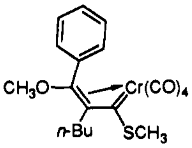
The transformation of **1** into **2** probably involves species related to metal carbene **3**, analogous to presumed intermediates in the Dötz and other reactions.[1] Yet although it has (*E*)-stereochemistry,[1a] **3** does not yield a naphthol or an indene. The reason we propose is that it is diverted by the adjacent sulfur atom, as pictured in structure **4**, to **5**, which transforms into **2** either by dimerizing or by combining with **3**.[23] This accords with the propensity of heteroatoms to bridge carbon–metal bonds,[25] the facility with which structures $Z(Et_2N)C{=}Cr(CO)_5$ convert to $(Et_2N)C{\equiv}Cr(CO)_4Z$ (Z is Se, Te, Cl, Br, I, Sn, and Pb),[26] the ready dimerizations of metal carbynes to acetylenes[27] and their derivatives,[28,29] and the instability of (alkylthio)methylenechromium pentacarbonyls.[30] In this connection, note that the metal carbene adds to the acetylene in the direction that should be favored electronically,[8] that is, in the way it adds to ynamines[3a–d] but not, seemingly,[2a,31] to most alkoxyacetylenes.[2]



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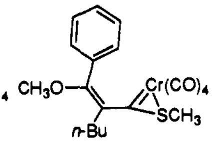

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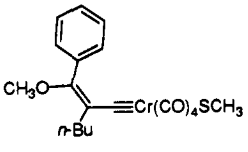

5

The transformation may be useful in mechanistic analysis for it is one of only two[1e] that appear to trap the presumed 2-propenylidene–metal precursor of products like phenols and indenes.[1a,b] It may also lead to new ways to couple molecules, for it suggests that chromium (alkyl- and arylthio)carbenes[30] in general may link to give acetylenes. The relevant previous work is ambiguous. On the one hand there is an assertion that they do link,[32] while on the other a structure related to **3** gave a 1-(alkylthio)indene instead.[33,34]

Acknowledgment. We thank the National Science Foundation for partial support (CHE 85-13274) and Diego Hoic and Shuhao Shi for help.

Supplementary Material Available: Preparative details, ^1H and ^{13}C NMR spectra of unlabeled **2** (the later with and without proton couplings), and ^{13}C NMR spectra of labeled **2**, showing ^{13}C couplings, and proton–carbon NOEs (6 pages). Ordering information is given on any current masthead page.

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[23] The eliminated $[Cr(CO)_4SCH_3]_2$ is not known, but the SePh[24a] and Me_2P analogues[24b] are, as is $[W(CO)_4SPh]_2$.[24c]

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Detection of a σ-Complex in the Reaction of Cobalt Atoms with Methane

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Received July 27, 1992
Revised Manuscript Received November 11, 1992

Although the occurrence of two-electron, three-center M⋯H⋯C bonds is now well-established for a large number of organometallic complexes in which the C–H bonds of a bound ligand interact with the metal center,[1] there is less evidence for the coordination of free hydrocarbon C–H bonds to transition-metal species.[2–5] These weak interactions are thought to be important in C–H activation.[6–8] The most direct evidence for alkane complexes came from the early work of Perutz and Turner[2] on $M(CO)_5$ fragments bound to alkanes in low-temperature matrices. Alkane complexes

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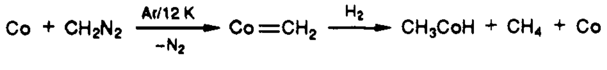
Table I. Measured Infrared Frequencies (cm^{-1}) for CH_4, $Co(CH_4)$, CD_4, $Co(CD_4)$, CH_3CoH, and CD_3CoD in Solid Argon

vibration mode	CH_4	$Co(CH_4)$	CD_4	$Co(CD_4)$	CH_3CoH	CD_3CoD
methane deformation	1305.3	1303.4 1299.3	993.6	992.9 989.8		
Co–C stretch					531.5	
Co–H stretch					1722.6 1716.6	1241.0

Scheme I



$$Co + CH_2N_2 \xrightarrow[-N_2]{Ar/12\ K} Co{=}CH_2 \xrightarrow{H_2} CH_3CoH + CH_4 + Co$$

have also been proposed on the basis of isotope labeling studies in the reductive elimination of alkyl hydride complexes in solution.[3-5] These and other recent gas-phase studies[9] on the oxidative addition of alkanes to metal complexes in which short-lived complexes have been identified prompt us to report the direct observation, by FTIR matrix isolation, of an intermolecular complex in which cobalt atoms are bound to methane. A salient feature of this work is the discovery of a route to a matrix environment in which a cobalt atom can be isolated with a single molecule of methane. In this way the dominance of free methane, which would otherwise mask the spectrum of the metal–methane complex in the infrared spectrum, is overcome.

The ternary reaction illustrated in Scheme I proceeds spontaneously to yield methane and CH_3CoH[10,11] when cobalt atoms, diazomethane, and dihydrogen are cocondensed with argon onto a rhodium-plated copper surface at 12 K.[12,13] Evidence for a cobalt–methane complex was found when wavelength-dependent photolysis studies were carried out. Thus photolysis using $\lambda \geq 400$ nm radiation leads to the reductive elimination of cobalt from CH_3CoH to yield the $Co(CH_4)$ complex, whereas the reverse process can be induced by UV photolysis (eq 1).[13] The $Co(CH_4)$

$$CH_3CoH \underset{UV}{\overset{\lambda \geq 400\ nm}{\rightleftharpoons}} Co(CH_4) \qquad (1)$$

complex produced in this reversible process has the triply degenerate $\nu_4(f_2)$ absorption of methane at 1305.3 cm^{-1} split into two peaks appearing at 1299.3 and 1303.4 cm^{-1}. The appearance of two peaks suggests that the $Co(CH_4)$ adduct has C_{3v} symmetry.[17-19]

Spectral evidence for these events is presented in the infrared spectra shown in Figure 1. Spectrum A was recorded when Co, CH_2N_2, and argon were cocondensed at 11 K. The weak methane peak results from the reaction of $Co{=}CH_2$ with residual dihydrogen.[20] Spectrum B was recorded after dihydrogen was cocondensed as a ternary reagent. Under these conditions both CH_4 and CH_3CoH are formed as illustrated in Scheme I. The photoextrusion of Co from CH_3CoH to give the $Co(CH_4)$ complex using $\lambda \geq 400$ nm radiation is illustrated in spectrum C. The reverse process is illustrated in D where UV photolysis leads to the insertion adduct CH_3CoH (eq 1). This sequence is repeated in E and F. Similar experiments using CD_2N_2 and D_2 gave rise to a $Co(CD_4)$ adduct with absorptions at 992.9 and 989.8 cm^{-1}. These data along with those of the $Co(CH_4)$ complex are presented in Table I.

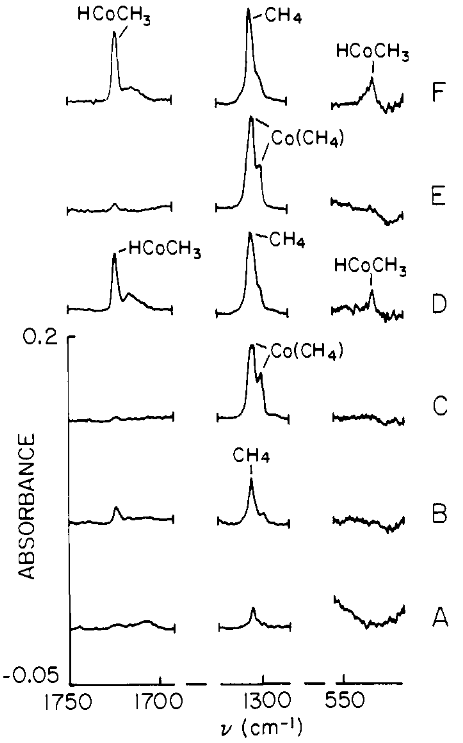


Figure 1. Partial FTIR spectra of CH_4, $Co(CH_4)$, and CH_3CoH obtained from the cocondensation of Co, CH_2N_2, and dihydrogen in argon matrices: A, without dihydrogen, $Co/CH_2N_2/Ar$ = 1.0/0.9/100; B, dihydrogen added during deposition, $Co/CH_2N_2/H_2/Ar$ = 1.0/0.9/5/100; C, after 10 min of photolysis of B with $\lambda \geq 400$ nm; D, after 10 min of photolysis of B with $360 \geq \lambda \geq 280$ nm; E, after 10 min of photolysis of B with $\lambda \geq 400$ nm; F, after 10 min of photolysis of B with $360 \geq \lambda \geq 280$ nm.

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

vibration mode	$CoCH_2$	$Co^{13}CH_2$	CoCHD	$CoCD_2$
CH_2 s-stretch	2918.0	2912.7		
CH_2 scissor	1327.0	1316.9	1186.5	993.2
CoC stretch	655.4	638.1	646.0	608.2
CH_2 a-stretch	2979.7	2969.1	2948.4	
CH_2 rock	587.5	583.6	494.4	455.4
CH_2 wag	757.4	749.9	681.5	599.5

Two structures, **1** and **2**, would satisfy the C_{3v} symmetry requirement. The adduct **3** would have C_{2v} symmetry. Although there is no basis to choose between either **1** or **2**, the adduct with three C–H bonds complexed to the cobalt would probably be more

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[9] *Chem. Eng. News* **1992**, January 27, 32–33.

[10] Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393.

[11] $Co{=}CH_2$ is accompanied in low yield by several $(N_2)_xCo{=}CH_2$ species. The yield of these products can be enhanced by cocondensing dinitrogen with the other matrix components.

[12] For a description of the apparatus, see: Hauge, R. H.; Fredin, L.; Kafafi, Z. H.; Margrave, J. L. *Appl. Spectrosc.* **1986**, *40*, 588.

[13] The stoichiometry of these reactions was determined from a concentration study in which the Co/Ar molar ratio was increased from 0.0 to 1.4. The addition of a small amount of CO gave rise to a band at 1990.7 cm^{-1} resulting from $Co(CO)_3$, which served as an internal standard. A log–log plot[14,15] of the intensity of this band versus one at 655.4 cm^{-1} (Co—C stretch assigned to $Co{=}CH_2$) gave a slope of 0.93, confirming that only one cobalt atom is involved.

[14] Moskovits, M.; Ozin, G. A. *Cryochemistry*; Wiley-Interscience: New York, 1976.

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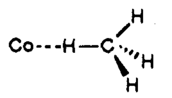
[17] Herzberg, G. *Molecular Spectra and Molecular Structure, II*; D. Van Nostrand: New York, 1955.

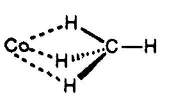
[18] The splitting of this band can be observed up to 38 K. Above this temperature the matrix boils away rapidly. This observation mitigates strongly against multiple matrix site perturbation of methane by the cobalt atom as the origin of this effect.

[19] A referee has pointed out 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 exhibited in Figure 1.

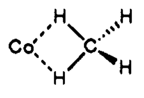
[20] A small amount of dihydrogen may be produced by the cracking of pump oil.



1

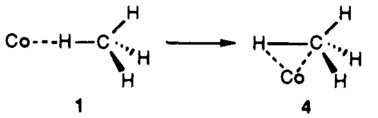


2



3

stable. Another argument in favor of **2** is the facile insertion of the Co atom into a C–H bond of methane to yield CH_3CoH.[10] Complex **1** would require extensive reorganization (1 → 4) prior to C–H activation.



The $Co{=}CH_2$ intermediate illustrated in Scheme I can be isolated and characterized in the absence of dihydrogen. The vibrational frequencies assigned to this species as well as those of the isotopically labeled species, $Co{=}^{13}CH_2$, $Co{=}CD_2$, and $Co{=}CHD$, used to make the vibrational assignments are presented in Table II.[21]

Future studies will extend this work to other metal atom–alkane adducts.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (CHE-9112530), the 3M Company, and the Robert A. Welch Foundation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Dr. Z. H. Kafafi for many helpful discussions.

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[21] $Co{=}^{13}CH_2$, $Co{=}CD_2$, and $Co{=}CHD$ were prepared from $^{13}CH_2N_2$, CD_2N_2, and $CHDN_2$, respectively.

Production of Polymers from Polymers. Novel Template Polymerization via Radical Ring-Opening Isomerization

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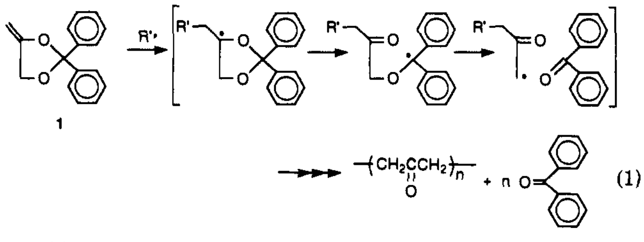
Received August 3, 1992

The 4-methylene-1,3-dioxolanes have been investigated[1-7] as rare monomers which can undergo radical ring-opening polymerization. However, their polymers consist of two or more kinds of repeating units, since the polymerization is sometimes accompanied by not only ring-opening but also elimination of carbonyl compounds $R_2C{=}O$. Recently, Hiraguri et al. reported the first example of radical ring-opening polymerization accompanied by quantitative elimination of the carbonyl compound, achieved by using 2,2-diphenyl-4-methylene-1,3-dioxolane (**1**), which affords polyketone and benzophenone[7] (eq 1).



(1)

This quantitative elimination in the radical ring-opening polymerization stimulated us to establish a novel template polymerization. It is anticipated that if the polymer (named prepolymer) has the structure of **1** in the side chain of repeating units, then the polyketone (newborn polymer) will also be formed from the prepolymer with radical initiation. This means that *polymers bear polymers* (Scheme I). This polymerization differs from conventional template polymerizations in that polymerization and separation take place simultaneously on the *prepolymer* to afford both the *newborn* and the *template polymer* without chemical treatment after polymerization.

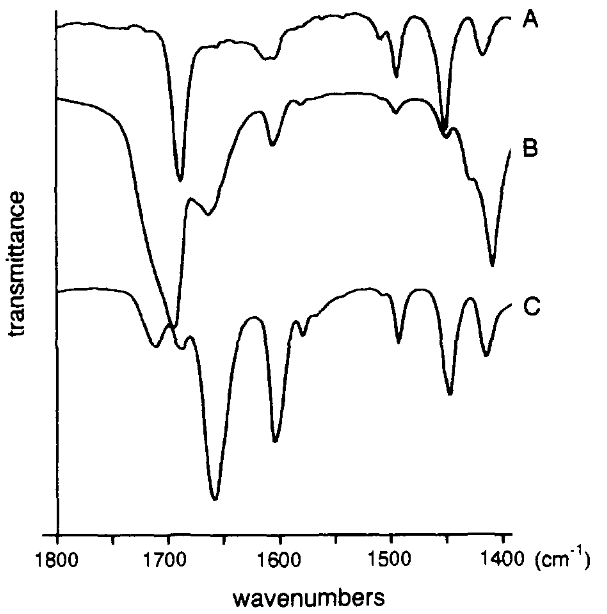
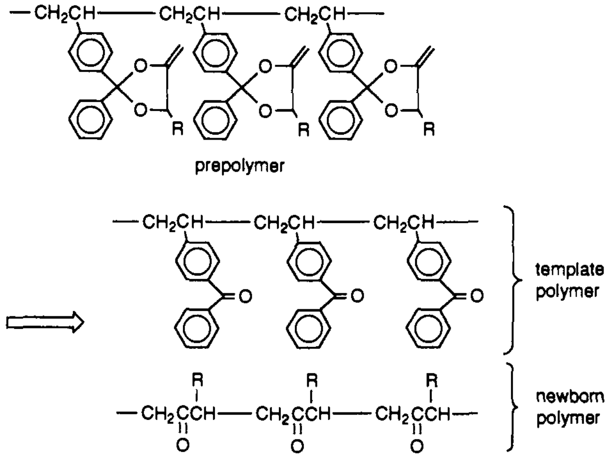


Figure 1. IR absorption of **2a**, **4a**, and **5a**. (A) Prepolymer **2a**. (B) Newborn polymer **4a**. (C) Template polymer **5a**.

Scheme I



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