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EXPERIMENTS IN NITROGEN FIXATION - PARTIAL REDUCTION OF BENZOTRICHLORIDE AND RELATED COMPOUNDS

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Whereas biological activation of molecular nitrogen occurs under mild conditions, all industrial processes utilizing gaseous nitrogen employ very forcing conditions. Considerable interest centres on the possibility of developing a mild, catalytic, nitrogen-fixation method. Recently hydrido- and nitrogen complexes of cobalt,[1] ruthenium,[2] osmium,[3] iridium,[4] and rhodium[5] have been described. The cobalt complex (I), $(\emptyset_3P)_3\,CoHN_2$, was originally prepared with difficulty by the reaction of cobalt acetylacetonate with trialkyl aluminium, triphenylphosphine, and nitrogen gas. We find that the complexes I and II, $(\emptyset_3P)_3CoH_3$ may be prepared more simply by the reaction of sodium borohydride, triphenylphosphine and cobalt chloride in diglyme under nitrogen (I) or hydrogen (II).

The products in this case are moderately stable yellow-brown (I) or red-brown (II) solids with spectral and other characteristics in agreement with those reported.[1] The corresponding trioctylphosphine and tributylphosphine analogues may be prepared as unstable oils. We have also prepared the previously unreported iron and nickel analogues.

As part of an investigation directed to the trapping of nitrogen contained in these complexes, we examined the reaction of both hydride and hydridonitrogan complexes with halogeno compounds in diglyme as solvent. A more or less vigorous reaction occurred with carbon tetrachloride, bromotrichloromethane, and other compounds containing $-CX_3$ groups, resulting in the evolution of nitrogen and the displacement of one halogen atom by hydrogen. Thus, both carbon tetrachloride and bromotrichloromethane were converted into chloroform (a bromine atom being displaced preferentially). Benzotrichloride, benzylidene bromide, 2,5-dichlorobenzotrichloride, and hexachloroethane gave respectively benzylidene chloride, benzyl bromide, 2,5-dichlorobenzylidene chloride, and pentachloroethane. When ethanol was used as a solvent yields were drastically reduced and a number of so-far unidentified materials were obtained. Yields were highest for each metal with the nitrogen-containing complexes. Yields were lowest with iron complexes and highest with nickel complexes.

For example the following yields of benzylidene chloride were obtained from benzotrichloride using tris(triphenylphosphine) complexes

Metal	Hydrido-	Hydridonitrogen
Fe	15	25
Co	40	70
N~~o~~i	50	85

In a typical reaction hydridonitrogen tris(triphenylphosphine) cobalt (1g.) in diglyme, under N_2, was stirred with slow addition of excess benzotrichloride (2.5g.). Vigorous evolution of gas occurred. The reaction was worked up by partition between dilute hydrochloric acid and chloroform. Examination of the (suitably purified) extracts by gas-liquid chromatography (on fluorosilicone, silicone oil, and polyethyleneglycoladipate columns) revealed the presence of benzylidene chloride (70%), which could be isolated by fractional distillation.

The possible use of these complexes as catalytic reagents, and for the preparation of some less highly chlorinated analogues of DDT is under investigation.

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