Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Polyfluoroaromatic derivatives of metal carbonyls VII*. Dicarbonyl-π-cyclopentadienyl-σ-*S*-pentafluorophenylsulphonyliron, $C_6F_5SO_2Fe(CO)_2(\pi\text{-}C_5H_5)$: preparation, properties and structure

M.I. BRUCE

Department of Inorganic Chemistry, The University, Bristol, BS8 1TS (Great Britain)

A.D. REDHOUSE

Department of Chemistry and Applied Chemistry, University of Salford, Salford 5, Lancs. (Great Britain)

(Received June 1st, 1971)

The insertion of sulphur dioxide into metal—carbon σ-bonds has been reported for a variety of systems, including phenyl and benzyl derivatives containing the $(\pi\text{-}C_5H_5)Fe(CO)_2$ group[2]. However, no sulphinato complex could be obtained on treatment of $R_fFe(CO)_2(\pi\text{-}C_5H_5)$ ($R_f = C_6F_5$[2] or $C_6F_5CH_2$[3]) with liquid SO_2 for 24 h.

The complex $C_6F_5SO_2Fe(CO)_2(\pi\text{-}C_5H_5)$ (I) may be prepared from reactions between $C_6F_5SO_2Cl$ and the anion $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$, when a small amount of $C_6F_5Fe(CO)_2(\pi\text{-}C_5H_5)$ is also formed, or in higher yield with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, when an equivalent amount of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ is also formed. Complex (I) is air-stable, and surprisingly insoluble in non-polar solvents, although it may be recrystallised from tetrahydrofuran or aqueous acetone. It is involatile, and cannot be desulphonylated thermally; only ions from complex decomposition products were observed when attempts were made to obtain its mass spectrum. It is of some interest that no binuclear complex of the type $(\pi\text{-}C_5H_5)Fe(CO)_2C_6F_4SO_2Fe(CO)_2(\pi\text{-}C_5H_5)$ was found in the reaction with the anion, in contrast to results obtained with C_6F_5COCl[4,5].

Comparison of the ^{19}F NMR spectra of complex (I) (signals at 140.5, 153.4 and 161.6 ppm, upfield from internal $CFCl_3$) with that of $C_6F_5SO_2Cl$ (134.5, 140.3 and 157.6 ppm) suggests that strong Fe—S d_π—d_π bonding and weak ring π-system interaction with the sulphur *d* orbitals occur[5]. To investigate this in more detail, and to confirm the presence of the *S*-sulphinato group, the crystal and molecular structures of complex (I) have been determined.

Bright yellow-orange crystals of complex (I) separate from tetrahydrofuran. Crystal data: monoclinic, space group $P2_1/n$ (No. 14), $a = 10.97(2)$, $b = 12.12(2)$, $c = 12.06(2)$ Å, $\beta = 117.6(2)°$, $V = 1420$ Å^3, density 1.90g·ml^{-3}, calculated for $Z = 4$, 1.91g·ml^{-3}. A total of 893 independent reflections was recorded by visual estimation from precession photographs taken with Mo-K_α radiation. The structure was solved by standard heavy atom procedures and

---

[*] For part VI see ref. 1.

refined by using full matrix least squares methods, with isotropic thermal parameters for all atoms, to a conventional R factor of 10.9%.

The molecular structure of the complex is shown in Fig.1 and confirms that it is an S-bonded system. The Fe—S bond distance of 2.20(1) Å is in good agreement with that found in $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CHC_6H_5$ [6] (2.218 Å), and considerably shorter than the estimated Fe—S single-bond length of 2.38 Å. The C—S distance is 1.83(2) Å and compares favourably with the distance of 1.78 Å calculated from the covalent radii of sulphur (1.04 Å) and sp^2 carbon (0.74 Å). These facts accord with a strong π-interaction between the iron and sulphur d orbitals, but minimal interaction between the π-system of the phenyl group and the sulphur d orbitals, and support Wojcicki's observations[2] and the ^{19}F NMR results reported previously[5]. Some other parameters are indicated in Fig.1.

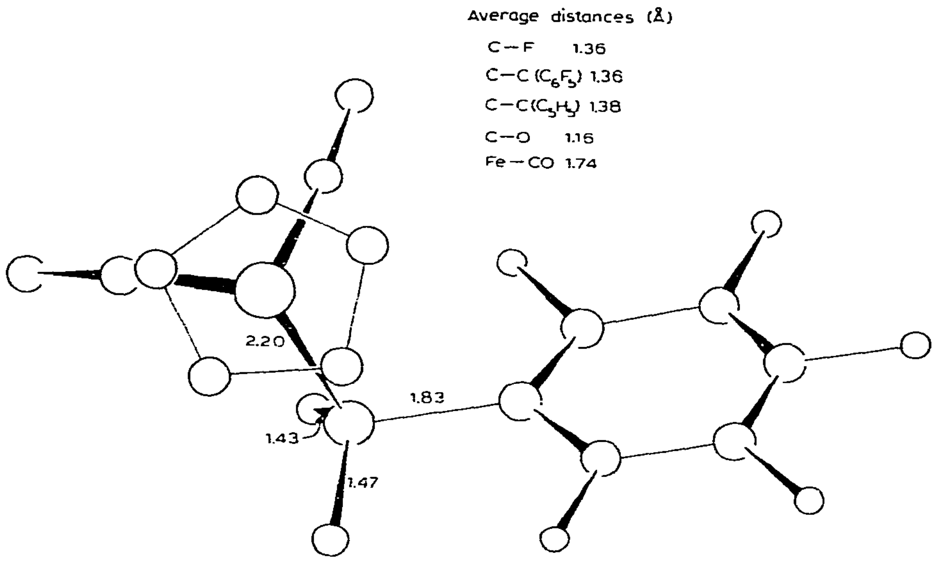

Fig.1. Molecular structure of $C_6F_5SO_2Fe(CO)_2(\pi\text{-}C_5H_5)$.

EXPERIMENTAL

Chromatography of the reaction product from equimolar amounts of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ and $C_6F_5SO_2Cl$ on Florisil, gave small amounts of $C_6F_5Fe(CO)_2(\pi\text{-}C_5H_5)$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, and a bright yellow band eluted with acetone. Evaporation and recrystallisation gave pure complex (I) as bright yellow-orange blocks, m.p. 165—170° (decomp.). The same complex could also be obtained in over 70% yield, along with an equivalent amount of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$, from a reaction between $C_6F_5SO_2Cl$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ in tetrahydrofuran for 25 h at room temperature (Found: C, 38.22; H, 1.19; F, 23.55; S, 7.72; $C_{13}H_5F_5FeO_4S$ calcd.: C, 38.24; H, 1.22; F, 23.20; S, 7.85%. Infrared spectrum ($CHCl_3$): 2070vs, 2023vs [ν(CO)]; 1644m, 1518m, 1512sh, 1489vs, 1385w, 1288w, 1140w; 1095vs, 1076vs, 990vs [ν(SO)]; 855m (C_5H_5), 650m cm^{-1}).

REFERENCES

1 M.I. Bruce, *J. Organometal. Chem.*, 21 (1970) 415.
2 J.P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, 88 (1966) 4862.
3 M.I. Bruce, unpublished observations.
4 T. Blackmore, M.I. Bruce, P.J. Davidson, M.Z. Iqbal and F.G.A. Stone, *J. Chem. Soc., A*, (1970) 3153; T. Blackmore, M.I. Bruce and F.G.A. Stone, *J. Chem. Soc., A*, (1968) 2158.
5 M.I. Bruce, *J. Chem. Soc., A*, (1968) 1459.
6 M.R. Churchill and J. Wormald, *Inorg. Chem.*, 10 (1971) 572.