CHEMISTRY LETTERS, pp. 583-586, 1973. Published by the Chemical Society of Japan

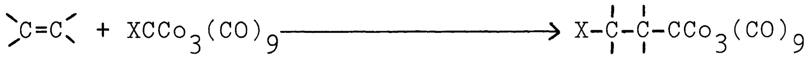
REACTIONS OF METHINYLTRICOBALT ENNEACARBONYL WITH OLEFINS

Noritoshi SAKAMOTO, Takanori KITAMURA, and Takashi JOH
The Institute of Scientific and Industrial Research,
Osaka University, Yamada-kami, Suita, Osaka

Alkyl or alkenyl substituted methinyltricobalt enneacarbonyls were formed in the reactions of methinyltricobalt enneacarbonyl with mono- or diolefins.

The unusual chemistry of the apical carbon of the tricobalt carbon cluster, $XCCo_3(CO)_9$, has become of interest in recent years. In the previous paper,[1)] we reported that the three different types of reactions took place in the reactions of $XCCo_3(CO)_9$ with norbornadiene, depending upon the apical substituent X. The reactions of $HCCo_3(CO)_9$ or $DCCo_3(CO)_9$ with norbornadiene afforded the complexes $(C_7H_8X)CCo_3(CO)_9$ and $(C_7H_8XCO)CCo_3(CO)_9$ (X=H or D), whereas norbornadiene complexes $XCCo_3(CO)_7(C_7H_8)$ were formed when X was alkyl, aryl, or F. $BrCCo_3(CO)_9$ or Cl-$CCo_3(CO)_9$ catalyzed the selective dimerization reaction of norbornadiene.

The present communication describes the formation of alkyl or alkenyl substituted methinyltricobalt enneacarbonyls from the reactions of $XCCo_3(CO)_9$ (X=H or D) with mono- or diolefins.

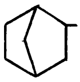
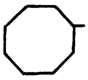
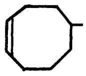
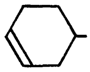
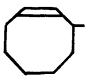
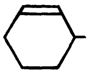
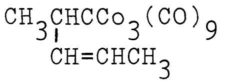
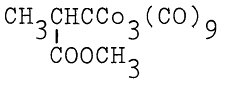


$$>C=C< + XCCo_3(CO)_9 \longrightarrow X\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}CCo_3(CO)_9$$

X=H or D

An example illustrating the reactions of $HCCo_3(CO)_9$ with olefins is as follows. When $HCCo_3(CO)_9$ (442 mg, 1 mmole) in heptane (5 ml) was heated at 130°C for 5 hrs. under 20 kg/cm^2 pressure of ethylene in an autoclave, the reaction took place to give the complex $C_2H_5CCo_3(CO)_9$ in about 20% yield. It was found that the reactions of $HCCo_3(CO)_9$ with mono- or diolefins took place generally in a similar manner (see Table 1).

Table 1. Reaction of $HCCo_3(CO)_9$ with olefins

Olefin	Product	M.p. (°C)	Yield (%)
ethylene[a)]	$C_2H_5CCo_3(CO)_9$	189-191	20
propylene[a)]	$n\text{-}C_3H_7CCo_3(CO)_9 + i\text{-}C_3H_7CCo_3(CO)_9$ (5 : 1)	-	10
norbornene	 -$CCo_3(CO)_9$	74	11
cyclooctene	 -$CCo_3(CO)_9$	89	4
1,5-cyclooctadiene	 -$CCo_3(CO)_9$	104-106	26
1,4-cyclohexadiene	 -$CCo_3(CO)_9$	79-81	11
1,3-cyclooctadiene	 -$CCo_3(CO)_9$	114	45
1,3-cyclohexadiene	 -$CCo_3(CO)_9$	94	25
1,3-butadiene	$CH_3CH{=}CHCH_2CCo_3(CO)_9$	49-51	32
1,3-pentadiene	 $CH_3CH(CH{=}CHCH_3)CCo_3(CO)_9$	58-60	11
methyl acrylate	 $CH_3CH(COOCH_3)CCo_3(CO)_9$	81-84	19
vinyl acetate	$C_2H_5CCo_3(CO)_9$	189-191	10
allyl bromide	$CH_2{=}CHCH_2CCo_3(CO)_9$	140-143	21

Reaction condition; $HCCo_3(CO)_9$, 1 mmole; olefin, 0.5 ml; solvent, heptane, (5 ml); 100°C for 5 hrs. a) reaction temperature, 130°C.

Non-conjugated diolefins reacted with $HCCo_3(CO)_9$ in a similar manner as monoolefins, whereas 1,3-diolefins afforded the 1,4-adducts. In the reaction of acrylonitrile, the complex was perfectly destroyed and the expected product could not be obtained. The reaction of vinyl acetate or allyl bromide proceeded in a different manner from the above. Details on these reactions will be presented in a subsequent paper.

In the reactions of $DCCo_3(CO)_9$ with olefins, it was found that the incorporation of deuterium atom into the products took place. The results are shown in Table 2.

Table 2. Reaction of $DCCo_3(CO)_9$ with olefins

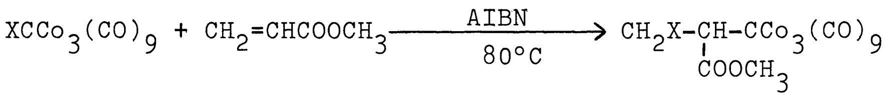
Olefin	Product	Relative intensity ratio of parent peaks in mass spectrum
ethylene	$C_2H_5CCo_3(CO)_9/C_2H_4DCCo_3(CO)_9$	0.7/1
propylene	$C_3H_7CCo_3(CO)_9/C_3H_6DCCo_3(CO)_9$	1/1
norbornene	$C_7H_{11}CCo_3(CO)_9/C_7H_{10}DCCo_3(CO)_9$	1/17
methyl acrylate	$C_4H_7O_2CCo_3(CO)_9/C_4H_6DO_2CCo_3(CO)_9$	1.4/1
1,3-cyclooctadiene	$C_8H_{13}CCo_3(CO)_9/C_8H_{12}DCCo_3(CO)_9$	0.7/1

Thus, it is considered that the insertion of olefins into the C-X bond of $XCCo_3(CO)_9$ (X=H or D) apparently took place at least in part. Several reaction paths, i.e., a) direct insertion of olefins into the C-X bond of $XCCo_3(CO)_9$, b) ionic mechanism involving $X^+\ CCo_3(CO)_9^-$, and c) radical reaction path, can be considered in these reactions. Recently, D.Seyferth et al.[2)] reported briefly the reactions which are shown by the following equations and suggested a radical mechanism.

$$HCCo_3(CO)_9 + CH_3COOCH_2CH{=}CH_2 \xrightarrow[80^\circ C]{AIBN} CH_3COOCH_2CH_2CH_2CCo_3(CO)_9$$

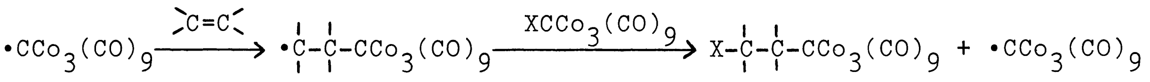
$$HCCo_3(CO)_9 + C_2H_5OCH_2CH{=}CH_2 \xrightarrow[80^\circ C]{AIBN} C_2H_5OCH_2CH_2CH_2CCo_3(CO)_9$$

We investigated the reactions of $XCCo_3(CO)_9$ (X=H or D) with methyl acrylate in the presence of azobisisobutyronitrile (AIBN). Although the reaction did not take place at 80°C without AIBN, the expected product was obtained in the presence of AIBN at the same reaction temperature. Further, the reaction of $DCCo_3(CO)_9$ gave the monodeuterated product. From these observations, it is reasonable to consider



$$XCCo_3(CO)_9 + CH_2{=}CHCOOCH_3 \xrightarrow[80°C]{AIBN} CH_2X-\underset{COOCH_3}{\underset{|}{C}}H-CCo_3(CO)_9$$

that the reaction proceeds with a radical mechanism, as shown in the following scheme.



$$\cdot CCo_3(CO)_9 \xrightarrow{>C=C<} \cdot\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CCo_3(CO)_9 \xrightarrow{XCCo_3(CO)_9} X-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CCo_3(CO)_9 + \cdot CCo_3(CO)_9$$

The reactions of $BrCCo_3(CO)_9$ were found to be more complex than those of $HCCo_3(CO)_9$. For example, the complexes $C_2H_5CCo_3(CO)_9$ and $CH_3CH{=}C(CH_3)CCo_3(CO)_9$ were formed in the reaction of $BrCCo_3(CO)_9$ with ethylene. It was also found that the reaction of $BrCCo_3(CO)_9$ with methyl acrylate afforded the product $CH_3OOCCH_2CH_2$-$CCo_3(CO)_9$. Further investigation in this area are now in progress.

References

1) T.Kamijo, T.Kitamura, N.Sakamoto, and T.Joh, J.Organometal.Chem., in press.

2) D.Seyferth, J.H.Hallgren, R.J.Spohn, A.T.Wehman, and G.H.Williams, XXIIIrd International Congress of Pure and Applied Chemistry, 6, 133 (1971).

(Received April 16, 1973)