Acknowledgment. We are grateful to the National Science Foundation for financial support of this work.

References and Notes

(1) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, 1967, Chapter 6; K. P. C. Vollhardt, *Fortschr. Chem. Forsch.*, **59**, 113 (1975).

(2) O. L. Chapman, C. C. Chang, and N. R. Rosenquist, *J. Am. Chem. Soc.*, **98**, 261 (1976).

(3) Werrer Winter and Henner Straub, *Angew. Chem., Int. Ed. Engl.*, **17**, 127 (1978).

(4) J. Michl, *Mol. Photochem.*, **4**, 257–286 (1972); Karl Tseng and J. Michl, *J. Am. Chem. Soc.*, **99**, 4840 (1977).

(5) T. Koenig and S. Southworth, *J. Am. Chem. Soc.*, **99**, 2807 (1977).

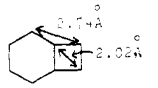
(6) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

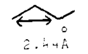
(7) (a) The structure representation procedure has been developed by Simpson[7b] with optical transitions in dyes. The method postulates the existence of many electron functions which can be associated with chemical structures (square root of the structure). These functions, though their mathematical form may be unknown, constitute a basis set. Linear combinations of this basis set are approximations to the many electron wave functions for a selected group of states of the molecule. The method discovers properties of the mathematically unknown basis functions by dediagonalization of symmetry-determined problems. The empirical matrix elements (bond ionization potentials for diagonals and splitting parameters for off diagonals) are postulated to be interchangeable among molecules with interchangeable structural features. The method could be considered as a simplified version of valence bond theory just as the Hückel method is a simplified version of molecular orbital theory. (b) W. T. Simpson and C. W. Looney, *J. Am. Chem. Soc.*, **76**, 6285, 6793 (1954).

(8) The HAM/3 procedure, as it applies to photoelectron spectra, has been described by Lindholm. L. Asbrink, C. Fridh, and E. Lindholm, *Chem. Phys. Lett.*, **52**, 63, 69 (1977). We are grateful to Professor Lindholm for supplying us with a copy of his HAM/3 program.

(9) The geometry used for the HAM/3 calculation was taken from the X-ray structure[3] of the di-*tert*-butyl derivative.

(10) In the SR procedure, a slight decrease in the $S_{2,3}$ value (1.50) and a slight increase in the $S_{3,4}$ value (1.75) gives agreement in the calculated positions of all the π bands with experiment. Such changes in these splitting parameters are in accord with the changes in interatomic distances of the 1,3 type for I compared with butadiene or 1,4-cyclohexadiene.





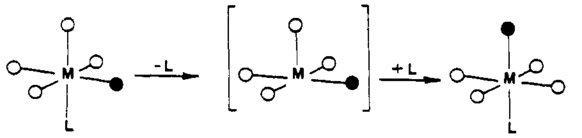
T. Koenig,* Daniel Imre, James A. Hoobler
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

Received April 9, 1979

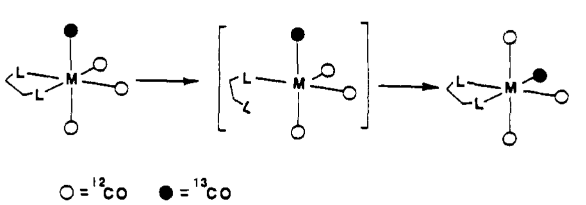
Intramolecular Rearrangement of Carbonyl Ligands in the Octahedral Complex $W(CO)_5P(OMe)_3$ by a Nondissociative Process: An Example of the Utility of the Oxygen-18 Isotope Shift on the ^{13}C NMR of the Carbonyl Ligand

Sir:

Frequently carbonyl ligand rearrangements in octahedral transition metal complexes have been observed to occur by means of a mechanism involving prior ligand dissociation, e.g., as depicted in eq 1 and 2.[1-8] On the other hand intramolecular permutation of ligands in complexes of octahedral symmetry by a process which does not involve ligand dissociation is less well documented. Indeed, the barrier to intramolecular rearrangements by a non-bond-breaking process in octahedral transition metal complexes has long been believed to be quite large.[9,10] Several recent studies, however, indicate that the process is the lowest energy mechanism for cis ⇌ trans isomerization reactions involving some of these complexes.[11-14] In this communication stereochemical nonrigidity in $W(CO)_5P(OMe)_3$ occurring by a non-bond-breaking process is unambiguously established.



(1)



(2)

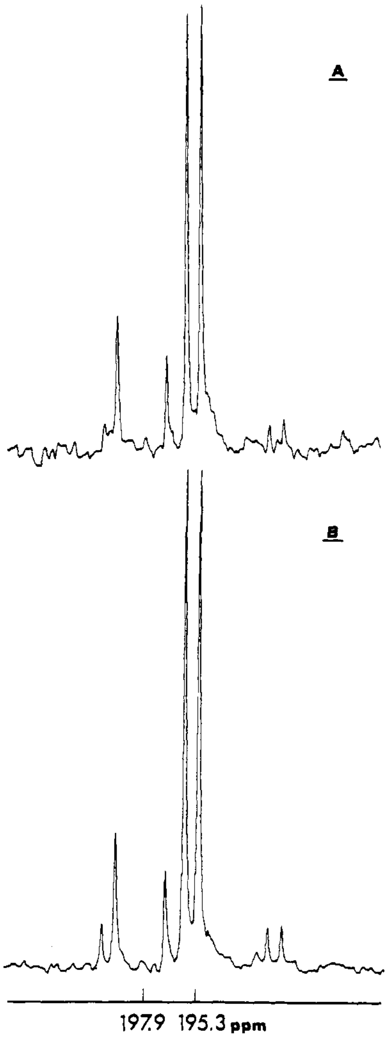


Figure 1. ^{13}C NMR spectra of $W(CO)_5P(OMe)_3$ in $CDCl_3$. (A) Natural abundance spectrum of $W(CO)_5P(OMe)_3$. $\delta(C_{trans})$ 197.9 ppm (J_{P-C} = 37.6 Hz) and $\delta(C_{cis})$ 195.3 ppm (J_{P-C} = 10.7 and J_{W-C} = 125 Hz). Note downfield portion of $\delta(C_{trans})$ overlapped with peak due to W-C_{cis} coupling (this is resolved in the spectrum determined at higher resolution; see Figure 2). (B) Spectrum of $W(CO)_5P(OMe)_3$ prepared from *cis*-$W(CO)_4[P(OMe)_3]NHC_5H_{10}$ and 93% enriched ^{13}CO in octane at 78 °C for 2 days. The ^{13}CO ligand is ~90% randomized.

Upon reacting *cis*-$W(CO)_4[P(OMe)_3]NHC_5H_{10}$ with [^{13}C]carbon monoxide in octane solvent at 78 °C for a prolonged period a nearly statistical mixture of *cis*- and *trans*-$W(CO)_4(^{13}CO)P(OMe)_3$ was obtained (see ^{13}C NMR spectra in Figure 1).[15] If the piperidine substitution reaction is stopped at an earlier stage in the substitutional process the $W(CO)_4(^{13}CO)P(OMe)_3$ product is more highly stereoselectively enriched in the equatorial position, thus indicating that a fluxional process is operative subsequent to the initial ^{13}CO incorporation. The possibility that this stereochemical nonrigidity in the $W(CO)_4(^{13}CO)P(OMe)_3$ species is occurring by a dissociative process is ruled out in that reaction of

0002-7863/79/1501-6447$01.00/0

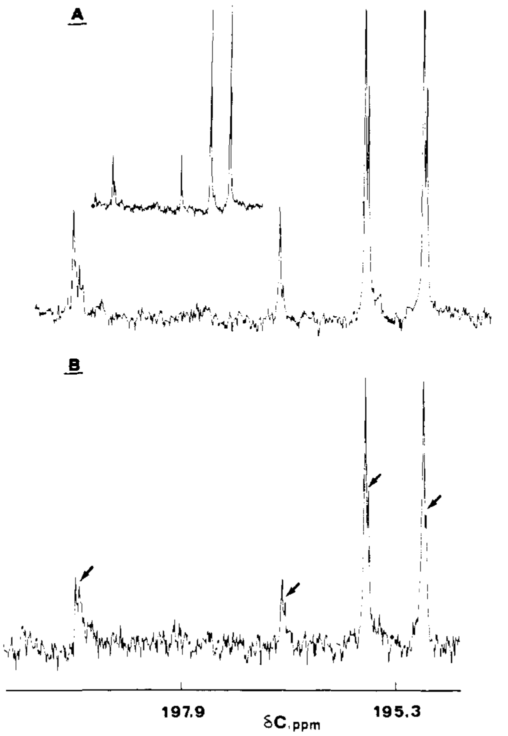


Figure 2. Natural abundance ^{13}C NMR spectra of oxygen-18-enriched $W(CO)_5P(OMe)_3$ in $CDCl_3$. (A) $W(CO)_5P(OMe)_3$ enriched in oxygen-18 stereoselectively (overlay allows for quantitative assessment of ^{18}O level in $\delta(C_{cis})$). (B) $W(CO)_5P(OMe)_3$ after 2 days in octane at 78 °C in the presence of $C^{16}O$. ^{18}O-shifted ^{13}C resonances are indicated by arrows. Both the axial and equatorial resonances are shifted upfield by 0.040 ppm.

$W(CO)_5P(OMe)_3$ with ^{13}CO in octane at 78 °C for 2 days resulted in *no* incorporation of ^{13}CO into the parent complex as well as no production of $W(CO)_5(^{13}CO)$.

These observations taken collectively are indicative of a non-bond-breaking mechanism for the ligand rearrangement process in $W(CO)_5P(OMe)_3$. Nevertheless, in order to illustrate this more dramatically, as well as to introduce a novel technique for probing these occurrences, a highly stereoselectively labeled $W(CO)_5P(OMe)_3$ species has been synthesized by the phase-transfer catalyzed oxygen-18 exchange reaction between the substrate and ^{18}O-enriched hydroxide ion.[16,17] Although the oxygen-18 incorporation reaction is carried out under condition where some rearrangement of ligands in the $W(CO)_5P(OMe)_3$ species occurs, it is possible to synthesize a complex which is highly selectively enriched in the equatorial carbonyl positions.[16-18]

Previously we have shown that the oxygen-18 isotope shift on the ^{13}C NMR of the carbon monoxide ligand in metal carbonyl derivatives provides an extremely useful method for establishing the degree of ^{18}O incorporation and its site specificity.[19] Figure 2 exhibits the natural abundance ^{13}C NMR spectra of $W(CO)_5P(OMe)_3$ enriched in oxygen-18 in both its initially prepared state and after 2 days of rearrangement in octane solvent at 78 °C in the presence of $C^{16}O$. It is possible to assess from these ^{13}C NMR spectral measurements that the initially synthesized ^{18}O-enriched $W(CO)_5P(OMe)_3$ is stereoselectively labeled in equatorial carbonyl sites, with 37% of the equatorial oxygens and 16% of the axial oxygens being oxygen-18 atoms.[20] Further these ^{13}C spectral data clearly demonstrate that, once the stereoselectively oxygen-18-enriched $W(CO)_5P(OMe)_3$ species has been heated in octane at 78 °C for 2 days in the presence of $C^{16}O$, the equatorial and axial carbonyl sites have equilibrated and, *more importantly*, the total ratio of oxygen-18 to oxygen-16 atoms has not been altered (33% of all the oxygen atoms being oxygen-18 in both the initial and rearranged complex) during the fluxional process.

These results provide for the first time clear-cut evidence that neutral, six-coordinate molecules of the type $M(CO)_5L$ can undergo ligand rearrangements in their *intact* state. Presumably this fluxional process occurs through either a trigonal-prismatic[21-24] or bicapped tetrahedron[25] intermediate or transition state. Further, it has been demonstrated that the small upfield shift in the ^{13}C resonance caused by oxygen-18 substitution at a carbon monoxide ligand permits an accurate determination of the ratio of oxygen-18 to oxygen-16 atoms in metal carbonyl derivatives to be made, thus providing a novel and alternative methodology for tracing labeled carbon monoxide ligands.[26-28] Studies in progress indicate the barrier to ligand rearrangement in $Mo(CO)_5P(OMe)_3$ by a non-bond-breaking mechanism to be greater than that observed for the tungsten species herein reported.[29-31] On the other hand $Cr(CO)_5P(OMe)_3$ has been found to undergo ligand rearrangement by a nondissociative process in an even more facile manner than $W(CO)_5P(OMe)_3$.[32] Thus the metal dependence for the ease of non-bond-breaking ligand rearrangements in the group 6b $M(CO)_5P(OMe)_3$ species is Cr > W > Mo. Quantitative investigations aimed at evaluating the activation parameters for these processes are underway.

Acknowledgment. The financial support of this research by the National Science Foundation through Grant CHE 78-01758 is greatly appreciated.

References and Notes

(1) Darensbourg, D. J.; Darensbourg, M. Y.; Dennenberg, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2807.

(2) Darensbourg, D. J.; Nelson, H. H., III *J. Am. Chem. Soc.* **1974**, **96**, 6511.

(3) Darensbourg, D. J.; Nelson, H. H., III; Murphy, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 896.

(4) Dobson, G. R.; Asali, K. J.; Marshall, J. L.; McDaniel, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 8100.

(5) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.

(6) Cohen, M. A.; Brown, T. L. *Inorg. Chem.* **1976**, *15*, 1417.

(7) Poliakoff, M. *Inorg. Chem.* **1976**, *15*, 2892.

(8) Dobson, G. R.; Asali, K. J. *J. Am. Chem. Soc.* **1979**, *101*, 5433.

(9) Muetterties, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5097.

(10) Muetterties, E. L. *Acc. Chem. Res.* **1970**, *3*, 266.

(11) Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1972**, *94*, 274.

(12) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.

(13) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4110.

(14) (a) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14. (b) Darensbourg, D. J.; Baldwin, B. J. *Inorg. Chem.*, submitted for publication.

(15) The slowness of this amine substitution process is attributed to hydrogen-bond formation between the -N-H grouping and an oxygen atom on the phosphite ligand. The presence of the hydrogen bond has been confirmed by an X-ray structure determination of this derivative. It has been shown as well that this piperidine substitution reaction takes place by a purely dissociative process when CO is the incoming ligand.

(16) Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 338.

(17) Darensbourg, D. J.; Baldwin, B. J.; Froelich, J. A. *J. Am. Chem. Soc.*, submitted for publication. Indeed, it has been shown that, in systems where intramolecular rearrangements are not occurring concomitantly with the oxygen-exchange reactions, this latter process is stereospecific.

(18) Reaction carried out using benzene solvent as the organic phase at 72 °C for ~2 days.

(19) Darensbourg, D. J. *J. Organomet. Chem.*, **1979**, *174*, C70.

(20) The ^{13}C resonances were resolved assuming symmetric peak shapes (Lorentzian) on expanded versions of the spectra shown in Figure 2 and the relative areas measured with a planimeter to arrive at the oxygen-18 content in the samples. This has been shown to be quite reliable in $W(CO)_6$ where both $\nu(CO)$ IR data and mass spectral data corroborate the findings by ^{13}C NMR.[19] The percent oxygen-18 content of a particular carbonyl ligand is believed to be accurate to better than ±10%. The ^{13}C NMR spectra were recorded on a JEOL FX60 operated at 15.03 MHz with an internal deuterium lock. Samples were run in $CDCl_3$ solvent in 10-mm tubes. The spectra resulted from the accumulation of 14 000 transients employing a sweep width of 500 Hz (16K data block) with an acquisition time of 16.4 s, a pulse repetition rate of 17.0 s, and a flip angle of 90°

(21) Bailar, J. C., Jr. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165.

(22) Ray, P.; Dutt, N. K. *J. Indian Chem. Soc.* **1943**, *20*, 81.

(23) Springer, C. S., Jr.; Sievers, R. E. *Inorg. Chem.* **1967**, *6*, 852.

(24) Majunke, W.; Leibfritz, D.; Mack, T.; TomDieck, H. *Chem. Ber.* **1975**, *108*, 3025.

(25) Hoffmann, R.; Howell, J. M.; Bossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.

(26) The advantage of this ^{13}C NMR technique over that employing ^{13}C labeling is that it does not require the presence of a ^{13}C "internal standard" in the molecule in order to quantitatively assess simultaneously the geometrical

distribution of the label and extent of labeling in the molecule.[4]

(27) The ^{18}O-isotope upfield shift on the ^{13}C 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*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ and ^{13}CO, the stereospecifically, equatorially ^{13}CO-labeled species, *cis*-$Mo(CO)_4(^{13}CO)P(OMe)_3$, 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*-$Cr(CO)_4[P(OMe)_3]NHC_5H_{10}$ and >90% ^{13}CO in heptane solvent. This species was found to rearrange at a convenient rate at 50 °C without either CO or $P(OMe)_3$ dissociation.

Donald J. Darensbourg,* Brenda J. Baldwin
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Received June 25, 1979

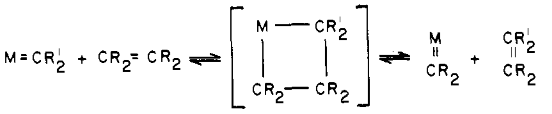
Properties and Reactions of Manganese Methylene Complexes in the Gas Phase. The Importance of Strong Metal-Carbene Bonds for Effective Olefin Metathesis Catalysts

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

$$CR'_2{=}CR'_2 + CR_2{=}CR_2 \rightleftharpoons CR'_2{=}CR_2 + CR'_2{=}CR_2 \qquad (1)$$

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

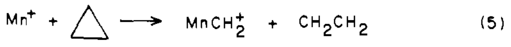


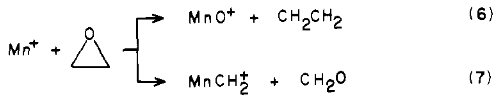
The synthesis, reactivity, and thermochemistry of transition metal carbenes have been focal points of recent studies in our laboratory, using the techniques of ion cyclotron resonance spectroscopy.[7] Previously we reported the preparation and reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_nCH_2^+$ (n = 1, 2).[8] In this communication the formation, properties, and reactions of the gas phase carbenes $MnCH_2^+$, $(CO)_5MnCH_2^+$, and $(CO)_4MnCH_2^+$ 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 $MnCH_2^+$. These include a reaction sequence beginning with the oxide MnO^+, prepared by reaction of Mn^+ [9] with N_2O, reaction 3.[10] For this and subsequent reactions, the neutral products are inferred and not detected. In the presence of ethylene, a new species, $MnCH_2^+$, is observed, arising from the metathesis of MnO^+ with CH_2CH_2, reaction 4. The $MnCH_2^+$ ion can be generated in a single step by reaction of Mn^+ with cyclopropane, reaction 5. Both MnO^+ and $MnCH_2^+$ are products of reaction of Mn^+ with ethylene oxide, reactions 6 and 7.

$$Mn^+ + NO_2 \rightarrow MnO^+ + N_2 \qquad (3)$$

$$MnO^+ + CH_2CH_2 \rightarrow MnCH_2^+ + CH_2O \qquad (4)$$





The carbene $MnCH_2^+$ reacts with the olefins CD_2CD_2, CH_3CHCH_2, and $(CD_3)_2CCD_2$ to yield the new carbene species $MnCD_2^+$, $MnCHCH_3^+$, and $MnC(CD_3)_2^+$, respectively; no $MnCD_2^+$ is produced in the reaction with $(CD_3)_2CCD_2$. These are the expected products from a metathesis reaction, as illustrated by reaction 8.[11] In the case of

$$MnCH_2^+ + CD_2CD_2 \rightarrow MnCD_2^+ + CH_2CD_2 \qquad (8)$$

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.

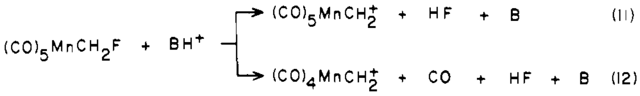
In competition with the metathesis reactions,[13] abstraction of the ligands from MnO^+ and $MnCH_2^+$ to yield Mn^+ is seen with olefins present, reactions 9 and 10.

$$MnO^+ + CH_2CH_2 \rightarrow Mn^+ + C_2H_4O \qquad (9)$$

$$MnCH_2^+ + CD_2CD_2 \rightarrow Mn^+ + C_3H_2D_4 \qquad (10)$$

These reactions are of particular importance in that they provide limits for the bond dissociation energies, $D(Mn^+\text{-}X)$. The ability of Mn^+ to abstract CH_2 from cyclopropane, reaction 5, establishes a lower limit to $D(Mn^+\text{-}CH_2)$ 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 $D(Mn^+\text{-}CH_2)$ of 100 kcal/mol.[16]

To compare the reactivity of the "bare" metal carbene $MnCH_2^+$ to species with more typical coordination, we explored the formation and reactions of the species $(CO)_n\text{-}MnCH_2^+$. Attempts to generate $(CO)_nMnCD_2^+$ ions by reaction of $(CO)_nMn^+$ with cyclopropane-d_6 result only in ions of formula $(CO)_mMn(C_3D_6)^+$, $m < n$. However, a variety of proton donors BH^+, where B is a base (e.g., CH_4, $(CH_3)_2O$), undergo reactions 11 and 12 to yield carbene complexes.[17,18]



$$(CO)_5MnCH_2F + BH^+ \rightarrow (CO)_5MnCH_2^+ + HF + B \qquad (11)$$

$$(CO)_5MnCH_2F + BH^+ \rightarrow (CO)_4MnCH_2^+ + CO + HF + B \qquad (12)$$

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

$$(CO)_5MnCH_2^+ + C_4H_8 \rightarrow (CO)_5Mn^+ + C_5H_{10} \qquad (13)$$

olefin or a cyclopropane. The bond energy $D[(CO)_5Mn^+\text{-}CH_2]$ is estimated from appearance potential data[19] to be 77 ± 5 kcal/mol,[20] making cyclopropane formation exothermic by approximately 15 kcal/mol. Reaction of olefins with $(CO)_4MnCH_2^+$ 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.[5a] Evidence for a carbene species generated by oxidative addition of alkyl cyclopropanes to a

0002-7863/79/1501-6449$01.00/0