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Reductive Coupling of Carbon Monoxide to C_2 Products

Progress Report

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Progress during the budget period beginning in May of 1990 is summarized in this report. Work proposed in the two major areas of the grant proposal has been successfully pursued. Advances in carbyne chemistry are addressed first below, followed by a brief outline of new initiatives in metal nitrene chemistry which completes the report.

Perhaps our flashiest result is the isolation and characterization of a terminal Fischer carbyne complex. Although several high oxidation state $L_nM{\equiv}CH$ complexes are known, the low oxidation state carbonyl containing species has proven elusive. We first prepared $Tp'(CO)_2W{\equiv}CH$ from a conversion of the cationic phosphonium carbyne $Tp'(CO)_2W{\equiv}CPMe_3^+$ to a neutral carbene by hydride addition at carbon. Removal of PMe_3 with a Lewis acid trap yielded milligram quantities of the desired terminal carbyne. More recently we have prepared a silylcarbyne precursor which reacts with Bu_4NF in wet THF to form substantial amounts of the CH carbyne. Dimerization to form an unusual vinylidene bridged complex is a facile decomposition route which consumes the $Tp'(CO)_2M{\equiv}CH$ monomer for both M=Mo and M=W. This work has been communicated.[1]

Preparation of other carbyne complexes has been achieved using $Tp'(CO)_2W{\equiv}C\text{-}Cl$ as a reagent. Both $Tp'(CO)_2W{\equiv}C\text{-}OAr$ and $[Tp'(CO)_2W{\equiv}C\text{-}PR_3][PF_6]$ have been synthesized in high yields by nucleophilic attack on the chlorocarbyne complex. Aryloxycarbyne complexes had not been reported previously. Surprisingly the one-bond coupling between the carbyne carbon and phosphorous is too small to observe in the ^{13}C NMR spectrum except for the tricyclohexyl phosphine derivative where $^1J_{PC} = 15$ Hz.[2]

Another carbyne derivative was synthesized from $Tp'(CO)_2Mo{\equiv}C\text{-}Cl$ by adding $K[CpFe(CO)_2]$ to displace the chloride. This rare example of a carbide bridged dinuclear complex has been protonated to form an agostic bridging methylene complex characterized by a low J_{CH} value of 72 Hz. Insertion into the iron-carbide bond and ligand substitution reactions have also been communicated for the carbide complex.[3]

Reduction of phenylacetylene in the coordination sphere of tungsten(II) by sequential H^-, H^+ addition also generates an agostic product. The net result is conversion of a four-electron donor PhC≡CH unit to $PhCCH_3$ which provides four electrons total, too, through the carbene lone pair and the C-H donation to the metal. The β-agostic carbene complexes formed this way have distinctive ^{13}C NMR properties and an x-ray structure has confirmed the agostic nature of the carbene ligand.[4]

We have found electrophilic addition to anionic isocyanide complexes to be an important route to new carbon based ligands. A mixture of molybdenum aminocarbyne, η^2-iminoacyl, and η^2-acyl complexes has been prepared via the addition of MeI to the anionic *tert*-butyl isocyanide complex $[Na][Tp'(CO)_2Mo(CNBu^t)]$. Addition of MeI to the analogous anionic methyl or phenyl isocyanide complex yields only aminocarbyne complexes. The η^2-iminoacyl complex can be deprotonated at the C_β methyl site to give an anionic η^2-enamide intermediate, and quenching with MeI yields the ethyl product, $Tp'(CO)_2Mo(\eta^2\text{-}C(NBu^t)Et)$. Protonation of $Tp'(CO)_2Mo{\equiv}CN(Me)(Bu^t)$ in the presence of phenylacetylene ultimately yields a cationic η^2-vinyliminium complex, $[Tp'(CO)_2Mo(\eta^2\text{-}C(Ph){=}C(H)C(H){=}N(Me)(Bu^t))][BF_4]$. This material is fluxional in the ^1H NMR spectrum due to rapid inversion at the vinyl β-carbon. A neutral η^2-vinylamine complex, $Tp'(CO)_2Mo(\eta^2\text{-}C(Ph){=}C(H)CH_2N(Me)(Bu^t))$, has been synthesized by addition of $LiEt_3BH$ to the cationic η^2-vinyliminium complex.[5]

Two forays into nitrene chemistry have clarified our ideas regarding the accessibility and reactivity of intermediate oxidation state metal complexes with amido and imido ligands. Organometallic products formed from the reaction of an electrophilic iron carbene complex with nitrosoarenes or azobenzene reflect net insertion of the ArN=X moiety into the Fe=CHAr bond. $Cp(CO)_2Fe\text{-}O\text{-}N(Ar'){=}CHAr^+$ and $Cp(CO)_2FeN(Ph)\text{-}N(Ph){=}CHAr^+$ have been isolated and spectroscopically characterized.[6]

More promising results for long term progress in building electrophilic nitrene complexes have been achieved with Group VI reagents. Simple methods for generating $Tp'(CO)_2W{=}NHR$ for R = Ar and Bu^t are encouraging. Furthermore, removal of H^- from the amido ligand with either I_2 or $[Ph_3C][BF_4]$ provides access to cationic nitrene complexes. Addition of BH_4^- to the $Tp'(CO)_2W{\equiv}NR^+$ cation regenerates the neutral amido complex, indicating that the nitrene here is electrophilic in terms of net chemistry regardless of the mechanism.[7]

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