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Preliminary communication

IMPROVED PREPARATION OF h^5-$C_5H_5Fe(CO)_2(h^1$-ALKYL) COMPLEXES FROM $[h^5$-$C_5H_5Fe(CO)_2(h^2$-ALKENE)$]^+ BF_4^-$

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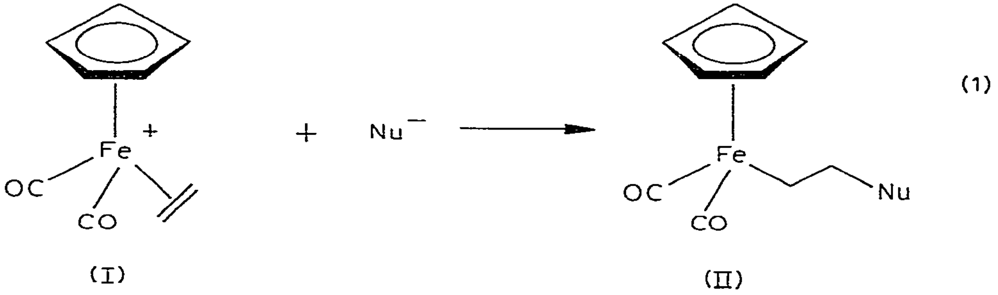
Summary

Sodium cyanoborohydride has been found to be very effective for the conversion of $[(h^5$-$C_5H_5)Fe(CO)_2(h^2$-alkene$)]^+ BF_4^-$ complexes to the corresponding h^1-alkyl derivatives.

The addition of nucleophiles to $[h^5$-$C_5H_5Fe(CO)_2(h^2$-alkene$)]^+ BF_4^-$ complexes (I) has been employed widely to prepare the iron alkyls II (eq. 1) [1a—d]. These, in turn, are convertible into hydrocarbons, alkyl halides, esters, etc. [2]. Although Green and coworkers reported that the reactions of I (alkene = ethylene, propene) with $NaBH_4$ produce the corresponding ethyl and isopropyl derivatives [1a], we and others [3] have found this reaction to be lacking in generality, often proceeding in poor yield with extensive formation of $[h^5$-$C_5H_5Fe(CO)_2]_2$.



We wish to report that sodium cyanoborohydride ($NaBH_3CN$) is much superior to $NaBH_4$ for the conversion I → II (Nu = H). Treatment of nitro-

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TABLE 1

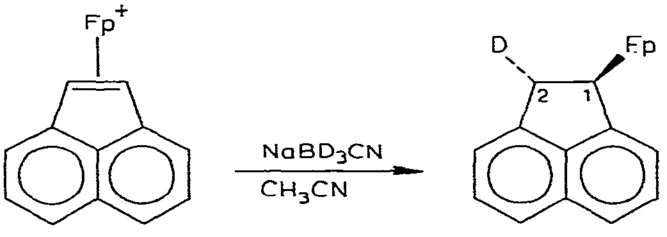
$$\underset{(\mathrm{I})}{[h^5\text{-}C_5H_5Fe(CO)_2(h^2\text{-alkene})]^+ BF_4^-} \ (\mathrm{I}) + NaBH_3CN \rightarrow \underset{(\mathrm{II})}{C_5H_5Fe(CO)_2(h^1\text{-alkyl})}$$

Alkene in I	Compound	Yield of II (%)
1-Heptene	Ia	81
Allylbenzene	Ib	71
Propene	Ic	96
Styrene	Id	56
Acenaphthylene	Ie	81
Cyclopentene	If	77
Isobutene	Ig	95
Cycloheptene	Ih	0
Cyclooctene	Ii	0
Norbornadiene	Ij	0

methane solutions of the olefin salts at 0°C with $NaBH_3CN$* (1:1.25 mol ratio) produced the corresponding alkyl complexes, usually within a few minutes. The products were isolated in good yield (Table 1) upon evaporation of the solvent, extraction of the residue with petroleum ether, and evaporation of the extracts. Steric factors appear to play an important role as the complexes of cycloheptene, cyclooctene and norbornadiene reacted only after several days and failed to give appreciable quantities of alkyls.

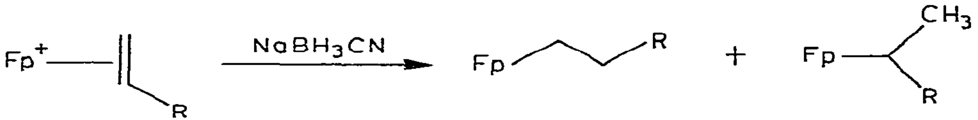
If $NaBD_3CN$ [4] is employed, stereospecifically labeled β-deuteroalkyls may be conveniently synthesized. For example, the *trans*-deuteroacenaphthene complex IIe was prepared from Ie ($J(H(1)\text{—}H(2)) < 2$ Hz)**. Such labeled complexes should prove useful in mechanistic studies.

Two isomeric alkyls (e.g. IIIa, IIIb) may be obtained from complexes of unsymmetrical alkenes (eq. 2). The propene salt with $NaBH_3CN$, as with $NaBH_4$ [1a] gave exclusively (within detection by NMR) the isopropyl complex IIIb ($R = CH_3$). The other monosubstituted olefin complexes (Ia, Ib, Id),



(Ie) (IIe)

Fp = $(h^5\text{-}C_5H_5)Fe(CO)_2$



(IIIa) (IIIb) (2)

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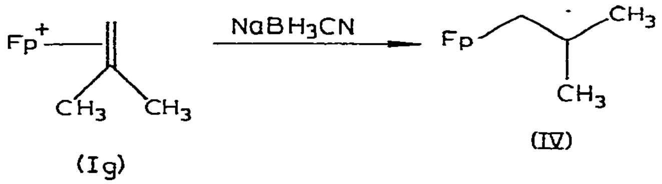
*Obtained from Aldrich Chemical Co.

**Other nucleophiles also give *trans* adducts with Ie [5].



(3)

however, yielded both isomers in varying ratios upon reaction with cyanoborohydride. Interestingly, reduction of Fp(h^2-isobutene)$^+$ BF_4^- (Ig) produced only the isobutyl derivative IV resulting from attack at the most substituted carbon. The corresponding reaction (eq. 3) with $NaBH_4$ produces a 3:1 mixture of the t-butyl and isobutyl complexes [6].

We are investigating further the factors which determine the regioselectivity of this reaction.

Acknowledgement

Helpful discussions with Prof. T. Whitesides (Wisconsin) on the use of sodium cyanoborohydride are acknowledged. We also thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support.

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