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REDUCTIVE COUPLING OF CARBON MONOXIDE TO C_2 PRODUCTS

Progress Report for the Period

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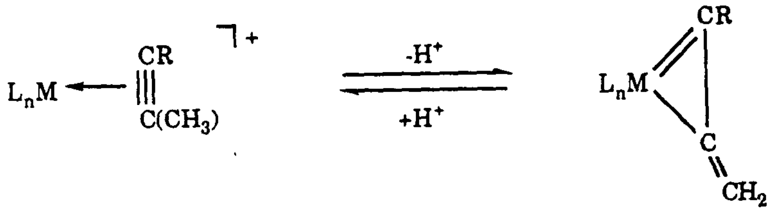
I. Introduction

Progress since the initiation of this two year award on May 1, 1988, has been divided into two areas for reporting purposes. We have been working on ideas described in the proposal submitted two years ago, and simultaneously we initiated chemistry in a distinct area in order to provide a springboard for the current proposal. Efforts directed toward reductive coupling of carbon monoxide have continued to focus on carbyne species as the central figure in coupling reactions. At the same time we have attempted to prepare intermediate oxidation state metal imido complexes with an eye to synthetic applications of nitrene transfer reagents. The results of carbyne chemistry, electrophilic addition reactions of anionic carbonyl and isonitrile complexes, and carbyne-carbonyl coupling reactions will be presented in this progress report, while the work with nitrene complexes will be included as preliminary results in the text of the accompanying proposal. The description of published work will be brief in this report; greater detail will be provided for unpublished material.

II. Alkyne Ligands as Four-Electron Donors

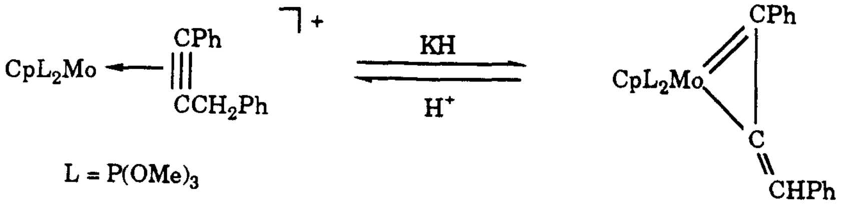
An extensive review of molybdenum and tungsten alkyne complexes has been published.[1] In addition to collecting synthetic, spectral, electrochemical and structural data for this class of compounds, this review developed some important concepts concerning alkyne ligands and their cousins.

For example, the isolobal character of four-electron alkyne ligands and anionic η^2-allenyl ligands anticipated that deprotonation and protonation should synthetically link these two ligands (Eq. 1). Indeed Green has



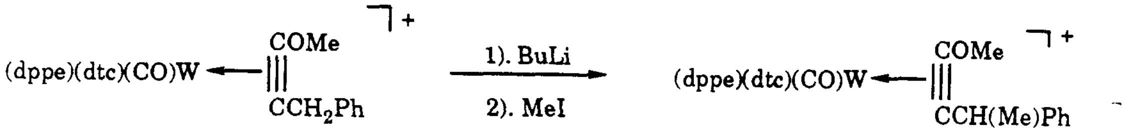
(1)

reported a reaction which confirms this relationship (Eq. 2).[2] We have recently deprotonated a cationic alkyne at the ß-position and added methyl iodide to alkylate the intermediate allenyl complex as a means of regioselective propargyl anion elaboration (Eq. 3).[3]



L = P(OMe)$_3$

(2)

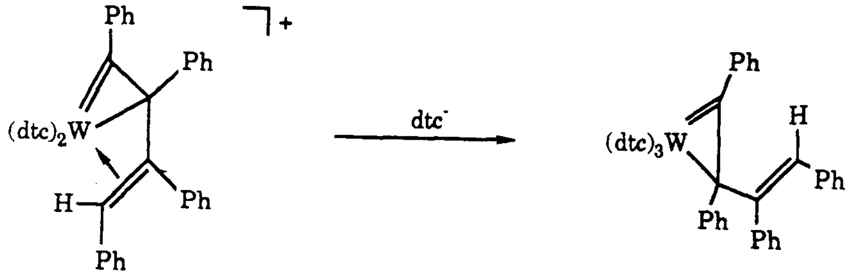


(3)

dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$

dtc = R$_2$NCS$_2^-$

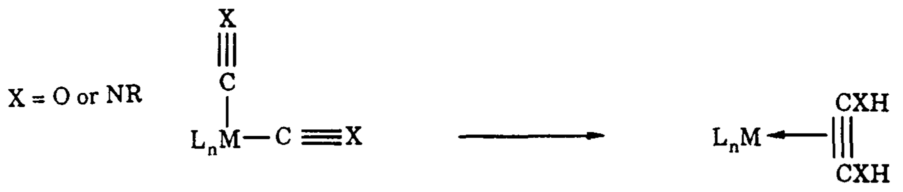
Although relatively few groups have prepared η^2-vinyl ligands[4] the number of η^2-vinyl complexes is growing, and again the conceptual link to four-electron alkyne ligands is synthetically useful. In addition to the d^4 η^2-vinyl complexes described in the review, alkyne analogs indicated that d^2 η^2-vinyl complexes should be accessible, and indeed $(dtc)_3W(\eta^2$-PhC=CHR) has recently been reported (Eq. 4).[5]



(4)

General features of alkyne ligand syntheses from C_1 ligands were described in the review. Particularly relevant for carbonyl coupling reactions were patterns evident in isonitrile coupling reactions. When viewed as an informative piece in the puzzle of C_1-ß-heteroatom coupling reactions

(Eq. 5), a first step involving conversion to a heteroatom carbyne by addition of an electrophile stood out as a unifying feature for reactions involving C_1 coupling of isonitriles, carbonyls, and carbynes (Eq. 6). Electrophilic addition to the oxygen of terminal carbonyl ligands in simple monomeric



$$L_nM(C{\equiv}X)-C{\equiv}X \longrightarrow L_nM \leftarrow (CXH{\equiv}CXH) \qquad (5)$$

$$L_nM{-}C{\equiv}X: \quad + \quad E^+ \longrightarrow [L_nM{\equiv}C{-}X{-}E]^+ \qquad (6)$$

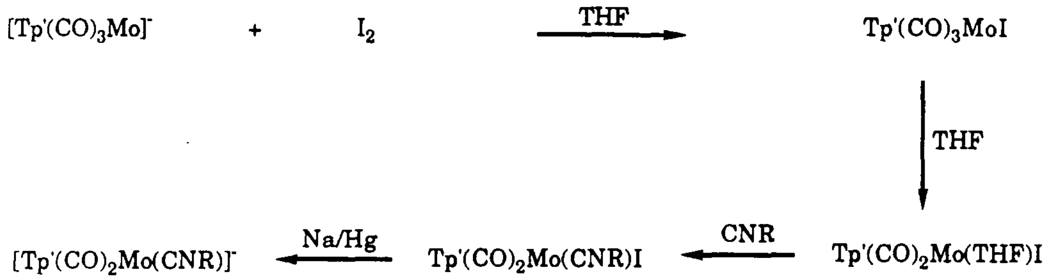
X = S or O

reagents has proven elusive, and we turned to isonitrile complexes to probe electrophilic addition at the heteroatom as a viable mechanism to generate heteroatom carbynes.

III. Chemistry from Electrophilic Addition to Isocyanide Ligands

In order to use the pool of data available for electrophilic addition to $[Tp'Mo(CO)_3]^-$ (Tp' = tris(3,5-dimethylpyrazolyl)borate) anions we wanted to explore the chemistry of $[Tp'(CO)_2Mo(CNR)]^-$ with electrophiles. Formation of this complex has recently been accomplished in our laboratory. The $[Tp'Mo(CO)_3]^-$ anion resists thermal carbonyl substitution and photochemical carbonyl replacement has not been an effective synthetic tool to $[Tp'(CO)_2MoL]^-$ reagents for us. Preparation of the desired anionic isonitrile complex has now been achieved by an oxidation/substitution/reduction sequence as shown in Scheme I.

Scheme I



Oxidation of the d^6 $[Tp'Mo(CO)_3]^-$ reagent with iodine in THF yields a labile d^4 complex. The solution infrared spectrum of this complex changes slowly at room temperature in THF; we postulate that the initial two bands at 2025 and 1937 cm^{-1} are due to the $Tp'(CO)_3MoI$ tricarbonyl with effective C_{3V} symmetry. Conversion to a species with carbonyl absorptions at 1998 and 1921 cm^{-1} is consistent with loss of one carbonyl ligand and coordination of THF, but we have no additional data to confirm this speculation. Regardless of the exact identity of the metal complex in solution, addition of RN≡C leads to $Tp'(CO)_2IMo(CNR)$ products in high yield for R = Me, Ph, or Bu^t.

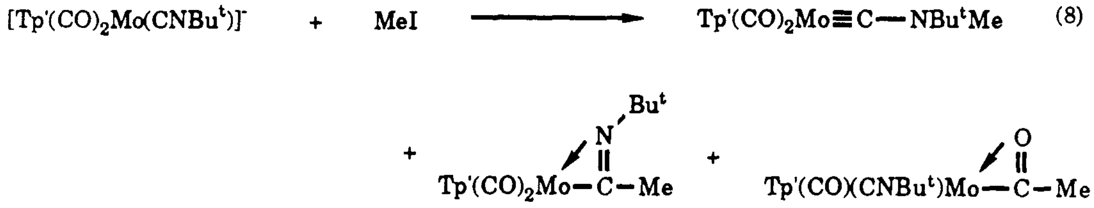
Reduction of $Tp'(CO)_2IMo(CNR)$ with sodium amalgam to form the $[Tp'(CO)_2Mo(CNR)]^-$ anion and NaI proceeds cleanly. The anionic product is quite reactive, and it has been characterized only by solution infrared spectroscopy. Subsequent alkylation or protonation reactions utilize the THF reaction solution directly after it has been filtered away from the spent amalgam.

Alkylation with methyl iodide of either the methylisocyanide or the phenylisocyanide complex with methyl iodide yields an aminocarbyne product (Eq. 7). Similar results have been reported by Lippard in monomeric rhenium complexes.[6] Alkylation of $[Tp'(CO)_2Mo{-}C{\equiv}NBu^t]^-$ yields multiple products

$$[Tp'(CO)_2Mo(CNR)]^- \quad + \quad MeI \longrightarrow Tp'(CO)_2Mo{\equiv}C{-}NMeR \qquad (7)$$

$$R = Me, Ph$$

(Eq. 8). It seems likely that the bulky tert-butyl group inhibits electrophilic addition at nitrogen, and hence metal methylation followed by

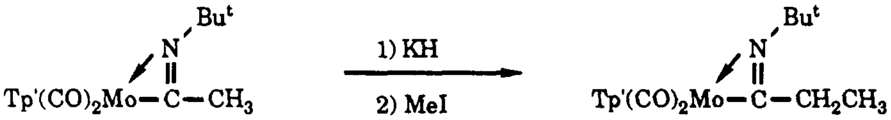


$$[Tp'(CO)_2Mo(CNBu^t)]^- \quad + \quad MeI \longrightarrow Tp'(CO)_2Mo{\equiv}C{-}NBu^tMe \qquad (8)$$

$$+ \quad Tp'(CO)_2Mo{-}\overset{\overset{\displaystyle N{-}Bu^t}{\|}}{C}{-}Me \quad + \quad Tp'(CO)(CNBu^t)Mo{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Me$$

insertion of either the isocyanide or a carbonyl to form η^2-iminoacyl or η^2-acyl products becomes competitive.

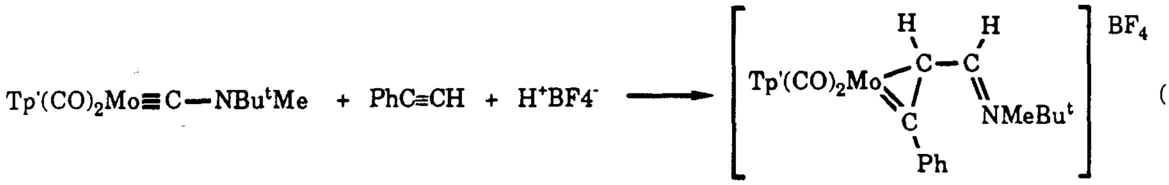
We have chosen not to pursue further chemistry of the η^2-acyl product which presumably would follow reactivity patterns previously established for related $Tp'(CO)LMo[\eta^2\text{-}C(O)R]$ complexes.[7] Both the η^2-iminoacyl and the aminocarbyne products have served as precursors to additional chemistry. In a reaction analogous to that of η^2-acyl elaboration we have deprotonated the η^2-iminoacyl ligand and then quenched the resulting anion with MeI to form an ethyl substituent (Eq. 9), so elaboration of the η^2-iminoacyl is accessible.



$$Tp'(CO)_2Mo{-}\overset{\overset{\displaystyle N{-}Bu^t}{\|}}{C}{-}CH_3 \xrightarrow[\text{2) MeI}]{\text{1) KH}} Tp'(CO)_2Mo{-}\overset{\overset{\displaystyle N{-}Bu^t}{\|}}{C}{-}CH_2CH_3 \qquad (9)$$

In studying the aminocarbyne product we have attempted direct coupling reactions of coordinated $\mathrm{CNBu^tMe}$ and CO without success. Addition of excess $\mathrm{PMe_3}$ and heating produces no observable net chemistry, and photolysis has not produced coupled products. We have observed that coupling reactions are strongly dependent on the carbyne substituent in closely related systems. For example, photolysis of $\mathrm{Tp'(CO)_2Mo{\equiv}C{-}Ph}$ yields the coupled ketenyl ligand, η^2-PhC=C=O, while photolysis of $\mathrm{Tp'(CO)_2Mo{\equiv}CMe}$ leads to retention of the methylcarbyne ligand and loss of carbon monoxide. While the presence of a cis-carbonyl carbyne unit in a Group VI monomer can lead to coupled products it is not sufficient to dictate that coupling will occur.

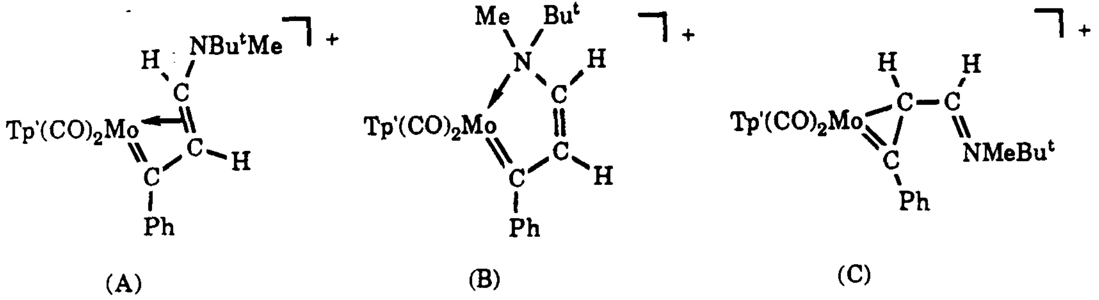
We have been more successful in pursuing reactivity of the aminocarbyne complexes with electrophilic reagents. Protonation in acetonitrile solution with $\mathrm{HBF_4}$ causes the two CO absorptions to move up roughly 30 $\mathrm{cm^{-1}}$, consistent with formation of cationic complex, perhaps a carbene. Only oils have been isolated from this reaction, and its characterization has not been definitive. Addition of $\mathrm{PhC{\equiv}CH}$ to the aminocarbyne prior to protonation, reminiscent of Geoffrey's recent studies[8] with $\mathrm{Cp(CO)_2W{\equiv}CAr}$, provides a trap which yields a single clean product (Eq. 10).



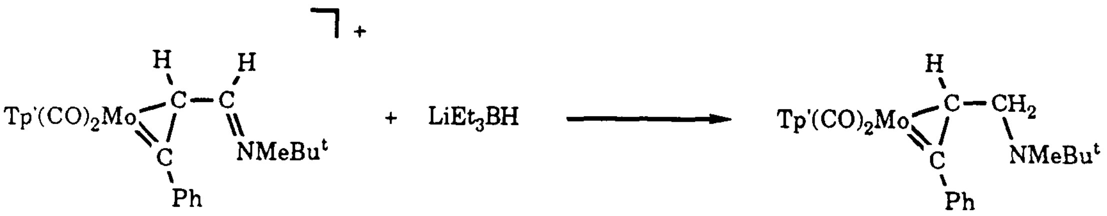
(10)

A dicarbonyl infrared pattern is still present (2027, 1944 $\mathrm{cm^{-1}}$), and ^{1}H and ^{13}C NMR clearly indicate a connectivity of $\mathrm{CPh{-}CH{-}CH{-}NMeBu^t}$ in the newly formed ligand. This carbon framework is consistent with initial formation of an electron-deficient carbene complex followed by alkyne insertion as observed by Geoffrey.[8] Several plausible structures can be constructed that would provide the four electrons required to saturate the metal in this cationic product (Scheme II). We felt that a vinylcarbene formulation (A) analogous to $[Cp(CO)_2Mo(\eta^3{=}CPh{-}CPh{=}CHAr)]^+$ or a chelated carbene (B) with the amine lone pair coordinated to the metal were more likely, but the NMR data indicate that an η^2-vinyl formulation (C) with an iminium substituent on the ß-carbon is accurate. The coordinated vinyl group proton appears far upfield (4.1 ppm) of the iminium proton (7.5 ppm). The presence of one metal coordinated and one free vinylic hydrogen is consistent with the η^2-vinyl, but not with either of the first two alternatives. Notice that the two protons in this ligand provide more relevant data in terms of ^1H chemical shift, H-H coupling constants, J_{CH} values and multiplicities than other substituents such as alkyl or aryl groups. In addition to the low field C_α (243 ppm) and high field C_β (41 ppm) signature of η^2-vinyl ligands, the iminium carbon resonates at 170 ppm with a $^1J_{CH}$ of 169 Hz. It may well be that coordination of the nitrogen to form a five-membered ring, as in coordination of the heteroatom of the metallocycles formed by alkyne insertion into metal acyl bonds,[1,7,8] is prohibited by the steric bulk of the nitrogen methyl and t-butyl substituents.

Scheme II



Confirmation of the η^2-vinyl iminium formulation was provided by reaction of the alkyne inserted cation with Et_3BH^- to form a neutral product. We find that H^- addition generates a CH_2 unit adjacent to the amine, i.e. simple nucleophilic attack at the iminium carbon leaves the η^2-vinyl metallocycle MoC_2 ring in tact (Eq. 11). Again ^1H and ^{13}C data are definitive. The $CHCH_2$ unit stands out as the two diastereotopic methylene protons differ substantially in chemical shift and in coupling to the vicinal proton. The AMX pattern has J_{HH} values of 2,9 (vicinal) and 13 (geminal) Hz. Typical C_α (285 ppm) and C_β (44 ppm) ^{13}C chemical shifts are observed for the η^2-vinyl carbons.[1] Notice that nucleophilic addition in Geoffrey's system occurs at the carbene carbon of the vinyl carbene ligand to form η^3-allyl products.[8] We find η^3-allyl products are a thermodynamic sink in other reactions of closely related complexes in our system. For example, addition of H^- to a four-electron donor PhC≡CMe ligand yields an η^3-$PhCHCHCH_2$ ligand, presumably by attack at the phenyl substituted carbon followed by hydrogen migration to the central carbon. We have seen related chemistry from putative η^2-vinyl ligands formed by CO loss from η^2-enone complexes[7] and Green has carried out labeling studies in η^2-vinyl to η^3-allyl rearrangements of cyclopentadienyl systems.[9]



(11)

A further point of interest is the stability of the cationic and neutral products we have isolated. They survive easily at room temperature and bulk crystals have been isolated. In contrast $[Cp(CO)_2Mo(\eta^3{=}CPhCPh{=}CHAr)][BF_4]$ is unstable at ambient temperatures.[8] The sequence of isonitrile conversion to an aminocarbyne by electrophile addition followed by protonation to form a reactive carbene which inserts alkyne to form η^2-vinyl products is important relative to our general understanding of reactions of electrophilic carbenes with olefins and alkynes. Stepwise reduction of the C≡NR bond via alkylation, protonation, insertion and hydride addition may provide a route to control of chirality at the nucleophilic addition step where nucleophiles other than H^- would yield diastereomers.

IV. Tantalum(I) Alkyne Chemistry

Publications in the area of carbonyl coupling by Lippard's group since the submission of our proposal two years ago have confirmed the sequence of events we postulated at that time. Since the first report that $Ta(CO)_2(dmpe)_2Cl$ could be converted to $Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl$ with a sequence of Mg dust, $HgCl_2$, $Cp^*_2ZrCl_2$ followed by Me_3SiCl (all in THF solvent),[10] subsequent publications have indicated that $[Ta(CO)_2(dmpe)_2]^-$ is the key reagent in this scheme.[11] Reductive loss of chloride occurs when $Ta(CO)_2(dmpe)_2Cl$ is reduced with sodium amalgam, and conversion of $[Ta(CO)_2(dmpe)_2]^-$ to the coupled product $Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)Y$ results from addition of Me_3SiY. Isolation of an intermediate siloxycarbyne was reported in 1988 when Pr^i_3SiCl was added to $Ta(CO)_2(dmpe)_2^-$ and the structure of $(dmpe)_2(CO)Ta{\equiv}COSiPr^i_3$ was determined.[12] Coupling of the cis siloxycarbyne and carbonyl ligands was induced by Me_3SiCl or $Pr^i_3Si(OTf)$ addition to yield the alkyne product. In a more recent publication hydrolysis of the $Me_3SiOC{\equiv}COSiMe_3$ ligand with aqueous HCl yielded a metal bound HOC≡COH ligand.[12]

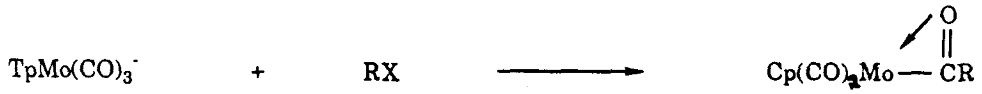
In summary it is the highly reduced d^6 $Ta(CO)_2(dmpe)_2^-$ anion which promotes coupling in Lippard's system rather than the d^4 $Ta(CO)_2(dmpe)_2Cl$ precursor. Electrophilic addition to the oxygen atom of one of the low frequency carbonyl ligands creates the requisite cis-carbyne carbonyl entity appropriate for ketenyl formation from these two C_1 fragments. Electrophilic addition to the ketenyl oxygen yields the observed C_2 alkyne product.

When we undertook our studies of potential carbonyl coupling products little was known concerning d^4 alkyne monomers in Group V. Given Lippard's earlier results and the electron rich properties of these low oxidation state complexes, we pursued the properties of several Ta(I) alkyne monomers in order to provide information relevant to alkyne products formed by coupling reactions. Our work with $Ta(CO)_2(RC{\equiv}CR)IL_2$ complexes [$L = PMe_3$ or $P(OMe)_3$], which included syntheses, ^1H, ^{13}C and ^{31}P NMR, IR, UV-VIS, experimental and theoretical barriers to alkyne rotation, electrochemical data and one x-ray structure, has been published.[13]

V. Formation and ^1H NMR Properties of Tungsten(II) Hydride Complexes

In pursuit of alternatives to Lippard's highly reduced $[Ta(CO)_2(dmpe)_2]^-$ coupling reagent we have examined reactions of less electron rich Group VI carbonyl anions with electrophiles. Different products are observed with alkylating reagents when anionic Cp and Tp derivatives are employed. Thus seven-coordinate metal alkyl products result from $CpM(CO)_3^-$ alkylation[14] (Eq. 12) while η^2-acyl products form in the analogous Tp system (Eq. 13).[15]

$$CpMo(CO)_3^- \quad + \quad RX \longrightarrow Cp(CO)_3Mo—R \qquad (12)$$



$$TpMo(CO)_3^- \quad + \quad RX \longrightarrow Cp(CO)_2Mo—\overset{O}{\overset{\|}{C}}R \qquad (13)$$

In an effort to gather data relevant to the role of steric and electronic factors in determining the distribution electrophilic addition products we have prepared a series of tris(pyrazolylborato)tungsten(II) hydride complexes. The NMR properties, including $^1J_{WH}$ values, vary dramatically as described below. To date we have seen no indication of protonation at a terminal carbonyl oxygen, and even with larger electrophiles no alkoxycarbyne species have been detected. We anticipate that even if methylation at oxygen took place, the resulting $Tp(CO)_2W{\equiv}COMe$ would be an efficient methylating reagent with $Tp(CO)_3W^-$ serving as an excellent leaving group. Isolation of $Tp(CO)_2W{\equiv}COMe$ in the presence of even weak nucleophiles seems unlikely.

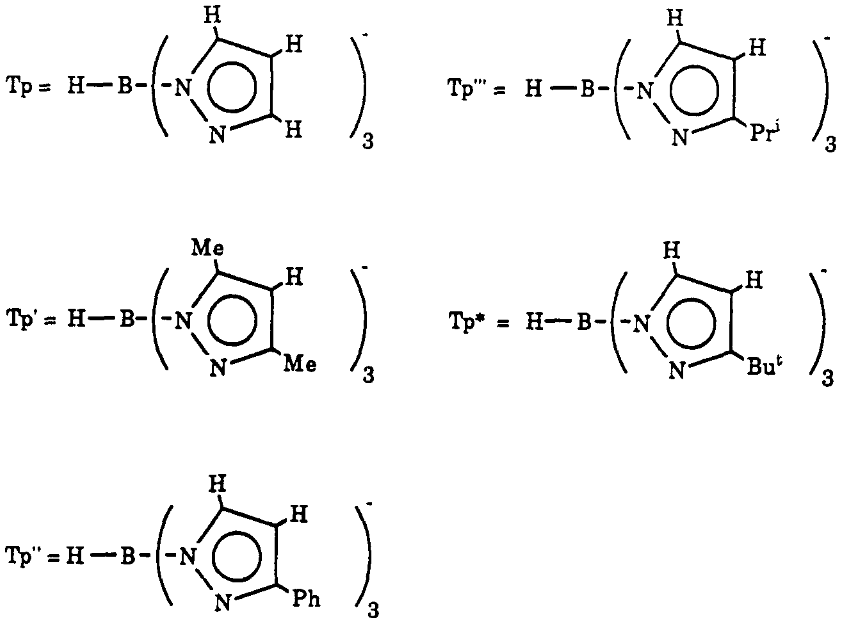
Direct protonation of $TpW(CO)_3^-$ reagents ($\nu_{CO} \sim 1900$ and $1750\ cm^{-1}$) with HCl in CH_3CN solution yields neutral $Tp(CO)_3WH$ products. We were motivated to pursue this apparently trivial chemistry by the unusually low $^1J_{WH}$ value of 6

Hz we observed for Tp'$(CO)_3$W-H. Note that the $^1J_{WH}$ value for Cp$(CO)_3$W-H is 37 Hz, a factor of six larger.[16]

Although NMR chemical shifts and IR data were consistent with a simple Tp'$(CO)_3$WH formulation, the low metal-hydrogen coupling constant to ^{183}W (I = 1/2 and 14% naturally abundant) seemed inappropriate for a metal-hydride bond. We have completed a crystal structure, and although the hydride was not located, the geometry of the metal coordination sphere and all of the ligands matches expectations for the simple hydride product. At the least this structure eliminates location of the hydrogen on a carbonyl or at any other site which would cause distortion of a carbonyl or pyrazole ring.

We have now prepared other derivatives (Scheme III) including the unsubstituted parent tris(pyrazolyl)borate ligand (Tp$(CO)_3$W-H) as well as those with phenyl[17] and isopropyl[18] substituted pyrazolyl rings. Efforts with t-butyl derivatives[17] are underway, but we have only IR data to indicate that [Tp(t-Bu)]$(CO)_3W^-$ is accessible, and the tricarbonyl pattern may be due to coordination of one or two pyrazole nitrogens rather than all three.

SCHEME III



The $^1J_{W-H}$ values for this series, all with δ between -2 and -3 ppm, are Tp 9 Hz, Tp' 6 Hz, Tp" 7 Hz, and Tp"' 4 Hz. Legzdins has published a thorough discussion of one bond $^1J_{WH}$ values.[19] It seems reasonable to conclude that the low one bond coupling values here are due to steric congestion at the metal which inhibits access of the hydride ligand to the metal center and results in long W-H bonds in this class of compounds.

A counterpoint to the NMR parameters for the Tp(CO)$_3$W-H series of hydride compounds is provided by Tp'(CO)(PhC≡CMe)W-H where the $^1J_{WH}$ value is normal (120 Hz), but the hydride chemical shift is unusual (11.4 ppm). This compound, also a tungsten(II) hydride when the alkyne is considered a neutral ligand, has been prepared from Tp'(CO)(PhC≡CMe)W(N≡CCH$_3$)$^+$ and Na$^+$BH$_4^-$ in THF. Although metal hydride chemical shifts in the 0-10 ppm range are common for d^0 metals, shifts below 10 ppm are rare. Nonetheless, the shift of 11.4 ppm that we observe for our tungsten(II) alkyne hydride can hardly be considered anomalous given Chisholm's report of terminal tungsten hydride signal at 20 ppm.[20] The difference in NMR properties carries over to chemical reactivity, too. Acidification of Tp'(CO)(PhC≡CMe)W-H in the presence of free L generates H$_2$ gas and Tp'(CO)(PhC=CMe)WL$^+$ while Tp(CO)$_3$W-H complexes are unreactive towards acid.

VI. [Tp'(CO)$_2$M≡C-PR$_3$][BF$_4$] as Carbyne Precursors

An awareness of the properties of Tp'(CO)$_2$M≡C-O-R carbyne complexes could be helpful in efforts to identify such intermediates in alkylation reaction of Tp'M(CO)$_3^-$ reagents. The phosphonium carbynes reported in 1987[21] are susceptible to nucleophilic attack at the carbyne carbon and several carbene complexes have been prepared by this route. Loss of PR$_3$ from the carbene species of course leads to carbyne products, so this offers a route to carbynes by net nucleophilic displacement at carbon. Lalor has observed related chemistry with the chlorocarbyne reagent where thiolates displace chloride.[22]

We have now investigated the synthesis and reactivity of Group VI oxycarbynes via nucleophilic attack of oxygen nucleophiles on cationic tungsten and molybdenum centers (Eq. 14). Hydride addition to cationic phosphonium carbynes has also been pursued, yielding a new tungsten methylidyne complex via displacement of phosphine at the carbyne carbon (Eq. 15).

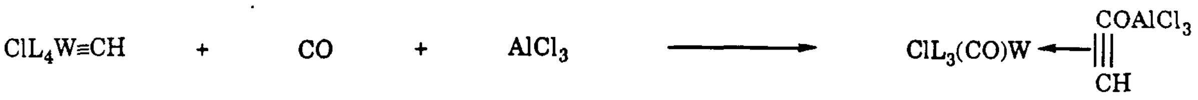
$$\left.\mathrm{Tp'(CO)2W{\equiv}C{-}PR_3}\right]^{+} \quad + \quad {}^{-}\mathrm{OAr} \longrightarrow \mathrm{Tp'(CO)_2W{\equiv}C{-}OAr} \qquad (14)$$

$$\left.\mathrm{Tp'(CO)2W{\equiv}C{-}PR_3}\right]^{+} \quad + \quad \mathrm{HBR_3^-} \longrightarrow \mathrm{Tp'(CO)_2W{\equiv}C{-}H} \qquad (15)$$

Chisholm has noted the formation of $(t\text{-BuO})_3W(CH)$ spectroscopically,[23] and Schrock and Churchill have reported the synthesis and characterization of several terminal carbyne W(IV) d^2 complexes and investigated their reactivity.[24] Protonation of $XL_4W(CH)$ (X = Cl, I; L = PMe_3) yields complexes with a WL_2 face-protonated moiety in which a bridging methylene group accounts for the unusual spectroscopic properties (Eq. 16). Lewis acids coordinate to the methylidyne ligand, yielding adducts with a methylidyne moiety still virtually intact. Finally, the methylidyne ligand can undergo Lewis acid-

$$\mathrm{XL_4W{\equiv}CH} \quad + \quad \mathrm{H^+} \longrightarrow \left.\mathrm{XL_4W(\mu\text{-}H)CH}\right]^{+} \qquad (16)$$

promoted carbyne-carbonyl coupling under CO pressure, yielding a tungsten-bound (aluminoxy)alkyne complex (Eq. 17). Elaboration of the tungsten



$$\mathrm{ClL_4W{\equiv}CH} + \mathrm{CO} + \mathrm{AlCl_3} \longrightarrow \mathrm{ClL_3(CO)W} \longleftarrow \overset{\mathrm{COAlCl_3}}{\underset{\mathrm{CH}}{|||}} \qquad (17)$$

methylidyne system to include carbonyl-containing complexes should allow further investigation into the coupling reactivity and properties of these compounds.

Extension of our earlier work[21] has led to the formation of three new cationic phosphonium carbynes which contain bulkier phosphines at the carbyne carbon. In the case of the dimethylphenylphosphonium derivative, addition of two equivalents of phosphine to C_α of the chlorocarbyne precursor can be avoided by employing slightly less than one equivalent of phosphine; isolation of the phosphonium carbyne is simplified in that it is not necessary to separate the carbyne from $[PMe_3Ph][I]$. The bulkier triphenyl- and tricyclohexylphosphines can be added in excess without complication of bis(phosphonium)carbene formation, presumably due to their steric bulk.

Note that the one-bond carbon-phosphorus coupling constant in the triphenyl- and dimethylphenylphosphonium carbynes is too small to detect. The tungsten-carbon coupling (212 and 207 Hz, respectively), agrees well with coupling constants in numerous other tungsten carbyne complexes.[25] Carbon-phosphorus coupling is observed in the ^{13}C NMR spectrum of the tricyclophexylphosphonium complex; to date it appears that this is the only complex which displays such coupling.

As with other cationic carbynes, nucleophilic addition takes place at the carbyne carbon, C_α, to form carbenes which can be converted to new carbynes by displacement of the original carbyne substituent. Our original attempts at hydridocarbyne formation involved addition of hydride to $[Tp'(CO)_2W{\equiv}C\text{-}PMe_2Ph][PF_6]$. Reaction occurred immediately to form a dark blue solution of hydridocarbene, definitively characterized by a low-field doublet at $\delta = 13.3$ ppm attributed to the proton bound to C_α. However, trapping of PMe_2Ph with MeI was slow, and very little conversion to $Tp'(CO)_2W{\equiv}CH$ could be realized before decomposition of the product occurred. Apparently PMe_2Ph does not readily dissociate from the carbene, perhaps due to its nucleophilicity or its relatively small size.

If addition of hydride to a bulkier phosphonium-substituted carbyne center could be realized we expected the larger phosphine leaving group would facilitate hydridocarbyne formation. More severe steric interactions between the phosphorus substituents and the bulky $[Tp'(CO)_2W]$ moiety might promote phosphine dissociation. Indeed, addition of $NaBH_4$ to the tricyclohexylphosphonium derivative, or addition of $KHB(Oi\text{-}pr)_3$ to the triphenylphosphonium complex results in hydride attack at C_α followed by spontaneous loss of phosphine, forming $Tp'(CO)_2W{\equiv}CH$ as the only carbonyl containing product according to solution IR studies. Separation of the hydridocarbyne complex from free PPh_3 or from $P(Cy)_3$ has been unsuccessful to date. The absence of a signal attributable to a hydridocarbene as well as the presence of the characteristic methylidyne singlet at $\delta = 8.23$ ppm with ${}^2J_{WH} = 80$ Hz indicate that the phosphine is not re-adding to the carbyne. Significant amounts of the carbyne are destroyed during column chromatography and only very small quantities of the carbyne/phosphine mixture have been recovered.

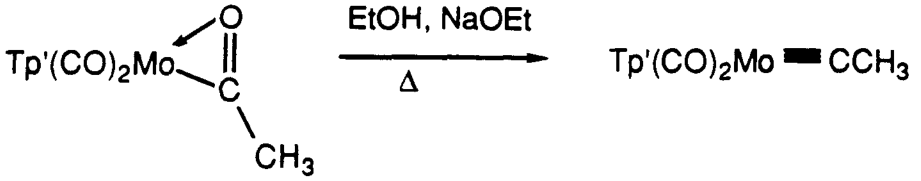
Attack of the substituted phenoxide anion $[p\text{-}OC_6H_4OCH_3]^-$ at C_α of $Tp'(CO)W{\equiv}C\text{-}PMe_2Ph][PF_6]$ gives the new aryloxycarbyne $Tp'(CO)_2W{\equiv}C\text{-}OC_6H_4OCH_3$. Lalor and Ferguson have reported the preparation of a series of non-first row organochalcogeno-substituted Group VI carbynes by direct substitution of organochalcogenide for halide;[22] the direct displacement of halide from the chlorocarbyne ligand of $Tp'(CO)_2W{\equiv}CCl$ by oxyanions reported here extends this methodology to include substitution by first row chalcogenides. With the exception of a tantalum siloxycarbyne,[12] no other stable transition metal oxycarbynes have been reported.

The extremely high-field ^{13}C NMR carbyne carbon resonance (227 ppm) suggests that there is substantial contribution of an oxygen lone pair into a π- orbital of the carbyne ligand. The contribution of electron density from nitrogen lone pairs in aminocarbynes manifests itself in relatively high-field carbyne chemical shifts, as well as lengthened $M-C_\alpha$ bonds and shortened $C_\alpha-N$ bonds.[25]

Initial investigations into intramolecular carbonyl-carbyne coupling in the aryloxycarbyne series suggest that the oxycarbynes are inert under typical coupling conditions. Photolysis for one hour at 254 nm of a THF solution of $Tp'(CO)_2W{\equiv}C-O(4-C_6H_4OCH_3)$ in the presence of excess trimethylphosphine has no effect on the ^1H NMR spectrum of the aryloxycarbyne. Similarly, thermolysis of the aryloxycarbyne in the presence of trimethylphosphine for one day leaves the complex unaffected.

VII. Vinylidene and η^2-Acyl Complexes as Carbyne Precursors

Additional carbyne chemistry, including carbyne-carbonyl coupling, has been developed following conversion of η^2-acyl complexes to carbynes by a net oxygen atom removal reaction driven with excess ethoxide in ethanol. In this reaction, formation of the carbyne product occurs without a change in the overall charge of the metal-containing species -- thus corresponding to formal removal of atomic oxygen (Eq. 18).



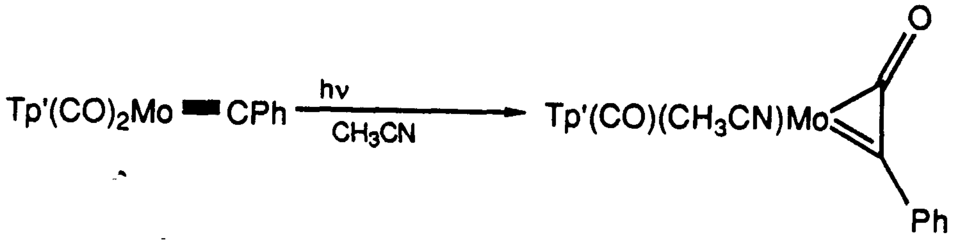
(Eq. 18)

Both $\mathrm{Tp'(CO)_2Mo{\equiv}CCH_3}$ and $\mathrm{Tp'(CO)_2Mo{\equiv}CCH_2CH_3}$ are susceptible to deprotonation by strong bases at the carbyne ß-carbon to yield thermally unstable vinylidene complexes (Eq. 19). Electrophiles such as methyl iodide readily attack these anions at the vinylidene ß-carbon, generating a carbyne ligand with an elaborated alkyl chain (Eq. 20).

$$\mathrm{Tp'(CO)_2Mo{\equiv}CCH_3 + Na[N(SiMe_3)_2] \xrightarrow{-78^\circ} Tp'(CO)_2Mo{=}C{=}CH_2{}^{1-}} \qquad \text{(Eq. 19)}$$

$$\mathrm{Tp'(CO)_2Mo{=}C{=}CH_2{}^{1-} + RX \longrightarrow Tp'(CO)_2Mo{\equiv}CCH_2R + X^{1-}} \qquad \text{(Eq. 20)}$$

Photolysis of an acetonitrile solution of $\mathrm{Tp'(CO)_2Mo{\equiv}CPh}$ produces an η^2-ketenyl complex (Eq. 21). The contrasting behavior of $\mathrm{Tp'(CO)_2Mo{\equiv}CMe}$ is noteworthy: loss of carbon monoxide occurs under these conditions rather than undergoing carbonyl-carbyne coupling (Eq. 22).



(Eq. 21)

$$\mathrm{Tp'(CO)_2Mo{\equiv}CCH_3 \xrightarrow[CH_3CN]{h\nu} Tp'(CO)(CH_3CN)Mo{\equiv}CCH_3 + CO} \qquad \text{(Eq. 22)}$$

The vinylidene anion prepared by deprotonating $\mathrm{Tp'(CO)_2Mo{\equiv}CMe}$ with excess $\mathrm{Na[N(SiMe_3)_2]}$ in THF, can be detected at low temperature by NMR spectroscopy (Eq. 19). When one equivalent of base is employed, only half of the methyl carbyne complex is deprotonated. Thus the $\mathrm{p}K_a$ of the carbyne methyl group is approximately equal to the pK_a of $HN(SiMe_3)_2$; the latter value is 25.8 in THF solvent.[26]

The vinylidene CH_2 group appears as a singlet at 3.74 ppm in the ^1H NMR spectrum. In the ^{13}C NMR spectrum, a resonance at 349.6 ppm is assigned to the α-carbon of the vinylidene ligand, while the ß-carbon resonates at 91.4 ppm (t, $^1J_{CH}$ = 153 Hz). This ß-carbon shift is slightly higher than typically observed (ca. 110-130 ppm).[27] However, its appearance as a triplet is conclusive as no other carbon atom in this complex is bound to two protons. The coupling information indicates that the ß-carbon is sp^2 hybridized as expected and the negative charge of the anion is extensively delocalized.

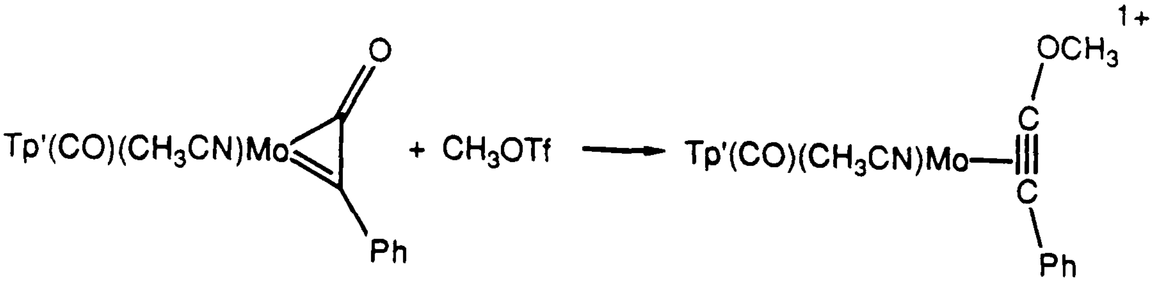
The vinylidene complex is susceptible to attack at the ß-carbon of the vinylidene ligand by methyl iodide or ethyl iodide to regenerate a metal carbyne (Eq. 20). Nucleophilic behavior at vinylidene C_β and was predicted from molecular orbital calculations[28] has been observed in other work.[29]

Photolysis of the methyl carbyne complex in acetonitrile gives red solutions of $Tp'(CO)(CH_3CN)Mo{\equiv}CCH_3)$ (Eq. 22). ^{13}C NMR spectroscopy confirms that the carbyne linkage remains intact: a resonance at 291.9 ppm is assigned to the carbyne carbon. The acetonitrile substitution product could not be isolated as a pure solid, however. A stable analog was obtained by photolysis in acetone and treating the resulting solution with excess trimethylphosphine (Eq. 23). An interesting feature of the ^1H NMR spectrum of the phosphine product is the appearance of a doublet ($^4J_{HP}$ = 5 Hz) assigned to the methyl group of the carbyne ligand. In the ^{13}C NMR spectrum, the carbyne carbon resonates at 288.1 ppm, coupled to phosphorus by 20 Hz. The carbonyl carbon, at 243.0 ppm, is coupled to phosphorus by 10 Hz. The coupling data are consistent with a metal-bound phosphine ligand. The presence of a single terminal CO absorption in the IR spectrum, at 1842 cm^{-1}, and the lack of a ketonic absorption associated with a metal-bound ketenyl ligand completes the characterization of this complex as the product of simple CO substitution from the methyl carbyne.

$$\mathrm{Tp'(CO)(Me_2CO)Mo{\equiv}CCH_3} \xrightarrow{\mathrm{PMe_3}} \mathrm{Tp'(CO)(PMe_3)Mo{\equiv}CCH_3} \qquad 23$$

In acetonitrile solvent, the phenyl carbyne complex is photochemically converted to an η^2-ketenyl complex, $Tp'(CO)(CH_3CN)Mo(\eta^2\text{-}C(O)CPh)$ by coupling a carbonyl and the carbyne ligand (Eq. 21). The ketenyl complex is characterized by a single terminal CO absorption in the infrared spectrum at 1884 cm^{-1} and by a broad, weak band at 1758 cm^{-1} that is assigned to the ketonic C=O moiety. NMR spectra of this product confirm the loss of mirror symmetry in the complex, as shown by the unique set of resonances for each pyrazole ring of the Tp' ligand. The α-carbon of the ketenyl ligand resonates at 232.1 ppm and appears as a triplet ($^3J_{CH}$ = 8 Hz). The ketenyl ß-carbon is found at 209.5 ppm. These values are similar to those of other η^2-ketenyl complexes.[30] The bound acetonitrile resonates at 143 ppm ($CH_3\underline{C}N$).[31]

Addition of Lewis acids to η^2-ketenyl complexes is a facile route to alkoxyalkyne complexes.[30] Accordingly, we find that the ketenyl product is readily alkylated by methyl triflate to give a cationic alkyne complex (Eq. 24).



24

VIII. Summary

As indicated in the introduction this report represents a transition in our research efforts during the past two years. Of the six sections describing different topics, only the review article (section II) and a paper concerning tantalum(I) alkyne complexes (section IV) have been published. The results of section VII addressing carbyne reactions have been incorporated into a full paper which will appear in Organometallics in late 1989 or early 1990. We are beginning to write manuscripts for the other three sections now: isonitrile to carbyne conversions (II), tungsten hydride NMR properties (V), and $L_nM{\equiv}C$-O-Ar complexes (VI). Further work with protonation of the aminocarbyne to form reactive heteroatom carbenes is planned. We have also successfully prepared an electron-deficient methylphenylcarbene complex, $[Tp'(CO)_2W{=}CPhCH_3][BF_4]$, by protonation of $Tp'(CO)_2W(\eta^2\text{-}PhC{=}CH_2)$. The NMR properties and x-ray structure indicate that the methyl carbon is interacting with the metal center (δ ^{13}C, -22 ppm; W-CH_3, 2.49 Å). We believe these $[Tp'(CO)_2W{=}CRR']^+$ cations may provide useful reagents for mechanistic carbene reaction studies.

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