

Synthesis, Structures and Spectroscopy of Metal Clusters

Containing Polycarbon and Heterocumulene Ligands

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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 $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_7(\text{SO}_2)_2(\text{CCO})]$ $[\text{PPN}]_2[\text{Ru}_3(\text{CO})_7(\text{SO}_2)_3]$, $[\text{Fe}_3(\text{CO})_7(\text{SO}_2)_2(\text{CCOCH}_3)]$ and $[\text{PPN}]_2[\text{Ru}_3(\text{CO})_9\text{SO}_2]$ were prepared and their reactivity with electrophiles was investigated. The reactions of $[\text{PPN}]_2[\text{Ru}_3(\text{CO})_7(\text{SO}_2)_2]$ with the electrophiles MeOTf, EtOTf and AcCl were found to yield $[\text{Ru}_3(\text{CO})_7(\text{SO}_2)_2(\text{OSOE})]^+$ (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 $[\text{PPN}]_2[\text{Ru}_3(\text{CO})_7(\text{SO}_2)_3]$, with AcCl, followed by reaction with metal nucleophiles such as $[\text{C}_6\text{H}_5)_4\text{P}][\text{Mn}(\text{CO})_5]$, $\text{Na}_2[\text{Fe}(\text{CO})_4]$, $[\text{PPN}][\text{CpMo}(\text{CO})_3]$. Similarly, the reaction of $[\text{PPN}]_2[\text{Ru}_2(\text{CO})_7(\text{SO}_2)_3]$ with $[\text{CH}_3\text{SO}_3\text{CF}_3]$ followed by the strong nucleophile, $\text{Na}_2[\text{Fe}(\text{CO})_4]$, was explored and the products have been characterized. These studies were performed by a graduate student, Randal Eveland.

A graduate student, Daphne Norton, explored $[\text{PPN}][\text{Fe}_3(\text{CO})_9\text{CCFeCp}(\text{CO})_2]$ as an alternate precursor to $[\text{PPN}]_2[\text{Fe}_6(\text{CO})_{18}\text{C}_4]$, which she had previously synthesized by the treatment of $[\text{Fe}_3(\text{CO})\text{CCO}]^{2-}$ with excess $(\text{SO}_3\text{CF}_3)_2$. She postulated that the reaction proceeds through an intermediate with the formula $[\text{PPN}][\text{Fe}_3(\text{CO})_9\text{CCOTf}]$, followed by loss of SO_3CF_3^- and subsequent dimerization to yield $[\text{PPN}]_2[\text{Fe}_6(\text{CO})_{18}\text{C}_4]$. She also discovered an alternate route to $[\text{Fe}_6(\text{CO})_{18}\text{C}_4]^{2-}$.

based on the treatment of $[\text{Fe}_3(\text{CO})_9\text{CCFeCp}(\text{CO})_2]^-$ with electrophiles.

DOE Sponsored Publications:

"Mixed-Metal Butterfly Acetamidate Clusters Derived from a Highly Reactive Ruthenium Oxo Cluster: Synthesis and Characterization of $[(\text{PPh}_3)_2\text{N}][\text{MRu}_3(\text{CO})_{12}(\eta^2-\mu_3\text{-NC}(\mu\text{-O})\text{CH}_3)]$, ($\text{M} = \text{Mn}$ 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 μ_4 -Sulfido Ligands: $[\text{PPN}][\text{Fe}_3\text{M}(\text{CO})_{12}(\mu_4\text{-E})]$ ($\text{E} = \text{O}$ or S and $\text{M} = \text{Mn}$ 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. Sleboznick, D. F. Shriver, *J. Organomet. Chem.*, **495** 33 (1995).

"Reaction of $[\text{PPN}][\text{Fe}_3(\text{CO})\text{CCOC}(\text{O})\text{CH}_3]$ with the Metal Nucleophile $[\text{Re}(\text{CO})_5]^-$ to Generate a Mixed-Metal Acetylidyne, $[\text{PPN}][\text{Fe}_3(\text{CO})_9\text{CCRe}(\text{CO})_5]^-$ ", 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 $\text{Os}_3(\text{CO})_9(\mu_3\text{-NPh})(\mu_3\text{-S})$, $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-(PhN)}_2\text{SO})(\mu_3\text{-S})$, and $\text{Os}_3(\text{CO})_8(\text{NCMe})(\mu_3\text{-NPh})(\mu_3\text{-S})$, W. H. Yeh, C. L. Stern and D. F. Shriver, *Inorg. Chem.*, **36**, 4408-4414 (1997).

"New SO_2 Iron Containing Cluster Compounds $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_9(\mu_3, \eta^2\text{-SO}_2)]$, $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_8(\mu\text{-SO}_2)\mu_3\text{-S}]$, $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_8(\mu\text{-SO}_2)(\mu_3\text{-CCO})]$, and $[\text{PPN}]_2[\text{Fe}_2(\text{CO})_6(\mu\text{-SO}_2)_2]$ From Heterometal Precursors", R. W. Eveland, C. C. Raymond, T. E. Albrecht-Schmitt, D. F. Shriver, *Inorg. Chem.*, **38**, 1282-1287 (1999).

" $[\text{PPN}][\text{Fe}_3(\text{CO})_9(\text{C}\equiv\text{CH})]$ and $[\text{Fe}_3(\text{CO})_9(\text{C}\equiv\text{COTi}(\text{THF})_4\text{Cl})]$ From the Reaction of Low-Valent Titanium with $[\text{Fe}_3(\text{CO})_9(\text{CCO})]^{2-}$ ", R. W. Eveland, C. C. Raymond, D. F. Shriver, *Organometallics*, **18**, 534-539 (1999).

"[PPN][Fe₃(CO)₉(C≡CH)] and [Fe₃(CO)₉(C≡COTi(THF)₄Cl)] From the Reaction of Low- Valent Titanium with [Fe₃(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