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Development of Molecular Precursors for the Synthesis of Mesostructured Metal Phosphides
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The goal of this ACS PRF program was to develop metal phosphide materials with precisely controlled nano- and meso-structures for heterogeneous catalyst in hydroprocessing of hydrocarbons. Currently, transition metal sulfides are deployed commercially for catalytic hydroprocessing, however their limits are quickly being realized as environmental regulations are increasing and diverse feedstocks are employed.

Building upon our previous success with the synthesis of novel nickel-phosphide molecular clusters, we have continued to investigate the synthesis, properties, and conversion to the catalytically active Ni_2P phase of these clusters. This report details our expansion of the metal phosphide cluster library, characterization of the properties of the molecular clusters, and the ongoing effort to develop mesostructured nickel-phosphides

We have designed and synthesized a family of nickel phosphide molecular clusters that can be readily converted to crystalline nickel phosphide phases via thermolysis. These clusters are synthesized by the room temperature reaction of bis(1,5-cyclooctadiene)nickel(0) with various organocyclophosphines in the presence of an excess of trialkylphosphine capping ligand. Single crystal x-ray diffraction (SCXRD) of the black crystals obtained from these reactions indicates that cluster nuclearity and degree of ligand passivation can be tuned depending on the choice of organocyclophosphine or capping ligand used. We sought to expand the cluster library to even larger or more nickel-nickel rich clusters using this synthetic approach. By increasing the equivalents of bis(1,5-cyclooctadiene)nickel(0), we have isolated clusters of previously observed nuclearity but with even fewer trialkylphosphine capping ligands, $\text{Ni}_{12}(\text{PMe})_{10}(\text{PEt}_3)_6$ (Figure 1a). When the common N-heterocyclic carbene, 1,3-dimethylimidazol-2-ylidene (IMe) is used in place of a trialkylphosphine ligand, SCXRD revealed that a cluster of also previously observed nuclearity was obtained, however it was totally ligated by the IMe ligands, $\text{Ni}_{12}(\text{PMe})_{10}(\text{IME})_8$ (Figure 1b). We were initially excited by the isolation of these clusters due to their nickel-rich nature, however poor fidelity in the isolation of the new clusters has prevented their use in the conversion to Ni_2P .

The reaction of bis(1,5-cyclooctadiene)nickel(0) with the organocyclophosphines proceeds very quickly at room temperature and we were interested in gaining insight into the mechanism of cluster formation to design reactions that produced novel clusters. We sought to “trap” an intermediate in the cluster formation reaction by increasing the amount of capping ligand present. We successfully isolated a species that appears to be one such intermediate, $\text{Ni}_2((\text{PMe})_5)_2(\text{PMe}_3)_2$ (Figure 1c). This dinuclear nickel cluster reveals that two organocyclophosphines first act as bridging ligands to two $\text{Ni}(0)(\text{PMe}_3)$ species. Our hypothesis is that these $\text{Ni}(0)$ centers then undergo a series of oxidative addition reactions on the organocyclophosphines to produce the isolated clusters. In a continuation of the ACS PRF project, we are currently investigating how this trapped intermediate can be used to further expand the cluster library.

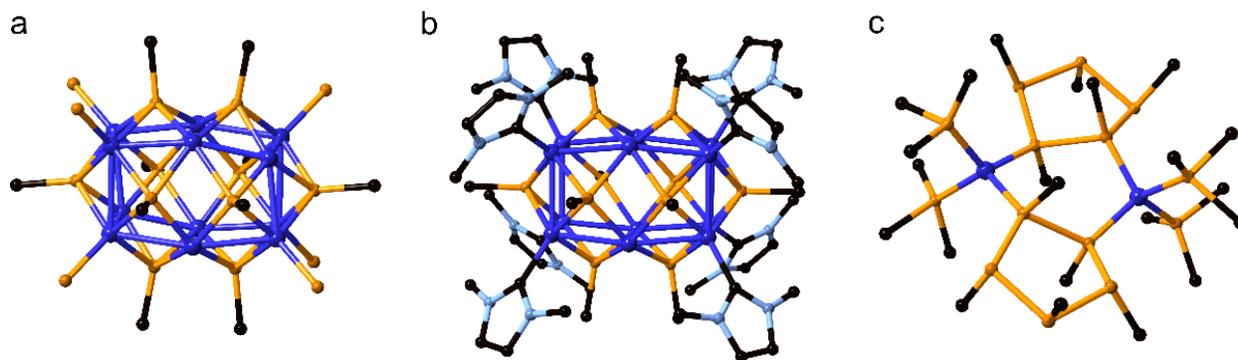


Figure 1. Crystal structures of (a) $\text{Ni}_8(\text{PMe})_6(\text{PMe}_3)_6$ and (b) $\text{Ni}_{12}(\text{PMe})_{10}(\text{IMe})_8$ and (c) $\text{Ni}_2((\text{PMe})_5)_2(\text{PMe}_3)_2$. The alkyl groups on the trialkylphosphine capping ligands in **a**, and the hydrogens are omitted for clarity. Legend: Blue, Ni; orange, P; black, C, light blue N.

Because this family of nickel phosphide clusters has few other literature examples, we were interested in examining the properties of these clusters. We first performed SQUID magnetometry measurements on the $\text{Ni}_{12}(\text{PMe})_{10}(\text{PEt}_3)_8$ cluster. These measurements revealed that the cluster is diamagnetic. Due to the highly crystalline nature of the isolated clusters, solubility of the clusters is low and this has limited our ability to further characterize this family of clusters and use them as precursors to create nanostructured nickel phosphides.

In order to overcome these challenges and allow us to make solution-based measurements, we have begun to examine the chemical oxidation of the $\text{Ni}_{12}(\text{PMe})_{10}(\text{PEt}_3)_8$. The addition of ferrocenium hexafluorophosphate to a $\text{Ni}_{12}(\text{PMe})_{10}(\text{PEt}_3)_8$ solution in tetrahydrofuran, results in the oxidation of the cluster to yield $[\text{Ni}_{12}(\text{PMe})_{10}(\text{PEt}_3)_8][\text{PF}_6]$. We are extremely excited by this result because of the enhanced solubility of the oxidized cluster as well as the potential for a change in magnetic properties. Investigations of the oxidized cluster are currently ongoing.

Again, building upon our successes previously, we are furthering the development of mesostructured nickel phosphides. We have discovered that the thermolysis of the $\text{Ni}_{12}(\text{PMe})_{10}(\text{PEt}_3)_8$ cluster in a sealed borosilicate glass tube within a tube furnace resulted in crystalline material that primarily consisted of the Ni_2P phase with some nickel metal impurities present. Continued thermolysis experiments revealed that by slowly ramping the temperature to 450°C and maintaining that temperature for several hours results in nearly complete conversion to the Ni_2P phase with few if any impurities as determined by powder x-ray diffraction (PXRD) experiments. This project is continuing by utilizing the slow thermolysis of the $\text{Ni}_{12}(\text{PMe})_{10}(\text{PEt}_3)_8$ cluster as a method to produce mesostructured Ni_2P materials by infiltrating a mesoporous template material with the $\text{Ni}_{12}(\text{PMe})_{10}(\text{PEt}_3)_8$ cluster precursors. We are working with MCM-41 as the mesoporous template due to its ideal pore size, ease of synthesis, and thermal stability.

Over the funding period, this ACS PRF grant has supported the continued work of one, graduate student, Evan Doud, with one manuscript describing the synthesis of utilization of the nickel-phosphide clusters currently under preparation. In addition to supporting Evan, the Petroleum Research Fund has been crucial in broadening our research interests beyond traditional transition metal chalcogenide chemistry and into transition metal pnictide chemistry. This project has also allowed us to begin exploring materials design for catalytic applications, which I anticipate will become an important dimension of our work moving forward. A publication describing our results is in preparation and should be submitted in the coming weeks.