A Simple Method for the Disengagement of Organic Ligands from Iron Complexes

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Summary A method is described for the disengagement of an organic ligand from its iron carbonyl complex by treating the latter with amine oxides in aprotic solvents.

IT frequently becomes necessary to disengage an organic ligand (L) from an iron carbonyl complex $(CO)_nFeL$. This may be achieved by oxidizing the complex with ceric ammonium nitrate or ferric chloride in acetone or ethanol solution. Although successful with structurally simple cases, the inherent disadvantage of the above method is the instability of the π-electron-rich organic ligands under the oxidative reaction conditions. Furthermore, easily oxidizable functional groups may not survive the above reaction conditions. Consequently, extensive deterioration of the product limits the scope of the above reaction.

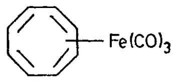
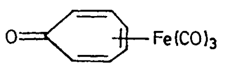
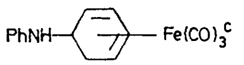
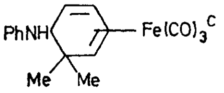
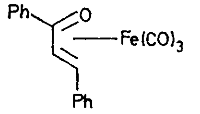
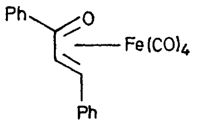
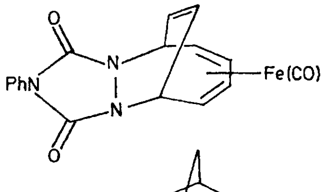
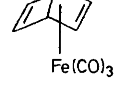
We have discovered that amine oxides, preferably trimethylamine oxide, induce the disengagement of organic ligands (L) from $(CO)_nFeL$ complexes in good yields and without any detectable deterioration of the product. The nature of the products are expressed in the following equation:

$$(CO)_nFeL + R_3NO \rightarrow L + R_3N + CO_2 + \text{"iron compounds"}$$

Notable advantages of this reaction are the relatively low temperature (25—81°), and the use of aprotic solvents. The results and conditions of our experiments using Me_3NO are presented in the Table. In each case the iron-free organic ligand of the listed complex has been obtained. Most instructive is the oxidation-sensitive complex, tricarbonyl(cyclohexadienylphenylamine)iron, from which the corresponding 5-anilino-1,3-cyclohexadiene was isolated in relatively good yield (45%). This, in our opinion indicates the mildness of the reaction, which may be suitable for other oxidation-sensitive complexes. In light of the variety of the complexes which were successfully decomposed it is reasonable to anticipate that this reaction is of general scope.

In order to drive the reaction to completion, and at reasonable rates, an eight-fold molar excess of the amine oxide must be used. This rather large excess, however, does not interfere with the isolation of the product, since the specific trimethylamine oxide is transformed (mostly) into the volatile trimethylamine, which escapes from the

TABLE. Results and conditions for disengagement of iron complexes[a]

Compound	Yield[b] /%	Reaction time/h	Solvent (temp)
	95	1	Benzene (reflux)
	71	12	Benzene (reflux)
	45[d]	24	Acetone (25°)
	85	12	Benzene (65°)
	70	12	Benzene (reflux)
	71	24	Benzene (25°)
	77	3	Benzene (reflux)
	75	12	Acetone (25°)

[a] All the reactions were carried out under nitrogen. [b] Yields were determined gravimetrically, by v.p.c. and n.m.r. depending on the particular substrate. [c] The *endo*-complex was used; see ref. 1. The *N*-phenylmaleimide adduct of the product was characterized by spectral methods and elemental analyses. [d] Accompanied by 35% of diphenylamine.

reaction mixture. At the time of complete disappearance of the complex (n.m.r.), we can account for 5·0 ± 0·1 moles of Me_3N and *ca* 0·3—0·5 moles of CO_2 which were evolved. The nature of the "iron compounds" which precipitate from the reaction mixture has not been elucidated.

The mechanism of this reaction has not yet been investigated. Other workers[2,3] have found that amine oxides can be reduced to the corresponding amines with $Fe(CO)_5$. We have reversed the usefulness of the above reaction in the sense that the organic ligand of a complex $(CO)_nFeL$, rather than the amine, is the desired and indeed the isolable product.

This reaction is also promising with neutral π-allyl complexes.

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[1] Y. Becker, A. Eisenstadt, and Y. Shvo, *Tetrahedron Letters*, 1972, 3183.

[2] J. M. Landesberg, L. Katz, and C. Alsen, *J. Org. Chem.*, 1972, **37**, 930 and reports cited in ref. 21.

[3] H. Alper and J. T. Edward, *Canad. J. Chem.*, 1970, **48**, 1543.