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Preliminary communication

A facile synthesis of tricarbonylferrole–iron tricarbonyl derivatives from benzalacetonetricarbonyliron and alkynes

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SUMMARY

Alkynes react with the benzalacetone complex $[C_6H_5CH{=}CHC(O)CH_3]Fe(CO)_3$ in boiling benzene to give nearly exclusively the corresponding tricarbonylferrole–iron tricarbonyl derivatives.

Alkynes react with the various iron carbonyls (*e.g.* $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Fe(CO)_5$) to give a complex variety of products[1,2]. We have now found that reactions of a variety of alkynes with benzalacetonetricarbonyliron, recently[3] shown to be a convenient source of $Fe(CO)_3$ groups under mild conditions, proceed readily in boiling benzene to give the corresponding yellow tricarbonylferrole–iron tricarbonyl derivatives (I) free from other organoiron carbonyl derivatives (Table 1). Simple alkynes (*e.g.* diphenylacetylene and hexyne-3) give ~50% yields of the tricarbonylferrole–iron tricarbonyl derivatives (I) thereby providing the first method suitable for preparation of tricarbonylferrole–iron tricarbonyl derivatives (I) in quantities sufficient for a detailed study of their chemistry.

Macrocyclic alkadiynes (II: m = 4, n = 4, 5, and 6; m = 5 and 6) also form a complex variety of products with iron carbonyls[4]. However, reactions of these macrocyclic alkadiynes with benzalacetonetricarbonyliron in boiling benzene in a 1/1 molar ratio give yellow compounds $(alkadiyne)_2Fe_2(CO)_6$ as the major iron carbonyl product (Table 1). Only in the case of 1,7-cyclotridecadiyne (II: m = 4, n = 5) was a product of this type, *i.e.* yellow $(C_{13}H_{18})_2Fe_2(CO)_6$, previously obtained from macrocyclic alkadiynes (II) and simple iron carbonyls[4]. The compounds $(alkadiyne)_2Fe_2(CO)_6$ are believed[4] to have tricarbonylferrole–iron tricarbonyl structures of the type III, but this has not yet been confirmed by X-ray crystallography. However, the formation of the $(alkadiyne)_2Fe_2(CO)_6$

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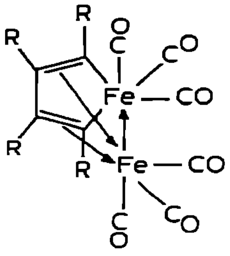
TABLE I

TRICARBONYLFERROLE–IRON TRICARBONYL DERIVATIVES OBTAINED FROM BENZALACETONETRICARBONYLIRON AND ALKYNES

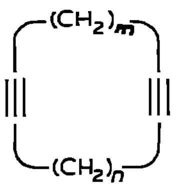
Alkyne	*Product*[a]	*Structure*	*M.p.*	*Yield (%)*
$CH_3C{\equiv}CCH_3$	$(CH_3C_2CH_3)_2Fe_2(CO)_6$	I (R = CH_3)	149–151°	25
$C_2H_5C{\equiv}CC_2H_5$	$(C_2H_5C_2C_2H_5)_2Fe_2(CO)_6$	I (R = C_2H_5)	>150° (dec.)	50
$C_6H_5C{\equiv}CC_6H_5$	$(C_6H_5C_2C_6H_5)_2Fe_2(CO)_6$	I (R = C_6H_5)	>150° (dec.)	50
1,7-$C_{12}H_{16}$ (II: $m = 4, n = 4$)	$(C_{12}H_{16})_2Fe_2(CO)_6$	III ($m = 4, n = 4$)	174–177°	21
1,7-$C_{13}H_{18}$ (II: $m = 4, n = 5$)	$(C_{13}H_{18})_2Fe_2(CO)_6$	III ($m = 4, n = 5$)	128–129° [b]	30
1,8-$C_{14}H_{20}$ (II: $m = 5, n = 5$)	$(C_{14}H_{20})_2Fe_2(CO)_6$	III ($m = 5, n = 5$)	173–175°	4
1,7-$C_{14}H_{20}$ (II: $m = 4, n = 6$)	$(C_{14}H_{20})_2Fe_2(CO)_6$	III ($m = 4, n = 6$)		23
1,8-$C_{15}H_{22}$ (II: $m = 5, n = 6$)	$(C_{15}H_{22})_2Fe_2(CO)_6$	III ($m = 5, n = 6$)	168–170°	8

[a] The products were identified by analyses for at least two elements, proton NMR spectra, and the presence of the characteristic tricarbonylferrole–iron tricarbonyl ν(CO) frequencies at 2069 ± 5, 2031 ± 3, 1984 ± 4 and 1930 ± 8 cm^{-1} in the infrared spectrum.

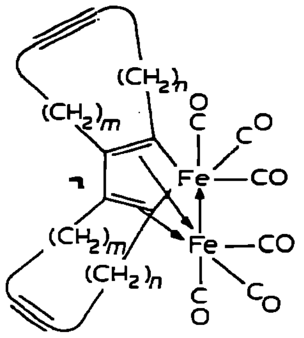
[b] Lit.[4] m.p. 133°.



(I)



(II)



(III)

derivatives from the macrocyclic alkadiynes II under conditions where tricarbonylferrole–iron tricarbonyl derivatives (I) are exclusively formed from simple alkynes provides further evidence for tricarbonylferrole–iron tricarbonyl structures III for the (alkadiyne)$_2$Fe$_2$(CO)$_6$ derivatives.

The facile formation of tricarbonylferrole–iron tricarbonyl derivatives (I) from alkynes and benzalacetonetricarbonyliron clarifies certain aspects of the complex reactions between alkynes and metal carbonyls[1,2] by indicating that the stable products normally formed by interaction of alkynes with Fe(CO)$_3$ groups are tricarbonylferrole–iron tricarbonyl derivatives rather than, for example, cyclobutadiene–iron tricarbonyl derivatives. The absence of significant quantities of products other than I from reactions of alkynes with benzalacetonetricarbonyliron can be attributed to the fact that benzalacetonetricarbonyliron, unlike the simple iron carbonyls, provides a source of Fe(CO)$_3$ groups free from Fe(CO)$_4$ groups.

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