

## Rearrangement of the Mo/Fe/S Cluster under the Reducing Conditions; Alternative Synthesis of $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$ Cluster from $[(\text{Cl}_4\text{-cat})\text{Mo}(\text{MeCN})\text{Fe}_3\text{S}_4\text{Cl}_3](\text{Et}_4\text{N})_2$

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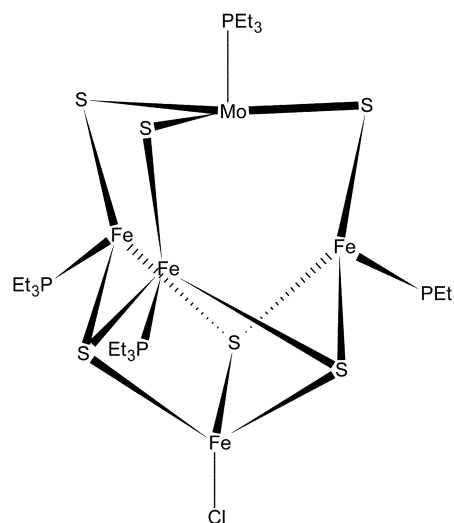
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Synthetic model compounds for FeMo-cofactor have been pursued persistently by synthetic inorganic chemists. Continuous efforts resulted in P-cluster analogs of  $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SH})_2]^{3-}$  and  $[(\text{Fe}_4\text{S}_3)_2(\mu_6\text{-S})]^{4+}$  clusters, recently.<sup>1,2</sup> Our ongoing efforts to synthesize FeMo-cofactor model compounds has produced many new Mo/Fe/S clusters, including  $(\text{Cl}_4\text{-cat})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PR}_3)_6$  ( $\text{R} = \text{Et}$ ,  $^n\text{Pr}$ , and  $^n\text{Bu}$ ),<sup>3</sup>  $\text{Fe}(\text{DMF})\text{Cl}(\text{Cl}_4\text{-cat})_2\text{Mo}_2\text{Fe}_2\text{S}_4(\text{PET}_3)_2\text{ClFe}_4\text{S}_4(\text{PET}_3)_3(\text{CO})_6\text{Cl}$ ,<sup>4</sup>  $[(\text{Cl}_4\text{-cat})_2\text{Mo}_2\text{Fe}_2\text{S}_3\text{O}(\text{PET}_3)_3\text{Cl}]^+$ ,<sup>5</sup>  $(\text{Cl}_4\text{-cat})_2\text{Mo}_2\text{Fe}_3\text{S}_5(\text{PET}_3)_5$ ,<sup>5</sup> and  $(\text{Cl}_4\text{-cat})\text{LMoFe}_3\text{S}_3(\text{PR}_3)_n(\text{CO})_m$  ( $\text{L} = \text{none}$ ,  $\text{PR}_3$ , Pyridine, or  $\text{O}$ ,  $n = 2$  or  $3$ ,  $m = 4, 5$  or  $6$ ,  $\text{R} = \text{Et}$  or  $^n\text{Pr}$ ).<sup>6</sup> These Mo/Fe/S clusters are synthesized by rational synthetic designs instead of so-called spontaneous self-assembly (SSA). One of the established methods to prepare high nuclearity Mo/Fe/S clusters is the reductive coupling of the  $\text{Fe}_2\text{S}_2$  and  $\text{MoFeS}_2$  rhombic building blocks in the presence of  $\text{S}^{2-}$ -scavenging trialkylphosphine.<sup>4,7</sup> Reductive coupling rationale can also explain reactivity of many Mo/Fe/S clusters in the presence of CO and trialkylphosphine.<sup>8</sup> This approach has advantage over SSA method because the product can be predicted and explained, while SSA method cannot be. For examples, high pressure CO reaction of  $[\text{Fe}_4\text{S}_4(\text{PcHex}_3)_4](\text{BPh}_4)$  cluster produces the  $\text{Fe}_3\text{S}_2(\text{CO})_7\text{-}(\text{PcHex}_3)_2$  cluster<sup>9</sup> and  $\text{Fe}_4\text{S}_4(\text{P}^t\text{Bu}_3)_4$  cluster couples itself to form  $\text{Fe}_{16}\text{S}_{16}(\text{P}^t\text{Bu}_3)_8$  cluster.<sup>10</sup>

Here we report the new synthesis of high nuclearity Mo/Fe/S cluster,  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$ , from the reaction between  $[(\text{Cl}_4\text{-cat})\text{Mo}(\text{MeCN})\text{Fe}_3\text{S}_4\text{Cl}_3](\text{Et}_4\text{N})_2$ <sup>11</sup> and  $\text{Fe}(\text{PET}_3)_2\text{Cl}_2$ <sup>12</sup> in MeCN. The reaction conditions had been used for the preparation of  $(\text{Cl}_4\text{-cat})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PET}_3)_6$  cluster before, and which is not soluble in MeCN. After a day stirring, the reaction mixture was filtered to remove  $(\text{Cl}_4\text{-cat})_2\text{Mo}_2\text{Fe}_6\text{S}_8\text{-}(\text{PET}_3)_6$  cluster<sup>5</sup> and the filtrate was dried under reduced pressure. The residue was extracted by ether and black solution was obtained. Black crystalline product was crystallized by slow evaporation of the solvent. CHN analysis and FAB<sup>+</sup>-MS data matched  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$  cluster (Figure 1). The <sup>1</sup>H-NMR spectrum of the product showed four peaks at  $\delta$  1.510 ppm, 0.871 ppm, 0.504 ppm, and -2.107 ppm, which are almost same as the reported values.<sup>13</sup> Finally the unit cell determination of a single crystal identified  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$  cluster.<sup>14</sup> Since elemental analysis, <sup>1</sup>H-NMR spectrum, and unit cell parameters matched with  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$  cluster, X-ray diffraction

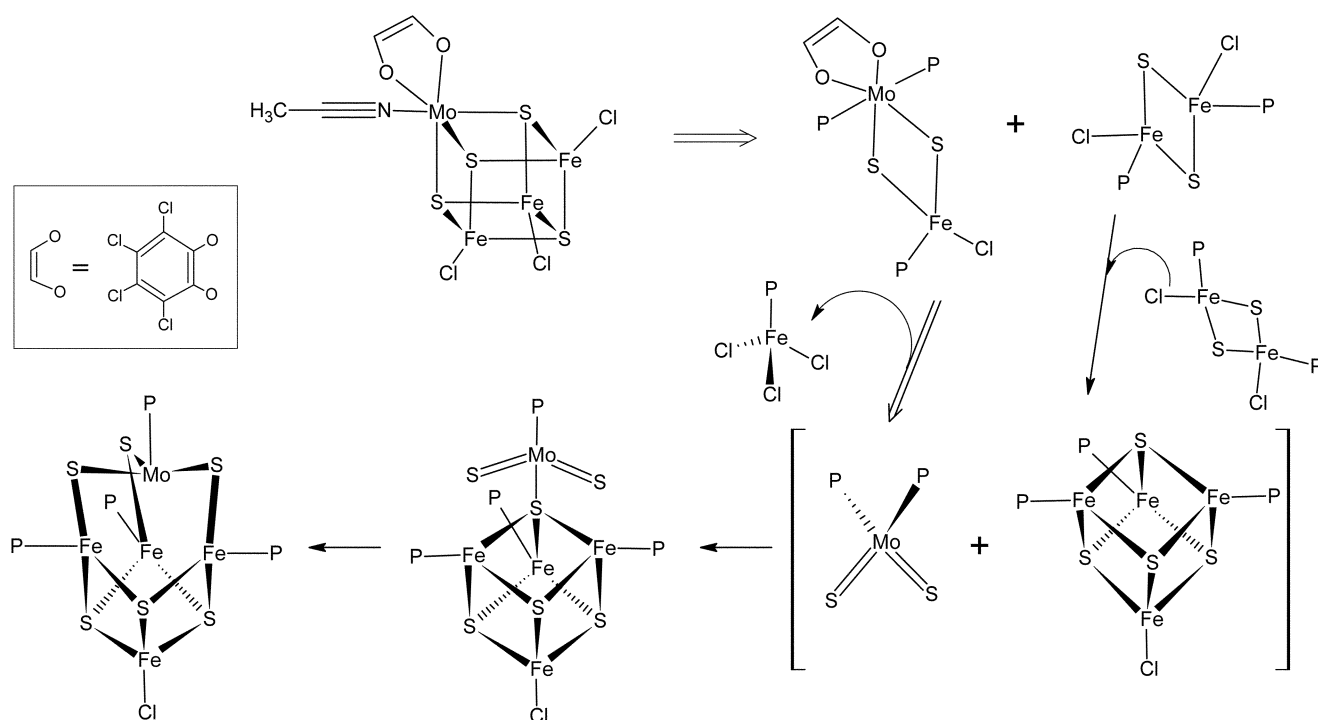


**Figure 1.** Molecular structure of the heterometal cuboidal  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$  cluster.

data collection was not tried. The IR data of  $\text{MoFe}_4\text{S}_6\text{-}(\text{PET}_3)_4\text{Cl}$  cluster has not been reported before. It has characteristic strong peaks at  $1034\text{ cm}^{-1}$  and  $763\text{ cm}^{-1}$ . Four alkyl C-H stretchings of  $\text{PET}_3$  at  $2965\text{ cm}^{-1}$ ,  $2934\text{ cm}^{-1}$ ,  $2904\text{ cm}^{-1}$ , and  $2887\text{ cm}^{-1}$  as well as a strong Fe-S stretching at  $366\text{ cm}^{-1}$  in far-IR range were assigned.

The heterometal cuboidal  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$  cluster was structurally considered to be one of the best model compounds resembling the core of FeMo-cofactor<sup>15</sup> and the Ru analogs was also synthesized by SSA.<sup>16</sup> The reported synthesis of  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$  cluster involves SSA and accompanies concomitant formation of  $\text{Fe}_6\text{S}_6(\text{PET}_3)_4\text{Cl}_2$  cluster.<sup>13</sup> But the new synthetic method of  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$  cluster from  $[(\text{Cl}_4\text{-cat})\text{Mo}(\text{MeCN})\text{Fe}_3\text{S}_4\text{Cl}_3](\text{Et}_4\text{N})_2$  in the presence of reducing agent  $\text{Fe}(\text{PET}_3)_2\text{Cl}_2$  didn't produce any  $\text{Fe}_6\text{S}_6(\text{PET}_3)_4\text{Cl}_2$  byproduct based on <sup>1</sup>H-NMR. The isolation of the product can be achieved by simple extraction.

The formation of  $\text{MoFe}_4\text{S}_6(\text{PET}_3)_4\text{Cl}$  cluster from  $[(\text{Cl}_4\text{-cat})\text{Mo}(\text{MeCN})\text{Fe}_3\text{S}_4\text{Cl}_3](\text{Et}_4\text{N})_2$  in the presence of  $\text{Fe}(\text{PET}_3)_2\text{Cl}_2$  can be envisioned as indicated in Scheme 1. The dissociation of the cubic units of  $[(\text{Cl}_4\text{-cat})\text{Mo}(\text{MeCN})\text{-}\text{Fe}_3\text{S}_4\text{Cl}_3](\text{Et}_4\text{N})_2$  makes available the solvated  $[\text{MoFeS}_2]$  and  $[\text{Fe}_2\text{S}_2]$  rhombic dimers, and this type of oxidative decoupling was reported.<sup>7</sup> The  $[\text{MoFeS}_2]$  unit can further dissociate



**Scheme 1.** Suggested synthetic mechanism for  $\text{MoFe}_4\text{S}_6(\text{PEt}_3)_4\text{Cl}$  from the reaction between  $[(\text{Cl}_4\text{-cat})\text{Mo}(\text{MeCN})\text{Fe}_3\text{S}_4\text{Cl}_3](\text{Et}_4\text{N})_2$  and  $\text{Fe}(\text{PEt}_3)_2\text{Cl}_2$ . P represents  $\text{PEt}_3$  or solvent molecules. Decoupling and coupling steps are designated by  $\Rightarrow$  and  $\rightarrow$ , respectively.

into the solvated  $[\text{MoS}_2]$  and  $[\text{Fe}]$  monomers. Cleavage of the  $[\text{MoFeS}_2]$  unit into the monomers under similar conditions was observed before.<sup>17</sup> Reductive coupling of  $[\text{Fe}_2\text{S}_2]$  dimers occurs to form the  $[\text{Fe}_4\text{S}_4(\text{PEt}_3)_3\text{Cl}]$  and further association of  $[\text{Fe}_4\text{S}_4(\text{PEt}_3)_3\text{Cl}]$  and  $[\text{MoS}_2(\text{PEt}_3)]$  results in  $\text{MoFe}_4\text{S}_6(\text{PEt}_3)_4\text{Cl}$  cluster. Formation of  $[\text{Fe}_4\text{S}_4(\text{PEt}_3)_3\text{Cl}]$  unit from the  $[\text{MoFe}_3\text{S}_4]$  core under the reducing conditions has also reported.<sup>4</sup> The unique  $\mu_3\text{-S}$  ligand among the three  $\text{Fe}(\mu_3\text{-S})_3(\text{PEt}_3)$  in the electron rich  $[\text{Fe}_4\text{S}_4(\text{PEt}_3)_3\text{Cl}]$  cluster can coordinate to the fourth metal center.<sup>18</sup> In this case, the unique  $\mu_3\text{-S}$  ligand binds to Mo atom of  $[\text{MoS}_2]$  monomer. Successive coordination of terminal sulfide ligands of  $[\text{MoS}_2]$  to the cuboidal Fe atoms produces the  $\text{MoFe}_4\text{S}_6(\text{PEt}_3)_4\text{Cl}$  cluster as a final product. This work is an additional expansion of the new Mo/Fe/S cluster synthesis methodology. Rational Syntheses of new Mo/Fe/S clusters exploiting the reductive coupling are currently underway for a FeMo-cofactor model compound.

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- Black crystals, 12% yield, FT-IR (KBr,  $\text{cm}^{-1}$ ) 2965 (m), 2934 (m), 2903 (w), 2887 (m), 1414 (m), 1410 (m), 1379 (m), 1033 (s), 763 (s), 423 (m), 413 (m), 366 (s), 362 (s), 331 (m). <sup>1</sup>H-NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.510 (br. s., 9H,  $\text{MoPCH}_2\text{CH}_3$ ), 0.871 (t,  $J = 6.6$  Hz, 27H,  $\text{FePCH}_2\text{CH}_3$ ), 0.504 (br. s., 6H,  $\text{MoPCH}_2$ ), -2.107 (br. s., 18H,  $\text{FePCH}_2$ ). Anal. Calcd for  $\text{C}_{24}\text{H}_{60}\text{ClFe}_4\text{MoP}_4\text{S}_6$ : C, 28.27; H, 5.93. Found: C, 28.36, H, 5.88. FAB-MS (3-nitrobenzoyl alcohol):  $M^+$  cald  $m/e$  1020.81, found  $m/e$  1020.80.
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