

## Preliminary communication

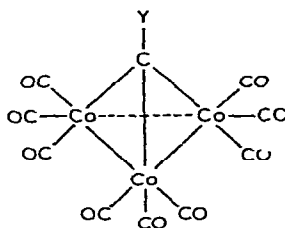
### The C-arylation and alkylation of methylidyne-cobalt nonacarbonyls by organomercury compounds

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Although methylidyne-cobalt nonacarbonyls (I) have been known for some time<sup>1-5</sup>, very little is known about their chemical transformations, in particular, the reactions of the C–Y bond. Ligand substitution processes involving the Co–CO moieties of I have been studied<sup>6-8</sup>, and the thermolysis<sup>9-11</sup> and the degradation by halogens<sup>2</sup> of compounds of type I have been reported. One reaction involving a C–Y bond is the coupling of  $\text{CCO}_3(\text{CO})_9$  units to  $(\text{OC})_9\text{Co}_3\text{C}-\text{CCO}_3(\text{CO})_9$  by the action of a tertiary arsine on  $\text{ClCCO}_3(\text{CO})_9$ <sup>6</sup>.

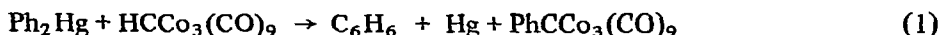


(I)

In  $\text{CH}_3\text{CCO}_3(\text{CO})_9$  the average Co–C–Co bond angle is  $81.1^\circ$ <sup>12</sup>, far from the tetrahedral angle of  $sp^3$  carbon, and the carbon atom in such  $\text{CCO}_3(\text{CO})_9$  clusters is in a rather unusual environment. We feel that the chemistry of the C–Y bond in compounds of type I should be quite novel and interesting and have commenced a broad study of the transformations of such compounds in which the  $\text{CCO}_3(\text{CO})_9$  cluster is preserved. In the present communication we report the successful arylation and alkylation of methylidyne-cobalt nonacarbonyl (Y = H).

We have found that a wide variety of organomercury compounds, both  $\text{R}_2\text{Hg}$  and  $\text{RHgX}$ , are capable of alkylating methylidyne-cobalt nonacarbonyl. Our initial experiments were carried out under dry nitrogen with diphenylmercury. In general, the reaction of one molar equivalent of the mercury compound with one molar equivalent of  $\text{HCCO}_3(\text{CO})_9$  proceeded within a few hours to give  $\text{PhCCO}_3(\text{CO})_9$  in yields of 45–65% based on eq. 1. The other major products were metallic mercury and benzene, thus eq. 1 seems applicable.

These reactions could be carried out in benzene, THF, 1,2-dimethoxyethane (DME), or



cyclohexane. A similar reaction occurred with phenylmercuric bromide. Thus reaction of  $\text{HCCo}_3(\text{CO})_9$  with one molar equivalent of  $\text{PhHgBr}$  in refluxing DME gave  $\text{PhCCo}_3(\text{CO})_9$  in 47% yield during a one hour reaction time. This reaction appeared to proceed less well in benzene, very likely because of the lower solubility of the mercurial in this solvent. Other  $\text{RCCo}_3(\text{CO})_9$  prepared using the respective  $\text{R}_2\text{Hg}$  compound were  $\text{C}_6\text{F}_5\text{CCo}_3(\text{CO})_9$  (64%), m.p. 128–129° dec., and  $\text{PhCH}_2\text{CCo}_3(\text{CO})_9$  (62%), m.p. 68° (lit.<sup>2</sup> m.p. 68°). Prepared via the  $\text{RHgX}$  compound ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) were  $p\text{-FC}_6\text{H}_4\text{CCo}_3(\text{CO})_9$  (66%), m.p. 94–95°,  $p\text{-ClC}_6\text{H}_4\text{CCo}_3(\text{CO})_9$  (54%), m.p. 141–143° dec.,  $\alpha\text{-C}_{10}\text{H}_7\text{CCo}_3(\text{CO})_9$  (11%), and  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CCo}_3(\text{CO})_9$  (14%), m.p. 75–77°.

A significant improvement of this reaction was effected after a minor by-product was identified as  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ . The presence of this compound suggested to us that some degradation of the  $\text{CCo}_3(\text{CO})_9$  cluster was taking place during the arylation or alkylation reaction, and thus it was decided to carry out some of these reactions under an atmosphere of carbon monoxide rather than of nitrogen. If decomposition of  $\text{HCCo}_3(\text{CO})_9$  or of the product  $\text{RCCo}_3(\text{CO})_9$  under the reaction conditions involved initial, reversible loss of carbon monoxide ligand, then the introduction of external carbon monoxide could be beneficial. The improvement which resulted was substantial. The reaction of  $\text{HCCo}_3(\text{CO})_9$  with diphenylmercury in refluxing benzene, carried out while bubbling carbon monoxide at atmospheric pressure into the reaction mixture, was complete within 2 h, and  $\text{PhCCo}_3(\text{CO})_9$  could be isolated in 91% yield. Similar reaction conditions (reaction times as indicated; reaction progress followed by TLC\*) gave  $p\text{-ClC}_6\text{H}_4\text{CCo}_3(\text{CO})_9$  in 83% yield (6 h),  $\text{C}_6\text{F}_5\text{CCo}_3(\text{CO})_9$  in 73% yield (36 h),  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CCo}_3(\text{CO})_9$  in 92% yield (7 h),  $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CCo}_3(\text{CO})_9$  in 64% yield (4 h) and  $\text{PhCH}_2\text{CCo}_3(\text{CO})_9$  in 75% yield (4 days). In each case the respective diarylmercury compound was used.

This improved procedure also was applicable to the synthesis of alkyl derivatives. The reaction of di-*n*-amylmercury with  $\text{HCCo}_3(\text{CO})_9$  (8 days) under carbon monoxide resulted in formation of  $n\text{-C}_5\text{H}_{11}\text{CCo}_3(\text{CO})_9$ , m.p. 73–74°, in 38% yield, while a similar reaction carried out with  $\text{MeOCH}_2\text{CH}_2\text{HgCl}$  gave (after 14 days)  $\text{MeOCH}_2\text{CH}_2\text{CCo}_3(\text{CO})_9$ , m.p. 34–35°, in 32% yield.

Such reactions are easily carried out. The organomercury reagent and the  $\text{HCCo}_3(\text{CO})_9$  (1/1 molar ratio) are mixed with the appropriate solvent (50 ml for a 1–2 mmol reaction) and the reaction mixture is stirred at reflux for the appropriate length of time while bubbling carbon monoxide at a fairly slow rate into the reaction solution. The reaction mixtures are worked up by filtration, evaporation of the filtrate and subsequent column chromatography using Mallinckrodt silicic acid (100 mesh, pH 4 grade) with hexane as eluent. In the isolation of  $\text{ArCCo}_3(\text{CO})_9$  compounds a 200 x 40 mm column suffices, but separation of alkyl- $\text{CCo}_3(\text{CO})_9$  from  $\text{HCCo}_3(\text{CO})_9$  requires a 2.5 m x 25 mm column. Final purification can be effected by recrystallization or by sublimation in vacuum.

\*Eastman Chromagram Sheet 6060 (silica gel with fluorescent indicator) is used and the eluent is hexane. The organocobalt compounds are colored ( $\text{Y} = \text{H}$ , alkyl: purple;  $\text{Y} = \text{aryl}$ : brown) and the colorless starting mercurials can be visualized by treatment with iodine vapor.

Although reaction times in some cases are rather long, it is apparent that we have in hand a very useful and fairly generally applicable synthesis of substituted methylidyne-tricobalt nonacarbonyls, one more general than that based on the reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{RCX}_3$  compounds<sup>3-5</sup>. Of special interest is the transfer of the  $\beta$ -methoxyethyl group intact from mercury to carbon since this example suggests that introduction of diverse functionality into methylidyne tricobalt nonacarbonyls should be possible via the olefin mercuration-HCCo<sub>3</sub>(CO)<sub>9</sub> alkylation sequence. This point is receiving special attention.

This new reaction of organomercury compounds is a rather unusual one. The alkylation or arylation of C-H bonds by organomercurials usually involves free radical intermediates and requires rather high energy input (photolysis,  $\gamma$ -radiolysis or high temperature) (e.g., ref. 13 and 14). The formation of radicals from  $\text{R}_2\text{Hg}$  under the mild conditions of our experiments would not be expected unless some initiating radical source was present. Further studies will be directed to a consideration of the mechanism of this novel reaction. Satisfactory ( $\pm 0.3\%$ ) analyses were obtained for all new compounds.

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