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Homogeneous Dehydrogenation of Amines by μ-(η^1:η^5-Cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium(*Ti–Ti*)

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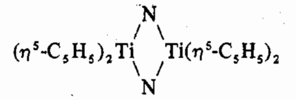
Solutions of μ-(η^1:η^5-cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium(*Ti–Ti*) (I) react readily with NH_3 and primary and secondary amines with the evolution of H_2. The reaction with ammonia results in the consumption of 2 mol of NH_3 and the loss of 1 mol of H_2/Ti_2 unit and leads to a new material formulated as



$$(\eta^5\text{-}C_5H_5)_2Ti\overset{N}{\underset{N}{\diamond}}Ti(\eta^5\text{-}C_5H_5)_2$$

II

A framework structure consisting of a planar array of the two Ti atoms and two nitrogen atoms as well as the location of the η^5-C_5H_5 rings above and below this plane has been determined by single-crystal x-ray diffraction studies. The nitrogen atoms in II are not simply "nitridic". The stoichiometry as well as both chemical and physical evidence suggests that three additional hydrogen atoms ought to be included in the above structure. The reactivity of I with organic amines varies according to the following sequence: $NH_3 > C_2H_5NH_2 \gg (CH_3)_2NH \geq (C_2H_5)_2NH \gg t\text{-}C_4H_9NH_2 \gg (C_2H_5)_3N$ (which does not appear to yield any H_2 at all). In addition, compound I reacts with urea or substituted ureas to yield 1 mol of H_2/Ti_2 unit. The importance of these results with respect to the desired catalytic properties of the low-valent titanium metallocene I will be discussed.

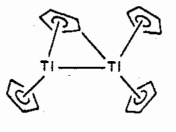
Introduction

With the discovery of ferrocene in 1951,[1,2] the field of organometallic chemistry has evolved with often unpredictable results. One of the more recent developments in organometallic as well as inorganic chemistry is the capability of some metal complexes to coordinate molecular nitrogen. In this respect, the early work of Vol'pin and Shur,[3,4] Shilov,[5] Brintzinger,[6-8] and Bercaw[9-11] was concentrated primarily on the use of low-valent titanium[12-14] organometallics to bind dinitrogen.

Several years ago, Pez,[15-17] in these laboratories, prepared μ-(η^1:η^5-cyclopentadienyl)-tris(η-cyclopentadienyl)dititanium(*Ti–Ti*) by the low-temperature reduction of (η^5-$C_5H_5)_2TiCl_2$ with potassium naphthalene in THF.

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 + 2KC_{10}H_8 \xrightarrow[-80\text{ to }+25\ ^\circ C]{THF} \underset{I}{\text{a "bis(titanocene)"}}$$

Although this was originally thought to be the true metallocene dimer of titanium, recent single-crystal x-ray diffraction work has shown conclusively that the molecule (as the THF adduct) actually has the bridged structure



I

Besides being a catalyst for the hydrogenation of olefins, compound I is able to form several different molecular nitrogen complexes in which the dinitrogen can be reduced with potassium naphthalene.[17] After acidification of the reduced nitrogen complex with anhydrous HCl, up to 1.4 mol of NH_4^+/mol of Ti_2 has been obtained. During the course of this work, it was discovered that even anhydrous ammonia reacts with I to yield hydrogen and a new red compound, $(TiC_{10}H_{10}N)_2H_3$ (II).[18] This new compound has now been isolated from the reaction, and its structure determined by single-crystal x-ray studies.

Generally, the reactions of ammonia with metallocenes proceed by direct addition to the metal center or not at all. The homogeneous reaction of a metallocene with ammonia is fascinating not only because hydrogen gas is evolved but also because the latter result would seem to indicate that "titanocene" complexes might not be suitable for the catalytic reduction of N_2. For the most part, the impetus in the field of titanium metallocenes had been provided by the fact that these low-valent titanium complexes, in the presence of a strong reducing agent, were capable of reducing molecular nitrogen.[4,5,11,19-21] Compound I coordinates N_2 to give several different nitrogen complexes which yield NH_3 upon reduction and hydrolysis.[17] The fact that I is also capable of dehydrogenating ammonia[22] brings out the parallel in chemical properties between the homogeneous, organometallic compound, I, and the iron-based heterogeneous ammonia synthesis catalyst.

This report will describe the preparation and characterization of the reaction product of I with ammonia and organic amines; a subsequent report[23] will discuss the reactions and catalytic properties of this new compound. Prior to this work no complex which coordinates N_2 has been observed to also dissociate NH_3 into H_2. The latter property is to be expected

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti1	0.5782 (3)	0.2949 (7)	0.2500 (0)	0.0039 (2)	0.0168 (9)	0.00443 (15)	0.0020 (10)	0.0001 (4)	0.001 (1)
Ti2	0.6458 (2)	0.1995 (6)	0.4161 (3)	0.0028 (1)	0.0119 (6)	0.00266 (9)	−0.0016 (9)	0.0011 (3)	−0.003 (1)
N1	0.649 (1)	0.465 (3)	0.3355 (12)	0.0039 (9)	0.022 (5)	0.0046 (8)	0.002 (4)	−0.001 (2)	−0.007 (4)
N2	0.576 (1)	0.034 (3)	0.3303 (9)	0.0066 (10)	0.013 (5)	0.0023 (6)	0.007 (4)	−0.004 (1)	0.002 (3)
C1	0.429 (2)	0.333 (4)	0.301 (2)	0.0053 (13)	0.023 (8)	0.0055 (12)	0.008 (6)	−0.001 (2)	−0.001 (5)
C2	0.425 (1)	0.241 (4)	0.231 (2)	0.0020 (8)	0.025 (9)	0.0106 (17)	−0.004 (5)	−0.005 (2)	−0.005 (6)
C3	0.452 (2)	0.400 (8)	0.183 (2)	0.0086 (19)	0.129 (19)	0.0054 (12)	0.035 (10)	0.001 (3)	0.037 (7)
C4	0.477 (2)	0.576 (5)	0.226 (2)	0.0054 (14)	0.027 (8)	0.0100 (19)	0.014 (6)	−0.001 (3)	0.004 (7)
C5	0.464 (2)	0.543 (6)	0.297 (1)	0.0042 (12)	0.081 (15)	0.0034 (10)	0.022 (7)	0.001 (2)	0.008 (7)
C6	0.731 (2)	0.235 (5)	0.219 (1)	0.0064 (14)	0.042 (10)	0.0036 (9)	0.015 (6)	0.001 (2)	−0.004 (6)
C7	0.705 (2)	0.392 (6)	0.186 (1)	0.0114 (21)	0.055 (13)	0.0029 (11)	−0.022 (9)	0.005 (2)	−0.001 (6)
C8	0.639 (2)	0.344 (6)	0.136 (2)	0.0211 (21)	0.126 (13)	0.0037 (9)	0.094 (7)	0.015 (2)	0.035 (6)
C9	0.623 (2)	0.111 (6)	0.149 (1)	0.0080 (18)	0.063 (13)	0.0034 (10)	0.011 (8)	0.004 (2)	−0.012 (6)
C10	0.692 (2)	0.079 (6)	0.200 (2)	0.0149 (23)	0.061 (11)	0.0042 (11)	0.040 (8)	0.005 (3)	−0.015 (6)
C11	0.591 (2)	0.466 (5)	0.501 (1)	0.0096 (18)	0.058 (10)	0.0037 (9)	−0.021 (8)	0.006 (2)	−0.025 (5)
C12	0.614 (2)	0.259 (7)	0.536 (2)	0.0097 (19)	0.078 (16)	0.0034 (10)	0.028 (9)	−0.002 (3)	−0.007 (8)
C13	0.550 (2)	0.102 (5)	0.513 (2)	0.0154 (21)	0.028 (9)	0.0049 (10)	−0.010 (8)	0.014 (2)	−0.008 (5)
C14	0.501 (2)	0.230 (9)	0.466 (2)	0.0047 (14)	0.142 (25)	0.0043 (11)	0.019 (12)	0.002 (2)	−0.019 (10)
C15	0.531 (3)	0.436 (6)	0.467 (2)	0.0191 (35)	0.029 (11)	0.0065 (15)	0.006 (11)	0.008 (4)	−0.009 (7)
C16	0.790 (2)	0.207 (7)	0.465 (2)	0.0065 (15)	0.064 (14)	0.0043 (11)	0.018 (8)	−0.003 (2)	−0.003 (8)
C17	0.799 (2)	0.218 (5)	0.388 (2)	0.0037 (12)	0.028 (8)	0.0084 (16)	0.002 (6)	−0.001 (2)	0.006 (7)
C18	0.769 (2)	−0.001 (5)	0.376 (2)	0.0045 (12)	0.064 (9)	0.0084 (11)	0.027 (6)	−0.008 (2)	−0.041 (5)
C19	0.714 (2)	−0.172 (5)	0.422 (1)	0.0096 (14)	0.055 (9)	0.0011 (6)	0.034 (6)	0.006 (2)	0.010 (6)
C20	0.761 (2)	0.001 (6)	0.482 (2)	0.0057 (15)	0.081 (12)	0.0048 (10)	0.014 (8)	0.002 (2)	0.034 (5)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

Table II. Bond Distances (Å)

Atom 1	Atom 2	Distance[a]	Atom 1	Atom 2	Distance[a]	Atom 1	Atom 2	Distance[a]
Ti1	Ti2	3.392 (4)	Ti2	C11	2.46 (3)	C6	C7	1.23 (4)
Ti1	N1	2.224 (16)	Ti2	C12	2.38 (2)	C6	C10	1.19 (4)
Ti1	N2	2.237 (15)	Ti2	C13	2.43 (2)	C7	C8	1.41 (5)
Ti1	C1	2.453 (20)	Ti2	C14	2.39 (2)	C8	C9	1.49 (5)
Ti1	C2	2.360 (15)	Ti2	C15	2.47 (3)	C9	C10	1.45 (4)
Ti1	C3	2.38 (2)	Ti2	C16	2.36 (2)	C11	C12	1.50 (4)
Ti1	C4	2.357 (20)	Ti2	C17	2.372 (19)	C11	C15	1.11 (4)
Ti1	C5	2.47 (2)	Ti2	C18	2.358 (17)	C12	C13	1.45 (4)
Ti1	C6	2.40 (2)	Ti2	C19	2.527 (20)	C13	C14	1.41 (4)
Ti1	C7	2.35 (2)	Ti2	C20	2.47 (2)	C14	C15	1.36 (5)
Ti1	C8	2.38 (3)	C1	C2	1.47 (3)	C16	C17	1.48 (3)
Ti1	C9	2.35 (2)	C1	C5	1.41 (3)	C16	C20	1.39 (4)
Ti1	C10	2.37 (2)	C2	C3	1.40 (3)	C17	C18	1.45 (3)
Ti2	N1	2.261 (19)	C3	C4	1.42 (5)	C18	C19	1.61 (4)
Ti2	N2	2.204 (15)	C4	C5	1.39 (4)	C19	C20	1.71 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

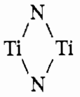
for any true catalyst of activating N_2 for reduction by H_2.

Results

Stoichiometry. Treatment of crystalline "bis(titanocene)" (I) (0.13 mmol) with 0.55 mmol of ammonia liberates 0.12 mmol of hydrogen and consumes 0.28 mmol of ammonia in ~10 mL of benzene or toluene. This suggests the following stoichiometry:

$$\underset{\text{I}}{1.0Cp_2TiC_5H_4TiCp} + 2.0NH_3 \rightarrow 1.0H_2 + \underset{\text{II}}{Ti_2Cp_4N_2H_3}$$

Molecular Structure. Crystals of the major product from the reaction of I with NH_3 (II) were submitted to the Molecular Structure Corp.[24] for structural analysis. The structural framework of the molecule is given in Figure 1. It consists of a binuclear Ti complex (3.392 (4) Å Ti–Ti) bridged by two nitrogen atoms. The titanium atoms are in pseudotetrahedral environments with the



(∠Ti–N–Ti ~ 99°, Ti–N = 2.23 Å) framework in a planar array. The relevant structural data are listed in Tables I–V. With a distance of 2.896 Å between the N atoms there can be no bonding interaction between the two nitrogen atoms in the plane. Unlike the starting material all four C_5H_5 ligands are symmetrically displaced around the titanium atoms with no observed interaction of any single C_5H_5 ring with both Ti atoms. The mean Ti–C distance is 2.4 Å. These distances compare well with those reported for other Ti metallocenes (e.g., I,[16] $[(C_5H_5)Ti(OH)]_2C_{10}H_8$,[25] $(C_5H_5)_2TiCl_2$,[26] and $[(C_5H_5)_2TiSiH_2]$[27]). The observed conformation as well as

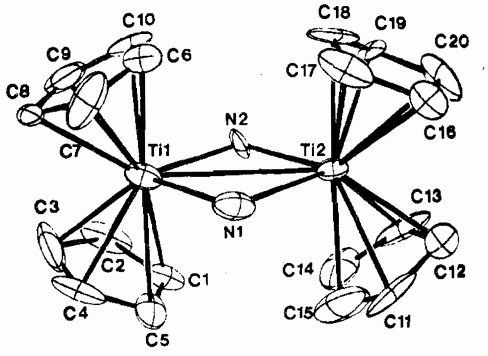


Figure 1. X-ray structure of the "bis(titanocene)"–ammonia complex: N1–Ti1–N2 = 80°, Ti1–N2–Ti2 = 98°, Ti–C = 2.4 Å, N1–N2 = 2.9 Å, Ti–Ti = 3.39 Å, Ti–N = 2.2 Å.

Table III. Bond Angles (deg)

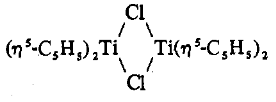
Atom 1	Atom 2	Atom 3	Angle[a]	Atom 1	Atom 2	Atom 3	Angle[a]	Atom 1	Atom 2	Atom 3	Angle[a]
Ti2	Ti1	N1	41.3 (5)	C4	Ti1	C8	88.4 (11)	C12	Ti2	C13	35.0 (10)
Ti2	Ti1	N2	39.8 (4)	C4	Ti1	C9	112.4 (13)	C12	Ti2	C14	54.6 (9)
Ti2	Ti1	C1	85.1 (5)	C4	Ti1	C10	143.5 (13)	C12	Ti2	C15	51.9 (11)
Ti2	Ti1	C2	114.5 (7)	C5	Ti1	C6	148.1 (10)	C12	Ti2	C16	78.3 (9)
Ti2	Ti1	C3	142.3 (8)	C5	Ti1	C7	126.3 (12)	C12	Ti2	C17	114.0 (10)
Ti2	Ti1	C4	120.4 (9)	C5	Ti1	C8	121.2 (9)	C12	Ti2	C18	123.7 (9)
Ti2	Ti1	C5	88.7 (5)	C5	Ti1	C9	143.1 (10)	C12	Ti2	C19	100.1 (9)
Ti2	Ti1	C6	85.3 (6)	C5	Ti1	C10	175.8 (13)	C12	Ti2	C20	74.1 (9)
Ti2	Ti1	C7	107.1 (9)	C6	Ti1	C7	30.0 (9)	C13	Ti2	C14	34.2 (10)
Ti2	Ti1	C8	140.0 (10)	C6	Ti1	C8	55.1 (10)	C13	Ti2	C15	55.2 (10)
Ti2	Ti1	C9	127.1 (9)	C6	Ti1	C9	56.5 (8)	C13	Ti2	C16	104.4 (13)
Ti2	Ti1	C10	93.5 (8)	C6	Ti1	C10	28.9 (10)	C13	Ti2	C17	139.8 (12)
N1	Ti1	N2	81.1 (6)	C7	Ti1	C8	34.6 (11)	C13	Ti2	C18	125.8 (13)
N1	Ti1	C1	95.6 (6)	C7	Ti1	C9	57.4 (9)	C13	Ti2	C19	88.6 (9)
N1	Ti1	C2	130.7 (8)	C7	Ti1	C10	49.6 (13)	C13	Ti2	C20	84.5 (11)
N1	Ti1	C3	130.4 (12)	C8	Ti1	C9	36.6 (11)	C14	Ti2	C15	32.4 (12)
N1	Ti1	C4	95.8 (9)	C8	Ti1	C10	55.2 (10)	C14	Ti2	C16	132.8 (10)
N1	Ti1	C5	76.7 (7)	C9	Ti1	C10	35.7 (9)	C14	Ti2	C17	167.2 (11)
N1	Ti1	C6	78.3 (7)	Ti1	Ti2	N1	40.5 (4)	C14	Ti2	C18	152.8 (17)
N1	Ti1	C7	82.7 (8)	Ti1	Ti2	N2	40.6 (4)	C14	Ti2	C19	115.2 (15)
N1	Ti1	C8	115.5 (15)	Ti1	Ti2	C11	113.5 (9)	C14	Ti2	C20	118.6 (12)
N1	Ti1	C9	134.7 (8)	Ti1	Ti2	C12	145.2 (6)	C15	Ti2	C16	118.1 (13)
N1	Ti1	C10	102.7 (11)	Ti1	Ti2	C13	125.7 (10)	C15	Ti2	C17	137.7 (12)
N2	Ti1	C1	77.4 (6)	Ti1	Ti2	C14	95.0 (8)	C15	Ti2	C18	172.5 (12)
N2	Ti1	C2	89.5 (7)	Ti1	Ti2	C15	93.5 (10)	C15	Ti2	C19	143.8 (9)
N2	Ti1	C3	123.9 (10)	Ti1	Ti2	C16	130.0 (8)	C15	Ti2	C20	125.8 (13)
N2	Ti1	C4	131.5 (9)	Ti1	Ti2	C17	93.9 (7)	C16	Ti2	C17	36.5 (8)
N2	Ti1	C5	101.1 (8)	Ti1	Ti2	C18	91.1 (7)	C16	Ti2	C18	54.6 (8)
N2	Ti1	C6	94.1 (8)	Ti1	Ti2	C19	109.1 (6)	C16	Ti2	C19	68.0 (10)
N2	Ti1	C7	124.0 (11)	Ti1	Ti2	C20	140.7 (7)	C16	Ti2	C20	33.3 (9)
N2	Ti1	C8	136.7 (9)	N1	Ti2	N2	81.0 (5)	C17	Ti2	C18	35.8 (8)
N2	Ti1	C9	102.6 (10)	N1	Ti2	C11	88.0 (9)	C17	T12	C19	70.2 (8)
N2	Ti1	C10	82.8 (10)	N1	Ti2	C12	123.4 (10)	C17	T12	C20	57.2 (8)
C1	Ti1	C2	35.5 (7)	N1	Ti2	C13	135.9 (9)	C18	T12	C19	38.4 (9)
C1	Ti1	C3	57.5 (9)	N1	Ti2	C14	103.6 (13)	C18	T12	C20	49.7 (9)
C1	Ti1	C4	54.7 (9)	N1	Ti2	C15	81.6 (9)	C19	T12	C20	40.0 (9)
C1	Ti1	C5	33.2 (7)	N1	Ti2	C16	103.5 (9)	Ti1	N1	Ti2	98.3 (7)
C1	Ti1	C6	170.2 (8)	N1	Ti2	C17	77.6 (7)	Ti1	N2	Ti2	99.6 (6)
C1	Ti1	C7	157.7 (11)	N1	Ti2	C18	98.2 (10)	C2	C1	C5	108.7 (19)
C1	Ti1	C8	134.7 (10)	N1	Ti2	C19	133.6 (6)	C1	C2	C3	108.0 (23)
C1	Ti1	C9	129.6 (8)	N1	Ti2	C20	134.0 (7)	C2	C3	C4	104.4 (28)
C1	Ti1	C10	150.6 (13)	N2	Ti2	C11	130.2 (8)	C3	C4	C5	114.3 (28)
C2	Ti1	C3	34.4 (8)	N2	Ti2	C12	134.4 (10)	C1	C5	C4	104.5 (25)
C2	Ti1	C4	56.3 (8)	N2	Ti2	C13	99.8 (9)	C7	C6	C10	109.5 (30)
C2	Ti1	C5	57.8 (8)	N2	Ti2	C14	84.3 (9)	C6	C7	C8	113.8 (28)
C2	Ti1	C6	151.0 (9)	N2	Ti2	C15	104.1 (12)	C7	C8	C9	102.4 (22)
C2	Ti1	C7	138.4 (11)	N2	Ti2	C16	137.8 (8)	C8	C9	C10	97.3 (28)
C2	Ti1	C8	104.4 (14)	N2	Ti2	C17	108.4 (9)	C6	C10	C9	116.7 (33)
C2	Ti1	C9	94.6 (9)	N2	Ti2	C18	83.2 (6)	C12	C11	C15	107.7 (32)
C3	Ti1	C10	124 (13)	N2	Ti2	C19	78.7 (7)	C11	C12	C13	106.3 (22)
C3	Ti1	C4	34.8 (11)	N2	Ti2	C20	118.6 (10)	C12	C13	C14	99.4 (27)
C3	Ti1	C5	58.1 (11)	C11	Ti2	C12	36.1 (10)	C13	C14	C15	110.0 (29)
C3	Ti1	C6	132.2 (9)	C11	Ti2	C13	57.7 (9)	C11	C15	C14	116.3 (40)
C3	Ti1	C7	107.1 (12)	C11	Ti2	C14	51.4 (12)	C17	C16	C20	107.6 (28)
C3	Ti1	C8	77.2 (12)	C11	Ti2	C15	26.1 (10)	C16	C17	C18	94.9 (24)
C3	Ti1	C9	85.2 (13)	C11	Ti2	C16	92.0 (10)	C17	C18	C19	133.4 (23)
C3	Ti1	C10	120.9 (4)	C11	Ti2	C17	116.4 (9)	C18	C19	C20	75.2 (16)
C4	Ti1	C5	33.3 (9)	C11	Ti2	C18	146.6 (9)	C16	C20	C19	123.5 (23)
C4	Ti1	C6	132.9 (11)	C11	Ti2	C19	136.0 (11)				
C4	Ti1	C7	103.2 (13)	C11	Ti2	C20	103.8 (13)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

the crystal packing is shown in Figure 2.

For comparison, the Ti–N distance in $Cp_2Ti(NCO)_2$[28] is 2.01 Å. Since the $Cp_2Ti(NCO)_2$ complex probably contains some degree of conjugation in the Ti–N–C–O bonding array, it is difficult to draw any significant conclusion regarding the length of the Ti–N bond in compound II. Bercaw[29] has reported a distance of 2.019 Å in $(Me_5C_5)_2TiN{=}NTi(C_5Me_5)_2$. Titanium silylamides have a Ti–N bond distance of 1.93 Å[30] which is appreciably different from that expected for other metal–nitride–metal complexes (for Ru, Ru–N = 1.724 Å; for Fe, Fe–N = 1.6605 Å).[31] Preliminary structural data on the dehydrodiimide, amine bridged Pt(II) complex, $[PtN_2H_x(PPh_3)_2]_2(BPh_4)_2$, provided an estimate of 2.09 ± 0.05 Å for the Pt–N bond.[32] Therefore, it would appear that the bridging nitrogen atoms in compound II are not simply nitridic in character as the framework structure would lead one to believe.

The Ti–Ti bond is only slightly longer than that reported[16] for compound I but substantially less than that reported for



$$(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)_2Ti(\eta^5\text{-}C_5H_5)_2$$

Table IV. Weighted Least-Squares Planes[a]

Plane no.	*A*	*B*	*C*	*D*	Atom[b]	*X*	*Y*	*Z*	Distance	Esd
1	0.8733	−0.3456	−0.3433	5.3116	Ti1*	8.6898	1.8325	4.7895	−0.000	0.004
					Ti2*	9.7057	1.2395	7.9708	−0.000	0.004
					N1*	9.7586	2.8911	6.4280	0.005	0.020
					N2*	8.6574	0.2097	6.3286	0.004	0.019
2	0.8720	−0.3488	−0.3435	5.2332	Ti1*	8.6898	1.8325	4.7895	−0.000	0.004
					Ti2*	9.7057	1.2395	7.9708	−0.000	0.004
					N1*	9.7586	2.8911	6.4280	−0.000	0.020
					N2	8.6574	0.2097	6.3286	0.009	0.019
3	−0.9315	0.3547	−0.0807	−5.7559	C1*	6.4545	2.0685	5.7721	0.011	0.026
					C2*	6.3824	1.4990	4.4199	−0.015	0.021
					C3*	6.7958	2.4842	3.5114	0.023	0.035
					C4*	7.1741	3.5774	4.3263	−0.007	0.027
					C5*	6.9758	3.3727	5.6852	−0.005	0.027
					Ti1	8.6898	1.8325	4.7895	−2.075	0.004
					Ti2	9.7057	1.2395	7.9708	−3.489	0.003
					N1	9.7586	2.8911	6.4280	−2.828	0.020
					N2	8.6574	0.2097	6.3286	−2.745	0.019
4	0.6846	−0.1949	−0.7024	4.2976	C6*	10.9887	1.4602	4.1947	−0.006	0.028
					C7*	10.5986	2.4375	3.5568	−0.015	0.031
					C8*	9.6014	2.1352	2.6085	0.027	0.032
					C9*	9.3590	0.6875	2.8496	−0.026	0.029
					C10*	10.3961	0.4889	3.8382	0.028	0.034
					T11	8.6898	1.8325	4.7895	−2.070	0.003
					T12	9.7057	1.2395	7.9708	−3.493	0.005
					N1	9.7586	2.8911	6.4280	−2.695	0.021
					N2	8.6574	0.2097	6.3286	−2.857	0.0019
5	0.6109	0.2376	0.7552	−2.5094	C11*	8.8783	2.8980	9.5892	0.002	0.029
					C12*	9.2342	1.6101	10.2711	0.010	0.032
					C13*	8.2642	0.6328	9.8265	−0.014	0.031
					C14*	7.5272	1.4320	8.9224	0.029	0.034
					C15*	7.9836	2.7098	8.9549	−0.021	0.041
					Ti1	8.6898	1.8325	4.7895	3.765	0.003
					Ti2	9.7057	1.2395	7.9708	2.124	0.005
6	−0.8960	0.4411	−0.0508	−10.5995	C16*	11.8765	1.2859	8.9045	0.073	0.031
					C17*	12.0123	1.3557	7.4296	0.057	0.025
					C18*	11.5534	−0.0040	7.1978	−0.120	0.026
					C19*	10.7330	−1.0665	8.0937	0.101	0.026
					C20*	11.4419	0.0045	9.2268	−0.119	0.038
					Ti1	8.6898	1.8325	4.7895	3.379	0.004
					Ti2	9.7057	1.2395	7.9708	2.045	0.003
					N1	9.7586	2.8911	6.4280	2.805	0.020
					N2	8.6574	0.2097	6.3286	2.613	0.019

[a] The equation of the plane is of the form $A^*X + B^*Y + C^*2 - D = 0$, where A, B, C, and D are constants and X, Y, and Z are orthogonalized coordinates. [b] Asterisks signify atoms in planes.

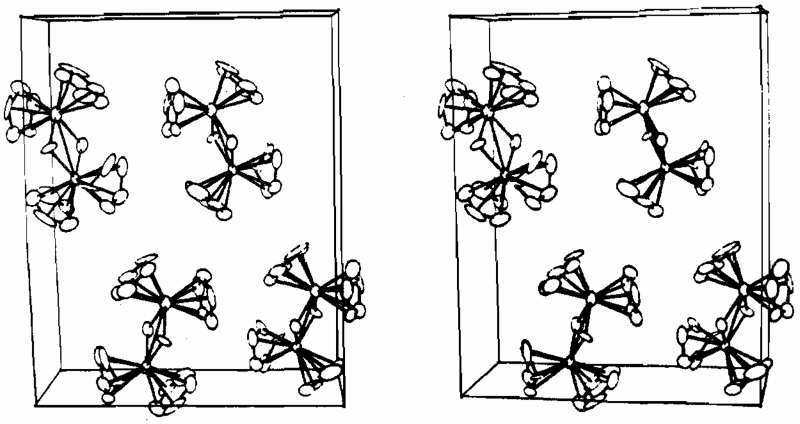


Figure 2. Conformation and crystal packing in compound II.

(Ti–Ti = 3.9 Å).[26] A much shorter Ti–Ti bond distance of 3.110 (7) Å has been reported[33] for $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$, and the value[34] for the Ti–Ti bond distance in the pure metal (α form) is 2.8956 Å. While the Ti–Ti bond length may appear to indicate some degree of bonding interaction between the Ti atoms, this may simply result from the presence of μ-nitrogen atom bridges symmetrically disposed around the Ti–Ti bond axis which served to bring the two Ti atoms closer together. One of the best structural analogies that we can find is the $[H_2NFe(CO)_3]_2$ complex[35] with Fe–N–Fe angle of 75° and N–Fe–N angle of 77°, Fe–Fe = 2.406 Å and Fe–N = 1.98 Å. In the latter structure the Fe–Fe distance corresponds very closely to that observed in iron metal α form (2.482 Å). Dahl, Costello, and King[35] demonstrated that the Fe–N–Fe angle is responsible for counterbalancing the effect on the Fe–Fe bond length.

Table V. Dihedral Angles (deg) between Planes

Plane no.	Plane no.	Dihedral angle	Plane no.	Plane no.	Dihedral angle
1	2	0.2	2	6	−23.4
1	3	−24.7	3	4	−49.4
1	4	25.0	3	5	−53.7
1	5	29.0	3	6	5.6
1	6	−23.4	4	5	5.7
2	3	−24.7	4	6	−48.4
2	4	25.0	5	6	−52.1
2	5	29.0			

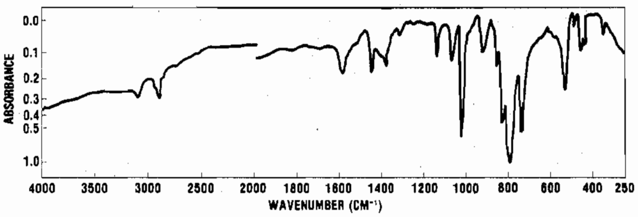
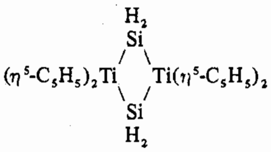


Figure 3. Infrared spectrum of compound II in Nujol mull, corrected for solvent absorptions.

The general structure for compound II is surprisingly similar to that presented[27] for $[(C_5H_5)_2TiSiH_2]_2$:



The Ti–Si–Ti bond angle is 102.8°, and the Ti–Ti distance is 3.37 Å with Ti–Si as 2.16 Å. The authors did not comment on the possibility of an H bridge along the Ti–Ti axis.

Additional H Atoms in Molecular Structure. In our complex, we could not observe any H 1s electron density within 1.7 Å of the N atoms; however, the quality of the crystal may not have been sufficient to allow precise location of additional H atoms in the structure. The location of the hydrogen atoms on the C_5H_5 ring also could not be precisely defined; however, the four C_5H_5 rings are planar. The final difference Fourier map for the $[TiCp_2N]_2$ framework showed two peaks of about the intensity expected for hydrogen atoms located near N1 and N2. (These were the only peaks in the difference Fourier analysis of density greater than 0.5 e/Å^3.) Because of the imperfections existing in the best of our single crystals, x-ray analysis was limited in its resolution.[36] These two extra peaks could not be refined in the final analysis.

Infrared Spectrum and Raman Spectrum. The infrared spectrum of compound II (Nujol) is illustrated in Figure 3. The most notable features are the new bands with respect to compound I at 1585 (m), 1240 (w), 910 (m), and 430 (m) cm^{-1}. Other bands in the spectrum are consistent with vibrations due to the $TiCp_2$ component of the complex.[16,37] It is interesting to note the absence of bands above 3120 cm^{-1} which are often indicative of nitrogen–hydrogen bonds.[38] The use of $^{15}NH_3$ in place of $^{14}NH_3$ results in a shift of the 1585-cm^{-1} band by 6 cm^{-1}. Using ND_3 in place of NH_3 results in the expected shift of the band at 1585 cm^{-1}. Pressurizing a toluene solution of compound II with D_2 at 66 psi does not produce a shift in any of the bands. Besides using *n*-hexadecane-d_{34} as the solvent, we ran numerous difference, low-temperature (−196 °C), and solution spectra in an unsuccessful effort to find new bands assignable to metal hydride or N–H vibrations.[39–44] However, later reactions of II with CO_2 resulted[23] in the appearance of N–H vibrations above 3200 cm^{-1}. These results will be discussed in the following paper and strongly support the argument for N–H bonds in the framework structure obtained from x-ray crystallography.

The Raman spectrum of compound II in the solid state could not be obtained due to decomposition of the solid in the laser beam. In THF solution (568.2-nm excitation), a series of four or perhaps five new bands was observed below 500 cm^{-1} (453, 326, 267, 218, and 198 cm^{-1}). In addition, new bands observed at 1135 and 1185 cm^{-1} may be due to the solute. The band at 453 cm^{-1} shifted ~10 cm^{-1} upon substitution of ^{15}N for ^{14}N.

UV–Vis–Near-IR Absorption Spectra. (1) Solution. Benzene was used as the solvent for all solution spectra. Unlike compound I which shows an absorption[16,45,46] band at 1130 nm (ϵ 138 M^{-1} cm^{-1}) and additional bands at 640 nm (175 M^{-1} cm^{-1}) and 486 (244 M^{-1} cm^{-1}), compound II shows no absorption band in the near-IR (800–2000 nm) but a very intense, broad band at 495 nm (ϵ 3.7 × 10^3 M^{-1} cm^{-1}) ($\Delta\lambda$ = 80 nm at $^1/_2\epsilon_{max}$). The solution obeys Beer's law in the range of 1.15–2.5 × 10^{-3} M. The intensity of the band decays very slowly over a period of weeks. However, the addition of excess NH_3 to a benzene solution of II raises the value of ϵ at 495 nm by 10–20%. This suggests that NH_3 may inhibit the dissocation of compound II, and the value which we observe may only represent the equilibrium concentration of compound II in solution. Alternatively, perhaps a secondary reaction of NH_3 with compound II is occurring. For the most part, the vis–near-IR spectrum of the crude preparation of compound II was identical with that obtained using crystalline sources of compound II reported above.

When the vis–near-IR spectrum is recorded simultaneously with the stoichiometric experiments described earlier, an immediate reaction occurs (<3 min with a three- to fivefold excess of NH_3) resulting in the complete disappearance of the 1130-nm intervalence band for "bis(titanocene)". Over the next few hours, small changes occur in the visible spectrum attributable to compound II with the growth of a new absorption at 497 nm which reaches a maximum in about 48 h. The maximum 497 nm corresponds to an ϵ 5.2 × 10^3 M^{-1} cm^{-1}. The high value of ϵ may be due in part to errors related to the small quantities of reactants being used or to a small amount of a side product produced during the course of the reaction. It is also possible that the slight excess of NH_3 may react further with compound II. Nonetheless, the major reaction leads to compound II. From the changes in the spectrum with time, it is apparent that at least two (or perhaps three) successive steps are involved in the formation of compound II from "bis(titanocene)" I.

(2) Solid-State Reflectance Spectra in the Visible/and Near-IR. The reflectance spectrum of compound II (crystals ground to powder) indicated a broad maximum centered at 495 ± 10 nm.

Additional near-IR bands were observed at 1300, 1540, 1650, and 1860 nm of intensity comparable to that observed at 495 nm. This is markedly different from the spectrum recorded in solution and strongly suggests that there are different species present in solid and solution.

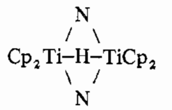
Mass Spectrum. We have not been able to obtain any useful information regarding the identity of compound II from mass spectrographic analysis. The only peak observed in the mass spectrum corresponded to *m*/*e* 178 (probably $TiCp_2$). Compound II does not visibly appear to sublime even at 200 °C and 10^{-3} Torr; however, the sampling procedures on our AEI-MS9 do not allow us to obtain the mass spectrum of solids without first breaking open the capillary tube (containing the sample) in air.

Molecular Weight. The molecular weight was determined using a device designed and built[16] by Pez which is based on the isopiestic method.[47] With benzene or THF as solvent (vs. azobenzene as the reference solute), we could not obtain consistent molecular weights using the crude preparation of compound II. Using the crystalline form of compound II, we obtained a plateau in the plot of observed molecular weight vs. solute concentration at 172 g/mol (solute concentration = 0.027–0.032 *m* based on a molecular weight of 193 g). The value of 172 g/mol is within the probable error limits (i.e., limitations due to Raoult's law, trace oxidants, temperature drifts, etc.) for a mononuclear complex having the formula, $TiCp_2NH$, (mol wt = 193 g/mol). The residue from the molecular weight determination still contained almost all of the original nitrogen in the sample. These results strongly indicate that in solution the binuclear complex dissociates into mononuclear species which are probably capable of forming polymers at high solute concentrations.

Reactivity of Compound II with Hydride Scavengers. Recently, Pez has demonstrated[16] that CH_3I is an effective reagent for determining the presence of Ti–H bonds in several compounds. Treating 0.149 mol of compound II (crystals) with a large excess of CH_3I (neat) gave 0.15 mmol of CH_4 as determined by Toepler pump techniques and confirmed by mass spectrometry.

The addition of an excess of gaseous HCl to 0.072 mmol of compound II (crystals) yields 0.072 mmol of hydrogen within a few hours corresponding to 1.0 mol of H_2/mol of $Ti_2C_{20}H_{23}N_2$.

Both of these independent methods strongly suggest the presence of a hydridic type of hydrogen in the dimeric complex. One possible formulation, consistent with the lack of any metal–hydride stretching frequency above 1700 cm^{-1}, is arrived at by assuming the presence of an additional symmetrical, bridging hydride in the framework structure which was obtained from x-ray analysis:



$$\begin{array}{c} N \\ / \quad \backslash \\ Cp_2Ti\text{–}H\text{–}TiCp_2 \\ \backslash \quad / \\ N \end{array}$$

Since hydrides bridging two metal centers are extremely difficult to detect, x-ray diffraction analysis could neither confirm nor rule out this possibility. However, the H/D exchange experiments described in the next paragraph coupled with the CH_3I and HCl experiments support the presence of one unique, exchangeable H atom in compound II.

Exchange Experiments. Reaction with D_2. Several experiments were performed at 1 atm of D_2 (0.5 mmol) over a toluene solution of compound II (0.06–0.11 mmol) (3, 5, and 10 days). In addition, similar solutions were prepared in pressure tubes using a minimum gas volume above the solutions. The solutions were pressured with 30 psi of D_2 (0.5 mmol) for 7 and 12 days. Analysis of the gas phase by mass spectroscopy indicated that exchange was complete in the minimum amount of time noted above and that the extent of exchange corresponded to 1 H atom/mol of compound II. (Recall that no new bands were observed in the IR spectrum of compound II exposed to D_2.)

Reaction with ND_3. Duplicate measurements were obtained using a slight excess of ND_3 (0.22 mmol) over a solution of compound I ($\sim$0.10 mmol) in toluene. After a few days, the mass spectrum of the noncondensable gases above the solution (after freezing the solution with liquid nitrogen) indicated 85% H_2, 5% HD, and only 9% D_2. The infrared spectrum indicated a substantial amount of C–H (>80%) still present in the residue of the reaction. Repeating the reaction with a large excess of ND_3 gave the same isotopic distribution of D_2/HD/H_2 but considerable exchange of the C_5H_5 ring protons with deuterium as well (vide IR). Treatment of the residue with CH_3I and freezing of the products with liquid nitrogen gave a gaseous product containing both CH_3D ($\sim$40%) and CH_4. This means that the H_2 gas ultimately comes from the hydrogen atoms on the C_5H_5 rings of I. If one assumes, from the stoichiometry, that 6 hydrogen atoms (from two molecules of ammonia) are available to exchange with the 19 hydrogen atoms in compound I, then the 9% D_2 which we observe is consistent with the production of D_2 and immediate exchange of this D_2 with all the H atoms in I. Since H atoms from the C_5H_5 ring on compound II do not exchange with D_2, then exchange must be occurring before compound II is produced. Recalling the results from the experiments measuring the spectral changes observed on treating compound I with NH_3, an intermediate(s) is produced which might be responsible for exchange of D_2 with the C_5H_5 rings.

Gouy Magnetic Measurements. We have obtained preliminary magnetic susceptibility measurements on compound II (crystals) using the Gouy technique.[48] Applying a correction for the change in weight of the empty sample tube, a value of $\chi_{20\,°C} = 3.8 \times 10^{-6}$ cgs units (duplicate measurements) was determined. Using a molecular weight of 387 g/mol, the effective magnetic moment is 1.9 μ_B. The calculated value for Ti^{3+} in a tetrahedral field at 27 °C is 1.9 μ_B after applying the normal spin–orbit coupling parameters.[49] Thus, the Gouy measurements suggest that the compound behaves as if it contains *one unpaired* electron per Ti_2 unit. This suggests two possibilities (i.e., Ti^{II}–Ti^{III} or Ti^{III}–Ti^{IV}) for the oxidation states of the two titanium atoms in the dimer.

An effort was made to determine the magnetic moment by the Evans method.[50] No splitting was observed at 10^{-3} M solutions of compound II in toluene or benzene. Although some splitting was observed at 10^{-4} M, the results were not reproducible. Even with solvents over Na/K alloy *very* dilute solutions of compound II over a period of hours are susceptible to decomposition due to trace amounts of oxidants.

Nuclear Magnetic Resonance. Several attempts at obtaining the ^1H NMR spectrum of the crystals of compound II were made using a Varian HR-100 spectrometer. No signal was observed in toluene-d_8. However, several broad bands were observed using THF-d_8. The absence of a hydride signal at high fields in the ^1H NMR spectrum may be indicative of a paramagnetic species. As the temperature was varied, the bands were observed to vary in shape and intensity (30 °C, δ 8.4, 7.3, and 7.2; −60 °C, δ 6.4, 5.9, and 5.6, using cyclohexane as the lock signal). This suggests antiferromagnetic behavior of the complex at lower temperatures. This agrees with the results from ESR experiments described below.

The ^{13}C NMR in THF and 30% THF-d_8 exhibited only one very week signal at 100 ppm.

Electron Spin Resonance. The ESR spectrum of compound II in the solid state (crystals) or in toluene displays a derivative spectrum which is a singlet with a *g* value of 1.979. This agrees with the *g* value obtained for other Ti(III) complexes.[51] Further, the measurement of the spin density gave a value of μ(obsd) = 2.1 μ_B corresponding closely to that determined by the Gouy method. The value of μ(obsd) for the solid state obeyed the Curie–Weiss law (to −196 °C). The ESR spectrum of a solution of compound II (crystals) in toluene yielded a broadened singlet with a shoulder. Upon lowering the temperature to −100 °C, a new singlet appears at $g \simeq 4$ and the $g \sim 2$ region splits into a quintet (Figure 4). A singlet at $g = 4$ is indicative of a singlet–triplet equilibrium.[52,53] This would be consistent with the decomposition of a binuclear complex (in solution) into mononuclear Ti(III) species which could interact in the frozen state giving rise to singlet–triplet states in equilibrium. This interpretation would corroborate earlier evidence which was presented that suggested the presence of different forms of the complex in the solid state and in solution.

Reaction of I with Organic Amines. Treatment of compound I, dissolved in toluene, with a tenfold excess of gaseous $C_2H_5NH_2$ (dried over BaO and then over compound II[54]) slowly yields H_2 gas. While the reaction is not as vigorous

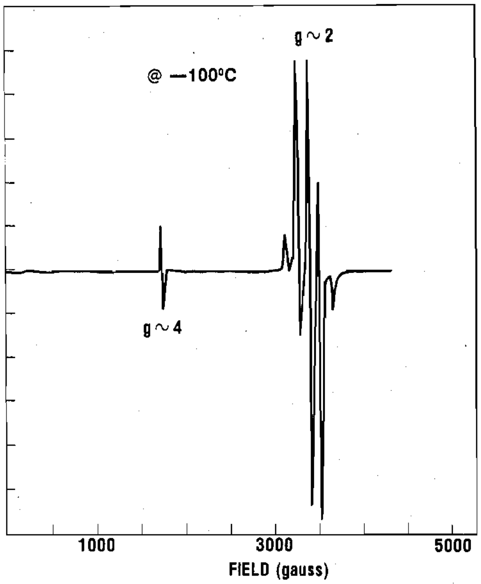
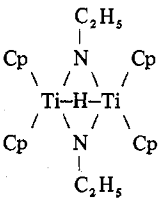


Figure 4. Spectrum of toluene "solution" at −100 °C of compound II at 10^{-4} M.

as that observed with NH_3, the solution does undergo a color change from deep green to brown with the generation of ∼1 mol of H_2/Ti_2 (as determined by Toepler pump techniques). The infrared spectrum of the resulting octane-washed residue (III) does not contain a new band at >3200 cm^{-1} which could be indicative of a coordinated amine or amide. By measuring the consumption of $C_2H_5NH_2$, the stoichiometry is the same as that reported for reaction 1, that is 2 $C_2H_5NH_2/Ti_2$. Microanalysis of the red solid corresponds to 6.5% N (Dumas method, implies 1 N/Ti). Pressurizing a toluene solution of this product (III) with D_2 over a period of 3 days does not produce a compound containing any significant C–D vibrations in the IR spectrum. This suggests that there is no longer a Ti–C σ bond as in I (which readily exchanges D_2/H_2 via the C_5H_4 ring). Addition of CH_3I to III does not produce substantial quantities of CH_4, although the addition of HCl(g) to a toluene solution of III results in the generation of H_2 (∼0.5 H_2/Ti_2). Since we do not observe any Ti–H or N–H vibrations above 1700 cm^{-1}, the stoichiometry and the HCl experiment suggest that a H atom may be bridging the Ti atoms. This new compound can best be tentatively formulated as



III

Treating compound I with a fourfold excess of $(C_2H_5)_2NH$ (dried over Na/K alloy) also results in the slow (1 week) evolution of H_2 (∼1.0 mol of H_2/Ti_2). With a 40-fold excess of the secondary amine, the reaction occurs within several days. The resulting red solution yields a solid having no significant absorption above 3100 cm^{-1} in the infrared spectrum. Treating compound I with $(C_2H_5)_3N$ yields no significant amounts of H_2. The use of a fourfold excess of $(CH_3)_2NH$ (dried over the corresponding amide and then over compound II)[54] results in the very slow evolution of H_2 (days).

Reaction of I with Ureas. The generation of H_2 from N donors containing an N–H bond is not limited to simple amines. Treating the deep green "titanocene" complex (I) (in toluene or THF) with at least a twofold excess of urea results in an immediate discoloration of the solution with the vigorous evolution of H_2 (∼1.0 mol of H_2/Ti_2). Using urea-d_4, one obtains a mixture of H_2, HD, and D_2.[55] The resulting blue-gray solution yields, upon evaporation of the solvent, a solid (IV) which displays numerous bands in the IR spectrum (i.e., 3400 and 1583 cm^{-1}) which can be assigned to N–H vibrations. The mass spectrum of the product displays numerous peaks, most notably at m/e = 414 which might be attributable to $Cp_2TiN(H)C({=}O)N(H)TiCp_2$ and one at m/e 237 which could be $Cp_2TiN(H)C({=}O)NH_2$ indicating a mixture of complexes. The formulation of the products (IV) as ureylene complexes[56] is consistent with the loss of H_2 in the reaction. Analogous ureylene complexes[57] of iron carbonyls have been prepared by the reaction of organic azides (via a nitrene intermediate) with $Fe_2(CO)_9$.[58] However, the absence of a C–O vibration above 1680 cm^{-1} (in IV) suggests that the oxygen atom of urea may also be coordinated to the titanium center. An additional IR band is observed at 1065 cm^{-1} which may be the Ti–O(urea) vibration.

Treatment of a toluene solution of compound I and 1,3-dimethylurea also yields H_2 (∼1 mol of H_2/Ti_2) and a blue residue upon evaporation of the solvent. However, the addition of tetramethylurea (dried over molecular sieves) to I does not generate any significant amount of H_2 over a period of days.

Discussion

Dehydrogenation of Ammonia. The reaction of I with ammonia represents the first observed homogeneous dehydrogenation of ammonia yielding H_2.[22] Generally, ammonia adds to metal complexes to form ammine complexes.[58-60] For example, Knoth[61] has reported that $[(C_6H_5)_3P]_3Ru(N_2)H_2$ reacts reversibly with NH_3 to yield $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ and N_2.

Titanium dialkylamides are generally prepared by the much more rigorous treatment of titanium chlorides with group 1 alkylamides.[62-64] The insolubility of $LiNH_2$ probably limits the parallel reaction with $TiCp_2Cl_2$. By analogy, the complex, $[(C_5H_5)_2TiSiH_2]_2$, was prepared via the treatment of $(C_5H_5)_2TiCl_2$ with SiH_3K, via the intermediate $(C_5H_5)_2Ti(SiH_3)_2$ which decays[27] according to the following equation:

$$2n(C_5H_5)_2Ti(SiH_3)_2 \rightarrow n[(C_5H_5)_2TiSiH_2]_2 + (SiH_2)_n + nH_2$$

In a similar manner, compound I could react with NH_3 to yield a transient ammine or amide complex which immediately decomposes to yield compound II and H_2.

The dehydrogenation of ammonia which occurs with strong reducing agents (e.g., Na^0, K^0 in the presence of iron), especially on metal surfaces[65]

$$Na + NH_3 \xrightarrow[Fe]{} NaNH_2 + {}^1/_2H_2$$

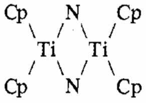
represents the closest analogy to the reaction reported here. Actually, the reaction we have observed is of general interest since heterogeneous surfaces[66] are known to dehydrogenate ammonia to yield H_2:

$$NH_3 + M(surface) \rightarrow MNH_2 \text{ (or NH)} + MH$$
$$2MH \rightarrow 2M + H_2$$

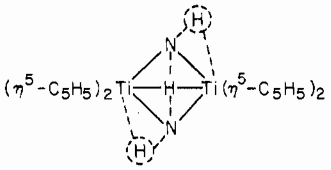
Indeed, the same iron catalysts which are used for the reduction[67] of N_2 by H_2 are also capable of decomposing NH_3 to yield H_2. Therefore, the reactivity of compound I with ammonia and with N_2 may be an indication that under the appropriate conditions compound I may be capable of functioning as a catalyst for the hydrogenation of N_2.

Dehydrogenation of Amines and Ureas. The relative order of reactivity of amines with I (toward H_2 evolution) is $NH_3 >_{min} C_2H_5NH_2 \gg_{days} (CH_3)_2NH \geq (C_2H_5)_2NH \gg_{weeks} t\text{-}C_4H_9NH_2$. Thus, it is apparent that while compound I reacts with primary or secondary amines, steric factors are also very important. If the amine must approach the titanium dimer via the exposed metal-metal bond, the accessibility of the lone pair of electrons on the nitrogen atom for prior coordination of the amine must be important. Certainly another possible step in the mechanism for the reaction of amines with compound I is the oxidative addition of the amine, which should be reflected in the acidity of these amines in solution. While they have not been measured, the acidities should be fairly comparable[68] (by analogy with the corresponding alcohols). Thus, the large difference in the rates of H_2 evolution for $C_2H_5NH_2$ and t-$C_4H_9NH_2$ suggests that steric constraints associated with the approach of the amine to the complex must be very important. Using more acidic amines such as 2,4-diaminotoluene or p-toluidine results in a rapid evolution of H_2 which approaches 1 mol of H_2/Ti_2.

Molecular Structure. The x-ray diffraction study is conclusive on the basic framework of compound II in the solid state. Unlike compound I there is no bridging cyclopentadienyl ring, and thus there is no facile mechanism for H–D exchange on the rings. The stoichiometry for the reaction of ammonia with $(C_5H_5)Ti(C_5H_4)Ti(C_5H_5)_2$ requires that II have the formula $[Ti(C_5H_5)_2N]_2H_3$. The reactions of II with CH_3I and HCl as well as the D_2 exchange experiments strongly suggest that one hydridic, hydrogen atom is present. This hydrogen atom may either be a terminal or bridging hydride (see the "Results" section on hydride scavengers). Further, since no N–H vibration is seen above 3200 cm^{-1}, a typical bridging amide or imide structure is unlikely. The appearance of a vibration at 1585 cm^{-1} which is sensitive to ^{15}N deuterium substitution is assigned to hydrogen atoms interacting with both the titanium and nitrogen atoms. When compound II is treated with CO_2, the product displays a N–H vibration above 3200 cm^{-1} characteristic of a carbamate complex. The following formula best represents compound II on the basis of all the experimental evidence gathered to date:



A



B

An analogous type of interaction was recently reported for the structure of bis(tertiary phosphine)platinum(0) complexes[69] with one of the hydrogens of the C_6H_5 groups interacting with the Pt center over a distance of 2.8 Å. As in the past, very rarely does one obtain positive evidence from the x-ray data alone.[34,70–72]

Solution vs. Solid State. Molecular weight, ESR, and reflectance measurements all indicate the presence of a second species (derived from compound II) in solution. The most likely formula for this compound in solution is a mononuclear complex derived from the partial dissociation of the binuclear complex in solution. Some possibilities are Cp_2Ti^{IV}–$\bar{\underline{N}}$–H, Cp_2Ti^{III}–NH_2, and $Cp_2Ti^{III}(H)(-\bar{N}-H)$. Anyone of these monomers would be expected to be reactive since they are either coordinatively unsaturated, contain an "imine" nitrogen, or contain a low-valent Ti center.

The absence of any D_2 exchange on the cyclopentadienyl ring strongly rules out a mononuclear complex in solution containing a C_5H_4 ligand. The addition of the N–H group to the $TiCp_2$ molecule may prevent the abstraction of ring hydrogens[11] from the cyclopentadienyl ligand(s).

Nevertheless, the equilibrium between mononuclear and binuclear species must be facile since the crystals are prepared from dissolution of the crude preparations of compound II. The reactivity which we have observed for compound II with small molecules[23] such as nitrogen, carbon monoxide, or ethylene can be easily explained by assuming that any of the above low-valent, mononuclear, coordinatively unsaturated species are present and may be the active species in solution.

In conclusion, compound I reacts readily with primary and secondary aliphatic amines, aromatic amines, and urea and monosubstituted ureas to yield H_2 gas. To our knowledge, this is the first general type of a homogeneous dehydrogenation of organonitrogen complexes to yield H_2. However, the reaction of I with aliphatic amines is facilitated by the presence of a sterically unhindered N–H bond. A series of new organometallic complexes is generated containing organonitrogen ligands which must result from deprotonated N donors. The structural framework of compound II has been determined by single-crystal x-ray diffraction studies. Evidence has also been presented that this binuclear compound (II) apparently dissociates into mononuclear species in solution.

While these unique, homogeneous, dehydrogenation reactions of amines may be limited to the titanocene system, additional examples may emerge if investigators simply look for them, since amines are often used as chemically inert solvents in some organometallic systems. Indeed, we may find that the homogeneous dehydrogenation of amines and ureas is a feature of low-valent, coordinatively unsaturated organometallic complexes.

Experimental Section

Apparatus and Reagents. All chemicals used were of the highest purity available. The extremely air-sensitive nature of the metallocenes used throughout this work required the rigorous exclusion of air and water. All solids were transferred or handled in a Vacuum Atmospheres drybox[73] filled with argon containing <5 ppm O_2 or H_2O. The titanium complexes were dissolved in solvents using glassware fitted with Kontes Teflon, vacuum valves. The solvents were handled using standard vacuum line (10^{-4} Torr) techniques.

Chromatoquality grade solvents were used when available. Hydrocarbon solvents were treated with Na/K alloy under argon or vacuum. Tetrahydrofuran was first treated with $LiAlH_4$ and then distilled into a flask containing Na/K alloy and anthracene. The ether was then distilled, as required, from the blue radical anion solutions of Na/K–anthracene. For physical measurements on very dilute solutions ($\leq 10^{-3}$ M), it was necessary to distill the solvents (prepared in the above manner) onto "bis(titanocene)" before distilling the solvents onto our titanocene complexes.

Research quality gases such as H_2, N_2 Ar, and NH_3 were transferred by expansion (using a heavy gauge steel pressure line—fitted with bellows valves) into clean, spun-steel cylinders (Hoke Inc.)[74] containing ~1 mL of Na/K alloy. The cylinders were fitted 2000 psi rupture disks and double sealed with a combination of a high-pressure valve followed by a steel "Nupro" bellows valve. Reactions could be pressurized on the steel line to 150 psi using heavy-wall 1 in. glass tubes, fitted with 8-mm Kontes Teflon valves tapered to heavy-wall $^3/_8$ in. o.d. glass tubing. The tube was attached to the line using Teflon ferrules (R. S. Crum & Co.) and a Swagelok nut. For reactions at <1 atm, the "Nupro" valves of the steel cylinders were adapted with the Teflon ferrules and a Swagelok nut to couple a heavy-wall $^3/_8$-in. glass tube fitted with a suitable ground-glass joint.

Stoichiometry. The stoichiometry was determined with the aid of a Toepler pump. Crystals of compound I in toluene or benzene were treated with a fivefold excess of anhydrous ammonia. After several days, the solution was frozen in liquid N_2 and the product gases were collected using a Toepler pump. Hydrogen gas was determined volumetrically (and confirmed by mass spectrometry) by burning the product gases over CuO at 400 °C and weighing the H_2O produced. Using an octane/N_2 slush (−56 °C), the unreacted ammonia was collected and measured with the Toepler pump.

Physical Measurements. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Mulling agents (Nujol or

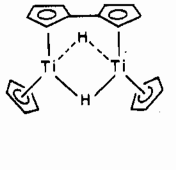
Nujol-*d* (*n*-hexadecane-d_{34}, Merck & Co., Inc.)) were purified by treatment with Na/K alloy followed by distillation under vacuum at ~100 °C. Vis–near-IR spectra were recorded on a Cary 14 recording spectrophotometer. Samples were weighed to within 0.01 mg (in an argon atmosphere) and transferred to a 250-mL high-vacuum glass bulb appended with a 2-mm quartz spectrophotometer cell. The solvent was then condensed into the glass bulb, warmed to room temperature, and weighed to within 1 mg using a Mettler balance. After filtering the solutions and sealing off the NMR tube under vacuum, proton NMR spectra were recorded on a Varian HR 100 spectrometer. Cyclohexane was used as an internal reference. The ^{13}C NMR were recorded on a Varian CFT-20 NMR spectrometer. Raman spectra were recorded on a Spex-Model 1401, using a coherent radiation krypton ion laser at 568.2 nm. The finely ground crystals were mounted in a capillary sealed under argon. Reflectance spectra were recorded on finely ground crystals contained in a 2-mm quartz spectrophotometer cell sealed under argon.

Molecular weight was determined by an isopiestic method. Benzene solutions of compound II and zone-refined azobenzene were equilibrated at constant temperature in separate tubes connected to a closed glass loop previously evacuated to 10^{-4} Torr. Using a Capacitance Monometer (Granville-Phillips) to monitor the ΔP between the two solutions, the solvent was withdrawn from the appropriate tube until the vapor pressures were equal. The molecular weight was then determined from the weight of the solute and the solvents. Gouy measurements (at 24 °C) were obtained with the assistance of Dr. David Ostwald, Seton Hall University. The crystals of compound II were ground and added to a 3-mm (o.d.) quartz tube, sealed under argon and weighed to five places. Deflections were noted reproducibly to tenths of a milligram, and corrections for the magnetism of the quartz tubes were made using the deflections observed in air as well as with a similar volume of $HgCo(NCS)_4$ ($\chi_g = 16.44 \times 10^{-6}$ at 20 °C). ESR spectra were recorded on a Varian E-12 spectrometer fitted with a low-temperature chamber. The spin density was determined on a known weight of compound II (ground crystals, under argon). The quartz ESR tube was fitted with a 4-mm Kontes Teflon valve so that solvents could be added or withdrawn as necessary.

Purification of Anhydrous Ammonia. Commercially available NH_3 (99%) contains both H_2O and $C_2H_5NH_2$. Since both of these impurities react with compound I, it was necessary to exhaustively scrub the ammonia. Ammonia (Matheson) was first distilled onto fresh Na/K alloy in a glass pressure tube using a dry ice/G-11 slush at −80 °C. When the tube was three-fourths full and the liquid ammonia solution was deep blue (indicating the absence of O_2), the −80 °C slush was removed and replaced with a chloroform slush (−63 °C). The cylinder (having a spun-steel bottom)[74] containing a few drops of Na/K alloy was immersed in a liquid nitrogen to collect the NH_3 from the glass tube at −63 °C. A few millimeters of ammonia remained at the end of the distillation, and this was vented in the hood. The ammonia prepared in this manner showed almost no trace of $C_2H_5NH_2$. On occasion, the cylinder was immersed in liquid nitrogen to pump off small amounts of hydrogen formed from the slow reaction of the alloy with NH_3.

Preparation of "Bis(titanocene)": $(\eta\text{-}C_5H_5)_2Ti\text{-}\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)\text{-}Ti(\eta\text{-}C_5H_5)$ (I). This preparation is described in detail in several previous reports.[15–17] Basically this involves the low-temperature reduction of $(\eta\text{-}C_5H_5)_2TiCl_2$ with potassium naphthalene. For the preparation of the crude complex from ammonia and I, the impure form of "bis(titanocene)" was used. When the stoichiometry of the reaction of I with ammonia was determined, crystalline $Cp_2TiC_5H_4TiCp{\cdot}2THF$ was used (after taking care to remove the THF by two successive washings with *n*-octane).

Preparation of Compound II, $(TiC_{10}H_{10}N)_2H_3$. The general method of preparation involves the addition of 0.8 g (2.2 mmol) of compound I to ~8 mL of toluene, contained in one leg of an "H-shaped reactor" (volume ~ 150 mL; two vertical tubes ~ 1.25-in. in diameter, joined by a horizontal tube containing a M-porosity frit). The starting material, "bis(titanocene)", I, is crude and probably contains $\mu\text{-}H_2\text{-}\mu\text{-}(\eta^5{:}\eta^5\text{-}C_{10}H_8)\text{-}(\eta\text{-}C_5H_5)_2Ti_2$ as well as other impurities.[7] This deep green solution is stirred for approximately 5 min at room temperature, frozen with liquid nitrogen, and outgassed to 10^{-4} Torr. Anhydrous ammonia (~5 mol) is then condensed onto the toluene layer. On thawing, hydrogen is immediately evolved, and the solution begins to turn brown. After 6–18 h, the solution is frozen with liquid N_2, and most of the H_2 is pumped from the reactor. The reaction is allowed to stir for 3–4 days at room temperature. The red solid which precipitates from the solution is allowed to settle, and the solution is filtered into the empty leg of the H reactor. About one-half of the toluene is distilled back onto the red solid. The product is washed with the toluene and filtered again. After pumping off the toluene, 50 mL of *n*-octane is condensed onto the red solid. The product is washed with octane, filtered, washed again, and refiltered. After the octane is evaporated to dryness, a dry, red, power of compound II remains. The purity of the power is best characterized by analysis[75] for nitrogen by the Dumas method. Early in the course of this work some difficulty was observed in recovering all the nitrogen from some titanium complexes. Even samples of titanium nitride[76] gave very low values for total percent N by the standard Dumas methods. However, the addition of Cr_2O_3 to the ceramic boats used in the Dumas analyses[75] led to the complete recovery of nitrogen. Apparently, during the normal Dumas or Kjeldahl analysis, compound II decomposes to yield intractable nitrides of titanium.[76] These can only be detected by extreme methods involving the use of strong oxidants. Anal. Calcd for $Ti_2C_{20}H_{23}N_2$: Ti, 24.7; N 7.23; C, 62.2; H, 6.00. Found: N, 7.42; C, 62.5; H, 5.65. Numerous earlier preparations yielded red solids generally having 3% nitrogen (conventional Dumas).



Direct Preparation of $(TiC_{10}H_{10}N)_2H_3$ (II), from $TiCp_2Cl_2$. Two grams (8.1 mmol) of $TiCp_2Cl_2$ was added to a large (total volume = 1 L) "H reactor" containing 2.2 equiv (0.12 g; 17.8 mmol) of Li powder. A catalytic amount of naphthalene (0.18 g, 1.4 mmol) was added to the side arm of the reactor and then sealed under argon. After evacuating to 10^{-4} Torr, approximately 100 mL of anhydrous diethyl ether (over "bis(titanocene)") was distilled into the flask and the mixture stirred for 15 min at ~0 °C. Naphthalene from the side arm was then added and the solution allowed to stir overnight. The next day, ammonia (8.1 mmol) was added to the frozen $(C_2H_5)_2O$ solution, the solution was allowed to thaw, and the reaction mixture was vigorously stirred for 4 days. The red-brown solution was filtered and the $(C_2H_5)_2O$ was removed under vacuum. The crude red residue was washed with a minimum amount of toluene and a large excess of octane. Crystals of compound II could be grown by the technique described in the next paragraph. The resulting crystals contained no Cl^-. The purity of the compound was confirmed by microanalysis, its distinctive vis–near-IR spectrum, and its x-ray powder pattern (12 strongest lines in Å (relative to I): 9.5 (45); 7.0 (89); 5.74 (100); 5.50 (72); 5.20 (28); 4.79 (42); 4.27 (8); 4.02 (15); 3.91 (4); 3.71 (6); 3.38 (4); 2.69 (8)). Apparently, compound II can also be prepared by adding the NH_3 at the start of the lithium naphthalene reduction. During the course of the reduction, an intermediate sea green solid forms. The latter compound may actually be the same compound that Green and Lucas[77] reported as $(\eta\text{-}C_5H_5)_2TiCl(NH_3)$. The color gradually changes from a green to red-brown and the resulting red solid contains as much as 5% Cl^-. It can be purified by the crystallization procedures described below.

Preparation of Crystalline $(TiC_{10}H_{10}N)_2H_3$. In general, single crystals of compound II could only be grown from toluene solutions. Other solvents were tried (THF, C_6H_6, THF/octane, toluene/octane, toluene/hexane, glyme, and C_6H_6/isopentane) without success. X-ray quality crystals were grown using an H reactor containing a saturated solution of compound II. The deep red solution was filtered into the empty leg and allowed to evaporate slowly using a temperature differential of ~2 °C. When almost all of the toluene had evaporated into the cooler leg, crystals remained in the other leg of the reactor. The remaining toluene solution over the crystals was then filtered into the leg of the reactor containing the bulk of the toluene distillate. All of the toluene was evaporated to dryness. The crystals were washed and filtered four times with ~10-mL portions of *n*-octane.

Collection of X-Ray Data and Structure Determination. Single-crystal x-ray diffraction data for compound II were collected on a prismatic crystal (approximate dimensions 0.5 × 0.32 × 2.0 mm) mounted in a 0.5-mm glass capillary. The crystal was mounted in an argon atmosphere (Vacuum Atmosphere drybox) using mineral oil to keep the crystal from slipping during the collection of data. Preliminary Weissenberg and precession photographs indicated an orthorhombic cell (*Pca*2$_1$ or *Pbcm*). While we were repeatedly able to grow crystals suitable for single-crystal x-ray crystallography, the quality of these crystals was never quite as good as the one upon which the following structure was determined.

Subsequent structural analysis[24] was carried out using a Syntex P_1 automatic diffractometer with graphite monochromatic Mo Kα radiation (λ 0.710 73 Å). Cell constants were obtained by computer centering of 15 reflections followed by a least-squares refinement of the setting angles. The following results were obtained: $a = 15.029$ (10) Å, $b = 6.214$ (3) Å, $c = 19.158$ (11) Å, $V = 1789$ (2) Å^3, empirical formula $Ti_2N_2C_{20}H_{22}$, structural formula $(TiC_{10}N)_2$, four molecules per unit cell, calculated density = 1.374 g/cm^3. The density of the crystals was 1.42 ± 0.06 g/cm^3 as determined by the displacement of isopentane from a tube containing a known weight of crystals (using 0.616 g/cm^3 for the density of isopentane at 20 °C). This is in good agreement with the density calculated from the x-ray data. The system is orthorhombic and systematic absences of $(0kl)$, $l \neq 2n$, $(h0l)$, $h \neq 2n$, $(h00)$, $h \neq 2n$, and $(00l)$, $l \neq 2n$, indicated a space group of $Pca2_1$ as confirmed by the successful refinement of the structure.

For the collection of structural data, using Mo Kα radiation, data were collected at a temperature of 23 ± 1 °C in the range $0 < 2\theta$(Mo Kα) $< 50°$ with a scan width ranging from 2θ(Mo Kα_1) $- 1.1°$ to 2θ(Mo Kα_2) $+ 1.1°$. The total number of reflections collected was 1936 of which 1876 were independent reflections. As a check on the crystal and electron stability, three representative reflections were measured periodically and no significant change was observed.

Intensities and standard deviations on intensities were calculated using the following formulas: $I = S(C - RB)$, $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = scan time/background count time, and B = total background count. Unit weights were used. Lorentz and polarization corrections were applied to the data. Extinction and absorption corrections were not necessary.

The structure was solved using heavy-atom, direct methods. In subsequent use of a full-matrix least-squares refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized where the weight, w, is defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors and values of $\Delta f'$ and $\Delta f''$ were taken from published data and anomalous dispersion effects were included in F_c. Only 777 reflections having $F_o^2 < 3\sigma(F_o^2)$ were used in the refinement. The R factors, defined as

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$$

were 0.079 and 0.089, respectively. The final positional and thermal parameters for the nonhydrogen atoms are given in Table I.

A listing of observed and calculated structure factors is available.[78]

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Registry No. I, 61529-60-0; II, 64611-27-4; III, 64611-26-3; $Cp_2TiN(H)C({=}O)N(H)TiCp_2$, 64600-01-7; $Cp_2TiN(H)C({=}O)NH_2$, 64600-00-6; $TiCp_2Cl_2$, 1271-19-8; NH_3, 7664-41-7; $C_2H_5NH_2$, 75-04-7; $(C_2H_5)_2NH$, 109-89-7; $(CH_3)_2NH$, 124-40-3; urea, 57-13-6; 1,3-dimethylurea, 96-31-1; t-$C_4H_9NH_2$, 75-64-9.

Supplementary Material Available: A listing of the structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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it does not react with amines. This latter result makes it a particularly good drying agent for amines.

(55) This has been confirmed by mass spectrographic analyses. If only D_2 was produced in the reaction, it would be expected to undergo rapid H–D exchange with any unreacted starting material (ref 17).

(56) The formulation of the complexes through a definite Ti–N linkage is based on the amount of H_2 evolved. Since the IR spectrum of monodentate ureylene complexes has not been reported, we can only suggest that the shifts in the N–H and CO frequencies which we observe are consistent with the proposed formulation.

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Reactions of an Imidohydridobis(dicyclopentadienyltitanium) with N_2, CO, and CO_2 and Olefins[1]

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The chemical reactivity of the new, red, crystalline complex isolated from the reaction of NH_3 with $(C_5H_5)Ti(C_5H_4)Ti(C_5H_5)_2$ (I) has been investigated. The original interest in I was in its demonstrated ability to activate molecular nitrogen; however, compound I is so reactive that it readily reacts with many of the very same organonitrogen products which we sought to synthesize. Surprisingly, the product of the NH_3 reaction above, $[TiCp_2NH]_2H$ (II), is itself quite reactive. Carbon monoxide or CO_2 react with compound II to yield an isocyanate or carbamate complex, respectively. Despite the formal oxidation of I by NH_3, the product II is still capable of coordinating N_2. This latter N_2 complex can also be reduced further by potassium naphthalene to NH_3 (after addition of HCl). Further, compound II is an effective, low-pressure, homogeneous catalyst for the hydrogenation of olefins.

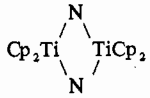
Introduction

Over the last few years, experiments have been conducted in these laboratories to determine if it might be possible to catalytically generate organonitrogen compounds (especially primary amines) directly from dinitrogen (or alternatively from NH_3). Extensive studies have been focused on the preparation and properties of a new, low-valent, coordinatively unsaturated titanium[2,3] metallocene, $(C_5H_5)_2\overline{TiC_5H_4Ti}(C_5H_5)$ (I). One feature of this complex[4] is its unusual $\eta^1{:}\eta^5$-bonded C_5H_4 group; another is its high reactivity toward small, unsaturated molecules such as N_2. Treatment of I with N_2 in the presence of potassium naphthalene followed by acid hydrolysis results in the transformation of most of the N_2 to NH_3. However, compound I is so reactive that it readily reacts with many of the very same organonitrogen products which we sought to synthesize. For example, compound I readily reacts with ammonia[5,6] and aliphatic and aromatic amines as well as ureas[7,8] to yield H_2. In the case of ammonia, the stoichiometry is

$$\underset{\text{I}}{Cp_2TiC_5H_4TiCp} + 2.0NH_3 \rightarrow \underset{\text{II}}{(Cp_2TiNH)_2H} + H_2 \qquad (1)$$

$$Cp = \eta\text{-}C_5H_5$$

While the precise location of the H atoms in II is based upon indirect arguments, the framework structure incorporating a planar array of the titanium and nitrogen atoms, has been defined by x-ray crystallography.[5] We now report that II, prepared by the spontaneous reaction of I with NH_3, is still capable of coordinating N_2. Surprisingly, we also find that II is an olefin hydrogenation catalyst which is still active in the presence of free NH_3 or $C_2H_5NH_2$. Further, the reactivity of II with CO and CO_2 is described.



Results and Discussion

Reaction with Dinitrogen. Pressurizing a toluene solution of II with 150 psi of N_2 results in an immediate deepening in the color of the red solution. Evaporation of the solvent to dryness at 0 °C followed by washing with *n*-octane leaves a dark red solid, III, which analyzes for 10.3% N ($\sim$3 N/Ti). (The parent compound (II) contains 7.3% N, using the same Dumas method). The product slowly loses N_2 while stored in the cold or with exhaustive pumping. Attempts to determine the actual amount of coordinated N_2 using HCl, ICl, or KIO_3 to oxidize the complex resulted in an incomplete accounting of the total nitrogen originally present (probably due to the formation of stable titanium nitrides). Debye–Scherrer x-ray powder photographs (Vanadium-filtered Cr radiation) of this

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