Azobenzene Complexes of Zerovalent Nickel

By H.-F. KLEIN† and J. F. NIXON*

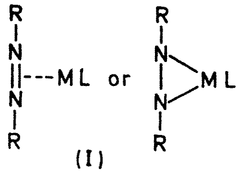
(*School of Molecular Sciences, University of Sussex, Brighton,* BN1 9QJ; *and †Institut für Anorganische Chemie der Universität, Wurzburg, Germany*)

Summary A new and convenient synthesis of azobenzene complexes of nickel(0) is described, which can be extended to certain olefin–nickel complexes, and some reactions of the azobenzene complexes are reported.

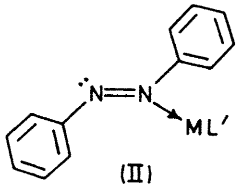
THERE are relatively few examples of complexes which contain ligands co-ordinated to a transition metal solely by an azo-function.[1,2] Although the metal–azo bond could be considered formally analagous to that known in metal–olefin complexes co-ordination *via* a nitrogen lone pair is also possible[1,3] (II) and azobenzene is known to form 2-(phenylazo)phenyl–metal complexes (III) which also contain a σ-bond between the metal and the *ortho*-carbon atom of one phenyl ring.[4]

Recent very brief references[5] to the first examples of azobenzene complexes of type (I) prompts us to report a simple convenient high-yield synthesis of the dark red, crystalline, air-sensitive azobenzene–nickel compounds, Ni(R_3P)$_2$(azobenzene) (IV; R = Me, Bu, Ph), by treatment of the appropriate bis(phosphine)nickel dichloride complex with azobenzene and metallic lithium in tetrahydrofuran solution below room temperature. The use of lithium as reducing agent, *via* formation of the dilithio intermediate, seems to have general applicability; certain olefin–nickel complexes *e.g.* (R_3P)$_2$Ni (stilbene) (V; R = Ph, Bu) are also readily accessible by this route. Compound (IV; R = Ph) was also obtained by displacement of stilbene from (V; R = Ph) or by displacement of triphenylphosphine from Ni(Ph_3P)$_4$. (See Scheme). On the other hand, the phosphite–nickel(0) complex Ni[P(OMe)$_3$]$_4$ did not react with azobenzene even at 100° and was readily formed when (IV; R = Ph) was treated with (MeO)$_3$P.

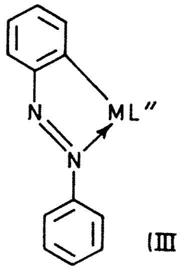
We have studied some reactions of the azobenzene–nickel complexes since the simplest azo-compound, di-imide (HN=NH), co-ordinated to a transition metal might be a possible intermediate in the fixation of dinitrogen in biological systems. We find that (IV; R = Ph) reacts readily with oxygen in tetrahydrofuran solution even at −40°, affording almost quantitative amounts of metallic nickel, together with a mixture of azobenzene, triphenylphosphine, and triphenylphosphine oxide. Oxidation of ligands attached to Ni, Pd, and Pt have been reported previously.[6] Reduction of the co-ordinated azobenzene was effected by treatment of (IV; R = Me) with either (a) aqueous ethanol at 60° or (b) dimethylglyoxime in tetrahydrofuran solution, readily affording high yields (90—95%) of hydrazobenzene (see Scheme).



(I)

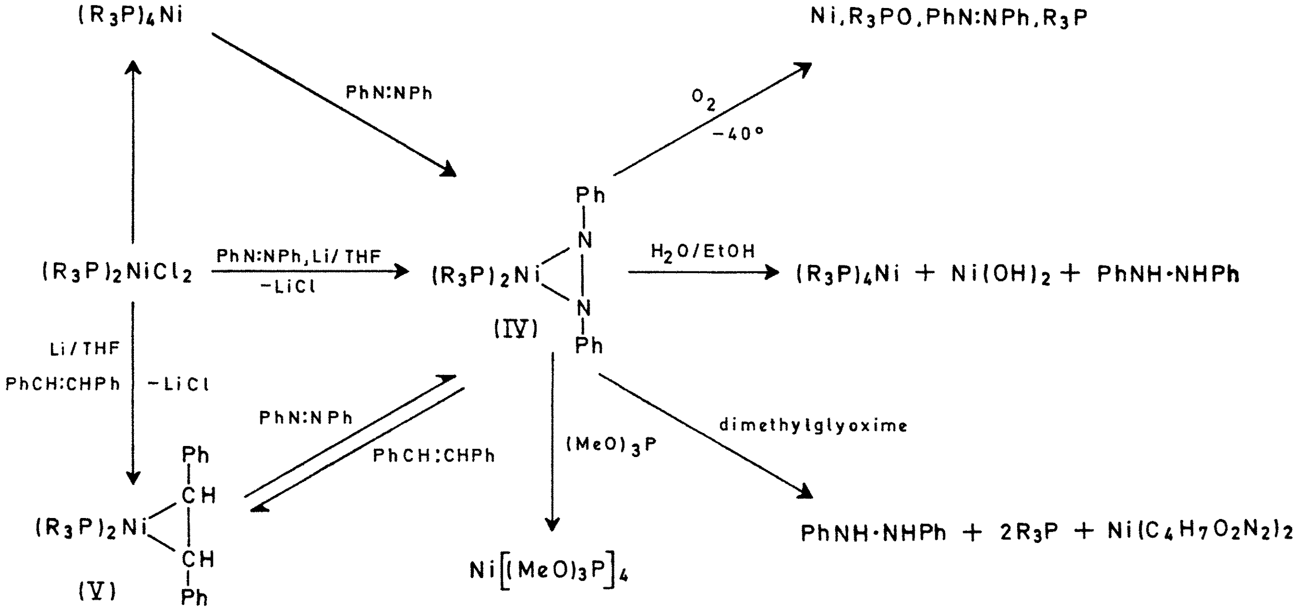


(II)



(III)

(M = transition metal; L or L′ represents all other ligands attached to the metal)



SCHEME

We thank Albright and Wilson Ltd. for financial support for part of this work.

(*Received, October 26th,* 1970; *Com.* 1856.)

---

[1] R. Murray, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 811; A. L. Balch and D. Petridis, *Inorg. Chem.*, 1969, **8**, 2247 and refs. therein.

[2] M. Dekker and G. R. Knox, *Chem. Comm.*, 1967, 1243; M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 3083.

[3] I. D. Brown and J. D. Dunitz, *Acta Cryst.*, 1960, **13**, 28; O. Diels and W. Koll, *Annalen*, 1925, **443**, 262.

[4] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272; H. Takahashi and J. Tsuji, *J. Organometallic Chem.*, 1967, **10**, 511; J. P. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, 1963, **85**, 1544; R. F. Heck, *ibid.*, 1968, **90**, 313.

[5] S. Otsuka, A. Nakamura, and H. Minamida, *Chem. Comm.*, 1969, 1169; and paper presented at the Organometallic Symposium, Bristol, 1969.

[6] R. Ugo, *Coordination Chem. Rev.*, 1968, **3**, 319.