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REACTIONS OF MOLECULAR NITROGEN WITH TITANOCENE AND ITS DERIVATIVES

by

Robert Hyman Marvich

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
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to tiger

and

to my faithful truck, blimpy

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INTRODUCTION

The chemistry of titanocene derivatives, and their importance as models in the bioinorganic chemistry of N_2 fixation, has recently received considerable research attention. In fact, the growth in this research area since this study was initiated has been tremendous. Several excellent and comprehensive review articles have been published concerning the recent developments in inorganic models of N_2 fixation and their relationship to biological reduction by nitrogenase[1,2] and an extensive review will not be attempted here. It seems appropriate, however, to briefly outline those findings which are related to the chemistry of titanocene, and those which have contributed to clarifying the question of how the coordination of N_2 by transition metals to form stable complexes may be related to the actual reduction of N_2 that occurs in biological systems.

The versatility of N_2 as a ligand is now clear: well-confirmed N_2 complexes have been isolated for ten of the transition elements and the number and variety is steadily increasing. Allen and Senoff isolated the first transition metal N_2 complex from the reduction of $RuCl_3$ with excess N_2H_4 in aqueous solution, the NH_3 and N_2 ligands being formed by the Ru-catalyzed decomposition of hydrazine.[3] This extremely stable N_2 complex has since been prepared in a variety of other reactions.[4,5] An interesting procedure involves the reduction of a Ru-N_2O complex by Cr(II)[6] or amalgamated Zn.[7]

$$[(NH_3)_5Ru(N_2O)]^{2+} \xrightarrow{Zn/Hg} [(NH_3)_5Ru(N_2)]^{2+}$$

Conceivably, findings such as this may lead to an understanding of

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how to effect the reverse reaction, i.e. some modification of the coordinated N_2.

It would seem, however, that the most significant synthetic routes involve the direct utilization of N_2 since this obviously parallels the behavior of nitrogenase in biological systems. For example, a direct coordination of molecular nitrogen has been observed with coordinatively unsaturated complexes of the Fe-group metals.[8,9]

$$[P(C_2H_5)(C_6H_5)_2]_3FeH_2 + N_2 \longrightarrow [P(C_2H_5)(C_6H_5)_2]_3FeH_2(N_2)$$

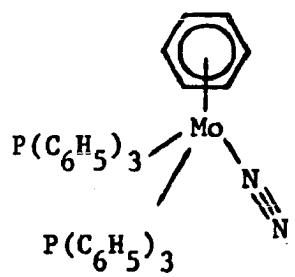
$$[P(C_6H_5)_3]_3RuH_2 + N_2 \longrightarrow [P(C_6H_5)_3]_3RuH_2(N_2)$$

N_2 is also capable of replacing other ligands, e.g. coordinated H_2O in the following complex.[10]

$$[(NH_3)_5RuCl]^{2+} \xrightarrow[H_2O]{Zn} [(NH_3)_5Ru(H_2O)]^{2+} \xrightarrow{N_2} [(NH_3)_5Ru(N_2)]^{2+}$$

N_2 is even more effective in this regard than halide ions.[2]

The trapping of reactive intermediate species by N_2 upon reduction of various transition metals by aluminum alkyls[11-14] or metallic Zn,[15] in the presence of tertiary phosphines, has proven to be one of the most successful methods of preparing transition metal N_2 complexes. This synthetic method has led to the isolation of N_2 complexes of Fe[8,16] and Mo,[17,18] providing some of the first substantial evidence for the ability of these nitrogenase metals to bind N_2. The evidence for the structures of the Mo compounds, for example the π-arene complex



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is not unambiguous, but the coordination of N_2 by molybdenum in these species seems certain. A N_2 complex of molybdocene has just recently been observed in this laboratory[19] although its structure has not yet been completely characterized.

The enthusiasm surrounding the isolation of the first discrete transition metal N_2 complexes has been dampened somewhat as a result of the failure to induce the coordinated N_2 in any of these complexes to undergo reduction. It is apparent, however, that, at least in some respects, the chemistry of these inorganic N_2 complexes does resemble that of nitrogenase. For example, the reversible displacement of hydrogen by N_2 from the following cobalt dihydride complex[20]

$$[P(C_6H_5)_3]_2CoH_2 + N_2 \longrightarrow [P(C_6H_5)_3]_2Co(N_2) + H_2$$

obviously parallels the competitive inhibition of N_2 reduction by H_2 that is observed in the enzymatic systems.[1]

Although the nitrogenase-catalyzed reduction of nitriles and acetylenes does not find any close analogy in the inorganic model systems, with the possible exception of a recently reported molybdenum-thiol system,[21,22] transition metal complexes of nitriles and acetylenes are well known. A cobalt acetonitrile complex actually exhibits a reversible interaction with molecular nitrogen.[23]

$$[P(C_6H_5)_3]_3CoH(CH_3CN) + N_2 \longrightarrow [P(C_6H_5)_3]_3CoH(N_2) + CH_3CN$$

In addition, nitrile analogs of $[(NH_3)_5Ru(N_2)]^{2+}$ have been isolated, with the N_2 being replaced by CH_3CN[24] or HCN.[25] The ability of a transition metal site to bind both N_2 and acetylenes has been demonstrated by Collman and Kang[26] who found that various disubstituted

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acetylenes readily replace N_2 in the Ir complex $[P(C_6H_5)_3]_3IrCl(N_2)$.[27] The acetylenes could in turn be displaced by carbon monoxide.

The inability of the monomeric N_2 complexes to lead to the formation of ammonia, or any reduced nitrogen derivative at all, has prompted several workers to seek dimeric bridged complexes, in which the N_2 molecule would hopefully be more highly activated by coordination to two transition metals. This approach has gathered some momentum from the fact that most of the currently favored mechanisms for biological N_2 fixation include such dimeric N_2-bridged intermediates, postulating either an Fe-Fe[28] or an Fe-Mo[29,30] dinuclear site. The recent isolation of several dimeric N_2-bridged complexes of Ru[2,31] and Os,[2] for example by the following reaction,

$$[(NH_3)_5Os(N_2)]^{2+} + [(H_2O)Ru(NH_3)_5]^{2+} \longrightarrow$$

$$[(NH_3)_5Os\text{-}N_2\text{-}Ru(NH_3)_5]^{4+} + H_2O$$

has provided experimental evidence for the ability of N_2 to form such complexes, but, at the same time, has shown that merely coordinating two metal atoms does not appreciably increase the activation of the N_2 molecule. The infrared N_2-stretching frequencies, which are usually assumed to be indicative of the strength of the M-N_2 interaction, occur at 2010 cm^{-1} and 2100 cm^{-1}, respectively, in the mononuclear complexes $[(NH_3)_5Os(N_2)]^{2+}$ and $[(NH_3)_5Ru(N_2)]^{2+}$, while in the mixed N_2-bridged dimer shown above it is found at 2047 cm^{-1}, remaining virtually unchanged. However, Chatt has reported[32] some apparently bridged complexes of Re and Mo which do exhibit extremely low N_2-stretching frequencies, e.g. 1680 cm^{-1} for a complex formed from $[P(CH_3)_2(C_6H_5)]_4ReCl(N_2)$ and excess $MoCl_4 \cdot 2\ (C_2H_5)_2O$, but, given the absence of further reports, contain

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N_2 which is still insufficiently activated to undergo reduction.

In all of the mononuclear and dinuclear transition metal N_2 complexes reported to date, an end-on, or linear, coordination of the N_2 molecule has either been established[33-36] or inferred from infrared data and comparative geometries.[2,37] Several authors have suggested that while such an end-on coordination may result in the formation of stable N_2 complexes, it is possibly an edge-on coordination of the N_2 molecule which leads to reduction.[38,39]

Since the early work of Volpin and Shur with titanocene dichloride, $(C_5H_5)_2TiCl_2$,[40] numerous other $(C_5H_5)_2Ti$ derivatives have been found which promote the fixation and reduction of molecular nitrogen.[41-44] Although many examples of N_2 reduction with other transition metals have been observed, most notably a stoichiometric reaction involving $FeCl_3$,[45] and several active systems with Mo,[46,47] titanium has remained the most active of the transition metals towards N_2 reduction and has been studied in the most detail. Despite many interesting developments in the Ti systems, no titanium complex of molecular nitrogen has been isolated, and the actual mechanism of N_2 coordination and reduction in these systems remains unclear.

Volpin and coworkers have reported that the reduction of N_2 by mixtures of $(C_5H_5)_2TiCl_2$ and phenyllithium leads to significant amounts of aniline.[51] These authors postulated that the formation of aromatic amines in this reaction proceeded via insertion of N_2 into a titanium aryl bond to yield an arylazo titanium derivative, $Ti-N=N-C_6H_5$. Similar azo derivatives, although not obtained directly from N_2, have been reported for platinum,[52] molybdenum,[53] and tungsten.[54] In these compounds the N=N bond can indeed be cleaved upon reduction to yield

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amines. Substantial evidence was found for the occurrence of a benzyne intermediate in this system: triphenylene (the product of the cyclotrimerization of benzyne) was detected in the products of the reaction of $(C_5H_5)_2TiCl_2$ with C_6H_5Li, and, when the reaction was carried out using o-tolyllithium, considerable amounts of the rearrangement products m- and p-toluidine were formed in addition to the expected o-toluidine. The occurrence of such an intermediate had been postulated earlier by Dvorak[55] to occur in the thermal decomposition of $(C_5H_5)_2Ti(C_6H_5)_2$.

Similarly, van Tamelen has found that N_2 can be directly utilized in the synthesis of organic amines and nitriles.[56] Mixtures of $(C_5H_5)_2TiCl_2$ and Mg powder, in tetrahydrofuran under N_2, convert, for example, various ketones to amines in an overall reductive deoxygenation process. Rather than the N_2 insertion mechanism discussed above, this author proposes that an intermediate titanocene nitride complex, formed in these mixtures, is the species which actually reacts with the organic carbonyl.

Nitrogen-reducing systems involving Ti have recently been shown to catalyze the formation of aluminum nitride from N_2 either in a mixture of Al in molten $AlBr_3$[48] or upon electrolysis with an Al anode.[49] However, these examples, as well as many other N_2 reducing systems which utilize highly-reducing metals, almost seem to have more in common with the heterogeneous nitriding of Li wire[50] than with biological N_2 reduction.

Various conflicting proposals as to the mechanism of N_2 reduction in the titanocene systems have been put forth. Highly reactive titanium hydride species, observed by their epr spectra, were originally thought to be responsible for this reactivity[38,40,57] although there was little

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agreement as to the actual hydride complex involved. Several analogous hydride-transfer mechanisms have been postulated to explain biological reduction by nitrogenase.[29,30] Later, other authors suggested, on the basis of new epr studies, that the species which binds the N_2 molecule was probably diamagnetic, and possibly a Ti(0) complex.[58] Still other reports have stated, although without much experimental support, that Ti(II) complexes are actually the species which coordinate and reduce N_2.[42,59] The numerous reports and proposals based on studies with the green titanium compound $C_{20}H_{20}Ti_2$, often referred to as titanocene in the literature, have contributed to the confusion regarding the mechanism of N_2 coordination and reduction in these systems, since this compound is not titanocene at all, but a titanium hydride complex with a rather complicated structure.[60]

It would seem, however, that most of the titanium systems in which reduction of N_2 occurs have been too complex to unambiguously define a mechanistic pathway, or to allow isolation of intermediate nitrogen complexes, so that the numerous proposals concerning the actual mechanism of the N_2 fixation have been largely speculation. In particular, it seems that considerable ambiguity has resulted from a failure to distinguish between epr-active species, the species which binds the N_2 molecule, and the mechanism by which the bound N_2 is reduced, perhaps to a nitride, which can then be hydrolyzed to yield ammonia.

This work on titanocene chemistry was initiated primarily with the objectives of isolating and characterizing intermediate titanocene complexes formed in these systems, and of gaining an understanding of the reaction chemistry of these highly reactive species, which could then possibly be correlated to their observed behavior towards N_2.

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CHAPTER 1

ISOLATION OF A NITROGEN-REDUCING TITANOCENE DERIVATIVE FROM THE VOLPIN-SHUR SYSTEM

A reaction mixture which reduces N_2 in an essentially stoichiometric reaction is obtained when titanocene dicloride is allowed to react with excess Grignard reagent in an ethereal solvent.[40] In an effort to identify intermediates in these systems, the electron paramagnetic (epr) spectra of several alkyl and hydride complexes of titanocene, which form in these reaction mixtures, had been investigated in this laboratory.[61] More recently, it was found that on addition of ethylmagnesium chloride to a suspension of $(C_5H_5)_2TiCl_2$ in diethyl ether, the reactive ingredient of this reaction mixture can be isolated as a yellow microcrystalline powder.

Isolation and Characterization

The yellow precipitate begins to snow out from solutions containing a 6-8 fold excess of C_2H_5MgCl after about 10-15 minutes. If the solution is quickly filtered after most of the precipitate has formed, the remainder of the yellow material will usually crystallize from the brownish filtrate in the form of rather well-shaped platelets of about 0.5 mm diameter, growing on the walls of the vessel. The material directly precipitated from the reaction mixture appeared sufficiently pure and uniform, however, to be used for the chemical studies discussed below. For this purpose it was filtered, washed with fresh ether at -80°C, and dried *in vacuo*, as described in the experimental section of this thesis.

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The stoichiometry of a number of reactions of the yellow solid establishes its formulation as a titanocene ethyl complex with a composition $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$. Upon heating to 125°C, for example, the yellow complex darkens and decomposes, liberating 0.5 mmol of C_2H_4 and 0.5 mmol of C_2H_6 per mmol of Ti. In controlled reactions of the highly air-sensitive complex with pure O_2, the evolution of equimolar amounts of ethylene and ethane is also observed. These results are consistent with a disproportionation of the two Ti-C_2H_5 units in the complex, to yield one mmol each of C_2H_4 and C_2H_6.

In reactions of the yellow solid with acidic reagents, such as H_2O or HCl, only ethane is liberated. The reaction of the complex with H_2O vapor results in the evolution of 1.0 mmol of C_2H_6 and 0.5 mmol of H_2 per mmol of Ti. The yellow solid initially turns light blue upon exposure to H_2O vapor, possibly the result of formation of $(C_5H_5)_2TiOH$, which then slowly oxidizes to a yellowish-green product. The H_2 evolved in the reaction likely results from the oxidation of Ti(III) to Ti(IV). The yellow solid reacts with HCl gas to form $(C_5H_5)_2TiCl_2$. The reaction is not quite stoichiometric, however, and only about 90% of the titanium can be reconvered as pure titanocene dichloride. In this reaction with HCl, and similarly in a number of other reactions, one finds that slightly more than one C_2H_6 is obtained per titanium center. This observation indicates that the $MgCl_2$ in the yellow solid contains a small admixture of C_2H_5MgCl. The determination of the magnesium, chloride, and ether content of the compound are detailed in the experimental section.

The ethyl complex exhibits bulk diamagnetism, as determined by Gouy balance measurements. This rules out the possibility that the compound is monomeric, since the titanocene species $(C_5H_5)_2TiC_2H_5$

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would have a formal Ti(III) center and, therefore, one unpaired electron. The complex might, therefore, be a dimer, analogous to the violet hydride compound $[(C_5H_5)_2TiH]_2$,[62] or a higher polymeric species with titanium ethyl bridges. The equivalent weight, based on the titanium content, is in good agreement with the proposed composition.

This composition still leaves some ambiguity as to the anion associated with the $(C_5H_5)_2Ti$ moiety: in principle, the yellow solid could also be formulated as $[(C_5H_5)_2TiCl]_2 \cdot 2\ C_2H_5MgCl \cdot 4\ MgCl_2 \cdot 7\ (C_2H_5)_2O$. The ease with which the ethyl groups are lost as C_2H_4 and C_2H_6 upon moderate warming, and the formation of titanocene derivatives not containing chloride in numerous reactions of the yellow complex, is much more indicative, however, of a titanium alkyl structure than of a Grignard compound. It therefore seems likely that the formation of the yellow precipitate occurs essentially according to the following equation:

$$2\ (C_5H_5)_2TiCl_2 + 8\ C_2H_5MgCl \xrightarrow{(C_2H_5)_2O}$$

$$[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O + C_2H_6 + C_2H_4 + 2\ (C_2H_5)_2Mg \qquad (1)$$

This equation is in satisfactory accord with most observations on this reaction system,[63] for instance with a minimum of 4 $C_2H_5MgCl/(C_5H_5)_2TiCl_2$ required for the formation of the yellow solid.

In previously published studies on various titanocene alkyl compounds it was observed that all titanocene monoalkyl compounds, except for the methyl derivative, are unstable and decompose even at -80°C.[61] While one might invoke stabilization of the ethyl titanocene structure by the lattice in the yellow solid, it appears remarkable that this unit would survive at room temperature for ca. thirty minutes

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until the precipitation is complete. Similarly, Mr. Stanley Wreford, an undergraduate research assistant in this laboratory, has observed that the yellow solid can be dissolved in tetrahydrofuran (THF) at -80°C to form a yellow-brown solution which retains the titanium-ethyl groups almost completely.[64] Obviously, some ingredient of these solutions, either the magnesium chloride, or the small admixture of C_2H_5MgCl, act to stabilize the ethyl titanium species present.

Reactivity of the Complex

Upon dissolution in THF or other solvents at room temperature, however, the yellow solid disintegrates with the loss of the titanium-ethyl bonds. Depending on the reaction partners present, the primary product of this decomposition might be a hydride species arising from the elimination of C_2H_4 (equation 2).

$$[(C_5H_5)_2TiC_2H_5]_2 \longrightarrow 2/x\ [(C_5H_5)_2TiH]_x + 2\ C_2H_4 \qquad (2)$$

In other cases, however, a $[(C_5H_5)_2Ti]_2$ intermediate appears to be formed directly by elimination of both C_2H_4 and C_2H_6 from the titanocene alkyl derivative (equation 3).

$$[(C_5H_5)_2TiC_2H_5]_2 \longrightarrow [(C_5H_5)_2Ti]_2 + C_2H_4 + C_2H_6 \qquad (3)$$

The availability of a hydride species is evident in numerous reactions of the yellow complex which are uniquely characteristic of a $(C_5H_5)_2TiH$ intermediate.[62] The complex reacts, for example, with diborane in THF to give, in about 20% yield, the violet titanocene borohydride complex:[65]

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$$[(C_5H_5)_2TiC_2H_5]_2 + B_2H_6 \xrightarrow{THF} 2\ (C_5H_5)_2TiBH_4 + 2\ C_2H_4 \qquad (4)$$

Similarly, the complex reacts with 1,3-pentadiene to yield the blue allyl complex:[66]

$$[(C_5H_5)_2TiC_2H_5]_2 + 2\ C_5H_8 \longrightarrow 2\ (C_5H_5)_2Ti(\pi\text{-}C_5H_9) + 2\ C_2H_4 \qquad (5)$$

The epr spectrum of a mixture of the yellow $(C_5H_5)_2TiC_2H_5$ complex and triphenylphosphine in 2-methyltetrahydrofuran exhibits two doublets identical with those observed for a mixture of violet $[(C_5H_5)_2TiH]_2$ and $P(C_6H_5)_3$, and assigned to the complex $(C_5H_5)_2Ti(H)P(C_6H_5)_3$.[62] When the yellow solid is stirred with excess $P(C_6H_5)_3$ in ether, the formation of $(C_5H_5)_2Ti(H)P(C_6H_5)_3$ takes place concurrent with the evolution of essentially pure C_2H_4.[64] When evacuated these solutions turn bright purple upon loss of H_2 to form a titanocene triphenylphosphine complex, $[(C_{10}H_{10})TiP(C_6H_5)_3]_2$. (see chapter 3)

The yellow compound reacts with methyl iodide to form a bright orange solution with the evolution of 0.5 mmol of CH_4, 0.8 mmol of C_2H_4, and 0.3 mmol of C_2H_6. The formation of methane in this reaction, and the predominance of ethylene in the evolution products, indicates that this reaction proceeds, at least in part, via a hydride intermediate. The amount of CH_4 produced, which is almost equal to the increase of C_2H_4 formed over that expected for a simple disproportionation, is in accord with equation 2, which requires that each hydride moiety formed be accompanied by the evolution of one C_2H_4 molecule.

The evolution of substantial amounts of C_2H_6 indicates that the formation of a titanocene intermediate according to equation 3 competes appreciably with the hydride formation 2. In accord with this,

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substantial amounts of the oxidative-addition product $(C_5H_5)_2TiICH_3$ are formed in the reaction mixture.

Reactions with Molecular Nitrogen

Most significant, however, is the observation that the yellow compound $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ reacts with N_2 upon stirring in the autoclave with an ethereal solvent to form a titanocene nitride derivative which can be hydrolyzed to give ammonia. The stoichiometry of the reduction reaction and the nature of the species containing the reduced nitrogen indicate that the reactivity of the yellow ethyl complex towards molecular nitrogen results from its ability to act as a source of the highly reactive species $[(C_5H_5)_2Ti]_2$.(1)

Since the yellow solid does not react with N_2 to any appreciable extent in the absence of solvents, an apparatus was designed to carry out the reaction at high pressure while minimizing the competitive degradation reactions in solution. The apparatus described in the experimental section of this thesis was used with good results. The most consistent results were obtained using 1,2-dimethoxyethane (DME) as the solvent for the N_2 reactions. The reaction in DME is complete after 10-15 minutes at room temperature. Reproducible yields of 60% NH_3 were obtained in this solvent, the highest observed yield being 64.2%. In THF somewhat irreproducible yields ranging from 25 to 60%

(1). In accord with the results presented in Chapter 2, this titanocene intermediate will generally be formulated as a dimer. However, it is obvious that the reactive species in many of the reactions discussed could also be the monomeric $(C_5H_5)_2Ti$, either formed *in situ*, or in equilibrium with the dimer.

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were observed.

The presence of excess ethylmagnesium chloride enhances the NH_3 yields somewhat. In the presence of a 1.5 fold excess of C_2H_5MgCl in THF, the yield of NH_3 was 66.3%. Increasing the amount of Grignard to a ten-fold excess raised the yield only slightly to 72.6% Since C_2H_5MgCl is only slighly soluble in DME, large excess of Grignard could not be used in that solvent.

An analysis of the gases evolved from the reduction reaction shows that roughly equal amounts of ethane (0.54 mmol/mmol Ti) and ethylene (0.36 mmol/mmol Ti) are liberated when the yellow complex reacts with N_2. By analogy to the reactions discussed above, these results indicate that the decomposition of the ethyl complex yields $[(C_5H_5)_2Ti]_2$ as an intermediate under these conditions (equation 3). Furthermore, when the yellow solid is reacted with 100 atmospheres of carbon monoxide under conditions identical to those used in the N_2 reduction, $(C_5H_5)_2Ti(CO)_2$ is formed, providing additional evidence for the occurrence of a $(C_5H_5)_2Ti$ species under the conditions of the N_2 reaction.

Excess hydrogen, present at a pressure of 30 atm, completely suppresses the nitrogen reduction by $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ in the presence of 125 atm of N_2. This result is to be expected if $[(C_5H_5)_2Ti]_2$ is in fact an intermediate in the reduction of N_2 (see chapter 2), and eliminates the possibility that a hydride species like $[(C_5H_5)_2TiH]_x$ is responsible for the N_2 reduction, since the occurence of such a species could only be favored by the presence of excess H_2.

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Chacterization of the N_2 Reduction Product

From the crude product mixture of the reaction of the yellow complex with N_2 in 1,2-dimethoxyethane, a black powdery solid has been isolated which contains the reduced nitrogen. The hydrolysis of the black solid with HCl leads to the formation of $(C_5H_5)_2TiCl_2$ and NH_3, in a ratio of 2 NH_3/3 Ti.

The black material contains, in addition, $MgCl_2$ and coordinated ethers, complicating the complete characterization of this reaction product. However, the virtual absence of H_2 evolution upon hydrolysis establishes a formal oxidation state of +IV for the titanium center in the N_2 reduction product, in accord with its formulation as a titanocene nitride complex:

$$[(C_5H_5)_2Ti^{2+}]_3[N^{3-}]_2 + 6\ HCl \longrightarrow 3\ (C_5H_5)_2TiCl_2 + 2\ NH_3 \qquad (6)$$

While the nitrogen in the product is quantitatively liberated as N_2 gas by strong oxidizing agents such as Cl_2, no N_2 is evolved upon hydrolysis or upon heating the black solid to 200°C in vacuum.

The observation that the titanocene nitride species has normal π-bound rings, as evidenced by the formation of $(C_5H_5)_2TiCl_2$ upon reaction with HCl, indicates that the reactive titanocene intermediate must retain its $(h^5\text{-}C_5H_5)_2Ti$ configuration in order to coordinate and reduce N_2.

Since a $(C_5H_5)_2Ti(II)$ species can provide no more than 2 of the 3 reduction equivalents required for the formation of a N^{3-} species, 0.67 mmol of NH_3/mmol Ti is the theoretical maximum yield, if $(C_5H_5)_2Ti$ is in fact the sole reducing agent in this reaction system. Maximum yields of 60-64% obtained in the N_2 reductions with the yellow complex

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in the absence of additional reducing agents, and the stoichiometry of the titanocene nitride product, therefore provide substantial evidence that a $(C_5H_5)_2Ti(II)$ species is responsible for the reduction of N_2 that is observed in the Volpin-Shur system. Direct evidence for the ability of a $(C_5H_5)_2Ti$ species to coordinate molecular nitrogen is presented in the following chapter.

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CHAPTER 2

A METASTABLE FORM OF TITANOCENE, $[(C_5H_5)_2Ti]_2$

The reaction between dimethyl titanocene, $(C_5H_5)_2Ti(CH_3)_2$, and H_2 gas has, for some time, been known to yield a dark green compound, which, although having the correct elemental composition for titanocene, $C_{10}H_{10}Ti$,[67] has been shown to be a dimeric titanium hydride derivative with two of its four cyclopentadienyl ligands present in the form of C_5H_4 units.[60]

$$(C_5H_5)_2Ti(CH_3)_2 + H_2 \longrightarrow \frac{1}{2}\,[(C_5H_5)(C_5H_4)TiH]_2 + 2\ CH_4 \qquad (7)$$

Dr. John E. Bercaw, in this laboratory, succeeded in isolating and characterizing the violet titanocene hydride complex $[(C_5H_5)_2TiH]_2$, which forms as an intermediate in the above reaction.[62]

$$(C_5H_5)_2Ti(CH_3)_2 + \frac{3}{2}\,H_2 \longrightarrow \frac{1}{2}\,[(C_5H_5)_2TiH]_2 + 2\ CH_4 \qquad (8)$$

This compound represented the first hydride complex of its kind to be isolated.

When heated <u>in vacuo</u>, the violet soild liberates H_2, turning dark green to form the less reactive $[(C_5H_5)(C_5H_4)TiH]_2$. Apparently, a highly reactive $(h^5\text{-}C_5H_5)_2Ti$ species, formed by elimination of H_2 from the violet hydride, readily undergoes deactivation via an α-hydrogen shift in much the same way as a carbene does.[68] A similar abstraction of cyclopentadienyl protons has recently been observed with analogous niobium and tantalum hydrides.[69]

The violet hydride, $[(C_5H_5)_2TiH]_2$, while relatively stable as a solid when stored at -80°C, was observed to convert to a green-gray

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product rather rapidly at room temperature, especially if any traces of impurities were present. This green-gray isomer, however, exhibited chemical reactivity identical with that of violet $[(C_5H_5)_2TiH]_2$.[68]

Characterization of the Green-Gray Hydride, $[(C_5H_5)_2TiH]_x$

Recently, it was found that the green-gray complex can be prepared directly by reacting saturated hexane solutions of $(C_5H_5)_2Ti(CH_3)_2$ with excess H_2 gas at 0°C. The formation of $[(C_5H_5)(C_5H_4)TiH]_2$, as shown in equation 7, is virtually eliminated when this reaction is carried out with efficient stirring and cooling at 0°C. Traces of this green impurity can easily be removed from the green-gray hydride by washing with toluene at -80°C.

The composition of the green-gray hydride is established as $[(C_5H_5)_2TiH]_x$ by a number of reactions which are virtually identical with those of $[(C_5H_5)_2TiH]_2$. For example, $[(C_5H_5)_2TiH]_x$ is converted to the green form of titanocene upon thermal decomposition at 100°C, as in equation 9:

$$\frac{1}{x}\,[(C_5H_5)_2TiH]_x \longrightarrow \frac{1}{2}\,[(C_5H_5)(C_5H_4)TiH]_2 + \frac{1}{2}\,H_2 \qquad (9)$$

Its reaction with DCl leads to titanocene dichloride and HD:

$$\frac{1}{x}\,[(C_5H_5)_2TiH]_x \xrightarrow{DCl} (C_5H_5)_2TiCl_2 + HD + \frac{1}{2}\,D_2 \qquad (10)$$

Formation of the dicarbonyl complex[70] and evolution of H_2 is observed upon exposure to CO:

$$\frac{1}{x}\,[(C_5H_5)_2TiH]_x \xrightarrow{CO} (C_5H_5)_2Ti(CO)_2 + \frac{1}{2}\,H_2 \qquad (11)$$

The green-gray hydride also resembles $[(C_5H_5)_2TiH]_2$ in its extreme (pyrophoric) air sensitivity. In contrast to the latter, however, it

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can be stored as a solid for months under Ar without noticeable decomposition. The insolubility of $[(C_5H_5)_2TiH]_x$ in ethereal solvents, which readily dissolve the violet hydride even at -80°C, indicate that the green-gray hydride is polymeric. An analogous Zr hydride complex, $[(C_5H_5)_2ZrH_2]_x$, showed a similar lack of solubility and was, in fact, postulated to be polymeric.[71]

The ir spectrum of $[(C_5H_5)_2TiH]_x$ (Figure 1) shows all the features of bona fide $(h^5\text{-}C_5H_5)_2Ti$ derivatives. It is nearly identical, for instance, to that of violet $[(C_5H_5)_2TiH]_2$. However, instead of the absorption at 1450 cm^{-1} attributed to the antisymmetric vibration of the TiH_2Ti ring in the violet compound,[62] a similarly broad band is observed at 1140 cm^{-1} in the green-gray isomer. In a deuterated sample, prepared by reacting $(C_5H_5)_2Ti(CH_3)_2$ with D_2, the broad absorption is shifted to 800-850 cm^{-1}. The absence of any absorption at 1230 cm^{-1}, or any observable splitting in the out-of-plane C-H bending mode at 800 cm^{-1}, which dominate the spectrum of $[(C_5H_5)(C_5H_4)TiH]_2$,[60] confirms the absence of this impurity in the green-gray hydride.

Formation of $[(C_5H_5)_2Ti]_2$ from the Green-Gray Hydride

The hydride $[(C_5H_5)_2TiH]_x$ is a convenient source of a highly reactive form of titanocene: when the hydride is suspended and stirred at room temperature in solvents such as toluene or diethyl ether, the gray solid slowly disappears. In the course of several hours a homogeneous dark solution is produced concurrent with the evolution of 0.5 mmol H_2 per mmol Ti. The resulting solutions must therefore contain a species of composition $[(C_5H_5)_2Ti]_x$. This species is definitely different from $[(C_5H_5)(C_5H_4)TiH]_2$: the intense green color typical of

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$[(C_5H_5)(C_5H_4)TiH]_2$ is completely absent from the $[(C_5H_5)_2Ti]_x$ solutions. When heated to 100°C, however, such a toluene solution turns bright green. Subsequently, pure $[(C_5H_5)(C_5H_4)TiH]_2$ can be isolated from the solution. This stoichiometric conversion shows that the $[(C_5H_5)_2Ti]_x$ species originally formed from the green-gray hydride must be a metastable isomer of $[(C_5H_5)(C_5H_4)TiH]_2$. Exactly analogous observations are made with toluene solutions obtained by hydrogen elimination from the violet hydride $[(C_5H_5)_2TiH]_2$.

The ir spectra of solutions of the metastable $[(C_5H_5)_2Ti]_x$, or of residues obtained by removal of the solvent (Figure 1) do not exhibit any of the band splittings characteristic of $[(C_5H_5)(C_5H_4)TiH]_2$.[62] Rather a simple metallocene spectrum, with two bands at 790 cm^{-1} and 1010 cm^{-1}, is observed for $[(C_5H_5)_2Ti]_x$.

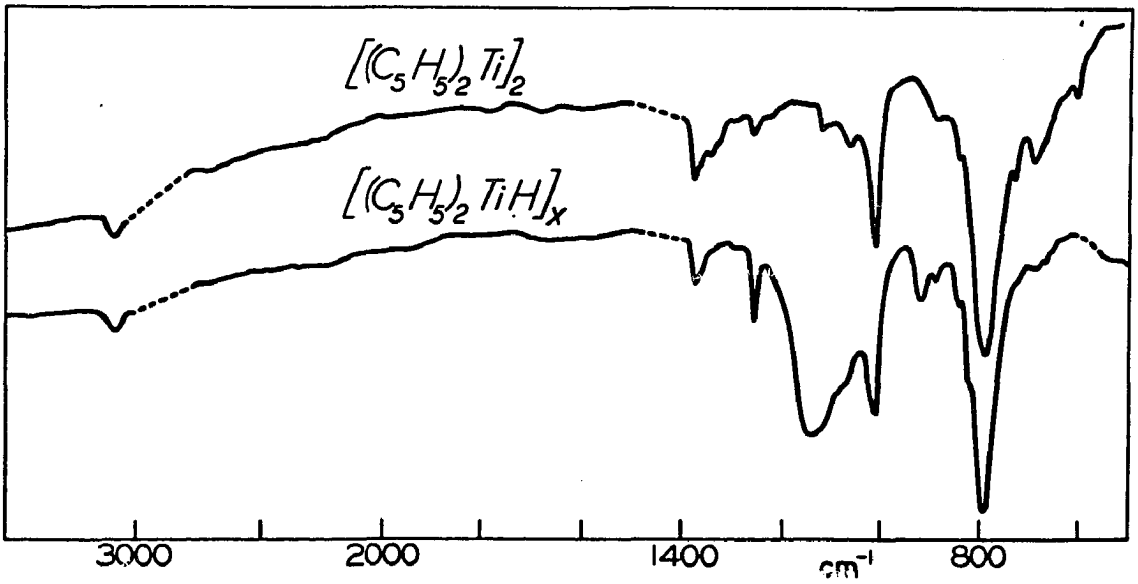

Figure 1. Ir spectra of $[(C_5H_5)_2Ti]_2$ (top) and $[(C_5H_5)_2TiH]_x$ (bottom), taken in nujol on KBr.

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Molecular weight studies by cryoscopy in benzene show that the complex is dimeric in solution. An average apparent molecular weight of 385 ± 30 was obtained for 0.2 to 0.06 F solutions in fairly good agreement with the value of 356 calculated for $[(C_5H_5)_2Ti]_2$.

Properties of $[(C_5H_5)_2Ti]_2$

Magnetic susceptibility determinations on ca. 0.1 M solutions of $[(C_5H_5)_2Ti]_2$ in toluene at 30°C[72] indicate a noticeable paramagnetism, which could be explained by the presence of a small fraction of the complex as monomeric $(C_5H_5)_2Ti$ with two unpaired electrons, possibly as a result of a monomer-dimer equilibrium. Such an equilibrium has been observed by Bercaw with solutions of decamethyltitanocene, $[C_5(CH_3)_5]_2Ti$.[68] While $[(C_5H_5)_2Ti]_2$ and $[C_5(CH_3)_5]_2Ti$ resemble each other in many of their reaction paterns, as will be shown in detail below, they do exhibit some interesting differences in behavior which are related to the steric crowding of the decamethyltitanocene sandwich. Whereas the unsubstituted titanocene, $[(C_5H_5)_2Ti]_2$, is preponderantly dimeric in solution, monomeric and dimeric decamethyltitanocene are present in almost equal concentrations in 0.1 M solutions of this complex. While a titanium-titanium bond of appreciable strength appears to exist in both of the dimeric titanocenes, the steric crowding of the methylated ring ligands undoubtedly favors the mononuclear species $[C_5(CH_3)_5]_2Ti$.

Attempts to obtain $[(C_5H_5)_2Ti]_2$ as a crystalline solid have not been successful. Cooling solutions of $[(C_5H_5)_2Ti]_2$ in toluene or in mixtures of toluene and hexane leads only to a tarry solid material. The titanocene species is sufficiently stable in solution, however,

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to allow quantitative studies to be carried out directly with solutions prepared from purified samples of $[(C_5H_5)_2TiH]_x$. Toluene solutions of $[(C_5H_5)_2Ti]_2$ can be kept at room temperature for several days without noticeable decomposition. The presence of impurities seems to increase the sensitivity of $[(C_5H_5)_2Ti]_2$ to decomposition, in particular, to deactivation to $[(C_5H_5)(C_5H_4)TiH]_2$.

In tetrahydrofuran, however, $[(C_5H_5)_2Ti]_2$ is not stable at room temperature: initially a bright green THF adduct forms which, in the course of ca. thirty minutes, further reacts to yield a brown decomposition product. Removal of the THF from solutions of the initially formed green adduct yields a dark green solid, which, although containing coordinated THF, can be redissolved in toluene to regenerate the reactive $[(C_5H_5)_2Ti]_2$ species. The brown product, possibly a titanocene alkoxide derivative resulting from insertion into THF, no longer exhibits any of this characteristic reactivity. This observed reactivity of $[(C_5H_5)_2Ti]_2$ towards tetrahydrofuran could explain some of the earlier observations concerning green and brown THF adducts of titanocene.[73,74]

The presence of normal h^5-C_5H_5 rings in $[(C_5H_5)_2Ti]_2$ is also supported by its chemical behavior. When exposed to HCl gas at -80°C, solutions of $[(C_5H_5)_2Ti]_2$ rapidly react to form $(C_5H_5)_2TiCl_2$. The formation of the magenta chloride complex $[(C_5H_5)(C_5H_4)TiCl]_2$, characteristic of the green compound $[(C_5H_5)(C_5H_4)TiH]_2$,[75] was not observed in the reaction of $[(C_5H_5)_2Ti]_2$ solutions with HCl. When exposed to carbon monoxide, an ether solution of $[(C_5H_5)_2Ti]_2$ immediately absorbs CO to form, in essentially quantitative yields, the dicarbonyl complex, $(C_5H_5)_2Ti(CO)_2$.[70]

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Reactions of $[(C_5H_5)_2Ti]_2$ with H_2 and N_2

When solutions of $[(C_5H_5)_2Ti]_2$ in toluene or ether are stirred in an atmosphere of hydrogen gas, somewhat variable amounts of H_2 are absorbed. When these solutions are cooled to -80°C, evacuated, and then warmed again to room temperature, 0.2 to 0.4 mmols of H_2/ mmol of Ti are released. Although the reaction of $[(C_5H_5)_2Ti]_2$ with H_2 is not stoichiometric, molecular weight determinations by cryoscopy in benzene indicate that the dimeric titanocene is cleaved to a significant extent upon exposure to H_2. By analogy to the reaction of $[C_5(CH_3)_5]_2Ti$ with H_2, which leads to the formation of the hydride complex $[C_5(CH_3)_5]_2TiH_2$,[68] it seems probable that formation of some monomeric hydride complex occurs in the unsubstituted titanium compound as well.

When toluene solutions of $[(C_5H_5)_2Ti]_2$ are stirred with D_2 gas for several hours, a complete exchange of deuterium between the gas phase and all hydrogen positions of the cyclopentadienyl rings occurs. Obviously, one of the species in the equilibrium mixture must undergo a facile rearrangement which exchanges hydride ligands with ring hydrogen atoms. Most likely, the species in which this exchange occurs is either $[(C_5H_5)_2Ti]_2$ or the monomer $(C_5H_5)_2Ti$ in equilibrium with it. A similar D_2-exchange, which occurs with a titanocene triphenylphosphine complex, is described in chapter 3.

Slightly cooled solutions of $[(C_5H_5)_2Ti]_2$, upon exposure to nitrogen gas, instantaneously absorb N_2 to form an intensely blue complex. At -80°C one mmol of N_2 is retained by one mmol of $[(C_5H_5)_2Ti]_2$. The coordination is completely reversible, the N_2 being released upon warming to room temperature, or by evacuation at about -20°C. In very concentrated solutions of $[(C_5H_5)_2Ti]_2$ in toluene, the blue complex

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persists even at room temperature. The nitrogen complex can be obtained as a solid since it is much less soluble in toluene than $[(C_5H_5)_2Ti]_2$. By cooling toluene solutions of the complex to -80°C, filtering, washing with butane and drying in vacuum, all operations carried out at -80°C, the nitrogen complex is isolated as a dark blue powder which can be stored under N_2 at room temperature without noticeable decomposition. When dissolved in toluene, it releases one mmol of N_2 per mmol of $[(C_5H_5)_2Ti]_2$ in accord with the proposed stoichiometry of the complex as $[C_5H_5)_2Ti]_2N_2$.

Attempts to observe any infrared absorption attributable to the coordinated N_2 moiety were unsuccessful. The ir spectrum of the solid $[(C_5H_5)_2Ti]_2N_2$ exhibits only the plain metallocene bands observed with $[(C_5H_5)_2Ti]_2$ (see Figure 3). This observation is in accord with the symmetrical dimeric structure $(C_5H_5)_2Ti\text{-}N_2\text{-}Ti(C_5H_5)_2$. The complex is too intensely colored to yield a Raman spectrum; no significant emission could be observed upon irradiation of a solid sample of $[(C_5H_5)_2Ti]_2N_2$ with either neon or argon lasers.

Due to its intense blue color and instability in highly diluted solutions, it is rather difficult to obtain exact quantitative optical absorption data for $[(C_5H_5)_2Ti]_2N_2$. The extinction coefficient at λ_{max} = 597 nm is definitely greater than 10^4.

Interestingly, an obviously related observation has been reported by Shilov et al.[42] When THF solutions of $(C_5H_5)_2TiCl_2$ are treated with 2 equivalents of C_2H_5MgBr at -70°C in a nitrogen atmosphere, a transient intensely blue species (λ_{max} = 600 nm)

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appears in solution. From the similarity of its color and a concentration dependence proportional to $[Ti]^2$, there can be little doubt that the species observed in solution by these authors is in fact identical to the complex $[(C_5H_5)_2Ti]_2N_2$ which we have isolated.

A remarkably similar N_2 complex has been observed to form by J. E. Bercaw when solutions of $[C_5(CH_3)_5]_2Ti$ are exposed to N_2.[68,76] This purple-blue (λ_{max}= 568 nm) N_2 complex is also relatively unstable, evolving N_2 upon warming to ca. -10°C in vacuo to yield $[C_5(CH_3)_5]_2Ti$.

The blue complex $[(C_5H_5)_2Ti]_2N_2$ can be reduced to some ammonia derivative of titanocene. When a diethyl ether solution of $[(C_5H_5)_2Ti]_2N_2$ is treated with two equivalents of lithium naphthalide at -80°C, and then warmed to room temperature under a pressure of ca. 150 atmospheres of N_2, most of the coordinated N_2 is reduced, and, upon subsequent hydrolysis, released as NH_3. The reaction is somewhat irreproducible, however, and variable yields of NH_3, from 35 to 95%, have been obtained.

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CHAPTER 3

SOME RELATED EXPERIMENTS WITH A TITANOCENE TRIPHENYLPHOSPHINE COMPLEX, $[C_{10}H_{10}TiP(C_6H_5)_3]_2$

Another highly reactive derivative of titanocene is obtained in reaction systems containing triphenylphosphine. In a variety of such systems, discussed below, an intensely purple phosphine complex is obtained. Shilov *et al.* have reported similar observations.[42] However, these authors have interpreted their results in terms of the formation of a N_2-containing triphenylphosphine complex of titanocene. In contrast to this, we find that the purple complex (λ_{max} = 521 nm) is a species of composition $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ which forms in the absence of N_2.(2)

The phosphine complex was first observed by J. E. Bercaw, who found that the previously described hydride complex $(C_5H_5)_2Ti(H)P(C_6H_5)_3$, formed in the reaction[62]

$$\frac{1}{2}\,[(C_5H_5)_2TiH]_2 + P(C_6H_5)_3 \longrightarrow (C_5H_5)_2Ti(H)P(C_6H_5)_3 \qquad (12)$$

readily eliminates H_2 to form an intensely purple complex. Spectral studies have shown that this reaction is in fact a reversible equilibrium, according to:[68]

$$[C_{10}H_{10}TiP(C_6H_5)_3]_2 + H_2 \rightleftharpoons 2\ (C_5H_5)_2Ti(H)P(C_6H_5)_3 \qquad (13)$$

---

(2). Several aspects of the reactivity and properties of this phosphine complex (its dimeric nature, reactions with H_2, N_2, HCl, and its thermal decomposition to $[(C_5H_5)(C_5H_4)TiH]_2$ and $P(C_6H_5)_3$) have been discussed in detail earlier by J. E. Bercaw, reference 68.

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A completely analogous reaction sequence is observed when the green-gray polymeric hydride, $[(C_5H_5)_2TiH]_x$, is substituted for the violet dimer. Reaction of the metastable titanocene, $[(C_5H_5)_2Ti]_2$, with triphenylphosphine in toluene yields the purple complex directly without evolution of hydrogen.

The most convenient preparation of the purple phosphine complex is the reaction of $(C_5H_5)_2Ti(CH_3)_2$ with hydrogen in the presence of triphenylphosphine in hexane at 0°C. Under these conditions the compound precipitates cleanly from the reaction mixture.

$$(C_5H_5)_2Ti(CH_3)_2 + H_2 \xrightarrow[P(C_6H_5)_3]{0°C} \frac{1}{2}[C_{10}H_{10}TiP(C_6H_5)_3]_2 + 2\ CH_4 \quad (14)$$

The indication that this phosphine complex might be an intermediate in the deactivation of a h^5-C_5H_5 titanocene species, possibly via an α-hydrogen shift to a compound like $[(C_5H_5)(C_5H_4)TiH]_2$, led us to believe that the complete characterization of this purple complex might shed some light on the mechanism by which this rearrangement occurs in these reactive titanocene compounds. It seemed probable that some distortion of the cyclopentadienyl ligands was present in $[C_{10}H_{10}TiP(C_6H_5)_3]_2$: treatment of the purple compound with HCl did not yield $(C_5H_5)_2TiCl_2$, but, rather, the magenta chloride complex,[75] $[(C_5H_5)(C_5H_4)TiCl]_2$. In addition, the possibility of some kind of rearrangement product is indicated by the ir spectrum of the phosphine complex: in contrast to $[(C_5H_5)_2Ti]_2$, the out-of-plane bending mode of the ring ligands at ca. 800 cm^{-1} is split in $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ in a manner quite similar to that observed in $[(C_5H_5)(C_5H_4)TiH]_2$. The strong absorption at 1230 cm^{-1}, characteristic of $[(C_5H_5)(C_5H_4)TiH]_2$,[60] is completely absent, however. The possibility that the phosphine

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complex is simply a triphenylphosphine adduct of $[(C_5H_5)(C_5H_4)TiH]_2$ is ruled out by the fact that, upon stirring the dark green hydride with triphenylphosphine in toluene solution for three days, the formation of the purple compound was not observed.

It is clear, however, that, if the cyclopentadienyl ligands are distorted in $[C_{10}H_{10}TiP(C_6H_5)_3]_2$, this distortion is reversible, and that a h^5-C_5H_5 structure can be regenerated in this compound. The reversible formation of the phosphine hydride complex, $(C_5H_5)_2Ti(H)P(C_6H_5)_3$, from the purple complex seems conclusive of this. In addition to the epr spectra of the hydride complex, which indicated the presence of normal h^5-C_5H_5 rings,[62] ir spectra taken with solutions of the phosphine hydride complex(3) exhibit none of the deviations from normal metallocene spectra that are observed with $[(C_5H_5)(C_5H_4)TiH]_2$,[60,75] $[(C_5H_5)(C_5H_4)TiCl]_2$,[60] and even with $[C_{10}H_{10}TiP(C_6H_5)_3]_2$.[68]

Supporting chemical evidence for the presence of normal π-bound rings in $(C_5H_5)_2Ti(H)P(C_6H_5)_3$ was found in the essentially quantitative conversion of this complex to $(C_5H_5)_2TiBH_4$[65] upon treatment with excess diborane.

$$(C_5H_5)_2Ti(H)P(C_6H_5)_3 \xrightarrow{B_2H_6} (C_5H_5)_2TiBH_4 + P(C_6H_5)_3 \qquad (15)$$

Furthermore, when toluene solutions of the purple triphenylphosphine complex were exposed to excess CO, significant amounts of the dicarbonyl

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(3). Attempts to observe any ir absorption attributable to the terminal hydride moiety in $(C_5H_5)_2Ti(H)P(C_6H_5)_3$ have been unsuccessful. The epr spectra of this complex, and spectra of deuterated samples, seem to be conclusive proof of such a structure, however. Examples of metal hydrides in which no conclusive evidence for infrared M-H stretching vibrations was found are known in the literature.[77-82]

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complex were formed.

If D_2 is substituted for H_2 in equilibrium 13, the following phenomena are observed: (1) H_2 appears in the gas phase, (2) replacing the gas phase several times with fresh D_2 leads to a completely deuterated complex, and (3) thermal decomposition of this resulting complex yields $[(C_5D_5)(C_5D_4)TiD]_2$ and $P(C_6H_5)_3$. This isotope exchange is indicative of a facile ring-to-titanium hydrogen shift in one of the species in the equilibrium mixture. While either $(C_5H_5)_2Ti(H)P(C_6H_5)_3$ or $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ might be responsible for the observed ring-D_2 exchange, the absence of any deuterium exchange with the aromatic ortho positions in $P(C_6H_5)_3$, frequently observed in other systems,[83] suggests that the reactive species involved in the exchange is void of triphenylphosphine. It therefore seems likely, by analogy to the isotope exchange observed with the metastable $[(C_5H_5)_2Ti]_2$, that this species, $[(C_5H_5)_2Ti]_2$, is in fact in equilibrium with $[C_{10}H_{10}TiP(C_6H_5)_3]_2$. That some $[(C_5H_5)_2Ti]_2$ occurs in equilibrium with $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ in solution is also indicated by the stabilization of the latter in the presence of excess $P(C_6H_5)_3$,[68] and by its reaction with carbon monoxide to form $(C_5H_5)_2Ti(CO)_2$, as discussed above.

The question of how, exactly, the cyclopentadienyl ligands are bound to the titanium in this phosphine complex has not been answered, and its structure remains unclear. It is apparent, however, that a highly reactive form of titanocene, as contrasted to the unreactive $[(C_5H_5)(C_5H_4)TiH]_2$, is preserved in $[C_{10}H_{10}TiP(C_6H_5)_3]_2$. The observed reactivity of the phosphine complex toward carbon monoxide, molecular hydrogen and molecular nitrogen strongly support this supposition.

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CHAPTER 4
DISCUSSION

In view of the numerous unsuccessful attempts to isolate $(C_5H_5)_2Ti$ and the ease with which the less reactive isomer $[(C_5H_5)(C_5H_4)TiH]_2$ is formed instead of $(C_5H_5)_2Ti$,[60,84] it is indeed surprising to find that a dimeric, yet highly reactive form of this compound, $[(C_5H_5)_2Ti]_2$, is stable in solution at room temperature. The normally occurring rearrangement to $[(C_5H_5)(C_5H_4)TiH]_2$ via a ring-to-titanium hydrogen shift is apparently suppressed when $[(C_5H_5)_2Ti]_2$ is formed slowly under mild conditions from a titanocene hydride complex. In the absence of any other reactants, highly reactive monomeric $(C_5H_5)_2Ti$ species, generated by H_2 elimination from $[(C_5H_5)_2TiH]_x$, rapidly dimerize to form the metastable compound $[(C_5H_5)_2Ti]_2$.

A high affinity of the titanium center for hydrogen is also evident from the behavior of titanocene toward molecular hydrogen: not only is there a reversible hydrogen complexation observed when $[(C_5H_5)_2Ti]_2$ is exposed to H_2, but, in addition, one also finds that exchange occurs between D_2 gas and all the hydrogen positions in the C_5H_5 rings. A <u>reversible</u> ring-to-titanium hydrogen shift must be invoked to explain this observation. A similar exchange between D_2 and all the cyclopentadienyl hydrogens has been observed before by Martin and deJongh when solutions of the grayish hydrogenation product of 1-methylallyl titanocene are exposed to D_2.[85] From the properties of the hydrogenation product, as described by Martin,[86] it seems likely that this material is identical to the green-gray $[(C_5H_5)_2TiH]_x$ described here.

The structure of the titanocene species resulting from such a

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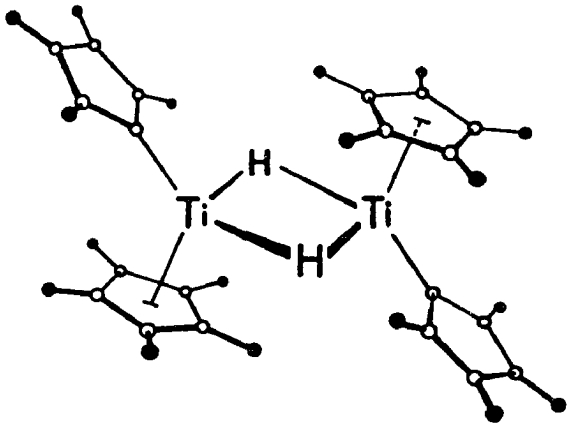
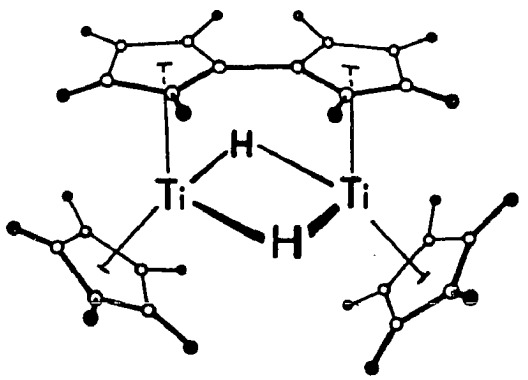
reversible hydrogen shift could for instance be 1, or the corresponding monomer.[60]



1

The concentration of a species such as 1 must be rather small, however, since ir spectra of $[(C_5H_5)_2Ti]_2$ solutions do not exhibit any deviations from those of *bona fide* $(h^5\text{-}C_5H_5)_2Ti$ derivatives, or any absorption attributable to a double hydrogen bridged structure, such as the strong absorption at 1450 cm^{-1} in $[(C_5H_5)_2TiH]_2$.[62]

Judging from the isotope exchange rate, the reversible conversion to a hydride structure like 1 is much faster than the degradation to the green dimer $[(C_5H_5)(C_5H_4)TiH]_2$. The possibility that two C_5H_4 units have to couple to a $C_{10}H_8$ ligand, as in structure 2, might provide a reasonable explanation for the higher activation energy of this latter rearrangement.[60]



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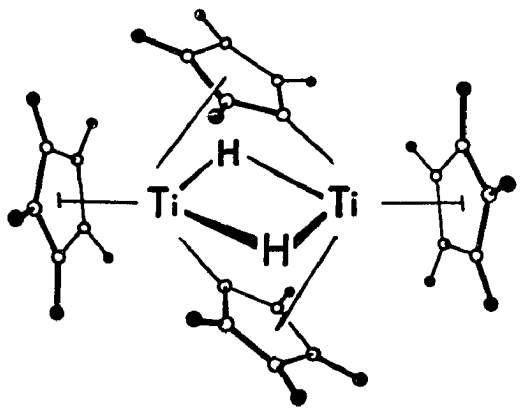
The only substantial evidence for the presence of a fulvulene ligand in the green dimer $[(C_5H_5)(C_5H_4)TiH]_2$ is the occurrence of an unusally intense peak at m/e = 128, corresponding to $C_{10}H_8^+$, in the mass spectrum of this compound. It is not clear, however, whether this moiety is actually present in $[(C_5H_5)(C_5H_4)TiH]_2$, or if it is formed in the source of the mass spectrometer.

An alternate structure for this compound can be envisioned, as in structure 3; containing bridging C_5H_4 ligands in a manner similar to that observed in $(C_5H_5)(CO)\overline{Mo\text{-}\mu\text{-}C_5H_4\text{-}Mn(CO)_4}$,[87] and in the recently reported dimer of "niobocene", $[(C_5H_5)(C_5H_4)NbH]_2$.[69]



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This titanocene structure has been postulated recently by Parshall *et al.*[1,69] by analogy to their findings with the similar niobocene system. The occurrence of a bridging C_5H_4 ligand has also been established for the titanocene derivative $[(C_5H_5)Ti\text{-}\mu\text{-}C_5H_4\text{-}Al(C_2H_5)_2]_2$.[88-90] The preparation of this compound directly from the green dimer, as in equation 16,[90] strongly suggests the actual presence of bridging C_5H_4 units in $[(C_5H_5)(C_5H_4)TiH]_2$ rather than the $C_{10}H_8$ moiety postulated

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earlier.[60]

$$[(C_5H_5)(C_5H_4)TiH]_2 + Al_2(C_2H_5)_6 \longrightarrow \quad (16)$$

$$[(C_5H_5)Ti\text{-}\mu\text{-}C_5H_4\text{-}Al(C_2H_5)_2]_2 + 2\ C_2H_6$$

Despite the ambiguity about the structure of the green dimer, it seems apparent that the observed exchange between D_2 and all the hydrogen positions of the cyclopentadienyl rings requires a reversible ring to metal hydrogen shift of the kind represented in structure 1. For the actual mechanism of the exchange, several pathways can be envisioned: one possibility is the formation of a mixed dimeric species, $(C_5H_5)(C_5H_4)TiHDTi(C_5H_5)_2$, formed from the monomeric moieties of structure 1 and $[(C_5H_5)_2TiD]_x$ arising from the D_2 addition. This dimer can then revert to $(C_5H_5)(C_5H_4D)Ti$, and so forth, leading, in the presence of excess D_2, to a completely deuterated product.

The results presented here would seem to rule out earlier postulates[38,40,57] that a titanium hydride species is responsible for the reduction of N_2 that is observed in these systems. Hydrogen was found to inhibit N_2 reduction by $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$, and, in view of the affinity of the titanium center for hydrogen, this excess H_2 could only favor the formation of hydride species. In accord with this, the green-gray hydride $[(C_5H_5)_2TiH]_x$ was found to eliminate H_2 upon stirring with solvents such as toluene or ether, yielding a metastable titanocene species, $[(C_5H_5)_2Ti]_2$, which, upon exposure to N_2, formed a bright blue complex, $[(C_5H_5)_2Ti]_2N_2$. This result, and, in addition, the coordination of N_2 by decamethyltitanocene, $[C_5(CH_3)_5]_2Ti$, to form a blue-violet complex, have provided direct evidence concerning the mode of interaction between titanocene and molecular nitrogen. In both cases N_2-bridged dimeric complexes are formed. Although the com-

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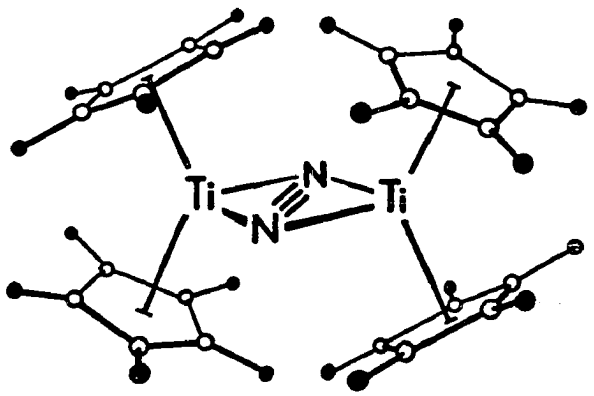
plete structural assignment of these complexes will have to await an x-ray diffraction study, some inferences concerning their structures can be made. The absence of any observable infrared absorption attributable to an N_2 stretching mode in spectra of $[(C_5H_5)_2Ti]_2N_2$ indicates a centrosymmetric Ti-N_2-Ti structure, i.e. these four atoms must be essentially coplanar. This is compatible with two possible geometries: the bridging N_2 ligand could either be coordinated in an end-on, or linear, fashion; as in $(NH_3)_5Ru\text{-}N{\equiv}N\text{-}Ru(NH_3)_5$;[33] or else be coordinated edge-on between the titanium centers (structure 4).



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Of these two possibilities we favor the latter, structure 4, for the following reasons: in all titanocene derivatives known to date, one finds, in addition to the cyclopentadienyl rings, two ligand atoms occupying coordination sites in the equatorial plane of the molecule. Such a pseudo-tetrahedral coordination seems to be universal for $(C_5H_5)_2Ti$ derivatives; in particular, no structure with only one equatorial ligand atom has been established. Structure 4 is in accord with this requirement for a pseudo-tetrahedral coordination. As stated above, in all of the previously described mononuclear and binuclear

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transition metal N_2 complexes, the nitrogen molecule is coordinated end-on. However, in all of these complexes the N_2 molecule is coordinated to a 16-electron species, i.e. donation of one electron pair from the N_2 ligand completes the 18-electron valence shell. In contrast to this, $(h^5\text{-}C_5H_5)_2Ti(II)$ has to be considered a 14-electron species and would, therefore, require two electron pairs to complete its valence shell. An edge-on coordination of the N_2 molecule would allow such a 4-electron donation, being comparable to the bonding situation of those alkyne complexes in which the acetylene ligand substitutes for two monodentate ligand groups, i.e. where the acetylene ligand is bound to a 14-electron species. In these complexes the shift of the C≡C stretching vibrations to lower energy is several times larger than in those alkyne complexes where the acetylene is bound to a species with 16 valence electrons.[91,26]

The utility of the titanocene systems as a model for biological N_2 reduction arises primarily as a result of its simplicity: if we can determine the mechanism of N_2 reduction in one simple case, it will unquestionably add to our understanding of the very complex reaction mechanisms which involve nitrogenase. It would seem unreasonable to expect that such a simple system could imitate all of the reactivity characteristic of nitrogenase, although it is clear that, at least in some respects, the chemistry of titanocene does parallel that of the enzyme systems.

$[(C_5H_5)_2Ti]_2$ reacts reversibly with N_2 and H_2 to form complexes, and irreversibly with CO to yield the dicarbonyl complex, $(C_5H_5)_2Ti(CO)_2$. Titanocene derivatives such as $(C_5H_5)_2Ti(CO)_2$[92] and $(C_5H_5)_2TiCl_2$ with various Grignard reagents[93] are known to catalytically hydrogenate

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alkynes and alkenes. In some cases, alkynes can be reduced almost exclusively to the corresponding alkenes. Such a specificity, as opposed to the complete hydrogenation to alkanes, is regarded as one of the most striking characteristics of nitrogen-reducing enzyme systems.[94.95] It is known, however, that some alkenes, e.g. C_2H_4, do interact strongly with titanium derivatives, such as Ziegler catalysts, while no similar interaction of C_2H_4 and nitrogenase has been observed.[1]

Most importantly, the fixation and reduction of molecular nitrogen has been observed in numerous titanocene systems. The results presented here suggest that the species responsible for this reactivity is $(h^5\text{-}C_5H_5)_2Ti(II)$. However, it is still unclear why, with some of the titanocene derivatives, such as $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ and $[C_{10}H_{10}TiP(C_6H_5)_3]_2$, reduction of N_2 to a nitride occurs directly, without further reducing agents; whereas, in other cases, the reduction is incomplete and either hydrazine is recovered,[42] or N_2 remains unreduced. The yellow ethyl complex, for example, reacts with N_2 under pressure to yield a nitride product from which N_2 gas can be regenerated only with strong oxidizing agents such as Cl_2, while, with the metastable species $[(C_5H_5)_2Ti]_2$, a reversible coordination of N_2 was observed, and no evidence for the direct formation of a titanocene nitride species was found.

The instability of $[(C_5H_5)_2Ti]_2N_2$ towards loss of N_2, and the observation that the coordinated nitrogen in this complex can be reduced only by very strong reducing agents, indicate that the dimeric species $[(C_5H_5)_2Ti]_2$, while having demonstrated the ability of titanocene to bind molecular nitrogen, is not the actual species which reduces the N_2. By analogy to the complexes $[(NH_3)_5Ru\text{-}N_2\text{-}Ru(NH_3)_5]^{4+}$ and

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$[(NH_3)_5RuN_2]^{2+}$,[2] and the discussion above, it seems likely that the monomeric species $(C_5H_5)_2Ti$ would also have the ability to coordinate N_2. In the absence of a rather strong titanium-titanium interaction, it is conceivable that such a monomeric species might be more highly reactive than the dimeric complex $[(C_5H_5)_2Ti]_2N_2$. In complex reaction mixtures, such as that obtained from the yellow titanocene ethyl complex, this short-lived monomeric species, generated in the presence of N_2, might react with some other low valent metallic species present in solution, leading, by some still unknown mechanism, to the reduction of its coordinated N_2.

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CHAPTER 5

EXPERIMENTAL

Materials and General Techniques

Most of the techniques used for the handling of the highly air-sensitive compounds described in this thesis have been detailed earlier[62,68] and will, therefore, be only briefly described here where appropriate.

Titanocene dichloride was obtained from Alfa Inorganics, Beverly, Massachusetts, and recrystallized from dry chloroform saturated with HCl gas. Ethyl magnesium chloride was prepared using a slight excess of magnesium and filtered prior to use. Dimethyltitanocene, $(C_5H_5)_2Ti(CH_3)_2$, was prepared by the method of Clauss and Bestian[67] with several modifications outlined in detail earlier.[62]

Reagent grade diethyl ether and THF were stored over $LiAlH_4$ under vacuum and distilled *in vacuo* just prior to use. Hexane and petroleum ether were dried with n-butyllithium in hexane and stored in vacuum. Toluene and benzene were stored over CaH_2 and prepurified before use by distillation onto $[(C_5H_5)(C_5H_4)TiH]_2$. Matheson research grade n-butane was used without further purification. Argon, nitrogen, hydrogen, and carbon monoxide were Matheson prepurified grade.

Intermediate in the Volpin-Shur System, $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$

1. Preparation of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$

Eight milliliters of *ca.* 1.5 M C_2H_5MgCl (12 mmol) in diethyl

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ether was added rapidly with a syringe to a stirred mixture of 500 mg (2.0 mmol) of $(C_5H_5)_2TiCl_2$ in 15 ml of $(C_2H_5)_2O$ under Ar at room temperature. The mixture immediately turned yellowish-brown with a vigorous gas evolution. After stirring for about 10 min the formation of a yellow precipitate was observed. The mixture was stirred for an additional 30 min, when the precipitation appeared complete, and then filtered. The yellow filter cake was washed with about 20 ml of diethyl ether until the washings, initially a dark violet, were colorless. The filtration and washings were carried out at -80°C as the yellow solid, although fairly stable in the presence of C_2H_5MgCl, decomposes slowly in diethyl ether. The yellow material was dried *in vacuo*, scraped loose from the frit under an Ar stream, and tapped into a clean flask. Yield: 950 mg [64% based on $(C_5H_5)_2TiCl_2$].

The yellow solid was stored at -80°C to prevent the gradual decomposition which is observed upon prolonged storage at room temperature.

2. Analyses

Titanium was determined colorimetrically as the Ti(IV)-H_2O_2 complex, using standard solutions prepared from potassium titanyl oxalate, $K_2TiO(C_2O_4)_2 \cdot 2\ H_2O$, as a reference. A weighed sample of the yellow solid was slowly air-oxidized and digested in hot conc H_2SO_4 with a small amount of decolorizing charcoal. The resulting solution was filtered through a sintered glass frit and quantitatively diluted with 2.0 N H_2SO_4. Calcd: Ti, 6.29%. Found: 6.31%, corresponding to an equivalent weight of 749 g (calcd 752).

Magnesium was determined volumetrically by titration with

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standard EDTA using Eriochrome black T indicator. The solution obtained for the Ti(IV) analysis was used for the magnesium determination. Calcd: Mg, 9.70%. Found: 9.61%.

Chloride was determined by the Mohr method. A weighed sample of the yellow complex was oxidized slowly and extracted with hot conc KOH. The resulting solution was filtered, neutralized with HNO_3, and quantitatively diluted. Calcd: Cl, 28.32%. Found: 28.29%.

Coordinated diethyl ether was determined by treatment of the yellow solid with excess ethylene glycol. On the vacuum line, 841 mg (1.12 mequiv) of the yellow solid was treated with ca. 5 ml of ethylene glycol. The $(C_2H_5)_2O$ liberated (3.85 mmols) was collected, fractionated and identified by its ir spectrum. Calcd: 3.50 mmol $(C_2H_5)_2O$/mmol Ti. Found: 3.52 $(C_2H_5)_2O$/Ti.

3. Thermal Decomposition of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$

The yellow solid (948 mg, 1.27 mequivs) was heated slowly under vacuum with an oil bath. The evolution of ethylene and ethane began at 60°C, and was complete after heating for one hour at 125°C. The coordinated $(C_2H_5)_2O$ was evolved continuously upon heating but liberation was not complete even on heating to 200°C. The yellow complex darkened upon warming and appeared brownish-black at 125°C. Ethane and ethylene were fractionated from the evolved diethyl ether on the vacuum line by repeated passage through a -130°C pentane slush bath, which retained the $(C_2H_5)_2O$. Mixtures of C_2H_4 and C_2H_6 were analyzed by infrared spectroscopy and concentrations determined by reference to calibrated Beer's law plots. Found: 0.62 mmol C_2H_4 (0.49/Ti), 0.60 mmol C_2H_6 (0.47/Ti).

No green $[(C_5H_5)(C_5H_4)TiH]_2$ was observed upon extraction of

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the brownish-black residue with toluene. Treatment of the residue with HCl gas gave an intensely colored green solution upon evolution of 1.43 mmols of H_2 (1.13/Ti).

4. Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with Oxygen

Yellow $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ (995 mg, 1.28 mequivs) was reacted with oxygen by recycling excess O_2 at a pressure of ca. 20 torr over the solid via a Toepler pump. The yellow solid turned bright orange as the highly exothermic reaction proceeded. The ethylene and ethane evolved in the reaction were collected and analyzed as described above. Found: 0.68 mmol C_2H_4 (0.53/Ti), 0.68 mmol C_2H_6 (0.53/Ti).

5. Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with H_2O

Yellow $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ (879 mg, 1.17 mequivs) was reacted with excess H_2O vapor utilizing a Toepler pump to recycle the H_2O and the gaseous evolution products over the yellow solid. A bright blue transient intermediate was formed in the initial stages of the reaction. After about 2 hours the solid appeared uniformly greenish-yellow, and the recycling was stopped. The gas mixture was repeatedly passed through several liquid nitrogen traps to remove the condensable evolution products and the excess H_2O vapor. H_2 (0.62 mmol, 0.53/Ti) was collected and its purity confirmed by its quantitative conversion to H_2O upon passage over CuO at 300°C. Ethane (1.19 mmols, 1.02/Ti) was collected by the fractionation procedure described above, and its purity confirmed by a comparison of its ir spectrum to that of pure C_2H_6.

6. Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with HCl

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Excess HCl gas was recycled over a solid sample of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ (780 mg, 1.04 mequivs) via a Toepler pump. The solid turned green immediately upon exposure to HCl, and then slowly to a dark red-brown in the course of about 2 hours. The excess HCl was removed by recycling the gas mixture over KOH pellets and H_2O. The remaining volatile material was fractionated and analyzed as described above. Found: 1.23 mmols C_2H_6 (1.20/Ti), 0.5 mmol H_2 (0.51/Ti).

Extraction of the dark red solid residue with $CHCl_3$ yielded a bright red solution. Removal of the solvent, and drying in vacuum, gave 232 mg of $(C_5H_5)_2TiCl_2$ (0.92 mmol) as red needles. The nmr spectrum of the material indicated the presence of a slight trace of $(C_5H_5)TiCl_3$.

7. Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with Diborane

Diborane (2.04 mmols) and 15 ml of THF were distilled onto the yellow solid (751 mg, 1.00 mequiv) at -80°C. The mixture was allowed to warm slowly to room temperature. After stirring for ca. 30 min, the solvent was removed from the brownish-violet solution leaving a dark brown residue. Sublimation of this residue at 80°C, 10^{-2} torr, yielded bright violet needles of $(C_5H_5)_2TiBH_4$ (45 mg, 0.24 mmol) identified by comparison of its ir spectrum to that given by Nöth and Hartwimmer.[65] Fractionation and analysis of the evolution products showed that predominantly ethylene was formed in the reaction.

8. Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with 1,3-Pentadiene

1,3-Pentadiene (5 ml) and THF (5 ml) were distilled onto the

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yellow solid (ca. 1.0 mequiv) at -80°C, and the mixture allowed to warm to room temperature. After stirring for ca. 30 min, the mixture was evaporated to dryness and the dark residue extracted with 15 ml of hexane. The deep blue hexane solution was filtered, and the solvent removed in vacuo, leaving dark blue needles of π-(1,3-dimethyl) allyl titanocene, identified by comparison of its ir spectrum to that given by Martin.[86]

9. Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with Methyl Iodide

Excess CH_3I was distilled onto the yellow solid (917 mg, 1.22 mequiv) at -80°C. Upon warming to room temperature, the mixture turned orange-red. CH_4 (0.58 mmol, 0.48/Ti) was evolved during the reaction. Fractionation and analysis of the evolution products by the methods described above showed that ethylene and ethane were also formed in the reaction. Found: 1.07 mmols C_2H_4 (0.87/Ti), 0.42 mmol C_2H_6 (0.35/Ti). Extraction of the solid residue from the reaction with hexane yielded an orange-red solution from which bright orange crystals of $(C_5H_5)_2Ti(CH_3)I$ could be isolated.

10. Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with Acetylenes

Diphenylacetylene (800 mg, 4.5 mmols) and $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ (730 mg, 0.97 mequiv) were stirred with 10 ml of diethyl ether for 3 hrs at room temperature, during which time the mixture turned dark brown. The volatile products formed in the reaction were fractionated and analyzed as given above. Found: 0.14 mmol C_2H_4. No C_2H_6 or H_2 were observed.

Excess hexafluoro-2-butyne was condensed into a mixture of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ (ca. 1.0 mequiv) and 10 ml of

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THF at -80°C. Upon warming to room temperature, the mixture turned dark red-brown, and became quite thick with the apparent polymerization of the hexafluoro-2-butyne. Fractionation of the volatile material yielded 0.4 mmol of C_2H_4 and 0.15 mmol of C_2H_6. No H_2 was observed.

11. Reactions of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with Molecular Nitrogen

Reactions of the yellow solid with N_2 were carried out a high pressure in an autoclave. The apparatus used allowed solvents to be added at high N_2 pressures, thus minimizing the competitive decomposition reactions of the complex in solution. The apparatus illustrated below was used with good results.

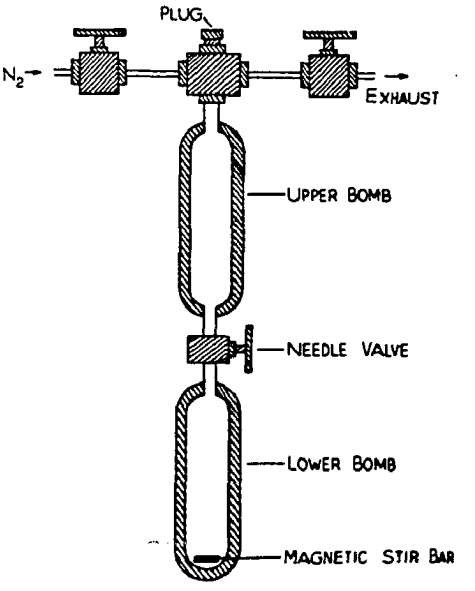

Figure 2. Double bomb apparatus used in high pressure reactions.

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In a glove box, the yellow solid was transferred from a tared storage ampoule to the lower cylinder, and the needle valve attached. The apparatus was assembled on the high pressure line and the upper cylinder flushed with N_2. Both cylinders were then pressurized to 130 atmospheres with prepurified N_2. The pressure was then released from the upper cylinder and the solvent added with a syringe to the upper cylinder. After flushing several times, the pressure in the upper cylinder was increased to 230 atm, forcing the N_2-saturated solvent through the needle valve onto the yellow solid in the lower cylinder.

In a typical experiment, $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ (741 mg, 0.99 mmol) was reacted with nitrogen at 230 atm in 10 ml of 1,2-dimethoxyethane (DME) for 15 min at room temperature. The pressure was then released, the mixture hydrolyzed with 10 ml of ca. 2.5 N H_2SO_4, and the ammonia liberated determined by the Kjeldahl method. Found: 0.63 mmol NH_3 (0.64/Ti). The distillate gave a positive test for NH_4^+ with Nessler's reagent, and a negative spot test for N_2H_4 with p-dimethylaminobenzaldehyde.

In another experiment, 719 mg of the yellow solid (0.95 mequiv) was reacted with N_2 at 230 atm in DME and the evolution products trapped out by releasing the pressure slowly through a cooling coil at -196°C. The cold trap was attached to the vacuum line and the condensed material fractionated and analyzed as previously described. Found: 0.51 mmol C_2H_6 (0.54/Ti), 0.34 mmol C_2H_4 (0.36/Ti). A subsequent Kjeldahl determination on the autoclave mixture yielded 0.56 mmol of NH_3 (0.59/Ti). The reactions of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with molecular nitrogen are summarized in Table 1.

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Table 1. Nitrogen Reduction by $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$

Solvent	Additional Reactants	Reaction Time (hours)	Reaction Temp. (°C)	N_2 Pressure (atm)	Yield (NH_3/Ti)
DME	none	0.25	25	230	0.64
DME	none	0.50	25	230	0.60
DME	none	2.0	25	210	0.59
THF	none	0.25	25	230	0.54
DME	none	1.0	0	180	0.41
none	none	8.0	25	160	0.02
DME	1.5 C_2H_5MgCl/Ti	0.25	25	180	0.65
THF	10.0 C_2H_5MgCl/Ti	0.25	25	180	0.72

12. Characterization of the N_2 Reduction Product

The crude product from the reaction of ca. 800 mg (1 mequiv) of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6\ MgCl_2 \cdot 7\ (C_2H_5)_2O$ with 230 atm of N_2 in 10 ml of DME was transferred from the autoclave cylinder to a small flask which was then attached to a filtration assembly on the vacuum line while flushing with Ar. The dark green solution was cooled to -80°C and ca. 10 ml of toluene distilled in with stirring. The black precipitate which formed was filtered and washed with fresh toluene until the washings were colorless. The black solid obtained was dried in vacuo and transferred to a storage ampoule in the glove box.

Upon exposure to excess HCl gas, a 274 mg sample of the black powder turned dark red. Only a very small amount of H_2 (ca. 0.01 mmol) was evolved during the reaction. Extraction of the dark red solid

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with a mixture of $CHCl_3$ and dilute HCl yielded a bright red $CHCl_3$ solution from which 75 mg of $(C_5H_5)_2TiCl_2$ (0.30 mmol) was obtained upon removal of the solvent. The purity of the $(C_5H_5)_2TiCl_2$ was confirmed by nmr. A Kjeldahl determination on the aqueous layer yielded 0.202 mmol of NH_3.

A sample of the black solid was treated with excess Cl_2 and the N_2 evolved (0.073 mmol) collected through several liquid N_2 traps and identified by its mass spectrum. The residue from the reaction was extracted with hot conc H_2SO_4, and the [Ti] determined colorimetrically as previously described. Found: 0.236 mmol Ti (3.08 Ti/1.0 N_2).

Metastable Form of Titanocene, $[(C_5H_5)_2Ti]_2$

1. Preparation of $[(C_5H_5)_2TiH]_x$

Fifty milliliters of ca. 0.14 M $(C_5H_5)_2Ti(CH_3)_2$ in hexane was syringed under Ar into a 250 ml flask attached to a filtration assembly on the vacuum line. Approximately 20 ml of the hexane was removed *in vacuo* to obtain a slurry of $(C_5H_5)_2Ti(CH_3)_2$ crystals. H_2 gas (1 atm) was introduced at 0°C. After several minutes incubation, the reaction proceeded smoothly, beginning with the film of crystalline, yellow $(C_5H_5)_2Ti(CH_3)_2$ on the sides of the flask and spreading rapidly through the solution. The formation of violet $[(C_5H_5)_2TiH]_2$ was observed where the dry crystals adhered to the sides of the flask. The solution initially turned dark brown, and began to deposit a grayish precipitate after several minutes. The H_2 atmosphere was renewed periodically, after applying a slight vacuum to insure removal of the

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evolved methane. Excess H_2, efficient stirring, and cooling are necessary to avoid formation of green $[(C_5H_5)(C_5H_4)TiH]_2$. The precipitation appeared complete after stirring for about 40 minutes. The mixture was filtered and the solid washed with about 20 ml of fresh hexane. The green-gray product was dried *in vacuo* and transferred to a storage ampoule in a glovebox under Ar. Yield: 1.1 g [*ca.* 85% based on $(C_5H_5)_2Ti(CH_3)_2$].

2. *Thermal Decomposition of* $[(C_5H_5)_2TiH]_x$

Green-gray $[(C_5H_5)_2TiH]_x$ (85 mg, 0.48 mequiv) was transferred to a small flask in a glovebox under prepurified Ar. The flask was attached to the vacuum line and the green-gray solid heated *in vacuo* with an oil bath. The evolution of non-condensable gas began at *ca.* 60°C and was essentially complete after heating for 2 hours at 100°C. The green-gray solid turned dark green as the reaction proceeded. The non-condensable gas (0.26 mmol, 0.55/Ti) was identified as pure H_2 by its quantitative conversion to H_2O upon passage over CuO at 320°C. The dark green product was identified by comparison of its ir spectrum to that of a genuine sample, prepared by the method of Salzmann and Mossimann.[75]

3. *Reaction of* $[(C_5H_5)_2TiH]_x$ *with Deuterium Chloride*

All exposed surfaces in the vacuum line were wetted with several portions od 38% DCl in D_2O, and then with two 25 torr portions of DCl gas (*ca.* 91.5% isotopic purity). Green-gray $[(C_5H_5)_2TiH]_x$ (162 mg, 0.90 mequiv) was slurried with 5 ml of toluene at -80°C and excess DCl gas distilled in at this temperature. The reaction began immediately with vigorous bubbling; the mixture turning bright red with the formation of $(C_5H_5)_2TiCl_2$ after several minutes stirring at

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-50°C. 1.07 mmol (1.19/Ti) of non-condensable gas was collected via a Toepler pump. Mass spectral analysis of this gas mixture showed 6.7% D_2, 89.6% HD, and 3.7% H_2. The yield of D_2 in this reaction is somewhat lower than that predicted by equation 10. A similar and undoubtedly related observation was made previously in the reaction of violet $[(C_5H_5)_2TiH]_2$ with DCl.[62]

4. Reaction of $[(C_5H_5)_2TiH]_x$ with Carbon Monoxide

Green-gray $[(C_5H_5)_2TiH]_x$ (153 mg, 0.86 mequiv) was slurried with about 5 ml of toluene at -80°C and 1 atm of CO introduced at this temperature. Upon slowly warming the mixture to room temperature, the color changed from green-gray to red-brown. After stirring for 30 min the toluene was removed in vacuo leaving a dark red solid. A sublimation probe was inserted under Ar and the red solid sublimed at 45-60°C, 10^{-2} torr, for 3 hours and an additional hour at 90°C. Bright red crystals of $(C_5H_5)_2Ti(CO)_2$ (133 mg, 0.64 mmol), identified by its ir spectrum,[70] were obtained.

5. Preparation of $[(C_5H_5)_2Ti]_2$ Solutions

In a typical experiment, green-gray $[(C_5H_5)_2TiH]_x$ (242 mg, 1.35 mequiv) was stirred with 10 ml of toluene at room temperature for about two hours. The solid hydride slowly dissolved yielding a dark, slightly greenish solution. Hydrogen (0.64 mmol, 0.47/Ti) was evolved during the reaction and collected and analyzed as described above. Solutions of $[(C_5H_5)_2Ti]_2$ in diethyl ether were prepared in a similar manner, but were used immediately as $[(C_5H_5)_2Ti]_2$ is prone to rearrange to $[(C_5H_5)(C_5H_4)TiH]_2$ upon standing in ethereal solvents. $[(C_5H_5)_2Ti]_2$ is only slightly soluble in aliphatic hydrocarbons, such

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as hexane, and was not prepared directly in these solvents.

6. Thermal Decomposition of $[(C_5H_5)_2Ti]_2$

A solution of $[(C_5H_5)_2Ti]_2$ (0.53 mmol) in 10 ml of toluene was heated under Ar with an oil bath. The solution turned bright green upon heating to 110°C. The toluene solution was refluxed for ca. 2 hours. Removal of the toluene in vacuo yielded a dark green solid which was identified as essentially pure $[(C_5H_5)(C_5H_4)TiH]_2$ by its ir spectrum.[75]

7. Reaction of $[(C_5H_5)_2Ti]_2$ with Hydrogen Chloride

Green-gray $[(C_5H_5)_2TiH]_x$ (122 mg, 0.67 mequiv) was stirred with 5 ml of toluene for two hours at room temperature until all the hydride had dissolved. The H_2 evolved (0.32 mmol) was removed, and the toluene solution cooled to -80°C. Excess HCl was introduced at this temperature. The reaction began immediately, with a vigorous gas evolution, the solution turning brownish-red. The mixture was warmed to room temperature to insure complete reaction and the evolved H_2 (0.55 mmol) was collected and identified as above. Removal of the toluene from the red-brown solution yielded a dark red solid from which $(C_5H_5)_2TiCl_2$ (166 mg, 0.56 mmol) was obtained upon extraction with chloroform.

8. Reaction of $[(C_5H_5)_2Ti]_2$ with Carbon Monoxide

Green-gray $[(C_5H_5)_2TiH]_x$ (152 mg, 0.85 mequiv) was stirred with 10 ml of $(C_2H_5)_2O$ at room temperature for 2 hours to form $[(C_5H_5)_2Ti]_2$. The H_2 released (0.44 mmol, 0.52/Ti) was collected and analyzed as described above. The $[(C_5H_5)_2Ti]_2$ solution was cooled

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to -80°C and 1 atm of CO introduced. A reaction began immediately, and upon warming to room temperature the solution appeared homogeneously dark red. The excess CO was removed and excess HCl gas distilled in at -80°C. Non-condensable gas (2.53 mmol), a mixture of CO and H_2, was evolved upon warming the ether solution to room temperature. The gas mixture was recycled over CuO at 320°C for 2 hours to form CO_2 and H_2O, which were then quantitatively separated by passage through a -80°C trap. The composition of the gas mixture, determined by this procedure, was 1.65 mmol CO (1.94/Ti) and 0.87 mmol H_2 (1.04/Ti).

9. Reaction of $[(C_5H_5)_2Ti]_2$ with Deuterium

A solution of $[(C_5H_5)_2Ti]_2$ (1.04 mmol) in 5 ml of toluene was stirred overnight under D_2 gas (1 atm, 2.4 mmol). No visible change occurred during this period. The non-condensable gas was collected via a Toepler pump and its composition determined by mass spectroscopy. Found: 89.0% H_2, 10.5% HD, 0.5% D_2. Expected for a random scrambling between $[(C_5H_5)_2Ti]_2$ and the gas phase: 77.7% H_2, 18.7% HD, and 3.6% D_2.

10. Reaction of $[(C_5H_5)_2Ti]_2$ with Molecular Nitrogen

Green-gray $[(C_5H_5)_2TiH]_x$ (162 mg, 0.91 mequiv) was converted to $[(C_5H_5)_2Ti]_2$ in diethyl ether as described above. The solution was cooled to -80°C and 1 atm of N_2 introduced at this temperature. The solution immediately turned intensely blue. After stirring for about 20 minutes at -80°C, the excess N_2 was removed and the blue solution allowed to warm slowly. At ca. -20°C a vigorous gas evolution was observed and the solution lost most of its blue color. Some blue color persisted, however, until the solution was warmed to room

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temperature and all the N_2 was removed via a Toepler pump. The N_2 collected (0.43 mmol, 0.47/Ti) was identified by its mass spectrum. Upon readmission of N_2 to the solution, and cooling to -80°C, the blue complex was regenerated. The amount of complexed N_2 (0.45 mmol) found upon repeating the above procedures illustrated the reversibility of the reaction.

11. Isolation of $[(C_5H_5)_2Ti]_2N_2$

Green-gray $[(C_5H_5)_2TiH]_x$ (368 mg, 2.06 mequiv) was stirred with ca. 15 ml of toluene for 3 hours at room temperature until a homogeneous solution of $[(C_5H_5)_2Ti]_2$ was obtained. The solution was cooled to -80°C and N_2 91 atm) introduced. After stirring for about 10 min at -80°C, a small amount of blue solid was observed. Approximately 10 ml of hexane was distilled in at -80°C and the mixture became quite thick with the formation of a dark blue precipitate. The mixture was filtered cold and the dark blue complex washed with an additional 10 ml of hexane at -80°C. The blue material was slurried with 10 ml of fresh hexane under 1 atm of N_2 at -80°C. The slurry was filtered, the solid washed with about 5 ml of iso-butane a -80°C, and dried in vacuo while cold. The blue solid (ca. 200 mg) was transferred to a storage ampoule in a glove box filled with prepurified N_2.

To determine whether the complexed N_2 was stoichiometrically retained in the solid, a sample of the dark blue complex $[(C_5H_5)_2Ti]_2N_2$ (83 mg, 0.22 mmol) was dissolved in 10 ml of toluene a -80°C and allowed to warm slowly. The intially bright blue solution bubbled vigorously upon warming to -20°C, changing color to a dark, greenish hue characteristic of $[(C_5H_5)_2Ti]_2$ solutions. Passage of the evolved

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gas through several liquid N_2 traps, and collection via a Toepler pump, yielded 0.20 mmol (0.47/Ti) of N_2.

12. Reduction of $[(C_5H_5)_2Ti]_2N_2$

$[(C_5H_5)_2TiH]_x$ (362 mg, 2.02 mequiv) was stirred with 15 ml of diethyl ether for about 2 hours at room temperature until all the green-gray hydride dissolved. The resulting $[(C_5H_5)_2Ti]_2$ solution was transferred with a syringe into the lower cylinder of the double bomb apparatus (Figure 2) under a N_2 stream, and the solution pressurized to 180 atm with prepurified N_2 and cooled to -80°C to insure complete formation of $[(C_5H_5)_2Ti]_2N_2$. The pressure in the top cylinder was released and 12 ml of a 0.194 M solution of lithium naphthalide (LiNp) in THF (2.33 mmol, 1.15/Ti) was added. After pressurizing to 210 atm with N_2, the LiNp in the top cylinder was added to the $[(C_5H_5)_2Ti]_2N_2$ solution at -80°C. The mixture was stirred at -80°C for 1 hour, warmed slowly to room temperature over a two hour period, and then hydrolyzed with 10 ml of 2.5 N H_2SO_4. The NH_3 formed (1.92 mmol, 0.95/Ti) was determined by the Kjeldahl method. A positive test for NH_3 was obtained with Nessler's reagent. A negative spot test with p-dimethylamino-benzaldehyde indicated that no hydrazine was formed in the reaction. The reduction with LiNp seems to be somewhat irreproducible, however, and varying yields of NH_3 have been observed. The reduction reactions of $[(C_5H_5)_2Ti]_2N_2$ are summarized in Table 2.

Titanocene Triphenylphosphine Complex, $[C_{10}H_{10}TiP(C_6H_5)_3]_2$

The complex $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ was prepared from dimethyl-titanocene, $(C_5H_5)_2Ti(CH_3)_2$, by a procedure described in detail

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Table 2. Reduction of $[(C_5H_5)_2Ti]_2N_2$ by various reducing agents.

Reducing Agent	Molar Excess	Solvent	N_2 Pressure (atm)	Temperature °C (min/max)	NH_3/Ti
LiNp	1.50	THF/ether	180	-80/25	0.41
LiNp	1.04	THF/ether	170	-80/25	0.57
LiNp	1.15	THF/ether	180	-80/25	0.95
LiNp	ca. 10	THF/ether	1	0/25	0.30
LiNp	1.04	THF/ether	1	25/25	0.34
Na/K[a]	--	ether	150	25/25	0.25
Na/Hg[b]	--	ether	160	25/25	0.00
Al[c]	--	ether	170	25/25	0.05

a. large excess liquid sodium-potassium alloy (1:4)

b. large excess 1% sodium amalgam

c. large excess Al powder

earlier.[68]

1. Reaction of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with H_2

The purple phosphine complex (365 mg, 0.415 mmol) was dissolved in 10 ml of toluene containing 282 mg (1.07 mmol) of $P(C_6H_5)_3$ and the mixture exposed to 1 atm of H_2 at room temperature. The purple solution immediately turned yellowish-brown with the uptake of H_2. Upon cooling the solution to -80°C and removing the excess H_2, the yellow-brown color persisted. The absorbed H_2 was released upon warming to room temperature in vacuo and the purple color of the complex $[C_{10}H_{10}TiP(C_6H_5)_2]_2$ reappeared. The evolved H_2 (0.43 mmol, 0.52/Ti) was collected and analyzed as described above.

2. Reaction of $(C_5H_5)_2Ti(H)P(C_6H_5)_3$ with Diborane

Purple $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ (361 mg, 0.41 mmol) was dissolved in THF and stirred for 1 hour under 1 atm of H_2 to form the yellow-brown hydride complex $(C_5H_5)_2Ti(H)P(C_6H_5)_3$. The solution was then frozen with liquid nitrogen, the excess H_2 removed, and B_2H_6 (ca. 2.0 mmol) distilled in. The mixture was allowed to warm slowly to room temperature under an atmosphere of fresh H_2. Upon melting, a reaction began almost immediately, the solution changing in color from yellow-brown to blue-violet. Difficulty in separating the titanocene borohydride complex, $(C_5H_5)_2TiBH_4$, from $P(C_6H_5)_3$ required that the yield in this reaction be determined colorimetrically by comparison to standard solutions of $(C_5H_5)_2TiBH_4$, prepared by the method of Nöth and Hartwimmer.[65] Spectral analysis (at 510 nm) showed that the reaction was essentially quantitative.

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3. Reaction of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with Carbon Monoxide

The purple phosphine complex (284 mg, 0.32 mmol) and $P(C_6H_5)_3$ (520 mg, 1.96 mmol) were dissolved in 15 ml of toluene at -80°C and allowed to warm slowly with stirring under 1 atm of CO. Upon stirring at room temperature, the solution slowly turned red, until, after 2 hours, it appeared dark red-brown. The solution was cooled to -80°C and the non-condensable material collected via a Toepler pump. Analysis of this gas by the procedures described above showed that it consisted of pure CO. The toluene was removed from the reaction mixture, leaving a dark red-brown solid. Sublimation of this residue at 45-60°C, 10^{-2} torr, yielded bright red crystals of $(C_5H_5)_2Ti(CO)_2$ (49 mg, 0.21 mmol).

4. Hydrogen Exchange of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with D_2

Purple $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ (425 mg, 0.48 mmol) was dissolved in ca. 25 ml of toluene containing 240 mg of $P(C_6H_5)_3$ (0.92 mmol) in a 400 ml flask. The solution was stirred under 1 atm of D_2 (ca. 20 mmol) for 4 hours at room temperature. After this period the D_2 atmosphere was renewed and the yellow-brown solution stirred for an additional 4 hours. This procedure was carried out once more with a third portion of D_2. The D_2 was then completely removed, whereupon the solution again turned bright purple with the formation of the purple phosphine complex. The purple compound was then thermally decomposed by heating the solution with an oil bath to 110°C for 3 hrs under Ar. The green decomposition product was precipitated from the toluene solution by the addition of 40 ml of hexane, filtered, washed with hexane, and dried in vacuo. Mass spectral analysis of the green solid identified it as $[(C_5D_5)(C_5D_4)TiD]_2$. The presence of a parent peak at m/e = 376, and loss of D_2 in the mass spectrometer, giving rise to a large peak at

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m/e = 372, confirmed that complete deuteration of cyclopentadienyl ligands had occurred. The nmr spectrum, as the oxide, of the $P(C_6H_5)_3$ which was recovered from the toluene-hexane washings showed no apparent decrease in the o-hydrogen signal relative to a pure sample of triphenylphosphine oxide, confirming that the phenyl rings are not involved in the exchange reaction.

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