The Absence of Valence Tautomerism in *trans*, *trans*-1,4-Bis(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene

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Summary The 100 and 251 MHz proton n.m.r. spectra of *trans,trans*-1,4-bis(dicarbonyl-π-cyclopentadienyliron)-buta-1,3-diene show no evidence for valence tautomerism.

CHURCHILL *et al.*[1] recently reported that the reaction of (π-C_5H_5)Fe(CO)$_2$Na with *cis*-3,4-dichlorocyclobutene yielded an orange crystalline complex which, according to two independent *X*-ray diffraction studies,[1,2] is 1,4-bis(dicarbonyl-π-cyclopentadienyliron)-*trans,trans*-buta-1,3-diene, (I). The 60 MHz spectrum of this compound in tetrahydrofuran and *sym*-$C_2H_2Cl_4$ was reported to consist of two sharp singlets of relative intensities 5 : 2 at τ 5·05 and 3·76.[1] The peak at τ 5·05 was assigned to the cyclopentadienyl protons, leaving an unexpected single resonance line at τ 3·76 for the remaining four protons of the butadienyl system.[1] Churchill and his co-workers gave two possible explanations for the appearance of the butadienyl moiety as a single line in the 60 MHz spectrum: (i) the protons on C(1) and C(2) have accidentally the same chemical shifts or (ii) an averaging process is taking place which interchanges the environments of the proton on C(1) and C(1′) with C(2) and C(2′), respectively. The first possibility was considered unlikely because of the rather different environments of the two types of protons and because the vinyl protons in (π-C_5H_5)Fe(CO)$_2$(σ-C_2H_3) do have different chemical shifts. The second explanation (*i.e.* valence tautomerism) was considered likely because of a broadening of the τ 3·76 resonance at low temperatures, and a 1,2-shift was suggested as the averaging process. Recently, Campbell and Green

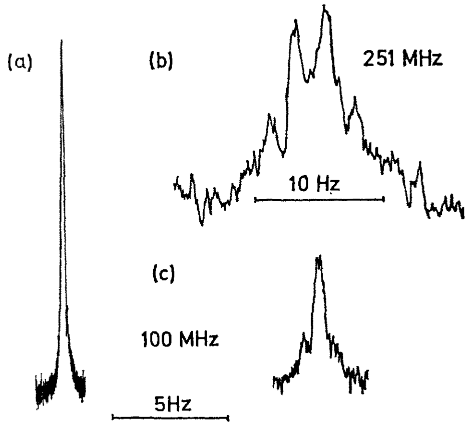

FIGURE 1. *Spectra of* [(π-C_5H_5)Fe(CO)$_2$]$_2$$C_4H_4$ (a) 100 *MHz spectrum of the cyclopentadienyl protons*, (b) 251 *MHz spectrum of the butadienyl protons*, (c) 100 *MHz spectrum of the butadienyl protons.*

accepted that an averaging process was taking place but rejected the 1,2-shift in favour of a 1,3-shift.

Contrary to the above conclusions, we now report that the 100 and 251 MHz spectra of the complex (I) clearly show the absence of any valence tautomerism. In perdeuteriotetrahydrofuran the 100 MHz n.m.r. spectrum of (I) shows a singlet at τ 5·05 due to the cyclopentadienyl protons (Figure 1,a) and a broader peak with some fine structure at τ 3·76 corresponding to the butadienyl protons (Figure 1,c). At 251 MHz the cyclopentadienyl protons appear as a single peak but the butadienyl protons appear as a multiplet (Figure 1,b). The 100 MHz resonance pattern of the butadienyl protons spreads out at low temperatures (Figure 2). Thus, all the protons of the butadienyl residue do not have the same chemical shift at room temperature, and therefore there is neither evidence nor need for a 1,2- or 1,3-shift. The 60 MHz spectrum of the butadienyl protons is virtually a single line[1] at room temperature because of the combination of a small chemical shift difference and relatively large coupling constants. The broadening reported to take place at low temperatures[1] is not the result of an averaging process becoming slow on the n.m.r. time scale, but is a reflection of an increased chemical shift difference as the temperature is lowered. All the 100 MHz spectra can be fitted to AA′BB′ systems calculated on the basis of expected values of coupling constants (J_{AB} 17; $J_{AB'}$ $-0·8$; $J_{AA'}$ 0·7; $J_{BB'}$ 10·4 Hz) and with the following chemical shifts (temperatures in bracket): 5 Hz (room temp.); 10 Hz ($-32°$); 15 Hz ($-58°$); 20 Hz ($-93°$). Also, the 251 MHz spectrum at room temperature fits a chemical shift of 12·5 Hz (*i.e.*, 0·05 p.p.m., corresponding to 5 Hz at 100 MHz). The variation of the chemical shifts is most likely due to different populations of rapidly interconverting rotamers at different temperatures.

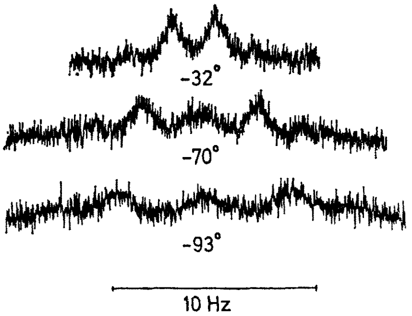

FIGURE 2. *100 MHz spectra of the butadienyl protons of* $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2]_2C_4H_4$ *at various temperatures.*

The evidence presented by Campbell and Green[3] for a 1,3-shift was based on the structure of one of the ^{13}C satellite of a dimethyl derivative of (I), and on the spectrum of a monomethyl derivative of (I). The analysis of the ^{13}C satellite spectrum was based on a first-order treatment which at best appears to be a poor approximation. In our view the data[3] presented are not inconsistent with our conclusions.

We find that the small chemical shift difference is not unique for the butadienyl system among the cyclopentadienyl iron complexes. King[4] reported the preparation of the complex $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_3$ and found that the trimethylene moiety appears as a singlet in the 60 MHz spectrum. At both 100 and 251 MHz, we find that the trimethylene protons give rise to complex multiplets, so that here also there is no evidence for valence tautomerism.

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