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Bond Forming Reactions of Carbyne and Nitrene Complexes

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Templeton, J. L.
Institution: University of North Carolina Phone: 919-966-4575
Department: Department of Chemistry Fax: 919-843-8005
Address: Chapel Hill, NC 27514 Email: joetemp@unc.edu

An isolobal relationship among terminal carbyne, nitrene and oxo ligands provided the basis for our efforts to explore new synthetic routes to such complexes and to probe bond forming reactions of these ligands. The specific goals of this project were to explore reactions of carbyne and nitrene ligands, and a summary of our results follows. Manipulation of metal-ligand pi bonds to control reactivity patterns provided the conceptual basis for this work. New transformations and coupling reactions of the CR and NR moieties bound to metal centers have been explored and transformations of carbyne or nitrene ligands have been achieved.

Perhaps the most exciting results have come in the area of the simplest ligand: the CH carbyne unit. Treatment of $[Tp'(CO)_2W\equiv C\text{-}PPh_3][PF_6]$ (Tp' = hydridotris(3,5-dimethylpyrazolylborate) with $Na[HBEt_3]$ forms the methylidyne complex $Tp'(CO)_2W\equiv C\text{-}H$ via formyl and carbene intermediates. Protonation of the $Tp'(CO)_2W\equiv C\text{-}H$ methylidyne complex yields the cationic agostic methylidene complex, $[Tp'(CO)_2W{=}CH_2][BF_4]$. The methylidyne complex with a pK_a of 28.7 can be deprotonated to provide the anionic terminal carbide $Tp'(CO)_2W\equiv C\text{-}Li$; a resonance at 556 ppm in the ^{13}C NMR spectrum has been assigned to the carbide carbon. Addition of excess $Na[HBEt_3]$ to $Tp'(CO)_2W\equiv C\text{-}H$ generates the anionic methylidene complex $[Na][Tp'(CO)_2W{=}CH_2]$.

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Mark P. Dvorscak Sept 30, 2002
Date
(630) 252-2393
E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office

Complexes that contain metal-carbon multiple bonds are activated toward deprotonation and alkylation reactions at the site beta to the metal. One application is in the case of methylcarbyne complexes which form reactive nucleophilic vinylidene anions when deprotonated. We used this reagent to derivatize carbyne ligands and to develop a new series of hydrocarbon bridged metal dimers. Combination of the nucleophilic vinylidene anion with an array of electrophiles yielded a range of monomeric carbyne derivatives, and dimers with terminal carbyne linkages to each metal were also prepared. Both C_3 and C_4 bridged skeletons linking metal centers in new dimeric products were synthesized, and examples of C_1 and C_2 connectors were also been prepared.

We have exposed interconversions among carbyne, allyl, and vinyl isomers. Isomers of the carbyne unit (C_3H_4R) in $Tp'(OC)_2W{\equiv}CCH_2CH_2R$ include η^2-vinyl ligands in complexes of the type $[Tp'(OC)_2W(\eta^2\text{-}CH_2CCH_2R)]$, and these can rearrange to η^3-allyl complexes $[Tp'(OC)_2W(\eta^3\text{-} CH_2CHCHR)]$. The thermodynamic and kinetic relationships of these three isomeric ligands have been revealed in our studies.

We have also examined catalytic conversion of PhINR and olefins to aziridines with copper complexes. Electronic effects on the catalytic transfer of a nitrene fragment using a copper(I) complex as the catalyst have been investigated. Perhaps most importantly we proved that simple Lewis acids can convert imines and carbene precursors to aziridines, too.

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