

**Preliminary communication**

**A NEW AND UNUSUAL ISOMERISM IN  $[\text{Fe}(\text{CO})_2 \{ \text{P}(\text{OR})_3 \}_2 (\text{SO}_2)]$  COMPLEXES (R = ARYL)**

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**Summary**

$[\text{Fe}(\text{CO})_2 \{ \text{P}(\text{OR})_3 \}_2 (\text{SO}_2)]$  complexes (R = aryl) exist in solution as equilibrium mixtures of two isomers; both have been shown by X-ray diffraction studies (where R = Ph or *o*-MeC<sub>6</sub>H<sub>4</sub>) to have planar coordination about SO<sub>2</sub> and trigonal bipyramidal coordination about Fe, but in one isomer (R = Ph) the equatorial plane is occupied by SO<sub>2</sub> and two CO ligands whilst in the other one (R = *o*-MeC<sub>6</sub>H<sub>4</sub>) it is occupied by the SO<sub>2</sub> and two P ligands.

Sulphur dioxide is an unusually flexible ligand in that it may adopt a number of different modes of coordination in transition metal complexes, and may cause variations in the coordination polyhedra about those metal atoms [1].

Here, we describe a totally unexpected and previously unreported type of isomerism which is found in complexes of the type  $[\text{Fe}(\text{CO})_2 \{ \text{P}(\text{OR})_3 \}_2 (\text{SO}_2)]$  (R = aryl), prepared by the reaction of  $[\text{Fe}(\text{CO})_2 \{ \text{P}(\text{OR})_3 \}_2 (\text{CS}_2)]$  with SO<sub>2</sub> [2]. These exist as solvent dependent mixtures of two species in solution; isomer A (which predominates when R = Ph or *p*-MeC<sub>6</sub>H<sub>4</sub>) gives rise to two  $\nu(\text{CO})$  vibrations whilst isomer B (predominating when R = *o*-MeC<sub>6</sub>H<sub>4</sub>) gives only one. The P(OR)<sub>3</sub> ligand affects not only the position of the equilibrium in solution, but also the isomer which is found in the solid state.

To identify these two isomers unambiguously, we have carried out 3d X-ray diffraction studies on single crystals of  $[\text{Fe}(\text{CO})_2 \{ \text{P}(\text{OPh})_3 \}_2 (\text{SO}_2)]$  [Crystal data: C<sub>38</sub>H<sub>30</sub>O<sub>10</sub>P<sub>2</sub>SFe, mol.wt. 796.5, Triclinic, *a* 11.027(5), *b* 11.374(5), *c* 15.328(8) Å,  $\alpha$  88.3(1),  $\beta$  97.7(1),  $\gamma$  108.6(1)°, *U* 1805.9 Å<sup>3</sup>, *D*<sub>M</sub> 1.45 g cm<sup>-3</sup> (by flotation), *Z* = 2, *D*<sub>C</sub> = 1.464 g cm<sup>-3</sup>; *F*(000) = 820,  $\mu(\text{Mo-K}\alpha)$  6.3 cm<sup>-1</sup>; space group *P*1 or *P* $\bar{1}$ , solved and refined in *P* $\bar{1}$  to *R* = 0.083, *R'* = 0.115 from 2427 independent non-zero reflexions from precession photographs

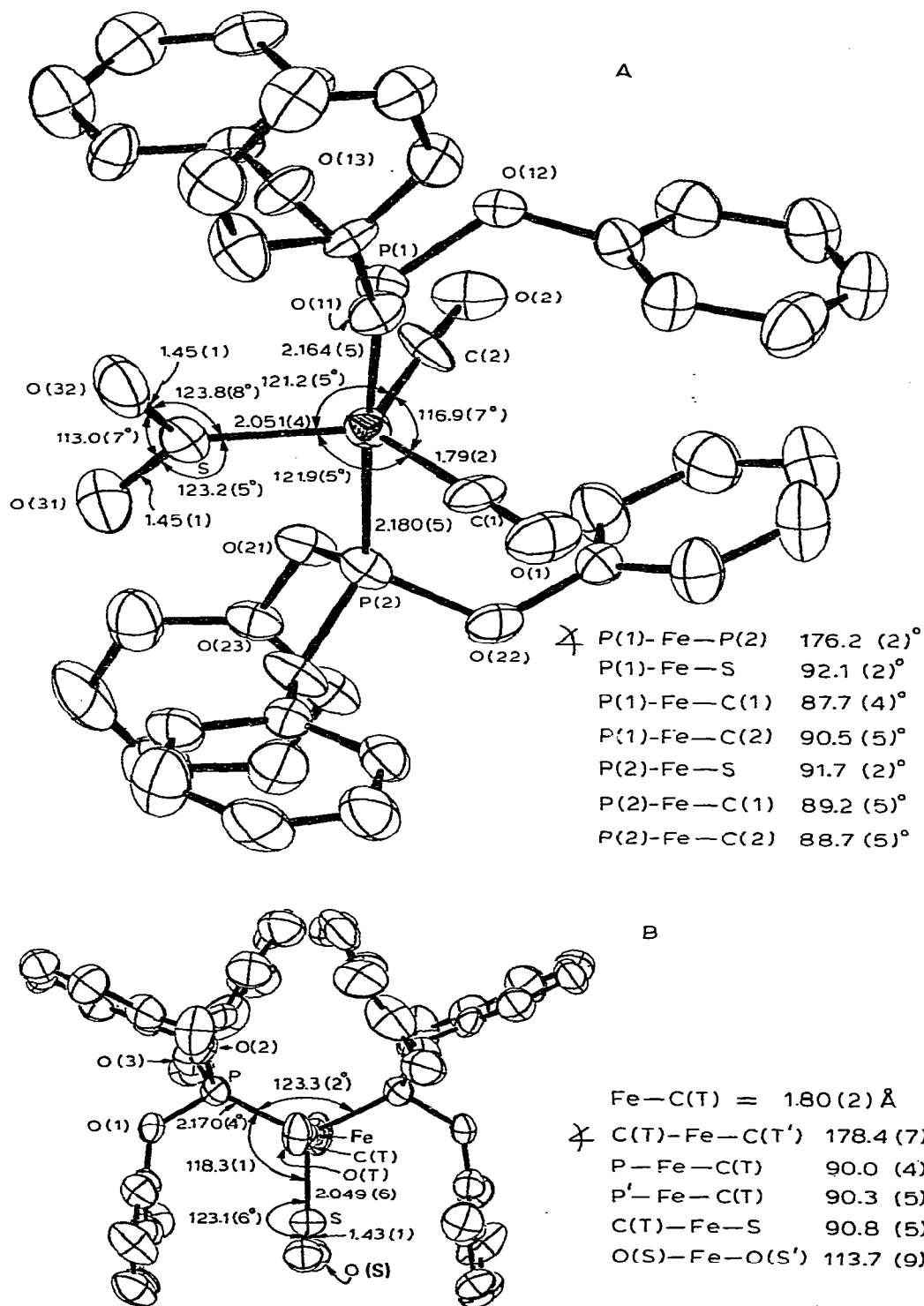


Fig. 1. Structures of  $[Fe(CO)_2\{P(OPh)_2\}_2(SO_2)]$  (isomer A) and  $[Fe(CO)_2\{P(OC_6H_4Me-o)_2\}_2(SO_2)]$  (isomer B) in the solid state. Angles in degree, distances in Å.

for layers 0 — 3,  $k, l; l, k, 0 — 4$  and (101) 0 — 3.], and  $[\text{Fe}(\text{CO})_2 - \{\text{P}(\text{OC}_6\text{H}_4\text{Me-}o)_3\}_2(\text{SO}_2)]$  [Crystal data:  $\text{C}_{44}\text{H}_{42}\text{O}_{10}\text{P}_2\text{SFe}$ , mol.wt. 880.7, monoclinic,  $a$  19.873 (11),  $b$  10.725 (5),  $c$  20.798 (11) Å,  $\beta$  100.7 (1)°,  $U = 4355.4$  Å<sup>3</sup>,  $Z$  4,  $D_C$  1.343 g cm<sup>-3</sup>,  $F(000) = 1832$ ,  $\mu(\text{Mo-K}\alpha) 5.3$  cm<sup>-1</sup>, systematic absences  $h, k, l$  if  $h + k \neq 2n$  and  $h, 0, l$  if  $l \neq 2n$ . Space group  $Cc$  or  $C2/c$ , solved and refined in  $C2/c$  (hence molecule has space group imposed  $C_2$  symmetry) to  $R = 0.086$ ,  $R' = 0.119$  for 1309 independent non-zero reflexions from precession photographs from layers 0 — 4,  $k, l; h, k, 0 — 6$  and (101) 0 — 4]. Infrared spectral data show the first of these two compounds adopts the A configuration in the solid state whilst the second adopts the B form. The two structures are illustrated in Fig. 1.

It can be seen that in both there is ca. planar coordination about sulphur and an almost exact trigonal bipyramidal ligand distribution about iron with bond angles deviating by only a few degrees from the ideal values. It is remarkable that the isomerism arises from the axial disposition of the phosphorus ligands in A changing to equatorial in B. In general  $[\text{Fe}(\text{CO})_2\{\text{PR}_3\}_2(\text{L})]$  complexes adopt structure A (e.g.  $\text{L} = \text{CO}$  [3],  $\text{CS}$  [4], or  $\text{CS}_2$  [5]). This is attributed, at least in part, to the steric interactions between the phosphorus ligands which are probably much greater in configuration B than in (A). In these sulphur dioxide complexes, however, the larger ligands ( $\text{P}(\text{OC}_6\text{H}_4\text{Me-}o)_3$  cone angle 141°;  $\text{P}(\text{OPh})_3$  cone angle 121° [6]) prefer the bis-equatorial to the bis-axial arrangement. Although this suggests, at first sight, that electronic effects are important, we do not think that this is so. The  $\text{P}(\text{OC}_6\text{H}_4\text{Me-}p)_3$  derivative exists in solution mainly as isomer A and in the solid state solely as this form. The *o*- and *p*-methyl groups are unlikely to differ greatly in their electronic effects at the phosphorus (or iron) atom, but they do have markedly different steric consequences within the triarylphosphite ligands.

A careful examination of the structure of  $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2(\text{SO}_2)]$  (form A) shows that the planar  $\text{SO}_2$  ligand is almost perpendicular to the equatorial plane of the complex (dihedral angle 108°), and that there is a close contact between its oxygen atoms and a phenyl ring of each of the  $\text{P}(\text{OPh})_3$  ligands. This interaction would be minimised by conformational changes within the phosphite ligands. It is possible that the presence of *ortho*-methyl groups prevents these necessary conformational changes. The resultant ring- $\text{SO}_2$  interactions destabilize isomer A in preference to isomer B where, of course, they are absent and in consequence the plane of the  $\text{SO}_2$  ligand lies exactly perpendicular to the equatorial plane of the complex.

## References

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