Bis(pentamethylcyclopentadienyl)titanium(II) and Its Complexes with Molecular Nitrogen

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Abstract: The synthesis of $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$ (**2**) from $[\eta^5\text{-}C_5(CH_3)_5]_2TiH_2$ is described. Physical properties for **2**, including ^1H nmr and ir spectra, molecular weight, and magnetic properties, are presented. In solution at room temperature **2** is observed to undergo a reversible ring methyl-to-titanium hydrogen shift to yield another isomer, $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiH$, and in the presence of D_2 **2** exchanges all 30 ring methyl hydrogens for deuterium. Above 60°, **2** decomposes predominantly to $[(C_5(CH_3)_5][C_5(CH_3)_4CH_2]Ti$. When **2** is treated with N_2 under appropriate conditions, $[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2$ (**4**), $[C_5(CH_3)_5]_2TiN_2$ (**6**), or $[(C_5CH_3)_5]_2Ti(N_2)_2$ (**7**) is obtained. **4** is isolated as a blue-black crystalline solid, and its physical and chemical properties are described. **6** is characterized in solution utilizing ^1H, ^{13}C, and ^{15}N nmr and ir data. Two isomers, $[C_5(CH_3)_5]_2Ti(\eta^1\text{-}N_2)$ and $[C_5(CH_3)_5]_2Ti(\eta^2\text{-}N_2)$, are detected at −61°, the forms having comparable concentrations at this temperature. On warming, these two forms are in rapid equilibrium on the nmr time scale Treatment of **6** with hydrogen chloride yields $[C_5(CH_3)_5]_2TiCl_2$, N_2, H_2, and N_2H_4. The product distribution of this reaction is not inconsistent with the suggestion that the reactive configuration which ultimately leads to N_2H_4 is that of the η^2 dinitrogen complex $[C_5(CH_3)_5]_2Ti(\eta^2\text{-}N_2)$.

The intermediacy of bis(cyclopentadienyl)titanium(II) in titanocene-based N_2-reducing systems has recently been recognized.[1–7] It has been shown that solutions of a metastable form of titanocene, $[(C_5H_5)_2Ti]_2$, prepared from a titanocene hydride,[1,2] sodium[7] or lithium amalgam[6] reduction of titanocene dichloride, or by treatment of $(C_5H_5)_2TiCl$ with CH_3MgI,[5c] absorb N_2 *in situ* in rapid reversible reactions to yield the blue[1,2,6,7] or black[5c] binuclear dinitrogen complex $[(C_5H_5)_2Ti]_2N_2$. The exact nature of this dinitrogen complex, particularly with respect to the crucial TiN_2Ti bonding situation, has not been established however. Furthermore, there still exist certain unresolved disparities concerning the preparation and properties of "$[(C_5H_5)_2Ti]_2N_2$," so that it now appears likely that there may indeed be more than one dinitrogen complex of titanocene.[8] These apparent contradictions are probably related to the fact that in no case has a uniform crystalline material been obtained. The inherent instability of the metastable species $[(C_5H_5)_2Ti]_2$ with respect to rearrangement to titanium hydride complexes *via* a ring-to-titanium α-hydrogen shift[1,7,9,10] is undoubtedly contributory. In view of the above, we have described the synthesis and partial characterization of the closely related bis(cyclopentadienyl)titanium(II) derivative, $[(\eta^5\text{-}C_5(CH_3)_5]_2Ti$.[1,3] More recently we have obtained some results which were not adequately explained on the basis of these earlier reports, so that a closer examination of permethyltitanocene and its behavior toward N_2 has been undertaken. This paper describes the results of that study.

Results

1. Dissociative Decomposition of Permethyltitanocene Hydrides. We have reported that the reaction of $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3$ with hydrogen yields permethyltitanocene dihydride, $[C_5(CH_3)_5]_2TiH_2$[1,3] (**1**).

$$[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3 + 2H_2 \longrightarrow [C_5(CH_3)_5]_2TiH_2 + CH_4 \qquad (1)$$

When dissolved in hydrocarbon solvents at room temperature *in vacuo*, **1** was found to slowly release H_2 with the formation of permethyltitanocene.[1,3]

On the basis of new experiments below, the decomposition of **1** is best described by the step-wise sequence, equilibria 2 and 3. (i) The course of the decomposition

$$\underset{\mathbf{1}}{[C_5(CH_3)_5]_2TiH_2} \rightleftharpoons \underset{\mathbf{2}}{[C_5(CH_3)_5]_2Ti} + H_2 \qquad (2)$$

$$\underset{\mathbf{1}}{[C_5(CH_3)_5]_2TiH_2} + \underset{\mathbf{2}}{[C_5(CH_3)_5]_2Ti} \rightleftharpoons \underset{\mathbf{3}}{2[C_5(CH_3)_5]_2TiH} \qquad (3)$$

of **1** in toluene was followed by monitoring the rate of hydrogen evolution. Initially there occurs a relatively rapid evolution of H_2 and after approximately 2 hr at 20°, 0.50 mmol of H_2/mmol of Ti is released. Continued stirring *in vacuo* results in additional H_2 evolution, however, at a rate which slows gradually; after 11 hr at 20° the total hydrogen released amounts to 0.86 mmol of H_2/mmol of Ti. Thus the rate H_2 evolution does not follow a simple first-order behavior as would be expected if (2) adequately described the decomposition of **1**. (ii) Cooling the solution which results after 0.50 mmol of H_2/mmol of Ti has been released from orange **1** yields a red-brown crystalline compound nearly quantitatively. This complex must therefore be of stoichiometry $[C_5(CH_3)_5]_2TiH$ (**3**). (iii) Cryoscopic

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[1] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972).

[2] R. H. Marvich and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **93**, 2048 (1971).

[3] J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **93**, 2046 (1971).

[4] E. E. van Tamelen, *Accounts Chem. Res.*, **3**, 361 (1970), and literature cited herein.

[5] (a) A. E. Shilov, A. K. Shilova, and E. F. Kvashina, *Kinet. Katal.*, 10, 1402 (1969); (b) A. E. Shilov, E. F. Kvashina, and T. A. Vorontsova, *Chem. Commun.*, 1590 (1971); (c) Y. G. Borod'ko, I. N. Ivleva, L. M. Kachapina, S. I. Salienko, A. K. Shilova, and A. E. Shilov, *J. Chem. Soc., Chem. Commun.*, 1178 (1972); (d) Y. G. Borod'ko, I. N. Ivleva, L. M. Kachapina, E. F. Kvashina, A. K. Shilova, and A. E. Shilov, *ibid.*, 169 (1973).

[6] C. Ungurenasu and E. Streba, *J. Inorg. Nucl. Chem.*, **34**, 3753 (1972).

[7] E. E. van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, *J. Chem. Soc., Chem. Commun.*, 481 (1972).

[8] Compare, for example, ref 1–3, 6, and 7 with 4 and 5.

[9] H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, **92**, 6182 (1970).

[10] M. E. Vol'pin, A. A. Belyi, V. B. Shur, Y. I. Lyakhovetsky, R. V. Kudryavtsev, and N. N. Bubnov, *J. Organometal. Chem.*, **27**, C5 (1971).

molecular weight determinations of a solution containing 112 mg of **3** per gram of C_6H_6 indicate a molecular weight of 331 ± 20; 319 is calculated for monomeric **3**. (iv) ^1H nmr spectra of **3** in toluene-d_8 exhibit a broad singlet attributable to the methyl hydrogens whose position varies according to the expected Curie dependence from 27.7 ppm at −30° to 22.2 ppm +30°.

On the basis of these new results, it appears that the original synthesis of $[C_5(CH_3)_5]_2Ti$, *via* cooling the solution which results from stirring **1** *in vacuo* for several hours, may be expected to yield a mixture[11] of **3** and **2**. Therefore the properties previously reported for $[C_5(CH_3)_5]_2Ti$ must be considered largely incorrect. We now find that the most convenient method to obtain analytically pure samples of $[C_5(CH_3)_5]_2Ti$ is *via* the binuclear dinitrogen complex described below.

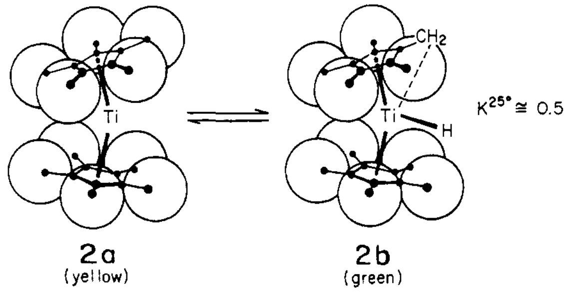
2. Synthesis of $[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2$ and $[C_5(CH_3)_5]_2Ti$. Properties of $[C_5(CH_3)_5]_2Ti$. Admission of 1 atm of N_2 to the yellow-green solution obtained by stirring **1** in toluene, until approximately 0.9 mmol of H_2/mmol of Ti has been evolved, results in darkening of the solution. After cooling at 0° for several minutes, a blue-black microcrystalline precipitate is obtained. This material may be filtered off, washed with pentane at −80°, and dried *in vacuo* without decomposition. Large well-formed crystals are obtained by slow diffusion of N_2 into unstirred pentane solutions of $[C_5(CH_3)_5]_2Ti$ at 0°. Such crystalline samples are stable for weeks under an atmosphere of pure nitrogen.

The blue-black complex is moderately soluble in toluene, pentane, and diethyl ether, and evolution of N_2 is observed under reduced pressure. Quantitative measurements of the amount of N_2 which is slowly released at room temperature *in vacuo* indicate the stoichiometry $[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2$ (**4**) for this dinitrogen complex (the properties of **4** are described more fully in section 3). Complete removal of solvent from the resulting solution at room temperature yields a yellow-orange crystalline material which, on the basis of the results below, has been identified as permethyltitanocene, $[C_5(CH_3)_5]_2Ti$ (**2**).

2 is extremely soluble in diethyl ether and hydrocarbon solvents, yielding yellow solutions at low temperature. On warming, however, a gradual transformation of the solution from yellow to yellow-green is observed. Slow removal of solvent from the resulting yellow-green solution at room temperature yields only the original yellow-orange crystalline material.[12] The above sequence may be carried out repeatedly with identical results indicating a slow, *reversible* rearrangement of **2** in solution. On the basis of the following evidence, these observations are attributed to a tautomeric behavior for permethyltitanocene. (i) Visible spectral changes of **2** in toluene illustrate the reversibility of the yellow ⇌ green conversion, wherein the yellow-to-green transformation follows first-order behavior with a half-life of 8 ± 0.5 min at 4.5°, 2 ± 1 min at 25°. (ii) Solvent participation in the equilibrium is excluded since the yellow ⇌ green behavior is observed in pentane as well as in toluene, benzene, and diethyl ether. (iii) The molecular weight, determined cryoscopically for a yellow-green solution containing 76.5 mg of **2** per gram of benzene, was 318 ± 20; 318 is the calculated molecular weight for monomeric **2**. (iv) Magnetic susceptibility measurements for yellow-orange microcrystalline samples of **2** indicate a gram magnetic susceptibility of 8.03×10^{-6} cgsu at 25°. The corrected effective magnetic moment varies slightly from 2.60 ± 0.01 BM at 298°K to 2.48 ± 0.02 BM at 129°K, values in reasonable agreement with that expected for a Ti(II) species with two unpaired electrons. (v) The infrared spectrum of **2** (Nujol mull of yellow-orange crystalline material) exhibits bands similar in position and intensity to those of $[\eta^5\text{-}C_5(CH_3)_5]_2Fe$ and $[\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2$ in the region 400–4000 cm^{-1} (see Experimental Section). In particular there are no absorptions in the region 1500–2000 cm^{-1} which may be attributed to Ti–H stretching frequency.

These data suggest that yellow-orange **2** is $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$ and that the green form is a *monomeric* complex of the same composition. Nmr studies are in accord with this suggestion. When yellow-orange microcrystalline samples of **2** are dissolved in toluene-d_8 at −80°, and the ^1H nmr spectrum is measured at −51° without further warming, the only signal observed is a moderately broadened (WHM = 150 Hz) singlet 86.2 ppm downfield of TMS. When this orange sample is then warmed to room temperature for 15 min so that green **2** grows in, cooled quickly back to −51°, and the spectrum again recorded, the original singlet is observed to decrease to 65% of its original intensity. Furthermore, a new set of resonances are now observed which consist of a series of sharp singlets at 2.18 (3 H), 1.80 (15 H), 1.62 (3 H), 1.36 (3 H), and 1.08 ppm (3 H) together with at least four smaller signals in this region. This new set of signals is quite reminiscent of that observed for $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3$[1,3] and strongly suggests that green **2** has the analogous structure $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiH$ (**2b**).

On the basis of these nmr experiments and the properties listed above, the tautomeric character of **2** in solution is best described by the rearrangement shown in eq 4. Thus the paramagnetically shifted singlet is attributed to the 30 equivalent methyl hydrogens of yellow **2a**. The position of this signal varies according to the Curie dependence from 86.2 ppm at −51° to 62.0 ppm at +27° and extrapolates at $1/T \rightarrow 0$ to 1 ± 5 ppm, in



(4)

2a (yellow)

2b (green)

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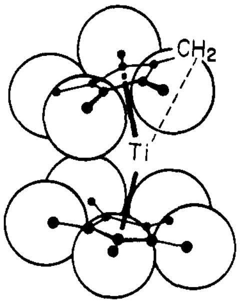
[11] The disparities noted previously[1] in the ir and nmr spectra of "$[C_5(CH_3)_5]_2Ti$" are now reconciled on the basis that this material was severely contaminated with **3**. For example, the nmr signal previously reported for **2**, the position of which did *not* deviate from Curie dependence as was expected due to interference of a monomer–dimer equilibrium, is now assigned to **3** impurity. Apparently the true ^1H signal due to **2**, which is shifted far downfield (see below), was not located in these earlier experiments. The unexplained absorption at 1575 cm^{-1} in the previously reported ir spectrum of **2** is now readily assigned to the Ti–H stretching frequency for this hydride impurity (*cf.* 1560 cm^{-1} for **1**).

[12] Rapid removal of solvent from these yellow-green solutions yields both yellow and green crystalline residues; however, after several minutes at room temperature the green crystals disintegrate to a yellow powder, indicating that yellow-orange **2** is the more stable crystalline form.

the region of the methyl resonance for diamagnetic $[\eta^5\text{-}C_5(CH_3)_5]_2TiX_2$ (X = Cl, CH_3, H) derivatives. The singlet at 1.80 ppm is attributed to the $[\eta^5\text{-}C_5(CH_3)_5]$ ring, and the singlets at 2.18, 1.62, 1.36, and 1.08 ppm are assigned to the four methyl groups of the $[C_5(CH_3)_4CH_2]$ ring of **2b**. The remaining smaller signals may be the multiplet expected for the methylene hydrogens of this ring which are necessarily nonequivalent. A resonance attributable to the Ti–H moiety has not been located unequivocally.

When a toluene solution of **2** was stirred with D_2 (composition: 97.0% D_2, 0.5% DH, 2.5% H_2; 0.85 mmol of D_2/mmol of Ti) for 2 hr at 20°, the gas on quantitative reversion to **2** consisted of 8.7% D_2, 41.3% DH, and 50.0% H_2, corresponding to 74.5% theoretical scrambling between the gas phase and all 30 hydrogen positions of the pentamethylcyclopentadienyl rings (ignoring kinetic isotope effects). After identical treatment with another equal portion of D_2 for an additional 12 hr, 93.1% theoretical scrambling had been achieved. The *reversible* ring methyl-to-titanium hydrogen shift which must be invoked for such D–H exchange is readily accommodated by equilibrium 4.[13]

While **2** undergoes this reversible rearrangement in solution at room temperature, this process does not seriously restrict its use in the preparation of other $[\eta^5\text{-}C_5(CH_3)_5]_2Ti^{II}$ derivatives (see below). However, **2** is of marginal stability only, and prolonged storage at room temperature or warming above 60° results in its decomposition with evolution of hydrogen. The major product of such a thermal decomposition of **2** is a dark violet crystalline complex which may be purified by sublimation at 80°, 10^{-3} Torr. Based on the evidence which follows, this violet complex is assigned the structure $[\eta^5\text{-}C_5(CH_3)_5][C_5(CH_3)_4CH_2]Ti$ (**5**). (i) The molecular weight, determined cryoscopically for a solution containing 193 mg of **5** per gram of benzene, was 325 ± 20; 317 is the calculated molecular weight for monomeric $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]Ti$. (ii) Magnetic susceptibility measurements for microcrystalline **5** indicate a gram magnetic susceptibility of 2.38×10^{-6} cgsu at 25°. The corrected effective magnetic moment is 1.53 ± 0.05 BM, a value in accord with that expected for a formal Ti(III) species with one unpaired electron. (iii) The infrared spectrum of **5** (see Experimental Section) is very similar to that of $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3$[14] and is considerably more complex in the region 1200–400 cm^{-1} than that observed for permethyltitanocene derivatives with only normal $[\eta^5\text{-}C_5(CH_3)_5]$ rings, entirely in accord with the spectrum expected for a compound with structure **5**.



5

The ^1H nmr spectrum for **5** in toluene-d_8 at +30° exhibits at least three severely broadened and shifted resonances: a very broad (WHM ≅ 1500 Hz) asymmetric signal centered 24.0 ppm downfield of TMS, a smaller broad (WHM ≅ 1000 Hz) signal centered 12.6 ppm downfield of TMS, and a third broad (WHM ≅ 400 Hz) singlet centered 10.9 ppm upfield of TMS. This spectrum is in accord with structure **5**; however, the signals were not sufficiently well resolved to allow unambiguous assignments. Cooling to −50° results in larger paramagnetic shifts of all signals concurrent with a marked further broadening (WHM ≅ 3000 Hz).[15]

3. Reactions of $[C_5(CH_3)_5]_2Ti$ with N_2. When solutions of permethyltitanocene, **2**, are exposed to N_2, any or all of three different dinitrogen complexes are formed. The specific dinitrogen complex which predominates in solution is markedly dependent upon the solubility of N_2 in the solvent, N_2 pressure, temperature, and total titanium concentration.

$[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2$ (**4**) whose synthesis has been described in section 2, is the least-soluble of these complexes and thus readily isolated as a blue-black crystalline solid. **4** is characterized by the following chemical and physical properties. (i) Crystalline **4** is moderately soluble in hydrocarbons, diethyl ether, and 1,2-dimethoxyethane, and quantitatively, but slowly, releases its nitrogen under reduced pressure, as expected from eq 5. (ii) The dark blue color of **4** arises from two characteristic, intense absorptions with λ_{max} at 512 and 642 nm ($\epsilon^{512} > 3 \times 10^3$, $\epsilon^{642} > 3.5 \times 10^3$). (iii) Magnetic susceptibility measurements for microcrystalline **4** yield a gram magnetic susceptibility of 5.83×10^{-6} cgsu at 25°. The corrected effective magnetic moment is thus 2.28 ± 0.01 BM[16] (per Ti), a value which

$$\underset{\mathbf{4}}{[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2} \rightleftharpoons \underset{\mathbf{2}}{2[C_5(CH_3)_5]_2Ti} + N_2 \qquad (5)$$

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[13] Several pathways can be envisioned for the actual D–H exchange mechanism. One possibility is that of the four species (**1**, **3**, **2a**, and **2b**) in mutual equilibrium under the reaction conditions, the reaction between $[C_5(CH_3)_5]_2TiD_2$ and **2b** leads to $[C_5(CH_3)_5]_2TiD$ and $[C_5(CH_3)_5][C_5(CH_3)_4CH_2D]TiD$, etc., or, similarly, the reaction between $[C_5(CH_3)_5]_2TiD$ and **2b** yields $[C_5(CH_3)_5]_2Ti$ and $[C_5(CH_3)_5][C_5(CH_3)_4CH_2D]TiH$, etc. In any event, D_2 exchange with ring-methyl protons requires a ring-metal hydrogen shift of the type represented in structure **2b**.

[14] J. E. Bercaw, Thesis, The University of Michigan, 1971.

[15] This empirical observation of extremely broad nmr signals appears to be a general feature of these Ti(III) derivatives. In contrast, the Ti(II) derivatives with two unpaired electrons exhibit nmr signals which are only slightly broadened to a degree (50–150 Hz) which is nearly temperature independent in the region −65 to +40°. These differences are undoubtedly reflections of the much shorter electron spin-lattice relaxation times for Ti(II) as compared to Ti(III) complexes. Thus, although very large nmr contact shifts are often observed, ^1H nmr studies of these paramagnetic Ti(II) complexes yield spectra sufficiently well resolved to provide much useful information (see below). For a complete discussion of these effects, see H. J. Keller and K. E. Sehwarzhans, *Angew. Chem., Int. Ed. Engl.*, **9**, 196 (1970).

[16] This magnetic moment is considerably lower than the spin-only value of 2.83 BM for two unpaired electrons (per Ti) predicted for two magnetically decoupled, high spin Ti(II) centers. Similarly the magnetic moment for **2a** of 2.60 BM is significantly lower than the spin-only of 2.83 BM. Very little magnetic data appear to be available for Ti(II) compounds for comparison; however, quite curiously, Na_2TiCl_4 exhibits a magnetic moment of only 2.43 BM at 27°, a value which could not be readily explained.[17] Organometallic Ti(III) derivatives also exhibit moments below the 1.73 BM spin-only value, *e.g.*, 1.69 BM for $(C_5H_5)_3Ti$,[18] 1.60 BM for $(C_5H_5)(C_8H_8)Ti^{III}$,[19] and 1.60 BM for $(C_5H_5)_2TiC_6H_5$.[20] The factors responsible for the apparent negative orbital contributions to the magnetic moments of these compounds are not understood.

[17] J. Lewis, D. J. Machin, I. E. Newnham, and R. S. Nyholm, *J. Chem. Soc.*, 2036 (1962).

[18] E. O. Fischer and A. Löchner, *Z. Naturforsch. B*, **10**, 353 (1955).

[19] H. O. van Oven and H. J. deLiefde Meijer, *J. Organometal. Chem.*, **19**, 373 (1969).

[20] J. H. Teuben and H. J. deLiefde Meijer, *Recueil*, **90**, 360 (1971).

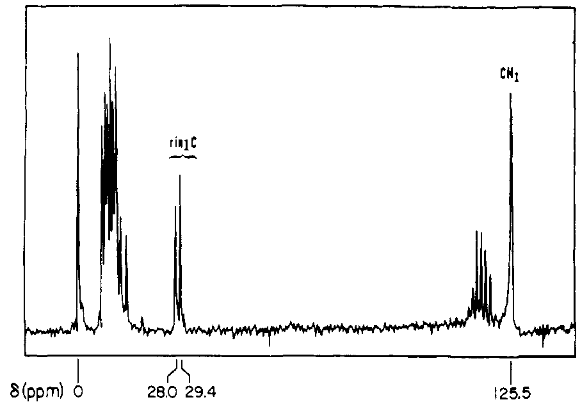
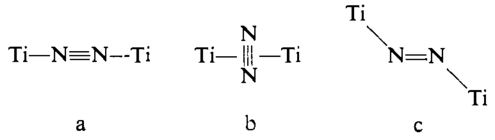


Figure 1. A 15.09-MHz ^1H decoupled ^{13}C nmr spectrum of $[C_5(CH_3)_5]_2TiN_2$ in toluene-d_8 at −65°. All unlabeled signals are attributable to $C_6D_5CD_3$.

is invariant over the region 107–298°K. (iv) The infrared spectrum of **4** (Nujol mull) is quite simple exhibiting only those few bands characteristic of $[\eta^5\text{-}C_5(CH_3)_5]$ rings in the region 4000–700 cm^{-1}, nearly identical with the spectrum of **2** in this region. Between 700 and 400 cm^{-1} the two spectra are also similar except for a band of medium intensity at 617 cm^{-1} observed only for **4**. A significant feature is the absence of any band in the region 1600–2300 cm^{-1} which could be attributed to a N≡N stretching mode, indicative of a centrosymmetric TiN_2Ti substructure (a, b, or c).



a b c

The ^1H nmr spectra for **4** in toluene-d_8 (Table I) exhibit a paramagnetically shifted, slightly broadened singlet at −55°, illustrating the equivalence of all methyl groups in the dimer. Upon stepwise warming to +30°, this signal undergoes an upfield shift which does not, however, follow the usual Curie dependence. Furthermore, there occurs a concurrent severe broadening of the signal. Both of these observations are attributed to the onset of the dissociative reaction (eq 5)[21] which occurs on the nmr time scale at approximately +30°, so that the two higher temperature resonances represent an average signal due to **4** and **2a** (see above).

Table I. The 220 MHz ^1H Nmr Data for the Methyl Resonance of $[\eta^5\text{-}C_5(CH_3)_5]_2TiN_2Ti[\eta^5\text{-}C_5(CH_3)_5]_2$. [**4**] = 0.025 *M* in toluene-d_8

T, °C	δ (ppm)[a]	WHM (Hz)
−55	60.9	70
−40	56.9	90
−16	53.5	320
+30	48.2	2080

[a] Calculated relative to the residual aromatic protons of toluene-d_8 and converted to values relative to (and downfield of) TMS at δ 0.

On cooling toluene solutions of **2** or **4** below −10° under 1 atm of nitrogen there occurs a rapid color change to intense purple-blue. At −80° the ligated dinitrogen in this complex is entirely retained, even under reduced pressure. Measurements of the nitrogen released on reversion to **2** at room temperature are in quantitative agreement with the stoichiometry $[C_5(CH_3)_5]_2TiN_2$ (**6**), for this low-temperature-stable, purple-blue dinitrogen complex. The purple-blue color of **6** is due to an intense absorption with λ_{max} at 578 nm ($\epsilon > 10^4$). **6** is extremely soluble in toluene, diethyl ether, hexane, and 1,2-dimethoxyethane, but from very concentrated hexane solutions, a dark purple microcrystalline precipitate may be obtained at −80°. This material is quite unstable with respect to conversion to **4**, even as a solid, on warming to room temperature, thus thwarting all attempts to obtain a uniform crystalline material suitable for further studies in the solid state. However, its extreme solubility does conveniently allow a study of its structure in solution.

The ^1H nmr spectrum of **6** in toluene-d_8[22] at −52° shows a single, somewhat broadened, resonance centered at δ 1.78 ppm. On cooling to −62°, this signal splits into two resonances of approximately equal intensity at 1.88 and 1.68 ppm. Further cooling to −72° results in no substantial further change, whereas warming to above −45° leads to severe broadening of the signal, probably due to the onset of dissociative exchange with **2** (eq 6) and/or **4** (eq 7). Below −45°,

$$\underset{\mathbf{6}}{[C_5(CH_3)_5]_2TiN_2} \rightleftharpoons \underset{\mathbf{2}}{[C_5(CH_3)_5]_2Ti} + N_2 \qquad (6)$$

$$\underset{\mathbf{6}}{2[C_5(CH_3)_5]_2TiN_2} \rightleftharpoons \underset{\mathbf{4}}{[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2} + N_2 \qquad (7)$$

2 and **4** do not appear to be present to a significant extent as judged by the absence of their characteristic ^1H nmr signals. The results thus imply the presence of two forms of **6** which are in rapid equilibrium on nmr time scale above −62°.

This interpretation is supported by ^{13}C nmr spectra of the same sample (Figure 1). Below −45°, two resonances of approximately equal intensity are observed at 28.0 and 29.4 ppm (upfield of the C_1 resonance of toluene-d_8), attributable to the ring carbons of the two forms of **6**. At higher field, a single, slightly broadened resonance attributable to the methyl carbons of **6** appears at 125.5 ppm. These assignments were confirmed by comparison with ^{13}C shifts of $[\eta^5\text{-}C_5(CH_3)_5]_2Ti(CH_3)_2$,[23] and by the spectrum at −58° without proton decoupling, the highest field signal being then the expected quartet. Clearly, the two forms of **6** differ only slightly in structure because only the ring carbons exhibit resolvable chemical-shift differences.

The ^{15}N nmr studies of **6** were undertaken using a sample prepared as before except substituting 1 atm of doubly labeled $^{15}N_2$[24] for ordinary dinitrogen. The ^1H-decoupled ^{15}N nmr spectrum at −61° (Figure 2) showed two doublets centered 84.6 and 134.0 ppm, respectively, upfield of a third, rather sharp, singlet resonance. These signals, taken in conjunction with

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(21) After warming above −40°, additional resonances, attributable to the other two dinitrogen complexes **6** and **7** as well as a small amount of **2b**, grow into the spectrum also. However, **2a** and **4** are the major species present under these experimental conditions.

(22) A total of 210 mg of **2** in 3.3 ml of $C_6D_5CD_3$ was stirred under 1 atm of nitrogen, filtered into a 10-mm nmr tube, and sealed off under N_2, with all operations being carried out at −80°.

(23) The ^1H decoupled ^{13}C nmr spectrum (toluene-d_8): $[\mathit{C}_5(CH_3)_5]_2Ti(CH_3)_2$, s, δ 17.8 ppm; $[C_5(\mathit{C}H_3)_5]_2Ti(CH_3)_2$, s, 118.8; $[C_5(CH_3)_5]_2Ti(\mathit{C}H_3)_2$, s, 88.6.

(24) Merck Sharpe, and Dohme "$^{15}N_2$" with a composition (mass spectrum) of $^{15}N{\equiv}^{15}N$, 91.6%; $^{15}N{\equiv}^{14}N$, 7.6%; and $^{14}N{\equiv}^{14}N$, 0.87%.

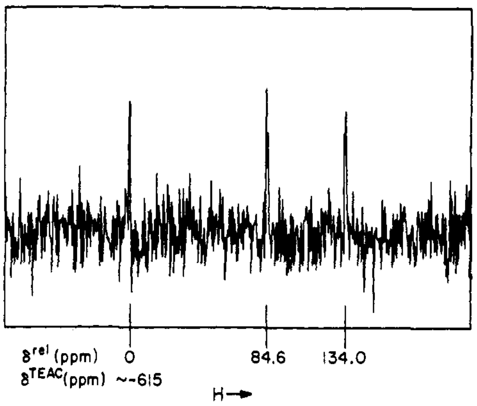
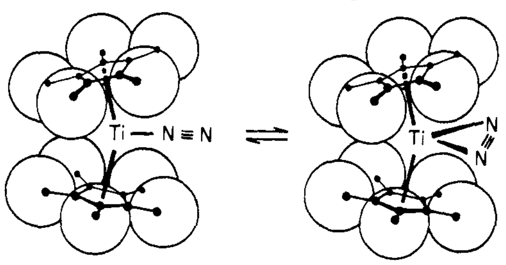


Figure 2. A 6.08-MHz ^1H decoupled ^{15}N nmr spectrum of $[C_5(CH_3)_5]_2Ti(^{15}N{\equiv}^{15}N)$ in toluene-d_8 at −61°. The low field signal is observed approximately 615 ppm downfield of a separate sample of 11 *M* aqueous $(C_2H_5)_4{}^{15}NCl$.

the ^1H and ^{13}C nmr data, are indicative of an "end-on" (η^1-N_2) ⇌ "edge-on" (η^2-N_2) equilibrium for **6** (eq 8),



(8)

η^1-**6** η^2-**6**

with the forms having comparable concentrations at this temperature. The two doublets are attributed to η^1-**6** wherein the nonequivalent ^{15}N nuclei are magnetically coupled with $^1J_{^{15}N-^{15}N} = 7 \pm 2$ Hz.[25] The remaining singlet resonance[26] is highly indicative of the presence of η^2-**6**, because this configuration, in which the $[C_5(CH_3)_5]$ rings and nitrogen ligand atoms are positioned in a pseudotetrahedral arrangement about Ti, appears to be the only possible monomeric structure containing magnetically equivalent nitrogen nuclei.

The infrared spectrum of **6** in heptane[27] at −65° (Figure 3) provides quite convincing evidence for two distinct isomers which differ in their modes of nitrogen coordination to Ti. As can be seen there is a band at 2056 cm^{-1} of medium intensity and a strong band at 2023 cm^{-1}, which may be attributed to the N≡N stretching frequencies of η^2-**6** and η^1-**6**. Although we are unable to make specific assignments, the observation of two bands is clearly consistent with eq 8 (further discussion of these ir data is deferred to the Discussion section below).

Gradual warming to +3° results in a decreased intensity for both bands and a small but measurable change in their relative intensities in favor of the species responsible for the 2023-cm^{-1} band (most likely η^1-**6**) at higher temperatures. Concurrent with the decrease in the bands arising from **6**, two new bands at 2086 and 1980 cm^{-1} grow in at the same rate. These bands are attributed to the symmetric and asymmetric N≡N stretching modes of the bis-dinitrogen complex $[C_5(CH_3)_5]_2Ti(N_2)_2$ (**7**), probably formed *via* the N_2 exchange reaction (eq 9). **7** has a transient existence only,

$$\underset{\mathbf{6}}{3[C_5(CH_3)_5]_2TiN_2} \rightleftharpoons \underset{\mathbf{4}}{[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2} + \underset{\mathbf{7}}{[C_5(CH_3)_5]_2Ti(N_2)_2} \quad (9)$$

however, and warming to above 20° results in near disappearance of all four ir bands. Under these conditions **4** and **2** (eq 5) are the predominant species in solution, **6** and **7** now being represented by only very small concentrations.

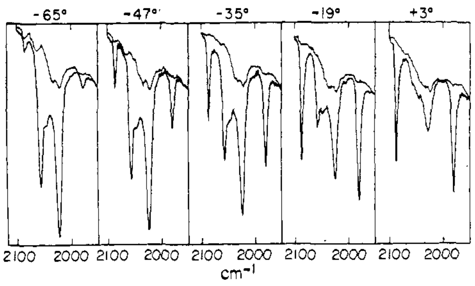


Figure 3. Infrared spectra of **6** (−65°) and of a mixture of **6** and **7** (four higher temperatures) in heptane. The thin lines represent the spectra of pure heptane.

7 appears to have the most elusive existence of the three dinitrogen complexes of permethyltitanocene, and no conditions were found under which it either precipitated cleanly or was formed exclusively in solution. **7** is favored, however, at low Ti concentrations in solvents for which N_2 is very soluble (*e.g.*, diethyl ether, pentane). Apart from the ir data above, **7** is characterized by the following properties. (i) Its yellow-brown color results from two characteristic absorptions with λ_{max} 354 nm ($\epsilon > 2 \times 10^4$) and λ_{max} 424 nm ($\epsilon > 2 \times 10^4$). (ii) Under conditions where its formation is expected on the basis of ir experiments (between −16 and −55° in toluene-d_8, 1 atm N_2), a singlet (WHM = 50 Hz) attributable to **7** is observed 13.7 ppm downfield of TMS at −55° in addition to the characteristic signals assigned to **4** and **6** (see above). The position of this signal varies according to the expected Curie dependence in this temperature region, but cooling below −55° results in disappearance of the signals due to both **4** and **7** and a corresponding increase in the signal due to **6**, as expected from eq 9.

4. Reactions of Permethyltitanocene and Its Dinitrogen Complexes. The expected $[\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2$ is obtained in high yield on treatment of **2** with excess HCl at −80° in toluene. Slightly less than the required amount of H_2 (0.865 mmol of H_2/mmol of **2**) is evolved in this reaction (eq 10).[28] Similar treatment

$$[\eta^5\text{-}C_5(CH_3)_5]_2Ti + 2HCl \longrightarrow [\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2 + H_2 \quad (10)$$

of a toluene solution of **6** with HCl at −80° yields $[\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2$ with the evolution of a mixture of N_2 and H_2 (composition: Ti:N_2:H_2 = 1.000:0.730:

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[25] When account is taken of the difference in gyromagnetic ratios, this coupling is comparable to the ^{13}C–^{15}N coupling of 19.8 Hz observed for HC≡N: G. Binsch and J. D. Roberts, *J. Phys. Chem.*, **72**, 4310 (1968).

[26] The possibility of the singlet resonance arising from free $^{15}N_2$ seems remote because its solubility at −60° is at least 200 times less than the experimental concentration of **6**.

[27] Except for minor frequency shifts, nearly identical results were observed in toluene; however, this solvent was less suitable than heptane due to the interference of several weaker solvent peaks in the region of interest.

[28] The nmr spectrum of this product shows the presence of 16% $[\eta^5\text{-}C_5(CH_3)_5]TiCl_3$ but is otherwise identical with that of an authentic sample of $[\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2$. The formation of this by-product is probably related to the lower yield of H_2.

0.425). A white crystalline solid, identified as $N_2H_4 \cdot 2HCl$ is obtained *via* extraction of the residue from this reaction with 6 *M* HCl. This product distribution is indicative of the occurrence of two reactions (eq 11 and 12).

$$6 + 2HCl \begin{cases} \xrightarrow{45\%} [\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2 + N_2 + H_2 & (11) \\ \xrightarrow{55\%} [\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2 + \tfrac{1}{2}N_2 + \tfrac{1}{2}N_2H_4 & (12) \end{cases}$$

The reaction of the dimeric dinitrogen complex, **4**, with excess HCl under same conditions yields a mixture of $[\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2$ and $[C_5(CH_3)_5]TiCl_3$, again with evolution of N_2 and H_2 (composition: $Ti:N_2:H_2 = 1.000:0.454:0.555$).[28] A very low yield (<5%) of ammonium chloride was extracted from the residue of this reaction with 6 *M* HCl.

It was not possible, however, to effect direct reduction of the ligated N_2 in these dinitrogen complexes. Treatment of a benzene solution of **4** with excess Mg/Hg for 92 hr at room temperature (1 atm of N_2) resulted in no visible change, and neither ammonia nor hydrazine was obtained upon subsequent hydrolysis of this reaction mixture. Furthermore, treatment of toluene solution of **2** with an N_2/H_2 mixture ($Ti:N_2:H_2 = 1.000:4.000:0.447$) for 8 hr at 3° resulted in no reduction of N_2 to either NH_3 or N_2H_4.

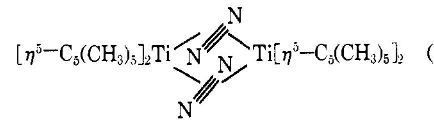
Discussion

In sections 1 and 2 of this paper, the synthesis and isolation of a coordinatively unsaturated, highly reactive bis(cyclopentadienyl)titanium(II) species, $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$, has been described. A more direct synthesis of this complex *via* reduction of $[\eta^5\text{-}C_5(CH_3)_5]_2TiCl_2$ would certainly be desirable; however, the relatively slow rates observed for Mg/Hg, Na/Hg, or Na–K alloy reductions of permethyltitanocene dichloride were found to be comparable with the decomposition rate for the desired product **2**, so that the major complex isolated from each of these reaction mixtures is, in fact, the thermal decomposition product **5**. Analytically pure samples of **2** are thus most conveniently obtained *via* the indirect route described previously,[1,3] with the modifications described in sections 1 and 2. The results described herein appear to reconcile most of the previously noted[1,3] disparities concerning the nature of permethyltitanocene.

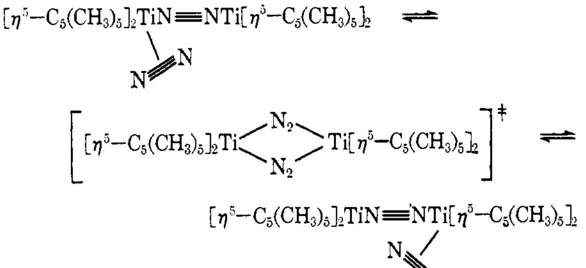
While $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$ appears to be sufficiently stable for determination of its structure and chemical reactivity, a favored rearrangement appears to be ring methyl hydrogen abstraction by the titanium center, in close analogy to the facile α-hydrogen shift from ring to Ti observed for $[(\eta^5\text{-}C_5H_5)_2Ti]_2$.[1,7,9,10] The propensity for these electron-deficient, 14-electron species to insert intramolecularly into their C–H bonds is undoubtedly a reflection of their tendency to expand their valence shells into the two adjacent empty coordination sites. While in both cases this C–H insertion process is easily reversed, there appears to be no readily accessible secondary reaction pathway to a more stable, dimeric complex available for $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$. Thus, whereas $[(\eta^5\text{-}C_5H_5)_2Ti]_2$ eventually rearranges to the green "titanocene" dimer,[29] the steric crowding and concomitant preference for monomeric complexes appear to make for a rather clear-cut, almost totally reversible C–H insertion process for $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$ (eq 4).

These differences attributable to the increased steric crowding in dimeric permethyltitanocene derivatives are also manifested in reactions with N_2. Stable binuclear complexes are obtained in rapid, reversible reactions of both $[\eta^5\text{-}C_5(CH_3)_5]_2Ti$ and $[(C_5H_5)_2Ti]_2$ with N_2, but here again the preponderance of monomeric derivatives of permethyltitanocene is evidenced by the formation of two new dinitrogen complexes, $[\eta^5\text{-}C_5(CH_3)_5]_2TiN_2$ and $[\eta^5\text{-}C_5(CH_3)_5]_2Ti(N_2)_2$.

The data presented in section 3 are interpreted in terms of a dinitrogen complex, $[\eta^5\text{-}C_5(CH_3)_5]_2TiN_2$, which contains an N_2 ligand bonded "edge-on" to a transition metal in rapid equilibrium with another isomer with a "more conventional" end-on bonded N_2 ligand. While this equilibrium (eq 8) appears to be the most straightforward interpretation of the data, the complexity of the system elicits other alternative explanations. For example, an equilibrium involving η^1-**6** and a dimer such as $[\eta^5\text{-}C_5(CH_3)_5]_2Ti(\mu\text{-(di-}\eta^2\text{-)}N_2)_2\text{-}Ti[\eta^5\text{-}C_5(CH_3)_5]_2$ could be invoked (eq 13). Although eq 13 could equally well explain the nmr and ir results at one temperature, the small shift in the equilibrium observed in the ^1H and ^{13}C nmr and ir experiments over a range of temperatures is much more indicative of an intramolecular process.


(13)

Other choices of an intramolecular equilibrium (eq 14 and 15) could also be offered as alternative interpretations of the data.[30] Although such fluxional dimeric complexes do appear attractive in that either offers an alternative to some of the more puzzling aspects of eq 8 (*e.g.*, the observation of comparable concentra-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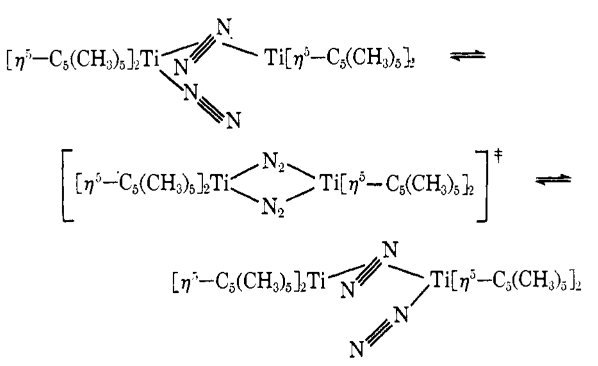
(15)

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(29) The structure of this green "titanocene" appears to be the fulvalenide and hydride bridged complex $[(\eta^5\text{-}C_5H_5)TiH]_2(C_{10}H_8)$ in view of recent results by L. J. Guggenberger and F. N. Tebbe, *J. Amer. Chem. Soc.*, **95**, 7870 (1973).

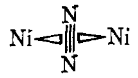
(30) W. E. Newton, J. L. Corbin, J. W. McDonald, and G. D. Watt, private communication.

tions of η^1-**6** and η^2-**6** and the temperature dependence of the stabilities for **4**, **6**, and **7**),[30] they are less attractive than eq 8 in other respects (*e.g.*, the relative intensities of the ^{15}N nmr signals and the change in relative intensities of the two ir bands, Figures 2 and 3). Unfortunately, reliable molecular weight measurements, which could unequivocally differentiate between equilibria 8 and 13 and 14 and 15, do not appear experimentally feasible due to the instability of **6** with respect to conversion to **4** at temperatures above −45°. Further speculation appears unjustified at this point. Hopefully the results of the structural determination for **4** together with studies presently under way on a related zirconium system[31] will help to clarify the nature of **6**.

One significant feature common to equilibrium 8 and the three most viable alternatives, equilibria 13, 14, and 15, is the edge-on coordination of dinitrogen. Orgel[32] was first to consider the possibility of such a η^2 bonding mode for an N_2 ligand, and he concluded η^2-N_2 is favored relative to η^1-N_2 more than is η^2-CO relative to η^1-CO, although no decision was possible concerning the relative stabilities of η^2-N_2 and η^1-N_2 on the *absolute* scale. More recently Yatsimirskii and Kraglyak[33] have concluded that, on the basis of extended Hückel molecular orbital calculations, η^2-N_2 is less stable than η^1-N_2 for FeN_2. Experimentally, end-on coordination of N_2 has either been established by structural studies or inferred from ir data in the overwhelming majority of previously described metal–N_2 complexes.[34] These observations thus strongly suggest that η^1-N_2 is favored relative to η^2-N_2 for the "stable" dinitrogen complexes, of which those containing a formal d^6 metal center (*e.g.*, Mo(0), W(0), Mn(I), Re(I), Fe(II), Ru(II), Os(II)) are particularly well represented.

Concurrent with these studies, Ozin and Voet[35] recently reported cobalt dinitrogen isotopic species $Co^{14}N_2$, $Co^{14}N^{15}N$, and $Co^{15}N_2$ formed in the cocondensation reaction of atomic cobalt with dilute nitrogen–argon matrices at 10°K. Their infrared data could only be interpreted in terms of a $Co(\eta^2\text{-}N_2)$ species, providing the first unambiguous spectroscopic evidence for a dinitrogen molecule bonded in a "side ways" (edge-on) fashion to a transition metal atom. Two features of their infrared data are similar to those of the spectra observed for $[\eta^5\text{-}C_5(CH_3)_5]_2Ti(\eta^2\text{-}N_2)$ and $[\eta^5\text{-}C_5(CH_3)_5]_2Ti(\eta^1\text{-}N_2)$ (Figure 3): (1) a comparison of the relative intensities for the N≡N stretching mode in $Co(\eta^2\text{-}N_2)$ and $Ni(\eta^1\text{-}N_2)$ indicates that while the η^1 configuration results in a stronger band, η^2-bonded N_2 exhibits a band of sufficient intensity to be easily detected;[36] (2) the N≡N stretching frequency for $Co(\eta^2\text{-}N_2)$, 2101 cm^{-1}, is 12 cm^{-1} *above* that of $Ni(\eta^1\text{-}N_2)$, 2089 cm^{-1}. The spectra of $Co(\eta^2\text{-}N_2)$ and of η^1-**6** and η^2-**6** appear to dispel preconceived expectations that edge-on N_2 complexes may exhibit their ν_{NN} band at considerably lower frequencies and of much lower intensity than end-on bonded N_2 complexes.

A structure related to η^2-**6**, containing a bridging η^2-N_2 has been suggested for $(C_5H_5)_2TiN_2Ti(C_5H_5)_2$ on the basis of chemical intuition.[1] Recent reports by Jonas[37] and Krüger and Tsay[38] describe the crystal structure of a binuclear nickel dinitrogen complex which contains such a η^2-N_2 bridge.[39]



While this observation and the findings described in this work concerning the structure of **6** do lend credence to this proposed structure for $(C_5H_5)_2TiN_2Ti(C_5H_5)_2$, a "more conventional" linear TiN≡NTi substructure must also be considered, since η^1-N_2 coordination for titanocene dinitrogen complexes has now been established as well. An X-ray structure determination for $[\eta^5\text{-}C_5(CH_3)_5]_2TiN_2Ti[\eta^5\text{-}C_5(CH_3)_5]_2$, in progress at the time of this writing, should settle the questions concerning the favored mode of Ti–N_2–Ti bonding in dimeric titanocene dinitrogen complexes.

Previous attempts to protonate and reduce η^1 dinitrogen complexes usually leads to protonation and oxidation of the metal with liberation of N_2, sometimes together with H_2.[40] Chatt and coworkers have observed protonation of one of the ligated dinitrogens in complexes of the type *trans*-$[M(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2]$, M = Mo, W;[41] however, the release and further reduction of the resulting $[N_2H_2]$ moiety have not as yet been realized. In section 4 of this paper, reactions of **4** and **6** with excess HCl were described. It is interesting to note that for **6** (eq 11 and 12), two pathways, which contribute nearly equally to the net reaction, are implied by the product distribution. Although the mechanisms of these reaction pathways are at present not completely understood,[42] the relative concentrations of η^1-**6** and η^2-**6**, based on the nmr and ir results described herein, may well suggest that the reactive configuration which ultimately leads to N_2H_4 is that of the η^2 dinitrogen complex η^2-**6**.

Experimental Section

Physical Measurements. ^{1}H nmr spectra were recorded on Varian 220 (CW), XL-100 (FT), T-60, and A-60A spectrometers. ^{13}C and ^{15}N nmr spectra were obtained at 15.09 and 6.08 MHz, respectively, on a DFS-60 (FT) spectrometer described earlier.[43] Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer. Low-temperature spectra were obtained in a vacuum-tight solution cell equipped with sapphire windows mounted in a Research and Industrial Instrument Co. VLT-2 dewar with KBr windows. Uv-visible spectra were run on Cary 14 and 17 spectrophotometers. Magnetic susceptibilities were measured on Par Model FM-1 vibrating sample magnetometer modified by Professor George Rossman of this institute as described earlier[44] and cali-

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(31) J. M. Manriquez and J. E. Bercaw, unpublished results.

(32) L. E. Orgel, "An Introduction to Transition-metal Chemistry," Metheun, London, 1966.

(33) K. B. Yatsimirskii and Yu A. Kraglyak, *Dokl. Akad. Nauk SSSR*, **186**, 885 (1969).

(34) A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens, and R. N. Whiteley, *Chem. Rev.*, **73**, 11 (1973).

(35) G. A. Ozin and A. V. Voet, *Can. J. Chem.*, **51**, 637 (1973).

(36) Approximately half that of η^1-N_2, assuming comparable matrix concentrations of $Co(\eta^2\text{-}N_2)$ and $Ni(\eta^1\text{-}N_2)$ in ref 35.

(37) K. Jonas, *Angew. Chem., Int. Ed. Engl.*, **12**, 997 (1973).

(38) C. Krüger and Y.-H. Tsay, *Angew. Chem., Int. Ed. Engl.*, **12**, 998 (1973).

(39) This complex, $[(C_6H_5Li)_6Ni_2N_2(Et_2O)_2]_2$, has a centrosymmetric dimeric structure containing at least four lithium atoms, in addition to the two Ni atoms, within bonding distances of each N_2 unit.

(40) J. Chatt, J. E. Fergusson, R. L. Richards, and J. R. Sanders, *Nature (London)*, **221**, 551 (1969).

(41) J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1010 (1972).

(42) The formation of diimide, which subsequently disproportionates to hydrazine and N_2, has been suggested to explain the formation of hydrazine in the reaction of a titanocene–dinitrogen complex with HCl (ref 5c).

(43) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970).

(44) H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Amer. Chem. Soc.*, **94**, 2683 (1970).

brated against $HgCo(SCN)_4$. Molecular weights were obtained cryoscopically in benzene using an air-tight cell equipped with a Cu *vs.* constantan thermocouple well. Thermocouple potentials (*vs.* a 0° reference junction) were continuously monitored and amplified by an HP Model 425 AR dc microvolt ammeter and recorded on a Moseley Model 135 xy recorder operating in the time base mode. At least eight cooling curves were measured for each sample, the freezing points so obtained deviating by less than $\pm 5\%$, and the molecular weights were calculated using $(C_5H_5)_2Fe$ calibration.

Materials. All manipulations were performed either on a vacuum line or in a glove box which was evacuated to <0.1 Torr and filled just prior to use with either prepurified nitrogen or argon. Nitrogen and argon used in the experiments were prepurified grade and were rendered rigorously oxygen- and water-free *via* passage over MnO on vermiculite[45] and activated 4A molecular sieves. All hydrocarbon and ether solvents were purified by distillation first from $LiAlH_4$ and then from a mixture of $[(C_5H_5)_2Ti]_2$ and $[(C_5H_5)TiH]_2(C_{10}H_8)$ *in vacuo.* 1,2,3,4,5-Pentamethylcyclopentadiene was prepared as described earlier.[1] $[C_5(CH_3)_5]_2TiCl_2$ was prepared as described previously,[1] with only the following modifications which were found to increase the yield to *ca.* 65%: (1) 1,2-dimethoxyethane was substituted for THF; (2) after addition of the $Na[C_5(CH_3)_5]$ solution to $TiCl_3$ at −80°, the mixture was warmed slowly to room temperature, then heated to 80° for 20 hr.

Procedures. (1) $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3$. $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3$ was prepared *via* thermal decomposition of $[C_5(CH_3)_5]_2Ti(CH_3)_2$ as described in ref 1. Molecular weight determined cryoscopically for a solution containing 113 mg per gram of C_6H_6, 329; calculated, 332.

(2) Hydrogen Evolution Measurements for 1. $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3$ (1.449 g, 4.37 mmol) was dissolved in 35 ml of toluene and allowed to react with H_2 (1 atm) at 0° for 3 hr. The resulting bright orange solution of **1** was cooled to −80°, and all residual H_2 and CH_4 were removed. This solution was warmed quickly to 20° and opened by means of a needle valve to a series of three liquid nitrogen cooled traps and a Toepler pump. The H_2 so collected was measured at regular intervals and amounted to the following millimoles of H_2 (after time in minutes): 1.25 (30), 1.64 (60), 1.92 (90), 2.50 (180), 2.83 (270), 3.09 (360), 3.29 (450), 3.49 (540), 3.65 (630).

(3) Preparation of 4. $[C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3$ (1.51 g, 4.55 mmol) was converted to **1** as described above. This solution was then stirred vigorously and the toluene-H_2 mixture was removed at 20° over an 18-hr period (H_2 evolved = 3.96 mmol). When all toluene had been removed, the yellow-orange residue was dissolved in 25 ml of pentane and cooled to 0° and N_2 (1 atm) was slowly admitted. After 3 hr the resulting black crystalline mass was filtered off at 0°, washed several times with fresh pentane at −80°, and dried at < −20° *in vacuo* (yield 830 mg, 55%).[46]

Analysis. To 202 mg (0.304 mmol) of $[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2$ was added 15 ml of toluene at −80°. The slurry was allowed to warm slowly to room temperature whereupon the color changed from dark royal blue to dark blue-green with evolution of N_2. Quantitative collection of the gas evolved after vigorous stirring for 1 hr at room temperature *in vacuo* yielded 0.308 mmol of N_2 (1.011 mmol of N_2/mmol of **4**). Other identical experiments produced the following N_2:**4** ratios: 0.988, 0.997, 0.971, 0.965, 0.994, 0.985.

(4) Deuterium Exchange Reactions for 2. To 120 mg (0.367 mequiv of Ti) of **4** was added 25 ml of toluene. The resulting solution was stirred under reduced pressure until all **4** had been converted to **2**. D_2 (223 Torr) (composition: 97.0% D_2, 0.5% DH, 2.5% H_2) in a 25.7-ml volume (0.310 mmol) was expanded into the 50-ml flask containing the toluene solution of **2**, and vigorous stirring was maintained at 20°. After 0.75 hr, the D_2/H_2 mixture was passed through three liquid nitrogen cooled traps and collected *via* a Toepler pump over a 1.25-hr period. The gas collected (0.282 mmol) consisted of 8.7% D_2, 41.3% DH, and 50% H_2.

The toluene removed during D_2/H_2 collection was replaced, and a second portion of D_2 (203 Torr in 25.7 ml, 0.282 mmol) was treated for an additional 12 hr at 20°. The D_2/H_2 mixture was collected as before (0.307 mmol, 99% recovery) and was determined to consist of 1.6% D_2, 23.4% DH, and 75.0% H_2.

The residue was dissolved in toluene at −80° and treated with N_2 (1 atm) for 10 min. The residual N_2 was removed *in vacuo* at −80°, and purple-blue **6** was allowed to revert to **2** at room temperature. The N_2 so evolved amounted to 0.349 mmol, indicating that the D_2 exchange experiments above resulted in less than 5% net decomposition of **2**.

(5) Thermal Decomposition of 2. **2** (60.1 mg, 0.189 mmol) was dissolved in 5 ml of toluene and heated slowly to reflux under 1 atm of butane. After 12 hr the solution was evaporated to dryness under reduced pressure, and volatile gases were passed through a series of liquid nitrogen cooled traps and collected *via* a Toepler pump. Of the 0.115 mmol of gas so obtained, 0.108 mmol was identified as H_2 by its quantitative conversion to H_2O upon passage over CuO at 300°; the remaining 0.007 mmol was CH_4 (ir). The residue was heated to 80°, 10^{-3} Torr, and violet crystalline **5** was collected on a water-cooled sublimation probe (yield *ca.* 50%).[46]

(6) Reaction of 2 with N_2. (a) 6. **2** (56.6 mg, 0.179 mmol) was dissolved in toluene at *ca.* −20° and exposed to 1 atm of N_2, whereupon the color instantly changed from yellow-orange to intense purple-blue. With stirring, the solution was cooled gradually to −80° over a 10-min period. Residual N_2 was removed to 0.005 Torr at −80°, and the flask was closed off and warmed to room temperature. The N_2 evolved on this conversion from **6** to **2** was collected *via* the Toepler pump as described above: N_2 collected, 0.171 mmol, 0.956 mmol of N_2/mmol of Ti. Other identical experiments produced the following N_2:Ti ratios: 0.992, 1.05, 0.978, 1.04, 1.00.

(b) **7.** **4** (62.8 mg, 0.189 mequiv of Ti) was dissolved in 10 ml diethyl ether at room temperature. N_2 (1 atm) was introduced, and the solution was cooled gradually to −196°. Residual N_2 was removed from the resulting dull purple-blue solid mass at −196°; the flask was closed off and warmed to room temperature and the N_2 released on reversion to **2** was collected as before. Total N_2 collected, 0.272 mmol. A blank experiment with an equal volume of diethyl ether yielded 0.015 mmol of N_2 retained at −196°. Corrected N_2 retained, 0.257 mmol, 1.36 mmol of N_2/mmol of Ti.

(7) Reaction of 6 with Hydrogen Chloride. **2** (0.376 mmol) in 15 ml of toluene was treated with N_2 at −80° as described in 6(a). N_2 (0.391 mmol) was released when **6** reverted to **2**. This treatment with N_2 was repeated (exactly) except that immediately after the residual N_2 had been removed from **6**, *ca.* 5 mmol of HCl were distilled in at −80°. An immediate reaction took place, and the purple-blue color instantly faded to purple-brown with gas evolution. The gases were passed through a series of liquid nitrogen cooled traps, and the N_2–H_2 mixture was collected *via* a Toepler pump. $N_2 + H_2$ amounted to 0.433 mmol. This gas mixture was cycled over CuO at 320° to convert H_2 to H_2O, which was removed in a liquid nitrogen cooled trap. N_2 (0.273 mmol, 0.726 mmol/mmol of Ti) remained. Thus H_2 evolved was 0.160 mmol, 0.425 mmol/mmol of Ti. Composition of the $CDCl_3$-soluble portion of residue (nmr): 90% $[C_5(CH_3)_5]_2TiCl_2$, 10% $[C_5(CH_3)_5]TiCl_3$. The 6 *M* HCl-soluble product was evaporated to dryness to yield several milligrams of a white crystalline salt identified as $N_2H_4 \cdot 2HCl$ by its ir spectrum (Nujol mull). In similar experiments, variable amounts of NH_4Cl were also observed in the hydrazine dihydrochloride residue.

(8) Reaction of 4 with Hydrogen Chloride. To 66.9 mg (0.101 mmol) of **4** was added 5 ml of toluene at −80°. HCl (3 mmol) was admitted and the slurry was stirred at −80° until all microcrystalline **4** had disappeared. The N_2–H_2 mixture was fractionated from HCl, collected, and analyzed as described above. N_2 evolved 0.0919 mmol, 0.908 mmol/mmol of **4**; H_2 evolved 0.112 mmol, 1.110 mmol/mmol of **4**. The residue was extracted with 6 *M* HCl, which yielded after evaporation to dryness a small amount (<1 mg) of a white crystalline material identified as NH_4Cl by its ir spectrum (mull) and by a positive test with Nessler's reagent. The $CDCl_3$-soluble portion of the residue consisted of 77% $[C_5(CH_3)_5]_2TiCl_2$ and 23% $[C_5(CH_3)_5]TiCl_3$.

Infrared Spectra. (1) $[C_5(CH_3)_5]_2TiCl_2$ (KBr pellet): 2982 s, 2948 s, 2890 vs, 2850 s (sh), 2710 m, 1610 w, 1488 s, 1440 m (sh), 1420 s, 1388 m, 1373 vs, 1160 m, 1090 w, 1060 m, 1016 s, 950 w, 805 m, 595 w, 590 w, 410 s.

(2) **2a** (Nujol mull on KBr): 2720 m, 1640 w, 1570 w, 1475 s, 1155 w, 1059 w, 1019 s, 845 w, 795 w, 718 w, 628 w, 610 w, 565 m, 510 w, 450 s.

(3) **4** (Nujol mull on KBr): 2705 m, 1158 m, 1055 w, 1019 s, 941 w, 795 w, 617 m, 549 m, 450 m (sh), 392 s.

(4) **5** (Nujol mull on KBr): 3040 m, 3015 m, 2718 m, 1332 m, 1160 m (b), 1067 m, 1018 s, 870 m, 842 s, 824 s, 801 s, 749 ms, 721 m, 610 m, 582 m, 560 m (sh), 510 s.

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[46] Satisfactory elemental analyses for C, H, Ti (and N) were obtained.

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Theoretical Conformational Analysis of Saturated Heterocycles. Substituent Effects on Primary Ozonides

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Abstract: The theoretical conformational analysis of 12 substituted primary ozonides has been carried out. The results indicate that several conformers for each compound are approximately equal in stability and hence no conformer predominates. A study of O^{-}–O–C^{+}–R zwitterion conformation shows that the R group will rotate into an anti zwitterion if the O–O–C–R angle is greater than 90°; analysis of O–O–C–R angles in the primary ozonides indicates that all substituents will tend to form anti zwitterions upon ring fission. An analysis of the relative stability of various conformers indicates that, within the limitation of the investigation, lone-pair interactions are more important than substituent interactions in determining ring conformation.

Primary ozonides (1,2,3-trioxolanes) are intermediates in the reaction of ozone with olefins to produce final ozonides (1,2,4-trioxolanes) and a mixture of polymeric peroxides. A mechanism for this reaction was originally proposed by Criegee[1] and later modified by Bailey, *et al.*,[2] and more recently by Kuczkowski, *et al.*[3] The Bailey, *et al.*, mechanism, shown in Figure 1, involves the initial formation of the primary ozonide, followed by its decomposition into a carbonyl moiety and a zwitterion. The zwitterion formed is postulated to be anti (from equatorial primary ozonide substituents) or syn (from axial substituents). The anti and syn zwitterion then react with carbonyl compounds to orient bulky groups cis or trans, respectively, in the final ozonides. This mechanism was proposed to account for much of the stereochemical data obtained from the ozonolysis of olefins, but not all. In particular ^{18}O-labeling experiments indicate that the introduction of ^{18}O-carbonyl moieties into the reaction produce final ozonides with ^{18}O in the peroxide position and support an alternate mechanism proposed by Murray, *et al.*[4–7] An alternate mechanism to explain the ^{18}O data has been proposed[8] and more recent studies of ^{18}O-labeled final ozonides produced from phenylethylenes[9] and small alkenes[10,11] show no peroxide ^{18}O. The recent modification of the Criegee mechanism of Kuczkowski, *et al.*,[3] postulates that the primary ozonide ring fission proceeds through a single conformer and is consistent with orbital symmetry arguments. Additional discussion of all but the last of these mechanisms can be found in the initial report of these theoretical studies.[12]

In order to determine the validity of the Bailey, *et al.*, proposal, two theoretical studies have been performed.[12–14] These studies concentrated on determining the lowest energy conformer(s) of the primary ozonide intermediate to see if well-defined axial and equatorial substituents could be found for the most stable ring conformation. The conclusions reached can be summarized by stating that several conformers were found to be very close in energy and it is difficult to identify one as the predominant conformer in a reaction mixture. Among the lowest energy conformers are conformers with substituents which do not occupy axial or equatorial substituent positions.

The initial study was performed with the extended Hückel theory[13,14] and did not include all conformers of the primary ozonide ring and used a crude approximation to the ring geometry. The second study[12] included all conformers with the crude geometry, along with a proposal for an improved geometry and was based on the CNDO/2 method. The results presented here conclude the semiempirical studies using the improved geometry and considering the effect of bulky groups (up to *tert*-butyl) on the conformations of the primary ozonide molecule. These results also provide information on the relative importance of lone-pair and substituent interactions about the ring.

The molecules studied here are: propene, 1-butene,

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