chloride. The organic layer was separated, washed with H_2O, and dried over anhydrous sodium sulfate (GC yield, 60% on OV-17 as described above). The authentic sample was used to identify **5** from the kinetic pyrolyses. ^{13}C NMR (neat): δ –5.07 (q), 6.05 (t), 6.50 (q), 22.24 (t), 112.11 (t), 133.96 (d).

Synthesis of Dimethylpropylvinylsilane (6).[43] To a solution of propyl Grignard (from bromopropane (4.1 g, 33 mmol) and Mg (3.0 g, 125 mmol) in 30 mL of diethyl ether) in a 100-mL three-neck round-bottom flask equipped with a reflux condenser, dropping funnel, and magnetic stirring bar was added 1.70 g (14 mmol) of chlorodimethylvinylsilane. The reaction mixture was allowed to stir at room temperature for 2 h and at 45 °C for 1 h until the chlorosilane had disappeared. The typical Grignard workup afforded **6**, 70% GC yield (20% SF-96 on Chromosorb W, $^1/_4$ in. × 20 ft). ^{13}C NMR (neat): δ –4.10 (q), 16.84 (t), 17.60 (q), 17.63 (t), 130.51 (t), 138.32 (d).

Synthesis of 1-Ethyl-1,1-dimethyl-2-vinyl-2,2-dimethyl-1,2-disilane (8).[44] To a 100-mL flask containing 0.5 g (71 mmol) of Li wire $^1/_4$ in. × $^1/_8$ in. pieces) and 50 mL of tetrahydrofuran (THF), under Ar, was added a solution of 2.0 g (16 mmol) of chloroethyldimethylsilane and 2.0 g (16.3 mmol) of chlorodimethylvinylsilane. The flask was immersed in a water-filled ultrasound laboratory cleaner,[45] and after 3 h, the liquid in the flask was flash distilled under vacuum. Product **8** was isolated by fractional distillation, 40% yield (1.12 g, bp 77 °C (30 Torr). ^{13}C NMR (neat): δ –5.07 (q), –4.55 (q), 6.50 (t), 7.61 (q), 130.19 (t), 138.50 (d).

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Registry No. (*E*)-1, 117309-73-6; (*Z*)-1, 117309-74-7; 2, 590-18-1; 3, 115-07-1; 4, 624-64-6; 5, 18292-34-7; 6, 28857-41-2; 8, 57080-70-3; $(CH_3)_2Si(H)Cl$, 1066-35-9; $(CH_3)_2Si(Et)Cl$, 6917-76-6; $(CH_3)_2Si(CH{=}CH_2)Cl$, 1719-58-0; $(CH_3)_2Si{=}CHCH_3$, 55395-25-0; $(CH_3)_2Si{=}CH_2$, 4112-23-6; (R^*,R^*)-(3-chloro-2-methylbutyl)dimethylchlorosilane, 117309-71-4; (R^*,S^*)-(3-chloro-2-methylbutyl)dimethylchlorosilane, 117309-72-5; 3-chloro-2-methyl-1-butene, 5166-35-8.

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Photolysis of Acetyltetracarbonylcobalt(I) in Low-Temperature Matrices: Unusual Behavior for a Coordinatively Unsaturated Intermediate

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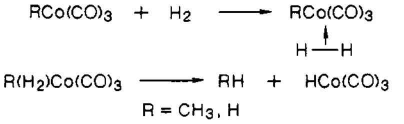
The ultraviolet photolysis of acetyltetracarbonylcobalt(I) in argon matrices produces $CH_3COCo(CO)_3$ which rearranges to form $CH_3Co(CO)_4$ upon subsequent irradiation. Although nominally coordinatively unsaturated, $CH_3COCo(CO)_3$ fails to react with CO or H_2 in the matrix, suggesting that the vacant coordination site is protected. The spectrum of the intermediate was fully characterized over the region from 2200 to 700 cm^{-1} by using both dispersive and Fourier transform infrared instruments. A band at 1685.9 cm^{-1} is assigned to the C–O stretch of the acetyl group. The anomolously low intensity exhibited by this band and the unusual lack of reactivity of a fragment which is nominally coordinatively unsaturated suggest that the carbonyl group is bonded in an unusual fashion, perhaps in an η^2 mode. The stabilization afforded $CH_3COCo(CO)_3$ by interactions with the acetyl group must become established as the CO is in the process of leaving because there is very little ^{13}CO incorporation during the formation of $CH_3COCo(CO)_3$ in a ^{13}CO matrix.

In the course of matrix-isolation studies of reactions of molecular hydrogen with coordinatively unsaturated transition-metal complexes, we have found that $RCo(CO)_3$ (R = H, CH_3) combines with dihydrogen to form complexes in which the hydrogen is coordinated, presumably as an η^2 ligand.[1] When irradiated with ultraviolet light, these complexes undergo cleavage reactions leading to RH and species derived from $HCo(CO)_3$.



$$RCo(CO)_3 + H_2 \longrightarrow \underset{H-H}{\overset{RCo(CO)_3}{\uparrow}}$$

$$R(H_2)Co(CO)_3 \longrightarrow RH + HCo(CO)_3$$

$$R = CH_3, H$$

Thinking that $CH_3COCo(CO)_4$ might behave in a similar fashion, we undertook studies of $CH_3COCo(CO)_4$ in hydrogen containing matrices. In this instance what was reasonably a coordinatively unsaturated complex was characterized, but it was surprising when it did not give any evidence of reaction with dihydrogen. Further investigation showed the species was unreactive toward CO as well. This prompted a detailed study of the nature of the intermediate.

Experimental Section

$CH_3Co(CO)_4$ was prepared by adding dimethyl sulfate to $NaCo(CO)_4$ while pumping on the mixture. $CH_3Co(CO)_4$, being the most volatile component, was pumped out. On occasion, it was redistilled at 0.1 mmHg pressure at 0 °C to remove dimethyl sulfate which had been carried over in the crude product. Typ-

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ically, some dimethyl sulfate was observed in the matrix even after additional purification. It proved inert to irradiation with 254-nm radiation. To obtain $CH_3COCo(CO)_4$, the $CH_3Co(CO)_4$ was warmed to 0 °C under a CO atmosphere for 30 min. $CH_3COCo(CO)_4$ was also formed from CH_3COCl and $NaCo(CO)_4$, but it was impossible to obtain matrices which were free of the acetyl chloride. Although the acetyl chloride was not affected by irradiation, its infrared spectrum interfered with observations of $CH_3COCo(CO)_4$ and its photoproducts. This method was used, however, to obtain ^{18}O-labeling in the acetyl group. To obtain ^{13}C-labeling in the acetyl group, $CH_3Co(CO)_4$ was exposed to ^{13}CO. Temperatures of 35 °C were required to get an isotopically labeled CO to exchange into the acetyl group.

Matrices of $CH_3COCo(CO)_4$ were obtained by subliming it into an argon gas stream at temperatures around −60 °C. Nondegenerate absorptions were 2–3 cm^{-1} in width at half-height and, routinely, there were no shoulders on the low-frequency side of absorptions. In addition, the photoproduct that was formed was a known mononuclear complex. These observations were taken as evidence of good isolation. Photolyses were performed with a variety of light sources in attempt to optimize the yield of $CH_3COCo(CO)_3$. Most commonly 254-nm light from a low-pressure mercury lamp (2.5 cm long) or $\lambda > 310$-nm light from a medium-pressure mercury lamp were used. The latter selection of wavelength was attained by using a crown glass filter. Spectra were recorded by using either a Beckman 4260 infrared spectrophotometer or a Perkin-Elmer 1760 Fourier transform infrared spectrometer. Most of the spectra taken by the Beckman spectrometer were recorded with 1.5–2 cm^{-1} resolution and were digitized every 0.2 cm^{-1}. Frequently the spectra were signal averaged. The FT-IR spectra were run at 1 cm^{-1} resolution with a 0.5 cm^{-1} point interval. The interferograms were transformed by using Norton–Beer apodization. Typically, 20 spectra were taken. Peak areas were obtained by fitting the digitized spectrum by a product of Gaussian and Lorentzian band shapes and then calculating the area of the theoretical peaks by using a trapezoidal sum. These procedures and those for obtaining the force fields have been described elsewhere.[1]

Results and Discussion

Perturbations in the Spectrum of $CH_3COCo(CO)_4$. The local symmetry at cobalt of $CH_3COCo(CO)_4$ (I) is presumed to be the same as that of $CH_3Co(CO)_4$ or $HCo(CO)_4$.[2,3] The latter molecules are of C_{3v} symmetry, with the methyl group or the hydride in an axial position of a trigonal bipyramid. The crystal structure of $CH_3COCo(CO)_3I^-$ is similar, with the iodide and acetyl groups in axial positions.[4] When $RCo(CO)_4$ is of C_{3v} symmetry, it is expected to give three bands in the region of the infrared spectrum in which terminal carbonyls absorb, two of A_1 symmetry and one of E symmetry. The spectrum of I shows four strong bands rather than three. Also, the band at 2011 cm^{-1} was broader than the others and unsymmetrical, occasionally exhibiting discrete peaks. If the acetyl group is indeed in the axial position, then it must strongly perturb the equatorial carbonyl groups.

This splitting of what in C_3 symmetry would be an E symmetry mode is abnormal. Therefore, a calculation of an energy factored force field for I and its isotopomers has been attempted. Calculations based on C_{2v}, C_s, and C_1 symmetries have been made. The force field of C_s symmetry yielded the best fit, with an average deviation from the observed frequencies of 0.3 cm^{-1} over 12 unique absorptions. If the true symmetry were C_s, then $CH_3COCo(CO)_4$ possesses a similar structure as $CH_3Co(CO)_4$ with some sort of distortion that makes one of the equatorial carbonyl groups unique. The values of the force constants are tabulated in Table I, while the results for fitting several isotopomers can be found in the supplementary material.

Table I. Force Constants ($N \bullet m^{-1}$) Used To Fit the Spectrum of $CH_3COCo(CO)_4$ and $CH_3COCo(CO)_3$

	$CH_3COCo(CO)_4$	$HCo(CO)_4$[a]	$CH_3COCo(CO)_3$
k_1[b]	1734.4 ± 2.8	1734.2	1712.2 ± 8.9
k_2[c]	1716.0 ± 2.8		
k_3[d]	1674.1 ± 1.5	1706.4	1621.0 ± 4.7
k_{12}[e]	24.7 ± 1.7		
k_{13}	36.5 ± 0.6	30.0	37.4 ± 3.3
k_{34}	40.9 ± 1.7	40.9	43.7 ± 5.0
k_{24}	28.9 ± 0.5		

[a] Taken from ref 1. [b] Force constant for the axial carbonyl. [c] Force constant for the unique equatorial carbonyl. [d] Force constant for the equatorial carbonyl which is equivalent to one or more other equatorial carbonyls which is identified as 4. [e] The index of the interaction force indicates which diagonal elements are linked.

Interestingly, the other symmetries gave results which, on average, fit the observed frequencies to within ±0.6 cm^{-1} and the magnitudes of the force constants were not grossly different from analogous constants of $HCo(CO)_4$ or the force field of C_s symmetry. Crude intensity calculations were made which could only fit the observed spectrum by assuming unrealistic bond angles. Darensbourg has made detailed studies of the infrared intensities observed from a series of molecules, $XM(CO)_4$, of C_{3v} symmetry.[8] He concluded that infrared intensities could not be used to calculate the structures of those molecules, especially when X possessed π bonding capabilities. The structure of $CH_3COCo(CO)_3I^-$ is instructive in understanding the perturbation that might cause the splitting of the E mode.[4] The methyl group eclipses one of the carbonyls and forces it to bend below the plane formed by the cobalt atom and the other two equatorial carbonyl carbon atoms. The Co–C–O bond angle is also distorted from the ideal 180°. The infrared spectrum of this molecule exhibits a large splitting of 12 cm^{-1} in what would be an E mode, were there no perturbation. With the assumption that $CH_3COCo(CO)_4$ is not more distorted than $CH_3COCo(CO)_3I^-$, these results support Darensbourg's reservations.

The magnitude of the force constants is compatible with a structure in which one of the carbonyl groups in the equatorial plane has been uniquely affected by the acetyl group. The 1716 $N{\cdot}m^{-1}$ is higher than what is observed for the other two carbonyl ligands in the equatorial plane and is also greater than the force constants for the equatorial carbonyls of the unencumbered $HCo(CO)_4$. If the unique carbonyl were bent out of the plane in the same way that is observed for $CH_3COCo(CO)_3I^-$, then it would participate less in π bonding with the metal, thus leading to a larger force constant.

The acetyl group of I gives rise to an infrared band at 1725 cm^{-1}. The deuterated molecule gives rise to two bands in the same region, at 1734.0 and 1705.4 cm^{-1}. Both bands are assigned to the carbonyl group of the deuteriated acetyl group for the following reasons: Warming a matrix caused the band at 1734.0 cm^{-1} to become attenuated as the other band grew. When the band at 1705 cm^{-1} is present, the band at 1734 cm^{-1} is not as intense as it should be relative to the bands in the terminal CO stretching region. Finally, ultraviolet irradiation causes both bands

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Table II. Positions of Terminal Carbonyl Absorptions of $CH_3COCo(CO)_4$ (I), $CH_3COCo(CO)_3$ (II), and $CH_3Co(CO)_4$ (III)

position (cm^{-1})^a	assignt	position (cm^{-1})^a	assignt
2112.0	I	2016.5	III^b
2108.6	III	2012.5	I^b
2081.1	II	2009.5	I^b
2051.3	I	2008	II^c
2037.6	III	2004.7	I^b
2030.3	I	1990.0	$CH_3Co(CO)_3$
2025.0	III^b	1977.3	II
2023.3	III^b		

^{a} Positions are ±1 cm^{-1}, except where the bands are poorly resolved. ^{b} Bands due to E mode appear split in these experiments. The splitting was not always resolved. ^{c} Band position obtained by computer subtraction.

to become attenuated by about the same amount. The two bands are assigned to the carbonyl modes of different rotomers of I. The spectra of matrix-isolated $CH_3COMn(CO)_5$ and $CH_3COFeCp(CO)_2$ give evidence of differentiable rotomers as well.[5,6] The fact that only a single rotomer of the protic form is observed in argon matrices must be due to a kinetic advantage. As the matrix-gas mixture impacts on the cold crystal surface, its temperature drops precipitously. These observations suggests that the protic acetyl group can attain its most stable configuration before it has lost too much thermal energy. The deuterium isomer must not be able to completely isomerize to the low-temperature form before the temperature has become too low. In methane, the protic form of I does exhibit a weak absorption that correlates with the band at 1705 cm^{-1}. Interestingly, the two rotomers are not differentiable by changes in the terminal CO stretching region of the spectrum. The absence of strong coupling will be a key argument in what follows.

Table III. Wavenumbers Observed for $CH_3COCo(CO)_4$ and $CH_3COCo(CO)_3$^{a}

isotopic composition of the acetyl group				
$CH_3{}^{12}C^{16}O$	$CD_3{}^{12}C^{16}O$	$CH_3{}^{13}C^{16}O$	$CH_3{}^{12}C^{18}O$	assignt
1723.5 (58.4)^b	1733.5 (29.1)^b	1685.7	1688.9	acyl C–O, I
	1704.8 br (13.4)			acyl C–O, I
1685.9 (9.4)^c	**1687.0 (10.0)**	*e*		acyl C–O, II
1421.2 (1.7)		1419.6		C–H deformation, I
1414.2 (1.1)		1413.2		C–H deformation, I
1344 (3.3)^c	**980.3 d (14.5)**	**1344.2 sh**		C–H deformation, II
1337.8 (2.4)	927.4 d (17.8)	1337.8		C–H deformation, I
1121.7 (10.0)^c	**1134.6 (10.0)**	**1101.2**	**1122.5**	CH_3–CO–Co skeletal, II
1060.1 (10.0)	1084.8 (10.0)	1049.3	1058.8	CH_3–CO–Co skeletal, I
936 sh (2.7)^c		**934 sh**		CH_3–CO–Co skeletal, II
910.2 (4.4)		896.6	909.8	CH_3–CO–Co skeletal, I

^{a} Error in each frequency is ±1.0 when a band is well resolved. All data has been corrected to vacuum conditions by using calibration spectra of DCl, NH_3, H_2O, and CH_4. ^{b} Relative intensities in parentheses. ^{c} Data that are in boldface type are due to $CH_3COCo(CO)_3$ (II). ^{d} The C–D band appears with anomolous intensity due to Fermi resonance. ^{e} Position is obscured by the C–O stretch of the acetyl group of the $^{13}C^{18}O$ isotoper of I. A shoulder does grow in at about 1947 cm^{-1} which may be the C–O of the acetyl group of II.

Photochemistry of $CH_3COCo(CO)_4$. When argon matrices of I are irradiated with ultraviolet light with λ > 310 nm or with a low-pressure mercury lamp, new bands are observed which are due to $CH_3Co(CO)_4$.[1] Also, after brief periods of photolysis new bands appear which behave as if they belong to an intermediate (II). A band at 2137.9 cm^{-1} which is due to free CO also becomes more intense after brief exposure. The observation of the spectrum of II is complicated by the fact that bands due to the parent $CH_3COCo(CO)_4$ (I) and the product $CH_3Co(CO)_4$ (III) are observed in the same regions of the spectrum. Consistent with the behavior of an intermediate, the bands due to II are never observed in high yield or in the absence of bands due to the other species. In fact, one of the carbonyl bands at 2008 cm^{-1} is best seen by computer subtraction. Bands at 2081, 2008, 1977, 1686, 1344, 1122, and 936 cm^{-1} are assigned to II. The positions and relative intensities of the three terminal CO stretching modes are similar to the spectrum of one of the isomers of $CH_3Co(CO)_3$, a molecule which can be viewed as a derivative of its parent, $CH_3Co(CO)_4$ (C_{3v}), with an equatorial vacancy.[1] The bands at lower frequency correlate with bands assigned to the acetyl group of I suggesting that the acetyl group is still intact[9] (see Table III). A force field calculation has also been attempted by using the carbonyl bands of II and those of isotopomers. These results are summarized in Table I and in the supplementary material. The resulting force constants are less than what is observed for I. A decrease in the magnitudes is expected for a coordinatively unsaturated complex. From these data, II is best formulated as $CH_3COCo(CO)_3$. The chemistry can be described by the following scheme.

$$CH_3COCo(CO)_4 \xrightarrow{h\nu} CH_3COCo(CO)_3 + CO$$

$$CH_3COCo(CO)_3 \xrightarrow{h\nu} CH_3Co(CO)_4$$

The ultraviolet spectrum of I exhibits an intense absorptions for λ < 250 nm. There is a shoulder at 270 nm. The photochemistry of I that is observed is independent of wavelength. A medium-pressure mercury lamp is capable of converting I into II with soda-lime glass filtering for which λ > 310 nm. When λ < 300 nm, the product $CH_3Co(CO)_4$ is also photosensitive and some amounts of $CH_3Co(CO)_3$ are observed, especially with prolonged irradiation periods. Although no absorptions are apparent in the visible for II, it does convert slowly into $CH_3Co(CO)_4$ when exposed to the visible radiation from the Nernst glower. This conversion is also affected by ultraviolet photons. A variety of filters were used in attempts to optimize the yield of II, with no success.

The characterization of the CO stretch of the acetyl group of II has been problematic. The band that appears at 1686 cm^{-1} is not as intense as one might expect it to be, based on the spectrum of I. The frequency of the CO stretch of the acetyl group is enough displaced from that of the terminal carbonyls that large coupling of the modes is not expected. Any changes of energy or intensity of the acetyl carbonyl stretch should reflect real changes in the bonding between the acetyl group and cobalt. The intensity of the band at 1686 cm^{-1} is approximately 10% of the intensity of the most intense band in the carbonyl region. By contrast, the carbonyl stretch of the acetyl group of I is approximately 40% as intense as the most intense bands of I. The weakness of the carbonyl stretch can be evaluated by another criterion. In II the skeletal mode at 1122 cm^{-1} is nearly as intense as the carbonyl stretch of the acetyl group, whereas the carbonyl stretch of the acetyl group of I is considerably more intense than

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[9] In particular, this appears to rule out the possibility that ketene is formed and coordinates the unsaturated complex. Hommeltoft, S. I.; Baird, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 2548–2549.

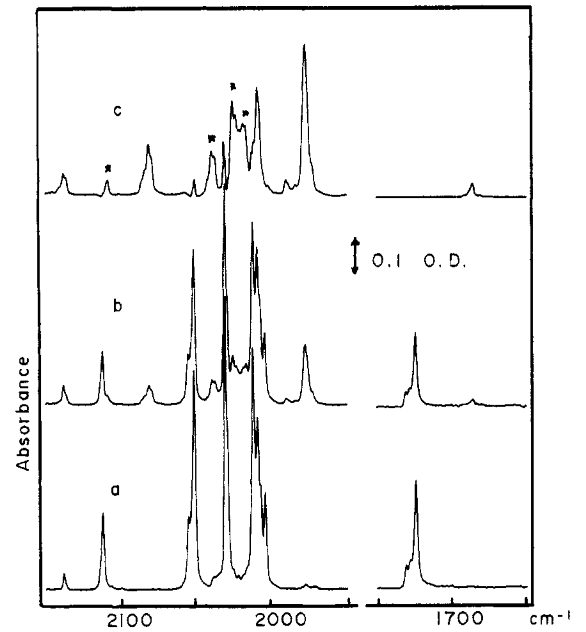

Figure 1. (a) Spectrum of $CH_3COCo(CO)_4$ in argon matrix having been deposited for 90 min from subliming solid at -60 °C. Data taken using FT-IR with 1 cm^{-1} resolution. (b) After 10 min of irradiation with a phosphor-coated low-pressure mercury lamp designed to give maximum intensity at 302 nm. (c) This spectrum was obtained by subtracting the spectrum of (a) from that of (b) in such a way as to just remove the band at 1724 cm^{-1}. The scale is expanded 4× that used in spectra (a) and (b). Peaks marked by an asterisk are due to $CH_3Co(CO)_4$. The weak absorption at 1990 cm^{-1} is due to $CH_3Co(CO)_3$.

any of the other skeletal vibrations of the acetyl group. This evidence is one of several data that indicate that the acetyl group is considerably perturbed. Also, the skeletal modes of the acetyl group are considerably shifted by 37 and 61 cm^{-1} when a terminal carbonyl ligand is lost.[10]

The nature of the interaction between the acetyl group and the coordinatively unsaturated cobalt center of II cannot be easily deduced from the spectra, but it is clear from the behavior of II that the acetyl group has imparted some very unusual properties to the complex. Whereas $CH_3Co(CO)_3$ and $HCo(CO)_3$ react with H_2 in matrices to give complexes,[1] II does not. Instead, the formation of II and subsequent formation of $CH_3Co(CO)_4$ are unaffected by added H_2. II is unique in another way. Whereas $CH_3Co(CO)_3$ reacts readily with CO in a matrix to form $CH_3Co(CO)_4$,[1] II cannot recombine with CO to give I. Rather, II decarbonylates to form $CH_0Co(CO)_4$ upon further irradiation. While it is difficult to form CO-deficient species in CO matrices, II forms readily even in a CO matrix. Amazingly, when I is photolyzed in a ^{13}CO matrix, the $CH_3Co(CO)_4$ that forms shows little evidence of ^{13}CO incorporation. (See Figure 2.) From these experiments, it appears that II cannot react with potential ligands in the matrix. The same behavior has been noted by Rest in studies of $CH_3COMn(CO)_5$[5] and $CH_3COFeCp(CO)_2$.[6] Clearly, the rate constant for reaction with ligand is slower than for decarbonylation, but it is also true that the rate constant for CO uptake is uncharacteristically slow with respect to $CH_3Co(CO)_3$ or $HCo(CO)_3$; II is stabilized.

At ambient conditions, this stabilization of II might prolong the lifetime of the intermediate and might also lower the transition-state energy for the thermal reaction leading from I and II. Indeed, this appears to be the case. The activation enthalpies for decarbonylation of $CH_3COCo(CO)_4$[11] and $C_4H_9COCo(CO)_4$[12] are both around 19 kcal/mol. The bond energy estimate derived from these kinetic studies is substantially less than what was proposed as a typical Co-CO bond energy taken from thermochemical measurements of cobalt carbonyl clusters;[13] the reason for this being so may reside in the fact that the acetyl carbonyl group stabilizes the transition state. In both of the forementioned kinetic studies, the activation entropy was near zero, suggesting that the transition state was not purely dissociative.

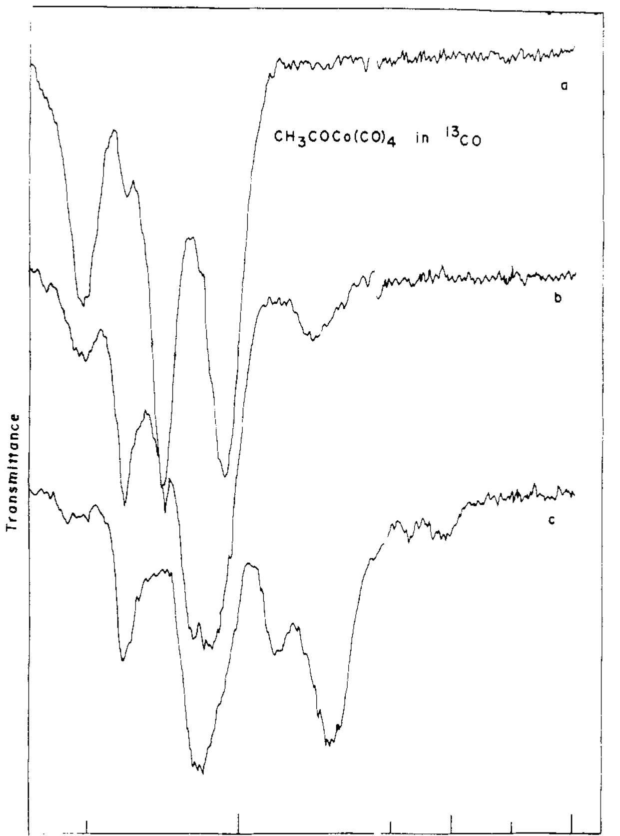

Figure 2. (a) Spectrum of $CH_3COCo(CO)_4$ in a ^{13}CO matrix having been deposited for 40 min at -60 °C. Data taken by the dispersive infrared spectrophotometer without signal averaging. (b) After 26 min of irradiation with a medium-pressure mercury lamp filtered by soda-lime glass. Large quantities of II do not accumulate with such irradiation. The spectrum shows the growth of $CH_3Co(CO)_4$ with mostly natural isotope abundances. This is to be contrasted with the behavior of $CH_3Co(CO)_4$ when it is irradiated at slightly higher frequencies as shown in trace c. (c) After 4 min of irradiation with an unfiltered medium-pressure mercury lamp.

Consider three possible explanations for the stabilization of II. (1) The steric crowding of I is relieved in forming II. To add a ligand requires a energetically significant deformation to attain the transition state. (2) The relaxation of crowding and the increase of electron density at cobalt make π bonding of the acetyl group much more important in II than in I. To add another ligand, this π bonding must be disrupted before attaining the transition state. (3) The acetyl group of II binds the metal as an η^2 ligand, affording a measure of stability. Of the three explanations, the first does not seem to be compatible with

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[10] Because of the mixing between the valence coordinates, it is difficult to assign an absorption to a vibration which is uniquely H_3C-C stretching and the CH_3-C-O deformation coordinate. Gordan, A. J.; Ford, R. A. *The Chemist's Companion*, Wiley: New York, 1972, p 197.

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[12] Kovacs, I.; Unvary, F.; Marko, L. *Organometallics* **1986**, *5*, 209-215.

[13] Skinner, H. A.; Conner, J. A. *Pure Appl. Chem.* **1985**, *57*, 79-88.

the near zero activation entropy.[11,12] Also, it is unlikely that the spectrum of the acetyl group would be so dramatically affected because the bond angles in the CH_3CO group of $CH_3COCo(CO)_3I^-$ are little perturbed from expected angles.[4] Finally, if the weak Co–CO bond energy found in kinetic studies were due to strain in I, then the magnitude of the strain might be on the order of 10 kcal/mol. This seems high when one realizes how readily five-coordinate complexes undergo fluxional processes.[14] The second and third explanations seem more in accord with the data because in either case one expects major perturbations in the spectrum of the acetyl group.

The substantially reduced intensity of the acetyl carbonyl stretch can best be explained by the η^2 formulation. The dipole moment derivative of the carbonyl group that is responsible for infrared intensity can be shorted out via the cobalt atom in a cyclic η^2 arrangement. During an extension of the C–O bond, the evolving charge on oxygen makes it a better donor to cobalt while the evolving positive charge on carbon makes the carbon a better acceptor from cobalt.[15] The C–O stretching frequency of the acetyl carbonyl group is not as low as is expected for stable η^2 complexes. Since there is no evidence to suggest that II is stable at ambient conditions, it would be surprising to find the frequency to be similar to those exhibited by stable η^2 complexes. In a recent study, Hermes and Girolami have reported crystal structures of an η^1-acyl complex and an η^2 complex related to the former by CO loss.[16] The C–O stretching frequency of the acyl group was reduced by approximately 40 cm^{-1}, a very similar shift as observed for I going to II. If the acyl group is bonded in an η^2 fashion, then the Co–C–O angle will certainly be less than 120°. The p character in the orbital that bonds to oxygen should be greater than what is found in a purely sp^2-hybrid orbital. Hence, the s character in the orbital that bonds to the methyl carbon might be expected to increase, making the bond stronger. This would lead one to expect a vibrational band shifted to higher energy than the corresponding band of the parent, as is observed for the bands at 1122 and 1060 cm^{-1} which are assigned to II and I, respectively.

It is difficult to understand how such a low intensity might arise if the acetyl group were bonded as an η^1 ligand. The C–O stretch of such a ligand would behave more as an isolated mode, and its intensity would not be expected to be very much different from that observed for I. Although changes in the Co–C bonding might impact the intensity, it has been observed that the greatest intensity for a terminal C–O stretch is associated with a carbonyl group the C–O stretching frequency of which is lowest.[8] Thus, one might expect the intensity of the C–O stretch of II to be more intense than that for I, if the bonding were η^1. Just the opposite is observed.

For the reasons stated above, II is assigned a structure in which the acetyl carbonyl group is bonded in an η^2 fashion. This interaction is established early as a carbonyl group is being lost. Bellus and Brown have claimed that acyl groups are cis labilizing;[17] from the behavior of I and the structure of II this property can be understood. It is probable that $Mn(CO)_4COCH_3$ and $CpFeCO(COCH_3)$ exhibit η^2 bonding.[7] Rest has assumed that the frequencies of the acetyl CO stretches were not low enough to support a claim of η^2 coordination. One should not expect, however, such a low carbonyl stretch in complexes which are not sufficiently stable to be observed at ambient temperatures. It should be pointed out that Ziegler has calculated a large stabilization for η^2 coordination of the acetyl group of $CH_3COMn(CO)_4$ by using HFS methods.[18] This contradicted results obtained by using extended Hückel calculations.[19] It is also important to point out that the η^2-complex may be a dead-end on the reaction path leading from $CH_3COCo(CO)_4$ to $CH_3Co(CO)_4$. The interaction may have to be disrupted so that methyl–cobalt interactions can be established.

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Registry No. I, 13964-92-6; I (isotopomer II), 117469-49-5; I (isotopomer IV), 117557-84-3; I (isotopomer V), 117469-51-9; I (isotopomer VII), 117557-85-4; I (isotopomer IX), 117469-52-0; I (isotopomer XI), 117557-86-5; I (isotopomer XII), 117469-54-2; II, 107556-38-7; II (isotopomer II), 117469-50-8; II (isotopomer IV), 117497-40-2; II (isotopomer VI), 117469-53-1; III, 14709-64-9; $NaCo(CO)_4$, 14878-28-5; $CH_3Co(CO)_3$, 112172-97-1; $CD_3{}^{12}C^{16}OCo(CO)_4$, 117469-43-9; $CD_3{}^{12}C^{16}OCo(CO)_3$, 117469-44-0; $CH_3{}^{13}C^{16}OCo(CO)_4$, 117469-45-1; $CH_3{}^{13}C^{16}OCo(CO)_3$, 117469-46-2; $CH_3{}^{12}C^{18}OCo(CO)_4$, 117469-47-3; $CH_3{}^{12}C^{18}OCo(CO)_3$, 117469-48-4.

Supplementary Material Available: A listing of the results of factored force field calculations for $CH_3COCo(CO)_4$ and $CH_3COCo(CO)_3$ (3 pages). Ordering information is given on any current masthead page.

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(14) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 8187–8194. Furthermore, ^{13}C NMR signals for unique axial and equatorial carbonyls were not observed. See ref 11.

(15) A weak band at 1490 cm^{-1} was characterized for an η^2-acyl complex of molybdenum: Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550–1561. Another η^2-acyl complex of molybdenum for which a moderately intense band at 1505 cm^{-1} is assigned to the C–O stretch. Carmona, E.; Sanchez, L.; Marin, J.; Poveda, M. L.; Atwood, J. L.; Priester, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214–3222.

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