# A New Route to Molecular Nitrogen Complexes

By G. M. BANCROFT, M. J. MAYS,* and B. E. PRATER
(*University Chemical Laboratory, Lensfield Road, Cambridge*)

*Summary* A new molecular nitrogen complex of iron has been prepared by the displacement of chloride ion from *trans*-hydridochlorodi(bisdiethylphosphinoethane)iron(II) by nitrogen in the presence of sodium tetraphenylborate.

MOLECULAR nitrogen complexes have been obtained from nitrogen gas either by the displacement of a neutral molecule such as $H_2O$ {from $[Ru(NH_3)_5H_2O]^{2+}$}[1] or $H_2$ [*e.g.* from $CoH_3(PPh_3)_3$][2] or by simple addition to a species containing a vacant co-ordination site [*e.g.* $FeH_2(PEtPh_2)_3$].[3] We report the preparation of a new molecular nitrogen complex of iron by the displacement of chloride ion under mild conditions. This method is potentially of general applicability.

Passage of nitrogen through an acetone solution of *trans*-hydridochlorodi(bisdiethylphosphinoethane)iron(II)[4] in the presence of sodium tetraphenylborate causes the precipitation of NaCl and the formation of *trans*-$FeH(N_2)depe_2^+ BPh_4^-$† (depe=$Et_2PH_2CCH_2PEt_2$). The complex is obtained as orange needles, which are stable in dry air, darken rapidly above 100°, and melt with decomposition at 135—145°. Its i.r. spectrum shows a very strong, sharp band at 2090 cm.$^{-1}$, assigned to $\nu(N_2)$, and a weak, rather broad absorption at 1870 cm.$^{-1}$ [$\nu$(FeH)].

In a similar way, the corresponding carbonyl complex, *trans*-$FeH(CO)depe_2^+ BPh_4^-$† can be prepared. This has a higher thermal stability than the nitrogen complex, darkening rapidly above 160°, and melting with decomposition at 170°. It exhibits a carbonyl stretching frequency at 1918 cm.$^{-1}$, and a weak $\nu$(FeH) at about 1875 cm.$^{-1}$. This compound is also formed when carbon monoxide is passed through a solution of the nitrogen complex.

Further support for the formulation of these complexes comes from conductivity measurements and $^1H$ n.m.r. spectra. The specific conductivities of $10^{-3}$M solutions of the compounds in nitromethane are in the region expected for 1 : 1 electrolytes, and their $^1H$ n.m.r. spectra show, in addition to resonances associated with the anion and phosphine ligands, high-field quintets (Table), with $J_{PH}$ values similar to those found in other compounds of known *trans* configuration.[4]

The Mössbauer spectra of the two complexes illustrate the very different bonding characteristics of $N_2$ and CO. For example, the much lower centre shift in the carbonyl complex suggests that CO is an appreciably better $\sigma$-donor and/or $\pi$-acceptor than $N_2$.[5] Furthermore, the larger quadrupole splitting in the carbonyl complex is also indicative of more back-donation to CO than $N_2$.[5]

*N.m.r. and Mössbauer data*

| Compound | $\tau_{MH}$[a] | $J_{PH}$(Hz) | δ (mm./sec.)[b] | $\Delta E_Q$ (mm./sec.)[b] |
|---|---|---|---|---|
| *trans*-$FeH(N_2)depe_2^+ BPh_4^-$ .. .. | 28·2 | 49 | +0·16 | 0·33 |
| *trans*-$FeH(CO)depe_2^+ BPh_4^-$ .. .. | 20·9 | 47 | −0·04 | 1·00 |

[a] In acetone solution, relative to $Me_4Si$ as internal standard.
[b] Room temperature data; values are quoted relative to stainless steel. Error ±0·01 mm./sec.

Preliminary studies on the nitrogen complex indicate that, in solution, it is extremely reactive and that the nitrogen is readily lost under an atmosphere of hydrogen or argon, and can be replaced by carbon monoxide and other $\pi$-bonding ligands.

A number of crystalline products have been obtained from these reactions and these are under study. Also, an analogous nitrogen complex can be prepared using bisdimethylphosphinoethane [$\nu(N_2)$ at 2093 cm.$^{-1}$], and the possibility of forming nitrogen complexes with other ditertiary phosphines is being examined.

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† Satisfactory elemental analyses were obtained for these new compounds.

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