Future Directions

A new ion source has been constructed for us by Mr. Kenneth Ehlers of the Lawrence Berkeley Laboratory. This source also produces ions in an arc plasma. However, the ion extraction orifice is in the anode itself, and this feature should give us a lessened "spread" of energies at a given ion energy. That, in turn, should give us better energy control in the important below 5 eV region, and may aid us in achieving controllable energies below 2 eV. In addition, the new ion source appears to be a superior one in handling CH_4 as the source gas. Consequently, we hope soon to be able to effect irradiations with $^{14}CH^+$, $^{14}CH_2^+$, and $^{14}CH_3^+$ ions. This may enable us to settle some of the problems, recounted above, about the time at which hydrogens are picked up by intermediates.

The advent of "total effluent" gas chromatographic-mass spectrometric (gc-ms) techniques, enabling the investigator to detect and identify 1–10 ng of organic compounds,[38] provides a method that should lead to a considerable advance in our ion-beam studies. A 1-hr operation of our 1-μA beam of $^{14}C^+$ gives (for example, in the case of toluene, at a 0.2% yield) 4×10^{13} molecules, which equals 6 ng. Consequently, the new gc-ms technique appears about as sensitive for detecting products, and has a far greater potentiality (through the mass spectra) for product identification. We can, therefore, use

$^{13}C^+$ instead of $^{14}C^+$ as our irradiating ion, and we can hope to identify many more of the products of our irradiations. Among these as yet unidentified products we may expect unusual benzene isomers (and their methyl and phenyl derivatives) such as benzvalene, Dewar benzene, fulvene, prismane, and bicyclopropenyl[39,40]—the first three of which have already been successfully handled *via* gc-ms techniques.[41]

We also intend to use the new technique to reveal the fate of the "secondary" carbons, that is, the carbon atoms ejected from the benzene, or from another target, by the irradiating carbons. With the ^{14}C technique described in this Account, the fate of ejected ^{12}C atoms is unknown. However, the gc-ms method should enable us to irradiate benzene-^{13}C with $^{12}C^+$ ions and to identify the compounds into which the ^{13}C is incorporated.

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Tricobalt Carbon, an Organometallic Cluster

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The metal cluster is now a well-known structural feature among the compounds of transition metals in

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their lower valency states.[1-3] Metal cluster compounds occur especially among the carbonyls of iron, cobalt, nickel, and their congeners, mostly with the metal in a state of zero valence. There are authenticated examples which contain triangular, tetrahedral, square-pyramidal, and octahedral clusters of metal atoms.[2,3] In these compounds the metal-metal bonds which hold the clusters together are strong, and metal-metal bond formation is a dominating influence in their chemistry.[1,4]

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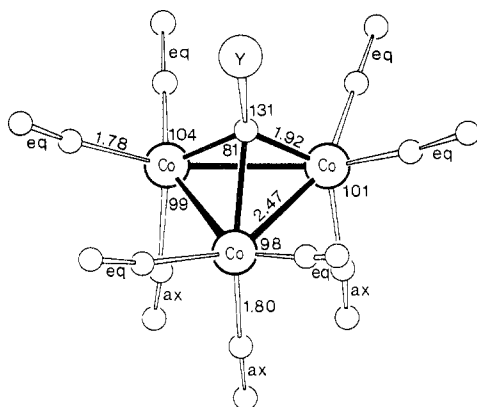
Figure 1. Molecular structure for compounds of general formula $YCCo_3(CO)_9$. Bond lengths (Å) and angles (degrees) are mean values over a number of independent structure determinations. Estimated standard deviations in these mean values are not greater than 0.01 Å or 1°.

In some of the metal cluster carbonyls, nonmetal atoms form symmetrical bridges across two or more atoms of the cluster. The triangular tricobalt cluster appears to be uniquely amenable to this type of bridging. For example, many carbonyls have been prepared in which a sulfur[5-9] (or one of its higher congeners)[10] or a carbon atom is symmetrically bridged to a Co_3 triangle to form a tetrahedral grouping. The tetrahedral Co_3C unit is the structural core of a whole series of methinyltricobalt enneacarbonyls of general composition $YCCo_3(CO)_9$ (Y = halogen, alkyl, aryl, carboxyl etc.) first prepared in 1958[11] and whose basic molecular structure, as illustrated in Figure 1, was elucidated by X-ray diffraction 8 years later.[12]

In the $YCCo_3(CO)_9$ compounds, three of the CO groups will be referred to as *axial* and the remaining six as *equatorial*, as indicated in Figure 1. The $-C-Co_3(CO)_9$ group possesses idealized C_{3v} symmetry and the essential molecular dimensions averaged over all appropriate compounds are given in the same figure. In all cases the equatorial CO groups are bent out of the Co_3 plane toward Y. For those compounds where the size of Y does not introduce additional constraints, the dihedral angle between the Co_3 triangle and a $CoCO(eq)CO(eq)$ triangle is 30°, on the average. These dimensions are highly consistent. Significant departures from average values may be related to special features of individual compounds: these are noted below in the section on molecular structures.

The principles governing the reactivity and stereochemistry of metal cluster carbonyls in general are fairly well understood, but this cannot be said for the methinyltricobalt compounds which are in many ways unique. They are, without exception, unusually stable to oxidation and thermal degradation, relative to the other cobalt carbonyls and comparable tetra-

hedral metal cluster compounds. The tricobalt carbon group in these compounds is the only authenticated cluster which is truly organometallic in the sense that traditional inorganic and organic reactions may both be carried out on the $YCCo_3$ unit. Reactivity is determined by steric and electronic requirements of the cluster as a whole. (Other cluster compounds, such as $Ru_6(CO)_{18}C$[13,14] and $Fe_5(CO)_{15}C$,[15] which contain an isolated carbon atom have been prepared, but these are best considered as carbides.)

When we commenced our studies, we decided to focus on three basic questions. First, was the four-coordinate apical carbon atom indeed aliphatic (sp^3), or did the basal cobalt triangle alter the nature of this carbon atom? If the Co_3C fragment was an integrated unit, would the reactivity of the apical substituent in turn be affected? Second, would intramolecular steric interactions place any constraints on the coordination behavior of the basal cobalt triangle? Third, could a satisfactory description of the bonding be formulated which could explain the unusual stability of these compounds as well as the details of molecular stereochemistry which began to emerge from the accompanying sequence of X-ray diffraction studies? Answers at least to the first two of these questions are now appearing.

Preparation

A comprehensive review of the synthetic routes has appeared recently;[16] we shall consider only those aspects pertinent to this Account. The original preparation[11] from acetylene complexes $Co_2(CO)_6RCCH$ is restricted to terminal acetylenes, and a $-CH_2$ is necessarily introduced.

$$Co_2(CO)_6RC_2H \xrightarrow{H_2SO_4\text{-methanol}} RCH_2CCo_3(CO)_9 \quad (1)$$
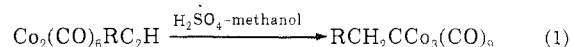
A general method utilizing α,α,α-trihalo compounds was announced independently from two laboratories[17,18] in 1961, and clusters with a wide variety of apical substituents were described.

$$5Co_2(CO)_8 + 3CYX_3 \rightleftharpoons$$
$$2Co_3(CO)_9CY + 4CoX_2 + 22CO + [YCX] \quad (2)$$
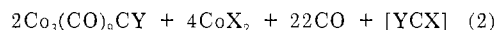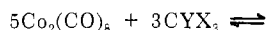
Extraneous carbon is not necessary, however. In fact these clusters, easily recognizable by their distinctive purple or dark purple-brown color, turn up in many reactions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$,[16] reflecting the high stability of the Co_3C unit. The source of carbon in these reactions is undoubtedly coordinated CO, although the actual intermediates have not been isolated.

A significant development is the recent preparation[19] of the anion $[OCCo_3(CO)_9]^-$ derived from the

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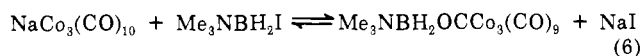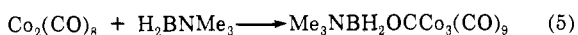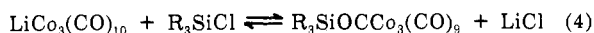
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Table I
### Reactions of Methinyltricobalt Enneacarbonyls, $YCCo_3(CO)_9$, Involving Substitution of CO

Apical group, Y	Ligand	Product	Comments	Ref
Me, Ph, F, Cl, Br	Phosphines Arsines	$YCCo_3(CO)_8L$	Equatorial substitution or CO-bridged structure	28, 35
		$YCCo_3(CO)_7L_2$	Limited formation	
		$YCCo_3(CO)_6L_3$	Et_2PhP only	
Me, Ph, F	Arenes	$YCCo_3(CO)_6$arene	Very labile	40
	Cyclooctatetraene	$YCCo_3(CO)_6COT$	Labile, fluxional	38
	Trienes	$YCCo_3(CO)_6$triene	Static structure, stable	41
Me, Ph, F, Cl	Norbornadiene	$YCCo_3(CO)_7$norb	Nonrigid structure	40
Me, Ph, F, Cl	Cyclopentadiene	$YCCo_3(CO)_4Cp_2$	Stable, CO bridged	40, 41, 64
Me, Ph, F	Olefins	Brown insoluble powders, carbonylation products?		41
Me, Ph, F	Acetylenes	Decomposition; $Co_2(CO)_6RCCR$ etc.		41
Me, Cl	Phosphine oxides	Co(II) phosphine complexes		42
Me	Diarsines	$YCCo_3(CO)_7[(CH_3)_2As]_2C_2(CF_2)_2$	CO-bridged structure	43, 44
CF_3	Diarsines	Rearrangement to give tetrahedral Co_4 structure		43, 45

$$Co_2(CO)_8 \xrightarrow{\text{K or Na-ether}} [OCCo_3(CO)_9]^- \quad (3)$$
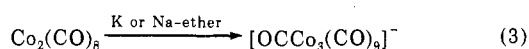
hydroxy cluster $HOCCo_3(CO)_9$. A CO-bridged configuration is adopted by the anion presumably as a means of dissipating the negative charge. At this point it is worth noting that $HOCCo_3(CO)_9$ is unknown. Our current ideas on the electronic structure of these clusters lead us to predict that it would be stable only in a strongly acidic medium. The anion could be the precursor for a myriad of compounds of the type $R'OCCo_3(CO)_9$ where R' is a metallic or nonmetallic moiety. Some boron[20,21] and silicon[20-22] derivatives have been described.

$$LiCo_3(CO)_{10} + R_3SiCl \rightleftharpoons R_3SiOCCo_3(CO)_9 + LiCl \quad (4)$$

$$Co_2(CO)_8 + H_2BNMe_3 \longrightarrow Me_3NBH_2OCCo_3(CO)_9 \quad (5)$$

$$NaCo_3(CO)_{10} + Me_3NBH_2I \rightleftharpoons Me_3NBH_2OCCo_3(CO)_9 + NaI \quad (6)$$

In theory, the following reaction should provide methinyltricobalt enneacarbonyls and analogs in which carbon is replaced by a main group or transition element (eq 7). However, these reactions with

$$3NaCo(CO)_4 + MX_3 \rightleftharpoons 3NaX + MCo_3(CO)_9 + 3CO \quad (7)$$
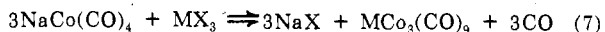
heavier main group elements give open polymeric structures, e.g., $RSn[Co(CO)_4]_3$,[23] or simpler carbonyls, e.g., $AsCo(CO)_4$.[24] The major metallic products when boron or silicon is involved do not contain boron or silicon bonded to cobalt but are in fact CCo_3 cluster compounds,[25] and reports of silicon analogs have been refuted.[26] We believe that boron or silicon clusters may have a transient existence but that CO insertion or transfer is so facile that anionic intermediates (say $[OCCo_3(CO)_9]^-$) are produced.

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which subsequently undergo electrophilic attack by the boron or silicon reagent, e.g.

$$NaCo(CO)_4 \longrightarrow NaCo_3(CO)_{10} + RSiX_3 \longrightarrow$$
$$NaCl + RCCo_3(CO)_9 + [\text{siloxanes, etc.}] \quad (8)$$
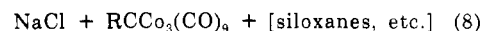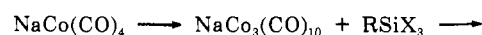
The only proven analogs to the carbon clusters are the paramagnetic group VI derivatives in which the carbon has been replaced by S, SR, Se, and Te,[6,10] although there is strong indirect evidence for the germanium analog $PhGeCo_3(CO)_9$.[26]

Reactions of Methinyltricobalt Enneacarbonyls

The chemistry of these cluster compounds has two facets, (a) the coordination chemistry of the basal Co_3 triangle (summarized in Table I) and (b) reactions involving transformation of the apical group, Y. Both aspects are interrelated in the sense that it is the steric and electronic requirements of the Co_3C core which govern the overall reactivity.

Coordination Chemistry of the Basal Triangle. Several years ago Ercoli and coworkers[27] found that three CO groups (presumably axial) exchange with ^{14}CO faster than the other six and that the relative rates fall in the order Y = H < Br < Cl < F. When Y = $COOCH_3$, only one CO group appeared to exchange. It is difficult to reconcile these observations with the structures of the clusters, but the influence of the apical group is significant and is reminiscent of the trans effect in classical inorganic reactions. In fact, the thermodynamic stability of any derivative and the conformation adopted follow a definite pattern based on the type of apical group. As a general rule aryl derivatives are the most resistant to thermal and oxidative decomposition. Apical C–halogen bonds are very susceptible to nucleophilic attack and heterolytic fission. For this reason many simple derivatives cannot be isolated; compounds with direct C–C linkages are produced instead. For instance, dehalogenation occurs on reaction with Ph_3As.[28]

$$2ClCCo_3(CO)_9 + Ph_3As \xrightarrow{373 \text{ K}} [CCo_3(CO)_9]_2 + Ph_3AsCl_2? \quad (9)$$
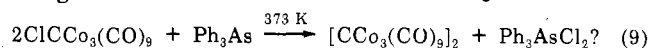
Even more intriguing are the acetylene com-

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pounds, $[CCo_3(CO)_9]_2C_2$, $[CCo_3(CO)_9][Co_2(CO)_6-C_2H]$, and $[CCo_3(CO)_9]_2C_2[Co_2(CO)_6C_2]$, formed in many reactions with organic molecules such as arenes[29-33] and also with nucleophiles. The clusters themselves appear, from deuteriation studies, to be the source of carbon, but the mechanism is unknown. Seyferth and coworkers[34] have shown that $[CCo_3(CO)_9]_2C_2[Co_2(CO)_6C_2]$ can also be prepared from hexachlorocyclopropane.

Lewis base derivatives illustrate how the coordination behavior and electronic structure of the cluster are interrelated. Generally solid-state structures correspond to simple substitution of L in an equatorial position for complexes $YCo_3(CO)_8L$. However, when Y = CH_3, the cluster may reorganize to a CO-bridged configuration.[35] Both nonbridged and bridged isomers coexist in solution, irrespective of the group Y. A CO-bridged configuration is also adopted by the more highly substituted phosphine derivatives $YCCo_3(CO)_7L_2$ and $YCCo_3(CO)_6L_3$, probably because a bridging CO is more effective in dissipating the increased charge on the cluster from σ donation. Activation energies [E_A (Y): 105 (CH_3), 83 (C_6H_5), 63 (H), 51 (F)] derived in a kinetic study[36] of the reactions

$$YCCo_3(CO)_9 \underset{-CO}{\rightleftharpoons} YCCo_3(CO)_8 \xrightarrow{L} YCCo_3(CO)_8L$$
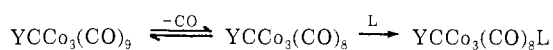
which proceed by the usual dissociative S_N1 mechanism are in accord with the concept of an electron-delocalized Co_3C core. The cobalt–CO bond is strongest with an electron-donating apical substituent and as expected the $\nu(CO)$ frequencies decrease from the fluoro to methyl derivative.[35]

Certain of the polyene and diene complexes have interesting spectral properties. The cyclooctatetraene derivatives, $YCCo_3(CO)_6COT$, where the polyene is coordinated to all three cobalt atoms,[36,37] are typical nonrigid (fluxional) molecules. An analysis of the pmr spectrum of $PhCCo_3(CO)_6COT$ strongly indicates that the predominant rearrangement pathway is a sequence of 1,2 shifts.[38] A different type of nonrigid behavior is exhibited by the complexes, $YCCo_3(CO)_7norb$.[39] From scale models it seems that the diene should be coordinated to one cobalt atom, but there are still two conformational possibilities: cis (adjacent to the apical group),cis or cis,trans. An analysis of the pmr spectra at low temperatures indicates that the instantaneous configurations are cis-trans (a 2:3:1:2 spectrum). As the temperature in-

creases the individual resonances collapse and a time-averaged 4:2:2 spectrum is observed at ~223 K, while at room temperature the olefin and bridgehead protons become equivalent (6:2 spectrum).[40-45] A mechanism involving (cis,trans)–(cis,cis) isomerization is probably operating. At temperatures above ~60° the norbornadiene complexes also undergo a reverse Diels–Alder reaction giving cyclopentadienyl complexes[41,46] and at the same time function as catalysts in the formation of the norbornadiene dimers.[41]

A number of derivatives have a tremendous affinity for CO, due to the lability of the ligand, and thus are ideal substrates for catalytic reactions. In fact, where the cluster–ligand bond is weak (alkenes, cyclooctadiene, acetylenes) the organic products are usually those formed through CO incorporation or polymerization.[41] The possibility that the phosphine complexes may act as carbonylation catalysts is currently being explored. A patent has already been granted to Bor[47] for the application of the parent clusters as antiknock agents, and Bamford[48] found that $PhCH_2CCo_3(CO)_9$ is an adept initiator of vinyl polymerization.

Reactions Involving the Apical Carbon and Apical Substituent (Y). The chemistry of the apical linkage, C–Y, is influenced by electronic effects and the severe stereochemical constraints imposed on the clusters. Certain physical features of the clusters suggest that the apical linkage has properties inconsistent with a saturated (sp^3) carbon atom. In particular, a number of C–Y bond lengths are shorter than expected for a "single" bond[30,31,37,49,50] and C–halogen stretching frequencies are unusually high; for example $\nu(C-Cl)$ in $ClCCo_3(CO)_9$ appears at 906 cm^{-1}.[18] These observations may be explained using the concept of a delocalized electron-rich Co_3C core which is electron-withdrawing with respect to the apical group. The high electron density in C–Y bonds may be due to polarization of this core by an electronegative halogen or to π bonding,[16] although the availability of suitable orbitals for π bonding is open to question. On these arguments it is anticipated that the apical carbon atom should be activated toward nucleophilic attack and intermediate carbonium ions stabilized. Moreover, the C–Y bond is sterically protected from "backside" attack and a dissociative S_N1 mechanism will be favored.

Reactions with Electrophiles. The Friedel–Crafts substitution of halo clusters is an important route to aryl clusters and illustrates the steric constraint on such reactions. These substitution reactions may be accomplished, often in high yields, using a nitrogen atmosphere,[51,52] *e.g.*

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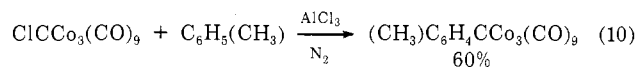
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(51) R. Dolby and B. H. Robinson, *Chem. Commun.*, 1058 (1970).

$$ClCCo_3(CO)_9 + C_6H_5(CH_3) \xrightarrow[N_2]{AlCl_3} (CH_3)C_6H_4CCo_3(CO)_9 \quad (10)$$
$$60\%$$

Substitution is almost wholly para because of interference from the equatorial carbonyls in the ortho product. With small substituents the isomer distribution is kinetically controlled; for example, in reaction 10 the isomer distribution is

Temp, °C	Solvent	Ortho, %	Para, %
40	CH_2Cl_2, PhMe	62	38
110	PhMe	36	64

Unstable green intermediates, $[HRCCo_3(CO)_9]^+$-$AlCl_4^-$, have been isolated from some reactions. Other more versatile routes to aryl clusters, employing, for example, Grignard and mercury reagents,[53] are now available. The coordinated aromatic moieties in these aryl clusters also undergo typical aromatic Friedel–Crafts reactions.[54,55]

All clusters are protonated in strong acids, and the deep red solutions exhibit the characteristic highfield resonance ($\tau \sim 30$) of a coordinated hydrogen.[42] Only monoprotonation is achieved, an observation difficult to interpret on a structural basis although other clusters (*e.g.*, $Ru_3(CO)_{12}$[56]) exhibit similar behavior. A useful approach might be to describe this protonation in terms of acid–base interaction and as a logical extension to derive a basicity function for the Co_3CY unit.

Substituents with basic functions are protonated in weak acids also and a range of salts of the type shown in (11) have been studied.[55] Physicochemical

$$Me_2NC_6H_4CCo_3(CO)_9 + HX \text{ (or } RX) \rightleftharpoons$$

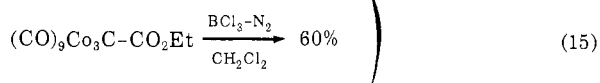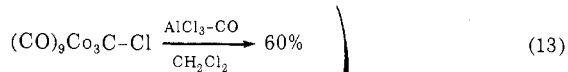$$[H(\text{or } R)Me_2NC_6H_4CCo_3(CO)_9]^+X^- \quad (11)$$
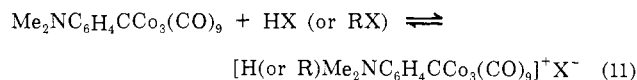
measurements on these salts have provided Hammett functions for the tricobaltcarbon cluster which resemble those of a typical deactivating group, CO_2H. Analysis of pK_b (for the salts) and pK_a (for phenol derivatives prepared by route 12) values also suggest that the cluster is a strongly deactivating entity.[53]

$$MeOC_6H_4CCo_3(CO)_9 \xrightarrow[CH_2Cl_2]{BBr_3} HOC_6H_4CCo_3(CO)_9 \quad (12)$$
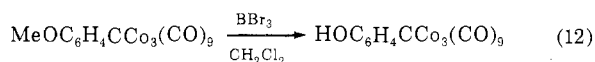
Recently it has been demonstrated[57,58] that the acid, $HO_2CCCo_3(CO)_9$, and esters dissolve in concentrated H_2SO_4 to generate the acylium cation, $^+OCCCo_3(CO)_9$, a precursor of considerable importance. This reaction is a direct consequence of the sterically hindered environment of the apical group. The following examples show the proton is only one of several electrophiles which give the acylium cation in high yield. Since reactions with halo clusters involve CO insertion, these reactions must be carried out under CO for maximum yield.
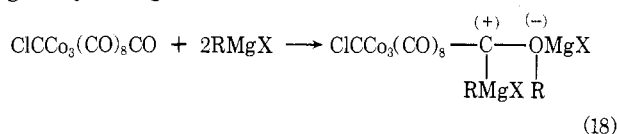
$$(CO)_9Co_3C{-}Cl \xrightarrow[CH_2Cl_2]{AlCl_3{-}CO} 60\% \quad (13)$$

$$(CO)_9Co_3C{-}Cl\cdot \xrightarrow[Et_2O]{BF_3{-}CO} 50\% \quad \Big\} \quad ^+OCCo_3(CO)_9 \quad (14)$$

$$(CO)_9Co_3C{-}CO_2Et \xrightarrow[CH_2Cl_2]{BCl_3{-}N_2} 60\% \quad (15)$$

The above reactions may be quenched with an appropriate nucleophile (see ref 57) and probably (13) is the most convenient route (quench with H_2O) to the acid from $Co_2(CO)_8$. For steric reasons it is difficult to esterify the carboxylic acid cluster by conventional procedures, but esterification may be accomplished using oxonium salts.[55]

$$(CO)_9Co_3C{-}CO_2H \xrightarrow{R_3O^+BF_4^-} (CO)_9Co_3C{-}CO_2R \quad (16)$$
$$80\%$$
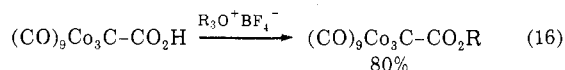
Reactions with Nucleophiles. Nucleophiles such as Grignards, RMgX, attack the apical carbon atom of halo clusters, yielding the expected substituted cluster provided R is an aryl group, the reaction is carried out under nitrogen, and the cluster/nucleophile ratio is greater than 1:9[55] (eq 17). Yields from the

$$ClCCo_3(CO)_9 + RMgX \rightarrow RCCo_3(CO)_9 + MgXCl \quad (17)$$
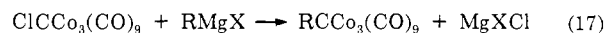
Grignard reactions are high (80%) and it is a stereospecific synthesis (*cf.* (10)). The reaction conditions suggest that there is initial attack on coordinated CO followed by attack by R^- on the apical carbon atom. Moreover, when R is a primary or secondary alkyl a coordinated CO is attacked by 2 mol of RMgX (eq 18) which on work-up leads to complete decomposition of the cluster (not substitution as originally thought[51]).

$$ClCCo_3(CO)_8CO + 2RMgX \longrightarrow ClCCo_3(CO)_8 \overset{(+)}{\underset{\underset{RMgX}{|}}{C}} \overset{(-)}{\underset{\underset{R}{|}}{OMgX}}$$

$$(18)$$

In contrast nucleophilic substitution *under CO* invariably gives compounds resulting from CO insertion.[42,55,59] Clearly, the initial step is again nucleophilic attack on coordinated CO, but the nature of the intermediates (possibly $ClOCCo_3(CO)_9$) is un-

$$(19)$$
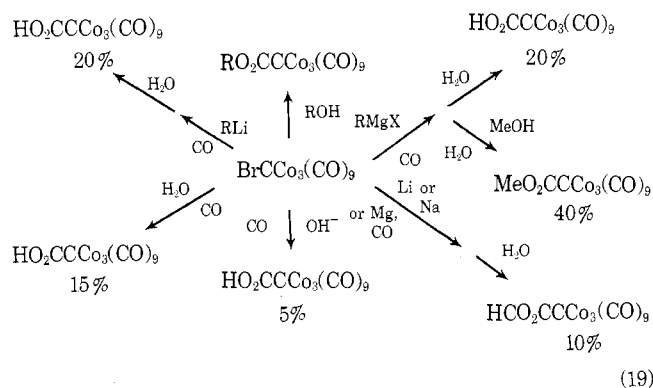
(52) R. Dolby and B. H. Robinson, *J. Chem. Soc., Dalton Trans.*, in press.

(53) D. Seyferth, J. E. Hallgren, and R. J. Spohn, *J. Organometal. Chem.*, **23**, C55 (1970).

(54) D. Seyferth and A. T. Wehman, *J. Amer. Chem. Soc.*, **92**, 5520 (1970).

(55) R. Dolby and B. H. Robinson, unpublished work.

(56) A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 2967 (1970).

(57) J. E. Hallgren, C. S. Eschbach, and D. Seyferth, *J. Amer. Chem. Soc.*, **94**, 2547 (1972).

(58) D. Seyferth, J. E. Hallgren, R. J. Spohn, A. T. Wehman, and E. H. Williams, Special Lectures, XXIIIrd Congress, IUPAC, Boston, Mass., 1971.

(59) R. Ercoli, E. Santambrigio, and E. Tattamanti-Cassagrande, *Chim. Ind. (Milan)*, **44**, 1344 (1962).

known. The crucial step is the intramolecular CO insertion which we postulate goes *via* a cyclic transition state. In fact, the close proximity of an equatorial CO to the apical group in these clusters is ideal for the formation of such a transition state. It seems likely that the majority of CO insertions in these compounds proceeds by this mechanism rather than the alternative intermolecular CO insertion into a strong C–Y bond, and this would account for the large number of insertion products (see ref 16). Significant yields of the derivatives $HCCo_3(CO)_9$,[C-$Co_3(CO)_9]_2C_2$, $[CCo_3(CO)_9]_2CO$, and $[CCo_3(CO)_9]$-$[Co_2(CO)_6C_2H]$ are always obtained in the above reactions. It has been proved[42] by deuteriation experiments that the hydrogen in $HCCo_3(CO)_9$ is derived from H_2O, but the mechanism for its formation is still uncertain.

Conclusion. The unique electronic and steric properties of methinyltricobalt enneacarbonyls give rise to novel reactivity patterns, but there are large areas yet to be explored. Apart from an isolated report that the double bond in $HO_2CC{=}CCo_3(CO)_9$ can be hydrogenated under mild conditions, little is known about the reactivity of coordinated apical aryl and alkyl groups;[16] profitable routes to a variety of organic substrates should result from work in this area (see, for example, the work reviewed in ref 58).

The coordination chemistry of the basal triangle is modified by the apical group, and it will be interesting to see if there is a synergic relationship. Finally, the concept of a delocalized electron-withdrawing Co_3C core adequately explains the known chemical and spectral data.

Molecular Structures

Detailed crystal structures have been determined for 13 compounds containing the Co_3C cluster. In none of these structures is there any pronounced intermolecular association, so that we may reasonably regard the solid-state molecular dimensions as applying also to the free molecules. The structures so far determined may be classified into five groups, each of which we shall discuss in turn relative to the basic $YCCo_3(CO)_9$ structure.

1. Substitution of Y only. Besides the methyl compound already referred to,[12] the only structure reported is that of $(C_2H_5)_3NBH_2OCCo_3(CO)_9$, where Y is triethylamine–oxyborane, arising from the reaction of triethylamine–borane with $Co_2(CO)_8$ in benzene.[21] This is the only structure reported in which an oxygen atom is directly bonded to the cluster carbon although compounds of general formula R_3Si-$OCCo_3(CO)_9$ presumably contain this feature. The C–O bond length of 1.28 (2) Å approximates to that of a double bond if the carbon atom is assumed to be sp^2 hybridized, but is also consistent with an interpretation in terms of a single bond involving an approximately sp-hybridized carbon atom.

2. Substitution of CO by σ Donor. The only structure reported[33] is that of $CH_3CCo_3(CO)_8P(C_6H_5)_3$ in which a single *equatorial* carbonyl has been replaced by triphenylphosphine following the reaction of $CH_3CCo_3(CO)_9$ with $P(C_6H_5)_3$ in hexane. There are no other major consequential structural changes, although infrared spectra show that in solution there

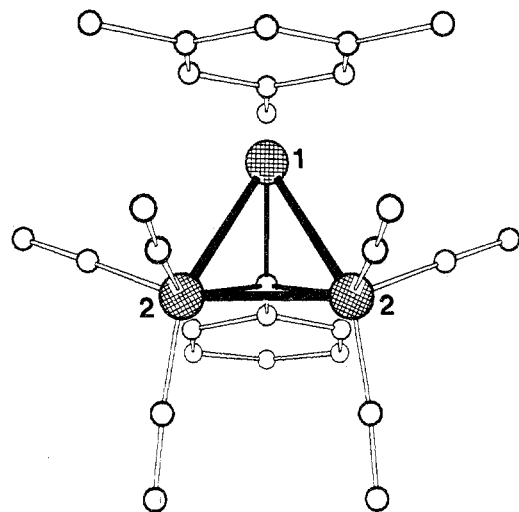**Figure 2.** Molecular structure of the π-mesitylene complex $C_6H_5CCo_3(CO)_6 \cdot (CH_3)_3C_6H_3$. The mean value of the distance from Co(1) to the mesitylene ring carbon atoms is 2.15 (3) Å.[60]

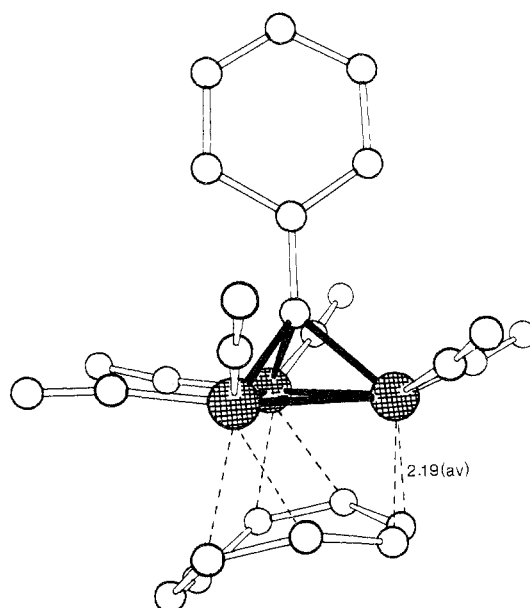**Figure 3.** Molecular structure of the π-cyclooctatetraene complex $C_6H_5CCo_3(CO)_6 \cdot C_8H_8$.[36,37]

exists an isomer containing bridging as well as terminal carbonyl groups.[35]

3. Substitution of CO by π Donors. Two structures are known,[36,37,60] $C_6H_5CCo_3(CO)_6 \cdot \pi$-$(CH_3)_3C_6H_3$ and $C_6H_5CCo_3(CO)_6 \cdot \pi$-$C_8H_8$, in which three of the carbonyl groups have been replaced by one molecule of mesitylene and one molecule of cyclooctatetraene, respectively, as a result of the direct reaction of $C_6H_5CCo_3(CO)_9$ with the π-donor compounds. In the mesitylene complex (Figure 2) all three carbonyls (two equatorial and one axial) associated with a single cobalt have been replaced and the unique Co atom is approximately equidistant (mean value 2.15 (3) Å) from all atoms of the mesitylene ring.[60] The Co–Co bonds involving the unique Co atom are 0.036 (4) Å shorter than the remaining Co–Co bond.

In the cyclooctatetraene complex (Figure 3) the three axial carbonyls have been replaced and the

(60) R. J. Dellaca and B. R. Penfold, *Inorg. Chem.*, 11, 1855 (1972).

Table II
Known Molecular Structures Containing the CCo_3 Cluster, Grouped as in the Text

1	2	3	4	5
$CH_3CCo_3(CO)_9$[12]	$CH_3CCo_3(CO)_8$-$P(C_6H_5)_3$[33]	$C_6H_5CCo_3(CO)_6$·π-$(CH_3)_3C_6H_3$[60]	$[CCo_3(CO)_9]_2$[50]	$CH_3CCo_3(CO)_8P$-$(C_6H_{11})_3$[63]
$(C_2H_5)_3NBH_2OCCo_3(CO)_9$[21]		$C_6H_5CCo_3(CO)_6$·π-C_8H_8[36,37]	$[CCo_3(CO)_9]_2CO$[61]	$CH_3CCo_3(CO)_7$-$[(CH_3)_2As]_2C_2(CF_2)_2$[44]
$R_3SiOCCo_3(CO)_9^{a,20}$			$[CCCo_3(CO)_9]_2$[31]	$[OCCo_3(CO)_9]^{-a,19}$
			$[Co_2(CO)_6]$-$HC_2CCo_3(CO)_9$[30]	$CH_3CCo_3(CO)_4$·$(\pi$-$C_5H_5)_2$[64]
			$[Co_2(CO)_6]$-$[C_2CCo_3(CO)_9]_2$[34,49]	

a Structure assumed from indirect evidence but not yet confirmed.

$CCo_3(CO)_6$ group retains idealized C_{3v} symmetry. The manner in which the cyclooctatetraene molecule (in the tub conformation) is attached to the Co_3 triangle is most interesting. Three of the four double bonds in the polyene ring are associated respectively with the three Co atoms, while the fourth double bond is bent away from the Co_3 triangle.[36,37] The mean value for the close Co-C(ring) contacts is 2.19 (2) Å. Notable also in this compound are the short Co-CO bonds which are in this case all equatorial. Their mean length is 1.69 (3) Å or 0.09 Å less than the mean value for all compounds in which no substitution of axial carbonyls has occurred. The indication is that axial-equatorial carbonyl repulsions may be a factor controlling the length of the Co-CO bonds, but further confirmation is required. The reason why the mesitylene molecule does not replace three axial carbonyls may be rationalized in a similar way—a model suggests that the nonbonded repulsions between equatorial carbonyls and a planar aromatic ring symmetrically placed below the Co_3 triangle would be prohibitive.[60]

4. Linkage of Two Clusters. There are five distinct examples of the linkage of one Co_3C cluster through its carbon atom to another cluster either directly or through an intermediate carbon chain.[30,31,34,49,50,61] These structures are compared in Figure 4 which shows the Co_3C clusters in corresponding orientations and which also indicates the bond lengths in the carbon chains. All compounds were formed in the reaction of $YCCo_3(CO)_9$ (Y = Cl, Br) with toluene, *m*-xylene, or mesitylene.[31] Compound A is a special case in that the Y group is not strictly a cluster but rather a dicobalt hexacarbonyl fragment coordinated by an acetylene.[30] However, it is properly to be included in this group of compounds because of its close structural relation to compound C.

In all three compounds, A, B, and C, an acetylene bond has been linked to the carbon atom of one Co_3C cluster. In A and C this bond is coordinated to $Co_2(CO)_6$. In compounds B and C the acetylene is linked to a second Co_3C cluster, in the case of C through a second acetylene bond. In compound D the two Co_3C clusters are linked through a carbonyl bridge, and in E the link is direct. In compound E, $[CCo_3(CO)_9]_2$, the Co-C bonds within the clusters are significantly longer [1.96 (1) Å] than the mean value (1.92) found for all of the other compounds. This lengthening may be associated with the minim-
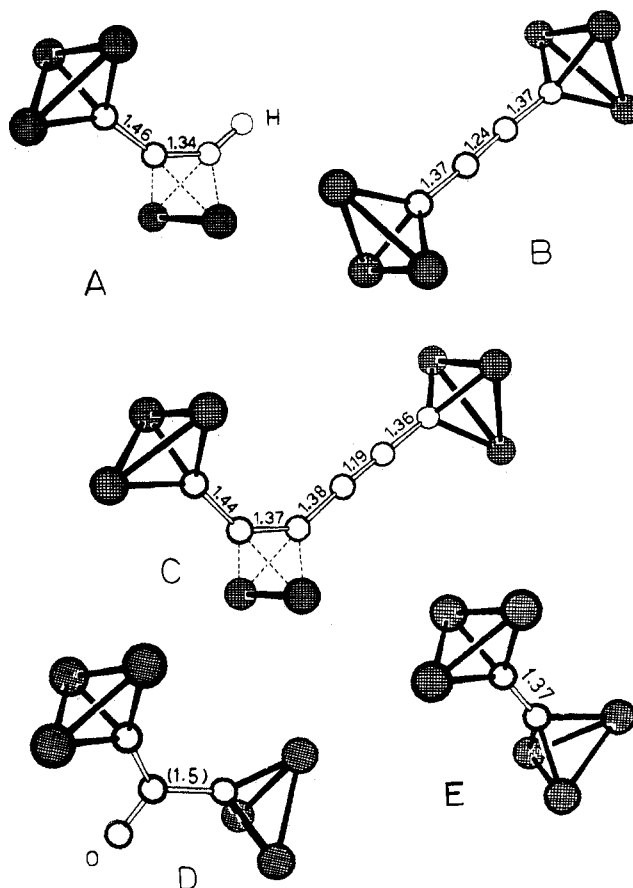
(61) G. Allegra and S. Valle, *Acta Crystallogr.*, *Sect. B*, **25**, 107 (1969).

Figure 4. Molecular skeletons of compounds containing linked clusters. Carbonyl groups (except for the bridging carbonyl in compound D) have been omitted for clarity. A is $[Co_2(CO)_6]$-$HC_2CCo_3(CO)_9$; B is $[CCCo_3(CO)_9]_2$; C is $[Co_2(CO)_6][C_2CCo_3(CO)_9]_2$; D is $[CCo_3(CO)_9]_2CO$; E is $[CCo_3(CO)_9]_2$. (See ref 30, 31, 34, and 49, 61, 50 respectively.)

ization of nonbonded repulsions between equatorial carbonyls from the two halves of the molecule.[50] These equatorial carbonyls are already significantly bent back toward the Co_3 planes (mean dihedral angle between Co_3 and CoC(eq)C(eq) is 24°, compared with a mean value of 30° in compounds where there are no such intermolecular interactions), and a lengthening of the Co-C cluster bonds will still further lengthen the nonbonded contacts. As it is, there are O···O contacts as short as 3.08 Å.

This series of compounds provides quantitative data concerning the bonds formed by the carbon atom of the cluster. Compound E, the dimer $[CCo_3(CO)_9]_2$, is particularly important. Although

Figure 5. Molecular structure of $CH_3CCo_3(CO)_8 \cdot P(C_6H_{11})_3$.[63]

Figure 6. Molecular structure of $CH_3CCo_3(CO)_7 \cdot [(CH_3)_2As]_2$-$C_2(CF_2)_2$.[44]

there appears to be no way in which the central C–C bond may possess π character (see, however, Kettle and Khan[62]), the length of 1.37 (1) Å for this bond is very short and if it is a single bond there will be very much reduced p character in the orbitals of the carbon atoms which point to each other. Given this information, there is no need to attribute π contributions to any of the C–C bonds formed by the cluster carbon atoms in this series of compounds.[50] The observed lengths in the carbon chains of compounds A, B, C, and E are all consistent with a description in terms of formally single bonds from the cluster carbon atom, triple bonds for the uncoordinated acetylene and double bonds for the coordinated acetylene. The C–C bond lengths in compound D are unfortunately not of sufficiently high precision to be considered in detail in this context.

5. Rearrangement of Carbonyls to Form Metal Bridges. The compound $CH_3CCo_3(CO)_8P(C_6H_{11})_3$ (Figure 5) results from the replacement of one axial carbonyl group by a molecule of tricyclohexylphosphine[63] while the compound $CH_3CCo_3(CO)_7$-$[(CH_3)_2As]_2C_2(CF_2)_2$ (Figure 6) results from the replacement of two axial carbonyl groups by one molecule of 1,2-bis(dimethylarsino)tetrafluorocyclobutene.[44] In both cases there has been a rearrangement of the equatorial carbonyl groups so that three of them are no longer terminal to the cluster but form bridges across each of the sides of the Co_3 triangle. The CCo_3 cluster is, however, only slightly distorted as a result. The mean value of the Co–CO (bridge) bond lengths is 1.94 Å.

In the compound $CH_3CCo_3(CO)_4(\pi$-$C_5H_5)_2$ (Figure 7) a rather different rearrangement has occurred.[64] The two cyclopentadienyl groups have replaced five of the carbonyl groups associated with two cobalt atoms and the single bridging carbonyl is axial rather than equatorial. The mean value of the Co–CO (bridge) bond lengths is 1.84 (2) Å.
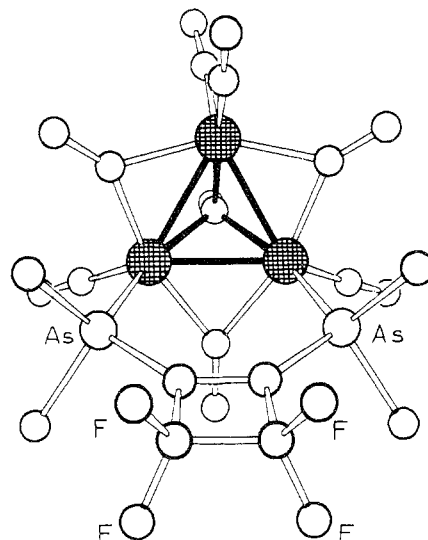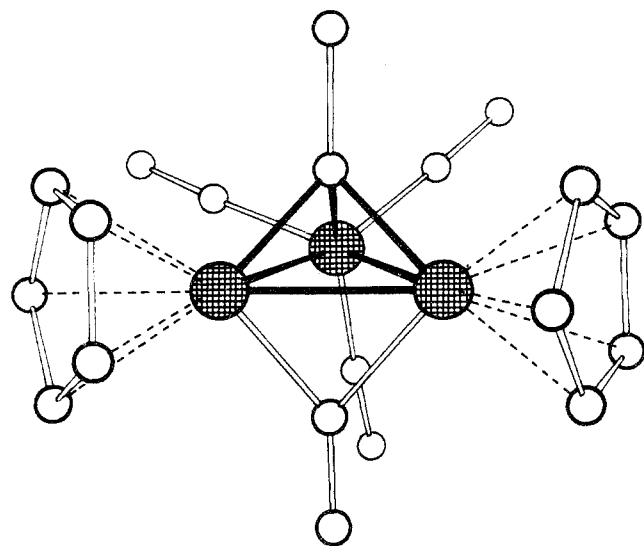

Figure 7. Molecular structure of the π-cyclopentadienyl complex $CH_3CCo_3(CO)_4(C_5H_5)_2$. The mean value of the distance from each ring carbon atom to its associated Co atom is 2.08 (2) Å.[64]

Bonding

We have presented evidence that the Co_3C cluster is capable of a unique type of bonding through the apical carbon atom. Moreover, the cluster is a complete entity with the electrons at least partially delocalized over all four atoms. Valence bond treatments[12] based on the concept of "bent bonds" and on sp³-hybridized carbon atom are therefore unsatisfactory. Descriptions in terms of the carbon as sp² or sp offer no advantages. The theoretical problems are essentially the same as encountered in tackling simpler metal clusters; all orbitals must be considered. From topological arguments Kettle[62] concluded that all available orbitals in the Co_3C cluster were just filled by the 30 valence electrons but only if three orbitals of the carbon are used in bonding. A better approach would be to consider a Co_3CR rather than Co_3C unit as in this way a MO treatment would permit the calculation of accessible experimental parameters such as bond lengths, magnetic anisotropy, etc.

(62) S. F. A. Kettle and J. Khan, *J. Organometal. Chem.*, 5, 588 (1961).
(63) T. W. Matheson and B. R. Penfold, unpublished results.
(64) R. S. McCallum and B. R. Penfold, unpublished results.