CN-bridged species. One way to direct and/or control the formation of low-dimensional extended networks consists of making clusters with mixed ligands that have different binding energies or labilities, so that one can selectively coordinate bidentate ligands by replacing the thermodynamically less favorable or labile ligands while leaving the thermodynamically more favorable or inert ligands unaffected. As illustrated for the series of site-differentiated hexanuclear  $[\text{Re}_6(\mu\text{-Se})_8(\text{PET})_6\text{I}_{6-n}]^{(n-4)+}$  ( $n = 4-6$ ) clusters, the remarkable stability of phosphane ligands is very suited for this purpose because it allows one to selectively

replace iodide by solvent or bidentate ligands.<sup>17</sup> This might not only offer us a variety of extended structures but also help to circumvent the insolubility problem mentioned above.

Recently, our group have been involved in the preparation of cubane-type  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  complexes bearing diphosphane ligands and the study of their non linear optical,<sup>18</sup> electrochemical, and catalytic properties.<sup>19</sup> The two  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  moieties are topologically related. The trinuclear cluster core in  $\text{Mo}_3\text{S}_4$  is formed by three molybdenum atoms defining an equilateral triangle, one capping sulfur and three bridging sulfur ligands, which can be regarded as an incomplete-cuboidal structure (see Figure 1). The vacant corner of the cube can be occupied by a copper atom leading to the cubane-type  $\text{Mo}_3\text{CuS}_4$  arrangement in which the four chalcogen atoms are capping each face of the tetrahedra defined by the  $\text{Mo}_3\text{Cu}$  core (see Figure 1). The coordination environment around the Mo sites is filled by halide and diphosphane ligands, the latter being substitutionally inert so that they can lock the desired ligand configurations onto the clusters, retain the overall  $\text{C}_3$  symmetry of the complex, and in our experience, promote the stability and crystallinity of the new  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  formed products.<sup>18,20</sup>

The use of these  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  clusters as building blocks of larger mixed-metal assemblies remains largely unexplored. In this sense, for cubane-type  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  cluster complexes to serve as molecular building blocks, it must be possible to connect things together with them. This implies complete control of substitution reactions in the labile Cu-Cl and Mo-Cl positions by bidentate ligands to subsequently explore their assembly. Herein, we describe such a study in which we have used cyanide ligands that have the capability of bridging to other metal centers and thereby enable, in principle, the assembly of mixed-metal complexes retaining the  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  clusters. The pentacarbonyl molybdenum  $\text{Mo}(\text{CO})_5$  fragment is chosen because of its great spectroscopic utility because of the fact that the carbonyl infrared stretching frequencies are extremely sensitive probes of the electronic structure of the complex. A combination of experimental techniques are used to investigate the intrinsic stability of the  $\text{M}'\text{-}\mu\text{CN}\cdots\text{Mo}(\text{CO})_5$  ( $\text{M}' = \text{Cu}, \text{Mo}$ ) linkages as well as the spectroscopic and electrochemical consequences of CN coordination as well as  $\text{Mo}(\text{CO})_5$  ligation either on the Mo or the Cu site in  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  clusters.

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## Experimental Section

**General Procedures.** In the sections that follow, clusters are designated as  $1^+ - 6^+$  according to Figure 1. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Compound  $\text{Na}[\text{NCMo}(\text{CO})_5]$  and tetra- and trinuclear  $[\text{Mo}_3(\text{CuCl})\text{S}_4(\text{dmpe})_3\text{Cl}_3]\text{PF}_6$  (**[1]PF<sub>6</sub>**) and  $[\text{Mo}_3\text{S}_4(\text{dmpe})_3\text{Cl}_3]\text{PF}_6$  (**[4]PF<sub>6</sub>**) clusters were prepared according to literature methods.<sup>21</sup> The general procedure for metathesis of  $\text{PF}_6^-$  by  $\text{BPh}_4^-$  was carried out by addition of an excess of  $\text{NaBPh}_4$  to methanol solutions of a given  $[\text{M}]\text{PF}_6$  complex precipitating the desired  $[\text{M}]\text{BPh}_4$  compound.<sup>22</sup>  $(\text{THF})\text{Mo}(\text{CO})_5$  was generated in situ by UV light irradiating a suspension of  $\text{Mo}(\text{CO})_6$  in THF for 1 h. The remaining reactants were obtained from commercial sources and used as received. Solvents for synthesis were dried and degassed by standard methods before use.

**Physical Measurements.** Elemental analyses were performed on an EA 1108 CHN microanalyzer.  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra were recorded on Varian MERCURY 300 MHz spectrometer, using  $\text{CD}_2\text{Cl}_2$  as solvent and are referenced to external 85%  $\text{H}_3\text{PO}_4$  and to the residual solvent signal for  $^{31}\text{P}$  and  $^1\text{H}$ , respectively. IR spectra were recorded on a JASCO FTIR 6200 in the 300–3000  $\text{cm}^{-1}$  range using  $\text{CH}_2\text{Cl}_2$  as solvent. Electronic spectra (250–800 nm) were recorded with a VARIAN UV/vis spectrophotometer (model CARY 500 SCAN) using different solvents. Cyclic voltammetry experiments were performed with a Echochemie Pgst 20 electrochemical analyzer. All measurements were carried out with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvent used in all experiments was  $\text{CH}_2\text{Cl}_2$  (Merck HPLC grade). The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate.  $E_{1/2}$  values were determined as  $1/2(E_a + E_c)$ , where  $E_a$  and  $E_c$  are the anodic and cathodic peak potentials, respectively.

**Electrospray Ionization (ESI) Mass Spectrometry and Energy-Dependent ESI Tandem Mass Spectrometry.** Electrospray ionization (ESI) mass spectra were recorded on a Q-TOF Premier (quadrupole-T-wave-time-of-flight) instrument using  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$  mixtures as solvent. A capillary voltage of 3.5 KV was used in the positive scan mode and the cone voltage ( $U_c$ ) was set to 20 V to control the extent of fragmentation of the identified ions. For ESI-MS reaction monitoring, after mixing cluster **[2]BPh<sub>4</sub>** or **[5]BPh<sub>4</sub>** and tetrahydrofuran solutions of  $(\text{THF})\text{Mo}(\text{CO})_5$ , a drop of the solution was extracted and diluted in THF and a positive-ion mass spectrum collected. The reaction solution was reexamined at 15 min intervals until no change in solution speciation was observed. The chemical composition of each peak was assigned by comparison of the isotope experimental pattern with that calculated using the MassLynx 4.1 program. ESI-MS/MS spectra were recorded in a convenient way to obtain energy dependent ESI-MS/MS (EDESI-MS/MS) representations as previously reported.<sup>23</sup> Typically, the cations of interest were mass-selected using the first quadrupole (Q1) and interacted with argon in the T-wave collision cell at variable collision energies (stepped by increments of 2 eV after 40 scans in the  $E_{\text{laboratory}} = 0\text{--}70$  eV range) while mass analyzing the

products with the time-of-flight analyzer (TOF). The isolation was ca. 1 Da and argon was used as a collision gas to produce a pressure of  $9 \times 10^{-4}$  mbar in the T-wave collision cell. EDESI-MS/MS representations were carried out with the aid of the EDIT computer program.<sup>24</sup>

**Syntheses.**  $[\text{Mo}_3(\text{CuCN})\text{S}_4(\text{dmpe})_3\text{Cl}_3]\text{PF}_6$  (**[2]PF<sub>6</sub>**). To a green solution of **[4]PF<sub>6</sub>** (0.095 g, 0.085 mmol) in  $\text{CH}_3\text{CN}$  (25 mL) was added an excess of  $\text{CuCN}$  (0.114 g, 1.270 mmol) under nitrogen. The solution color turned brown within 5 min. After the mixture was stirred for 1 h, it was filtered to eliminate the excess of  $\text{CuCN}$ . The filtrate was concentrated and the desired product precipitated with diethyl ether (20 mL). The precipitate was washed with water, isopropanol, and diethyl ether. Finally, the precipitate was redissolved in  $\text{CH}_3\text{CN}$  and an air stable microcrystalline brown solid was obtained by slow diffusion of diethyl ether (0.066 g, 64%). (Found: C, 18.78; H, 4.06; N, 1.05.  $\text{Mo}_3\text{S}_4\text{C}_{19}\text{H}_{48}\text{Cl}_3\text{NP}_7\text{F}_6$  requires: C, 18.90; H, 4.01; N, 1.16%). IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2140m (CN).  $^{31}\text{P}$  NMR ( $T = 30^\circ\text{C}$ ):  $\delta$  31.40 (d,  $J_{\text{P-P}} = 11$  Hz), 26.35 (d,  $J_{\text{P-P}} = 11$  Hz).  $^1\text{H}$  NMR ( $T = 30^\circ\text{C}$ ):  $\delta$  1.04 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 12.8$  Hz), 1.62 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 12.5$  Hz), 1.88 (m, 3H), 1.91 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 13.6$  Hz), 2.09 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 12.1$  Hz), 2.08 (m, 3H), 2.32 (m, 3H), 2.71 (m, 3H). ESI-MS(+)  $m/z$ : 1061.7  $[\text{M}]^+$ .

$\text{Mo}_3(\text{Cu-}\mu\text{CN}\cdots\text{Mo}(\text{CO})_5)\text{S}_4(\text{dmpe})_3\text{Cl}_3]\text{BPh}_4$  (**[3]BPh<sub>4</sub>**). To a brown solution of **[2](BPh<sub>4</sub>)** (0.05 g, 0.036 mmol) at  $T = 0^\circ\text{C}$  in THF (8 mL) was added a 10-fold excess of  $(\text{THF})\text{Mo}(\text{CO})_5$  under nitrogen. The solution color turned red immediately. After the mixture was stirred for 1 h, the red solution was taken to dryness, redissolved in  $\text{CH}_2\text{Cl}_2$  and absorbed onto a silica gel column. A very concentrated brown solution was eluted with  $\text{CH}_2\text{Cl}_2$ . This solution was taken to dryness to yield an air-stable brown solid characterized as **[3](BPh<sub>4</sub>)** (0.021 g, 36%). (Found: C, 34.92; H, 4.36; N, 0.91.  $\text{Mo}_4\text{S}_4\text{C}_{43}\text{H}_{68}\text{NP}_6\text{O}_5\text{Cu}$  requires: C, 35.64; H, 4.24; N, 0.87). IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2151w (CN); 2064m, 1984m, 1939s, 1901m (CO).  $^{31}\text{P}$  NMR ( $T = 30^\circ\text{C}$ ):  $\delta$  29.85 (d,  $J_{\text{P-P}} = 10$  Hz), 25.67 (d,  $J_{\text{P-P}} = 10$  Hz).  $^1\text{H}$  NMR ( $T = 30^\circ\text{C}$ ):  $\delta$  1.03 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 9.3$  Hz), 1.69 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 11.2$  Hz), 1.97 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 9.8$  Hz), 2.02 (m, 3H), 2.08 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 10.3$  Hz), 2.12 (m, 3H), 2.32 (m, 3H), 2.72 (m, 3H). ESI-MS(+)  $m/z$ : 1299.5  $[\text{M}]^+$ .

$[\text{Mo}_3\text{S}_4(\text{dmpe})_3(\text{CN})_3]\text{PF}_6$  (**[5]PF<sub>6</sub>**). To a green solution of **[4]PF<sub>6</sub>** (0.090 g, 0.081 mmol) in MeOH (15 mL) was added an excess of KCN (0.026 g, 0.400 mmol) under nitrogen and the reaction mixture was refluxed for 2 h, without any apparent color change. After the mixture was cooled to room temperature, the resulting solution was taken to dryness, redissolved in  $\text{CH}_2\text{Cl}_2$ , and filtered in order to eliminate the insoluble KCN inorganic salt. The resulting green solution was adsorbed onto a silica gel column. After washing the column with  $\text{CH}_2\text{Cl}_2$ /acetone mixtures (4:1), elution with a  $\text{KPF}_6$  solution in acetone (10 mg  $\text{mL}^{-1}$ ) afforded a very concentrated green solution. This solution was taken to dryness, redissolved in  $\text{CH}_2\text{Cl}_2$ , and filtered in order to eliminate the insoluble  $\text{KPF}_6$  inorganic salt. Finally, an air-stable microcrystalline green solid was obtained by slow diffusion of diethyl ether into the filtrate (0.044 g, 50%). (Found: C, 23.62; H, 4.96; N, 3.91.  $\text{Mo}_3\text{S}_4\text{C}_{21}\text{H}_{48}\text{N}_3\text{P}_7\text{F}_6$  requires: C, 23.15; H, 4.44; N, 3.86). IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2118m, 2098m (CN).  $^{31}\text{P}$  NMR ( $T = 30^\circ\text{C}$ ):  $\delta$  31.15 (d,  $J_{\text{P-P}} = 11$  Hz), 16.50 (d,  $J_{\text{P-P}} = 11$  Hz).  $^1\text{H}$  NMR ( $T = 30^\circ\text{C}$ ):  $\delta$  0.78 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 14.5$  Hz), 1.53 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 12.1$  Hz), 1.95 (m, 3H), 2.06 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 12.6$  Hz), 2.17 (d, 9H,  $\text{CH}_3$ ,  $^2J_{\text{HP}} = 13.5$  Hz), 2.31 (m, 3H), 2.41 (m, 3H), 2.85 (m, 3H). ESI-MS(+)  $m/z$ : 943.8  $[\text{M}]^+$ .

$[\text{Mo}_3\text{S}_4(\text{dmpe})_3(\mu\text{CN}\cdots\text{Mo}(\text{CO})_5)]\text{BPh}_4$  (**[6]BPh<sub>4</sub>**). To a green solution of **[5](BPh<sub>4</sub>)** (0.02 g, 0.015 mmol) at  $T = 0^\circ\text{C}$  in THF (10 mL) was added a solution of  $(\text{THF})\text{Mo}(\text{CO})_5$

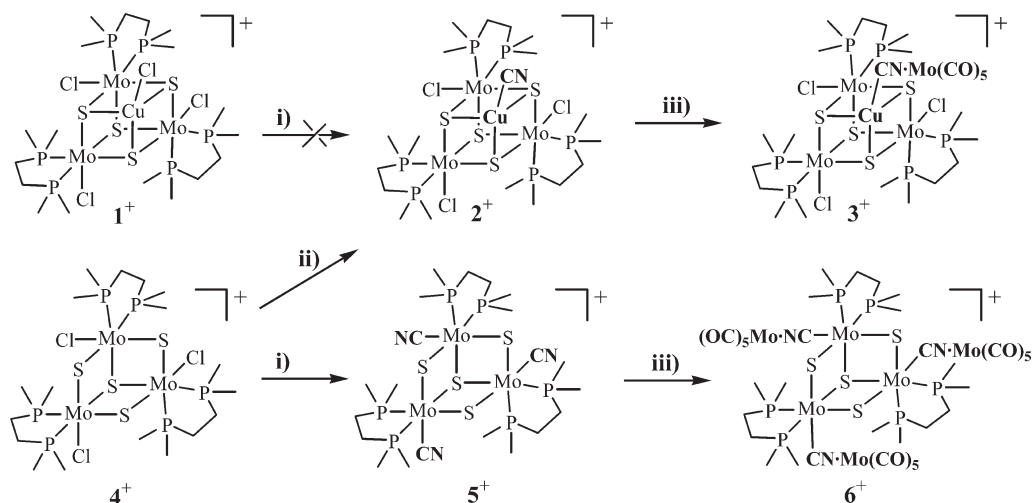
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Scheme 1.



(i) KCN in CH<sub>3</sub>OH; (ii) CuCN in CH<sub>3</sub>CN; (iii) (THF)Mo(CO)<sub>5</sub> in THF.

(0.025 mg, 0.091 mmol) in THF (7 mL) under nitrogen, producing a color change to dark red within 5 min. After the mixture was stirred for 30 min, it was taken to dryness to afford an air-stable dark red solid characterized as [6](BPh<sub>4</sub>) (0.03 g, 99%). (Found: C, 36.62; H, 3.26; N, 1.91. Mo<sub>6</sub>S<sub>4</sub>C<sub>60</sub>H<sub>68</sub>N<sub>3</sub>P<sub>6</sub>O<sub>15</sub> requires: C, 36.45; H, 3.48, N, 2.13). IR (cm<sup>-1</sup>):  $\nu_{\max}$  (cm<sup>-1</sup>): 2124w, 2104w (CN); 2070m, 1984m 1941s, 1908m (CO). <sup>31</sup>P NMR (*T* = 0 °C):  $\delta$  35.79 (d, *J*<sub>P-P</sub> = 10 Hz), 20.85 (d, *J*<sub>P-P</sub> = 10 Hz). <sup>1</sup>H NMR (*T* = 0 °C):  $\delta$  0.81 (d, 9H, CH<sub>3</sub>, <sup>2</sup>*J*<sub>HP</sub> = 10.5 Hz), 1.73 (d, 9H, CH<sub>3</sub>, <sup>2</sup>*J*<sub>HP</sub> = 10.1 Hz), 1.95 (m, 3H), 2.04 (d, 9H, CH<sub>3</sub>, <sup>2</sup>*J*<sub>HP</sub> = 11.6 Hz), 2.20 (d, 9H, CH<sub>3</sub>, <sup>2</sup>*J*<sub>HP</sub> = 11.3 Hz), 2.25 (m, 3H), 2.40 (m, 3H), 3.06 (m, 3H). ESI-MS(+) *m/z*: 1653.5 [M]<sup>+</sup>.

**X-ray Crystallographic Study.** Suitable crystals for X-ray studies for compounds [2]PF<sub>6</sub>·1/2CH<sub>2</sub>Cl<sub>2</sub> and [5]PF<sub>6</sub> were grown by slow diffusion of diethylether into dichloromethane sample solutions. X-ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at room temperature. Data were collected with a frame width of 0.3° in  $\omega$  and a counting time of 30 s per frame for both compounds at a crystal to detector distance of 4 cm. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.<sup>25</sup> The structures were solved by direct methods and refined by the full-matrix method based on F<sup>2</sup> using the SHELXTL software package.<sup>26</sup> Compound [2]PF<sub>6</sub>·1/2CH<sub>2</sub>Cl<sub>2</sub>: despite all angles being close to 90°, the structure was successfully refined in the monoclinic space group *P2*(1)/*n* considering a merohedral twinning. All cluster atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. One PF<sub>6</sub><sup>-</sup> anion was found in a general position compatible with the 1+ charge of the cluster. Half a molecule of dichloromethane was found in the last Fourier map and was refined isotropically as rigid group. Hydrogen atoms in this molecule were not included in the refinement. Empirical formula C<sub>19.50</sub>H<sub>49</sub>Cl<sub>4</sub>CuF<sub>6</sub>Mo<sub>3</sub>NP<sub>7</sub>S<sub>4</sub>; FW = 1249.79; crystal system, monoclinic; unit-cell dimensions *a* = 12.729(7) Å; *b* = 23.199(12) Å, *c* = 16.397(8) Å,  $\beta$  = 90.150(14), *V* = 4842(4) Å<sup>3</sup>; *T* = 293(2) K; space group *P2*(1)/*n*; *Z* = 4; no. of reflns collected = 27 808; no. of independent reflns = 8536 [*R*(int) = 0.0860];

final *R* indices [*I* > 2 $\sigma$ (*I*)] *R*<sub>1</sub> = 0.0539, *wR*<sub>2</sub> = 0.1327; *R* indices (all data) *R*<sub>1</sub> = 0.1003, *wR*<sub>2</sub> = 0.1586. Compound [5]PF<sub>6</sub>: The structure was successfully solved in the *I23* space group considering a merohedral twinning. All cluster atoms were refined anisotropically, whereas the positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. One of the PF<sub>6</sub><sup>-</sup> anion lies on a special position (intersection of three 2-fold axis), and its atoms were also refined anisotropically. This accounts for six out of the eight negative charges within the unit cell. The other set of independent PF<sub>6</sub><sup>-</sup> ions, revealed in the Fourier map as highly disordered, were refined as a rigid group with perfect octahedral geometry, placing the phosphorus atom on the highest electron density peak. The site occupancies of the highly disordered PF<sub>6</sub><sup>-</sup> anions were assigned to ensure a cluster:PF<sub>6</sub> ratio of 1, compatible with the observed cluster charge. This kind of disorder is often observed in isostructural tungsten [W<sub>3</sub>Q<sub>4</sub>(dmpe)<sub>3</sub>X<sub>3</sub>]PF<sub>6</sub> (Q = S, Se; X = OH, Br) complexes that crystallize in the cubic space group *I23*.<sup>20,27</sup> Empirical formula C<sub>21</sub>H<sub>48</sub>F<sub>6</sub>Mo<sub>3</sub>N<sub>3</sub>P<sub>7</sub>S<sub>4</sub>; FW = 1089.47; crystal system, cubic; unit-cell dimensions *a* = 21.039 (7) Å; *V* = 9304.6(5) Å<sup>3</sup>; *T* = 293(2) K; space group *I23*; *Z* = 8; no. of reflns collected = 20 215; no. of independent reflns = 2729 [*R*(int) = 0.1089]; final *R* indices [*I* > 2 $\sigma$ (*I*)] *R*<sub>1</sub> = 0.0599, *wR*<sub>2</sub> = 0.1659; *R* indices (all data) *R*<sub>1</sub> = 0.1015, *wR*<sub>2</sub> = 0.1923.

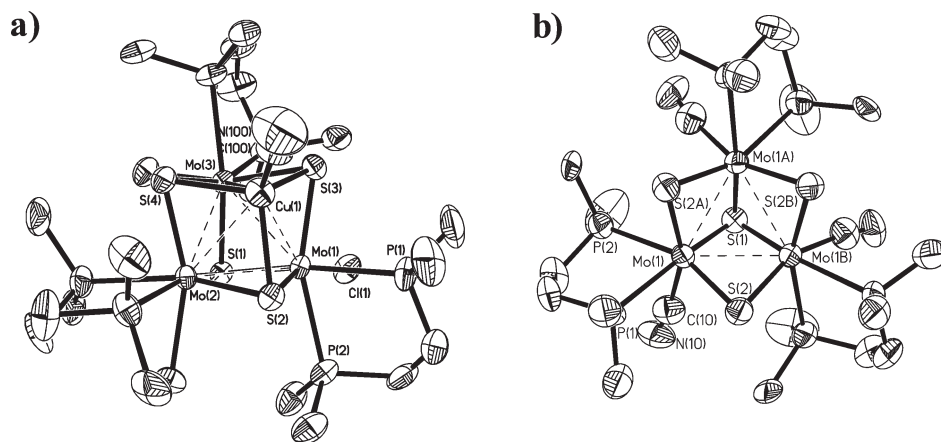
## Results and Discussion

**Cyanide-Terminated Clusters.** The present study focused primarily on two aspects of the reactivity of Mo<sub>3</sub>-Cu<sub>4</sub> and Mo<sub>3</sub>S<sub>4</sub> complexes. First, the substitutional lability of the chloride ligands attached to the Cu or Mo sites toward cyanide ligands is investigated. Second, we explore the use of the resulting cyanide-terminated complexes to generate mixed-metal assemblies that retain the cubane-type Mo<sub>3</sub>-Cu<sub>4</sub> and Mo<sub>3</sub>S<sub>4</sub> cores. The previously reported clusters [Mo<sub>3</sub>(CuCl)S<sub>4</sub>(dmpe)<sub>3</sub>Cl<sub>3</sub>]PF<sub>6</sub> ([1]PF<sub>6</sub>) and [Mo<sub>3</sub>S<sub>4</sub>(dmpe)<sub>3</sub>Cl<sub>3</sub>]PF<sub>6</sub> ([4]PF<sub>6</sub>) are tested as convenient starting materials.<sup>18</sup> Cyano-terminated [Mo<sub>3</sub>(CuCN)S<sub>4</sub>(dmpe)<sub>3</sub>Cl<sub>3</sub>]PF<sub>6</sub> ([2]PF<sub>6</sub>) and [Mo<sub>3</sub>S<sub>4</sub>(dmpe)<sub>3</sub>(CN)<sub>3</sub>]PF<sub>6</sub> ([5]PF<sub>6</sub>) compounds are accessible by reactions summarized in scheme 1 and were isolated as air-stable PF<sub>6</sub><sup>-</sup> salts.

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**Figure 2.** ORTEP representation (50% probability level ellipsoids) of the cationic cluster (a)  $2^+$  and (b)  $5^+$ .

Reaction of methanol solutions of  $[1]PF_6$  with 1 equiv. of KCN was investigated aimed at obtaining cluster  $2^+$ . This reaction invariably leads to cluster degradation to afford  $Mo_3S_4$  clusters, the trinuclear  $[Mo_3S_4(dmpe)_3Cl_3]PF_6$  ( $[4]PF_6$ ) complex being the only characterizable product as judged by ESI-MS. These results suggest that the presence of free  $CN^-$  in the reaction media is not compatible with compounds featuring a  $Mo_3CuS_4$  cluster core. Thus, an alternative strategy was necessary to selectively obtain the desired  $Mo_3CuS_4$  complex with  $Mo-Cl$  and  $Cu-CN$  groups. For this purpose, we use the trinuclear  $[4]PF_6$  complex and  $CuCN$  as a source of copper. This approach is so-called  $[3 + 1]$  building block strategy and has proven to be the most efficient route to construct cuboidal complexes with a  $Mo_3M'S_4$  ( $M'$  = transition metal) core both in aqueous and organic media.<sup>28</sup> In these reactions, the preassembled  $Mo_3$  trinuclear complex is typically reacted with a second  $M'$ -containing reagent to afford the desired compound. The reaction of complex  $[4]PF_6$  with a 3-fold excess of  $CuCN$  cleanly affords  $[Mo_3(CuCN)_4(dmpe)_3Cl_3]PF_6$  ( $[2]PF_6$ ) in 64% yield. We believe that the low solubility of  $CuCN$  in the reaction media and the short reaction time avoid possible  $Mo_3CuS_4$  cluster degradation because of the presence of free  $CN^-$ . Regarding the  $Mo_3S_4$  clusters, reaction of methanol solutions of  $[4]PF_6$  and a 5-fold excess of KCN affords  $[5]PF_6$  in 50% yield. Clusters  $[2]PF_6$  and  $[5]PF_6$  exhibit characteristic  $\nu(CN)$  stretching frequencies in their IR spectra. An IR spectrum of dichloromethane solutions of  $[2]PF_6$  shows a  $\nu(CN)$  stretching frequency at  $2140\text{ cm}^{-1}$ . Compound  $[5]PF_6$  displays two stretching frequencies at 2111 and  $2094\text{ cm}^{-1}$  which are comparable to those found for other sulfur-rich molybdenum complexes featuring terminal  $CN$  ligands, namely the trinuclear  $K_5[Mo_3S_4(CN)_9]$  ( $\nu(CN) = 2122$  and  $2118\text{ cm}^{-1}$ ),<sup>29</sup> and the hexanuclear  $K_7[Mo_6S_8(CN)_6]$  ( $\nu(CN) = 2095\text{ cm}^{-1}$ ) complex.<sup>30</sup> Suitable single crystals for X-ray analysis were obtained for compounds  $[2]PF_6$

and  $[5]PF_6$ . ORTEP representations for both  $2^+$  and  $5^+$  cations are shown in structures a and b in Figure 2.

The metal cluster core in the  $2^+$  cation consists of a slightly distorted tetrahedral arrangement of one copper and three molybdenum atoms from which the essential cubane-type motif is readily inferred. The coordination sphere on the copper atom appears in a tetrahedral environment defined by three bridging sulfur atoms and one cyanide ligand whereas the coordination sphere around each molybdenum atom is octahedral with three sulfurs, one chlorine and two phosphorus atoms of the diphosphane ligand. For the trinuclear  $5^+$  cation, ligand distribution around the molybdenum sites is essentially the same as that found in  $2^+$  except that the chlorine atoms are replaced by cyanide ligands. In general, cation  $5^+$  shares the main geometric features with other incomplete cubane-type  $Mo_3S_4$  complexes bearing diphosphane ligands.<sup>31</sup> Cations  $2^+$  and  $5^+$  preserve the stereochemistry of their  $1^+$  and  $4^+$  precursors, possess an idealized  $C_3$  symmetry and are conveniently identified in solution by  $^{31}P\{^1H\}$  and  $^1H$  NMR spectroscopy. Two phosphorus resonances (typical  $^2J_{P-P}$  values of 11 Hz) are observed for the  $2^+$  and  $5^+$  cations, as expected for three equivalent diphosphane ligands, whereas  $^1H$  NMR spectra comprise four doublets (corresponding to the four nonequivalent methyl groups of the diphosphane coupled with the neighbouring P atoms) together with four strongly coupled diastereotopic H atoms from the ethylene bridged backbone. Further support on the integrity of compounds  $[2]PF_6$  and  $[5]PF_6$  in solution is provided by ESI mass spectrometry where the  $2^+$  ( $m/z = 1061.7$ ) and  $5^+$  ( $m/z = 943.7$ ) cations are observed as the base peaks in their respective spectra.

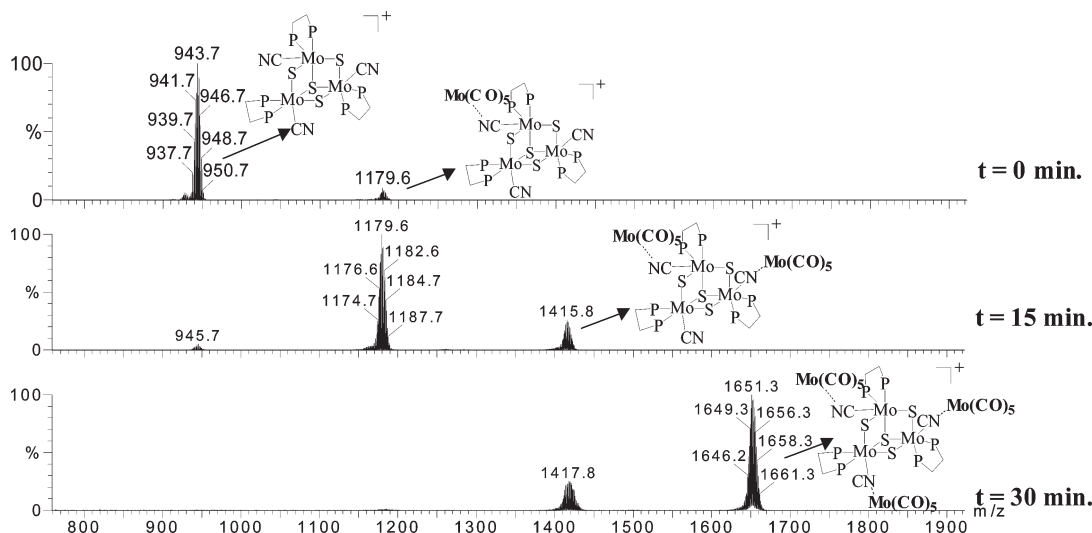
**Cyanide-Bridged Mixed-Metal Clusters.** Once selective cyanide coordination is achieved at the Cu site in  $[2]PF_6$  or Mo sites in  $[5]PF_6$ , it is now possible to use them as secondary building units to clusters of higher nuclearities. Hence, the reaction of complexes  $2^+$  and  $5^+$  with  $(THF)Mo(CO)_5$  in tetrahydrofuran (THF) was investigated. Because of the limited solubility of the  $PF_6^-$  salts in THF, we use as precursors the corresponding tetraphenylborate salts, namely  $[2]BPh_4$  and  $[5]BPh_4$  (see Experimental Section).

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**Figure 3.** ESI mass spectra of the reaction of compound [5]BPh<sub>4</sub> with a 6-fold excess of (THF)Mo(CO)<sub>5</sub> in tetrahydrofuran at different reaction times.

Reaction of complexes [2]BPh<sub>4</sub> and [5]BPh<sub>4</sub> with (THF)Mo(CO)<sub>5</sub> was monitored by electrospray ionization mass spectrometry (ESI-MS). ESI mass spectra of the reaction of complex [2]BPh<sub>4</sub> with (THF)Mo(CO)<sub>5</sub> reveal a progressive decrease of the signal of the 2<sup>+</sup> cation ( $m/z = 1061.7$ ) concomitant with the formation of cation 3<sup>+</sup> ( $m/z = 1299.5$ ). Completion of the reaction was achieved within 1 h. Both the mass-to-charge ratio and the isotopic pattern of 3<sup>+</sup> confirm that incorporation of a Mo(CO)<sub>5</sub> fragment has occurred. Even though ESI mass spectra suggest a clean incorporation of Mo(CO)<sub>5</sub> fragments into 2<sup>+</sup>, chromatographic workup was necessary to obtain [3]BPh<sub>4</sub> in analytically pure form. Treatment of THF solutions of [5]BPh<sub>4</sub> with a 6-fold excess of (THF)Mo(CO)<sub>5</sub> at 0 °C produces a gradual color change from green to dark violet. The temporal evolution of this reaction was also monitored using ESI-MS and representative spectra are shown in Figure 3.

At the early stages of the reaction, the solution mostly consists of the starting 5<sup>+</sup> cation at  $m/z = 943.7$  together with a small amount of [5 + Mo(CO)<sub>5</sub>]<sup>+</sup> cation centered at  $m/z = 1180.7$ . After 15 min, the 5<sup>+</sup> cation signal has considerably diminished and new signals due to higher nuclearity species are observed; these include the [5 + 2Mo(CO)<sub>5</sub>]<sup>+</sup> cation centered at  $m/z = 1417.6$  and the 6<sup>+</sup> species at  $m/z = 1653.5$  (formally corresponding to the [5 + 3Mo(CO)<sub>5</sub>]<sup>+</sup> cation). After half an hour, changes are essentially in intensity rather than speciation and complete coordination of Mo(CO)<sub>5</sub> fragments to the three Mo<sub>3</sub>S<sub>4</sub>-cyanide groups can be inferred (see Figure 3 bottom). All attempts to grow diffraction-quality crystals of complexes [3]BPh<sub>4</sub> and [6]BPh<sub>4</sub> were unsuccessful; however, the presence of Mo(CO)<sub>5</sub> fragments in [3]BPh<sub>4</sub> and [6]BPh<sub>4</sub> was further supported by elemental analysis, IR, UV-vis, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies.

**IR and UV-Vis Spectroscopies.** The characteristic  $\nu(\text{CN})$  stretching vibration shifts from 2140 cm<sup>-1</sup> (for 2<sup>+</sup>) to 2151 cm<sup>-1</sup> (in cluster 3<sup>+</sup>) upon coordination of one Mo(CO)<sub>5</sub> fragment. On going from compound 5<sup>+</sup> to 6<sup>+</sup>,  $\nu(\text{CN})$  stretching frequencies also shift from 2111/2094 cm<sup>-1</sup> to 2124/2104 cm<sup>-1</sup> as expected on going from terminal to bridged CN ligands.<sup>2</sup> Both compounds 3<sup>+</sup> and 6<sup>+</sup> exhibit the expected three-band pattern

(two A<sub>1</sub> and one E vibration mode) in the  $\nu(\text{CO})$  region of the infrared spectra, consistent with the presence of a monosubstituted molybdenum hexacarbonyl moiety.<sup>32</sup> These  $\nu(\text{CO})$  stretching frequencies are sensitive probes of the electronic nature of metalloligands Mo<sub>3</sub>S<sub>4</sub>Cu and Mo<sub>3</sub>S<sub>4</sub> in complexes 3<sup>+</sup> and 6<sup>+</sup>. Specifically, the lower A<sub>1</sub> frequency band (which derives most of its character from the CO vibration trans to the CN group) can be used as a probe of the electronic nature of the substituted ligand in hexacarbonyl derivatives. Hence, an inherently richer electron donor (or poorer electron acceptor) metalloligand coordinated to the Mo(CO)<sub>5</sub> fragment should cause a greater amount of the charge to be displaced into the vacant antibonding  $\pi$ -orbital of the trans-carbonyl, thus decreasing the stretching frequency. In the present case, the lower A<sub>1</sub> band frequency remains almost unchanged for 3<sup>+</sup> and 6<sup>+</sup> (1901 and 1908 cm<sup>-1</sup>, respectively), therefore suggesting similar electron donor (acceptor) abilities for the metalloligands Mo<sub>3</sub>S<sub>4</sub>Cu and Mo<sub>3</sub>S<sub>4</sub>. This experimental evidence indicates that a similar intrinsic stability of the Cu- $\mu\text{CN}\cdots\text{Mo}(\text{CO})_5$  and Mo- $\mu\text{CN}\cdots\text{Mo}(\text{CO})_5$  linkages is expected on the basis of electronic considerations, although the distinctive steric hindrance for the Cu-CN and Mo-CN groups in 2<sup>+</sup> and 4<sup>+</sup> also play an important role as we will discuss below.

UV-vis spectra of compounds 1<sup>+</sup>–6<sup>+</sup> are dominated by intense bands at high energy (below 360 nm), less intense bands in the 380–490 nm range, and weak bands at lower energy in the 530–640 nm range. Absorption bands in the visible are ubiquitous in Mo<sub>3</sub>S<sub>4</sub> and Mo<sub>3</sub>S<sub>4</sub>Cu clusters and are typically associated to transitions involving predominantly metal-based molecular orbitals (1e → 2a<sub>1</sub> for Mo<sub>3</sub>S<sub>4</sub> clusters and 3e → 4e for Mo<sub>3</sub>S<sub>4</sub>Cu clusters) whereas higher energy bands are associated with metal to ligand charge transfer or intraligand transitions.<sup>33</sup> Table 1 collects absorption maxima positions and intensities in the UV-vis spectra for the series 1<sup>+</sup>–6<sup>+</sup>.

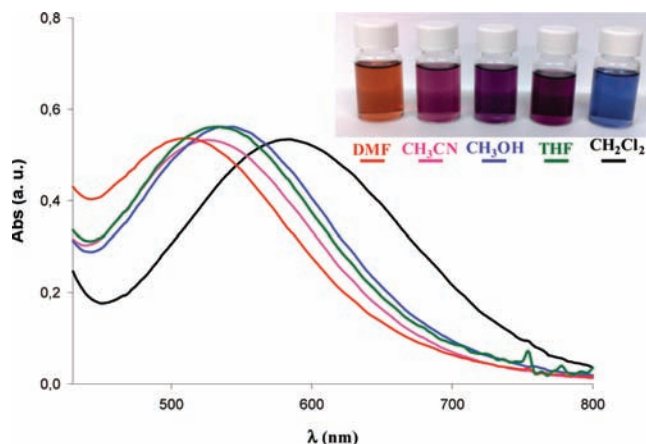
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**Table 1.** Spectroscopic Data in CH<sub>3</sub>CN (ca. 1 × 10<sup>-5</sup> M) and Redox Potentials of Mo<sub>3</sub>CuS<sub>4</sub> and Mo<sub>3</sub>S<sub>4</sub> Clusters 1<sup>+</sup>–6<sup>+</sup> in Dichloromethane<sup>a</sup>

compd	λ <sub>abs</sub> (nm) (ε (× 10 <sup>3</sup> dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> ))	oxidation E <sub>c</sub> <sup>b</sup> (V)	reduction E <sub>1/2</sub> (ΔE <sup>c</sup> ) (V)
[1]PF <sub>6</sub>	364(5.4), 493 (2.4), 649 (0.42)		–0.36 (57)
[2]PF <sub>6</sub>	360(5.9), 470 (3.1), 621 (0.49)		–0.34 (70)
[3]BPh <sub>4</sub> <sup>d</sup>	355(5.8), 485 (2.0), 612 (0.49)	0.95	–0.32 (137)
[4]PF <sub>6</sub>	341(6.0), 398 (4.6), 634 (0.42)		–0.75 (89)
[5]PF <sub>6</sub>	328(5.8), 400 (4.1), 590 (0.62)		–0.52 (68)
[6]BPh <sub>4</sub> <sup>d</sup>	290(6.2), 380 (2.85), 529 (0.55)	0.91	–0.24 (131)

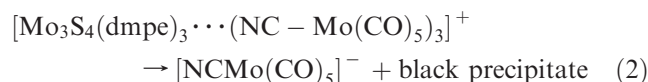
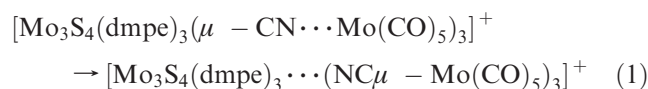
<sup>a</sup> Referenced to Fc/Fc<sup>+</sup> at E<sub>1/2</sub> = 0.44 V (vs Ag/AgCl). <sup>b</sup> Potentials measured at 100 mV/s. <sup>c</sup> ΔE = |E<sub>a</sub> – E<sub>c</sub>|. <sup>d</sup> An irreversible oxidation wave corresponding to the BPh<sub>4</sub><sup>-</sup> anion was observed at E<sub>a</sub> = 1.05 V.

**Figure 4.** UV–vis spectra of solutions of compound [6]BPh<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>, THF, CH<sub>3</sub>OH, CH<sub>3</sub>CN, and DMF.

Selective substitution of halide by cyanide ligands at the Cu or Mo sites has allowed us to investigate the spectroscopic consequences of sequential replacing at both the Cu and Mo sites in Mo<sub>3</sub>CuS<sub>4</sub> and Mo<sub>3</sub>S<sub>4</sub> complexes. For cubane-type Mo<sub>3</sub>CuS<sub>4</sub> clusters, replacement of Cl by CN at the Cu site in proceeding from 1<sup>+</sup> to 2<sup>+</sup> results in a blue shift of 28 cm<sup>-1</sup>. An analogous blue shift (44 cm<sup>-1</sup>) is observed upon Cl by CN replacement at the Mo sites in proceeding from 4<sup>+</sup> to 5<sup>+</sup>. Introduction of Mo(CO)<sub>5</sub> fragments in proceeding from 2<sup>+</sup> to 3<sup>+</sup> results in a blue-shift in the absorption maximum of 9 cm<sup>-1</sup>, whereas a more significant blue-shift (61 cm<sup>-1</sup>) is observed on going from 5<sup>+</sup> to 6<sup>+</sup>. Within the whole 1<sup>+</sup>–6<sup>+</sup> series, only the lowest energy absorption band in the absorption spectrum of 6<sup>+</sup> is strongly dependent on the solvent used. The absorption spectra in five different solvents shifts from λ = 510 nm in dimethylformamide to 585 nm in CH<sub>2</sub>Cl<sub>2</sub>. This is also evidenced by a color change of the solution from dark red to dark violet on going from DMF to dichloromethane solutions (see Figure 4). This lowest energy band displays significant negative solvatochromism (ca. 75 nm) with increasing solvent polarity, which means that a change in the solvent polarity leads to differential stabilization of the ground and excited states involved in this electronic transition. Because of the absence of solvatochromism for the whole series 1<sup>+</sup>–5<sup>+</sup>, we hypothesize a prominent involvement of the Mo<sub>3</sub>S<sub>4</sub> to Mo(CO)<sub>5</sub> moieties in the HOMO–LUMO orbitals of the ground and excited states.

**Solution vs Gas-Phase Stability of the M'–μCN···Mo(CO)<sub>5</sub> Linkage (M' = Cu, Mo) in Mo<sub>3</sub>CuS<sub>4</sub> and Mo<sub>3</sub>S<sub>4</sub> Clusters.** Unlike extended solids based on cyanide-bridged complexes, discrete mixed-metal assemblies 3<sup>+</sup> and 6<sup>+</sup> offer the opportunity to study in detail the fundamental properties of both terminal Cu–CN and

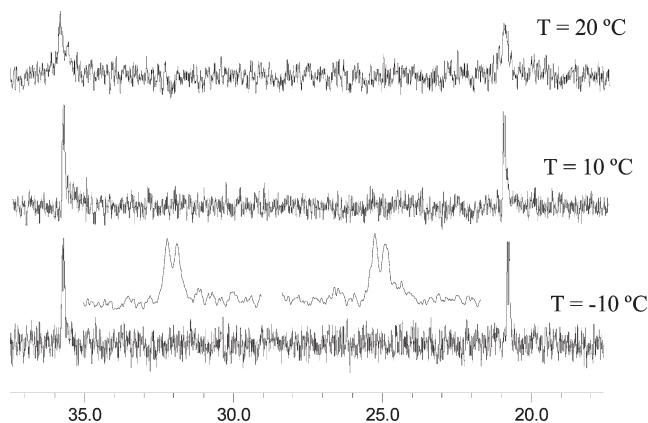
Mo–CN functional groups. Understanding of interactions between both cyanide-terminated Mo<sub>3</sub>CuS<sub>4</sub> or Mo<sub>3</sub>S<sub>4</sub> clusters and the Mo(CO)<sub>5</sub> fragment is of fundamental importance in developing further discrete or extended materials based on these clusters. In particular, the strength of the interaction of both entities as well as the tendency toward cyanide/isocyanide isomerization can be easily addressed by solution or gas-phase techniques such as NMR or ESI tandem mass spectrometry. In this context, cyanide/isocyanide conversion involving group 6 pentacarbonyls is not common,<sup>34</sup> the only example reported to date being the isomerization of [(PPh<sub>3</sub>)<sub>3</sub>Cu–μ–CN···W(CO)<sub>5</sub>] to [(PPh<sub>3</sub>)<sub>3</sub>Cu···NCμ–W(CO)<sub>5</sub>].<sup>35</sup> In the present study, we observe that compound 3<sup>+</sup> was stable in common organic solvents at room temperature for days. Solutions of 6<sup>+</sup> were also stable for days at low temperature (typically below T = 0 °C); however, after allowing to stand THF solutions of 6<sup>+</sup> at room temperature for hours, gradual rearrangement of the CN bridge was observed as evidenced by the presence of the free anion [(NC)Mo(CO)<sub>5</sub>]<sup>-</sup> in solution (a prominent species centered at m/z = 262 is observed in the ESI(–) mass spectrum) accompanied by the appearance of a black precipitate, characteristic of cluster decomposition. For compound 6<sup>+</sup>, we did not observe direct evidence (neither IR spectrum nor color change) of the presence of the linkage isomer of compound 6<sup>+</sup>, that is, the putative [Mo<sub>3</sub>S<sub>4</sub>(dmpe)<sub>3</sub>···(NCμ–Mo(CO)<sub>5</sub>)<sub>3</sub>]<sup>+</sup> species, which is believed to irreversibly undergo rapid [(NC)Mo(CO)<sub>5</sub>]<sup>-</sup> liberation once formed, according to reactions 1 and 2. In agreement with this hypothesis, all attempts to coordinate the anion [(NC)Mo(CO)<sub>5</sub>]<sup>-</sup> to Mo<sub>3</sub>S<sub>4</sub> clusters by reacting Na[(NC)Mo(CO)<sub>5</sub>] and [3]PF<sub>6</sub> were unsuccessful.



The higher ability of C-bound cyanide to accept electron density from the electron richer Mo(CO)<sub>5</sub> fragments rather than from the Mo<sub>3</sub>S<sub>4</sub> cluster is likely the driving force of

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**Figure 5.** VT- $^{31}\text{P}\{^1\text{H}\}$  NMR spectra in the  $T = -10$  to  $T = 20$  °C range of compound **[6]BPh<sub>4</sub>** in  $\text{CD}_2\text{Cl}_2$ . The insets show the expanded regions in the  $\delta = 35\text{--}36$  and  $20\text{--}21$  range.

such isomerization process in compound **6<sup>+</sup>**. This would also apply for compound **3<sup>+</sup>** featuring a  $\text{Cu}-\mu\text{CN}\cdots\text{Mo}(\text{CO})_5$  linkage; however, no isomerization was observed in this latter case, therefore suggesting that besides electronic considerations, steric factors may also play an important role at triggering cyanide/isocyanide conversion. In particular, the environment provided by diphosphane ligands around each Mo-CN group (in compound **6<sup>+</sup>**) is more congested than that in Cu-CN groups (in compound **3<sup>+</sup>**) and may preclude an effective approximation of the  $\text{Mo}(\text{CO})_5$  fragment, thus yielding labile  $\text{Mo}-\mu\text{CN}\cdots\text{Mo}(\text{CO})_5$  linkages that would permit facile rearrangement of the cyanide bridge. This is also manifested in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of compounds **[3]BPh<sub>4</sub>** and **[6]BPh<sub>4</sub>**.  $\text{CD}_2\text{Cl}_2$  solutions of compound **[3]BPh<sub>4</sub>** display a  $^{31}\text{P}\{^1\text{H}\}$  NMR pattern identical to that registered for the **[2]PF<sub>6</sub>** precursor with two doublets at 29.85 and 25.67 ppm, in agreement with preservation of the  $C_3$  symmetry upon  $\text{Mo}(\text{CO})_5$  coordination. Conversely,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of  $\text{CD}_2\text{Cl}_2$  solutions of **[6]BPh<sub>4</sub>** were broad with unresolved  $^2J_{\text{P-P}}$  coupling at room temperature in contrast to the sharp signals observed for the starting **[5]BPh<sub>4</sub>**. On cooling from 30 to  $-40$  °C, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **[6]BPh<sub>4</sub>** progressively narrow and  $^2J_{\text{P-P}}$  coupling is evident at near 0 °C. This dynamic behavior confirms that the  $C_3$  symmetry of **[6]BPh<sub>4</sub>** is frozen on the NMR time scale. Representative VT- $^{31}\text{P}\{^1\text{H}\}$  NMR spectra are shown in figure 5 in the 20 to  $-10$  °C range.

Solvent-mediated fluxionality has been invoked to account for the line broadening in cyanide mixed-metal assemblies involving group 6 pentacarbonyl groups. For example, compound  $[(\text{PPh}_3)_3\text{Cu}\cdots\text{NC}\mu\text{-W}(\text{CO})_5]$  undergoes a rapid exchange reaction that involves the insertion of a solvent molecule into the cyanide-bridging unit to yield the putative  $[(\text{PPh}_3)_3\text{Cu}\cdots\text{CH}_2\text{Cl}_2\cdots\text{NC}\mu\text{-W}(\text{CO})_5]$  species, which causes the  $^{13}\text{C}$  resonances to broaden; however, no solvent insertion was observed, and consequently, narrow  $^{13}\text{C}$  resonances were registered for its linkage isomer  $[(\text{PPh}_3)_3\text{Cu}-\mu\text{-CN}\cdots\text{W}(\text{CO})_5]$ .<sup>35</sup> For compound **[6]BPh<sub>4</sub>**, VT- $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were identical regardless of the solvent used, thus suggesting that solvent insertion on the CN bridging unit is unlikely. Moreover, this temperature-dependent behavior is reproducible over different temperature cycles from  $-40$  to 20 °C with the same sample (above  $T = 40$  °C, cluster

decomposition is accelerated), in agreement with a thermally driven dynamic process. On the basis of this experimental evidence, we tentatively propose that  $^{31}\text{P}$  NMR line broadening is caused by thermally induced lability of the  $\text{Mo}(\text{CO})_5$  fragments attached to the Mo-CN groups.

To obtain further details on the fundamental features of the  $\text{M}'-\mu\text{CN}\cdots\text{Mo}(\text{CO})_5$  linkages ( $\text{M}' = \text{Cu}, \text{Mo}$ ) in clusters **3<sup>+</sup>** and **6<sup>+</sup>**, we investigate their intrinsic stability in the gas phase. As shown above on the basis of IR spectra, electron donor abilities of metalloligands  $\text{Mo}_3\text{-CuS}_4$  (in **3<sup>+</sup>**) and  $\text{Mo}_3\text{S}_4$  **6<sup>+</sup>** (in **6<sup>+</sup>**) are similar, whereas the distinctive steric hindrance at the Cu-CN or Mo-CN sites in complexes **3<sup>+</sup>** and **6<sup>+</sup>** seem to play an important role on the intrinsic stability of the  $\text{M}'-\mu\text{-CN}\cdots\text{Mo}(\text{CO})_5$  linkages ( $\text{M}' = \text{Cu}, \text{Mo}$ ) in solution. In this regard, gas phase studies provide valuable complementary information in the absence of solvent or counterion effects, which can be easily obtained from tandem mass spectrometric techniques such as collision-induced dissociation (CID) experiments. In the particular case of carbonyl cluster compounds, CID typically causes progressive stripping of all CO ligands down to the metal core.<sup>36</sup> Because of their rich dissociation patterns, such compounds can be studied in detail using energy-dependent ESI tandem mass spectrometry (EDES-MS/MS) methodologies, to afford the complete fragmentation pattern as a two-dimensional map.<sup>23</sup> EDES-MS/MS is essentially a two-dimensional projection (collision energy vs  $m/z$ ) of a three-dimensional surface (ion intensity). Each crosspeak on the map represents different product ions generated as the collision energy is increased. EDES-MS/MS representations of cations **3<sup>+</sup>** and **6<sup>+</sup>** are shown in Figure 6.

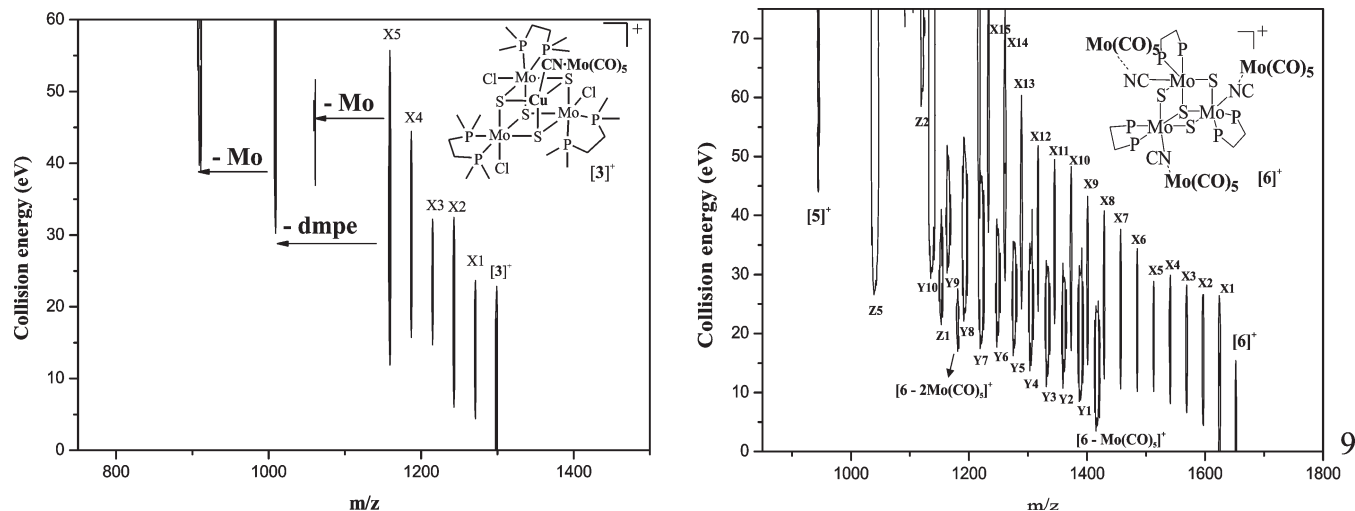
Each series of peaks (namely X, Y, or Z) correspond to singly charged species, and each peak in their respective series is 28 mass units apart, corresponding to the sequential loss of carbonyl ligands. For cation **3<sup>+</sup>**, upon increasing the collision energy (thus moving up the y axis, see Figure 6 a), up to five carbonyl ligands are stripped from the metal core denoted as  $\text{Xi}$  ( $i = 1\text{--}5$ ) species. At higher collision energies (typically above collision energy = 30 eV), EDES-MS/MS of **3<sup>+</sup>** is dominated by the liberation of neutral diphosphane,<sup>37</sup> and further increasing the energy (near  $E_{\text{laboratory}} = 40$  eV) results in the formal expulsion of Mo fragments. These results indicate a remarkable stability of the  $\text{Cu}-\mu\text{CN}\cdots\text{Mo}(\text{CO})_5$  linkage in the gas phase, which is comparable to that of the Mo-diphosphane dissociation energy.

EDES-MS/MS map of cation **6<sup>+</sup>** is shown in Figure 6b, revealing the presence of the precursor **6<sup>+</sup>** ion ( $m/z = 1653$ , appears in the bottom right-hand corner of the map) at low collision energy. At a collision energy of 5 eV, the first CO ligand is lost, and as the  $E_{\text{laboratory}}$  is further increased (moving up the y axis), CO stripping continues, producing the series of ions marked with  $\text{Xi}$  in

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**Figure 6.** EDESI-MSMS representations of cations  $3^+$  (left) and  $6^+$  (right) in the  $E_{\text{laboratory}} = 0\text{--}70$  eV range. Product ions labeled as Xi denote sequential iCO losses; Product ions labeled as Yi and Zi refer to species of general formula  $[6\text{--}Mo(CO)_5\text{--}iCO]^+$  and  $[6\text{--}2Mo(CO)_5\text{--}iCO]^+$ , respectively.

Figure 6 ( $i = 1\text{--}15$ ; formally corresponding to  $[6\text{--}iCO]^+$ ). However, it is immediately evident that unlike to  $3^+$ , the loss of CO ligands does not occur in a regular fashion. These discontinuities are caused by a second type of dissociation that consist in the formal liberation of neutral  $Mo(CO)_5$  fragments. Once a  $Mo(CO)_5$  fragment is liberated, a similarly steady CO loss pattern is seen to produce the series of the metal cluster  $[6\text{--}(CO)_5Mo\text{--}iCO]^+$  ( $i = 0\text{--}10$ ) and  $[6\text{--}2(CO)_5Mo\text{--}iCO]^+$  ( $i = 0\text{--}5$ ) cations denoted as the series of Yi and Zi species, respectively. As can be inferred in Figure 6, the series of species Y and Z are significantly broader than that of X as a consequence of the polyisotopic nature of Mo.

This characteristic dissociation in turn provides information about the molecular organization of cation  $6^+$ , confirming the presence of up to 15 CO groups as expected for the coordination of three  $Mo(CO)_5$  fragments. From the distinctive dissociation patterns of cations  $3^+$  and  $6^+$ , it is possible to qualitatively compare the strength of  $Mo\text{--}\mu\text{CN}\cdots Mo(CO)_5$  linkage in  $6^+$  versus that found in  $3^+$ . The absence of breaking for the  $Cu\text{--}\mu\text{CN}\cdots Mo(CO)_5$  linkage in  $3^+$  at low collision energies contrasts with the easiness of  $Mo(CO)_5$  liberation in  $6^+$ , thus clearly proving that the  $Mo\text{--}CN\cdots Mo(CO)_5$  linkage is inherently less stable than  $Cu\text{--}\mu\text{CN}\cdots Mo(CO)_5$  in the gas phase. This experimental results closely parallel those found in solution on the basis of VT- $^{31}P$  NMR and once again suggest a less robust  $Mo\text{--}\mu\text{CN}\cdots Mo(CO)_5$  linkage in  $6^+$  than that of  $Cu\text{--}\mu\text{CN}\cdots Mo(CO)_5$  in compound  $3^+$ .

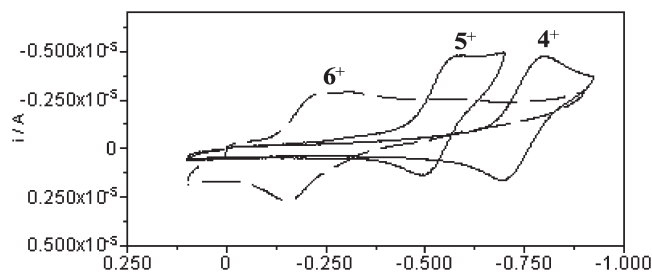
**Electrochemistry.** Electrochemical properties of the series of cubane-type  $1^+\text{--}3^+$  and incomplete cubane-type  $4^+\text{--}6^+$  complexes have been investigated by cyclic voltammetry (CV). The trinuclear molybdenum (IV)  $Mo_3S_4^{4+}$  clusters are electron precise with six electron available for the formation of three single metal–metal bonds. Copper insertion into the  $Mo_3S_4^{4+}$  affords cubane-type  $Mo_3CuS_4^{5+}$  compounds with 16 metal electrons and a formal oxidation of +1 for the copper atoms where the molybdenum oxidation state remains unchanged. In the case of the trinuclear  $[M_3S_4X_3(dmpe)_3]^+$  ( $M = Mo, W$ ;  $X = \text{halide}$ ) clusters, the most common behavior for the

first reduction process corresponds to a quasireversible two electron reduction attributed to  $Mo_3^{IV} \leftrightarrow Mo^{IV}Mo_2^{III}$ , although under certain experimental conditions (solvent, counterion, etc.), this process is seen as two one electron reduction waves.<sup>38</sup> Previous studies in our group have shown that insertion of Cu(I) into the  $Mo_3S_4$  units produces a significant anodic shift in the first reduction potential, which was tentatively assigned to the  $Mo_3^{IV}Cu^I \leftrightarrow Mo_2^{IV}Mo^{III}Cu^I$  process. Table 1 lists relevant electrochemical data for the  $Mo_3CuS_4$  and  $Mo_3S_4$  cluster cations  $1^+\text{--}6^+$  (for sake of comparison, all measurements were done in dichloromethane).

A comparison of the first reduction potential of  $Mo_3CuS_4$  cluster cations  $1^+\text{--}2^+$  reveals minor differences regardless of the X ( $X = Cl$  or  $CN$ ) ligand attached at the Cu site. Coordination of the neutral  $Mo(CO)_5$  unit does not have any significant effect on the redox potential of the  $Mo_3CuS_4$  clusters, the most remarkable feature being the presence of an irreversible oxidation wave at  $E_{1/2} = 0.95$  V that is characteristic of the  $Mo(CO)_5$  fragment. Incorporation of CuCl and CuCN fragments to compound  $4^+$  shows comparable anodic shift already reported when inserting CuCl to  $4^+$ .<sup>18</sup> Cyclic voltammograms of trinuclear complexes  $[Mo_3S_4(dmpe)_3(X)_3]^+$  where ( $X = Cl, CN, CN\cdots Mo(CO)_5$ ), numbered as  $4^+$ ,  $5^+$ , and  $6^+$ , are shown in Figure 7.

The trinuclear  $Mo_3S_4$  clusters  $4^+$ ,  $5^+$ , and  $6^+$  reveal a unique reduction wave displaying features of chemical reversibility in the cyclic voltammetric time scale at  $E_{1/2} = -0.74, -0.52,$  and  $-0.24$  V, respectively. Replacement of Cl by CN produces a strong anodic shift (ca. 220 mV) which is further pronounced upon coordination of  $Mo(CO)_5$  fragments (ca. 500 mV). These experimental evidence essentially means that CN and  $CN\cdots Mo(CO)_5$  fragment exert a dramatic electron-withdrawing effect on the  $Mo_3S_4$  cluster core as compared to Cl, whereas minor differences are found upon ligand substitution at the Cu site. Like compound  $3^+$ , cyclic voltammograms of complexes  $[6]BPh_4$  display an irreversible oxidation wave at

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**Figure 7.** Cyclic voltammogram of compounds  $4^+$ ,  $5^+$ , and  $6^+$  recorded in  $\text{CH}_2\text{Cl}_2$  at 250 mV/s scan rate.

$E_{1/2} = 0.91$  V, which is attributed to the presence of the three  $\text{Mo}(\text{CO})_5$  fragments. The observation of a single reduction step is indicative of negligible electronic communication between  $\text{Mo}(\text{CO})_5$  fragments through the  $\text{Mo}_3\text{S}_4$  cluster core.

### Conclusions

Synthetic procedures have been explored to facilitate the replacement of terminal chlorine ligands in cubane-type  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  cluster complexes to afford the cyanide-terminated complexes at the Cu or Mo site, namely  $[2]\text{PF}_6$  and  $[5]\text{PF}_6$ , respectively, for ultimate use in the preparation of mixed-metal assemblies. Clean replacement of terminal  $\text{CuCl}$  by  $\text{CuCN}$  groups in compound  $[1]\text{PF}_6$  is not generally possible in a direct ligand substitution reaction, but can be done by  $[3 + 1]$  building block synthesis starting from the trinuclear  $[4]\text{PF}_6$  and  $\text{CuCN}$ . The present study represents the first in which cubane-type  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  complexes have been incorporated into mixed-metal assemblies in which  $\text{Mo}(\text{CO})_5$  fragments are bound to the  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  cores through CN-containing linkages. Electronic features of Cu-CN and Mo-CN groups in  $3^+$  and  $6^+$  are similar while Mo-CN groups in  $6^+$  are more sterically crowded than Cu-CN sites in  $3^+$ . Consequently one may expect differences in the strength of the interaction between the molybdenum carbonyl fragments at both the Cu or the Mo sites. This is clearly demonstrated in solution where thermal cyanide/isocyanide isomerization is observed for  $6^+$ . Fundamental information about the intrinsic stability of cations  $3^+$  and  $6^+$  in the gas phase is provided by energy-dependent electrospray ionization tandem mass spectrometry (EDESI-MS/MS). EDESI-MS/MS representations present, besides the progressive loss of carbonyl ligands as

$\text{CO}$ , ease disruption of the  $\text{Mo}-\mu\text{CN}-\text{Mo}(\text{CO})_5$  linkages. These results suggest a stronger interaction for the  $\text{Cu}-\text{CN}-\text{Mo}(\text{CO})_5$  than the  $\text{Mo}-\text{CN}-\text{Mo}(\text{CO})_5$  linkage. The electrochemical measurements reported herein further complete the knowledge gathered on the effect of ancillary ligands on the redox characteristics of  $\text{Mo}_3\text{M}'\text{S}_4$  ( $\text{M}' = \text{Cu}, \text{Ni}, \text{Co}$ ) and  $\text{Mo}_3\text{S}_4$  clusters. For example, we have previously reported that the S/Se exchange in their  $[\text{Mo}_3\text{M}'\text{Q}_4]^+$  ( $\text{M}' = \text{Cu}, \text{Co}; \text{Q} = \text{S}, \text{Se}$ ) and  $[\text{Mo}_3\text{Q}_4]^+$  starting materials does not significantly affect the redox behavior.<sup>39</sup> In the present work, we demonstrate that for the cubane-type  $\text{Mo}_3\text{CuS}_4$  and  $\text{Mo}_3\text{S}_4$  complexes, redox variations are strongly affected upon CN ligation at the Mo site, whereas CN coordination to the Cu site produces only a moderate effect on the redox potentials as compared with their Cl counterparts. An identical effect has been previously reported for other cubane-type clusters. For example, redox potentials of cubane-type  $\text{Fe}_4\text{S}_4$  clusters can be increased by means of cyanide ligation, facilitating the isolation of the first synthetic cluster in the all-ferrous  $[\text{Fe}_4\text{S}_4]^{10}$  oxidation state.<sup>40</sup> Likewise, cyanide coordination at the iron sites in cubane-type clusters  $\text{MFe}_3\text{S}_4$  ( $\text{M} = \text{Mo}, \text{V}$ ) produce a profound influence on the redox potentials.<sup>41</sup>

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**Supporting Information Available:** Crystallographic data (excluding structure factors) for the structures reported in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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