Electrophilic Reactions of $ClCCo_3(CO)_9$. A New Preparation of Arylmethinyltricobalt Enneacarbonyls

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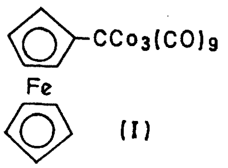
Summary A convenient new preparation of arylmethinyltricobalt enneacarbonyls, involving the reaction of $ClCCo_3(CO)_9$ with the arene in the presence of a typical Friedel–Crafts reagent like $AlCl_3$, is described.

RECENTLY we investigated the reactions of methinyltricobalt enneacarbonyls, $YCCo_3(CO)_9$, with arenes and showed that while arene complexes $YCCo_3(CO)_6(arene)$ can be prepared when Y = Me, Ph, and F, the chloro- and bromo-clusters yield the cobalt carbonyl carbides $Co_5(CO)_{15}C_3H$, $Co_6(CO)_{18}C_4$, and $Co_8(CO)_{24}C_6$.[1] In an attempt to prepare Cl(or Br)$CCo_3(CO)_6$(arene) derivatives, we tried $AlCl_3$ as catalyst, a method used successfully by Fischer and his co-workers.[2] However, instead of an arene complex forming, a ready Friedel–Crafts reaction occurred to give arylmethinyltricobalt enneacarbonyls in up to 80% yield. (Other Friedel–Crafts reagents such as $FeCl_3$ can be used).

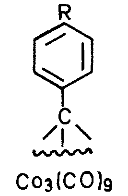
$$ClCCo_3(CO)_9 + RH \xrightarrow{AlCl_3} RCCo_3(CO)_9 + HCl.$$

This is a very convenient route to the aryls, as $ClCCo_3(CO)_9$ is very easily prepared from $Co_2(CO)_8$, whereas the other routes to the aryls are limited (where the preparation of $Co_2(CO)_6RC{\equiv}CH$ compounds are involved[3]) or impossible if the 1,1,1-trichloroaryl is required.[4] This method can be extended to solid arenes using dichloromethane as a solvent and a number of new aryl derivatives have been characterized including $R{=}ClC_6H_4$,BrC_6H_4, biphenyl, and *o*-, *m*-, and *p*-$C_6H_3(CH_3)_2$ and the novel ferrocene derivative $(\pi\text{-}C_5H_5)Fe[\pi\text{-}C_5H_4CCo_3(CO)_9]$ of probable structure (I).

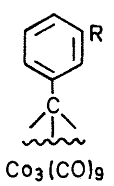


(I)

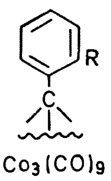
Isomeric derivatives (II), (III), and (IV) could conceivably form in these Friedel–Crafts reactions, and n.m.r., i.r., and mass spectra have been used to elucidate the stereochemistries of the product isolated. In some cases isomers have been separated by gas chromatography using a 6 ft. 10% Carbowax 20M column. The spectral features that are thought to characterize compounds of structures (IV), (V) and (VII) are (i) common fragments in the mass spectra are migration fragments of the type Co_3R^+, Co_2R^+, CoR^+, and Co_3CR^+ which are absent in the spectra of *para*- and *meta*-substituted derivatives, the comparable migration fragments of the latter spectra being $Co_nH^+ (n{=}3—1)$ and Co_nCH^+ ($n{=}3—1$); appropriate metastable transitions are observed. (ii) $YCCo_3(CO)_9$ derivatives of idealised C_{3v} symmetry, and those where there is no steric interaction between Y and the cluster, exhibit a typical i.r. spectrum in the carbonyl stretching region of four bands *ca.* 2100, 2050, 2040, and 2020 cm^{-1}, although five bands are predicted.[5] However, in those cases where there are gross deviations from C_{3v} symmetry (for example the ferrocene derivative) or where there is steric interaction [structures (IV), (V), and (VII)], the band at 2050 cm^{-1} (two accidentally degenerate *E* modes[5]) becomes very broad and splits into two components.



(II)



(III)



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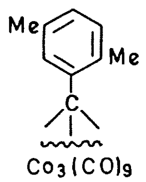

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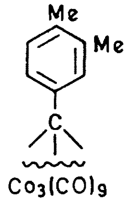
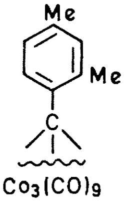


(VI)



(VII)

With these criteria as a guide and using the ^1H n.m.r. spectra to confirm our structural assignments, it was found that iodobenzene, bromobenzene, and most alkylbenzenes are substituted in the *para*-position whereas chlorobenzene undergoes *ortho*-substitution. Only one structure is possible for the *p*-xylene derivative (V) but *o*- and *m*-xylene were substituted in the *para*- and *ortho*-position, respectively, (VI) and (VII). *meta*-Substitution was never observed, and strongly deactivated arenes *e.g.* nitrobenzene did not undergo these Friedel–Crafts reactions. Steric requirements are also important, as shown by the failure of mesitylene to react and the slow reactions and poor yields with *m*- and *p*-xylene and ferrocene.

The chloro-cluster also reacts with typical Grignard and lithium reagents and thus a wide variety of alkyl, alkene, and aryl substituted cluster derivatives can be prepared using these reagents and Friedel–Crafts reactions.

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