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Preliminary communication

The methylenation of methylidynetricobalt nonacarbonyl with monohalomethylmercurials

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In recent investigations of methylidynetricobalt nonacarbonyl systems we have found that a wide variety of organomercurials will alkylate $HCCo_3(CO)_9$ at carbon to give $RCCo_3(CO)_9$ compounds, very often in excellent yield[1]. We have extended these studies to include some halomethyl-mercury compounds since we were interested in obtaining haloethylidynetricobalt nonacarbonyls of type $CH_nX_{3-n}CCo_3(CO)_9$ (n = 0–3) which might be useful intermediates in further transformations. Since the $R_2Hg/HCCo_3(CO)_9$ reaction proceeded so readily under mild conditions, one might expect that compounds such as $Hg(CH_2Br)_2$ and $Hg(CH_2I)_2$ would serve as reagents for the synthesis of $XCH_2CCo_3(CO)_9$ compounds*. However, such was not the case, and a different reaction of some interest and potential utility was observed instead.

The reaction of 2 mmoles each of $Hg(CH_2I)_2$[5] and $HCCo_3(CO)_9$ was carried out in 50 ml of dry benzene, at reflux and under a carbon monoxide atmosphere, for 24 h. The progress of the reaction was followed by thin layer chromatography (Eastman Chromagram Sheet 6060, hexane eluant) via a perceptible color change of the organocobalt spot from purple to reddish. Filtration of the reaction mixture was followed by evaporation of the filtrate. The residue was dissolved in a minimal amount of hexane and purified by column chromatography (silicic acid, hexane eluant). A single product was obtained which was sublimed in vacuum at 50° and identified as $CH_3CCo_3(CO)_9$ by comparison of its IR and NMR spectra with those of an authentic sample prepared by reaction of CH_3CCl_3 with $Co_2(CO)_8$[6] and by its m.p. of 183–185° dec. (lit.[7] m.p. 185° dec.) and an undepressed mixture m.p. The yield of this product was 77% based on starting $HCCo_3(CO)_9$.

A reaction of $HCCo_3(CO)_9$ and $Hg(CH_2I)_2$ in 2:1 molar ratio was carried out in order to see if both CH_2 groups of the mercury reagent could be utilized. This reaction, however, gave a mixture of starting cobalt compound and $CH_3CCo_3(CO)_9$ whose resolution on our column proved not to be possible. A similar situation was encountered in the reaction of ICH_2HgI[8] with $HCCo_3(CO)_9$. Bis(bromomethyl)mercury[3] also reacted with

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*Although the principal synthetic application of monohalomethyl-mercury compounds has been their use as CH_2 transfer agents[2,3], there are some examples of their use as alkylating agents, as in the reaction of $Hg(CH_2Cl)_2$ with arsenic trichloride to give $ClCH_2AsCl_2$[4].

$HCCo_3(CO)_9$ (in refluxing benzene, under nitrogen, 48 h, 1:1 molar ratio) to give the methylated cluster compound in 57% yield based on $HCCo_3(CO)_9$. In contrast to the iodomethyl-mercury reagents, however, a 2:1 $HCCo_3(CO)_9/Hg(CH_2Br)_2$ and a 1:1 $HCCo_3(CO)_9/BrCH_2HgBr$ reaction gave $CH_3CCo_3(CO)_9$ in substantial yields, 59% and 42%, respectively.

Reactions of this type are useful for the controlled introduction of deuterium into ethylidynetricobalt nonacarbonyl. Thus, treatment of $DCCo_3(CO)_9$ (prepared via reaction of DCl_3 with $Co_2(CO)_8$) with $Hg(CH_2Br)_2$ (refluxing benzene, under nitrogen, 48 h, 1:1 molar ratio) gave $CH_2DCCo_3(CO)_9$ in 75% yield (NMR in $CDCl_3$: δ 3.67 ppm, t [$J(H-D) = 2.0$ Hz] *vs.* NMR of $CH_3CCo_3(CO)_9$ in $CDCl_3$: δ 3.65 ppm, s), while the reaction of $HCCo_3(CO)_9$ with $Hg(CD_2I)_2$[9] gave $CHD_2CCo_3(CO)_9$ in 61% yield (NMR in $CDCl_3$: δ 3.61 ppm, quintet [$J(H-D) = 2.2$ Hz].

At the present time nothing is known about how these reactions proceed. *Formally*, they could be considered carbenoid CH_2 insertions into the C–H bond of $HCCo_3(CO)_9$, but it is more probable that a more complicated process is operative. In these reactions of $Hg(CH_2Br)_2$ with $HCCo_3(CO)_9$ metallic mercury is formed in variable amounts, but in the $HCCo_3(CO)_9$ reactions with $Hg(CH_2I)_2$, metallic mercury does not seem to be present. Clearly, more work is required in order to obtain an understanding of these novel reactions. We report these results at this time because the $HCCo_3(CO)_9/\alpha$-haloalkylmercurial reaction is a most unexpected one which may well prove to be very useful in our further development of methylidynetricobalt nonacarbonyl chemistry.

Another class of organomercury divalent carbon transfer reagents, the phenyl(trihalomethyl)mercurials, which readily release dihalocarbenes on being heated[10], did not show the hoped-for methylenation reaction. Thus, treatment of $HCCo_3(CO)_9$ with $PhHgCCl_2Br$ in benzene, under nitrogen, for 2.5 h at reflux gave $PhCCo_3(CO)_9$ (59%) as the only organocobalt product. A similar reaction (1 h) with $PhHgCBr_3$ gave this compound in 60% yield, while the reaction of $HCCo_3(CO)_9$ with $PhHgCF_3$[11] (1.5 h) resulted in formation of $PhCCo_3(CO)_9$ in 87% yield. Here then the usual $R_2Hg/HCCo_3(CO)_9$ reaction[1] was observed, but with a very striking preference for transfer of the phenyl group.

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