literature. Surprisingly enough, however, no comparable stoichiometric N_2 reduction has been reported yet for complexes of iron, which is such a prominent constituent of both enzymatic and heterogeneous N_2-reduction catalysts.[6] A number of complexes have been found which contain N_2 coordinated to an iron atom,[7-9] but these complexes do not appear to be susceptible to reductive cleavage of the $N \equiv N$ bond. In this communication we describe conditions for a clean, stoichiometric reduction of N_2 to NH_3 by iron compounds.

Whereas reaction systems derived from alkali naphthalides (Napht$^-$) and several titanium, vanadium, or chromium compounds bring about efficient reduction of N_2,[2,3] we find that the potential of Napht$^- \rightleftarrows$ Napht^0 + e^- is not quite reducing enough to promote this reaction efficiently in the presence of the corresponding iron compounds. Observed yields do not exceed *ca.* 0.5 mmol of NH_3 per mmol of $FeCl_3$ employed, even in the presence of a 25-fold excess of lithium naphthalide, and they are drastically diminished by the addition of free naphthalene (for experimental conditions see footnote 10). In keeping with this view, a large increase in N_2 reduction is observed when the more strongly reducing naphthalene dianion[11] (Napht^{2-}) is used as a reductant. With 8 mmol of Napht^{2-} per mmol of $FeCl_3$ (so that no free napth^0 is formed and the potential of the final reaction mixture is still governed by the equilibrium Napht$^{2-} \rightleftarrows$ Napth$^-$ + e^-) a yield of 0.82 mmol of NH_3/mmol of Fe is observed (Figure 1a). Stoichiometric yields (0.98 mmol of NH_3/mmol of Fe) are obtained when 2,6-dimethylnaphthalene dianion (DMNpht^{2-}) is employed as a reductant instead of Napht^{2-}. The electron-releasing methyl substituents undoubtedly make the aromatic dianion even more reducing.

The same stoichiometric yields are obtained with reaction systems containing naphthalene, if the concentration of Napht^{2-} is kept at the attainable maximum by an excess of metallic lithium (20 mmol per mmol of $FeCl_3$).[12] For this reduction four naphthalene moieties per iron appear to be required in the critical reaction step, as indicated by the sharp drop-off of reaction yields when less than 4 mmol of naphthalene/mmol of $FeCl_3$ is present in the reaction mixture (Figure 1b).

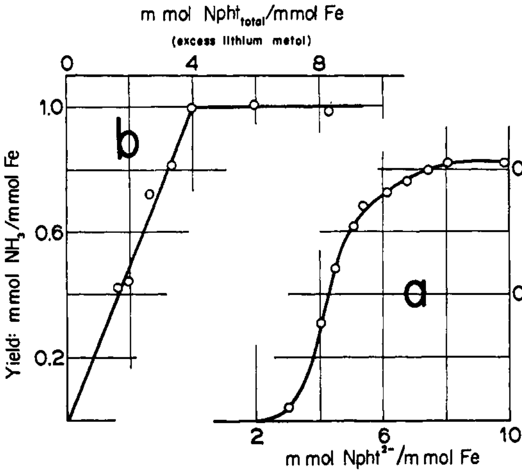

Figure 1. Requirements for iron-induced N_2 reduction: (a) dependence of NH_3 yields on the ratio of dilithium naphthalene/$FeCl_3$ employed, (b) effect of total naphthalene concentration (expressed as mmol of Napht$_{total}$/mmol of Fe) on the extent of N_2 reduction in the presence of 20 mmol of Li metal/mmol of $FeCl_3$. Experimental conditions are as follows. (a) A 0.05 *M* solution of $FeCl_3$ in THF (10 ml) was added, under Ar, to varying amounts of a solution of dilithium naphthalide in THF (0.16 *M* in naphthalene, 0.27 *M* in Li). The reaction flask was placed in an autoclave and heated, under 1600 psi of N_2, to 60° for 4 hr. NH_3 yields were determined by hydrolysis, removal of THF and naphthalene, and subsequent Kjeldahl distillation. (b) Metallic lithium (69 mg) was added to the reaction mixture under argon; otherwise the procedure is identical with the one given above.

The iron-containing N_2 reduction systems described above differ from related systems containing titanium, vanadium, or chromium compounds in that the reaction yields do not approach a limiting value of 2 mmol of NH_3/mmol of metal (see, *e.g.*, ref 3), but clearly have 1 mmol of NH_3/mmol of metal as their limit. This feature, as well as the considerably more negative potential required here to induce the reduction of N_2, will hopefully find its explanation in a more detailed mechanistic study of this reaction.

Of particular interest is the question of which kind of N_2 complexes are intermediates in this reaction and why interaction with the metal renders the N_2 molecule so much more susceptible to reduction in these species than in any of the known iron–N_2 complexes.

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Unusual Coordination in a Cobalt(II) Complex with the Tripod Ligand Tris(2-diphenylphosphinoethyl)amine

Sir:

The ligand tris(2-diphenylphosphinoethyl)amine, $(Ph_2PCH_2CH_2)_3N$, (NP_3), which contains both high-spin and low-spin stabilizing donor atoms (potential donor set 1N and 3P), has been used in order to obtain five-coordinate Ni(II) and Co(II) complexes

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(6) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968).

(7) C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito, and M. G. Swanwick, *J. Organometal. Chem.*, **14**, 349 (1968).

(8) G. M. Bancroft, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 585 (1969).

(9) In reaction systems containing iron compounds and reductants such as Grignard reagents or lithium alkyl compounds, N_2 reduction has been observed, but these reactions yielded only on the order of 0.1 mmol of NH_3/mmol of iron complex: M. L. Khidekel and Y. B. Grebenschchikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 761 (1965). These low reduction yields and the concomitant dominance of side reactions would render mechanistic studies quite difficult.

(10) The reactions are carried out in tetrahydrofuran at 60° (see also the legend for Figure 1). Yields of NH_3, determined by hydrolysis and Kjeldahl distillation, initially increase with time, but level off after about 4 hr. The rate and extent of N_2 reduction are independent of N_2 pressure in the range of 30–100 atm; at atmospheric pressure, it is diminished to roughly one-third. N_2 reductions proceed also at room temperature; substantially longer times are required for completion, however.

(11) J. Smid, *J. Amer. Chem. Soc.*, **87**, 655 (1965).

(12) The possibility that the known reaction, $6Li + N_2 \rightarrow 2Li_3N$, is responsible for the observed N_2 reduction can be excluded. In the absence of $FeCl_3$, otherwise identical reaction systems yield only 0.02–0.03 mmol of NH_3, compared to 0.99 mmol in the presence of 1 mmol of $FeCl_3$.

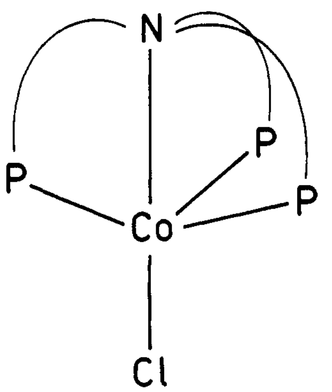

Figure 1. A sketch of the coordination in $[Co(NP_3)Cl]PF_6$.

with formula $[M(NP_3)X]Y$, where $X = Cl, Br, I$, or NCS; $Y = X, BF_4, PF_6$, or BPh_4.[1]

The nickel complexes are all diamagnetic and trigonal-bipyramidal coordination has been found for $[Ni(NP_3)I]I$.[2]

The cobalt complexes with $X = Cl$ or Br are all high spin; low-spin complexes are only found when $X = I$ or NCS. The low-spin $[Co(NP_3)I]I$ is square pyramidal, with a phosphorus atom in the apical position.[3]

We have now determined the structure of the high-spin complex $[Co(NP_3)Cl]PF_6$. Crystals of this compound are monoclinic, space group $P2_1/c$; $a = 21.685$ (13), $b = 14.248$ (15), $c = 17.715$ (15) Å, $\beta = 130.13$ (7)°, $D_c = 1.417$ g cm^{-3}, $Z = 4$, $D_m = 1.39$ g cm^{-3}. Multiple-film equiinclination Weissenberg data have been collected, using Fe Kα radiation. The structure has been solved by standard heavy-atom techniques and refined by full-matrix least squares with anisotropic temperature factors for all atoms except carbon, to an R value of 7.5% over 2025 observed reflections.

The metal atom is surrounded by a set of four ligands, one chlorine and three phosphorus atoms, with metal–ligand distances in the normal range. A fifth ligand (N) lies at a distance of 2.675 Å from the metal. The arrangement of the four closest donor atoms is distorted tetrahedral and the additional ligand atom may be visualized to complete either a very distorted trigonal bipyramid or a capped tetrahedron, about the cobalt (Figure 1). According to the former view, the ligands N and Cl occupy the apices of the bipyramid (N–Co–Cl angle, 178.9°) and the metal atom lies as much as 0.6 Å below the equatorial plane defined by the phosphorus atoms. Distances (Å) and angles (deg) in the coordination polyhedron are: Co–Cl, 2.226; Co–P_1, 2.378; Co–P_2, 2.374; Co–P_3, 2.355; Co–N, 2.675; Cl–Co–P_1, 105.0; Cl–Co–P_2, 104.5; Cl–Co–P_3, 104.3; P_1–Co–P_2, 118.4; P_1–Co–P_3, 110.1; P_2–Co–P_3, 113.0; N–Co–P_1, 75.4; N–Co–P_2, 76.1; and N–Co–P_3, 74.6. Standard deviations are less than 0.010 Å for bond distances and less than 0.3° for angles.

The contribution to the field of the ligands by the nitrogen atom is significant. The spectrum of the complex is indeed indicative of five coordination and definitely differs from that of tetrahedral Co(II). This is apparent from Figure 2, where the reflectance spectrum of $[Co(NP_3)Cl]PF_6$ is compared with those of the five-coordinate $[Co(Me_6tren)Br]Br$ (ref 4), of the tetrahedral $CoCl_2(PPh_2)_2$ (ref 5), and of $[Co(NOP_2)Cl]PF_6$, which has revealed a coordination geometry similar to that of the present complex.[6]

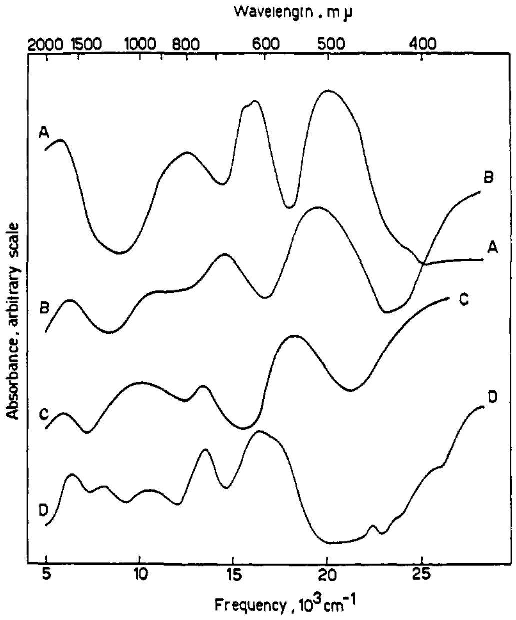

Figure 2. Reflectance spectra of (A) $[Co(Me_6tren)Br]Br$, (B) $[Co(NOP_2)Cl]PF_6$, (C) $[Co(NP_3)Cl]PF_6$ (present case), (D) $CoCl_2(PPh_3)_2$.

The spin state of complexes of the series $[Co(NP_3)X]Y$ shows a dependence on the softness of the ligand atom X, as measured by the value of the overall nucleophilic reactivity constant $\Sigma n°$ (ref 7). Indeed, the observed tendency of the ligand X to stabilize the low-spin state[1] (which increases in the order $Cl = Br < I < NCS$) parallels the ordering for $\Sigma n°$ ($Cl < Br < I < NCS$). Moreoever, the geometry of coordination, other factors being unchanged, is of importance. In fact, for the $Co(NP_3)I$ chromophore both spin isomers are known[1] and the square-pyramidal geometry is ascertained for the low-spin case,[3] whereas a structure of the $[Co(NP_3)Cl]PF_6$ type may be reasonably assumed for the other case, on the basis of the spectral analogy.[1] This would indicate that the square pyramid favors low-spin states.

The unusual geometry found for $[Co(NP_3)Cl]PF_6$ probably originates from a tendency of Co(II) toward tetradehral coordination. A tendency of this sort has been noticed for other Co(II) complexes[8] and may originate from stability of the $e^4t_2^3$ configuration for seven d electrons in the T_d ligand field. In order to shed more light on the last points, further structural investigations have been undertaken on complexes of this series.

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