Reaction of Tricarbonylcycloheptatrieneiron with Base: the Tricarbonylcycloheptatrienyliron Anion

By HENRY MALTZ* and BARBARA A. KELLY

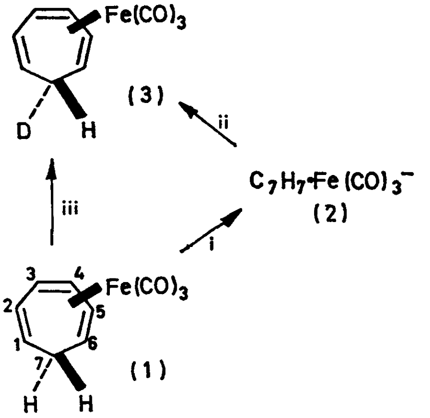
(*Department of Chemistry, Boston College, Chestnut Hill, Massachusetts* 02167)

Summary. Tricarbonylcycloheptatrieneiron (**1**) exchanges stereoselectively with MeO^- in MeOD immeasurably faster than the uncomplexed hydrocarbon; reaction of (**1**) with butyl-lithium in tetrahydrofuran gives the first reported complex of the cycloheptatrienyl anion.

WE were prompted to look for the tricarbonylcycloheptatrienyliron anion (**2**) after we discovered a dramatic difference in the rates of methoxide-catalysed deuterium exchange of cycloheptatriene and tricarbonylcycloheptatrieneiron (**1**). Whereas cycloheptatriene does not react in 10% NaOMe–MeOD even on heating to 110° for 24 h,[1] the complex (**1**) gives *exo*-tricarbonyl[7-$^2H_1$]cycloheptatrieneiron (**3**) {6%[$^2H_0$], 93%[$^2H_1$], and 1%[$^2H_2$] (mass spec.)} on similar treatment but for 1 h at room temperature.

That the exchange occurs at C-7 is shown by comparing the n.m.r. spectra (C_6D_6) of (**1**)[2] and the deuteriated material. Both substances show similar signals at τ 4·39 (2-H), 4·86—5·34 (1-, 4-, and 5-H), and 7·13 (3 and 6-H) but the band at 7·88 (7-H) is approximately half as intense in (**3**) as in (**1**). Although prolonged reaction leads to further deuteriation, the predominance of [$^2H_1$]-complex after only short reaction time indicates high stereoselectivity. *exo*-Deuteriation (on the less hindered side of the ring) is suggested by the i.r. spectrum (neat) of (**3**) which lacks the absorption at 2795 cm^{-1} observed for (**1**). Other such anomalously low C–H stretching frequencies in polyolefin–metal complexes have always come from *exo*-hydrogens.[3] The exchange could occur by proton abstraction to give (**2**) or by reversible Michael addition of MeO^- to (**1**).

Definitive evidence for (**2**) has come from reaction of (**1**) with butyl- or phenyl-lithium in tetrahydrofuran (THF). Addition of the alkyl-lithium (at −78°) immediately gave a red colour, followed by separation of a deep red viscous oil.† The i.r. spectrum (THF), ν_{max} 1942 and 1868 cm^{-1} ($C{\equiv}O$), is consistent with an $Fe(CO)_3$ anion.[4] The room-temperature n.m.r. spectrum ($[^2H_8]$THF) revealed (ignoring solvent absorptions) only one singlet at τ 5·35 with no change down to the m.p. (*ca.* −65°). These spectra are most consistent with a fluxional tricarbonylcycloheptatrienyliron anion (**2**), analogous to the isoelectronic, but neutral, $C_7H_7{\cdot}Co(CO)_3$ [τ 4·49 (CS_2)].[5] The uncomplexed anion, $C_7H_7^-$, by contrast is unstable[6] in THF above 0° and its n.m.r. spectrum has still not been reported.



SCHEME

Reagents: (*i*) *butyl-lithium*–THF; (*ii*) D_2O; *and* (*iii*) MeO^-–MeOD.

Although we have not yet isolated a heavy-cation salt, (**2**) has been further characterized by its reaction with D_2O to give (**3**) {71%; 4%$[^2H_0]$, 96%$[^2H_1]$ (mass spec.)} (see Scheme). Reaction of this deuteriated material with butyl-lithium, followed by H_2O gave (**1**) {76%$[^2H_0]$, 10%$[^2H_1]$, 6%$[^2H_2]$, 9%$[^2H_3]$ (mass spec.)} indicating again stereoselectivity for both the deuterium abstraction and the protonation.

The simple formation of (**2**) could be due to "removal" of 4 π-electrons from the otherwise anti-aromatic $C_7H_7^-$ by $Fe(CO)_3$ to give an "allyl" anion. Another possibility is metal interaction with all 8 π-electrons, lifting the anti-aromaticity. Further studies of (**2**) and related anions to test these alternatives are in progress.

We thank Mr. C. M. Lukehart (M.I.T.) for some of the mass spectra and acknowledge support from a N.A.T.O. Research Grant.

(*Received, August* 19*th*, 1971; *Com.* 1454.)

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† Wilkinson[2] has reported that 'treatment of $C_7H_8Fe(CO)_3$ with . . . phenyl-lithium . . . under a variety of conditions gave none of the expected products.' With solvents other than tetrahydrofuran, decomposition ensues; alternatively, aqueous work-up from tetrahydrofuran of the 'expected products' would lead to (**1**) (*vide infra*).

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[6] H. J. Dauben, jun., and M. R. Rifi, *J. Amer. Chem. Soc.*, 1963, **85**, 3041.