Low-Temperature Reactions of Atomic Cobalt with CH_2N_2, CH_4, CH_3D, CH_2D_2, CHD_3, CD_4, H_2, D_2, and HD

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Abstract: Cobalt atoms react spontaneously with diazomethane in solid argon at 12 K to yield $CoCH_2$, N_2CoCH_2, and at least two $(N_2)_xCoCH_2$ complexes. CH_3CoH is formed when dihydrogen is cocondensed as a ternary reagent. Photolysis of CH_3CoH ($\lambda \geq 400$ nm) gives the σ-complex $Co(CH_4)$ as a spectroscopically detectable species. Photolysis of this complex using an ultraviolet source regenerates CH_3CoH. The σ-complex has the triply degenerate $\nu4(f2)$ absorption of methane at 1305.3 cm^{-1} split into two peaks, suggesting C_{3v} symmetry. Studies using isotopically labeled methane show that these σ-complexes do not have rigid structures. UV photolysis of a $Co/H_2/Ar$ matrix at 12−15 K gives CoH_2. $Co(H_2)$ complexes could not be detected. Photolysis of $Co/D_2/Ar$ and Co/DH/Ar matrices gave CoD_2 and CoHD, respectively.

Introduction

The activation of alkanes by transition metal complexes is an area of considerable current interest.[1] Evidence has been presented which suggests that two-electron three-center $M{\cdots}H{\cdots}C$ bonds[2] may play an important role in those reactions where the C−H bonds of coordinated ligands are activated at a metal center.[3−5] There is considerably less information on the coordination of free hydrocarbon C-H bonds to organometallic species. The most direct evidence for alkane complexes came from the early work of Perutz and Turner[6] on $M(CO)_5$ fragments bound to alkanes in low-temperature matrices. Alkane complexes have also been proposed on the basis of isotope labeling studies in the reductive elimination of alkyl hydride complexes in solution.[7−9] More recently, transient organometallic σ-complexes of alkanes have been detected in the gas phase.[10] We have reported the direct observation of a $Co(CH_4)$ σ-complex by FTIR matrix isolation spectroscopy in solid argon.[11] A salient feature of this work was the discovery of a route to a matrix environment in which a cobalt atom could be isolated with methane in an argon cage. In this way the dominance of free methane, which would otherwise mask the spectrum of the metal methane complex in the infrared spectrum, can be overcome. In this paper, we report the results of a more detailed study of these complexes.

Experimental Section

A description of the multisurface matrix isolation apparatus has been reported previously.[12] Cobalt atoms were generated by vaporizing cobalt (Fisher, 99.5%) 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 Co. Hydrogenation studies were carried out by introducing dihydrogen (Air Products, 99.99%) or dideuterium (Air Products, 99.99%) into the matrix during deposition (H_2 or $D_2/Ar \approx 1.5-5/100$). Matrices were usually irradiated subsequent to 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), were used for wavelength dependent photolysis studies. The syntheses of CH_2N_2, CD_2N_2, $CHDN_2$, and $^{13}CH_2N_2$ were reported earlier.[13]

Results and Discussion

Reactions of Cobalt Atoms with CH_2N_2 in Solid Argon. $CoCH_2$ and N_2CoCH_2 were the major species[14,16−18] formed when cobalt atoms were cocondensed with diazomethane and argon onto a rhodium-plated copper surface over a period of approximately 30 min at 12 K. At least two other complexes ligated by N_2 were also formed in low yield.[19]

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(14) Since the synthesis of the first transition metal carbene complex by Fischer and Maasböl in 1964,[15] these versatile compounds have been recognized as important intermediates in both homogeneous and heterogeneous catalysis and have found wide application in organic synthesis. Surprisingly, metal complexes of the simplest carbene, CH_2, has been found in only a few cases.

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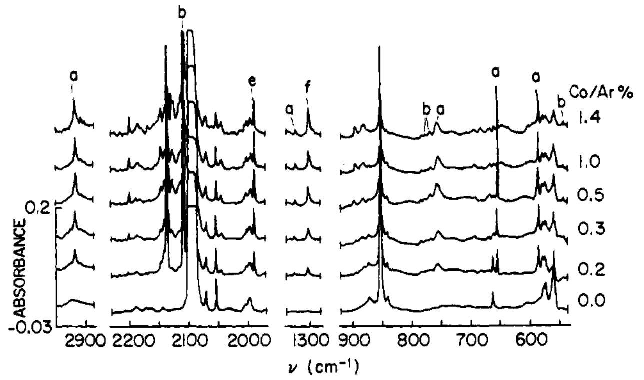

Figure 1. A cobalt concentration study. Molar ratio of $CH_2N_2/Ar \approx 0.9/100$. CO ($CO/Ar \approx 0.01/100$) added to form $Co(CO)_3$ as an internal standard: (a) $CoCH_2$, (b) N_2CoCH_2, (e) $Co(CO)_3$, (f) CH_4.

The stoichiometry of the reaction leading to $CoCH_2$ was established from a cobalt concentration study in which the Co/Ar molar ratio was increased gradually from 0.0 to 1.4 (Figure 1). An internal standard was formed by the addition of a small amount of CO, molar ratio of $CO/Ar \approx 0.01\%$. This gave bands at 1990.7 and 1953.3 cm^{-1} arising from $Co(CO)_3$ and CoCO, respectively. A log−log plot[20] (Figure 2) of the intensity of the stronger band at 1990.7 cm^{-1} versus one at 655.4 cm^{-1} (Co−C stretching frequency assigned to $CoCH_2$) gave a slope of 0.93 confirming that the major product absorptions (a bands in Figure 1) arise from a species containing only one cobalt atom. Since these absorptions were found in regions characteristic of other MCH_2 species, they were assigned to $CoCH_2$. The bands labeled b were assigned to N_2CoCH_2.

Studies using $^{13}CH_2N_2$, $CHDN_2$, and CD_2N_2 were carried out to identify the absorptions assigned to $CoCH_2$. The spectrum of $CoCH_2$ and the spectra of the isotopically labeled species $Co^{13}CH_2$, CoCHD, and $CoCD_2$ are presented in Figure 3. The observed frequencies were in good agreement with those calculated from a normal coordinate analysis. Both sets of frequencies are shown in Table 1 and the symmetry coordinates and force constants used for the calculations are listed in Table 2.

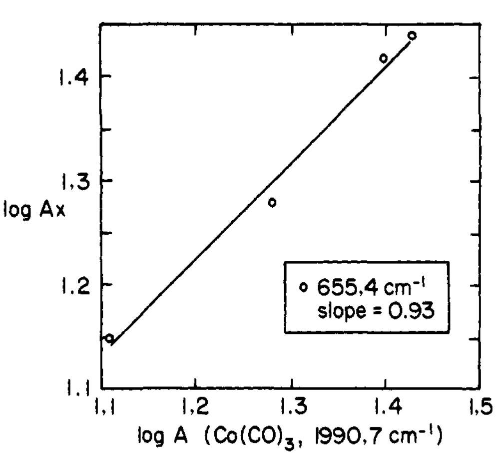

Figure 2. A plot of log Ax versus log A [$Co(CO)_3$, 1990.7 cm^{-1}]. Ax represents the absorbance measured at peak height (mm) of the 655.4 cm^{-1} peak assigned to $CoCH_2$.

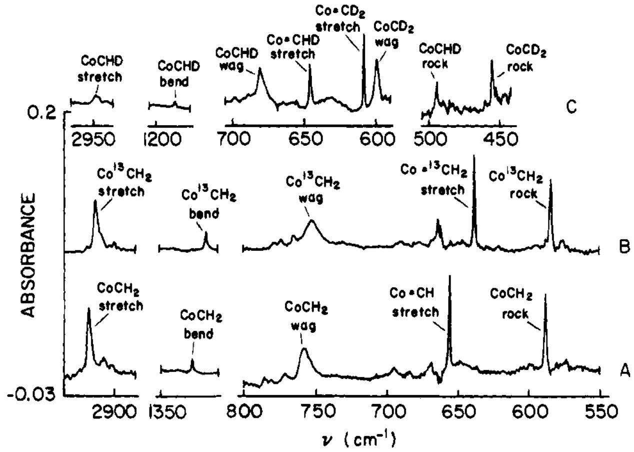

Figure 3. An isotope study. Partial FTIR spectra recorded in argon matrices of (A) $CoCH_2$, (B) $Co^{13}CH_2$, and (C) CoCHD and $CoCD_2$.

Two minor $(N_2)_xCoCH_2$ species are associated with the weaker absorptions labeled c and d (Figure 4). These bands as well as those assigned to N_2CoCH_2 could be enhanced (and thus identified) when N_2 was cocondensed with Co, CH_2N_2, and argon. This effect is illustrated in the figure where the 500−800 cm^{-1} region of spectrum A is compared with one (spectrum B) which was recorded after N_2 had been introduced. The c bands decreased during $\lambda \geq 500$ nm, $\lambda \geq 400$ nm, and UV photolysis, whereas the d bands showed significant bleaching by $\lambda \geq 500$ nm photolysis. No products could be identified from these photolyses. The N_2CoCH_2 complex could be photodissociated using either a visible or UV source as shown by an increase in the absorptions assigned to $CoCH_2$ with a concomitant decrease in the bands assigned to N_2CoCH_2.

$$N_2CoCH_2 \xrightarrow[UV]{\lambda > 400\ nm} CoCH_2 + N_2$$

Although labeling experiments to establish the mode of bonding in the N_2 complexes have not been carried out, it is tempting to postulate that the N_2 is bound "side-on" since the N=N stretching band of N_2CoCH_2 at 2109.5 cm^{-1} is very close to the one reported for CoN_2 at 2101.0 cm^{-1}, a species which is known to have the N_2 ligated in the less common "side-on" mode.[21]

Cobalt atoms were also found to react spontaneously with CH_2N_2 in N_2 matrices to yield $(N_2)_xCoCH_2$ complexes. The spectrum of a N_2 matrix is presented in Figure 5 along with the spectrum of $CoCH_2$ which was recorded in argon. Competing reactions between Co atoms and N_2 obscured the N=N

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Table 1. Measured and Calculated Infrared Frequencies (cm^{-1}) for $CoCH_2$, $Co^{13}CH_2$, CoCHD, and $CoCD_2$ in Solid Argon

	$CoCH_2$		$Co^{13}CH_2$		CoCHD		$CoCD_2$	
vibrational mode	obs	cal	obs	cal	obs	cal	obs	cal
CH_2 s-stretch	2918.0	2918.3	2912.7	2912.5		2160.8		2120.6
CH_2 scissor	1327.0	1326.0	1316.9	1320.3	1186.5	1181.2	993.2	996.5
CoC stretch	655.4	655.5	638.1	638.0	646.0	645.0	608.2	608.9
CH_2 a-stretch	2979.7	2979.5	2969.1	2969.4	2948.4	2948.3		2199.1
CH_2 rock	587.5	590.2	483.6	486.7	494.4	491.5	455.4	448.1
CH_2 wag	757.4	758.4	749.9	751.9	681.5	681.2	599.5	593.9

Table 2. Molecular Geometry, Symmetry Coordinates, and Force Constants Used for $CoCH_2$, $Co^{13}CH_2$, CoCHD, and $CoCD_2$ in the Normal Coordinate Analyses

	$r_1 = r_2 = r(\text{C-H}) = 1.07$ Å	$F_{11} = 4.793$	mdyn/Å
	$r_3 = r(\text{Co-C}) = 1.9$ Å	$F_{12} = -0.224$	mdyn/Å
	$\phi_1 = \phi_2 = \angle(\text{CoCH}) = 123.5°$	$F_{13} = 0.157$	mdyn/rad
	$\phi_3 = \angle(CH_2) = 113°$	$F_{22} = 2.902$	mdyn/Å
	$\theta_1 = \angle(CoCH_2) = 180.0°$	$F_{23} = -0.131$	mdyn/rad
		$F_{33} = 0.367$	mdyn Å/rad^2
		$F_{44} = 4.784$	mdyn/Å
A'	$S_1 = 2^{1/2} (\Delta r_1 + \Delta r_2)$	$F_{45} = 0.349$	mdyn/rad
	$S_2 = \Delta r_3$	$F_{55} = 0.220$	mdyn Å/rad^2
	$S_3 = 6^{1/2} (2\Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3)$	$F_{66} = 0.184$	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''	$S_6 = \Delta\theta_1 \sin\phi_1$		

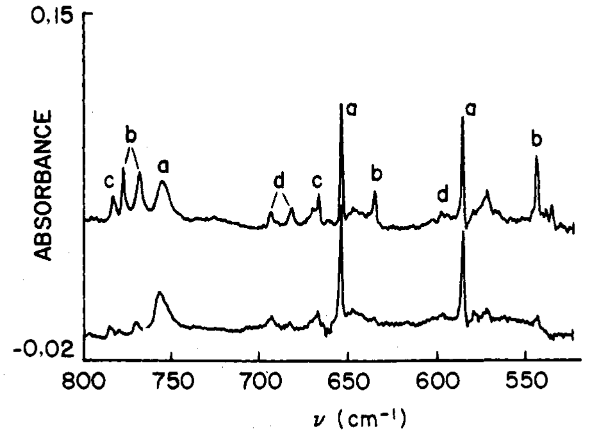

Figure 4. N_2 complexes of $CoCH_2$: (A) $Co/CH_2N_2/Ar = 1.0/0.9/100$, (B) $Co/CH_2N_2/N_2/Ar = 1.0/0.9/?/100$; (a) $CoCH_2$, (b) N_2CoCH_2, (c and d) $(N_2)_xCoCH_2$.

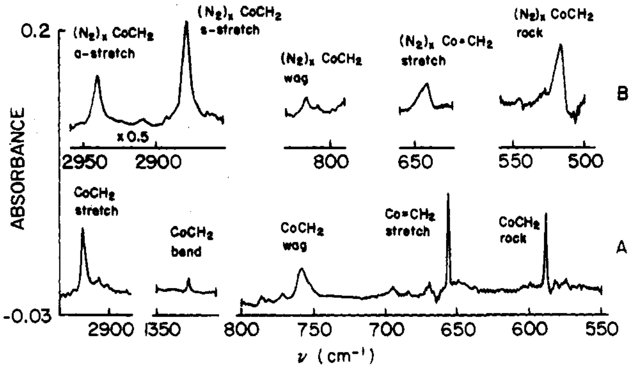

Figure 5. Partial FTIR spectra of $CoCH_2$ and $(N_2)_xCoCH_2$: (A), $CoCH_2$ in solid argon, (B) $(N_2)_xCoCH_2$ in a nitrogen matrix.

stretching absorptions of these complexes and the degree of coordination of N_2 could not be evaluated. The infrared frequencies exhibited by the various nitrogen coordinated complexes are presented in Table 3.

Table 3. Measured Infrared Frequencies (cm^{-1}) of Nitrogen Coordinated Cobalt Methylenes in Solid Argon and Solid Nitrogen[a]

vibration mode		$(N_2)_xCoCH_2$	$(N_2)_xCo^{13}CH_2$	$(N_2)_xCoCHD$	$(N_2)_xCoCD_2$
CH_2 s-stretch	B	2916.0	2908.0		
	C	2907.2	2900.0		
	N	2877.8	2872.9		
CH_2 bend	N	1353.8	1347.3		
					593.7
Co=C stretch	B	636.6	620.5	625.0	597.1
	N	640.7	628.2		
CH_2 a-stretch	N	2940.0	2930.1	2890.5	
CH_2 rock	B	544.6	540.5	453.0	411.0
	C	668.5	664.0		
	D	598.9	593.2		
	N	515.6	511.5	420.9	
CH_2 wag	B	770.7	764.2		
		779.6	772.6		
	C	785.9	778.1		
	D	683.4	668.2		
		695.0	688.9		
	N	815.5			636.9
N=N stretch	B	2109.5	2109.5	2109.5	2109.5

[a] B = N_2CoCH_2; C, D = $(N_2)_xCoCH_2$ ("c" and "d" bands) isolated in argon matrices. N = $(N_2)_xCoCH_2$ isolated in nitrogen matrices.

Scheme 1

$$Co + CH_2N_2 \xrightarrow[-N_2]{Ar/12\,K} CoCH_2 \xrightarrow{H_2} CH_3CoH + CH_4 + Co$$

A particularly salient feature of this work was the discovery of a route to a matrix environment in which a cobalt atom can be isolated in an argon cage with a single molecule of methane. Thus the ternary reaction illustrated in Scheme 1 was shown to proceed spontaneously when H_2 was cocondensed with cobalt atoms, diazomethane, and argon at 12 K. A competing hydrogenolysis reaction gave methane.[22]

Photolysis of the matrix using visible light ($\lambda \geq 400$ nm) led to the reductive elimination of cobalt from CH_3CoH to yield a $Co(CH_4)$ σ-complex.[23] CH_3CoH could be regenerated after UV photolysis.[24] The $Co(CH_4)$ adduct formed during this process had the triply degenerate $\nu4(f2)$ absorption of methane at 1305.3 cm^{-1} split into two peaks at 1303.4 cm^{-1} and 1299.3 cm^{-1}. The formation of two peaks implies that the σ-complex is a C_{3v} species.[25]

$$CH_3CoH \underset{280\text{ nm} < \lambda < 360\text{ nm}}{\overset{\lambda > 400\text{ nm}}{\rightleftharpoons}} Co(CH_4)$$

These events are illustrated in the infrared spectra presented in Figure 6. The weak methane peak in spectrum A results from the reaction of $CoCH_2$ with residual H_2.[25] When H_2 was added to the matrix (spectrum B), both CH_4 and CH_3CoH were

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(22) A small amount of dihydrogen may be produced by the cracking of pump oil.

(23) For an earlier example, see: Ozin, G. A.; McCaffrey, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 7351.

(24) For earlier examples of methane activation by photoexcited metal atoms, see: Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393. Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A.; Garcia-Prieto, J. *J. Am. Chem. Soc.* **1981**, *103*, 1574. Ozin, G. A.; McCaffrey, J. G.; Parnis, J. M. *Angew. Chem.* **1986**, *98*, 1076; *Angew. Chem., Int. Ed.* Engl. **1986**, *25*, 1072.

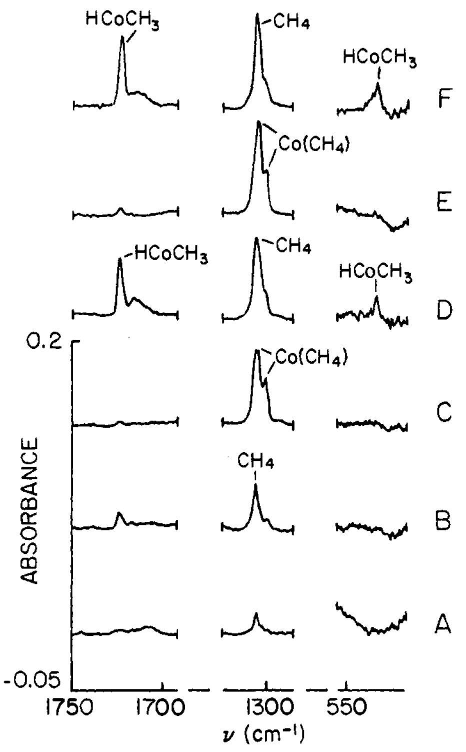
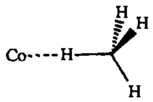


Figure 6. Partial FTIR spectra of CH_4, $Co(CH_4)$, and CH_3CoH formed by the cocondensation of Co, CH_2N_2, and H_2 in an argon matrix: (A) without H_2, $Co/CH_2N_2/Ar = 1.0/0.9/100$; (B) H_2 added during codeposition, $Co/CH_2N_2/H_2/Ar = 1.0/0.9/5/100$; (C) after 10-min photolysis of B with $\lambda \geq 400$ nm; (D) after 10-min photolysis of B with $360 \geq \lambda \geq 280$ nm; (E) after 10-min photolysis of B with $\lambda \geq 400$ nm; (F) after 10-min photolysis of B with $360 \geq \lambda \geq 280$ nm.

produced (Scheme 1). Photolysis using the visible source (spectrum C) led to extrusion of Co, whereas UV photolysis (spectrum D) gave the reverse process. This sequence is repeated in spectra E and F. These effects are displayed more clearly in Figure 7 with difference spectra and in Figure 8 for a $Co(CD_4)$ complex.



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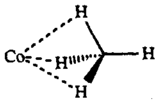

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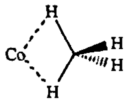

3

Two structures, **1** and **2**, would satisfy the C_{3v} symmetry requirement. The adduct **3** would have C_{2v} symmetry. An argument in favor of **2** is the facile insertion of the Co atom into one of the C−H bonds of methane to yield CH_3CoH. Complex **1** would probably require extensive reorganization (**1** → **4**) prior to C−H activation. In addition, the adduct with

1 4

three C−H bonds complexed to the cobalt would probably be the more stable one.[26]

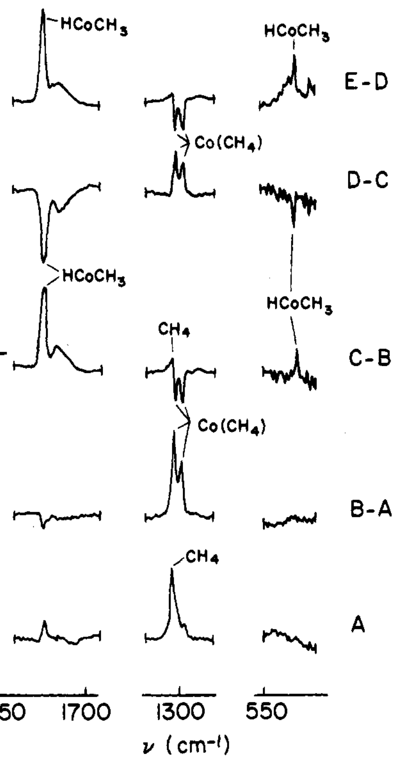

Figure 7. Partial FTIR spectra of CH_4, $Co(CH_4)$, and CH_3CoH formed by the cocondensation of Co, CH_2N_2, and H_2 in an argon matrix: (A) $Co/CH_2N_2/H_2/Ar = 1.0/0.9/5/100$; (B) after 10-min photolysis with $\lambda \geq 400$ nm; (C) after 10-min photolysis with $360 \geq \lambda \geq 280$ nm; (D) after 10-min photolysis with $\lambda \geq 400$ nm; (E) after 10-min photolysis with $360 \geq \lambda \geq 280$ nm.

Deuterium-Labeled Complexes $Co(CH_3D)$, $Co(CH_2D_2)$, and $Co(CD_4)$. In order to define the structures of these σ-complexes in greater detail, studies using deuterium-labeled compounds were carried out. Fortunately the scheme used to prepare CH_3CoH (Scheme 1) is readily emendable to the synthesis of these complexes. The synthesis of $Co(CH_2D_2)$ is illustrated in Scheme 2 and the absorption frequencies attributed to each of the σ-complexes investigated during this study are shown in Table 4. Curiously, irradiation of this matrix using the $\lambda \geq 400$ nm source led initially to an increase in the absorptions assigned H_2DCCo-D, followed by a gradual decrease. This observation suggests that visible light provides enough energy to diffuse (or to increase the mobility of) the D_2 to a neighboring $CoCH_2$ to form more H_2DCCo-D. This process competes with the formation of the $Co(CH_2D_2)$ σ-complex. However, as shown in Figure 9, nearly all of the H_2DCCo-D species was converted to the σ-complex after about 1.5 h. HD_2CCo-H was not observed during the photolysis.

When the $Co(CH_2D_2)$ complex from Scheme 2 was subjected to UV photolysis, a mixture of H_2DCCo-H and HD_2CCo-D was formed in about a 2/1 ratio (Scheme 3). Several cycles of visible−ultraviolet irradiations led to product ratios which were consistently 2.0−2.2. The same ratio of products was formed by irradiating a $Co/CH_2D_2/Ar$ matrix through several cycles of visible−UV photolyses.

These results show that reductive elimination of Co from CH_2DCo-D does not give a σ-complex in which the Co maintains an intimate relationship with the C−D bond. Other-

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(25) Herzberg, G. *Molecular Spectra and Molecular Structure II*; D. Van Nostrand: New York, 1955. The splitting of this band can be observed up to 38 K. Above this temperature the argon matrix boils away rapidly. This observation mitigates strongly against multiple matrix site perturbation of methane by the cobalt atom as the origin of this effect. It is possible that on lowering the symmetry to C_{2v} the degeneracy of this mode is lifted entirely yielding a_1, b_2, and b_1 modes. If two of these IR active modes should overlap, then one might observe the doublet observed here.

(26) For theoretical calculations see: Anderson, A. B.; Baldwin, S. *Organometallics*, **1987**, *6*, 1621.

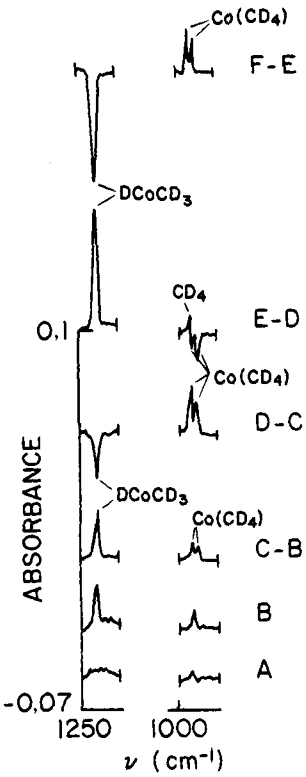


Figure 8. Partial FTIR spectra of CD_4, $Co(CD_4)$, and CD_3CoD formed by the cocondensation of Co, CD_2N_2, and D_2 in an argon matrix: (A), without D_2, $Co/CD_2N_2/Ar = 0.9/0.9/100$; (B) D_2 added during codeposition, $Co/CD_2N_2/D_2/Ar = 0.9/0.9/5/100$; (C) after 10-min photolysis of B with $\lambda \geq 500$ nm; (D) after 10-min photolysis of B with $\lambda > 400$ nm; (E) after 10-min photolysis of B with $360 \geq \lambda \geq 280$ nm; (F) after 10-min photolysis of B with $\lambda > 400$ nm.

Scheme 2

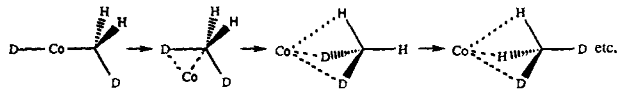
$$Co + CH_2N_2 \xrightarrow[-N_2]{Ar/12\ K} CoCH_2 \xrightarrow{D_2} CH_2DCo\text{-}D \xrightarrow{\lambda \geq 400\ nm} Co(CH_2D_2)$$

Table 4. Absorption Frequencies for $Co(CH_4)$, $Co(CH_2D_2)$, $Co(CD_4)$, and $Co(CH_3D)$

CH_4	$Co(CH_4)$	vibration mode	CD_4	$Co(CD_4)$	vibration mode
1305.8	1303.4 1299.3	CH_3 d-def	993.6	992.9 989.8	CD_3 d-def

CH_2D_2	$Co(CH_2D_2)$	vibration mode	CH_3D	$Co(CH_2D)$	vibration mode
3020.2	3015.4	CH_2 a-str	3026.5	3019.3	CH_3 d-str
2981.9	2974.0	CH_2 s-str			
1431.4	1430.0	CH_2 scis	1302.4	1303.1 1298.6	CH_3 s-def
1232.3	1229.3	CH_2 wag	1155.4	1155.1 1151.8	CH_3 rock
1028.6	1026.5	CD_2 scis			

wise, only $H_2DCCo\text{-}D$ would have been formed. A weakly bound complex in which the methane is free to rotate on the metal provides the best model.



Analogous routes to the two remaining deuterated σ-complexes $Co(CH_3D)$ and $Co(CD_4)$ are illustrated in Schemes 4 and 5, respectively.

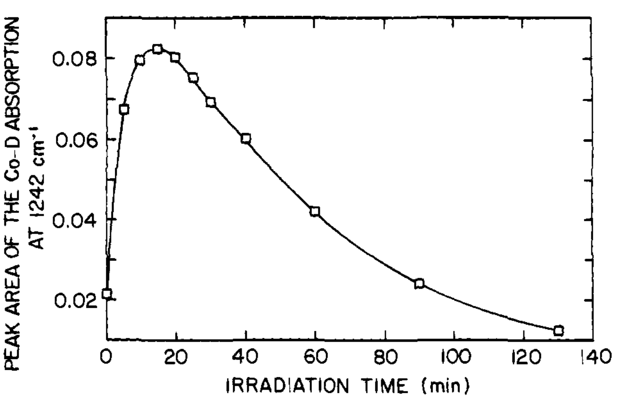
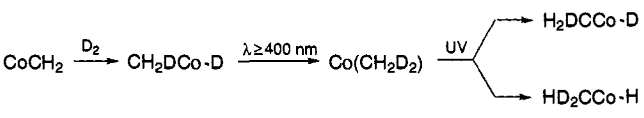
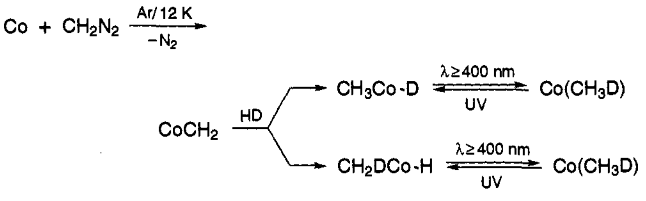


Figure 9. A plot of the 1242-cm^{-1} absorption band of $H_2DCCo{-}D$ ($CoCH_2 + D_2$) versus irradiation time using visible light.

Scheme 3



Scheme 4



Scheme 5

$$Co + CD_2N_2 \xrightarrow[-N_2]{Ar/12\ K} CoCD_2 \xrightarrow{D_2} CD_3Co\text{-}D \underset{UV}{\overset{\lambda \geq 400\ nm}{\rightleftharpoons}} Co(CD_4)$$

Table 5. Infrared Absorptions (cm^{-1}) of the Oxidative Addition Products Formed by Photolysis of Cobalt Atoms and CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4

assignments	$H_3CCo\text{-}H$	$HD_2CCo\text{-}H$	$H_2DCCo\text{-}D$	$H_2DCCo\text{-}H$	$H_3CCo\text{-}D$
$\nu(CH_3)$	2982.0 2942.1				
$\nu(Co\text{-}H)$, $\nu(Co\text{-}D)$	1722.6	1722.1	1242.2	1722.6	1244.3
$d(CH_3)$	1168.5				
$pr(CH_3)$, $r(CH_2)$	573.2 568.9		538.4	537.0	
$\nu(Co\text{-}C)$	530.8	507.9	511.8		531.5

The spontaneous reaction of $CoCH_2$ with HD illustrated in Scheme 4 was found to give both possible regioisomers $H_2DCCo\text{-}H$ and $H_3CCo\text{-}D$. Unfortunately, the yield of this reaction was low and furnace light led to the reductive elimination reaction making product ratios difficult to obtain. However, the results from four experiments showed that the $H_2DCCo\text{-}H/H_3CCo\text{-}D$ ratio was slightly greater than 1 (molar ratios from 1.1 to 1.6). Unfortunately, information relevant to the mechanism of this process is not available. If this reaction is initiated by oxidative addition of HD to $CoCH_2$, then the regiochemistry of the reduction may reflect the migratory aptitude of the isotopes.

Reactions of Cobalt Atoms with CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 in Solid Argon. The infrared absorptions of the oxidative addition products obtained by UV photolysis of Co/CH_4, Co/CH_3D, Co/CH_2D_2, Co/CHD_3, and Co/CD_4 matrices are presented in Table 5. The $Co(CH_4)$ σ-complexes cannot be observed in these matrices since the dominance of free methane masks the spectrum of the complex.

The Co-H and Co-D stretching absorptions and force constants for each compounds formed during this study are listed in Table 6. The stretching frequencies of the oxidative addition

Table 6. Frequencies ($\mathrm{cm^{-1}}$) of Co-H and Co-D Stretching Vibrations, and Their Force Constants (mdyn/Å)

reaction	product	str (Co-H)	str (Co-D)	*f*(Co-H)	*f*(Co-D)
Co + H_2	HCo-H	1684.5		1.65	
Co + HD	DCo-H	1733.7		1.74	
Co + CH_4	H_3CCo-H	1722.6		1.72	
Co + CH_2D_2	HD_2CCo-H	1722.1		1.72	
Co + CH_3D	H_2DCCo-H	1722.4		1.72	
$CoCH_2$ + H_2	H_3CCo-H	1723.1		1.72	
$CoCH_2$ + D_2	HD_2CCo-H	1722.4		1.72	
$CoCH_2$ + HD	H_2DCCo-H	1722.8		1.72	
Co + D_2	DCo-D		1223.4		1.71
Co + HD	HCo-D		1244.6		1.77
Co + CD_4	D_3CCo-D		1241.0		1.76
Co + CH_2D_2	H_2DCCo-D		1241.7		1.76
Co + CH_3D	H_3CCo-D		1244.3		1.77
$CoCH_2$ + D_2	H_2DCCo-D		1242.2		1.76
$CoCH_2$ + HD	H_3CCo-D		1244.6		1.77
CoD_2 + D_2	D_3CCo-D		1241.0		1.76

products formed H_2, D_2, and HD are listed for comparison. These reactions are discussed in greater detail in the following section. The force constants, *f* (in mdyn/Å), of the Co-H and Co-D stretching vibrations were calculated using the diatomic oscillator approximation (Hooke's law). With the exception of the CoH_2, CoD_2, and CoHD, the stretching frequencies for each RCo-H and RCo-D species appear over a narrow range, indicating that the absorptions are not influenced by other vibrations. This finding is further supported by comparing the stretching frequencies and force constants of RCo-H and RCo-D to those of CoH_2, CoD_2, and CoHD. The stretching modes of the RCo-H and RCo-D species behave much like those of CoHD.

The isotope effect determined for the oxidation addition step using a Co/CH_2D_2/Ar matrix formed by cocondensing Co, CH_2N_2, and Ar in a molar ratio of 0.8−0.9/1.0−1.1/100 was 2.2. Similar experiments using CH_3D gave a value of 2.4. Unfortunately, we are unaware of any protocol which would allow us to evaluate isotope effects determined for photochemically induced reactions in frozen argon. However, using conventional arguments one might conclude that the transition state for the oxidative addition would involve a three-center transition state with a significant Co- - -H interaction and a weakened C-H bond.

Reactions of Cobalt Atoms with H_2, D_2, and HD in Solid Argon. Although H_2 cannot be condensed onto the matrix surface at 12 K, molecules of H_2 and cobalt atoms can be trapped in argon cages. In a typical experiment, cobalt atoms, argon, and H_2 were codeposited for 30 min onto the matrix surfaces at 12−15 K. The Co/Ar molar ratio was approximately 0.85/100. No evidence was found for either the spontaneous activation of H_2 or for the formation of a Co(H_2) complex as observed earlier for nickel.[27] However, rapid formation of CoH_2 was observed when the matrix was photolyzed using the UV source. As observed earlier for FeH_2, subsequent irradiation of the matrix with visible light led to the reductive elimination of Co from the CoH_2 species.[28]

Table 7. Stretching Frequencies ($\mathrm{cm^{-1}}$) for CoH_2, CoD_2, and CoHD in Solid Argon

reaction	product	Co-H	Co-D	abs. ratio of Co-H/Co-D
Co + H_2	H-Co-H	1684.5		
Co + D_2	D-Co-D		1223.4	
Co + HD	H-Co-D	1733.7	1244.6	1.27

$$\mathrm{Co} + \mathrm{H_2} \underset{\lambda\,>\,400\ \mathrm{nm}}{\overset{280\ \mathrm{nm}\,<\,\lambda\,<\,360\ \mathrm{nm}}{\rightleftharpoons}} \mathrm{CoH_2}$$

Analogous reactions were observed when D_2 and HD were used.

$$\mathrm{Co} + \mathrm{D_2} \underset{\lambda\,>\,400\ \mathrm{nm}}{\overset{280\ \mathrm{nm}\,<\,\lambda\,<\,360\ \mathrm{nm}}{\rightleftharpoons}} \mathrm{CoD_2}$$

$$\mathrm{Co} + \mathrm{HD} \underset{\lambda\,>\,400\ \mathrm{nm}}{\overset{280\ \mathrm{nm}\,<\,\lambda\,<\,360\ \mathrm{nm}}{\rightleftharpoons}} \mathrm{CoHD}$$

The stretching frequencies corresponding to each product are listed in Table 7. The CoH_2 and CoD_2 species each exhibit a single absorption corresponding to the Co-H and Co-D stretching vibrations. Since the symmetric stretching vibrations of linear A−B−A molecules are IR inactive, these species must be nonlinear.

Vibrational modes were observed at higher frequencies for CoHD. Since the stretching modes in CoHD do not belong to the same symmetry group, these absorptions were used throughout this work to evaluate the relative molar extinction coefficients of the RCo-H and RCo-D stretching vibrations. The ratio of the Co-H/Co-D absorptions for CoHD was determined by careful peak area measurements and found to be 1.27 (Table 7).

Conclusions

We have found that $CoCH_2$ can be synthesized by cocondensing Co atoms with CH_2N_2 and argon at 12 K. The $CoCH_2$ species is accompanied by N_2CoCH_2 and at least two $(N_2)_xCoCH_2$ complexes. The $CoCH_2$ reacts with H_2 to give CH_3CoH. This species can also be synthesized by the oxidative addition of cobalt to a C-H bond of methane when Co/CH_4/Ar matrices are photolyzed using a UV source. Photolysis of CH_3CoH using visible light yields a Co(CH_4) σ-complex. Spectroscopic studies show that the σ-complex is a C_{3v} species. Studies using deuterium-labeled σ-complexes have shown that the methane is bound loosely to the Co, probably through a three-bond interaction.

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(27) Park, M. Ph.D. Thesis, (Rice University, Houston, TX, 1988). See also: Ozin, G. A.; McCaffrey, J. G. *J. Am. Chem. Soc.* **1984**, *106*, 807.

(28) Ozin, G. A.; McCaffrey, J. G. *J. Phys. Chem.* **1984**, *88*, 645.