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ORGANOCOBALT CLUSTER COMPLEXES

XII. THE ARYLATION AND ALKYLATION OF METHYLIDYNETRICOBALT NONACARBONYL WITH ORGANOMERCURY COMPOUNDS[*]

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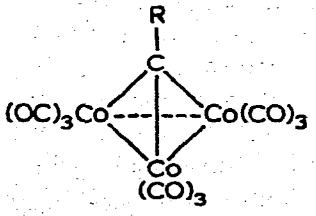
Summary

The reaction of diarylmercurials and arylmercuric halides with methylidynetricobalt nonacarbonyl in benzene or THF at reflux results in formation of benzylidynetricobalt nonacarbonyl complexes, $ArCCo_3(CO)_9$, in good yield, especially when the reactions are carried out under an atmosphere of carbon monoxide. The alkylation of $HCCo_3(CO)_9$ with dialkylmercurials or alkylmercuric halides proceeds much more slowly and in much lower yields. Similar reactions of (α-haloalkyl)mercurials, $(RCHX)_2Hg$, with $HCCo_3(CO)_9$, gives reduced products, $RCH_2CCo_3(CO)_9$, rather than the expected $RCHXCCo_3(CO)_9$. Similar arylation of the apical carbon atom of the CCo_3 cluster occurred in the reactions of $XCCo_3(CO)_9$ (X = Cl, Br, I) with diphenylmercury, and in reactions of tetraphenyltin and tetraphenyllead with $HCCo_3(CO)_9$.

Introduction

Two procedures are available for the conversion of dicobalt octacarbonyl to alkylidynetricobalt nonacarbonyl cluster complexes (I):



$[RCCo_3(CO)_9]$

(I)

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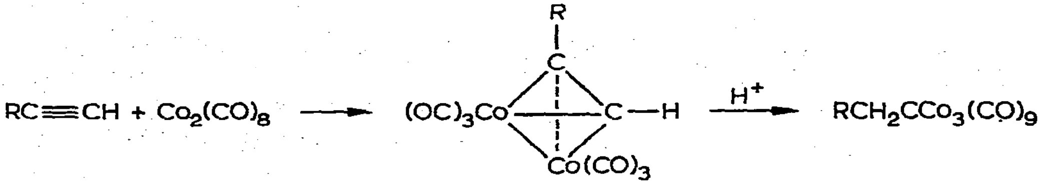
[*] Part XI, see ref. 1; Preliminary communications see refs. 2 and 3.

(*1*) the direct reaction of an organic trihalo or dihalo compound with dicobalt octacarbonyl [eqn. (1)] [4, 5] and (*2*) the reaction of a terminal acetylenedicobalt hexacarbonyl complex with strong acid [eqn. (2)] [6].

$$RCX_3 + Co_2(CO)_8 \rightarrow RCCo_3(CO)_9 \qquad (1)$$



(2)

However, at the outset of our work in this area, there was no general procedure for the preparation of $RCCo_3(CO)_9$ (R = alkyl and aryl) compounds starting with already intact cluster complexes such as $XCCo_3(CO)_9$, $HCCo_3(CO)_9$, etc. Our early attempts to alkylate the $CCo_3(CO)_9$ cluster by reactions of its C-halogen derivatives with organolithium and organomagnesium compounds showed little promise and in order to minimize competitive processes such as attack at carbon monoxide ligands, we decided to investigate the reactions of such simple methylidynetricobalt nonacarbonyl derivatives with less reactive alkylating agents. We report here concerning the reactions of organomercury compounds with methylidynetricobalt nonacarbonyl, reactions which serve excellently in the preparation of diversely substituted benzylidynetricobalt nonacarbonyls and moderately well in the preparation of alkylidynetricobalt nonacarbonyls [eqn. (3)].

$$R_2Hg \text{ (or } RHgX) + HCCo_3(CO)_9 \longrightarrow RCCo_3(CO)_9 \qquad (3)$$

Results and Discussion

Initial experiments with phenylmercurials showed that both diphenylmercury and monophenylmercurials such as the phenylmercuric halides and phenylmercuric hydroxide served to phenylate $HCCo_3(CO)_9$. These reactions could be effected very readily. An equimolar mixture of $HCCo_3(CO)_9$ and the mercurial (usually 1 - 2 mmol) in about 50 ml of solvent [usually benzene or tetrahydrofuran (THF)] was stirred and heated at reflux under nitrogen. The progress of the reaction could be followed conveniently by thin layer chromatography (TLC). Upon completion of the reaction, the metallic mercury which usually formed was filtered and column chromatography, crystallization and sublimation served in the separation of the cobalt-containing products. Most of these were air-stable, deeply colored (violet through brown and purple-black), volatile solids. The extension of these reactions to other organomercurials was examined. The results are summarized in Table 1. Both diarylmercurials and arylmercuric halides reacted with $HCCo_3(CO)_9$ to give $ArCCo_3(CO)_9$ compounds. The yields were moderate (20 - 60%), except in those cases where sterically hindered aryl groups (α-naphthyl, mesityl, pentachlorophenyl) were involved. The effect of varying the solvent on the $Ph_2Hg/HCCo_3(CO)_9$ and $PhHgBr/HCCo_3(CO)_9$ reactions was examined (Table 2). Phenylmercuric

TABLE 1
REACTIONS OF R_2Hg AND RHgX WITH $HCCo_3(CO)_9$ UNDER NITROGEN

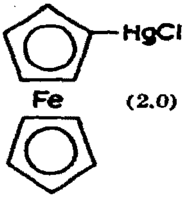
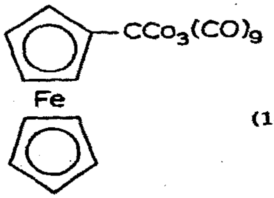
Mercurial (mmol)	$HCCo_3(CO)_9$ (mmol)	Solvent	Reaction time (h)	Product (% yield)	Hg^0 (% yield)
Ph_2Hg (3.0)	2.0	C_6H_6	6	$PhCCo_3(CO)_9$ (56)	60
Ph_2Hg (2.0)	2.0	THF	5	$PhCCo_3(CO)_9$ (51)	
$(C_6F_5)_2Hg$ (2.0)	2.0	C_6H_6	5	$C_6F_5CCo_3(CO)_9$ (63)	22
$(2,4,6\text{-}Me_3C_6H_2)_2Hg$ (3.0)	3.0	C_6H_6	5	Only $HCCo_3(CO)_9$ (7)	13
$(C_6Cl_5)_2Hg$ (1.5)	1.5	C_6H_6	36	Only $HCCo_3(CO)_9$ (73)	
$(PhCH_2)_2Hg$ (3.0)	2.0	THF	1	$PhCH_2CCo_3(CO)_9$ (61)	3
PhHgBr (1.5)	1.5	C_6H_6	3.75	$PhCCo_3(CO)_9$ (21) [$HCCo_3(CO)_9$ (44)]	7
PhHgOH (2.0)	2.0	C_6H_6	48	$PhCCo_3(CO)_9$ (51)	100
$p\text{-}FC_6H_4HgBr$ (2.0)	2.0	THF	12	$p\text{-}FC_6H_4CCo_3(CO)_9$ (66)	75
$p\text{-}ClC_6H_4HgBr$ (1.0)	1.0	C_6H_6	8	$p\text{-}ClC_6H_4CCo_3(CO)_9$ (54)	32
$\alpha\text{-}C_{10}H_7HgBr$ (1.5)	1.5	C_6H_6	4	$\alpha\text{-}C_{10}H_7CCo_3(CO)_9$ (11)	21
 (2.0)	2.0	C_6H_6	48	 (14) [$HCCo_3(CO)_9$ (21)]	46
$CH_3OCH_2CH_2HgCl$ (2.0)	2.0	C_6H_6	48	$CH_3OCH_2CH_2CCo_3(CO)_9$ (17) [$HCCo_3(CO)_9$ (40)]	93
$CCl_2 = CClHgBr$ (3.0)	2.0	THF	7	Only $HCCo_3(CO)_9$ (9)	

TABLE 2
EFFECT OF SOLVENT ON $Ph_2Hg/HCCo_3(CO)_9$ AND $PhHgBr/HCCo_3(CO)_9$ REACTIONS (UNDER NITROGEN)

Solvent	Reaction time (min)	Reaction temp.(°C)	$PhCCo_3(CO)_9$ yield (%)	Mercury yield (%)	$HCCo_3(CO)_9$ recovery (%)
Ph_2Hg reactions					
Cyclohexane	150	81	62	43	18
Benzene	360	80	56	60	0
1,2-Dimethoxyethane	45	85	65	40	0
Tetrahydrofuran	225	66	47	52	11
PhHgBr reactions					
Cyclohexane	165	81	30	7	22
Benzene	225	80	21	7	44
1,2-Dimethoxyethane	60	85	47	92	14
Tetrahydrofuran	150	66	53	97	16
Diglyme	75	90-93	52	100	14
Acetonitrile	60	82	5	7	0

TABLE 3

REACTIONS OF R_2Hg AND RHgX WITH $HCCo_3(CO)_9$ UNDER CARBON MONOXIDE

Mercurial (mmol)	$HCCo_3(CO)_9$ (mmol)	Solvent	Reaction time (h)	Product (% yield)	Hg^0 (% yield)
Ph_2Hg (1.0)	1.0	C_6H_6	2.5	$PhCCo_3(CO)_9$ (93)	
$(p\text{-}CH_3OC_6H_4)_2Hg$ (2.0)	2.0	C_6H_6	4	$p\text{-}CH_3OC_6H_4CCo_3(CO)_9$ (64)	39
$(p\text{-}CH_3C_6H_4)_2Hg$ (2.0)	2.0	C_6H_6	7	$p\text{-}CH_3C_6H_4CCo_3(CO)_9$ (92)	49
$(m\text{-}CH_3C_6H_4)_2Hg$ (2.0)	2.0	C_6H_6	7	$m\text{-}CH_3C_6H_4CCo_3(CO)_9$ (96)	74
$(o\text{-}CH_3\text{-}C_6H_4)_2Hg$ (4.77)	4.55	C_6H_6	3.5	$o\text{-}CH_3C_6H_4CCo_3(CO)_9$ (49)	
$(p\text{-}ClC_6H_4)_2Hg$ (2.0)	2.0	C_6H_6	6	$p\text{-}ClC_6H_4CCo_3(CO)_9$ (83)	30
$(m\text{-}ClC_6H_4)_2Hg$ (7.1)	7.0	C_6H_6	3.5	$m\text{-}ClC_6H_4CCo_3(CO)_9$ (93)	
$(o\text{-}ClC_6H_4)_2Hg$ (8.05)	7.9	C_6H_6	4	$o\text{-}ClC_6H_4CCo_3(CO)_9$ (57)	
$(m\text{-}FC_6H_4)_2Hg$ (4.01)	4.05	C_6H_6	4	$m\text{-}FC_6H_4CCo_3(CO)_9$ (85)	
$(p\text{-}BrC_6H_4)_2Hg$ (2.0)	2.0	C_6H_6	6.5	$p\text{-}BrC_6H_4CCo_3(CO)_9$ (86)	44
$(p\text{-}IC_6H_4)_2Hg$ (1.13)	1.13	C_6H_6	8	$p\text{-}IC_6H_4CCo_3(CO)_9$ (51)	58
$(C_6F_5)_2Hg$ (1.5)	1.0	C_6H_6	5	$C_6F_5CCo_3(CO)_9$ (69)	37
$(PhCH_2)_2Hg$ (1.5)	1.5	C_6H_6	96	$PhCH_2CCo_3(CO)_9$ (75)	88
$(2,4,6\text{-}Me_3C_6H_2)_2Hg$ (2.0)	1.5	C_6H_6	6 days	Only $HCCo_3(CO)_9$ (21)	54
PhHgBr (2.0)	1.0	C_6H_6	4	$PhCCo_3(CO)_9$ (58)	14
$p\text{-}FC_6H_4HgBr$ (1.5)	1.5	THF	24	$p\text{-}FC_6H_4CCo_3(CO)_9$ (57)	80
$p\text{-}H_2NC_6H_4HgCl$ (3.0)	2.0	THF	19	$p\text{-}H_2NC_6H_4CCo_3(CO)_9$ (26)	82
$CH_3OCH_2CH_2HgCl$ (3.0)	2.0	C_6H_6	14 days	$CH_3OCH_2CH_2CCo_3(CO)_9$ (32) [$HCCo_3(CO)_9$ (43)]	56
$(n\text{-}C_5H_{11})_2Hg$ (1.5)	1.5	C_6H_6	8 days	$n\text{-}C_5H_{11}CCo_3(CO)_9$ (32)	57

bromide reacted more rapidly and more completely in THF, 1,2-dimethoxyethane (DME) and diglyme than in cyclohexane or benzene, possibly due to the greater solubility of phenylmercuric bromide in ethereal solvents. Such effects were much less apparent with diphenylmercury, and, in fact, the differences observed may be simple temperature effects.

While the product yields on the whole were quite acceptable, a more effective utilization of the $HCCo_3(CO)_9$ starting material was desirable, since the preparation of the latter is not a high yield process. The observation and identification of a minor by-product of these reactions as $Hg[Co(CO)_4]_2$ provided the clue which allowed the achievement of such an improvement. The formation of this by-product implies partial degradation of the $CCo_3(CO)_9$ cluster of the starting material and/or product, and such a process may be the one which limits the yield of the desired product. The most common mode of decomposition of metal carbonyls involves the loss of a carbon monoxide ligand (usually reversible) as an initial step [eqn. (4)]. (It may be pertinent that

$$M(CO)_n \rightleftharpoons M(CO)_{n-1} + CO \qquad (4)$$

methylidynetricobalt nonacarbonyl complexes were found [7] to exchange carbon monoxide ligand with gaseous carbon monoxide at a reasonable rate at 35 - 55°; only three of the nine carbon monoxide ligands were reactive in such exchange processes). Such a reversible loss of a carbon monoxide ligand may be followed by irreversible degradation of the cluster complex. Such degradation

$$\begin{tikzcd} RCCo_3(CO)_9 \arrow[r, shift left] & RCCo_3(CO)_8 + CO \arrow[l, shift left] \arrow[d, "\text{decomposition}"] \\ & {} \end{tikzcd}$$

possibly may be minimized or completely prevented if reversal of the initial step is made more favorable. Accordingly, the $R_2Hg/HCCo_3(CO)_9$ reactions were carried out in the presence of external carbon monoxide, simply by initially saturating the reaction medium with carbon monoxide and then maintaining a slow stream of gaseous carbon monoxide through the reaction mixture during the reflux period. The effects of this change in reaction conditions were dramatic (Table 3). Qualitatively, the reactions proceeded more cleanly. Filtration left a pool of mercury with no other residue, in contrast to the reactions carried out under a nitrogen atmosphere. In quantitative terms, the yields of $ArCCo_3(CO)_9$ products, which before had been in the 50 - 60% range, were increased to the 70 - 95% range, although the required reaction times often were longer. Even a straight chain dialkylmercurial, di-n-amylmercury, reacted with $HCCo_3(CO)_9$ to give $n\text{-}C_5H_{11}CCo_3(CO)_9$ in 38% yield (but the reaction time required was 8 days). Eqn. (5) provides an idealized description

$$R_2Hg + HCCo_3(CO)_9 \longrightarrow RCCo_3(CO)_9 + RH + Hg \qquad (5)$$

of the $R_2Hg/HCCo_3(CO)_9$ reaction. Mercury usually was formed and in some reactions we isolated and identified the arene as well. A reaction of

$DCCo_3(CO)_9$ [5] with di-*p*-tolylmercury gave toluene which contained 89% toluene-d_1, 2% toluene-d_2 and 9% undeuterated toluene. In all cases examined, the carbon atom of the phenyl ring originally bonded to mercury became attached to the carbon atom of the cluster unit. No isomerizations were observed. For instance, in the tolyl series, the following chemical proof of structure was provided by oxidation of the three tolyl-substituted cluster complexes:

$$(CH_3C_6H_4)_2Hg + HCCo_3(CO)_9 \longrightarrow CH_3C_6H_4CCo_3(CO)_9$$

$$CH_3C_6H_4CCo_3(CO)_9 \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } KM_nO_4 \text{ aq./acetone}} CH_3C_6H_4CO_2H$$

The product derived from di-*o*-tolylmercury gave *o*-toluic acid upon oxidation, the *m*-tolylmercurial reacted to give a complex which gave *m*-toluic acid, while di-*p*-tolylmercury gave *p*-$CH_3C_6H_4CCo_3(CO)_9$, as indicated by oxidation of the latter to *p*-toluic acid.

The cobalt cluster derivatives obtained by the reactions of the three bis(chlorophenyl)mercurials with methylidynetricobalt nonacarbonyl, $ClC_6H_4CCo_3(CO)_9$, also were oxidized to the corresponding chlorobenzoic acids. Again the results showed that the substitution of $CCo_3(CO)_9$ for mercury had occurred without rearrangement.

In connection with the oxidation of substituted benzylidynetricobalt nonacarbonyls, we note that potassium permanganate in aqueous acetone serves well, no matter what the substitution pattern of the aryl group may be. On the other hand, oxidation with ceric ammonium nitrate [9] gave consistently good yields of the expected substituted benzoic acid only with *p*-substituted benzylidynetricobalt nonacarbonyls. In the case of the *m*-substituted compounds only low-to-moderate yields were obtained, while none of the *o*-substituted benzoic acid was formed when some *o*-substituted (CH_3 and Cl) benzylidynetricobalt nonacarbonyls were treated with ceric ammonium nitrate, although degradation of the cluster did take place.

The reactions of some functionally-substituted organomercurials with methylidynetricobalt nonacarbonyl were of special interest. Alkylation of $HCCo_3(CO)_9$ with the methoxymercuration product of ethylene was especially noteworthy [eqn. (6, 7)], although the reaction time was rather long. In principle, such reactions should allow the introduction of a wide variety of β-functional alkyl groups at carbon into the $CCo_3(CO)_9$ cluster system since the solvomercuration of olefins can be accomplished in wide scope [8].

$$Hg(OAc)_2 + CH_2{=}CH_2 + MeOH \longrightarrow \xrightarrow{NaCl} MeOCH_2CH_2HgCl \qquad (6)$$

$$MeOCH_2CH_2HgCl + HCCo_3(CO)_9 \xrightarrow[80^\circ\text{, CO gas}]{\text{Benzene, 14 days}} MeOCH_2CH_2CCo_3(CO)_9 \text{ (32\%)} \qquad (7)$$

In concurrent studies, we have developed the CH_2 transfer chemistry of (halomethyl)mercurials of type $Hg(CH_2X)_2$ and XCH_2HgX (X = Br, I) and have reported improved procedures for their preparation [10]. A reaction of such mercurials with $HCCo_3(CO)_9$ in the sense of eqn. (3) would be expected to give $XCH_2CCo_3(CO)_9$ derivatives which could be useful intermediates in the preparation of other functionally-substituted alkylidynetricobalt nonacarbonyl complexes. However, reactions of all four (halomethyl)mercury compounds, $Hg(CH_2I)_2$, $Hg(CH_2Br)_2$, ICH_2HgI and $BrCH_2HgBr$, with $HCCo_3(CO)_9$ in benzene at reflux invariably gave the reduced product, $CH_3CCo_3(CO)_9$, rather than the expected halomethyl derivative, e.g., eqn. (8). The source of the

$$Hg(CH_2I)_2 + HCCo_3(CO)_9 \xrightarrow[24\text{ h}]{\text{Benzene, }80^\circ} CH_3CCo_3(CO)_9 \text{ (77\%)} \quad (8)$$

"extra" hydrogen is the organocobalt starting material. Reaction of $DCCo_3(CO)_9$ with $Hg(CH_2Br)_2$ gave $CH_2DCCo_3(CO)_9$, while $CHD_2CCo_3(CO)_9$ was obtained when $HCCo_3(CO)_9$ and $Hg(CD_2I)_2$ were allowed to react. Other α-haloalkylmercury compounds reacted similarly [eqns. (9) and (10)]:

$$Hg(CHBrSiMe_3)_2 + HCCo_3(CO)_9 \longrightarrow Me_3SiCH_2CCo_3(CO)_9 \text{ (70\%)} \quad (9)$$

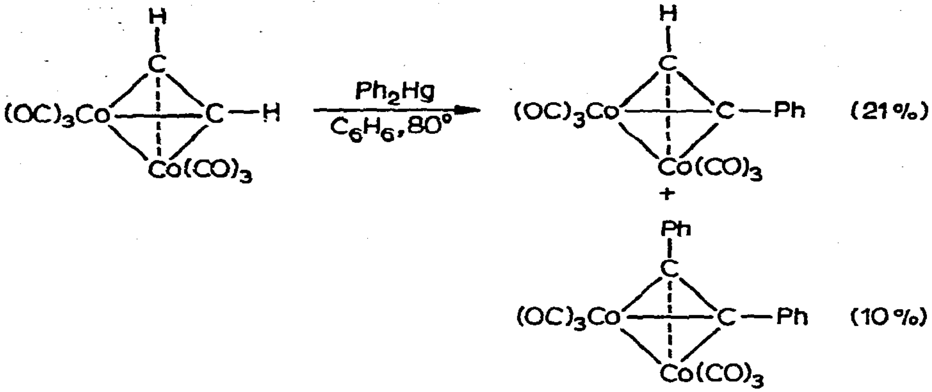
$$Hg(CHICH_3)_2 + HCCo_3(CO)_9 \longrightarrow CH_3CH_2CCo_3(CO)_9 \text{ (88\%)} \quad (10)$$

The high yields obtained in these reactions and their relatively rapid rate [compared with alkyl—HgX and $(alkyl)_2Hg$ reactions with $HCCo_3(CO)_9$] suggest that such $(RCHX)_2Hg/HCCo_3(CO)_9$ reactions might serve more generally in the preparation of alkyl—$CCo_3(CO)_9$ compounds. Moreover, the use of (α-haloalkyl)mercurials appears to allow the preparation of compounds not accessible by the $R_2Hg/HCCo_3(CO)_9$ reaction. In contrast to the results in eqn. (9), the reaction of $(Me_3SiCH_2)_2Hg$ with $HCCo_3(CO)_9$ did not give Me_3SiCH_2 $CCo_3(CO)_9$. A fuller development of these $(RCHX)_2Hg/HCCo_3(CO)_9$ reactions is, however, not to be expected. While (α-iodoalkyl)mercurials are readily prepared by reaction of the appropriate (α-iodoalkyl)zinc iodide with mercuric chloride in THF [10], the *gem*-diiodoalkanes required for the preparation of such zinc reagents are not easily accessible nor are they very stable.

The reaction of ethyl chloro(chloromercuri)acetate with methylidynetricobalt nonacarbonyl was less satisfactory, giving the expected $EtO_2CCH_2CCo_3(CO)_9$ in only 2% yield. A product formed in greater (5%) yield was $CH_3CCo_3(CO)_9$, which can be accounted for in terms of the unexpected reductive cleavage of the ethoxycarbonyl group.

The action of several phenyl(trihalomethyl)mercury compounds on $HCCo_3(CO)_9$ also was examined in the hope that the trihalomethyl group might be transferred to the cluster. However, such was not the case; the phenyl group was transferred in high yield, giving $C_6H_5CCo_3(CO)_9$: $PhHgCF_3$ (87%), $PhHgCCl_2Br$ (59%), $PhHgCBr_3$ (60%). Phenyl(trifluoromethyl)mercury was unexpectedly reactive. When its reaction with $HCCo_3(CO)_9$ was carried out in benzene at reflux, under nitrogen, the characteristic change in color – from the purple color of $HCCo_3(CO)_9$ to the brown color of $PhCCo_3(CO)_9$ – occurred within 10 min and within 90 min the starting materials were consumed.

Acetylenedicobalt hexacarbonyl complexes are related structurally to the alkylidynetricobalt nonacarbonyls in that they contain a pseudotetrahedral array of two carbon and two cobalt atoms. In such complexes also, C—H bonds can be phenylated with diphenylmercury [eqn. (11) and (12)], but the product yields are rather low.



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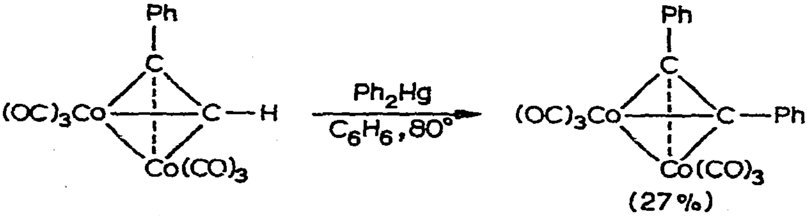

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While organomercurials appear to be the most effective alkylating agents for $HCCo_3(CO)_9$, organic derivatives of tin and lead also can be used to effect organic group transfer to the $CCo_3(CO)_9$ cluster. Thus, a reaction of tetraphenyltin with $HCCo_3(CO)_9$ in refluxing benzene for 48 h gave $PhCCo_3(CO)_9$ in 27% yield, while a similar reaction carried out for 12 h with tetraphenyllead as phenyl group source gave this product in 18% yield.

It is of interest to consider possible mechanisms of the novel reactions reported above. Usually, when organomercurials are used to alkylate or arylate C—H bonds, e.g., those of benzene and its derivatives or of condensed aromatic compounds, prior homolytic scission of the C—Hg bonds is required to produce the radicals which then react in a typical homolytic aromatic substitution process. Thus, usually such reactions require conditions which serve to break the mercury—carbon bond: photolysis, γ-radiolysis or thermolysis [11]. The arylation of a C—H bond under the rather mild conditions of our experiments therefore are rather surprising. One may still consider a radical process, one in which the initiation is provided by radicals generated in the homolytic decomposition of some $HCCo_3(CO)_9$ molecules, i.e.:

$$HCCo_3(CO)_9 \longrightarrow \text{radicals} + CO\ ?$$

$$r^{\bullet} + Ph_2Hg \longrightarrow PhHgr + Ph^{\bullet}$$

$$\mathrm{PhHgr} \longrightarrow \mathrm{Ph}^{\bullet} + \mathrm{r}^{\bullet} + \mathrm{Hg}$$

$$\mathrm{HCCo_3(CO)_9} + \mathrm{Ph}^{\bullet} \longrightarrow \mathrm{PhCCo_3(CO)_9} + \mathrm{H}^{\bullet}$$

A radical process however, is not supported by our observation that arylmercurials are much more reactive than alkylmercurials. Neither the presence of a radical catalyst, azobisisobutyronitrile (AIBN), nor of a radical inhibitor, Galvinoxyl, appeared to affect the rate or the course of the reaction of dianisylmercury with $HCCo_3(CO)_9$. In these instances, however, it was not known if the additives survived the reaction conditions sufficiently long to have any effect on the reaction. In this connection, we note other evidence [27] that AIBN can initiate the addition of $HCCo_3(CO)_9$ to the C=C bond of olefins.

An alternative mechanism involves electrophilic cleavage of the mercury—carbon bond by $HCCo_3(CO)_9$. The NMR spectrum of methylidynetricobalt nonacarbonyl in $CDCl_3$ consists of a single resonance at δ 12.1 ppm downfield from tetramethylsilane. This suggests that the hydrogen atom is very deshielded and that it might be acidic in nature, $H^{\delta+}{-}C^{\delta-}CO_3(CO)_9$. Relatively weak acids such as thiophenols can cause cleavage of the Hg—C(aryl) bond [12] and hence if $HCCo_3(CO)_9$ is somewhat acidic, it also might cleave the mercury—carbon bond. Such a mechanism would serve to explain the greater reactivity of the arylmercurials, compared with alkylmercurials. Such a process might proceed as follows:

$$\mathrm{Ar_2Hg} + \mathrm{HCCo_3(CO)_9} \longrightarrow \mathrm{ArH} + \mathrm{ArHgCCo_3(CO)_9} \tag{13}$$

$$\mathrm{ArHgCCo_3(CO)_9} \longrightarrow \mathrm{ArCCo_3(CO)_9} + \mathrm{Hg} \tag{14}$$

Attempts were made to prepare and isolate the postulated intermediate, $ArHgCCo_3(CO)_9$, but compounds of this type could not be isolated.

At the present time, decisive evidence concerning the mechanism of the $R_2Hg/HCCo_3(CO)_9$ reaction in not available, and further speculation on this question is not justified. An observation of possible significance in this connection is that in cases where no $ArCCo_3(CO)_9$ product is formed in such reactions, both the $HCCo_3(CO)_9$ and the mercurial are consumed. Thus in an experiment in which equimolar quantities of dimesitylmercury and $HCCo_3(CO)_9$ were heated in refluxing benzene under CO for 6 days, the mercurial was consumed (by TLC) and the mercury yield was 54%. Only 21% of the organocobalt starting material was recovered.

Also of interest to the question of mechanism is the fact that (halomethylidyne)tricobalt nonacarbonyl complexes, $XCCo_3(CO)_9$ (X = Cl, Br, I), also react with diphenylmercury to give $PhCCo_3(CO)_9$, although the yields of the latter are only moderate. Especially interesting is the formation of by-products derived from CO incorporation when the $Ph_2Hg/ICCo_3(CO)_9$ reaction was carried out in a stream of carbon monoxide [eqn. (15)]. Clearly, these reactions merit further study.

$$\mathrm{Ph_2Hg} + \mathrm{ICCo_3(CO)_9} \xrightarrow[\text{CO, 24 h}]{\text{Benzene, 58}^{\circ}} \begin{array}{l} \mathrm{PhCCo_3(CO)_9}\ (41\%) \\ \mathrm{PhC(O)CCo_3(CO)_9}\ (26\%) \\ \mathrm{(OC)_9Co_3C\text{-}CCo_3(CO)_9}\ \text{(trace)} \\ \mathrm{(OC)_9CO_3CCO_2H}\ \text{(trace)} \end{array} \tag{15}$$

In conclusion, we note that alternate routes to $RCCo_3(CO)_9$ and $ArCCo_3(CO)_9$ compounds have become available since this work was completed. A wide variety of alkylidynetricobalt nonacarbonyls of type $RCH_2CCo_3(CO)_9$ is available via reduction of $RC(O)CCo_3(CO)_9$ complexes with Et_3SiH/CF_3CO_2H [13]. $ArCCo_3(CO)_9$ compounds can be prepared by the aluminum chloride-induced reaction of chloromethylidynetricobalt nonacarbonyl with arenes [14] and by the reaction of $ClCCo_3(CO)_9$ with large excesses of aryl Grignard reagents under unspecified conditions [15]. An earlier claim [16] that such reactions with Grignard reagents could be used to introduce alkyl groups at the apical carbon atom of the $CCo_3(CO)_9$ cluster has been withdrawn [17]. Also, it appears that the previously claimed alkylation of $ClCCo_3(CO)_9$ [16] with organolithium reagents is not correct [17].

The formation of reduced products in the reactions of (α-haloalkyl)-mercurials with $HCCo_3(CO)_9$ also is not well understood. Formally, the products formed, e.g., $CH_3CCo_3(CO)_9$ in the case of the $Hg(CH_2I)_2/HCCo_3(CO)_9$ reaction, could be considered divalent carbon insertion products into the C—H bond. However, a more complicated course involving alkylation and reduction steps also is possible. In this connection, we note that the formation of unexpected reduction products is common in methylidynetricobalt nonacarbonyl chemistry. For instance, the reaction of hexachloroethane with dicobalt octacarbonyl gave $CH_3CCo_3(CO)_9$ [18] while the reaction of alcohols of type CX_3CR_2OH with $Co_2(CO)_8$ resulted in formation of $CHR_2CCo_3(CO)_9$ complexes, rather than the expected $HOCR_2CCo_3(CO)_9$ [19]. It is obvious that the question of mechanism in the $R_2Hg/HCCo_3(CO)_9$ and $(RCHX)_2Hg/HCCo_3(CO)_9$ reactions requires further attention. Nevertheless, these reactions have good preparative utility. In view of the facile direct mercuration of a wide variety of aromatic compounds to give compounds of type ArHgX, and of the ease of preparation of arylmercurials via aryl derivatives of other metals, the preparation of $ArCCo_3(CO)_9$ compounds via arylmercurials should find useful application.

Experimental

General comments

Most reactions were carried out in a flame-dried 100 ml, three-necked flask equipped with a magnetic stirring unit, a reflux condenser and a gas inlet tube ("standard apparatus"). Column chromatography was used extensively for separation of products. In general a 40 × 600 mm column fitted with a fritted glass disc and a Teflon stopcock was used. Silicic acid(Mallinckrodt reagent, 100 mesh) served well in most separations. Thin layer chromatography (TLC) was used for monitoring the progress of reactions (Eastman Chromagram Sheet No. 6060). The cobalt-containing species are intensely colored and can readily be observed directly. Mercury-containing species were observed upon visualization with iodine vapor as white spots, while cobalt-containing species turned brown.

Infrared spectra were obtained using Perkin—Elmer 237B, 337, 257 or 457A double beam grating infrared spectrophotometers. NMR spectra were obtaining using Varian T60 or Perkin—Elmer R20 NMR spectrometers. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Tetrahydrofuran (THF) was distilled either from sodium benzophenone ketyl or lithium aluminum hydride immediately before use; benzene was distilled from potassium benzophenone ketyl and stored under nitrogen.

Dicobalt octacarbonyl was purchased from Strem Chemical Co. Methylidynetricobalt nonacarbonyl was prepared as described in ref. [5]. The organomercurials used were prepared by standard literature methods, usually the Grignard procedure.

Reactions of organomercurials with methylidynetricobalt nonacarbonyl under nitrogen

With diphenylmercury. The standard apparatus was charged with 0.884 g (2.0 mmol) of methylidynetricobalt nonacarbonyl, 1.035 g (3.0 mmol) of diphenylmercury and 70 ml of dry benzene. The mixture was stirred under nitrogen to effect solution and then was stirred and heated at reflux for 6 h. After this time, TLC (hexane) showed that the starting materials had been consumed. The mixture was filtered and the pool of mercury was washed repeatedly with 10% aqueous nitric acid and then with acetone to leave 0.360 g (60%) of mercury. The filtrate was evaporated at reduced pressure, leaving a brown solid residue. The latter was dissolved in the minimum quantity of hexane and purified by column chromatography (hexane). A single brown solid was eluted, which after sublimation in vacuo at 50°, yielded 0.57 g (56%) of brown, crystalline solid whose IR spectrum was identical to that of an authentic sample of $PhCCo_3(CO)_9$.

Similar reactions were carried out with other R_2Hg compounds (Table 1).

With p-chlorophenylmercuric bromide. The standard apparatus was charged with 0.442 g (1.0 mmol) of $HCCo_3(CO)_9$, 0.391 g (1.0 mmol) of *p*-chlorophenylmercuric bromide and 50 ml of dry benzene. The mixture was stirred at reflux under nitrogen for 8 h. TLC (hexane) indicated the presence of two cobalt-containing compounds but the absence of organomercurial. The mixture was filtered and the residue washed with 10% nitric acid and acetone to leave 0.063 g (32%) of mercury. Evaporation of the filtrate at reduced pressure was followed by column chromatography of the residue (hexane). A purple material, m.p. 104 - 106°, eluted first and was identified as starting material. The brown solid which was eluted next was recrystallized from hexane to give 0.30 g (54%) of $p\text{-}ClC_6H_4CCo_3(CO)_9$.

Similar reactions were carried out with other RHgX compounds (Table 1) and with phenylmercuric bromide in other solvents (Table 2).

Isolation of other products

A reaction of 2.0 mmol each of diphenylmercury and $HCCo_3(CO)_9$ in 15 ml of dry THF at reflux for 5 h under nitrogen was followed by trap-to-trap distillation of volatiles at 50°/0.1 mm. GLC analysis of the distillate (10% Carbowax 20M on Chromosorb W at 75°) showed the presence of benzene (57% yield, identified by its IR spectrum) in addtion to solvent. The residue was extracted with hexane. The hexane extracts were chromatographed (silicic acid column, hexane eluant) to give a light purple solid (starting material) and a dark brown solid. The latter was sublimed at 60°/0.05 mm, giving first traces (< 0.01 g) of $Hg[Co(CO)_4]_2$, a yellow solid, m.p. 81 - 82°, and then 0.54 g (51%) of $PhCCo_3(CO)_9$. The residue from the hexane extraction was washed with 10% HNO_3 and acetone, leaving 0.2 g (50%) of metallic mercury.

When more $Hg[Co(CO)_4]_2$ was formed, as was the case in some reactions it could be separated by column chromatography. Thus in another Ph_2Hg/$HCCo_3(CO)_9$ reaction in THF, column chromatography gave, in this order, $HCCo_3(CO)_9$ (11%), $Hg[Co(CO)_4]_2$ and $PhCCo_3(CO)_9$ (47%). The second fraction was treated with an excess of triphenylphosphine and cooled to give the insoluble $Hg[Co(CO)_3PPh_3]_2$ (5%), whose IR spectrum was identical to that of an authentic sample.

Reactions of organomercurials with methylidynetricobalt nonacarbonyl under carbon monoxide

With Di-p-tolylmercury. The standard apparatus was charged with 0.886 g (2.0 mmol) of $HCCo_3(CO)_9$, 0.766 g (2.0 mmol) of di-*p*-tolylmercury and 60 ml of dry benzene. In the reactions carried out under CO, the gas inlet tube extended below the surface of the reaction mixture. Carbon monoxide was bubbled through the solution for 30 min and then the mixture was heated at reflux for 7 h while a slow carbon monoxide stream was maintained. After this time, TLC showed that the starting materials had been consumed. The volatiles were removed by trap-to-trap distillation at 0.01 mm and the distillate was analyzed by GLC (10% Carbowax 20M at 80°) to show the presence of toluene (1.2 mmol). Extraction of the residue with hexane was followed by treatment of the hexane-insoluble material with 10% HNO_3 and acetone to leave metallic mercury (49%). The hexane extracts were purified by column chromatography. A single fraction was eluted which, after sublimation in vacuo at 50°, yielded 0.97 g (92%) of p-$CH_3C_6H_4CCo_3(CO)_9$.

A similar reaction was carried out between di-*p*-tolylmercury and $DCCo_3(CO)_9$ [5] on a 3 mmol scale in 50 ml of dry benzene for 2 h at reflux under carbon monoxide. Trap-to-trap distillation of the reaction mixture at 0.02 mm gave 53.14 g of distillate. GLC (20% General Electric Co. SE-30 on Chromosorb P at 110°) showed the presence of toluene (0.91 mmol). The mass spectrum of a collected sample indicated the composition 9.7% toluene-d_0, 88.5% toluene-d_1 (ring deuterated) and 1.8% toluene-d_2, by comparison of relative intensities of peaks at *m/e* 89 - 95 [20]. Further work-up of the residue as described above showed the presence of elemental mercury (38%), starting $HCCo_3(CO)_9$ (4%) and p-$CH_3C_6H_4CCo_3(CO)_9$ (89%).

This procedure was used in reactions of other diarylmercurials with $HCCo_3(CO)_9$.

With phenylmercuric bromide. This reaction was carried out in the same manner on a 1.0 mmole scale in 50 ml of benzene, at reflux for 2 h; after this time another 1.0 mmole of PhHgBr was added and the reaction mixture was refluxed under carbon monoxide for another h. TLC showed the presence of two mercury compounds. After a total of 4 h, the starting materials were consumed. The usual work-up gave a 2% recovery of $HCCo_3(CO)_9$, mercury metal (14%) and $PhCCo_3(CO)_9$ in 58% yield.

With di-n-amylmercury. The reaction was carried out using 1.5 mmol each of di-n-amylmercury and $HCCo_3(CO)_9$ in 50 ml of benzene, at reflux under carbon monoxide for a period of 8 days. The usual work-up gave metallic mercury (57%), $n\text{-}C_5H_{11}CCo_3(CO)_9$, a red solid, in 38% yield, trace amounts of $HCCo_3(CO)_9$ and $Hg[Co(CO)_4]_2$ (4%).

In a reaction of 2 mmol of $HCCo_3(CO)_9$ and 3 mmol of $CH_3OCH_2CH_2HgCl$ in 60 ml of dry benzene at reflux under CO for 7 days the starting material recovery was 43%; $CH_3OCH_2CH_2CCo_3(CO)_9$ was isolated in 32% yield by the usual procedure.

Reactions of (halomethyl)mercurials with methylidynetricobalt nonacarbonyl (summarized in Table 4)

Bis(bromomethyl)mercury. A mixture of 2 mmol each of $Hg(CH_2Br)_2$ [10a,b] and $HCCo_3(CO)_9$ in 50 ml of benzene was stirred and heated at reflux under nitrogen for 48 h. The usual work-up gave elemental mercury (14%) and a purple solid which was sublimed at 55°/0.07 mm to give 0.513 g (1.13 mmol, 57%) of $CH_3CCo_3(CO)_9$, whose infrared spectrum was identical with that of an authentic sample. Its NMR spectrum in $CDCl_3$ showed a singlet at δ 3.67 ppm, at 3.60 ppm in CCl_4.

A similar reaction was carried out between 2 mmol each of this mercurial and $DCCo_3(CO)_9$ [5]. Mercury metal was isolated in 28% yield. The organocobalt product was identified as $CDH_2CCo_3(CO)_9$, m.p. 181.5 - 183° (dec), obtained in 75% yield. NMR ($CDCl_3$): δ 3.67 ppm (t, J_{HD} 2 Hz).

Bis(iodomethyl)mercury. A reaction, under CO at reflux, of 2 mmol each of $Hg(CH_2I)_2$ [10b, c] and $HCCo_3(CO)_9$ in 60 ml of benzene for 24 h gave as organocobalt product $CH_3CCo_3(CO)_9$ in 77% yield. A similar reaction between 2 mmol of $HCCo_3(CO)_9$ and 2 mmol of $Hg(CD_2I)_2$ [10] in 50 ml of benzene resulted in formation of $CD_2HCCo_3(CO)_9$ (0.55 g, 61%), m.p. 184 - 185° (dec). The atom % excess deuterium (falling drop method, J. Nemeth Urbana Ill.) found was 55.3; calcd. for $C_{10}HD_2O_9Co_3$: 66.7%. [The $Hg(CD_2I)_2$ contained 97.2% CD_2I and 2.8% CHDI group, via I_2 cleavage of the mercurial and mass spectrometric analysis of the diiodomethane produced [10b]]. The NMR spectrum in $CDCl_3$ of $CD_2HCCo_3(CO)_9$ showed a quintet (J_{HD} 1 Hz) at δ 3.60 ppm.

A similar reaction of 2 mmol each of $HCCo_3(CO)_9$ and $(Me_3SiCHBr)_2Hg$ [21] in 50 ml of benzene at reflux under nitrogen for 21 h gave 0.74 g (70%) of $Me_3SiCH_2CCo_3(CO)_9$ and metallic mercury (44%).

Ethyl chloro(chloromercuri)acetate. This mercurial was prepared by reaction of 20 mmol of mercuric acetate with 20 mmol of 1,2-dichlorovinyl ethyl ether in 70 ml of absolute ethanol under nitrogen. After 2 h, 20 mmol of NaCl in 150 ml of water was added and the mixture was stirred overnight and extracted with chloroform. The mercurial was precipitated by adding diethyl ether to the chloroform solution to give white needles m.p. 80 - 81°. (Found: C, 13.70; H, 1.87. $C_4H_6O_2Cl_2Hg$ calcd.: C, 13.43; H, 1.69%.) NMR ($CDCl_3$): δ 1.34 (t, 3H, CH_3), 4.23 (q, 2H, CH_2) and 4.73 ppm (s, 1H, CHCl, $J(H\text{—}^{199}Hg)$ 256 Hz). IR ($CHCl_3$): ν(C=O) 1750 cm^{-1}. The yield of $ClHgCHClCO_2Et$ thus obtained was 66%.

TABLE 4

REACTIONS OF (HALOMETHYL) MERCURIALS WITH $HCCo_3(CO)_9$ IN BENZENE

Mercurial (mmol)	$HCCo_3(CO)_9$ (mmol)	Reaction time (h)	Product (% yield)[a]	Hg^0 (%) yield)
$Hg(CH_2Br)_2$ (2.0)	2.0	48[b]	$CH_3CCo_3(CO)_9$ (57)	14
$BrCH_2HgBr$ (2.0)	2.0	41[b]	$CH_3CCo_3(CO)_9$ (59)	71
$Hg(CH_2Br)_2$ (2.0)	$DCCo_3(CO)_9$ (2.0)	48[b]	$CDH_2CCo_3(CO)_9$ (75)	28
$Hg(CH_2I)_2$ (2.0)	2.0	24[c]	$CH_3CCo_3(CO)_9$ (77)	
$Hg(CD_2I)_2$ (2.0)	2.0	22[c]	$CHD_2CCo_3(CO)_9$ (61)	
$Hg(CHICH_3)_2$ (2.0)	2.0	24[c]	$C_2H_5CCo_3(CO)_9$ (88)	51
$Hg(CHBrSiMe_3)_2$ (2.0)	2.0	21[c]	$Me_3SiCH_2CCo_3(CO)_9$ (70)	54
$ClHgCHClCO_2Et$ (2.0)	2.0	24[c]	$EtO_2CCH_2CCo_3(CO)_9$ (2) + $CH_3CCo_3(CO)_9$ (5)	74
$PhHgCF_3$ (2.0)	2.0	1.5[b] (in C_6H_6)	$PhCCo_3(CO)_9$ (87)	
$PhHgCF_3$ (2.0)	2.0	8[b] (in THF)	$PhCCo_3(CO)_9$ (73)	41
$PhHgCCl_2Br$ (2.0)	1.5	2.5[b]	$PhCCo_3(CO)_9$ (59)	
$PhHgCBr_3$ (2.0)	1.5	1[b]	$PhCCo_3(CO)_9$ (60)	

[a] Based on utilization of one R in R_2Hg or RHgX. [b] Reaction carried out under nitrogen. [c] Reaction carried out under carbon monoxide.

A reaction of 2 mmol each of this mercurial and $HCCo_3(CO)_9$ in 50 ml of benzene, at reflux under CO, for 24 h was followed by the addition of an additional 1 mmol of the mercurial and a further 6 day reflux period. The usual work-up gave metallic mercury (74%) Column chromatography gave two fractions: (1) a red solid which was sublimed at 50° in vacuo to give 0.400 g, m.p. 102 - 104°. This was shown by NMR to contain $HCCo_3(CO)_9$ (41% recovery) and $CH_3CCo_3(CO)_9$ (5% yield); (2) red $(OC)_9Co_3CH_2CO_2CH_2CH_3$ (0.02 g 2% yield).

Phenyl(trifluoromethyl)mercury. A benzene solution containing 2 mmol each of $HCCo_3(CO)_9$ and phenyl(trifluoromethyl)mercury [22] (50 ml) was stirred and heated at reflux under nitrogen. Within 10 min, the initially purple solution became brown. After 90 min, TLC no longer detected the presence of $HCCo_3(CO)_9$. The usual work-up failed to find metallic mercury. Column chromatography and sublimation at 50° in vacuo gave 0.90 g (1.74 mmol, 87%) of $PhCCo_3(CO)_9$.

A similar reaction in THF (under nitrogen, 8 h reflux) gave metallic mercury (41%) and $PhCCo_3(CO)_9$ in 73% yield.

Reaction of acetylenedicobalt hexacarbonyl with diphenylmercury

The standard apparatus was charged with 2.0 mmol of Ph_2Hg in 60 ml of dry benzene and the solution was stirred and saturated with carbon monoxide for 30 min. Acetylenedicobalt hexacarbonyl [red liquid, bp 62° (3 mm)] [23] (2.0 mmol) was added by syringe. The resulting mixture was heated at reflux while maintaining a slow stream of carbon monoxide through the solution for 3 h, until the mercurial was consumed (by TLC). Filtration was followed by evaporation of the filtrate at reduced pressure. The residue was dissolved in hexane and resolved into its components by column chromatography (silicic acid; hexane eluant). The first fraction, a red oil, was starting cobalt complex (0.25 g, 40% recovery). The second was $Hg[Co(CO)_4]_2$ and was isolated as $Hg[Co(CO)_3PPh_3]_2$ (0.51 g, 25%). The third fraction gave, after sublimation at 50° in vacuo, 0.17 g (21%) of brown solid whose IR spectrum was superimposable with that of authentic phenylacetylenedicobalt hexacarbonyl [23]. A fourth fraction was sublimed in vacuo at 50° to give 0.09 g (10%) of black solid, m.p. 108°, whose IR spectrum was identical to that of authentic diphenylacetylenedicobalt hexacarbonyl (m.p. [23] 110°).

A similar reaction of 10 mmol of diphenylmercury with 4 mmol of acetylenedicobalt hexacarbonyl in 50 ml of benzene, at reflux under CO, for 3 h gave little, if any, product. Instead, large amounts of $Hg[Co(CO)_4]_2$ were produced.

Reaction of phenylacetylenedicobalt hexacarbonyl with diphenylmercury

The standard apparatus was charged with 2.0 mmol of diphenylmercury, 2.0 mmol of phenylacetylenedicobalt hexacarbonyl [23], a brown oil of better than 95% purity (by TLC), and 50 ml of benzene. The solution was saturated with carbon monoxide and then was stirred and heated at reflux while CO was bubbled through the mixture for 4 h. Filtration and evaporation of the filtrate at reduced pressure left an oil. Column chromatographic resolution of the latter gave a brown oil identified by IR as starting material (0.50 g, 70%) and black solid which was sublimed at 70° in vacuo to give 0.25 g (27%) of diphenylacetylenedicobalt hexacarbonyl, m.p. 108°.

Reaction of Group IV tetraphenyls with methylidynetricobalt nonacarbonyl

The standard apparatus was charged with 1.0 mmol each of $HCCo_3(CO)_9$ and tetraphenyltin and 50 ml of dry benzene. The reaction mixture was stirred and heated at reflux under nitrogen for 48 h. TLC showed the presence of starting material and an additional brown component. The mixture was filtered and the filtrate was evaporated at reduced pressure. Column chromatography of the residue gave starting material (30% recovery after one sublimation) and 0.14 g (27%) of benzylidynetricobalt nonacarbonyl.

A similar reaction was carried out on a 2 mmol scale with tetraphenyllead in benzene (12 h reflux under nitrogen). Filtration left a residue which was pyrophoric in air. Work-up of the filtrate as in the case of the tetraphenyltin reaction gave $HCCo_3(CO)_9$ (4%) and $PhCCo_3(CO)_9$ (18%).

Reactions of diphenylmercury with halomethylidynetricobalt nonacarbonyls

With chloromethylidynetricobalt nonacarbonyl. A solution containing 1.5 mmol each of diphenylmercury and $ClCCo_3(CO)_9$ in 50 ml of benzene was stirred and heated at reflux under nitrogen for 12 h, until the mercurial had been consumed (by TLC). The mixture was filtered and the residue washed repeatedly with hexane to leave 60 mg of PhHgCl. The filtrate was evaporated at reduced pressure and column chromatography of the residue gave (after sublimation of the isolated products) 0.12 g (21%) of $ClCCo_3(CO)_9$ and 0.215 g (28%) of $PhCCo_3(CO)_9$.

With bromomethylidynetricobalt nonacarbonyl. A similar reaction was carried out using 1.5 mmol each of Ph_2Hg and $BrCCo_3(CO)_9$ in benzene, at reflux under nitrogen, for 3 h, until consumption of the mercurial. The usual work-up gave metallic mercury (31%), $BrCCo_3(CO)_9$ (18%) and $PhCCo_3(CO)_9$ (34%).

With iodomethylidynetricobalt nonacarbonyl. The $ICCo_3(CO)_9$ used contained a small amount of $ClCCo_3(CO)_9$, having been prepared by reaction of CI_4 with $Co_2(CO)_8$ in carbon tetrachloride solution [5].

The procedure described above was used in the reaction of 2 mmol each of diphenylmercury and $ICCo_3(CO)_9$ in 50 ml of benzene at reflux under nitrogen for 30 h. The usual work-up gave $PhCCo_3(CO)_9$ in 42% yield.

Another reaction was carried out between 2.3 mmol of Ph_2Hg and 2.0 mmol of $ICCo_3(CO)_9$ in 50 ml of benzene at 58° for 24 h while carbon monoxide was passed slowly through the stirred reaction mixture. The reaction mixture was filtered to remove 0.70 g (87%) of phenylmercuric iodide. The filtrate was evaporated at reduced pressure. Column chromatography served in the resolution of the residue. Five components were separated (silicic acid, hexane eluant) in the order listed: $ICCo_3(CO)_9$ (27%); $PhCCo_3(CO)_9$ (41%); $(OC)_9Co_3C\text{-}CCo_3(CO)_9$ (see below) (trace); $PhC(O)CCo_3(CO)_9$ (26%) and $(OC)_9Co_3CCO_2H$ (trace). An authentic sample of $PhC(O)CCo_3(CO)_9$ was available [5] for spectroscopic comparison, as was a sample of the cluster-substituted carboxylic acid [24].

Preparation of an authentic sample of bis(methylidynetricobalt) nonacarbonyl

The standard apparatus was charged with 2 mmol of $BrCCo_3(CO)_9$, 1.26 g of activated copper bronze [25], 3.4 g of *p*-bromotoluene and 25 ml of benzene. The reaction mixture was stirred and heated at reflux while a stream of carbon monoxide was passed slowly into the solution for a period of 3 h. The mixture was filtered and the filtrate was evaporated at reduced pressure. The residue was recrystallized from hexane to give 0.30 g (35%) of the title compound. (Found: C, 27.47. $C_{20}O_{18}Co_6$ calcd.: C, 27.24%.) Its IR spectrum was identical to that reported in the literature [26].

A similar reaction carried out with 2.0 mmol of $ClCCo_3(CO)_9$, 20 mmol of *p*-iodotoluene, 1.26 g of activated copper bronze in 25 ml of n-octane at 120° in a stream of CO for 2 h gave $p\text{-}CH_3C_6H_4CCo_3(CO)_9$ in 20% yield.

Oxidation of substituted benzylidynetricobalt nonacarbonyl complexes

(a). With potassium permanganate. A 300 ml round-bottomed flask was charged with 1.06 g (2.00 mmol) of $CH_3C_6H_4CCo_3(CO)_9$ obtained from the reaction of di-*p*-tolylmercury and methylidynetricobalt nonacarbonyl, 150 ml of reagent grade acetone and 25 ml of distilled water. The mixture was stirred

vigorously and 3.18 g (20.0 mmol) of solid $KMnO_4$ was added in portions. An exothermic reaction resulted. After the reaction mixture had been stirred for 1 h it was diluted with 400 ml of water and acidified with 50 ml of concd. HCl. This mixture was extracted with 250 ml of ethyl acetate. Evaporation of the extracts at reduced pressure left a white solid which was dissolved in 10% aqueous NaOH. Acidification of this solution gave a flocculent white precipitate which was recrystallized from methanol-water to give 0.18 g (66%) of *p*-toluic acid, m.p. 178 - 180°, identical (m.p. and IR) with an authentic sample.

Similar oxidations were carried out as follows: $CH_3C_6H_4CCo_3(CO)_9$, from di-*m*-tolylmercury and methylidynetricobalt nonacarbonyl, to *m*-toluic acid, m.p. 110 - 112°, in 56% yield. $CH_3C_6H_4CCo_3(CO)_9$, from di-*o*-tolylmercury and methylidynetricobalt nonacarbonyl, to *o*-toluic acid, m.p. 103 - 104°, in 58% yield. $ClC_6H_4CCo_3(CO)_9$, from di-*o*-chlorophenylmercury and methylidynetricobalt nonacarbonyl, to *o*-chlorobenzoic acid, m.p. 141.5 - 142.5°, in 58% yield.

All acids were identified by comparison of their melting points with literature values and by comparison of their IR spectra with those of the respective isomers in the Sadtler Standard Spectra collection.

(b). With ceric ammonium nitrate. A 300 ml three-necked flask equipped with a gas outlet tube was charged with 0.822 g (1.5 mmol) of $CH_3OC_6H_4CCo_3(CO)_9$, obtained from the reaction of di-*p*-anisylmercury with methylidynetricobalt nonacarbonyl, 150 ml of reagent grade acetone and 15 ml of distilled water. Ceric ammonium nitrate (8.22 g, 15 mmol) was added in portions to the vigorously stirred mixture. The reaction mixture was stirred for 1 h. Subsequently, the acetone was removed at reduced pressure, leaving a suspension of white solid in water. Ethyl acetate and more water were added. After separation of layers, the aqueous phase was extracted twice with ethyl acetate. Evaporation of the organic layer left a white solid which was dissolved in aqueous NaOH. Acidification gave a flocculent white solid. A second base/acid treatment gave 0.19 g (83%) of *p*-methoxybenzoic acid, m.p. 183 - 184.5°.

This procedure also was applied successfully in the following cases: $ClC_6H_4CCo_3(CO)_9$, from di-*p*-chlorophenylmercury and methylidynetricobalt nonacarbonyl, to *p*-chlorobenzoic acid, m.p. 238 - 240°, in 79% yield. $ClC_6H_4CCo_3(CO)_9$, from di-*m*-chlorophenylmercury and methylidynetricobalt nonacarbonyl, to *m*-chlorobenzoic acid, m.p. 153 - 155°, in 51% yield. $CH_3C_6H_4CCo_3(CO)_9$, from di-*p*-tolylmercury and methylidynetricobalt nonacarbonyl, to *p*-toluic acid, m.p. 178 - 180°, in 82% yield.

When this procedure was applied in the case of *m*-$CH_3C_6H_4CCo_3(CO)_9$, evaporation left an oil which solidified at −78°. When a sodium hydroxide solution of this material was acidified, only a negligible amount of precipitate resulted. The original water layer was made basic, concentrated to 100 ml and acidified, but no solid was obtained. Several variations of the above procedure were equally unsuccessful.

Attempted oxidation of the substituted benzylidynetricobalt nonacarbonyl complexes prepared via di-*o*-tolylmercury and di-*o*-chlorophenylmercury with ceric ammonium nitrate failed to give any substituted benzoic acids.

(c) With bromine. A 200 ml 3-necked flask was equipped with an addition funnel, a reflux condenser, a magnetic stirring unit and a nitrogen inlet tube. The funnel was charged with 2.24 g of $ClC_6H_4CCo_3(CO)_9$, obtained by reaction of di-*p*-chlorophenylmercury and methylidynetricobalt nonacarbonyl, and 10 ml of warm ethanol, while 50 ml of ethanol and 2.2 ml (ca. 41 mmol) of bromine were added to the reaction flask. The cluster solution was added to the bromine over a period of 5 min. Gas evolution was immediate. The reaction mixture was stirred at room temperature for 30 min and then was evaporated at reduced pressure. The solid residue was extracted with dichloromethane and water. The organic layer was dried and evaporated. The solid obtained was treated with excess of sodium thiosulfate and water, followed by an excess of sodium hydroxide. The resulting mixture was heated on the steam bath for 15 min, filtered, and the filtrate was acidified. The solid acid which precipitated was recrystallized from chloroform/dichloromethane to give 0.228 g (36%) of *p*-chlorobenzoic acid, m.p. 240 - 241°.

New compounds

The new compounds prepared during the course of this study whose properties and analyses are not given in the text are listed in Table 5.

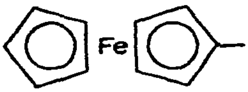
The IR and NMR spectra of all compounds were recorded. In general, all alkylidynetricobalt nonacarbonyl complexes show five bands in their IR spectrum in the region 2150 to 1950 cm^{-1} (terminal carbonyl region) with the intensity pattern: medium, very strong, strong, weak, very weak. As such, they serve to identify an $RCCo_3(CO)_9$ cluster complex, but shifts in these bands with change in the apical substituent R among organic groups are so minimal as to have little diagnostic value. Accordingly, only a few such spectra in this region are described as typical examples. IR spectra, in carbon tetrachloride solution; terminal CO region (in cm^{-1}):

o-$CH_3C_6H_4CCo_3(CO)_9$, 2108m, 2065vs, 2045s, 2030w, 1980vw;
$C_6F_5CCo_3(CO)_9$, 2108m, 2068vs, 2050s, 2025w, 1990vw;
n-$C_5H_{11}CCo_3(CO)_9$, 2103m, 2060vs, 2042s, 2010w, 1975vw;
$CH_3OCH_2CH_2CCo_3(CO)_9$, 2090m, 2080vs, 2065s, 2020w, 1965vw;
$CH_3CH_2O_2CCH_2CCo_3(CO)_9$, 2115m, 2075vs, 2050s, 2020w, 1985vw.

NMR spectra, in carbon tetrachloride solution unless otherwise specified, of $RCCo_3(CO)_9$ in δ units, ppm downfield from internal TMS: R = *p*-$CH_3C_6H_4$: 2.37 (s, CH_3), 7.0 - 7.4 (AA'BB' m); *m*-$CH_3C_6H_4$, 2.43 (s, CH_3), 7.0 - 7.3 (m); *o*-$CH_3C_6H_4$, 2.48 (s, CH_3), 7.6 - 7.8 (m); *p*-$CH_3OC_6H_4$, 3.83 (s, OCH_3), 6.8 - 7.4 (AA'BB' m); *p*-FC_6H_4: 6.8 - 7.3 and 7.4 - 7.8 (m); *m*-FC_6H_4, 6.8 - 7.4 (m); *p*-ClC_6H_4, 7.52 (AA'BB' m); *m*-ClC_6H_4, 7.30 and 7.45 (broad s); *o*-ClC_6H_4, 7.24 and 7.70 (broad s); *p*-BrC_6H_4, 7.33 (s); *p*-IC_6H_4, 7.42 (A_2B_2, *J* 18 Hz); C_6F_5, ^{19}F (vs. fluorobenzene): 17.0 (s, ortho F), 43.0 (s, *para*F), 50.0 (s, *meta*F); *p*-$H_2NC_6H_4$ (in acetone-d_6), 2.53 (broad, NH_2), 6.53 and 7.30 (m); $FeC_{10}H_9$ (in $CDCl_3$), 4.47 (s, 4H), 4.25 (s, 5H); $C_6H_5CH_2$, 4.80 (s, CH_2), 7.28 (s); $CH_3OCH_2CH_2$ (in $CDCl_3$), 3.33 (s, OCH_3), 3.83 (AA'BB' m); n-C_5H_{11}, 0.6 - 2.0 (m, n-C_4H_9), 3.70 (t, CH_3C); CH_3, 3.60 (s); C_2H_5 (in $CDCl_3$), 1.53 (t, *J* 8 Hz, CH_3), 3.77 (q, *J* 8 Hz, CH_2); Me_3SiCH_2, 0.20 (s,

TABLE 5

$RCCo_3(CO)_9$ COMPOUNDS PREPARED

R in $RCCo_3(CO)_9$	M.p.(°C)[a]	Color	Analysis[b] found (calcd.) %		
			carbon	hydrogen	other
C_6H_5	105—107	Brown black	(Known compound)[c]		
p-$CH_3C_6H_4$	105—107	Brown	38.52(38.38)	1.52(1.33)	
m-$CH_3C_6H_4$	94—96	Brown	38.45(38.38)	1.57(1.33)	
o-$CH_3C_6H_4$	93—94	Brown	38.48(38.38)	1.56(1.33)	
p-$CH_3OC_6H_4$	97—98	Brown	37.47(37.24)	1.44(1.38)	
p-FC_6H_4	93—95	Brown	35.90(35.85)	0.33(0.75)	
m-FC_6H_4	84—85	Brown	35.93(35.85)	0.97(0.75)	
p-ClC_6H_4	141—143(d)	Brown	34.75(34.79)	0.94(0.72)	
m-ClC_6H_4	104—106	Black	34.92(34.79)	0.84(0.72)	Cl:6.38 (6.42)
o-ClC_6H_4	113—114	Black	34.87(34.79)	0.81(0.72)	Cl: 6.51 (6.42)
p-BrC_6H_4	144—145	Brown	32.17(32.19)	0.88(0.68)	
p-IC_6H_4	115—117	Brown	30.01(29.84)	0.83(0.63)	
C_6F_5	128—129(d)	Bronze	31.58(31.61)		Co: 29.40 (29.08)
p-$H_2NC_6H_4$	133(d)	Bronze	36.11(36.05)	1.28(1.13)	N: 2.65 (2.62)
α-$C_{10}H_7$	64—66	Brown	42.40(42.28)	1.40(1.24)	
	75—77	Black	38.46(38.38)	1.59(1.45)	Co: 27.96 (28.25) Fe: 9.06 (8.92)
$C_6H_5CH_2$	66—68	Red	(Known compound)[d]		
$CH_3OCH_2CH_2$	34—35	Purple	31.16(31.23)	1.41(1.44)	
n-C_5H_{11}	72.5—75	Red	35.24(35.19)	2.34(2.15)	
CH_3	183—184(d)	Red	(Known compound)[e]		
C_2H_5	190—192(d)[f]	Red			
$(CH_3)_3SiCH_2$	36—37	Black	31.79(31.84)	2.49(2.10)	
$CH_3CH_2O_2CCH_2$		Red	31.94(31.85)	1.34(1.33)	

[a] A number of the compounds in this list have been reported by Dolby and Robinson [14] as having been prepared by the Friedel—Crafts procedure. However, although all of these compounds are crystalline solids when pure, these workers did not report a single melting point. [b] Dolby and Robinson [14] have reported difficulties in obtaining acceptable analyses for $ArCCo_3(CO)_9$ compounds, claiming occlusion of unspecified solvent. We have experienced no such difficulties in our work, irregardless of reaction or recrystallization solvent used. [c] Ref. [4] reports m.p. 105—106°. [d] Ref. [4] reports m.p. 68°. [e] Ref. [6] reports m.p. 185° (dec); [f] Ref. [13] reports m.p. 190—192°.

Me_3Si), 3.82 (s, CH_2); $CH_3CH_2O_2CCH_2$, 1.30 (t, *J* 7 Hz, CH_3), 4.31 (q, *J* 7 Hz, OCH_2).

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