# A New Method for the Synthesis of Organic Iron Carbonyl Complexes

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*Summary* Amine oxides induce a very fast reaction, even at low temperatures, between $Fe(CO)_5$ and various dienes, giving $Fe(CO)_3$-diene complexes in good yields.

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RECENTLY we reported a simple method for the disengagement of organic ligands from iron carbonyl complexes.[1] When an iron carbonyl complex of an organic ligand (L), usually a diene, is heated in an aprotic solvent in the presence of an excess of amine oxide (usually $Me_3NO$) the reaction shown in equation 1 takes place. The reaction is characterized by high yields, excellent purity of the liberated oxidation sensitive ligands and convenience of work-up.

$$L\text{-}Fe(CO)_3 + Me_3NO \xrightarrow{\text{solvent}} L + Me_3N + CO_2 + \text{iron compounds} \qquad (1)$$

We now report the formally reversed reaction, namely a very fast complexation of diene ligands (L) with $Fe(CO)_5$ in the presence of amine oxide, preferably $Me_3NO$. The reduction of amine oxides by $Fe(CO)_5$ has been described by Alper *et al.*[2] It can be assumed that amine oxides are capable of generating $Fe(CO)_4$ from $Fe(CO)_5$ and apparently this reaction is an exceedingly fast one. In the presence of a diene ligand the reaction is as shown in equation 2. Practically, when $Fe(CO)_5$ (2 mol) is added to a suspension of the amine oxide (4 mol) in benzene containing diene

$$L + Fe(CO)_5 + Me_3NO \rightarrow LFe(CO)_3 + Me_3N + CO_2 + CO \qquad (2)$$

Table. Results and conditions of complexation reaction.

| Amine oxide | Structure of Fe(CO)$_3$ complex | Reaction time/h | Solvent | Yield[a] |
|---|---|---|---|---|
| Me$_3$ NO | Cyclo-octatetraene | 1 | Benzene | 78 |
| Me$_3$ NO | Cyclo-octatetraene | 1 | Tetrahydrofuran | 80 |
| Me$_3$ NO | Cyclo-octatetraene | 1 | Acetone | 68 |
| PhNMe$_2$O | Cyclo-octatetraene | 1·5 | Benzene | 40 |
| Me$_3$ NO | Tropone | 1 | Benzene | 62 |
| Me$_3$ NO | *o*-Xylylene | 1 | Benzene | 4[b] |
| Me$_3$ NO | 6-Anilinocyclohexa-1,3-diene | 0·75 | Benzene | 7[c] |

[a] The yields are related to a 1 h reflux in the respective solvents after the low-temperature reaction was completed. [b] A 6% yield was reported when the complexation was carried out with Fe$_2$(CO)$_9$.[3] [c] This complex was prepared in 25% yield by an indirect reaction of 1-phenyl-3,6-dihydro-oxazine and Fe$_2$(CO)$_9$.[4]

(1 mol) under nitrogen at 0 °C, an immediate evolution of gas occurs and the solution turns violet. Good stirring is required. At this stage, *ca.* 50% yield of the complex L-Fe(CO)$_3$ is obtained upon filtration, evaporation and crystallization of the residue. The yield may be increased by 20—30% if, after the low temperature reaction is completed, the mixture is refluxed for 1 h. Considering that the solubility of amine oxide (Me$_3$NO) in benzene at 0 °C is extremely small, the reaction must be a very fast one. Indeed when acetone was used as a solvent the reaction mixture had to be cooled to dry-ice temperature in order to moderate the reaction.

It should be noted that the direct complexation of Fe(CO)$_5$ with dienes requires high temperatures (*ca.* 120 °C), and complexation with Fe$_2$(CO)$_9$ proceeds at about room temperature. The present reaction offers a practically instantaneous complexation which may be carried out at very low temperature. It was ascertained that Fe$_2$(CO)$_9$ is not formed during this reaction. Also, it was demonstrated that complexation does not take place in the presence of the amine instead of its oxide. As the yields indicate, the reverse reaction, namely the disengagement of the L-Fe(CO)$_3$ complex, is insignificant, most probably due to the low temperature and smaller molar ratio of amine oxide : Fe(CO)$_5$ which are employed in this reaction. The results of several experiments are presented in the Table.

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