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Preliminary communication

(η^4-C_7H_8)Fe(CO)$_3$: A FLUXIONAL MOLECULE, OR "THE DOG THAT WHIMPERED IN THE NIGHT-TIME" [1]

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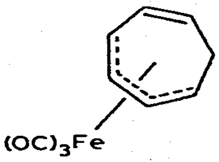
Summary

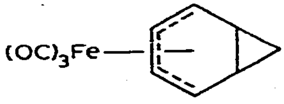
(η^4-C_7H_8)Fe(CO)$_3$ is shown to be fluxional by use of the Forsén—Hoffman spin saturation method in the ^{13}C NMR spectrum.

Over the past ten years, the case for 1,2 shifts in fluxional organometallic compounds has been developed to the exclusion of 1,3 shifts. Cotton [1] has cited the absence of fluxionality in a number of compounds, where 1,2 shifts are unlikely, e.g., (η^4-C_7H_8)Fe(CO)$_3$ (I), as evidence for 1,2 shifts. Recently, the existence of 1,3 shifts has been proven for [(η^3-C_7H_9)PdL$_2$]$^+$, [(η^3-C_8H_{11})PdL$_2$]$^+$ [2], (η^6-C_8H_8)Cr(CO)$_3$ [3], and (η^6-C_8H_8)W(CO)$_3$ [4]. It therefore seems strange that (η^4-C_7H_8)Fe(CO)$_3$, should not be fluxional, albeit at higher energy than would be expected for an unhindered 1,2 shift mechanism. An examination of the variable temperature ^{13}C NMR spectrum showed only a little broadening of the signals before decomposition became rapid at ca. 130°C. However, recently the Forsén—Hoffman spin saturation method [5] has been developed [6] to permit the determination of slow exchange rates in ^{13}C NMR spectra. This method was applied to (η^4-C_7H_8)Fe(CO)$_3$ at 94°C to yield an approximate rate of 0.2 s^{-1} which corresponds to a $\Delta G^{\ddagger}$ of ca. 23 kcal/mol. An accurate rate could not be obtained on account of significant decomposition during the measurements.

The fluxionality of (η^4-C_7H_8)Fe(CO)$_3$ may arise via two mechanisms. Two sequential 1,2 shifts may be occurring via II. It is known that the 1,2 shifts in (η^4-C_8H_8)Fe(CO)$_3$ has E_a of ca. 7 kcal/mol [7]. Thus ca. 16 kcal/mol would be



(I)



(II)

attributed to the formation of the high energy norcaradiene structure, II. This energy is reasonable. It has been estimated that cycloheptatriene is 10.2 kcal/mol more stable than norcaradiene [8]. When, by substitution, significant quantities of the cycloheptatriene and norcaradiene are present in solution, E_a has been determined to be in the range 7 to 15 kcal/mol [9]. Thus two sequential 1,2 shifts for I via II is not an unreasonable mechanism. A direct 1,3 shift mechanism is also possible. It has been shown for $(\eta^2\text{-}CH_2{=}CHPh)Fe(CO)_4$ that $\Delta H^{\ddagger}$ = 29 kcal/mol for the reaction with CO to give $Fe(CO)_5$ via $Fe(CO)_4$ [10]. Thus a mechanism involving the 16 electron intermediate $(\eta^2\text{-}C_7H_8)Fe(CO)_3$ is unlikely, but if the free double bond enters as the other double bond leaves producing a transition state which is 18 electron in character, then the activation energy could be reduced to the observed value. Intermediates of the type $[(\eta^5\text{-}C_7H_7)\text{-}Fe(CO)_3]^+$ [11] can be eliminated as the spin saturation experiments show pairwise exchange without the CH_2 carbon atom being involved in the exchange mechanism. It is therefore clear that $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ is fluxional via either 1,2 or 1,3 shifts and cannot be quoted as proof that the 1,3 shift mechanism is forbidden.

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