Gas-Phase Chemistry of Methenyltricobalt Nonacarbonyl Radical Anions

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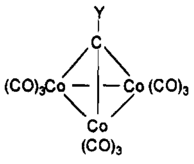
The gas-phase chemistry of the radical anions of methenyltricobalt nonacarbonyls, $YCCo_3(CO)_9$, where Y is H, CH_3, C_6H_5, C_6H_4F, CO_2CH_3, F, and Cl, is reported. Molecular anions are not stable, and $YCCo_3(CO)_n$ fragments are formed by losses of carbon monoxide via dissociative electron capture. The fragmentation that occurs upon ionization (seen in full-scan mass spectra) or collisional activation (seen in tandem mass spectra) is minor and is in accord with the proposed electron-rich, delocalized core of the $YCCo_3$ moiety. Bimolecular reactions of the methenyltricobalt nonacarbonyl radical anions with their neutral precursor or with neutral ligands were studied by Fourier transform mass spectrometry (FTMS). The reactions with the neutral precursors result in higher-order clusters containing five or six cobalt atoms and both apical substituents (i.e., $[(YC)_2Co_5(CO)_{11}]^-$ or $[(YC)_2Co_6(CO)_{13}]^-$). In mixtures of the methenyltricobalt nonacarbonyls with neutral ligands, substitution reactions are observed in which carbon monoxide is replaced by π-bonding ligands but not σ-bonding ligands.

Introduction

Methenyltricobalt nonacarbonyls, $YCCo_3(CO)_9$, occupy an interesting area in both structural and heteronuclear chemistry. The deep-purple metal-cluster complexes are remarkably stable in air and solvents compared to other complexes containing an isolated Co—C σ-bond.[1] Their inherent stability is underscored by the numerous and facile synthetic routes[2] and can be attributed, in part, to the high symmetry of the complexes. The molecular configuration possesses C_{3v} symmetry and consists of an apical-carbon substituent, symmetrically coordinated by three Co—C bonds to a basal $Co_3(CO)_9$ fragment containing identical $Co(CO)_3$ groups positioned at the corners of an equilateral triangle and bound to one another by Co—Co bonds (see structure 1). In the $YCCo_3(CO)_9$ compounds, three of the carbonyls are in axial positions whereas the remaining six are in equatorial positions.



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Since their discovery, methenyltricobalt nonacarbonyls have garnered considerable attention as possible heteronuclear catalysts. The complexes have been utilized as catalysts for the reduction of aromatic nitro compounds,[3] the hydroformation of alkenes,[4] and the hydrogenation of CO.[5] Furthermore, it was suggested that the complexes may serve as models for absorbed C-containing species on metal surfaces.[6]

Aside from their interest as catalysts, various efforts have been made to investigate the physical properties of these metal-cluster complexes. Photoelectron spectroscopy has been used to demonstrate the existence of substantial delocalization of π-type Y orbitals throughout the complexes.[7] Electrochemical studies have shown that the complexes readily undergo a chemically reversible, one-electron reduction to produce stable radical anions, but that they decompose upon oxidation or upon two-electron reduction.[8] Investigation by positive-ion mass spectrometry shows strong retention of the $YCCo_3$ core followed by cleavage of Co—Co bonds rather than Co—C bonds.[9]

Although reactions of the metal-cluster complexes have been previously studied in the gas-phase as radical cations,[9,10] no investigations of these complexes as radical anions have been reported. From a synthetic viewpoint, these types of investigations are of interest because several methods for transition-metal-mediated organic synthesis employ reactions involving either

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metal-anion intermediates or anionic nucleophiles with metal-coordinated ligands.[11] Thus, the aim of this study is to investigate the gas-phase reactivity of the methenyltricobalt nonacarbonyl radical anions.

Appropriate methods for the gas-phase reactivity study of the methenyltricobalt nonacarbonyl radical anions are tandem mass spectrometry[12] (MS/MS) and Fourier transform mass spectrometry[13] (FTMS). Providing information on the unimolecular reactivity of gas-phase ions is only one of the many inherent features of MS/MS. In these experiments, ions of a specific mass can be selected from other ions by using the first stage of a tandem instrument. The selected ions may fragment by metastable-ion decomposition or upon collisional activation to form product ions, which can then be detected by the second stage of the mass spectrometer. FTMS is ideally suited for bimolecular reactivity studies because it has the ability to trap, select, and store ions for extended periods of time. This methodology permits one to "follow" ion–molecule reactions by isolating the reactant ion and allowing it to react in the presence of a selected neutral for varying amounts of time. Collisional activation of ions can also be performed in the FTMS experiment.

Experimental Methods

Tandem Mass Spectrometer. The methenyltricobalt nonacarbonyl compounds were admitted, via a solids probe, into an electron-ionization source of a Kratos MS-50 triple-analyzer mass spectrometer of EBE design.[14] Full-scan experiments (resolution, R, = 2000; 10% valley definition) were calibrated with perfluorokerosene in the negative-ion mode. For the MS/MS experiments, precursor ions were selected (R = 2500) by using MS-1 (ESA-1 and magnetic sector), and ESA-2 was scanned to give a spectrum of the resulting fragment ions. Collisionally activated decomposition (CAD) experiments were performed with helium as a collision gas at pressures sufficient to reduce the ion signal by 80%, a regime in which principally double collisions of the ion occur.

Typical operating conditions for the tandem mass spectrometer experiments were accelerating voltage 8 kV, ionizing energy 70 eV, emission current 10 μA, and source temperature 50 °C. Frequent cleaning of all source components and replacement of rhenium filaments were necessary throughout this study.

Fourier Transform Mass Spectrometer. Ion–molecule reactions were investigated on a custom-built Fourier transform mass spectrometer and controlled by a Nicolet FTMS 2000 data system. The mass spectrometer was equipped with a 5.08-cm cubic cell in a 1.2-T magnetic field. The methenyltricobalt nonacarbonyl compound was admitted into the FT mass spectrometer cell via a solids probe to uncalibrated pressures of (3–20) × 10^{-7} Torr. Typical ionizing energies were 0.5–2.0 eV at an emission current of 0.2 μA, and the trapping plates were held at 1 V. Several experiments were done with the trapping plates held at 2 V to distinguish the doubly-charged anions from second-harmonic artifacts. The presence of dianions was also confirmed by the disappearance of the peak at the doubly-charged mass upon ion ejection.

Table 1. Partial Negative-Ion Mass Spectra of $YCCo_3(CO)_9$ Compounds at 70 eV

species	H	CH_3[a]	C_6H_5	C_6H_4F	F	CH_3CO_2	Cl[b]
$[YCCo_3(Co)_9]^-$	0	0	0	0	0	0	0
$[YCCo_3(CO)_8]^-$	5.7	15.5	8.5	2.6	1.2	2.5	0.3
$[YCCo_3(CO)_7]^-$	100	100	100	100	100	65.2	0.2
$[YCCo_3(CO)_6]^-$	17.2	36.2	22.5	20.8	44.5	100	100
$[YCCo_3(CO)_5]^-$	5.2	3.8	9.7	1.6	5.5	66.6	67.5
$[YCCo_3(CO)_4]^-$	3.4	0	5.7	4.2	0.9	16.2	10.1
$[YCCo_3(CO)_3]^-$	1.4	0	2.6	2.5	0.3	5.8	8.4
$[YCCo_3(CO)_2]^-$	0.4	0	1.1	0.4	0	5.4	2.6
$[YCCo_3(CO)]^-$	0	0	0.3	0.2	0	0.1	0.7
$[YCCo_3]^-$	0	0	0	0	0	0	0.2

[a] Also shows loss of $[M - nCO - 2H]^-$ for n = 3–7. [b] Relative abundance of ^{35}Cl-containing ion.

The reagents used in the ligand substitution experiments were purchased from Matheson Gas Products, Inc. (acetylene, 1,3-butadiene, and dimethyl ether), Fischer Scientific (methanol), and MSD Isotopes (ethylene-d_4) and used without further purification. The reagents were introduced into the FT mass spectrometer cell through Varian leaks valves to obtain uncalibrated pressures ranging from (5 to 100) × 10^{-7} Torr. The pressure measurements of acetylene and 1,3-butadiene for the rate constant determinations were calibrated, in separate experiments, by using the reactions of the acetylene radical cation with neutral acetylene[15] and the 1,3-butadiene radical cation with neutral 1,3-butadiene,[16] both of which have known rate constants. The rate constants for the methenyltricobalt nonacarbonyl radical anions were calculated from experiments in which the selected ion was allowed to react with a neutral reagent at varying times and then the products formed in each reaction were measured.

Synthesis. The substituted methenyltricobalt nonacarbonyls were synthesized according to literature methods.[17]

Tandem Mass Spectrometer Results

Full-Scan Mass Spectrometry. The methenyltricobalt nonacarbonyl compounds display behavior similar to that of other polynuclear cobalt carbonyls.[18] The molecular anions are not stable, and the principal ions, formed via dissociative electron capture by loss of CO groups (see eq 1), account for nearly 100% of the

$$YCCo_3(CO)_9 + e^- \rightarrow [YCCo_3(CO)_{9-n}]^{\bullet -} + nCO \quad (1)$$

fragment ions (see Table 1). Each compound loses varying numbers of CO groups; only in the chloride compound is the carbonyl-free ion detected. Additionally, the spectrum for the methyl compound shows a series of ions formed by the loss of H_2 (or 2H) from the apical substitutent and in conjunction with loss of a CO molecule. The mechanism for these losses will be discussed in more detail in the section on tandem mass spectrometry.

The negative-ion mass spectra of these compounds provide some evidence for the stability of the anionic $YCCo_3$ core within the complexes. Complete retention of the $YCCo_3$ core was observed for all the compounds. These results are consistent with the concept of a delocalized $YCCo_3$ core, which has been reported to

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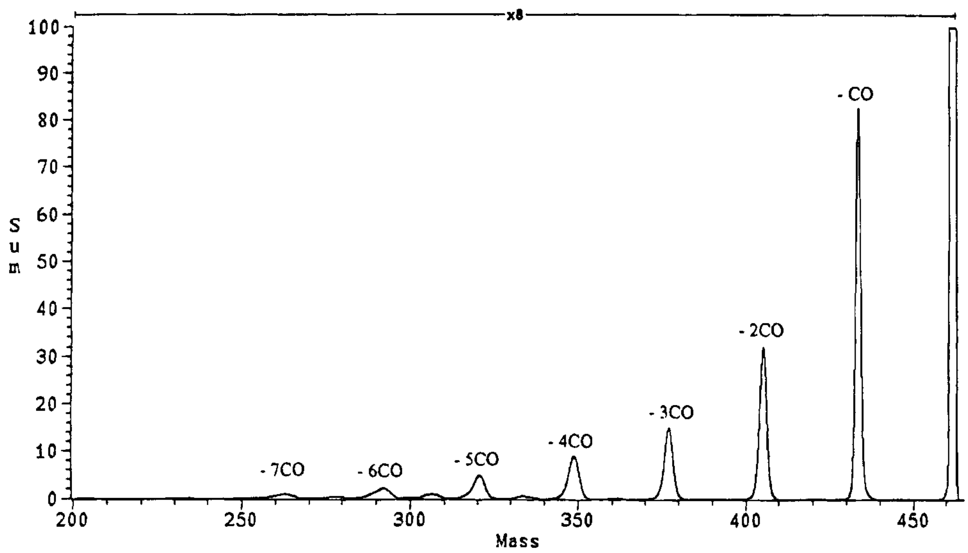
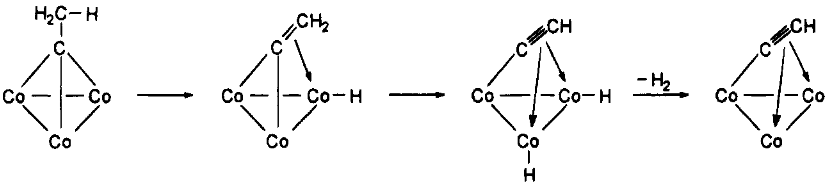


Figure 1. CAD spectrum of the $[C_6H_5CCo_3(CO)_7]^-$ radical anion. Data were taken by using a Kratos MS-50 tandem mass spectrometer.

Scheme 1



function as an electron reservoir that provides stability to the molecule.[8]

It is interesting to note here that the electron-deficient methenyltricobalt nonacarbonyl radical cation undergoes fragmentation of the $YCCo_3$ core. Multiphoton ionization of the methyl compound shows only a small degree of retention (<5%) of the $YCCo_3$ core; photolysis at 337 nm favors greater retention than at 450 nm.[19] Fragmentation upon electron ionization at 70 eV gives approximately 80% retention of the $YCCo_3$ core for some of the same compounds investigated here.[9] It should be mentioned, however, that each compound does produce a detectable positive molecular ion.[9]

Tandem Mass Spectrometry. Although full-scan mass spectrometry can provide some information on the unimolecular reactivity of the methenyltricobalt nonacarbonyl radical anions, a more detailed understanding can be achieved by use of MS/MS. Under metastable or collisional activation conditions, the fragmentations of a preselected ion can be observed and recorded. In metastable-ion decomposition (MID) experiments, the observed product ions are generally formed via low-energy fragmentation or rearrangement processes whereas product ions from collisional activation decomposition (CAD) experiments are formed via both low- and high-energy processes.

Table 2. Percent Product Ion Yield[a] of $[YCCo_3(CO)_7]^-$ Radical Anions

Y	% product ion yield	Y	% product ion yield
F	21.4	C_6H_4F	7.5
Cl	15.4	CH_3	6.8
CH_3CO_2	11.4	H	5.2
C_6H_5	7.9		

[a] Relative error estimated at approximately 20%.

The MID spectra of $[YCCo_3(CO)_7]^-$ for each compound show that losses of one or two CO molecules occur. MID spectra for the $[CH_3CCo_3(CO)_n]^-$ ions, where $n = 5-8$, were also obtained to determine the origin of H_2 (or 2H) loss. Losses of one or two CO molecules occur for ions of $n = 6-8$ and the loss of hydrogen occurs from ions of $n = 5$ and 6. The $[CH_3CCo_3(CO)_6]^-$ ion loses hydrogen only in conjunction with the loss of CO whereas the $[CH_3CCo_3(CO)_5]^-$ ion loses hydrogen nearly exclusively. The mechanism for this breakdown, however, is difficult to establish at the present, but a concerted 1,1-H_2 elimination seems improbable. A more reasonable mechanism is shown in Scheme 1.

To observe high-energy fragmentation processes, CAD spectra were recorded for the $[YCCo_3(CO)_7]^-$ ion of each compound. The ions exhibit stepwise losses of all seven CO molecules and minor fragmentation of the $YCCo_3$ core (see Figure 1). Notable is the ion of m/z 171 in the CAD spectrum of $[CH_3CCo_3(CO)_7]^-$. This ion is presumably $[Co(CO)_4]^-$, which was postulated to be the starting reactant in the preparation of $CH_3CCo_3(CO)_9$.[20]

Further distinctions between the apical substituents of the methenyltricobalt nonacarbonyl radical anions can be made by measuring the product ion yield of each $[YCCo_3(CO)_7]^-$ ion in the CAD spectrum (see Table 2). The product ion yield is defined as the ratio of product ion abundances to the precursor ion abundance measured after beam suppression and then corrected for beam attenuation. The yields are generally higher for compounds containing electron-withdrawing apical substituents, whereas they are lower for compounds containing electron-donating apical substituents.

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These differences are attributed, in part, to the ability of electron-donating apical substituents to add strength to the Co—CO bonds, thereby allowing for less fragmentation and lowering the yield of product ions. Electron-donating substituents increase the charge on the Co atoms which, although weakening the Co—CO σ bonding, raises the energy of the metal π-orbitals and increases back-donation.[21] Other factors, however, such as the propensity for electron detachment[22] or the collision cross-sections,[23] both of which cannot be measured on this instrument, may also influence the product ion yield.

The product ion yields for $[CH_3CCo_3(CO)_8]^-$ and $[CH_3CCo_3(CO)_6]^-$ were determined to be 8.1 and 4.5%, respectively. These values are consistent with a decrease in the number of fragmentation pathways; that is, the ion with the least number of CO molecules gives the smallest product ion yield.

Fourier Transform Mass Spectrometer Results

As in the negative-ion sector mass spectrometry experiments, no molecular anions are detected in a normal FTMS experiment, even at a low ionizing energy (~1 eV). At an ionizing energy of 70 eV, the fragmentation pattern for each compound is comparable with that obtained in the tandem mass spectrometer experiments, except for small differences in relative abundances owing to variations in instrumental and experimental conditions. At low ionizing energy, the principal ions formed are $[YCCo_3(CO)_7]^-$ for the hydrido, methyl, phenyl, fluoride, *p*-fluorophenyl, and acetyl compounds. Small abundances of $[YCCo_3(CO)_6]^-$ and $[YCCo_3(CO)_8]^-$ are also observed for these compounds. For the chloride compound, the principal ions are $[YCCo_3(CO)_5]^-$ and $[YCCo_3(CO)_6]^-$.

Doubly-charged species of the principal ions are also observed in low abundance (<1%) for all of the compounds at low and high ionizing energies. These species are of interest because their lifetime in solution is short[8] and because the existence of doubly-charged anions in the gas phase is rare.[24] In the present study, the dianions are most likely formed by electron capture (see eq 2) of low-energy secondary electrons (~1 eV),[25] which are stored, along with the monoanions, in the FTMS cell.

$$[YCCo_3(CO)_7]^{\bullet-} + e^- \rightarrow [YCCo_3(CO)_7]^{2-} \quad (2)$$

Evidence for electron capture is demonstrated by use of multiple-resonance techniques,[26] where an ion of interest can be ejected from or isolated in the FTMS cell. The doubly-charged species of $[(C_6H_4F)CCo_3(CO)_7]^-$ is not detected when its precursor is ejected from the cell. Moreover, the production of $[(C_6H_4F)CCo_3(CO)_7]^{2-}$ increases when $[(C_6H_4F)CCo_3(CO)_7]^-$ is isolated and then allowed to react over increasing periods of time. The dianions are absent in the tandem mass spectrometry experiments, where the electrons used for ionization are highly energetic (~70 eV) and are not stored.

Bimolecular Reactions. To study the bimolecular reactivity of the methenyltricobalt nonacarbonyl radical anions, multiple-resonance techniques were utilized. Two types of reactions were observed when the principal ion for each compound was allowed to react with its neutral precursor. The addition of a CO molecule to the reactant ion occurs in conjunction with the formation of clusters containing either five or six cobalt atoms and both apical substituents.

The structure of the $[YCCo_3(CO)_8]^-$ ion formed in the bimolecular reaction (see eq 3)[27] is likely to be the same as that formed by electron ionization in the normal FTMS experiment. Both ions are unreactive in the presence of the neutral precursor, and their inertness may be attributed to the presence of a bridging carbonyl that occupies two metal centers. Such species, irrespective of the apical substituent, are known to exist in solution.[20]

$$[YCCo_3(CO)_7]^{\bullet-} + YCCo_3(CO)_9 \rightarrow [YCCo_3(CO)_8]^{\bullet-} + YCCo_3(CO)_8 \quad (3)$$

For the bimolecular reactions in which higher-order clusters are formed, the principal product ions possess five or six cobalt atoms as well as both apical substituents (see Table 3). The types of products are determined, in large part, by the number of CO molecules in the reactant ion. For example, in the reaction of the $[YCCo_3(CO)_7]^-$ ion, where Y is the hydrido, fluoride, methyl, acetyl, phenyl, or fluorophenyl apical substituent, the predominant product ion contains five cobalt atoms and both apical substituents. For the $[YCCo_3(CO)_6]^-$ reactant ion, where Y is a fluoride or chloride substituent, the product ions include all six cobalt atoms as well as both apical substituents. Both types of reactions, however, occur when mixtures of hydrido or methyl and chloride compounds are introduced into the FTMS cell; that is, the formation of product ions containing either five or six cobalt atoms and both apical substituents is observed when the $[HCCo_3(CO)_7]^-$ or $[CH_3CCo_3(CO)_7]^-$ ion reacts with $ClCCo_3(CO)_9$. Similarly, products that include five or six cobalt atoms as well as both apical substituents are formed in the reaction of the $[ClCCo_3(CO)_6]^-$ ion with $HCCo_3(CO)_9$ or $CH_3CCo_3(CO)_9$.

Additional product ions from the cluster reactions are formed by losses of one or more CO molecules from the major product ions, but they are in low abundance. Investigation of the $[(HC)_2Co_5(CO)_{11}]^-$ and $[(ClC)_2Co_6(CO)_{11}]^-$ ions by CAD in the FT mass spectrometer also shows only loss of one or more CO molecules. No further reactions of the product ions with their neutral precursor were detected.

Numerous reports have demonstrated that methenyltricobalt nonacarbonyls can bond with other clusters.[28]

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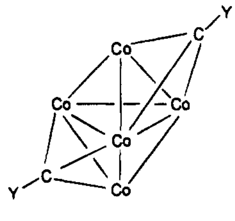
Table 3. Bimolecular Reactions Forming Co_5 and Co_6 Cluster Anions

precursor ion	neutral precursor	product ion	neutral product	abundance
$[HCCo_3(CO)_7]^-$	$HCCo_3(CO)_9$	$[(HC)_2Co_5(CO)_{11}]^-$	"$Co(CO)_5$"	100
		$[(HC)_2Co_5(CO)_{10}]^-$	"$Co(CO)_6$"	5
		$[(HC)_2Co_6(CO)_{13}]^-$	3CO	8
		$[(HC)_2Co_6(CO)_{12}]^-$	4CO	9
		$[(HC)_2Co_6(CO)_{11}]^-$	5CO	3
$[CH_3CCo_3(CO)_8]^-$	$CH_3CCo_3(CO)_9$	$[(CH_3C)_2Co_5(CO)_{11}]^-$	"$Co(CO)_6$"	100
		$[(CH_3C)_2Co_5(CO)_{10}]^-$	"$Co(CO)_7$"	5
		$[(CH_3C)_2Co_6(CO)_{13}]^-$	4CO	9
$[CH_3CCo_3(CO)_7]^-$	$CH_3CCo_3(CO)_9$	$[(CH_3C)_2Co_5(CO)_{11}]^-$	"$Co(CO)_5$"	100
		$[(CH_3C)_2Co_6(CO)_{13}]^-$	3CO	3
$[CH_3CCo_3(CO)_6]^-$	$CH_3CCo_3(CO)_9$	$[(CH_3C)_2Co_5(CO)_{11}]^-$	"$Co(CO)_4$"	100
		$[(CH_3C)_2Co_5(CO)_{10}]^-$	"$Co(CO)_5$"	15
		$[(CH_3C)_2Co_6(CO)_{13}]^-$	2CO	20
		$[(CH_3C)_2Co_6(CO)_{12}]^-$	3CO	13
		$[(CH_3C)_2Co_6(CO)_{11}]^-$	4CO	3
$[C_6H_5CCo_3(CO)_7]^-$	$C_6H_5CCo_3(CO)_9$	$[(C_6H_5C)_2Co_5(CO)_{11}]^-$	"$Co(CO)_5$"	100
		$[(C_6H_5C)_2Co_6(CO)_{12}]^-$	4CO	10
$[C_6H_4FCCo_3(CO)_7]^-$	$C_6H_4FCCo_3(CO)_9$	$[(C_6H_4FC)_2Co_5(CO)_{11}]^-$	"$Co(CO)_5$"	100
$[FCCo_3(CO)_6]^-$	$FCCo_3(CO)_9$	$[(FC)_2Co_5(CO)_9]^-$	"$Co(CO)_6$"	48
		$[(FC)_2Co_5(CO)_8]^-$	"$Co(CO)_7$"	90
		$[(FC)_2Co_6(CO)_{11}]^-$	4CO	93
		$[(FC)_2Co_6(CO)_{10}]^-$	5CO	100
$[FCCo_3(CO)_7]^-$	$FCCo_3(CO)_9$	no detected products		
$[CH_3CO_2CCo_3(CO)_6]^-$	$CH_3CO_2CCo_3(CO)_9$	$[(CH_3CO_2C)_2Co_5(CO)_{10}]^-$	"$Co(CO)_6$"	12
		$[(CH_3CO_2C)_2Co_6(CO)_{12}]^-$	4CO	18
		$[(CH_3CO_2C)_2Co_6(CO)_{11}]^-$	5CO	12
		$[(CH_3CO_2C)_2Co_6(CO)_{10}]^-$	6CO	20
		$[(CH_3CO_2C)_2Co_6(CO)_9]^-$	7CO	100
$[ClCCo_3(CO)_6]^-$	$ClCCo_3(CO)_9$	$[(ClC)_2Co_6(CO)_{11}]^-$	4CO	100
		$[(ClC)_2Co_6(CO)_{10}]^-$	5CO	38
$[HCCo_3(CO)_6]^-$	$ClCCo_3(CO)_9$	$[(HC)(ClC)Co_5(CO)_{10}]^-$	"$Co(CO)_6$"	45
		$[(HC)(ClC)Co_5(CO)_9]^-$	"$Co(CO)_7$"	23
		$[(HC)(ClC)Co_6(CO)_{11}]^-$	5CO	100
		$[(HC)(ClC)Co_6(CO)_{10}]^-$	6CO	32
		$[(HC)(ClC)Co_6(CO)_9]^-$	7CO	43
$[ClCCo_3(CO)_6]^-$	$HCCo_3(CO)_9$	$[(HC)(ClC)Co_6(CO)_{11}]^-$	4CO	100
$[FCCo_3(CO)_7]^-$	$ClCCo_3(CO)_9$	$[(FC)(ClC)Co_5(CO)_{10}]^-$	"$Co(CO)_6$"	100
$[CH_3CCo_3(CO)_6]^-$	$ClCCo_3(CO)_9$	$[(CH_3C)(CCl)Co_6(CO)_{11}]^-$	5CO	44
		$[(CH_3C)(CCl)Co_6(CO)_{10}]^-$	6CO	100

[a] Relative abundance of Co_5 and Co_6 cluster anions; the major peak is designated as 100%.

The products in these previous studies are linked from the carbon atom of one CCo_3 cluster to the other cluster, either by a direct linkage or through an intermediate carbon chain. This circumstance, however, is unlikely for the clusters formed in the FTMS experiments because the apical substituents are retained. The initial linkage of the cluster is more likely through one or more cobalt atoms, where there can be two or three open coordination sites depending on the number of carbonyls in the reactant ion.

Possible structures for the polynuclear cluster anions can be considered as a function of their total number of electrons. For the Co_5 species, likely core structures are trigonal bipyramidal (see structures **2** and **3**) or square pyramidal (see structures **4** and **5**). The relatively high stability of the $[(YC)_2Co_5(CO)_{11}]^-$ ions in all cases examined, except for Y = F or CO_2CH_3, can be explained in terms of structures **3** or **4**. These ions have 72 and 74 total electrons, respectively, and are electron-precise. Although the individual cobalt atoms do not all have 18-electron configurations, some redistribution of electronic charge can be achieved by having edge- or face-bridging CO groups. Losses of CO molecules result in species which are electron-deficient. The square pyramidal cluster **5**, in which an alkyne C_2Y_2 caps the square face, is a 72-electron species if 11 CO groups are also attached to the cobalt atoms.



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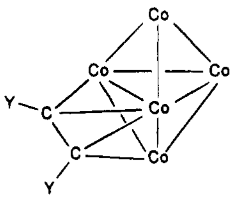

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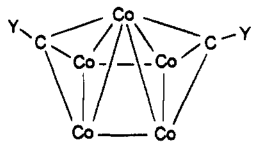

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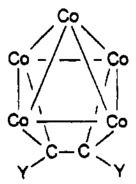

5

The problem of whether the two CY units are linked (to form an alkyne-type group) or are separate cannot be resolved definitively on the evidence available here. Coupling of the CY units on clusters has many precedents in vitro; reactions of alkynes with other Co-triad clusters have resulted in the fission to two CY units.[29] It is noted here, however, that the CY unit can donate six electrons, whereas the alkyne C_2Y_2 can only donate

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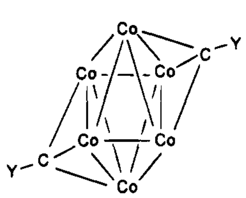
(29) Clauss, A. D.; Shipley, J. R.; Wilker, C. N.; Hoffman, R. *Organometallics* **1984**, *3*, 619.

four electrons. It is possible therefore, that the loss of CO from **3** or, alternatively, the greater relative stabilities of $[(YC)_2Co_5(CO)_{11}]^-$ ions for Y = F or CO_2CH_3 are related to the C—C bond breaking of the C_2Y_2 ligand in **3** to give a similar structure **2**, in which the two CY groups each cap a triangular face of the trigonal pyramidal cluster.

Similar considerations apply to the hexanuclear cluster anions. In this case, it is not possible to have an electron-precise structure as there is an even number of metal atoms. This feature can, however, be accommodated by partial occupancy of one of the cluster molecular orbitals and, indeed, may be the driving force for fragmentation to the Co_5 anions.

The anions of highest stability have 12 or 13 CO ligands and are likely to possess an octahedral geometry (see structure **6**) with 87 total electrons. This structure is closely related to that of the hexanuclear carbonyl $Co_6(CO)_{16}$,[30] in which two face-bonding CO groups have been replaced by two CY moieties. Alternative structures in which a C_2Y_2 unit caps a triangular face or is incorporated into the cluster core can be proposed (see structure **7**), but the present evidence does not warrant detailed consideration.



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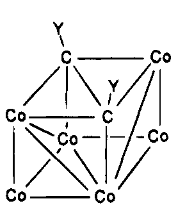

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Ligand Substitution. Mixtures of each compound and a variety of ligands were examined to delineate the occurrence of substitution reactions. The $[YCCo_3(CO)_7]^-$ ion was isolated as the reactant ion for each compound, except the chloride compound, which did not form the $[ClCCo_3(CO)_7]^-$ ion. The various species investigated include σ-bonding, unidentate ligands (CH_3OH and CH_3OCH_3), π-bonding, unidentate ligands (C_2D_4 and C_2H_2), and a π-bonding, multidentate ligand (1,3-butadiene). The reactions were typically conducted over the time frame of 5 ms to 5 s.

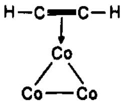
The reactions of several methenyltricobalt nonacarbonyl radical anions with CH_3OH or CH_3OCH_3 give no prominent products at low (~1 × 10^{-7} Torr) or at high (~(5−10) × 10^{-7} Torr) pressure. The nonoccurrence of substitution may be attributed to the weak π-acceptor abilities of CH_3OH and CH_3OCH_3 compared to those of the CO molecule.[31] It was previously suggested that the relative metal—ligand bond strengths that affect whether or not substitution occurs for electron-rich cobalt complexes are largely determined by the ability of the ligand to π-back-bond to the metal; the σ-donor ability of the ligand plays a less important role.[32] The results obtained here are in accord with solution chemistry for which there are only a few reports of ligand substitution of CO by a σ-donor, the most notable being the triphenylphosphine ligand.[20,30a]

Mixtures of each methenyltricobalt nonacarbonyl compound with various π-bonding ligands were also investigated. Ethylene has well-recognized π-bonding ability and can form a large number of organometallic complexes.[33] Reaction of C_2D_2 with several anionic clusters, however, produces no detectable substitution products at low or high pressures. The π-bonding ability of C_2D_4 does not appear to play a significant role in its CO substitution reactions. This may occur because ethylene has only one π* orbital available for backbonding to the metal, whereas the CO molecule has two.

The reaction of each $[YCCo_3(CO)_7]^-$ ion with the acetylene ligand yields one prominent product (see eq 4), although a minor loss of CO is observed from this product. For the fluoride compound, a second acetylene molecule is added to form the $[FCCo_3(CO)_5(C_2H_2)_2]^-$ ion, presumably to impart more stability to the electron-deficient core.

$$[YCCo_3(CO)_7]^{\bullet-} + C_2H_2 \rightarrow [YCCo_3(CO)_6(C_2H_2)]^{\bullet-} + CO \quad (4)$$

The structure of the acetylene complex may be viewed as a η^2-complex (see structure **8**), a μ-η^2-complex (see structure **9**), or a product of insertion, of which there are two possibilities for addition into two or three cobalt bonds (see structures **10** and **11**).[34] The fact that a second acetylene can be added to these complexes, however, suggests that the acetylene ligand functions as a two-electron π-donor[35] and, therefore, disfavors **9**. Collisional activation of the $[CH_3CCo_3(CO)_6(C_2H_2)]^-$ ion in the FT mass spectrometer produces preferential loss of C_2H_2 compared to that of CO, strongly indicating that the acetylene complex is a weakly-bound product, as in **8**, rather than the more strongly-bound insertion products.



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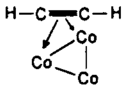

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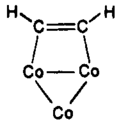

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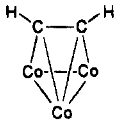

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The minor loss of CO from the acetylene product, $[YCCo_3(CO)_6(C_2H_2)]^-$, is most likely the result of acetylene acting as a four-electron donor. This behavior is known in metal-cluster chemistry.[34] Further evidence is the CAD spectrum of the $[CH_3CCo_3(CO)_5(C_2H_2)]^-$ ion, which shows loss of CO to be more favorable than loss

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(30) Albano, V. G.; Chini, P.; Scatturin, V. J. *J. Chem. Soc., Chem. Commun.* **1968**, 163.

(31) (a) Horrocks, W. D., Jr.; Taylor, R. C. *Inorg. Chem.* **1963**, *2*, 723. (b) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702. (c) Strohmeir, W.; Muller, F. J. *Chem. Ber.* **1967**, *100*, 2812.

(32) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1977**, *16*, 3135.

(33) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; Chapter 26.

(34) For a review of alkyne-substituted metallic carbonyl clusters, see: Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, 203.

(35) A similar argument was used in the reaction of $[Fe(CO)_3]^-$ with acetylene: McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095.

Table 4. Kinetic Data[a] for the Ion–Molecule Reactions of $[YCCo_3(CO)_7]^-$ with C_2H_2

Y	$10^{11}k_{total}$ (cm^3 $molecule^{-1}$ s^{-1})	$10^{10}k_L$ (cm^3 $molecule^{-1}$ s^{-1})
CH_3CO_2	7.9	8.43
CH_3	1.3	8.46
H	3.5	8.47
C_6H_5	1.1	8.42
C_6H_4F	1.6	8.41
F	6.4	8.45

[a] Relative error estimated at approximately 10%.

of C_2H_2. Several modes of attachment are possible although bridging to all three cobalt atoms is the most probable.

To study the electronic effects of the apical substituents, the rate of CO substitution with acetylene was investigated for each ion (see Table 4). The reaction efficiency can be estimated by comparing the experimental rate constant (k_{total}) to the theoretical collision rate (k_L),[36] which is mass dependent, for each reaction. The efficiency of each reaction varies from approximately 1% (i.e., one reaction per 100 collisions) for the phenyl compound to nearly 10% for the acetyl compound.

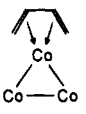
It is clear, however, from comparison of the rate constants for each compound that the reactions are governed more by the electronic behavior of the substituent than by the mass of the reactant ion. The rate constants are in accord with the concept of an electron-delocalized core where reactant ions with electron-withdrawing substituents (i.e., acetyl and fluoride) react more rapidly than ions with electron-donating substituents (i.e., methyl and phenyl); that is, the cobalt–CO bond is stronger in compounds with electron-donating apical substituents.[20]

Rate constants for the ion–molecule reactions of the $[CH_3CCCo_3(CO)_6]^-$ and $[CH_3CCo_3(CO)_8]^-$ ions with acetylene were determined to be 3.5×10^{-11} and $<10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The reactivity increases as the degree of coordinative saturation decreases, presumably to provide more stability to ions with a lesser number of CO molecules. These results are consistent with other investigations which demonstrated a direct correlation between the relative rate constants of the reactant ion species and their electron deficiencies.[37]

Ligand substitution reactions similar to those of acetylene occur in mixtures of a methenyltricobalt nonacarbonyl compound and the 1,3-butadiene ligand (see eq 5). As with the acetylene complexes, several

$$[YCCo_3(CO)_7]^{\bullet-} + C_4H_6 \rightarrow [YCCo_3(CO)_6(C_4H_6)]^{\bullet-} + CO \quad (5)$$

bonding possibilities exist in the formation of complexes of methenyltricobalt nonacarbonyl radical anions and butadiene. For the 1,3-butadiene ligand, perhaps the most common bonding mode is that of the η^4-cis complex involving one metal atom (see structure **12**).[38] The butadiene ligand can also bind as a σ-metallacyclopentene (see structure **13**) in which the π-bond may or may not interact with the other cobalt atoms.[39] When two or more metal atoms are proximate, the number of bonding modes increases. The butadiene ligand may bind not only to give a η^4-trans complex to a two metal center (see structure **14**) but also to form an insertion product whereby extensive rearrangements occur (see structures **15–17**). Investigation by CAD demonstrates that the $[CH_3CCo_3(CO)_6(C_4H_6)]^-$ ion favors loss of CO to that of C_4H_6, suggesting that the butadiene ligand binds to give an insertion product. Furthermore, studies of the $Fe(CO)_3(C_4H_6)$ radical anion show substitution of the η^4-butadiene ligand by stronger π-acceptors including the CO molecule.[40] In the present study, substitution of a CO molecule from the neutral precursor to the butadiene complex is not observed.



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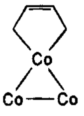

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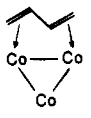

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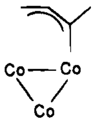

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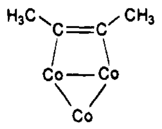

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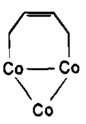

17

Trends in rate constants for the 1,3-butadiene ligand displacement reactions are similar to those of the acetylene reactions, although the reactions occur more slowly ($k_{total} \sim 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}).

A mixture of $CH_3CCo_3(CO)_9$ and equimolar amounts of C_2H_2 and C_4H_6 was examined for the purpose of determining the preferred direction of ligand substitution (see eq 6). Although both product anions, $[CH_3CCo_3(CO)_6(C_2H_2)]^-$ and $[CH_3CCo_3(CO)_6(C_4H_6)]^-$, are formed

$$[YCCo_3(CO)_6(C_2H_2)]^{\bullet-} + C_4H_6 \rightleftharpoons [YCCo_3(CO)_6(C_4H_6)]^{\bullet-} + C_2H_2 \quad (6)$$

in approximately equal abundance, each ion shows only minimal substitution of other ligands when selected for varying amounts of time. The failure to observe a preferred direction of ligand substitution is not well understood, but it is possible that the reactions are too slow to observe (i.e., $k_{total} < 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) in the time frame of these experiments.

Conclusion

Although the methenyltricobalt nonacarbonyls incorporate unusual bonding within the molecule, the unimolecular reactivity of the radical anion parallels that of other polynuclear cobalt complexes.[17] The molecular

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(36) Giousmousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

(37) (a) Meckstroth, W. K.; Freas, R. B.; Reents, W. D., Jr.; Ridge, D. P. *Inorg. Chem.* **1985**, *24*, 3139. (b) Freeden, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 3903.

(38) The less stable η^4-trans complex has also been observed in butadiene complexes of the formula $(\eta^4\text{-}C_4H_6)M(\eta^5\text{-}C_5H_5)_2$ where M = Zr and Hf: (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. (b) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470. (c) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

(39) For a review on the structure of σ-metallacyclopentane complexes, see: Erker, G.; Kruger, C.; Muller, G. *Adv. Organomet. Chem.* **1965**, *24*, 1.

(40) Wang, D.; Squires, R. R. *Organometallics* **1987**, *6*, 905.

anion for each compound is not observed and the principal mode for formation of negative ions is dissociative electron capture. Studies by tandem mass spectrometry demonstrate that most of the $YCCo_3$ core is retained, even under high-energy collisional activation conditions. The CAD spectra are in accord with the concept of an electron-rich delocalized core where compounds with electron-withdrawing substituents produce more fragment ions than do those with electron-donating substituents.

FTMS experiments show that the methenyltricobalt nonacarbonyl radical anions react with their neutral precursor to form higher-order cobalt clusters. The five-cobalt clusters are hypothesized to form in a trigonal bipyramidal or in a square pyramidal geometry whereas the six-cobalt clusters form in an octahedral geometry. Ligand substitution reactions occur more readily with π-bonding ligands such as acetylene and 1,3-butadiene than with σ-bonding ligands. These reactions are also consistent with an electron-rich delocalized $YCCo_3$ core; that is, the compounds with electron-withdrawing apical substituents react more rapidly with acetylene and 1,3-butadiene than do those with electron-donating apical substituents.

These investigations with FTMS have demonstrated its utility in the study of the *intrinsic* reactivity of methenyltricobalt nonacarbonyl radical anions with their neutral precursor or with another cobalt cluster. Another interesting possibility in which FTMS might be useful is the study of metal–metal exchange reactions, where one or more metal–ligand groups of a cluster are replaced by a different metal–ligand group to yield a new cluster that contains the same total number of metal atoms.[41] Solution-phase reactions have been shown to occur in mixtures of methenyltricobalt nonacarbonyls and $CpM(CO)_3AsMe_2$, where M is Cr, Mo, or W.[42] The mechanism for the metal–metal exchange process, however, is not completely understood. Moreover, these exchange reactions could lend insight into the formation of the higher-order cobalt clusters described in this report.

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(41) Adams, R. D. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. H., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; p 159.

(42) (a) Beurich, H.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2385. (b) Beurich, H.; Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2409. (c) Blumhofer, R.; Fischer, K.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 194.