

- distribution of the label and extent of labeling in the molecule.⁴
- (27) The ¹⁸O-isotope upfield shift on the ¹³C resonances in all group 6b metal carbonyl derivatives thus far investigated range from 0.61 to 0.67 Hz (observed at 15.03 MHz).
- (28) For a theoretical discussion of the origin of isotope shifts in NMR, see Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4983.
- (29) In the more facile reaction between *cis*-Mo(CO)₄[P(OMe)₃]NHC₅H₁₀ and ¹³CO, the stereospecifically, equatorially ¹³CO-labeled species, *cis*-Mo(CO)₄(¹³CO)P(OMe)₃, is afforded.^{30,31}
- (30) Atwood, J. L.; Darensbourg, D. J. *Inorg. Chem.* **1977**, *16*, 2314.
- (31) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 0000.
- (32) Stereoselectively carbon-13-enriched Cr(CO)₅P(OMe)₃ was prepared from the room-temperature reaction of *cis*-Cr(CO)₄[P(OMe)₃]NHC₅H₁₀ and >90% ¹³CO in heptane solvent. This species was found to rearrange at a convenient rate at 50 °C without either CO or P(OMe)₃ dissociation.

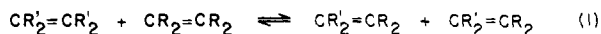
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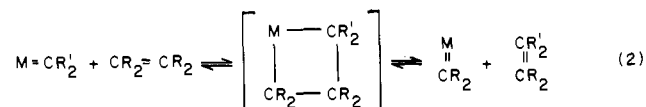
Properties and Reactions of Manganese Methylene Complexes in the Gas Phase. The Importance of Strong Metal-Carbene Bonds for Effective Olefin Metathesis Catalysts

Sir:

Transition metal carbene complexes are proving to be remarkably versatile species. They are implicated as intermediates in a variety of reactions, including the decomposition of metal alkyls,¹ polymerization of olefins by Ziegler-Natta catalysts,² olefin homologation,³ and cyclopropane formation from olefins.⁴ One reaction for which a substantial body of evidence supports the intermediacy of a metal carbene is olefin metathesis,⁵ an example of which is given in reaction 1. The

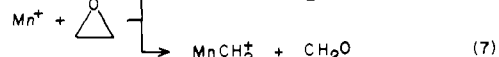
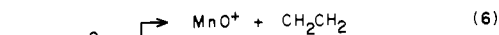
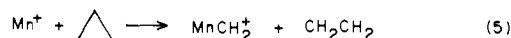
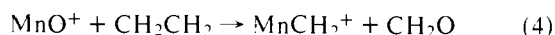
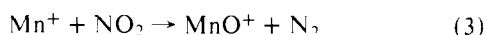


mechanism for metal carbene catalysis of this reaction is suggested to be that shown in eq 2.



The synthesis, reactivity, and thermochemistry of transition metal carbenes have been focal points of recent studies in our laboratory, using the techniques of ion cyclotron resonance spectroscopy.⁷ Previously we reported the preparation and reactions of (η^5 -C₅H₅)Fe(CO)_{*n*}CH₂⁺ (*n* = 1, 2).⁸ In this communication the formation, properties, and reactions of the gas phase carbenes MnCH₂⁺, (CO)₅MnCH₂⁺, and (CO)₄MnCH₂⁺ are described. Reported results include observation of metathesis and abstraction reactions of the methylene ligand with olefins and the first experimental determination of metal-carbene bond dissociation energies.

Several reaction pathways result in the formation of MnCH₂⁺. These include a reaction sequence beginning with the oxide MnO⁺, prepared by reaction of Mn⁺ with N₂O, reaction 3.¹⁰ For this and subsequent reactions, the neutral products are inferred and not detected. In the presence of ethylene, a new species, MnCH₂⁺, is observed, arising from the metathesis of MnO⁺ with CH₂CH₂, reaction 4. The MnCH₂⁺ ion can be generated in a single step by reaction of Mn⁺ with cyclopropane, reaction 5. Both MnO⁺ and MnCH₂⁺ are products of reaction of Mn⁺ with ethylene oxide, reactions 6 and 7.

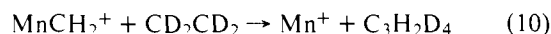


The carbene MnCH₂⁺ reacts with the olefins CD₂CD₂, CH₃CHCH₂, and (CD₃)₂CCD₂ to yield the new carbene species MnCD₂⁺, MnCHCH₃⁺, and MnC(CD₃)₂⁺, respectively; no MnCD₂⁺ is produced in the reaction with (CD₃)₂CCD₂. These are the expected products from a metathesis reaction, as illustrated by reaction 8.¹¹ In the case of



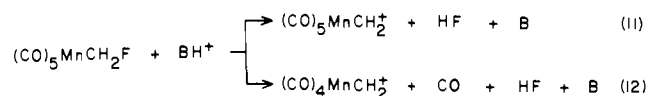
the manganese ethylidene and propylidene ions, it is possible the organic ligand has rearranged to a coordinated olefin.¹² The complexity of the reaction systems in which these species are formed precluded investigation of their structure via further reactions.

In competition with the metathesis reactions,¹³ abstraction of the ligands from MnO⁺ and MnCH₂⁺ to yield Mn⁺ is seen with olefins present, reactions 9 and 10.

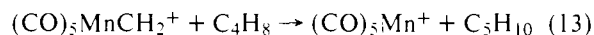


These reactions are of particular importance in that they provide limits for the bond dissociation energies, *D*(Mn⁺-X). The ability of Mn⁺ to abstract CH₂ from cyclopropane, reaction 5, establishes a lower limit to *D*(Mn⁺-CH₂) of 92 kcal/mol.^{14,15} Since the reverse of reaction 5 would be endothermic, the product of the ligand abstract, reaction 10, is most likely propylene, the olefin homologation product. This provides an upper limit to *D*(Mn⁺-CH₂) of 100 kcal/mol.¹⁶

To compare the reactivity of the "bare" metal carbene MnCH₂⁺ to species with more typical coordination, we explored the formation and reactions of the species (CO)_{*n*}MnCH₂⁺. Attempts to generate (CO)_{*n*}MnCD₂⁺ ions by reaction of (CO)_{*n*}Mn⁺ with cyclopropane-*d*₆ result only in ions of formula (CO)_{*m*}Mn(C₃D₆)⁺, *m* < *n*. However, a variety of proton donors BH⁺, where B is a base (e.g., CH₄, (CH₃)₂O), undergo reactions 11 and 12 to yield carbene complexes.^{17,18}



Pentacarbonylmanganese methylene ion reacts with the olefins *cis*-2-butene and isobutylene to give (CO)₅Mn⁺, reaction 13; the neutral hydrocarbon product could be either an



olefin or a cyclopropane. The bond energy *D*[(CO)₅Mn-CH₂] is estimated from appearance potential data¹⁹ to be 77 ± 5 kcal/mol,²⁰ making cyclopropane formation exothermic by approximately 15 kcal/mol. Reaction of olefins with (CO)₄MnCH₂⁺ results only in CO displacement products. No metathesis reactions are observed for either of these carbenes.

These results are important in several respects. Although evidence exists suggesting metal carbenes act as olefin metathesis catalysts, speculation on the mechanism of this reaction continues. This is due in part to difficulties in establishing how these species can be generated, as well as inability to characterize them in known catalytic systems. For example, the metathesis of a metal oxide with olefins to generate carbenes has been implicated, but not documented, in a number of homogeneous systems.²¹ Evidence for a carbene species generated by oxidative addition of alkyl cyclopropanes to a

metal center, followed by loss of an olefin, has been obtained in phenyltungsten trichloride-aluminum chloride mixtures.²¹ The results reported here confirm that each of these reactions can provide metal carbene complexes.

Several metal carbenes have been suggested as active catalytic species in solution, among these $(\text{CO})_4\text{WCPh}_2^{22}$ and $(\text{CO})_4\text{ReCHCH}_2\text{CH}_3^+$.²³ It was expected that $(\text{CO})_4\text{MnCH}_2^+$ would exhibit similar chemistry, but the activated complex formed in its reaction with olefins only loses CO.

Olefin homologation processes (e.g. reaction 10) are documented for $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCH}_2\text{AlCl}(\text{CH}_3)_2^{3a}$ and several tantalum alkylidenes,^{3b} as well as being observed in systems catalyzing the metathesis reaction.⁵ The results reported here show that the carbene complex MnCH_2^+ undergoes competing metathesis and homologation reactions.

The present results include the first experimental determinations of metal-carbene bond dissociation energies. Important points are that (a) metal-methylene bond energies are extremely strong and (b) the Mn^+ -methylene bond energy is decreased substantially on addition of five carbonyls to the metal center.²⁴ There is no obvious requirement that an effective metathesis catalyst possess a strong metal-carbene bond. However, if the metal-carbene bond energy exceeds 100 kcal/mol, then transfer of the carbene to an olefin to give a cyclopropane or new olefin will be endothermic and thus will not compete with the metathesis reaction. In order to avoid low turnover numbers resulting from consumption of carbene intermediates, strong metal-carbene bonds are a desirable feature of practical metathesis catalysts.

We are continuing to explore the effects of a variety of ligands on metal-carbene bond strengths, as well as periodic trends in reactivities and thermochemistry of these species.

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- (9) Mn^+ was produced by 100-eV electron impact ionization of $\text{Mn}_2(\text{CO})_{10}$ (obtained from Alfa Products).
- (10) All reactions are identified by double resonance techniques.⁷ In reaction 3, for example, a decrease in abundance of MnO^+ is observed on irradiating Mn^+ . In addition, double resonances were repeated with and without neutral reactants present, as well as with manganese ions absent.
- (11) Deuterium transfer is consistent with alkylidene units remaining intact; for example no MnCHD^+ is observed from reaction of MnCH_2^+ with CD_2CD_2 .
- (12) This type of rearrangement is observed for $(\text{CO})_5\text{WC}(\text{C}_6\text{H}_5)(\text{CH}_3)$ in solution: Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533.
- (13) Owing to the complexities of the reaction pathways, rates of reactions were not measured; we estimate rate constants to be on the order of 10^{-10} cm³ molecule⁻¹ s⁻¹. Comparable product intensities resulted from the competing reactions 4 and 9, and 8 and 10.
- (14) Thermochemical data is taken from Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds", Academic Press: New York, **1975**. Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1971**, No. 37. An exception is $\Delta H_f^\circ(\text{CH}_2) = 92.4$ kcal/mol: Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data, Suppl.* **1975**, *4*, No. 1. Another is $\Delta H_f^\circ(\text{CH}_2\text{F}) = -4.9$ kcal/mol: Blint, R. J.; McMahon, T. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1269. All data are at 298 K.
- (15) The method of obtaining Mn^+ ions⁹ raises the possibility of producing manganese ions in excited states. However, the appearance potential curve for MnCH_2^+ produced by reaction 5 is superimposable on that of Mn^+ ,

- consistent with reaction of ground state Mn^+ ions (s^1d^5 , ⁷S).
- (16) Exothermicity of reactions 6, 9, and 4 similarly requires 84 kcal/mol $\leq D(\text{Mn}^+-\text{O}) \leq 106$ kcal/mol.
 - (17) Pentacarbonyl(fluoromethyl)manganese was prepared by decarbonylation of $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_2\text{F}$ and purified by sublimation: Noack, K.; Schaerer, U.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *8*, 517. Traces of $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_2\text{F}$ remained in the sample, as evidenced by the presence of $(\text{CO})_5\text{Mn}^+$ in the mass spectrum.
 - (18) These reactions are similar to those used to generate molybdenum perfluorocarbene complexes in solution: Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153*, 67.
 - (19) The bond energy $D[(\text{CO})_5\text{Mn}^+-\text{CH}_2]$ is calculated from the ~ 1.7 -eV difference in appearance potentials of the two fragments $(\text{CO})_5\text{MnCH}_2^+$ and $(\text{CO})_5\text{Mn}^+$. The thresholds for these reactions are being determined more precisely using photoionization mass spectrometry.
 - (20) Schrock^{3b} has estimated $D(\text{Cp}_2\text{TaCH}_3-\text{CH}_2)$ to be on the order of 75 kcal/mol.
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Dihydrogen Reduction of Isocyanides Promoted by Permethylzirconocene Dihydride. A Modeling Study of Carbon Monoxide Reduction

Sir:

We have reported the stoichiometric reduction of carbon monoxide by $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ (**1**) leads to *trans*- $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}(\mu\text{-OCH=CHO})]$ (**4**) or $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{OCH}_3)$ (**5**), depending on the reaction conditions (Scheme 1).^{1,2} The proposed key intermediate, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\eta^2\text{-CHO})$ (**3**), generated by migratory insertion of CO into a Zr-H bond, was postulated to exhibit an oxy-carbenoid reactivity undergoing dimerization (**3** \rightarrow **4**) or insertion into a Zr-H bond of **1** eventually leading to **5**.³ In light of recent results³ which indicate that formyl complexes of transition metals from groups 7 and 8 spontaneously decompose in most cases to the corresponding carbonyl hydrides, one might question whether the rearrangement of **2** to **3** is thermodynamically accessible even with a substantial Zr-O interaction for **3**.⁴ In addition, our findings that **1** is capable of the facile reduction of coordinated carbon monoxide to "zirconoxy" carbenes⁵ suggest an alternative mechanism for the generation

Scheme I

