1,3-Shifts in $[(\eta^6\text{-}C_8H_8)Cr(CO)_3]$. Application of the Forsen–Hoffman Spin Saturation Method to a Four-site ^{13}C Nuclear Magnetic Resonance Problem†

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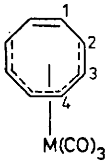
Summary $[(\eta^6\text{-}C_8H_8)Cr(CO)_3]$ has been shown to be fluxional by means of 1,3- and, to a lesser extent, 1,2-shifts; this work clearly proves the earlier suggestion of random shifts to be wrong.

Recently, Cotton[1] has examined the dynamic ^{13}C n.m.r. spectra of $[(\eta^6\text{-}C_8H_8)M(CO)_3]$ (M = Cr, Mo, or W) (I) and found that, at room temperature, the cyclo-octatetraene ring is fluxional. As it was found that all four ^{13}C resonances of the cyclo-octatetraene ring broadened at the same rate, it was possible to show that the ring must be either undergoing 1,3- or random-shifts. Cotton[1] argued that random shifts *via* the symmetric 20-electron intermediate, $[(\eta^8\text{-}C_8H_8)M(CO)_3]$ occur. Subsequently, Whitesides[2] argued that the 1,3-shift *via* a 16-electron intermediate, $[(1\text{—}4\text{-}\eta\text{-}C_8H_8)M(CO)_3]$ was more likely. This mechanism is even more likely in view of the observation of 1,3-shifts in $[(\eta^3\text{-cycloheptadienyl})PdL_2]^+$ complexes involving the reverse mechanism with an 18-electron intermediate, $[(\eta^5\text{-cycloheptadienyl})PdL_2]^+$.[3]



(I)

In order to resolve this controversial problem, the Forsén–Hoffman[4,5] spin saturation method has been applied to $[(\eta^6\text{-}C_8H_8)Cr(CO)_3]$. As originally described, the method was only applicable to sensitive nuclei, but it has been extended to become a very powerful tool in dynamic ^{13}C n.m.r. spectroscopy.[6] In the original method, in order to determine the exchange rate in an n-site problem, it was necessary to decouple $n - 1$ sites; a problem fraught with difficulties. When the method is applied to pulse Fourier transform n.m.r. spectroscopy, the difficulties vanish. It may be shown[5] that if a pulse Fourier transform ^{13}C n.m.r. spectrum is measured with at least $5T_1$ between each pulse in the absence and in the presence of a saturating decoupling field at one site, then for the Kth site equation (1) holds, where $M_0{}^K$ is the magnetisation of the

$$(M_0{}^K - M_z{}^K)/T_{1K} = M_z{}^K \sum_{\nu \neq K} \lambda_{K\nu} + \sum_{\nu \neq K} \lambda_{\nu K} M_z{}^{\nu} \qquad (1)$$

Kth site in the absence of irradiation, $M_z{}^{\nu}$ is the equilibrium magnetisation of the νth site in the presence of irradiation at one site, T_{1K} is the spin–lattice relaxation time of the Kth site, and $\lambda_{K\nu}$ is the exchange rate between the Kth and νth site. Note that λ_{12} is not the rate of a 1,2-shift as it arises from both the movement of 1 to 2 and to 2′ in (I), *i.e.*, if $k_{\alpha\beta}$ is the rate of the α,β-shift, then $\lambda_{12} = k_{12} + k_{13}$, and other similar relations may be derived. A typical set of spectra is shown in the Figure. T_{1K} was measured during the usual $(\pi\text{–}\tau\text{–}\frac{\pi}{2}\text{–}5T_1)_n$ pulse sequence. This method is valid provided that all the exchanging sites have the same T_1,[7] which is true in this case. For $[(\eta^6\text{-}C_8H_8)Cr(CO)_3]$ there are in principle 12 independent equations derivable and only 4 unknown rates. In practice, as the two resonances at δ 104·8 and 102·5 p.p.m. were too close to saturate one without affecting the other, only 6 independent equations were derived.

An inspection of the spectra in the Figure shows that the saturation transfer is not random. One signal is not affected as much as the other two remaining signals. In order to analyse the data quantitatively, it is necessary to assign the spectra. The signal at δ 130·6 p.p.m. is close to that of cyclo-octatetraene,[8] δ 133 p.p.m., and may be assigned to C(1), the unco-ordinated carbon atom. The remaining signals were assigned by relating the ^{1}H n.m.r. signals to the ^{13}C n.m.r. signals by ^{13}C{^{1}H} decoupling.[9] Then ^{1}H{^{1}H} decoupling at 220 MHz was used to assign the hydrogen atoms, starting with H(1), already assigned from C(1). The ^{1}H n.m.r. assignments are in agreement with those previously published for $[(\eta^6\text{-}C_8H_8)Cr(CO)_3]$.[10] Quantitative analysis of the spectra gave, at −22·5 °C, $k_{12} = 0{\cdot}03 \pm 0{\cdot}02$ and $k_{13} = 0{\cdot}29 \pm 0{\cdot}03\ s^{-1}$, and at −15 °C, $k_{12} = 0{\cdot}12 \pm 0{\cdot}06$ and $k_{13} = 0{\cdot}58 \pm 0{\cdot}09\ s^{-1}$; k_{14} and k_{15} are zero. It is therefore clear that the dominant mechanism is the 1,3-shift as argued by Whitesides.[2] However, k_{12} is large enough to raise the possibility of a competing 1,2-shift mechanism, but not large enough to prove that such a mechanism is occurring. When the variable temperature ^{13}C n.m.r. spectrum was reinvestigated, it was found, contrary to previous work,[1] that all the cyclo-octatetraene resonances do not broaden at the same rate. The signals due to C(2) and C(3) broaden faster, confirming a competing 1,2-shift. Line-shape analysis gave $k_{12} = 24$ and $k_{13} = 48\ s^{-1}$ at 26·5 °C. It is therefore concluded that 1,2-shifts are also occurring.

There are now three proven examples of 1,3-shifts, *i.e.*, $[(\eta^6\text{-}C_8H_8)Cr(CO)_3]$, $[(\eta^3\text{-}C_7H_9)PdL_2]^+$,[3] and $[(\eta^3\text{-}C_8H_{10})\text{-}$

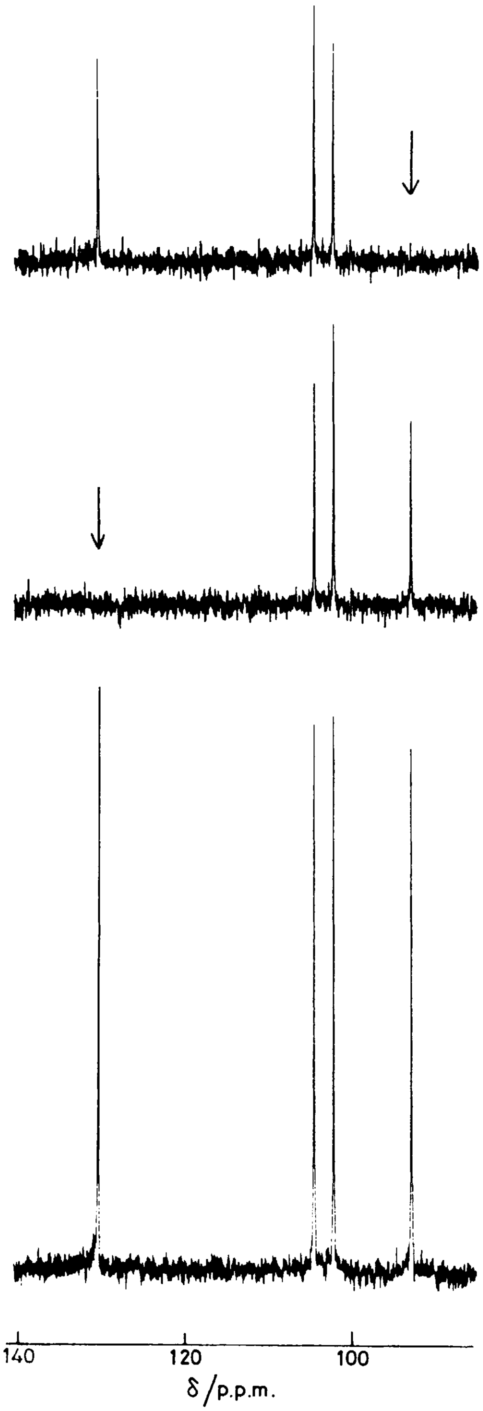


FIGURE. The application of the Forsén–Hoffman spin saturation method to the cyclo-octatetraene ^{13}C n.m.r. resonances of $[(\eta^6\text{-}C_8H_8)Cr(CO)_3]$ in $CD_2Cl_2\text{–}CH_2Cl_2$ at −15 °C. The places irradiated are indicated by arrows.

$PdL_2]^+$.[3] It is to be expected that $[(\eta^6\text{-}C_8H_8)Mo(CO)_3]$,[1] $[(\eta^6\text{-}C_8H_8)W(CO)_3]$,[1] and $[(\eta^6\text{-}C_8H_8)Ru(\eta^4\text{-norbornadiene})]$[11] will also be shown to undergo 1,3-shifts rather than the random shifts previously suggested. It would be strange if 1,3-shifts are restricted to just these compounds and work is in progress to look for further examples.

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† No reprints available.

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