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Preliminary communication

PHASE TRANSFER CATALYZED *ortho*-METALATION

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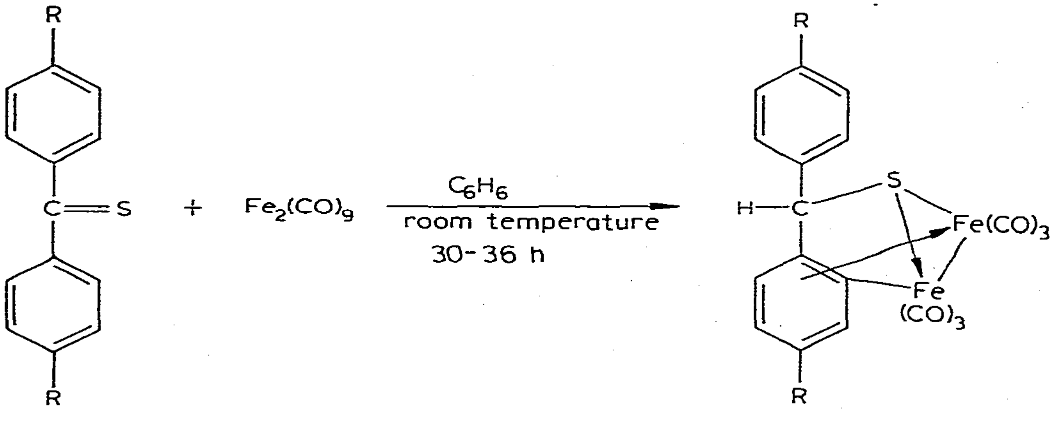
Summary

The first examples of the application of phase transfer catalysis to *ortho*-metalation are described.

One of the major developments in organic chemistry in recent years is the use of phase transfer catalysis in synthesis [1]. The application of this process to organometallic chemistry has yet to be explored*. We now wish to report that sulfur-donor ligand *ortho*-metalated complexes can be readily prepared by a facile phase transfer catalyzed reaction.

Transition metal intramolecular *ortho*-metalation reactions is a subject of great interest in organometallic chemistry [3]. Several years ago, one of us [4] described the first examples of sulfur-donor ligand *ortho*-metalated complexes II, prepared by reaction of thiobenzophenones (I) with diiron enneacarbonyl in benzene for 30—36 h. Although these complexes have proven to



(I)

(II)

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* The phase transfer catalyzed reduction of nitrobenzenes to anilines has recently been observed [2].

be valuable intermediates for organic synthesis [4,5], their preparation requires long reaction times. A dramatic enhancement of reaction rate, as well as simple reaction work-up, occurred by the use of phase transfer catalysis.

Treatment of a benzene solution of a thiobenzophenone (I) with triiron dodecacarboxyl [$Fe_3(CO)_{12}$, 2.5 equivalents], aqueous sodium hydroxide, and benzyltriethylammonium chloride as the catalyst for 30—45 min afforded

$$\mathrm{I} \xrightarrow[\mathrm{C_6H_5CH_2N^+(C_2H_5)_3Cl^-}]{\mathrm{Fe_3(CO)_{12},\ 2N\ NaOH}} \mathrm{II}$$

30—45 min, C_6H_6
roomtemperature

the *ortho*-metalated complexes in 36—80% yields [R = $N(CH_3)_2$, 76%; OCH_3, 80%; H, 70%; CH_3, 36%]. These yields are higher or lower than those obtained using $Fe_2(CO)_9$, depending on the nature of the R group. However, even in those instances where the phase transfer catalyzed reaction gives lower yields of II, the reaction is very fast and can be easily recycled (note that this reaction is much faster than the base promoted conversion of I to the corresponding benzophenone). Less than 3% *ortho*-metalation occurred in the absence of the catalyst.

It is assumed, on the basis of previous work with iron carbonyl hydrides [6,7], that $Fe_3(CO)_{12}$ and NaOH generate the hydridoundecacarbonyltriferrate anion, $HFe_3(CO)_{11}^-$, and that this is an important species in the reaction. It is noteworthy that II, R = $N(CH_3)_2$, was obtained by reaction of I, R = $N(CH_3)_2$, with $Fe_3(CO)_{12}$ and $NaOD/D_2O$ under phase transfer catalyzed conditions. Therefore, the benzylic hydrogen in II arises from the *ortho*-position of I by intramolecular transfer, and not from aqueous sodium hydroxide. The hydrogen transfer is also intramolecular in the reaction of I with $Fe_2(CO)_9$ [4], although the reaction pathway would be different since the phase transfer catalyzed process likely occurs by initial nucleophilic attack of $HFe_3(CO)_{11}^-$ at the sulfur atom of the thione.

The following procedure is typical: Into a 125 ml filtering flask was added benzene (20 ml), I (R = $N(CH_3)_2$, 2.0 mmol), amhydrous $Fe_3(CO)_{12}$ (5.0 mmol), benzyltriethylammonium chloride (1.0 mmol), and 2 *N* NaOH (20 ml) [nitrogen atmosphere]. The mixture was stirred at room temperature for 45 min. The organic layer was separated by centrifugation or by use of a separatory funnel, dried ($MgSO_4$), and flash evaporated to give crude II. The latter was treated with a small amount of hexane, filtered, and the concentrated filtrate was chromatographed (thin-layer, silica gel) with benzene affording pure II (R = $N(CH_3)_2$) in 76% yield.

In conclusion, phase transfer catalysis is an extremely useful method for affecting *ortho*-metalation. The application of this technique to other *ortho*-metalated systems, and to other areas of organometallic chemistry, is under active investigation.

Acknowledgments

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