Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802

Photoinduced Declusterification of $HCCo_3(CO)_9$, $CH_3CCo_3(CO)_9$, and $HFeCo_3(CO)_{12}$

GREGORY L. GEOFFROY* and RONALD A. EPSTEIN

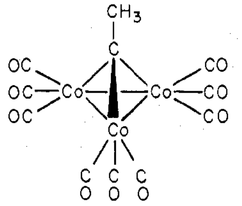
Received April 13, 1977 AIC70268O

Irradiation of solutions of $HCCo_3(CO)_9$ under an H_2 atmosphere with visible or UV light leads to quantitative formation of $Co_4(CO)_{12}$ and production of methane. Under a 3:1 H_2/CO atmosphere irradiation produces $Co_2(CO)_8$ with a 366-nm quantum yield of 0.03. Photolysis in the presence of D_2 has shown that the methane derives from the apical CH group and not from CO. Irradiation of $HCCo_3(CO)_9$ in the presence of H_2 and 1-hexene leads to catalytic isomerization to *cis*- and *trans*-2-hexene. The photochemical properties of $CH_3CCo_3(CO)_9$ parallel those of $HCCo_3(CO)_9$, except that no reaction is observed under an H_2/CO atmosphere. Irradiation of $HFeCo_3(CO)_{12}$ and $HFeCo_3(CO)_{10}(PPh_3)_2$ in degassed solutions also leads to declusterification with subsequent formation of $Co_4(CO)_{12}$ and $Co_2(CO)_6(PPh_3)_2$, respectively.

Introduction

Numerous organometallic cluster complexes have been prepared and studied in recent years, and the thermal reactivity of a large number of these is well documented.[1-3] The photochemical properties of organometallic clusters, however, have not been studied in detail although a few interesting reports have appeared.[4,5] Since photolysis of monomeric complexes often leads to very active species of both synthetic and catalytic utility, it is likely that photolysis of clusters may yield similar results. For this reason we have set out to explore the photochemistry of selected transition metal cluster complexes in detail and aim to develop an understanding of those factors which control cluster photoreactivity.

The first class of compounds that we have chosen to examine are the alkylidynetricobalt nonacarbonyl clusters, $YCCo_3(CO)_9$. A very large number of such clusters is known,[6-8] and Y can vary through a wide range of substituent groups. The structure of $CH_3CCo_3(CO)_9$ has been determined by x-ray diffraction[9] and is depicted in **1**. The core of this cluster consists of a triangle of metal–metal bonded cobalt atoms with a symmetrical triply bridging carbon atom forming the apex of a trigonal pyramid. The carbonyl groups are terminal in this example, although bridging carbonyls are found in some substituted $YCCo_3(CO)_{9-x}L_x$ clusters.[10] The chemistry of this class of compounds has been explored in great detail, although the majority of studies have centered on modifications of the substituent Y.[6-8] Studies of the chemistry of the Co_3C portion have focused mainly on reactions in which CO is replaced by other ligands, principally phosphines and arsines.[6-8,10]



1

We report herein the spectral and photochemical properties of $HCCo_3(CO)_9$ and $CH_3CCo(CO)_9$, the two simplest members of this class of compounds. These are compared to the structurally similar $HFeCo_3(CO)_{12}$ and $HFeCo_3(CO)_{10}(PPh_3)_2$, where in effect an $Fe(CO)_3$ unit has replaced the YC group and the hydride is believed to bridge the opposite face of the Co_3 triangle.[11]

Experimental Section

The complexes $HCCo_3(CO)_9$,[12] $CH_3CCo_3(CO)_9$,[13] $CH_3CCo_3(CO)_8PPh_3$,[10] $CH_3CCo_3(CO)_7(PPh_3)_2$,[10] $HFeCo_3(CO)_{12}$,[14] $HFeCo_3(CO)_{10}(PPh_3)_2$,[15] $Co_4(CO)_{12}$,[16] $Na[Co_3(CO)_{10}]$,[17] and $Co_2(CO)_6(PPh_3)_2$[18] were prepared by published procedures. All solvents were distilled from $LiAlH_4$ and degassed on a vacuum line prior to use. A 3:1 H_2/CO gas mixture was obtained from Matheson Gas Products and was used without further purification.

General Irradiation Procedures. Solutions to be irradiated were prepared on a vacuum line using specially constructed degassable quartz UV cells or Schlenk vessels. After heating the evacuated vessel to remove traces of adsorbed water, the compound to be studied was added and the vessel reevacuated. Due to the volatility of $HCCo_3(CO)_9$ and $CH_3CCo_3(CO)_9$, it was necessary to cool these samples in liquid nitrogen during evacuation. Dry and degassed solvent was then distilled into the vessel and the appropriate atmosphere placed over the sample. Irradiations were conducted at room temperature (21–25 °C) using a 450-W Hanovia medium-pressure Hg lamp equipped with the appropriate Corning glass filters ($\lambda \geq 500$ nm, Corning no. 3-69; λ 366 nm, Corning no. 7-83 narrow band-pass filter), a 100-W Blak-Ray B100A lamp equipped with a 366-nm narrow band-pass filter, and a Rayonet photoreactor equipped with 16 fluorescent tubes with λ_{max} 350 nm or with 254-nm low-pressure Hg lamps. Lamp intensities for quantum yield measurements were determined using ferrioxalate actinometry[19] and were of the order of 6.36×10^{-7} einstein/min at 366 nm.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer using 0.5-mm path length NaCl solution infrared cells. These cells were sealed with serum caps and purged with N_2 in order to record spectra of air-sensitive compounds. A Varian 1400 gas chromatograph with a 25-ft SE-30 column was used for analysis of the hexene solutions. A du Pont Model 830 liquid chromatograph equipped with a 254-nm UV detector and a 100 cm × 2.1 mm Corasil II-C_{18} reverse phase column was used for analysis of the $HFeCo_3(CO)_{10}(PPh_3)_2$ photolysis solutions. Mass spectra were recorded with an AEI MS902 mass spectrometer, and electronic absorption spectra were recorded on a Cary 17 spectrophotometer using 1.0-cm path length quartz cells. Spectra at 77 K were recorded in 5:5:2 diethyl ether/isopentane/ethanol (EPA) or 1:1 diethyl ether/isopentane solution using a quartz Dewar. Low-temperature spectra were corrected for solvent contraction.

Results

Electronic Absorption Spectra. Electronic absorption spectral data for $HCCo_3(CO)_9$, $CH_3CCo_3(CO)_9$, $CH_3CCo_3(CO)_8PPh_3$, $HFeCo_3(CO)_{12}$, and $HFeCo_3(CO)_{10}(PPh_3)_2$ are set out in Table I. The 300 and 77 K spectra of $CH_3CCo_3(CO)_9$ are shown in Figure 1, and these spectra are representative of all the compounds examined. Each of the clusters shows a broad band in the visible spectral region with a maximum between 502 and 592 nm and two well-defined shoulders at 370–400 and 290–325 nm on a rising absorption into the UV. These bands sharpen considerably upon cooling to 77 K and the broad absorption in the visible region is seen to be comprised of two distinct transitions. To aid interpretation, spectral data for $Na[Co_3(CO)_{10}]$ was obtained and is included for comparison in Table I.

Photolysis of $HCCo_3(CO)_9$. Irradiation of degassed solutions of $HCCo_3(CO)_9$ with 254-, 350-, or 366-nm light leads only to very slow decomposition. For example, a benzene solution of the cluster that had been irradiated at 350 nm for 6 h showed only a 2% decrease in the principal absorption band

Table I. Electronic Absorption Spectral Data

	300 K[a]		77 K[b]	
Cluster	λ_{max}, nm	ϵ_{max}	λ_{max}, nm	ϵ_{max}
$HCCo_3(CO)_9$	505	1 590	470	2 240
	370 sh	3 740	360	3 780
	290 sh	13 500		
$CH_3CCo_3(CO)_9$	510	1 840	475	2 430
			448	2 320
	370 sh	3 680	360	3 750
	295 sh	13 600		
$CH_3CCo_3(CO)_8PPh_3$	502[c]	2 490	485	3 830
			466	3 770
	400 sh	5 320	390	8 080
	310 sh	16 170		
$HFeCo_3(CO)_{12}$	528	3 980	591[d]	
			525	5 150
	380 sh	6 940	377	9 510
	324 sh	11 000	324	13 270
	280 sh	12 400		
$HFeCo_3(CO)_{10}(PPh_3)_2$	680 sh[c]	2 450	660	4 070
	592	4 590	580	7 790
	381	12 140	380	17 370
	308	16 350	305	16 290
$Na[Co_3(CO)_{10}]$	505 sh			
	371 sh			

[a] 2,2,4-Trimethylpentane solution. [b] Diethyl ether/isopentane/ethyl alcohol (5:5:2) solution. [c] CH_2Cl_2 solution. [d] Diethyl ether/isopentane (1:1) solution.

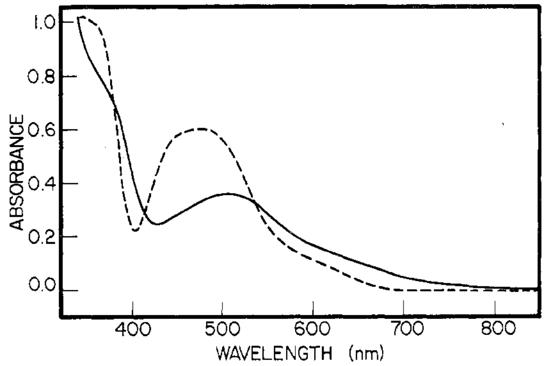


Figure 1. Electronic absorption spectra of $CH_3CCo_3(CO)_9$ at 300 K (—) and 77 K (---) in EPA solution.

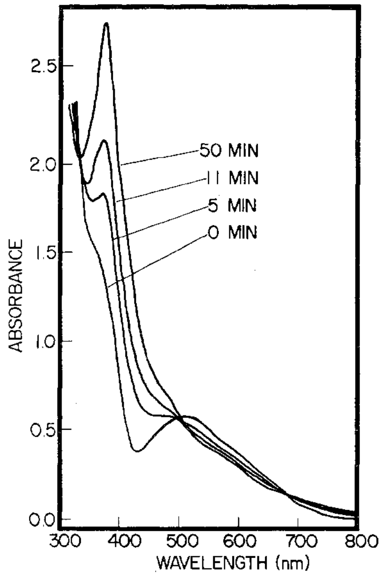


Figure 2. Electronic absorption spectral changes during 366-nm irradiation of $HCCo_3(CO)_9$ in hexane solution under an H_2 atmosphere.

at 505 nm. The cluster showed similar stability when irradiated with 254 nm.

The cluster is quite photosensitive, however, when irradiated with visible or UV light *in the presence of* H_2. As the irradiation proceeds, solutions rapidly change color from reddish purple to yellow-brown, and the electronic absorption spectral changes shown in Figure 2 are obtained. The final spectrum shown is identical with that of a pure sample of $Co_4(CO)_{12}$ and indicates its formation. Further evidence for production of $Co_4(CO)_{12}$ comes from monitoring the photolysis in the infrared spectral region where a smooth decrease in the ν_{CO} bands due to $HCCo_3(CO)_9$ is observed, and bands at 2063, 2055, 2038, 2028, and 1867 cm^{-1}, characteristic of $Co_4(CO)_{12}$,[20] grow in. Mass spectral analysis of the gases above irradiated solutions showed formation of substantial quantities of methane, and hence the overall reaction is that summarized in eq 1. Production of $Co_4(CO)_{12}$ was shown to be quantitative by measuring the final intensity of its characteristic absorption band at 373 nm (ϵ 10 500).[21] The photoreaction can be induced by irradiation with $\lambda \leq 500$ nm, but spectral overlap has precluded quantum yield measurements. Importantly, no reaction was observed when solutions of $HCCo_3(CO)_9$ were stored under a hydrogen atmosphere in the dark, although decomposition to $Co_4(CO)_{12}$ plus other unidentified products did occur when hexane solutions of $HCCo_3(CO)_9$ were heated to reflux under an H_2 purge.

$$4HCCo_3(CO)_9 + 6H_2 \xrightarrow{h\nu} 3Co_4(CO)_{12} + 4CH_4 \quad (1)$$

Photolysis of benzene, pentane, or isooctane solutions of $HCCo_3(CO)_9$ under a 3:1 mixture of hydrogen and carbon monoxide also leads to rapid photoreaction. Mass spectral analysis confirmed the production of CH_4, but other carbon-containing products were not detected. The growth of bands at 2070, 2043, 2025, and 1858 cm^{-1} in the infrared region[22] and the appearance of a band at 350 nm[23] in the electronic absorption spectrum indicate that $Co_2(CO)_8$ is produced. Formation of $Co_2(CO)_8$ was shown to be quantitative by monitoring the 350 nm (ϵ 5500)[23] absorption band, and the overall reaction under H_2/CO is summarized in eq 2. The reaction can be induced by photolysis with $\lambda \leq 500$ nm, and the quantum yield of disappearance of $HCCo_3(CO)_9$ measured at 366 nm under a 3:1 H_2/CO atmosphere is 0.03. Photolysis of the cluster under a pure CO atmosphere leads to very slow formation of $Co_2(CO)_8$. For example, after 3 h photolysis with 350 nm, only 20% disappearance of $HCCo_3(CO)_9$ was detected whereas under an H_2/CO atmosphere the reaction is complete within 1 h. The organic products from photolysis under CO were not identified.

$$2HCCo_3(CO)_9 + 3H_2 + 6CO \xrightarrow{h\nu} 2CH_4 + 3Co_2(CO)_8 \quad (2)$$

It was of obvious importance to determine the source of the methane produced. Mass spectral analysis of the gases above a solution of $HCCo_3(CO)_9$ that had been irradiated under a D_2/CO atmosphere showed only the presence of CHD_3, and no CD_4 was detected. We thus conclude that all the methane formed comes from the initial apical CH group and no hydrogenation of carbon monoxide occurs.

The conversion of $HCCo_3(CO)_9$ into $Co_4(CO)_{12}$ cannot be direct and must proceed through formation of several intermediates. This is evidenced by our observation of a slow continual 2–5% increase in intensity of the 373-nm band of $Co_4(CO)_{12}$ for several days after irradiation had ceased. Attempts to identify the initially produced fragments have been largely unsuccessful, but we have observed that at least one is a catalyst for the isomerization of 1-hexene. When $HCCo_3(CO)_9$ is irradiated in neat 1-hexene under H_2, isomerization to *cis*- and *trans*-2-hexene (1:2.5) occurred but with no hydrogenation. Photolysis in degassed 1-hexene gave no change in the cluster nor isomerization. Hydrogen is thus essential for the reaction. Experiments have shown that the isomerization is photocatalytic since it continued long after the irradiation had ceased. For example, in a typical experiment a sample was irradiated for 1 h, giving 30% isomerization. After storage of the irradiated solution in the dark for 4 days, the isomerization had increased to 85%. In a separate experiment, we also observed that photolysis of $Co_4(CO)_{12}$ under H_2 in 1-hexene gave isomerization, but at a rate much slower than $HCCo_3(CO)_9$.

The photochemical properties of $HCCo_3(CO)_9$ were also examined in the presence of excess PPh_3. At room temperature, a slow thermal substitution of CO by PPh_3 occurs, giving approximately 10% conversion in 24 h. When degassed benzene solutions containing excess PPh_3 were irradiated with 350 nm, a very rapid reaction was indicated by the electronic absorption spectral changes. Infrared and thin-layer chromatographic analysis of a solution irradiated for 45 min showed the formation of $HCCo_3(CO)_8(PPh_3)$, $HCCo_3(CO)_7(PPh_3)_2$, and at least one other unidentified product. It appears that substitution of CO by PPh_3 can be photoinduced, but that progressive photochemical reactions complicate the process. These reactions were not examined further.

Photolysis of $CH_3CCo_3(CO)_9$. The photochemical properties of $CH_3CCo_3(CO)_9$ parallel those of $HCCo_3(CO)_9$. No photoreaction was observed in the absence of H_2, but when $CH_3CCo_3(CO)_9$ was irradiated under an H_2 atmosphere nearly quantitative formation of $Co_4(CO)_{12}$ occurred. The organic products of the reaction, as identified by mass spectroscopy, were ethylene and ethane in a ratio estimated as 1:2. When the irradiation was conducted under a D_2 atmosphere, complete scrambling of hydrogen and deuterium was found in the organic products. Surprisingly, no reaction occurred when the complex was irradiated under a mixture of H_2 and CO. The quantum yield of disappearance of $CH_3CCo_3(CO)_9$ under H_2 could not be measured but is at least an order of magnitude less than that of $HCCo_3(CO)_9$ under comparable conditions.

Photolysis of $HFeCo_3(CO)_{12}$ and $HFeCo_3(CO)_{10}(PPh_3)_2$. Although $HFeCo_3(CO)_{12}$ is photosensitive, its reactions are inefficient and the chemistry is not as simple as that observed for $HCCo_3(CO)_9$. Photolysis of degassed benzene or isooctane solutions with 350 nm leads to formation of $Co_4(CO)_{12}$ over a period of several days. A similar reaction is observed under an H_2 atmosphere. When irradiation was done under carbon monoxide, slow but nearly quantitative production of $Co_2(CO)_8$ occurred. The iron-containing products could not be isolated in a state of purity sufficient for identification.

The photochemistry of $HFeCo_3(CO)_{10}(PPh_3)_2$ is also complex and inefficient. Photolysis of degassed benzene solutions of $HFeCo_3(CO)_{10}(PPh_3)_2$ leads over a period of several days to cluster fragmentation and formation of $Co_2(CO)_6(PPh_3)_2$, as evidenced by monitoring the dimer's electronic absorption band at 392 nm.[23] High-pressure liquid chromatographic analysis[24] of a degassed benzene solution that had been irradiated for 2 days showed the presence of $HFeCo_3(CO)_{10}(PPh_3)_2$, $Co_2(CO)_6(PPh_3)_2$, and at least two other unidentified products.

Thermal Reactivity of $CH_3CCo_3(CO)_8PPh_3$ and $CH_3CCo_3(CO)_7(PPh_3)_2$. The triphenylphosphine derivatives of $CH_3CCo_3(CO)_9$ were prepared in order to examine their photoreactivity. They proved too thermally unstable, however, to examine under our reaction conditions. Although $CH_3CCo_3(CO)_8PPh_3$ was indefinitely stable in degassed isooctane solution, it slowly decomposed when placed under an atmosphere of hydrogen. $CH_3CCo_3(CO)_7(PPh_3)_2$ was even more reactive, giving slow decomposition even in degassed benzene solution. The electronic absorption spectrum taken after nearly all the original cluster had disappeared showed a band at 392 nm characteristic[23] of $Co_2(CO)_6(PPh_3)_2$ and shoulders at 318 and 333 nm. An immediate thermal reaction occurred when H_2 was admitted to a benzene solution of $CH_3CCo_3(CO)_7(PPh_3)_2$, and the electronic absorption spectrum of this solution indicated formation of $Co_2(CO)_6(PPh_3)_2$, along with other products.

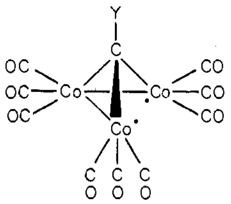
Discussion

Electronic Absorption Spectra. Examination of the available literature[6-8] leads to the observation that nearly all of the $YCCo_3(CO)_9$ clusters are similar in color, purple or reddish-purple, regardless of the nature of the Y group. This is illustrated by the spectral data summarized in Table I. The spectra of $HCCo_3(CO)_9$ and $CH_3CCo_3(CO)_9$ are virtually identical. Further, the spectrum of $HFeCo_3(CO)_{12}$ is remarkably similar to that of $HCCo_3(CO)_9$, showing only a slight red shift in the lower two absorption bands. This latter observation is surprising, since in effect the apical HC group is replaced by the vastly different $Fe(CO)_3$. Yet the spectral pattern does not change. A similar spectrum is also obtained for $[Co_3(CO)_{10}]^-$, in which a triply bridging carbonyl replaces the CY group, and substitution of phosphines for carbonyls in $CH_3CCo_3(CO)_9$ and $HFeCo_3(CO)_{12}$ leads only to an energy shift in the lower bands.

The similar color of nearly all the $YCCo_3(CO)_9$ clusters and the spectral data reported herein clearly indicate that the nature of the apical group perturbs only slightly, if at all, the low-lying electronic transitions in these clusters. Hence the transitions must be localized primarily within the Co_3 framework. Furthermore, the conclusion that the lowest unoccupied molecular orbital is localized within the Co_3 framework is supported by recent ESR studies.[25,26] The ESR spectra of the one-electron reduction products from a number of $YCCo_3(CO)_9$ clusters have been shown to be compatible with the added electron residing in an orbital encompassing only the three cobalt atoms, with little spin density delocalized onto the apical carbon. A molecular orbital analysis performed by Strouse and Dahl[27] for the $XCo_3(CO)_9$ (X = S, Se) clusters would suggest that the observed bands in the $YCCo_3(CO)_9$ clusters are due to transitions from nonbonding to antibonding metal–metal orbitals.

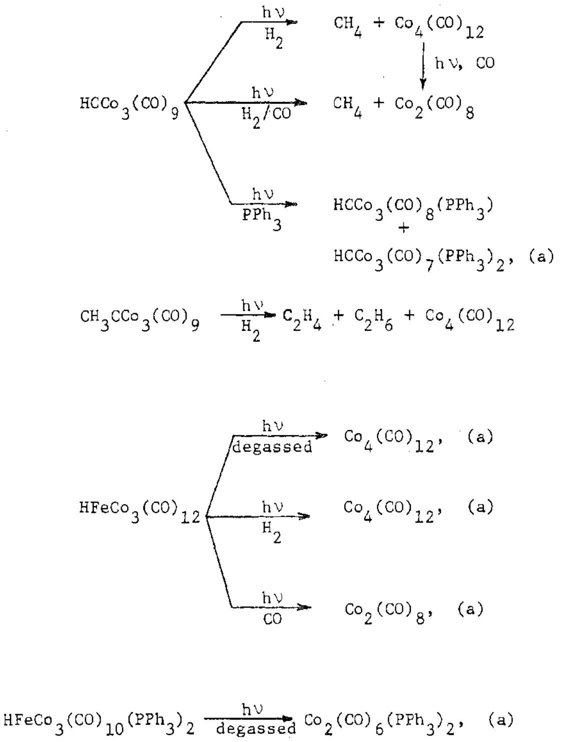
Photochemistry. The photochemical reactions observed in this study are summarized in Scheme I. In general, they represent photoinduced declusterification followed by redistribution of the $Co(CO)_3$ units. In the absence of CO, $Co_4(CO)_{12}$ is obtained, whereas $Co_2(CO)_8$ results when CO is available. It is further necessary to have H_2 present in order to observe rapid declusterification of $HCCo_3(CO)_9$ and $CH_3CCo_3(CO)_9$, although $HFeCo_3(CO)_{12}$ and $HFeCo_3(CO)_{10}(PPh_3)_2$ are photoactive even in degassed solution.

If, as we propose, the lowest excited states in these clusters correspond to population of metal–metal antibonding orbitals, the overall bonding in the Co_3 triangle should be greatly weakened upon excitation. It is reasonable to assume that cleavage of one of the Co–Co bonds would result to generate a diradical such as that shown in **2**. Support for the assumption of metal–metal bond cleavage comes from studies of the $Ru_3(CO)_{12}$[28] and $H_3Re_3(CO)_{12}$[29] trimers, each of which



2

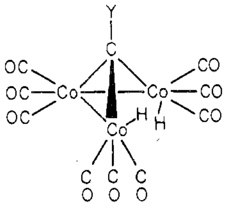
Scheme I



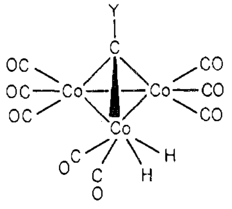
(a) plus unidentified products

gives photoinduced fragmentation to monomeric and dimeric compounds, respectively, and from the numerous studies[30] of metal–metal dimers which have been demonstrated to give cleavage of the metal–metal bond upon photolysis.

Two distinctly different mechanisms, each of which begins from **2**, can be written to explain the net photochemical transformation. The reaction can proceed by H_2 addition across the open Co–Co bond to generate a dihydride such as that shown in **3**. This complex could then eliminate H_2 to re-form $YCCo_3(CO)_9$, or hydrogen could migrate to the CY group. In the presence of additional H_2, this migration would likely be followed by further rapid hydrogenation to form H_3CY and $HCo(CO)_3$ fragments. Combination of these cobalt fragments with concomitant H_2 loss would generate $Co_4(CO)_{12}$ in the absence of CO or $Co_2(CO)_8$ in the presence of CO. The proposed formation of $HCo(CO)_3$ is supported by the observation of catalytic olefin isomerization when $HCCo_3(CO)_9$ is irradiated under H_2 in the presence of 1-hexene. $HCo(CO)_3$ has been implicated as the key intermediate in the isomerization of olefins catalyzed by $HCo(CO)_4$.[31]



3



4

The second mechanism would invoke thermal or photochemical dissociation of carbon monoxide from the radical centers which result from initial cleavage of the Co–Co bond. Such dissociation would leave open a coordination site on one of the cobalt atoms even if it were followed by rapid re-formation of the metal–metal bond. Oxidative addition of H_2 at this open site to give an intermediate such as **4** could occur, followed by hydrogen transfer to the apical carbon to yield declusterification as in the mechanism discussed above. Such an overall mechanism has close parallel to that proposed by Byers and Brown[32] to account for CO substitution in $HRe(CO)_5$. In this study, thermal dissociation of CO from the $\cdot Re(CO)_5$ radical intermediate was suggested to occur much faster than from nonradical $HRe(CO)_5$ and $Re_2(CO)_{10}$.

Support for the second mechanism comes from our observation that photolysis can lead to substitution of PPh_3 by CO in $HCCo_3(CO)_9$. Furthermore, if the second mechanism is operative, then the net photoinduced declusterification should be retarded in the presence of CO, since CO would compete with H_2 for the open coordination site. Although $CH_3CCo_3(CO)_9$ gives $Co_4(CO)_{12}$ when irradiated under an H_2 atmosphere, the declusterification was completely inhibited under a 3:1 H_2/CO atmosphere. In direct contrast, however, no CO inhibition of the declusterification of $HCCo_3(CO)_9$ was observed, and identical rates were obtained for photolysis under 10:25:75 $CO/H_2/N_2$ and 75:25 CO/H_2 atmospheres. It can also be argued that phosphine substitution is not inconsistent with the first mechanism since phosphine attack directly at the open coordination site resulting from metal–metal bond cleavage and subsequent loss of CO would lead to substitution.

The available experimental evidence does not allow us to define the overall mechanism for the photoinduced declusterification. The electronic absorption spectra and precedence from previous studies of metal trimers[28,29] and dimers[30] strongly suggest that the primary photochemical reaction is cleavage of one of the Co–Co bonds. Importantly, these studies do show that it is necessary to have H_2 present in order to induce declusterification of $YCCo_3(CO)_9$ since fragmentation can only proceed by removal of the CY group, and such removal is best accomplished through hydrogenation.[33]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant MPS 7505909) for support of this research.

Registry No. $HCCo_3(CO)_9$, 51900-20-0; $CH_3CCo_3(CO)_9$, 12328-59-5; $CH_3CCo_3(CO)_8PPh_3$, 22338-03-0; $HFeCo_3(CO)_{12}$, 21750-96-9; $HFeCo_3(CO)_{10}(PPh_3)_2$, 56009-83-7; $Na[Co_3(CO)_{10}]$, 26248-46-4; 1-hexene, 592-41-6.

References and Notes

(1) R. B. King, *Prog. Inorg. Chem.*, **15**, 287 (1972).
(2) P. Chini, *Inorg. Chim. Acta, Rev.*, **2**, 31 (1968).
(3) P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).
(4) M. S. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
(5) B. F. G. Johnson, J. W. Kelland, J. Lewis, and S. K. Rehani, *J. Organomet. Chem.*, **113**, C42 (1976).
(6) G. Palyi, F. Piacenti, and L. Marko, *Inorg. Chim. Acta, Rev.*, **4**, 109 (1970).
(7) B. R. Penfold and B. H. Robinson, *Acc. Chem. Res.*, **6**, 73 (1973).
(8) D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976).
(9) P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 261 (1967).
(10) T. W. Matheson, B. H. Robinson, and W. S. Tham, *J. Chem. Soc. A*, 1457 (1971).
(11) B. T. Huie, C. B. Knobler, and H. D. Kaesz, *J. Chem. Soc., Chem. Commun.*, 684 (1975).
(12) R. Ercoli, E. Santambrogio, and G. T. Casagrande, *Chim. Ind.* (*Milan*), **44**, 1344 (1962).
(13) W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc., London*, 169 (1961).
(14) P. Chini, L. Colli, and M. Peraldo, *Gazz. Chim. Ital.*, **90**, 1005 (1960).
(15) C. G. Cooke and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 455 (1975).
(16) P. Chini, V. Albano, and S. Martinengo, *J. Organomet. Chem.*, **16**, 471 (1969).
(17) S. A. Fieldhouse, B. H. Freeland, C. D. M. Mann, and R. J. O'Brien, *Chem. Commun.*, 181 (1970).
(18) A. R. Manning, *J. Chem. Soc. A*, 1135 (1968).
(19) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(20) G. Bor and L. Marko, *Spectrochim. Acta*, **16**, 1105 (1960).
(21) C. Frazier, Ph.D. Thesis, California Institute of Technology, 1975; H. B. Gray and W. C. Trogler, private communication.
(22) J. W. Cable, R. S. Nyholm, and R. K. Sheline, *J. Am. Chem. Soc.*, **76**, 3373 (1954).

(23) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Libienthal, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, **16**, 1554 (1977).
(24) C. T. Enos, G. L. Geoffroy, and T. H. Risby, *J. Chromatogr. Sci.*, **15**, 83 (1977).
(25) J. C. Kotz, J. V. Petersen, and R. C. Reed, *J. Organomet. Chem.*, **120**, 433 (1976).
(26) B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *Inorg. Chem.*, **16**, 405 (1977).
(27) C. E. Strouse and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 6032 (1971).
(28) B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organomet. Chem.*, **67**, C75 (1974).
(29) G. L. Geoffroy, R. Henderson, and W. L. Gladfelter, unpublished results; H. D. Kaesz, private communication.
(30) M. S. Wrighton, *Top. Curr. Chem.*, **65**, 37 (1976), and references therein.
(31) (a) D. S. Breslow and R. F. Heck, *Chem. Ind. (London)*, 467 (1960); (b) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961); (c) R. F. Heck, *ibid.*, **85**, 651 (1963).
(32) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **99**, 2527 (1977).
(33) $PhCCo_3(CO)_9$ was recently reported to catalyze the hydroformylation of 1- and 2-pentene (R. C. Ryan, C. U. Pittman, and J. P. O'Connor, *J. Am. Chem. Soc.*, **99**, 1986 (1977)), and an intermediate similar to **3** was suggested. No declusterification was observed, however, implying that hydrogen transfer to the apical PhC group does not readily occur in this cluster. Consistent with this notion, we have observed that $PhCCo_3(CO)_9$ is completely inert to photolysis even under an H_2 atmosphere.

Contribution from the Department of Biochemistry, College of Agricultural and Life Sciences,
and the School of Pharmacy, University of Wisconsin-Madison, Madison, Wisconsin 53706

Phosphorus-31 NMR Studies of Complexes of Adenosine Triphosphate, Adenosine Diphosphate, Tripolyphosphate, and Pyrophosphate with Cobalt(III) Ammines[1a]

R. D. CORNELIUS,*[1b] P. A. HART, and W. W. CLELAND

Received February 23, 1977 AIC701306

The complexes $Co(NH_3)_nHATP$ (n = 2, 3, or 4) and $[Co(NH_3)_nADP]$ (n = 4 or 5) have been prepared and isolated in solution. The complexes $Co(en)_2HP_2O_7$, $Co(NH_3)_nHP_2O_7$ (n = 4 or 5), and $Co(NH_3)_nH_2P_3O_{10}$ (n = 3 or 4) have been synthesized and crystallized. These and other phosphato complexes have been examined by ^{1}H and ^{31}P NMR. The ^{31}P NMR spectra of the simpler phosphato complexes provide definitive evidence of pyrophosphate both as a monodentate and as a bidentate ligand and of tripolyphosphate both as bidentate and as a tridentate ligand. In these simpler complexes chemical shift differences between the coordinated phosphates and the corresponding free ligands range from −7 to −14 ppm and provide a basis for the assignment of the spectra of $[Co(NH_3)_4ATP]^-$, in which ATP is entirely bidentate, and of $[Co(NH_3)_3ATP]^-$, in which a mixture of bidentate and tridentate isomers is observed. Sufficient differences in the chemical shifts of diastereomers of the nucleotide complexes make it possible to distinguish differences between the spectra of the two isomers of bidentate $[Co(NH_3)_4ATP]^-$ and of bidentate $Co(NH_3)_4ADP$ and among the spectra of the four isomers of tridentate $[Co(NH_3)_3ATP]^-$.

Introduction

The substitution-inert complexes between chromium(III) and ATP[2] prepared by DePamphilis and Cleland[3] have been used with considerable success to elucidate the kinetic mechanism of yeast hexokinase[4] and other enzymes.[5] In addition, chromium(III)–nucleotide complexes are of some value in determining the state of coordination of the nucleotide substrate with enzymes such as hexokinase, for which the β,γ-bidentate complexes show substrate activity.[4,6] Unfortunately, efforts to crystallize the isomers of CrATP have been unsuccessful, and the paramagnetism of d^3 chromium(III) precludes fruitful NMR studies as a means of structure determination. This paper describes the preparation in solution, characterization, and NMR spectra of diamagnetic substitution-inert complexes of cobalt ammines: $Co(NH_3)_4HATP$, $Co(NH_3)_3HATP$, and $Co(NH_3)_2HATP$. The tetraammine and the triammine exhibit substrate activity with yeast hexokinase[1] and can be used as models to establish the coordination state of the naturally occurring MgATP complex as it binds to the enzyme.

The desire for a definitive interpretation of the ^{31}P and ^{1}H NMR spectra of the ATP complexes described here demanded the preparation and characterization of simpler phosphato complexes for which assignment of the NMR spectra was straightforward; these complexes would serve as a good basis for chemical shift–coordination state correlations. Several phosphato complexes of cobalt amines have previously been reported. These include $Co(NH_3)_5PO_4$,[7,8] $Co(NH_3)_4PO_4$,[9] $[Co(NH_3)_4H_2O(HPO_4)]ClO_4$,[9] $Na[Co(NH_3)_5P_2O_7]$,[7] $Co(en)_2PO_4$,[10] and $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,HPO_4)\text{-}Co(NH_3)_4](NO_3)_3$.[11] Minimal characterization in solution of the product of the reaction between $[Co(NH_3)_4(H_2O)_2]^{3+}$ and $P_3O_{10}{}^{5-}$ has also been presented.[12] Interest in these complexes has been centered on the rates of formation, ring opening, and hydrolysis, but very little NMR data have been reported. The NMR spectra of complexes previously prepared are also recorded so that eventual correlations between O–P–O bond angles and chemical shifts of coordinated phosphates might be made. Such a correlation has recently been made for uncoordinated phosphates.[13]

The complexes of pyrophosphate and tripolyphosphate reported here provide data on the same metal coordination sphere as contained in the nucleotide complexes. Crystal structures of these complexes are of direct value in revealing for coordinated phosphates the spatial relationships which give rise to substrate activity for enzymes that accept the cobalt(III)–nucleotide complexes as substrates.

Experimental Section

Analytical Procedures. Elemental microanalyses of solid materials were performed by Galbraith Laboratories, Knoxville, Tenn. For solution samples, cobalt was determined spectrophotometrically[14] as cobalt(II) after reduction by stannous chloride,[8] the Kjeldahl method was used for nitrogen determination, and phosphorus was estimated spectrophotometrically as phosphomolybdate.

Previously Reported Complexes. The method of Schmidt and Taube[8] was used to prepare $[Co(NH_3)_5PO_4]\cdot 2H_2O$ from commercially obtained $[Co(NH_3)_5H_2O]Cl_3$. An attempt to prepare $Co(en)_2PO_4$ as described by Lincoln and Stranks,[10] but from *trans*-$[Co(en)_2Cl_2]Cl$[15] instead of the perchlorate salt, yielded a material which exhibited a visible spectrum in agreement with that reported but which had a ^{31}P NMR chemical shift not displaced from free orthophosphate ion at the same pH. The nature of the species actually prepared was not further investigated. A sample of $[(NH_3)_4Co\text{-}\mu\text{-}(NH_2,HPO_4)\text{-}Co$