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Synthesis and Structure of the Unligated Carbene of Chromium

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Introduction

Complexes with metal–carbon double bonds have found applications as intermediates in many important catalytic reactions including cyclopropanation of alkenes by diazoalkanes, Fischer–Tropsch synthesis, olefin metathesis, Ziegler–Natta polymerization, alkane activation, and in the decomposition of transition metal alkyl complexes.[1,2] However, complexes with the simplest carbene, CH_2, coordinated to the metal center are relatively rare. In this paper we report the synthesis and characterization of the simple unligated carbene of chromium by FTIR matrix isolation spectroscopy.

Experimental Details

A description of the multisurface matrix isolation apparatus[3] as well as the preparation of CH_2N_2, CD_2N_2, $CHDN_2$, and $^{13}CH_2N_2$ has been reported previously.[4] Chromium atoms were generated by vaporizing chromium (A. D. Mackay, 99.95%) from an alumina crucible enclosed in a resistively heated tantalum furnace over the range 1270–1400 °C. A quartz crystal microbalance mounted on the matrix block was used to monitor the chromium concentration. Argon (99.9995%) and dinitrogen (99.9995%) were obtained from Matheson Chemical Co. Hydrogenation studies were carried out by introducing dihydrogen (Air Products, 99.9995%) or dideuterium (Air Products, 99.99%) into the matrix during deposition (H_2 or $D_2/Ar = 15–50$ mm Hg/1000 mmHg). Matrices were usually irradiated subsequent to deposition by exposure to a focused 100-W medium-pressure short arc Hg lamp. The typical exposure time was 10 min. A water filter with various Corning long-pass cutoff filters and a band filter, 280–360 nm (UV), were used for wavelength dependent photolysis studies. In a typical experiment chromium atoms and diazomethane were cocondensed with argon onto a rhodium-plated copper surface over a period of 30 min at 12 K.

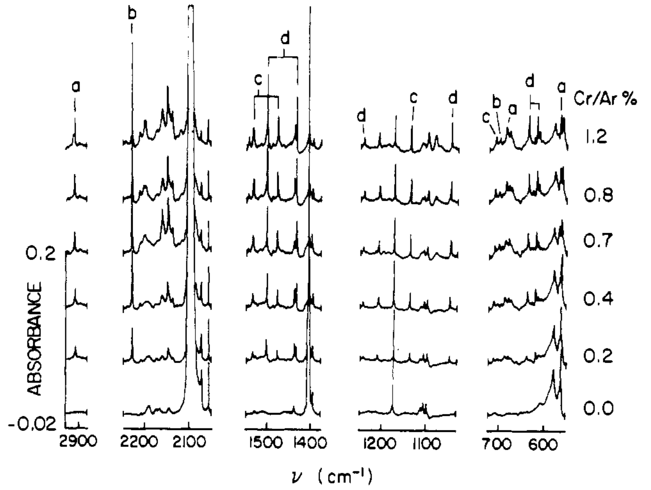

Figure 1. A chromium concentration study. Molar ratio of $CH_2N_2/Ar \approx 0.8/100$. a = $CrCH_2$, b = N_2CrCH_2, and c and d = $Cr(CH_2N_2)$ complexes.

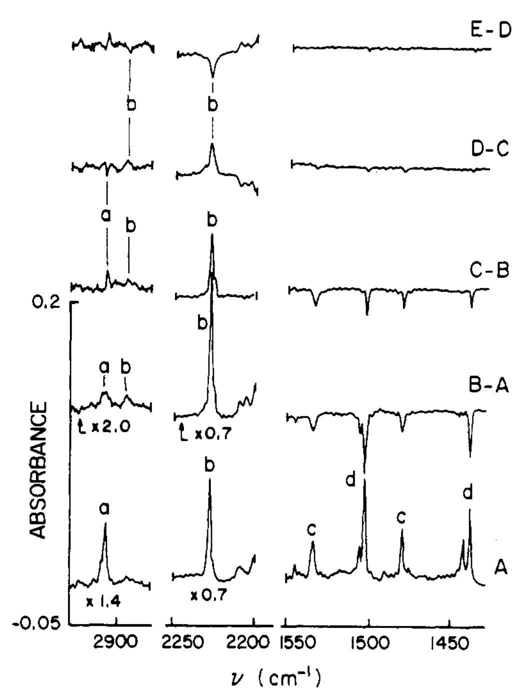

Figure 2. A photolysis study. $Cr/CH_2N_2/Ar \approx 0.8/0.8/100$. A, no photolysis; B, after 10-min photolysis with $\lambda \geq 500$ nm; C, after 10-min photolysis with $\lambda \geq 400$ nm; D, after 10-min photolysis with $360 \geq \lambda \geq 280$ nm. a = $CrCH_2$, b = N_2CrCH_2, and c and d = $Cr(CH_2N_2)$ complexes.

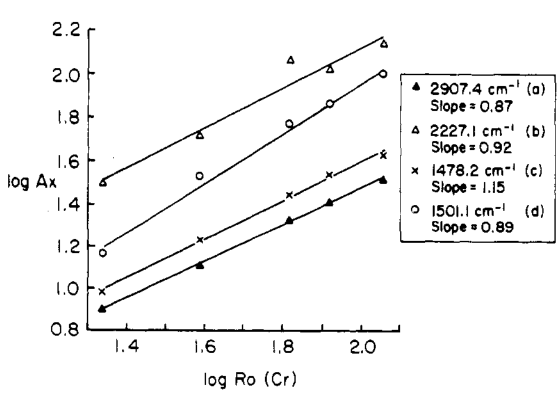

Figure 3. Plot of log A_x versus log R_0(Cr) plots. A_x represents the absorbance of peak x measured as peak height in mm. R_0(Cr) is the molar ratio of chromium to argon, Cr/Ar × 10 000.

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(2) For a comprehensive coverage, see also: *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany 1983. For several relevant reviews, see: Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545–574. Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487–613. 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. *Prog. Inorg. Chem.* **1980**, *27*, 1–122. 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*, 407–423. Fischer, E. O. *Pure Appl. Chem.* **1972**, *30*, 353–372. Kreiter, C. G.; Fischer, E. O. In *XXIII International Congress of Pure and Applied Chemistry*; Butterworths: London, 1971; pp 151–168. Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857–870. 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, Germany, 1986. Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

(3) Hauge, R. H.; Fredin, L.; Kafafi, Z. H.; Margrave, J. L. *Appl. Spec.* **1986**, *40*, 588.

(4) Chang, S. C.; Kafafi, Z. H.; Hauge, R. H.; Billups, W. E.; Margrave, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 4508.

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Table I. Measured and Calculated Infrared Frequencies (cm^{-1}) for $CrCH_2$, $Cr^{13}CH_2$, CrCHD, and $CrCD_2$ in Solid Argon

	$CrCH_2$		$Cr^{13}CH_2$		CrCHD		$CrCD_2$	
vibr mode	obs	cal	obs	cal	obs	cal	obs	cal
CH_2 s-str	2907.4	2907.6	2901.9	2901.7		2155.6		2114.2
CH_2 bend[a]		1327.4		1321.4		1178.1		996.0
CrC str	567.0	566.5	552.5	551.9	554.7	554.3	525.7	527.4
CH_2 a-str	2966.7	2966.7	2956.5	2956.5	2934.4	2934.4		2189.4
CH_2 rock	450.3	451.2	447.4	448.5		379.3	346.2	342.8
CH_2 wag	687.7	687.3	682.0	681.4	615.7	617.3	538.8	538.3

[a] CH_2 bending frequencies are based on measured values for $NiCH_2$ in argon matrices.

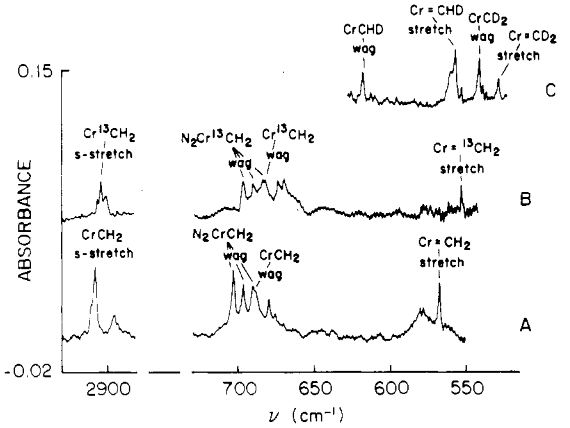

Figure 4. An isotope study. Partial FTIR spectra of selected regions of A, $CrCH_2$ and N_2CrCH_2; B, $Cr^{13}CH_2$ and $N_2Cr^{13}CH_2$; and C, CrCHD and $CrCD_2$ in argon matrices.

Table II. Symmetry Coordinates Used in the Normal Coordinate Analysis and Calculated Force Constants for $CrCH_2$, $Cr^{13}CH_2$, CrCHD, and $CrCD_2$

$r_1 = r_2 = r(\text{C–H}) = 1.07$ Å
$r_3 = r(\text{Cr–C}) = 1.9$ Å
$\phi_1 = \phi_2 = \angle x(\text{CrCH}) = 123.5°$
$\phi_3 = \angle x(\text{CH}_2) = 113°$
$\theta_1 = \angle x(\text{CrCH}_2) = 180.0°$

A′ $S_1 = 2^{1/2}(\Delta r_1 - \Delta r_2)$
$S_2 = \Delta r_3$
$S_3 = 6^{1/2}(2\Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3)$
$S_4 = 2^{1/2}(\Delta r_1 - \Delta r_2)$
$S_5 = 2^{1/2}(\Delta\phi_2 - \Delta\phi_3)$
A″ $S_6 = \Delta\theta_1 \sin\phi_1$

$F_{11} = 4.716$ mdyn/Å
$F_{12} = -0.574$ mdyn/Å
$F_{13} = 0.264$ mdyn/rad
$F_{22} = 2.195$ mdyn/Å
$F_{23} = -0.116$ mdyn/rad
$F_{33} = 0.375$ mdyn Å/rad^2
$F_{44} = 4.742$ mdyn/Å
$F_{45} = 0.340$ mdyn/rad
$F_{55} = 0.138$ mdyn Å/rad^2
$F_{66} = 0.151$ mdyn Å/rad^2

Table III. Measured Infrared Frequencies (cm^{-1}) for Nitrogen Coordinated $CrCH_2$ in Solid Argon and Solid Nitrogen

vibr mode	n[a]	$(N_2)_nCrCH_2$	$(N_2)_nCr^{13}CH_2$	$(N_2)_nCrCHD$	$(N_2)_nCrCD_2$
CH_2 s-stretch	1	2894.4			
	2	2862.8	2854.7		
CH_2 a-stretch	1	2950.3	2940.2	2922.1	
	2	2908.9	2898.4		
CH_2 wag	1	702.4	696.4	632.1	557.1
		695.9	689.9	626.8	554.9
		689.2	683.8	620.5	550.6
N-N stretch	1	2227.1	2227.1	2227.1	2227.1
	2	2171.2	2171.2		
		2162.3	2162.3		

[a] $n = 1$ species were isolated in argon; $n = 2$ species were isolated in nitrogen.

Table IV. Measured Infrared Frequencies (cm^{-1}) for Diazomethane and Chromium–Diazomethane Complexes in Solid Argon[a]

vibr mode		$Cr(CH_2N_2)$	$Cr(^{13}CH_2N_2)$	$Cr(CD_2N_2)$
CH_2 wag	A	427.6	423.1	324.0
	C	712.6	706.5	
	D	618.8	615.7	
		638.1	636.4	524.7
CH_2 scissor	A	1172.5	1158.1	965.0
	C	1136.8	1128.9	927.4
	D	1046.7	1038.2	895.5
C═N stretch	A	1407.8	1398.4	
	C	1478.2	1463.5	
		1532.9	1518.2	
	D	1436.2	1435.0	
		1501.1	1481.3	

[a] A = CH_2N_2; C = $Cr(CH_2N_2)$, "c" bands; D = $Cr(CH_2N_2)$, "d" bands.

Results

Chromium atoms react spontaneously with diazomethane in solid argon at 11 K to yield $CrCH_2$ and N_2CrCH_2. Absorptions assigned to these species (labeled a and b, respectively) are presented in the chromium concentration study shown in Figure 1 where the CH_2N_2/Ar molar ratio was kept constant as the Cr/Ar molar ratio was increased from 0.0 to 1.2%. Two additional sets of absorptions labeled c and d were found in regions characteristic of diazomethane and are assigned to $Cr(CH_2N_2)$ complexes. Photolysis of the matrix using $\lambda \geq 500$ nm radiation results in the bleaching of the bands assigned to the $Cr(CH_2N_2)$ complexes with the concomitant enhancement of the peaks assigned to the carbenes by ~20% and 120%, respectively (Figure 2, B-A). Similar observations were made when $\lambda \geq 400$ nm radiation was used to photolyze the matrix (Figure 2, C-B). Other photolysis studies showed that the dinitrogen ligand of N_2CrCH_2 can be photo-dissociated by UV photolysis (Figure 2, D-C), whereas $\lambda \geq 400$ nm photolysis regenerates the N_2CrCH_2 species (Figure 2, E-D).

The stoichiometry of the Cr/CH_2N_2 reactions was determined from log–log plots of the intensities of selected bands versus chromium concentration as depicted in Figure 3.

The assignment of each product absorption was confirmed by analysis of the products using isotopically labeled diazomethane. Figure 4 shows the partial infrared spectra of $CrCH_2$, $Cr^{13}CH_2$, CrCHD, and $CrCD_2$ in argon matrices. The vibrational mode assignments for $CrCH_2$ and the isotopically labeled species are supported by a normal coordinate analysis. The observed and calculated frequencies and calculated force constants are listed in Tables I and II, respectively. Frequency assignments for N_2CrCH_2, $N_2Cr^{13}CH_2$, N_2CrCHD, and N_2CrCD_2 are presented in Table III along with those obtained for the species isolated in dinitrogen matrices where the dominant product was provisionally identified as $(N_2)_2CrCH_2$.

The infrared frequencies for the $Cr(CH_2N_2)$ complexes and the corresponding isotopically labeled molecules are listed in Table IV.

Hydrogenolysis of the Cr–C bond was observed when dihydrogen was added to the matrix.[5] It was not possible to detect the addition product CH_3CrH.[6]

Discussion

The chromium atom/diazomethane reactions in argon matrices are summarized in the following scheme:

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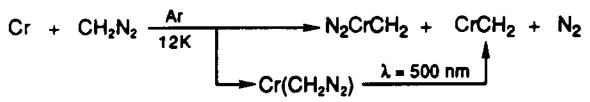
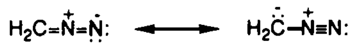
(5) For similar studies using other metals see: Chang, S.-C.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L.; Billups, W. E. *J. Am. Chem. Soc.* **1988**, *110*, 7975. Chang, S.-C.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L.; Billups, W. E. *Inorg. Chem.* **1990**, *29*, 4373.

(6) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1793.



Although the insertion of Cr atoms into the CN bond of CH_2N_2 is expected to be exothermic and clearly does occur spontaneously, the formation of stable $Cr(CH_2N_2)$ complexes is consistent with previous observations.[5] It is tempting to speculate that the isolable $Cr(CH_2N_2)$ complexes arise from the chromium atom interacting with the dinitrogen of CH_2N_2, whereas the spontaneous reaction leading to the carbene would result from the metal complexing with the CH_2 group. In view of the structure of diazomethane it is not surprising that several complexes might be formed.



$$\mathrm{H_2C{=}\overset{+}{N}{=}\overset{-}{\underset{\cdot\cdot}{N}}{:}} \longleftrightarrow \mathrm{H_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N{:}}$$

The most salient observation made during photolysis using long wavelength radiation is the decrease in intensity of bands assigned to $(N_2)CrCH_2$ after photolysis by $\lambda \geq 400$ nm radiation. Thus the set of absorptions assigned to $(N_2)CrCH_2$ decreased in intensity after photolysis but regained intensity after UV photolysis. This observation can be explained in terms of the photo-reversible reaction shown in eq 1. It is apparent from the longer wavelength absorption behavior of N_2CrCH_2 that complexation of $CrCH_2$ with dinitrogen causes a red shift of the electronic absorption of $CrCH_2$.

$$\mathrm{N_2CrCH_2} \underset{\mathrm{UV}}{\overset{\lambda \geq 400\ \mathrm{nm}}{\rightleftharpoons}} \mathrm{CrCH_2 + N_2} \qquad (1)$$

The spontaneous reaction of chromium atoms with diazomethane in dinitrogen matrices to yield $(N_2)_nCrCH_2$ species has been observed in the reactions of other metals with CH_2N_2.[5] Two strong absorptions at 2908.9 cm^{-1} and 2862.8 cm^{-1} can be assigned to a-stretching and s-stretching modes, respectively. Absorptions arising from Cr/N_2 reaction products prevent the assignment of bands in the N≡N stretching region. Two bands at 2171.2 cm^{-1} and 2162.3 cm^{-1} were found to be associated with the two CH_2 stretching bands, suggesting that two dinitrogen molecules may be involved. Absorptions below 800 cm^{-1} were too weak to be identified. Thus, although conclusive assignments cannot be made, the four observed absorptions can be tentatively assigned to $(N_2)_2CrCH_2$.

It is interesting that the reaction with dihydrogen yielded only the hydrogenolysis product methane rather than CH_3CrH. This observation is consistent with an earlier result with methane/Cr matrices where it was not possible to observe the insertion product.[6] The chemistry observed upon doping the matrix with a ternary reagent would, of course, depend on the state of the organometallic species. In this regard some preliminary calculations using the Hartree–Fock self-consistent-field (SCF) method and configuration interaction including all single and double excitations (CISD) identified the ground electronic state of $CrCH_2$ as the $^3A''$ state arising from the $12a'^2 1a'^1 3a''^2 1a''^1$ electronic configuration in C_s symmetry.[7]

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(7) We thank Dr. Gustavo Scuseria for these calculations.