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Preliminary communication

THE CARBONYL INSERTION REACTION OF SULFUR-DONOR LIGAND *ortho*-METALATED IRON CARBONYL COMPLEXES

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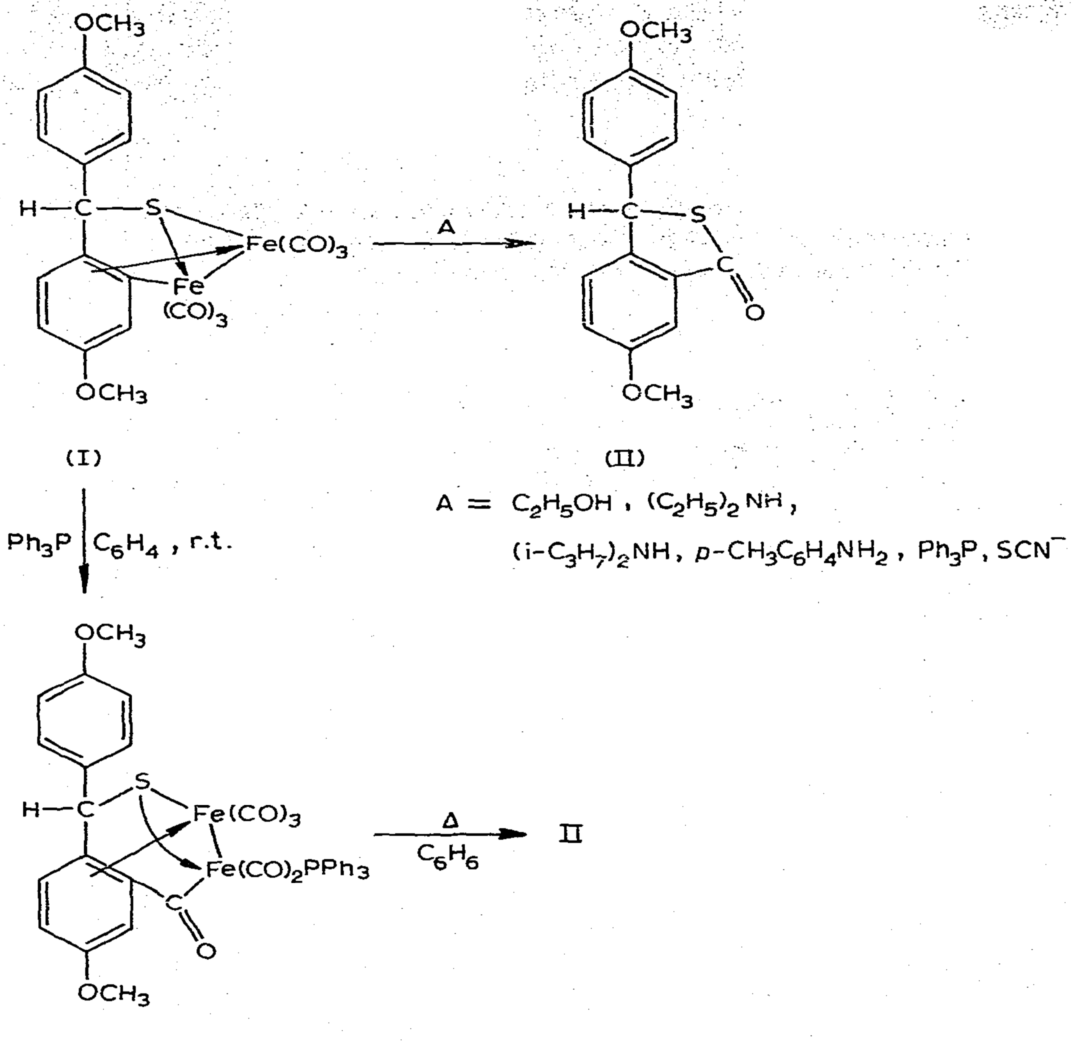
Summary

Amines, phosphines, alcohols, and thiocyanate ion are useful reagents for effecting carbonyl insertion of sulfur-donor ligand *ortho*-metalated iron carbonyl complexes. The apparent intermediate in these reactions has been isolated.

Treatment of thiobenzophenones with diiron enneacarbonyl affords sulfur-donor ligand *ortho*-metalated iron carbonyl complexes [e.g. I] in good to excellent yields [1]. Oxidative cleavage of these complexes with ceric ion gave isobenzothiophene derivatives [e.g. II]. The carbonyl insertion product II was also formed under non-oxidative conditions, i.e. by thermolysis of I in ethanol [1]. The generality of this insertion process, and the isolation of the reaction intermediate, are the subjects of this communication.

Reaction of I with diethylamine [$A = (C_2H_5)_2NH$] or diisopropylamine [$A = (i\text{-}C_3H_7)_2NH$] in benzene at 60° for two days gave II in 49 and 77% yields, respectively. Carbonyl insertion was also observed using *p*-toluidine in benzene. Treatment of I with triphenylphosphine [$A = (C_6H_5)_3P$] in refluxing benzene afforded II in 42% yield. An almost quantitative yield of II was realized by the use of sodium thiocyanate in refluxing benzene—methanol (6/1).

The fact that the same conversion [I→II] could be effected with the different reagents noted suggested the occurrence of initial carbonyl insertion into the aromatic carbon-iron σ bond, analogous to other carbonyl insertion reactions (e.g. $RMn(CO)_5$ [2]). Complex I was treated with triphenylphosphine under mild conditions [room temperature, 12 h, hexane as solvent] in an attempt to isolate the carbonyl inserted organometallic complex. Filtration, thorough washing (hexane), and subsequent drying in vacuo gave the orange complex III in 80% yield, m.p. 125—127° dec. (Found: C, 58.87; H, 4.01; Fe, 14.25; S, 3.62; Mol. wt., 781. $C_{39}H_{29}Fe_2O_8PS$ calcd.: C, 58.52;



H, 3.65;Fe, 13.95; S, 4.00; Mol. wt., 800.4). Terminal metal carbonyl stretching bands were observed in the infrared (KBr) at 2062s, 2021s, 1990vs, 1962vs and 1946ms cm^{-1}. The carbonyl stretching absorption for the benzoyl group appeared at 1604cm^{-1}, in excellent accord with the position [1603cm^{-1}] of the same type of band for the related $C_6H_5C(=O)Fe(CO)_2C_5H_5$ system [3]. The proton NMR spectrum [$CDCl_3$-internal TMS] displayed singlets for the methoxy groups at δ 3.78 and 3.81 ppm, and a singlet at δ 6.18 ppm for the methine proton. Signals in the δ 6.4—7.8 ppm region are due to the aromatic protons, the ratio of methoxy to aromatic protons being 3/11.

Conversion of III to II was carried out in refluxing benzene (22 h work-up by column chromatography). By-products of the reaction were triphenylphosphineiron tetracarbonyl [4] and an, as yet, unidentified complex (ν(CO)(CCl_4)2042s, 1981s cm^{-1}, no benzoyl band).

Finally, it is noteworthy that an intermediate, structurally related to III, has been postulated in the carbonylation of the nitrogen-donor ligand *ortho*-metallated complex derived from benzaldehyde anil and dicobalt octacarbonyl [5]

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