**Acknowledgment.** P.L.S. is indebted to the British Council for partial financial support.

**Registry No.** $Co_2(CO)_6(HC_2H)$, 12264-05-0; $Co_2(CO)_6(CH_3C_2CH_3)$, 12282-08-5; $Co_2(CO)_6(C_6H_5C_2C_6H_5)$, 14515-69-6; $Co_2(CO)_6(COOCH_3C_2COOCH_3)$, 37685-64-6; $Co_2(CO)_6(CF_3C_2CF_3)$, 12557-89-0; $Fe_2(CO)_6S_2$, 58500-79-1; $Co_2(CO)_6(n\text{-}C_3H_7C_2\text{-}n\text{-}C_3H_7)$, 34766-99-9; $Co_2(CO)_6(CH_2N(C_2H_5)_2C_2CH_2N(C_2H_5)_2)$, 61395-31-1; $Co_2(CO)_6(CH_3C_2C_6H_5)$, 53556-74-4; $Co_2(CO)_6(HC_2\text{-}t\text{-}C_4H_9)$, 56792-69-9; $Co_2(CO)_6(HC_2\text{-}i\text{-}C_5H_{11})$, 61395-32-2; $Co_2(CO)_6(HC_2C_6H_5)$, 12154-91-5; $Co_2(CO)_6(CH_2ClC_2CH_2Cl)$, 37685-62-4.

**Supplementary Material Available:** Normal-coordinate calculations on CO vibrators and tables of force and interaction constants of $Co_2(CO)_6(RC_2R')$ species and of $Fe_2(CO)_6S_2$ (5 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) G. Bor, *Chem. Ber.*, **96**, 2644 (1963).

(2) I. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).

(3) Y. Iwashita, A. Ishikawa, and M. Kainosho, *Spectrochim. Acta, Part A*, **27**, 271 (1971).

(4) Y. Iwashita, *Inorg. Chem.*, **9**, 1178 (1970).

(5) G. Bor, *Discuss. Faraday Soc.*, **47**, 65 (1969).

(6) G. Bor, *Inorg. Chim. Acta*, **3**, 169 (1969); *Chem. Commun.*, 696 (1969); A. R. Manning and J. K. Millen, *J. Chem. Soc. A*, 3352 (1970); R. J. Ziegler, J. M. Murtitch, S. E. Hayes, and W. M. Riesen, Jr., *Inorg. Chem.*, **11**, 720 (1972); G. Bor and G. Sbrignadello, *J. Chem. Soc., Dalton Trans.*, 440 (1974).

(7) G. Bor, *J. Organomet. Chem.*, **94**, 181 (1975).

(8) W. M. Scovell and T. G. Spiro, *Inorg. Chem.*, **13**, 303 (1974).

(9) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 556.

(10) S. F. A. Kettle, in preparation.

(11) G. Cetini, O. Gambino, P. L. Stanghellini, and G. A. Vaglio, *Inorg. Chem.*, **6**, 1225 (1967).

(12) T. G. Spiro, *Prog. Inorg. Chem.*, **11**, 1 (1970).

(13) E. Maslowsky, Jr., *Chem. Rev.*, **71**, 507 (1971).

(14) F. J. Farrell and T. G. Spiro, *Inorg. Chem.*, **10**, 1606 (1971).

(15) G. J. Kubas and T. G. Spiro, *Inorg. Chem.*, **12**, 1797 (1973).

(16) C. V. Berney, L. R. Cousins, and T. A. Miller, *Spectrochim. Acta*, **19**, 2019 (1963).

(17) R. S. Dickson and P. J. Frazer, *Adv. Organomet. Chem.*, **12**, 323 (1974), and references therein.

(18) J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *Chem. Ind. (London)*, 1137 (1960).

---

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

# Organocobalt Cluster Complexes. 21. Conversion of Halomethylidynetricobalt Nonacarbonyl Complexes to the Tricobaltcarbon Decacarbonyl Cation by the Action of Aluminum Halides. A New and Useful Route to α-Functional Alkylidynetricobalt Nonacarbonyl Complexes[1,2]

DIETMAR SEYFERTH,* GARY H. WILLIAMS, and CYNTHIA L. NIVERT

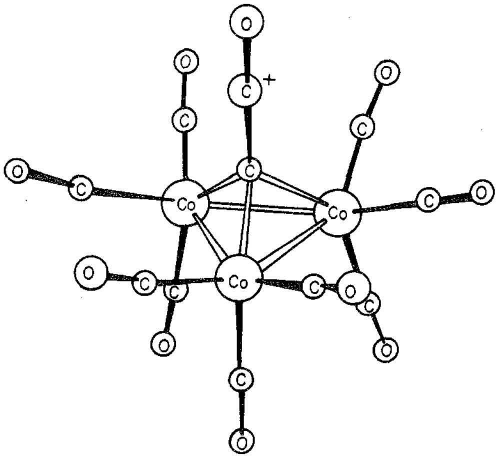
*Received December 1, 1976* AIC60861Q

The action of aluminum halides, $AlX_3$ (X = Cl, Br, I), on halomethylidynetricobalt nonacarbonyl complexes, $XCCo_3(CO)_9$ (X = Cl, Br), results in formation of the acylium haloaluminate salt $(OC)_9Co_3CCO^+[AlX_4{\cdot}AlX_3^-]$, even when the reaction is carried out under nitrogen. Addition of a diversity of nucleophiles (alcohols, phenols, amines, thiols, $R_4Sn$ compounds, reactive aromatics, silicon hydrides) to such reagents produces cluster complexes of type $YC(O)CCo_3(CO)_9$ with Y = RO, ArO, RR′N, RS, R, Ar, H) in moderate to good yields. The possible mechanism of this novel Co-to-C carbon monoxide transfer is discussed.

## Introduction

We have reported recently the preparation (eq 1) and chemistry of the hexafluorophosphate salt of the tricobaltcarbon decacarbonyl cation, I.[3] The reaction of this salt with a broad spectrum of nucleophiles provided access to many new functionally α-substituted alkylidynetricobalt nonacarbonyl complexes. We report here a new route to reagent I, the discovery of which, in contrast to that shown in eq 1, was entirely serendipitous.

$$(OC)_9Co_3CCO_2R + (EtCO)_2O + H^+PF_6^- \rightarrow (OC)_9Co_3CCO^+PF_6^- + EtCO_2R + EtCO_2H \qquad (1)$$



I

In 1970, Dolby and Robinson[4] described a new, general synthesis of benzylidynetricobalt nonacarbonyl complexes from chloro- or bromomethylidynetricobalt nonacarbonyl (eq 2).

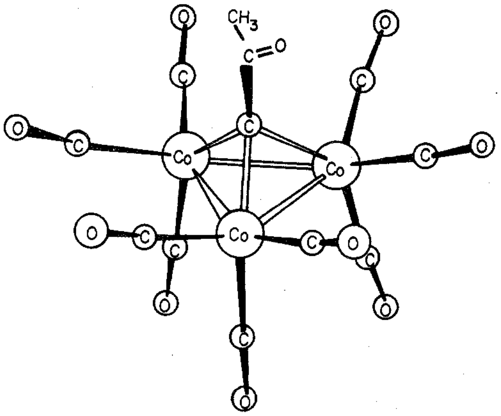
$$ClCCo_3(CO)_9 + ArH \xrightarrow{AlCl_3/CH_2Cl_2} ArCCo_3(CO)_9 \qquad (2)$$

At that time we were particularly interested in developing new routes to alkylidynetricobalt nonacarbonyls, $RCCo_3(CO)_9$ (R = alkyl), and the fact that the halomethylidynetricobalt nonacarbonyls were reactive Friedel–Crafts halides suggested to us a possible route to such compounds based on known organotin chemistry.

Tetramethyltin reacts with acyl chlorides in the presence of aluminum chloride as shown in eq 3.[5] It therefore might have been expected that the reaction of tetramethyltin with $ClCCo_3(CO)_9$ in the presence of aluminum chloride would give the methylated complex $CH_3CCo_3(CO)_9$. However, when this reaction was carried out in dichloromethane solution under a nitrogen atmosphere, the product which was isolated (in 26%

$$(CH_3)_4Sn + RC(O)Cl \xrightarrow{AlCl_3} RC(O)CH_3 + (CH_3)_3SnCl \qquad (3)$$

yield) was the acetyl derivative $CH_3C(O)CCo_3(CO)_9$, II. We had found tetramethyltin to react with $(OC)_9Co_3CCO^+PF_6^-$ to give this compound,[3] so it seemed reasonable to assume that in the aluminum chloride induced reaction the same cation was being formed with an $AlCl_4^-$ or $[AlCl_4{\cdot}nAlCl_3]^-$ counterion. This new reaction of $ClCCo_3(CO)_9$ seemed well worth examining in some detail. First, it represented a potentially useful route to new alkylidynetricobalt nonacarbonyl complexes. Second, if the $(OC)_9Co_3CCO^+$ ion was indeed being formed, a most intriguing transfer of a carbon monoxide ligand from a cobalt atom to the apical carbon atom of the cluster must necessarily be involved.



II

## Results and Discussion

Among the reactions of $(OC)_9Co_3CCO^+PF_6^-$ which proceeded particularly well were those with methanol and ethanol to give the respective $(OC)_9Co_3CCO_2R$ cluster esters. These nucleophilic substrates were used in a series of experiments designed to define the best conditions for the synthesis and preparative utilization of the $(OC)_9Co_3CCO^+[AlCl_4{\cdot}nAlCl_3]^-$ reagent (Table IV). In these initial studies it was found that at least 2, and preferably 3 or more, molar equiv of aluminum chloride was required. Also, the reaction of $ClCCo_3(CO)_9$ with 3 molar equiv of aluminum chloride in dichloromethane required 20–30 min of stirring at room temperature in order to go to completion. A large excess of aluminum chloride (e.g., 10 molar equiv) accelerated the formation of the $(OC)_9Co_3CCO^+$ reagent. A control reaction established that $ClCCo_3(CO)_9$ reacted only very slowly with ethanol in the absence of aluminum chloride. After such a solution had been stirred at room temperature under nitrogen for 15 days, the yield of $(OC)_9Co_3CCO_2Et$ was only 6%, and 78% of the starting material was recovered.

An indication of the extent of conversion of $ClCCo_3(CO)_9$ to the acylium ion is given by a change of the reaction mixture from its original purple color to yellow-brown. The rate of consumption of $ClCCo_3(CO)_9$ also can be followed by thin-layer chromatography (TLC). The final reaction mixture appears to be heterogeneous, but most of the $(OC)_9Co_3CCO^+$ reagent is in solution. Thus treatment of the reagent obtained by allowing $ClCCo_3(CO)_9$ and $AlCl_3$ to react in a 1:3 molar ratio in dichloromethane under nitrogen at room temperature for 30 min with methanol gave $(OC)_9Co_3CCO_2Me$ in 83% yield. The yield of this ester in a similar experiment in which the reaction mixture was filtered and methanol added to the filtrate was 67%. Furthermore, the $(OC)_9Co_3CCO^+$ reagent is quite stable at room temperature: a similar reaction mixture gave the methyl ester in 72% yield upon addition of methanol after it had been stirred under nitrogen for 73 h.

The chemistry of the $(OC)_9Co_3CCO^+$ ion had been delineated in our earlier study of the hexafluorophosphate salt.[3] The reactions of $(OC)_9Co_3CCO^+[AlCl_4{\cdot}nAlCl_3]^-$ with various nucleophiles gave very similar results and are shown in Table I. In these reactions 2–3 molar equiv of aluminum chloride was added to the chloromethylidynetricobalt nonacarbonyl in dichloromethane under nitrogen, the mixture was stirred for 20–30 min at room temperature, and then the nucleophile was added. The product yields in general ranged from 50 to 85%, based on the starting $ClCCo_3(CO)_9$. Several new functionally substituted cluster complexes were prepared in this manner. Reactions with alcohols gave the respective esters; reactions with phenols, the aryl esters; reactions with thiols, the thioesters; and reactions with ammonia and primary and secondary amines, the expected amides. Tetraorganotin compounds reacted to give acylmethylidynetricobalt nonacarbonyl complexes. The $(OC)_9Co_3CCO^+[AlCl_4{\cdot}nAlCl_3]^-$ reagent acylated reactive aromatic and heterocyclic substrates such as *N,N*-dimethylaniline, indole, pyrrole, *N*-methylpyrrole, and ferrocene. Of special interest was the reduction of the $(OC)_9Co_3CCO^+[AlCl_4{\cdot}nAlCl_3]^-$ complex by silicon hydrides to give the aldehyde $(OC)_9Co_3CCHO$. This reaction was one which $(OC)_9Co_3CCO^+PF_6^-$ did not undergo, except in the presence of aluminum chloride.[3] One may speculate that a reaction of a chloroaluminum hydride, rather than of a silicon hydride, with the cation is involved. The acylium ion chloroaluminate also may be formed from $(OC)_8(Ph_3P)Co_3CCl$; its reaction with methanol gave $(OC)_8(Ph_3P)Co_3CCO_2CH_3$.

Other Lewis acid systems were examined for their effectiveness in the $(OC)_9Co_3CCl$ to $(OC)_9Co_3CCO^+$ conversion (Table IV). The action of aluminum bromide on chloromethylidynetricobalt nonacarbonyl in a 4:1 ratio in dichloromethane for 2 min, followed by treatment of the reaction mixture with methanol, gave $(OC)_9Co_3CCO_2CH_3$ in 59% yield. The use of aluminum iodide in a similar reaction sequence gave this product in 70% yield.

Bromomethylidynetricobalt nonacarbonyl also was examined for its utility in this reaction. Treatment with aluminum chloride in a 3:1 ratio in dichloromethane at room temperature during 20 min, followed by reaction of the reagent formed with methanol, gave the expected methyl ester in 74% yield. The $(OC)_9Co_3CBr/AlBr_3$ reagent was given more detailed study and found to be quite effective, as the results in Table II show. The formation of the reagent $(OC)_9Co_3CCO^+[AlBr_4{\cdot}nAlBr_3]^-$ is best carried out in carbon disulfide. In this solvent a virtually instantaneous reaction precipitated the reagent. Addition of dichloromethane dissolved the precipitate; the nucleophilic substrate then was added to the solution. The product yields were somewhat less in the $AlBr_3$-induced reactions than in those carried out in the presence of aluminum chloride. It may be that the stronger Lewis acid, $AlBr_3$, also causes more decomposition of the cluster than does $AlCl_3$. In other experiments it was found that by using iodomethane as solvent or by carrying out the $ClCCo_3(CO)_9/AlCl_3$ reaction in dichloromethane in the presence of a large excess of iodomethane, a rapid conversion to the $(OC)_9Co_3CCO^+$ reagent was obtained, with excellent product yields upon addition of nucleophiles. Thus, an 80% yield of $(OC)_9Co_3CCO_2CH_3$ was realized after methanol was added to the reaction mixture 5 min after the original reactants had been mixed. Several other reactions were carried out using this $ClCCo_3(CO)_9/AlCl_3/CH_3I$ system; the results are given in Table III. Of the two possible modes of reaction of iodomethane in this mixture, $AlCl_3$-catalyzed reaction with $ClCCo_3(CO)_9$ to give $ICCo_3(CO)_9$ or simply exchange with $AlCl_3$ to give $AlI_3$, a more reactive Lewis acid, we favor the latter. This question, however, was not pursued.

Further experiments showed chloroform freed of its usual ethanol stabilizer can be used as a solvent for the 1:3 $(OC)_9Co_3CCl/AlBr_3$ reaction (68% yield of the methyl ester after reaction with methanol) and that dibromomethane also

**Table I.** Reactions of the $ClCCo_3(CO)_9/AlCl_3$ Reagent with Nucleophiles

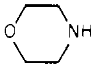
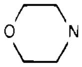
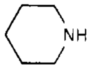
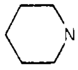
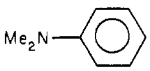
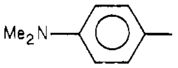
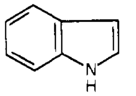
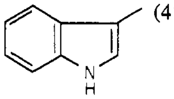
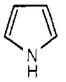
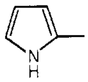
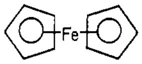
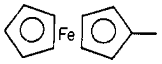
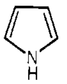
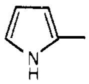
| Amt, mmol | | | |
|---|---|---|---|
| $ClCCo_3(CO)_9$ | $AlCl_3$ | Nucleophile (amt) | Product, R in $RC(O)CCo_3(CO)_9$ (% yield) |
| 2.2 | 6.1 | $CH_3OH$ (10 mL) | $CH_3O$ (83) |
| 2.5 | 6.1 | $C_2H_5OH$ (20 mL) | $C_2H_5O$ (78) |
| 2.1 | 5.4 | $Me_2CHOH$ (5 mL) | $Me_2CHO$ (78) |
| 2.2 | 6.2 | $Me_3COH$ (20 mL) | $Me_3CO$ (77) |
| 11.0 | 38.5 | $BrCH_2CH_2OH$ (50 mmol) | $BrCH_2CH_2O$ (74) |
| 2.2 | 7.7 | $CH_2{=}CHCH_2OH$ (73 mmol) | $CH_2{=}CHCH_2O$ (66) |
| 2.2 | 7.7 | $HC{\equiv}CCH_2OH$ (17 mmol) | $HC{\equiv}CCH_2O$ (62) |
| 2.2 | 7.7 | $CCl_3CH_2OH$ (10 mmol) | $CCl_3CH_2O$ (62) |
| 1.7 | 4.7 | $C_6H_5OH$ (93 mmol) | $C_6H_5O$ (66) |
| 2.2 | 7.7 | *p*-$CH_3OC_6H_4OH$ (5 mmol) | *p*-$CH_3OC_6H_5O$ (39) |
| 2.2 | 7.7 | *p*-$O_2NC_6H_4OH$ (20 mmol) | *p*-$O_2NC_6H_4O$ (30) |
| 2.2 | 7.7 | *p*-$MeC_6H_4OH$ (20 mmol) | *p*-$MeC_6H_4O$ (54) |
| 2.2 | 7.7 | *p*-$ClC_6H_4OH$ (20 mmol) | *p*-$ClC_6H_4O$ (38) |
| 2.2 | 7.7 | $Me_3CSH$ (18.5 mmol) | $Me_3CS$ (51) |
| 2.1 | 7.9 | $C_6H_5SH$ (3 mL) | $C_6H_5S$ (58) |
| 4.1 | 9.5 | $NH_3$ (large excess) | $H_2N$ (64) |
| 2.1 | 5.0 | $(CH_3)_2NH$ (large excess) | $(CH_3)_2N$ (55) |
| 2.1 | 7.8 | $Et_2NH$ (70 mmol) | $Et_2N$ (75) |
| 2.2 | 7.7 | $Me_3CNH_2$ (10 mmol) | $Me_3CNH$ (55) |
| 2.6 | 6.9 | $C_6H_5NH_2$ (3.5 mL) | $C_6H_5NH$ (76) |
| 2.2 | 7.7 |  (11.5 mmol) |  (64) |
| 2.2 | 7.7 |  (10 mmol) |  (50) |
| 2.3 | 6.3 | $H_2O$ (large excess) | HO (29) |
| 2.1 | 5.2 | $(CH_3)_4Sn$ (5 mL) | $CH_3$ (61) |
| 2.2 | 5.3 | $(C_2H_5)_4Sn$ (5 mL) | $C_2H_5$ (68) |
| 2.2 | 7.7 | $(n\text{-}C_4H_9)_4Sn$ (15 mmol) | *n*-$C_4H_9$ (34) |
| 2.0 | 6.0 | $(CH_2{=}CHCH_2)_4Sn$ (5.0 mmol) | $CH_2{=}CHCH_2$ (69) |
| 16.7 | 47.0 | $Et_3SiH$ (51.0 mmol) | H (68) |
| 2.3 | 5.9 | $Ph_3SiH$ (9.0 mmol) | H (40) |
| 2.2 | 6.2 |  (3 mL) |  (69) |
| 2.2 | 7.7 |  (5.0 mmol) |  (47) |
| 2.2 | 7.7 |  (5.0 mmol) |  (68) |
| 2.0 | 5.0 |  (5.4 mmol) |  (41) |

**Table II.** Reactions of the $BrCCo_3(CO)_9/AlBr_3$ Reagent with Nucleophiles

| Amt, mmol | | | |
|---|---|---|---|
| $BrCCo_3(CO)_9$ | $AlBr_3$ | Nucleophile[a] (amt) | Product, R in $RC(O)CCo_3(CO)_9$ (% yield) |
| 2.0 | 6.0 | $CH_3OH$ (5 mL) | MeO (68) |
| 2.0 | 2.0 | $CH_3OH$ (5 mL) | MeO (38)<br>(recovery of $BrCCo_3(CO)_9$ was 22%) |
| 3.0 | 9.0 | $C_2H_5OH$ (4 mL) | $C_2H_5O$ (66) |
| 2.0 | 6.0 | $CCl_3CH_2OH$ (1 mL, 10 mmol) | $CCl_3CH_2O$ (55) |
| 2.0 | 5.3 | $CH_2{=}CHCH_2OH$ (1 mL, 15 mmol) | $CH_2{=}CHCH_2O$ (53) |
| 2.0 | 6.0 | *p*-$CH_3C_6H_4SH$ (10 mmol) | *p*-$CH_3C_6H_4S$ (80) |
| 2.0 | 6.7 | $NH_3$ (large excess) | $H_2N$ (46) |
| 2.0 | 6.0 | $Et_2NH$ (1 mL, 20 mmol) | $Et_2N$ (60) |
| 2.0 | 6.0 | $Me_3CNH_2$ (10 mmol) | $Me_3CNH$ (58) |
| 2.0 | 6.0 |  (1 mL) |  (58) |
| 2.0 | 6.04 | $Me_2NC_6H_5$ (1 mL) | *p*-$Me_2NC_6H_4$- (42) |

[a] The reagent mixture should be chilled to 0 °C before the nucleophile is added.

can serve as a solvent in this reaction.

Subsequent work has provided some information concerning the constitution of the $(OC)_9Co_3CCO^+[AlX_4{\cdot}nAlX_3]^-$ reagents. The $AlCl_3$-derived reagent may be precipitated from its dichloromethane solution by adding carbon disulfide. The brown powdery crude solid which was isolated approximated the

**Table III.** Reactions of the $ClCCo_3(CO)_9/AlCl_3/CH_3I$ Reagent with Nucleophiles

| Amt,[a] mmol | | | |
|---|---|---|---|
| $ClCCo_3$-$(CO)_9$ | $AlCl_3$ | Nucleophile (amt) | Product, R in $RC(O)CCo_3(CO)_9$ (% yield) |
| 2.08 | 3.0 | $CH_3OH$ (20 mL) | $CH_3O$ (80) |
| 2.2 | 7.7 | $CH_3OH$ (5 mL) | $CH_3O$ (78) |
| 2.2 | 7.35 | $C_2H_5OH$ (0.5 mL) | $C_2H_5O$ (71) |
| 2.2 | 7.7 | $BrCH_2CH_2OH$ (1 mL, 14 mmol) | $BrCH_2CH_2O$ (65) |
| 2.2 | 7.7 | $NH_3$ (excess) | $H_2N$ (45) |
| 2.2 | 7.7 | $Et_2NH$ (1 mL, 20 mmol) | $Et_2N$ (49) |
| 2.2 | 7.7 | $Me_2NC_6H_5$ (1 mL) | *p*-$Me_2NC_6H_4$- (60) |

[a] The amount of $CH_3I$ for all reactions was 10 mL.

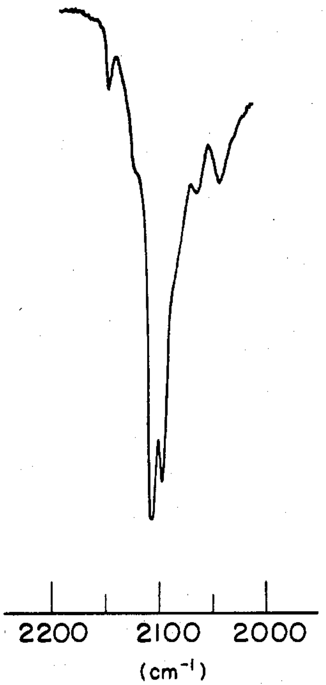
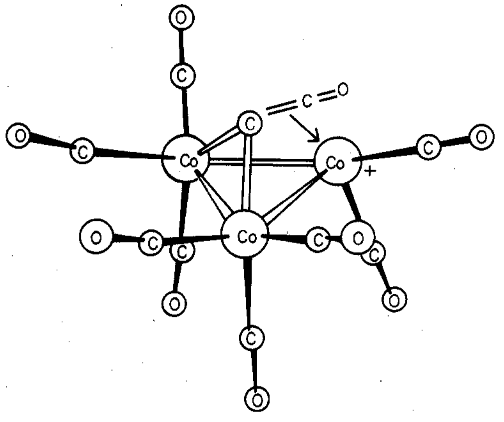


**Figure 1.** Infrared spectrum of $(OC)_9Co_3CCO^+[AlCl_4{\cdot}AlCl_3]^-$ in dichloromethane (terminal carbonyl region).

composition $(OC)_9Co_3CCO^+[AlCl_4{\cdot}AlCl_3]^-$. The crude solid which was obtained by the reaction of $BrCCo_3(CO)_9$ with aluminum bromide in carbon disulfide also was analyzed and found to approximate $(OC)_9Co_3CCO^+[AlBr_4{\cdot}AlBr_3]^-$. The infrared spectra of both reagents (in dichloromethane) were virtually identical, showing seven bands in the terminal carbonyl region, e.g., 2147 (w), 2121 (sh), 2107 (s), 2099 (s), 2082 (sh), 2068 (w), and 2046 (w) cm$^{-1}$ in the case of $(OC)_9Co_3CCO^+[AlCl_4{\cdot}AlCl_3]^-$ (Figure 1). In comparison, the infrared spectrum of $(OC)_9Co_3CCO_2CH_3$ shows absorptions at 2115 (m), 2065 (vs), 2040 (s), 2020 (w), and 1980 (vw) cm$^{-1}$ in this region, and shifts in these bands as the apical carbon substituents are changed in neutral alkylidynetricobalt nonacarbonyl complexes generally are minimal. In the cluster acylium ion salt we thus find a shift of the group of terminal CO absorptions to higher energy by about 40 cm$^{-1}$. The general features of the infrared spectrum of $(OC)_9Co_3CCO^+PF_6^-$ in acetonitrile solution were identical, but the bands were not shifted so far to higher energy. It is likely that the solvent and the anion are important factors. No band in the infrared spectra of the cluster acylium ion haloaluminate salts can be identified as being due to the carbonyl group attached to the apical carbon atom. The C=O stretching frequency in the $CH_3CO^+$ species is reported to occur at 2300 cm$^{-1}$,[6] but the spectra of our $(OC)_9Co_3CCO^+$ salts showed no bands above 2150 cm$^{-1}$. It may be that one of the seven bands in the infrared spectrum of the cluster acylium ion is due to the C=O attached to the apical carbon atom.

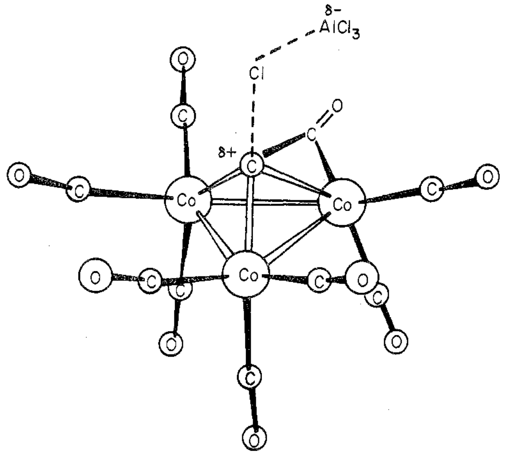
The location of the "extra" mole of $AlX_3$ in these acylium ion salts is not known. It could be present in the form of the $Al_2X_7^-$ ion or it could be coordinated to an oxygen atom of one of the CO ligands on cobalt. In this connection, it may be noted that the oxygen atom of a CO ligand attached to a transition metal is known to coordinate to Lewis acids, in particular, boron and aluminum halides and alkyls.[7,8] The $(OC)_9Co_3CCO^+$ ion is a relatively poor carbon electrophile in that it will acylate only the most reactive aromatic nucleophiles such as the ones mentioned above, but not benzene, toluene, or anisole. This suggests that the positive charge is delocalized away from the CO substituent on the apical carbon atom. The shift in the CO stretching frequency of carbon monoxide ligands bound to cobalt to higher energy, compared to neutral cluster derivatives, indicates that a greater amount of positive charge accumulates on the cobalt atoms when the cation is formed. This raises the question of the structure and bonding of the $(OC)_9Co_3CCO^+$ ion. A structure with gross geometry unchanged from that of neutral $RCCo_3(CO)_9$ complexes, e.g., I, would provide the means for transfer of electron density from the cluster to the electron-deficient CO group attached to the apical carbon atom. In the $(OC)_9Co_3CCO^+$ ion of structure I the three cobalt–carbon framework orbitals of the cluster possess $C_{3v}$ symmetry and transform as $a_1 + e$. The two $\pi$-antibonding orbitals of the acylium CO are of e symmetry and appropriate for interaction with one of the filled e framework orbitals. However, other structures with more complete electron transfer from cobalt to carbon with a change in geometry, e.g., the complex ketene structure III, are possible. Experimental information bearing on this question is not available at this time, so further speculation is not justified.



III

The formation of the $(OC)_9Co_3CCO^+$ species from $ClCCo_3(CO)_9$ represents a novel and unusual transformation. The question of its mechanism is an intriguing one. The experimental facts are as follows. The reagents obtained with $AlCl_3$ and $AlBr_3$ require more than 1 molar equiv of aluminum halide for their formation. These reactions proceed well in the absence of external carbon monoxide. In fact, when carbon monoxide is bubbled through such solutions during reagent formation, neither the rate of $(OC)_9Co_3CCO^+$ formation nor the ultimate product yield is increased. (No reactions were carried out at higher CO pressure.) The product yields listed in Table I are quite variable, but yields as high as 83% based on $ClCCo_3(CO)_9$ charged have been obtained. This implies very efficient transfer of carbon monoxide from cobalt to the apical carbon atom and from one cobalt atom to the other. If one recalculates the 83% yield of $(OC)_9Co_3CCO_2CH_3$ based on available $(OC)_9Co_3CCO^+$ from the $ClCCo_3(CO)_9$ used (assuming the destruction of an amount of $ClCCo_3(CO)_9$ equivalent to the theoretically required amount of CO to replace at cobalt the CO which was transferred to carbon), it is 92%.

On the basis of the available information, we suggest that initially a $(OC)_9Co_3CCl{\cdot}AlCl_3$ complex is formed in which there is substantial polarization of the C–Cl bond and which is capable of Friedel–Crafts substitution on aromatic systems. Subsequent coordination of a second molecule of $AlCl_3$ at a carbon monoxide ligand (a known process, as pointed out above) then provides the activation for migration of CO from cobalt to the electron-deficient apical carbon atom. This could be an intra- or an intermolecular process. The concept of $AlX_3$-assisted CO migration from a terminal position on cobalt via a bridged intermediate, IV, to a terminal position on the apical carbon atom seems a reasonable one. It is known that in binuclear metal carbonyls (such as $Co_2(CO)_8$) the oxygen atoms of bridging carbonyl ligands are stronger Lewis base sites than are the oxygens of terminal carbon monoxides.[7,8] In fact, aluminum alkyls were found to promote a terminal-to-bridging CO shift in a binuclear ruthenium complex.[9] Such a Co-to-C carbon monoxide transfer in our system would leave a coordinatively unsaturated cobalt atom in the cluster acylium ion which would require very efficient CO transfer from other molecules in order to obtain the $(OC)_9Co_3CCO^+$ species in high yield.



IV

Regardless of mechanism, this new procedure for the preparation of cluster complexes of the type $RC(O)CCo_3(CO)_9$ represents a very useful addition to the arsenal of alkylidynetricobalt nonacarbonyl chemistry in that it allows the preparation of a wide variety of organofunctional derivatives of the $CCo_3(CO)_9$ cluster.

## Experimental Section

**General Comments.** All reactions were carried out under an atmosphere of dry nitrogen. Column chromatography was used extensively for the separation of products. In general, a 40 × 600 mm column fitted with a fritted-glass disk and a Teflon stopcock was used. Silicic acid (Mallinckrodt reagent, 100 mesh) served well in most separations. Thin-layer chromatography (TLC) was used for monitoring the progress of reactions (Eastman Chromagram Sheet No. 6060). The cobalt-containing species are intensely colored and can be observed directly. Solid samples of new compounds were, in general, further purified by sublimation in vacuo or by recrystallization.

Infrared spectra were obtained using a Perkin-Elmer 457A double-beam grating infrared spectrophotometer; NMR spectra, using a Varian T60 spectrometer. Chemical shifts are reported in $\delta$ units, ppm downfield from internal tetramethylsilane. All solvents were of reagent grade and were used without further purification. The nucleophilic substrates were distilled or recrystallized before use. Glassware was flame-dried under nitrogen before use.

Dicobalt octacarbonyl was purchased from Strem Chemical Co. Bromo- and chloromethylidynetricobalt nonacarbonyl were prepared by reaction of the appropriate carbon tetrahalide with dicobalt octacarbonyl. Aluminum chloride from freshly opened bottles was used (Baker & Adamson, Allied Chemical). Not all batches were acceptable for use in this work. The material should be white or at the most light gray and should be granular and free-flowing. Yellow material should not be used. When it is dissolved in dichloromethane, it should give a solution only very palely colored and the solution should contain only minor amounts of undissolved solids. Commercially obtained (Alfa/Ventron) aluminum bromide was purified as follows. The solid (usually highly colored) was dissolved in carbon disulfide and the solution was filtered under nitrogen through glass wool. The filtrate was evaporated at reduced pressure to leave a light yellow, free-flowing solid which was stored in the absence of atmospheric moisture.

The standard reaction apparatus consisted of a three-necked, round-bottom flask of appropriate size (usually 100 or 200 mL) equipped with a nitrogen inlet tube and a magnetic stirring assembly.

**Reaction of Chloromethylidynetricobalt Nonacarbonyl/Aluminum Chloride with Nucleophiles.** The standard apparatus was charged with 3 molar equiv of aluminum chloride, 1 molar equiv of chloromethylidynetricobalt nonacarbonyl, and dichloromethane solvent (25 mL/mmol of the cobalt complex used). The initially purple, homogeneous solution became brown and somewhat heterogeneous after it had been stirred under nitrogen for 20–30 min. At this point TLC indicates that no $ClCCo_3(CO)_9$ remains; only a single brown spot, $R_f$ 0, was observed. Addition of the nucleophile effects an instantaneous color change and results in a homogeneous solution. The resulting solution usually was stirred under nitrogen until TLC showed only spots due to product.

The standard workup consisted of pouring the reaction mixture into 200–300 mL of cold 5% or 10% hydrochloric acid, separating and drying the organic layer (anhydrous sodium sulfate), filtering and removing the solvent at reduced pressure. Many products were isolated by filtration chromatography, a procedure in which the solid obtained is dissolved in hexane and poured onto a bed of silicic acid (ca. 50 mL) in a 60-mL glass-frit filter funnel. The appropriate solvent then is passed through with suction filtration. When more than a single product was formed, column chromatography often was used. Final purification generally was accomplished by sublimation in vacuo or by recrystallization (from hexane or hexane/dichloromethane in most cases).

Many of the products obtained in this study had been prepared earlier by reactions of $(OC)_9Co_3CCO^+PF_6^-$ with appropriate nucleophiles;[3] authentic samples and/or their IR and proton NMR spectra were available for comparison.

A few specific examples of such preparative reactions follow.

**Reaction of $(OC)_9Co_3CCO^+[AlCl_4{\cdot}AlCl_3]^-$ with Specific Substrates. (a) Methanol.** To a solution of 0.81 g (6.1 mmol) of aluminum chloride and 1.0 g (2.2 mmol) of chloromethylidynetricobalt nonacarbonyl in 50 mL of dichloromethane, prepared under nitrogen in the standard apparatus, was added 10 mL of anhydrous methanol. The yellow-brown reagent solution immediately turned reddish brown. TLC showed the presence of a single brown product. The solution was poured into 200 mL of cold 5% HCl. The layers were separated and the red-brown organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated at reduced pressure. The solid residue was dissolved in hexane and poured onto a bed of silicic acid. Dichloromethane was used to elute the major product. The solvent was removed and the residue was sublimed in vacuo to give 0.90 g (83%) of pure $(OC)_9Co_3CCO_2CH_3$.[3]

**(b) Ammonia.** The reagent was prepared from 9.5 mmol of $AlCl_3$ and 4.1 mmol of $ClCCo_3(CO)_9$ in 100 mL or dichloromethane. Gaseous ammonia was passed through a second gas-inlet tube over the stirred solution for 10 min until the color change which indicated consumption of the reagent had taken place. Standard workup was followed by filtration chromatography (silicic acid, dichloromethane). The crude product was recrystallized from hexane/dichloromethane to give 1.26 g (64%) of black solid $(OC)_9Co_3CC(O)NH_2$.[3]

**(c) Triethylsilane.** The reagent was prepared as before from 47.0 mmol of aluminum chloride and 16.7 mmol of $ClCCo_3(CO)_9$ in 250 mL of dichloromethane. The resulting solution was diluted with 200 mL of dichloromethane and chilled in ice water and then 6.14 g (51

Table IV. Orientational Experiments[a]

| X in $XCCo_3(CO)_9$ (mmol) | Y in $AlY_3$ (mmol) | Solvent | Product of ROH reaction, $(OC)_9Co_3CCO_2R$ (% yield) | Remarks |
|---|---|---|---|---|
| Cl (1.9) | None | | Et (6) | $ClCCo_3(CO)_9$ in 50 mL of EtOH stirred at room temperature for 15 days; 78% recovery of $ClCCo_3(CO)_9$ |
| Cl (1.5) | Cl (4.0) | $CH_2Cl_2$ | Et (0) | EtOH added to initial purple solution 1 min after reagents were mixed; 92% recovery of $ClCCo_3(CO)_9$ |
| Cl (1.7) | Cl (1.75) | $CH_2Cl_2$ | Et (0) | At room temperature for 26 h under CO atmosphere; solution remained purple |
| Cl (2.5) | Cl (6.1) | $CH_2Cl_2$ | Et (78) | Solution turned yellow-brown during 30 min at room temperature under nitrogen; EtOH added at that point |
| Cl (2.0) | Cl (5.5) | $CH_2Cl_2$ | Et (74) | At room temperature for 60 min under CO before EtOH was added |
| Cl (2.2) | Cl (6.1) | $CH_2Cl_2$ | Me (83) | MeOH added to yellow-brown solution after 30 min |
| Cl (2.1) | Cl (6.8) | $CH_2Cl_2$ | Me (72) | Reagent solution kept under nitrogen at room temperature for 73 h before MeOH was added |
| Cl (2.1) | Cl (6.5) | $CH_2Cl_2$ | Me (67) | Reagent solution kept under nitrogen at room temperature for 1 h and then was filtered; MeOH added to the filtrate |
| Br (2.2) | Cl (6.4) | $CH_2Cl_2$ | Me (80) | Reagent solution formed within 15 min, more rapidly than with $ClCCo_3(CO)_9$ |
| Cl (2.1) | Cl (3.0) | $CH_3I$ | Me (80) | Reagent formed within 5 min |
| Cl (2.2) | Br (7.7) | $CHCl_3$ | Me (68) | 2 h required for reagent to form; solvent washed with concentrated $H_2SO_4$, dried over $CaCl_2$ and distilled to remove EtOH stabilizer |
| Cl (1.1) | Cl (3.8) | $CS_2$ | Me (5) | MeOH added after 5 h; $AlCl_3$ not soluble in $CS_2$ |
| Cl (1.1) | Cl (3.8) | $CCl_4$ | Me (0) | MeOH added after 2 h; $AlCl_3$ not soluble in $CCl_4$ |
| Cl (1.1) | Cl (3.4) | $CH_3NO_2$ | Me (0) | Massive decomposition |
| Cl (2.2) | Cl (7.7) | $CH_2Br_2$ | Me (55) | Much slower rate of reagent formation; MeOH added after 3 h under nitrogen at room temperature |
| Cl (2.2) | Br (8.1) | $CH_2Cl_2$ | Me (59) | Rapid reagent formation; MeOH added after 2 min |
| Cl (1.1) | Br (3.4) | $CS_2$ | Me (71) | Reagent precipitated, leaving solution almost colorless; mixture cooled to 0 °C before MeOH added (5 min after initial reactant mixing) |
| Cl (2.2) | I (7.4) | $CH_2Cl_2$ | Me (70) | Rapid reagent formation; MeOH added after 10 min after mixture had been cooled to 0 °C |
| Br (1.0) | Br (3.0) | $CS_2$ | Me (60) | Reagent precipitated immediately; MeOH added at room temperature |
| Br (2.0) | Br (6.0) | $CS_2$ | Me (68) | Reagent precipitated immediately; MeOH added at 0 °C |
| Br (2.0) | Br (2.0) | $CS_2$ | Me (38) | MeOH added at 0 °C |
| Br (2.2) | Br (6.6) | $CS_2$ | Me (64) | Reagent precipitated; reaction carried out with CO bubbling through solution; MeOH added at 0 °C after 10 min |

[a] All reactions were carried out in the "standard reaction apparatus" under an atmosphere of dry nitrogen, unless otherwise noted. The initial reactants were stirred until TLC indicated that the starting halomethylidynetricobalt nonacarbonyl had been consumed. At that point the alcohol was added to the reaction mixture.

mmol) of $Et_3SiH$ (PCR Inc.) was added. The resulting brown solution was stirred for 15 min and then worked up in the usual manner. The crude product was purified by filtration chromatography (silicic acid, 70:30 hexane/dichloromethane). The brown solid thus obtained was recrystallized from pentane to give 5.31 g (68%) of the aldehyde, $(OC)_9Co_3CCHO$. The compound decomposed without melting at 120–130 °C.

**(d) Tetraethyltin.** The reagent was prepared from 5.3 mmol of aluminum chloride and 2.2 mmol of $ClCCo_3(CO)_9$ in 50 mL of dichloromethane and then 5 mL of tetraethyltin was added. The resulting brown solution was stirred for 19 h; the standard workup followed. Chromatography on silicic acid (70:30 hexane/dichloromethane eluent) gave crude product which was recrystallized from hexane to yield 0.71 g (66%) of brown $(OC)_9Co_3CC(O)C_2H_5$.[10]

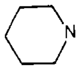
**(e) *N,N*-Dimethylaniline.** The reagent was prepared from 6.2 mmol of aluminum chloride and 2.2 mmol of $ClCCo_3(CO)_9$ in 50 mL of dichloromethane. The solution obtained was chilled in an ice-water bath for 30 min and then 3 mL of *N,N*-dimethylaniline was added dropwise with stirring. An intense blue color resulted immediately. The reaction mixture was stirred for 5 min and then worked up in the standard manner. Chromatography on silicic acid (elution with dichloromethane and chloroform) gave a single product which was recrystallized from dichloromethane/pentane to give 0.88 g (69%) of red-brown solid, $(OC)_9Co_3CC(O)C_6H_4NMe_2$-*p*.

**Reaction of Bromomethylidynetricobalt Nonacarbonyl/Aluminum Bromide with Nucleophiles.** The standard reaction apparatus was charged with bromomethylidynetricobalt nonacarbonyl, and carbon disulfide (15 mL/mmol of the complex) was added. Aluminum bromide (3 molar equiv) was added to this solution from a transfer vial. Immediate precipitation of the cluster acylium ion bromoaluminate salt occurred. TLC demonstrated that the starting $BrCCo_3(CO)_9$ had been consumed; only a brown spot of $R_f$ 0 in hexane was observed. Addition of 10 mL of dichloromethane dissolved this solid.

The reaction of this reagent with 2,2,2-trichloroethanol is described to illustrate the procedure used.

The reagent was prepared as described above from 1.04 g (2.0 mmol) of $BrCCo_3(CO)_9$ and 1.60 g (6.0 mmol) of aluminum bromide

Table V. New $(OC)_9Co_3CC(O)R$ Compounds

| R in $RC(O)CCo_3(CO)_9$ | Mp, °C | Color | Purification procedure | % carbon | | % hydrogen | | IR (in $CCl_4$), $cm^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calcd | Found | Calcd | Found | $\nu(C{\equiv}O)$ | $\nu(C{=}O)$ |
| $CH_2{=}CHCH_2O$ | 42–43 | Purple | Sublimn | 31.97 | 32.00 | 0.96 | 1.01 | 2105 m, 2065 vs, 2040 s, 2020 sh, 1990 w | 1675 |
| $HC{\equiv}CCH_2O$ | 59–60 | Purple | Sublimn | 32.09 | 32.19 | 0.57 | 0.64 | 2105 m, 2040 vs, 2035 s, 2020 sh, 1990 w | 1685 |
| $CCl_3CH_2O$ | 59–60 | Purple | Sublimn | 25.29 | 25.60 | 0.33 | 0.44 | 2105 m, 2065 s, 2045 vs, 2020 sh, 1990 w | 1685 |
| $BrCH_2CH_2O$ | 34–35 | Purple | Sublimn | 26.33 | 26.66 | 0.68 | 0.79 | 2110 m, 2070 s, 2040 vs, 2020 sh, 1985 w | 1685 |
| $p$-$MeOC_6H_4O$ | 54–55 | Purple | Sublimn | 36.51 | 36.73 | 1.19 | 1.37 | 2105 m, 2065 vs, 2045 s, 2015 sh, 1987 w | 1690 |
| $p$-$ClC_6H_4O$ | 56–57 | Purple | Recrystallizn from hexane | 34.23 | 34.52 | 0.68 | 0.79 | 2108 m, 2067 vs, 2047 s, 2030 sh, 2010 sh, 1983 w | 1700 |
| $p$-$MeC_6H_4O$ | 62–63 | Purple | Recrystallizn from hexane | 37.53 | 37.50 | 1.23 | 1.22 | 2108 m, 2065 vs, 2045 s, 2015 sh, 1984 w | 1698 |
| $p$-$NO_2C_6H_4O^a$ | 85–86 | Purple | Recrystallizn from hexane | 33.64 | 33.66 | 0.67 | 0.81 | 2115 m, 2070 vs, 2050 s, 2020 sh, 1990 w | 1707 |
| $Me_3CS$ | 74–75 | Purple | Sublimn | 32.28 | 32.32 | 1.63 | 1.70 | 2105 m, 2065 s, 2045 vs, 2015 sh, 1985 w | 1623 |
|  N | 63–64 | Purple | Recrystallizn from hexane | 34.74 | 34.34 | 1.82 | 1.90 | 2105 m, 2060 s, 2040 s, 2025 sh, 2005 sh, 1990 vw | 1623 |
| $Me_3CNH^b$ | 72–73 | Purple-brown | Recrystallizn from hexane | 33.30 | 33.15 | 1.87 | 2.01 | 2107 m, 2063 s, 2043 s, 2010 sh, 1980 w | 1632 |
| $H^c$ | Dec 120–130 °C without melting | Brown | Recrystallizn from pentane | 28.12 | 28.15 | 0.21 | 0.24 | 2110 m, 2065 s, 2050 s, 2020 sh, 1985 w | 1632 |
| $CH_2{=}CHCH_2$ | 51–52 | Purple-black | Recrystallizn from pentane | 32.97 | 32.84 | 0.99 | 1.19 | 2104 s, 2025 vs, 1989 sh | |

[a] % N: calcd, 2.31; found, 2.27. [b] % N calcd, 2.59; found, 2.62. [c] $^1H$ NMR ($DCCl_3$) spectrum shows aldehyde proton at 10.78 ppm.

in 30 mL of carbon disulfide. Ten milliliters of dichloromethane was added; the resulting solution was cooled in an ice bath and then 10 mmol of 2,2,2-trichloroethanol (Aldrich) was added by means of a syringe. The reaction mixture was stirred for 10 min and then poured into 100 mL of cold 10% HCl. The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. Column chromatography (silicic acid/dichloromethane) and subsequent sublimation in vacuo at 50 °C gave 0.73 g (55%) of purple $(OC)_9Co_3CCO_2CH_2CCl_3$.

**Reaction of Chloromethylidynetricobalt Nonacarbonyl/Aluminum Chloride/Iodomethane with Nucleophiles.** A solution of 2.2 mmol of $ClCCo_3(CO)_9$ in 10 mL of iodomethane and 40 mL of dichloromethane was prepared in the standard apparatus. To this purple solution was added 1.02 g (7.7 mmol) of aluminum chloride from a transfer vial. The formation of the reagent was complete within 10 min as indicated by TLC. After addition of the appropriate nucleophile (Table III), the further procedure was identical with that used in reactions carried out in the absence of iodomethane.

**Orientational Reactions.** A number of reactions of the halomethylidynetricobalt nonacarbonyl/aluminum halide systems were carried out to examine different reaction conditions. These are summarized in Table IV. After addition of the nucleophile, further workup followed the general procedure indicated above.

**Preparation of Cluster Acylium Ion Haloaluminate Salts for Analysis and Spectroscopic Examination.** (a) The following procedure was carried out in a drybox. An oven-dried 100-mL round-bottomed flask was charged with 2.00 mmol of $BrCCo_3(CO)_9$ and 25 mL of carbon disulfide. To the resulting solution was added dropwise with stirring at room temperature a solution of 6.00 mmol of $AlBr_3$ in 25 mL of carbon disulfide. The precipitate was transferred to a Schlenk tube, removed from the drybox, and dried in vacuo overnight. The Schlenk tube was returned to the drybox where samples of the dark brown solid were taken for further examination. Anal. Calcd for $(OC)_9Co_3CCO^+[AlBr_4{\cdot}AlBr_3]^-$: C, 12.21; Co, 16.34; Al, 4.99; Br, 51.69. Found: C, 11.61; Co, 18.30; Al, 4.44; Br, 50.75. IR ($CH_2Cl_2$): 2148 (w), 2122 (sh), 2110 (s), 2100 (s), 2084 (sh), 2068 (w), 2044 (w) $cm^{-1}$.

(b) The following procedure was carried out in a Schlenk apparatus consisting of a 100-mL round-bottomed flask modified by attachment of a coarse-glass frit at right angles to the neck and a nitrogen inlet collinear to the frit. This apparatus was equipped with a magnetic stir bar and a serum cap and was attached via the joint at the frit to another 100-mL three-necked flask equipped with a nitrogen inlet. The flame-dried reaction apparatus was charged with 2.2 mmol of $ClCCo_3(CO)_9$ and 25 mL of dichloromethane and to the resulting purple solution was added 6.6 mmol of aluminum chloride from a transfer vial. The mixture was stirred under nitrogen for 1 h and then 50 mL of carbon disulfide was added dropwise from a pressure-equalizing addition funnel. The mixture was filtered under a positive pressure of nitrogen and the solid which had precipitated was filtered with five 5-mL portions of carbon disulfide. The flask containing the solvents was replaced by a sealed tube and the solid on the frit was dried in vacuo overnight. The apparatus then was transferred to the drybox. Anal. Calcd for $(OC)_9Co_3CCO^+[AlCl_4{\cdot}AlCl_3]^-$: C, 17.13; Co, 22.93; Al, 7.00; Cl, 32.19. Found: C, 15.80; Co, 23.46; Al, 7.44; Cl, 37.96. IR ($CH_2Cl_2$): 2147 (w), 2121 (sh), 2107 (s), 2099 (s), 2082 (sh), 2068 (w), 2046 (w) $cm^{-1}$.

The infrared spectra were taken using a Perkin-Elmer 457A spectrophotometer utilizing an expanded scale of 2.5 and calibrated against polystyrene and referenced against dichloromethane. The samples were prepared from saturated, filtered dichloromethane solutions. A demountable NaCl cell and path length of 0.1 mm was used for best results.

**Comparison of $(OC)_9Co_3CCO^+[AlCl_4{\cdot}AlCl_3]^-$ Formation under Nitrogen and under Carbon Monoxide.** These reactions were carried out in pairs for reaction times of 5 and 15 min. Conditions were duplicated in all runs as closely as possible. Both gases were bubbled through the reaction mixtures at the same rates as monitored by a Nujol bubbler.

**(a) Under Nitrogen.** A flame-dried 100-mL three-necked flask equipped with a gas bubbler and magnetic stirring bar was charged with 2.2 mmol of $ClCCo_3(CO)_9$ and 50 mL of dichloromethane. Nitrogen was bubbled through the solution for 15 min. Aluminum chloride (6.6 mmol) then was added via a transfer vial and the nitrogen stream was continued. After 5 min 2 mL of methanol was added by syringe. The reaction mixture was stirred for 5 min and then was poured into 100 mL of 10% HCl. The organic layer was dried ($MgSO_4$) and evaporated in vacuo. The residue was dissolved in hexane and resolved by filtration chromatography. Hexane eluted 0.47 g (47%) of $ClCCo_3(CO)_9$. Subsequent elution with dichloromethane gave crude $(OC)_9Co_3CCO_2CH_3$ which was crystallized from hexane to give 0.32 g (29%) of pure material, mp 108–109 °C.

An identical experiment, except for a 15-min reaction time of the $ClCCo_3(CO)_9$ and aluminum chloride before the methanol was added, gave only a trace of unconverted $ClCCo_3(CO)_9$ and the ester in 81% yield.

**(b) Under Carbon Monoxide.** A procedure identical with that described above was used in these experiments except that carbon monoxide was bubbled through the reaction mixture instead of nitrogen. A 5-min reaction time before methanol was added gave a 41% recovery of $ClCCo_3(CO)_9$ and $(OC)_9Co_3CCO_2CH_3$ in 30% yield. A 15-min reaction time gave only a trace of the starting material and the methyl ester in 84% yield.

**Triphenylphosphine-Substituted Complexes. (a) Preparation of Chloromethylidynetricobalt Octacarbonyl Triphenylphosphine.** The standard apparatus was charged with 2.2 mmol of $ClCCo_3(CO)_9$, 2.2 mmol of triphenylphosphine (M&T Chemicals, Inc.), and 50 mL of dichloromethane. Nitrogen was bubbled through the resulting solution while it was stirred at room temperature for 90 min. Removal of the solvent at reduced pressure was followed by filtration chromatography (silicic acid/dichloromethane). The solid obtained was recrystallized from hexane to give 0.61 g (85%) of green-black $ClCCo_3(CO)_8PPh_3$, mp 114–116 °C dec. IR ($CCl_4$), $cm^{-1}$: 2080 (s), 2042 (s), 2035 (s), 1998 (w), 1988 (sh), 1975 (m) ($C{\equiv}O$ region). Anal. Calcd for $C_{27}H_{15}O_8ClPCo_3$: C, 45.63; H, 2.13. Found: C, 46.26; H, 2.48.

**(b) Reaction of Chloromethylidynetricobalt Octacarbonyl Triphenylphosphine with Aluminum Chloride.** A solution of the title compound was prepared by the above procedure from 2.2 mmol each of $ClCCo_3(CO)_9$ and triphenylphosphine in 50 mL of dichloromethane. To this solution was added 4.4 mmol of aluminum chloride and the resulting mixture was stirred at room temperature under nitrogen for 45 min. During this time a color change from purple to yellow brown was observed. Two milliliters of methanol was added and the reaction mixture was stirred for a few minutes more before being poured into 200 mL of cold 10% HCl. The dried organic layer was evaporated and the residue was resolved by column chromatography (silicic acid/$CH_2Cl_2$). The product, $Ph_3P(OC)_8Co_3CCO_2CH_3$, a dark greenish brown solid, was recrystallized from hexane to give pure material, 0.93 g (58%), mp 130–132 °C dec. IR ($CCl_4$), $cm^{-1}$: 2082 (s), 2047 (s), 2030 (s), 2020 (sh), 1997 (w), 1989 (sh), 1975 (m) ($C{\equiv}O$ region), 1673 ($\nu(C{=}O)$). Anal. Calcd for $C_{29}H_{18}O_{10}PCo_3$: C, 47.45; H, 2.47. Found: C, 47.40; H, 2.58.

**(c) Reaction of $(OC)_9Co_3CCO_2CH_3$ with Triphenylphosphine.** A solution of 1.0 mmol each of $(OC)_9Co_3CCO_2CH_3$ and triphenylphosphine in 30 mL of dichloromethane was stirred at room temperature for 45 min while nitrogen was being bubbled through the solution. A color change from purple to green-brown was noted. Evaporation of the solvent was followed by column chromatography of the residue and recrystallization of the product from hexane to give 0.61 g (83%) of $Ph_3P(OC)_8Co_3CCO_2CH_3$ which was identical in all respects with the product obtained in (b).

**Purification and Characterization of Products. (a) Known Compounds.** Many of the products obtained in this work had been prepared by the $(OC)_9Co_3CCO^+PF_6^-$ route in our previous investigations[3] or in another previous study.[10] The melting and/or decomposition points, the IR spectra, and in some cases the NMR spectra of these products were obtained and in all cases were found to be in full agreement with those of samples characterized in these previous studies. An error in ref 3 requires correction: the correct value of $\nu(C{=}O)$ of $(OC)_9Co_3CC(O)SC_6H_5$ is 1640 $cm^{-1}$.

**(b) New Compounds.** Characterization data for the new compounds prepared in this study are recorded in Table V.

**Acknowledgment.** The authors are grateful to the National Science Foundation (Grants GP 31429X, MPS75-21215) for generous support of this work.

**Registry No.** $CH_2{=}CHCH_2OC(O)CCo_3(CO)_9$, 36834-89-6; $HC{\equiv}CCH_2OC(O)CCo_3(CO)_9$, 61587-45-9; $CCl_3CH_2OC(O)CCo_3(CO)_9$, 61587-44-8; $BrCH_2CH_2OC(O)CCo_3(CO)_9$, 61587-43-7; $p$-$MeOC_6H_4OC(O)CCo_3(CO)_9$, 61587-42-6; $p$-$ClC_6H_4OC(O)CCo_3(CO)_9$, 61587-41-5; $p$-$MeC_6H_4OC(O)CCo_3(CO)_9$, 61587-40-4; $p$-$NO_2C_6H_4OC(O)CCo_3(CO)_9$, 61587-39-1; $Me_3CSC(O)CCo_3(CO)_9$, 61587-38-0; (piperidyl)$C(O)CCo_3(CO)_9$, 61587-37-9; $Me_3CNHC(O)CCo_3(CO)_9$, 60583-97-3; $HC(O)CCo_3(CO)_9$, 37541-28-9; $CH_2{=}CHCH_2C(O)CCo_3(CO)_9$, 61587-36-8; $ClCCo_3(CO)_9$, 19512-60-8; $CH_3OC({=}O)CCo_3(CO)_9$, 36834-85-2; $C_2H_5OC({=}O)CCo_3(CO)_9$, 19425-32-2; $Me_2CHOC({=}O)CCo_3(CO)_9$, 36834-86-3; $Me_3COC({=}O)CCo_3(CO)_9$, 36834-87-4; $C_6H_5OC({=}O)CCo_3(CO)_9$, 36834-95-4; $C_6H_5SC({=}O)CCo_3(CO)_9$, 36955-53-0; $H_2NC({=}O)CCo_3(CO)_9$, 37541-23-4; $(CH_3)_2NC({=}O)CCo_3(CO)_9$, 37541-24-5; $Et_2NC({=}O)CCo_3(CO)_9$, 37541-25-6; $C_6H_5NHC({=}O)CCo_3(CO)_9$, 37541-26-7; (morpholino)$C({=}O)CCo_3(CO)_9$, 52519-03-6; $HOC({=}O)CCo_3(CO)_9$, 61587-35-7; $CH_3C({=}O)CCo_3(CO)_9$, 36834-97-6; $C_2H_5C({=}O)CCo_3(CO)_9$, 36834-96-5; $n$-$C_4H_9C({=}O)CCo_3(CO)_9$, 40741-76-2; $Me_2N$-$p$-$C_6H_4C({=}O)CCo_3(CO)_9$, 37604-01-6; (3-indyl)$C({=}O)CCo_3(CO)_9$, 52519-08-1; (2-pyrrollyl)$C({=}O)CCo_3(CO)_9$, 52519-07-0; (ferrocenyl)$C({=}O)CCo_3(CO)_9$, 52501-89-0; $BrCCo_3(CO)_9$, 19512-61-9; $p$-$CH_3C_6H_4SC({=}O)CCo_3(CO)_9$, 61587-49-3; $(OC)_9Co_3CCO^+[AlBr_4{\cdot}AlBr_3]^-$, 61587-47-1; $(OC)_9Co_3CCO^+[AlCl_4{\cdot}AlCl_3]^-$, 61587-48-2; $ClCCo_3(CO)_8PPh_3$, 15633-23-5; $Ph_3P(OC)_8Co_3CCO_2CH_3$, 61587-46-0; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; methanol, 67-56-1; ammonia, 14798-03-9; triethylsilane, 617-86-7; tetraethyltin, 597-64-8; $N,N$-dimethylaniline, 121-69-7; 2,2,2-trichloroethanol, 115-20-8.

## References and Notes

(1) Part 20: D. Seyferth, M. O. Nestle, and C. S. Eschbach, *J. Am. Chem. Soc.*, **98**, 6724 (1976).

(2) Preliminary communication: D. Seyferth and G. H. Williams, *J. Organomet. Chem.*, **38**, C11 (1972).

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

(4) R. Dolby and B. H. Robinson, *Chem. Commun.*, 1058 (1970); *J. Chem. Soc., Dalton Trans.*, 2046 (1972).

(5) K. Dey, C. Eaborn, and D. R. M. Walton, *Organomet. Chem. Synth.*, **1**, 151 (1970/1971).

(6) A. Germain, A. Commeyras, and A. Casadevall, *Bull. Soc. Chim. Fr.*, 3177 (1972).

(7) J. C. Kotz and D. G. Pedrotty, *Organomet. Chem. Rev., Sect. A*, **4**, 479 (1969).

(8) D. F. Shriver, *Acc. Chem. Res.*, **3**, 231 (1970).

(9) A. Alich, N. J. Nelson, and D. F. Shriver, *Chem. Commun.*, 254 (1971).

(10) D. Seyferth, J. E. Hallgren, and P. L. K. Hung, *J. Organomet. Chem.*, **50**, 265 (1973).