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Reductive Coupling of Carbon Monoxide

To C₂ Products

Progress Report for the Period
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INTRODUCTION

This progress report covers the two broad areas of research addressed during the period since May 1, 1990. As proposed in 1989, studies of carbyne transformations have been pursued with a variety of carbyne substituents. Perhaps the most noteworthy carbyne results are also the simplest: preparation and properties of the parent $M\equiv CH$ unit. The other topic addressed with DOE support has metal nitrene chemistry as the cornerstone. Publications with iron, tungsten and copper complexes reflect our efforts to access intermediate oxidation state metal nitrene monomers. This new thrust was a central theme of the proposal submitted in 1989, and progress to date is sufficiently encouraging that detailed plans for expanding our nitrene project are an integral part of the accompanying proposal. References in this progress report are kept to a minimum; extensive references in the papers cited here place the work in perspective relative to the literature landscape.

I. CARBYNE CHEMISTRY

The impetus for exploring carbyne chemistry was crafted into our original 1985 proposal as a reflection of our hypothesis that carbyne species were feasible intermediates in reductive carbon monoxide coupling reactions.¹ During the intervening years several research groups have made significant contributions to our understanding of the role of carbyne ligands in coupling reactions.² The Lippard group at MIT has led the charge to expose reaction pathways and capitalize on the potential of this ubiquitous class of reactions.³

As a result of studies directed toward conversion of metal carbonyls to metal carbynes utilizing thiocarbonyl model compounds,⁴ tantalizing quantities of $Tp'(CO)_2W\equiv CH$ were prepared in our laboratory (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate) (Scheme 1). Since removal of one phosphine from the cationic carbene $[Tp'(CO)_2W=C(PMe_3)_2]^+$ was efficiently realized with MeI as a mild

Scheme 1

Tp' = hydridotris(3,5-dimethylpyrazolyl)borate

electrophilic trap for $P(Me)_3$,⁵ it followed that removal of phosphine from $Tp'(CO)_2W=CH(PMe_3)$ should yield the desired $Tp'(CO)_2W\equiv CH$. While this reaction proceeded as expected to form the parent carbyne (eq. 1), only small quantities could be synthesized, and it was not possible for us to scale up this reaction to more than a few milligrams.

Since the chemistry of a low oxidation state terminal Fischer carbyne complex with ancillary carbonyl ligands had not been previously accessible, we sought a more generous route to the $Tp'(CO)_2W\equiv CH$ monomer. We have now developed a more efficient synthesis involving fluoride-induced desilylation of silylcarbyne precursors.⁶ Beginning with $M(CO)_6$ ($M=Mo, W$) and following Mayr's multistep Fischer carbyne synthesis,⁷ we incorporated Tp' into the metal coordination sphere and isolated silylcarbynes of both molybdenum and tungsten in low yield following chromatography (Scheme 2). These silylcarbyne complexes were smoothly desilylated with Bu_4NF to generate hydridocarbynes $Tp'(CO)_2W\equiv CH$. For the tungsten derivative we isolated the product as a bright yellow powder in 30% yield; a downfield singlet in the proton NMR at 8.22 ppm with 83 Hz coupling to tungsten (^{183}W , $I=1/2$, 14% abundant) and a carbon resonance at 281 ppm with large couplings to both tungsten (192 Hz) and hydrogen (142 Hz) unambiguously identified the CH ligand.

Scheme 2

The molybdenum carbyne complex undergoes a secondary reaction to form a new dimeric compound at low temperatures, while dimerization of the tungsten analog takes days at room temperature (eq. 2). The structure of the tungsten dimer has been determined, and the most interesting geometrical feature of the structure is the W_2C_2 core. A short C-C distance of 1.51 Å indicates a carbon-carbon single bond. The

bridging carbide links the two tungsten atoms with bond distances of 2.00 Å and a W-C-W angle of 167°. The methylene carbon lies about 2.35 Å from each tungsten, and given that this carbon is five-coordinate, a non-classical bonding description is no doubt appropriate for the planar W₂C₂ framework.

Informative NMR data include low field signals for the bridging carbide in both dimers (347 ppm for Mo and 304 ppm for W). These chemical shift values and the 45 Hz coupling to tungsten are compatible with a vinylidene-like carbide center (Chart I). The bridging methylene carbon appears as a triplet near TMS (7 ppm for Mo and -3 ppm for W) in the gated decoupled C-13 spectrum.

Chart I

In an effort to bring into focus the bonding in the W₂C₂ skeleton, an extended Hückel molecular orbital calculation was carried out on the isoelectronic model compound [H₃(CO)₂W(CCH₂)W(CO)₂H₃]⁴⁻ in which hydride ligands were substituted for the Tp' ligands.⁸ This model system has a large HOMO-LUMO gap of 4.3 eV, a characteristic of stable diamagnetic complexes.

The nonclassical bonding in the W₂C₂ core can be understood in terms of two orthogonal three-center interactions. A set of molecular orbitals can be identified which involves combinations of tungsten d_{xz} atomic orbitals with the unhybridized p_x orbital at the bridging methylene carbon (refer to the coordinate system in Figure 1). A low-lying filled bonding combination of two out-of-phase metal d_{xz} orbitals with the methylene p_x constitutes a three center-two electron σ-bonding scheme; the nonbonding combination (the molecule's LUMO) and the antibonding combination remain empty.

The carbide nucleus of the vinylidene bridge can use sp² hybrid orbitals for bonds to the methylene carbon and both tungsten nuclei, leaving an unhybridized p_y orbital at the carbide atom. The carbide p_y is of the proper symmetry to interact with the metal d_{xy} orbitals, generating a set of three molecular orbitals which define a three center-four

Figure 1. Qualitative Molecular Orbital
Scheme for $\text{Tp}'(\text{CO})_2\text{M}(\mu\text{-}\eta^2\text{:}\eta^2\text{-CCH}_2)\text{M}(\text{CO})_2\text{Tp}'$

M-C-M Bonding: 3-center, 4-electron

M-CH₂-M Bonding: 3-center, 2-electron

electron p-bond. Both low-lying bonding ($d_{xy} + p_y - d_{xy}$) and nonbonding ($d_{xy} + d_{xy}$) molecular orbitals are doubly occupied, leaving an empty antibonding combination well above the frontier orbitals (Figure 1).

Cyclic voltammograms reveal that both the molybdenum and tungsten vinylidene dimers are readily oxidized. The molybdenum derivative exhibits a quasi-reversible redox couple at $E_{1/2} = +0.64$ V vs SCE, while the tungsten analog displays a quasi-reversible oxidation at 0.44 V. As is typical the tungsten complex is more easily oxidized than its molybdenum congener.

Although NMR spectra of the molybdenum dimer indicate a structure possessing mirror symmetry at room temperature, the tungsten analog displays spectra which suggest fluxional behavior. Upon cooling a sample of the tungsten dimer to -75 °C, the broad ^1H NMR signals observed in the room temperature dimer spectrum separate, so that the downfield resonances occur as three sharp singlets and six separate Tp' methyl singlets are observed upfield. As the sample is warmed, the two lower field aromatic resonances coalesce (Figure 2) and the methyl resonances undergo corresponding changes. A $\Delta G^\ddagger$ of 13.9 kcal/mol characterizes the fluxional process for tungsten while the molybdenum dimer behaves similarly with a $\Delta G^\ddagger$ of 10.7 kcal/mol.

At low temperature pairwise equivalence characterizes the six pyrazole rings and four terminal carbonyls in the vinylidene dimers. Citing the geometry of the tungsten dimer in the solid state and invoking an idealized octahedral geometry at each metal center, a plausible ground state at low temperature would possess a C_2 symmetry axis coincident with the C-C bond of the bridging vinylidene ligand. In this manner pyrazoles C and C' are equivalent as are pyrazoles A and A', and B and B'. There will be two pairs of equivalent carbonyls also, each comprised of one carbonyl from each metal.

One process which can explain the observed NMR behavior involves a net rotation of the bridging methylene unit about the M-C-M axis by 180° to regenerate an equivalent conformer wherein pyrazoles A and A', and B and B' have exchanged; pyrazoles C and C' are unchanged. As the methylene rotates freely about the M-C-M axis, the four off-axis pyrazoles all become equivalent, as do all four terminal carbonyls; the pyrazoles along the axis remain distinct.

Displacement of chloride from the group 6 chlorocarbene complexes $\text{Tp}'\text{W}(\text{CO})_2\equiv\text{CCl}$ with aryloxide anions produces neutral aryloxycarbene derivatives⁹ for

both molybdenum and tungsten, $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{COAr}$ ($\text{Ar} = \text{Ph}, \text{Tol}, \text{p-C}_6\text{H}_4\text{OMe}$) (eq. 3). Tertiary phosphines ($\text{PMe}_2\text{Ph}, \text{PPh}_3, \text{PCy}_3$) also displace chloride from the tungsten halocarbene precursor to give the cationic phosphonocarbynes $[\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CPR}_3][\text{PF}_6]$ (eq. 4).

Members of this new class of carbene complexes display relatively high field methyldiene resonances in their C-13 NMR spectra, presumably due to resonance stabilization by the aryloxy substituent. Note that unlike common aminocarbene complexes which bear an NR_2 group, the phosphonocarbynes with PR_3 substituents lack a heteroatom lone pair to stabilize the carbene carbon. The absence of a detectable one-bond coupling between the carbene carbon and the attached phosphorus atom in all but the PCy_3 derivative is a curious feature of these $[\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CPR}_3]^+$ cations.

Upon electrophilic activation with HBF_4 , tungsten aryloxycarbene regioselectively insert phenylacetylene to generate cationic tungsten η^2 -vinylxonium complexes $[\text{Tp}'(\text{CO})_2\text{W}(-\text{C}(\text{Ph})=\text{CH}-\text{CH}=\text{OAr})][\text{BF}_4]$ (eq. 5). An x-ray structural investigation reveals interatomic distances which indicate substantial electron delocalization in the new organic ligand, suggesting that the tungsten nucleus is saturated by η^2 -vinyl coordination and that the oxygen atom bears some positive charge. Free iodide acts to cleave the aryl-oxygen bond to form a neutral metallocene, $\text{Tp}'(\text{CO})_2\text{W}(=\text{C}(\text{Ph})=\text{CH}-\text{CH}=\text{O})$ (eq. 6). This example of $\text{S}_{\text{N}}2$ attack on the aromatic ring is compatible with the description of the oxygen atom as positively charged.

Although the electron poor aryloxide $\text{K}[\text{O}(\text{p-C}_6\text{H}_4\text{NO}_2)]$ displaces chloride from tungsten chlorocarbene $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CCl}$ to form $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{COAr}$, the phosphonium carbene $[\text{Tp}'(\text{CO})_2\text{W}\equiv\text{C-PMe}_2\text{Ph}]^+$ reacts with this aryloxide to form an η^2 -phosphoranylidene ketene, $\text{Tp}'(\text{CO})(\text{OAr})\text{W}(\eta^2\text{-C(PMe}_2\text{Ph)CO})$ (eq. 7). This nucleophile induced coupling reaction combines the carbene and carbonyl ligands to generate a ketenyl analog. The resulting phosphine substituted ketenyl ligand can be methylated at the oxygen site to form a cationic alkyne complex along the lines of the now classical coupling and electrophilic addition sequence (eq. 8). Even though the phosphine substituted ketenyl and alkyne ligands display unusual ^{13}C chemical shift values, the structures of both of these complexes are consistent with current understanding of metal-ketenyl and metal-alkyne bonding interactions in $d^4 \text{L}_n\text{M}(\text{CO})$ complexes.

A mixture of molybdenum aminocarbene, η^2 -iminoacyl, and η^2 -acyl complexes, $\text{Tp}'(\text{CO})_2\text{Mo}\equiv\text{CN}(\text{Me})(\text{Bu}^t)$, $\text{Tp}'(\text{CO})_2\text{Mo}(\eta^2\text{-C}(\text{NBu}^t)\text{Me})$, and $\text{Tp}'(\text{CO})(\text{Bu}^t\text{NC})\text{Mo}(\eta^2\text{-C}(\text{O})\text{Me})$, was prepared via the addition of MeI to the anionic tert-butyl isocyanide complex $[\text{Tp}'(\text{CO})_2\text{Mo}(\text{CNBu}^t)]^-$ (eq. 9).¹⁰ Addition of MeI to the analogous anionic methyl or phenyl isocyanide complex yields only aminocarbene complexes (eq. 10). The iminoacyl complex can be deprotonated at the C β methyl site with KH to give an anionic η^2 -enamide intermediate, and quenching with MeI yields the ethyl product. The iminoacyl complex undergoes cleavage in air to give tert-butylacetamide.

Protonation of $\text{Tp}'(\text{CO})_2\text{Mo} \equiv \text{CN}(\text{Me})(\text{Bu}^t)$ in the presence of phenylacetylene ultimately yields a cationic η^2 -vinyliminium complex, $[\text{Tp}'(\text{CO})_2\text{Mo}(\eta^2\text{-C}(\text{Ph})=\text{CHCH}=\text{N}(\text{Me})(\text{Bu}^t))]^+$ (eq. 11). This monomer is fluxional on the NMR timescale due to rapid inversion at the vinyl β -carbon. The x-ray structure of the η^2 -vinyl cation has been determined, and it is qualitatively similar to the structure of the aryloxy analog discussed above. Addition of LiEt_3BH to the cationic η^2 -vinyliminium complex generates a neutral η^2 -vinyl amine product (eq. 12).

In view of the success we encountered in substitution reactions utilizing Lalor's chlorocarbene as a reagent, we attempted to replace the chloride with the $[\text{CpFe}(\text{CO})_2]^-$ fragment (Fp). Indeed the reaction of $\text{Tp}'(\text{CO})_2\text{Mo} \equiv \text{CCl}$ with Fp anion rapidly formed $\text{Tp}'(\text{CO})_2\text{Mo} \equiv \text{C-Fp}$ (eq. 13).¹¹ A vinylidene resonance form with both metals in the same oxidation state is no doubt an important contributor to the bonding as shown in Chart 2. The bridging carbide resonates at 381 ppm in the ^{13}C NMR spectrum, near the range expected for vinylidene C_α chemical shifts and below carbene chemical shift values in related complexes.

Chart 2

The x-ray structure of the bridging carbide unit reveals a single carbon between the iron and molybdenum atoms in an almost linear unit. The molybdenum-carbon bond is definitely a triple bond and the iron-carbon bond length is appropriate for a σ -bond between an sp-type carbon and an iron center.

Protonation of the central carbide with fluoroboric acid at low temperature forms a cationic μ^2 -methyne complex (eq. 14). Prominent NMR data include a proton singlet at 1.94 ppm and a ^{13}C signal at 344 ppm which splits into a doublet with $J_{\text{CH}} = 72$ Hz in the coupled spectrum. One-bond CH coupling constants in this range are the most reliable spectral diagnostic for agostic bonds.

Efforts to add electrophiles to the oxygen site of a carbonyl ligand in anionic metal complexes led us to explore steric factors which might inhibit metal based attack and thus indirectly favor oxygen addition. Proton addition was particularly prone to occur at the metal, and as a result we were led to study $\text{Tp}'\text{W}(\text{CO})_3\text{H}$ and related seven-coordinate tungsten compounds.

Unusual W-H one bond coupling constants were found for $\text{Tp}'\text{W}(\text{CO})_3\text{H}$ analogs (4-10 Hz) and $\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CMe})\text{H}$ (120 Hz).¹² NMR studies have been extended to inverse detection methods for ^{183}W where remote J_{WH} couplings to pyrazole protons can be used effectively in heteronuclear shift correlation experiments to obtain ^{183}W spectra in less than an hour.¹³ NOESY spectra are particularly informative in these small molecules where the three pyrazole rings provide convenient probe protons for geometry correlations.

Seven-coordinate complexes are accessible in the d^4 Tp' system outside of the hydride derivatives. Although the extensive series of seven-coordinate Cp complexes is not matched, as exemplified by the difference between $\text{Cp}(\text{CO})_3\text{MR}$ and $\text{Tp}'\text{M}(\text{CO})_2(\eta^2\text{-C}(\text{O})\text{R})$ where the Tp' system adopts the six-coordinate acyl geometry (Chart 3), steric

factors are not prohibitive in achieving seven coordination. Oxidation of the $\text{Tp}'\text{W}(\text{CO})_3$ radical with ferrocenium followed by addition of phosphine yields a series of cationic tungsten(II) complexes of the type $[\text{Tp}'\text{W}(\text{CO})_3]^+$ (eq. 15).¹⁴ Spectral data indicate that three of these phosphine complexes adopt a 3:3:1 capped octahedral geometry both in solution and in the solid state. In addition, x-ray analysis has confirmed this aesthetically pleasing geometry for the PMe_3 and PMe_2Ph derivatives. For steric reasons, the PPh_3 complex prefers the more common 4:3 piano stool geometry.

Chart 3

A route to metal-carbon multiple bonds by addition reactions of coordinated alkynes has been uncovered. Nucleophilic addition at the terminal acetylene carbon of $[\text{Tp}'(\text{CO})_2\text{W}(\text{PhC}\equiv\text{CH})]^+$ can be achieved with either $\text{Li}[\text{Et}_3\text{BH}]$ or MeLi to form neutral η^2 -vinyl complexes (eq. 16). The carbenoid character of C_α , bearing the phenyl group, is evident in the low-field ^{13}C chemical shift (234 ppm for $\eta^2\text{-CPh=CH}_2$ and 265 ppm for $\eta^2\text{-CPh=CHMe}$). Protonation of the original alkyne terminal carbon results from addition of tetrafluoroboric acid to the neutral η^2 -vinyl monomers. The net result of sequential H^- , H^+ addition to the terminal alkyne carbon is conversion of $\text{PhC}\equiv\text{CH}$ to PhCCH_3 .¹⁵ While electrophilic addition to the C_β site of η^1 -vinyl ligands to form carbenes maintains the full electron count at metal, simple carbene formation from an η^2 -vinyl ligand leaves the metal unsaturated (eq. 17).

The only unusual piece of spectral data we obtained for the methylphenylcarbene complex was a high-field ^{13}C chemical shift for the methyl carbon (-22.8 ppm). Fortunately the ethyl analog gave rise to two distinct proton signals for the methylene group of the ethyl substituent at -60°C . The keystone that definitively characterizes the cationic ethylcarbene complex as agostic was the doublet of doublets revealed in the low temperature ^{13}C NMR spectrum. The smaller J_{CH} value of 96 Hz is the signature of an agostic bond, and the larger value of 145 Hz reflects rehybridization from sp^3 toward sp^2 for the methylene carbon. Coalescence of the methylene protons at -5°C indicates a barrier of 11.7 kcal/mol for enantiomer interconversion. The x-ray structure of the methyl derivative is compatible with an agostic formulation. The metal to methyl carbon distance of 2.49 Å is consistent with a three-center, two-electron linkage tying the W-H-C unit together. The $\text{W}=\text{C}-\text{C}$ angle of 91° to the methyl carbon is reminiscent of protonated carbynes, the analogy here being a methylated phenylcarbyne ligand.

In contrast, hydride addition to the bis(phenylacetylene) complex $[\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CH})_2]^+$ forms an alkyne σ -vinyl complex, $\text{Tp}'(\text{CO})(\text{PhC}\equiv\text{CH})\text{W}(\eta^1\text{-CPh}=\text{CH}_2)$ (eq. 18). Protonation of this η^1 -vinyl complex at $\text{C}\beta$ results in the formation of an 18-electron alkyne carbene cation, $[\text{Tp}'(\text{CO})(\text{PhC}\equiv\text{CH})\text{W}=\text{C}(\text{Me})\text{Ph}]^+$ (eq. 19).¹⁶

Other fundamental ligand transformations have been observed when nucleophiles react with cationic internal alkyne complexes. Evidently the steric hindrance of the alkyne substituents and the electron richness of the alkyl group relative to hydrogen inhibit nucleophilic attack at the coordinated alkyne. As a result cuprate reagents transfer R^- to a carbonyl to form acyl ligands.

Reaction of $[\text{Tp}'\text{W}(\text{CO})_2(\text{PhC}\equiv\text{CMe})]^+$ with LiCuR_2 ($\text{R} = \text{Me}, \text{Ph}$) generates neutral η^1 -acyl complexes $\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CMe})(\eta^1\text{-C}(\text{O})\text{R})$ in which the alkyne ligand remains as a four-electron donor (eq. 20).¹⁷ Addition of base deprotonates the alkyne methyl group rather than the acyl methyl group, and the nucleophilic propargyl synthon which results reacts with MeI to yield an ethyl alkyne complex (eq. 21). Electrophilic addition at the acyl oxygen of the neutral η^1 -acyl complexes forms Fischer-type hydroxy- or methoxycarbene cations (eq. 22). The structure of the methoxy(butyl)carbene complex shows that the alkyne ligand aligns itself parallel to the cis metal-carbonyl axis and perpendicular to the plane of the carbene ligand. Deprotonation of $[\text{Tp}'(\text{CO})(\text{PhC}\equiv\text{CMe})\text{W}=\text{C}(\text{OMe})\text{Me}]^+$ with sodium hydroxide in methanol generates a neutral s-vinyl complex, $\text{Tp}'(\text{CO})(\text{PhC}\equiv\text{CMe})\text{W}(\eta^1\text{-C}(\text{OMe})=\text{CH}_2)$ (eq. 23). Reaction of $[\text{Tp}'(\text{CO})(\text{PhC}\equiv\text{CMe})\text{W}=\text{C}(\text{OMe})\text{Ph}]^+$ with two equivalents of cyanide in methanol yields a neutral azavinylidene complex, $\text{Tp}'(\text{CO})(\text{PhC}\equiv\text{CMe})\text{W}-\text{N}=\text{C}(\text{CN})\text{CH}(\text{OMe})\text{Ph}$ (eq. 24), in which the lone pair of electrons on the nitrogen of the azavinylidene ligand competes with the alkyne π donor orbital for donation to the lone vacant metal $d\pi$ orbital.

II. NITRENE CHEMISTRY

Several avenues of exploratory nitrene synthesis have been pursued in a collaborative effort with Professor M. S. Brookhart, also here at UNC. In the majority of cases here the term nitrene will be used for the NR entity. This is formally a neutral fragment that can donate either two or four electrons depending on the disposition of the nitrogen lone pair. Alternatively, and equally accurately, one can use the imido nomenclature for the NR^{2-} unit. The oxidation state formalism is thus brought into play indirectly, and the imido dianion would then bring either four or six electrons into the bonding scheme. Of course the ultimate electron count and bonding description will be equivalent regardless of whether one combines M^{n+} and NR or $\text{M}^{(n+2)+}$ and NR^{2-} .

Initial studies with $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CHAr}]^+$ reagents and nitrosobenzene yielded nitrene products rather than nitrenes (eq. 1).¹⁸ In fact the organometallic products formed from the reaction of an electrophilic iron carbene complex with either nitrosoarene or azobenzene reagents (eq. 2) reflect net insertion of the $\text{ArN}=\text{X}$ moiety into the $\text{Fe}=\text{CHAr}$ bond. Both $[\text{Fp}-\text{O}-\text{N}(\text{Ar})=\text{CHAr}]^+$ and $[\text{Fp}-\text{N}(\text{Ph})-\text{N}(\text{Ph})=\text{CHAr}]^+$ have been isolated and characterized, and the crystal structure of the nitrene product was solved. Acetone solutions of both metal products gave imine products when exposed to light. Aldehyde products were available from the nitrene reagent by hydrolysis reactions. An important conclusion from these results was that one can postulate reasonable pathways to the aldehyde and imine organic products without invoking metallacycles.

Preparative routes to intermediate oxidation state metal nitrene monomers proved elusive in the iron system, but our efforts were rewarded once we turned to the pyrazolyl borate tungsten system. We now have a nice array of synthetic methods for generating tungsten nitrene complexes as summarized in the next section of this progress report.

Conversion of terminal oxo monomers to nitrene complexes is probably the most common method of forming an $\text{M}=\text{NR}$ linkage. Thus an intermediate oxidation state metal oxo reagent in the d^2 manifold would offer a simple route to a nitrene complex. The limiting factor here is the availability of monomers containing both carbonyl and oxo

units. Mayer had shown that tungsten can support both of these diverse ligands in a single coordination sphere by oxidatively adding carbon dioxide to L_4Cl_2W to form $L_2Cl_2(OC)W=O$ products.¹⁹

We were surprised to find that oxidation of a W(II) carbonyl compound, $Tp'(CO)_3WI$, with molecular oxygen led to a monomeric W(IV) oxo product with retention of one carbonyl ligand (eq. 3). Reaction of aniline with $Tp'(CO)IW=O$ indeed gave $Tp'(CO)IW=NPh$ in roughly 50% yield (eq. 4).²⁰ The spectroscopic data for this complex provided a base for quickly recognizing other nitrene derivatives when we sought more innovative preparative methods for tungsten nitrene complexes containing ancillary carbon monoxide ligands. Salient spectral features included a CO stretching absorption at 1930 cm^{-1} , roughly 45 cm^{-1} below the oxo analog, and a low field ^{13}C NMR signal at 279 ppm for the carbonyl carbon. The ipso carbon of the phenyl group exhibited two-bond coupling to tungsten of 35 Hz which has proven to be diagnostic for carbyne and nitrene entities bound to tungsten while no measurable coupling characterizes related carbenes or amidos.

A more general approach to nitrene complexes unfolded as we expanded the chemistry accessible from $Tp'(CO)_3WI$ and amines. Reaction of either aniline or tert-butylamine with $Tp'(CO)_3WI$ forms dicarbonyl(amido)tungsten (II) d^4 monomers, $Tp'(CO)_2W(NHR)$ (eq. 5).²¹ These products each display a low-field proton NMR signal assigned to the amido proton (15.4 ppm for Ph and 14.2 ppm for t-butyl).

Oxidation of either of the amido complexes with iodine produces a cationic nitrene monomer with iodide as the counterion (eq. 6). The net result of this oxidation is simple hydride abstraction from the amido nitrogen; alternate syntheses are accessible with trityl cation as the oxidant (eq. 7).

Electrophilic character is evident at the nitrogen atom in the cationic nitrene complexes as they undergo facile hydride addition to reform the amide starting materials (eq. 8). Treatment of the phenyl nitrene complex with lithium borohydride at low temperature in acetonitrile results in spectroscopically pure amido product which can be isolated in 80% yield. Likewise, the t-butyl nitrene complex yields only the amido monomer upon hydride reduction.

An important mechanistic point regarding formation of the amide product was obtained by a low temperature NMR study of the reaction solution.²² When $[\text{Tp}'(\text{CO})_2\text{W}(\text{NPh})]^+$ and a large excess of lithium borohydride were combined in an NMR tube at -40°C and monitored by proton NMR, a single product was evident. This initial product is not the amide, but rather an isomer of the amide. The 1:1:1 pattern observed for the pyrazole rings indicates that the mirror plane characteristic of both the reagent and product is absent in this intermediate. A proton signal at 16.5 ppm with 20 Hz coupling to tungsten and a carbon signal at 293 ppm are signatures for the formyl ligand (eq. 9). Furthermore the infrared spectrum of the intermediate shows one strong absorption at 1948 cm^{-1} for the terminal carbonyl and a weak absorption at 1680 cm^{-1} for the formyl CO stretch.

The formyl complex $\text{Tp}'(\text{WCO})(\text{NPh})(\text{CHO})$ is fluxional at low temperatures. We interpret the data as reflecting degenerate hydride migration from the formyl to the carbonyl ligand. The ^{13}C spectrum of a ^{13}C carbon monoxide enriched sample exhibits line broadening of the CO and CHO signals, and line-width analysis indicates a $\Delta G^\ddagger$ value of 11.5 kcal/mol. This is the same activation energy that characterizes coalescence of the pyrazole proton signals.

A first-order rate process was established for the conversion of the formyl intermediate to the amide product. Analysis of the NMR data obtained at -70°C was indicative of a $\Delta G^\ddagger$ of 16.5 kcal/mol, so hydride migration between the two CO units is orders of magnitude faster than hydride migration from the formyl to the nitrene. The fact that a carbonyl ligand is the kinetic site of hydride addition is also noteworthy as we

construct plans for generating electrophilic nitrene complexes for nitrene transfer applications.

A breakthrough in preparing $\text{Tp}'(\text{CO})_2\text{WNHR}$ complexes resulted when we generated the unsaturated $\text{Tp}'(\text{CO})_2\text{WI}$ monomer for use as the metal reagent in place of $\text{Tp}'(\text{CO})_3\text{WI}$. Loss of carbon monoxide from $\text{Tp}'(\text{CO})_3\text{WI}$ forms a paramagnetic $\text{Tp}'(\text{CO})_2\text{WI}$ monomer in refluxing THF solution (eq. 10), and this material can be isolated as a clean solid for use in numerous reactions. It is sufficiently reactive to allow the use of relatively mild conditions for reactions where heating would be required if $\text{Tp}'(\text{CO})_3\text{WI}$ were used as the source of the $\text{Tp}'(\text{CO})_2\text{W}$ moiety. With $\text{Tp}'(\text{CO})_2\text{WI}$ as the metal reagent we were able to extend the amido chemistry to the simple NH_2^- ligand, and as a result both NH_2^- and N^{3-} derivatives have now been prepared.²³

The synthesis and reactions of these complexes are summarized in Scheme 1. $\text{Tp}'(\text{CO})_2\text{W}(\text{NH}_2)$, prepared from ammonia and $\text{Tp}'(\text{CO})_2\text{WI}$ in THF, is a rare example of a metal complex with both carbonyl and amido ligands. Two broad signals in the ^1H NMR spectrum (13.5 and 11.6 ppm) are assigned as the amido protons, one proximal to the pyrazole rings, the other distal. Rotation around the $\text{W}=\text{NH}_2$ bond is restricted, and the coalescence observed at 103°C establishes a barrier to rotation of 17 kcal/mol.

This amido complex shows ambiphilic character and can react as either a hydride donor or a proton donor. Treatment of $\text{Tp}'(\text{CO})_2\text{W}(\text{NH}_2)$ with $[\text{Ph}_3\text{C}][\text{PF}_6]$ produces two nitrene products: $[\text{Tp}'(\text{CO})_2\text{W}(\text{NH})]^+$ and $[\text{Tp}'(\text{CO})_2\text{W}(\text{NCPh}_3)]^+$. Addition of excess lithium diisopropyl amide and then MeI affords the dimethylamido derivative, $\text{Tp}'(\text{CO})_2\text{W}(\text{NMe}_2)$. An x-ray structure of this complex reveals a planar WNMe_2 fragment with a W-N distance (1.96 Å) in the range typical of metal-nitrogen multiple bonds. The acute angle of 72° between the two carbonyl ligands is compatible with optimal $d\pi$ orbital interactions. Here the vertical NMe_2 fragment will donate into the lone vacant $d\pi$ orbital, while the two filled $d\pi$ orbitals will be preferentially stabilized by back-bonding to the two π -acid carbonyl ligands.

Reaction of the parent nitrene cation $[\text{Tp}'(\text{CO})_2\text{W}(\text{NH})]^+$ with base yields the unique nitride monomer $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{N}$. Isolation of analytically pure solid has proven difficult, but the preparation of this tungsten(IV) species which simultaneously accommodates the powerful π donor nitride and π acceptor carbonyl ligands deserves

Scheme 1

advertising. The reactivity of this species confirms its composition. Reaction of the nitride complex with appropriate electrophiles generates cationic nitrene derivatives, $[\text{Tp}'(\text{CO})_2\text{W}(\text{NR})]^+$, for $\text{R} = \text{H}, \text{Me}, \text{or CPh}_3$.

In addition to the synthetic methods mentioned above which rely on amines as the source of the nitrene moiety, we have undertaken studies designed to utilize coordinated nitriles as the precursor nitrogen sources for nitrene formation. Efforts to add H^- and then H^+ to the nitrile carbon in $[\text{Tp}'(\text{CO})_3\text{W}(\text{N}\equiv\text{CMe})]^+$ have recently been successful and will be described more fully in the proposal, but at this juncture suffice it to say that our nitrene project led us to explore nucleophilic addition reactions of coordinated nitriles with amine reagents.

Cationic amidine products result when $[\text{Tp}'(\text{CO})(\text{PhC}_2\text{Me})\text{W}(\text{N}\equiv\text{CR})]^+$ reacts with primary amines (eq. 11).²⁴ These reactions reflect net addition of H-NHR across the nitrile triple bond. Deprotonation of the α -nitrogen of $[\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}(\text{NH}=\text{C}(\text{Ph})\text{NHPH})]^+$ with ammonia results in the formation of a neutral azavinylidene alkyne complex, $\text{Tp}'(\text{CO})(\text{PhC}_2\text{H})\text{W}-\text{N}=\text{C}(\text{Ph})\text{NHPH}$ (eq. 12). When a terminal alkyne complex and ammonia are combined, a coupling of the alkyne and the nitrile ligand occurs (eq. 13), linked by the added ammonia nitrogen, to form a six-membered metallacycle. An x-ray structure of $\text{Tp}'(\text{CO})\text{W}=\text{C}(\text{Ph})-\text{C}(\text{H})=\text{N}-\text{CR}=\text{N}$ reveals a planar metallacycle with surprisingly short tungsten bonds to both the carbon (2.08 Å) and the nitrogen (1.77 Å) in the ring. An aromatic metallocycle description of the bonding in this product is probably helpful.

Nitrene transfer to olefins remains an important goal in organometallic chemistry, and significant advances in this area have recently been reported from several laboratories. The use of copper catalysts has proven to be a successful approach, and we have found that a trispyrazolylborate copper(I) complex effects nitrene transfer from PhINTs to olefins to form aziridines.²⁵

The hypothesis that nitrene transfer can mimic carbene transfer led us to explore carbene transfer as a method of seeking potential nitrene transfer catalysts. Once the efficacy of $\text{Tp}'\text{Cu}(\text{CH}_2=\text{CH}_2)$ as a catalyst for carbene transfer from ethyl diazoacetate to both olefins and alkynes had been established, reactions of PhINTs with olefins in the presence of this copper(I) catalyst were explored. Conversion of styrene, cyclooctene, and 1-hexene to aziridines with PhINTs as the nitrene source and 0.5% $\text{Tp}'\text{Cu}(\text{CH}_2=\text{CH}_2)$ as catalyst proceeded to give isolated yields ranging from 40 to 90% (eq. 14). These reactions require anhydrous conditions in order to avoid forming TsNH_2 from the PhINTs reagent.

The range of carbyne and nitrene chemistry summarized in this progress report serves as background information for future plans presented in the accompanying proposal.

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