Tetracarbonylallyliron Cations. A Synthetic Route to 2-Substituted Butadiene Complexes

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Summary Tetracarbonylallyliron cations have been prepared by electrophilic addition to tetracarbonyltetramethylalleneiron; deprotonations of the salts are attended by loss of CO resulting in the formation of tricarbonylbutadieneiron derivatives with 2-substituents.

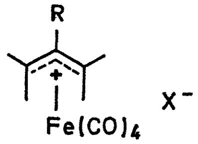
COMPOUNDS reported to contain carbonium ion ligands bound to an iron carbonyl moiety fall into two general classes:[1] (i) those in which iron can attain the krypton configuration (π pentadienyl or homopentadienyl complexes) and (ii) electron deficient systems (π-allyl complexes). Data concerning π-allyl carbonium ion complexes in which iron can attain the preferred inert gas configuration are sparse; the first example of such a compound appears to be the unstable adduct formed between tetracarbonylbutadieneiron and HCl.[2] This adduct decomposed into the known[3] covalent chloride upon treatment with aqueous acetone.

We report the preparation of salts having the general structure (I) by electrophilic addition to tetracarbonyltetramethylalleneiron (II).[4] Treatment of (II) with HBF_4 in acetic anhydride followed by precipitation in cold ether affords (Ia) as a fine yellow powder in nearly quantitative yield. Recrystallization from dichloromethane provides yellow needles which decompose without melting when heated above 100°.† The i.r. spectrum of the salt (CH_2Cl_2) exhibits $\nu(C{\equiv}O)$ at 2140, 2095, 2050, and 2015 cm^{-1} and the n.m.r. spectrum [$(CD_3)_2CO$] exhibits singlets at τ 4·33, 7·60, and 7·70 with relative areas 1:6:6, respectively.

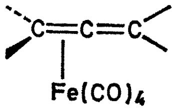
Friedel–Crafts acylation of (II) in dichloromethane solution, as described for tricarbonylbutadieneiron,[5] followed by precipitation in cold ether provides the corresponding acetyl (Ib) and benzoyl (Ic) derivatives as their $AlCl_4^-$ salts. The i.r. spectra of these also shows 4 bands in the region 2000—2150 cm^{-1}. The values for the C≡O stretching vibrations in these salts are thus in agreement with the values obtained for other iron carbonyl carbonium ion complexes.[6] Contrary to the suggestion[7] that systems containing π-allyl ligands with *anti* substituents might be unstable if four additional ligands were bound to iron, the tetracarbonylallyliron cations with *anti* methyl substituents are comparable in stability to their tricarbonyl-*cis*-π-pentadienyl analogues.[6]

Deprotonation and loss of a carbon monoxide ligand occurs upon slight warming of (Ia) in acetone solution to give tricarbonyl-2,4-dimethylpenta-1,3-dieneiron[4] (IIIa). Similar treatment of the acylated salts provides (IIIb) and (IIIc) in 60% overall yield. The n.m.r. spectrum of (IIIb)† $[(CD_3)_2CO]$ exhibits singlets at τ 7·49, 7·92, 8·52, and 8·84 and doublets at 8·30 and 8·45; (IIIc)† $(CD_3)_2CO$ exhibits multiplets at τ 1·80 and 2·20, singlets at 7·98, 8·62, and 8·67 and a pair of doublets centred at τ 8·22. Work on other tetracarbonylallyliron cations is in progress to establish the generality of this route to 2-substituted butadiene complexes.

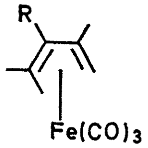
We thank the Research Corporation, the University of Louisville for an Arts and Sciences grant, and General Aniline and Film Corporation for a gift of iron pentacarbonyl.



(I) a; R = H; $X^- = BF_4^-$
b; R = Ac; $X^- = AlCl_4^-$
c; R = PhCO; $X^- = AlCl_4^-$



(II)



(III) a; R = H
b; R = Ac
c; R = PhCO

(*Received, March* 17*th*, 1971; *Com.* 334.)

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† Satisfactory analytical data have been obtained on this compound.

[1] E. W. Abel and S. P. Tyfield, "Advances in Organometallic Chemistry," Academic Press, New York, 1970, vol. 8, p. 146.
[2] H. D. Murdoch and E. Weiss, *Helv. Chim. Acta.*, 1962, **45**, 1156.
[3] F. J. Impastato and K. G. Ihrman, *J. Amer. Chem. Soc.*, 1961, **83**, 3726.
[4] R. Ben-Shoshan and R. Pettit, *J. Amer. Chem. Soc.*, 1967, **89**, 2231.
[5] E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Comm.*, 1969, 1124.
[6] J. E. Mahler, D. H. Gibson, and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3959.
[7] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968.