# Organocobalt Cluster Complexes. XVIII. Friedel–Crafts Acylation of Diarylacetylenedicobalt Hexacarbonyl Complexes. The Dicobalt Hexacarbonyl Unit as a Protecting Group for the Acetylene Function[1,2]

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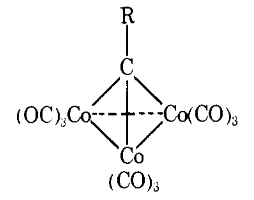
**Abstract:** Friedel–Crafts acetylation of diarylacetylenedicobalt hexacarbonyl proceeds readily and in high yield. Introduction of the first acetyl substituent is a very rapid process, but the second acetyl group is introduced more slowly. In all cases, para substitution was observed, presumably because of steric factors. Deactivation of aluminum chloride by its coordination at the newly formed ketone function caused some difficulties in some cases. Competition experiments showed diphenylacetylenedicobalt hexacarbonyl to be somewhat less reactive toward $CH_3COCl-AlCl_3$ than anisole. The $Co_2(CO)_6$ unit serves as a protecting group for the $C\equiv C$ function; diarylacetylenes cannot be acetylated directly, but their $Co_2(CO)_6$ complexes can. Oxidation of the acetylated complex with ceric ammonium nitrate releases the acetylated acetylene in good yield.

In the previous paper of this series,[1] we reported the facile acylation of benzylidynetricobalt nonacarbonyl complexes of type 1. The fact that these reactions proceeded so rapidly and in high yield was attributed to the high degree of stabilization imparted to intermediates such as 2 by delocalization of the positive charge into the $CCo_3(CO)_9$ cluster substituent.



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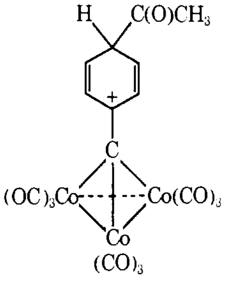


2

A class of organocobalt complexes structurally related to the alkylidynetricobalt nonacarbonyls is that of the acetylenedicobalt hexacarbonyls. In these the central core of two carbon and two cobalt atoms is arranged in a roughly tetrahedral fashion (Figure 1).[3] These complexes are formed readily by the reaction of the respective acetylene with dicobalt octacarbonyl.[4] They are best understood in terms of the interaction of the acetylene in its first excited state with the dicobalt hexacarbonyl unit.[5] They are less robust than the alkylidynetricobalt nonacarbonyls, decomposing noticeably when heated to 60–75°. At the time we began this research, the study of their chemistry had been limited to ligand substitution processes, the protonation–rearrangement sequence which converts terminal acetylenedicobalt hexacarbonyls to alkylidynetricobalt nonacarbonyls [$(RC_2H)Co_2(CO)_6 \rightarrow RCH_2CCo_3(CO)_9$][6] and reactions with acetylenes at higher temperatures to give other organocobalt complexes and organic products such as benzenes and cyclopentadienone derivatives.[7] Like the alkylidynetricobalt nonacarbonyls, the acetylenedicobalt hexacarbonyl complexes are deeply colored crystalline solids or oils, depending on the substituents on the carbon atoms.[8]

The physical and structural similarities between these two classes of organocobalt carbonyl complexes suggested to us that there might be some similarities in their chemical reactivity. For instance, if $PhCCo_3(CO)_9$ can be acylated readily by the Friedel–Crafts procedure, then the mono- and diphenylacetylenedicobalt hexacarbonyl complexes also might be capable of undergoing such nuclear acylation. This was an intriguing possibility since nuclear acylation of diphenylacetylene itself cannot be accomplished because of the faster competing attack of the $RCO^+$ species at the $C\equiv C$ bond. Such Friedel–Crafts acylation of arylacetylenedicobalt hexacarbonyl complexes would be of synthetic utility only if the acetylene could be released from its complex after the functionalization reaction.

## Results and Discussion

Initial experiments showed that Friedel–Crafts acylation of diphenylacetylenedicobalt hexacarbonyl indeed could be accomplished. Thus, addition of this complex to 2 mol equiv of $CH_3COCl-AlCl_3$ in dichloromethane at 0° gave, after a 2-hr reaction time at room temperature, a mixture of a monoacetylated (51% yield) and a diacetylated (36% yield) product. A similar reaction carried out with 5 mol equiv of $CH_3COCl-AlCl_3$ per equivalent of the acetylene complex gave only the diacetylated product. The NMR spectra of the products indicated that only para acetylation had occurred.

In this particular case, the NMR spectra of the products were definitive. This was not the case with some of the other acetylated diarylacetylenedicobalt hexacarbonyls and, with these, the position of acetylation was determined by chemical degradation. It was found that ceric ammonium nitrate oxidation of acetylenedicobalt hexacarbonyls regenerated the coordinated acetylene in high (generally >85%) yield while converting the $Co_2(CO)_6$ unit to cobalt salts and carbon monoxide (Scheme I). The acetylated acetylenes pre-

Scheme I. Degradation of Diarylacetylenedicobalt Hexacarbonyl Complexes

$$(ArC_2Ar')Co_2(CO)_6 \xrightarrow{Ce(NH_4)_2(NO_3)_6} ArC\equiv CAr' + \text{Co salts} + 6CO$$

$$\downarrow KMnO_4 \text{ or } KMnO_4\text{-}NaIO_4$$

$$ArCO_2H + Ar'CO_2H$$

$$\downarrow CH_2N_2$$

$$ArCO_2CH_3 + Ar'CO_2CH_3$$

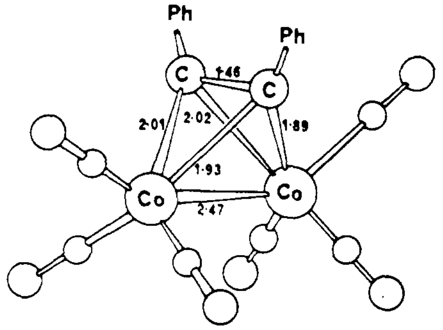


Figure 1. Structure of diarylacetylenedicobalt hexacarbonyl complexes.

pared in this manner during the course of this work were oxidized to the corresponding benzoic acids with potassium permanganate in aqueous acetone or, if this procedure failed, by sequential treatment with potassium permanganate and sodium periodate. In the case of symmetrically substituted acetylenes, it sufficed to isolate and identify the substituted benzoic acids produced. Oxidation of the unsymmetrically substituted acetylenes, on the other hand, gave two acids. These were converted to their methyl esters which were analyzed and separated by gas chromatography (GLC).

In order to obtain more information concerning this novel Friedel–Crafts reaction, a number of substituted diphenylacetylenedicobalt hexacarbonyl complexes was prepared and treated with the acetyl chloride–aluminum chloride reagent. The results obtained in these reactions depended very much on how the reactions were carried out. Initially, the acetylenedicobalt hexacarbonyl was added to the 1:1 $CH_3COCl–AlCl_3$ mixture in dichloromethane. The results of these experiments are presented in Table I. Subsequently, some reactions were carried out in which the $CH_3COCl–AlCl_3$ mixture was added to the acetylene complex instead (the last three entries in Table I).

An examination of the results shown in Table I leads to the following conclusions. In every case only para acetylation was observed, no matter what other substituents (electron-releasing, ortho,para directing methyl or electron-attracting chlorine) were present. If the para position were blocked, acetylation did not occur at all; attempts to force it merely resulted in decomposition of the complex. This parallels the observations made in the acetylation of benzylidynetricobalt nonacarbonyl complexes[1] and indicates that, in the diarylacetylenedicobalt hexacarbonyl complexes, also steric factors are quite important. Friedel–Crafts acetylation of the three unsymmetrically substituted acetylene complexes yielded only a single monoacetylated product in each case. As expected for electrophilic aromatic substitution, a methyl group activates the ring, while a chlorine substituent has a deactivating effect.

The reactions in Table I would be more useful for preparative purposes if they could be made to proceed more cleanly, that is, if the 1:1 reactions would give exclusively the monoacetylation product and the 2:1 reactions only the diacetylation product. The change in mode of addition to one in which the $CH_3COCl–AlCl_3$ mixture was added to the acetylene complex (Table I) in the case of the 1:1 reactions resulted in a greater relative proportion of the monoacetylation product, a fact which suggests that the rate of introduction of the first acetyl group is faster than that of the second. With further investigation, conditions were found for carrying out diacetylation in high yield in most cases and monoacetylation in high yield in some. More importantly, the results of these experiments provided a better picture of the interactions of the $CH_3COCl–AlCl_3$ reagent with the acetylene complexes. The experiments carried out are summarized in Table II. It was confirmed that the introduction of the first acetyl group is an extremely rapid process. As noted in the seventh entry in Table II, when the reaction mixture work-up followed immediately after the $CH_3COCl–AlCl_3$ reagent solution had been added to diphenylacetylenedicobalt hexacarbonyl, the yield of the monoacetyl product obtained was 86%. The rate of introduction of the second acetyl group is slower. In the case of the diphenylacetylene and the two chlorine-containing diphenylacetylene complexes, this rate is sufficiently slower so that quite clean monosubstitution can be effected with a 1:1 reagent ratio. The rate of introduction of the second acetyl group is to some extent competitive with that of the first in the Friedel–Crafts acetylation of the two ditolylacetylenes, and a mixture of mono- and diacetylated products, in which the former predominates, was obtained when a 1:1 reagent ratio was used.

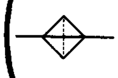
The amount of aluminum chloride used is a critical factor and can determine the products isolated. Thus, in one experiment, a mixture of 4 mol equiv of acetyl chloride and 5 mol equiv of aluminum chloride was added to 2 mol equiv of diphenylacetylenedicobalt hexacarbonyl in dichloromethane. Examination of the reaction mixture by thin layer chromatography (TLC) immediately after mixing showed that only the monoacetylated complex was present. Stirring was continued, and the progress of the reaction was followed by TLC. Even after the reaction mixture had been stirred for 10 hr, a mixture of the mono- and diacetylated products was present. However, when another 4 mol equiv of $AlCl_3$ was added, complete conversion to the diacetyl derivative was effected within 20 min. In another reaction with diphenylacetylenedicobalt hexacarbonyl in which such a larger excess of $AlCl_3$ was used, complete reaction to form the diacetyl compound was accomplished within 10–15 min after the reactants had been mixed.

Observations relating to the stability of acetylenedicobalt hexacarbonyl complexes in the presence of aluminum chloride are of interest in this connection. During the course of this work, it was discovered that aluminum chloride can cause decomposition of diarylacetylenedicobalt hexacarbonyl complexes. Acetylation of the benzene nucleus appears to hinder the decomposition process since the diacetylated complexes are quite stable toward aluminum chloride, the monoacetylated complexes somewhat less so, while the action of a fivefold excess of aluminum chloride on diphenylacetylenedicobalt hexacarbonyl in dichloromethane resulted in decomposition of the acetylene complex within 10 min. This explains why starting acetylene complexes usually were not recovered in reactions where conversion to products was not complete. At this time it is not known whether the stabilizing effect of the acetyl substituents involves a simple electronic effect or if further complexation of aluminum chloride at the acetyl function is involved.

In order to obtain a better understanding of the Friedel–Crafts acetylation of diarylacetylenedicobalt hexacarbonyl complexes, an infrared study was undertaken. The spectral changes accompanying the addition of varying amounts of aluminum chloride to dichloromethane solutions of diphenylacetylenedicobalt hexacarbonyl and its monoacetyl derivative were examined. In addition, similar studies were carried out with benzylidynetricobalt nonacarbonyl and its *p*-acetyl derivative since somewhat similar observations had been made in the Friedel–Crafts acetylation of $ArCCo_3(CO)_9$ compounds.[1] The results of the studies with the benzylidynetricobalt nonacarbonyls are summarized in Figures 2 and 3.

Spectrum A in Figure 2 shows the ir spectrum of benzylidynetricobalt nonacarbonyl in dichloromethane (1 mmol in 50 ml) in the terminal carbonyl region. Another spectrum

Table I. Acetylation of Arylacetylenedicobalt Hexacarbonyl Complexes



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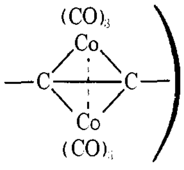

| Cobalt complex (mmol) | $\frac{\text{mmol of } CH_3COCl-AlCl_3}{\text{mmol of } (ArC_2Ar')Co_2(CO)_6}$ | Products (% yield[a]) |
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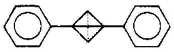
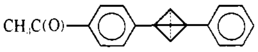
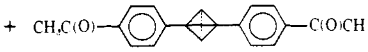
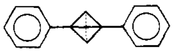
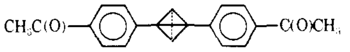
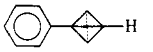
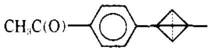
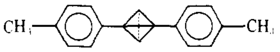
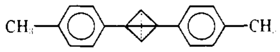
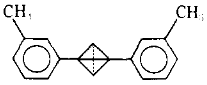
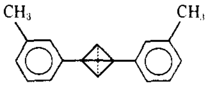
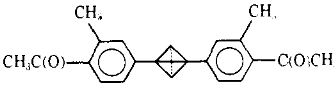
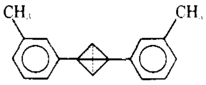
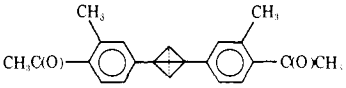
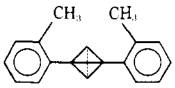
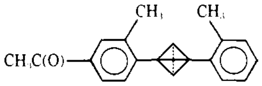
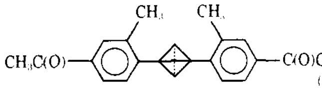
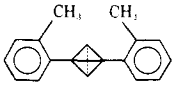
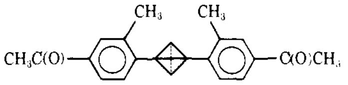
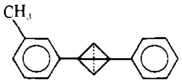
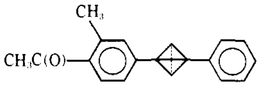
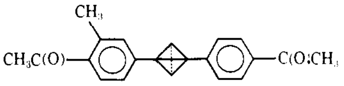
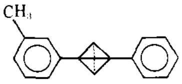
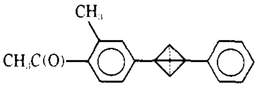
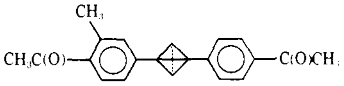
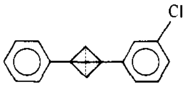
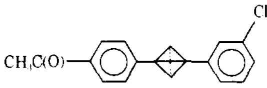
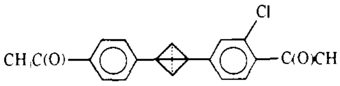
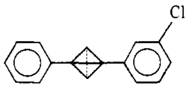
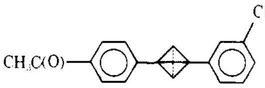
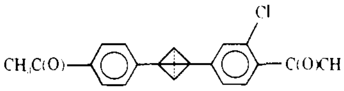
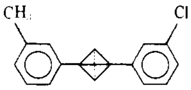
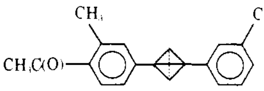
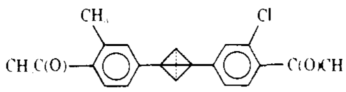
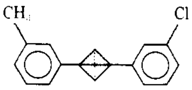
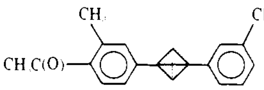
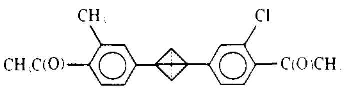
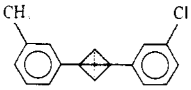
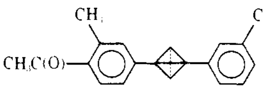
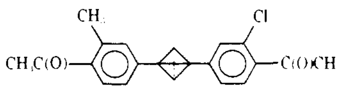
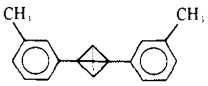
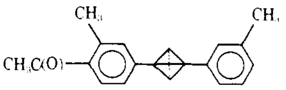
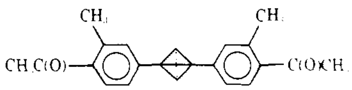
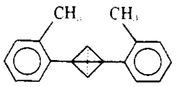
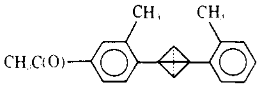
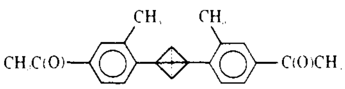
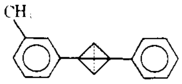
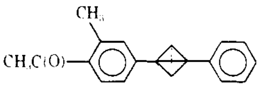
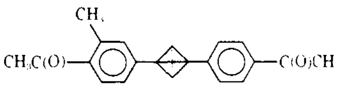
|  (2) | 2[b] |  (51) +  (36) |
|  (2) | 5[b] |  (62) |
|  (3.2) | 1[b] |  (51)[d] |
|  (1) | 1[b] | Starting material (99) |
|  (2) | 2[b] | Starting material (40); some decomposition |
|  (5) | 1[b] |  (45) +  (47) |
|  (10) | 2[b] |  (98) |
|  (2.2) | 1[b] |  (58) +  (15) |
|  (4) | 2[b] |  (92) |
|  (2.1) | 1[b] |  (50) +  (14) |
|  (3.1) | 2[b] |  (39) +  (50) |
|  (3.7) | 1[b] |  (75) +  (trace) |
|  (4) | 2[b] |  (85) +  (2) |
|  (5) | 1[b] |  (79) +  (5) |
|  (10) | 2[b] |  (63) +  (12) |
|  (4.4) | 5[b] |  (32) +  (17) |
|  (7.7) | 1[c] |  (62) +  (15) |
|  (1.8) | 1[c] |  (65) +  (12) |
|  (5) | 1[c] |  (68) +  (9) |

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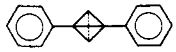
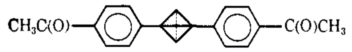
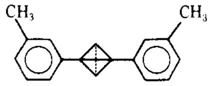
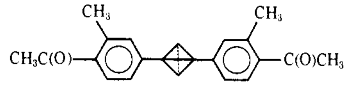
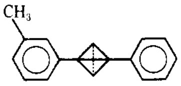
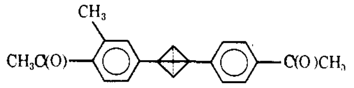
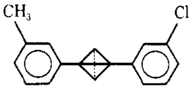
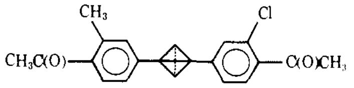
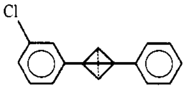
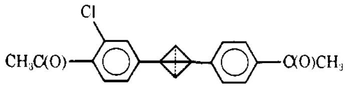
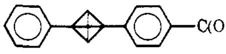
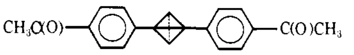
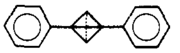
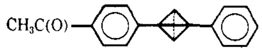
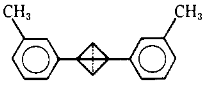
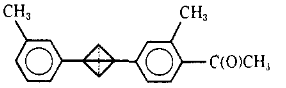
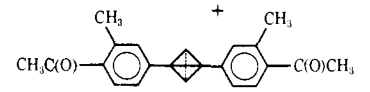
[a] Based on the acetylene complex. [b] The acetylenedicobalt hexacarbonyl was added to the $CH_3COCl-AlCl_3$ reagent in dichloromethane. [c] The $CH_3COCl-AlCl_3$ reagent was added to the acetylenedicobalt hexacarbonyl in dichloromethane. [d] Experiment by G. H. Williams.

Table II. Preferential Mono- and Diacetylation of Diarylacetylenedicobalt Hexacarbonyls

| Cobalt complex (mmol) | | $CH_3COCl$, mmol | $AlCl_3$, mmol | Reaction time, min | Products (% yield) |
|---|---|---|---|---|---|
|  | (2) | 4 | 8 | 15 |  (91) |
|  | (2) | 4 | 5 | 5 |  (94) |
|  | (1) | 2 | 10 | 10 |  (91) |
|  | (1) | 2 | 10 | 20 |  (88) |
|  | (2) | 4 | 10 | 40 |  (89) |
|  | (2) | 4 | 16[a] | 10 |  (97) |
|  | (1) | 1 | 2 | 0[b] |  (86) |
|  | (2) | 2 | 5 | 0[b] |  (60)<br>+<br> (16) |

[a] Ten millimoles of $AlCl_3$ stirred with the cobalt complex in $CH_2Cl_2$ for 30 min prior to addition of 4 mmol of $CH_3COCl$ and 6 mmol of $AlCl_3$ in $CH_2Cl_2$. [b] Work-up immediately after the $CH_3COCl-AlCl_3$ mixture had been added to the cobalt complex.

was obtained after 1 mmol of aluminum chloride had been added and the mixture had been stirred for a few minutes; only a minor change (a shoulder on the 2104 cm$^{-1}$ band) was observed. Spectrum B was recorded after a second millimole of aluminum chloride had been added. It can be seen that the 2104 cm$^{-1}$ band has begun to split. Addition of a third millimole of aluminum chloride was followed by the measurement of spectrum C: the splitting of the 2104 cm$^{-1}$ band is even more pronounced and other carbonyl bands show some broadening. Finally, spectrum D was obtained after another 5 mmol of aluminum chloride had been added; resolution was lost, and the entire collection of carbonyl absorptions was shifted to a frequency approximately 40 cm$^{-1}$ higher. The results of a similar set of experiments carried out with *p*-acetylbenzylidynetricobalt nonacarbonyl are shown in Figure 3. Spectrum A shows the ir spectrum of the pure cluster complex in dichloromethane (1 mmol in 50 ml). The acetyl group's C═O stretching frequency is observed at 1690 cm$^{-1}$. Upon addition of 0.5 mmol of aluminum chloride (spectrum B), the terminal carbonyl region remains unchanged, but the band at 1690 cm$^{-1}$ has decreased in intensity and two new absorptions have appeared at 1555 and 1513 cm$^{-1}$. Spectrum C was recorded after a total of 1 mmol of aluminum chloride had been added. The terminal carbonyl region still has not changed, but the 1690 cm$^{-1}$ absorption has almost disappeared and the bands at 1555 and 1513 cm$^{-1}$ have broadened. Another 4 mmol of aluminum chloride was added, and then spectrum D was obtained. The terminal carbonyl region now shows considerable splitting as well as a shift to higher frequency by 40-45 cm$^{-1}$. The bands which were at 1555 and 1513 cm$^{-1}$ in spectrum C have shifted to higher frequency by 30-35 cm$^{-1}$.

Similar studies were carried out with diphenylacetylenedicobalt hexacarbonyl and 4,4′-diacetyldiphenylacetylenedicobalt hexacarbonyl. As aluminum chloride was added to a dichloromethane solution of $(PhC_2Ph)Co_2(CO)_6$, slight splitting of some of the terminal carbonyl bands was observed. However, this splitting never became as sharp or as extensive as in the case of benzylidynetricobalt nonacarbonyl. Also, the bands never broadened or shifted position. However, these observations may be of no significance since aluminum chloride causes rapid decomposition of diphenylacetylenedicobalt nonacarbonyl. As the aluminum chloride was added, the cobalt complex solution became heterogeneous and began turning green, an indication of decomposition to inorganic cobalt halide. 4,4′-Diacetyldiphenylacetylenedicobalt hexacarbonyl, on the other hand, was stable to aluminum chloride. Its ketonic stretching frequency in dichloromethane solution (1 mmol in 50 ml) was observed at 1690 cm$^{-1}$. As aluminum chloride was added to this solution, there was no change in the terminal carbonyl region. The changes in the acetyl group's C═O absorption caused by addition of aluminum chloride were very similar to those seen in the case of benzylidynetricobalt nonacarbonyl. Addition of 1 mmol of aluminum chloride resulted in a decrease in the intensity of the 1690 cm$^{-1}$ band, and two new bands were observed at 1568 and 1530 cm$^{-1}$. The 1690 cm$^{-1}$ band disappeared completely when another millimole of aluminum chloride was added, and the two new bands broadened. Finally, after 6 mmol of aluminum chloride had been added, all bands had broadened, but no change in the terminal carbonyl region was perceptible.

These experiments with the acetylated products show quite clearly that aluminum chloride coordinates to the ketonic carbonyl function. This explains why a minimum of 1 mol of aluminum chloride per acetyl group introduced is required in these reactions. However, there also may be an in-

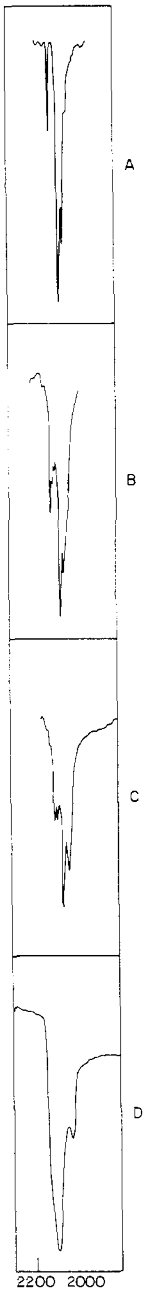


**Figure 2.** Effect of $AlCl_3$ on benzylidynetricobalt nonacarbonyl in dichloromethane: (A) 1 mmol of $C_6H_5CCo_3(CO)_9$ in 50 ml of $CH_2Cl_2$; (B) after addition of 2 mmol of $AlCl_3$; (C) after addition of a third mmol of $AlCl_3$; (D) after addition of another 5 mmol of $AlCl_3$.

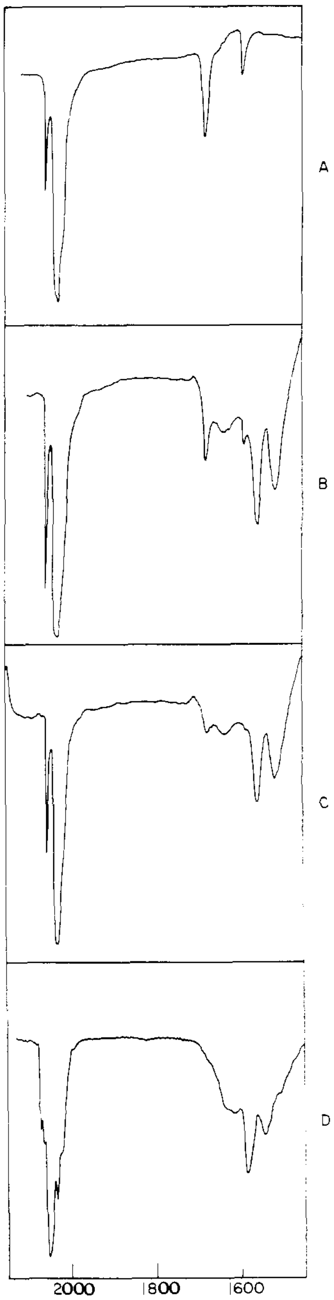
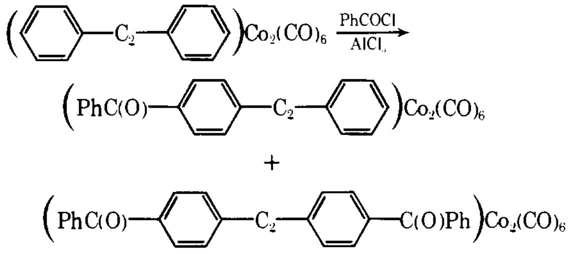


**Figure 3.** Effect of $AlCl_3$ on *p*-acetylbenzylidynetricobalt nonacarbonyl: (A) 1 mmol of $p$-$CH_3COC_6H_4CCo_3(CO)_9$ in 50 ml of $CH_2Cl_2$; (B) after addition of 0.5 mmol of $AlCl_3$; (C) after addition of another 0.5 mmol of $AlCl_3$; (D) after addition of another 4 mmol of $AlCl_3$.

teraction of aluminum chloride with these cobalt carbonyl clusters of another kind which, in the case of the nonacetylated complexes, ultimately leads to their decomposition. In this connection, the changes which occurred in the terminal carbonyl region in the infrared spectra of such cluster complexes as increasing amounts of aluminum chloride were added to their solutions in dichloromethane are to be noted. These, however, provide no useful information concerning possible cluster-$AlCl_3$ interactions. It is known that various polynuclear metal carbonyls will complex Lewis acids but, in most cases, it is the interaction of a bridging carbonyl group with the Lewis acid which is involved.[9]

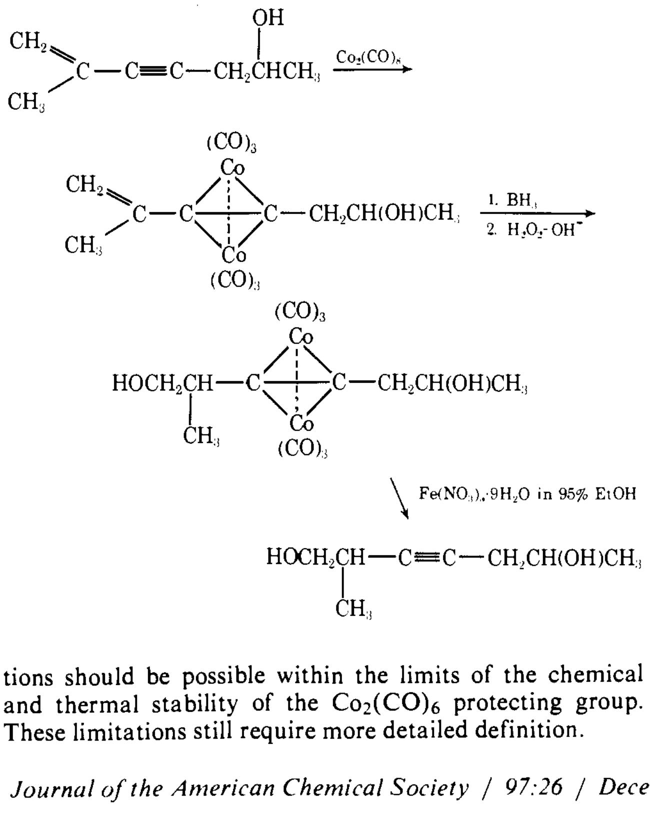
As we have noted, the introduction of the first acetyl group into a diarylacetylenedicobalt hexacarbonyl is a very rapid process, and so it was of interest to obtain more quantitative information concerning reaction rates. Benzylidynetricobalt nonacarbonyl (**1**, Ar = $C_6H_5$) had been shown to be exceedingly reactive toward $CH_3COCl$-$AlCl_3$ (slightly more so than *N,N*-dimethylaniline), and so an assessment of the reactivity of $(PhC_2Ph)Co_2(CO)_6$ relative to that of this related organocobalt complex was undertaken. A competition reaction in which 10 mmol each of $PhCCo_3(CO)_9$ and $(PhC_2Ph)Co_2(CO)_6$ were allowed to compete for 1 mmol of $CH_3COCl$-2 mmol of $AlCl_3$ in dichloromethane gave only the acetylation product (in 88% yield) of benzylidynetricobalt nonacarbonyl. A similar competition reaction between $(PhC_2Ph)Co_2(CO)_6$ and anisole gave both possible products, $(4\text{-}CH_3C(O)C_6H_4C_2C_6H_5)Co_2(CO)_6$ in 31% yield and *p*-methoxyacetophenone in 58% yield. No anisole-derived product was formed in a competition reaction between $PhCCo_3(CO)_9$ and anisole for $CH_3COCl$-$AlCl_3$[1] and so it is clear that, although the diphenylacetylenedicobalt hexacarbonyl is quite reactive, it is considerably less reactive than $PhCCo_3(CO)_9$. As we have indicated, the three cobalt atoms in the latter play an important role in stabilizing the positively charged intermediate **2** in its Friedel-Crafts acetylation.[1] In $(PhC_2Ph)Co_2(CO)_6$ there are only two cobalt atoms which can play such an assisting role in the stabilization of the analogous positively charged intermediate in its acetylation, and also, the other phenyl substituent may have a destabilizing effect. As a result, $(PhC_2Ph)Co_2(CO)_6$ is less reactive than $PhCCo_3(CO)_9$. In general agreement with this view is the demonstrated lesser stability of carbonium ions of type $[(RC_2CMe_2)Co_2(CO)_6]^+$,[10] compared with $[(OC)_9Co_3CRR']^+$.[11,12]

This work has shown that diarylacetylenedicobalt hexacarbonyl complexes can be acetylated in high yield with the acetyl chloride–aluminum chloride reagent. Benzoylation also is possible (eq 1) and trichloroacetylation failed. However, no attempt has been made to extend the scope of this reaction. No doubt, many other acid halides and, very likely, acid anhydrides can acylate such arylacetylene complexes. The acylated acetylene ligand can be recovered in high yield by oxidation of the acetylenedicobalt hexacarbonyl complex with ceric ammonium nitrate. Thus the $Co_2(CO)_6$ unit is an effective protecting group for the acetylene function in a molecule. Conversion of an acetylenic function to the $Co_2(CO)_6$ complex allows one to carry out chemical conversions elsewhere in the molecule which would not be possible in the presence of the reactive, uncomplexed C≡C bond. This principle was demonstrated first in our preliminary communication in 1970.[2] Later work by Nicholas and Pettit[13] provided another example of the application of this principle (Scheme II). Other applications should be possible within the limits of the chemical and thermal stability of the $Co_2(CO)_6$ protecting group. These limitations still require more detailed definition.



(1)

Scheme II



## Experimental Section

**General Comments.** Unless otherwise indicated, reactions were carried out in an apparatus which was assembled, flame-dried, evacuated, refilled with dry nitrogen. 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. Dichloromethane was distilled from $P_2O_5$ and stored under nitrogen. Acetyl chloride was distilled and stored under nitrogen. Dicobalt octacarbonyl was purchased from Strem Chemical Co. Column chromatography was used extensively for the separation of products. A 40 × 600 mm column fitted with a fritted glass disk and a Teflon stopcock was used. The columns were packed with Mallinckrodt silicic acid, reagent grade, 100 mesh. The progress of reactions usually was monitored by thin layer chromatography (TLC) using Eastman silica gel TLC sheet, type 6061, and hexane, hexane–dichloromethane (70:30), dichloromethane, and benzene as eluents. The intense colors of the acetylenedicobalt hexacarbonyl complexes made further treatment for visualization unnecessary. Infrared spectra were recorded using a Perkin-Elmer Model 457A infrared spectrophotometer and NMR spectra using a Varian Associates T60 spectrometer. Chemical shifts are reported in $\delta$ units, ppm downfield from internal tetramethylsilane.

**Preparation of Acetylenes.** Diphenylacetylene was purchased from Aldrich Chemical Co. Di-*p*-tolyl- and di-*m*-tolylacetylene were prepared by mercuric oxide oxidation of the appropriate dihydrazones.[14] The following acetylenes were prepared by reaction of $C_6H_5C{\equiv}CCu$ with the appropriately substituted iodobenzenes:[15] **3-chlorodiphenylacetylene**, mp 30–31°, in 53% yield (Anal. Calcd for $C_{14}H_9Cl$: C, 79.09; H, 4.27; Cl, 16.66. Found: C, 78.74; H, 4.34; Cl, 16.64); **3-methyldiphenylacetylene**, mp 30–31°, in 37% yield (Anal. Calcd for $C_{15}H_{12}$: C, 93.70; H, 6.29. Found: C, 93.50; H, 6.27), NMR ($CCl_4$) $\delta$ 2.31 (s, 3 H) and 6.9–7.5 ppm (m, 9 H). A third route to acetylenes used in this work is shown in eq 2–4; this procedure (eq 3) is based on the phosphorus ylide chemistry of Bestmann.[16] The preparation of 3-chloro-3′-methyldiphenylacetylene was accomplished as follows. A 1-l. three-necked flask equipped with a nitrogen inlet, a reflux condenser fitted with a nitrogen outlet, a stirrer, and an addition funnel was charged with 99.4 g (0.2 mol) of $m\text{-}CH_3C_6H_4CH_2PPh_3{}^+Br^-$ suspended in 200 ml of dry ether. *n*-Butyllithium in hexane (0.2 mol) was added dropwise, and the resulting mixture was stirred at room temperature for 4 hr. 3-Chlorobenzaldehyde (30.9 g, 0.22 mol, washed with 5% $Na_2CO_3$, dried and distilled) was added to the orange Wittig reagent solution, causing the color to be discharged and a white precipitate to form. Filtration was followed by evaporation of the filtrate. The residue was recrystallized three times from hexane to give 20.6 g (45%) of 3-chloro-3′-methylstilbene: mp 78–79.5°; NMR ($CCl_4$) $\delta$ 2.36 (s, 3 H), 6.89 (s, 2 H), and 6.8–7.5 ppm (m, 8 H). Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.59; H, 5.79; Cl, 15.47.

Treatment of 3-chloro-3′-methylstilbene (0.09 mol) with an equimolar amount of bromine in 200 ml of carbon tetrachloride, filtration to remove product, and recrystallization of the latter from dichloromethane gave 1-*m*-tolyl-2-*m*-chlorophenyl-1,2-dibromoethane in 48% yield. Dehydrobromination of this compound gave the desired acetylene using the following procedure. A 300-ml three-necked flask equipped with a reflux condenser and magnetic stirrer was charged with 30 g of potassium hydroxide and 50 ml of ethanol. Solution was effected by heating the mixture in an oil bath at 140°. The resulting solution was cooled slightly and the dibromide was added (43 mmol) in several portions, allowing the exotherm which resulted with each addition to subside before more was added. The reaction mixture was heated at reflux for 24 hr (oil bath at 135°) and then poured into 250 ml of cold water while still hot. The acetylene precipitated and was separated by filtration. Recrystallization from ethanol and sublimation at 60° (0.2 mmHg) gave 3-chloro-3′-methyldiphenylacetylene, mp 140–142°, in 96% yield; NMR ($CCl_4$) $\delta$ 2.39 (s, 3 H) and 7.0–7.6 ppm (m, 8 H). Anal. Calcd for $C_{15}H_{11}Cl$: C, 79.47; H, 4.89; Cl, 15.64. Found: C, 79.36; H, 4.95; Cl, 15.94.

The first of these routes served in the preparation of di-*o*-tolylacetylene. The same procedure was used in the reaction of *o*-methylbenzyltriphenylphosphonium bromide (0.2 mol) with *n*-butyllithium (0.2 mol) in diethyl ether to generate the phosphorus ylide.

Table III. Acetylenedicobalt Hexacarbonyl Complexes

| Complex | Mp, °C | Color | Anal. Found (Calcd) | | Ir (in $CCl_4$), $cm^{-1}$ terminal C≡O frequencies | NMR (in $CCl_4$) δ, ppm |
|---|---|---|---|---|---|---|
| | | | Carbon | Hydrogen | | |
| $(4\text{-}CH_3C_6H_4C_2C_6H_4CH_3\text{-}4)Co_2(CO)_6$ | 98.5–99 | Brown | 53.22 (53.68) | 3.09 (2.86) | 2088, 2053, 2010, 1980 (sh) | 2.41 (s, 6 H)<br>7.0–7.7 (m, AA'BB') |
| $(3\text{-}CH_3C_6H_4C_2C_6H_4CH_3\text{-}3)Co_2(CO)_6$ | 53–54 | Red–brown | 53.27 (53.68) | 2.81 (2.86) | 2086, 2050, 2010, 1984 (sh) | 2.43 (s, 6 H)<br>6.9–7.6 (m) |
| $(2\text{-}CH_3C_6H_4C_2C_6H_4CH_3\text{-}2)Co_2(CO)_6$ | 113.5–114.5 | Green | 53.81 (53.68) | 2.94 (2.86) | 2087, 2048, 2005, 1967 (sh) | 2.12 (s, 6 H)<br>7.0–7.7 (m) |
| $(C_6H_5C_2C_6H_4CH_3\text{-}3)Co_2(CO)_6$ | 75.5–76.5 | Brown | 52.57 (52.75) | 2.57 (2.53) | 2086, 2054, 2024, 1982 (sh) | 2.42 (s, 3 H)<br>7.0–7.7 (m) |
| $(C_6H_5C_2C_6H_4Cl\text{-}3)Co_2(CO)_6$ | 91.0–92.5 | Brown | 48.05 (48.18) | 1.97 (1.82) | 2080, 2045, 2015, 1980 (sh) | 7.1–7.7 (m) |
| $(3\text{-}CH_3C_6H_4C_2C_6H_4Cl\text{-}3)Co_2(CO)_6$ | Slightly below room temp | Brown | 49.15 (49.20) | 2.38 (2.16) | 2087, 2055, 2023, 2000, 1985 (sh) | 2.44 (s, 3 H)<br>6.9–7.6 (m) |

$$\mathrm{ArCH_2Br \xrightarrow{Ph_3P} ArCH_2PPh_3{}^+Br^- \xrightarrow{\textit{n}\text{-}BuLi} ArCH{=}PPh_3} \quad (2)$$

$$\mathrm{ArCH{=}PPh_3 \xrightarrow{O_2} ArCH{=}CHAr \xrightarrow{Br_2} ArCHBrCHBrAr \xrightarrow{KOH} ArC{\equiv}CAr} \quad (3)$$

$$\mathrm{ArCH{=}PPh_3 \xrightarrow{Ar'CHO} ArCH{=}CHAr' \xrightarrow{Br_2} ArCHBrCHBrAr' \xrightarrow{KOH} ArC{\equiv}CAr'} \quad (4)$$

Subsequently, dry air was bubbled through the bright orange ylide solution (approximately 1 bubble every 5 sec) until the solution became colorless and a white precipitate formed. Filtration was followed by evaporation of the filtrate and recrystallization of the residue from hexane to give 2,2'-dimethylstilbene, mp 82.5-84° (lit.[16] mp 83°), in 76% yield.

Bromination of this stilbene derivative gave 1,2-di-*o*-tolyl-1,2-dibromoethane, mp 170-173° (lit.[18] mp 171-172°). Dehydrobromination was effected using the same procedure as above with 19.05 g (0.052 mol) of this dibromide. The acetylene did not precipitate when the reaction mixture was poured into cold water. The dichloromethane layer was dried and evaporated. The oil which remained was purified by column chromatography (silicic acid) using benzene as eluent. The resulting liquid product was further purified by molecular distillation at 86.3° (0.01 mmHg) to give di-*o*-tolylacetylene, $n^{20}D$ 1.6231 (lit.[18] $n^{20}D$ 1.6228) in 37% yield.

**Preparation of Diarylacetylenedicobalt Hexacarbonyl Complexes.** The preparation of di-*p*-tolylacetylenedicobalt hexacarbonyl is described to illustrate the procedure used. A 250-ml three-necked flask equipped with a nitrogen inlet and outlet, magnetic stirrer, and addition funnel was charged with 6.25 g (18.3 mmol) of $Co_2(CO)_8$ and 50 ml of anhydrous diethyl ether. Di-*p*-tolylacetylene (3.61 g, 18.3 mmol) in 50 ml of ether was added with stirring. The reaction mixture was stirred until evolution of carbon monoxide ceased (ca. 1.5 hr) and then was filtered. The filtrate was evaporated at reduced pressure and the solid residue purified by column chromatography using hexane as eluent. Recrystallization of the solid thus obtained from hexane at −19° gave 7.54 g (84%) of di-*p*-tolylacetylenedicobalt hexacarbonyl, mp 98.5-99.0° as brown crystals.

Physical, spectroscopic, and analytical data for all acetylenedicobalt hexacarbonyl complexes prepared in this study are given in Table III. Yields of the pure complexes obtained ranged from 84 to 96%. These complexes are relatively air stable as the pure solids. However, in solution they decompose in a matter of hours when exposed to air.

**Friedel-Crafts Acetylation of Diarylacetylenedicobalt Hexacarbonyl Complexes.** The acetylation of 3-chloro-3'-methyldiphenylacetylenedicobalt hexacarbonyl is described to illustrate the procedure used.

A 300-ml three-necked flask equipped with a nitrogen inlet and outlet, addition funnel, and magnetic stirring unit was oven dried, flamed out, evacuated, flushed with dry nitrogen, and charged with 2.94 g (22.0 mmol) of aluminum chloride and 1.57 g (20.0 mmol) of acetyl chloride in 50 ml of dichloromethane. The mixture was stirred under nitrogen for 10 min. Then 5.13 g (10.0 mmol) of the acetylenedicobalt hexacarbonyl complex dissolved in 50 ml of dichloromethane was added. The reaction mixture was stirred for 10 min and then was poured into 400 ml of distilled water. The aqueous phase was extracted with four 250-ml portions of dichloromethane. The combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure. The products in the residue were separated by column chromatography, using first hexane as eluent and slowly switching to dichloromethane. The first product to be eluted was 4-acetyl-3'-chloro-3-methyldiphenylacetylenedicobalt hexacarbonyl; the second was the 4,4'-diacetylated complex. Table I gives details of this experiment, as well as of other acetylations carried out in this manner.

Three of the reactions listed in Table I were carried out in a slightly different manner. The apparatus was assembled as described above, and the flask was charged with the diarylacetylenedicobalt hexacarbonyl and 50 ml of dichloromethane. Into the addition funnel was charged the aluminum chloride, acetyl chloride, and 50 ml of dichloromethane, as well as a magnetic stirring bar, and both mixtures were stirred for 10 min. The acetyl chloride–aluminum chloride complex then was added to the cobalt complex solution, and the reaction mixture was stirred for 10 min. Further work-up procedures were the same.

In some cases, the acetylated diarylacetylenedicobalt hexacarbonyl complexes were isolated as oils that could not be induced to crystallize. These then were converted to corresponding diarylacetylenedicobalt tetracarbonylbis(triphenylphosphine) complexes. The following procedure was used. A 300-ml three-necked flask equipped as described above was charged with 0.53 g (2.0 mmol) of triphenylphosphine (M & T Chemicals, Inc.) and 50 ml of dry benzene. 4-Acetyl-3-methyldiphenylacetylenedicobalt hexacarbonyl (0.42 g, 0.81 mmol), an oil, dissolved in 50 ml of benzene, was added. The reaction mixture was heated at reflux for 2 hr, cooled, and treated with 1 ml of iodomethane. The mixture was stirred at room temperature overnight and then was evaporated at reduced pressure. The brown solid which remained was purified by column chromatography using 1:1 hexane–dichloromethane as eluent. The solid obtained was recrystallized from hexane–dichloromethane and obtained in 83% yield.

The reactions listed in Table II all were carried out by adding the premixed acetyl chloride–aluminum chloride mixture in dichloromethane to a solution of the diarylacetylenedicobalt hexacarbonyl in dichloromethane.

The acetylated diarylacetylenedicobalt hexacarbonyl and tetracarbonylbis(triphenylphosphine) complexes prepared in this study are listed in Table IV together with physical, analytical, and spectroscopic data.

**Benzoylation of Diphenylacetylenedicobalt Hexacarbonyl.** To a cold slurry of 10 mmol of aluminum chloride in 25 ml of dichloromethane was added 10 mmol of benzoyl chloride, and the resultant complex was stirred for 10 min. A solution of 0.928 g (2 mmol) of diphenylacetylenedicobalt hexacarbonyl in 50 ml of dichloromethane was added with stirring under nitrogen, and the reaction mixture was stirred at 0° for 15 min and for 2 hr at room temperature. It then was poured into ice-water. Extraction of the aqueous phase

Table IV. Acetylation (Benzoylation) Products of Diarylacetylenedicobalt Hexacarbonyl Complexes

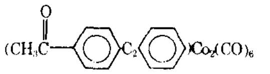
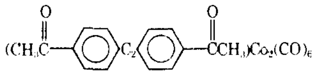
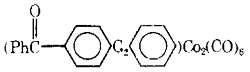
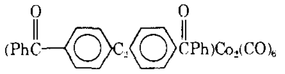
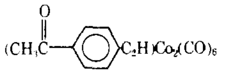
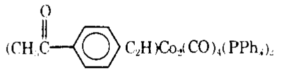
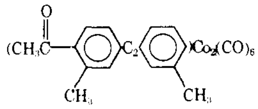
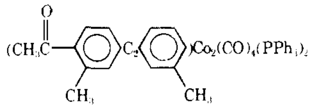
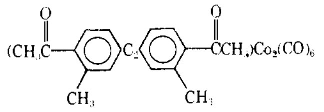
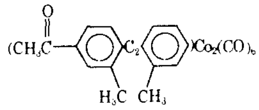
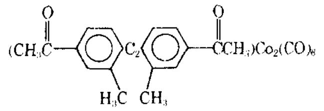
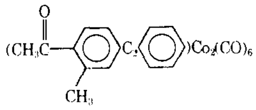
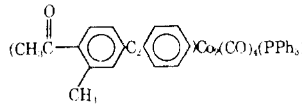
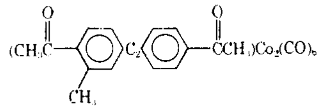
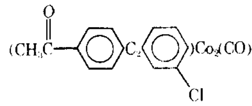
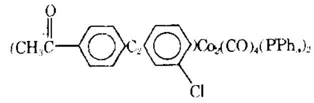
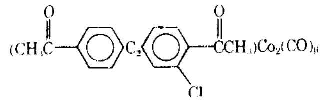
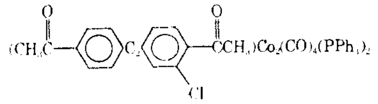
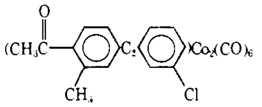
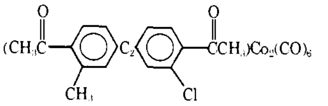
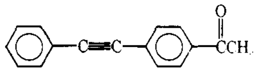
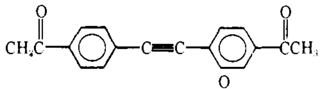
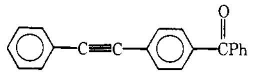
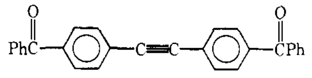
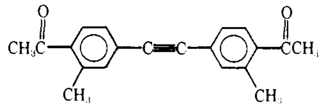
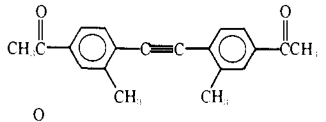
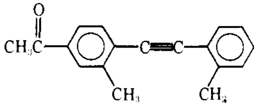
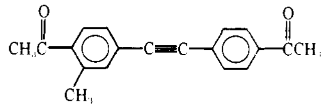
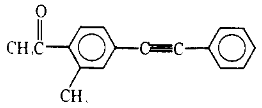
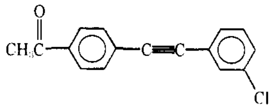
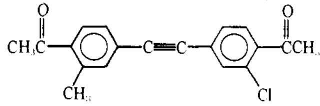
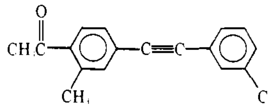
| Complex | Mp, °C | Color | Anal. Found (Calcd) | | Ir (in $CCl_4$), cm$^{-1}$ | | NMR (in $CCl_4$) δ, ppm |
|---|---|---|---|---|---|---|---|
| | | | Carbon | Hydrogen | Terminal CO | Acyl CO | |
|  | 63–63.5 | Brown | 51.81 (52.19) | 2.75 (2.41) | 2095, 2060, 2030, 2020, 1990 | 1690 | 2.54 (s, 3 H), 7.10–8.10 (m, 9 H) |
|  | 93–94 | Brown | 52.90 (52.57) | 2.76 (2.57) | 2090, 2060, 2030, 2020, 1990 | 1690 | 2.57 (s, 6 H), 7.53, 7.66, 7.87, 8.01 (AA'BB', 8 H, aromatic) |
|  | 133–134 | Brown | 57.57 (57.06) | 2.64 (2.48) | 2090, 2060, 2040, 2020, 1990 | 1665 | 7.2–8.0 (m) |
|  | Dec >65° | Red–brown | 60.72 (60.71) | 2.76 (2.70) | 2100, 2065, 2040, 2020 | 1665 | 7.1–8.0 (m) |
|  | Oil | Red | | | | 1675 | 2.56 (s, 3 H), 6.40 (s, 1 H), 7.50, 7.63, 7.86, 7.99 (AA'BB', 4 H) |
|  | 224–227 | Tan | 66.59 (66.83) | 4.20 (4.26) | 2014, 1965, 1942 | 1667 | 2.22 (s, 3 H), 6.86–7.53 (m) |
|  | Oil | Red–brown | | | 2092, 2056, 2024, 2017, 1982 | 1681 | |
|  | 171–172.5 | Yellow–brown | 69.40 (69.46) | 4.63 (4.62) | 2030, 1983, 1970, 1942 | 1675 | 2.03 (s, 3 H), 2.20 (s, 3 H), 2.56 (s, 3 H), 6.5–7.7 (m) |
|  | 99.5–100 | Red–brown | 54.56 (54.18) | 3.44 (3.14) | 2093, 2058, 2028, 2018, 1986 | 1686 | 2.57 (s, 12 H), 7.2–7.8 (m) |
|  | Oil | Green | | | 2087, 2055, 2025, 2015, 1989 | 1685 | 2.10 (s, 3 H), 2.17 (s, 3 H), 2.53 (s, 3 H), 7.1–8.0 (m) |
|  | 115.5–117 | Green | 54.51 (54.18) | 3.31 (3.14) | 2080, 2050, 2018, 2005, 1978 | 1685 | 2.17 (s, 6 H), 2.57 (s, 6 H), 7.5–8.0 (m) |
|  | Oil | Red–brown | | | 2089, 2054, 2020, 1986 | 1682 | 2.43 (br s, 6 H), 7.1–7.8 (m) |
|  | 151–152 | Yellow–brown | 68.12 (68.24) | 4.65 (4.49) | | | (In $CDCl_3$) 2.20 (s, 3 H), 2.54 (s, 3 H), 6.6–7.9 (m) |
|  | 73.5–75 | Red–brown | 53.85 (53.40) | 2.98 (2.87) | 2093, 2060, 2030, 2022, 1985 | 1686 | 2.57 (s, 9 H), 7.3–8.1 (m) |
|  | Oil | Brown | | | 2089, 2054, 2020, 1986 | 1684 | 2.51 (s, 3 H), 7.1–8.1 (m) |
|  | 129–130 | Yellow–brown | 66.29 (66.64) | 4.25 (4.09)$^a$ | 2032, 1983 (sh) 1976, 1947 | 1677 | |
|  | Oil | Red–brown | | | 2095, 2061, 2035, 1970 | 1687 | 2.65 (s, 3 H), 2.70 (s, 3 H), 7.3–8.2 (m) |
|  | 122–125 (dec) | Yellow–brown | 65.78 (66.26) | 4.11 (4.12)$^b$ | 2022, 1986, 1972, 1947 | 1676 | 2.47 (s, 3 H), 2.56 (s, 3 H), 6.69–7.4 (m) |

Table IV (*Continued*)

| Complex | Mp, °C | Color | Anal. Found (Calcd) |  | Ir (in $CCl_4$), $cm^{-1}$ |  | NMR (in $CCl_4$) δ, ppm |
|---|---|---|---|---|---|---|---|
|  |  |  | Carbon | Hydrogen | Terminal CO | Acyl CO |  |
|  | 79–80.5 | Red–brown | 50.19 (49.80) | 2.51 (2.36)[c] | 2090, 2055, 2015, 1985 | 1688 | 2.57 (s, 3 H), 2.59 (s, 3 H), 7.2–7.9 (m) |
|  | 100–101 | Red–brown | 50.70 (50.32) | 2.65 (2.53)[d] | 2094, 2061, 2030, 2020, 1989 | 1686 | 2.60 (s, 3 H), 2.65 (s, 3 H), 2.72 (s, 3 H), 7.2–7.9 (m) |

[a] Cl: found, 3.73; calcd, 3.51. [b] Cl: found, 3.51; calcd, 3.37. [c] Cl: found, 6.43; calcd, 6.39. [d] Cl: found, 6.03; calcd, 5.94.

Table V. Acylated Diarylacetylenes

| Acetylene compd | Mp, °C | Anal. Found (Calcd) |  | Ir, ν (C=O), $cm^{-1}$ ($CCl_4$) |
|---|---|---|---|---|
|  |  | Carbon | Hydrogen |  |
|  | 98–98.5 | 87.11 (87.24) | 5.45 (5.49) | 1685 |
|  | 198.5–200 | 82.15 (82.43) | 5.36 (5.38) | 1680 |
|  | 110–111.5 | 89.09 (89.32) | 5.03 (4.88) | 1655 |
|  | 226–227.5 | 86.78 (87.02) | 4.61 (4.73) | 1655 |
|  | 98.5–99.5 | 82.38 (82.73) | 6.20 (6.25) | 1690 |
|  | 166.5–168 | 82.30 (82.73) | 6.27 (6.25) | 1678 |
|  | 120–121.5 | 86.10 (87.06)[b] | 6.73 (6.49) | 1688 |
|  | 83.5–84.5 | 82.33 (82.58) | 6.05 (5.84) | 1685 |
|  | 62–63 | 87.20 (87.15) | 5.97 (6.02) | 1686 |
|  | 91.5–92.5 | 75.54 (75.45) | 4.45 (4.35)[a] | 1686 |
|  | 83–83.5 | 73.42 (73.43) | 4.99 (4.86) | 1688 |
|  | 55.5–56 | 75.66 (75.95) | 4.78 (4.88) | 1685 |

[a] Cl: found, 13.75; calcd, 13.91. [b] Insufficient sample to permit further purification.

with dichloromethane was followed by evaporation of the combined organic layers at reduced pressure. Column chromatography (dichloromethane eluent) gave two products: (1) 0.33 g (28%) of a brown oil which crystallized on addition of hexane (recrystallization from methanol-water gave a solid, mp 133–134°, the monobenzoyl derivative); (2) 0.48 g (36%) of red-brown solid, recrystallized from methanol-water, which decomposed above 65°, the 4,4′-dibenzoyl derivative. Details concerning these products are given in Table IV.

When this reaction was carried out with a larger excess of the benzoyl chloride-aluminum chloride reagent, both products again were obtained in approximately the same yields as in the experiment above.

**Competition Reactions. (a) Diphenylacetylenedicobalt Hexacar-**

**bonyl and Benzylidynetricobalt Nonacarbonyl.** The usual apparatus was charged with 4.64 g (10.0 mmol) of the acetylene complex, 5.18 g (10.0 mmol) of $PhCCo_3(CO)_9$, and 50 ml of dichloromethane. This mixture was stirred for 10 min to ensure complete mixing. The addition funnel was charged with 0.079 g (1.0 mmol) of acetyl chloride, 0.26 g (2.0 mmol) of aluminum chloride, and 50 ml of dichloromethane. This mixture also was stirred for 10 min and then was added to the mixture of cobalt complexes. The reaction mixture was stirred under nitrogen at room temperature for 10 min and then was poured into 500 ml of water. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed twice with water, dried, and evaporated under reduced pressure. The unconverted starting materials were separated from the acetylated products by column chromatography using hexane as eluent. Using 30:70 dichloromethane-hexane as eluent, 0.49 g (88%) of *p*-acetylbenzylidynetricobalt nonacarbonyl was isolated. The product was recrystallized once from hexane and identified by its melting point and ir and NMR spectra which were identical with those of an authentic sample.[1] A trace of 4-acetyldiphenylacetylenedicobalt hexacarbonyl may have been formed as evidenced by a faint band on the column, but insufficient quantity was present to isolate and identify.

**(b) Diphenylacetylenedicobalt Hexacarbonyl and Anisole.** Essentially the same procedure was used in the reaction in which 4.64 g (10.0 mmol) of the acetylene complex and 1.08 g (10.0 mmol) of anisole were allowed to compete for the reagent prepared from 0.079 g (1.0 mmol) of acetyl chloride and 0.26 g (2.0 mmol) of aluminum chloride in dichloromethane solution. Column chromatography (hexane eluent) served to remove unconverted starting materials. Subsequently, 20:80 dichloromethane-hexane removed 4-acetyldiphenylacetylenedicobalt hexacarbonyl, 0.16 g (31%), identified by means of its melting point and ir spectrum, and elution with dichloromethane finally removed *p*-methoxyacetophenone, 0.09 g (58%), identified by its melting point of 38-39.5° (lit.[19] 39°) and its ir spectrum (comparison with Sadtler Standard Spectrum No. 3883).

**Oxidation of Diarylacetylenedicobalt Hexacarbonyl Complexes with Ceric Ammonium Nitrate.** The liberation of the acetylene ligand from 4,4′-diacetyl-3,3′-dimethyldiphenylacetylenedicobalt hexacarbonyl is described to illustrate the procedure used.

A 250-ml round-bottomed flask equipped with a magnetic stirring unit was charged with 3.0 g (5.21 mmol) of the cobalt complex and 100 ml of reagent grade acetone. Ceric ammonium nitrate (8.6 g, 15.6 mmol) was added slowly in portions, and the mixture was stirred for 2 hr. Gas evolution was observed during the course of the reaction and the initial brown color of the solution decreased in intensity and eventually changed to orange. The solvent was removed under reduced pressure, and the residue was dissolved by addition of dichloromethane and water. The aqueous phase was extracted with dichloromethane, and the combined organic phases were dried and evaporated. The residue was recrystallized three times from methanol-water to give 1.40 g (92%) of the acetylene.

The yields in such oxidations were uniformly high, from 80 to 95%. The new acetylenes prepared in this manner are listed in Table V.

**Oxidation of Diarylacetylenes to the Corresponding Substituted Benzoic Acids. (a) Potassium Permanganate Procedure.** The oxidation of 4,4′-diacetyl-3,3′-dimethyldiphenylacetylene is described. A 200-ml round-bottomed flask was charged with 0.20 g (0.63 mmol) of the acetylene and 100 ml of reagent grade acetone. Potassium permanganate (0.32 g, 2.0 mmol) dissolved in 50 ml of water was added dropwise over a 1-hr period, and the reaction mixture was stirred overnight. Acidification was followed by dilution with 150 ml of water and extraction with three 50-ml portions of ethyl acetate. The extracts were evaporated under reduced pressure, leaving a white, flocculent solid which was recrystallized from methanol-water to give 0.18 g (80%) of 4-acetyl-3-methylbenzoic acid, mp 146.5-148° (lit.[1] mp 147-148°), whose identity was confirmed by comparison of its ir spectrum with that of an authentic sample.

This procedure was successful in the oxidation of 3-chloro-4,4′-diacetyl-3′-methyldiphenylacetylene and 4-acetyl-3′-chlorodiphenylacetylene. In both cases a mixture of two acids resulted. Identification of the products was achieved by methylating the mixture of acids with diazomethane in ether (via Du Pont EXR-101) and separating the methyl ester mixture by GLC (6-ft UC W98, 190°; injection of ether solution). Methyl 4-acetyl-3-chlorobenzoate, mp 51-52°, was identified by mixture melting point and NMR comparison with an authentic sample. The latter was prepared by ceric ammonium nitrate oxidation of 4-acetyl-3-chlorobenzylidynetricobalt nonacarbonyl (whose structure had been established[1]) followed by methylation of the 4-acetyl-3-chlorobenzoic acid obtained: NMR ($CCl_4$) $\delta$ 2.61 (s, 3 H, $CH_3CO$), 3.91 (s, 3 H, $CH_3O$), and 7.4-9.1 ppm. Methyl 4-acetyl-3-methylbenzoate, mp 68-69°, showed the following resonances in its NMR spectrum (in $CCl_4$): $\delta$ 2.56 (s, 6 H); 3.90 (s, 3 H, $CH_3O$); and 7.5-8.0 ppm (m). An authentic sample of this ester was prepared by methylation of 4-acetyl-3-methylbenzoic acid (Table V) obtained by oxidative degradation of the appropriate acetylene. The melting points and spectral data of methyl 3-chlorobenzoate (mp 20-22°) and methyl 4-acetylbenzoate (mp 94.5°-95.5°) agreed well with literature values (21 and 95-95.5°, respectively, as reported in ref 20 and 1, respectively).

**(b) Potassium Permanganate-Sodium Periodate Procedure.** A 100-ml round-bottomed flask was charged with 0.15 g (0.5 mmol) of 4,4′-diacetyl-2,2′-dimethyldiphenylacetylene and 50 ml of water. Potassium permanganate (0.40 g, 2.5 mmol) was added, and the mixture was stirred overnight. The mixture was diluted with 100 ml of water and acidified and extracted three times with ethyl acetate. Evaporation of the extracts at reduced pressure left an oil which was diluted with 50 ml of water and treated with 0.53 g (2.5 mmol) of sodium metaperiodate. The pH was adjusted to about 7 by careful addition of sodium hydroxide, and the mixture was stirred overnight and filtered. The precipitated solid was washed twice with dichloromethane, and the filtrate was acidified with HCl and extracted three times with ethyl acetate. The organic phases were evaporated at reduced pressure, and the residue was dissolved in 10 ml of aqueous NaOH. Filtration was followed by acidification of the filtrate to give 0.10 g (56%) of 4-acetyl-2-methylbenzoic acid. The ir spectrum of the product was identical with that of an authentic sample.[1]

The oxidation of 4-acetyl-3-methyldiphenylacetylene was carried out in similar fashion. The mixture of acids was separated as described above, giving the known methyl benzoate, $n^{25}D$ 1.5208, and methyl 4-acetyl-3-methylbenzoate.

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