Inorg. Chem. **1990**, *29*, 4373-4376

they nevertheless show promising possibilities, since high selectivity and high yields can be achieved through new reaction pathways.

In particular, the surface-mediated synthesis of $H_4M_4(CO)_{12}$ (M = Ru, Os) from silica-supported $M_3(CO)_{12}$ presents significant advantages over the conventional synthesis in solution: (1) milder reaction conditions; (2) direct formation of the products via one-step reactions, leading to higher yield and selectivity (absence of unreacted $M_3(CO)_{12}$ and other cluster compounds); (3) easy recovering of the products by simple solvent extraction at room temperature.

Therefore, a new field of preparative inorganic chemistry on the gas-solid interphase is now being developed, with unexpected and promising improvements over the conventional methods in solution.

Acknowledgment. This work was supported by a grant from Progetto Finalizzato Chimica Fine II of the Italian CNR; D.R. is indebted to the Canadian Natural Sciences and Engineering Research Council for a postdoctoral NATO fellowship. We wish to thank Prof. A. Pasini for fruitful discussions.

Contribution from the Department of Chemistry,
Rice University, Houston, Texas 77251

Low-Temperature Reactions of Atomic Nickel with Diazomethane

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

Received September 25, 1989

The reactions of atomic nickel with diazomethane have been investigated by FTIR matrix-isolation spectroscopy. In argon matrices, $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ are formed spontaneously. Photolysis of the matrix with $\lambda \approx 400$–500 nm radiation enhances the yield of $N_2Ni{=}CH_2$, suggesting that photoinduced diffusion of reagents may become important under these conditions. Dihydrogen reacts with $Ni{=}CH_2$ to give methane, whereas $N_2Ni{=}CH_2$ is less reactive to hydrogenolysis. Ultraviolet photolysis of a $Ni/CH_2N_2/H_2/Ar$ matrix yields CH_3NiH from insertion of photoexcited nickel atoms into the C–H bonds of methane. In nitrogen matrices, $(N_2)_xNi{=}CH_2$ complexes are formed spontaneously. The yield of these species can be increased by photolysis with $\lambda \approx 400$–500 nm radiation or by ultraviolet photolysis.

Introduction

Since the landmark paper by Fischer and Massböl[1] in 1964 describing the synthesis of (methoxymethylcarbene)pentacarbonyltungsten, the synthesis and characterization of transition-metal carbene complexes has occupied a critical position in the development of organometallic chemistry. Indeed, the chemistry of metal–carbon double bonds is now well entrenched in organometallic chemistry and is even used in efforts to understand surface chemistry and homogeneous catalysis.[2] In this paper, we describe the synthesis and characterization of naked $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ by FTIR matrix-isolation spectroscopy.[3]

Experimental Section

A description of the multisurface matrix-isolation apparatus[4] as well as the preparation of CH_2N_2, CD_2N_2, $CHDN_2$, and $^{13}CH_2N_2$ has been reported previously.[5] Nickel atoms were generated by vaporizing nickel (MC&B, 99.5%) from an alumina crucible enclosed in a resistively heated tantalum furnace over the range 1250–1420 °C. 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/Ar or $D_2/Ar \approx 15$–50 mmHg/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, nickel atoms and diazomethane were cocondensed with argon onto a rhodium-plated copper surface over a period of 30 min at 12 K.

Results

Although the infrared spectra exhibited by the products of atomic nickel and diazomethane are complicated by additional absorptions arising from residual dihydrogen[6] reacting with nickel atoms and clusters, the primary products can be characterized readily as $Ni{=}CH_2$ and $N_2Ni{=}CH_2$. The infrared spectra from a study in which the concentration of nickel is increased gradually are shown in Figure 1. The product absorptions associated with $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ are labeled a and b, respectively.

A small amount of CO was added to provide NiCO[7] (c band) as an internal standard. Log–log plots[8] of the intensities of bands corresponding to each species versus the absorption of NiCO at 1994.5 cm^{-1} (Figure 2) suggest that the absorption labeled e, as well as those assigned to the carbenes, correspond to atomic nickel reactions. The d band may arise from a Ni_2 reaction product.

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Table I. Measured and Calculated Infrared Frequencies (cm^{-1}) for $NiCH_2$, $Ni^{13}CH_2$, NiCHD, and $NiCD_2$ in Solid Argon

	$NiCH_2$		$Ni^{13}CH_2$		NiCHD		$NiCD_2$	
vibrn mode	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
CH_2 sym str	2917.1	2917.3	2910.5	2910.2		2162.7		2133.0
CH_2 scissor	1328.5	1326.6	1319.7	1321.3		1180.3	993.6	994.5
NiC str	696.2	696.2	677.8	677.8	683.6	681.4	641.7	644.5
CH_2 asym str	2973.2	2972.9	2963.6	2963.6	2943.1	2943.1		2187.3
CH_2 rock	586.7	588.6	584.6	584.6	495.6	493.5	455.1	450.0
CH_2 wag	791.9	792.8	785.7	785.7	712.3	712.7	627.0	622.3

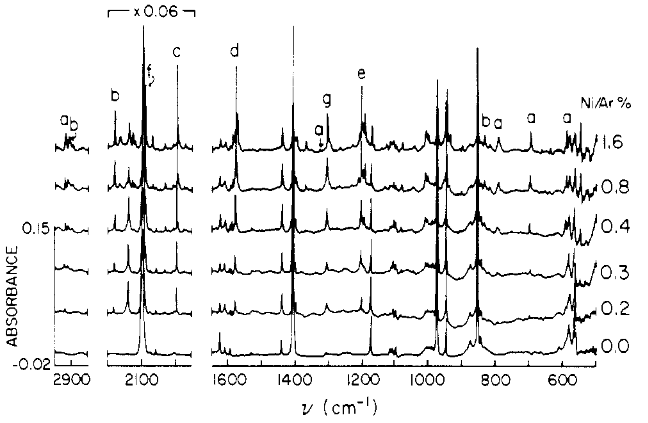

Figure 1. Nickel concentration study. Molar ratio of $CH_2N_2/Ar \cong 0.86/100$. a = $NiCH_2$, b = N_2NiCH_2, c = NiCO, d = $Ni_2(CH_2N_2)$ complexes, e = $Ni(CH_2N_2)$ complexes, f = NiN_2, and g = CH_4.

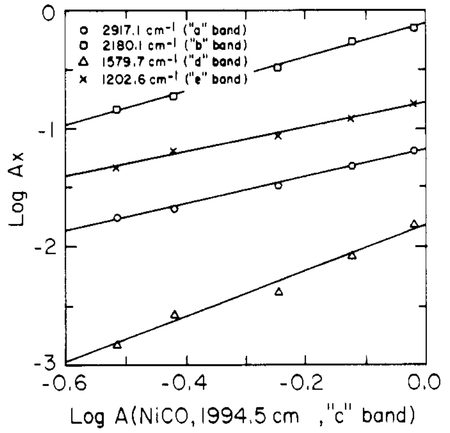

Figure 2. Plot of log A(x) versus log A(NiCO). A(x) is the absorbance of peak x. a, b, d, and e refer to the absorptions of $NiCH_2$, N_2NiCH_2, $Ni_2(CH_2N_2)$ complexes, and $Ni(CH_2N_2)$ complexes, respectively, as shown in Figure 1. The slopes of lines a, b, d, and e are 1.1, 1.4, 1.9, and 1.0, respectively.

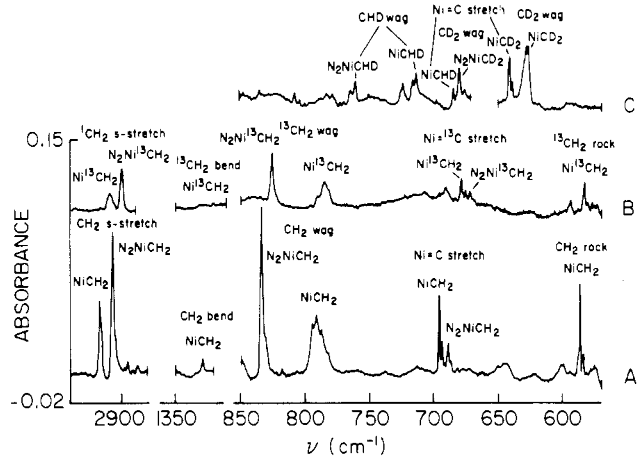

Figure 3. FTIR spectra of selected regions: (A) $NiCH_2$ and N_2NiCH_2; (B) $Ni^{13}CH_2$ and $N_2Ni^{13}CH_2$; (C) NiCHD, N_2NiCHD, $NiCD_2$, and N_2NiCD in argon matrices.

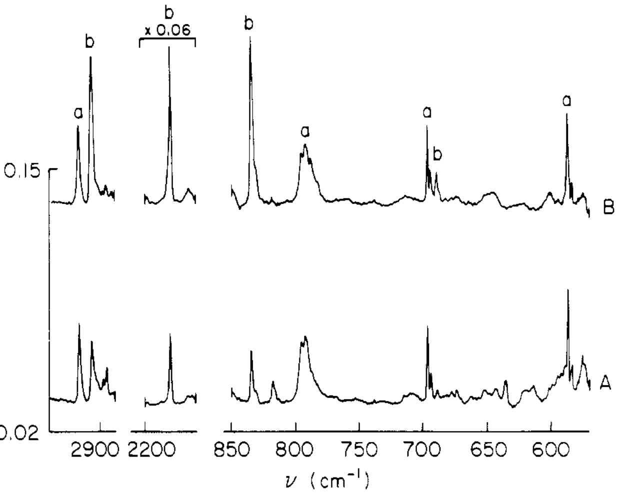

Figure 4. Partial FTIR spectra from photolysis of $Ni/CH_2N_2/Ar \cong 0.91/1.0/100$ with $\lambda \geq 400$ nm: (A) without photolysis; (B) after 10 min photolysis. a = $NiCH_2$, and b = N_2NiCH_2.

Table II. Symmetry Coordinates Used in the Normal-Coordinate Analysis and Calculated Force Constants for $NiCH_2$, $Ni^{13}CH_2$, NiCHD, and $NiCD_2$

	$r_1 = r_2 = r(C\text{-}H) = 1.071$ Å	$F_{11} = 4.736$	mdyn/Å
	$r_3 = r(Ni\text{-}C) = 1.78$ Å	$F_{12} = -0.587$	mdyn/Å
	$\phi_1 = \phi_2 = \angle(NiCH) = 123.5°$	$F_{13} = 0.148$	mdyn/rad
	$\phi_3 = \angle(CH_2) = 113°$	$F_{22} = 3.355$	mdyn/Å
	$\theta_1 = \angle(NiCH_2) = 180.0°$	$F_{23} = -0.176$	mdyn/rad
		$F_{33} = 0.370$	mdyn Å/rad^2
		$F_{44} = 4.779$	mdyn/Å
A′	$S_1 = 2^{1/2}(\Delta r_1 + \Delta r_2)$	$F_{45} = 0.475$	mdyn/rad
	$S_2 = \Delta r_3$	$F_{55} = 0.238$	mdyn Å/rad^2
	$S_3 = 6^{1/2}(2\Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3)$	$F_{66} = 0.200$	mdyn Å/rad^2
	$S_4 = 2^{1/2}(\Delta r_1 - \Delta r_2)$		
	$S_5 = 2^{1/2}(\Delta\phi_2 - \Delta\phi_3)$		
A″	$S_6 = \Delta\theta_1 \sin\phi_1$		

The use of log–log plots in the analysis of concentration dependent data derived from matrix-isolation studies is based on the assumption that the formation of a complex formed from two species striking the matrix surface simultaneously obeys a simple mass-action law. Thus the rate of formation of the complex is proportional to the product of the flux of the two species, and the order of the metal dependence can be considered without concern for the actual rate. It should be noted that the use of this plot does not imply that all of the metal atoms have reacted or are in a state of equilibrium.

The absorptions assigned to the primary products are located in regions characteristic of other $M{=}CH_2$ species.[5,9-11] Results from isotopic studies were used to verify these assignments. The relevant absorptions of $Ni{=}CH_2$, $N_2Ni{=}CH_2$, and the isotopic species are presented in Figure 3. A normal-coordinate analysis has been carried out for $Ni{=}CH_2$ and the isotopically labeled species to confirm the vibrational mode assignments. The observed and calculated frequencies are listed in Table I. The symmetry coordinates[12] used for these calculations and the calculated force

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Table III. Measured Frequencies (cm^{-1}) of $Ni_2(CH_2N_2)$ ("d" bands) and $Ni(CH_2N_2)$ ("e" bands)[a] Complexes in Solid Argon

	frequency				
band	Ni/ CH_2N_2	Ni/ $^{13}CH_2N_2$	Ni/ $CHDN_2$	Ni/ CD_2N_2	possible assignts
d	1575.6	1566.4	1575.5	1576.9	N═N str
	1579.7	1570.7	1579.7	1580.9	
	1583.3				
				1240.0	
e1	1192.5	1175.2	1184.3	1242.2	CH_2 bend
e2	1196.9	1182.4			CH_2 bend
	2895.6	2889.1			CH_2 bend
e3	1202.6	1185.3			CH_2 bend

[a] "e" bands consist of three different species labeled e1, e2, and e3, respectively.

constants can be found in Table II. A doublet splitting with a 3:1 ratio for the various Ni═C stretching bands (natural abundance of ^{58}Ni = 67.8%; that of ^{60}Ni = 26.2%) further supports the conclusion that these absorptions arise from atomic nickel reactions. The absorption at 2180.1 cm^{-1} (Figure 1) can be assigned to the N═N stretching band of $N_2Ni{=}CH_2$. The position of this absorption, which is about 100 cm^{-1} higher than that of NiN_2 (2089.3 cm^{-1}),[13] may indicate that dinitrogen is bound "end on".

Photolysis of the matrix using $\lambda \geq 400$ nm radiation resulted in a pronounced enhancement of the absorptions assigned to $N_2Ni{=}CH_2$ (b bands), as shown in Figure 4, suggesting that photoinduced diffusion of reagents may become important under these conditions. The dinitrogen group of $N_2Ni{=}CH_2$ cannot be photodissociated as observed in previous studies with Cu/CH_2N_2 reactions.[5] The coordination of dinitrogen seems to enhance the intensities of CH_2 stretching and wagging modes but reduces the intensity of the Ni═C stretching mode. Red shifts are observed for the CH_2 stretching and Ni═C stretching bands, whereas a blue shift is found for the CH_2 wagging band (Figure 4).

The species labeled d and e (Figure 1) exhibit strong absorptions in the N═N stretching and CH_2 bending regions. These absorptions are assigned to $Ni_2(CH_2N_2)$ and $Ni(CH_2N_2)$ complexes, respectively. Photolysis of the matrix with $\lambda \geq 500$ nm led to a bleaching of these absorptions by photodissociation into Ni_2, Ni, and CH_2N_2. Table III lists the observed frequencies of these complexes.

In addition to the species described above, absorptions arising from NiN_2[13] (2089.3 cm^{-1}, f band) and CH_4 (1305.6 cm^{-1}, g band) were also detected when nickel atoms were condensed with diazomethane in argon matrices (Figure 1). Each of these species is a product of a secondary reaction. The NiN_2 would, of course, arise from nickel atoms reacting with N_2, a coproduct of $Ni{=}CH_2$. Methane formation can be rationalized most readily in terms of a reaction with residual dihydrogen.[6] Confirmation of this hypothesis came from an experiment in which dihydrogen was cocondensed with the other matrix materials. Under these conditions, the absorptions assigned to $Ni{=}CH_2$ were eliminated completely with the concominant formation of methane. Surprisingly, the $N_2Ni{=}CH_2$ species appears to be nearly inert to hydrogenolysis.[9] These results stand in contrast to those obtained during a similar study with iron where coordinated dinitrogen activated the metal-carbon double bond in its reactions with hydrogen.[10]

Photolysis of the matrix with $\lambda \approx 400$–500 nm yielded only a slight increase in the absorptions arising from methane. Photolysis with ultraviolet radiation, however, led to the formation of CH_3NiH, a species characterized previously in Ni/CH_4/Ar reactions.[14] The formation of CH_3NiH indicates that the methane formed from the hydrogenolysis of $Ni{=}CH_2$ is closely sited, as expected, with the Ni atom. In this regard, the deformation band of methane at 1305.3 cm^{-1} experiences significant perturbation, probably through an agostic interaction.[11] A more detailed analysis of this phenomenon is not possible because of strong features arising from Ni/H_2 reactions.[15]

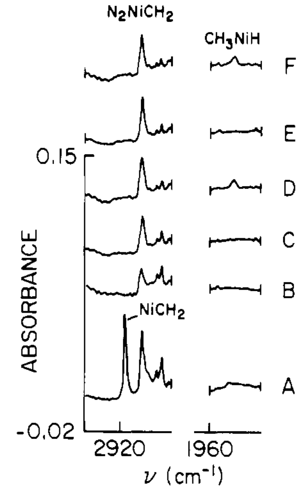

Figure 5. Partial FTIR spectra of selected regions of $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ in a matrix hydrogenation reaction with Ni/CH_2N_2/H_2/Ar ≅ 0.9/1.0/100: (A) symmetric C—H stretching bands for $Ni{=}CH_2$ and $N_2Ni{=}CH_2$; (B) spectrum after addition of dihydrogen; (C) spectrum after photolysis with $\lambda \geq 400$ nm; (D) spectrum after UV photolysis; (E) same as C; (F) same as D.

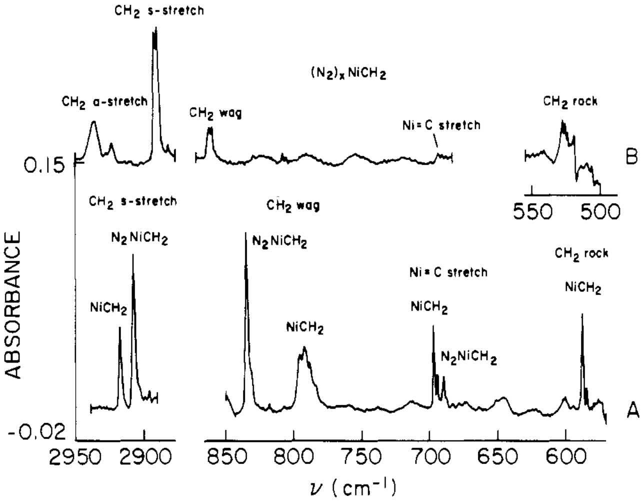

Figure 6. FTIR spectra of selected regions: (A) $NiCH_2$, N_2NiCH_2, and CH_3NiH in an argon matrix; (B) $(N_2)_xNiCH_2$ in a nitrogen matrix.

The wavelength dependent photoinduced reductive elimination/oxidative addition reactions that are characteristic of CH_3NiH can be detected during prolonged photolysis of a Ni/CH_2N_2/H_2/Ar matrix.[14,16]

$$Ni(CH_4) \underset{\lambda \approx 400\text{–}500\ \text{nm}}{\overset{\text{UV}}{\rightleftharpoons}} CH_3NiH$$

These results are presented in Figure 5 where the symmetric C—H stretching bands for both $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ are present in spectrum A. When dihydrogen is added to the matrix (spectrum B), the absorption assigned to $Ni{=}CH_2$ disappears, whereas the remaining absorption of $N_2Ni{=}CH_2$ is only diminished somewhat, as described above. Photolysis with $\lambda \approx 400$–500 nm leads to a slight enhancement of the $N_2Ni{=}CH_2$ absorption (spectrum C). Ultraviolet irradiation (spectrum D) results in C–H activation of methane by photoexcited nickel to yield CH_3NiH. The weak Ni–H stretching band of this species can be seen at 1945.1 cm^{-1}.

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Table IV. Measured Infrared Frequencies (cm^{-1}) for Nitrogen Coordinated Nickel Methylene in Solid Argon and Solid Nitrogen[a]

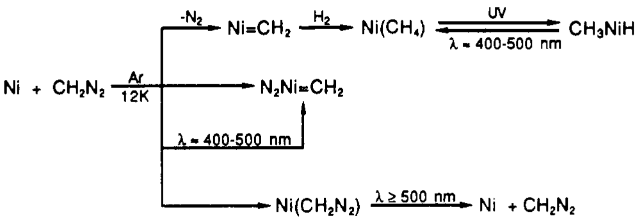
		frequency			
vibrn mode	x	$(N_2)_x$-$NiCH_2$	$(N_2)_x$-$Ni^{13}CH_2$	$(N_2)_x$-NiCHD	$(N_2)_x$-$NiCD_2$
CH_2 s-stretch	1	2907.2	2901.4		
	x	2889.1	2883.3		
		2890.8	2885.2		
CH_2 bend	1	1328.5	1319.7		
Ni=C stretch	1	688.9	671.5	677.0	633.0
	x	692.8			
CH_2 a-stretch	1	2960.2	2948.9	2932.7	
	x	2934.9	2927.2		
CH_2 rock	1	538.5	534.4		409.5
	x	528.6	523.0		
		525.5	519.7		
CH_2 wag	1	834.3	826.3	759.6	679.1
	x	860.1	850.7		
		862.0	852.6		
N≡N stretch	1	2180.1	2180.1	2180.1	2180.1

[a] $(N_2)NiCH_2$ was isolated in argon matrices. $(N_2)_xNiCH_2$ was isolated in nitrogen matrices.

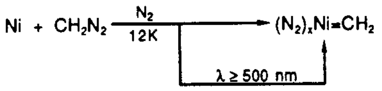
Prolonged photolysis with $\lambda \approx$ 400–500 nm leads to reductive elimination (spectrum E), whereas ultraviolet photolysis regenerates CH_3NiH (spectrum F).

Discussion

These nickel atom/diazomethane reactions in argon matrices can be summarized as follows:

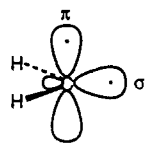


The reactions of Ni with CH_2N_2 in nitrogen matrices yields $(N_2)_xNi{=}CH_2$, $x \geq 1$, as the only product. The number of dinitrogen molecules adducted to the nickel cannot be determined because of the complex Ni/N_2 reactions.[13] A comparison of the Ni/CH_2N_2 reaction in argon and nitrogen matrices is presented in Figure 6.



The observed frequencies of $N_2Ni{=}CH_2$ and $(N_2)_xNi{=}CH_2$ are listed in Table IV.

The nature of the bonding in $Ni{=}CH_2$ is of interest. The rather high Ni–C stretching frequency would seem to indicate that the species can be represented in its ground state with significant double-bond character. As a basis for describing this bonding, the CH_2 ligand in its ground state ($^3B_1$) with a single electron in each of two nonbonding orbitals denoted as σ and π in **1** would



1

bond to the Ni 4s orbital through the σ orbital, whereas the weak π interaction would result from overlap of the π lobe with nickel d orbitals. Theoretical calculations support this assumption.[12]

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation and the 3M Co. for support of this work.

Registry No. Ni, 7440-02-0; CH_2N_2, 334-88-3; $Ni{=}CH_2$, 60187-22-6; $N_2Ni{=}CH_2$, 129391-83-9; CH_3NiH, 86392-32-7; $Ni^{13}CH_2$, 129391-84-0; NiCHD, 129391-85-1; $NiCD_2$, 129391-86-2.

Contribution from the Dipartimento di Chimica, Centro di Fotochimica del CNR, Università di Ferrara, Via Borsari 46, 44100 Ferrara, Italy, and Laboratorium für Anorganische Chemie, ETHZ, Universitätstrasse 6, CH-8092 Zürich, Switzerland

Generation of Reactive Intermediates in the Photochemistry of Binuclear Trihydridodiplatinum Complexes

P. Bergamini,[†] S. Sostero,[†] O. Traverso,*[,†] and L. M. Venanzi[‡]

Received October 12, 1989

The photochemistry of the complexes trans–trans monohydrido-bridged $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) and trans–cis dihydrido-bridged $[(PEt_3)_2HPt(\mu\text{-}H)_2Pt(PEt_3)_2][BPh_4]$ (**2**) is reported. Photolysis of **1** and **2** using 334-nm light occurs with good quantum yields to give *trans*-$[PtH_2(PEt_3)_2]$ (**3a**) and *trans*-$[PtH(S)(PEt_3)_2]^+$ (**4**) (S = solvent, e.g. acetonitrile). Photoproducts **3a** and **4** are highly reactive and undergo a multiplicity of reactions depending upon experimental conditions. Evidence of H_2 elimination, photoinduced insertion of CO_2 into the Pt–H bond of **3a**, and abstraction of Cl from chlorocarbon solvents by **3a** and **4** is reported.

Introduction

The photoinduced elimination of H_2 from cis hydride ligands in transition-metal complexes has proven to be a very general photochemical reaction.[1] Photolysis of inorganic and organometallic complexes is a convenient method for generating coordinatively unsaturated compounds that undergo potentially important reactions such as activation of molecular H_2, CO_2 fixation, and saturated carbon–hydrogen bond cleavage.[2,3] This paper reports the photolysis of trans–trans monohydrido-bridged complex **1** and trans–cis dihydrido-bridged complex **2** and describes a useful route to highly reactive mononuclear platinum(II) intermediates.

[†] University of Ferrara.
[‡] ETHZ.

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0020-1669/90/1329-4376$02.50/0