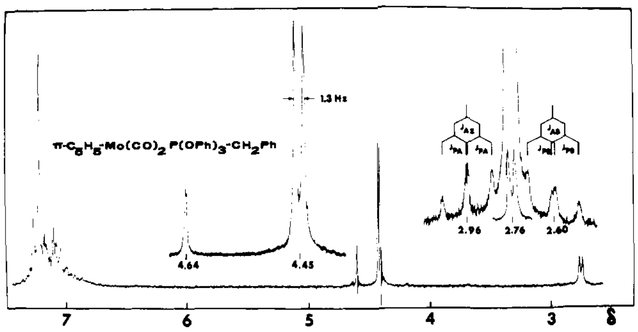

Figure 3. The pmr spectrum of σ-benzyl-π-$C_5H_5Mo(CO)_2$-$P(OC_6H_5)_3$ in chloroform-d_1 at ambient temperature.

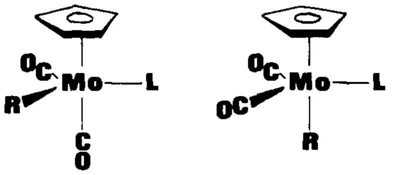

Figure 4. Two of several possible intermediates or transition states expected in the intramolecular rearrangement processes.

of five-coordinate complexes appears likely. Hence intermediates or transition states such as those indicated in Figure 4 might be anticipated.[12]

We are currently investigating the thermodynamics and kinetics of these complexes in order to determine the steric and electronic factors responsible for the stability of a given configuration, the barriers to interconversion, and the plausibility of suggested mechanism of ligand interchange. We tentatively assume that the lowest energy pathway of rearrangement would suggest an intermediate or transition state with the least bulky group in the "apical" position. Hence, in the hydride the lowest energy pathway would involve movement of a hydrogen atom to an apical position. In the alkyl complexes, placing either the carbonyl or the alkyl group in the apical position could result in a comparable situation energetically, and more than one pathway might be important.[14,15]

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(12) The structures in Figure 4 are only meant to imply relative ligand orientation, not bond angles. These structures were suggested by the most stable conformations of seven-coordinate complexes[13] and the possibility of a rapid 3:4 = 3:3:1 = 3:4 conformational interconversion.

(13) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

(14) The benzyl and methyl derivatives exist in the *trans* form in the solid; hence, one can observe the kinetics of interconversion by measuring concentrations as a function of time at low temperature and nmr line-shape analysis at high temperatures. This allows very accurate determinations of barriers since one can measure rate constants over a range of 10^6 in rate constant and 150° in temperature.

(15) We wish to acknowledge the financial support of the Connecticut Research Commission and the Petroleum Research Fund administered by the American Chemical Society. We wish to thank the National Science Foundation for Grant GP-6938 which allowed the purchase of the Varian HA-100 spectrometer.

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Titanium(II) in the Fixation–Reduction of Molecular Nitrogen under Mild Conditions

Sir:

In previous communications[1-3] we have described the facile room-temperature, atmospheric pressure conversion of molecular nitrogen (N_2) to ammonia by means of an over-all catalytic, titanium-based process involving a fixation–reduction–protonation sequence. In the reaction, aerial N_2 can be utilized,[2] and the reduction can be effected by either chemical or electrolytic means.[3] The central role of a titanium(II) species had served from the outset as an ideological guide in the design of our experiments,[1,4,5] and the function of this unusual, lower valent titanium type has now been clarified by findings which include the first case of the detention and subsequent reductive conversion to ammonia of a given transition metal compound made directly by reaction with N_2 or by other means.[6]

In a typical experiment dicyclopentadienyltitanium ("titanocene") (1.50 g, 8.40 mmol), dissolved in 95 ml of anhydrous, oxygen-free benzene at 20–25°, was exposed with stirring to an atmosphere of N_2.[7] During the course of approximately 3 weeks, 7.56 mmol of the gas was absorbed, after which N_2 uptake ceased. Similar behavior was observed when a preparation of titanium(II) *n*-hexoxide (prepared by reaction of titanium(III) chloride, *n*-hexyl alcohol, and methyllithium in a 1:2:3 molar ratio)[5] was dissolved in benzene and exposed to an atmosphere of N_2. Significantly, titanium(II) alloxide and benzoxide, useful for achieving coupling of hydrocarbon units,[5] were ineffectual in fixing nitrogen, possibly because of stabilization due to internal coordination with titanium of the π electrons of the unsaturated ligands. The titanocene–N_2 reaction is reversible under the conditions described. Thus, in one run, the reaction was interrupted after 30% reaction by quickly flushing argon through the system; during 50 successive hr all of the chemically bound N_2 was released into the argon atmosphere, as indicated by the volume change.

Treatments of this titanium–nitrogen complex in benzene with excess sodium naphthalide (NaNp) and subsequent hydrolysis produced high yields of ammonia. Further, a solution of this complex in benzene showed an infrared absorption at *ca.* 1960 cm^{-1} which may be attributable to an N–N stretch and which disappeared after the solution was exposed overnight to an argon atmosphere. An osmometric molecular weight determination in benzene indicates that the nitrogen complex is dimeric.

In order to ascertain the stoichiometry of the over-all

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(1) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Am. Chem. Soc.*, **89**, 5707 (1967).

(2) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968).

(3) E. E. van Tamelen and B. Åkermark, *ibid.*, **90**, 4492 (1968).

(4) E. E. van Tamelen and M. A. Schwartz, *ibid.*, **87**, 3277 (1965).

(5) For the role of titanium(II) species in the one-step coupling of alcohols to hydrocarbons, see E. E. van Tamelen, B. Åkermark, and K. B. Sharpless, *ibid.*, **91**, 1552 (1969).

(6) Previously, an order of stability sufficient to permit isolation of transition metal compounds with N_2 ligands apparently also precluded reduction or oxidation of the ligand: J. Chatt, R. C. Richards, J. E. Ferguson, and J. L. Love, *Chem. Commun.*, 1522 (1968).

(7) The use of titanocene for the *over-all* conversion of molecular nitrogen to ammonia was first described in a publication from this laboratory.[1] The metallocene was prepared according to the directions of G. W. Watt, L. J. Baye, and F. O. Drummond, *J. Am. Chem. Soc.*, **88**, 1138 (1966).

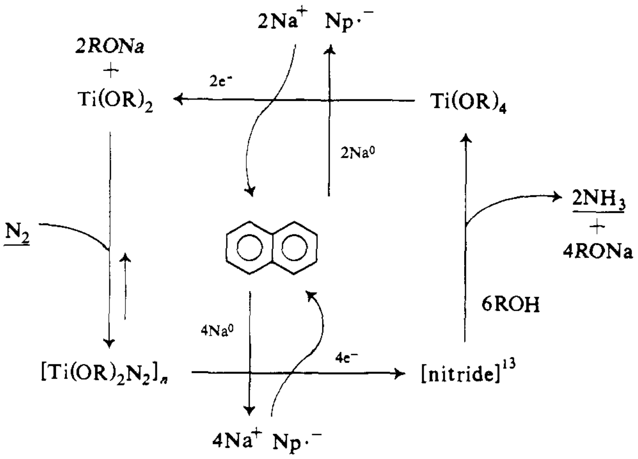
N_2-reducing reaction involving titanium, a Job plot[8] was constructed in which the yield of ammonia was measured as a function of the starting titanium(IV) isopropoxide/sodium naphthalide ratio. The absence of either reagent precluded ammonia formation, while a maximum yield of product was observed with a 1:6 ratio, reflecting the redox relationship required for the over-all conversion of N_2 to ammonia. Independently of the Ti/NaNp molar ratio, there was formed approximately 2 mol of ammonia per mol of N_2 taken up. Although the maximum ammonia yield observed per run in this system was 60-65%, essentially quantitative yields have been realized with titanium(IV) chloride under higher N_2 pressures.[9]

On the basis of early observations made on a slow, over-all aprotic reaction based on titanium(IV) chloride, alkoxide ion, and potassium metal, it was suggested that hydrogen in the product ammonia molecules originated under these conditions in the ethereal solvent used in the fixation–reduction reaction.[1] This claim is now qualitatively confirmed by experiments carried out with perdeuterated solvent, but otherwise in the same fashion as the earlier runs. By employing potassium *t*-butoxide and perdeuteriotetrahydrofuran and sweeping the system periodically with N_2 gas over a period of about 4 weeks, there was obtained solvent distillate which contained about 10% deuterium bound to ammonia nitrogen, as indicated by high-resolution mass spectral means. The amount of nitrogen-bound deuterium lost by exchange with water before or during the analytical determination is not known. Neither has the intermediate stage at which hydrogen abstraction takes place been identified; but because of the slower rate of formation and poor yield (about 10%) of ammonia in this reaction modification, it is likely that hydrogen abstraction from solvent does not intervene to any measurable extent in the runs featuring the efficient and rapid naphthalide reduction.[10]

On the basis of the evidence accumulated thus far, we believe the scheme in Chart I represents the titanium-based cycle by which N_2 is converted to ammonia in our system. Cyclical operation thus depends on the N_2-fixing ability of titanium(II), as well as regenerability of titanium(II) and reduction of the titanium-bound N_2, both brought about by NaNp available from a naphthalene pool by periodic reaction with reagent sodium metal. The over-all net process can be expressed as

$$N_2 + 6e^- + 6ROH \rightarrow 2NH_3 + 6RO^-$$

Chart I



It is evident that this mode of N_2 fixation—the first room-temperature, atmospheric pressure process to be operated in an over-all catalytic fashion—differs from the original Vol'pin reaction,[11] wherein transition metal compounds are used in conjunction with alkyl Grignard reagents or metal hydrides as reducing species and hydrogen sources.[12] Finally, this cycle serves as a crude parallel or model for the biological N_2-fixation process, which in its simplest form probably involves initial interaction of lower valent transition metal with N_2 from the air, reduction of the coordinated N_2 species, followed by protonation of the fixed-reduced entity to give ammonia and regenerated lower valent metal.[13]

Acknowledgment. The authors are indebted to the National Institutes of Health for grant support (GM 13797).

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[8] M. M. Jones, "Elementary Coordination Chemistry," Prentice Hall Inc., Englewood Cliffs, N. J., 1964, p 282.

[9] G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **79**, 898 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 873 (1967).

[10] The Ti–H bonds postulated on the basis of esr data for the titanocene–naphthalide system [G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **80**, 398 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 386 (1968)] might be formed by such reactions. However, this phenomenon would probably be unrelated to the normal N_2 fixation–reduction process under discussion in that, whereas reaction with N_2 by titanium(IV)–naphthalide reagent prepared under N_2 is very rapid (~30–80 min), N_2 fixation is considerably slower by the titanium–naphthalide reagent prepared in advance under argon. It is clear that some additional reaction is superimposed, possibly hydrogen abstraction from solvent.

[11] (a) M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966); (b) H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4305, 4307 (1966).

[12] The difference is illustrated by the result, *viz.*, no N_2 uptake and no ammonia formation, of treating titanium(IV) isopropoxide with α-naphthylmagnesium bromide, the Grignard counterpart of the naphthalene radical anion.

[13] Our efforts to characterize the nonprotonated fixation–reduction product have been only modestly rewarding. After a purification sequence involving selective organic solvent extractions and precipitations, there could be obtained an unstable, air-sensitive, black, powdery product, apparently a nitride which contained titanium, nitrogen, sodium, and isopropoxide units and which liberated ammonia on reaction with water or alcohols. Reliable evidence on the homogeneity of the intermediate is lacking.

[14] National Institutes of Health Postdoctoral Fellow, 1966–1968.

[15] National Institutes of Health Postdoctoral Fellow, 1968–present.

[16] Max Kade Foundation, Inc., Research Fellow, 1967–1968.

[17] National Science Foundation Predoctoral Fellow, 1966–present.

[18] Fellowship provided by Swedish Council for Applied Research, 1967–1968.

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Mechanism of the Titanium-Promoted Deoxygenative Coupling of Allyl and Benzyl Alcohols to Hydrocarbons

Sir:

As a convenient method for the synthesis of bibenzyls and 1,5-dienes, the direct reductive coupling of benzyl and allyl alcohols was recently innovated and developed in this laboratory.[1,2] Involving either identical or nonidentical

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[1] E. E. van Tamelen and M. A. Schwartz, *J. Am. Chem. Soc.* **87**, 3277 (1965).

[2] K. B. Sharpless, R. P. Hanzlik, and E. E. van Tamelen, *ibid.*, **90**, 209 (1968).