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Cobalt Atom–Ethylene Cryochemistry: Synthesis and Spectroscopic Studies of $\text{Co}(\text{C}_2\text{H}_4)_l$, $\text{Co}_2(\text{C}_2\text{H}_4)_m$, and $\text{Co}_4(\text{C}_2\text{H}_4)_n$ and Chemisorption Models for Ethylene Adsorbed on Bulk Cobalt

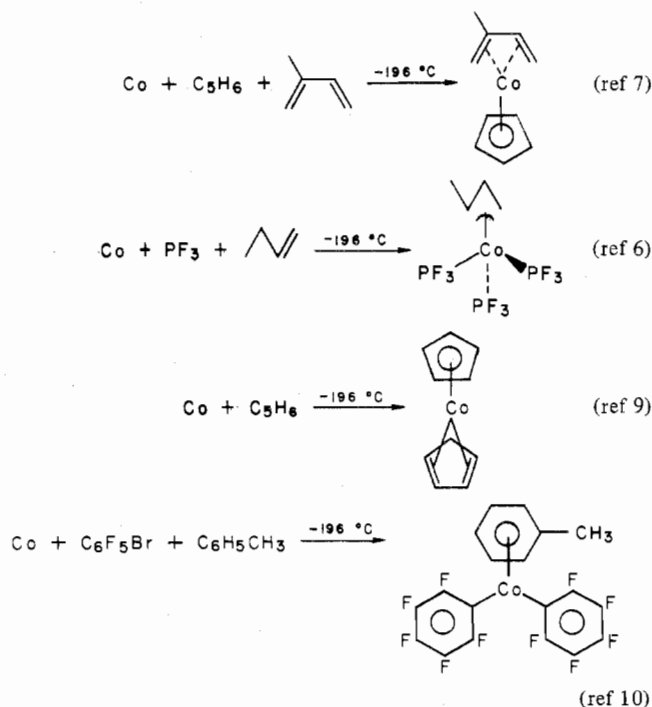
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The propensity of cobalt atoms to engage in facile matrix aggregation reactions in both low-temperature, weakly interacting supports (e.g., inert gases, alkanes, aromatics) and reactive supports (e.g., CO, N_2 , O_2) is found to extend to $\text{C}_2\text{H}_4/\text{Ar}$ and pure C_2H_4 matrices. By employing extensive Co atom matrix concentration and deposition-temperature techniques, $^{12}\text{C}_2\text{H}_4/\text{Ar}$ matrix ratio variations, $^{13}\text{C}_2\text{H}_4/\text{Ar}$ and $^{12}\text{C}_2\text{H}_4/^{13}\text{C}_2\text{H}_4/\text{Ar}$ isotopic substitution, Co/CO₂ matrix photochemical and bulk matrix annealing procedures, as monitored by infrared and UV-visible spectroscopy, it has proven possible to synthesize a novel series of mononuclear and binuclear binary cobalt–ethylene complexes $\text{Co}(\text{C}_2\text{H}_4)_l$ (where $l = 1, 2$) and $\text{Co}_2(\text{C}_2\text{H}_4)_m$ (where $m = 1, 2$) as well as a suspected tetranuclear species $\text{Co}_4(\text{C}_2\text{H}_4)_n$. Trends in their infrared and ultraviolet spectra with ethylene stoichiometry and cobalt cluster size, as well as comparisons with other binary ethylene complexes of nickel and copper, are considered. The usefulness of these kinds of binary ethylene complexes as localized bonding representations for ethylene chemisorbed on the corresponding bulk metal is also contemplated.

Introduction

The group 8 transition metals are renown for their pervasive catalytic activity¹ with the cobalt group being particularly useful for the hydroformylation of olefins in the well-known Oxo reaction.² In fact both homogeneous and heterogeneous catalytic reactions involving transition metals and olefins are extremely widespread,³ and this has recently stimulated considerable interest in metal atom–olefin cryochemistry on both a matrix spectroscopic^{4,5} and macropreparative scale.⁵ Although considerable emphasis has been placed on the metal atom–olefin chemistry of the Ni, Pd, and Pt^{4,5} triad, not a great deal is presently known about the corresponding Co, Rh, and Ir groups of metals. In brief, atomic cobalt has been shown to catalytically isomerize terminal olefins to internal olefins and nonconjugated dienes to their conjugated analogues,⁶ to disproportionate 1,3-cyclohexadiene to benzene and cyclohexene,⁷ to trimerize (and oligomerize) butadiene (in the absence or presence of other metals or ligands) to cyclododecatriene,⁸ and to be a generally useful atomic reagent for the synthesis of organocobalt complexes exemplified by



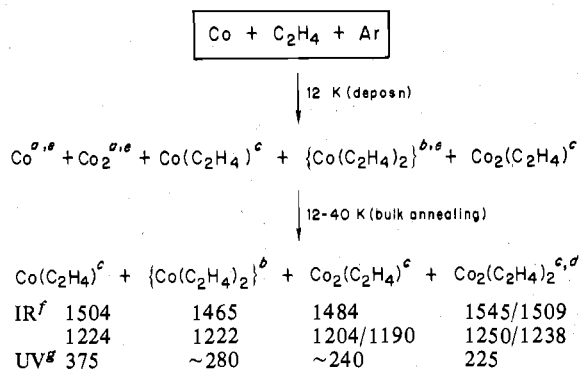
However, other than a brief conference report¹¹ on some highly labile $\text{Co}(\text{C}_2\text{H}_4)_3$, $\text{Co}(\text{C}_7\text{H}_{10})_3$, and $\text{Co}(\text{C}_8\text{H}_{12})_2$ compounds ($\text{C}_7\text{H}_{10} \equiv$ norbornene, $\text{C}_8\text{H}_{12} \equiv$ cyclooctadiene), whose stoichiometries were based solely on comparative infrared studies with the known, more stable nickel analogues, very little is actually understood about reactive intermediates and/or stable products formed from the interaction of atomic cobalt and olefins.

In view of our standing interest in “chemisorption models”, i.e., experimental representations of surface reaction intermediates composed of ligands interacting with atomic and small, well-defined metal cluster sites,¹² the cobalt–ethylene system is of special interest because of the facile matrix aggregation reactions of cobalt atoms recently demonstrated by Hanlan and Ozin¹³ and Klabunde and co-workers.¹⁴ Unlike atomic Ni¹⁵ and Pd,^{16a} where forcing conditions are required to form even metal diatomics, in the case of Co, the opposite was true; that is, it was difficult to isolate atoms at 12 K without the “contamination” of a fair proportion of dimer species.¹³ This suggested that the matrix synthesis of mononuclear and binuclear and possibly higher cobalt cluster–ethylene species might be practical under reproducible conditions allowing one to assess the effect of cobalt cluster size on the bonding, structural, and spectral properties of coordinated ethylene. In this way one can experimentally evaluate the boundary conditions suitable for a localized bonding description of ethylene chemisorbed on bulk cobalt and hopefully evaluate the general applicability of M_nL (supercoordinatively unsaturated) chemisorption models.¹²

In this context it is interesting to note that, in spite of the particular relevance of cobalt–ethylene interactions in catalysis, relatively few chemisorption surface spectroscopic studies have centered on this system.^{16b} Nihira and co-workers¹⁷ studied the competitive hydrogenation of olefins over cobalt oxide and deduced that the olefin was coordinated to the surface cobalt atoms in a π -complexed manner, where increasing alkyl substituents on the olefin decreased the energy of chemisorption. Wojtczak and co-workers¹⁸ examined the chemisorption of olefins on evaporated films of cobalt while Blyholder and Wyatt⁴⁶ studied olefins on silica-supported cobalt, in both the presence and absence of H_2 and CO, but neither made comment on the mode of olefin coordination in the unsaturated form.

In the report that follows we present, for the first time, matrix synthetic and spectroscopic details for a number of new binary cobalt–ethylene complexes. Both mononuclear $\text{Co}(\text{C}_2\text{H}_4)_l$ and binuclear $\text{Co}_2(\text{C}_2\text{H}_4)_m$ and a probable tetranuclear

Scheme I. Dilute Matrices



^a Seen in UV-visible (ref 13 and Figures 5, 7, 8). ^b Seen in 1/20 to 1/50 range; highly dependent on deposition conditions. No isotopic confirmation (see text). ^c ¹²C₂H₄/¹³C₂H₄(Ar) isotopic confirmation. ^d Predominates at high Co concentrations and after 35 K bulk annealing experiments. ^e { } indicate minor products under these reaction conditions. ^f Units in cm⁻¹. ^g Units in nm.

Co₄(C₂H₄)_n species are reasonably well characterized from these studies; their convergence behavior toward C₂H₄ ads is scrutinized and discussed. Furthermore, comparisons between these cobalt species and the recently reported nickel analogues¹⁹ have proven to be particularly enlightening in terms of analyzing vibrational and electronic spectral trends and cross-checking earlier stoichiometric, structural, and spectral assignments.

Experimental Section

Cobalt vapor was generated by directly heating a 0.01-in. ribbon filament of the metal with ac in a furnace similar to that previously described.²⁰ The rate of cobalt atom deposition was continuously monitored using a quartz crystal microbalance.²¹ The cobalt (99.99%) was supplied by McKay, N.Y. Research grade ethylene and argon (both 99.99%) were supplied by Matheson of Canada. Labeled ethylene (¹³C₂H₄, 91%) was supplied as research grade by Stohler Isotopes, Montreal.

In the infrared experiments matrices were deposited onto a CsI optical window cooled to the deposition temperature by means of an Air Products Displex closed-cycle helium refrigerator. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer. UV-visible spectra were recorded on a standard Varian Techtron in the range 190–900 nm, the matrix being deposited onto a NaCl optical window. Pure ethylene matrices were evaporated by continuous pumping (<10⁻⁵ torr) at 75 K.

Results and Discussion

Infrared Experiments. In comparison to the nickel atom-ethylene system,^{19,22} the cobalt atom-ethylene system appears at first somewhat confusing, due to the facile matrix aggregation of atomic cobalt¹³ as opposed to that of nickel¹⁵ and the prevalent overlap complications of the ν(C=C) and δ-(CH₂) modes of a number of the cobalt-ethylene complexes. These were only discernible with the aid of ¹²C₂H₄/¹³C₂H₄ mixed-isotope substitution and careful concentration and bulk annealing experiments. The end result of an extensive series of experiments is therefore summarized at the outset of this discussion in reaction Schemes I and II. These should greatly assist the reader with the spectral interpretive puzzle that follows.

Dilute Ethylene/Argon Matrices. Let us formalize the infrared experiments by initially focusing our attention on dilute C₂H₄/Ar ≈ 1/50 matrix condensations under Co concentration conditions which favor the isolation of mononuclear complexes in the presence of binuclear complexes; that is, Co/Ar ≈ 1/10⁴ at 12–15 K (note that we were never

Table I. Infrared Spectral Data (cm⁻¹) for M(C₂H₄)_m and M₂(C₂H₄)_m (Where M = Co or Ni and m = 1 or 2) in the ν(C=C) and δ(CH₂) Regions

	M = Co ^a	M = Ni ^a	assign
M(C ₂ H ₄)	1504	1490	ν(C=C)
	1224	1160	δ(CH ₂)
M(C ₂ H ₄) ₂	1465	1465	ν(C=C)
	1222	1223	δ(CH ₂)
M ₂ (C ₂ H ₄)	1484	1488	ν(C=C)
	1204/1190	1208/1180	δ(CH ₂)
M ₂ (C ₂ H ₄) ₂	1545/1509	1504	ν(C=C)
	1276/1250/1238	1232	δ(CH ₂)

^a ν(M-C) modes observed at 340 and 320 cm⁻¹ for Co₂(C₂H₄)₂ and at 446 and 416 cm⁻¹ for Ni₂(C₂H₄)_{1,2} are in line with the greater thermal stability of the cobalt-ethylene complexes.

Table II. ¹²C/¹³C Infrared Isotopic Data for Co(C₂H₄)₁, Co₂(C₂H₄)₁, and Co₂(C₂H₄)₂ in the ν(C=C) and δ(CH₂) Regions

ν(C=C)	δ(CH ₂)	complex
1504	1224	Co(¹² C ₂ H ₄)
1482	1204	Co(¹³ C ₂ H ₄)
1484	1204, 1190	Co ₂ (¹² C ₂ H ₄)
1454	1178	Co ₂ (¹³ C ₂ H ₄)
1545, 1509	1276, 1250, 1238	Co ₂ (¹² C ₂ H ₄) ₂
1516, 1488	1256, 1220, 1206	Co ₂ (¹³ C ₂ H ₄) ₂

Table III. Complete Infrared Spectra for Co₂(¹²C₂H₄)₂ and Co₂(¹³C₂H₄)₂

Co ₂ (¹² C ₂ H ₄) ₂ ^a	Co ₂ (¹³ C ₂ H ₄) ₂ ^a	assign
3048 w, sh		ν(CH ₂)
3000 m	2988	
2900 w	2986	
2876 w	2872	
1544 w	1516	ν(C=C)
1508 s	1488	
1420 w, sh	1416	δ(CH ₂)
1276 w	1256	
1248 w	1220	δ(CH ₂)
1234 s	1206	
340 w	332	
320 w	314	ν(Co-C)

^a Spectrum recorded after having sublimed away the pure ethylene matrix at 75–80 K (see text for details).

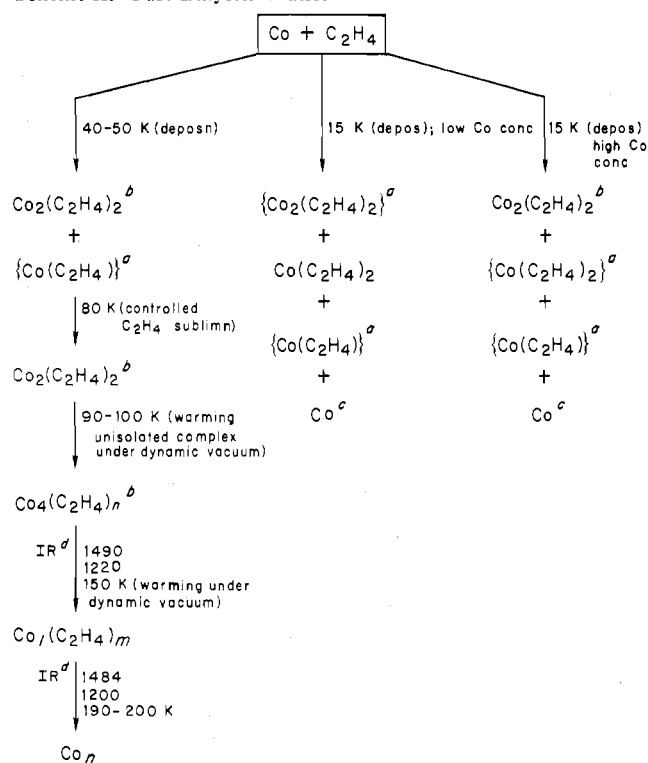
Table IV. Complete Infrared Spectrum of the Proposed Tetranuclear Complex Co₄(C₂H₄)_n^a Formed from the Dimerization of Co₂(C₂H₄)₂

2 Co ₂ (C ₂ H ₄) ₂	→ Co ₄ (C ₂ H ₄) _n ^a	assign
3048	3057	ν(CH ₂)
3000	2984	
2900	2948	
2876	2888	
1544/1508	1496/1492	ν(C=C)
1420	1416	δ(CH ₂)
1276/1248	1224	δ(CH ₂)
1234	1216	
340	460	ν(Co-C)
320	384	

^a The value of n is most likely 4 or 1 (see text).

entirely successful in eliminating binuclear complex formation; this was not surprising in view of the Co/Co₂/Ar aggregation studies of Ozin and Hanlan¹³). Under these circumstances, aside from the absorptions associated with uncomplexed ethylene in the Ar matrix (labeled E in all figures), new absorptions were observed at 1504, 1484, 1224, 1204, and 1190 cm⁻¹, the spectral range characteristic of ν(C=C) and δ(CH₂) vibrations of coordinated ethylene. A typical spectral trace is depicted in Figure 1A, complete spectra being listed in Tables I–IV (the method of identification of the cobalt-

Scheme II. Pure Ethylene Matrices



^a { } indicate minor products under these reaction conditions.
^b ¹²C₂H₄/¹³C₂H₄ isotopic data point to an *n* value of 1 or 4 (see text). ^c Seen in UV-visible spectrum (Figure 9). ^d Units in cm⁻¹.

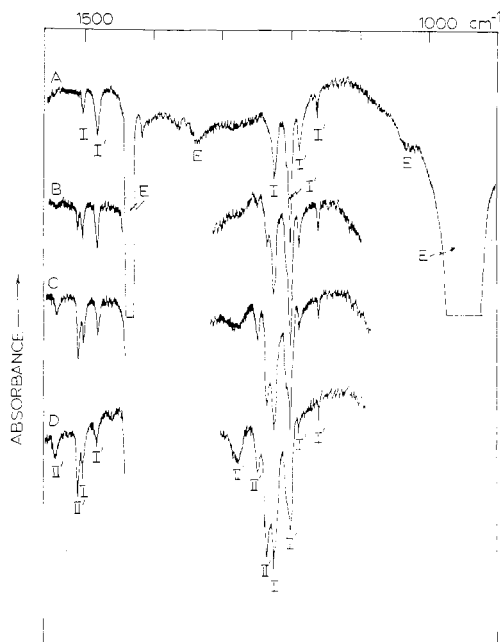


Figure 1. Matrix infrared spectra of Co atoms deposited with ¹²C₂H₄/Ar ≈ 1/50 mixtures, with Co/Ar ≈ 1/10⁴ at (A) 12 K and after warming to (B) 25, (C) 35, and (D) 40 K and recoiling to 12 K for spectral recording. E refers to unreacted ¹²C₂H₄ in the matrix, and I ≡ Co(C₂H₄), I' ≡ Co₂(C₂H₄), and II' ≡ Co₂(C₂H₄)₂.

ethylene complexes in this paper will, for the most part, make use of bands in the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ spectral regions such as was the case for the nickel,^{19,22} copper,²³ and palladium²⁴ ethylene studies, both because of their favorably high absorbances relative to other vibrational modes and because of their sensitivity to ¹²C/¹³C isotopic substitution in mixed ¹²C₂H₄/¹³C₂H₄/(Ar) matrices). In these discussions we, like

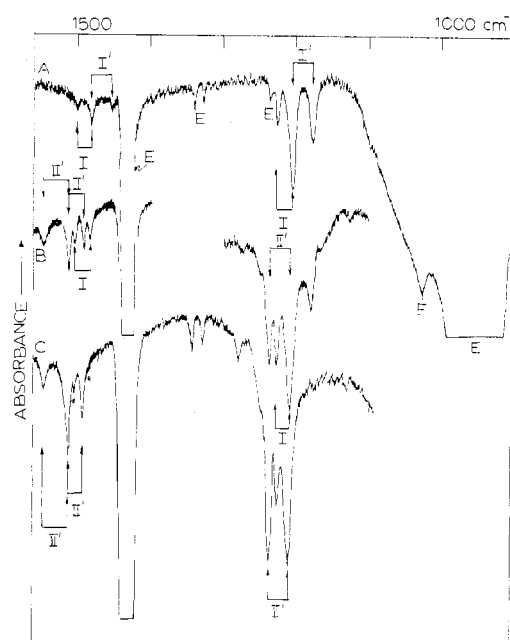


Figure 2. Similar experiments to those of Figure 1 except that ¹²C₂H₄/¹³C₂H₄/Ar ≈ 1/1/50 mixtures were used.

others, are aware of the vibrational coupling complications between the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ modes;²⁵ for the sake of clarity of presentation we will retain these labels without actually implying anything about the potential energy distribution between these two modes. At this point it should also be noted that the optical spectrum of the matrix corresponding to Figure 1A showed the presence of large amounts of unreacted cobalt atoms (Figures 7, 8), which, as we shall demonstrate later on, react on warming with free ethylene to yield cobalt-ethylene complexes. The results of successive annealing experiments at 25, 35, and 40 K of this matrix are depicted in Figure 1B, 1C, and 1D, respectively. From consideration of growth-decay behavior of the observed spectral bands, one can discern the presence of *three* distinct cobalt-ethylene complexes labeled I, I', and II' with associated $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ modes at 1504/1224, 1484/1204/1190, and 1545/1509/1250/1238 cm⁻¹, respectively. Retaining the matrix concentration at C₂H₄/Ar ≈ 1/50, experiments were conducted at gradually increasing concentrations of cobalt metal. Essentially the same three species were observed under conditions which favored mononuclear and binuclear complexation. Species labeled I' and II' displayed binuclear concentration behavior while I conformed more to that expected for a mononuclear complex.^{12,26}

By performing a corresponding series of ¹²C₂H₄/¹³C₂H₄/Ar mixed isotopic substitution experiments, the isotopic patterns associated with I, I', and II' could be examined with the intention of establishing ethylene stoichiometry. A typical series of experiments at roughly 1/1/50 are depicted in Figure 2A,B,C from which three "mono-type" ¹²C/¹³C isotopic patterns can be extracted, once one realizes the frequency locations of coincidental isotopic overlap complications for these species. These assignments are indicated in Figure 2A-C by arrows joining related sets of ¹²C/¹³C isotopic components in the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ spectral regions. The actual isotopically related frequencies are listed in Tables II-IV.

At this stage of the experimentation in dilute C₂H₄/Ar matrices deposited at 12 K, we can summarize by stating that *only three complexes* can be generated in spectroscopically detectable concentrations of which I and I' are respectively mononuclear and binuclear, as far as the cobalt is concerned. As I and I' are favored on deposition under dilute C₂H₄/Ar conditions and display ¹²C₂H₄/¹³C₂H₄/Ar isotopic patterns

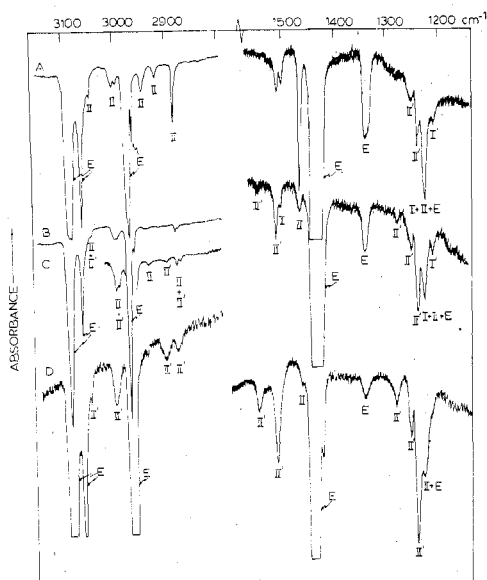
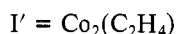
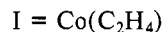
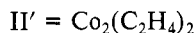


Figure 3. Matrix infrared spectra of Co atoms deposited with $^{12}\text{C}_2\text{H}_4$ at 12 K: (A) $\text{Co}/\text{C}_2\text{H}_4 \approx 1/10^4$, (B) $\text{Co}/\text{C}_2\text{H}_4 \approx 1/10^3$, where (C) is a roughly $2 \times$ ordinate expansion of (B), and (D) is the matrix infrared spectrum of Co atoms deposited at 40–50 K with $\text{Co}/\text{C}_2\text{H}_4 \approx 1/10^4$. E refers to unreacted ethylene and I = $\text{Co}(\text{C}_2\text{H}_4)$, I' = $\text{Co}_2(\text{C}_2\text{H}_4)$, II = $\text{Co}(\text{C}_2\text{H}_4)_2$, and II' = $\text{Co}_2(\text{C}_2\text{H}_4)_2$.

indicative of *monoethylene* complexes, one can confidently propose the assignments



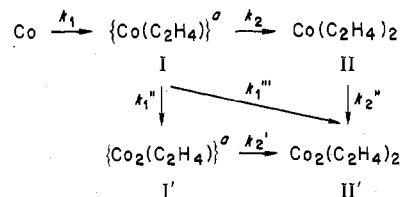
The ethylene is almost certainly coordinated to the cobalt in a normal side-on, π -complexed manner (more on this point later). Species II' is especially interesting, in that it displays binuclear Co atom concentration behavior, is the favored warm-up product from $\text{C}_2\text{H}_4/\text{Ar} \approx 1/50$ matrices, predominates in more concentrated $\text{C}_2\text{H}_4/\text{Ar}$ mixtures (under binuclear cobalt conditions), and yields *two* $\nu(\text{C}=\text{C})$ stretching modes in the spectral region typical of a normal side-on π -ethylene complex, but yet it shows a $^{12}\text{C}_2\text{H}_4/^{13}\text{C}_2\text{H}_4/\text{Ar}$ isotopic pattern (Figure 2C) characteristic of a *monoethylene* complex. Weighing all of the evidence collected for species II', one is obliged to make the assignment



in which the ethylene ligands are *noncentrosymmetrically* π -coordinated to *different* cobalt atoms. Weak vibrational coupling between the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ modes of the ethylene ligands (across the cobalt-cobalt bond) must be primarily responsible for the observation of a "pseudo-monoethylene" $^{12}\text{C}_2\text{H}_4/^{13}\text{C}_2\text{H}_4$ isotopic multiplet. We note that this assignment is consistent with the observation throughout this study (and the corresponding Ni/ C_2H_4 study) of *only two detectable binuclear cobalt-ethylene complexes* I' and II'.

Pure Ethylene Matrices. In the initial stages of our experimentation with Co atom condensations into pure ethylene matrices, our expectations were prejudiced by the tendency of Ni,^{22,27} Pd,^{24,28} and Pt²⁹ to form $\text{M}(\text{C}_2\text{H}_4)_3$ species as the highest stoichiometry ethylene complex. A conference paper¹¹ had reported a macroscale synthesis of $\text{Co}(\text{C}_2\text{H}_4)_3$ via Co atom deposition into excess ethylene at 77 K (with the assignment based on infrared spectroscopic comparisons with $\text{Ni}(\text{C}_2\text{H}_4)_3$), this complex being stable to ~ 200 K. However, as we shall demonstrate from our experiments in pure C_2H_4 matrices, the highest stoichiometry observed for the mononuclear cobalt-

Scheme III



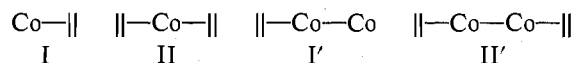
^a { } indicate minor products under these reaction conditions.

ethylene complexes was $\text{Co}(\text{C}_2\text{H}_4)_2$. The previously reported compound¹¹ may well be our observed $\text{Co}_4(\text{C}_2\text{H}_4)_n$.

Let us formalize the infrared spectroscopic experiments in pure ethylene by initially focusing on mononuclear-type conditions in cobalt and 12 K depositions. An infrared trace which typified this situation is displayed in Figure 3A. Immediately apparent from these spectral data is the predominance of a species labeled II associated with $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ modes at 1465 and 1222 cm^{-1} (note that II had been seen in concentrated $\text{C}_2\text{H}_4/\text{Ar}$ matrices under mononuclear Co conditions). Accompanying II on deposition are small amounts of I and II' (also seen in $\text{C}_2\text{H}_4/\text{Ar}$ matrices) as evidenced by the observation of weak absorptions at 1502/1224 cm^{-1} and 1545/1509/1250/1238 cm^{-1} , respectively (Figure 3A, 3B) (traces of I' can sometimes be detected under these conditions). Cobalt atom concentration studies conducted in pure C_2H_4 matrices at 12 K clearly pointed toward a mononuclear formulation for I and II and a binuclear assignment for II', the latter being in accordance with the observations in dilute $\text{C}_2\text{H}_4/\text{Ar}$ matrices. (We note here that the appearance of I in C_2H_4 matrices deposited at 12 K is not surprising in view of the presence of substantial amounts of unreacted Co atoms seen in the corresponding UV-visible spectra; these are described later.) In fact using $\text{Co}/\text{C}_2\text{H}_4 \approx 1/10^3$ mixtures deposited at 12 K (Figure 3B) and/or $\text{Co}/\text{C}_2\text{H}_4 \approx 1/10^4$ mixtures deposited at 40–50 K (Figure 3C), almost spectroscopically pure II' could be easily generated. A typical trace illustrating the 40–50 K case is shown in Figure 3C.

That II' in pure C_2H_4 genuinely represents $\text{Co}_2(\text{C}_2\text{H}_4)_2$ and not an unsuspected overlap with, for example, $\text{Co}(\text{C}_2\text{H}_4)_3$ was convincingly demonstrated by $^{12}\text{C}_2\text{H}_4/^{13}\text{C}_2\text{H}_4$ mixed-isotope experiments. *These infrared spectra portrayed isotopic multiplets essentially identical with those described earlier for II' in $\text{C}_2\text{H}_4/\text{Ar}$ matrices, Figure 2C (not at all like that anticipated for a tris(ethylene) complex, exemplified by $\text{Pd}(\text{C}_2\text{H}_4)_n(\text{C}_2\text{H}_4)_{3-n}$ (where $n = 0-3$)²⁴. Isotopic overlap complications of the 1465- cm^{-1} absorption of the mononuclear species II with the intense 1430 cm^{-1} deformational mode of the ethylene matrix unfortunately prevented an unequivocal ethylene stoichiometry assignment for II. However, consideration of the high ethylene concentrations required for generation of substantial amounts of II, together with the closeness of the $\nu(\text{C}=\text{C})$ and $\delta(\text{CH}_2)$ modes to those assigned to $\text{Ni}(\text{C}_2\text{H}_4)_2$ ²² and $\text{Pd}(\text{C}_2\text{H}_4)_2$ ²⁴, suggest a bis(ethylene) formulation for II.*

Collecting together the infrared spectroscopic evidence in pure C_2H_4 and $\text{C}_2\text{H}_4/\text{Ar}$ matrices, we conclude that it is possible to synthesize *two* mononuclear $\text{Co}(\text{C}_2\text{H}_4)_{1,2}$ and *two* binuclear $\text{Co}_2(\text{C}_2\text{H}_4)_{1,2}$ binary cobalt- π -ethylene complexes with the structures



The *absence of any other matrix-isolated complexes* under the wide variety of reaction conditions used in this study argues strongly against other likely stoichiometries, such as, $\text{Co}(\text{C}_2\text{H}_4)_{3,4}$ or $\text{Co}_2(\text{C}_2\text{H}_4)_{3,4}$.

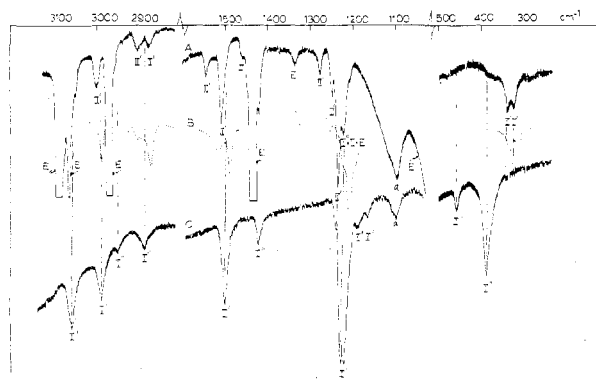


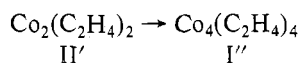
Figure 4. (A) The same as Figure 3D, (B) the same as Figure 3D but using 91% $^{13}\text{C}_2\text{H}_4$, and (C) the spectrum obtained after controlled $^{12}\text{C}_2\text{H}_4$ sublimation at 75–80 K from the matrix in A and further warming to 90–100 K showing the transformation of $\text{II}' = \text{Co}_2(\text{C}_2\text{H}_4)_2$ to $\text{I}' = \text{Co}_4(\text{C}_2\text{H}_4)_n$.

To rationalize the generation of spectroscopically detectable concentrations of I, II, I', and II' in pure C_2H_4 matrices at 12 K (Figure 3) in terms of the competitive kinetics in the reaction network shown in Scheme III, we first note the infrared spectroscopic evidence of only trace amounts of $\text{Co}_2(\text{C}_2\text{H}_4)_2$ and the UV spectroscopic absence of Co_2 (Figure 9A). The formation of I and II are the surface-diffusion and/or bulk-diffusion pathways normally observed for mononuclear complexes. Although mass-size arguments would tend to favor pathway k_2'' rather than k_2' and k_1''' , the latter two routes must *predominate* to be consistent with the $(\text{C}_2\text{H}_4)\text{Co}-\text{Co}(\text{C}_2\text{H}_4)$ structure proposed for II'. This mechanism is in accord with the observation of some I in pure C_2H_4 matrices and might also explain the observation that II is rarely seen in dilute $\text{C}_2\text{H}_4/\text{Ar}$ matrices.

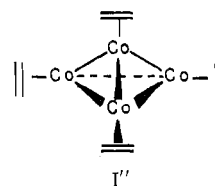
In the context of the proposed dimerization $2\text{Co}(\text{C}_2\text{H}_4) \rightarrow \text{Co}_2(\text{C}_2\text{H}_4)_2$, it is interesting to consider the further reactions that have been discovered on *controlled ethylene sublimation* from a pure ethylene matrix containing mainly $\text{Co}_2(\text{C}_2\text{H}_4)_2$. After a cobalt atom deposition with pure C_2H_4 at $1/10^4$ ratios at 40–50 K, II' is the dominant product with a trace of II (Figure 3C and Figure 4A).

When the matrix is slowly warmed to 75–80 K, II' is the only detectable product after the C_2H_4 matrix support is allowed to sublime away into the vacuum system. That species II' under non-matrix-isolated conditions was one and the same as compound II' observed at low temperatures in $\text{C}_2\text{H}_4/\text{Ar}$ and C_2H_4 matrices was confirmed by $^{12}\text{C}_2\text{H}_4/^{13}\text{C}_2\text{H}_4$ isotopic substitution. However, a remarkable spectral transformation was observed on allowing II' (adhering to the low-temperature optical window) in its "nonisolated" state to slowly warm to 90–100 K under dynamic vacuum conditions. The molecular conversion of II' to a new species I' is illustrated in Figure 4A and 4B and was complete by 160 K. At 190–200 K (very close to the decomposition temperature reported for the proposed $\text{Co}(\text{C}_2\text{H}_4)_3$ complex¹¹) the spectrum of I' gradually decays to zero, presumably as a result of the subsequent decomposition of I' to naked cobalt clusters (cf. $\text{Cu}_2(\text{C}_2\text{H}_4)_n \xrightarrow{50\text{K}} \text{Cu}_n$ ²³).

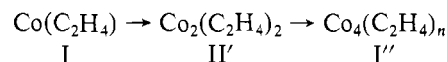
Parallel $^{12}\text{C}_2\text{H}_4/^{13}\text{C}_2\text{H}_4$ infrared experiments displayed broad, poorly resolved bands for the new species I' although a *doublet isotopic* envelope in the $\delta(\text{CH}_2)$ (1200-cm^{-1}) region was suggestive of a "monoethylene" formulation for I'. In view of the spectral transformation of II' to I' and the suggested monoethylene stoichiometry for I', we are tempted to speculate that the dimerization reaction



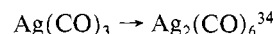
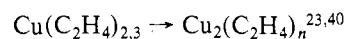
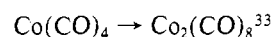
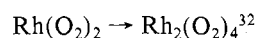
has been observed, most likely with a pseudotetrahedral structure for I' and minimal vibrational coupling between the



coordinated ethylenes.³⁰ It is most intriguing to note that the postulated sequence of aggregation events



is not an unprecedented observation in matrix reactions involving the cobalt group as well as other metals. For instance, the reactions



have been monitored by matrix infrared spectroscopy and therefore provide indirect support for our proposed conversion of I to II' to I'. The loss of signal at 190–200 K for I' could therefore represent the cluster decomposition reaction $m\text{Co}_4(\text{C}_2\text{H}_4)_n \rightarrow 4\text{Co}_m + nm\text{C}_2\text{H}_4$, analogous to the decompositions observed previously for $\text{Cu}_2(\text{C}_2\text{H}_4)_n$ ²³ and $\text{Ag}_2(\text{CO})_6$.³⁴ It is interesting to speculate that the observed thermal lability of C_2H_4 on cobalt may well be the reason that cobalt metal was once used as a hydroformylation catalyst² and could explain the sparsity of surface spectroscopic data for C_2H_4 chemisorbed onto bulk cobalt.

Ultraviolet-Visible Experiments. Dilute Ethylene/Agron Matrices. Examination of the optical spectra of cobalt atoms deposited into dilute $\text{C}_2\text{H}_4/\text{Ar}$ mixtures at 12 K always showed the presence of dominant cobalt atom absorptions. Atomic Co can be seen even in a $\text{C}_2\text{H}_4/\text{Ar} \approx 1/10$ matrix after deposition at 12 K (see Figure 5A and compare with $\text{Co}/\text{Co}_2/\text{Ar}$ spectrum shown in Figure 6A,B). Under these conditions the infrared spectrum shows mainly I, I', and a trace of II. Matrix annealing to 25 K reveals the growth of a molecular absorption at 375 nm ascribed to I (Figure 5B) in the presence of the atomic cobalt absorptions. Further annealing to 30 K induces collapse of the atomic cobalt spectrum and the exposure of a new broad absorption centered around 240 nm and ascribed to I' (Figure 5C). The choice of assignments for I and I' was based on a series of $\text{Co}/\text{C}_2\text{H}_4/\text{Ar}$ concentration and bulk annealing experiments with close reference to the corresponding infrared observations. The breadth of the 240-nm, I' absorption most likely arises from an overlap with the absorption due to II which is expected to be present under these conditions. (Actually II is found to absorb at roughly 280 nm from pure C_2H_4 experiments to be described.) Incidentally, the assignments for I and I' at 375 and 240 nm seem quite reasonable in view of the similar trend¹⁹ observed for $\text{Ni}(\text{C}_2\text{H}_4)$, 320 nm, $\text{Ni}_2(\text{C}_2\text{H}_4)$, 240 nm, and $\text{Cu}(\text{C}_2\text{H}_4)$, 382 nm/ $\text{Cu}_2(\text{C}_2\text{H}_4)_n$, 240 nm (see Table V and later discussion).

Aside from some inhomogeneous band-broadening effects and loss of fine structural detail, the spectra of atomic Co in $\text{C}_2\text{H}_4/\text{Ar} \approx 1/10$ mixtures are essentially identical with those observed for pure argon matrices. A typical cobalt concentration-temperature study is illustrated in Figure 6 (see Ozin

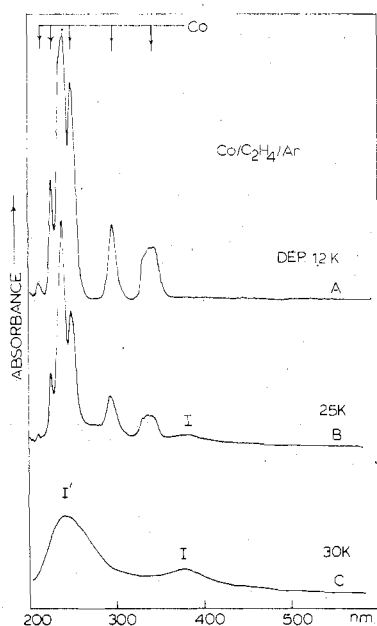


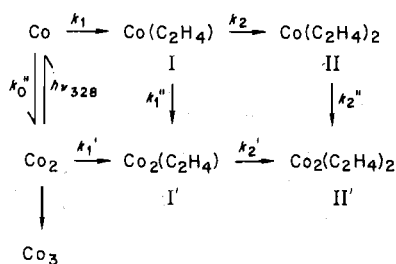
Figure 5. Ultraviolet-visible spectra obtained on depositing Co atoms with $C_2H_4/Ar \approx 1/10$ mixtures with $Co/Ar \approx 1/10^4$ at (A) 12 K and after warm-up to (B) 25 K and (C) 30 K and recoiling to 12 K for recording purposes.

Table V. Ultraviolet Spectral Data^a for $M(C_2H_4)_m$ and $M_2(C_2H_4)_m$ (Where $M = Co$ or Ni and $m = 1$ or 2)

complex	Co	Ni ^{19,22}	Cu ²³
$M(C_2H_4)$	375	320	382
$M(C_2H_4)_2$	~280 ^b	280	276
$M_2(C_2H_4)$	240	}240	}240
$M_2(C_2H_4)_2$	225		

^a Units in nm. ^b Appears as a broad shoulder on the 240-nm absorption of $Co_2(C_2H_4)$.

Scheme IV



and Hanlan¹³). The absence of Co_2 in Figure 5A,B is noteworthy in that it implies the main pathway to I' is via route k_1'' rather than k_1' in the reaction network shown in Scheme IV.

The generation of detectable quantities of Co_2 in the presence of Co becomes apparent in $C_2H_4/Ar \approx 1/50$ matrices, an example of which is shown in Figure 7A. Considerable insight into the competing diffusion-reaction processes occurring in these mixtures can be gleaned by surveying the UV-visible spectral alterations which ensue in these 1/50 matrices during 12–40 K bulk annealing experiments (Figure 7B,C). In essence, atomic Co is consumed rapidly (compared with identical experiments in pure Ar matrices¹³), Co_2 maintains an approximate steady-state concentration up to about 35 K and then gradually decays around 40 K, at which time detectable amounts of Co_3 (316, 287 nm)¹³ and $Co_2(C_2H_4)$, I', being to appear. Under these conditions, the expected formation of I (375 nm) would be obscured by the intense low-energy absorption of Co_2 . Although interesting,

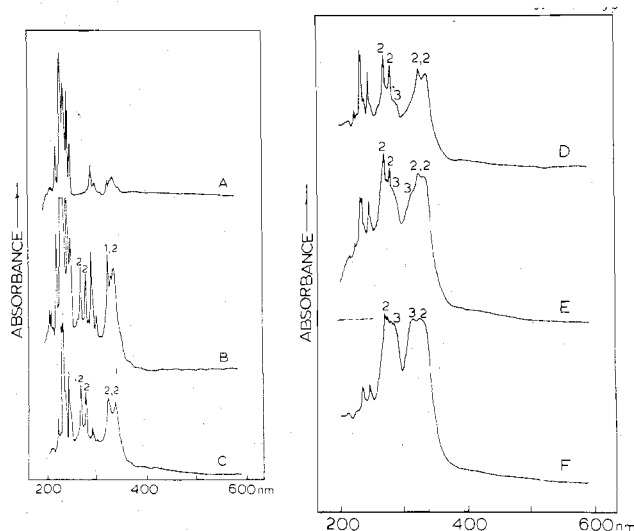


Figure 6. Ultraviolet-visible spectra of $Co/Ar \approx 1/10^4$ mixtures deposited at (A) 4.2 K, (B) 12 K, (C) 20 K, (D) 25 K, (E) 30 K, and (F) 35 K showing the gradual progression from isolated Co atoms to Co/Co_2 to $Co/Co_2/Co_3$ mixtures. See ref 13 for details.

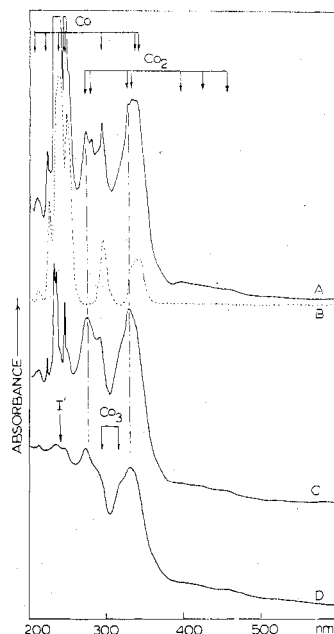


Figure 7. Ultraviolet-visible spectra obtained on depositing Co atoms at 12 K with (A) $C_2H_4/Ar \approx 1/50$ mixtures showing mainly Co and Co_2 , (B) $C_2H_4/Ar \approx 1/10$ mixtures showing mainly Co, and (C and D) the matrix shown in A after bulk annealing at 25 and 40 K showing the rapid consumption of Co atoms, slower loss of Co_2 , and gradual appearance of Co_3 and $I' = Co_2(C_2H_4)$. Complex I [$Co(C_2H_4)$], expected to weakly absorb around 375 nm, is probably masked by the tail end of the low-energy Co_2 band.

these observations cannot be used to distinguish pathways k_1' or k_1'' as the route to I'. Clearly competing cobalt atom aggregation reactions accompany Co/C_2H_4 complexation under dilute $C_2H_4/Ar \approx 1/50$ conditions, while under 1/10 conditions these cobalt atom nucleation events are more efficiently quenched.

Photolysis of the 328-nm Co/Co_2 overlap region of a $C_2H_4/Ar \approx 1/50$ matrix deposited at 12 K (Figure 8A) results in rapid photodepletion of Co_2 essentially to disappearance (Figure 8B) and slight photodecay of Co with concomitant photoproduction of $I = Co(C_2H_4)$ as seen by the growth of the 375-nm absorption (Figure 8C,D). In view of Hanlan and Ozin's Co photoaggregation and Co_2 cluster

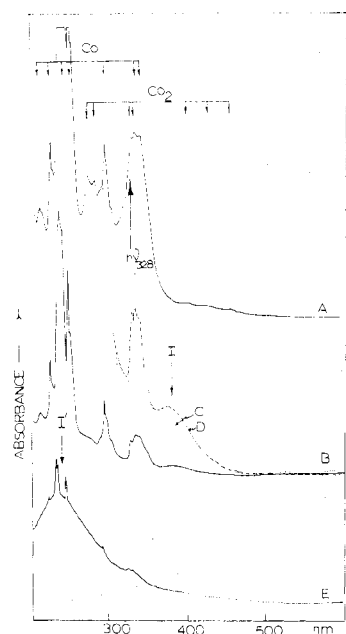
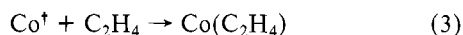


Figure 8. Ultraviolet-visible spectra of a $C_2H_4/Ar \approx 1/50$ matrix deposited (A) at 12 K showing mainly Co and Co_2 absorptions and (B) after 15 min of photolysis at 328 nm (600-W Xe lamp, Schoeffel monochromator assembly) showing photodecay of Co/ Co_2 and photoproduction of I. C is the same as B but scale $\times 5$, D is the same as C but after a further 15 min of photolysis, and E is the same as D after 35–40 K bulk annealing with scale $\times 1$ showing the thermal generation of mainly I.

photodissociation studies in Co/ Co_2 /Ar matrices,¹³ we would like to rationalize the outcome of the 328-nm photoexcitation of Co/ Co_2 / C_2H_4 /Ar mixtures in terms of the reaction sequence of eq 1–3, where (1) represents the photodissociation



of Co_2 to photomobile Co^{\dagger} atoms concurrent with (2) photoexcitation of atomic Co, electronic to lattice phonon energy transfer, and production of a photomobile Co^{\dagger} atom culminating in (3) the simple reaction of a photodiffusing Co atom with matrix-entrapped C_2H_4 to yield $Co(C_2H_4)$.

Pure Ethylene Matrices. After we realized that substantial concentrations of atomic cobalt can be isolated even in concentrated C_2H_4/Ar mixtures at 12 K, pointing to the existence of a small, yet finite activation energy for Co/ C_2H_4 complexation, it was not too surprising to discover that atomic cobalt could also be isolated in $Co/C_2H_4 \approx 1/10^3$ mixtures at 12–15 K (Figure 9A). Remember that under these conditions some compound formation has occurred as seen by the infrared observation of mainly II and II' (Figure 3 and Scheme II). This implies that the UV molar absorbances of unreacted Co atoms under these deposition conditions must greatly outweigh and/or overlap with those associated with II and II'. By gradually increasing the deposition temperature from 12–15 to 25 to 50 K, the delicate kinetic balance which must exist between isolating (i) *only* Co atoms, (ii) Co atoms and Co/C_2H_4 complexes, and (iii) *only* Co/C_2H_4 complexes, can be monitored and analyzed in terms of overlapping absorptions of II at roughly 280 nm and of II' at roughly 225 nm (Figure 9A–D and Table V). Collected together in Table V are the optical assignments for both $M(C_2H_4)_{1,2}$ and $M_2(C_2H_4)_{1,2}$ (where $M = Co, Ni, Cu$) which appear to form a reasonable set, the interpretation and discussion of which

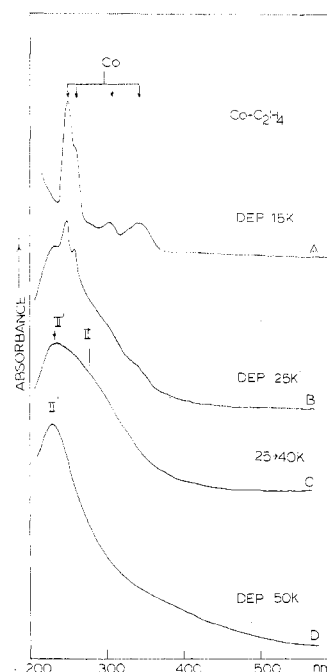


Figure 9. Ultraviolet-visible spectra of the products formed when Co atoms are condensed with C_2H_4 matrices (A) at 15 K, (B) at 25 K, and (C) after warming the matrix in B to 40 K and recoiling to 12 K for spectral recording purposes. D is the spectrum of the Co/C_2H_4 cocondensation at 50 K.

are left to the following section.

Discussion

In the cobalt–ethylene system, as now seems to be universal in binary transition-metal– π -ethylene complexes, the “mainly intraligand” infrared modes are relatively insensitive to both ethylene stoichiometry and metal cluster size. However, this does not seem to be quite the case for the metal–ligand stretching modes so far observed for the nickel– and cobalt–ethylene systems (see Tables I, III, and IV). For example, on passing from $Ni(C_2H_4)$ to $Ni_2(C_2H_4)_{1,2}$, the observed $\nu(Ni-C)$ stretching modes shift from 376 to 416 and 446 cm^{-1} , respectively. In the case of $Co_2(C_2H_4)_2$ and $Co_4(C_2H_4)_4$, the observed $\nu(Co-C)$ modes shift from 332 and 314 to 384 and 460 cm^{-1} , respectively. The point to notice here is the reasonably large sensitivity of the $\nu(M-C)$ modes to both metal cluster size and the nature of the metal. The higher $\nu(M-C)$ energies observed for the nickel complexes relative to the cobalt complexes are in line with the correspondingly greater thermal stabilities of the former compared to those of the latter; this property would probably be manifested in the adsorption energies for chemisorbed ethylene on Ni and Co surfaces (which as far as we are aware have not yet been reported in the literature) and probably reflects on the superior hydroformylation catalytic properties of cobalt relative to nickel.

Although vibrational data for ethylene chemisorbed onto cobalt metal has not yet been reported, it is nevertheless instructive to compare the infrared data for our proposed Co/C_2H_4 chemisorption models with the HREELS (high-resolution electron energy loss spectroscopic) data for ethylene chemisorbed on Ni(111) single-crystal surfaces³⁵ (Table VI).

On surveying the available data in Table I–IV for $Co(C_2H_4)/Co_2(C_2H_4)_{1,2}/Co_4(C_2H_4)_n$ and $Ni(C_2H_4)/Ni_2(C_2H_4)_{1,2}$, one can make certain useful statements about the suitability of finite cluster–ethylene complexes as localized bonding models for chemisorbed ethylene. Aside from the rather special $\nu(CH_2)$ “softened mode” at 2690 cm^{-1} (a surface hydrogen-bonding interaction in the terminology of Demuth, Ibach, and Lehwald³⁵) the $\nu(CH_2)$ region of so-called π -

Table VI. Comparison of HREELS for C_2H_4 on Ni(111) with $Co_n(C_2H_4)_m$ Chemisorption Models

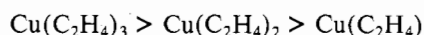
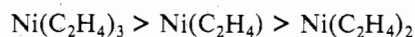
HREELS C_2H_4 / Ni(111) (ref 35)	$Co_2(C_2H_4)_2$ (this work)	$Co_4(C_2H_4)_4$ (this work)	assign ^b
2940	3048 w, sh 3000 m 2900 m 2876 w	3057 s 2984 s 2948 w 2888 w, br	} $\nu(CH_2)$
2690 ^a			
1500	1544 w/1508 s	1496/1492 s	$\nu(CH_2)^a$
1430	1420 w	1416 w	$\nu(C=C)$
1090	1276 w/1248 w/ 1234 s	1224/1216 s	$\delta(CH_2)$
880			$\rho_r(CH_2)$
440	332 w 314 w	460 w 384 s	} $\nu(M-C)$

^a Softened mode. ^b The paper by J. P. Sorzano and J. P. Fackler Jr., *J. Mol. Spectrosc.*, **22**, 80 (1967), is a useful reference source for detailed vibrational-normal-coordinate studies of coordinated C_2H_4 .

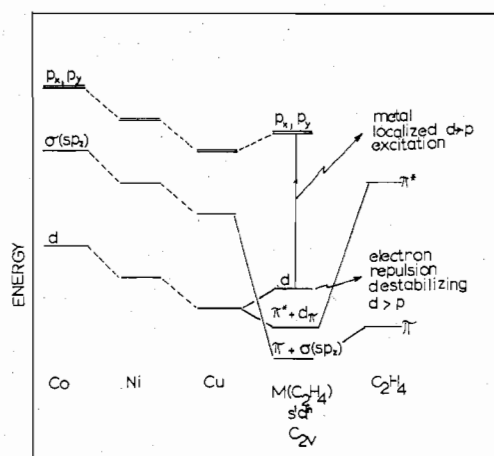
chemisorbed ethylene is dominated by a broad vibrational loss around 2940 cm^{-1} (Table VI). Clearly this band "envelope" corresponds to bands observed in the 3050–2875- cm^{-1} region of our finite cluster-ethylene complexes. Significantly, the crucial $\nu(C=C)$ stretching modes of ethylene π bonded to the surface metal atom sites and π bonded in our complexes are relatively insensitive to cluster size or ethylene stoichiometry, being observed as a weak band around 1500 cm^{-1} (surface selection rule arguments) on the Ni(111) surface and around 1504 (I), 1484 (I'), 1508 (II'), and 1494 (I') cm^{-1} for the cobalt complexes and 1499 (I), 1488 (I'), and 1504 (II') cm^{-1} for the nickel complexes¹⁹ (Table VI). The observed $\delta(CH_2)$ deformational modes in the 1400- and 1200- cm^{-1} regions also seem to be relatively insensitive to cluster size and the nature of the metal although the 1200- cm^{-1} group of bands are shifted by roughly 100 cm^{-1} with respect to the corresponding surface modes (Table VI).

It would seem, therefore, that the $\delta(CH_2)$ modes around 1200 cm^{-1} and the $\nu(M-C)$ modes around 300–450 cm^{-1} are likely to be most informative in terms of localized bonding discussions. In particular it would appear that increasing the cluster size from 1 to 2 to 4 causes a monotonic blue shift of $\nu(M-C)$ toward the value observed for the corresponding ethylene chemisorption mode, being already reasonably close for 2–4 metal atom clusters. Broadly speaking, one can reasonably conclude that it is possible to represent π -chemisorbed ethylene by a finite cluster-ethylene complex containing as few as 2–4 metal atoms in the case of Co and Ni.

In spite of the general insensitivity of the intraligand vibrational modes to cluster size, there are a few specifics worth mentioning, particularly with respect to the trends in $\nu(C=C)$. (We realize in these discussions that to infer strength of bonding from $\nu(C=C)$ frequencies involves the naive assumption that coupling effects with other modes, especially $\delta(CH_2)$ vibrations, are either minimal or roughly constant throughout a given series.⁴⁷) The first point relates to the observed $\nu(C=C)$ orderings



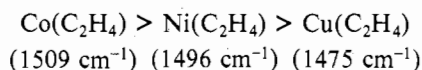
The amonotonic order for cobalt and nickel compared to the monotonic order for copper mononuclear ethylene complexes (like earlier $M(CO)_n$ discussions²²) can best be rationalized in terms of a finite positive $k_{C=C-C}$ interaction force constant

**Figure 10.** Schematic representation of the $\sigma(sp_2)$, p_x, p_y , and d metal orbital energy variations on passing from Co to Ni to Cu in C_{2v} $M(C_2H_4)$ π -ethylene complexes.**Chart I**

Co-	Ni-
1504 cm^{-1}	1499 cm^{-1}
(C_{2v})	(C_{2v})
Co-Co-	Ni-Ni-
1484 cm^{-1}	1488 cm^{-1}
(C_{2v})	(C_{2v})
-Co-Co-	-Ni-Ni-
1508 cm^{-1}	1504 cm^{-1}
	(D_{2h})

for Co and Ni rather than the outcome of amonotonicity in the principle $k_{C=C}$ stretching force constants.

At this point it is significant to note that $\nu(C=C)$ (or $k_{C=C}$) for $M(C_2H_4)$ adopts the order



If we accept the GVB-CI conclusion¹⁹ that the nickel atom in $Ni(C_2H_4)$ adopts the s^1d^9 electronic configuration (in line with the ESR interpretation of a s^1d^{10} copper atom in $Cu(C_2H_4)$ ³⁶) with a major $\pi(C_2H_4) \rightarrow \sigma(sp)Ni$ donor yet a minimal $\pi^*(C_2H_4) \leftarrow d_\pi(Ni)$ acceptor interaction, then we would predict the monotonic $\sigma(sp)/d_\pi$ metal orbital variations illustrated in Figure 10 to hold true on passing from (s^1d^8)Co to (s^1d^9)Ni to (s^1d^{10})Cu. Thus for a dominant $\pi(C_2H_4) \rightarrow \sigma(sp)M$ bonding interaction, one would expect the strongest metal-ethylene bond to occur for Cu and the weakest for Co in $M(C_2H_4)$ complexes. This would be consistent with the highest $\nu(C=C)$ for $Co(C_2H_4)$ and the $\nu(C=C)$ ordering $Co > Ni > Cu$. Such a rationale would not be expected to hold true for the bis- and tris(ethylene) complexes as the electronic configuration of the metal is likely to move away from s^1d^8/s^1d^9 in $Co(C_2H_4)_2/Ni(C_2H_4)_2$ to p^1d^8/p^1d^9 or d^9/d^{10} in $Co(C_2H_4)_{2,3}/Ni(C_2H_4)_{2,3}$ and s^1d^{10} in $Cu(C_2H_4)$ to p^1d^{10} in $Cu(C_2H_4)_{2,3}$ (in line with ESR evidence for $Cu(C_2H_4)_{1,2,3}$ ³⁶ and $Cu(C_2H_2)_{1,2}$ ³⁷).

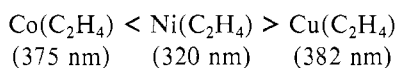
Some other fascinating parallels in the $\nu(C=C)$ frequencies worthy of consideration are shown in Chart I. To begin with, we note a roughly constant difference of 4–5 cm^{-1} on passing from $M(C_2H_4)$ to its dimer, $M_2(C_2H_4)_2$. Secondly, the $\nu(C=C)$ frequencies first red shift on passing from $M(C_2H_4)$ to $M_2(C_2H_4)_2$ and then blue shift from $M_2(C_2H_4)_2$ to $M_2(C_2H_4)_2$.

Within the GVB-CI description of the bonding interactions in $M(C_2H_4)$,¹⁹ we note that on adding the second metal atom in an s^1d^n -promoted (valence) state (which is very close in energy to the s^2d^n repulsive ground state) to the s^1d^n metal

atom in $M(C_2H_4)$, the repulsive interaction between the charge density in the $\sigma(sp)$ -nonbonding orbital and the π -charge density of the incoming ethylene ligand in $M(C_2H_4)$ is reduced slightly in $M_2(C_2H_4)$. In other words the (sp) -charge density is polarized more away from the ethylene in $M_2(C_2H_4)$ compared to that in $M(C_2H_4)$.¹⁹ The outcome is a closer approach of the ethylene to the metal atom site in $M_2(C_2H_4)$ relative to $M(C_2H_4)$, resulting in a greater delocalization of charge from the π orbital of the ethylene onto the metal site in $M_2(C_2H_4)$ and hence a lower $\nu(C=C)$ frequency with respect to $M(C_2H_4)$.

The subsequent blue shift in the $\nu(C=C)$ stretching frequency on passing from $M_2(C_2H_4)$ to $M_2(C_2H_4)_2$ most probably arises from increased charge repulsion effects between the π -electron densities of the ethylenes and the mainly s -charge density localized in the metal-metal bond. One therefore anticipates a weaker $\pi(C_2H_4) + \sigma(sp)M$ bonding interaction in $M_2(C_2H_4)_2$ which is manifested in a blue $\nu(C=C)$ shift with respect to $M_2(C_2H_4)$. Finally, we note in passing that the detection of two $\nu(C=C)$ stretching modes for $Co_2(C_2H_4)_2$ (sym $\nu(C=C)$ 1545 cm^{-1} , asym $\nu(C=C)$ 1508 cm^{-1}) necessitates a noncentrosymmetric geometry. The observation of a single $\nu(C=C)$ for $Ni_2(C_2H_4)_2$ suggests that the geometry is either centrosymmetric D_{2h} or that it is noncentrosymmetric but the symmetric $\nu(C=C)$ has remained undetected. This difference, if real, could conceivably be a reflection of stabilization differences necessitated by an s^{1d^8} cobalt atom in $Co_2(C_2H_4)_2$ relative to an s^{1d^9} nickel atom in $Ni_2(C_2H_4)_2$.

The discussion of $d_{\pi}/\sigma(sp)$ orbital trends for the $M(C_2H_4)$ complexes leads us to the interesting ordering of observed UV transition energies:



If we accept the GVB-CI assignment for the 320-nm UV transition of $Ni(C_2H_4)$ in terms of a $d \rightarrow p$ excitation, localized on an s^{1d^9} nickel atom¹⁹ (in line with recent UV studies of nickel-olefin complexes for a wide variety of substituted olefins³⁸), then one has to account for a metal-localized $d \rightarrow p$ energy ordering in $M(C_2H_4)$ of the form $Co < Ni > Cu$. In terms of effective nuclear charge-orbital penetration arguments one would initially expect the $d \rightarrow p$ energy gap to take on the order $Co < Ni < Cu$. Clearly this is an oversimplified explanation and account must be taken of the effect of a monotonically increasing $\pi(C_2H_4) \rightarrow \sigma(sp)M$ charge donation from the ethylene to the metal. This will clearly have the opposite effect to Z^* -penetration effects alone and could well account for the "anomalously" low energy of the $d \rightarrow p$ excitation observed for $Cu(C_2H_4)$ and the resulting a monotonic $d \rightarrow p$ metal-localized ordering $Co < Ni > Cu$ (Figure 10). This intriguing point will hopefully be scrutinized in future ab initio CI molecular orbital calculations of $M(C_2H_4)$ systems. It will be fascinating to discover whether the corresponding UV surface excitations anticipated for $M(C_2H_4_{ads})$, possibly observable by HREELS techniques of the type recently reported by Rubloff (IBM)³⁹ for CO on Ni(111) will display a parallel energy trend to that observed for $M(C_2H_4)$.

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Registry No. I, 67951-75-1; I', 67951-76-2; I'', 67951-77-3; II, 67951-78-4; II', 67951-79-5; $Co_2(^{13}C_2H_4)$, 67951-80-8; $Co_2(^{13}C_2H_4)_2$,

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Characterization of Some Mixed-Halide Copper(II) Dimers of the General Formula $[\text{Cu}_2\text{X}_n\text{X}'_{6-n}]^{2-}$ ($\text{X} = \text{Cl}^-$ and $\text{X}' = \text{Br}^-$): Evidence for the Preference of Chloride Bridges in the Mixed-Halide Species

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Magnetic and spectral properties are reported for several halogen-bridged dimeric copper(II) clusters of the general form $\text{A}_2\text{Cu}_2\text{X}_n\text{X}'_{6-n}$ where $\text{A} = (\text{C}_6\text{H}_5)_4\text{P}^+$, $(\text{C}_6\text{H}_5)_4\text{Sb}^+$, or $(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5)_3\text{P}^+$, $\text{X} = \text{Cl}^-$, and $\text{X}' = \text{Br}^-$. All of the compounds exhibit ferromagnetic exchange coupling between pairs of copper(II) ions with $2J$ values ranging from 5.4 to 112 cm^{-1} . Infrared data and the magnitudes of the exchange interactions suggest that chloride bridges are preferred in the mixed-halide complexes. An analysis of the electron paramagnetic resonance data and the low-temperature magnetization data suggests that deviations from the simple pair model for the exchange interactions can be attributed to zero-field splittings of the triplet states instead of to interdimer exchange.

Introduction

The existence of ferromagnetic intracenter exchange in paramagnetic transition-metal cluster complexes has been documented only within the last decade.¹⁻³ Although the number of ferromagnetically coupled cluster complexes of known crystal structure is still relatively small, examples are being found at a rapidly increasing rate as a result of careful, systematic studies of magnetic and structural properties.^{4,5} For several comprehensive reviews of this field see ref 4-8. Since the available theoretical methods for treating the spin-spin coupling problem are unmanageable for a large number of interacting spins, the use of small clusters of well-isolated interacting systems as models for the larger, more complicated magnets is of considerable importance.⁹⁻¹¹ With the model approach it should be possible to more fully understand the various magnetic and structural features which are necessary for the ultimate realization of insulating magnets.^{12,13}

The rich variety of cluster complexes of the d^9 copper(II) ion make these systems especially attractive for magnetic and structural studies. Although large numbers of compounds containing oxygen bridges between copper(II) ions have been fully characterized,⁴⁻⁸ only a few dimeric clusters containing halogen bridge atoms have been studied.^{4,14-18} A general class of halocuprates(II) represented by the general formula ACuX_3 (where $\text{X} = \text{Cl}^-$ or Br^- and A is an alkali metal or monovalent organic cation) are of particular interest since structures of this type are known to vary from simple bimetallic clusters as in $[(\text{C}_6\text{H}_5)_4\text{AsCuCl}_3]_2$ ^{16a} to complicated arrays of dimers joined into chains as in KCuCl_3 .¹⁹ Apparently, the geometry about the $\text{Cu}_2\text{X}_6^{2-}$ ion is dictated by the size and packing requirements of the cation. Thus, with small cations these complexes possess complicated structures loosely based on the quasi-planar dimeric $\text{Cu}_2\text{X}_6^{2-}$ moiety, but with very large organic cations, the structures lose their quasi-planar nature and become isolated bimetallic clusters consisting of two distorted tetrahedra sharing an edge.^{16a,17a}

Shortly after the initial discovery of the ferromagnetically coupled $\text{Cu}_2\text{Cl}_6^{2-}$ dimers in the tetraphenylarsonium tri-

chlorocuprate(II),¹⁶ Textor et al.^{17a} showed that the tetraphenylphosphonium analogue was isomorphous and very nearly isostructural to the $\text{Ph}_4\text{AsCuCl}_3$ ($\text{Ph} = \text{C}_6\text{H}_5$) salt. One of the more important differences between the structures was a decrease in the $\text{Cu}-\text{Cl}_6-\text{Cu}$ bridge angle from 93.7 (1) to 93.3 (1)°. Since earlier work on an extensive series of hydroxo-bridged copper(II) dimers has shown that the magnitude and sign of the exchange coupling constant are very sensitive to small changes in the bridging geometry,¹³ we expected to find analogous behavior in halide-bridged copper(II) systems. To study this problem we have prepared and characterized the dimeric Ph_4P^+ complexes of mixed halides. In addition, two other complexes with the cations tetraphenylstibonium and triphenyl-*n*-propylphosphonium have been prepared as their chloride salts. The results of these studies are described in this paper.

Experimental Section

Tetraphenylphosphonium chloride and bromide were obtained from Columbia Organic Chemicals, Inc. (Columbia, S.C.). Triphenyl-*n*-propylphosphonium bromide was obtained from Aldrich Chemical Co. (Atlanta, Ga.) and converted to the chloride salt via ion-exchange chromatography. Tetraphenylstibonium chloride was prepared and purified after the method of Doak et al.²⁰ Reagent grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and CuBr_2 were obtained from J. T. Baker Chemical Co. (Phillipsburg, N.J.) and used without additional purification.

Preparation of the Complexes. The complexes containing only one type of halide per formula unit were synthesized by adding equimolar amounts of the cation and the appropriate copper(II) halide in warm methanol or absolute ethanol. The orange-red ($\text{Cu}_2\text{Cl}_6^{2-}$) or maroon-black ($\text{Cu}_2\text{Br}_6^{2-}$) complexes were readily recrystallized from methanol or dichloromethane. The mixed-halide complexes of the Ph_4P^+ cation ($\text{Ph} = \text{C}_6\text{H}_5$) were prepared by the following method: Carefully weighed stoichiometric amounts of the phosphonium bromide and copper(II) chloride dihydrate were dissolved in separate amounts of warm absolute ethanol. These solutions were quickly mixed and allowed to cool until crystallization occurred. The precipitated mixed-halogen complexes were separated by filtration and air-dried. These compounds could not be recrystallized even from inert organic solvents such as dichloromethane since the process always led to preferential crystallization of a pure-halide compound. Analytical