Synthesis, Structures and Spectroscopy of Metal Clusters Containing Polycarbon and Heterocumulene Ligands

Final Technical Report

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by

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Summary of Accomplishments:

The thrust of the above named project was the investigation of transformations of the SO_2, CO and CCO ligands bound to metal clusters with the thought that this metal cluster chemistry will mimic reactions on supported metal catalysts. The SO_2 containing clusters $[PPN]_2[Fe_3(CO)_7(SO_2)_2(CCO)]$ $[PPN]_2[Ru_3(CO)_7(SO_2)_3]$, $[Fe_3(CO)_7(SO_2)_2(CCOCH_3)]^-$ and $[PPN]_2[Ru_3(CO)_9SO_2]$ were prepared and their reactivity with electrophiles was investigated. The reactions of $[PPN]_2[Ru_3(CO)_7(SO_7)_2]$ with the electrophiles MeOTf, EtOTf and AcCl were found to yield $[Ru_3(CO)_7(SO_2)_2(OSOE)]^+$ (where E = CH_3, CH_3CH_2, or CH_3CO).

This research was extended to clusters of higher nuclearity, which were prepared by reaction of $[PPN]_2[Ru_3(CO)_7(SO_2)_3]$, with AcCl, followed by reaction with metal nucleophiles such as $[C_6H_5)_4P][Mn(CO)_5]$, $Na_2[Fe(CO)_4]$, $[PPN][CpMo(CO)_3]$. Similarly, the reaction of $[PPN]_2[Ru_2(CO)_7(SO_2)_3]$ with $[CH_3SO_3CF_3]$ followed by the strong nucleophile, $Na_2[Fe(CO)_4]$, was explored and the products have been characterized. These studies were performed by a graduate student, Randal Eveland.

A graduate student, Daphne Norton, explored $[PPN][Fe_3(CO)_9CCFeCp(CO)_2]$ as an alternate precursor to $[PPN]_2[Fe_6(CO)_{18}C_4]$, which she had previously synthesized by the treatment of $[Fe_3(CO)CCO]^{2-}$ with excess $(SO_3CF_3)_2$. She postulated that the reaction proceeds through an intermediate with the formula $[PPN][Fe_3(CO)_9CCOTf]$, followed by loss of $SO_3CF_3^-$ and subsequent dimerization to yield $[PPN]_2[Fe_6(CO)_{18}C_4]$. She also discovered an alternate route to $[Fe_6(CO)_{18}C_4]^{2-}$

based on the treatment of $[Fe_3(CO)_9CCFeCp(CO)_2]^-$ with electrophiles.

DOE Sponsored Publications:

"Mixed-Metal Butterfly Acetamidediato Clusters Derived from a Highly Reactive Ruthenium Oxo Cluster: Synthesis and Characterization of $[(PPh_3)_2N][MRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]$, (M = Mn or Re)", E. J. Voss, M. Sabat, D. F. Shriver, Inorg. Chim. Acta, 240, 49-61 (1995).

"Synthesis, Structure and Bonding of Butterfly Clusters that Contain μ_4-Oxo and μ4-Sulfido Ligands: $[PPN][Fe_3M(CO)_{12}(\mu_4\text{-}E)$ (E = O or S and M = Mn or Re)", C. K. Schauer, S. Harris, M. Sabat, E. J. Voss and D. F. Shriver, *Inorg. Chem.*, 34, 5017 (1995).

"Substitution of SO_2 for CO in Triruthenium Carbonyl Anions," G. B. Karet, C. L. Stern, J. A. Cody, S. J. Lange, M. A. Pell, C. Slebodnick, D. F. Shriver, J. Organomet. Chem.,495 33 (1995).

"Reaction of $[PPN][Fe_3(CO)CCOC(O)CH_3]$ with the Metal Nucleophile $[Re(CO)_5]^-$ to Generate a Mixed-Metal Acetylide, $[PPN][Fe_3(CO)_9CCRe(CO)_5]$", D. M. Norton, R. W. Eveland, J. C. Hutchison, C. Stern, and D. F. Shriver, Organometallics, 15, No. 19, 3916-3919 (1996).

"Syntheses, Characterization, and Structures of Tri- and Tetraruthenium Clusters Containing Sulfido, Phenylimido, and (Phenylimino)thio Ligands", W. Y. Yeh, C. L. Stern, and D. F. Shriver, Inorg. Chem., 35 No. 26, 7857-7862 (1996).

"Reactions of Triosmium Carbonyl Clusters with Thionylaniline. Crystal Structures of $Os_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}S)$, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(PhN)_2SO)(\mu_3\text{-}S)$, and $Os_3(CO)_8(NCMe)(\mu_3\text{-}NPh)(\mu_3\text{-}S)$, W. H. Yeh, C. L. Stern and D. F. Shriver, Inorg. Chem., 36, 4408-4414 (1997).

"New SO_2 Iron Containing Cluster Compounds $[PPN]_2[Fe_3(CO)_9(\mu_3,\eta^2\text{-}SO_2)]$, $[PPN]_2[Fe_3(CO)_8(\mu\text{-}SO_2)\mu_3\text{-}S]$, $[PPN]_2[Fe_3(CO)_8(\mu\text{-}SO_2)(\mu_3\text{-}CCO)]$, and $[PPN]_2[Fe_2(CO)_6(\mu\text{-}SO_2)_2]$ From Heterometal Precursors", R. W. Eveland, C. C. Raymond, T. E. Albrecht-Schmitt, D. F. Shriver, Inorg. Chem., 38, 1282-1287 (1999).

"$[PPN][Fe_3(CO)_9(C{\equiv}CH)]$ and $[Fe_3(CO)_9(C{\equiv}COTi(THF)_4Cl)]$ From the Reaction of Low-Valent Titanium with $[Fe_3(CO)_9(CCO)]^{2-}$," R. W. Eveland, C. C. Raymond, D. F. Shriver, Organometallics, 18, 534-539 (1999).

"[PPN][$Fe_3(CO)_9(C{\equiv}CH)$] and [$Fe_3(CO)_9(C{\equiv}COTi(THF)_4Cl)$] From the Reaction of Low- Valent Titanium with $[Fe_3(CO)_9(CCO)]^{2-}$," R. W. Eveland, C. C. Raymond, D. F. Shriver, Organometallics, 18, 534-539 (1999).

"The Reaction of Tri-ruthenium Clusters with Sulfur Dioxide," R. E. Eveland and D. F. Shriver, Inorg. Chim. Acta, submitted.

Ph.D.'s Granted:
Daphne M. Norton - PhD 1996
Randal W. Eveland - PhD 1998