Organocobalt Cluster Complexes. 28. Highly Stabilized (Nonacarbonyltricobalt)carbon-Substituted Carbonium Ions[1,2]

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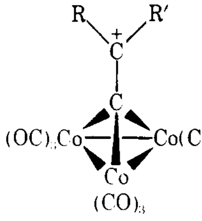
Abstract: The action of concentrated sulfuric acid, trifluoroacetic acid, or aqueous hexafluorophosphoric acid/propionic anhydride on $(OC)_9Co_3CCH(OH)R$ resulted in formation of carbonium ions of type $[(OC)_9Co_3CCHR]^+$. Very stable hexafluorophosphate salts of these cations were isolated in analytical purity. On the basis of their reactivity toward nucleophilic reagents (alcohols, PhSH, $PhNH_2$, and very reactive aromatic nucleophiles), their ^1H and ^{13}C NMR spectra, and their IR spectra it was concluded that most of the positive charge generated at the carbon atom at which C–O heterolysis has occurred is delocalized onto the cobalt atoms.

Introduction

In previous papers of this series we have reported two preparative routes to the tricobaltcarbon decacarbonyl cation, $(OC)_9Co_3CCO^+$, and presented evidence which showed this species to be a very stable and rather deactivated carbon electrophile.[3,4] These observations that the $(OC)_9Co_3C$ cluster substituent appeared to stabilize a positive charge on an adjacent carbon atom suggested to us that an examination of cobalt cluster-substituted carbonium ions of type $[(OC)_9Co_3CCRR']^+$, of expected structure I, might be of considerable interest. During the attempted synthesis of α-hydroxyalkylidynetricobalt nonacarbonyl complexes of type $(OC)_9Co_3CCH(OH)R$ (II) for this investigation we obtained an early hint that such cluster-substituted carbonium ions do indeed enjoy high stability.[5] In the attempted reduction of the aldehyde $(OC)_9Co_3CCH{=}O$ and of the ketone $(OC)_9Co_3CC(O)CH_3$ to the respective alcohols using the triethylsilane/trifluoroacetic acid system it was found that both compounds were reduced completely to the alkyl derivatives instead, $(OC)_9Co_3CCH_3$ and $(OC)_9Co_3CC_2H_5$, respectively. Such reduction past the alcohol stage by the Et_3SiH/CF_3CO_2H system usually occurs if one of the carbonyl substituents is capable of strong stabilization of a positive charge.[6] Thus, such reduction of $(OC)_9Co_3CC(O)R$ in those cases where R = H and CH_3, both nonstabilizing substituents,[6] suggests that the cobalt cluster substituent is one which can stabilize a positive charge on an adjacent carbon atom.



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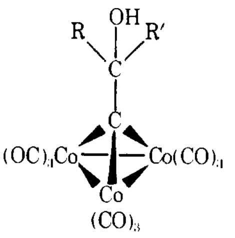


II

In the present paper we describe the results of a study which has provided two routes to such carbonium ions of type I and which has provided strong confirmation of the idea that the $(OC)_9Co_3C$ cluster stabilizes adjacent carbonium ion centers.

Results and Discussion

1. Synthesis. One of the routes to the cobalt-cluster-substituted acylium ion used the reaction of aqueous hexafluorophosphoric acid with a cluster-substituted ester:[3]

$$(OC)_9Co_3CCO_2R \xrightarrow{H^+PF_6^-,\ (EtCO)_2O} [(OC)_9Co_3CCO]^+[PF_6]^- \quad (1)$$

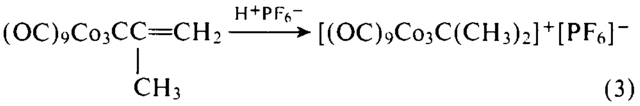
This procedure was nicely adaptable to the synthesis of cobalt-cluster-substituted carbonium ions from the alcohols:

$$(OC)_9Co_3CCH(OH)R \xrightarrow{H^+PF_6^-,\ (EtCO)_2O} [(OC)_9Co_3CCHR]^+[PF_6]^- \quad (2)$$

$$(R = H, CH_3, n\text{-}C_9H_{19}, C_6H_5)$$

The best results were obtained when the reactions were carried out in benzene solution using only small amounts of propionic anhydride. The carbonium hexafluorophosphate salts precipitated rapidly in high yield as microcrystalline, black solids, but occasionally as brown, amorphous powders. The reaction which forms them must be a clean process since the three salts with R = H, CH_3, and C_6H_5 could be isolated in analytical purity simply by washing the initial precipitate with several portions of dichloromethane. The carbonium ion hexafluorophosphates are thermally stable at room temperature and are quite air stable, but they react readily with water and other reactive nucleophiles. They are totally insoluble in nonpolar organic solvents (hexane, benzene, dichloromethane), but are partially soluble in oxygen-containing solvents (ethers, propionic anhydride) and quite soluble in nitromethane. They generally dissolve to give a brown to red-brown solution. The cobalt-cluster-substituted carbonium ions also may be generated by dissolving the alcohols in cold, concentrated sulfuric acid, in which they presumably are present as the soluble bisulfate or sulfate salts. In this solvent system the possibilities for developing their reaction chemistry are, of course, somewhat limited.

A second route to such cluster-substituted carbonium ions could be developed when vinyl-substituted methylidynetricobalt nonacarbonyl complexes became available.[2c,7] Protonation of such compounds gave the expected carbonium ions, and this route is useful in particular for the preparation of tertiary carbonium ion salts (eq 3).



$$(OC)_9Co_3C\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow{H^+PF_6^-} [(OC)_9Co_3C(CH_3)_2]^+[PF_6]^- \quad (3)$$

A third potential route to such carbonium ions, hydride

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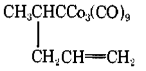
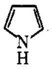
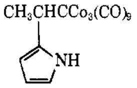
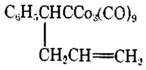
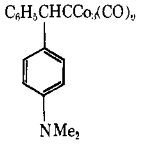
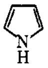
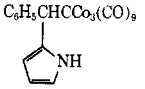
Table I. Reactions of $(OC)_9Co_3C$-Substituted Carbonium Ion Hexafluorophosphate Salts

R in $[RCHCCo_3(CO)_9]^+$	reactant	product (% yield)	mp, °C
H	MeOH	$MeOCH_2CCo_3(CO)_9$ (85)	128-129
H	EtOH	$EtOCH_2CCo_3(CO)_9$ (76)	54-56
H	$C_6H_5NH_2$	$C_6H_5NHCH_2CCo_3(CO)_9$ (67)	69-71
H	$C_6H_5NMe_2$	p-$Me_2NC_6H_4CH_2CCo_3(CO)_9$ (49)	90-105[a]
CH_3	MeOH	$CH_3CH(OMe)CCo_3(CO)_9$ (85)	176-177
CH_3	EtOH	$CH_3CH(OEt)CCo_3(CO)_9$ (82)	61-63 dec
CH_3	C_6H_5SH	$CH_3CH(SC_6H_5)CCo_3(CO)_9$ (42)	73-75
CH_3	$C_6H_5NH_2$	$CH_3CH(\underset{H}{N}C_6H_5)CCo_3(CO)_9$ (73)	117-119
CH_3	$C_6H_5NMe_2$	$CH_2{=}CHCCo_3(CO)_9$ (68)	144-146
CH_3	$(CH_2{=}CHCH_2)_4Sn$	 $\underset{CH_2CH=CH_2}{CH_3CHCCo_3(CO)_9}$ (65)	75-77
CH_3		 (36)	137-139
C_6H_5	MeOH	$C_6H_5CH(OMe)CCo_3(CO)_9$ (59)	70-72
C_6H_5	EtOH	$C_6H_5CH(OEt)CCo_3(CO)_9$ (75)	77-79
C_6H_5	C_6H_5SH	$C_6H_5CH(SC_6H_5)CCo_3(CO)_9$ (38)	93-95
C_6H_5	$C_6H_5NH_2$	$C_6H_5CH(NHC_6H_5)CCo_3(CO)_9$ (59)	126-127
C_6H_5	$(CH_2{=}CHCH_2)_4Sn$	 $\underset{CH_2CH=CH_2}{C_6H_5CHCCo_3(CO)_9}$ (76)	56-58
C_6H_5	$C_6H_5NMe_2$	 (54)	101-103
C_6H_5		 (44)	124-126

[a] Product unstable in air.

abstraction from an alkyl-substituted methylidynetricobalt nonacarbonyl cluster, was not successful. Thus trityl hexafluorophosphate in dichloromethane at reflux was without effect on $(OC)_9Co_3CCH_3$. Hydrolysis of the reaction mixture gave an 82% recovery of the starting cluster complex and no evidence for formation of $(OC)_9Co_3CCH_2OH$. In refluxing 1,2-dichloroethane medium this attempted reaction only resulted in partial decomposition of the cluster complex.

2. Reactivity. The $[(OC)_9Co_3CCRR']^+$ salts prepared in this study react with diverse nucleophilic substrates. As might be expected, they are sensitive to hydrolysis and are converted back to the starting alcohols on reaction with water. They react readily with alcohols to give ethers, $(OC)_9Co_3CC(OR'')RR'$, with benzenethiol to give the thioether, $(OC)_9Co_3CC(SPh)RR'$, with aniline to give the secondary amine, $(OC)_9Co_3CC(NHPh)RR'$, and with tetraallyltin to give the allylated product, $(OC)_9Co_3CC(CH_2CH{=}CH_2)RR'$. *N,N*-Dimethylaniline was alkylated by $[(OC)_9Co_3CCH_2]^+$ and $[(OC)_9Co_3CCHC_6H_5]^+$ but its reaction with $[(OC)_9Co_3CCHCH_3]^+$ resulted in deprotonation of the latter to give $CH_2{=}CHCCo_3(CO)_9$. However, $[(OC)_9Co_3CCHCH_3]^+$ as well as $[(OC)_9Co_3CC(CH_3)_2]^+$ and $[(OC)_9Co_3CCHC_6H_5]^+$ alkylated pyrrole. These carbonium ion salts did not alkylate less nucleophilic aromatic substrates. The $[(OC)_9CO_3CCHCH_3]^+[PF_6]^-$ salt did not even react with ferrocene, a known highly reactive aromatic nucleophile,[8] under the conditions used for its successful reaction with pyrrole. Anisole and toluene also are unreactive, and, as noted above, benzene is a satisfactory medium for the preparation of these salts and for carrying out their further conversions. It would appear that the $[(OC)_9Co_3CCRR']^+$ cations are rather deactivated carbon electrophiles, an observation made previously in the case of the related acylium ion, $[(OC)_9Co_3CCO]^+$. They do, however, have useful chemistry and provide the means for the preparation of many new carbon-functional alkylidynetricobalt nonacarbonyl complexes. Such applications, however, do seem somewhat limited. In many cases where successful reactions of these $[(OC)_9Co_3CCRR']^+$ salts might have been expected, decomposition of the cobalt cluster was the only process observed. This was the case on attempted reactions with *p*-tolylmagnesium bromide, ammonia, 1-*N*-piperidylpropene, acetonitrile, tetramethyltin, and triphenylphosphine. With the latter, the phosphonium salt, $[(OC)_9Co_3CH(Ph)PPh_3]^+[PF_6]^-$ was the expected product of the reaction with $[(OC)_9Co_3CCHC_6H_5]^+[PF_6]^-$. However, on addition of the phosphine to a brown solution/suspension of the salt in tetrahydrofuran an immediate color change to black-green and violent evolution of carbon monoxide occurred instead.

An attempt was made to develop the chemistry of $[(OC)_9Co_3CCHCH_3]^+$ without its prior isolation as the hexafluorophosphate salt. To this end, $(OC)_9Co_3CCH(OH)CH_3$ was treated with propionic anhydride and trifluoroacetic acid in benzene for 1 h, followed by addition of methanol. Even after long reaction times (12 h), the expected $(OC)_9Co_3CCH(OCH_3)CH_3$ was isolated in only 35% yield and a large part (32%) of the starting material was recovered unchanged. One reaction, however, proceeded more readily with the cation generated in solution than with the preformed salt: reduction by triethylsilane. Thus treatment of $[(OC)_9Co_3CCHC_6H_5]^+[PF_6]^-$ with Et_3SiH in THF gave $(OC)_9Co_3CCH_2Ph$ in only 7% yield, but reaction of $(OC)_9Co_3CCH(OH)CH_3$ with Et_3SiH/CF_3CO_2H in THF resulted in formation of $(OC)_9Co_3CCH_2CH_3$ in 72% yield.

Table I summarizes the chemical conversions of the car-

Table II. Proton Magnetic Resonance Spectra of $(OC)_9Co_3C$-Substituted Alcohols and Derived Carbonium Ions[a]

alcohol δ, ppm	cation δ (solvent), ppm	Δδ, ppm
$(OC)_9Co_3CCH_2OH$	$[(OC)_9Co_3CCH_2]^+$	
CH_2 5.21	5.8 (H_2SO_4)	0.6
	5.7 (CF_3COOH)	0.5
$(OC)_9Co_3CCH(OH)CH_3$	$[(OC)_9Co_3CCHCH_3]^+$	
CH 5.4	6.7 (H_2SO_4)[b]	1.3
	6.9 (CF_3COOH)	1.5
	6.9 (PF_6^- salt in CH_3NO_2)	1.5
CH_3 1.8	2.4 (H_2SO_4)[c]	0.6
	2.5 (CF_3COOH)	0.7
	2.4 (PF_6^- salt in CH_3NO_2)	0.6
$(OC)_9Co_3CCH(OH)C_6H_5$	$[(OC)_9Co_3CCHC_6H_5]^+$	
CH 6.2	7.7 (H_2SO_4)	1.5
	8.2 (CF_3COOH)	2.0
C_6H_5 7.4	7.2 (H_2SO_4)	−0.2
	7.6 (CF_3COOH)	0.2
$(OC)_9Co_3CCH(OH)C_9H_{19}$-*n*		
CH 5.09[d]		
$(OC)_9Co_3CC(CH_3)_2OH$	$[(OC)_9Co_3CC(CH_3)_2]^+$	
CH_3 1.77	2.08 (H_2SO_4)	0.31

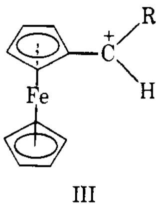
[a] Alcohol spectra were obtained in $CDCl_3$ and are referenced to internal tetramethylsilane. Cation spectra are referenced to external tetramethylsilane contained in a capillary tube inside the NMR tube. [b] Quartet, $J = 7$ Hz. [c] Doublet, $J = 7$ Hz. [d] In CCl_4 solution.

bonium ions $[(OC)_9Co_3CCHR]^+$ (R = H, CH_3, C_6H_5). The reactions of $[(OC)_9Co_3CC(CH_3)_2]^+$ have been described in a previous paper.[7]

3. Spectroscopy. The fact that the $[(OC)_9Co_3CRR']^+$ salts are carbon electrophiles of considerably diminished reactivity suggested that the positive charge was being delocalized into the $CCo_3(CO)_9$ cluster, i.e., that the cluster substituent was donating electron density to the electron-deficient, positively charged carbon center formed by heterolytic cleavage of the C–OH bond of the $(OC)_9Co_3CH(OH)R$ complex. Additional evidence in support of this view was desirable and to this end ^1H and ^{13}C NMR and IR spectroscopic studies of both neutral complexes, $(OC)_9Co_3CCH(OH)R$ and $(OC)_9Co_3CCH_2R$, and of the derived carbocations, were undertaken.

a. Proton Magnetic Resonance Spectra. Table II provides proton chemical shift data for $(OC)_9Co_3CCH(OH)R$ (R = H, CH_3, *n*-C_9H_{19}, and C_6H_5)[5] and $(OC)_9Co_3CC(OH)(CH_3)_2$[7] and for the carbocations derived from them when they were dissolved in concentrated sulfuric acid or in neat trifluoroacetic acid. In two cases, the ^1H NMR spectrum of the cobalt-cluster-substituted carbonium ion hexafluorophosphate salt in freshly prepared nitromethane solution was recorded as well.

^1H NMR spectroscopy has been used in the past to obtain estimates of the degree of stabilization of metal-substituted carbonium ions. In general, the $R'CH(R)OH$ protons in secondary alcohols become less shielded when the alcohol is converted to the carbonium ion, $R'CHR^+$.[9] When the carbonium ion is one which is not highly stabilized, e.g., for the process $(CH_3)_2CHOH \rightarrow (CH_3)_2CH^+$, this change in chemical shift, Δδ, is relatively large (+8.5 ppm in the example cited). On the other hand, when the carbonium ion is highly stabilized, then Δδ is small.[10] For instance, diverse techniques have shown ferrocenyl-substituted carbonium ions, III, to be



III

highly stabilized by the organoiron substituent.[11] On conversion of ferrocenyl-substituted alcohols, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH(OH)R)$, to the carbonium ions, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CHR)]^+$, by solution in trifluoroacetic acid, Δδ for the resonance of the indicated proton is in the range 2.6–2.9 ppm when R = alkyl or aryl and 1.57 ppm when R = H.[12] Similarly, for the conversion of $(\eta^6\text{-}p\text{-}CH_3C_6H_4CH(OH)CH_3)Cr(CO)_3$ to the stabilized carbonium ion Δδ = 2.13.[13] The Δδ values for the cluster-substituted carbonium ions reported in Table II are considerably smaller, but, in view of the caveat already made,[10] one cannot infer that the $(OC)_9Co_3C$-substituted cations are more stable, only that they also are highly stabilized by the metal substituents.

b. ^{13}C Nuclear Magnetic Resonance Spectra. In the processes $R_3COH \rightarrow R_3C^+$ and $R_3CH \rightarrow R_3C^+$ the change in the shielding of the indicated carbon atom, $\Delta\delta_C = \delta_C(\text{cation}) - \delta_C(\text{alcohol})$ or $\delta_C(\text{cation}) - \delta_C(\text{alkane})$, provides some measure of the stabilization of the cation.[14] When there is little stabilization, as in the case of the carbonium ions formed in the processes $Me_2CHOH \rightarrow Me_2CH^+$ and $Me_2CH_2 \rightarrow Me_2CH^+$, $\Delta\delta_C$ is large, 255.7 and 303.5 ppm, respectively.[14a] On the other hand, if the cation is highly stabilized, then $\Delta\delta_C$ invariably is much smaller; e.g., see Scheme I. It is believed that the charge density at a carbonium ion center is the major factor governing its shielding, so as a first approximation these Δδ values do reflect changes in charge density at the carbon atom upon formation of the cation from the neutral compound. However, ^{13}C chemical shifts depend on other factors as well (on hybridization and on anisotropic, diamagnetic, and paramagnetic effects),[14] and, therefore, a ranking of the stabilities of metal-complexed carbonium ions on the basis of Δδ values is not possible. A more illuminating comparison would be that between the Δδ values for the metal-complexed alcohol and its derived cation and the uncomplexed alcohol and its respective carbonium ion. Such a comparison was possible in the case of the tricarbonylchromium complexes of benzyl alcohols and benzhydrols,[17] but in many other cases the free, uncomplexed organic ligands are not available as stable species. In the present instance, the organic ligands are carbynes, $R\dot{C}$:, which triply bridge the three cobalt atoms of the $Co_3(CO)_9$ unit, and free carbynes are known only as reactive intermediates.[21]

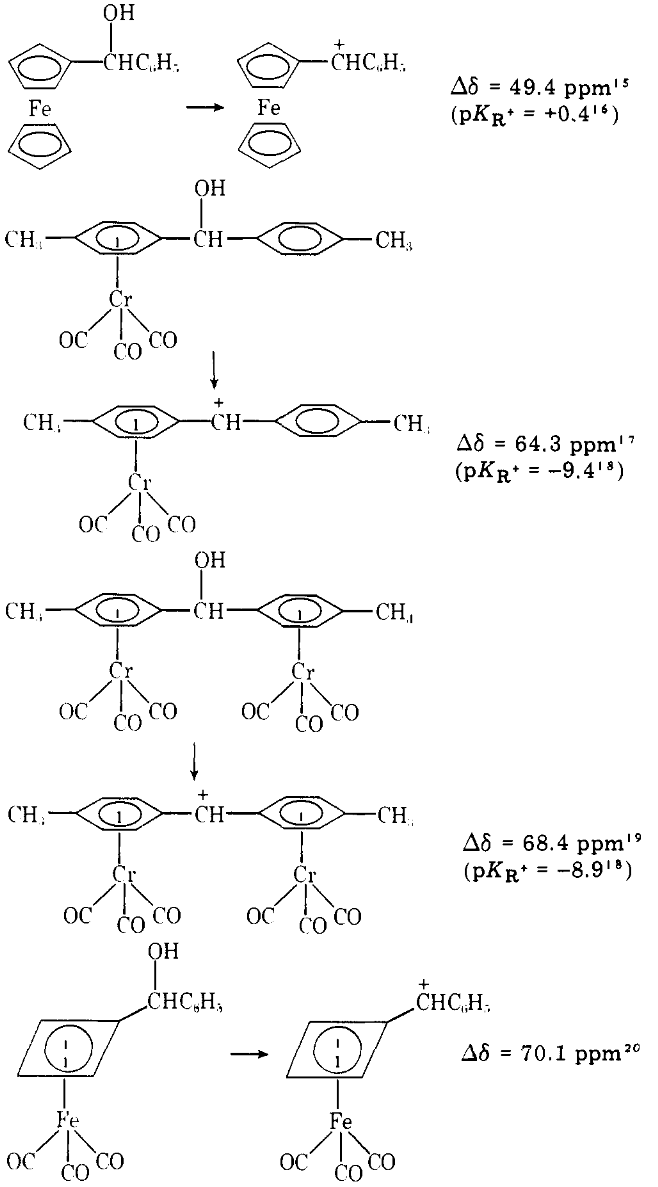
^{13}C NMR data for a number of neutral alkylidynetricobalt nonacarbonyl complexes and for several cobalt-cluster-substituted carbonium ions are given in Table III. The carbonium ions were generated by dissolving the respective alcohols in cold, concentrated H_2SO_4. Difficulty was encountered initially

Table III. ^{13}C NMR Spectra of Neutral and Charged Alkylidynetricobalt Nonacarbonyl Complexes[a]

complex: R in $RCCo_3(CO)_9$	δ_C, C≡O carbon	δ_C, α carbon	δ_C, other, ppm
CH_3	200.7	45.7	
CH_3CH_2	200.9	52.6	21.3 (CH_3)
n-$C_9H_{19}CH_2$	201.2	60.1	
$C_6H_5CH_2$	199.7	64.0	C_6H_5: 143.9 (C_1), 130.0 (C_2), 127.9 (C_3), 129.4 (C_4)
$HOCH_2$	200.6	77.6	
$CH_3(OH)CH$	200.5	82.5	28.5 (CH_3)
n-$C_9H_{19}(OH)CH$	200.7	87.3	
$(CH_3)_2(OH)C$	200.8	86.0	36.5 (CH_3)
$C_6H_5(OH)CH$	200.0	88.8	C_6H_5: 146.2 (C_1), 128.8 (C_2), 126.8 (C_3), 128.6 (C_4)
n-$C_6H_{13}C(O)$	199.9	211.5 (>C=O)	
n-$C_9H_{19}C(O)$	199.6	211.2 (>C=O)	
$CH_3CH_2OC(O)$	199.0	177.6 (>C=O)	61.3 (CH_3), 13.8 (CH_2)
n-$C_{10}H_{21}OC(O)$	199.1	179.1 (>C=O)	
trans-$(CH_3)_3SiCH{=}CH$	200.8		162.4, 132.2 (CH=CH), 0.86, $(CH_3)_3Si$
CH_2^+	192.7	91.1	
CH_3CH^+	193.2	119.9	26.2 (CH_3)
n-$C_9H_{19}CH^+$	193.1	123.7	
$(CH_3)_2C^+$	193.3	157.9	33.7 (CH_3)
$C_6H_5CH^+$	192.4	124.5	C_6H_5: 135.4 (C_1), 129.9 (C_2), 129.3 (C_3), 132.6 (C_4)

[a] Spectra of neutral complexes were obtained in $CDCl_3$ solution and are referenced to internal tetramethylsilane. Cation spectra were obtained in concentrated sulfuric acid solution and are referenced to external tetramethylsilane through the ^{19}F lock signal. All spectra were proton decoupled.

Scheme I



$\Delta\delta$ = 49.4 ppm[15] (pK_{R^+} = +0.4[16])

$\Delta\delta$ = 64.3 ppm[17] (pK_{R^+} = −9.4[18])

$\Delta\delta$ = 68.4 ppm[19] (pK_{R^+} = −8.9[18])

$\Delta\delta$ = 70.1 ppm[20]

in observing the signal due to the carbon atom of the CCo_3 core of these complexes, and this was not unexpected. Theoretically, the signal due to the cluster carbon atom should be a 22-line pattern resulting from spin-spin coupling to the three cobalt atoms, each possessing a nuclear spin of $^7/_2$.[22] Furthermore, the line width would be broadened by the nuclear quadrupole moment of the cobalt atoms, and, an additional difficulty, the apical carbon atom might have too short a relaxation time to permit observation of its signal in solution. Finally, the methylidynetricobalt nonacarbonyl complexes generally have limited molar solubility in organic solvents. However, the use of very concentrated and very viscous solutions of suitable neutral complexes in $CDCl_3$ or of the neat liquid complexes themselves overcame these difficulties. It also was found that the apical carbon atom resonance of the cobalt-cluster-substituted carbonium ions could be observed when efforts were made to prepare concentrated solutions. Subsequent to our preliminary communication of these results,[2d] an Italian group reported further apical carbon atom resonances for neutral complexes.[23] From their results and those which we report, it would appear that the viscosity of the medium is the deciding factor in the success of these measurements, i.e., fast relaxation of the apical carbon atom is a decisive complication. In recording our spectra, it was discovered that the addition of even a small quantity of $CDCl_3$ to liquid samples markedly decreased the intensity of the apical carbon atom signal. This can be attributed to a decrease in the viscosity of the solution. In support of this idea, the spectra of the cluster carbonium ions showed the apical carbon atom signals even though the solutions were not very concentrated; however, they were very viscous.

The apical carbon atom signals in the ^{13}C NMR spectra of neutral $(OC)_9Co_3CR$ complexes were observed as broad multiplets about 40–50 Hz in width in the region δ_C 255–315 ppm (Table IV). These chemical shifts are well downfield from those of most carbon atoms in organic and organometallic compounds except for those of alkylcarbonium ions,[14] some transition metal–carbene complexes (e.g., $(OC)_5CrC^*(OMe)Ph$, δ (C^*) 351.4 ppm;[24] $(OC)_5WC^*(OEt)C{\equiv}CPh$, δ (C^*) 286.1 ppm[25]) and -carbyne complexes (e.g., $CH_3C^*{\equiv}W(CO)_4Cl$, δ (C^*) 288.8 ppm;[26] $PhC{\equiv}C{-}C^*{\equiv}W(CO)_4Br$, δ (C^*) 230.6 ppm[25]). As noted above, $RCCo_3(CO)_9$ compounds are best viewed as carbyne complexes, so this low-field position of the apical carbon atom is

Table IV. Apical Carbon Atom Resonances of Some Neutral and Charged Alkylidynetricobalt Nonacarbonyl Complexes[a]

complex: R in $RCCo_3(CO)_9$	NMR sample	δ_C, apical carbon, ppm
n-C_5H_{11}	$CDCl_3$ solution	305.9
n-$C_{10}H_{21}$	$CDCl_3$ solution	306.4
trans-$(CH_3)_3SiCH{=}CH$	$CDCl_3$ solution	283.0
n-$C_6H_{13}C(O)$	neat sample	276.3
n-$C_9H_{19}C(O)$	neat sample	276.2
$C_2H_5OC(O)$	neat sample	258.4
n-$C_{10}H_{21}OC(O)$	$CDCl_3$ solution	257.6
CH_2^+	H_2SO_4 solution[b]	286.2
CH_3CH^+	H_2SO_4 solution[b]	273.5
n-$C_9H_{19}CH^+$	H_2SO_4 solution[b]	273.3
$C_6H_5CH^+$	H_2SO_4 solution[b]	267.0
$(CH_3)_2C^+$	H_2SO_4 solution[c]	257.8

[a] Satisfactory spectra were obtained in about 3000 pulses for neat samples, about 10 000 pulses for $CDCl_3$ solutions, and about 8000 pulses for 1-2 M solutions in concentrated sulfuric acid, using a pulse width of 8 μs (corresponding to a nutation angle of ca. 30°), a data acquisition time of 0.41 s, and 0.80 s between pulses. The field positions of the lines were calculated using the plotting parameters and are referenced to external tetramethylsilane through the ^{19}F lock signal. [b] Via solution of the respective alcohol in concentrated sulfuric acid. [c] Via solution of $(OC)_9Co_3CC(CH_3){=}CH_2$[7] in concentrated sulfuric acid.

Table V. Observed $\Delta\delta_C$ Values for the α Carbon Atoms and the C≡O Ligand Carbon Atoms for the $RCH_2CCo_3(CO)_9 \rightarrow [RCHCCo_3(CO)_9]^+$ and $RCH(OH)CCo_3(CO)_9 \rightarrow [RCHCCo_3(CO)_9]^+$ Processes[a]

neutral complex	cation	$\Delta\delta_C$, ppm	
$CH_3CCo_3(CO)_9$	$[CH_2CCo_3(CO)_9]^+$	αC	45.4
		C≡O	−8.0
$CH_3CH_2CCo_3(CO)_9$	$[CH_3CHCCo_3(CO)_9]^+$	αC	67.3
		C≡O	−7.7
n-$C_9H_{19}CH_2CCo_3(CO)_9$	$[n$-$C_9H_{19}CHCCo_3(CO)_9]^+$	αC	63.6
		C≡O	−7.8
$C_6H_5CH_2CCo_3(CO)_9$	$[C_6H_5CHCCo_3(CO)_9]^+$	αC	60.5
		C≡O	−7.3
$HOCH_2CCo_3(CO)_9$	$[CH_2CCo_3(CO)_9]^+$	αC	13.5
		C≡O	−7.9
$CH_3CH(OH)CCo_3(CO)_9$	$[CH_3CHCCo_3(CO)_9]^+$	αC	37.4
		C≡O	−7.2
n-$C_9H_{19}CH(OH)CCo_3(CO)_9$	$[n$-$C_9H_{19}CHCCo_3(CO)_9]^+$	αC	41.2
		C≡O	−7.4
$C_6H_5CH(OH)CCo_3(CO)_9$	$[C_6H_5CHCCo_3(CO)_9]^+$	αC	35.7
		C≡O	−7.6
$(CH_3)_2C(OH)CCo_3(CO)_9$	$[(CH_3)_2CCCo_3(CO)_9]^+$	αC	71.9
		C≡O	−7.5

[a] $\Delta\delta_C = \delta_C(\text{cation}) - \delta_C(\text{neutral complex})$.

not surprising. The carbon monoxide ligand carbon atom resonances in the ^{13}C NMR spectra of the neutral alkylidynetricobalt nonacarbonyl complexes were observed as broad singlets (with some fine structure). On the basis of the known structure of the neutral alkylidynetricobalt nonacarbonyl complexes,[27] one would have expected two CO carbon atom resonances in 2:1 ratio. However, as has been reported,[23] even at low temperature, only a single, now sharp C≡O resonance was observed. One may assume that an intramolecular exchange process is taking place. The CO ligand carbon atom resonances in the ^{13}C NMR spectra of the $(OC)_9Co_3C$-substituted alcohols became much sharper in the spectra of the derived carbonium ions, presumably owing to the increased viscosity of the sulfuric acid solvent system.

An analysis of the NMR data in Table III provides strong confirmation that the positive charge has been delocalized to a large extent from the carbon atom α to the $CCo_3(CO)_9$ cluster to the cobalt atoms, leaving nearly electroneutral α carbon atoms. Table V presents Δδ values for the α carbon atom signals for several $(OC)_9Co_3CCH_2R \rightarrow [(OC)_9Co_3CCHR]^+$ and $(OC)_9Co_3CCH(OH)R \rightarrow [(OC)_9Co_3CCHR]^+$ ionization processes, as well as for the C≡O ligand resonances. It is immediately apparent that the Δδ (C_α) values are small and comparable to those observed for other transition-metal-stabilized carbocations. In fact, comparison (Table VI) with Δδ (C_α) values with comparable ferrocenyl carbonium ions, which are very highly stabilized ($pK_{R^+} = 0 \pm 2$[11]), suggests that the $(OC)_9Co_3C$-substituted carbonium ions are very highly stabilized as well. However, as noted before, quantitative differences in stabilization cannot be extracted from Δδ values.

Table VI. Comparison of $\Delta\delta_C(C_\alpha)$ Values[a] for $[RCHCCo_3(CO)_9]^+$ and $[RCHC_5H_5FeC_5H_5]^+$ Cations

R in cation	$\Delta\delta_C$ in $[RCHCCo_3(CO)_9]^+$, ppm	$\Delta\delta_C$ in $[RCHC_5H_4FeC_5H_5]^+$ ppm[b]
H	13.5	26.2
CH_3	37.4	52.1
C_6H_5	35.7	49.4

[a] For the process $R'RCHOH \rightarrow [R'RCH]^+$. [b] Data from ref 15.

The observed shieldings for the α carbon atoms in the $[(OC)_9Co_3CCHR]^+$ cations fall in the olefinic region rather than in the region of the relatively unstabilized (>300 ppm) or even the phenyl-stabilized (~200-250 ppm) carbonium ions. In our further analysis this olefin analogy is useful. To facilitate our further examination of the observed ^{13}C NMR data, the cluster alcohols $(OC)_9Co_3CCH(OH)R$ (R = H, CH_3, C_6H_5) are compared with the series ethanol, 2-propanol, and 1-phenylethanol, while the derived cationic species are compared with ethylene, propene, and styrene, respectively. These model systems correlate amazingly well with the spectra observed for the cationic cobalt cluster complexes. The shieldings of the α carbon atoms in the cations follow the normal order observed when substituents on a fully substituted carbon atom are varied from hydrogen to methyl to phenyl: the substitution of a methyl group for hydrogen deshields the carbon atom of attachment, as does the substitution of a phenyl group for a methyl substituent. In contrast, for normal carbonium ions, the resonance of the methyl derivative of a series invariably is farther downfield (less shielded) than is that of the phenyl derivative.[14a] The cobalt-cluster-substituted alcohols show the same

Table VII. Terminal Carbonyl Stretching Frequencies (cm^{-1}) of $(OC)_9Co_3C$-Substituted Alcohols and of Their Derived Carbonium Ion Tetrafluoroborates in Dichloromethane Solution

$CH_3CH(OH)CCo_3(CO)_9$	2102 w	$[CH_3CHCCo_3(CO)_9]^+$	2134 w
	2052 s		2100 s
	2039 s		2085 s
	2019 sh		2055 sh
$(CH_3)_2C(OH)CCo_3(CO)_9$	2101 w	$[(CH_3)_2CCCo_3(CO)_9]^+$	2135 w
	2050 s		2097 s
	2039 s		2084 s
	2025 sh		2049 sh
$C_6H_5CH(OH)CCo_3(CO)_9$	2105 w	$[C_6H_5CHCCo_3(CO)_9]^+$	2141 w
	2051 s		2105 s
	2039 s		2090 s
	2025 sh		2058 w
in Nujol	2098 w	PF_6^- salt	2140 w
	2058 s	(in Nujol)	2112 s
	2039 s		2089 s
	2020 sh		2070 w

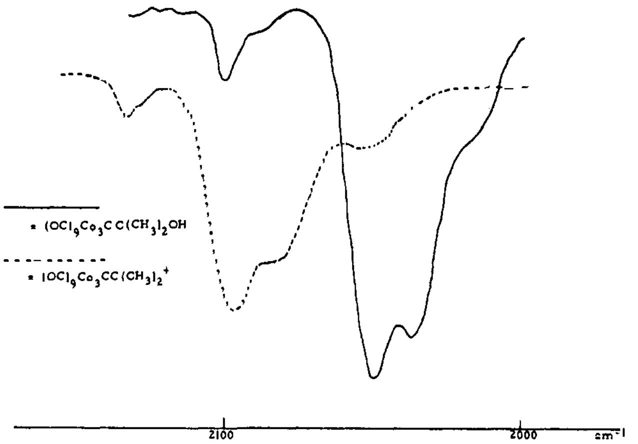


Figure 1. Infrared spectra of $(OC)_9Co_3CC(CH_3)_2OH$ and $(OC)_9Co_3CC(CH_3)^+$.

substitution effects as the cations. Furthermore, the observed shifts on going from alcohols to cations in the alkylidynetricobalt nonacarbonyl series are paralleled in the olefin model series: the unsubstituted carbon atom signal is shifted least on going from the alcohol to the cation, the phenyl-substituted carbon atom signal is shifted more, and the methyl-substituted carbon atom signal is shifted the most. These considerations provide good indication that the α carbon atom in the $[(OC)_9Co_3CCHR]^+$ cations is nearly fully bonded and only slightly electron deficient.

Examination of the remainder of the carbon atom shieldings in Table III does not show any significant deshielding on conversion of an alcohol to a cation. In fact, the carbon monoxide ligand carbon atom resonances are shifted slightly upfield ($\Delta\delta$ = −7–8 ppm), as are the signals due to the carbon atoms immediately bonded to the α carbon atom (CH_3 in $[(OC)_9Co_3CCHCH_3]^+$ and C-1 of the phenyl group in $[(OC)_9Co_3CCHC_6H_5]^+$). The latter shifts provide further confirmation that the α carbon atom in the $[(OC)_9Co_3CCHR]^+$ cations is nearly fully bonded and only slightly electron deficient, since an analogous upfield shift is observed in the alcohol/olefin model compound series. Thus the methyl carbon atom resonance of 2-propanol and that of the C-1 phenyl carbon atom of 1-phenylethanol move upfield on going from the alcohol to the olefin.[14a]

The upfield shift of the C≡O ligand carbon atom resonances shows clearly that the positive charge is being displaced onto the cobalt atoms. The C≡O ligands will become more tightly bonded to the cobalt atoms as positive charge accumulates on the latter, and the consequent movement of these carbon atoms to a position closer to the metal atoms would be expected to result in increased shielding due to the diamagnetic anisotropic shielding effect of the cobalt atoms. It is noteworthy that a linear correlation has been found to exist between the ^{13}C chemical shift and the Cotton-Kraihanzel metal-carbon force constant in several series of transition metal carbonyl complexes: the higher the ^{13}C shielding, the larger the force constant.[28]

c. Infrared Spectra. The infrared spectra of the alcohols $(OC)_9Co_3CCH(OH)CH_3$, $(OC)_9Co_3CC(OH)(CH_3)_2$, and $(OC)_9Co_3CCH(OH)C_6H_5$, and of their derived carbonium ion tetrafluoroborates, prepared by reaction of the alcohols with $HBF_4 \cdot OMe_2$ in dichloromethane solution, were examined in the terminal carbonyl region (2000–2200 cm^{-1}). The observed frequencies are listed in Table VII, and a representative spectrum is reproduced in Figure 1. The IR spectra of the alcohols display the same terminal carbonyl stretching pattern found by earlier workers for various alkylidynetricobalt nonacarbonyl complexes:[29] four bands at approximately 2100 w, 2050 s, 2040 s, and 2020 m cm^{-1}. These bands have been assigned to a_1, e, a_2, and e bands, respectively, of a CCo_3 cluster with local C_{3v} symmetry.[30] The cobalt cluster carbonium ion spectra, on the other hand, show absorptions which are 30–50 cm^{-1} higher than those of the respective alcohols. Such shifts to higher energy are in excellent agreement with the conclusion reached on the basis of the ^{13}C NMR spectra that the positive charge in these cationic complexes resides in the main on the cobalt atoms. A loss of electron density at the cobalt atom results in diminished donation of electron density from the cobalt atoms to the π^* orbitals of the C≡O ligands, which leads to a higher C—O bond order and a higher C—O stretching energy.[31] It has been shown that, for metal carbonyls, a net change of one unit of charge results in a 100-cm^{-1} shift.[32] In the $[(OC)_9Co_3CCHR]^+$ complexes, with one unit of positive charge being distributed equally over three cobalt atoms, the shifts of 30–50 cm^{-1} to higher energy are thus in the expected range.

Inspection of Figure 1 shows that the band contours of the C≡O stretching vibrations have not changed markedly on going from the neutral alcohol to the positively charged cation. However, there is noticeable broadening of the bands, but band splitting is not apparent. To ensure sufficient resolution in these spectra to detect any minor changes, the infrared spectra of $PhCH(OH)CCo_3(CO)_9$ and of $[(OC)_9Co_3CCHPh]^+[BF_4]^-$ were recorded using a Perkin-Elmer 180 infrared spectrophotometer with 1-cm^{-1} resolution. These are reproduced in Figure 2. In this better quality spectrum a 4–5-cm^{-1} splitting

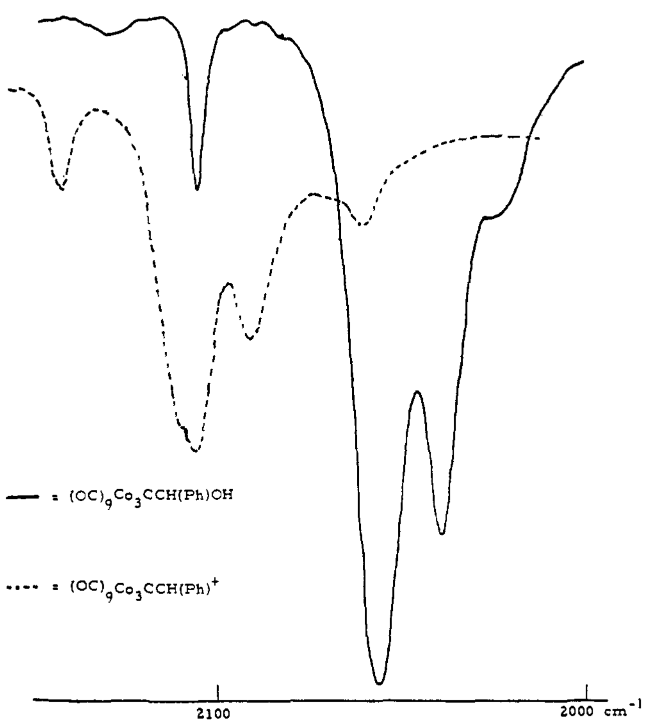


Figure 2. Infrared spectra of $(OC)_9Co_3CCH(Ph)OH$ and $(OC)_9Co_3CCH(Ph)^+$.

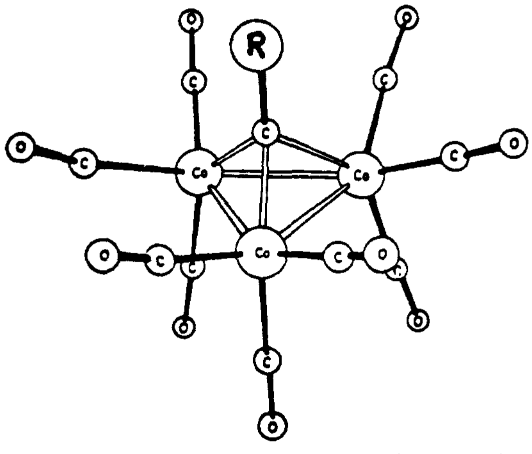


Figure 3. Structure of alkylidynetricobalt nonacarbonyl complexes.

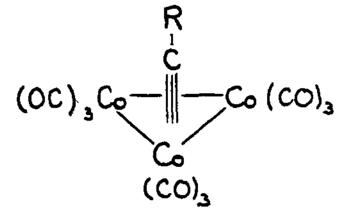


Figure 4. Carbyne complex representation of alkylidynetricobalt nonacarbonyl complexes.

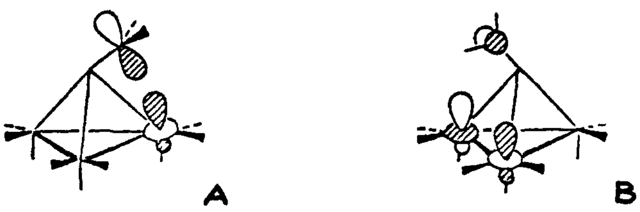


Figure 5. Favorable orbital interactions in the "tipped" model of $[CH_2CCo(CO)_9]^+$ (from ref 37).

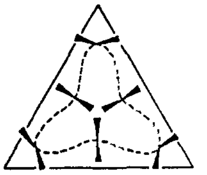
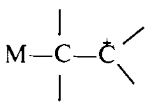


Figure 6. CH_2 circumambulation in the "tipped" model of $[CH_2CCo_3(CO)_9]^+$ (from ref 37).

of the higher energy e band is perceptible. The significance of this observation will be discussed in the next section.

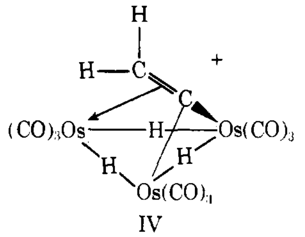
4. Bonding. A brief discussion of the bonding of the neutral alkylidynetricobalt nonacarbonyl complexes is in order before we consider the bonding in the derived cluster cations. The structures of a number of such complexes have been determined by X-ray crystallography.[33,34] The disposition of ligands about the CCo_3 tetrahedral core is as shown in Figure 3. Penfold and Robinson in a review[33] developed the concept of "a delocalized, electron-rich Co_3C core which is electron-withdrawing with respect to the apical group". ^{13}C NMR and IR spectroscopic studies have been cited[29] in support of a model in which the $CCo_3(CO)_9$ cluster "behaves as an electron sink capable of π interaction with the apical substituent", as an "electron reservoir analogous to an aromatic system". Further evidence of such a view is provided by electrochemical[35] and ^{59}Co nuclear quadrupole resonance spectroscopic studies.[36] In any case, a model in which the lines in Figure 3 which connect the core atoms are viewed as two-center, two-electron σ bonds clearly is not appropriate. Miller and Brill[36] have suggested the alternate representation shown in Figure 4 which stresses the visualization of these $(OC)_9Co_3CR$ compounds as carbyne complexes. More recently, a molecular orbital approach to the bonding in $(OC)_9Co_3CR$ clusters (and to M_3L_9(ligand) complexes in general) has been developed by Schilling and Hoffmann,[37] and this probably is the best description of the bonding in these clusters.

Our early view[2a,b,d] of the bonding in the $(OC)_9Co_3C$-substituted carbonium ions utilized the σ-π metal-carbon bond hyperconjugation approach which has been applied quite successfully to



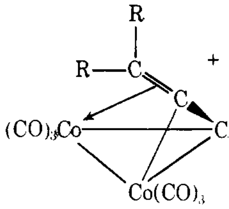
$$M-\underset{|}{\overset{|}{C}}-\overset{+}{C}\Big\langle$$

systems in main group organometallic chemistry.[38] The MO study of Schilling and Hoffmann,[37] however, also has dealt with the $[(OC)_9Co_3CCH_2]^+$ cluster ion. Favorable orbital interactions of types A and B (Figure 5) when the CH_2 group is tipped from the original perpendicular position lead to a fluxional species in which the CH_2 substituent circumambulates and rotates as indicated in Figure 6. In this model the transfer of electron density from cobalt to carbon to a large extent neutralizes the positive charge on carbon and leads to substantial positive charge accumulation on cobalt. This bonding model is similar to that proposed for the related osmium cluster, $[CH_2COs_3H_3(CO)_9]^+$ (IV), whose tipped-CH_2 structure was indicated by ^1H NMR studies.[39]



IV

An X-ray crystallographic study of a $(OC)_9Co_3C$-substituted carbonium ion salt will be required to settle this structural question: is the α carbon atom tipped from the Co_3–C perpendicular as in V, or is it not, as in I? To date, we have not been able to obtain crystals suitable for an X-ray diffraction study. However, the ^{13}C NMR and IR spectroscopic results offer hints that the "tipped" model may indeed be the correct one.



V

In the fluxional model of Schilling and Hoffmann which involves C_α–Co interactions, the ^{13}C NMR signal of the α carbon atom might be expected to show spin–spin coupling to the cobalt atoms. (Spin–spin coupling constants, $J(^{103}Rh-^{13}C)$, have been found to lie in the range 10–16 Hz for a number of olefin and diene complexes of rhodium.[40]) Coupling with the cobalt atom should result in an eight-line pattern for the α carbon atom signal. Although a resolved eight-line signal was not observed, the signals of the α carbon atoms in the spectra of the $[(OC)_9Co_3CCHR]^+$ ions are somewhat broader than those of the other carbon atoms of these complexes. For example, the line width at half height of the α C resonance in $[(OC)_9Co_3CCHC_9H_{19}\text{-}n]^+$ is 25 Hz, as compared to 5–12 Hz for the lines assigned to the alkyl carbon atom resonances. A temperature-dependent ^{13}C NMR study of such cobalt-cluster-substituted carbonium ions might provide clearer indication of $^{59}Co-^{13}C_\alpha$ spin–spin coupling.

If the model shown in V is the correct one, then also one might expect some changes in the terminal C≡O stretching region of the infrared spectra of these cations, compared with the IR spectra of the alcohols from which they were generated. As noted above, splitting of the higher energy e band is perceptible and broadening of the bands occurred on going from the neutral cluster to the cation. As Figure 2 shows, these effects are not large. Perhaps relevant to these spectral changes are the infrared spectra of the neutral cluster complexes of type $(OC)_9Co_3CCH{=}C(R)COOR'$.[30] In these, an apparent donor/acceptor-type interaction between the ester carbonyl oxygen and the cobalt atoms of the cluster results in significant band broadening and splitting (7–10 cm^{-1}).

In conclusion, the spectroscopic evidence that the positive charge which is generated at the α carbon atom upon heterolysis of the C–O bond of an $(OC)_9Co_3CCH(OH)R$ complex is distributed in large part to the cobalt atoms provides an adequate explanation of the chemistry of the $[(OC)_9Co_3CCHR]^+$ cations. They are poor carbon electrophiles and some nucleophiles, e.g., triphenylphosphine, react at cobalt, where most of the positive charge resides. Other chemical consequences of this great stabilization of positive charge generated at the α carbon atom of such complexes have been pointed out in previous papers of this series, i.e., the high Friedel–Crafts reactivity of benzylidynetricobalt nonacarbonyl complexes, $(OC)_9Co_3CAr$,[41] and the regioselectivity toward electrophiles of $(OC)_9Co_3CCH{=}CH_2$.[7]

Experimental Section

General Comments. Reactions were carried out in an apparatus which was assembled, dried under vacuum, and refilled with nitrogen. Solvents were rigorously dried before use and were transferred by syringe or cannula.

The progress of reactions usually was indicated by color changes and was routinely monitored by thin layer chromatography (TLC) using Eastman silica gel TLC sheet Type 6061 and hexane, hexane/dichloromethane (70/30), dichloromethane, or benzene as eluents. The intense colors of the compounds involved made further treatment unnecessary. Mixtures of reaction products in general were separated by column chromatography on silicic acid using hexane, hexane/dichloromethane (70/30), dichloromethane, or benzene as eluents. For separation of samples with widely differing retention times, a filtration chromatography technique was used. A slurry of silicic acid (15–30 cm^3) in the eluting solvent (50–100 mL) was prepared and poured into a filter funnel with a glass frit. Application of aspirator vacuum using a filter flask provided a packed bed of silicic acid for the filtration. The sample then was poured onto the filter pad and washed with hexane until the high R_f material had been completely eluted. Washing the filter bed with dichloromethane then eluted the lower R_f material. Samples recovered from chromatographic separations are reported in the order in which they eluted. Solid samples in general were further purified by sublimation (0.02–0.07 mmHg, 50–60 °C) or by recrystallization. The $(OC)_9Co_3C$-substituted carbonium ion salts as the solids or in solution are moisture sensitive and were prepared, handled, and brought into reaction under an inert atmosphere.

Infrared spectra were recorded using a Perkin-Elmer Model 337, 237B, 257, or 457A infrared spectrophotometer, ^1H NMR spectra using a Varian Associates T-60 spectrometer. Chemical shifts are given in δ units, parts per million downfield from internal tetramethylsilane. Tetramethylsilane, dichloromethane, and chloroform were used as internal standards.

^{13}C NMR spectra were obtained in the Fourier transform mode utilizing a modified Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 data system and are accurate to ±0.2 ppm. The field was locked using the ^{19}F signal of hexafluorobenzene contained in a capillary inside the sample tube. Satisfactory proton-decoupled spectra of approximately 1 M solutions were obtained in about 2000 pulses using a pulse width of 8 μs (corresponding to a nutation angle of about 30°), a data acquisition time of 0.41 s, and 0.80 between pulses. Proton noise decoupling was achieved using a decoupling frequency corresponding to 3.39 ppm upfield from the benzene proton resonance and a decoupling bandwidth of 1200 Hz. Off-resonance decoupling was achieved by irradiating in the CW mode at a frequency corresponding to 8.28 ppm upfield from the benzene proton resonance. A greater number of pulses was required to obtain proton-coupled spectra. The field positions of the lines were computer generated or calculated by measuring the distances between lines and using the plotting parameters. All the spectra of the alcohols are referenced to internal $CDCl_3$ and reported in parts per million downfield from tetramethylsilane. The spectra obtained in concentrated sulfuric acid are referenced to external tetramethylsilane through the ^{19}F lock signal. Assignments of the observed resonances were made on the basis of standard ^{13}C NMR correlations[14a,28] and were completely straightforward since relatively few carbon atoms are present in these complexes and since they are all of radically different character.

Starting Materials. The preparation of the alcohols required for this study has been described in a previous paper of this series.[5] The alcohol $(OC)_9Co_3CCH(OH)C_9H_{19}\text{-}n$ is a new compound. Its preparation, as well as that of its precursors, is described in the "New Compounds" section. Dicobalt octacarbonyl was purchased from Strem Chemical Co., and hexafluorophosphoric acid (65% by weight aqueous solution) from Matheson Coleman and Bell. Technical grade propionic anhydride was distilled prior to use and stored in sealed bottles under nitrogen.

Silicic acid for chromatography (Silicar CC7, pH 7, "Special for Chromatography") was obtained from Mallinckrodt.

Preparation of $(OC)_9Co_3C$-Substituted Carbonium Ion Hexafluorophosphates. The standard apparatus used consisted of a 200-mL, single-necked, round-bottomed flask which was modified by the addition of a second 24/40 standard taper joint at ca. 45° to the original joint. The flask was further modified by attachment of a straight, 30-mm glass tube with a coarse glass frit which was tapered below the frit to a 19/38 standard taper joint. This tube was collinear with the original neck of the flask as shown in Figure 7. When in use, this apparatus was equipped with a nitrogen inlet, a glass stopper, and, below the frit, a 100-mL, three-necked, round-bottomed flask which was equipped with a nitrogen inlet and a glass stopper. A magnetic stir bar was always placed inside the reaction (filter) flask. A powerful horseshoe magnet mounted alongside the reaction flask could be used to stir the solution. When solutions were present in the reaction flask, it was necessary to force nitrogen upward through the frit in order to prevent the solution from filtering. When it was necessary to filter the solution, the source of nitrogen to the bottom flask was opened to a vent and the nitrogen source over the solution was prevented from venting.

In the $[(OC)_9Co_3CCHR]^+[PF_6]^-$ preparations the standard apparatus was charged with about 2 mmol of the appropriate $(OC)_9Co_3CCH(OH)R$ complex, 50 mL of benzene, and 3-4 mL of propionic anhydride. The resulting mixture was stirred for 5-10 min to effect solution and then was treated with about 0.5 mL of 65% aqueous hexafluorophosphoric acid (ca. 4 mmol of "HPF_6" and 16 mmol of H_2O). The initially purple-red solution immediately began to deposit a black precipitate. After about 30 min precipitation was complete and the mixture was filtered. The black solid which remained on the frit was washed with dry benzene until the washings were colorless; usually one or two 10-mL portions were required. The filtrate was discarded and the reaction flask at the filter tube end was capped with a 50-mL, round-bottomed flask. In subsequent reactions the $[(OC)_9Co_3CCHR]^+[PF_6]^-$ thus prepared either was treated with the nucleophilic substrate directly or was slurried in dry benzene prior to reaction.

Samples of the $(OC)_9Co_3C$-substituted carbonium ion hexafluorophosphates were prepared for analysis in the following manner. Upon isolation of the $[(OC)_9Co_3CCHR]^+[PF_6]^-$ as described above it was dried under vacuum for 1 day. The vacuum was broken to nitrogen and the sample shaken into a small tube which was sealed under partial vacuum. The samples isolated in this manner were of very good purity. C/H analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and cobalt and fluorine analyses by Alfred Bernhardt.

$[(OC)_9Co_3CCH_2]^+[PF_6]^-$. Anal. Calcd for $C_{11}H_2O_9F_6PCo_3$: C, 22.02; H, 0.34; F, 19.00; Co, 29.47. Found: C, 21.97; H, 0.42; F, 19.45; Co, 30.07.

$[(OC)_9Co_3CCHCH_3]^+[PF_6]^-$. Anal. Calcd for $C_{12}H_4O_9F_6PCo_3$: C, 23.48; H, 0.66; F, 18.57; Co, 28.80. Found: C, 23.45; H, 0.74; F, 18.79; Co, 29.39.

$[(OC)_9Co_3CCHC_6H_5]^+[PF_6]^-$. Anal. Calcd for $C_{17}H_6O_9F_6PCo_3$: C, 30.21; H, 0.89. Found: C, 30.28; H, 0.99.

Reactions of $(OC)_9Co_3C$-Substituted Carbonium Ion Hexafluorophosphates. A few examples are described in detail to illustrate the procedures used. Product yields are given in Table I. For product characterization and analyses, see Table VIII.

a. Reaction of $[(OC)_9Co_3CCH_2]^+[PF_6]^-$ with Ethanol. The carbonium ion salt was prepared from 0.77 g (1.63 mmol) of $(OC)_9Co_3CCH_2OH$ in the standard manner. The resulting black solid was treated with 20 mL of absolute ethanol. An intensely red-purple solution was formed immediately. After 5 min, the mixture was poured into 250 mL of cold, saturated aqueous sodium bicarbonate solution. The organic layer was separated, dried, and evaporated under reduced pressure. The crude red oil which remained was diluted with hexane and filtered through a bed of neutral alumina (Woelm grade IV). The filtrate was evaporated and the residue was sublimed to give 0.62 g (76%) of purple solid identified as $(OC)_9Co_3CCH_2OEt$.

b. Reaction of $[(OC)_9Co_3CCHCH_3]^+[PF_6]^-$ with Aniline. The carbonium ion salt was prepared from 0.94 g (1.93 mmol) of $CH_3CH(OH)CCo_3(CO)_9$ in the standard manner. The resulting black solid was slurried in 50 mL of dry benzene and then was treated with 0.5 mL (0.55 g, 5.9 mmol) of freshly distilled aniline. The mixture was stirred for 10 min and then worked up as in (a). The resulting brown solid was dissolved in 70/30 hexane/dichloromethane and filtered through a bed of neutral alumina. The solvent was removed from the filtrate and the resulting solid dried under vacuum. Recrystallization from pentane afforded 0.79 g (73%) of $(OC)_9Co_3CCH(NHPh)CH_3$, a compound which is unstable in air and prone to decomposition on storage at room temperature.

c. Reaction of $[(OC)_9Co_3CCHCH_3]^+[PF_6]^-$ with *N,N*-Dimethylaniline. The carbonium ion salt was prepared from 0.75 g (1.77 mmol) of $(OC)_9Co_3CCH(OH)CH_3$ in the standard manner. The black solid was slurried in 50 mL of benzene and then was treated with 0.54 g (4.5 mmol) of *N,N*-dimethylaniline. After a reaction time of 1 h, normal workup gave crude product which was purified by filtration chromatography through neutral silicic acid. The resulting red-purple solid was recrystallized from pentane to give 0.49 g (68%) of purple solid, mp 144-146 °C, identified as $(OC)_9Co_3CCH{=}CH_2$ by comparison of its IR and ^1H NMR spectra with those of an authentic sample, mp 147-149 °C dec.[7]

d. Reaction of $[(OC)_9Co_3CCHC_6H_5]^+[PF_6]^-$ with Tetraallyltin. The carbonium ion salt was prepared from 1.06 g (1.94 mmol) of $(OC)_9Co_3CCH(OH)Ph$ in the standard manner. The resulting black solid was dissolved in a mixture of 50 mL of benzene and 10 mL of nitromethane (purified[42] and twice distilled). To the resulting brown solution was added 1.39 g (4.9 mmol) of tetraallyltin during the course of 10 min. A purple solution resulted. Normal workup was followed by filtration chromatography through neutral silicic acid which afforded a single product. The crude material was sublimed to give 0.84 g (76%) of purple solid $(OC)_9Co_3CCH(CH_2CH{=}CH_2)Ph$.

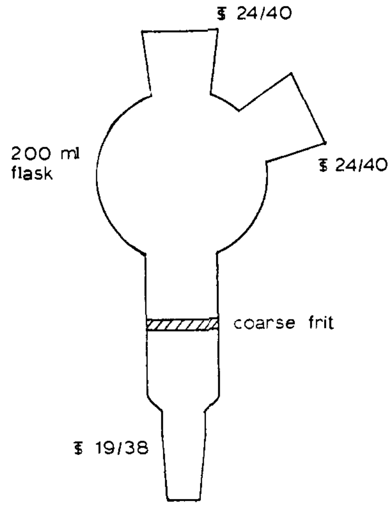


Figure 7. Apparatus for preparation of $(OC)_9Co_3C$-substituted carbonium ions.

e. Reaction of $[(OC)_9Co_3CCHC_6H_5]^+[PF_6]^-$ with Pyrrole. The carbonium ion salt was prepared from 1.19 g (2.18 mmol) of $(OC)_9Co_3CCH(OH)Ph$ in the usual manner. The resulting black solid was dissolved in a mixture of 50 mL of benzene and 20 mL of nitromethane, and the resulting brown solution was treated with 1.04 g (14.9 mmol) of pyrrole. After a 5-min reaction time, standard workup gave a crude solid which was chromatographed on neutral silicic acid (70/30 hexane/dichloromethane eluent). The single major fraction was isolated and recrystallized from pentane to give 0.58 g (44%) of purple solid. Alkylation of the pyrrole ring in the 2 position was assumed since this is the preferred position of electrophilic attack.[43]

Reaction of 2-Hydroxypropylidynetricobalt Nonacarbonyl with Triethylsilane and Trifluoroacetic Acid. A 100-mL, three-necked flask which was equipped with a nitrogen inlet tube, a reflux condenser, and a magnetic stir bar was charged with 1.05 g (2.16 mmol) of $(OC)_9Co_3CCH(OH)CH_3$, 50 mL of dry tetrahydrofuran, 0.69 g of triethylsilane, and 0.65 g (5.73 mmol) of trifluoroacetic acid. The resulting solution was stirred and heated at reflux for 4 h. Subsequently it was cooled and worked up in the standard manner. The purple solid which was obtained was dissolved in hexane and filtered through a bed of silicic acid. Evaporation of the filtrate gave a solid which was sublimed to give 0.73 g (72%) of purple $(OC)_9Co_3CCH_2CH_3$, mp 192-194 °C, which was identified by comparison of its IR and NMR spectra with those of an authentic sample, mp 190-192 °C.[7]

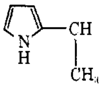
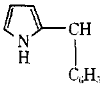
A reaction in which $[(OC)_9Co_3CCHC_6H_5]^+[PF_6]^-$ from 1.94 mmol of the respective alcohol in 50 mL of tetrahydrofuran (partial solution) was treated with 3.22 mmol of triethylsilane at room temperature for 90 min gave (usual workup) only 0.14 g (7%) of $PhCH_2CCo_3(CO)_9$, mp 62-64 °C.

Reaction of $[(OC)_9Co_3CCHC_6H_5]^+[PF_6]^-$ with Triphenylphosphine. The carbonium ion salt was prepared from 1.09 g (1.98 mmol) of the respective alcohol in the usual manner. The black solid was partially dissolved in 50 mL of dry tetrahydrofuran. To the resulting brown mixture was added 1.22 g (4.7 mmol) of triphenylphosphine. The solution immediately turned greenish-black and vigorous frothing ensued. No organocobalt products could be isolated.

A similar reaction in which 2.02 mmol of this carbonium ion salt dissolved in a mixture of 50 mL of benzene and 20 mL of nitromethane was treated with 2.1 mmol of triphenylphosphine resulted in a rapid color change to green, indicative of decomposition. Standard workup after 5 min failed to give isolable amounts of organocobalt products.

A reaction of 1.95 mmol of this carbonium ion salt (benzene slurry) with 5 mL of acetonitrile resulted in complete decomposition within 5 min. No organocobalt cluster compounds could be detected by TLC.

Table VIII. Characterization of New Compounds Prepared in This Study

R in $RCCo_3(CO)_9$[a]	color	anal. found (calcd), % C	H	N	NMR spectrum, δ ppm[b]
CH_3OCH_2	purple	29.64 (29.66)	1.06 (1.04)		3.59 (s, CH_3) 4.98 (s, CH_2)
$C_2H_5OCH_2$	purple	31.13 (31.23)	1.44 (1.41)		1.28 (t, J = 7 Hz, CH_3) 3.75 (q, CH_2 of Et) 5.04 (s, CH_2CCo_3)
$C_6H_5NHCH_2$	brown	37.38 (37.33)	1.53 (1.47)	2.58 (2.56)	4.18 (m, NH) 5.04 (d, J = 6 Hz, CH_2) 6.75, 7.23 (m, C_6H_5)[c]
p-$(CH_3)_2NC_6H_4CH_2$	brown	39.90 (39.68)	2.25 (2.10)		2.90 (s, CH_3) 4.63 (s, CH_2) 6.55, 7.03 (C_6H_4)
CH_3OCHCH_3	purple	31.24 (31.23)	1.42 (1.41)		1.63 (d, J = 7 Hz, CH_3) 3.53 (s, OCH_3), 4.74 (q, CH)
$C_2H_5OCHCH_3$	purple	32.89 (32.71)	1.85 (1.76)		1.23 (t, J = 9 Hz, CH_3 of Et) 1.69 (d, J = 7 Hz, CH_3) 3.74 (q, CH_2 of Et) 4.90 (q, CH)
$C_6H_5SCHCH_3$	brown	37.22 (37.40)	1.59 (1.57)		1.79 (d, J = 7 Hz, CH_3) 5.13 (q, CH) 7.38 (m, C_6H_5)
$C_6H_5NHCHCH_3$	brown	38.58 (38.53)	1.91 (1.80)	2.52 (2.50)	1.75 (d, J = 7 Hz, CH_3) 3.64 (d, J = 9 Hz, NH) 5.28 (m, CH) 6.63, 7.20 (m, C_6H_5)
$CH_2{=}CHCH_2CHCH_3$[e]	purple	35.38 (35.33)	1.88 (1.78)		1.54 (d, J = 7 Hz, CH_3) 1.93-3.03 (m, CH_2) 3.17-3.82 (m, CH) 4.85-5.38 (m, 2 vinyl H) 5.53-6.29 (m, 1 vinyl H)
	brown	35.97 (35.92)	1.69 (1.51)	2.66 (2.62)	1.86 (d, J = 7 Hz, CH_3) 4.76 (q, CH) 5.88-6.09 (m, 2 pyrrole H) 6.40-6.69 (m, 1 pyrrole H) 7.75 (broad, NH)
$CH_3OCHC_6H_5$	purple	38.46 (38.47)	1.66 (1.61)		3.48 (s, OCH_3) 5.58 (s, CH) 7.37 (m, C_6H_5)
$C_2H_5OCHC_6H_5$	purple	39.64 (39.61)	1.92 (1.93)		1.27 (t, J = 8 Hz, CH_3) 3.57 (q, CH_2) 5.63 (s, CH), 7.34 (m, C_6H_5)
$C_6H_5SCHC_6H_5$	brown	43.07 (43.15)	1.89 (1.73)		5.99 (s, CH) 7.23 (m, C_6H_5)
$C_6H_5NHCHC_6H_5$	black	44.43 (44.33)	2.08 (1.94)	2.24 (2.25)	4.20 (d, J = 6 Hz, NH) 5.79 (d, J = 6 Hz, CH) 6.86 (m, C_6H_5)
$CH_2{=}CHCH_2CHC_6H_5$[f]	purple	41.76 (41.99)	2.18 (1.94)		2.77-3.16 (m, CH_2) 4.37-5.78 (m, CH + $CH_2{=}CH$) 7.28 (s, C_6H_5)
p-$(CH_3)_2NC_6H_4CHC_6H_5$	brown	46.10 (46.11)	2.50 (2.48)	2.15 (2.15)	2.85 (s, CH_3) 5.62 (s, CH) 6.84 (m, C_6H_4 + C_6H_5)
	purple	42.35 (42.24)	1.81 (1.69)	2.42 (2.35)	5.70 (s, CH) 5.86-6.57, 6.94-7.68 (C_6H_5 + pyrrole) 7.85 (broad, NH)
n-$C_9H_{19}C{=}O$[g]	brown oil	41.50 (40.29)	3.70 (3.22)		0.54-1.32 (m, alkyl) 2.87 (t, J = 6 Hz, $CH_2C(O)$)[d]
n-$C_9H_{19}CH(OH)$	purple	39.67 (40.15)	3.90 (3.55)		0.80-2.00 (m, alkyl) 2.25 (d, J = 5 Hz, OH) 5.09 (m, CH)
n-$C_{10}H_{21}$	purple	41.19 (41.26)	3.66 (3.64)		0.5-2.4 (m, alkyl) 3.70 (t, J = 8 Hz, CH_2CCo_3)[c]
n-$C_{10}H_{21}OC(O)$[h]	red oil				0.6-2.0 (m, alkyl) 4.30 (t, J = 7 Hz, OCH_2)[c]
$(C_6H_5)_2CH$	black	45.55 (45.43)	1.95 (1.82)		5.84 (s, CH) 7.17-7.83 (m, C_6H_5)[c]
p-$C_2H_5OC(O)C_6H_4$[i]	black	38.52 (38.67)	1.59 (1.54)		1.37 (t, J = 8 Hz, CH_3) 4.38 (q, CH_2), 7.43, 7.59, 7.91, 8.09 (AA′BB′, C_6H_4)[c]

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[a] For melting points and percent yields, see Table I. [b] In CCl_4 unless otherwise specified. [c] In $CDCl_3$. [d] In benzene. [e] IR (CCl_4): $\nu(C{=}C)$ 1640 cm^{-1}. [f] IR (CCl_4): $\nu(C{=}C)$ 1641 cm^{-1}. [g] IR (CCl_4): $\nu(C{=}C)$ 1638 cm^{-1}. [h] IR (CCl_4): $\nu(C{=}C)$ 1676 cm^{-1}. [i] IR (CCl_4): $\nu(C{=}C)$ 1705 cm^{-1}.

Preparation of New Alkylidynetricobalt Nonacarbonyl Complexes. During the course of these studies a number of new $RCCo_3(CO)_9$ complexes were prepared, mainly for use in the spectroscopic studies.

a. (Nonacarbonyltricobalt)carbon Complexes Containing C_{10} Substituents. 1,1,1-Trichloro-2-hydroxyundecane was prepared by the method of Taguchi et al.[44] in 62% yield. It was isolated as a pale yellow liquid, bp 87–95 °C (0.004 mmHg). Its oxidation with chromium trioxide in glacial acetic acid gave the ketone n-$C_9H_{19}C(O)CCl_3$, bp 76–82 °C (0.01 mmHg), in 68% yield. Anal. Calcd for $C_{11}H_{19}OCl_3$: C, 48.28; H, 7.01; Cl, 38.86. Found: C, 48.23; H, 7.27; Cl, 38.62. ν(C=O) (CCl_4): 1757 cm^{-1}.

The reaction of n-$C_9H_{19}C(O)CCl_3$ (29.2 mmol) with dicobalt octacarbonyl (52.6 mmol) in 250 mL of THF under nitrogen at room temperature[46] gave $(OC)_9Co_3CC(O)C_9H_{19}$-n, a brown oil which was purified by column chromatography (silicic acid/benzene), in 72% yield. Reduction of this ketone with triethylsilane[7] afforded the alcohol $(OC)_9Co_3CCH(OH)C_9H_{19}$-$n$ as a waxy solid, mp 46.5–47.5 °C, in 58% yield. This product was purified by column chromatography (Silicar CC-7/hexane) and recrystallization from pentane. The reduction of the ketone with Et_3SiH/CF_3COOH[7] gave $(OC)_9Co_3CC_{10}H_{21}$-n, a solid, mp 30–31 °C, in 88% yield after purification by column chromatography (silicic acid/hexane) and recrystallization from hexane.

b. *n*-Decyl Ester of Carboxymethylidynetricobalt Nonacarbonyl. This ester was prepared by adding a solution of 10 mmol of $(OC)_9Co_3CCO_2Et$ in concentrated sulfuric acid (30 mL) into ice-cold 1-decanol using the procedure described in a previous paper of this series.[3] The product was purified by column chromatography (silicic acid/1:3 dichloromethane-hexane) and isolated in 57% yield as a red oil. IR (CCl_4): ν(C=O) 1682 sh, 1676 s. NMR ($CDCl_3$): δ 0.6–2.0 (m, 19 H) and 4.30 ppm (t, J = 7 Hz, 2 H).

c. 2,2-Diphenylethylidynetricobalt Nonacarbonyl, $(OC)_9Co_3CCH(C_6H_5)_2$. The reaction of 32.5 mmol (9.33 g) of 2,2-diphenyl-1,1,1-trichloroethane with 58.5 mmol of dicobalt octacarbonyl in 300 mL of THF at 50 °C for 48 h[46] gave the title compound as black nuggets, mp 159–161 °C, in 16% yield. The product was purified by filtration chromatography (silicic acid) and recrystallization from dichloromethane/hexane.

Attempted hydride abstraction from $(OC)_9Co_3CCH(C_6H_5)_2$ to give the $[(OC)_9Co_3CC(C_6H_5)_2]^+$ cation using $Ph_3C^+PF_6^-$ in propionic anhydride at room temperature or in nitromethane/propionic anhydride was unsuccessful. The starting complex was recovered in each case in greater than 85% yield.

d. *p*-Carboethoxybenzylidynetricobalt Nonacarbonyl, $(OC)_9Co_3CC_6H_4CO_2Et$-*p*. The reaction of 22.79 g (85.5 mmol) of ethyl p-trichloromethylbenzoate and 152 mmol of dicobalt octacarbonyl in 800 mL of THF at 45 °C using the procedure of ref 46 gave, after purification by filtration chromatography (neutral alumina/dichloromethane) and recrystallization from hexane, 11.49 g (19%) of the title compound, black needles, mp 108–110 °C. Attempted conversion to the acylium ion salt by treatment with 65% aqueous hexafluorophosphoric acid in propionic anhydride was unsuccessful, and the starting cobalt complex was recovered in 78% yield.

Preparation of Samples for NMR Study. The NMR tube was charged with the dry solid $(OC)_9Co_3C$-substituted alcohol, fitted with a rubber septum, and then evacuated for 10 min via a syringe needle through the septum. The vacuum was broken to dry nitrogen and the septum was removed with a heavy flow of nitrogen through the syringe needle. Sulfuric acid (or trifluoroacetic acid) was added to fill the tube to a depth of about 1.5 times that originally occupied by the solid sample. The mixture was shaken manually and additional acid was added until a homogeneous, brown solution resulted. The septum was removed and any lock or reference samples (sealed in glass capillaries) were added, again with a brisk nitrogen flow through the syringe needle. For those samples used for ^{13}C NMR spectra it was found necessary to fill the tube at least ¾ full, and to place the lower vortex plug near the surface in order to prevent vortexing in the sample. Evidently some slow decomposition was taking place and the evolved carbon monoxide forces the sulfuric acid solution above the vortex plug and allows vortexing to occur.

It should be noted that the $(OC)_9Co_3C$-substituted carbonium ions are considerably more stable in concentrated sulfuric acid than are the analogous ferrocenylcarbonium ions, III. The former could be dissolved in commercial concentrated sulfuric acid at room temperature and there was no problem in obtaining ^{13}C FT NMR spectra. In contrast, the ferrocenyl carbonium ions decomposed immediately and completely when the ferrocenyl alcohols were dissolved in commercial concentrated sulfuric acid. Only in cold, degassed sulfuric acid could usable solutions be obtained.

Characterization of New Compounds. Table VIII lists the new compounds prepared during the course of this study, together with their analyses and ^1H NMR spectra. Melting points are given in Table I. The presence of the $CCo_3(CO)_9$ cluster substituent in a molecule is indicated immediately by its infrared spectrum: four bands at about 2100 (weak), 2050 (strong to very strong), 2040 (strong), and 2020 (medium) cm^{-1} are present in the terminal carbonyl region. The positions of these bands vary only very little, if at all, when the apical carbon atom substituents are changed.

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References and Notes

(1) Part 27: Seyferth, D.; Merola, J. S.; Berry, D. H., *Z. Anorg. Allg. Chem.*, in press.

(2) Preliminary communications: (a) Seyferth, D.; Williams, G. H.; Hallgren, J. E., *J. Am. Chem. Soc.* **1973**, *95*, 266. (b) Seyferth, D.; Williams, G. H.; Traficante, D. D. *Ibid.* **1974**, *96*, 604. (c) Seyferth, D.; Eschbach, C. S.; Williams, G. H.; Hung, P. L. K.; Cheng, Y.-M. *J. Organomet. Chem.* **1974**, *78*, C13. (d) Seyferth, D.; Eschbach, C. S.; Nestle, M. O., *Ibid.* **1975**, *97*, C11.

(3) Seyferth, D.; Hallgren, J. E.; Eschbach, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 1730.

(4) (a) Seyferth, D.; Williams, G. H. *J. Organomet. Chem.* **1972**, *38*, C11. (b) Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, *16*, 758.

(5) Seyferth, D.; Williams, G. H.; Hung, P. L. K.; Hallgren, J. E. *J. Organomet. Chem.* **1974**, *71*, 97.

(6) Kursanov, D. N.; Loim, N. M., *Synthesis* **1974**, 633. See, however, Carey, F. A.; Tremper, H. A. *J. Org. Chem.* **1971**, *36*, 758, in which the reaction of trialkylcarbinols with silicon hydrides in the presence of trifluoroacetic acid to give tertiary alkyl carbonium ions is described. It was determined that in these reactions it is the olefin obtained by dehydration of the carbinol which is the species which leads to the cation.

(7) Seyferth, D.; Eschbach, C. S.; Williams, G. H.; Hung, P. L. K. *J. Organomet. Chem.* **1977**, *134*, 67

(8) Rosenblum, M. "Chemistry of the Iron Group Metallocenes", Wiley-Interscience: New York, 1965; Chapters 4 and 5.

(9) Olah, G. A.; Baker, E. B.; Evans, J. C.; Tolgyesi, W. S.; McIntyre, J. S.; Bastien, I. J. *J. Am. Chem. Soc.* **1964**, *86*, 1360.

(10) This is strictly an empirical correlation. The proton chemical shift is influenced by a number of factors other than the charge density at the carbon atom to which the proton in question is attached, so that this correlation has a tenuous theoretical basis.

(11) Watts, W. E. *J. Organomet. Chem. Lib.* **1979**, *7*, 399.

(12) Cerichelli, G.; Floris, B.; Ortaggi, G. *J. Organomet. Chem.* **1974**, *78*, 241.

(13) Acampora, M.; Ceccon, A.; Dal Farra, M.; Giacometti, G. *J. Chem. Soc., Chem. Commun.* **1975**, 871.

(14) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy", Academic Press: New York, 1972; Chapter 6. (b) Olah, G. A. *Science* **1970**, *168*, 1298. (c) Olah, G. A.; Westerman, P. W.; Nishimura, J. *J. Am. Chem. Soc.* **1974**, *96*, 3548.

(15) Williams, G. W.; Traficante, D. D.; Seyferth, D. *J. Organomet. Chem.* **1973**, *60*, C53.

(16) Cerichelli, G.; Floris, B.; Ortaggi, G. *J. Organomet. Chem.* **1974**, *78*, 241.

(17) Acampora, M.; Ceccon, A.; Dal Farra, M.; Giacometti, G.; Rigatti, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 483.

(18) Ceccon, A.; Gobbo, A.; Venzo, A. *J. Organomet. Chem.* **1978**, *162*, 311.

(19) Seyferth, D.; Merola, J. S.; Eschbach, C. S. *J. Am. Chem. Soc.* **1978**, *100*, 4124.

(20) Eschbach, C. S.; Reeves, P. C.; Seyferth, D. *J. Organomet. Chem.* **1976**, *104*, 363.

(21) E.g., Strausz, O. P.; DoMinh, T.; Fout, J. *J. Am. Chem. Soc.* **1968**, *90*, 1930. DoMinh, T.; Gunning, H. E.; Strausz, O. P. *Ibid.* **1967**, *89*, 6785.

(22) (a) Lauterbur, P. C. *J. Chem. Phys.* **1965**, *42*, 799. (b) Lowenstein, A.; Sporer, M. *Mol. Phys.* **1965**, *9*, 293.

(23) Aime, S.; Milone, L.; Valle, M. *Inorg. Chim. Acta* **1976**, *18*, 9.

(24) Kreiter, C. G.; Formaček, V. *Angew. Chem.* **1972**, *84*, 155.

(25) Köhler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* **1975**, *85*, C19.

(26) Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Müller, J.; Huttner, G.; Lorenz, H. *Angew. Chem.* **1973**, *85*, 618.

(27) Sutton, P. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 261.

(28) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135.

(29) Pályi, G.; Piacenti, F.; Markó, L. *Inorg. Chim. Acta Rev.* **1970**, *4*, 109.

(30) Pályi, G.; Váradi, G. *J. Organomet. Chem.* **1975**, *86*, 119.

(31) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(32) Abel, E. W. *Q. Rev., Chem. Soc.* **1963**, *17*, 133.

(33) Penfold, B. R.; Robinson, B. H., *Acc. Chem. Res.* **1973**, *6*, 73.

(34) Schmid, G. *Angew. Chem.*, **1978**, *90*, 417.

(35) Bond, A. H.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Watson, D. J. *Inorg. Chem.* **1977**, *16*, 410.

(36) Miller, D. C.; Brill, T. B. *Inorg. Chem.* **1978**, *17*, 240.
(37) (a) Schilling, B. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6274. (b) *Ibid.*, **1979**, *101*, 3456.
(38) Traylor, T. G.; Berwin, H. J.; Jerkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599.
(39) Deeming, A. J.; Hasso, S.; Underhill, M.; Canty, A. J.; Johnson, B. F. G.; Jackson, W. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Chem. Commun.* **1974**, 807.
(40) Bodner, G. M.; Storhoff, B. N.; Doddrell, D.; Todd, L. J. *Chem. Commun.* **1970**, 1530.
(41) Seyferth, D.; Williams, G. H.; Wehman, A. T.; Nestle, M. O. *J. Am. Chem. Soc.* **1975**, *97*, 2107.
(42) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis", Vol. 1; Wiley: New York, 1968; p 739.
(43) Jones, R. A.; Bean, G. P. "The Chemistry of Pyrroles", Academic Press: New York, 1977; Chapter 4.
(44) Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 3010.
(45) Bishop, D. C.; Meacock, S. C. R.; Williamson, W. R. N. *Chem. Commun.* **1966**, 670.
(46) Seyferth, D.; Hallgren, J. E.; Hung, P. L. K. *J. Organomet. Chem.* **1973**, *50*, 265.

Metal Clusters. 21.[1] Synthesis of Rhodium Phosphite Clusters

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Abstract: Reaction of η^3-C_3H_5Rh-1,5-cyclooctadiene with phosphites and phosphines has through the simple expedient of stoichiometry control yielded a series of quasi-four-coordinate and five-coordinate η^3-allylrhodium complexes, η^3-$C_3H_5RhL_2$ and η^3-$C_3H_5RhL_3$. All members of these two classes exhibited a fast hydrogen cleavage of the allylrhodium bond at 20 °C to form propene (initially) and rhodium hydrides. The cleavage reactions were always preceded or accompanied by ligand exchange so that the reactions typically yielded $HRhL_4$, H_3RhL_3, $\{HRhL_2\}_x$, and an unidentified hydride; the yield of the polynuclear $HRhL_2$ species was highest with the η^3-$C_3H_5RhL_2$ complexes. Fully identified were the polynuclear hydrides; $\{HRh[P(OCH_3)_3]_2\}_3$, $\{HRh[P(OC_2H_5)_3]_2\}_3$, and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. Stability of the phosphine analogues was substantially lower and rhodium metal was a pervasive and significant product in the $H_2 + \eta^3\text{-}C_3H_5Rh[PR_3]_n$ reactions. The polynuclear hydride complexes were very active catalyst precursors for olefin and acetylene hydrogenation reactions. Turnover rates for olefin hydrogenation were greater than ~two/s at 23 °C at olefin to polynuclear hydride ratios of 10 000:1. Because acetylenes competed far more effectively than olefins for coordination sites in the polynuclear hydrides, the catalyzed acetylene hydrogenation reactions, although much slower than olefin hydrogenation, yielded largely olefins. The dimer $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ was a catalyst precursor for arene hydrogenations: the rates were low, the hydrogen addition mode was nonselective (large amounts of *trans*-dimethylcyclohexanes were produced from xylenes), and in D_2-arene reactions there was substantial H-D exchange. In the reactions of $\{HRh[P(OR)_3]_2\}_n$ with hydrogen, there was no detectable cluster fragmentation. The intermediate in the case of the dimer was identified as $H[(i\text{-}C_3H_7O)_3P]_2RhH_3Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ and as $H_5Rh_3[P(OCH_3)_3]_6$ for the trimer. Both these hydrogen adducts were fluxional molecules; hydride ligand migration occurred in each adduct in two mechanistically distinct processes. In the catalytic reaction, the hydrogen addition step and the olefin addition step appear to be largely centered on adjacent rhodium sites.

Introduction

Allylcobalt phosphite and phosphine complexes, η^3-$C_3H_5Co[P{<}]_3$, are unique catalysts for the hydrogenation of aromatic hydrocarbons: rates run as high as 1 turnover/min at 20 °C and 1-3 atm and there is complete stereoselectivity with an all cis hydrogen addition.[2,3] However, these complexes all suffer hydrogenolysis of the allyl-cobalt bond.[3] We initiated a general study of allylmetal complexes to establish catalytic scope and the factors that promote the hydrogen cleavage reaction. Generally, we have found that the rates for catalytic hydrogenations and for hydrogenolysis of the allyl group correlate directly in these allylmetal complexes.[3,4] We describe here the synthesis and chemistry of a group of allylrhodium phosphite and phosphine complexes—a study that has led to the isolation of a novel class of coordinately unsaturated and very reactive clusters.[5,6]

Experimental Section

Reagents and Solvents. All operations with air-sensitive materials were effected in a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri Train under an argon or nitrogen atmosphere, or in a conventional vacuum system. Rhodium trichloride hydrate was obtained from Alfa Chemicals and Matthey Bishop, Inc. Trimethyl phosphite, triethyl phosphite, triphenylphosphine, *o*-xylene, *p*-xylene, and 1,5-cyclooctadiene were purchased from Aldrich Chemical Co., Inc.; triisopropyl phosphite and trimethylphosphine from Strem Chemicals; 1-hexene from Phillips Petroleum Co.; trifluoroacetic acid from Eastman Kodak Co.; allylbenzene and *trans*-propenylbenzene from Chemical Samples. Prepurified hydrogen (99.95%), deuterium, CP (99.5% (atom)), ethylene CP, ethane CP, propylene CP, and propane were purchased from Matheson & Co.

Rhodium trichloride hydrate, absolute ethanol, and the gases were used as obtained. The 1,5-cyclooctadiene was purified by passing it down an alumina column and degassing it prior to use. Acetonitrile, 1-hexene, and *trans*-propenylbenzene were stored over calcium hydride for at least 1 week and were vacuum distilled prior to use. Allylbenzene was stored over lithium aluminum hydride and vacuum distilled prior to use. The trifluoroacetic acid was vacuum distilled just before using it. Reagent grade *n*-pentane, benzene, toluene, diethyl ether, tetrahydrofuran, and the xylenes were vacuum distilled from sodium benzophenone ketyl. The trialkyl phosphites were stored over sodium for a minimum of 2 weeks (with periodic degassing) and distilled prior to their usage. Methanol was dried over magnesium methoxide and vacuum distilled prior to use. Allylmagnesium bromide was prepared by standard methods[7] and was isolated as a solid of ~80% activity.

Physical Measurements. ^1H NMR spectra were recorded at 60 MHz with a Varian Associates A-60A, and at 90 MHz with either a Varian Associates EM-390 or a Bruker HX-90 (with a Digilab Fourier accessory). Chemical shifts were referenced to internal tetramethylsilane and are reported in parts per million with increasing field in the positive direction. Solution ^{31}P spectra were recorded on the Bruker HX-90 and chemical shifts were referenced to external H_3PO_4. All NMR spectra were of C_6D_6 solutions except where stated otherwise. Unsaturated hydrocarbons and products of hydrogenations

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