Eliminations from Amino-carbene Complexes

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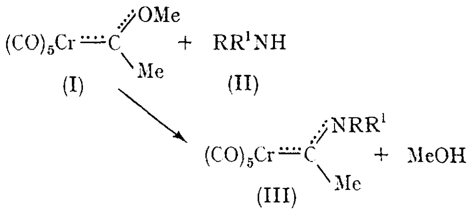
IN the course of a detailed study of substitution reactions of (methyl-, methoxy-)carbenechromium pentacarbonyl (I) with nucleophiles,[1,2] we have prepared complexes from secondary amines according to:



With (II; R=R^1 = Me or Et) the expected complexes (III) are obtained in good yield as pale yellow diamagnetic solids.[1,3]

Attempts to prepare the next higher homologue of this series (III; R = R^1 = Pr^i) gave instead the monoisopropylamino-derivative (III; R = Pr^i, R^1 = H), m.p. 88—89°, which had been prepared independently from the reaction between (I) and isopropylamine.[3] *N*-Methylbenzylamine (II; R = PhCH$_2$, R^1 = Me) in ether as solvent at room temperature, gave after 1 hr. the benzylamino-derivative (III; R = PhCH$_2$, R^1 = H), m.p. 147—148°. This product is identical with that obtained from the reaction between (I) and benzylamine.[3] The reaction with *N*-methylaniline (II; R = Ph, R^1 = Me) in ether has failed to yield any substitution product even after three months. This is in contrast to the behaviour of aniline which is less basic and yet which gives the expected product (III; R = Ph, R^1 = H).[1]

The most important features of these reactions are the ease with which they occur around room temperature, and the importance of steric factors. Whilst the behaviour of di-isopropylamine shows a certain similarity to a Hofmann elimination, in the case of *N*-methylbenzylamine, where it is necessary to postulate the elimination of a methylene fragment, a process of the Hofmann type cannot be involved.

We have also prepared a number of *p*-substituted aniline derivatives (III; R = H, R^1 = *p*-C$_6$H$_4$·X, X = NH$_2$, OCH$_3$, CH$_3$, H, Cl, CF$_3$) in order to observe the effect of substitution upon various physical properties of the (CO)$_5$CrCMeNH-fragment.[3] Treatment with lithium aluminium hydride results in hydrogenolysis and the corresponding *N*-ethylamine is obtained. The fate of the carbonyl residue in this reaction is still under investigation.

The identity of all the compounds reported has been established by total analysis, infrared, n.m.r., and mass spectroscopy.

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[1] U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, in the press.
[2] *cf.*, E. O. Fischer and R. Aumann, *Angew. Chem.*, 1967, **79**, 191.
[3] E. O. Fischer and J. A. Connor, unpublished results.