

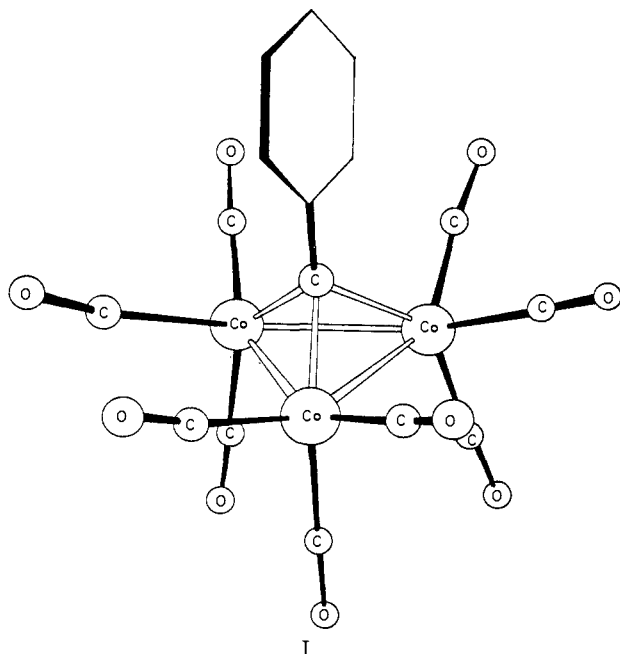
Organocobalt Cluster Complexes. XVII. Friedel–Crafts Acylation of Benzylidynecobalt Nonacarbonyl Complexes. Further Evidence for the Stabilization of Carbonium Ion Centers by the $(OC)_9Co_3C$ Moiety^{1,2}

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Abstract: The reaction of benzylidynecobalt nonacarbonyl and its *o*- and *m*-methyl and chloro derivatives with $CH_3COCl-AlCl_3$ gives in each case the para-acetylated cluster complex in good yield. Similar reactions were observed with the $C_6H_5COCl-AlCl_3$ reagent but not in the case of the Cl-substituted cluster complexes. Formylation of $C_6H_5CCO_3(CO)_9$ in low yield could be achieved with $CH_3OCHCl_2-AlCl_3$. Evidence indicating rapid deactivation of $AlCl_3$ was obtained. Competition experiments involving $C_6H_5CCO_3(CO)_9$, ferrocene, *N,N*-dimethylaniline, and anisole demonstrated the exceptionally high reactivity of benzylidynecobalt nonacarbonyl toward $CH_3COCl-AlCl_3$. An explanation is given in terms of substantial delocalization of the positive charge in the ionic intermediate into the $(OC)_9Co_3C$ cluster, possibly via $\sigma-\pi$ conjugation. Oxidation of these $ArCCO_3(CO)_9$ complexes with ceric ammonium nitrate gives the benzoic acids, $ArCOOH$.

Benzylidynecobalt nonacarbonyl (I) and its ring-sub-

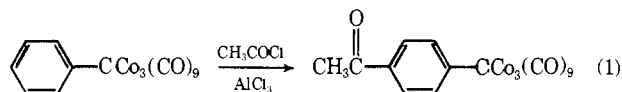


stituted derivatives are easily prepared by the direct reaction of the appropriate $ArCX_3$ or $ArCHX_2$ compound with dicobalt octacarbonyl,³ by the reaction of $HCCO_3(CO)_9$ with a diarylmercurial⁴ or by the $AlCl_3$ -induced reaction of $ClCCO_3(CO)_9$ with arenes.⁵ In our investigations of $RC-CO_3(CO)_9$ complexes (cf. previous papers of this series), we have been interested in particular in the introduction and subsequent conversions of R groups bearing functional substituents. The ready availability of such benzylidynecobalt nonacarbonyl complexes prompted us to examine their reactivity in aromatic substitution reactions. In view of the general instability of many $RCCO_3(CO)_9$ systems toward strongly basic and/or nucleophilic reagents, we decided to investigate electrophilic aromatic substitution reactions of $ArCCO_3(CO)_9$ complexes. Here also the scope of these studies was limited. Since $RCCO_3(CO)_9$ compounds are readily decomposed by oxidizing agents to inorganic cobalt species and organic derivatives containing the $RC\equiv$ moiety, certain electrophilic aromatic substitution processes

(halogenation, nitration, etc.) were excluded from this study, and we have thus far restricted ourselves to Friedel–Crafts acylation of $ArCCO_3(CO)_9$ complexes.

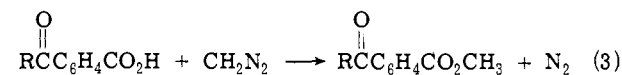
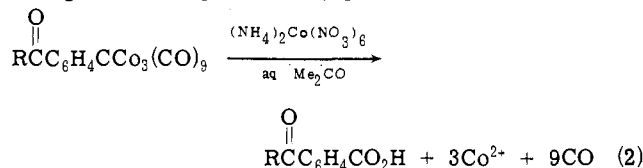
Results and Discussion

Our initial studies² showed that acetylation of benzylidynecobalt nonacarbonyl can be effected easily. Thus when $C_6H_5CCO_3(CO)_9$ was added to equimolar quantities of acetyl chloride and aluminum chloride in dichloromethane, acetylation of the phenyl ring exclusively in the para position occurred in nearly quantitative yield (eq 1). A simi-



lar reaction with benzoyl chloride gave *p*- $C_6H_5C(O)-C_6H_4CCO_3(CO)_9$ in 71% yield, and the $AlCl_3$ -induced reaction of benzylidynecobalt nonacarbonyl with CH_3OCHCl_2 , followed by hydrolysis, resulted in formation of the formyl derivative, *p*- $O=CHC_6H_4CCO_3(CO)_9$, in 20% yield.

Degradation experiments (eq 2 and 3) established that



acylation had occurred exclusively in the para position in the case of reactions with acetyl and benzoyl chloride. The methyl esters obtained were identified unambiguously as methyl *p*-acetylbenzoate and methyl *p*-benzoylbenzoate, respectively, and the absence of other isomers was established.

Since these acylation reactions proceeded in such high yield, apparently rapidly and under mild conditions, we extended the scope of this study to include benzylidynecobalt nonacarbonyl complexes bearing electron-attracting chlorine and electron-releasing methyl substituents (ortho-, meta-, and para-substituted), as well as *p*-bromobenzylidynecobalt nonacarbonyl and $C_6H_5CH_2CCO_3(CO)_9$. The

Table I. Acylation of Benzylidynetricobalt Nonacarbonyl Complexes

Ar in $\text{ArCCo}_3(\text{CO})_9$ (mmol)	Acyl chloride (mmol)	AlCl_3 (mmol)	Para-acylated product (% yield)	Recovered $\text{ArCCo}_3(\text{CO})_9$ (%)
C_6H_5 (5.0)	CH_3COCl (5.0)	5.0	93	
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$ (2.7)	(4.2)	3.4	88	
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$ (1.2)	(1.5)	1.4	91	8
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$ (1.6)	(2.3)	2.0	0	94
<i>o</i> - ClC_6H_4 (2.5)	(4.0)	3.8	58	26
<i>m</i> - ClC_6H_4 (2.6)	(3.8)	3.7	60	31
<i>p</i> - ClC_6H_4 (1.4)	(1.9)	1.5	0	89
<i>p</i> - BrC_6H_4 (0.85)	(1.27)	1.04	22	40
$\text{C}_6\text{H}_5\text{CH}_2$ (0.76)	(2.33)	1.85	0	40
C_6H_5 (4.0)	$\text{C}_6\text{H}_5\text{COCl}$ (10.0)	10.0	71	
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$ (1.4)	(1.5)	1.6	48	30
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$ (1.9)	(2.2)	2.3	67	20
<i>o</i> - ClC_6H_4 (1.4)	(2.0)	1.6	0	71
<i>m</i> - ClC_6H_4 (1.1)	(1.4)	1.4	0	87

results are shown in Table I; all reactions were carried out under the same conditions using the same general procedure.

The yields of the substitution products are, in general, higher for the complexes with the activating methyl substituent than for those with the deactivating chlorine substituent. All reactions of benzoyl chloride proceeded in lower yield than did those of acetyl chloride.

In all examples studied, acylation occurred at the para position, irrespective of the nature and position of the other substituents on the benzene ring. If the para position was blocked, either no Friedel-Crafts reaction was observed, even under forcing conditions, or, as was observed in the case of the *p*-bromo-substituted complex, the para substituent was displaced. Thus under no conditions could acetylation of *p*-methyl- or *p*-chlorobenzylidynetricobalt nonacarbonyl be achieved.

The success of these Friedel-Crafts reactions is very dependent upon reaction conditions because nonproductive interactions of aluminum chloride with the benzylidynetricobalt nonacarbonyl complexes also are possible. In virtually all of these reactions, the reaction mixture was examined by thin layer chromatography immediately after the reactants had been mixed. In those cases where reaction was not complete, longer reaction times or higher reaction temperatures were used in the hope of driving the reaction to completion. However, it soon became apparent that these reactions, when they occurred, were quite rapid initially but that a few moments after the reactants had been mixed the reaction ceased quite abruptly. Further stirring or heating served only to destroy starting material, product, or both. That these reactions are quite rapid was visually evident in every case where the reaction did go to completion. The intensely brown-colored starting material was converted into an intensely red-brown-colored product the moment it entered the solution of acetyl chloride and aluminum chloride. In these cases the reaction mixtures were worked up after only a few moments of stirring.

The most plausible explanation for such behavior is that one or more of the reactants is deactivated in some way very shortly after the reactants are mixed. Aluminum chloride is known to complex with carbonyl functions in ketones and with coordinated carbon monoxide ligands in metal carbonyls.⁶ Further work showed that in cases where the acetylation reaction did not go to completion immediately after mixing, e.g., entry 6 in Table I, complete reaction could be achieved by using a large excess of aluminum chloride. Thus, in contrast to the results of entry 6, Table I, a reaction of 1 mmol each of *m*- $\text{ClC}_6\text{H}_4\text{CCo}_3(\text{CO})_9$ and acetyl chloride in the presence of 10 mmol of aluminum chloride gave an 88% yield of para-acylated product. Because of this apparent deactivation of aluminum chloride, the way in

which these reactions are carried out is of critical importance. This is shown by some experiments with $\text{C}_6\text{H}_5\text{C-Co}_3(\text{CO})_9$, which, as entry 1 in Table I shows, gives high product yields under the proper reaction conditions. In one experiment, this compound was treated with an equimolar quantity of aluminum chloride in dichloromethane for 5 min. Addition of acetyl chloride in 20% excess, followed by a reaction time of 5 min and normal work-up gave the expected *p*- $\text{CH}_3\text{COC}_6\text{H}_4\text{CCo}_3(\text{CO})_9$ in only 32% yield, and 35% of the starting cluster complex was recovered. However, the use of an excess of aluminum chloride improved matters when this "wrong" mode of addition was used, as shown in an experiment in which $\text{C}_6\text{H}_5\text{CCo}_3(\text{CO})_9$ and aluminum chloride (1:1 molar ratio) in dichloromethane was stirred for 5 min and then added to a solution containing acetyl chloride and a molar equivalent of aluminum chloride. Work-up immediately after mixing gave *p*-acetylbenzylidynetricobalt nonacarbonyl in 82% yield.

It would be of interest to learn more about the nature of the $\text{ArCCo}_3(\text{CO})_9\text{-AlCl}_3$ complexes which are formed in these systems, and studies on this subject are in progress.

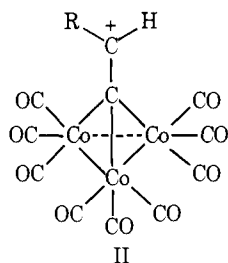
The almost instantaneous reactions which occurred when the proper mixing sequence of RCOCl , AlCl_3 , and $\text{ArCCo}_3(\text{CO})_9$ was used indicated that these aryl-substituted cluster complexes are quite reactive in the Friedel-Crafts reaction. In order to obtain a more quantitative idea of the reactivity of these $\text{ArCCo}_3(\text{CO})_9$ compounds, we carried out a few competition reactions. In these, a mixture of 10 molar equiv each of $\text{C}_6\text{H}_5\text{CCo}_3(\text{CO})_9$ and another aromatic substrate in dichloromethane was treated with a solution of 1 molar equiv of acetyl chloride and two of aluminum chloride in dichloromethane. A 10-min reaction period was followed by the usual work-up with suitable modifications to separate the acetylated products and unconverted starting materials. The results of these experiments are given in Table II. Although the relative rate constants are by no means highly accurate as determined by this procedure, it is clear that benzylidynetricobalt nonacarbonyl is a highly reactive aromatic nucleophile, comparable to and apparently exceeding ferrocene and *N,N*-dimethylaniline in reactivity toward the $\text{CH}_3\text{COCl-AlCl}_3$ reagent. Ferrocene is known to be exceptionally reactive toward this reagent,⁷ and the very high reactivity of anilines in electrophilic aromatic substitution processes is mentioned in every organic textbook.

An explanation for this high reactivity of $\text{ArCCo}_3(\text{CO})_9$ compounds toward Friedel-Crafts acylation may be found in the results of some of our studies on functional alkylidynetricobalt nonacarbonyl complexes. $(\text{OC})_9\text{Co}_3\text{C}$ -substituted carbonium ions of type II are exceptionally stable, and this appears to result from substantial delocalization of positive charge into the cluster, very likely via σ - π conjuga-

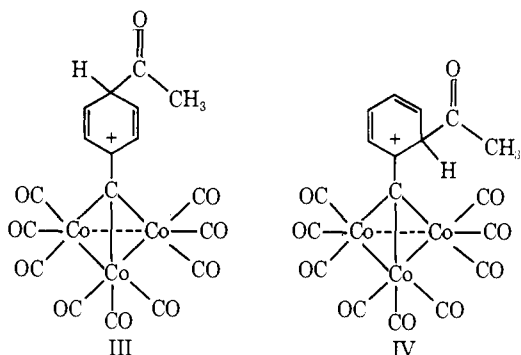
Table II. Competition Experiments: $10\text{C}_6\text{H}_5\text{CCO}_3(\text{CO})_9 + 10\text{X} + \text{CH}_3\text{COCl} + 2\text{AlCl}_3$

Compound X	Acetylated products (% yield, based on CH_3COCl)	$k(\text{PhCCO}_3(\text{CO})_9)/k_{\text{X}}$
	(85.6) (10.3)	1.2 ^{a,c}
	(38.9) (52.1)	1.3 ^b
	(0) (89.3)	

^a Calculation assuming that there are ten reactive positions in ferrocene and only one in $\text{PhCCO}_3(\text{CO})_9$. ^b Calculation assuming that there is only one reactive position in Me_2NPh and $\text{PhCCO}_3(\text{CO})_9$. (Me_2NPh undergoes exclusive para-acetylation under these conditions.) ^c k_{rel} values ranging from 0.9 to 1.2 were obtained in a series of four experiments in which reagent ratios and reaction times were varied (cf. Experimental Section).



tion.⁸ The attack of the $\text{CH}_3\text{COCl}-\text{AlCl}_3$ reagent (as $\text{CH}_3\text{CO}^+ \text{AlCl}_4^-$) at the para position of $\text{C}_6\text{H}_5\text{CCO}_3(\text{CO})_9$ would lead to an ionic intermediate in which positive charge can be displaced to the ring carbon atom which is bonded to the cluster carbon atom (III), and thus further delocaliza-

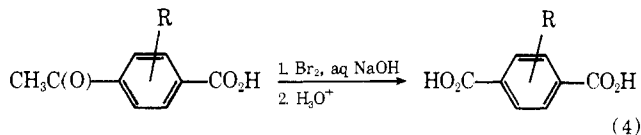


tion of positive charge into the cluster would be possible. The net stabilization gained must be considerable, in view of the high reactivity of these $\text{ArCCO}_3(\text{CO})_9$ compounds. Ortho-substitution in these systems also would lead to a cluster-stabilized intermediate, IV. However, the severely retarding steric effect of the carbon monoxide ligands on cobalt, six of which are disposed in the general direction of the cluster carbon atom and its substituent,⁹ would be expected to hinder or possibly completely prevent attack at an ortho position (cf. I). As a result, reactions of $\text{ArC}-\text{CO}_3(\text{CO})_9$ compounds with the $\text{RCOCl}-\text{AlCl}_3$ reagents are limited to para substitution, irrespective of electronic effects due to other substituent groups on the benzene ring.

Stabilization of the type shown in III as the decisive factor in the high reactivity of $\text{C}_6\text{H}_5\text{CCO}_3(\text{CO})_9$ is not possible in the case of $\text{C}_6\text{H}_5\text{CH}_2\text{CCO}_3(\text{CO})_9$ with its insulating

methylene bridge, and thus the lack of reactivity of this compound is understandable.

Some further comments are in order concerning the determination of the position of substitution in the case of the substituted benzylidynetricobalt nonacarbonyl complexes. Ceric ion oxidation of the acetylated products did give the expected substituted benzoic acids as shown in eq 2. However, these were not known compounds, and to establish the position of acetylation, they were oxidized to the diacids (eq 4). Alternatively, the acetylated benzylidynetricobalt non-



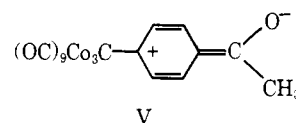
(R = Me or Cl)

carbonyl complexes could be oxidized directly to the corresponding terephthalic acids by bromine in aqueous base. Either the substituted terephthalic acids themselves or their dimethyl esters (via diazomethane) then were compared with the authentic compounds to confirm para substitution. It was assumed that such para substitution also occurred with the $\text{C}_6\text{H}_5\text{COCl}-\text{AlCl}_3$ and $\text{CH}_3\text{OCHCl}_2-\text{AlCl}_3$ reagents.

In summary, this study has provided another example of the very substantial stabilizing effect of the $(\text{OC})_9\text{Co}_3\text{C}$ cluster on a carbonium ion center. This stabilization serves to make $(\text{OC})_9\text{Co}_3\text{CC}_6\text{H}_5$ perhaps the most reactive monosubstituted benzene known with respect to electrophilic aromatic substitution.¹⁰ Unfortunately, the scope of such reactions is severely limited, due to the ready destruction of the $(\text{OC})_9\text{Co}_3\text{C}$ cluster by oxidizing agents and many strong bases and nucleophiles and, as we have found, by the competitive complexation of aluminum chloride by the cluster, which appears also to lead ultimately to its decomposition.

While the chemistry described above does not appear to have practical applications in synthesis, analogous acylation of $(\text{ArC}_2\text{Ar}')\text{Co}_2(\text{CO})_6$ cluster complexes does have potential synthetic utility.² Full details of our studies of this class of cobalt carbonyl complexes will be provided in the near future.

In conclusion, the $\text{C}=\text{O}$ stretching frequencies in the infrared spectra of the acetylated benzylidynetricobalt nonacarbonyls merit special comment. This frequency for $p\text{-CH}_3\text{COC}_6\text{H}_4\text{CCO}_3(\text{CO})_9$ (in dilute CCl_4) is $1685 \pm 1 \text{ cm}^{-1}$. Fuson et al.¹¹ had found that there was a good linear correlation between Hammett σ constants and $\nu(\text{C}=\text{O})$ for substituted acetophenones in dilute carbon tetrachloride solution. Thus $\nu(\text{C}=\text{O})$ for $p\text{-H}_2\text{N}$, $p\text{-HO}$, $p\text{-H}$, $p\text{-Br}$, and $p\text{-O}_2\text{N}$ acetophenone was 1677, 1686, 1692, 1693, and 1702 cm^{-1} , respectively. On this basis, one may estimate the σ constant for the $p\text{-CCO}_3(\text{CO})_9$ substituent to be about -0.35 . That this substituent is an electron-donor with respect to a para-carbonyl group in an attached benzene ring is not unexpected since charge delocalization into the cluster via V should be possible.



Experimental Section

General Comments. Unless otherwise indicated, reactions were carried out in an apparatus which was assembled, dried by evacuation, and refilled with nitrogen. Purification of reagents prior to use is indicated in the detailed experimental procedure of each reaction type. Where no indication is given, reagent grade chemicals were used as purchased. Reactive liquids and specially purified

solvents were weighed and transferred via syringe or cannula. Reactive solids (AlCl_3) were transferred to small vials and weighed by difference.

The progress of reactions was often indicated by color changes and was routinely monitored by thin layer chromatography (TLC) using Eastman silica gel TLC sheet, Type 6061, and hexane, hexane/methylene chloride (70/30), methylene chloride, and benzene as eluents. The intense colors of the compounds involved made further treatment unnecessary. Mixtures of reaction products were in general separated by column chromatography using hexane, hexane/methylene chloride (70/30), methylene chloride, and benzene as eluents. A standard column was prepared in the following manner. Silicic acid (300–400 cm^3) was placed in a 1-l. beaker with magnetic stirring bar. The eluent was added to bring the total volume to between 700 and 800 ml. The slurry was magnetically stirred for approximately 10 min and then quickly poured into a column previously prepared by placing approximately $\frac{1}{4}$ to $\frac{1}{2}$ in. of sand over the frit and covering this with the eluent to a depth of approximately 4 in. After the slurry had settled for a brief time, the stopcock was opened and the silicic acid was allowed to settle until further packing ceased. With a full column of solvent over the packed silicic acid, a second layer of sand was gently added. Removal of the solvent to the level of the sand afforded a column ready for use.

For separations of samples with widely different retention times, a filtration chromatography technique was used. A slurry of silicic acid (15–30 cm^3) in the eluting solvent (50–100 ml) was prepared as before and poured into a filter funnel with glass frit. Application of aspirator vacuum using a filter flask provided a packed bed of silicic acid for the filtration. The sample was then poured onto the filter pad and washed with hexane until the higher R_f material had completely eluted. Washing the filter bed with methylene chloride then eluted the lower R_f material.

Samples recovered from chromatographic separations are reported in the experimental procedure in the order in which they eluted.

Solid samples were in general isolated by sublimation (0.02–0.07 mm; 50–60°) or recrystallization. Recrystallized samples were dried under full vacuum for a period of from 10 min to several hours, depending principally on the solvent used for recrystallization. Samples for elemental analysis were prepared by triply recrystallizing and drying under vacuum or by triply subliming in an O-ring-type sublimation apparatus.

Infrared spectra were recorded using a Perkin-Elmer Model 337, 237B, 257, or 457A infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates T-60 spectrometer using concentrated samples. Chemical shifts are expressed in δ units: parts per million downfield from tetramethylsilane. Tetramethylsilane, methylene chloride, and chloroform were used as internal standards.

The preparation of the $\text{ArCCO}_3(\text{CO})_9$ complexes used in this work has been described in a previous paper of this series.⁴

Friedel-Crafts Acylation of Benzylidynetricobalt Nonacarbonyl Complexes. The acetylation of *o*-methylbenzylidynetricobalt nonacarbonyl is described to illustrate the procedure used.

A 200-ml, three-necked flask, equipped with nitrogen inlet, addition funnel, and magnetic stirring assembly, was dried by evacuation and refilled with nitrogen. Into the addition funnel were placed 1.45 g (2.72 mmol) of *o*-methylbenzylidynetricobalt nonacarbonyl and 40 ml of methylene chloride (reagent). The system then was agitated to effect solution. Into the reaction flask were placed 0.456 g (3.42 mmol) of aluminum chloride, 30 ml of methylene chloride (reagent), and (via syringe) 0.33 g (4.2 mmol) of acetyl chloride (distilled). The solution was stirred for 1 min, and the contents of the addition funnel were added as rapidly as possible. Immediate TLC analysis showed that only a trace of the starting cobalt compound was present. The red-brown solution immediately was poured into 200 ml of ice cold dilute, aqueous hydrochloric acid. The organic layer was isolated, dried, and filtered, and the solvent was removed. The remaining red-brown solid was chromatographed on silicic acid with hexane/methylene chloride (70/30) as eluent. The major fraction was isolated and recrystallized from hexane to yield 1.38 g (88%) of *p*-acetyl-*o*-methylbenzylidynetricobalt nonacarbonyl as black nuggets, mp 92–94° dec.

Table I lists the other reactions which were carried out, and characterizing data for the products are found in Table III.

The acetylation of *p*-methylbenzylidynetricobalt nonacarbonyl was attempted under more forcing conditions.

i. Using the standard apparatus and procedure, 0.81 g (1.5 mmol) of *p*-methylbenzylidynetricobalt nonacarbonyl was treated with 0.24 g (1.8 mmol) of aluminum chloride and 0.135 g (1.7 mmol) of acetyl chloride in methylene chloride. TLC analysis indicated that no reaction had occurred after mixing, so a reflux condenser was added to the apparatus and the system was heated at reflux for 23 hr. After it had been cooled, the mixture was worked-up in the standard manner and chromatographed on silicic acid with hexane eluent. The single brown product was purified by recrystallization from hexane and identified as starting *p*-methylbenzylidynetricobalt nonacarbonyl, by comparison of its ir spectrum to that of an authentic sample, 0.895 g (60%), mp 106–107°.

ii. Using the standard apparatus and procedure, 0.60 g (1.12 mmol) of *p*-methylbenzylidynetricobalt nonacarbonyl was treated with 0.133 g (1.0 mmol) of aluminum chloride and 0.110 g (1.4 mmol) of acetyl chloride in 75 ml of nitrobenzene (reagent). TLC analysis immediately after mixing showed that reaction had not occurred, so the flask was fitted with a reflux condenser and the reaction mixture was warmed at ca. 80° for 3 days. The solution was cooled and worked-up in the normal manner. The majority of the nitrobenzene was removed by vacuum distillation (0.2 mm, 40°). The sample then was diluted with hexane and chromatographed on silicic acid with hexane eluent. The product was recrystallized from hexane to yield 0.14 g (24%) of starting *p*-methylbenzylidynetricobalt nonacarbonyl. The sample had an ir spectrum identical with that of an authentic sample, mp 104–106°.

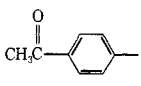
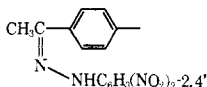
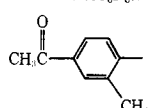
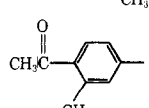
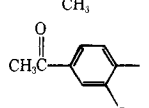
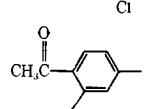
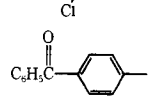
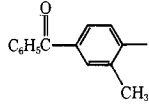
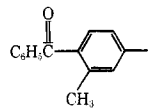
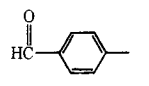
Friedel-Crafts Formylation of Benzylidynetricobalt Nonacarbonyl. To a cooled slurry of 1.04 g (2 mmol) of $\text{C}_6\text{H}_5\text{CCO}_3(\text{CO})_9$ and 0.267 g of AlCl_3 in 25 ml of dichloromethane was added dropwise a solution of 0.252 g (2.2 mmol) of $\text{CH}_3\text{OCHCl}_2$. The reaction mixture was stirred at ice bath temperature for 15 min, then at room temperature for 2 hr. The mixture was poured into ice water and extracted with dichloromethane. The combined organic extracts were dried (MgSO_4) and evaporated. The semisolid residue was chromatographed (silicic acid, CH_2Cl_2) to yield 0.22 g (20%) of brown solid, homogeneous by TLC, which was recrystallized from hexane to provide a black solid, mp 127–128°, for analysis, which was identified as $(\text{OC})_9\text{Co}_3\text{CC}_6\text{H}_4\text{CHO}$ -*p*.

Reaction of Acylated Benzylidynetricobalt Nonacarbonyls with Ceric Ammonium Nitrate. The oxidation of *p*-acetylbenzylidynetricobalt nonacarbonyl is described as an example of the procedure used.

A 100-ml, three-necked flask, equipped with nitrogen inlet and magnetic stirring assembly, was flushed with nitrogen. The flask was charged with 0.815 g (1.45 mmol) of *p*-acetylbenzylidynetricobalt nonacarbonyl, 75 ml of acetone (reagent), and 10 ml of distilled water. Solid ceric ammonium nitrate, 8.2 g (14.5 mmol), was added into the stirred solution in small portions. Gas evolution was evident with the addition of each portion of ceric salt. When the addition was complete, the intense red-brown color had dissipated and only a faint orange color remained. After the mixture had been stirred for a few minutes, the solvent was removed, and methylene chloride and water were added. The methylene chloride layer was isolated and combined with an ethyl acetate wash of the water layer. The solvents were removed, and the sample was dissolved in methylene chloride and extracted with dilute aqueous sodium hydroxide. The aqueous layer was washed with methylene chloride, separated, and acidified. The acid product then was extracted with ethyl acetate and recrystallized from ethanol–water to yield 0.164 g (83%) of *p*-acetylbenzoic acid, mp 208–210°, which was identified by comparison of its ir spectrum with that of an authentic sample, lit.¹² mp 209–210°. (*o*-Acetylbenzoic acid has mp 114–117°¹³ and *m*-acetylbenzoic acid has mp 165°.¹⁴)

Treatment of this acid with an excess of ethereal diazomethane gave methyl *p*-acetylbenzoate, mp 93.5–94° (lit.¹² mp 95–95.5°). (Methyl *o*-acetylbenzoate is a liquid, bp 114° (1 mm),¹⁵ and methyl *m*-acetylbenzoate has mp 39–39.5°.¹⁶) Our methyl acetylbenzoate showed an undepressed mixture melting point with authentic methyl *p*-acetylbenzoate. GLC analysis of a *N,N*-dimethylformamide (DMF) solution of our methyl ester (DC-200 silicone oil at 190°) showed the presence of only one component, retention time 5.8 min. Authentic methyl *p*-acetylbenzoate had the identical retention time, while that of the ortho isomer was 4.6 min.

Table III. New $\text{ArCCo}_3(\text{CO})_9$ Compounds Prepared

Ar^a	Mp, °C	Anal., found (calcd)		NMR, δ (ppm)	$\nu(\text{C}=\text{O})$, cm^{-1}
		Carbon, %	Hydrogen, %		
	107–108	38.63 (38.60)	1.25 (1.26)	2.55 (s, 3, CH_3), 7.4 (d, $J = 8$ Hz, 2), 7.9 (d, $J = 8$ Hz, 2)	1685
	>300	38.88 (38.94)	1.68 (1.50)		
	92–94 dec	39.88 (39.75)	1.62 (1.58)	2.52 (s, 6, CH_3), 7.70 (s, 3)	1676
	103–105	39.78 (39.75)	1.74 (1.58)	2.58 (s, 3, CH_3), 2.61 (s, 3, CH_3), 7.26–7.8 (m, 3)	1683
	79–80	36.41 (36.36)	1.19 (1.02) ^d	2.52 (s, 3, CH_3), 7.65–8.02 (m, 3)	1690
	73–75	36.50 (36.36)	1.09 (1.02) ^e	2.68 (s, 3, CH_3), 7.18–7.69 (m, 3)	1685
	173–174	44.55 (44.38)	1.76 (1.46)	7.0–8.0 (m, 9)	1660
	178–180	45.44 (45.31)	1.92 (1.74)	2.52 (s, 3, CH_3), 7.08–7.92 (m, 8)	1647
	163–164	45.22 (45.31)	1.84 (1.74)	2.45 (s, 3, CH_3), 7.2–7.95 (m, 8)	1663
	127–128	37.62 (37.66)	1.14 (0.94)	7.6 ^f (d, $J = 8.5$ Hz, 2), 7.8 (d, $J = 8.5$ Hz, 2), 10.0 (s, 1, CHO)	1700

^a All of these $\text{ArCCo}_3(\text{CO})_9$ are deeply colored (brown to black) and usually are isolated in the form of black nuggets or needles on recrystallization from hexane. ^b In CCl_4 solution unless otherwise noted. ^c Prepared in 39% yield by reaction with 2,4-dinitrophenylhydrazine in ethanol in the presence of a small amount of HCl. ^d % Cl: found, 6.04; calcd, 5.96. ^e % Cl: found, 6.17; calcd, 5.96. ^f In CDCl_3 .

Similar oxidation of the acetylation product of *o*-methylbenzylidynettricobalt nonacarbonyl gave *p*-acetyl-*o*-toluic acid: mp 128–130°, in 78% yield; NMR ($\text{DMSO-}d_6$, CH_2Cl_2) δ 2.63 (s, 6 H, CH_3 protons) and 7.93 ppm (s, 3 H, aromatic H).

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_3$: C, 67.41; H, 5.66. Found: C, 67.49; H, 5.76.

The acetylation product of *m*-methylbenzylidynettricobalt nonacarbonyl was oxidized in this way to give *p*-acetyl-*m*-toluic acid: mp 147–148°, in 51% yield; NMR ($\text{DMSO-}d_6$, CH_2Cl_2) δ 2.02 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), and 7.38 ppm (s, 3 H, aromatic).

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_3$: C, 67.41; H, 5.66. Found: C, 67.32; H, 5.81.

The reaction of the benzoylation product of benzylidynettricobalt nonacarbonyl with ceric ammonium nitrate gave crude *p*-benzoylbenzoic acid, mp 188–191°, in 79% yield (lit. mp: ortho isomer, 127°;¹³ meta, 162.5–163°;¹⁷ para, 195–195.5°¹⁷). The crude acid when methylated with ethereal diazomethane gave methyl *p*-benzoylbenzoate, mp 107–108° (lit mp: ortho isomer, 51.2°;¹⁸ meta, 62°;¹⁹ para, 107°²⁰). GLC examination (4 ft. UC W98 silicon column at 215°) of the methyl ester obtained and of authentic samples of methyl *o*- and *p*-benzoylbenzoate also served to demonstrate the identity of our product as the para isomer.

Reaction of Acylated Benzylidynettricobalt Nonacarbonyls with Bromine in Aqueous Sodium Hydroxide. The reaction of *p*-acetylbenzylidynettricobalt nonacarbonyl is described to illustrate the procedure used.

A 200-ml, three-necked flask equipped with magnetic stirring assembly, nitrogen inlet, and addition funnel was flushed with ni-

trogen. Into the addition funnel were placed 0.6 g (1.07 mmol) of *p*-acetylbenzylidynettricobalt nonacarbonyl and 50 ml of tetrahydrofuran (reagent). The reaction flask was charged with 50 ml of tetrahydrofuran, 10 ml of water, 6 g (37.5 mmol) of bromine, and 4 g (100 mmol) of sodium hydroxide. The contents of the addition funnel were added dropwise with stirring. Upon completion of addition, the solution was stirred for 1 hr. The reaction mixture then was filtered through a bed of Celite. Water then was added, and the layers were separated and washed twice with methylene chloride. The aqueous layer was acidified and filtered to yield 0.134 g (81%) of terephthalic acid. The sample did not melt but had an ir spectrum identical with that of an authentic sample (Sadtler No. 9178).

Similar oxidation of *p*-acetyl-*o*-methylbenzylidynettricobalt nonacarbonyl gave methylterephthalic acid in 35% yield, whose ir spectrum was in accord with the assigned structure. Oxidation of *p*-acetyl-*m*-methylbenzylidynettricobalt nonacarbonyl using this procedure gave methylterephthalic acid in 63% yield, while chloroterephthalic acid was obtained in 34% yield by such oxidation of *p*-acetyl-*m*-chlorobenzylidynettricobalt nonacarbonyl. The ir spectrum of the latter product agreed with that of an authentic sample (Sadtler No. 16400).

Oxidation of Acylated Benzoic and Toluic Acids with Bromine in Sodium Hydroxide. In view of the poor yields obtained in the direct oxidation of the acylated benzylidynettricobalt nonacarbonyls using $\text{Br}_2\text{-NaOH}$, the acylated benzoic and toluic acids resulting from the ceric ammonium nitrate oxidation of the acylated cluster complexes were oxidized to the terephthalic acids and these were

Table IV. Competition Experiments with Ferrocene

PhCCO ₃ (CO) ₉ (mmol)	Ferrocene (mmol)	CH ₃ COCl (mmol)	AlCl ₃ (mmol)	Reaction time (min)	Products (% yield)		<i>k</i> _{rel} ^a
					<i>p</i> -AcC ₆ H ₄ CCO ₃ - (CO) ₉	Acetylferrocene	
10	10	1	5	10	8.8	85.6	1.0
10	10	1	2	3	8.3	91.0	0.9
10	10	1	2	10	10.3	85.6	1.2
10	5	1	2	30	16.0	75.3	1.06

$$^a k_{\text{rel}} = k(\text{PhCCO}_3(\text{CO})_9)/k(\text{ferrocene}).$$

converted to the methyl esters. The procedure used in the case of *p*-acetylbenzoic acid is described in detail.

A 100-ml, three-necked flask with nitrogen inlet, stirring assembly, and addition funnel was flushed with nitrogen. Into the addition funnel were placed 0.155 g (0.95 mmol) of *p*-acetylbenzoic acid, 50 ml of distilled water, and one sodium hydroxide pellet. The reaction flask was charged with 50 ml of distilled water, 0.6 g (15 mmol) of sodium hydroxide, and 0.3 ml (0.8 g, 5 mmol) of bromine. The contents of the addition funnel were added dropwise. Upon completion of addition the solution was washed with hexane, separated, and acidified. Filtration yielded 0.142 g (90%) of terephthalic acid (ir spectrum vs. Sadtler No. 9178).

Similar oxidation of *p*-acetyl-*o*-toluic acid gave methylterephthalic acid in 82% yield (ir spectrum) which was methylated with diazomethane to produce dimethyl methylterephthalate, mp 71–73°, in 94% yield (lit.²¹ mp 73°). The ir spectrum was identical with that of an authentic sample (Sadtler No. 16390). The oxidation of *p*-acetyl-*m*-toluic acid by this method also gave methylterephthalic acid (75% yield), whose methylation with diazomethane resulted in dimethyl methylterephthalate, mp 70–72°, in 98% yield.

Competition Reactions. (a) Between Benzylidynetricobalt Nonacarbonyl and Ferrocene. A 300 ml, three-necked flask equipped with a magnetic stirring unit, a nitrogen inlet and outlet, and an addition funnel was oven-dried, flushed with nitrogen, and charged with 1.86 g (10.0 mmol) of ferrocene and 5.18 g (10.0 mmol) of C₆H₅CCO₃(CO)₉. Dichloromethane (50 ml) was added and the mixture was stirred for 15 min. The addition funnel was charged with 0.27 g (2.0 mmol) of aluminum chloride, 0.079 g (1.0 mmol) of acetyl chloride, and 50 ml of dichloromethane. This mixture was stirred thoroughly and added to the flask contents. The resulting mixture was stirred for 10 min at room temperature and then was poured into 400 ml of water. The organic layer was separated and the aqueous layer extracted with three 200-ml portions of dichloromethane. The combined organic phase was dried and evaporated at reduced pressure. Column chromatography was used in separation of products (Mallinckrodt silicic acid, reagent grade, 100 mesh). Elution with hexane removed both starting compounds as a mixture. Subsequent elution with 1:1 hexane-dichloromethane gave *p*-acetylbenzylidynetricobalt nonacarbonyl (0.058 g, 10.3%), identified by its melting point and ir spectrum. Finally, elution with dichloromethane gave monoacetylferrocene (0.19 g, 85.6%), identified by its infrared spectrum, melting point, and mixture melting point with authentic material (Alfa/Ventron). The relative rate constant was calculated by the method of Doering and Henderson,²² using the equation

$$k_{\text{rel}} = \frac{k(\text{PhCCO}_3(\text{CO})_9)}{k_X} = \frac{P_{\text{Co}} I_X}{P_X I_{\text{Co}}}$$

where *P*_{Co} and *P*_X are the millimoles of product derived from the cobalt complex and from its competitor, respectively, and *I*_{Co} and *I*_X represent the initial millimoles of the starting compounds. In the case of ferrocene, this value of 10.0 mmol must be multiplied by 10 since there are ten equal sites of initial reactivity in this molecule. The four experiments carried out with ferrocene are summarized in Table IV.

(b) Between Benzylidynetricobalt Nonacarbonyl and *N,N*-Dimethylaniline. This reaction was carried out in the same manner and on the same scale. However, *p*-acetyl-*N,N*-dimethylaniline and *p*-acetylbenzylidynetricobalt nonacarbonyl could not be separated by column chromatography, although hexane elution sepa-

rated the unconverted starting materials. Therefore, *p*-acetyl-*N,N*-dimethylaniline was converted to its methiodide derivative.

A 300-ml, round-bottomed flask fitted with a nitrogen inlet and outlet and a magnetic stirring unit was evacuated, flame-dried, and flushed with nitrogen. It then was charged with combined acetylated products from this experiment, 50 ml of dichloromethane and 1 ml of iodomethane. This mixture was stirred overnight and then was filtered. The white solid was washed with dichloromethane and dried to give 0.12 g (38.9%) of *p*-acetyl-*N,N,N*-trimethylanilinium iodide, mp 210–212° dec. The combined dichloromethane solutions were evaporated under reduced pressure to give 0.29 g (52.1%) of pure (melting point and ir) *p*-acetylbenzylidynetricobalt nonacarbonyl.

An authentic sample of *p*-acetyl-*N,N*-dimethylaniline was prepared by standard Friedel-Crafts acetylation of *N,N*-dimethylaniline in 96% yield (ir spectrum identical with that of authentic material, Sadtler spectrum No. 38174). Treatment with iodomethane as described above gave authentic *p*-acetyl-*N,N,N*-trimethylanilinium iodide, mp 210–212° dec, whose mixture melting point with the product above was undepressed.

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- (10) In this connection, we must take exception to the erroneous statement by R. Dolby and B. H. Robinson (*J. Chem. Soc., Dalton Trans.*, 2046 (1972)) concerning such reactions: "Moreover, PhCCO₃(CO)₉ undergoes Friedel-Crafts reactions but yields are low and reactions slow", referring to our preliminary communication² and unpublished results of Dolby. It is clear from our initial publication² that excellent yields can be obtained and that the reactions are rapid, results which have been amplified in the present work.
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