

spectra were recorded with a Tesla BS 487/C 80-MHz spectrophotometer using Me₄Si as the internal standard. Analysis of the volatile compounds was performed on an analytical Hewlett-Packard Model 5830A gas chromatograph using 30-m glass capillary column with 0.15- μ m OV-1 stationary phase and *n*-nonane internal standard. All manipulations involving air-sensitive organometallic compounds were carried out by using Schlenk techniques.¹⁴ Reactions above 3-bar pressure were performed with 10-mL samples in a 20-mL stainless-steel rocking autoclave.

Materials. The solvents were dried in the usual way and stored under CO. Commercial ethyl acrylate was freshly distilled under CO. Stock solutions of HCo(CO)₄ were prepared in *n*-octane from Co₂(CO)₈, DMF, and concentrated HCl.¹⁵ The concentration of HCo(CO)₄ solutions was determined by 0.1 N alkaline titration at 0 °C under CO. Dicobalt octacarbonyl was doubly recrystallized first from CH₂Cl₂ and then from *n*-heptane under CO.

Kinetic runs were performed in a gasometric apparatus fitted with a mercury-filled gas burette. A 5-L buffer flask was connected to the leveling vessel of the gas burette and kept at the pressure of the reaction vessel. All parts of the apparatus were thermostated (± 0.05 °C). The actual total pressure was determined in millimeters of Hg by using an open mercury manometer measuring the pressure difference between the atmosphere and the reaction

vessel. The reaction was started by injecting the ethyl acrylate into the vigorously stirred solution of HCo(CO)₄ and Co₂(CO)₈. In the case of ethyl (3-(ethoxycarbonyl)propionyl)cobalt tetracarbonyl formation the reaction was started by injecting freshly warmed up solutions of (1-(ethoxycarbonyl)ethyl)cobalt tetracarbonyl into the vigorously stirred solvent or into solutions of Co₂(CO)₈. The initial rate of CO uptake was calculated from the change of gas volume with time.

The PPh₃-substituted derivatives were prepared in a gasometric apparatus by adding 10% molar excess of PPh₃ (based on Co) as a 0.3 M solution in toluene/heptane (1:8, v/v) to the reaction mixture prepared from ethyl acrylate and HCo(CO)₄ under CO after the Co₂(CO)₈ crystals have been removed at -79 °C. Yellow crystals formed within 10 min.

The 2,4-dinitrophenylhydrazone derivatives were prepared by adding 10% molar excess of perchloric acid stabilized 2,4-dinitrophenylhydrazine in water to the reaction mixture followed by cooling overnight in the refrigerator and filtration of the precipitate.

Registry No. HCo(CO)₄, 16842-03-8; CH₂=CHCOOEt, 140-88-5; ethyl propionate, 105-37-3; ethyl 2-formylpropionate, 27772-62-9; (1-(ethoxycarbonyl)ethyl)cobalt tetracarbonyl, 85421-34-7; (2-(ethoxycarbonyl)propionyl)(triphenylphosphine)tricarbonyl cobalt, 104465-48-7; (1-(ethoxycarbonyl)ethyl)(triphenylphosphine)tricarbonyl cobalt, 104465-49-8; (3-(ethoxycarbonyl)propionyl)cobalt tetracarbonyl, 104465-50-1; (3-(ethoxycarbonyl)propionyl)(triphenylphosphine)tricarbonyl cobalt, 104465-51-2; ethyl 3-formylpropionate, 10138-10-0.

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¹³C NMR and EHMO Studies on Seyferth's [Co₃(CO)₉CCO]⁺ Cluster: To Bend or Not To Bend

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Variable-temperature ¹³C NMR studies on [Co₃(CO)₉CCO]⁺ and its Ph₃P-substituted analogue are described. At -110 °C, the 125.7-MHz ¹³C NMR spectrum of [Co₃(CO)₉CCO]⁺ exhibits a 3:6 pattern for the cobalt carbonyls. This is interpreted in terms of a tilted (C_s) geometry for the ketenylidene fragment rather than a perpendicular (C_{3v}) arrangement. It is proposed that [(Ph₃P)Co₃(CO)₈CCO]⁺ and [CpMoCo₂(CO)₈CCO]⁺ also have related structures in which localized Co(CO)₃ rotation cannot be slowed on the NMR time scale. Extended Hückel molecular orbital calculations consistently found the C_s geometry to be the most stable for [Co₃(CO)₉CCO]⁺ and for the related molecule [Fe₃(CO)₉CCO]²⁻, with the ketenylidene fragment leaning toward a metal vertex. The energy variation was found to be small over a large range of bending angles, in contrast with the [Co₃(CO)₉CCH₂]⁺ cluster. The difference between this latter cation and the ketenylidene clusters is analyzed.

Introduction

Among the more interesting systems which have emerged from studies on metal clusters are those containing the ketenylidene ligand, C=C=O, which are believed to be models for the reduction of CO on metal surfaces.¹ The first reported synthesis² of such a system described the tricobalt acylium ion 1, and since that time the chemistry of this cluster has been extensively developed.³ Nevertheless, despite numerous attempts to obtain good crystallographic data,⁴ the structure of 1 is still a

matter of conjecture and both the linear (C_{3v}) geometry, 1a, and bent (C_s) conformation, 1b, are viable candidates. The infrared spectroscopic data⁵ militate against structures involving bridging carbonyls between the metal vertices.

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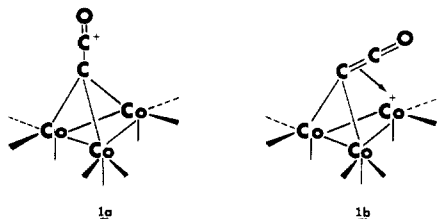
(4) Churchill, M. R., personal communication.

(5) (a) Co₃(CO)₉CCO⁺BF₄⁻: IR (CH₂Cl₂) ν_{CO} at 2260 (m), 2110 (m), 2070 (s), 2040 (vs), and 1990 (w) cm⁻¹. Reference 2. (b) Co₃(CO)₉CCO⁺AlCl₄⁻nAlCl₃: IR (CH₂Cl₂) ν_{CO} at 2147 (m), 2121 (sh), 2107 (s), 2099 (s), 2082 (sh), 2068 (w), and 2046 (w) cm⁻¹. Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* 1977, 16, 758.

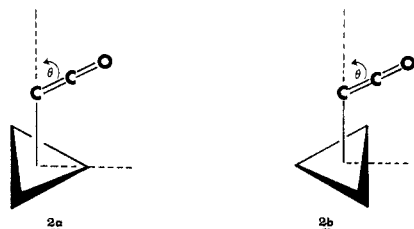
[†] McMaster University.

[‡] Bruker Spectrospin.

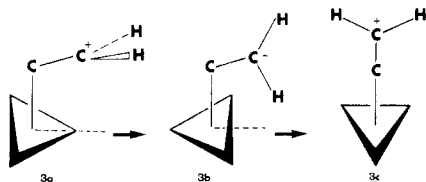
[§] Université de Rennes I.



In a series of elegant studies, Shriver⁶⁻⁸ and his colleagues have elucidated the structures of several anionic ketylidene clusters. In all cases, the C=C=O moiety is essentially linear and is tilted away from the perpendicular to the plane of the metal atoms. One can define an angle θ between the C=C=O vector and the threefold axis which passes through the trimetallic plane, as in 2.



A closely analogous problem has been analyzed in some detail by Schilling and Hoffmann⁹ who used an extended Hückel molecular orbital approach to show that $[\text{Co}_3(\text{CO})_9\text{CCH}_2]^+$ (3) has the favored structure 3a, in which the vinylidene fragment is tilted toward a metal atom. These three minima are interconverted by passing over saddle points 3b in which the methylene group not only eclipses a cobalt-cobalt bond but also rotates through 90° so as to be situated in the molecular mirror plane. In-



terestingly, the nondistorted structure 3c, in which the twofold axis of the methylene is coincidental with the threefold axis, is an energy maximum; furthermore, it is a forbidden transition state for the interconversion of the tilted structures.⁹ These theoretical predictions have been experimentally verified via an elegant and ingenious ¹³C NMR study by Edidin, Norton, and Mislow.¹⁰

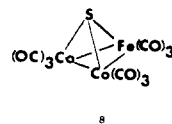
Returning to the ketylidene system, we note that $[\text{Fe}_3(\text{CO})_9\text{CCO}]^{2-}$ (4) and $[\text{Fe}_2\text{Co}(\text{CO})_9\text{CCO}]^-$ (5) adopt structure 2a with θ values of 33° and 24°, respectively.^{6,7} In contrast, $[\text{Ru}_3(\text{CO})_9\text{CCO}]^{2-}$ (6) has only an 11° tilt and leans toward the middle of a Ru-Ru bond as in 2b.⁸ Furthermore, in the neutral cluster $\text{H}_2\text{Os}_3(\text{CO})_9\text{CCO}$ (7) the C=C=O moiety is nearly perpendicular with respect to the metal plane,¹¹ i.e., analogous to structure 1a. In the

absence of crystallographic data on 1, we chose to use NMR spectroscopy and EHMO calculations to try to gain some insight into this problem and we here report the low-temperature ¹³C NMR spectra of 1 measured at 11.4 T (125.7 MHz for ¹³C; 500 MHz for protons).

Results and Discussion

In principle, it should be possible to use NMR spectroscopy to distinguish between the two proposed structures for $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$, viz., 1a and 1b, since their different point groups will impose different splittings in degeneracy on the metals and their associated carbonyls. In the limiting case, the C_{3v} isomer 1a maintains the equivalence of the cobalt atoms but splits the carbonyls into sets of six equatorial and three axial ligands. In contrast, structure 1b has only a single mirror plane which would thus give rise to five carbonyl environments in the ratio 2:2:2:2:1. (Indeed, this latter criterion was used to establish the C_s structure of 7 in solution.¹² Subsequently, the structure was confirmed X-ray crystallographically.¹¹) Furthermore, in 1b the three cobalt atoms are no longer degenerate and the possibility exists of observing two ⁵⁹Co resonances in a 2:1 ratio. In practice, however, ⁵⁹Co NMR signals are very broad except in the most favorable cases,¹³ and indeed for molecule 1 we could not detect anything other than a broad featureless resonance.

In clusters comprised of second- or third-row metals it is frequently possible to obtain a limiting low-temperature spectrum;¹⁴ in contrast, the barriers to carbonyl exchange in cobalt systems are invariably very low. Typically, in the 25.1-MHz ¹³C NMR spectrum of $\text{Co}_2\text{Fe}(\text{CO})_9\text{S}$ (8) the



room-temperature singlet splits, upon cooling, into a 3:6 pattern with chemical shifts appropriate for one $\text{Fe}(\text{CO})_3$ and two $\text{Co}(\text{CO})_3$ fragments. Subsequently, the $\text{Fe}(\text{CO})_3$ resonance splits again to yield different chemical shifts for the axial and equatorial carbonyls; the $\text{Co}(\text{CO})_3$ groups, however, always exhibit a sharp singlet.¹⁵ More significantly, perhaps, we have shown that at 9.4 T (100.6 MHz for ¹³C; 400 MHz for ¹H) the cobalt carbonyl resonance of $\text{Co}_3(\text{CO})_9\text{CCO}_2\text{CHMe}_2$ (9) at -110 °C is still a sharp singlet showing that the barrier to axial-equatorial exchange is very low in these systems.

In order to acquire ¹³C NMR data on 1 over a range of temperatures in a reasonable time frame, the chloro derivative 10 was enriched in ¹³CO to the extent of ~30%; subsequent treatment with 3 equiv of AlCl_3 yields the cation 1 in which the acylium carbon is also enriched since it is derived via migration of a cobalt carbonyl to the apical

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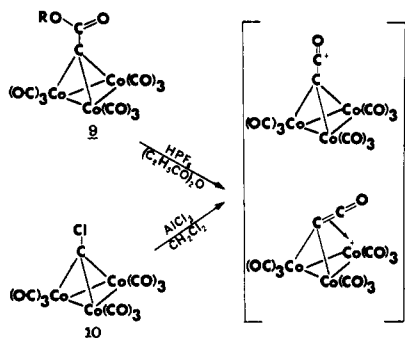
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Table I. ¹³C NMR Data (ppm) for Ketenylidene-Trimetallic Clusters and Related Molecules

	acylium carbon	apical carbon	J _{acyl-apical} , Hz	metal carbonyls		ref
[Fe ₃ (CO) ₉ CCO] ²⁻	182.2	90.1	74.0	222.3 ^a		6
[Fe ₃ (CO) ₉ (μ-CO)CH] ⁻		262.4		220.5 ^a		6
[Fe ₂ Co(CO) ₉ CCO] ⁻	172.5	82.8	79.4	213.5 ^b		7
[Ru ₃ (CO) ₉ (μ-CO) ₃ CCO] ²⁻	159.1	-28.3	96.0	273.3 [3] ^{b,c}		8
				204.0 [3]		
				202.3 [3]		
H ₂ Os ₃ (CO) ₉ CCO	160.3	8.6	86.0	175.6 [3]	165.8 [6] ^d	12
				179.6 [2]	173.0 [2] ^e	
				169.9 [1]	168.0 [2]	
					158.3 [2]	
[Co ₃ (CO) ₉ CCH ₂] ⁺	91.1 ^f	286.2		192.7 ^g		16
[Co ₃ (CO) ₉ CCO] ⁺	168.2	108.4		197.8 [3]	188.4 [6] ^h	this work
[(Ph ₃ P)Co ₃ (CO) ₈ CCO] ⁺	169.1			200.3 [2]	193.5 [6] ⁱ	this work
[CpMoCo ₂ (CO) ₈ CCO] ⁺	158.0			211.8 [2]	196.2 [6] ⁱ	this work

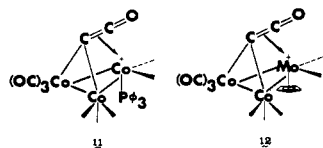
^a At 67.8 MHz (corresponds to 270 MHz for ¹H); temperature = -40 °C. ^b At 67.8 MHz; temperature = -90 °C. ^c Numbers in square brackets denote peak intensities. ^d At 67.8 MHz; temperature = +25 °C. ^e At 67.8 MHz; temperature = -60 °C. ^f Methylene carbon. ^g At 22.6 MHz (corresponds to 90 MHz for ¹H). ^h At 125.7 MHz (corresponds to 500 MHz for ¹H); temperature = -110 °C. ⁱ At 62.8 MHz (corresponds to 250 MHz for ¹H); temperature = -90 °C.

position. The alternative route to 1 from the ester 9 and HPF₆ does not enrich this acylium carbon. We note, however, that unlike Shriver's [Fe₃(CO)₉CCO]²⁻ and related molecules in which all carbons are derived from ¹³C-enriched CO, the apical carbon in 1 can only be enriched by using ¹³CCl₄ in the original synthesis of 10.



The room-temperature ¹³C NMR spectrum of 1 (see Figure 1) showed resonances at 191.2 and 168.2 ppm in the ratio 9:1, thus providing the first such chemical shift data for a cationic ketenylidene system. The cobalt carbonyl shift compares favorably with that of ~193 ppm in the [Co₃(CO)₉CCR₂]⁺ molecules previously examined by Seyferth and co-workers.¹⁶ An overnight run on 1 gave a broad peak (W_{1/2} = 280 Hz) at 108.4 ppm tentatively assigned to the apical carbon; a more definitive shift and measurement of the coupling constant between this nucleus and the contiguous acylium carbon would require a sample enriched via the ¹³CCl₄ route discussed above. A comparison of the ¹³C NMR chemical shifts of the known ketenylidene clusters and of some related molecules appears as Table I.

When the sample of 1 was cooled, the acylium peak at 168.2 ppm remained sharp but the metal carbonyl resonance eventually split into two peaks at 197.8 and 188.4 ppm in the ratio 3:6. Similar behavior was observed for the triphenylphosphine-substituted cluster 11 for which



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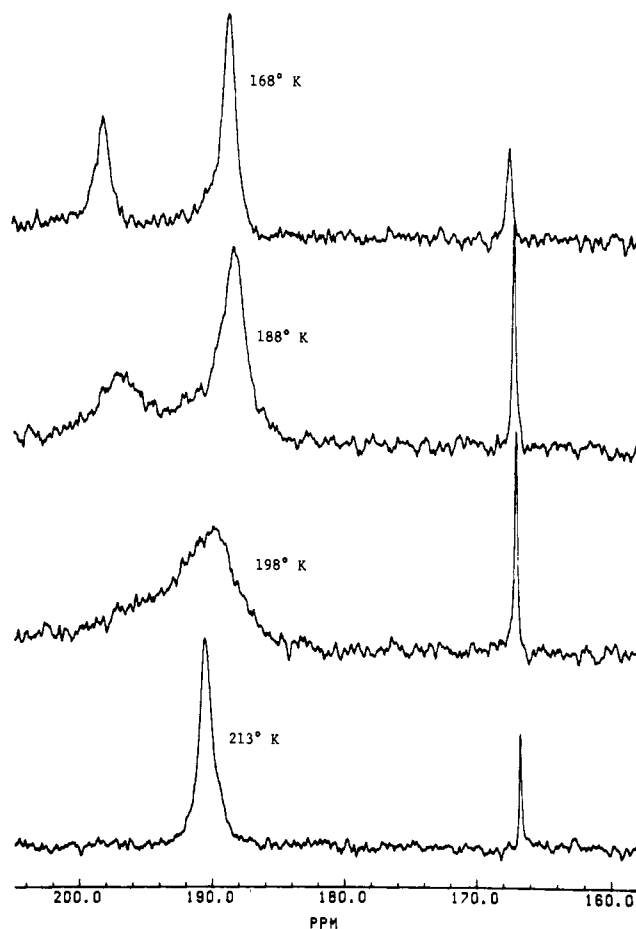


Figure 1. Variable-temperature 125.7-MHz ¹³C NMR spectra of [Co₃(CO)₉CCO]⁺ (1).

the low-temperature spectrum exhibited peaks at 200.3, 193.5, and 169.1 ppm in the ratio 2:6:1. It is noticeable, however, that in the phosphine cluster the onset of peak decoalescence was observed at a much higher temperature, and this is reflected in the ΔG[‡] values for carbonyl exchange which were measured to be 7.0 ± 0.5 and 9.0 ± 0.5 kcal mol⁻¹ for 1 and 11, respectively.

One can envisage two scenarios consistent with the 3:6 splitting of the carbonyl resonances in 1: the first would maintain the C_{3v} geometry 1a with slow exchange of the axial and equatorial ligands on the NMR time scale, while the second explanation would invoke tilting of the kete-

nylidene moiety so as to render two $\text{Co}(\text{CO})_3$ groups different from the third as in **1b**. We do not favor the first model since it is known that the barrier to $\text{Co}(\text{CO})_3$ rotation is very low in the neutral clusters.¹⁴ The second structure permits the continued rapid tripodal rotation of the $\text{Co}(\text{CO})_3$ moieties but allows for a clear differentiation of the two cobalt environments. Furthermore, the resonance position of the apical carbon is more typical of a π -bonded sp^2 carbon than of a carbyne. However, one cannot place too much diagnostic value on the chemical shift of the apical carbon since, as shown in Table I, they span a very large range.

If one takes the view that axial-equatorial carbonyl exchange is not the process responsible for the coalescence phenomenon, then one can envisage two viable mechanisms for equilibrating the carbonyl environments in the tilted structure **1b**. The first would involve migration of the ketenylidene moiety from one cobalt vertex to another, analogous to the proposal of Schilling and Hoffmann for $[\text{Co}_3(\text{CO})_9\text{CCH}_2]^+$. The observed barrier for **1** is 7 kcal mol⁻¹ compared to 10.5 kcal mol⁻¹ for **3**. The rather small barrier to migration of the ketenylidene unit from cobalt to cobalt may be a reflection of the decreased steric demand of the $\text{C}=\text{C}=\text{O}$ group relative to that of a $\text{C}=\text{CR}_2$ fragment. In the former case, rotation about the $\text{C}=\text{C}=\text{O}$ axis has no effect, whereas for the vinylidene unit the coupled rotations push an alkyl substituent closer to the metal triangle.^{9,10} However, one must also consider a second carbonyl exchange mechanism, viz., intermetallic carbonyl migration which is known to occur around the metal triangular face of RCM_3 tetrahedral molecules.^{15,17}

To investigate this further we prepared the triphenylphosphine-substituted cation **11**. Although the single positive charge is undoubtedly delocalized over the cluster, structure **1b** places a formal charge on the unique cobalt atom. We felt that incorporation of a phosphine would help alleviate this positive charge and so would enhance the tendency of the ketenylidene moiety to interact with the metal atom center. This molecule has C_s symmetry whether the capping unit is vertical or bent toward the cobalt atom which bears the phosphine. If the ketenylidene fragment were positioned proximate to one of the $\text{Co}(\text{CO})_3$ vertices, then the molecule would be chiral and the low temperature spectrum would be expected to show a 2:3:3 splitting, but the experimental observation is a 2:6 pattern. Clearly here one is measuring the barrier to inter-cobalt carbonyl migration, and the value of 9 kcal mol⁻¹ is in line with our previous results on related molecules.^{17d} We are, therefore, of the opinion that the coalescence phenomenon observed in **1** is indeed a measure of the barrier to $\text{C}=\text{C}=\text{O}$ migration rather than intermetallic carbonyl exchange. Furthermore, we note that in **11** the set of six cobalt carbonyls exhibits a sharp singlet even at low temperature suggesting that the barrier to axial-equatorial exchange is too low for us to stop the process on the NMR time scale.

Studies are continuing in this area with efforts being concentrated on $[(\text{diphos})\text{Co}_3(\text{CO})_7\text{CCO}]^+$ and $[(\text{triphos})\text{Co}_3(\text{CO})_6\text{CCO}]^+$; hopefully, variable-temperature ³¹P NMR spectra will help to clarify the situation. Finally, we note that the ¹³C NMR spectrum of the mixed-metal

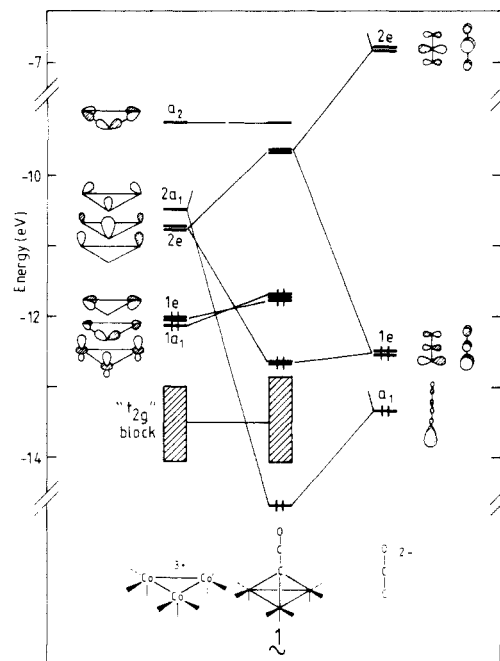


Figure 2. Orbital interaction diagram for $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ in C_{3v} symmetry.

cation $[\text{CpMoCo}_2(\text{CO})_8\text{CCO}]^+$ (**12**), the synthesis and chemistry of which has been described elsewhere,¹⁸ exhibits a single metal carbonyl resonance at room temperature but at -90°C has peaks at 211.8, 196.2, and 158.0 ppm in the ratio 2:6:1. These are clearly attributable to $\text{Mo}(\text{CO})_2$, $\text{Co}_2(\text{CO})_6$, and the acylium carbon, respectively. The sharpness of the cobalt carbonyl signal does not suggest the probability of stopping the axial-equatorial exchange of carbonyls on cobalt.

To complement our experimental data on $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ and related molecules, we have carried out molecular orbital calculations at the extended Hückel level. As mentioned previously, the bending of $\text{C}=\text{CH}_2$ fragment toward a metal vertex was predicted by Schilling and Hoffmann⁹ and subsequently experimentally verified.¹⁰ We commence with a description of the $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ in the C_{3v} geometry. As shown in Figure 2, the molecule can be constructed conceptually from the well-known tricobalt nonacarbonyl fragment⁹ and a ketenylidene moiety. The former presents a set of three orbitals ($2a_1 + 2e$) well oriented for interaction with a capping unit. Below them lies another set of three frontier orbitals ($1a_1 + 1e$). The ketenylidene fragment (regarded formally as $[\text{CCO}]^{2-}$) gives rise to five frontier orbitals of which the lowest is the σ lone pair (a_1) on the terminal carbon. Above this is situated a degenerate pair of filled nonbonding $1e$ orbitals of π symmetry; at considerably higher energy lies the vacant π^* system ($2e$). The π^* antibonding orbitals of the $[\text{CCO}]^{2-}$ unit lie at too high an energy to interact significantly with the occupied frontier orbitals of the cobalt triangle; furthermore, the localization of these orbitals on the terminal carbon is rather poor.

The major interaction of the ketenylidene lone pair is with the vacant $2a_1$ frontier orbital of the metal system (formally $[\text{Co}_3(\text{CO})_9]^{3+}$) and is, of course, strongly stabilizing. However, the ketenylidene a_1 orbital also interacts to some extent with the filled $1a_1$ of the metal triangle with some consequent destabilization. Analogously, within the e manifold, we have a favorable $1e$ ($[\text{CCO}]^{2-}$) and $2e$

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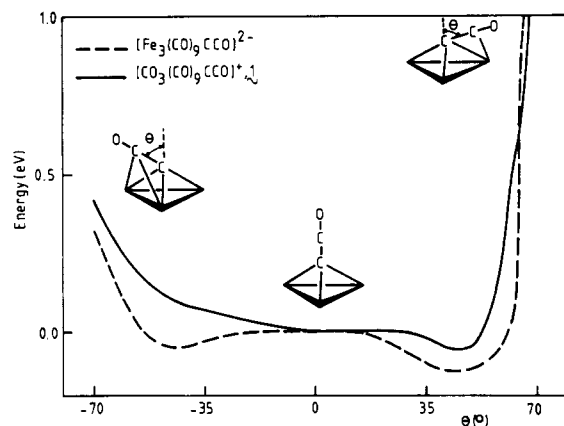


Figure 3. Energy level diagram showing the effect of tilting the capping ketenylidene unit from the threefold axis perpendicular to the plane of the metals in $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ and in $[\text{Fe}_3(\text{CO})_9\text{CCO}]^{2-}$.

($[\text{Co}_3(\text{CO})_9]^{3+}$) interaction which is partially counteracted by the repulsion with the filled metal $1e$ orbital. The ketenylidene π^* orbitals ($2e$) also play a rôle in that they interact significantly only with the $2e$ orbitals of the cobalt triangle, thus preventing the latter orbitals from giving rise to a relatively high-lying LUMO. To summarize, therefore, the cation **1** possesses six skeletal electron pairs in orbitals derived principally from the $1a_1$ and $1e$ sets of the $[\text{CCO}]^{2-}$ and $[\text{Co}_3(\text{CO})_9]^{3+}$ fragments.

It is instructive now to compare the energy level patterns of the apparently closely related $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ (**1**) and $[\text{Co}_3(\text{CO})_9\text{CCH}_2]^+$ (**3**) cations in which the capping groups are positioned along the C_3 axis. In the latter case, the π^* orbital of the vinylidene fragment lies at considerably lower energy (by ~ 2.4 eV) than do the corresponding π^* orbitals of the ketenylidene unit. The net result for the vinylidene-capped cluster **3** is a lowlying LUMO which, together with the relatively high-lying HOMO, produces a rather small HOMO–LUMO gap and leaves open the possibility of geometric deformation to stabilize the system. The HOMO–LUMO gap in **3** increases markedly on reorienting the vinylidene toward a metal atom, and this is, in fact, the observed geometry.

Returning now to the molecule of interest, viz., **1**, we note initially that the HOMO–LUMO gap is more than double that for **3**; this means that in **1** there is a weaker driving force for a second-order Jahn–Teller distortion away from the C_{3v} structure. In Figure 3 are shown the results of tilting the ketenylidene fragment away from the C_3 axis in the $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ and $[\text{Fe}_3(\text{CO})_9\text{CCO}]^{2-}$ molecules. As anticipated from the Jahn–Teller argument, the stabilization upon tilting the capping unit is small and indeed the curves are almost flat over a wide range of angles. Nevertheless, there is a distinct, though shallow, minimum when the ketenylidene is tilted toward a cobalt vertex.

In terms of orbital interactions, the overlap of the σ lone pair of the $[\text{CCO}]^{2-}$ with the metal triangle scarcely changes upon bending. In contrast, the π interactions are rather complicated. Typically, when bending toward a metal atom, the interaction of the symmetric component of the ketenylidene $1e$ set with the corresponding metal $2e$ orbital diminishes; however, there is a new and favorable overlap with the $2a_1$ orbital since the symmetry constraint disappears in C_s symmetry. Furthermore, similar stabilization and destabilization effects are observed for the metal $1e$ and $1a_1$, respectively. Overall, these effects are rather small and almost self-cancelling so that, as shown in Figure 3, the curve is almost flat and only rises steeply when steric interactions come into play.

There is a fundamental difference between the $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ case just discussed and the $[\text{Co}_3(\text{CO})_9\text{CCH}_2]^+$ cation previously analyzed by Schilling and Hoffmann.⁹ In the latter molecule, bending of the vinylidene cap toward a cobalt atom produces a very favorable interaction between the symmetrical component of the $2e$ set of the metal triangle and the π orbital of the $\text{C}=\text{CH}_2$ unit which is well-localized on the methylene carbon, thus creating direct bonding between this carbon and a cobalt atom. There is an analogous, but slightly weaker, interaction when the vinylidene unit is oriented toward a cobalt–cobalt vector. In contrast, for $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$ the localization of the $1e$ orbitals on the central carbon of the ketenylidene moiety is rather poor so this particular orbital interaction is disfavored. There is, however, favorable localization on the central carbon atom of the $[\text{CCO}]^{2-}$ unit in the π^* ($2e$) orbitals, but they are too high in energy to provide significant stabilization to the $1a_1$ or $1e$ orbitals of the triangle and so do not provide a strong driving force for the bending. Thus, the curve shown in Figure 3 is a compromise of numerous weak and opposing interactions.

Finally, we note that calculations on Shriver's $[\text{Fe}_3(\text{CO})_9\text{CCO}]^{2-}$ compound (see Figure 3) reveal two shallow minima of which the lower (depth ≈ 3 kcal mol⁻¹) corresponds to a tilting of the capping group by $\sim 45^\circ$ toward an iron vertex. Gratifyingly, the crystallographic data show a bend of 33° in this direction.⁶ Interestingly, in the ruthenium analogue⁸ the capping ketenylidene tilts the other way toward a ruthenium–ruthenium vector perhaps corresponding to the other minimum on the graph calculated for the iron complex.

To conclude, we feel that the available evidence strongly favors the bent configuration **1b** for $[\text{Co}_3(\text{CO})_9\text{CCO}]^+$, thus paralleling the situation for $[\text{Co}_3(\text{CO})_9\text{CCH}_2]^+$ and for $[\text{Fe}_3(\text{CO})_9\text{CCO}]^{2-}$. We propose that the low-temperature ^{13}C NMR spectrum of **1** can be interpreted in terms of a slow interconversion of molecules in which the ketenylidene capping unit is tilted toward one of the cobalt vertices; the exchange of axial and equatorial carbonyl ligands is very fast on the NMR time scale, but in clusters in which one $\text{Co}(\text{CO})_3$ vertex has been replaced by a $\text{Co}(\text{CO})_2\text{PPh}_3$ or $\text{CpMo}(\text{CO})_2$ fragment intermetallic carbonyl migration can be observed. EHMO calculations also favor the bending of the CCO capping moiety toward a cobalt atom, but energy stabilization thus achieved is markedly less than for the analogous $\text{C}=\text{CH}_2$ fragment.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen, and the solvents were dried and distilled before use. ^{13}C NMR spectra were recorded in CD_2Cl_2 on Bruker WM250 and AM500 spectrometers operating at 62.8 and 125.7 MHz, respectively. $\text{Co}_3(\text{CO})_9\text{CCl}$,¹⁹ $(\text{Ph}_3\text{P})\text{Co}_3(\text{CO})_8\text{CCl}$,^{5b} $\text{Co}_3(\text{CO})_9\text{CCO}^+$,^{5b} $(\text{Ph}_3\text{P})\text{Co}_3(\text{CO})_8\text{CCO}^+$,^{5b} and $\text{CpMoCo}_2(\text{CO})_8\text{CCO}_2\text{CHMe}_2$,²⁰ were prepared by literature methods. $\text{CpMoCo}_2(\text{CO})_8\text{CCO}^+$ was prepared as described elsewhere.¹⁸ All other cations were prepared as their $\text{AlCl}_4^-n\text{AlCl}_3$ salts.

^{13}C Enrichment of $\text{Co}_3(\text{CO})_9\text{CCl}$. A 1.0-g sample of $\text{Co}_3(\text{CO})_9\text{CCl}$ was dissolved in 15 mL of CH_2Cl_2 . The solution was degassed, and 760 torr of ^{13}C O was placed over the solution which was then stirred for 1 week at room temperature. The exchanged CO was then removed, the solution exposed to fresh ^{13}C O, and the process repeated. After filtration to remove any decomposed cluster, the CH_2Cl_2 was removed under vacuum. This procedure resulted in $\sim 30\%$ enrichment of all carbonyls in $\text{Co}_3(\text{CO})_9\text{CCl}$. The degree of enrichment was determined from the mass spectrum

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Table II. Extended Hückel Parameters

orbital	H_{ii} , eV	exponents ^a	
		ζ_1	ζ_2
C 2s	-21.40	1.625	
2p	-11.40	1.625	
O 2s	-32.30	2.275	
2p	-14.80	2.275	
Fe 4s	-9.1	1.90	
4p	-5.32	1.90	
3d	-12.60	5.35 (0.5336)	1.8 (0.6678)
Co 4s	-9.21	2.00	
4p	-5.29	2.00	
3d	-13.18	5.55 (0.5550)	1.9 (0.6460)

^aTwo Slater exponents are listed for the 3d functions. Each is followed in parentheses by the coefficients in the double- ζ expansion.

of the product. Similar methods were employed for the ¹³C enrichment of (Ph₃P)Co₃(CO)₈CCl and CpMoCo₂(CO)₈CCO₂CHMe₂.

Molecular Orbital Calculations. All calculations were carried out within the extended Hückel formalism²¹ using the

weighted H_{ij} formula.²² The atomic parameters utilized are listed in Table II. The idealized experimental structure⁶ of Fe₃(CO)₉CCO²⁻ serves as the basic geometry for the iron and cobalt cluster models. Co-Co and Fe-Fe separations were 2.50 and 2.57 Å, respectively. The ketylidene group was placed 1.30 and 1.25 Å, respectively, above the metallic core. In all cases M-C(carbonyl) = 1.80 Å, C-O = 1.15 Å, C-C(ketylidene) = 1.30 Å, and C-O(ketylidene) = 1.29 Å.

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Stereochemistry and Mechanism of Nickel-Catalyzed Hydrocyanation of Olefins and Conjugated Dienes

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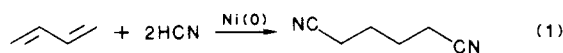
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The mechanism of nickel-catalyzed hydrocyanation of 3,3-dimethyl-1-butene and 1,3-cyclohexadiene has been studied. Formation of *erythro*-2,3-dideuterio-4,4-dimethylpentanenitrile (**2**) from nickel-catalyzed addition of DCN to (*E*)-1-deuterio-3,3-dimethyl-1-butene (**1**) shows that the DCN adds *cis* across the double bond. Nickel-catalyzed addition of DCN to 1,3-cyclohexadiene occurs both 1,4 and 1,2 with *cis* stereochemistry as shown by the formation of a 1:1 mixture of *cis*-4-deuterio-2-cyclohexene-1-carbonitrile (**8a**) and *cis*-6-deuterio-2-cyclohexene-1-carbonitrile (**8b**). A competitive experiment using HCN/DCN in a 1:1 ratio gave an isotope effect of 3.6 ± 0.4 in the hydrocyanation of 1,3-cyclohexadiene. The mechanism for the hydrocyanation reactions involves *cis* addition of nickel hydride followed by migration of coordinated cyanide to the coordinated hydrocarbon ligand formed.

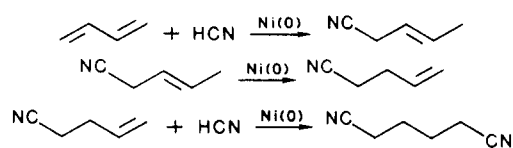
Introduction

The nickel-catalyzed hydrocyanation of butadiene (eq 1), known as the adiponitrile process,¹ is today the most



important process for industrial manufacture of adiponitrile. Approximately 75% of the total world production of adiponitrile is based on this process. The hydrocyanation reaction, which is catalyzed by nickel(0) phosphite complexes² in combination with a Lewis acid,^{3,4} proceeds in three discrete steps (Scheme I). All three steps, hydrocyanation of the diene, isomerization, and hydrocyanation of the terminal double bond, are catalyzed by nickel complexes.

Scheme I



Although nickel-catalyzed hydrocyanation has been known for some time, very little was reported in the literature concerning its mechanism until recently. In 1981 we reported in preliminary form on the stereochemistry of the nickel-catalyzed hydrocyanation of a monoolefin.⁵ Since then several groups^{4,6-8} have published mechanistic work on the hydrocyanation, and we⁹ have communicated

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