

Organocobalt Cluster Complexes. XV. A New Route to Organofunctional Organocobalt Cluster Complexes Based on the Tricobaltcarbon Decacarbonyl Cation^{1,2}

Dietmar Seyferth,* John E. Hallgren, and C. Scott Eschbach

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received October 26, 1973

Abstract: Carboxymethylidyne tricobalt nonacarbonyl and its esters dissolve in concentrated sulfuric acid to give the acylium ion, $(OC)_9Co_3CCO^+$. A stable, crystalline hexafluorophosphate salt of this acylium ion may be obtained by addition of hexafluorophosphoric acid to a solution of carboxymethylidyne tricobalt nonacarbonyl or of its ethyl ester in propionic anhydride. Further reactions of this salt may be carried out by treating it directly with a nucleophilic substrate or by bringing it into reaction in the form of its slurry in dichloromethane or its solution in nitromethane. Its reactions with alcohols gave the appropriate esters: with phenyl the phenol ester, with thiols the thio esters, with ammonia and primary and secondary amines the corresponding amides, with primary amides the corresponding secondary imides, with alkylating agents such as tetramethyltin or ethylzinc bromide the corresponding ketones. The acylium hexafluorophosphate salt could be used to acylate NH_2 groups of ethyl glycinate and of a tripeptide, and it acylated highly nucleophilic aromatic substrates such as *N,N*-dimethylaniline, pyrrole, indole, and ferrocene. Its reduction to the aldehyde, $(OC)_9Co_3CCHO$, by triethylsilane was successful only when the reaction was carried out in the presence of an excess of aluminum chloride.

The direct reaction of geminal organic di- and trihalides with dicobalt octacarbonyl,³ the arylation and alkylation of methylidyne tricobalt nonacarbonyl with organomercurials,⁴ and the aluminum chloride induced reaction of chloromethylidyne tricobalt nonacarbonyl with benzene and substituted benzenes⁵ have served well in the preparation of a large number of substituted $RCCO_3(CO)_9$ compounds. However, at the outset of this research, the interconversions of organic functional groups attached to the apical carbon atom of the $(OC)_9Co_3C$ cluster had not been examined. The discovery⁶ and the recognition of the novel structure^{7,8} of the methylidyne tricobalt nonacarbonyl complexes dates back to 1959–1961, but in 1970 a review article⁹ could still say about $(OC)_9Co_3CY$ compounds, "The reaction possibilities which may be performed as "organic" reactions of Y are very poorly explored." The main thrust of our research on organocobalt cluster complex chemistry since 1970 has been directed toward the development of the organofunctional chemistry of this class of compounds, and we have published the preliminary results of these studies.^{2, 10–13} We re-

port here the full details of our investigations of the chemistry of carboalkoxymethylidyne tricobalt nonacarbonyl complexes.

Results and Discussion

Esters of carboxymethylidyne tricobalt nonacarbonyl (or nonacarbonyl tricobaltacetic acid), $(OC)_9Co_3CCO_2R$, can be prepared readily by the reaction of esters of trichloroacetic acid with dicobalt octacarbonyl.^{3,8,14} A similar reaction of dicobalt octacarbonyl with trichloroacetic acid itself in our hands failed to give the expected $(OC)_9Co_3CCO_2H$, but this compound, in principle, should be readily obtained by hydrolysis of its esters. The availability of carboxymethylidyne tricobalt nonacarbonyl should make possible the synthesis of many new organofunctional derivatives of the $(OC)_9Co_3C$ cluster.

The hydrolysis of $(OC)_9Co_3CCO_2R$ esters, however, proved not to be straightforward. Attempted hydrolysis of the ethyl ester in aqueous tetrahydrofuran (THF) in the presence of sodium carbonate resulted in complete destruction of the cobalt cluster within 30 min, thus providing another example of the degradation of an $(OC)_9Co_3C$ derivative by a base. Attempted acid hydrolysis of $(OC)_9Co_3CCO_2Et$ using aqueous THF in the presence of catalytic, stoichiometric, or above stoichiometric quantities of mineral acids failed; the ester was recovered unchanged.

Examination of the molecular structure of $(OC)_9Co_3CCH_3$, as determined by Sutton and Dahl,¹⁵ provided a possible explanation of this lack of reactivity toward aqueous acid. The exocenter substituent on carbon in these complexes is located such that it is in a "pocket" composed of six carbonyl ligands (Figure 1) and it is well shielded from flank-side attack by an external reagent and totally shielded from back-side attack. The accepted mechanism for acid-catalyzed ester hy-

(1) Part XIV: D. Seyferth, G. H. Williams, and P. L. K. Hung, in press.

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

(3) D. Seyferth, J. E. Hallgren, and P. L. K. Hung, *J. Organometal. Chem.*, **50**, 265 (1973), and earlier references cited therein.

(4) D. Seyferth, J. E. Hallgren, R. J. Spohn, G. H. Williams, M. O. Nestle, and P. L. K. Hung, *J. Organometal. Chem.*, **65**, 99 (1974).

(5) R. Dolby and B. H. Robinson, *J. Chem. Soc., Dalton Trans.*, 2046 (1972).

(6) R. Markby, I. Wender, R. A. Friedel, F. A. Cotton, and H. W. Sternberg, *J. Amer. Chem. Soc.*, **80**, 6529 (1958).

(7) U. Krücker and W. Hübel, *Chem. Ind. (London)*, 1264 (1960).

(8) W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc., (London)*, 169 (1961).

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

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

(11) D. Seyferth and G. H. Williams, *J. Organometal. Chem.*, **38**, C11 (1972).

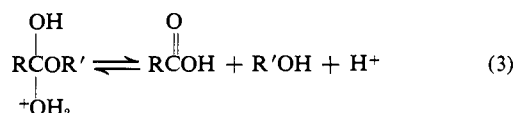
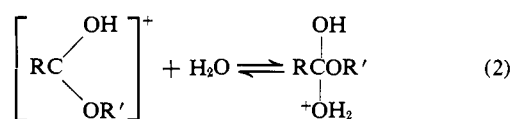
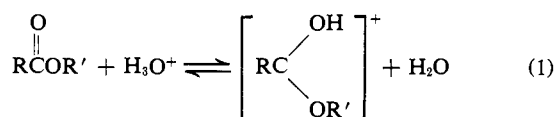
(12) D. Seyferth, P. L. K. Hung, and J. E. Hallgren, *J. Organometal. Chem.*, **44**, C55 (1972).

(13) D. Seyferth, G. H. Williams, and J. E. Hallgren, *J. Amer. Chem. Soc.*, **95**, 266 (1973).

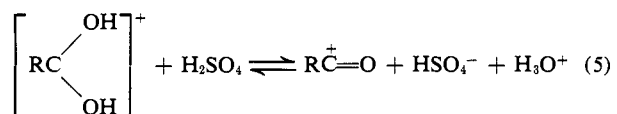
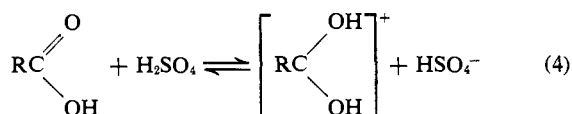
(14) R. Ercoli, E. Santambrogio, and G. T. Casagrande, *Chim. Ind. (Milan)*, **44**, 1344 (1962).

(15) P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 261 (1967).

drolisis (eq 1-3) thus may not be applicable to $(OC)_9Co_3CCO_2R$ because of these steric factors.



One procedure for effecting the hydrolysis of sterically hindered esters and the esterification of sterically hindered carboxylic acids¹⁶ is based on some observations of Hammett, *et al.*^{16a,b} It had been demonstrated that most carboxylic acids dissolved in concentrated sulfuric acid to give merely the monoprotonated species, $RCO_2H_2^+$. However, some few highly hindered carboxylic acids reacted further (eq 4 and 5)



to give the sterically much less hindered acylium ion, a very reactive species. When a sulfuric acid solution containing such an acylium ion was poured onto ice, the carboxylic acid was produced; when it was treated with an alcohol, $R'OH$, the ester, RCO_2R' , was formed. It is noteworthy that such acylium ion formation as observed only in the case of rather *weak* sterically hindered acids. Thus, 2,4,6-trimethylbenzoic acid ($K_a = 3.7 \times 10^{-4}$, ref 17) formed such an acylium ion in concentrated sulfuric acid, but the equally hindered but somewhat stronger 2,4,6-tribromobenzoic acid ($K_a = 3.9 \times 10^{-3}$, ref 17) or 3,5-dibromo-2,4,6-trimethylbenzoic acid did not. The magnitude of the steric factor was critical; in contrast to 2,4,6-trimethylbenzoic acid, the 2,4,5-trimethyl isomer was only protonated in concentrated sulfuric acid and did not form the acylium ion.

In spite of these steric and electronic restrictions on acylium ion formation, we examined the effect of concentrated sulfuric acid on $(OC)_9Co_3CCO_2Et$. This ester dissolved in concentrated sulfuric acid without evolution of carbon monoxide to give a yellow-brown solution which was stable at room temperature while it was maintained under a nitrogen atmosphere. When such a solution was poured onto cracked ice, the desired carboxymethylidynetricobalt nonacarbonyl was obtained in virtually quantitative yield. Esterification of this acid could be effected easily, generally in high yield, by pouring such a solution of the respective cluster complex into a large excess of the appropriate

(16) (a) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **55**, 1900 (1933); (b) H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937); (c) M. S. Newman, *ibid.*, **63**, 2431 (1941).

(17) J. Shorter and F. J. Stubbs, *J. Chem. Soc.*, 1180 (1949).

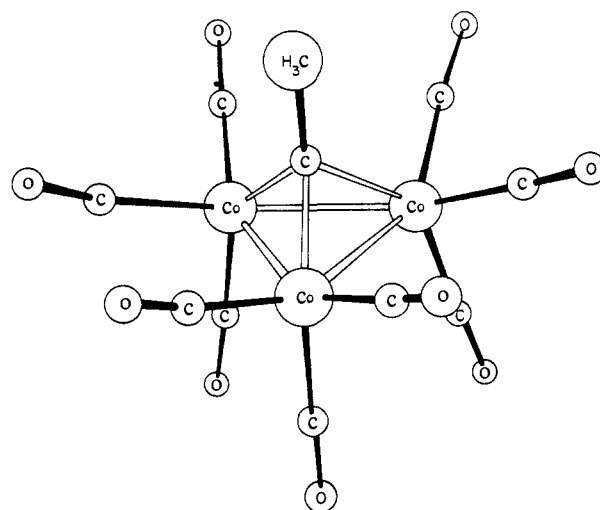


Figure 1. Structure of ethylidynetricobalt nonacarbonyl (Sutton and Dahl, ref 15).

alcohol. The results of these experiments are summarized in Table I. This procedure, however, was not applicable to the preparation of aryl esters.

Table I. Preparation of Esters of $(OC)_9Co_3CCO_2H$ by the Sulfuric Acid Procedure

| ROH | R in $(OC)_9Co_3CCO_2R$ | % yield |
|---------------------------------------|------------------------------------|---------|
| CH ₃ OH | CH ₃ | 95 |
| (CH ₃) ₂ CHOH | (CH ₃) ₂ CH | 96 |
| (CH ₃) ₃ COH | (CH ₃) ₃ C | 39 |
| CH ₂ =CHCH ₂ OH | CH ₂ =CHCH ₂ | 99 |
| HOCH ₂ CH ₂ OH | HOCH ₂ CH ₂ | 85 |

More normal esterification procedures were not very successful when tried with $(OC)_9Co_3CCO_2H$. For instance, reaction of this acid in ethanol solution with only 5 molar equiv of concentrated H_2SO_4 for 10 days at room temperature gave the expected ester in only 11% yield.

The observed reactivity of $(OC)_9Co_3CCO_2H$ and of its ethyl ester in concentrated sulfuric acid solution indicates that the solution process involves the sequence of reactions 4 and 5, *i.e.*, that these solutions contain $(OC)_9Co_3CCO^+$, the tricobaltcarbon decacarbonyl cation, as the reactive species. Furthermore, as we have pointed out, such behavior is quite rare and is restricted to *weak*, sterically hindered acids. Carboxymethylidynetricobalt nonacarbonyl must then be a rather weak acid, with a pK_a similar in magnitude to that of 2,4,6-trimethylbenzoic acid. This indirect evidence concerning the acidity of $(OC)_9Co_3CCO_2H$ is all that is presently available, the poor solubility of this compound in appropriate solvents thus far having precluded our attempts to determine its pK_a by standard procedures.

The availability of the desired acid should, in principle, make possible the preparation of a wide variety of new functional derivatives of the $(OC)_9Co_3C$ cluster. However, our attempts to convert the acid to a more reactive intermediate, the acid chloride $(OC)_9Co_3CCOCl$, were not successful. An even more reactive intermediate, the acylium ion $(OC)_9Co_3CCO^+$, was, of course, available, but the sulfuric acid solvent in

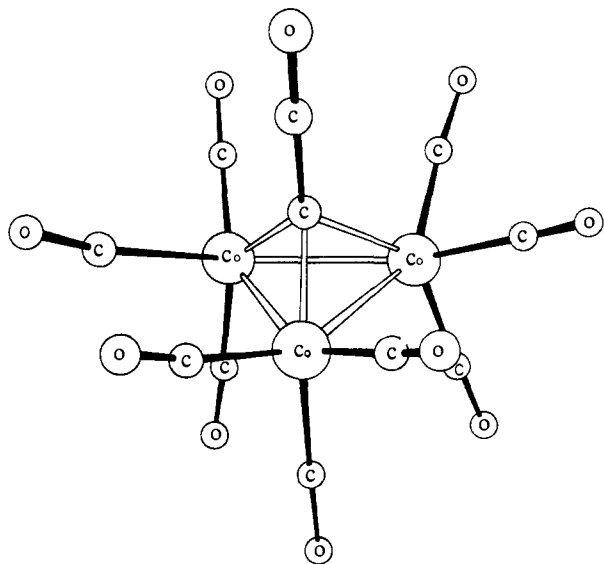


Figure 2. Proposed structure of the tricobaltcarbon decacarbonyl cation.

which it was generated imposed severe restrictions on its reactions which might be investigated.

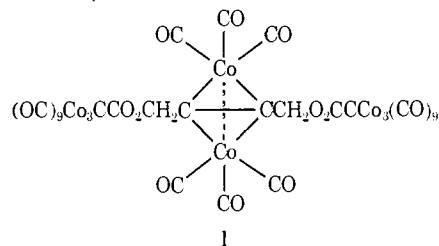
A well-established procedure for the conversion of triphenylcarbinol to trityl carbonium ion salts proved to be adaptable to the preparation of stable, isolable salts of the $(OC)_9Co_3CCO^+$ cation. Solution of either carboxymethyldynetricobalt nonacarbonyl or one of its esters in a minimum volume of propionic anhydride followed by addition of an excess of 65% aqueous hexafluorophosphoric acid resulted in the immediate precipitation of a black, microcrystalline solid. This solid was quite moisture-sensitive but was stable toward oxygen and could be handled using Schlenk tube techniques. It was insoluble in and unaffected by ethers, chlorinated hydrocarbons, acetone, and many arenes and was found to dissolve in nitromethane without reaction. A sample of this solid which had been washed well with dichloromethane was analyzed for all elements; the results were quite compatible with its formulation as $(OC)_9Co_3CCO^+PF_6^-$. Furthermore, all of the reactions of this solid (see below) are fully in accord with this structure, Figure 2.

The availability of this stable acylium methyldynetricobalt nonacarbonyl salt permitted a much broader development of the chemistry of the $(OC)_9Co_3CCO^+$ cation. In most of the reactions studied the solid salt was allowed to react directly with the nucleophilic substrate or it was brought into reaction as a slurry in dichloromethane. As shown in a few examples, reactions with $(OC)_9Co_3CCO^+PF_6^-$ may also be carried out in nitromethane solution. The moisture sensitivity of this salt involves its rapid hydrolysis to $(OC)_9Co_3CCO_2H$.

The chemistry of $(OC)_9Co_3CCO^+PF_6^-$ was examined in some detail. The results are summarized in Table II and are discussed below.

Reactions with Alcohols and Phenol. Acylium methyldynetricobalt nonacarbonyl hexafluorophosphate reacted readily with primary, secondary, and tertiary alcohols to give the corresponding esters. In contrast to the reaction of the $(OC)_9Co_3CCO^+$ cation with *tert*-butyl alcohol in the sulfuric acid system, the reaction

of the PF_6^- salt with this alcohol gave $(OC)_9Co_3CCO_2-CMe_3$ in high yield. Both the mono- and the diester could be prepared from ethylene glycol. Phenol, which could not be brought into successful reaction in the sulfuric acid system, reacted with $(OC)_9Co_3CCO^+PF_6^-$ in dichloromethane to give $(OC)_9Co_3CCO_2Ph$ in 72% yield. Of interest is the product of the reaction of 2 molar equiv of the PF_6^- salt with 1,4-butynediol, $(OC)_9Co_3CCO_2CH_2C\equiv CCH_2O_2CCC_3(CO)_9$, whose acetylenic linkage reacted with dicobalt octacarbonyl to form a complex containing two CCO_3 and one C_2CO_2 cluster, I. The $(OC)_9Co_3CCO_2R$ esters of lower molec-



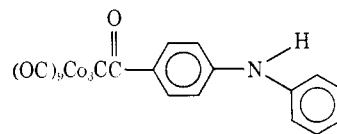
ular weight are volatile, deeply colored, crystalline solids which can be purified by sublimation *in vacuo* at 50° and which are air-stable. Their ester C=O stretching frequencies center around 1675 cm^{-1} , which is considerably lower than $\nu_{C=O}$ in normal organic esters.

Reactions with Thiols. Reactions of $(OC)_9Co_3CCO^+PF_6^-$ with ethyl mercaptan and with thiophenol gave $(OC)_9Co_3CC(O)SEt$ and $(OC)_9Co_3CC(O)SPh$, respectively, in high yield.

Reactions with Ammonia, Amines, and Other Nitrogen Compounds. Acylation of ammonia, aliphatic, and aromatic primary amines and aliphatic secondary amines could be accomplished readily with $(OC)_9Co_3CCO^+PF_6^-$, as indicated in Table II, when an excess of the amine was used (eq 6). The reaction of the PF_6^- $(OC)_9Co_3CCO^+PF_6^- + 2RNH_2 \rightarrow$



salt with diphenylamine gave the expected $(OC)_9Co_3CC(O)NPh_2$ in 42% yield, but a second product was formed and identified as II, *i.e.*, as a Friedel-Crafts



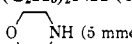
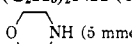
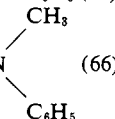
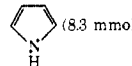
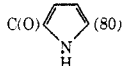
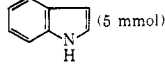
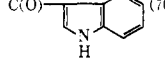
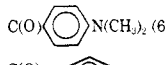
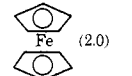
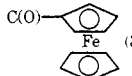
II

acylation product. The fact that such a product was not encountered in the case of *N*-methylaniline no doubt is due to the lower nucleophilicity of and the higher steric hindrance in diphenylamine.

The amides formed in these reactions were found to be less stable than the esters. They decomposed on being heated and on standing in air at room temperature for a few days. Their C=O stretching frequencies ranged from 1575–1635 cm^{-1} , again much lower than $\nu_{C=O}$ of their wholly organic analogs.

Acylation of primary amides (*e.g.*, formamide and acetamide) also was possible, although the imides formed, $(OC)_9Co_3CC(O)NHC(O)R$ ($R = H$ or CH_3), were even less stable than the cluster-substituted amides, decomposing slowly at 0° even under an inert atmosphere. The PF_6^- salt also reacted with *N*-methylacetamide, but the imide formed, $(OC)_9Co_3CCON-(CH_3)COCH_3$, was too unstable to isolate in analytical

Table II. Reactions of $(OC)_9Co_3CCO^+PF_6^-$

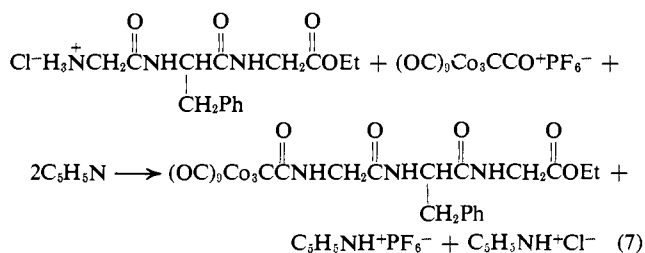
| Nucleophile (amount used) | $(OC)_9Co_3-$ CCO_2Et (mmol) (or H) | CH_2Cl_2 (ml) | R in $(OC)_9Co_3CR$ product (% yield) | Purified by method(s) | Ref for known compd |
|--|---|--------------------------------|---|--|---------------------------|
| CH_3OH (25 ml) | 2.0 | | CO_2CH_3 (82) | a | 3 |
| C_2H_5OH (10 ml) | 2.14 | | $CO_2C_2H_5$ (96) | a | 3 |
| $(CH_3)_2CHOH$ (1 ml) | 2.0 | 10 | $CO_2CH(CH_3)_2$ (89) | a | |
| $(CH_3)_3COH$ (1 ml) | 2.0 | 10 | $CO_2C(CH_3)_3$ (84) | a | 3 |
| $HOCH_2CH_2OH$ (1 mmol) | 2.0 | 25 | $CO_2CH_2CH_2O_2CCC(O)_9$ (35) | b (CH_2Cl_2) c (hexane) | |
| $HOCH_2C\equiv CCH_2OH$ (1.5 mmol) | 3.0 | 10 | $CO_2CH_2C\equiv CCH_2O_2CCC(O)_9$ (52) | b (CH_2Cl_2) c (hexane- $CHCl_3$) | |
| $HOCH_2C\equiv CCH_2OH$ (1.0 mmol) | 2.0 | 15 (CH_3NO_2) | $CO_2CH_2C\equiv CCH_2O_2CCC(O)_9$ (49) | b (CH_2Cl_2) c (hexane) | |
| C_6H_5OH (5 mmol) | 2.0 | 25 | $CO_2C_6H_5$ (72) | a | |
| C_2H_5SH (0.6 ml) | 2.0 | 10 | $C(O)SC_2H_5$ (80) | a | |
| C_6H_5SH (2.1 mmol) | 2.0 | 20 | $C(O)SC_6H_5$ (80) | c (hexane) | |
| NH_3 (g) (excess) | 2.0 | 15 | $C(O)NH_2$ (89) | c ($CHCl_3$ -hexane) | |
| CH_3NH_2 (g) (excess) | 2.0 | 10 | $C(O)NHCH_3$ (96) | c (hexane) | |
| $(CH_3)_2NH$ (g) (excess) | 3.0 | 15 | $C(O)N(CH_3)_2$ (84) | c (hexane) | |
| $(C_2H_5)_2NH$ (6 mmol) | 2.0 | 25 | $C(O)N(C_2H_5)_2$ (93) | c (hexane) | 3 |
|  (5 mmol) | 2.0 | 25 | $C(O)N$  (52) | b (CH_2Cl_2) c (hexane) | |
| $C_6H_5NH_2$ (5 mmol) | 2.0 | 20 | $C(O)NHC_6H_5$ (73) | c (hexane) | |
| $C_6H_5NHCH_3$ (5 mmol) | 2.0 | 20 | $C(O)N$  (66) | b (C_6H_6) c (hexane) | |
| $(C_6H_5)_2NH$ (5 mmol) | 2.0 | 20 | $C(O)N(C_6H_5)_2$ (42) | b (benzene) c (hexane) | |
| $HC(O)NH_2$ (5 mmol) | 2.0 | 25 | $C(O)NHC_6H_5$ (20) $C(O)NHC(O)H$ (42) | b (CH_2Cl_2) c ($CHCl_3$ -hexane) | |
| $CH_3C(O)NH_2$ (4 mmol) | 2.0 | 20 | $C(O)NHC(O)CH_3$ (65) | c (hexane) | |
| $Cl^-H_3N^+CH_2CO_2Et$ (4 mmol) | 2.0 | 15 (+10 mmol pyridine) | $C(O)NHCH_2CO_2Et$ (63) | b (CH_2Cl_2) c (hexane) | |
| $Cl^-H_3N^+CH_2C(O)NHCH(CH_2Ph)-$ $C(O)NHCH_2CO_2Et$ (1.15 mmol) | 2.0 | 15 (+4 mmol pyridine) | $C(O)NHCH_2C(O)NHCH(CH_2Ph)C-$ $(O)NHCH_2CO_2Et$ (58) | b (5% Et_2O , 95% CH_2Cl_2) c ($CHCl_3$ -hexane) | |
|  (8.3 mmol) | 2.0 | 20 | $C(O)$  (80) | b (30% hexane, 70% CH_2Cl_2) c ($CHCl_3$) | |
|  (5 mmol) | 2.0 | 20 | $C(O)$  (70) | b (CH_2Cl_2) c ($CHCl_3$) | |
| $(CH_3)_2NC_6H_5$ (5 mmol) | 2.0 | 20 | $C(O)$  (69) | b (benzene) c ($CHCl_3$ -hexane) | |
|  (2.0) | 2.0 | 20 | $C(O)$  (31) | b (benzene) c (hexane) | |
| $(CH_3)_4Sn$ (2.8 mmol) | 2.0 | 15 (5 day reaction time) | $C(O)CH_3$ (58) | a | 3 |
| $(C_2H_5)_4Sn$ (27.3 mmol) | 2.0 | 20 (5 day reaction time) | $C(O)C_2H_5$ (9) | b (30% hexane, 70% CH_2Cl_2) c (pentane) | 3 |
| C_2H_5ZnBr (3 mmol in THF) | 1.9 | 15 (THF) | $C(O)C_2H_5$ (54) | a | |
| C_2H_5MgBr (2 mmol) + $ZnCl_2$ (4 mmol) in Et_2O -THF | 2.0 | 20 (THF) | $C(O)C_2H_5$ (44) $CCO_3(CO)_9$ (11) $C(O)CO_3(CO)_9$ (18) | b (20% C_6H_6 , 80% hexane) c (hexane) | |

a Sublimation *in vacuo*. b Column chromatography. c Recrystallization.

purity and could only be characterized spectroscopically. In these imides, $\nu_{C=O}$ attributable to the carbonyl group adjacent to the $CCO_3(CO)_9$ cluster was found at 1650–1660 cm^{-1} .

The $CCO_3(CO)_9$ cluster also could be introduced into molecules of biological interest *via* $(OC)_9Co_3CCO^+PF_6^-$. Acylation of the amino function of ethyl glycinate was readily accomplished by reaction of the acylium hexafluorophosphate with $EtO_2CCH_2NH_3^+Cl^-$ in the presence of pyridine. A tripeptide hydro-

chloride was acylated in a similar manner (eq 7). The

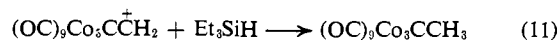
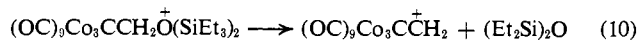
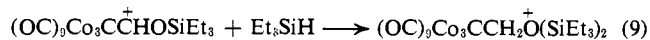
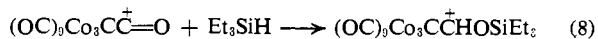


low value of the C=O (amide) stretching frequency, 1608 cm^{-1} , in this product indicated the assigned structure, rather than one in which an amide N-H function had been acylated. This reaction is of particular interest since it suggests that the $(\text{OC})_9\text{Co}_3\text{CCO}$ moiety can be introduced into more complex molecules of biological interest *via* acylation of N-H, O-H, or S-H bonds. Of importance in this connection is the availability of soluble systems containing the $(\text{OC})_9\text{Co}_3\text{CCO}^+$ cation: the PF_6^- salt in nitromethane, the BF_4^- salt in dichloromethane (ref 2 and work in progress), and the AlCl_4^- salt.¹¹ Applications in polypeptide X-ray crystallography and electron microscopy are conceivable.

Alkylation Reactions. Attempted alkylation of $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$ with organolithium or organomagnesium reagents was not successful. Decomposition and the formation, in low yield, of products attributable to complex electron transfer processes (*e.g.*, $(\text{OC})_9\text{Co}_3\text{CCC}_3(\text{CO})_9$, and $[(\text{OC})_9\text{Co}_3\text{C}]_2\text{C}=\text{O}$) were observed. However, milder alkylating agents did serve in the preparation of ketones from $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$. Ethylzinc halides reacted rapidly in THF with the PF_6^- salt to give $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{Et}$ in variable (20–55%) yield. Tetramethyl- and tetraethyltin also were found to react with $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$, but much less rapidly, to give the expected ketones. The acetyl complex, $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{CH}_3$, was formed in good yield, but the yield of the ethyl ketone was quite low. It may be that steric factors become more important as the size of R in R_4Sn increases. In any case, these reactions are much less useful than the quite general $\text{RC}(\text{O})\text{CCl}_3-\text{Co}_2(\text{CO})_8$ reaction³ for the synthesis of acylmethylidynetricobalt nonacarbonyl complexes.

Friedel-Crafts Reactions. As might be expected, $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$ acylates aromatic substrates. However, this reaction was observed only with highly nucleophilic substrates: ferrocene, pyrrole, indole, *N,N*-dimethylaniline, and, as mentioned above, diphenylamine. Anisole, which is fairly high on the Friedel-Crafts reactivity scale, was not acylated by the PF_6^- salt during a contact period of 2 weeks at room temperature nor did benzofuran react.

Reduction. Reaction of $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$ with an excess of triethylsilane in dichloromethane at room temperature gave a mixture of $(\text{OC})_9\text{Co}_3\text{CCH}_3$ (30%) and $(\text{OC})_9\text{Co}_3\text{CH}$ (43%) instead of the expected aldehyde, $(\text{OC})_9\text{Co}_3\text{CCH}=\text{O}$. While the formation of the C-C cleavage product is not readily explained, the observed complete reduction to the methyl derivative can be rationalized in terms of the reactions shown in eq 8–11. In a parallel study,¹¹ we had found that



$(\text{OC})_9\text{Co}_3\text{CCO}^+\text{AlCl}_4^-$ (in the presence of an excess of AlCl_3) reacts with triethylsilane to give the desired aldehyde in good yield, and, for this reason, the addition of aluminum chloride to the PF_6^- salt was investigated. Addition of 3 molar equiv of AlCl_3 to a

slurry of $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$ in dichloromethane resulted in the formation of a brown, homogeneous solution. Subsequent addition of an excess of triethylsilane to this solution gave $(\text{OC})_9\text{Co}_3\text{CCH}=\text{O}$ in 74% yield as the only product. This striking difference may possibly be explained in terms of the introduction of massive amounts of chloride ion which may intervene in the reaction sequence above to displace the Et_3Si group from the $(\text{OC})_9\text{Co}_3\text{C}^+\text{CHOSiEt}_3$ intermediate to give the aldehyde.

We note, in conclusion, that the initial objective of this research has been achieved. The tricobaltcarbon decarbonyl cation is easily prepared from the readily available $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{R}$ esters and is a moderately reactive acylating agent which reacts with a wide variety of nucleophilic substrates. As Tables I and II show, it already has permitted the preparation of many new organic derivatives of the tricobaltcarbon nonacarbonyl cluster. We indicated in a preliminary communication¹¹ that this versatile intermediate also is readily available *via* aluminum chloride induced conversion of $\text{ClCCO}_3(\text{CO})_9$ to $[(\text{OC})_9\text{Co}_3\text{CO}^+\text{AlCl}_4^-]_n\text{AlCl}_3$. The availability of two high yield preparations of this novel acylium ion should permit a much fuller development of its chemistry. Further work in this direction is in progress.

Experimental Section

General Comments. 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 readily be observed directly. Solid samples were, in general, further purified by sublimation *in vacuo* or by recrystallization.

Infrared spectra were obtained using Perkin Elmer 237B, 337, 257, or 457A double beam grating infrared spectrophotometers. Nmr spectra were obtained using Varian T60 or Perkin Elmer R20 nmr spectrometers. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. All solvents were rigorously dried before use; glassware was flame-dried under nitrogen.

Dicobalt octacarbonyl was purchased from Strem Chemical Co. Carboethoxymethylidynetricobalt nonacarbonyl was prepared by the direct reaction of ethyl trichloroacetate with dicobalt octacarbonyl.³ Hexafluorophosphoric acid (practical grade) was purchased in the form of a 65% by weight aqueous solution from Matheson Coleman and Bell.

Preparation of Carboxymethylidynetricobalt Nonacarbonyl by the Sulfuric Acid Technique. A 100-ml round-bottomed flask equipped with a magnetic stirring assembly and a nitrogen inlet tube was charged with 1.54 g (3.0 mmol) of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{Et}$ and 50 ml of concentrated sulfuric acid. The mixture was stirred at room temperature under a nitrogen atmosphere until all of the purple ester had dissolved to form a yellow-brown solution which appeared to be stable at room temperature for a limited time. No gas was evolved as the solid went into solution. This solution was poured onto 400 g of cracked ice. The resulting mixture was extracted with 150 ml of diethyl ether, and the ether extracts were dried (MgSO_4) and evaporated at reduced pressure to leave a purple solid which was recrystallized from chloroform to yield 1.33 g (92%) of purple-black needles of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{H}$, which decomposed when warmed above 120°.

Esterification of Carboxymethylidynetricobalt Nonacarbonyl by the Sulfuric Acid Procedure. A 100-ml round-bottomed flask equipped with a magnetic stirring assembly and a nitrogen inlet tube was charged with 2.0 mmol of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{H}$ and 40 ml of concentrated sulfuric acid. The mixture was stirred under nitrogen at room temperature to effect solution and then poured into 200 ml of the cold alcohol (*cf.* Table I). After 10 min, the solution was diluted with 600 ml of water and the cluster product was extracted

with hexane. The hexane extracts were dried and evaporated, leaving a red solid. Further purification by sublimation ($R = \text{Me}$, Me_2CH , allyl), recrystallization from hexane ($R = \text{HOCH}_2\text{CH}_2$) or column chromatography and sublimation ($R = \text{Me}_3\text{C}$) followed. In the initial extraction of the ethylene glycol-derived ester, diethyl ether was used, rather than hexane.

When such a sulfuric acid solution was poured into a solution of 50.0 g (0.47 mol) of phenol in 200 ml of dry THF, only the starting cluster acid could be recovered.

Preparation and Isolation of $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$. The apparatus used consisted of a 100-ml round-bottomed one-necked flask modified by attachment of a 15-mm coarse glass frit at right angles to the neck and a nitrogen inlet colinear with the frit. A 100-ml three-necked flask was attached to the frit with a nitrogen outlet. The first flask was charged with 1.04 g (2.0 mmol) of carboxymethylidyne-cobalt nonacarbonyl and 15 ml of propionic anhydride (Matheson Coleman and Bell, technical grade). The mixture was stirred to effect solution and 0.6 g (2.6 mmol) of 65% aqueous hexafluorophosphoric acid was added. A black precipitate formed immediately. After this mixture had been stirred under nitrogen for 5 min, the apparatus was rotated 90° and the mixture was filtered under nitrogen pressure. The black solid was washed with five 5-ml portions of dichloromethane and dried *in vacuo* at room temperature for 1 day. The black, microcrystalline solid thus obtained was found to be very moisture sensitive. It was insoluble in most common organic solvents but did dissolve in nitromethane.

Anal. Calcd for $\text{C}_{11}\text{O}_{16}\text{F}_6\text{PCo}_3$: C, 21.52; O, 26.06; F, 18.57; Co, 28.80. Found: C, 21.56; O, 27.50, 25.62; F, 17.84; Co, 28.30.

Reactions of $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$ with Alcohols, Phenol, Thiols, Amines, Amides, and Aromatic Substrates. (a) **Reaction with Undiluted Substrate.** The acylium hexafluorophosphate salt was prepared as described above from 1.0 g (2.0 mmol) of carboxymethylidyne-cobalt nonacarbonyl. The yield was 1.03 g (1.69 mmol). To this solid was added 25 ml of anhydrous methanol and the resulting mixture was shaken for 5 min. The red solution which formed was poured into 100 ml of water and the product was extracted with 50 ml of diethyl ether. The red ether layer was dried (MgSO_4) and evaporated under reduced pressure. The purple solid residue was sublimed *in vacuo* at 50° to give 0.82 g (98%, based on the acylium salt isolated; 82%, based on the starting acid) of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{CH}_3$.

(b) **Reaction in Dichloromethane Medium.** The acylium hexafluorophosphate salt was prepared from 2.0 mmol of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{Et}$ as described above and was slurried in 10 ml of dried dichloromethane. This suspension was treated with 0.6 ml of ethanethiol, added by syringe. The reaction mixture was stirred under nitrogen for 10 min and then was poured into 50 ml of water. Extraction with 50 ml of diethyl ether followed. The ether layer was washed with three 50-ml portions of 10% aqueous hydrochloric acid, dried, and evaporated under reduced pressure. The residue was extracted with benzene and the benzene solution was filtered through a pad of silicic acid to remove $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{H}$. The filtrate was evaporated and the residual solid was sublimed *in vacuo* at 50° to give 0.85 g (80%) of $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{SEt}$.

Reactions with gaseous substrates (NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$) were carried out by passing the gaseous amine over the surface of the acylium salt slurry in dichloromethane until all of the solid had dissolved to give a brown solution. In the case of the reactions with these (and all other) amines, the reaction mixture was treated with 100 ml of 5 or 10% aqueous HCl in the first step of the work-up procedure; extraction of the product with dichloromethane followed.

(c) **Reactions in Nitromethane Solution.** The acylium hexafluorophosphate was prepared from 2.06 mmol of carboxymethylidyne-cobalt nonacarbonyl as described above and then was dissolved, under nitrogen, in 25 ml of purified¹⁸ nitromethane. The resulting yellow-brown solution was filtered under nitrogen but left no observable residue on the frit. The filtered solution was treated with 5 ml of absolute ethanol (added by syringe). The solution immediately turned red-brown. After it had been stirred for 20 min under nitrogen, the solution was evaporated at reduced pressure. Sublimation of the oily residue *in vacuo* at 50° gave 0.83 g (79%) of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{Et}$.

(d) **Reaction with Ethyl Glycinate Hydrochloride in the Presence of Pyridine.** The $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$ was prepared from 2.0 mmol

of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{Et}$ and purified as before. A mixture of this solid and 0.56 g (4.0 mmol) of ethyl glycinate hydrochloride was slurried in 15 ml of dichloromethane under nitrogen and 0.80 g (10 mmol) of dry pyridine was added by syringe. The reaction mixture was stirred at room temperature for 10 min and then was treated with 100 ml of 5% aqueous HCl. The organic layer was dried and evaporated; the residue was dissolved in dichloromethane and separated into two components by column chromatography (silicic acid, dichloromethane eluent). First to be eluted was 0.04 g of $\text{HCCO}_3(\text{CO})_9$; this was followed by 0.72 g (63%) of $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{NHCH}_2\text{CO}_2\text{Et}$ (black needles).

(e) **Reaction with Ethyl Glycinyphenylalaninylglycinate Hydrochloride in the Presence of Pyridine.** The title peptide hydrobromide was obtained from Professor D. S. Kemp of this department. It was converted to the hydrochloride by anion exchange (Dowex 1-8X anion-exchange resin in the chloride form) after an initial experiment with the hydrobromide gave unsatisfactory results.

The acylium hexafluorophosphate prepared from 2.0 mmol of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{Et}$ was slurried in 15 ml of dichloromethane under nitrogen and 0.40 g (1.15 mmol) of the peptide hydrochloride was added. A slow evolution of gas commenced. After 5 min, 0.60 g (1.0 mmol) of pyridine was added. Further 0.06-g portions of pyridine were added every 5 min while the mixture was being stirred, until a total of 4.0 mmol had been added. The reaction mixture was stirred at room temperature for 25 min and then treated with 100 ml of water. Extraction with 100 ml of dichloromethane was followed by drying and concentration of the organic layer under reduced pressure. Column chromatography (silicic acid, 5% diethyl ether, 95% dichloromethane eluent) served in the separation of $\text{HCCO}_3(\text{CO})_9$ (0.12 g), $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{H}$ (0.25 g), and $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{NHCH}_2\text{C}(\text{O})\text{NHCH}(\text{CH}_2\text{Ph})\text{C}(\text{O})\text{NHCH}_2\text{CO}_2\text{Et}$ (0.53 g, 58%, based on the peptide, 34% based on the cobalt ester), in that order. The cluster-peptide compound was obtained as a black, crystalline solid which decomposed when it was warmed above 60°.

Reactions of $(\text{OC})_9\text{Co}_3\text{CCO}^+\text{PF}_6^-$ with Alkylating Agents. (a) **With Tetramethyltin.** The acylium hexafluorophosphate was prepared from 2.0 mmol of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{Et}$ and purified as before. The black solid was slurried in 15 ml of dichloromethane under nitrogen and treated with 0.5 g (2.8 mmol) of tetramethyltin (M&T Chemicals, Inc.). The progress of the reaction was followed by tlc. After 5 days at room temperature, no further reaction was evident. The solvent was removed at reduced pressure and the residue was extracted with benzene. The benzene extracts were filtered through a layer of silicic acid to remove carboxymethylidyne-cobalt nonacarbonyl and evaporated. The red solid residue was sublimed *in vacuo* at 50° to give 0.55 g (58%) of acetylmethylidyne-cobalt nonacarbonyl.

(b) **With Ethylzinc Bromide.** The acylium hexafluorophosphate prepared from 1.0 mmol of $(\text{OC})_9\text{Co}_3\text{CCO}_2\text{Et}$ was slurried in 15 ml of dry tetrahydrofuran (THF) under nitrogen and then was treated with 3.0 ml of a 1.0 M solution of EtZnBr^{19} in THF. The solution immediately turned red-brown. After it had been stirred at room temperature for 20 min, the mixture was treated with 100 ml of water and extracted with benzene. The organic layer was dried and filtered through a pad of silicic acid. Evaporation of the filtrate at reduced pressure was followed by sublimation of the red solid residue to give 0.51 g (54%) of $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{Et}$, a purple crystalline solid which decomposed around 74° without melting.


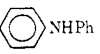

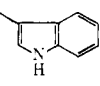
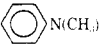

A similar reaction was carried out with the acylium hexafluorophosphate (THF slurry) prepared from 2.0 mmol of the ester and the reagent obtained by reaction of 2.0 mmol of ethylmagnesium bromide in diethyl ether with 4.0 mmol of anhydrous zinc chloride in THF. The brown reaction mixture was stirred for 1 hr, treated with 100 ml of 10% aqueous HCl, and extracted with diethyl ether. The organic layer was dried and evaporated and the brown solid residue was extracted with 1:1 hexane-benzene and resolved by column chromatography (silicic acid, 20% (v/v) benzene-80% hexane). Obtained, in order of elution, were bis(methylidyne-cobalt nonacarbonyl) $(\text{OC})_9\text{Co}_3\text{CCC}(\text{CO})_9$ (0.1 g, identified by comparison of its ir spectrum with that of an authentic sample⁴), bis(methylidyne-cobalt nonacarbonyl) ketone $(\text{OC})_9\text{Co}_3\text{CC}(\text{O})\text{CCO}_3(\text{CO})_9$ (0.17 g, mp 125° dec, in agreement with the identical literature²⁰ value), propionylmethylidyne-cobalt nonacarbonyl (0.45 g, 44%), and carboxymethylidyne-cobalt nonacarbonyl.

(19) Prepared by reaction of commercial diethylzinc with an equimolar quantity of anhydrous zinc bromide in THF.

(20) G. Allegra, E. Mostardini-Peronci, and R. Ercoli. *Chem. Commun.*, 549 (1959).

(18) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardin, *J. Amer. Chem. Soc.*, **86**, 1043 (1964).

Table III. New (OC)₉Co₃CR Compounds Prepared

| R | Mp, °C | Color ^a | Analysis, found (calcd) | | | Nmr, ^b δ (ppm) | Ir, ^b ν _{C=O} , cm ⁻¹ |
|---|---------------------------|--------------------|-------------------------|-------------|-------------|--|---|
| | | | Carbon | Hydrogen | Nitrogen | | |
| CO ₂ H | Dec ^c >120° | Purple-black | 27.19 (27.19) | 0.25 (0.21) | | 4.43 (s) (acetone- <i>d</i> ₆) | 1630 (CHCl ₃) 1636 (KBr) |
| CO ₂ CH(CH ₃) ₂ | 63–64 | Purple | 32.02 (31.84) | 1.41 (1.34) | | 1.35 (d, <i>J</i> = 6 Hz, 6 H), 5.15 (septet, <i>J</i> = 6 Hz, 1 H) | 1675 |
| CO ₂ CH ₂ CH=CH ₂ | 40–41 | Red | 32.14 (31.97) | 1.05 (0.96) | | 4.77 (d, <i>J</i> = 6 Hz with fine splitting, 2 H), 5.1–5.6 (m, 2 H), 5.7–6.4 (m, 1 H) | 1675 |
| CO ₂ CH ₂ CH ₂ OH | 66 | Red-black | 29.33 (29.46) | 1.13 (0.95) | | 2.07 (m, 1 H, OH), 3.91 (m, 2 H), 4.41 (t, <i>J</i> = 7 Hz, 2 H) [on adding 1 μl D ₂ O: 3.85 (t, <i>J</i> = 7 Hz, 2 H), 4.41 (t, <i>J</i> = 7 Hz, 2 H)] | 1675 |
| CO ₂ CH ₂ CH ₂ O ₂ CCCCo ₃ (CO) ₉ | Dec | Purple | 28.86 (28.88) | 0.58 (0.40) | | 4.58 (s) | 1677 (CHCl ₃) |
| CO ₂ CH ₂ C≡CCH ₂ O ₂ -CCCCo ₃ (CO) ₉ | Dec ^c ~97–100° | Purple | 30.61 (30.56) | 0.57 (0.40) | | 4.94 (s) | 1682 (CHCl ₃) |
| Compound I | 120–121 dec | Purple-red | 29.56 (29.39) | 0.48 (0.31) | | 5.58 (s) (CDCl ₃) | 1677 (CHCl ₃) |
| CO ₂ C ₆ H ₅ | 63–64 | Brown | 36.47 (36.33) | 0.97 (0.90) | | 7.17 (m) | 1697 |
| C(O)SC ₂ H ₅ | 61–62 dec | Black | 29.45 (29.45) | 1.02 (0.95) | | 1.42 (t, <i>J</i> = 7 Hz, 3 H), 3.07 (q, <i>J</i> = 7 Hz, 2 H) | 1632 |
| C(O)SC ₆ H ₅ | 91.5–92.5 dec | Black | 35.48 (35.32) | 0.99 (0.87) | | 7.53 (m) | 1590 |
| C(O)NH ₂ | Dec >130° without melting | Black | 26.97 (27.24) | 0.50 (0.41) | 2.95 (2.89) | | 1635 |
| C(O)NHCH ₃ | 124–126 dec | Black | 28.66 (28.88) | 0.94 (0.81) | 2.65 (2.81) | 3.07 (d, <i>J</i> = 5 Hz, 3 H), 6.0 (m, 1 H) | 1633 |
| C(O)N(CH ₃) ₂ | 121–123 dec | Black | 30.42 (30.44) | 1.30 (1.18) | 2.72 (2.73) | 3.22 (s) | 1590 |
| C(O)NHC ₆ H ₅ | 98–99 dec | Brown | 36.02 (36.39) | 1.21 (1.08) | 2.50 (2.50) | 7.38 (broad m) | 1648 |
| C(O)N(CH ₃)C ₆ H ₅ | 98–99 dec | Brown-black | 37.48 (37.59) | 1.50 (1.41) | 2.45 (2.44) | 3.37 (s, 3 H), 7.35 (m, 5 H) | 1582 |
| C(O)N(C ₆ H ₅) ₂ | 123–125 dec | Black | 43.38 (43.35) | 1.79 (1.59) | 2.23 (2.20) | 7.24 (m) | 1591, 1583 |
| C(O)N  | 74–75 dec | Brown-black | 32.36 (32.46) | 1.52 (1.46) | 2.59 (2.52) | 3.68 (m) | 1584 |
| C(O)NHC(O)H | Dec ^c ~120° | Brown | 28.28 (28.10) | 0.55 (0.39) | 2.71 (2.73) | | 1653, 1721 (CHCl ₃) |
| C(O)NHC(O)CH ₃ | Dec ^c | Black | 29.29 (29.63) | 0.94 (0.76) | 2.73 (2.66) | 1.78 (s, 3 H), 7.66 (m, 1 H) | 1655, 1710 |
| C(O)NHCH ₂ CO ₂ Et | 117 dec | Black | 31.35 (31.55) | 1.56 (1.41) | 2.54 (2.45) | 0.54 (t, <i>J</i> = 7 Hz, 3 H), 3.38 (d, <i>J</i> = 6 Hz, 2 H), 3.43 (d, <i>J</i> = 7 Hz, 2 H), 6.80 (m, 1 H) | 1620, 1735 |
| C(O)NHCH ₂ C(O)NHCH-(CH ₂ Ph)C(O)NHCH ₂ -CO ₂ CH ₂ CH ₃ | Dec >60° | Black | 39.69 (40.28) | 2.96 (2.58) | 5.42 (5.42) | | 1608, 1670, 1770 |
| C(O)  | 134–136 dec | Brown | 43.41 (43.35) | 1.57 (1.59) | | 6.17 (s, 1 H), 7.34 (m, 7 H), 8.07 (m, 2 H) | 1586 (ν _{N-H} 3420) |
| C(O)  | 144–146 dec | Brown | 33.50 (33.67) | 0.88 (0.76) | 2.58 (2.62) | 3.04 (m, 1 H), 6.34 (m, 1 H), 7.09 (m, 1 H), 7.30 (m, 1 H) (acetone- <i>d</i> ₆) | 1555 |
| C(O)  | 163–165 dec | Gold-brown | 38.92 (39.00) | 1.20 (1.04) | 2.44 (2.39) | 2.99 (s, 1 H), 7.40 (m, 3 H), 8.31 (m, 1 H), 8.57 (m, 1 H) | 1573 |
| C(O)  | 144–145 dec | Red-brown | 38.57 (38.73) | 1.81 (1.71) | 2.38 (2.38) | 3.02 (s, 6 H), 6.71–7.94 (AA'BB' m, 4 H) (acetone- <i>d</i> ₆) | 1582 |
| C(O)  | 104 dec | Black | 38.26 (38.57) | 1.65 (1.39) | | 4.20 (s, 5 H), 4.43–4.80 (AA'BB' m, 4 H) | 1590 |

^a The observed color depends on the crystallinity and particle size of the samples. A red-brown solid of small particle size on recrystallization often gave black needles or platelets. ^b In carbon tetrachloride solution unless otherwise specified. ^c Without melting.

Reduction of $(OC)_9Co_3CCO^+PF_6^-$ with Triethylsilane. (a) **In the Absence of Aluminum Chloride.** The acylium hexafluorophosphate prepared from 2.0 mmol of $(OC)_9Co_3CCO_2Et$ was slurried in 20 ml of dichloromethane under nitrogen, and 0.80 g (6.6 mmol) of triethylsilane (PCR Inc.) was added. The mixture was stirred at room temperature for 1 hr; a homogeneous solution resulted. The reaction mixture was evaporated under reduced pressure and the residue was extracted with hexane. The red extracts were filtered through a layer of silicic acid and evaporated. The red solid residue was sublimed *in vacuo* at 50° to give 0.65 g of red solid, melting in the range 95–115° with decomposition. Its ir spectrum suggested that a mixture of $CH_3CCO_3(CO)_9$ and $HCCO_3(CO)_9$ was present (bands at 2960 w, 2920 m, 2880 m, 2820 m, 1160 m, 1000 s, and 855 m cm^{-1}). The entire sample was dissolved in deuteriochloroform and the nmr spectrum which was taken showed that these two products were present in 1 to 1.44 ratio (30 and 43% yields, based on the 0.65 g isolated), respectively, by integration of the resonances at δ 3.76 and 12.10 ppm.

(b) **In the Presence of Aluminum Chloride.** The acylium hexafluorophosphate was prepared from 2.0 mmol of $(OC)_9Co_3CCO_2Et$ and slurried in 15 ml of dichloromethane under nitrogen. To this mixture was added 0.75 g (6.0 mmol) of aluminum chloride. A brief evolution of gas commenced but subsided quickly. Addition of 0.70 g (6.0 mmol) of triethylsilane followed. A brief evolution of gas again was observed and the solution turned from brown to red-brown. Tlc (benzene) showed the presence of a single brown material in the solution. After it had been stirred for 10 min at room temperature, the mixture was treated with 150 ml of 15% aqueous HCl and extracted with 100 ml of dichloromethane. The organic layer was dried and evaporated. The brown solid which remained was taken up in benzene. This solution was passed through a layer of silicic acid and evaporated. The residue was recrystallized from hexane to give 0.68 g (74%) of black needles which decomposed without melting around 115° and whose ir spectrum was identical with that of an authentic sample¹¹ of the aldehyde, $(OC)_9Co_3CCHO$.

An experiment in which only 2 mmol of aluminum chloride was added to the acylium hexafluorophosphate prepared from 2 mmol of the cluster-ester and in which this mixture was treated with 6 mmol of triethylsilane gave only $CH_3CCO_3(CO)_9$ (25%) and $HCCO_3(CO)_9$ (45%) and none of the aldehyde.

Reaction of $(OC)_9Co_3CCO_2CH_2C\equiv CCH_2O_2CCC_3(CO)_9$ with Dicobalt Octacarbonyl. A 100-ml three-necked flask equipped with a magnetic stirring unit, a nitrogen inlet tube, and a no-air stopper was charged with a solution of the cluster-substituted

acetylene (0.42 g, 0.47 mmol) in 20 ml of anhydrous diethyl ether. Subsequently, a solution of 2.3 g (6.7 mmol) of dicobalt octacarbonyl in 50 ml of diethyl ether was added. The mixture was stirred under nitrogen at room temperature for 90 min, during which time a very slow gas evolution and the separation of a solid were observed. The solvent was evaporated and the red-brown solid remaining was recrystallized from diethyl ether to give 0.41 g (78%) of I, mp 120–121° dec.

Characterization of Compounds. The new $(OC)_9Co_3C$ derivatives prepared during the course of this study are listed in Table III. The ir and nmr spectra of all compounds were recorded. In general, all alkylidynetricobalt nonacarbonyl complexes show five bands in their ir spectrum (Table IV) in the region 2150–1950 cm^{-1}

Table IV. Ir Spectra of $(OC)_9Co_3CR$ Complexes

| R | C≡O bands, cm^{-1} (in CCl_4 unless specified otherwise) |
|----------------------|--|
| CO_2H | 2120 m, 2075 vs, 2055 s, 2040 sh ($CHCl_3$) |
| CO_2CMe_3 | 2110 m, 2065 vs, 2044 s, 2018 w, 1980 vw |
| $C(O)SPh$ | 2110 m, 2065 vs, 2042 s, 2020 w, 1990 vw |
| $CONH_2$ | 2115 m, 2066 vs, 2044 s, 2015 w |
| $CONMe_2$ | 2114 m, 2065 vs, 2044 s, 2020 w, 1990 vw |
| $C(O)Et$ | 2110 m, 2065 vs, 2040 s, 2020 w, 1990 vw |
| $C(O)C_6H_4FeC_6H_5$ | 2108 m, 2065 vs, 2045 s, 2040 sh, 1983 vw |
| $C(O)C_6H_4NMe_2-p$ | 2108 m, 2065 vs, 2042 s, 2020 w, 1990 vw |

(terminal carbonyl region) with the intensity pattern medium, very strong, strong, weak, and very weak. As such, they serve to identify an $RCCO_3(CO)_9$ cluster complex, but shifts in these bands with change in apical substituent R among organic groups are so minimal as to have no diagnostic value. Accordingly, only a few such spectra in this region are described as typical examples.

Acknowledgments. The authors are grateful to the National Science Foundation (Grant GP 31429X) for generous support of this work and to the Massachusetts Institute of Technology for the award of a Forris Jewett Moore Fellowship and an Alfred P. Sloan Traineeship to J. E. H. We thank also Professor D. S. Kemp for a gift of the tripeptide used in this work.

Intramolecular Metal-Double Bond Interactions. VI. Metal- π -Electron Interactions Observed in Trialkenylaluminum and -gallium Derivatives

T. W. Dolzine and J. P. Oliver*

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Received August 7, 1973

Abstract: 1H nmr data and cryoscopic molecular weight data are presented for several terminal trialkenyl and trialkyl group III metal derivatives. The molecular weight data for the trialkenylaluminum derivatives correspond to a monomer in cyclohexane while under identical conditions the degree of association for the saturated trialkylaluminum derivatives is two. The nmr parameters for the trialkenyl group III metal derivatives are substantially perturbed. These data have been interpreted in terms of a direct intramolecular interaction between the metal center and the π -electron system of the olefinic site.

The interaction between a π -electron system and a metal atom has been shown to yield stable complexes with transition metals and it has been established that these complexes play an extremely important role in the stereochemically controlled reactions of these

systems. Similar metal-olefin complexes have been postulated for main group derivatives,¹ and a substantial body of evidence now exists supporting this type of

(1) K. Ziegler, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960.