Reactions of Azobenzene and Related Compounds with Rhodium Complexes: Cleavage of N:N and C:N Bonds

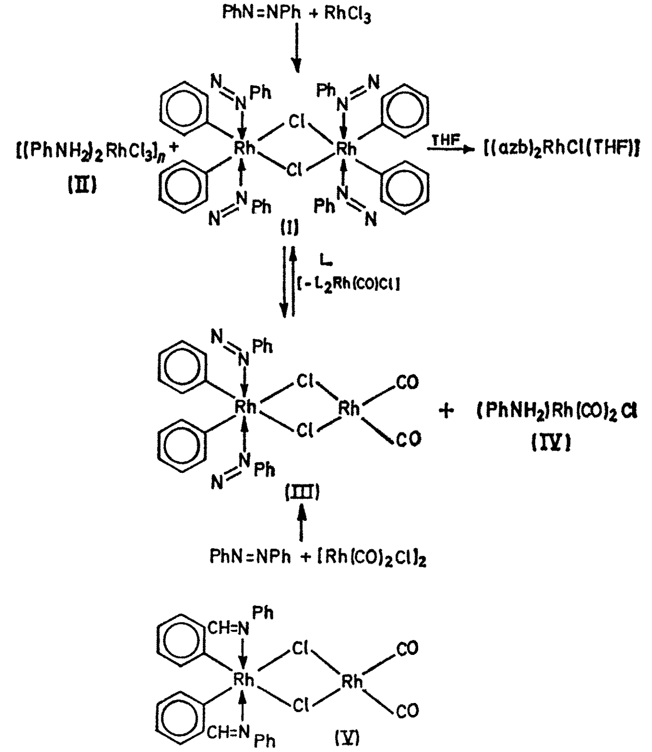
M. I. BRUCE,* B. L. GOODALL, M. Z. IQBAL, and F. G. A. STONE
(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

Summary The reactions of azobenzene and related compounds with rhodium complexes involve complexes containing chelated phenylazophenyl-2*C*,*N*′ ligands; complexes containing both Rh^{I} and Rh^{III}; transition-metal promoted hydrogen-transfer reactions; and rhodium-assisted hydration of CH=N bonds; a new catalytic reducing system is described.

THE reaction between azobenzene (azbH) and ethanolic rhodium(III) chloride affords a red dimeric complex, $[(azb)_2RhCl]_2$ (I), and a second, insoluble complex (II). Complex (I) was shown to contain a chelating phenylazophenyl-2*C*,*N*′ group, from its characteristic proton n.m.r. spectrum.[1] Recrystallisation from tetrahydrofuran (THF) gave the mononuclear adduct $[(azb)_2RhCl(THF)]$, previously described by Jo, Hagihara, and Murahashi.[2]

Treatment of (I) with $[Rh(CO)_2Cl]_2$ gives an orange complex $[(azb)Rh(CO)Cl]_2$ (III) (analysis, osmometric molecular weight, and high-resolution mass spectrometry). Its ^{1}H n.m.r. spectrum is similar to that of (I). Two sharp ν(CO) bands at 2080 and 2010 cm^{-1} suggest that both carbonyl groups are attached to the same metal atom. Addition of PPh_3 or $AsPh_3$ results in precipitation of *half* the rhodium as $L_2Rh(CO)Cl$ ($L = PPh_3$ or $AsPh_3$); from the filtrate, complex (I) can be isolated, in an amount corresponding to the other half of the rhodium content of (III). A reasonable structure for (III), containing both Rh^{I} and Rh^{III}, is shown, and accounts for both the ready formation of complexes $L_2Rh(CO)Cl$, and the similarity of the ^{1}H n.m.r. spectra of (I) and (III).

Complex (III) can also be obtained, together with other compounds, from the reaction between azobenzene and $[Rh(CO)_2Cl]_2$ as mentioned elsewhere,[3] although it was suggested that (III) is a tricarbonylrhodium complex.



The other products from the foregoing reactions are interesting. The insoluble orange complex (II) was shown to be $[(PhNH_2)_2RhCl_3]_n$ by comparison with an authentic sample. From the reaction between azobenzene and

$[Rh(CO)_2Cl]_2$, a volatile deep violet complex was obtained in addition to (III), identified as $(PhNH_2)Rh(CO)_2Cl$ (IV). Related compounds undergo similar reactions. Thus benzylideneaniline (bzaH) reacts with ethanolic $RhCl_3$ to give complex (II), and the filtrate afforded benzaldehyde. With $[Rh(CO)_2Cl]_2$, a binuclear complex, shown to have structure (V) [ν(CO), 2077 and 2006 cm^{-1}] was formed, together with (IV). In the presence of moisture, benzaldehyde was also obtained. These reactions provide unusual examples of cleavage of N=N bonds, and hydration of C=N bonds, assisted by transition metals.

In an aprotic solvent, *e.g.* C_6F_6, the aniline complex (IV) was still isolated from the reaction between azobenzene and $[Rh(CO)_2Cl]_2$, suggesting that reduction and cleavage of the N=N bond occurred *via* a metal-assisted hydrogen transfer from the *ortho*-position of the phenyl ring. In the course of reactions designed to elucidate the structure of (III), the formation of aniline, as well as of azobenzene, was observed on degradation of this complex with $LiAlH_4$. Normally, azobenzenes do not react with $LiAlH_4$, although reduction to hydrazobenzenes has been noted with certain metal halides.[4]

Addition of catalytic amounts of $[Rh(CO)_2Cl]_2$ to a mixture of $LiAlH_4$ and azobenzene rapidly gave a quantitative yield of hydrazobenzene, no trace of aniline being formed. This catalyst is extremely effective, no signs of exhaustion being observed during the reduction of over 60,000 times excess of the azo-compound, and the reaction is a convenient source of the hydrazo-compound free from amines. Other studies have shown that substituents have a profound effect on reduction. Azophenetole gives 4-ethoxyaniline, whereas azoxyanisole gives hydrazoanisole, both quantitatively.

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