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Highly Nucleophilic Acetylide, Vinyl, and Vinylidene Complexes

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Technical Report

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In the course of this research we found that the anionic alkynyl complex $[Cp'(CO)(PPh_3)Mn\text{-}C{\equiv}C\text{-}CH_3]^-$ (1) can be generated *in situ* by the addition of two equivalents of n-BuLi to a solution of the carbene complex $Cp'(CO)(PPh_3)Mn{=}C(OMe)CH_2CH_3$ (2). Complex 1 adds electrophiles such as H_2O, MeI, $MeOSO_2CF_3$, $[Et_3O][BF_4]$, EtI, Bu^tI, and RC{O}Cl (R = Me, Ph) to form vinylidene complexes $Cp'(CO)(PPh_3)Mn{=}C{=}CMe(R)$ {R = H, Me, Et, Bu^t, -C{O}Me (3), and -C{O}Ph}. Alkylation of 1 with MeOTf affords the vinyl carbyne complex $[Cp'(CO)(PPh_3)Mn{\equiv}C\text{-}C(Me){=}C(OMe)Me]^+CF_3SO_3^-$. The β-carbon of the propynyl ligand of 1 also adds to the central carbon atom of the heterocumulenes TolNCO, Ph_2CCO, and CO_2 to form, after protonation or alkylation, the vinylidene complexes $Cp'(CO)(PPh_3)Mn{=}C{=}CMe(\text{-}C\{O\}R)$ {R = NHTol, $CHPh_2$, OMe}, and 1 undergoes conjugate addition with *trans*-4-phenyl-3-buten-2-one to give after protonation the vinylidene complex $Cp'(CO)(PPh_3)Mn{=}C{=}CMe(CH(Ph)CH_2\text{-}C\{O\}Me)$. In the presence of $BF_3{\cdot}Et_2O$, complex 1 undergoes [2+3] cycloaddition of the C≡C bond of the propynyl ligand across the epoxide linkage of isobutylene oxide and cyclohexene oxide to form new cyclic carbene complexes 4 and 5. A similar [2+4] cycloaddition occurs with 3,3-dimethyloxetane to give yet another carbene complex 6. These latter reactions are highly stereospecific due to the chiral nature of 1 and give a single pair of enantiomers of 4 and 6.

It was also found that the highly nucleophilic propynyl complex $[Cp(CO)(PPh_3)\text{-}Mn\text{-}C{\equiv}C\text{-}Me]^-$ (7) reacts with a variety of aldehydes and ketones in the presence of $BF_3{\cdot}Et_2O$ to give, after quenching with MeOH, a series of cationic vinylcarbyne complexes of the general form $[Cp(CO)(PPh_3)Mn{\equiv}C\text{-}C(Me){=}C(R)(R')]BF_4$. The reactions of the R, R'= Ph derivative (8) with a series of nucleophiles ($LiAlH_4$, RMgX, $Bu^tC{\equiv}CLi$) has been studied, and addition occurs to both the α-carbon of the vinylcarbyne ligand to form vinylcarbene complexes $[Cp(CO)(PPh_3)\text{-}Mn{=}C(R)\text{-}C(Me){=}CPh_2]$ (R= H, Me, Et, $\text{-}C{\equiv}C\text{-}Bu^t$) and to the γ-carbon to give vinylidene complexes, with addition to C_α being electronically preferred but with addition to C_γ being favored sterically because of the bulky PPh_3 ligand. The vinylcarbyne complexes that have an acidic proton on the C_γ substituent undergo facile deprotonation to give vinyl-vinylidene derivatives of the general form $Cp(CO)(PPh_3)Mn{=}C{=}C(Me){-}C(R){=}C(R')_2$ (R'=H, R= *p*-Tol, Bu^t; R'=Me, R=H). The propynyl complex 7 also adds to the γ-carbon of 8 to form the binuclear bis(vinylidene) complex $[Cp(CO)(PPh_3)Mn{=}C{=}C(Me){-}]_2\{C(Ph)_2\}$ as a separable mixture of diastereomers. A related binuclear bis(vinylidene) complex $[Cp(CO)(PPh_3)Mn{=}C{=}C(Me){-}]_2{-}\{C(H)(Et)\}$ was also isolated in low yield from the reaction of propynyl complex 7 with both MeOH and Me_3SiCl.

The cationic alkylidyne complexes $[Cp(CO)_2M{\equiv}C{-}CH_2R]^+$ [M= Re, R= H; M= Mn, R= H, Me, Ph] have been found to undergo facile deprotonation to give the corresponding neutral vinylidene complexes $Cp(CO)_2M{=}C{=}C(H)R$. For $[Cp(CO)_2Re{\equiv}C{-}CH_3]^+$, this transformation occurs spontaneously at -78° C upon the addition of solvent (CH_2Cl_2 or THF) to the solid carbyne complex, but the manganese complexes $[Cp(CO)_2Mn{\equiv}C{-}CH_2R]^+$ (R= H, Me) require the addition of external base (*e.g.*, Et_3N) to induce their deprotonation. The manganese benzylcarbyne complex $[Cp(CO)_2Mn{\equiv}C{-}CH_2Ph]^+$ is intermediate in behavior. Except for $Cp(CO)_2Mn{=}C{=}C(H)Ph$, these vinylidene complexes are thermally unstable and must be generated and studied at low temperature. They are potent dipolarophiles which undergo net [2+2] cycloaddition with imines to give cyclic carbene complexes of the general form $Cp(CO)_2M{=}\overline{C{-}C(H)R{-}C(H)Ph{-}N}(R')$ [M = Re, R = H, R' = Me, Ph; M = Mn, R' = Ph, R = H, Me, Ph]. Identical manganese products form upon treatment of the manganese carbyne complexes first with imine followed by addition of Et_3N. Permanganate oxidation of the manganese cyclic carbene complexes gives the corresponding β-lactams in excellent yield. Also formed in the reactions of the rhenium complex $Cp(CO)_2Re{=}C{=}CH_2$ with imines are the products $Cp(CO)_2Re{=}\overline{C{-}C({=}C(H)Ph){-}C(H)Ph{-}N}(R')$ [R'= Me, Ph] that have an exocyclic double bond formed via an aldol-type condensation between the initial cycloadduct and excess imine. The vinylidene complexes $Cp(CO)_2M{=}C{=}C(H)R$ react with $HN{=}C(Ph)_2$ to give imino-carbene complexes of the general form $Cp(CO)_2M{=}C(CH_2R)\text{-}N{=}C(Ph)_2$ which derive by addition of the N-H bond across the vinylidene C=C bond. Similar products form upon benzophenone imine addition to the manganese carbyne complexes, followed by addition of Et_3N. Also formed in the reaction of $Cp(CO)_2Mn{=}C{=}C(H)Ph$ or $[Cp(CO)_2Mn{\equiv}C\text{-}CH_2Ph]^+$ with $HN{=}C(Ph)_2$ is the [2+2] cycloadduct $Cp(CO)_2Mn{=}\overline{C\text{-}C(H)Ph\text{-}C(Ph)_2\text{-}N}(H)$. Nitrile complexes, $Cp(CO)_2Mn\text{-}N{\equiv}C\text{-}CH_2R$, result from an organometallic analogue of the Beckmann rearrangement upon treatment of $Cp(CO)_2Mn{=}C{=}C(H)R$ [R= H, Ph] or $[Cp(CO)_2Mn{\equiv}C\text{-}CH_2R]^+$ [R= H, Me] with $Ph_2C{=}NNH_2$. Isocyanide complexes, $Cp(CO)_2Re\text{-}C{\equiv}N\text{-}R$, are the result of reaction of the vinylidene complex $Cp(CO)_2Re{=}C{=}CH_2$ with carbodiimides ($RN{=}C{=}NR$; R= Pr^i, Bu^t), a reaction that proceeds via net metathesis of the vinylidene Re=C bond with the carbodiimide C=N bond. A similar isocyanide product forms upon reaction of $[Cp(CO)_2Mn{\equiv}C\text{-}CH_3]^+$ with $Bu^tN{=}C{=}NBu^t$ and Et_3N, and a ^{13}C labelling experiment indicates a mechanism involving a [1,3]-migration of the $[Cp(CO)_2Mn]$ fragment in the intermediate $[Cp(CO)_2Mn\text{-}C({=}CH_2)\text{-}N(Bu^t){=}C{=}N(Bu^t)]$. Reaction of both $[Cp(CO)_2Mn{\equiv}C\text{-}CH_3]^+$ and $Cp(CO)_2Mn{=}C{=}CH_2$ with $Pr^iN{=}C{=}NPr^i$ gave the *ansa*-carbene carbene complex $\{\eta^5\text{-}C_5H_4\text{-}\overline{C({=}CH_2)\}(CO)_2Mn{=}C(N(H)Pr^i)(N}Pr^i)$ by a path involving a similar [1,3]-migration of the $[Cp(CO)_2Mn]$ fragment and insertion of the original vinylidene or carbyne α-carbon into the one of the C-H bonds of the cyclopentadienyl ligand. A byproduct of this reaction is the bis(amino)carbene complex $(\eta^5\text{-}C_5H_4\text{-}C\{O\}CH_3)(CO)_2Mn{=}C(NHPr^i)_2$, with an acetyl substituent on the cyclopentadienyl ligand, a product that likely results from hydrolysis of the above-mentioned *ansa*-carbene complex. An unusual zwitterionic vinylidene complex $Cp(CO)_2Mn{=}C{=}C(Me)\text{-}\overline{C\text{-}N(Bu^t)\text{-}\overset{-}{B}Cl_2\text{-}\overset{+}{N}}(Bu^t)$ is the principal product of the reaction of the propylidyne complex $[Cp(CO)_2Mn{\equiv}C\text{-}CH_2Me]^+$ with $Bu^tN{=}C{=}NBu^t$ and Et_3N. With benzalazine, $Ph(H)C{=}N\text{-}N{=}C(H)Ph$, the complexes $Cp(CO)_2Re{=}C{=}CH_2$ and $[Cp(CO)_2Mn{\equiv}C\text{-}CH_3]^+$ react to form the bimetallic bis(carbene) complexes $Cp(CO)_2M{=}\overline{C\text{-}C(H)_2\text{-}C(H)Ph\text{-}N}\text{-}\overline{N\text{-}C(H)Ph\text{-}C(H)_2\text{-}C}{=}M(CO)_2Cp$ (M = Re, Mn) that result from consecutive [3+2] cycloaddition reactions of the azine with two equivalents of the organometallic reagents.

We have also investigated reactions relevant to the halide promoted Fe and Ru catalyzed carbonylation of nitroaromatics. It was observed that the halides Cl^-, Br^-, I^- and the pseudo-halide NCO^- react with $Fe_3(CO)_{12}$ (9) in aprotic solvents to induce a disproportionation reaction yielding the radical anion $[Fe_3(CO)_{11}]^{-\bullet}$ (10). This species has been fully characterized by single crystal X-ray diffraction studies of its PPh_4^+ and PPN^+ salts, although the latter was disordered. In contrast to other related Fe_3 carbonyl clusters, the structures show that the anion has one semi-bridging CO and ten terminal CO ligands. Cluster **10** also forms upon reaction of $[Fe_3(CO)_{11}]^{2-}$ with $ArNO_2$, and it disproportionates under a CO atmosphere to yield $Fe(CO)_5$ and $[Fe_3(CO)_{11}]^{2-}$. The mixed metal cluster $Fe_2Ru(CO)_{12}$ also reacts with [PPN]Cl to yield [PPN]-$[Fe_2Ru(Cl)(CO)_{10}]$, a reaction which is similar to that previously observed for $Ru_3(CO)_{12}$. Reaction of $[Fe_3(CO)_{11}]^{-\bullet}$ with PhNO and $PhNO_2$ yields a mixture of clusters which, after workup, give azo- and azoxybenzene. When $Cl_5C_6NO_2$ was used in place of $PhNO_2$, the cluster $[Fe_3(CO)_9(\mu_3\text{-}NC_6Cl_5)]^{2-}$ (11) was obtained together with other products. Cluster **11** can be protonated by HBF_4 to yield $[HFe_3(CO)_9(\mu_3\text{-}NC_6Cl_5)]^-$ (12). The non-chlorinated analogue of 5, $[PPh_4]_2[Fe_3(CO)_9(\mu_3\text{-}NPh)]\cdot 2CH_2Cl_2$ has been characterized by an X-ray diffraction study. The cluster $[HFe_3(CO)_{11}]^-$ (13) has been found to react with PhNO and $ArNO_2$ by an initial electron transfer process to form $[HFe_3(CO)_9(\mu_3\text{-}NPh)]^-$ (14), with PhNO giving higher yields. Cluster 14 reacts with PhNO in the presence of radical activators to yield azo and azoxybenzene. The use of 2-Me-C_6H_4NO in this reaction gave only symmetrical azo and azoxyarenes, implying that these products do not derive from a coupling of the imido fragment in 14 with free ArNO. Cluster 14 reacts with water to yield aniline in the presence of $[Cp_2Fe][PF_6]$ but not in its absence. Competition experiments show that 14 is not a kinetically significant intermediate in the phase-transfer catalyzed reduction of $ArNO_2$ by $Fe_3(CO)_{12}$ and imply that radical intermediates are also involved in this reaction.

A final part of this work has involved investigations of metal-oxo complexes. It was found that in the presence of aqueous NaOH and air, Cp^*WCl_4 undergoes hydrolysis and oxidation to form $Cp^*W(O)_2Cl$. When air is excluded, two W(V) intermediates are detected in the above reaction for which spectroscopic evidence indicates the formulations $Cp^*WCl_3(OH)$ and $Cp^*WCl_2(OH)_2$. In the absence of air, Cp^*MoCl_4 reacts with NaOH(aq) to cleanly yield the Mo(V) compound $Cp^*Mo(O)Cl_2$, but in the presence of air oxidation occurs to give the Mo(VI) complex $Cp^*Mo(O)_2Cl$. Both Cp^*WCl_4 and Cp^*MoCl_4 react with aqueous Bu^tNH_2 in the presence of air to form the trioxo anions $[Cp^*M(O)_3]^-$ which have been isolated as their $[Bu^tNH_3]^+$ salts. The trioxo anions are also produced upon treatment of $Cp^*M(O)_2Cl$ or $[Cp^*M(O)_2]_2(\mu\text{-}O)$ with aqueous Bu^tNH_2. $[(Ph_3P)_2N]^+$ and $[Bu^n{}_4N]^+$ salts of $[Cp^*W(O)_3]^-$ were obtained by metathesis reactions, and the reaction of $[Bu^tNH_3][Cp^*W(O)_3]$ with $EtC\{O\}CH{=}CH_2$ gave the salt $[Bu^t(EtC\{O\}CH_2CH_2)NH_2][Cp^*W(O)_3]$. The complex Cp^*WCl_4 was also observed to react with anhydrous Bu^tNH_2 in the absence of air to form $Cp^*W(NBu^t)Cl_2$ which in turn gave $Cp^*W(O)(NBu^t)Cl$ upon exposure to moist air. With phenylhydrazine, Cp^*WCl_4 reacted in air to give the bis(hydrazinido) complex $Cp^*W(NNHPh)_2Cl$. With H_2S in air, both Cp^*WCl_4 and Cp^*MoCl_4 reacted to give mixtures of the known dinuclear compounds $[Cp^*M(S)]_2(\mu\text{-}S)_2$ and $[Cp^*M(S)]_2(\mu\text{-}S_2)$, but in the presence of NEt_3, Cp^*WCl_4 and H_2S reacted to give the new trisulfido anion $[Cp^*W(S)_3]^-$. In exploratory reactions of $[Cp^*W(O)_3]^-$ with unsaturated organic substrates, phenylketene was observed to react with this trioxo anion to give a new complex formed via net [2+2] cycloaddition of a W=O bond across the ketene C=C bond, and two molecules of $MeO\{O\}CC{\equiv}CC\{O\}OMe$ were taken up by $[Cp^*W(O)_3]^-$ to form a new complex with a six-membered W-O-C(R)=C(R)-C(R)=C(R) ring.

The trioxo anions $[Cp^*W(O)_3]^-$ and $[Cp^*Mo(O)_3]^-$ have been shown to be useful reagents for the formation of μ-oxo complexes via halide displacement reactions. For example, they react with $Cp^*M(O)_2Cl$ (M = Mo, W) to form the known homometallic μ-oxo complexes $Cp^*(O)_2M\text{-}O\text{-}M(O)_2Cp^*$ along with the heterometallic complex $Cp^*(O)_2Mo\text{-}O\text{-}W(O)_2Cp^*$. This latter species was also observed to form via a metal exchange process upon mixing the homometallic complexes $Cp^{*}(O)_2Mo\text{-}O\text{-}Mo(O)_2Cp^{*}$ and $Cp^{*}(O)_2W\text{-}O\text{-}W(O)_2Cp^{*}$. Reaction of the trioxo anions with $Cp_2M'Cl_2$ led to the new heterobimetallic complexes $Cp_2M'(Cl)\text{-}O\text{-}M(O)_2Cp^{*}$, (M' = Ti, Zr; M = Mo, W and M' = V, M = W). The corresponding trinuclear complexes $Cp^{*}(O)_2W\text{-}O\text{-}M'(Cp)_2\text{-}O\text{-}W(O)_2Cp^{*}$ were formed via addition of *two* equivalents of $[Cp^{*}W(O)_3]^{-}$ to $Cp_2M'Cl_2$ (M' = Ti, Zr). Addition of Et_2O to $Cp_2V(Cl)\text{-}O\text{-}W(O)_2Cp^{*}$ gave the solvated complex $[Cp_2V(Et_2O)\text{-}O\text{-}W(O)_2Cp^{*}]Cl$, and the tetrametallic complex $[\{Cp_2Ti\}_2\text{-}\{Cp^{*}W(O)_2\}_2(\mu\text{-}O)_4][BPh_4]_2$ was produced via halide abstraction from $Cp_2Ti(Cl)\text{-}O\text{-}W(O)_2Cp^{*}$ with $Na[BPh_4]$ followed by dimerization of the resulting monocations. The trioxo anion $[Cp^{*}W(O)_3]^{-}$ also displaced halides from $BrCPh_3$, chlorosilanes, and chlorogermanes to give the corresponding alkoxy $\{Cp^{*}W(O)_2\text{-}O\text{-}CPh_3\}$, siloxy $\{Cp^{*}W(O)_2\text{-}O\text{-}SiR_2R'$: R, R'= CH_2Ph; R= Bu^t, R'= H; R= Me, R'= Bu^t; R, R'= Me$\}$, and germoxy $\{Cp^{*}W(O)_2\text{-}O\text{-}GeR_3$: R = Me, Ph$\}$ complexes. The complex $Cp^{*}W(O)_2\text{-}O\text{-}SiMe_3$ was better prepared via reaction of $[Cp^{*}W(O)_3]^{-}$ with $CF_3C\{=NSiMe_3\}OSiMe_3$. However, reaction of $[Cp^{*}W(O)_3]^{-}$ with the tin analogue $ClSnMe_3$ did not give the corresponding bimetallic complex but instead produced $[\{Me_3Sn\}_4\text{-}\{Cp^{*}W(O)\}_4\{\mu\text{-}O\}_8]$ with a sixteen-membered ring and which is formally a $[\text{-}O\text{-}WCp^{*}(O)\text{-}O\text{-}Sn\text{-}Me_3\text{-}]_4$ tetramer. A variable temperature ^{17}O NMR study showed that this species undergoes a fluxional process which exchanges the bridging and terminal oxo ligands.

Personnel

The following posdoctoral scholars, graduate students, and undergraduates participated in this research program during this final grant period. The research contributed significantly to their training and education and helped prepare them for successful careers in the chemical profession.

A. Postdoctoral Fellows:

Name	Undergrad.	Ph.D. School	Present Location
Noël Lugan	U. Paul Sabatier, Toulouse, France	U. Paul Sabatier, Toulouse, France	CNRS, Toulouse
Chae Yi	U. Michigan	U. Wisconsin	Marquette Univ. (Asst Prof)
Fabio Ragaini	U. Milano	U. Milano	U. Milano (Assoc Prof)

B. Graduate Students

Name	Undergrad. School	Ph.D.	Present Location
David Ramage	U. South Alabama	1992	Postdoc, Colorado State (Norton)
Lisa Mercando	Ithaca College	1992	Air Products Corp.
Tom Snead	Worcester College	1991	Postdoc, Emory U. (Liebeskind)
Colleen Kelly	U. Richmond	1991	US Army (Walter Reed)
Michael Terry	U. Richmond	1993	Postdoc, U. Florida (McElwee-White)
Chris Kretz	Wilkes College	1993	Postdoc, U. Lausanne (Floriani)

C. Undergraduate Scholars:

Name	B.S.	Present Location
Anne Kaplin	1993	Grad student, Berkeley
Heather Beckman	1991	Working on Wall Street
Helen McMillan	1991	Ph.D./MD program, U. Virginia

D. Collaborators:

Prof. Arnold Rheingold, University of Delaware, X-ray crystallographer
Dr. R. Mathieu, CNRS, Toulouse, France
Professor Mark Wrighton, Massachusetts Institute of Technology

Progress Report in the Form of Publications Resulting from this DOE Grant

All of the research supported by this grant has been written up in the form of publications and is described in the following articles:

1. Handwerker, B. M.; Garrett, K. E.; Nagle, K. L.; Geoffroy, G. L. "Cycloaddition of Imines and $Bu^tN{=}O$ with the Carbyne Complexes $[Cp(CO)_2M{\equiv}CTol]^+$ ($M = Mn, Re$)" Organometallics 1990, 9, 1562-1575.
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