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Preliminary communication

ORGANOCOBALT CLUSTER COMPLEXES

XVI*. VINYL DERIVATIVES OF METHYLIDYNETRICOBALT NONACARBONYL: USEFUL PRECURSORS TO $(OC)_9Co_3C$-SUBSTITUTED CARBONIUM IONS AND FUNCTIONALLY SUBSTITUTED DERIVATIVES

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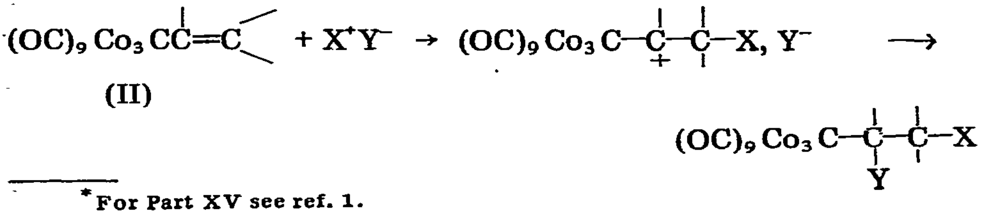
Summary

Vinyl-substituted derivatives of methylidynetricobalt nonacarbonyl of the type $RR'C{=}C(R'')CCo_3(CO)_9$ have been prepared, with vinylic groups $CH_2{=}CH$, $CH_2{=}C(CH_3)$, $Me_3SiCH{=}CH$ and $CH_3C(O)CH{=}CH$. Reaction of the first two with HPF_6 produced the carbonium ions via β-proton addition to the C=C bonds. Acetylium ion addition also could be achieved. Proton addition to the Me_3Si compound resulted in desilylation.

Carbonium ions of type I, generated from the appropriate alcohols, $RCH(OH)CCo_3(CO)_9$, in strong acid medium, are exceptionally stable, as our recent studies have shown [2,3], and this appears to be due to extensive delocalization of the positive charge into the cluster, very likely via σ—π conjugation. Since a positive charge on a carbon atom α to the cluster carbon atom is so highly stabilized, the addition of the positive part of an ionic reagent X^+Y^- to the terminal carbon of a C=C group attached to the cluster carbon atom should be a very favorable process (eqn. 1). We have found that this is indeed the case.



(II)

$$(OC)_9Co_3C\overset{|}{C}{=}C\!< \; + X^+Y^- \rightarrow (OC)_9Co_3C{-}\underset{+}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}X,\ Y^- \longrightarrow (OC)_9Co_3C{-}\underset{Y}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}X \qquad (1)$$

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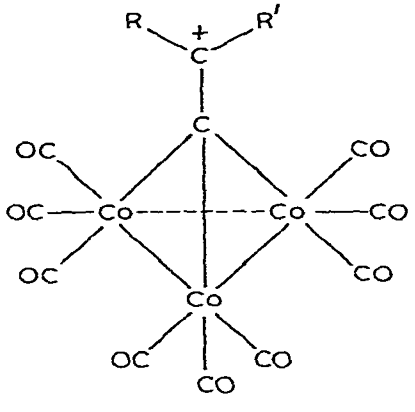
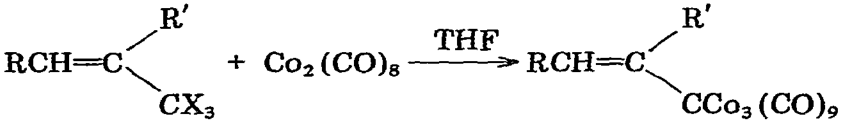
[*] For Part XV see ref. 1.



(I)

α,β-Unsaturated methylidynetricobalt nonacarbonyl complexes of type II can be prepared readily by the reaction between dicobalt octacarbonyl and the appropriate vinylic trihalomethyl derivative (eqn.2). The general procedure described in a previous paper of this series [4] is applicable. Use



$$RCH{=}C(R')CX_3 + Co_2(CO)_8 \xrightarrow{THF} RCH{=}C(R')CCo_3(CO)_9 \qquad (2)$$

(X = Cl, Br)

(IIIa) $R = R' = H$
(IIIb) $R = H; R' = CH_3$
(IIIc) $R = Me_3Si; R' = H$
(IIId) $R = CH_3C(O); R' = H$

of rigorously dried THF and a nonhydrolytic work-up are essential, or else saturated products are obtained instead, e.g., $Me_3SiCH_2CH_2CCo_3(CO)_9$ instead of $Me_3SiCH{=}CHCCo_3(CO)_9$. Presumably, this hydrogenation occurs via intermediate $HCo(CO)_4$ *.

All of the chemical reactions of these vinylic derivatives studied thus far proceed in the direction expected (eqn. 1), thus providing further evidence for the high stability of $(OC)_9Co_3C\overset{+}{C}RR'$ systems. Protonation of $CH_2{=}C(CH_3)$-$CCo_3(CO)_9$ using the 65% aqueous HPF_6/propionic anhydride reagent resulted in precipitation of the carbonium ion PF_6^- salt I ($R = R' = CH_3$) as a brown, powdery solid. Treatment of this product with methanol gave $CH_3OC(CH_3)_2$-$CCo_3(CO)_9$, a purple-black solid which does not melt but decomposes when heated rapidly above 200°, in 86% yield. The carbonium ion salt alkylated aniline at nitrogen, giving $C_6H_5NHC(CH_3)_2CCo_3(CO)_9$ in 49% yield, and pyrrole at carbon, giving III. The methyl ether and the anilino derivative are very sensitive to even mildly acidic conditions, which is another indication of the ease with which such carbonium ions of type I are formed. Attempted purification of the methyl ether by chromatography on pH 4 silicic acid

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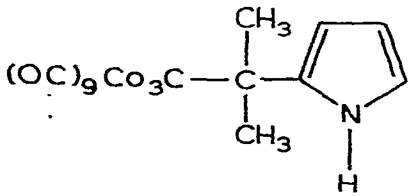
*In support of this idea, conversion of $CH_2{=}CHCCo_3(CO)_9$ to $C_2H_5CCo_3(CO)_9$ is easily effected by treatment with $Co_2(CO)_8$ and CF_3CO_2H in THF.



(III)

caused its conversion to the alcohol, $(OC)_9Co_3CC(CH_3)_2OH$, a black solid which decomposes on being heated but does not melt. Solution of $CH_2{=}C(CH_3)CCo_3(CO)_9$ in concentrated H_2SO_4 also generated the carbonium ion I ($R = R' = CH_3$), and when such a solution was poured onto ice, the alcohol was produced (52%), together with the starting olefin (33%). Still a further example of the facile formation of this carbonium ion is provided by the ready reduction of $CH_2{=}C(CH_3)CCo_3(CO)_9$ to the known [5] $(CH_3)_2CHCCo_3(CO)_9$ in good yield using zinc amalgam in concentrated HCl or in trifluoroacetic acid.

Similar protonation of $CH_2{=}CHCCo_3(CO)_9$ with $HPF_6/(EtCO)_2O$ gave the known [2] $(OC)_9Co_3CCHCH_3^+ PF_6^-$, whose reaction with methanol gave the expected methyl ether. On the other hand, protonation of $(OC)_9Co_3CCH{=}CHSiMe_3$ in concentrated H_2SO_4 resulted in desilylation (eqn. 3). Hydrolysis of the sulfuric acid solution gave only $CH_3CH(OH)$-

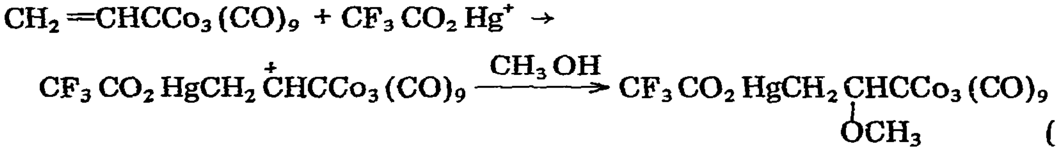
$$Me_3SiCH{=}CHCCo_3(CO)_9 + H_2SO_4 \rightarrow Me_3SiCH_2{-}\overset{+}{C}H{-}CCo_3(CO)_9, HSO_4^- \rightarrow$$

$$CH_2{=}CHCCo_3(CO)_9 + Me_3SiOSO_2OH \xrightarrow{H_2SO_4} CH_3{-}\overset{+}{C}H{-}CCo_3(CO)_9, \; HSO_4^- \qquad (3)$$

$CCo_3(CO)_9$ (78%) and hexamethyldisiloxane. Olefin elimination of this type from a species with a positive charge β to a silyl group is a known reaction [6].

Another reagent which adds to unsaturated cluster complexes of type II is $CH_3CO^+ AlCl_4^-$. Thus reaction of $CH_2{=}CHCCo_3(CO)_9$ with acetyl chloride/aluminum chloride in dichloromethane under a carbon monoxide atmosphere gave three products, all of which had the acetyl group attached to the terminal carbon as expected: $CH_3C(O)CH_2CH_2CCo_3(CO)_9$ (m.p. 70-71°, 13%); *trans*-$CH_3C(O)CH{=}CHCCo_3(CO)_9$ (m.p. 105-107°, 12%); $CH_3C(O)CH_2CH(OH)CCo_3(CO)_9$ (m.p. 109-111° dec., 6%). All of these can be readily derived from the initially formed $CH_3C(O)CH_2\overset{+}{C}HCCo_3(CO)_9$, through reduction, proton loss or hydrolysis, respectively. Similar addition of $CH_3CO^+ AlCl_4^-$ to $CH_2{=}C(CH_3)CCo_3(CO)_9$ produced $CH_3C(O)CH_2CH$-$(CH_3)CCo_3(CO)_9$ (m.p. 91-92.5°, 10% yield).

The organomercury derivative $ClHgCH_2CH(OCH_3)CCo_3(CO)_9$ was isolated from the oxymercuration of the vinyl-substituted cluster with $Hg(O_2CCF_3)_2$ in methanol, followed by anion exchange with aqueous NaCl, in 55% yield (m.p. 109-111° dec.). The direction of addition again is that expected (eqn. 4).



$$CH_2{=}CHCCo_3(CO)_9 + CF_3CO_2Hg^+ \rightarrow CF_3CO_2HgCH_2\overset{+}{C}HCCo_3(CO)_9 \xrightarrow{CH_3OH} CF_3CO_2HgCH_2\underset{OCH_3}{\underset{|}{C}}HCCo_3(CO)_9 \qquad (4)$$

Vinyl derivatives of the $CCo_3(CO)_9$ cluster thus open up a new and versatile route to diverse functionally substituted methylidynetricobalt nonacarbonyl complexes. The starting materials of type $RR'C{=}CHCX_3$ are easily prepared by radical-initiated addition of bromotrichloromethane or carbon tetrabromide to terminal olefins, followed by base-induced elimination of HBr from the adduct (see, for instance, the preparation of $Me_3SiCH{=}CHCBr_3$ [7].) The easy accessibility of the carbonium ions from such $RR'C{=}CHCCo_3(CO)_9$ complexes permits the synthesis of functional derivatives through their reactions with diverse nucleophiles.

All new compounds were characterized by analysis and by their IR and NMR spectra. The results of our further work in this area, including ^1H and ^{13}C NMR studies of the new carbonium ions generated by this procedure, will be reported in due course.

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