

Complexes of Azobenzenes and Schiff Bases

By M. M. BAGGA, P. L. PAUSON, F. J. PRESTON, and R. I. REED

(*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1, and Department of Chemistry, Glasgow University, Glasgow, W.2*)

THE appearance of a report concerning the formation of azobenzene complexes of platinum and palladium¹ prompts us to report at this stage our results with related iron complexes.² Schiff bases (I) derived from aromatic aldehydes or ketones are known³ to yield heterocyclic products (II) on carbonylation at high temperature and pressure

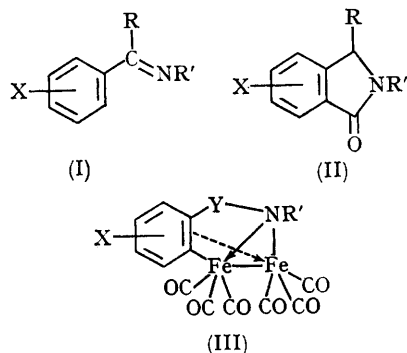
in the presence of cobalt carbonyl. We find that reaction with di-iron enneacarbonyl occurs under mild conditions to give a series of novel complexes (III; Y = CHR) in high yields. Formulation (III) is based on mass-spectroscopic, proton magnetic resonance, and chemical evidence; the latter includes degradation by ferric chloride oxidation

¹ A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.

² A brief account of this work was given at the 2nd International Symposium on Organometallic Chemistry at Madison, Wisconsin. (1.9.1965).

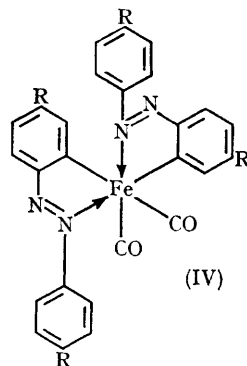
³ S. Murahashi and S. Horrie, *J. Amer. Chem. Soc.*, 1955, **77**, 6403; *Bull. Chem. Soc. Japan*, 1960, **33**, 247.

to the same lactams (II) obtainable in the catalytic reaction. The "dotted" bond is included solely to satisfy the "inert gas rule"; alternatively, the complex may be formulated with one iron atom having an incomplete (16 outer orbital) electron shell. Related complexes have been obtained from benzaldehyde phenylhydrazone and from ketazines such as benzophenone azine.



Probably analogous iron complexes (III; Y = NH) were isolated from the irradiation of azobenzene and its derivatives with iron pentacarbonyl. The complex from azobenzene (III; X = H; Y = NH; R' = Ph) undergoes rearrangement to *o*-semidine on reduction with lithium aluminium hydride. We consider an alternative formulation of the complex as derived from the

rearranged *o*-semidine skeleton to be less likely. When *p*-azotoluene or *p*-azoanisole are used the products (III) are accompanied by compounds which must be formulated as (IV; R = Me or OMe). The latter are very closely related to both the



platinum and palladium complexes of Cope and Siekman,¹ as well as the nickel complex of Kleiman and Dubeck⁴ and the formation of a bond between the metal atom and the *ortho*-position of the benzene ring is common to all these cases. Further work including X-ray-crystallographic studies is in progress.

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⁴ J. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, 1963, **85**, 1544.