Dr. U. Engelhardt and L. Centofanti kindly assisted him with gas determinations in the vacuum manifold system. This work was supported by U. S. Public Health Research Grant GM-12176.

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Formation of Ammonia by Insertion of Molecular Nitrogen into Metal–Hydride Bonds. II. Di-μ-imino-bis(dicyclopentadienyltitanium(III)) as a Product of the Reaction between Di-μ-hydrido-bis(dicyclopentadienyltitanium(III)) and Molecular Nitrogen[1]

Sir:

In a preceding publication[1] it was shown that a dimer of dicyclopentadienyltitanium(III) hydride, containing two μ-hydrido ligands, most likely is the species which reacts with molecular nitrogen in the reaction mixtures described by Vol'pin and Shur.[2] In order to investigate the mechanism of this reaction, an effort has been undertaken to establish the structure of the product of this reaction step. When a solution of 0.08 *M* dicyclopentadienyltitanium dichloride (Cp_2TiCl_2) and 0.8 *M* ethylmagnesium chloride (EtMgCl) in dry tetrahydrofuran was kept at room temperature under a nitrogen pressure of 150 atm for 15 days, the final solution liberated on treatment with 6 *N* aqueous HCl and subsequent Kjeldahl distillation *ca.* 1 mole of NH_3/mole of titanium complex. This final reaction solution showed only weak and complex epr signals. If the solution was slightly acidified, however (*ca.* 10 ml of HCl gas/2 ml of solution), a strong signal appeared, with a *g* value of 1.987 and a hyperfine pattern consisting of five lines spaced by 2.3 gauss (Figure 1).[3] On addition of ethylmagnesium chloride (0.5 ml of a 3.6 *M* solution) the signal disappears nearly completely (residual signal intensity *ca.* 2.5%). The signal reappears on addition of HCl. Prolonged treatment with HCl converts the compound *via* the green-brown $[Cp_2TiCl]_2$ ($g = 1.980$) to the starting material Cp_2TiCl_2 (absorption maximum 510 mμ).

Since there can be no reasonable doubt that the hyperfine quintuplet arises from two equivalent nitrogen nuclei in the complex, and since there is an equal number of nitrogens and of dicyclopentadienyltitanium cores, it is evident that the complex must be a dimeric dicyclopentadienyltitanium(III) species containing two bridging nitrogen ligands of some kind.

The most straightforward structural interpretation of the observed acid–base equilibrium is the following. If the di-μ-amino complex I occurs in the slightly acidified solutions, it could be expected to exhibit an antiferromagnetic interaction between the two Ti centers, comparable in size to that observed in related complexes with other bridging monoanions such as the chloride or hydride derivatives. This would explain the observation of a signal with appreciable intensity at room temperature or somewhat lowered temperatures. On addition of EtMgCl, I is to be expected to loose a proton from each of the μ-amino groups to give the di-μ-imino complex II. The bridging anion HN^{2-} will then induce an increased antiferromagnetic interaction between the two Ti cores, the concommitant

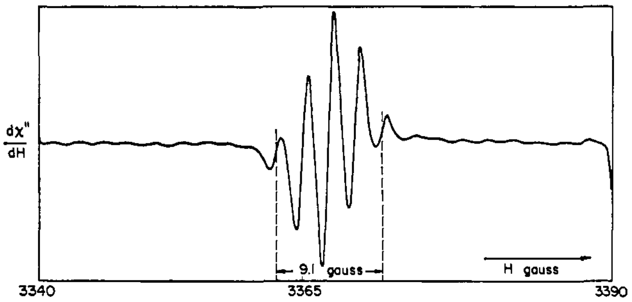
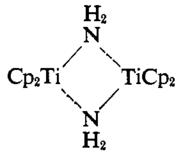


Figure 1. Electron paramagnetic resonance spectrum of a solution of 0.08 *M* Cp_2TiCl_2 and 0.8 *M* EtMgCl, which was kept under a nitrogen pressure of 150 atm for 15 days at room temperature after acidification of a 2-ml solution with 10 ml of hydrogen chloride gas. Microwave power 0.2 mw; microwave frequency 9.371 Gc; field modulation 0.25 gauss; temperature −57°.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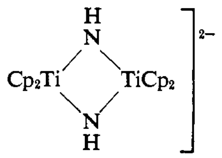
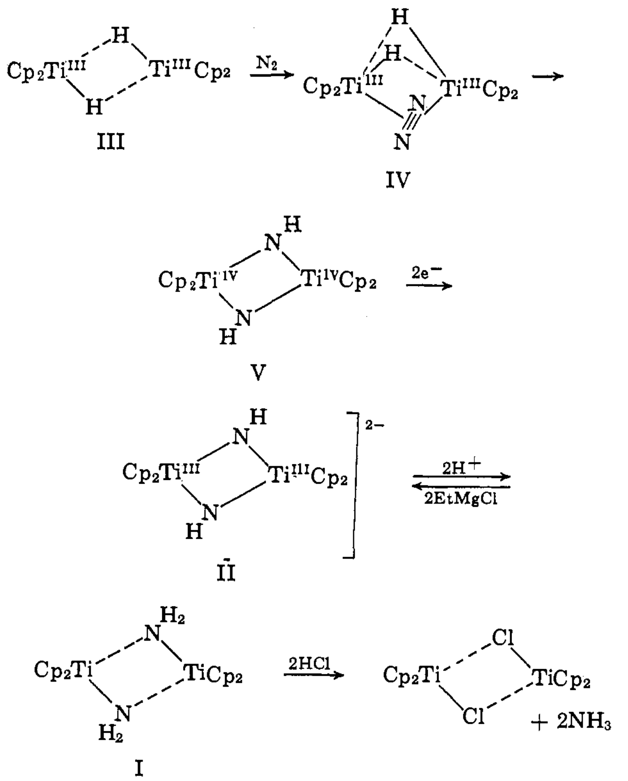

II

Scheme I



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(1) First communication of this series: H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 0000 (1966).

(2) M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966), and references cited therein.

(3) The weak titanium hyperfine lines are quite complex and their pattern is also superposed by traces of other products.

conversion of the complex to a diamagnetic ground state explaining the absence of detectable epr signals in the EtMgCl-treated solutions.

A conceivable alternative would be that the diamagnetic complex formed in the presence of EtMgCl is the di-μ-nitrido derivative, which then would be protonated to I and II. In this case, however, two different epr signals would be expected in the course of the protonation, which was not observed.

The identification of II as the product of the reaction between the hydride complex III and nitrogen (Scheme I) leaves no reasonable doubt that the reduction of molecular nitrogen N_2 has occurred *via* a double insertion of N_2 into the two metal–hydride bonds of III, presumably with a π-bonded nitrogen complex IV as intermediate. This complex IV is certainly too unstable to be directly detectable. However, such a slight nuclear displacement is necessary only to convert this species to the di-μ-imino complex V that quite small concentrations of IV might be sufficient to allow for the observed smooth reaction.

Though the six reduction equivalents, which are necessary to conduct the reduction of N_2 to the ammonia state, require that a titanium(IV) complex of structure V be the product of the insertion reaction proper, the identification of the corresponding titanium(III) compounds I and II in the reaction solution is not in contradiction with this mechanism; V is to be expected to be susceptible, like the corresponding dicyclopentadienyltitanium(IV) chloride, to reduction by the Grignard reagent which is present in excess in the reaction mixture.

The chemistry of this and related reactions will be considered in detail in a subsequent communication.

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A Linear Enthalpy–Free Energy Correlation as Supporting Evidence for Hammett's Indicator Overlap Method[1,2]

Sir:

We wish to report a remarkably good correlation between the heats of protonation of a series of primary amines in concentrated sulfuric acid and the estimated pK_a values of their conjugate acids in water. As shown in Figure 1, this correlation covers a very wide range, nearly 16 pK units and 30 kcal/mole. It is especially significant because many of the amines are weakly basic indicators whose pK_a values in water could only be estimated by a lengthy extrapolation using the Hammett overlap method.[3,4] Since this could easily result in serious cumulative errors,[4] it is important to have an independent test of the reliability of the overlap method. We believe that the results presented here help to meet this need.

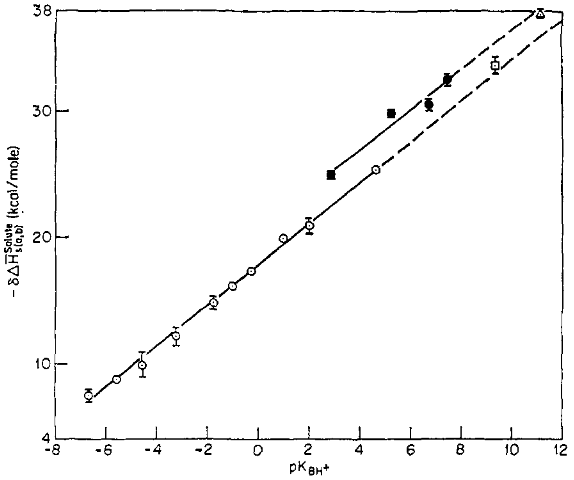

Figure 1. Partial molal heats of transfer $\Delta\bar{H}_a$ for amines from *sym*-tetrachloroethane to 96.48% sulfuric acid *vs.* the pK_a value of their conjugate acids in water. The solid points ● refer to pyridines with the following pK_a's: 2,4,6-collidine (7.43), 2,6-lutidine (6.72), pyridine (5.25), 3-bromopyridine (2.84). The open circles ○ refer to primary anilines of the following pK_a's: aniline (4.60), 2,4-dichloroaniline (2.00), *p*-nitroaniline (1.00), *o*-nitroaniline (−0.29), 4-chloro-2-nitroaniline (−1.02), 2,5-dichloro-4-nitroaniline (1.78), 2,6-dichloro-4-nitroaniline (−3.27), 2,4-dinitroaniline (−4.53), 2,6-dinitroaniline (−5.54), 2-bromo-4,6-dinitroaniline (−6.68). □ refers to benzylamine and △ refers to piperidine. The pK_a values used here were taken from M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963), or D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth, Inc., Washington, D. C., 1965.

Because of wide differences in basicity, there is no reliable analytical method that will permit measurement of the ionization constants of all of these amines in a single medium. However, their relative heats of ionization are measured easily (as described below) in a single acid solution of sufficient strength. In the present case, the heats of attenuation of the bases from their pure liquid or crystalline standard states to highly dilute (10^{-3} to 10^{-4}) solution in an inert solvent (*sym*-tetrachloroethane) were used to correct the heats of solution of the amines from the same liquid or crystalline standard states to concentrated sulfuric acid. The $\Delta\bar{H}_a$ values therefore represent standard heats of transfer for the amine from solution in the former solvent to the latter in which it is completely ionized.

The close correlation of heats of ionization in one medium with free energies in another suggests strongly that both properties are proportional to the same energy term, the internal energy of ionization at 25°. Following Hepler,[5] the standard free energy of ionization ($\Delta G_i°$) in a given medium can be considered in terms of internal (int) and external (ext) components, thus

$$\Delta G_i° = \Delta H°_{\text{int}} - T\Delta S°_{\text{int}} + \Delta H°_{\text{ext}} - T\Delta S°_{\text{ext}}$$

For a series of closely related compounds in aqueous media, the last two terms tend to compensate each other and the difference in $T\Delta S°_{\text{int}}$ is insignificant. Therefore, the structural variation (δ_s) of the measured free energy change corresponds to that of the internal

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(1) Paper II in the series Weak Bases in Strong Acids.

(2) Supported by National Institutes of Health Grant G.M. 10872.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(4) E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 223 (1963).

(5) L. G. Hepler, *J. Am. Chem. Soc.*, **85**, 3089 (1963), and earlier papers cited therein.