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Reactions of Atomic Manganese with CH_2N_2 in Solid Argon at 12 K

W. E. Billups,* Sou-Chan Chang, John L. Margrave, and Robert H. Hauge

Department of Chemistry, Rice University, Houston, Texas 77251

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Summary: The reactions of atomic manganese with diazomethane have been investigated by FTIR matrix isolation spectroscopy. In argon matrixes, $MnCH_2$ and $Mn(CH_2N_2)$ complexes are formed spontaneously. Photolysis of the matrix with $\lambda \geq 400$ nm radiation removes all but one of the $Mn(CH_2N_2)$ complexes as well as the $MnCH_2$ species. Wavelength-dependent photoreversibility is observed between a $N_2(CH_2N_2)$ complex and a species assigned to $N_2{\cdots}HMnCH$.

Introduction

The first transition metal carbene complexes were synthesized in E. O. Fischer's laboratory in 1964.[1,2] The Fischer carbenes have subsequently found wide application in organic synthesis. Carbene complexes have also been recognized as important intermediates in homogeneous and heterogeneous catalysis. However, metal complexes of the simplest carbene, CH_2, have been isolated under ambient conditions in only a few cases.[3] Naked $M{=}CH_2$ species have been isolated in solid argon for several of the group 2 metals and characterized by FTIR matrix isolation spectroscopy.[5] In this paper we report the synthesis and characterization of $Mn{=}CH_2$ and HMnCH using matrix isolation spectroscopy.[6]

Experimental Section

A description of the multisurface matrix isolation apparatus has been reported previously.[7] Manganese atoms were generated by vaporizing manganese (A. D. Mackay, 99.9%) from an alumina crucible enclosed in a resistively heated tantalum furnace over the range 1300−1500 °C. Argon (99.9995%) and dinitrogen (99.9995%) were obtained from Matheson Chemical Company. Matrixes were usually irradiated after deposition by exposure to a focused 100 W medium-pressure short arc Hg lamp. A water filter with various Corning long-pass cutoff filters and a band filter, 280−360 nm (UV), was used for wavelength-dependent photolysis studies. The syntheses of CH_2N_2, CD_2N_2, $CHDN_2$, and $^{13}CH_2N_2$ were reported in earlier work.[7]

Results and Discussion

Manganese atoms were found to react spontaneously with diazomethane in argon matrixes. FTIR spectra resulting from a study in which the concentration of manganese was gradually increased revealed that four different products are formed. Absorptions arising from these species are labeled a, b, c, and d in Figure 1. The log Ax − log R_0(Mn) plot shown in Figure 2 supports the assumption that bands c and d arise from reactions of monatomic manganese. The higher slope value for the a and b bands is inconclusive; however, isotopic work also supports the assignment of these species to atomic manganese.

The doublet bands labeled a are the only absorptions that can be assigned to a $Mn{=}CH_2$ species. The band at 2864.3 cm^{-1} is assigned to a C−H stretching mode and the 521.9 cm^{-1} band to a Mn=C stretching mode. The isotopic shift (13.9 cm^{-1}) observed for the Mn=C stretching band when $^{13}CH_2N_2$ was used supports the assignment of this species to atomic manganese. A diatomic model predicts a shift of 14.1 cm^{-1} for $MnCH_2$ and 15.7 cm^{-1} for Mn_2CH_2. Similar modes for $MnCD_2$ were not observed. This indicates that there is a strong isotope effect on the spontaneous reaction that prevents the formation of $MnCD_2$.

The bands labeled b, c, and d are assigned to $Mn(CH_2N_2)$ complexes. The formation of several Mn-

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[1] Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

[2] *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983; Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. Cotton, F. A.; Lukehart, C. M. *Progr. Inorg. Chem.* **1972**, *16*, 487. Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, pp 189−233. Brown, F. J. *Progr. Inorg. Chem.* **1980**, *27*, 1. Fischer, H. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley: Chichester, England, 1982; pp 181−231. Dötz, K. H. Carbene Complexes of Groups VIa, VIIa and VIIIa. *In Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: London. Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407. Fischer, E. O. *Pure Appl. Chem.* **1972**, *30*, 353. Kreiter, C. G.; Fischer, E. O. In *XXIII International Congress of Pure and Applied Chemistry*; Butterworth: London, 1971; pp 151−168. Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857. Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651. Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. Lappert, M. F. *J. Organomet. Chem.* **1975**, *100*, 139. Casey, C. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley: New York, 1981; Vol. 2, pp 135−174. Fischer, E. O.; Fischer, H. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; Verlag Chemie: Weinheim, FRG, 1986.

[3] One of the first derivatives, $Ta(C_5H_5)_2CH_3CH_2$, was reported by Schrock and co-workers.[4] The Schrock complexes differ from the Fischer carbenes in that the polarity of the M=C bond is such that the negative charge resides on carbon.

[4] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

[5] Billups, W. E.; Chang, S.-C.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 1387. Billups, W. E.; Chang, S.-C.; Hauge, R. H.; Margrave, J. L. *Inorg. Chem.* **1993**, *32*, 1529. Chang, S.-C.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L.; Billups, W. E. *Inorg. Chem.* **1990**, *29*, 4373. Chang, S.-C.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L.; Billups, W. E. *J. Am. Chem. Soc.* **1988**, *110*, 7975. Chang, S.-C.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L.; Billups, W. E. *Chem. Commun.* **1987**, 1682. Chang, S.-C.; Kafafi, Z. H.; Hauge, R. H.; Billups, W. E. Margrave, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 4508.

[6] Ab initio MO theory at the single configuration SCF level has been employed in an extensive study of several of the electronic states of $Mn{=}CH_2$. The electronic ground state is found to be of $^8B_1$ symmetry yielding r_e(M−C) = 1.26 Å. See: B. R, Brooks, H. F. Schaefer, III. *Mol. Phys.* **1977**, *34*, 193.

[7] Hauge, R. H.; Fredin, L.; Kafafi, Z. H.; Margrave, J. L *Appl. Spectrosc.* **1986**, *40*, 588.

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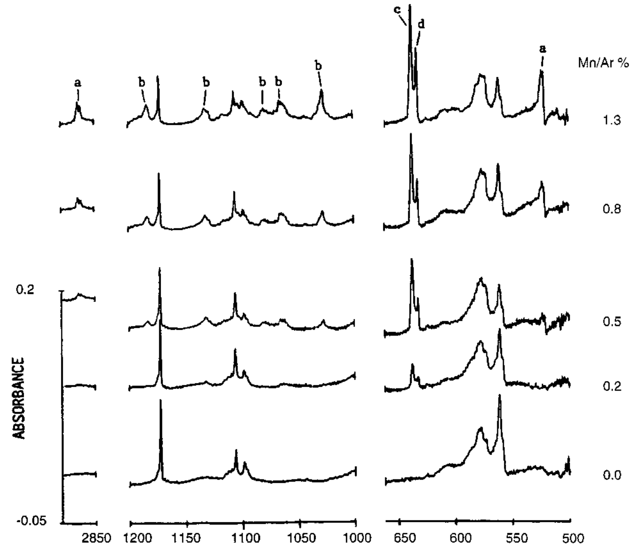


Figure 1. Manganesse concentration study. $CH_2N_2/Ar \approx 1.3/100$. a = $MnCH_2$; b, c, and d = $Mn(CH_2N_2)$ complexes.

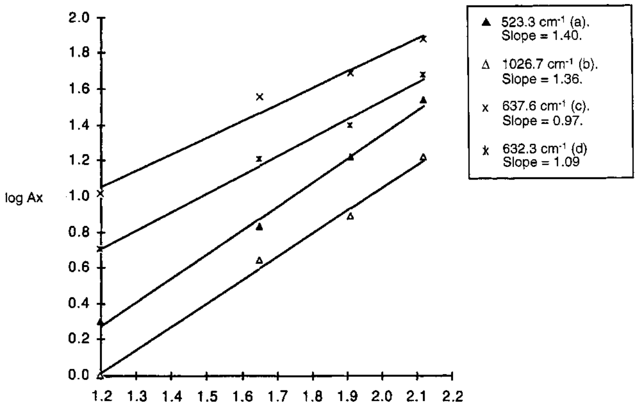


Figure 2. Plot of log Ax vs log R_0(Mn) plots. Ax represents the absorbance of peak x measured as peak height in mm. R_0(Mn) represents the molar ratio of manganese to argon, Mn/Arx1000.

(CH_2N_2) complexes is suggested by the dipolar resonance structures of diazomethane.

$$H_2\overset{-}{C}\text{-}\overset{+}{N}{\equiv}N: \longleftrightarrow H_2C{=}\overset{+}{N}{=}\overset{-}{N}: \longleftrightarrow H_2\overset{+}{C}\text{-}N{=}\overset{-}{N}:$$

The bands assigned to b appear only in the C=N stretching and CH_2 bending regions. This complex must differ significantly from the c and d species. In addition it does not form with N_2CD_2, which indicates a significant isotope effect on the rearrangement, which leads to the b species. The lack of formation of $MnCD_2$ as well suggests the b species may be an intermediate species which leads to the formation of $MnCD_2$.

The c and d bands are most likely due to very similar species. No other absorptions can be identified that are related to these peaks. The large 100 cm^{-1} isotopic shifts that are observed in the Mn/CD_2N_2 reactions (Figure 3) indicate that these bands are either CH_2 wagging or CH_2 rocking modes. In the absence of other information, we are forced to conclude that these absorptions also arise from $Mn(CH_2N_2)$ complexes.

The results of a photolysis experiment are displayed in Figure 4. The photolysis study revealed that the a bands arise from two different species labeled a_1 and a_2 (B−A, C−B) in Figure 4. The a_1 bands located at 2864.3 and 521.9 cm^{-1} decreased upon $\lambda \geq 500$ nm photolysis, while the a_2 bands at 2861.9 and 523.3 cm^{-1} were not affected. Each set of bands disappeared completely after $\lambda \geq 400$ nm photolysis. This observation is consistent with a free and a perturbed $MnCH_2$ species, possibly by a N_2 molecule.

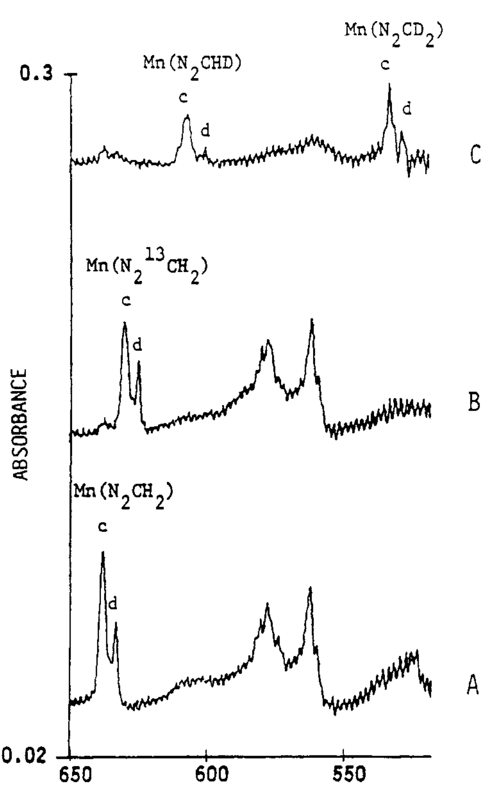


Figure 3. Isotope study showing c and d bands in (A) $Mn/CH_2N_2/Ar$ (B) $Mn/^{13}CH_2N_2/Ar$, and (C) $Mn/CHDN_2 + CD_2N_2/Ar$.

The absorptions arising from the $Mn(CH_2N_2)$ complex which exhibits the b bands disappeared after $\lambda \geq 500$ nm photolysis, but the d bands increased in intensity after $\lambda \geq 500$ nm and $\lambda \geq 400$ nm photolysis. These observations suggest that the species corresponding to a_1, a_2, and b may either return to starting materials, Mn and CH_2N_2, or give species with d absorptions. Similar reactions may occur for the complex associated with the c bands, since these also decreased upon $\lambda \geq 400$ nm photolysis. The similarity in frequency and concentration behavior suggests that species c and d are similar and may only be slightly different geometric isomers or the same species in different matrix sites.

New absorptions labeled e and g appeared after $\lambda \geq 400$ nm photolysis and increased significantly upon UV photolysis. The e bands can be assigned tentatively to HMnCH. Mn−H stretching bands are found in the 1600−1650 cm^{-1} region and an Mn−C stretching band near 600 cm^{-1} and C−H bending near 580 cm^{-1}. The calculated shifts from diatomic approximation are 17.7 and 18.7 cm^{-1} for the Mn≡C stretching frequency of the $HMn^{13}CH$ species. This compares to the measured values of 6.5 and 14.7 cm^{-1}, respectively. The measured shift for the $HMn^{13}CH$ e species is much lower than expected. We attribute this low value for the e species as most likely due to it being a mixed mode with the

Table 1. Measured Infrared Frequencies (cm^{-1}) and Tentative Assignments for Manganese/Diazomethane Reaction Products in Solid Argon

band	Mn/CH_2N_2	$Mn/^{13}CH_2N_2$	$Mn/CHDN_2$	Mn/CD_2N_2	assignment	species
a_1	2864.3	2859.0			$\nu(CH^2)$	$MnCH_2$
	521.9	508.0			$\nu(Mn{=}C)$	
a_2	2861.6	2856.0			$\nu(CH_2)$	
	523.3	510.0			$\nu(Mn{=}C)$	
b	1517.2	1493.0			$\nu(N{=}C)$	$Mn(CH_2N_2)$
	1183.4	1172.3			$\delta(CH_2)$	
	1126.5	1120.0				
	1079.0					
	1065.5	1061.1				
	1063.3	1056.0				
	1026.7	1023.3				
c	637.6	629.4	605.3	532.0	$\rho_w(CH_2)$/or $\rho_r(CH_2)$	$Mn(CH_2N_2)$
d	632.3	624.6	600.0	527.2	$\rho_w(CH_2)$/or $\rho_r(CH_2)$	
e	1608.6	1608.6		1158.0	$\nu(Mn{-}H)$	HMnCH
	601.7	595.2		587.0	$\nu(Mn{\equiv}C)$	
	580.7	578.5			$\delta(CH)$	
g	616.1	611.8			$\pi(CH^3)$	CH_3
h	1616.5	1616.8			$\nu(Mn{-}H)$	$HMnCH_3$

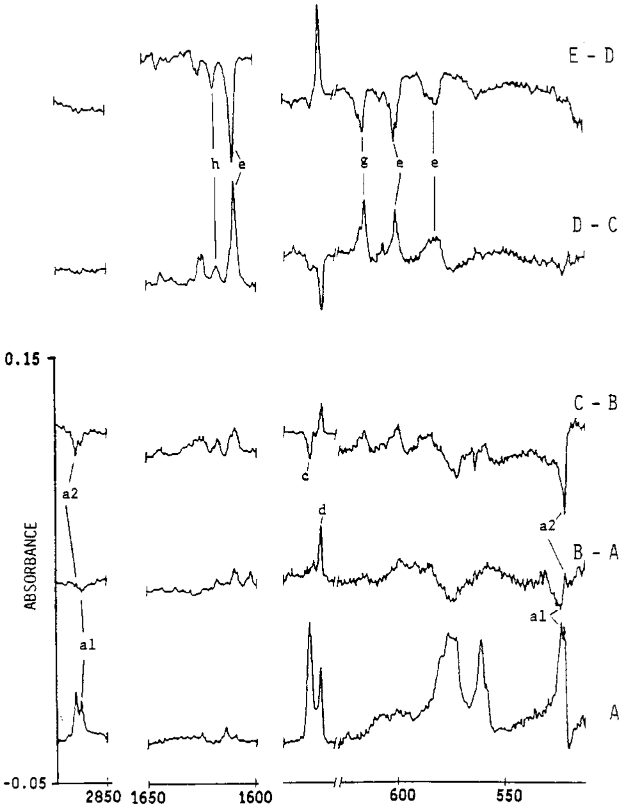


Figure 4. Photolysis study in an argon matrix. $Mn/CH_2N_2/Ar \approx 1.3/1.3/100$. A, without photolysis; B, after 10 min photolysis using $\lambda \geq 500$ nm; C, after 10 min photolysis using $\lambda \geq 400$ nm; D, after 10 min photolysis using $360 \geq \lambda \geq 280$ nm; E, after 10 min photolysis using $\lambda \geq 400$ nm. a = $MnCH_2$, c and d = $Mn(CH_2N_2)$ complexes, e = HMnCH, g = CH_3, h = CH_3MnH.

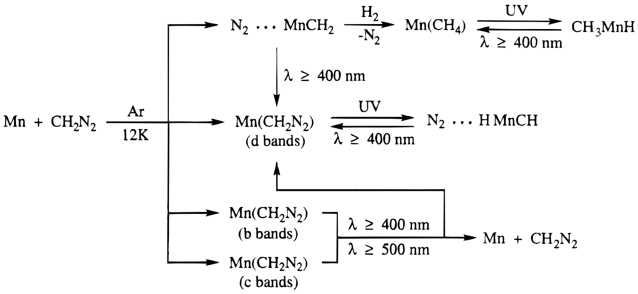
nearby CH bending mode at 580.7 cm^{-1}. This suggestion is supported by closer agreement between the measured value of 14.7 cm^{-1} versus the calculated value of 18.7 cm^{-1} for the DMnCD species. In this case the CD bending mode is further removed from the Mn≡C stretch and is thus less mixed with it.

A photoreversible phenomenon between $Mn(CH_2N_2)$ (d bands) and HMnCH (e bands) was observed as shown in Figure 4 (D−C and E−D). This reaction can be represented as follows.

$$Mn(CH_2N_2)\ (d) \underset{\lambda \geq 400\ nm}{\overset{UV}{\rightleftharpoons}} N_2\cdots MnNCH\ (e)$$

The g band at 616.1 cm^{-1} shifts to 611.8 cm^{-1} when $^{13}CH_2N_2$ is used. Although this absorption is characteristic of a methyl radical, the reaction pathway that leads to this species is not obvious. A CH_3MnH absorption, h band, at 1616.5 cm^{-1}, was observed after UV photolysis and is believed to result from the photoinduced Mn/CH_4 reaction. A small amount of dihydrogen that is formed by the cracking of pump oil probably reacts with a $MnCH_2$ species to yield methane. This process can be enhanced by adding H_2 during deposition. The Mn/CH_4 complex is a C_{3v} species, as evidenced by a doublet splitting at 1305.1 and 1303.1 cm^{-1} for the CH_4 deformation band.

The reactions of diazomethane with manganese atoms may be summarized as follows:



Finally, vibrational data are now available for all of the naked $M{=}CH_2$ species from chromium through zinc.[5] A compilation of this work will be published shortly in a review article.

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