Electrophilic Substitution of Tricarbonyl(norbornadiene)iron

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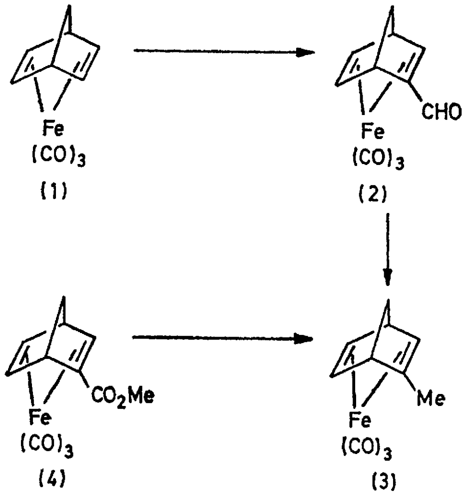
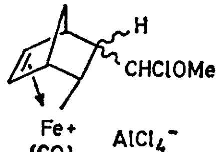
Summary Tricarbonyl(norbornadiene)iron (**1**), previously thought not to undergo electrophilic attack at carbon, gives tricarbonyl(norbornadiene-2-carbaldehyde)iron (**2**) on treatment with dichloromethyl methyl ether and titanium tetrachloride followed by hydrolysis.

Electrophilic substitution of transition metal-complexed conjugated dienes and polyenes has been reported.[1] Electrophilic substitution of non-conjugated diene-transition metal complexes has not been observed. Thus, tricarbonyl-(norbornadiene)iron (**1**) in the presence of sulphuric or fluorosulphonic acids undergoes protonation exclusively at iron, and no H–D exchange occurs in the presence of conc. D_2SO_4.[2]





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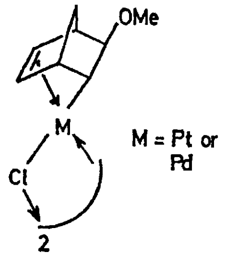

(6)

We now report electrophilic substitution of (**1**). Treatment of (**1**) with equivalent amounts of dichloromethyl methyl ether and titanium tetrachloride[3] in dichloromethane for 30 min at 0° and subsequent hydrolysis gave tricarbonyl(norbornadiene-2-carbaldehyde)iron (**2**), isolated by column chromatography (grade II alumina - Skellysolve B) as an orange oil in 27% yield. All analytical data support structure (**2**).† Further proof of structure (**2**) was accomplished by reduction with 1 : 4 $LiAlH_4$–$AlCl_3$[4] to give (**3**)† which was identical to a sample of (**3**) produced by a similar reduction of tricarbonyl-(2-methoxycarbonylnorbornadiene)iron (**4**).[5]† Attempts to acylate (**1**) using acetyl chloride and Lewis acids in dichloromethane have yielded small amounts of material which exhibited ketone carbonyl absorption in the i.r. Work to characterize this product further has been unsuccessful.

Production of (**2**) indicates existence of intermediate (**5**), a tricarbonyl(homoallyl)iron cation. Analogous platinum and palladium compounds (**6**) have been described,[6] but this is the first evidence for a homoallyl ligand attached to iron.[7] Previous evidence has indicated that tricarbonyl-(homoallyl)iron cations are much less stable than are their well-known conjugated analogues.[1b,c,e,f,2,8] Substitution of (**1**) by a carbon electrophile *vis à vis* lack of H–D exchange can be understood if formation of the new C–C bond is irreversible necessitating loss of a proton from (**5**). The exchange reaction could fail even if some homoallylic intermediate analogous to (**5**) were formed in equilibrium with the predominate iron-protonated species.[2] Whitesides and Arhart have shown that protonation of tricarbonyl(cyclohexa-1,3-diene)iron occurs from the *endo* side of the cyclohexadiene ligand in a highly stereospecific fashion.[1f] Stereospecificity[10] in *C*-deuteriation of (**1**) would lead, according to the principle of microscopic reversibility, to preferential cleavage of the newly made C–D bond when (**1**) is regenerated.

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† Characterized by i.r., n.m.r., mass spectrum, and elemental analysis.

[1] See, for example, (a) G. G. Ecke, U.S. P. 3,149,135, 1964; (b) E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Comm.*, 1969, 1124; (c) R. E. Graf as quoted in N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, 1970, **92**, 3065; (d) K. Erlich and G. F. Emerson, *ibid.*, 1972, **94**, 2464; (e) D. A. Young, J. R. Holmes, and H. D. Kaesz, *ibid.*, 1969, **91**, 6968; (f) T. H. Whitesides and R. W. Arhart *ibid.*, 1971, **93**, 5296.

[2] D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, 1967, **89**, 6387.

[3] A. Reiche, H. Gross, and E. Höft, *Org. Synth.*, 1967, **47**, 1.

[4] *Cf.* R. F. Nystrom, *J. Amer. Chem. Soc.*, 1955, **77**, 2544; J. H. Brewster and H. O. Beyer, *J. Org. Chem.*, 1964, **29**, 105; E. C. Ashby and J. Prather, *J. Amer. Chem. Soc.*, 1966, **88**, 729; M. Rosenblum, 'Chemistry of the Iron Group Metallocenes,' Part I, Wiley, New York, 1955, p. 146.

[5] R. Pettit, G. F. Emerson, and J. Mahler, *J. Chem. Educ.*, 1967, **40**, 175.

[6] J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, 1966, **88**, 5153; M. L. H. Green and R. I. Hancock, *J. Chem. Soc.* (*A*), 1967, 2054.

[7] For examples of other potentially homoconjugated ligands attached to iron see F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4624, 4626.

[8] D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, 1968, **90**, 2561.

[9] Either stereospecific *exo* or *endo* electrophilic attack is possible and will explain our observations. Tricarbonyl(1–4-η-cyclohepta-1,3,5-triene)iron has been observed to undergo stereospecific *exo* attack by electrophiles. *Cf.* B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *J. C. S. Dalton*, 1972, 457 and D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.* 1972, **38**, 349.