Isolation and Characterization of $ZnCH_2$ by Fourier Transform I.R. Matrix Isolation Spectroscopy and its Photolytic Rearrangement to HZnCH

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The 1 : 1 adduct produced by cocondensing monoatomic zinc, diazomethane and argon onto a cold surface at 12 K can be converted to $ZnCH_2$ with $\lambda \geqslant 400$ nm photolysis; a carbene$\rightarrow$carbyne rearrangement of $ZnCH_2$ to HZnCH is observed during u.v. photolysis.

The Clemmensen reduction[1] has been the object of considerable speculation with regard to mechanism.[2,3] The recent report of Burdon and Price,[4] in which zinc carbenes are invoked, as exemplified by the process illustrated in Scheme 1, prompts us to report our studies on the isolation and characterization of zinc carbene ($ZnCH_2$) by Fourier transform i.r. (f.t.i.r.) matrix isolation spectroscopy and its photolysis to HZnCH.

Zinc atoms were codeposited with diazomethane and argon onto a rhodium plated copper mirror at 12 K.[5] The molar ratio of zinc–diazomethane–argon, measured with a quartz crystal microbalance on the cold block, was varied from 0.0 : 8.7 : 1000 to 21.0 : 8.7 : 1000. In the presence of zinc atoms the i.r. spectrum showed absorptions very similar to those of diazomethane. These absorptions are thought to arise from vibrations of diazomethane perturbed by a zinc atom. The measured frequencies for this $Zn(CH_2N_2)$ adduct, as well as for CH_2N_2, are listed in Table 1. Photolysis through a cutoff filter with $\lambda \geqslant 400$ nm caused the disappearance of the adduct bands with the concomitant appearance of a new set of absorptions assigned to $ZnCH_2$. Assignment of these absorptions along with those of the isotopically labelled species

Table 1. Infrared frequencies (cm^{-1}) for diazomethane and Zinc–diazomethane adduct in solid argon at 12 K.

Vibration mode	CH_2N_2	$Zn(CH_2N_2)$
NNC bend	401.9	407.5
CH_2 bend	1105.5	1104.8
C=N stretch	1407.8	1407.3
N≡N stretch	2097.2	2091.7
CH_2 s-stretch	3070.1	3067.7

Table 2. Measured and calculated[a] i.r. frequencies (cm^{-1}) for $ZnCH_2$, $Zn^{13}CH_2$, ZnCHD, and $ZnCD_2$, in solid argon.

Vibration mode	$ZnCH_2$		$Zn^{13}CH_2$		ZnCHD		$ZnCD_2$	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
CH_2 s-stretch	2956.1 2958.5	2957.5	2951.3 2953.5	2950.0	2220.2	2220.2	2165.7	2165.5
CH_2 scissor	1341.5 1339.1	1341.8	1335.2 1332.4	1335.0	-	1195.7	1009.8	1009.6
ZnC stretch	513.7 512.0	512.9	499.2 497.0	499.6	511.3	513.1	472.2	471.8
CH_2 a-stretch	3047.2	3047.6	3034.7	3034.4	3002.9	3002.7	-	2274.1
CH_2 rock	543.8	545.0	541.2	542.2	445.0	441.8	412.2	409.2
CH_2 wag	524.8	524.4	516.1	519.9	470.0	471.0	419.0	410.7

[a] A planar structure with r(Zn=C) = 1.9, r(C–H) = 1.07 Å and ∠(CH_2) = 113° for $ZnCH_2$ was used in this calculation. The calculated force constant for ν(Zn=C) = 2.348, ν(C–H) = 4.721 mdyn/Å, δ(CH_2) = 0.410 mdyn Å/rad², $\rho_r(CH_2)$ = 0.174 mdyn Å/rad² and $\rho_w(CH_2)$ = 0.088 mdyn Å/rad².

Table 3. Measured and calculated[a] i.r. frequencies (cm^{-1}) for HZnCH, $HZn^{13}CH$, and DZnCD, in solid argon.

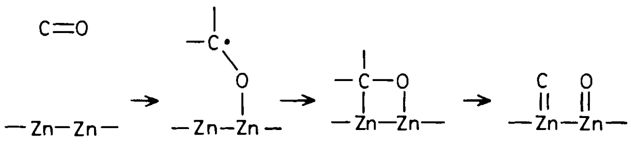
Vibration mode	HZnCH		$HZn^{13}CH$		DZnCD	
	obs.	calc.	obs.	calc.	obs.	calc.
Zn≡C stretch	647.5	650.4	628.4	631.1	627.2	621.0
HZnC bend	469.3	467.3	468.9	464.0	344.7	360.0
Zn–H stretch	1924.4	1924.8	1924.4	1924.2	1386.8	1386.2

[a] A convenient linear structure with r(H–Zn) = 1.5, r(Zn≡C) = 1.7 and r(C–H) = 1.07 Å was used in this calculation. The calculated force constant for ν(H–Zn) = 2.125, ν(Zn≡C) = 2.932 mdyn/Å and δ(C–H) = 0.121 mdyn Å/rad².

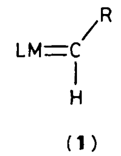
Table 4. Zinc–carbon stretching frequencies and force constants for matrix isolated organozinc compounds.

Compound	Matrix	ν (cm^{-1})	k (mdyn/Å)[a]	k (mdyn/Å)[b]	Reference
$HZn–CH_3$	CH_4	447.1	-	1.43	6
$Zn=CH_2$	Ar	513.7	2.35	1.79	this study
HZn≡CH	Ar	647.5	2.95	2.67	this study

[a] Obtained from a normal co-ordinate analysis. [b] Estimate based on a diatomic molecule approximation.



Scheme 1



(1)

(L = Ligand)

$Zn^{13}CH_2$, ZnCHD, and $ZnCD_2$ were verified and confirmed by a complete normal co-ordinate analysis (Table 2).

U.v. photolysis (360 ≥ λ ≥ 280 nm) of $ZnCH_2$ results in the formation of a new species with absorptions at 469.3, 647.5 and 1924.4 cm^{-1} (Figure 1). The band at 1924.4 cm^{-1} can be assigned readily to a Zn–H stretching mode. This band is shifted to 1386.8 cm^{-1} for the corresponding deuteriated species. The presence of a Zn≡C stretching band at 647.5 cm^{-1} as well as a HZnC bending absorption at 469.3 cm^{-1} allows assignment of this species to HZnCH. Isotopic studies using ^{13}C enriched diazomethane showed that the Zn≡C stretching absorption is shifted by 19.1 cm^{-1}. The observed isotopic data and calculated frequencies are presented in Table 3. The zinc–carbon stretching frequencies of the progression Zn–C,[6] Zn=C, Zn≡C (Table 4), provide convincing evidence for the increasing bond order of these species. The overall process can then be summarised as shown in equation (1)

$$\mathrm{Zn} + \mathrm{CH_2N_2} \xrightarrow[12\,\mathrm{K}]{\mathrm{Ar}} \mathrm{Zn(CH_2N_2)} \xrightarrow[-\mathrm{N_2}]{\lambda \geq 400\,\mathrm{nm}} \mathrm{Zn{=}CH_2} \xrightarrow{\mathrm{u.v.}} \mathrm{H{-}Zn{\equiv}CH} \qquad (1)$$

The detection of an adduct stands in contrast to previous work with iron and copper where spontaneous formation of $Fe=CH_2$[7] and $Cu=CH_2$[8] was observed. The photoinduced carbene→carbyne rearrangement is especially interesting in view of the geometry of several Schrock carbenes (**1**). For

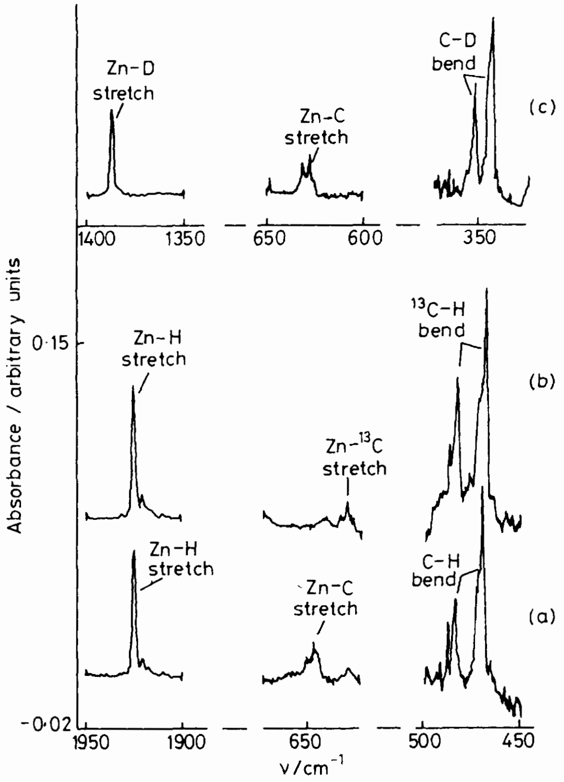


Figure 1. F.t.i.r. spectra of (a) HZnCH, (b) HZn^{13}CH, and (c) DZnCD, in argon matrices. These spectra were measured after u.v. photolysis for 10 min: (a) Zn : CH_2N_2 : Ar = 8.9 : 8.7 : 1000; (b) Zn : $^{13}CH_2N_2$: Ar = 9.7 : 8.7 : 1000; (c) Zn : CD_2N_2 : Ar = 8.4 : 8.7 : 1000.

example, remarkably small M–C–H angles, down to 78°, and correspondingly large M–C–R angles, up to 170°, have been observed for these metal complexes.[9] Thus one might expect that the M · · · H interaction responsible for this geometry would facilitate hydrogen transfer to the metal; however, this process appears to be forbidden, at least for the five co-ordinate, 14 electron complexes investigated.[10] This symmetry imposed barrier would not be present in the photoinduced reaction observed in this study.

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