

state and that there was a definite relationship between the extent of this reaction, the amount of carbon dioxide formed, and the quantity of chloride ion released from carbon tetrachloride. This preliminary communication describes the unusual and unexpected results obtained.

In each experiment, carbon tetrachloride was introduced into a solution of copper(I) chloride in dimethyl sulfoxide contained in a reaction vessel which was connected to an appropriate analytical train, the whole assembly being constantly swept out with pure dry nitrogen. The flow of nitrogen was continued for periods varying from 0.5 to 12 hr after addition of the carbon tetrachloride. In Table I a summary of the

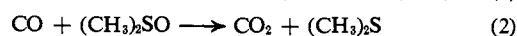
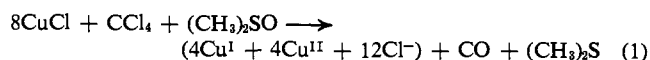
Table I. Reaction of Dimethyl Sulfoxide Solutions of CuCl with CCl₄^a

CuCl, mmoles	Cu(II) formed, mmoles	Final Cl ⁻ , mmoles	CO ₂ , mmoles	CCl ₄ , mmoles
2.31	1.20	3.20	0.32	5.0
2.24	1.15	3.47	0.29	5.0
6.05	3.12	9.02	0.73	5.0
6.60	3.33	9.66	0.91	5.0
6.09	3.08	8.85	0.73	5.0
10.14	5.07	14.85	1.25	5.0
10.08	5.21	14.69	1.26	5.0
10.42		14.34		1.00
10.66	3.98			1.00
18.82		23.04		1.00
19.56	3.96			1.00
9.29			0.71	1.00
10.20	4.17	13.85	0.84	1.00
19.89			0.63	1.00

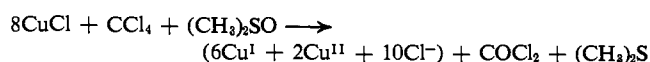
^a In each experiment, 5 ml of dimethyl sulfoxide was used and reaction was carried out at room temperature for 4 hr.

quantitative information obtained in 4-hr runs is given. The mixture of carbon dioxide and monoxide was converted completely to the dioxide by passage through a tower of iodine(V) oxide, followed by absorption in 1 *M* sodium hydroxide and potentiometric titration. The reaction mixture was diluted to a definite volume, and aliquots were appropriately treated and analyzed for chloride ion by potentiometric titration with standard silver nitrate solution and for copper(II) by iodometry.

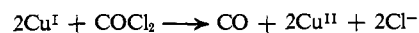
Examination of the data from those experiments in which 5 mmoles of carbon tetrachloride was used reveals a number of interesting points: (a) *half of the copper(I) initially present is converted to the di-positive state*; (b) *for each copper(II) ion formed one chloride ion is produced from carbon tetrachloride*; (c) *the total amount of carbon dioxide obtained is one-fourth of the quantity of copper(I) consumed or copper(II) formed*; and (d) *the increase in chloride ion content as a result of reaction is four times the amount of carbon dioxide obtained*. These results suggest the following over-all reactions:



It is conceivable that the precursor of the carbon monoxide is phosgene



and that this compound reacts further with copper(I)



Control experiments showed that solutions of phosgene in dimethyl sulfoxide react with copper(I) chloride with the liberation of chloride ion and oxides of carbon.

The participation of dimethyl sulfoxide as a reactant was demonstrated by the presence of dimethyl sulfide in the reaction mixture. Moreover, in a control it was shown that carbon monoxide is rapidly oxidized to the dioxide by dimethyl sulfoxide at room temperature.

Points b, c, and d cited above show unequivocally that any carbon tetrachloride attacked is completely converted to a mixture of carbon monoxide and dioxide. (Analysis of the gaseous mixture in a number of instances showed the ratio of dioxide to monoxide to be approximately 9:1.) Consistent with this are the results obtained in experiments in which 1 mmole of carbon tetrachloride was used. Only that amount of copper(I) required for complete consumption of carbon tetrachloride (4 mmoles of CuCl:1 mmole of CCl₄) was oxidized to copper(II). The increase in chloride ion (*ca.* 4 mmoles) is that expected from the complete removal of halogen from carbon tetrachloride. Finally, although the quantity of carbon dioxide obtained is only 62–84% of that expected, no carbon tetrachloride was detectable by a gas chromatographic analytical technique capable of detecting at least 2% of the compound.

The utilization, in experiments in which an excess (5 mmoles) of carbon tetrachloride was employed, of only half of the copper(I) present initially is undoubtedly governed by the relative order of stability of the copper(II) chloride and copper(I) chloride species which can be formed in dimethyl sulfoxide. The reduction potential of this mixture ($\text{Cu}^{\text{I}}\text{Cl}_n^{+1-n}$, $\text{Cu}^{\text{II}}\text{Cl}_{3-n}^{-1+n}$) must be sufficiently positive that copper(I) can no longer reduce carbon tetrachloride. In the absence of appropriate information, we do not feel that we can, at present, commit ourselves regarding the nature of the copper species present after reaction.

Acknowledgment. R. R. L. expresses his appreciation to the National Science Foundation for fellowship support for part of this work.

Robert R. Lavine, Reynold T. Iwamoto, Jacob Kleinberg
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044

Received July 22, 1966

Formation of Ammonia by Insertion of Molecular Nitrogen into Metal-Hydride Bonds. I. The Formation of Dimeric Dicyclopentadienyltitanium(III) Hydride as an Intermediate in the Vol'pin-Shur Nitrogen-Fixing System

Sir:

Until recently the reduction of molecular nitrogen under the mild conditions of the enzymatic nitrogen-fixing reactions was completely unparalleled by any nonenzymatic reaction of the N₂ molecule. Lately, however, among some other less efficient reaction systems, a procedure has been described by Vol'pin and

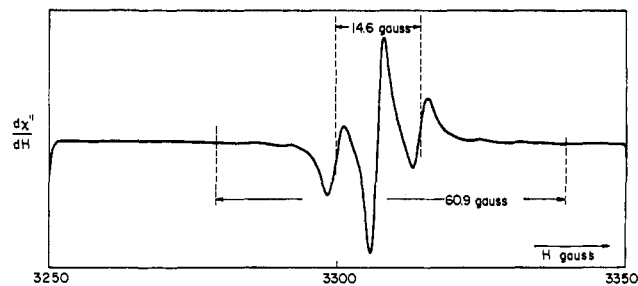


Figure 1. Electron paramagnetic resonance spectrum of a tetrahydrofuran solution containing 0.08 *M* Cp_2TiCl_2 and 0.8 *M* EtMgCl after 60 min. Microwave power 0.2 mw; microwave frequency 9.228 Gc; field modulation 0.7 gauss; temperature 23°.

Shur¹ wherein nitrogen is reduced to ammonia in an essentially stoichiometric reaction under very mild conditions. Dicyclopentadienyltitanium dichloride, in the presence of an ethylmagnesium halide in ethereal solution, reacts with nitrogen at room temperature and atmospheric pressure to yield, within some hours, a solution in which, after acid hydrolysis, NH_3 is found in an amount comparable to that of the titanium starting material; at elevated nitrogen pressures the reaction goes to completeness even faster. We wish to report here the results of an epr study, undertaken to establish the structure of the reactant, which is formed from dicyclopentadienyltitanium dichloride (Cp_2TiCl_2) and the ethylmagnesium halide (EtMgX), and which then supposedly enters the nitrogen fixation reaction proper.

If 1 equiv of EtMgCl is added to Cp_2TiCl_2 in tetrahydrofuran, gas evolution occurs and the red color of the solution changes to the green-brown of $[\text{Cp}_2\text{TiCl}]_2$ (absorption maximum at 710 $\text{m}\mu$). Concomittantly an epr signal appears at $g = 1.979$ (reported g value 1.980²). On addition of an excess of Grignard reagent the color of the solutions deepens to a very dark brown. Together with the color change the signal at $g = 1.979$ disappears and, instead, a very complex signal appears near $g = 2$, which has not been analyzed yet. This new signal is only of transient nature, however, and gives way in turn to a final, symmetric signal which is depicted in Figure 1. With a tenfold excess of EtMgCl over Cp_2TiCl_2 this change is essentially complete after *ca.* 1 hr at room temperature. Gas evolution continues during this period; ethane and ethylene are identified in the gas phase by their infrared spectra.

The resulting signal, which is indefinitely stable if the solution is kept under exclusion of air, is centered at $g = 1.993$ and consists of a hyperfine triplet with a 1:2:1 intensity ratio on which a weak hyperfine pattern of ten lines is superimposed. The splitting between the triplet lines is 7.3 gauss, the line width (peak-to-peak distance) 2.2 gauss. The ten-line pattern extends over 60.9 gauss, thus leaving 6.8 gauss for the individual spacings.

At lower temperatures the appearance of the spectrum changes very little. However, the spin concentration (evaluated by the double cavity-double integration method) is greatly decreased at lower temperatures compared to room temperature; at -32° it is only 78%, at -67° only 58% of that at room temperature.

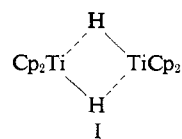
(1) M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966), and references cited therein.

(2) H. Nöth, J. Voitländer, and M. Nussbaum, *Naturwiss.*, **47**, 57 (1960).

If the reaction is performed with a perdeuterated Grignard reagent the hyperfine triplet is reduced in intensity and superposed by another, partly resolved hyperfine pattern of five equidistant lines with a spacing of 2.4 gauss (-74°).

If HCl is added to the final reaction product, it is reconverted, under evolution of hydrogen *via* the green-brown $[\text{Cp}_2\text{TiCl}]_2$ intermediate, to the starting material Cp_2TiCl_2 , as evidenced by its red color (absorption maximum 510 $\text{m}\mu$).

The experiment with the deuterated compound leaves no doubt that the triplet in Figure 1 arises from two equivalent hydrogens.³ The loss of spin concentration at lower temperature shows that the compound must contain two Ti(III) centers which, at low temperatures, will eventually go to a diamagnetic ground state. This, together with the fact that hydrochloric acid reconverts the compound, under release of hydrogen, to the titanocene chlorides, leads to the assignment of structure I for the reaction product.



This compound is the first paramagnetic hydride complex described. The meaning of the observed hyperfine parameters³ in terms of the electronic structure of the metal-hydride bond will be dealt with in another publication.

The way in which complex I is produced from $[\text{Cp}_2\text{TiCl}]_2$ might be visualized as involving ethylation of the titanocene by the Grignard reagent as a first step. From the metal alkyl, by a reversed insertion reaction, ethylene is then eliminated to yield the hydride. During this reaction period a mixture of mutual association products of Cp_2TiCl , Cp_2TiEt , and Cp_2TiH would then presumably be present, besides the respective dimers, a plausible explanation for the complexity observed in the transient epr spectrum.

Since complex I is the only detectable titanium species present in the reaction mixture during the period in which N_2 is being reduced to ammonia, there can be little doubt that it is the ingredient which enters into the reaction with the N_2 molecule. Moreover, its structure makes it very apt to do so. It contains, in the form of two hydride ions and two electrons of the Ti(III)-Ti(IV) couple, a total of 6 reducing equiv, exactly the number needed to conduct the reduction of N_2 to the NH_3 stage under circumvention of energetically unfavorable intermediates like diimine and others. Features of this reaction step will be discussed in subsequent communications.

Acknowledgments. The author wishes to thank Drs. R. H. Sands and R. W. Parry for helpful discussions about questions dealt with in this communication.

(3) The appearance of ten weak lines (those at the wings are readily discernible only at higher spectrometer amplification than that of Figure 1) explains itself by the near-equivalence of hydrogen and Ti^{49} hyperfine splittings (7.3 and 6.8 gauss, respectively); Ti^{49} ($I = 7/2$; $\mu = -1.102$), which occurs to only 5.5% in natural titanium and will therefore not be present twice in the same dimer to any detectable amount, splits each of the triplet components eightfold, so as to give the ten observed hyperfine lines. Hyperfine splitting due to Ti^{47} ($I = 3/2$; $\mu = -0.787$) should accordingly be 4.9 gauss. Since this splitting is not reinforced by coincidence with the hydrogen hyperfine splitting, it is observable only as weak shoulders on some of the more central Ti^{49} lines.

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.

(4) On leave from the University of Basel; travel support by the Privatdozenten-Fonds of the University of Basel and by the American-Swiss Foundation for Scientific Exchange is gratefully acknowledged.

Hans Brintzinger⁴

Biophysics Research Division and Department of Chemistry
The University of Michigan, Ann Arbor, Michigan

Received July 11, 1966

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 Nitrogen¹

Sir:

In a preceding publication¹ 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 $[\text{Cp}_2\text{TiCl}]_2$ (*g* = 1.980) to the starting material Cp_2TiCl_2 (absorption maximum 510 *m* μ).

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 anti-ferromagnetic interaction between the two Ti centers, comparable in size to that observed in related com-

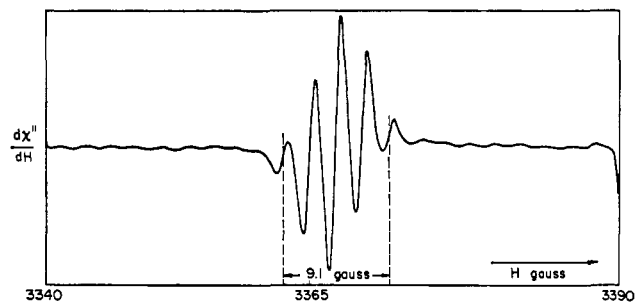
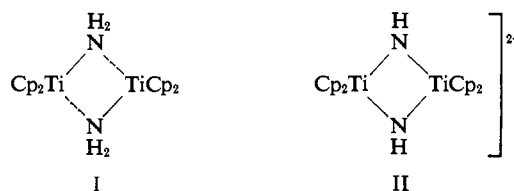


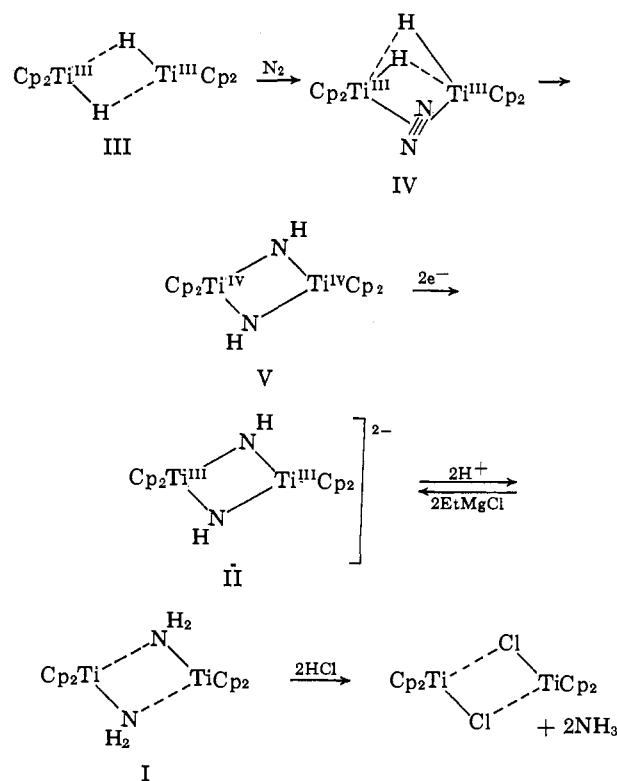
Figure 1. Electron paramagnetic resonance spectrum of a solution of 0.08 *M* Cp_2TiCl_2 and 0.8 *M* EtMgCl , which was kept under a nitrogen pressure of 150 atm for 15 days at room temperature after acidification of a 2-ml solution with 10 ml of hydrogen chloride gas. Microwave power 0.2 mw; microwave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

plexes 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



lose 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 anti-ferromagnetic interaction between the two Ti cores, the concomitant

Scheme I



(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.