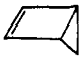
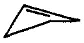
The electric dipole moment was measured by standard observations[10] of the Stark effect on the $1_{11} \rightarrow 2_{12}$ ($M = 0$), $1_{01} \rightarrow 2_{02}$ ($M = 1$), and $1_{01} \rightarrow 2_{02}$ ($M = 0$) transitions. The $J = 1 \rightarrow 2$, $M = 0$ transition of OCS[11] was used to calibrate the electric field strength in the absorption cell. The resultant moments were $\mu_a = 0.398 \pm 0.01$ D and $\mu_c = 0.025 \pm 0.002$ D. Thus, the total dipole is aligned very close to the a principal inertial axis with a value of $\mu = 0.398 \pm 0.01$ D. It is interesting to note the variation in the magnitude of the electric dipole moments in comparable molecules as shown below.

	0.398 ± 0.01 D	(this work)
	0.675 ± 0.01 D	(ref 7)
	0.190 ± 0.01 D	(ref 9)
	0.132 ± 0.01 D	(ref 6)
	0.419 ± 0.01 D	(ref 8)

In addition to the above molecular parameters, the molecular rotational Zeeman effect was also measured[12] which gives directly the molecular g values and magnetic susceptibility anisotropies.[13] Combining these parameters with the rotational constants (A, B, and C) gives the molecular quadrupole moments.[13] These values are listed below in Table II with the corresponding values for cyclobutene.[14]

Table II. Molecular g Values, Magnetic Susceptibility Anisotropies,[a] and Molecular Quadrupole Moments[b]

	Bicyclo[2.1.0]pent-2-ene	Cyclobutene[c]
g_{aa}	−0.0046 ± 0.0019	−0.0516 ± 0.0007
g_{bb}	−0.0342 ± 0.0011	−0.0663 ± 0.0006
g_{cc}	−0.0218 ± 0.0012	−0.0219 ± 0.0006
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	−14.9 ± 1.1	−0.9 ± 0.5
$-\chi_{aa} + 2\chi_{bb} - \chi_{cc}$	+7.8 ± 1.5	+5.0 ± 0.7
Q_{aa}	−1.9 ± 1.5	−0.3 ± 0.6
Q_{bb}	+2.7 ± 1.7	+1.6 ± 0.7
Q_{cc}	−0.8 ± 2.4	−1.3 ± 1.0

[a] In units of 10^{-6} erg/G^2 mol. [b] In units of 10^{-26} esu-cm^2. [c] The a axis in cyclobutene bisects the carbon–carbon double bond with a and b axes in the molecular plane.

The results of Table II indicate that **1** and cyclobutene possess similar magnetic properties and similar electric charge distributions. Values of $\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$ are also similar: +3.6 ± 1.4 for **1** and −2.0 ± 0.6 for cyclobutene. These anisotropies ($\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$) contrast sharply with the corresponding value of −34.3 in cyclopentadiene.[14,15] This large value of $\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$ in cyclopentadiene apparently indicates a ring current in this conjugated system.[16,17]

[10] S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

[11] J. S. Muenter, *ibid.*, **48**, 4544 (1968).

[12] For a description of the apparatus see: W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *ibid.*, **50**, 1417 (1969).

[13] W. Hüttner and W. H. Flygare, *ibid.*, **47**, 4137 (1967), and W. Hüttner, M. K. Lo, and W. H. Flygare, *ibid.*, **48**, 1206 (1968).

[14] R. C. Benson and W. H. Flygare, *ibid.*, in press.

[15] See ref 14; the numbers are cited in ref 16.

[16] J. H. S. Wang and W. H. Flygare, *J. Chem. Phys.*, **52**, 5636 (1970).

[17] J. M. Pochan and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 5928 (1969).

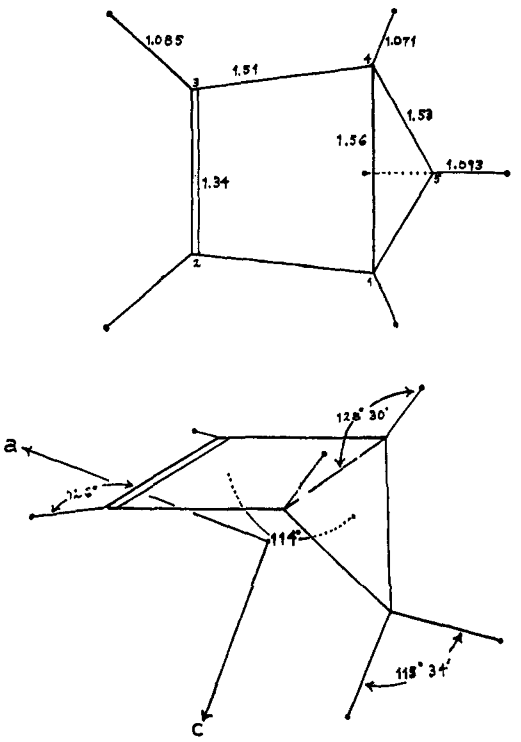


Figure 1. The molecular structure of bicyclo[2.1.0]pent-2-ene.

The small values of $\chi_{cc} - {}^1/_2(\chi_{aa} + \chi_{bb})$ in **1** and cyclobutene indicate small electron delocalization in these molecules relative to the apparent large electron delocalization in cyclopentadiene.[18,19]

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. We also thank Professor P. Beak for the use of his photochemical apparatus.

[18] D. H. Sutter and W. H. Flygare, *ibid.*, **91**, 4063 (1969).

[19] D. H. Sutter and W. H. Flygare, *ibid.*, **91**, 6895 (1969).

[20] University of Illinois Graduate Fellow.

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Intermediates in the Titanocene-Promoted Fixation–Reduction of Molecular Nitrogen

Sir:

Lower valent titanium species play an important role in the fixation of molecular nitrogen (N_2) under mild conditions, and have moved to center stage because of the chemical mutability of their nitrogen ligands and the mechanistic accessibility of these systems. Expressly basing experiments on the concept of titanium(II)[1] as the N_2-fixing type, this laboratory first reported: (1) the titanocene–naphthalide (Np) and

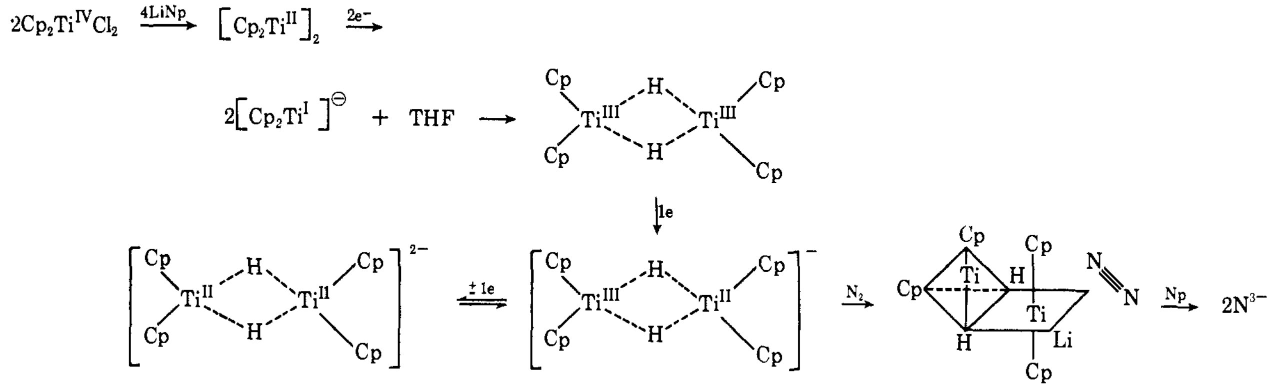
[1] E. E. van Tamelen and M. A. Schwartz, *J. Amer. Chem. Soc.*, **87**, 3277 (1965).

the titanium alkoxide-K^0 or Np induced conversion of N_2 to ammonia;[2] (2) the development of liquid-phase N_2 fixation–reduction cycles, fueled by electrical or chemical reduction means;[3-5] and (3) the preparation of a transition metal compound (titanocene–nitrogen), the ligand of which could be modified chemically.[6] Further study of the above systems now permits distinquishing among certain previously proposed fixation–reduction pathways and identification of the general course of the major reaction sequence.

In view of the above and other considerations this laboratory suggested route A, shown in generalized

$$N_2 + TiL_2 \rightleftharpoons (TiL_2\cdot N_2)_n \xrightarrow{e^-} 2nN^{3-} \qquad (A)$$

form, for the titanium-based fixation–reduction of N_2. On the other hand, Henrici-Olivé and Olivé later proposed a distinctly different scheme (B), based largely on esr studies carried out on Cp_2TiCl_2–LiNp *in the absence of N_2*.[7]



(B)

Summarized below are results which disallow scheme B as a major reaction pathway, but which are entirely consistent with the original proposal (A).

(1) A palpable feature of scheme B is the stoichiometric abstraction of protonic hydrogen from solvent THF by Cp_2Ti^- to give presumably THF anion and the hydrogen-bridged dimer of Cp_2TiH, the precursor of the nitrogen-fixing species. We have found that treatment with T_2O of a titanocene N_2 fixation–reduction reaction product does not lead to any isotopic labeling of the THF solvent, thereby indicating that no THF anion is present at the end of the fixation–reduction process. Further, by vpc criteria, no new products are formed in significant amount from THF solvent, and thus neither THF α radical nor carbonium ion is apparently formed by hydrogen loss from solvent. On the other hand, D_2O treatment of the reaction product does produce ratios of D_2, H_2, and HD (as high as 0.35:0.15:1.00) suggestive of one available hydrogen per titanium, a result indicating one reactive H deriving from the original titanium-bound C_5H_5 units.

(2) As reported early in 1969 by our laboratory[6] but not referred to in the later publication featuring proposal B, titanocene dimer is quantitatively converted by means of a reversible reaction in benzene

$$[(C_5H_5)_2Ti]_2 \underset{-N_2}{\overset{+N_2}{\rightleftharpoons}} [(C_5H_5)_2Ti\cdot N_2]_2$$

to the titanocene–nitrogen dimer, a result clearly demonstrating the ability of titanocene to fix N_2, as required by scheme A. In striking contrast, no N_2 is observably fixed by a reaction mixture prepared by treatment of titanocene dimer in THF with 3.0 equiv of sodium naphthalide, as would be expected on the basis of scheme B.

(3) Scheme B demands a maximum NH_3 yield of 1.0 per titanium center, and there was observed a value of 0.96 in a 16-hr reaction carried out in THF under 1 atm of N_2 with Li/Ti = 6. Starting with the titanocene–nitrogen compound, we have obtained in a more rapid reaction ~2.0 mol of NH_3 per titanium, a result in keeping with scheme A.

(4) In the case of both titanocene and titanium alkoxide N_2 fixation–reductions, the overall reaction proceeds much more slowly when the Ti(II) species is initially prepared under argon and used subsequently for the N_2 reaction, than when it is prepared and used, *in statu nascendi*, under N_2. Such results are consonant with generation of a highly reactive Ti(II) *monomer*, which rapidly fixes N_2 when available; but which, in the absence of N_2, is converted to Ti(II) polymer, an inefficient source of monomer in an equilibrium situation. As a titanium analog of a carbene, monomeric titanocene or titanium dialkoxide should react avidly with normally sluggish nucleophilic species, an early hypothesis[2] reinforced more recently on theoretical grounds.[8]

Although the above body of results negates scheme B as a *major* N_2 fixation–reduction pathway, reaction by a hydrogen abstraction route in a *slow*, low-NH_3-yield, process remains possible. In fact, this laboratory reported in 1967[2] and corroborated in 1969,[6] the *direct* production of NH_3 by means of a titanium-based process involving fixation–reduction of N_2 with some (10%) incorporation of solvent (THF) hydrogen into NH_3, but during the course of 4 weeks. It seems to us quite likely that the sensitive esr methods employed in the development of scheme B reveal minor constituents of a complex reaction mixture and have little to do with the major, *rapid* fixation–reduction process. In light of the foregoing, scheme A can be accepted and applied in expanded form to the titanocene case.[9]

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

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

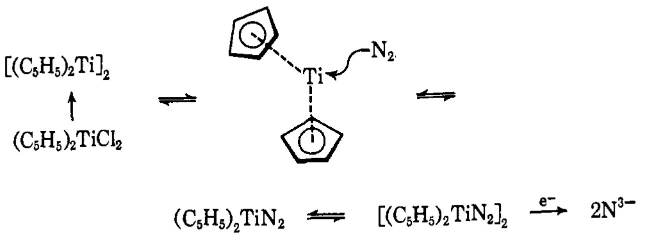
(4) E. E. van Tamelen and B. Åkermark, *ibid.*, **90**, 4492 (1968).

(5) E. E. van Tamelen and D. Seeley, *ibid.*, **91**, 5194 (1969).

(6) E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *ibid.*, **91**, 1551 (1969).

(7) G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **81**, 679 (1969).

(8) H. H. Brintzinger and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 1105 (1970).



Acknowledgment. The authors are grateful to the National Institutes of Health (Grant No. GM 13797) for financial support.

(9) In the pictorial presentation of titanocene monomer, the structure featuring noncoplanar C_5H_5 units is used, as suggested by Hückel calculations of Brintzinger and Bartell.[8]

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Utilization of Molecular Nitrogen in the Synthesis of Organic Amines and Nitriles

Sir:

Past efforts in this laboratory have led to the discovery of the first identifiable transition metal species bearing a nitrogen (N_2) ligand capable of chemical modification: $[(C_5H_5)_2TiN_2]_2$, stable in benzene solution under N_2, is quantitatively reducible to the ammonia level ($2NH_3/Ti$).[1] In the similar titanium alkoxide series, reduction of N_2 to hydrazine has been achieved.[2] We now wish to describe a reaction system, utilizing dicyclopentadienyltitanium chloride and magnesium metal as starting materials, which permits in one laboratory operation the incorporation of nitrogen from N_2 into various organic carbonyl compounds by means of an overall reductive deoxygenation process.[3]

In a typical experiment, a solution of Cp_2TiCl_2 (2.5 g, 10^{-2} mol) in anhydrous, oxygen-free THF (80 ml) is added portionwise to magnesium powder (1 g) in THF (10 ml), all under dry N_2. After a few minutes, the first portion of Cp_2TiCl_2 solution turns first green and then black while N_2 uptake begins. During 1 hr, about 60 ml of N_2 at 23° is absorbed. An excess (1.5 g) of diethyl ketone is added to the black solution, and the reactants are stirred at room temperature for 5 days. Water is added and the mixture extracted with Et_2O. The ethereal solution of amine is treated with aqueous acid; the acidic solution is then washed with Et_2O, made basic, and amine is extracted with Et_2O. A mixture of 3-pentylamine and di(3-pentyl)amine (2:1 ratio) is obtained in about 25–50% yield (based on fixed N_2). When the amination reaction is carried out at a higher temperature for a shorter period of time, a somewhat lower yield is observed. A similar result can be obtained using sodium naphthalide as the reducing agent with extra sodium being added after the addition of the ketone.

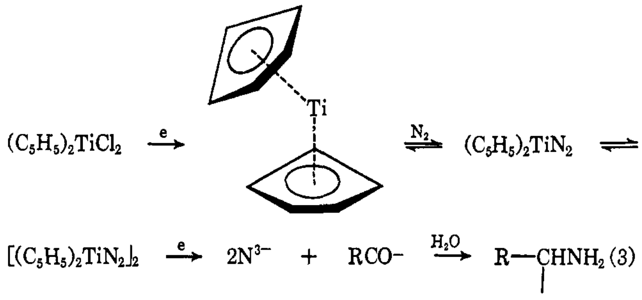
By means of reactions (eq 1) similar to that described above, di-*n*-butyl ketone is transformed into 5-nonyl- and di(5-nonyl)amines, and cyclohexanone can be converted to cyclohexylamine and dicyclohexylamine. In the aromatic series, benzaldehyde gives rise to benzylamine and some dibenzylamine, while benzophenone generates a poor yield (~5%) of benzhydrylamine. As an example of the acid chloride case, benzoyl chloride undergoes deoxygenation with incorporation of nitrogen, forming benzonitrile (eq 2). Low ester reactivity is revealed in the behavior of ethyl benzoate, which is minutely transformed into benzylamine. Product identification and yields are based on vpc and tlc data, including comparison with

$$R_2CO \longrightarrow R_2CHNH_2 + (R_2CH)_2NH \qquad (1)$$

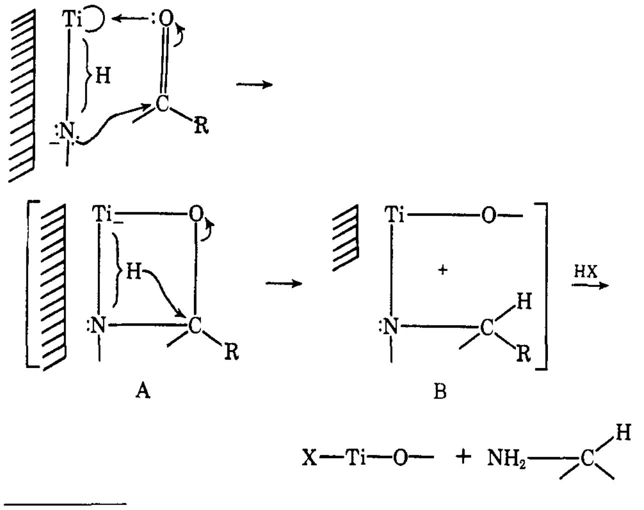
$$RCOCl \longrightarrow RCN \qquad (2)$$

authentic samples.

In view of prior studies on the course of titanium-based nitrogen fixation reactions[1,4] and the chronology of the presently described nitrogen incorporation, it seems likely that sequence 3 is operative.[5] Although the exact structural nature of the nitride intermediate is obscure,[1] a titanium–nitrogen(III) bond may be presumed available at this stage.[5] In that case there exists opportunity for an initial interaction with a carbonyl group in which an unshared electron pair on oxygen is accommodated by empty titanium orbitals while anionic nitrogen attacks carbon. In somewhat



(3)



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[1] E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969).

[2] E. E. van Tamelen, R. B. Fechter, and S. W. Schneller, *ibid.*, **91**, 7196 (1969).

[3] M. E. Vol'pin, V. B. Shur, R. V. Kudryavtsev, and L. A. Prodayco, *Chem. Commun.*, 1038 (1969), have reported the formation of aniline in 3% yield as a result of treatment of a mixture of dicyclopentadienyl titanium dichloride and phenyllithium with N_2.

[4] E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *J. Amer. Chem. Soc.*, **92**, 5251 (1970).

[5] The nonplanar representation of monomeric titanocene, proposed by H. H. Brintzinger and L. S. Bartell, *ibid.*, **92**, 1105 (1970), is used herein.