Substitution and Redox Reactions of Heptarhenium Cluster Derivatives

Scott W. Simerly   Final Seminar   August 16, 1991

Transition-metal clusters have long been studied as potential catalysts or as models for ligands bound to metal centers on surfaces [1]. One of the most interesting questions regarding metal cluster compounds is the extent to which one metal center interacts with one or more neighboring metal centers during reactions. As such, the investigation of ligand substitution reactions of metal cluster complexes are of interest in determining electronic effects, in which adjacent metal centers act as metallo-ligands, as well as structural interactions which involve cooperative coordination (multi-site binding).

Previous work has shown the heptarhenium cluster derivatives, $[Re_7C(CO)_{21}ML_n]^{2-}$ are analogous to the mononuclear species $CpML_n$ (M= Rh, Ir, etc.) [2]. The second-order rate constants for the reactivity of $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ towards phosphorus donors were determined in order to form a comparison with the classic work of Basolo and coworkers on the substitution reactions of $CpRh(CO)_2$ and related compounds [3]. In order to correlate the results to electronic and/or steric effects, steric profiles relating log k_2 to an intrinsic reactivity (α), an electronic parameter (β), and a steric parameter (θ) were constructed [4]. From differences in intrinsic reactivity for phosphines and phosphites, an intermediate configuration involving a bridging carbonyl has been proposed for the reaction of $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ with various phosphorus donors (PY_3).
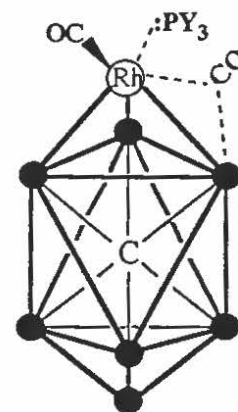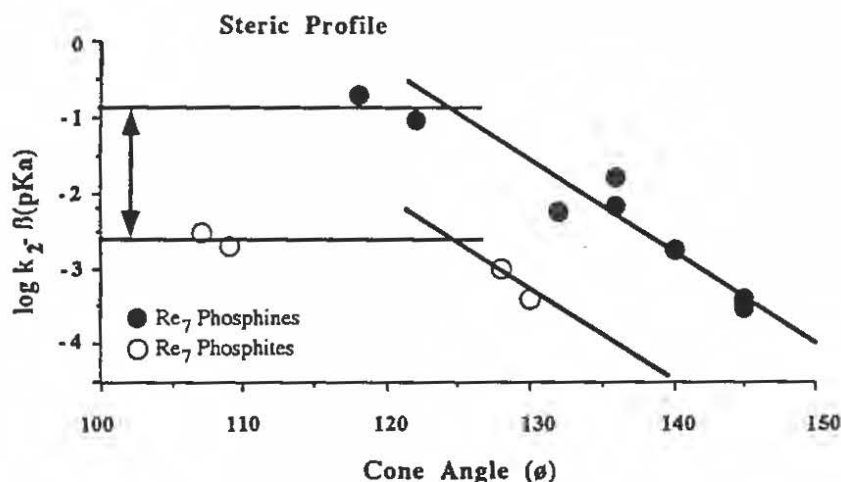

Proposed Transition State

Modifications of the coordination sphere of transition metal clusters may result in significant changes in cluster reactivity [5]. Nitrosylation of a series of mixed-metal heptarhenium clusters, $[Re_7C(CO)_{21}ML_n]^{2-}$, gave the mono-substituted products, $[Re_7C(CO)_{20}(NO)ML_n]^-$. A variety of spectroscopic techniques were used to characterize the reaction products. Variable temperature ^{13}C NMR studies determined the solution structure of $[Re_7C(CO)_{20}(NO)-Rh(CO)_2]^-$. From kinetic studies, the nitrosyl substituted cluster $[Re_7C(CO)_{20}(NO)Rh(CO)_2]^-$ exhibits enhanced reactivity toward phosphorus ligands in comparison with $[Re_7C(CO)_{21}-Rh(CO)_2]^{2-}$.

The carbonyl ligands bound to $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ display unusual intermolecular and intramolecular exchange. Upon treatment with ^{13}CO, $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$ is selectively ^{13}CO enriched to $[Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$. A capping $Re(CO)_3$ moiety trans to the rhodium cap remains unenriched. Formation of the radical species $[Re_7C(CO)_{21}Rh(CO)_2]^-$ by chemical oxidation results in complete carbonyl scrambling, which is revealed upon reduction to the parent cluster $[Re(^{13}CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$. The selectively ^{13}CO enriched cluster $[Re(CO)_3Re_6C(CO)_{18}]^{2-}$ has been formed in a decapping reaction of $[Re(CO)_3Re_6C(^{13}CO)_{18}Rh(^{13}CO)_2]^{2-}$ with excess PPh_3 in acetonitrile.
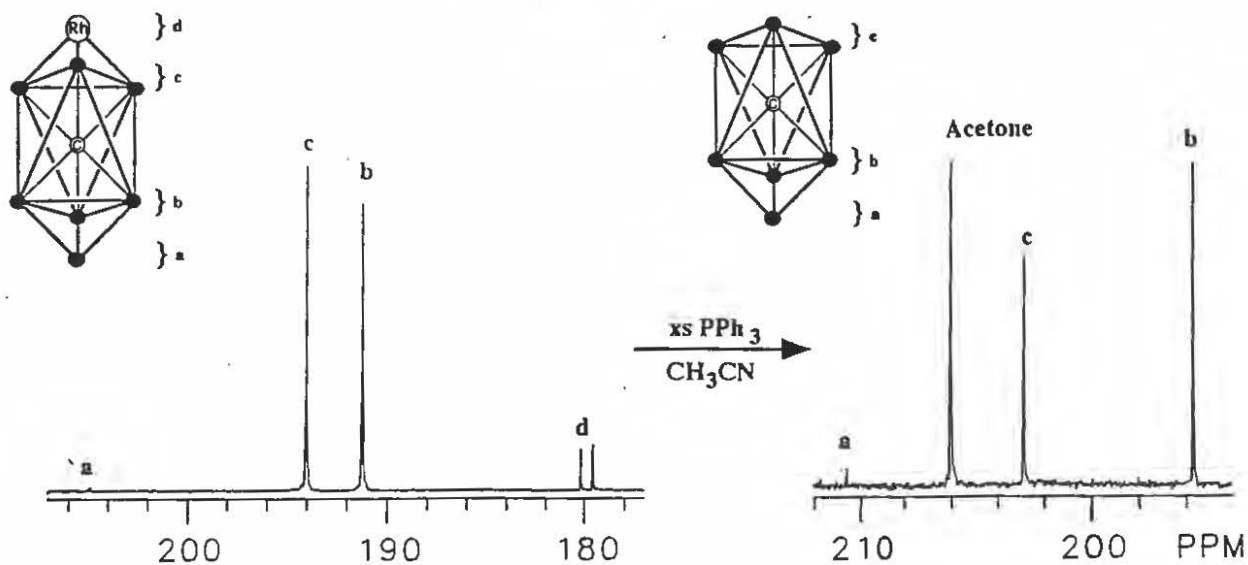
Electrochemical techniques have been used to increase the lability of clusters toward substitution reactions [6]. While ligand-ligand substitution reactions form the majority of such reactions, anionic charge-ligand substitutions also exist. For example, oxidation of $[Os_7C(CO)_{20}]^{2-}$ under a CO atmosphere affords $[Os_7C(CO)_{21}]$ [7]. In a similar reaction, two-electron oxidation of $[Re_7C(CO)_{21}]^{3-}$ in the presence of $P(OPh)_3$ affords $[Re_7C(CO)_{21}(P(OPh)_3)]^-$. ^{13}C NMR indicates that this cluster exhibits charge localization. $[Re_7C(CO)_{21}(P(OPh)_3)]^-$ decomposes in acetonitrile to form $[Re_6C(CO)_{19}]^{2-}$ and $[Re(CO)_3(P(OPh)_3)_2(NCCH_3)]^+$, and therefore it represents a directly observed intermediate in a cluster decapping reaction.
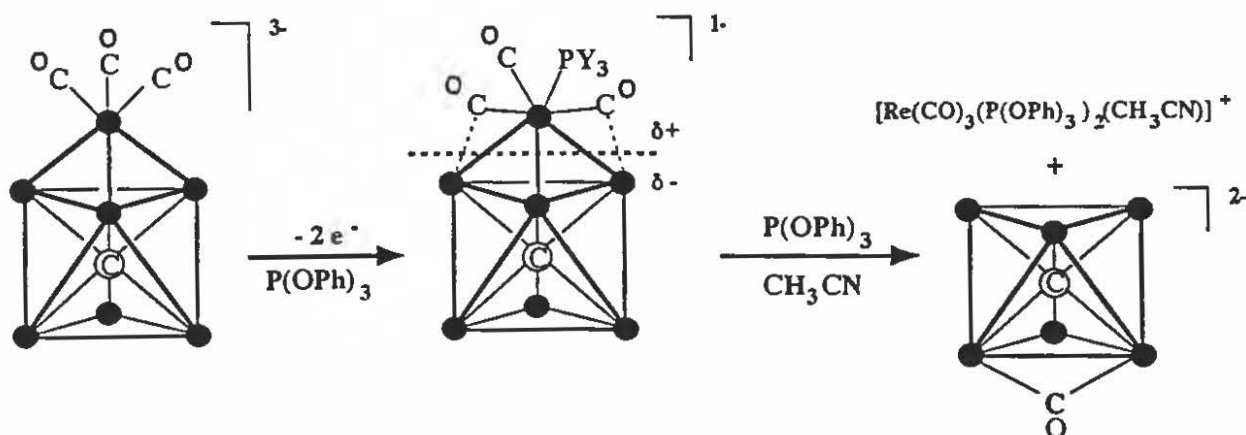
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