ortho-Metallation *vs.* Donor Ligand Complexation

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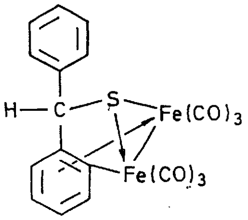
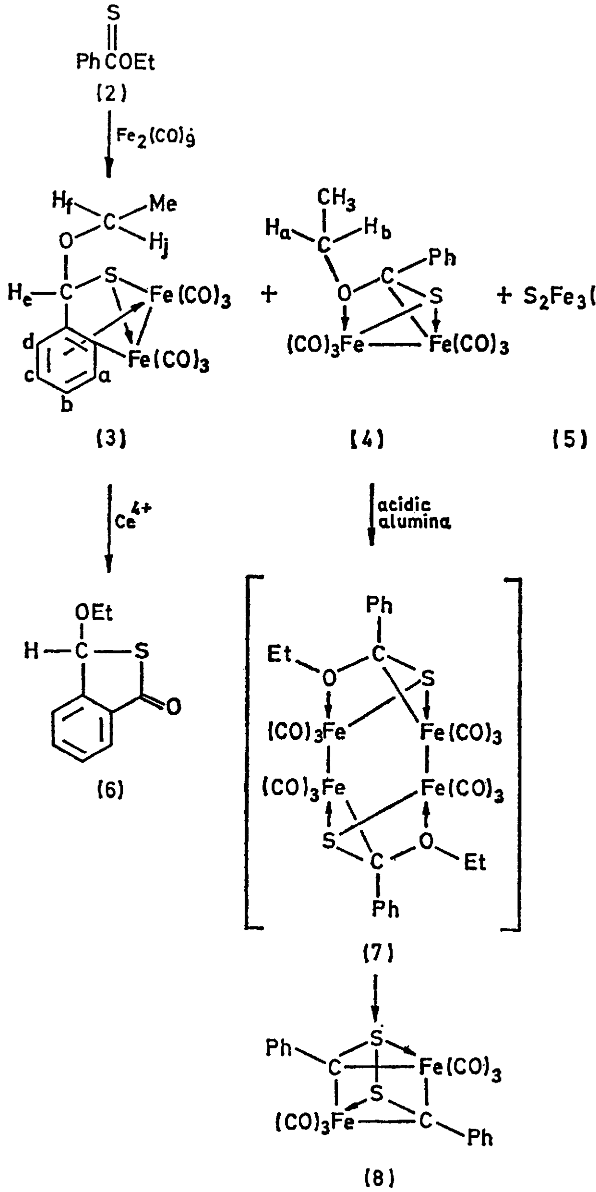
Summary The first *ortho*-metallated complex of a thiobenzoate is described; heteroatoms have an important influence on the *ortho*-metallation reaction.

ALTHOUGH a considerable amount of work has been published concerning the intramolecular *ortho*-metallation of nitrogen and phosphorus donor ligands by transition metals,[1] only recently have the first examples of sulphur donor ligand *ortho*-metallated complexes been described, *i.e.*, complexes derived from thiobenzophenones [*e.g.* (**1**)].[2]



(1)

We report the preparation of the first *ortho*-metallated complex of a thiobenzoate, a novel dimerization–elimination reaction, and, to our knowledge, the first study of competition between *ortho*-metallation and donor ligand complex formation within the same molecule.



Scheme 1

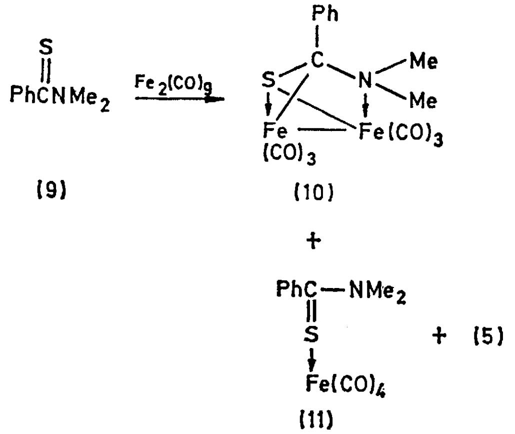
Treatment of *O*-ethyl thiobenzoate (**2**)[3] with enneacarbonyldi-iron [Scheme (1)] in benzene at room temperature for 43 h followed by chromatography, gave the *ortho*-metallated complex (**3**) (14·3%), the isomeric sulphur and oxygen donor complex (**4**) (49·0%), and (**5**) (5·5%).[2] The structures of (**3**) and (**4**) were assigned on the basis of their i.r.,[2] n.m.r., and mass spectra. In addition, irradiation of compound (**3**) at the centre of the methyl triplet at δ 1·06 resulted in collapse of the signals for H_f and H_j to an AB quartet with J_{fj} 10·5 Hz, indicative of geminal coupling of protons on a carbon atom adjacent to a hetero-atom.[4] Oxidative cleavage of (**3**) with ceric ammonium nitrate in acetone gave the thiolactone (**6**) (44·8%).

On passage of a solution of (**4**) in light petroleum through a column of acidic alumina a complex assigned structure (**8**) was obtained in (30%) [m.p. 113° (decomp.)].

Structure (**8**) was assigned on the basis of its i.r., n.m.r., and electron impact and methane chemical ionization[5] mass spectra.

The prismatic complex (**8**) may result from initial dimerization of (**4**) into (**7**), followed by acidic cleavage.

In order to determine the effect of a nitrogen donor on the *ortho*-metallation of the thiobenzoyl function, *NN*-dimethylthiobenzamide (**9**) was treated with $Fe_2(CO)_9$ in benzene at room temperature for 21 h to give the complex (**10**), analogous to (**4**), and compounds (**5**) and (**11**) as by-products [Scheme (2)].



Scheme 2

The i.r. terminal metal carbonyl stretching absorption bands for (**10**) are similar to those obtained for (**4**). The m.s. was consistent with structure (**10**). No *ortho*-metallated complex was isolated. *NN*-Dimethylthioacetamide reacts with $Fe_2(CO)_9$ to give analogues of (**10**), (**11**), and (**5**).

These results demonstrate the great influence of the heteroatom on the *ortho*-metallation reaction. Nitrogen being a better donor than oxygen, completely inhibits *ortho*-metallation. Oxygen, in turn, is a more effective donor than a benzene ring and consequently donor ligand complexation predominates over *ortho*-metallation.

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† Satisfactory analytical data were obtained for all new compounds.

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