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Preliminary communication

Direct observation of ion pair formation in dichloromethane solution and the crystal structure of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_3][BF_4]$

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Abstract

Infrared spectra of $[(\eta^5C_5Me_5)Fe(CO)_3][BF_4]$ in the ν(MC–O) region show separate peaks due to ion pairs and solvated molecules. The crystal structure of the complex determined at −110 °C showed no unexpected bond lengths or angles.

Ion pairing between metal carbonyl anions and various cations is well documented [1], but that between metal carbonyl cations and various anions is not. Certain nucleophilic anions attack sufficiently electrophilic MCO groups at carbon [2], but ion pairing involving simple metal carbonyl cations appears to be uncommon. We now report that $[(\eta^5C_5Me_5)Fe(CO)_3][BF_4]$ (**1**) has a MC–O stretch infrared spectrum, that is most simply explained as indicating that an ion pair is formed in dichloromethane solution. The ion separates on addition of acetonitrile.

Attempts to synthesise cationic diene complexes of the type $[(\eta^5\text{-}C_5Me_5)Fe(\eta^4\text{-diene})CO][BF_4]$ [1] gave small amounts of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_3][BF_4]$ (**1**) as a by-product. The latter complex was the major product in cases where no η^4-diene could be isolated. Infrared spectra of **1** in dichloromethane solution were more complex than those normally observed for cations containing the $M(CO)_3$ group (Fig. 1). These spectra indicate that an ion pair equilibrium is being directly observed in solution.

The identity of **1** was confirmed by analytical data, FAB mass spectrum and ^1H and ^{13}C NMR spectra. Attempts to obtain a crystal structure at room temperature were not successful. It was only possible to locate the Fe atom, the rest of the molecule was only poorly resolved. When data collection was repeated at −110 °C the structure refined satisfactorily and it is illustrated in Fig. 2 *. There were no

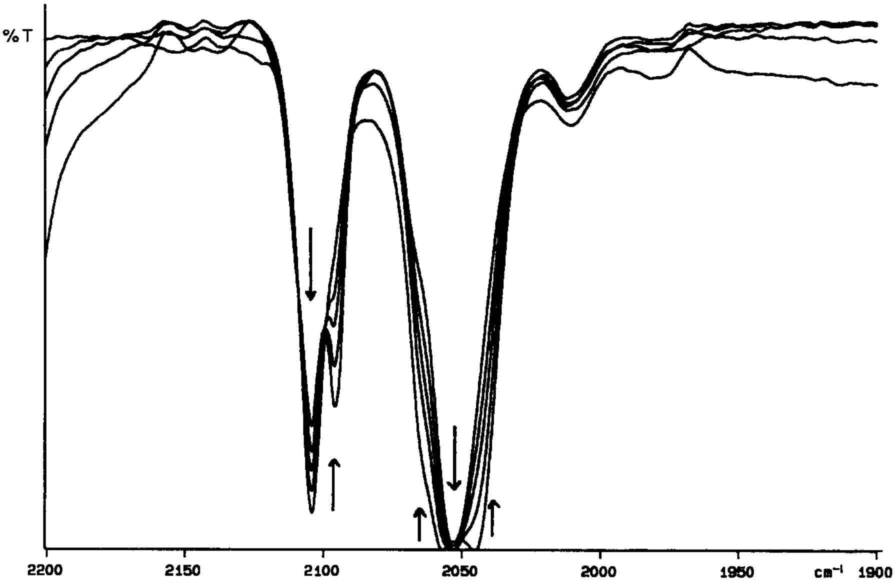

Fig. 1. IR spectra in dichloromethane solution with spectral changes in the direction of the arrows on dropwise addition of acetonitrile.

unusual bond lengths or angles. The closest anion–cation contact is a H···F contact of 2.47 Å.

The infrared spectra shown in Fig. 1 were obtained using the same batch of crystals from which a crystal was chosen for structure determination. In dichloromethane solution the complex displayed ν(MC–O) bands at 2105, 2096 and 2045 cm^{-1}. The band at 2045 cm^{-1} was not fully resolved into two peaks but was considerably broader than expected. Dropwise addition of acetonitrile to the dichloromethane solution gave spectral changes in the direction shown by the arrows. (On removal of solvents and redissolution of the residue in dichloromethane the process can be repeated.) It is reasonable to assume that the final spectrum obtained on addition of acetonitrile represents that of solvated ions only. The spectrum of the solvated ions lies at higher frequency than that of the ion pairs. This indicates that there is a significant reduction of charge on iron in the ion pairs leading to more extensive Fe–CO back bonding. Atomic charges calculated by the extended Hückel method [6], indicate that the bulk of the positive charge resides

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* *Crystal data for compound 1*: Orthorhombic; space group *Pbcm*; $a = 10.059(9)$, $b = 12.869(9)$, $c = 11.824(9)$ Å; $Z = 4$; $U = 1530.61$ Å; $\mu = 9.68$ cm^{-1}; $F(000) = 735.96$; 1213 unique reflections measured at −110 °C of which 885 were observed with $I > 3\sigma(U)$ using a CAD4 diffractometer and M-K_α radiation; $2\theta_{max} = 48$ °. The structure was solved by direct methods, SHELX86 [3], and refined with 144 variable parameters using SHELX76 [4]. Hydrogen atoms were located and refined with isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically. After full matrix refinement; $R = 4.27$ and $R_w = 4.68\%$. The maximum and minimum excursions in the final $F_o - F_c$ difference map were 0.26 and −0.22 e/Å^3. The ORTEP program was used to obtain the drawing [5]. Atomic coordinates, bond lengths and angles have been deposited at the Camridge Crystallography Data Centre.

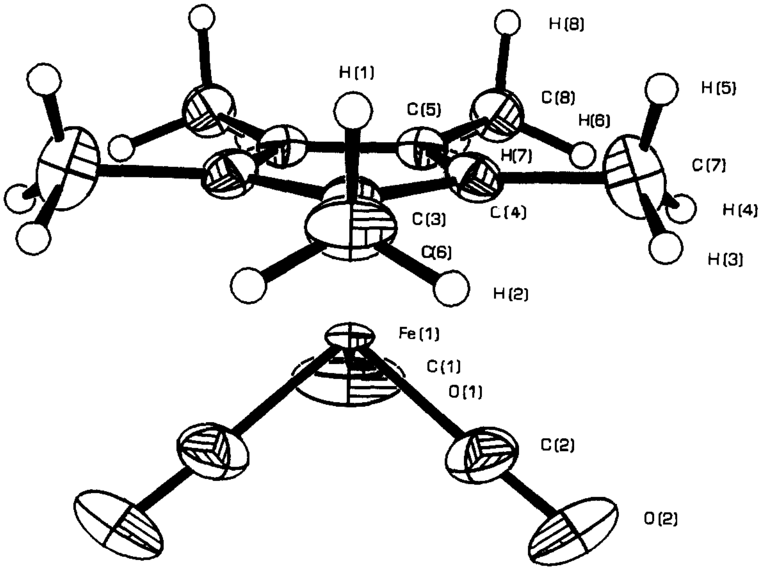

Fig. 2. ORTEP drawing of the cation of 1. Mean Fe–ring distance 2.11 and Fe–CO 1.78 Å. Calculated mean charges C(CO) 0.144, C(ring) 0.039, C(Me) 0.008, O −0.128 and Fe 0.777.

on iron and it is likely that ion association will involve the iron as the positive charges calculated for the other atoms are small, Fig. 2.

These results clearly show that ionic metal carbonyl species can be used for studies of ion pair equilibria using infra red spectroscopy.

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