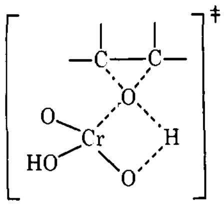

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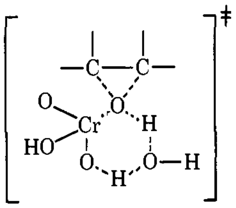

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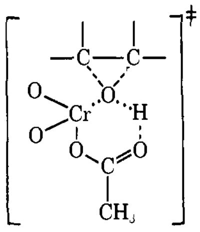

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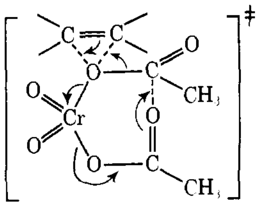
appears that a change in mechanism occurs in the chromic acid oxidation of styrenes.[41] An activated complex resembling **23** has been proposed for the chromyl acetate oxidation of alkenes and styrenes.[63,64] As stated above, **6** could also represent the activated complex in the rate-determining step for the chromyl chloride oxidation of alkenes and cycloalkenes. It is also of interest to note that epoxides have been isolated in the chromic acid oxidation of allylic alcohols,[65] cyclohexene,[66] and styrenes,[67] and in the chromyl acetate oxidation of alkenes and styrenes.[63,64] The carbonyl products obtained in the chromyl chloride oxidation could arise from isomerization of epoxide intermediates which could be formed from **5**, **6**, or **7**.



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We conclude from the relative rates, the solvent effects, the thermodynamic data, the magnitude of the ρ^+ value, and the secondary deuterium kinetic isotope effects that the electrophilic addition of chromyl chloride to styrene probably involves an activated complex resembling **5** or **6** in the rate-determining step.

Acknowledgment. We express our thanks to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Fillmore Freeman also thanks California State College, Long Beach, for the award of a Special Leave for Faculty Research during this investigation.

(64) M. A. Davis and W. J. Hickinbottom, *J. Chem. Soc.*, 2205 (1958), and earlier papers in series.

(65) P. S. Kalsi, K. S. Kumar, and M. S. Wadia, *Chem. Ind. (London)*, 71 (1971).

(66) J. Roček and J. C. Drozd, *J. Amer. Chem. Soc.*, **92**, 6668 (1970).

(67) Table I, footnotes *s* and *t*.

Titanocene as an Intermediate in Reactions Involving Molecular Hydrogen and Nitrogen

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Abstract: The bis(cyclopentadienyl)titanium(II) species $[C_5(CH_3)_5]_2Ti$, $([C_5(CH_3)_5]_2Ti)_2$, and $[(C_5H_5)_2Ti]_2$ have been prepared and characterized. These species react reversibly with molecular hydrogen to form hydride complexes, with molecular nitrogen to yield intensely colored N_2 complexes, and irreversibly with carbon monoxide to form the respective dicarbonyl derivatives. Triphenylphosphine forms a complex of composition $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with $[(C_5H_5)_2Ti]_2$. This phosphine complex reacts reversibly with H_2 to form a monomeric titanocene phosphine hydride, and irreversibly with N_2 and CO. $[(C_5H_5)_2Ti]_2$ rapidly exchanges cyclopentadienyl protons for deuterium in the presence of D_2. These unique reactions are utilized as a diagnostic to establish the occurrence of a transient titanocene species in other reaction systems in which the isolation of intermediates is not feasible. The participation of these Ti(II) sandwich compounds and their hydride derivatives in catalytic hydrogenation reactions and in the complexation and reduction of molecular nitrogen is discussed. The isolation and characterization of a titanocene ethyl complex, which is an intermediate in the Volpin–Shur nitrogen-reducing system, is reported, and evidence for the occurrence of $[(C_5H_5)_2Ti]_2$ in this system is described.

The unusual reactivity of reaction systems involving titanocene toward normally rather inert molecules such as H_2 and N_2 has recently been the subject of considerable interest. Reaction systems such as $TiCl_4$ with sodium cyclopentadienide,[1] $(C_5H_5)_2Ti(CO)_2$,[2] and $(C_5H_5)_2TiCl_2$ with various Grignard reagents[3] have been shown to catalytically hydrogenate alkenes and alkynes. The fixation and reduction of molecular nitrogen has been observed with mixtures of $(C_5H_5)_2TiCl_2$ and ethylmagnesium bromide and in other systems containing $(C_5H_5)_2Ti$ derivatives.[4-8] Highly reactive spe-

(1) M. E. Vol'pin, V. A. Dubovitskii, and O. V. Nogina, *Dokl. Akad. Nauk SSSR*, **151**, 1100 (1963).

(2) K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jap.*, **39**, 1178 (1966).

(3) K. Shikata, K. Nishino, K. Azuma, and Y. Takegami, *Kogyo Kogaku Zasshi*, **68**, 358 (1965).

cies, such as $(C_5H_5)_2TiH$ and $(C_5H_5)_2Ti$, have been postulated to explain the unusual reactivity associated with these systems; however, their role in these reaction sequences had been largely a matter of speculation.

A few years ago we began a systematic investigation of titanocene-based reaction systems. During the course of our research we have encountered many reactions, to be discussed in detail below, in which $(C_5H_5)_2TiH$ and $(C_5H_5)_2Ti$ appear to occur as reaction intermediates. In the course of these studies we also established that the compound referred to as "titanocene" in the literature is in fact a titanium hydride complex, which may be formulated as $[(C_5H_5)(C_5H_4)TiH]_2$.[9] It therefore appeared that $(C_5H_5)_2Ti$, if it does in fact exist as a reaction intermediate, exhibits a strong tendency to rearrange, *via* a ring-to-titanium α-hydrogen shift, to a less reactive isomer.[9]

In order to eliminate the occurrence of such a rearrangement, the synthesis of decamethyltitanocene, $[C_5(CH_3)_5]_2Ti$, was undertaken.[10] In this compound an α-hydrogen shift is impossible, even if the rings are σ (or h^1) bound. We have found that this compound did indeed provide an opportunity to investigate the reactivity associated with such a bis(cyclopentadienyl)titanium(II) intermediate in detail.[10] Subsequently we have succeeded in preparing a metastable form of titanocene, $[(C_5H_5)_2Ti]_2$, and characterized its reactivity.[11] Both compounds, $[C_5(CH_3)_5]_2Ti$ and $[(C_5H_5)_2Ti]_2$, form hydride and N_2 complexes upon exposure to molecular hydrogen and nitrogen, thus providing direct evidence for the intermediate existence of these species in the reaction systems mentioned above.

Results

(1) Bis(pentamethylcyclopentadienyl)titanium(II), $[C_5(CH_3)_5]_2Ti$, Synthesis and Properties. The obvious starting material in the synthesis of $[C_5(CH_3)_5]_2Ti(II)$ appeared to be $[C_5(CH_3)_5]_2TiCl_2$; however, this compound, decamethyltitanocene dichloride, had not yet been reported in the literature. King and Bisnette[12] reported that the reaction between lithium pentamethylcyclopentadienide and titanium tetrachloride, in a 1:1.3 mol ratio, respectively, yielded only the mono(pentamethylcyclopentadienyl) derivative, $[C_5(CH_3)_5]TiCl_3$.[13]

We found that treatment of titanium tetrachloride with a dimethoxyethane (DME) solution of sodium pentamethylcyclopentadienide, in a 1:4 mol ratio, respectively, yielded a mixture of red-orange $[C_5(CH_3)_5]TiCl_3$ and the desired product, $[C_5(CH_3)_5]_2TiCl_2$, in 14% yield. Higher yields, up to 40%, of purple-brown $[C_5(CH_3)_5]_2TiCl_2$ were obtained when $TiCl_3$ was treated first with saturated tetrahydrofuran (THF) solutions of $NaC_5(CH_3)_5$, and then with concentrated hydrochloric acid to oxidize the initial product, $[C_5(CH_3)_5]_2TiCl$, to $[C_5(CH_3)_5]_2TiCl_2$. The higher yield obtained from $TiCl_3$ is presumably due to lower steric interaction of the bulky pentamethylcyclopentadienyl rings in the initially formed $[C_5(CH_3)_5]_2TiCl$, as well as the elimination of the oxidation of $C_5(CH_3)_5^-$ by $TiCl_4$. Optimal reaction and purification procedures are outlined in the Experimental Section.

The equivalence of the ring methyl groups in $[C_5(CH_3)_5]_2TiCl_2$ is evident from its nmr spectrum. At 34° as well as at −50°, $CDCl_3$–TMS solutions of this compound show a singlet absorption at 2.00 ppm. This is in close analogy to the nmr spectra of $[C_5(CH_3)_5]_2Fe$ and $[C_5(CH_3)_5]TiCl_3$ which show nmr absorptions at 1.62 and 2.35 ppm, respectively.

The direct reduction of $[C_5(CH_3)_5]_2TiCl_2$ by sodium amalgam in toluene or by sodium naphthalide in THF gave solutions from which $[C_5(CH_3)_5]_2Ti(II)$ could not be isolated. When $[C_5(CH_3)_5]_2TiCl_2$ was reduced with sodium naphthalide in THF, only oily, apparently impure, products were isolated from the reaction mixture. A 1:5 mixture of $[C_5(CH_3)_5]_2TiCl_2$ and $[C_5(CH_3)_5]TiCl_3$ was obtained upon subsequent oxidation of the reaction mixture with HCl, implying some loss of pentamethylcyclopentadienyl ligands during the reduction by sodium naphthalide.

The failure of a direct reduction of decamethyltitanocene dichloride to yield the desired decamethyltitanocene species prompted the search for milder conditions for the formation of $[C_5(CH_3)_5]_2Ti(II)$. As noted earlier,[14] the reaction between dimethyltitanocene, $(h^5\text{-}C_5H_5)_2Ti(CH_3)_2$, and hydrogen gas leads to the formation of $[(C_5H_5)(C_5H_4)TiH]_2$ presumably *via* a $(h^5\text{-}C_5H_5)_2Ti$ intermediate. It therefore seemed reasonable to expect the analogous reaction, between $[C_5(CH_3)_5]_2Ti(CH_3)_2$ and H_2, to lead to $[C_5(CH_3)_5]_2Ti$, with the evolution of 2 mol of methane.

$[C_5(CH_3)_5]_2Ti(CH_3)_2$ was prepared by the reaction of methyllithium with decamethyltitanocene dichloride in diethyl ether. However, pentane solutions of $[C_5(CH_3)_5]_2Ti(CH_3)_2$ were found to show little or no reactivity toward hydrogen gas. Even when exposed to 100 atm of H_2, these solutions remained yellow, and no evidence of reaction was observed. It was found that if small amounts of methyllithium or $C_{10}(CH_3)_{10}CH_2Ti$ (see below) were present, a reaction did take place with evolution of the stoichiometric 2 mol of CH_4, but $[C_5(CH_3)_5]_2Ti$ could not be isolated from the resulting brown solutions. The nature of the product of this reaction remains to be clarified; the amount of hydrogen consumed in its formation indicates that it most likely has the composition $[C_5(CH_3)_5]_2TiH$.

The low reactivity of $[C_5(CH_3)_5]_2Ti(CH_3)_2$ toward hydrogen is probably related to its greater thermal stability compared to that of the unsubstituted $(h^5\text{-}C_5H_5)_2Ti(CH_3)_2$. Whereas $(C_5H_5)_2Ti(CH_3)_2$ decomposes at room temperature in the course of several minutes,[14] due to the high lability of the Ti–CH_3 bonds, $[C_5(CH_3)_5]_2Ti(CH_3)_2$ can be stored at room temperature for days without decomposition and is stable in solution to 90°. Heating the dimethyl derivative, $(C_5$-

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[4] M. E. Vol'pin and V. B. Shur, *Nature (London)*, **209**, 1236 (1966); *Dokl. Akad. Nauk SSSR*, **156**, 1102 (1964).

[5] G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **8**, 650 (1969).

[6] G. Henrici-Olive and S. Olive, *Angew. Chem.*, **80**, 398 (1968).

[7] A. E. Shilov, A. K. Shilova, and E. F. Kvashina, *Kinet. Katal.*, 10, 1402 (1969); A. E. Shilov, A. K. Shilova, E. F. Kvashina, and T. A. Vorontsova, *Chem. Commun.*, 1590 (1971).

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

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

[10] J. E. Bercaw and H. H. Brintzinger, *ibid.*, **93**, 2046 (1971).

[11] R. H. Marvich and H. H. Brintzinger, *ibid.*, **93**, 2048 (1971).

[12] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **8**, 287 (1967).

[13] $[C_5(CH_3)_5]TiCl_3$ was first obtained by treatment of $TiCl_4$ with isobutene at 300° and 30–60 atm pressure: H. Rohl, E. Lange, T. Gossel, and G. Roth, *Angew. Chem.*, **74**, 155 (1962).

[14] K. Clauss and H. Bestian, *Justus Liebigs Ann. Chem.*, **654**, 8 (1962).

$(CH_3)_5]_2Ti(CH_3)_2$, in toluene to 110° for 4 hr, however, yields, concurrent with the evolution of 1.0 CH_4 per titanium, a diamagnetic turquoise compound of composition $C_{10}(CH_3)_{10}CH_2Ti$, which sublimes at 75°, 10^{-3} Torr. The composition of this compound, inferred from the stoichiometry of its formation, is confirmed by its mass spectrum with a parent ion at *m/e* 332 (see Table I). No peaks at higher mass were observed with relative intensities in excess of 0.02; in particular there is no indication of the presence of dimeric species.

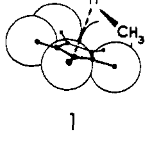
Table I. Mass Spectrum of the Turquoise Compound, $C_{10}(CH_3)_{10}CH_2Ti^a$

m/e	Intensity	Assignment
332	100	M^+
317	31	$M^+ - [CH_3]$
136^b	60	$C_5(CH_3)_5H^+$
134	77	$C_5(CH_3)_4CH_2^+$
121^b	28	$C_5(CH_3)_4H^+$
119	36	$C_5(CH_3)_3CH_2^+$

[a] M^+ represents the molecular ion. Given in the table are the monoisotopic species with ^{12}C, ^1H, and ^{48}Ti; the measured spectrum had a satisfactory isotopic distribution; ionizing voltage = 20 eV. [b] The occurrence of $C_5(CH_3)_5H^+$ and $C_5(CH_3)_4H^+$ in the spectrum is attributed to a small amount of more volatile pentamethylcyclopentadiene impurity which condenses on the sublimate during the sublimation of $C_{10}(CH_3)_{10}CH_2Ti$.

From its composition, $C_{10}(CH_3)_{10}CH_2Ti$ might be expected to be a CH_2 derivative of $[h^5\text{-}C_5(CH_3)_5]_2Ti$. This possibility is ruled out, however, by the nmr spectrum of this compound (Figure 1), which shows nonequivalent ring methyl groups, in contrast to nmr spectra of $[C_5(CH_3)_5]_2TiCl_2$ and $[C_5(CH_3)_5]_2Ti(CH_3)_2$. For a related structure, such as $[h^5\text{-}C_5(CH_3)_5][h^1\text{-}C_5(CH_3)_5]TiCH_2$, one would expect a coalescence of the methyl resonances at higher temperatures. The spectrum shown in Figure 1, however, persists unchanged over the temperature range −60 to +90°, thus eliminating this possibility.

Further examination of the mass spectrum of this turquoise intermediate provides most useful information. A structure which contains a $Ti{=}CH_2$ moiety would be expected to give rise to an ion with *m/e* 318 by loss of $[CH_2]$ from the molecular ion. This ion is not observed, but rather an ion with *m/e* 317, corresponding to the loss of a methyl group, is observed with moderate intensity. In addition, a predominant species in the spectrum is the ion $C_5(CH_3)_4CH_2^+$, arising from a pentamethylcyclopentadienyl ring by loss of one H atom. Although the occurrence of this ion might be explained as the result of *in situ* hydrogen abstraction from a $[C_5(CH_3)_5]$ ring by either $[CH_2]$ or the titanium center, its high abundance is suggestive of its presence in the parent molecule, $C_{10}(CH_3)_{10}CH_2Ti$. These observations seem to be consistent with structures **1** or **2**.



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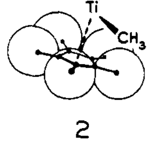

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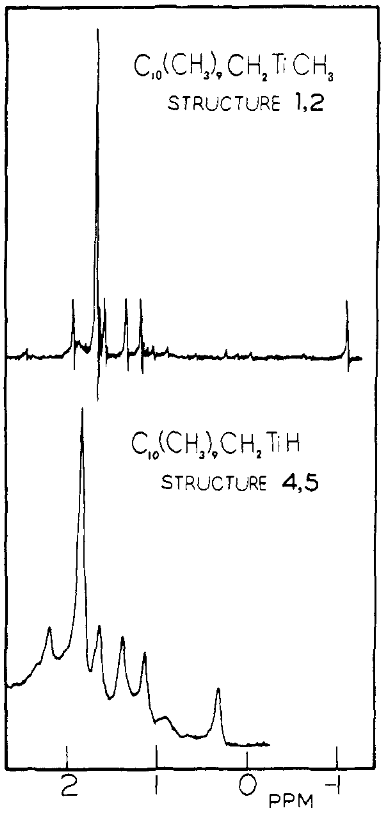

Figure 1. Nmr spectra of the turquoise intermediate, $C_{10}(CH_3)_9CH_2TiCH_3$, structures **1** and **2** (top), and of the thermal decomposition product, $C_{10}(CH_3)_9CH_2TiH$, structures **4** and **5** (bottom). The latter is obtained by warming $[C_5(CH_3)_5]_2Ti$ to 35° in benzene for 10 hr. Spectra were taken in C_6D_6 on a Varian T60 spectrometer.

There is essentially no difference between these two structures; rather, they may be thought of as related by resonance, or in MO theory, by assuming overlap of Ti atomic orbitals with those of the methyl-substituted fulvene ligand. At any rate, both structures contain a $TiCH_3$ moiety, consistent with the presence of a singlet nmr absorption at −1.07 ppm, the chemical shift and intensity of which are in accord with this assignment. (The dimethyl derivative similarly exhibits a singlet absorption at −0.97 ppm, attributable to the $Ti(CH_3)_2$ unit.) Another observation consistent with structure **1** is the presence of an olefinic C–H stretch at 3040 cm^{-1} in the ir spectrum of the turquoise intermediate. There is no evidence for this higher energy stretch in the ir spectra of other decamethyltitanocene derivatives with normal π-bound $[C_5(CH_3)_5]$ rings.

The formation of this compound from $[C_5(CH_3)_5]_2Ti(CH_3)_2$ may be thought of as a hydrogen abstraction from a ring methyl group by one of the $TiCH_3$ groups. A somewhat analogous reaction is observed in the thermal decomposition of $(C_5H_5)_2Ti(C_6H_5)_2$. Dvorak, *et al.*,[15] have recently shown that the initial product results from the abstraction of a proton from one coordinated (C_6H_5) unit by the other phenyl ligand group, under release of benzene (reaction 1). The proposed

$$(C_5H_5)_2Ti(C_6H_5)_2 \xrightarrow[\text{under reflux}]{\text{benzene}} [(C_5H_5)_2TiC_6H_4] + C_6H_6 \quad (1)$$

mechanism for the formation of the turquoise inter-

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[15] J. Dvorak, R. J. O'Brien, and W. Santo, *Chem. Commun.*, 411 (1970).

Table II. Mass Spectra of $[C_5(CH_3)_5]_2Ti$ and $[C_5(CH_3)_5]_2Ti(CH_3)_2$ (Given for Comparison)[a]

$[C_5(CH_3)_5]_2Ti(CH_3)_2$			$[C_5(CH_3)_5]_2Ti$		
m/e	Intensity	Assignment	*m/e*	Intensity	Assignment
348	9	M^+			
333	29	$M^+ - [CH_3]$			
332	5	$M^+ - CH_4$			
318	100[b]	$[C_5(CH_3)_5]_2Ti^+$	318	50	M^+
317	87	$[C_5(CH_3)_5]_2Ti^+ - [H]$	317	100[b]	$M^+ - [H]$
			316	17	$M^+ - H_2$
136[c]	49	$C_5(CH_3)_6H^+$	136[c]	91	$C_5(CH_3)_5H^+$
135	24	$C_5(CH_3)_5^+$	135	20	$C_5(CH_3)_5^+$
134	100[b]	$C_5(CH_3)_4CH_2^+$	134	100[b]	$C_6(CH_3)_4CH_2^+$
121[c]	30	$C_5(CH_3)_4H^+$	121[c]	25	$C_5(CH_3)_4H^+$
120	9	$C_5(CH_3)_4^+$	120	1	$C_5(CH_3)_4^+$
119	73	$C_5(CH_3)_3CH_2^+$	119	41	$C_5(CH_3)_3CH_2^+$

[a] M^+ represents the molecular ion for each compound. Given in the table are the monoisotopic species with ^{12}C, ^1H, and ^{48}Ti; the measured spectra had satisfactory isotopic distributions. Ionizing voltage = 20 eV. [b] Relative intensities grouped into Ti-containing and non-Ti-containing ions. [c] As noted in Table I, the occurrence of $C_5(CH_3)_5H^+$ and $C_5(CH_3)_4H^+$ in the spectrum is attributable to small amounts of more volatile pentamethylcyclopentadiene impurity.

mediate with either structure **1** or **2** (reaction 2) is in close analogy to this reaction sequence.

$$[C_5(CH_3)_5]_2Ti(CH_3)_2 \xrightarrow[110°]{\text{toluene}} [C_5(CH_3)_5][C_5(CH_3)_4CH_2]TiCH_3 + CH_4 \quad (2)$$

The turquoise compound, $C_{10}(CH_3)_{10}CH_2Ti$, readily reacts with H_2 in pentane at 0° to yield bis(pentamethylcyclopentadienyl)titanium(II), *via* a hydride complex (see below). The overall reaction requires 1.0 mmol of H_2 and evolves 1.0 mmol of CH_4 per mmol of starting material (reaction 3). When deuterium is substituted for hydrogen in the reaction, essentially pure CH_3D is evolved, presumably forming decamethyltitanocene-d_1 (reaction 4). This observation provides additional support for either structure **1** or **2**, assigned to the turquoise intermediate.

$$C_{10}(CH_3)_{10}CH_2Ti + H_2 \longrightarrow [C_5(CH_3)_5]_2Ti + CH_4 \quad (3)$$

$$C_{10}(CH_3)_{10}CH_2Ti + D_2 \longrightarrow [C_5(CH_3)_5][C_5(CH_3)_4CH_2D]Ti + CH_3D \quad (4)$$

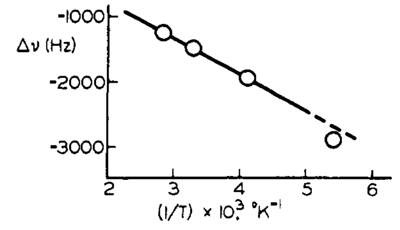

Figure 2. Temperature-dependent contact shift of the methyl resonance of $[C_5(CH_3)_5]_2Ti$ in toluene-d_8. Contact shifts are relative to the aromatic protons of toluene.

The identity of the product of this reaction with hydrogen as $[C_5(CH_3)_5]_2Ti$ is established, apart from the stoichiometry of its formation, by a mass spectrum with a parent ion at *m/e* 318 (see Table II). The appearance, next to the parent peak, of a strong peak at *m/e* 317 indicates that hydrogen loss is the favored fragmentation pathway. In accord with this one observes, in the *m/e* region 314–316, overlapping metastable peaks attributable to the loss of hydrogen from the ions with mass 317 and 318. It is obvious that $[C_5(CH_3)_5]_2Ti$, while relatively stable to a ring methyl–titanium hydrogen shift at low temperatures, is a rather fragile molecule at the temperatures necessary for volatilization (*ca.* 100°), and under electron impact (see, in addition, a discussion of the thermal decomposition, given below).

Freezing point depression experiments with a solution containing 60.0 mg of decamethyltitanocene per gram of benzene gave an apparent molecular weight of 520 ± 20; 318 is the calculated molecular weight for the monomer. These data indicate the existence of a monomer–dimer equilibrium with a constant (K_{eq}) of 0.022 ± 0.01 *M* (eq 5).

$$[C_5(CH_3)_5]_2Ti\text{–}Ti[C_5(CH_3)_5]_2 \rightleftharpoons 2[C_5(CH_3)_5]_2Ti \quad (5)$$

Magnetic susceptibility measurements of a benzene solution, using the nmr method described by Evans,[16] indicate a gram magnetic susceptibility of $2.8 \pm 0.1 \times 10^{-6}$ cgs units. If the above value of K_{eq} is used to calculate the concentration of monomeric $[C_5(CH_3)_5]_2Ti$ in solution, one obtains an effective magnetic moment of 3.0 ± 0.3 BM for the monomeric species. This value is in good agreement with a spin-only magnetic moment of 2.84 BM expected for a monomeric $[C_5(CH_3)_5]_2Ti(II)$ species with two unpaired electrons. The results further imply that the dimeric species is diamagnetic.

Nmr spectra of decamethyltitanocene in benzene-d_6 or toluene-d_8 at 34° show a broad singlet at 22.6 ppm. Rettig and Drago[17] have studied the nmr spectra of the 1,1′-dimethyldicyclopentadienyls of V, Cr, Co, and Ni, and observed methyl resonances very similar in both position and shape to that observed for decamethyltitanocene. They have attributed the observed contact shifts to delocalization of the unpaired electron density into the σ (in plane) cyclopentadienyl orbitals for V and Cr, and into the π (out of plane) orbitals for Co and Ni.[17] The temperature dependencies of the contact shifts indicated that the Curie law was obeyed in each case. Similarly, the position of the nmr resonance in spectra of decamethyltitanocene was found to vary reversibly from 19.6 ppm at +80° to 36 ppm at −90°. The close linearity of a plot of $\Delta\nu$ *vs.* $1/T$ indicates that the expected Curie law temperature dependence is obeyed for the $[C_5(CH_3)_5]_2Ti$ system also (Figure 2).[18]

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(16) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

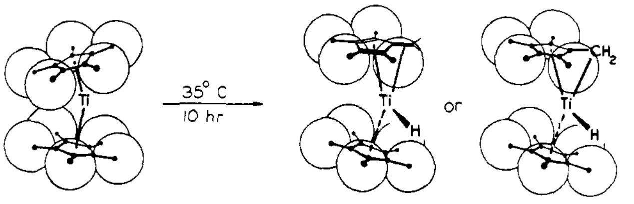
(17) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 1361 (1969).

(18) The interconversion between a paramagnetic monomer and a diamagnetic dimer discussed above should actually interfere with this $\Delta\nu$ *vs.* $1/T$ dependence. Possibly, the interconversion is frozen at the lower temperatures employed.

Extrapolation of the shifted resonance to $1/T \rightarrow 0$ yields a value of 2.0 ± 1.0 ppm for the origin of the resonance under consideration. This value closely coincides with the chemical shift of the methyl groups in diamagnetic $[C_5(CH_3)_5]_2TiX_2$ (X = Cl, H, CH_3, CO) derivatives.

The infrared spectrum of $[C_5(CH_3)_5]_2Ti$ is very similar to that of $[C_5(CH_3)_5]_2Fe$ and $[C_5(CH_3)_5]_2TiCl_2$, with only minor shifts and intensity differences. The occurrence of two bands at 1560 and 1575 cm^{-1} in the spectrum of decamethyltitanocene is a possible exception. Although peaks at 1550 and 1630 cm^{-1} are present in the ir spectrum of decamethylferrocene, they are considerably weaker. A possible explanation for their occurrence in the spectrum is the presence of some $[C_5(CH_3)_5]_2TiH_2$ impurity (see below), which exhibits a very strong absorbance in this region, or of the thermal decomposition product discussed below. In any case, the similarity of the spectrum of $[C_5(CH_3)_5]_2Ti$ to those of the other decamethyltitanocene derivatives and to that of decamethylferrocene,[19] is indicative of a structure with normal $[C_5(CH_3)_5]$ ligands.

Thermal decomposition of $[C_5(CH_3)_5]_2Ti$ is observed just slightly above room temperature. If pentane solutions of decamethyltitanocene are stirred under argon for *ca.* 10 hr at 35°, the color changes to dull purple brown. Nmr spectra (see Figure 1b) of benzene-d_6 solutions of the resulting compound exhibit strong absorptions from 2.20 to 0.25 ppm, in addition to the broad signal at 22.6 ppm attributable to some residual $[C_5(CH_3)_5]_2Ti$. The close resemblance, in position, shape, and relative peak intensities, of the new absorptions to those observed in the nmr spectrum of the turquoise compound, $C_{10}(CH_3)_{10}CH_2Ti$ (see Figure 1a), strongly suggests similar structures for the two species. The product of the thermal decomposition of $[C_5(CH_3)_5]_2Ti$ could therefore have structures **4** or **5**.



3 4 5

Examination of the mass spectrum of $[C_5(CH_3)_5]_2Ti$ (Table II) provides additional support for the occurrence of this thermal decomposition in the source of the mass spectrometer. The formation of **4** or **5** would explain the high abundance of the ions $C_5(CH_3)_5CH_2^+$ and $M^+ - [H]$ in the observed spectrum. The thermal decomposition product appears to have only a transient existence, however. The nmr spectrum decays to an undefinable series of absorptions within a few hours.

While the decamethyl-substituted titanocene, $[C_5(CH_3)_5]_2Ti$, is sufficiently stable for the determination of its structure and chemical reactivity, the favored deactivation mechanism appears to be a hydrogen abstraction by the titanium center in close analogy to the deactivation of $(h^5\text{-}C_5H_5)_2Ti$, discussed above.

When a toluene solution of $[C_5(CH_3)_5]_2Ti$ is treated with HCl at −80°, the expected $[C_5(CH_3)_5]_2TiCl_2$ is formed in high yield. The nmr spectrum of this product shows the presence of *ca.* 15% $[C_5(CH_3)_5]TiCl_3$, but is otherwise identical with that of an authentic sample of $[C_5(CH_3)_5]_2TiCl_2$.

A toluene or pentane solution of $[C_5(CH_3)_5]_2Ti$ readily absorbs 2 mol of carbon monoxide to form $[C_5(CH_3)_5]_2Ti(CO)_2$ (reaction 6). This yellow-brown sub-

$$[C_5(CH_3)_5]_2Ti + 2CO \longrightarrow [C_5(CH_3)_5]_2Ti(CO)_2 \qquad (6)$$

stance can be purified by sublimation at 80°, 10^{-3} Torr. Its nmr spectrum exhibits a single absorption at 1.69 ppm, indicating the equivalence of all ring methyl groups. The ir spectrum shows two carbonyl absorptions at 1930 and 1850 cm^{-1}. These frequencies are even lower than those observed in $(C_5H_5)_2Ti(CO)_2$, 1975 and 1897 cm^{-1},[20] illustrating the increased electron-donating capability of the titanium center in the decamethyl derivative.

(2) Hydride and Nitrogen Complexes of $[C_5(CH_3)_5]_2Ti$. While $[C_5(CH_3)_5]_2Ti(CO)_2$ does not lose its coordinated carbon monoxide upon mild heating or evacuation, reversible reactions are found to occur between $[C_5(CH_3)_5]_2Ti$ and N_2. If red-brown, crystalline decamethyltitanocene is dissolved in pentane at −100° and subsequently exposed to 1 atm of gaseous nitrogen, an olive-green nitrogen complex is formed. This nitrogen complex is unstable in a vacuum, even at −100°, thus thwarting all attempts of complete characterization. We believe that it is an analog of $[C_5(CH_3)_5]_2Ti(CO)_2$ containing the isoelectronic N_2 molecule substituting for CO, since it retains, at −200°, close to 2 mol of N_2 per mol of Ti.

When the N_2 atmosphere above the olive-green complex is partially removed at −100° a dramatic conversion to an intense purple-blue species is observed. This species is considerably more stable than the initially formed olive-green complex; however, it too decomposes, under evolution of N_2, yielding the original red-brown solution of $[C_5(CH_3)_5]_2Ti$ upon further warming to *ca.* −10° *in vacuo*. Readmission of nitrogen leads to darkening of the solution, and upon cooling below 0°, to the renewed formation of the intensely purple-blue complex. Quantitative measurements of the amount of N_2 released when this solution is again warmed to room temperature *in vacuo* indicate that the purple-blue complex contains 1.0 mol of N_2 per 2.0 mol of $[C_5(CH_3)_5]_2Ti$.

The purple-blue color of this complex results from an intense absorption with λ_{max} at 568 nm. A similar binuclear N_2 complex with λ_{max} 597 nm has been observed for the unsubstituted titanocene system (see section 4).

In addition to the reversible reactions with molecular nitrogen, $[C_5(CH_3)_5]_2Ti$ reversibly interacts with gaseous hydrogen. When red-brown pentane or toluene solutions of decamethyltitanocene are exposed to an atmosphere of H_2, hydrogen is absorbed concurrent with the formation of a bright orange solution. When this solution is cooled to −80°, the hydrogen is retained, even in a vacuum. When warmed to room temperature *in vacuo*, however, solutions of the resulting hydride species slowly release the coordinated hydrogen over a period of several hours.

Chemical and physical properties of this decamethyltitanocene hydride species indicate that it may be

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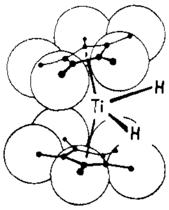
(19) K. Schlogl and M. Peterlik, *Monatsh. Chem.*, **93**, 1328 (1962).

(20) F. Calderazzo, J. J. Salzmann, and P. Mosimann, *Inorg. Chim. Acta*, **1**, 65 (1967).

formulated as $[C_5(CH_3)_5]_2TiH_2$ with structure **6**. When a benzene solution of $[C_5(CH_3)_5]_2Ti$ is exposed to 1 atm of hydrogen, the apparent molecular weight decreases significantly from 520 ± 20 to 395 ± 10. This observation indicates that the hydride is monomeric; the calculated molecular weight for monomeric **6** is 320.



6

In addition, magnetic susceptibility measurements show that the compound is diamagnetic. This observation eliminates the possibility that the compound is a monomeric species like $[C_5(CH_3)_5]_2TiH$, since such a compound contains a formal Ti(III) center and should therefore have one unpaired electron. The molecular weight rules out a decamethyl analog of $[(h^5\text{-}C_5H_5)_2TiH]_2$.[21]

The nmr spectra of benzene-d_6 solutions of **6**, under 1 atm of H_2, show a singlet absorption at 1.95 ppm, illustrating the equivalence of all ring methyl groups. In addition there is a singlet absorption at 0.28 ppm, the intensity of which is in accord with assignment to the TiH_2 moiety of structure **6**. The relatively small high-field shift of the proton which is bound to the titanium at first appears to be anomalous, since other transition metal hydride complexes exhibit resonances shifted upfield to δ −5 to −40 ppm. Although the nmr spectra of these hydride complexes have been the subject of much discussion, it is now well accepted that the large chemical shift of the proton is due to anisotropic polarization of the *partially* filled d shell by the magnetic field.[22] Metal hydrides which contain empty or completely filled d orbitals show considerably lower chemical shifts.[22] For example, tin and germanium hydrides show resonances at δ 2–5 ppm.[23,24] The ZrH hydride in $(C_5H_5)_2Zr(H)BH_4$ exhibits a resonance at δ 5.47 ppm,[25] while $(C_5H_5)_2TaH_3$ and $(C_5H_5)_2NbH_3$ have hydride resonances between δ −1.63 and −3.72 ppm.[26,27a] The hydride chemical shift of δ 0.28 ppm in the nmr spectrum of $[C_5(CH_3)_5]_2TiH_2$ is therefore perfectly in accord with its formally being a d_0 species.

The infrared spectrum of $[C_5(CH_3)_5]_2TiH_2$ measured in Nujol under 1 atm of H_2 is very similar to those of other decamethyltitanocene derivatives, except for the presence of a strong, broad band at 1560 cm^{-1}. This absorption must be associated with TiH stretch. The frequency of this metal–hydrogen stretch is considerably lower than those observed in the ir spectra of other cyclopentadienyl metal hydrides. These $(C_5H_5)_2MH_x$ compounds exhibit M–H stretching frequencies in the region 1825–2060 cm^{-1}.[28] The only exceptions appear to be $(C_5H_5)_2TaH_3$ and $(C_5H_5)_2NbH_3$, in which the M–H frequencies are 1735 and 1710 cm^{-1}, respectively.[26,27] Unfortunately there are no Ti–H stretching frequencies reported for comparison, since there were no titanium hydride complexes with terminal Ti–H bonds known prior to this work. The relative ease with which $[C_5(CH_3)_5]_2TiH_2$ loses its coordinated H_2 is apparently reflected in the low value of the force constant observed for the Ti–H stretch.

As noted earlier, $[C_5(CH_3)_5]_2TiH_2$ is formed in the reaction of the turquoise intermediate, $C_{10}(CH_3)_{10}CH_2Ti$, with hydrogen. Excess H_2 available in the system reacts with the initially formed $[C_5(CH_3)_5]_2Ti$, according to equilibrium 7. The hydride may be

$$[C_5(CH_3)_5]_2Ti + H_2 \rightleftharpoons [C_5(CH_3)_5]_2TiH_2 \qquad (7)$$

conveniently obtained from the pentane solution as large orange crystals by cooling to −90° under hydrogen. These crystals are stable to loss of H_2 at room temperature, even *in vacuo* or in an atmosphere of pure argon. If $[C_5(CH_3)_5]_2Ti$ is desired, the pentane solution of $[C_5(CH_3)_5]_2TiH_2$ is stirred at room temperature *in vacuo* for several hours to shift equilibrium 7 to the left, and the decamethyltitanocene is obtained as large red-brown crystals by cooling the resulting solution. Optimal preparative and purification procedures are detailed in the Experimental Section.

(3) Preparation and Properties of $[(C_5H_5)_2Ti]_2$. Meanwhile, we had found that it is in fact possible to obtain an unsubstituted species $[(C_5H_5)_2Ti]_2$, whose reactivity closely parallels that of decamethyltitanocene, by hydrogen elimination from titanocene hydride complexes.[11] We had previously observed that the violet hydride complex $[(C_5H_5)_2TiH]_2$, formed in the reaction of crystalline $(C_5H_5)_2Ti(CH_3)_2$ with H_2 gas, converts to a green-gray isomer upon standing at room temperature.[21] The green-gray compound exhibited chemical reactivity identical with that of violet $[(C_5H_5)_2TiH]_2$. Its insolubility in ethereal solvents, which readily dissolve the violet hydride even at −80°, however, leads us to believe that the green-gray isomer is polymeric. Recently, we found that the green-gray hydride complex can be prepared directly by treating saturated hexane solutions of $(C_5H_5)_2Ti(CH_3)_2$ with excess hydrogen gas at 0°. Although this reaction was originally reported to yield what has since been recognized as $[(C_5H_5)(C_5H_4)TiH]_2$, when carried out at room temperature,[14] efficient stirring with excess H_2 and cooling at 0° leads to a homogeneous green-gray product in which this green form of titanocene, $[(C_5H_5)(C_5H_4)TiH]_2$, is virtually absent. Traces of this impurity can easily be removed from the green-gray hydride by washing with toluene at −80°.

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 the violet compound $[(C_5H_5)_2TiH]_2$; $[(C_5H_5)_2TiH]_x$ is converted, for example, to the green form of titanocene upon thermal decomposition at 100° (reaction 8). Its reaction with DCl

$$(1/x)[(C_5H_5)_2TiH]_x \longrightarrow (1/2)[(C_5H_5)(C_5H_4)TiH]_2 + (1/2)H_2 \qquad (8)$$

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[21] J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **91**, 7301 (1969).

[22] A. D. Buckingham and P. J. Stevens, *J. Chem. Soc.*, 2747 (1964).

[23] J. E. Drake and W. L. Jolly, *ibid.*, 2807 (1962).

[24] P. E. Potter, L. Pratt, and G. Wilkinson, *ibid.*, 524 (1964).

[25] B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Inorg. Chem.*, **6**, 1979 (1967).

[26] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4845 (1961).

[27] (a) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971); (b) L. J. Guggenberger and F. N. Tebbe, *ibid.*, **93**, 5924 (1971).

[28] H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 285 (1964).

leads to titanocene dichloride and HD (reaction 9).

$$(1/x)[(C_5H_5)_2TiH]_x \xrightarrow{DCl} (C_5H_5)_2TiCl_2 + HD + (1/2)D_2 \quad (9)$$

Formation of the dicarbonyl complex and evolution of H_2 is observed upon exposure to CO (reaction 10).

$$(1/x)[(C_5H_5)_2TiH]_x \xrightarrow{CO} (C_5H_5)_2Ti(CO)_2 + (1/2)H_2 \quad (10)$$

The green-gray hydride also resembles $[(C_5H_5)_2TiH]_2$ in its extreme (pyrophoric) air sensitivity. In contrast to the latter, however, it can be stored as a solid under Ar for months without noticeable decomposition.

The ir spectrum of $[(C_5H_5)_2TiH]_x$ (Figure 3) shows all the features of *bona fide* $(h^5\text{-}C_5H_5)_2Ti$ derivatives. It is nearly identical, for instance, with 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,[21] a similarly broad band is observed at 1140 cm^{-1} in the green-gray isomer. The substantially lower frequency of this absorption is probably related to the different modes of coupling in the polymeric structure, containing, for instance, a linear $HTi(HTi)_xH$ chain, as opposed to the four-membered ring in the dimeric violet compound. In a deuterated sample, prepared by treating $(C_5H_5)_2Ti(CH_3)_2$ with D_2, the broad absorption is shifted from 1140 to 800–850 cm^{-1}. The lack of any observable splitting in the out-of plane C–H bending mode at 800 cm^{-1}, and the complete absence of any absorption at 1230 cm^{-1}, which dominates the spectrum of $[(C_5H_5)(C_5H_4)TiH]_2$, confirms the absence of $[(C_5H_5)(C_5H_4)TiH]_2$ impurity in 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 formed concurrent with the evolution of 0.5 mmol of H_2 per mmol of 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 $[(C_5H_5)(C_5H_4)TiH]_2$ is completely absent from the $[(C_5H_5)_2Ti]_x$ solutions. When heated to 100°, however, such a toluene solution turns bright green. Subsequently, pure $[(C_5H_5)(C_5H_4)TiH]_2$ is 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 3), do not exhibit any of the band splittings characteristic of $[(C_5H_5)(C_5H_4)TiH]_2$.[9] Rather, a simple metallocene spectrum with two strong bands at 790 and 1010 cm^{-1} is observed for $[(C_5H_5)_2Ti]_x$.

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 0.2–0.06 *F* solutions in fairly good agreement with the value of 356 calculated for $[(C_5H_5)_2Ti]_2$.

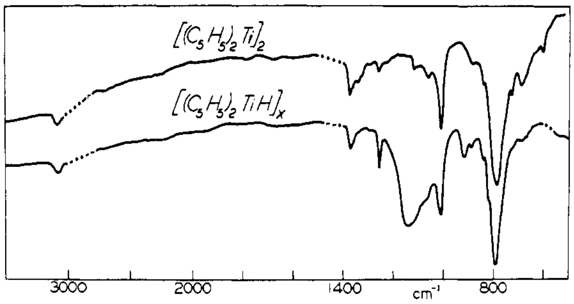

Figure 3. Ir spectra of $[(C_5H_5)_2Ti]_2$ (top) and $[(C_5H_5)_2TiH]_x$ (bottom), taken in Nujol on KBr.

Magnetic susceptibility determinations on *ca.* 0.1 *F* solutions of $[(C_5H_5)_2Ti]_2$ in toluene at 30°[16] 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, probably in a monomer–dimer equilibrium similar to that observed in solutions of $[C_5(CH_3)_5]_2Ti$.

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, 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 about 30 min, degrades to 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.[29] The brown product, possibly a titanocene alkoxide derivative resulting from insertion into THF, no longer exhibits any of this characteristic reactivity.

The presence of normal $h^5\text{-}C_5H_5$ rings in $[(C_5H_5)_2Ti]_2$ is also supported by its chemical behavior. When exposed to HCl gas at −80°, 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 form of "titanocene," 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 titanocene dicarbonyl complex, $(C_5H_5)_2Ti(CO)_2$. Reactions

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[29] (a) This observed reactivity of $[(C_5H_5)_2Ti]_2$ toward tetrahydrofuran could explain some of the earlier observations concerning green and brown titanocene THF adducts: see, A. K. Fischer and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 149 (1956), and G. A. Razuvaev, V. N. Latyaeva, L. I. Vyshinskaya, and G. A. Kilyakova, *Zh. Obshch. Khim.*, **36**, 1491 (1966). (b) A mass spectrum of titanocene, prepared by reduction of $(C_5H_5)_2TiCl_2$ with sodium amalgam, was reported by Y. Takegami, T. Ueno, T. Suzuki, and Y. Fuchizaki, *Bull. Chem. Soc. Jap.*, **41**, 2637 (1968), to exhibit a strong monomer peak at *m/e* 178 indicating the presence of some metastable $[(C_5H_5)_2Ti]_2$; the ir spectrum given by these authors indicates, however, that the rearrangement product $[(C_5H_5)(C_5H_4)TiH]_2$ is a major species present.

of $[(C_5H_5)_2Ti]_2$ with H_2 and N_2, which closely parallel the unique reaction behavior of decamethyltitanocene, are outlined in detail in the following section.

(4) 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°, evacuated, and then warmed again to room temperature, 0.2–0.4 mmol 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 studies by cryoscopy in benzene indicate that the dimer is cleaved to a significant extent upon exposure of $[(C_5H_5)_2Ti]_2$ solutions to hydrogen. By analogy to the reaction of $[C_5(CH_3)_5]_2Ti$ with H_2, which leads to the formation of the hydride complex $[C_5(CH_3)_5]_2TiH_2$, it seems probable that formation of some monomeric hydride complex occurs in the unsubstituted titanium compound as well. Whether the reaction with hydrogen proceeds *via* an insertion of H_2 into the dimer, with the subsequent formation of a monomeric Ti(III) hydride derivative, or *via* an oxidative addition of H_2 to the $(C_5H_5)_2Ti$ monomer, leading to a Ti(IV) dihydride, is not clear at present. 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 occurs with a titanocene–triphenylphosphine complex (see below).

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° 1 mmol of N_2 is retained by 1 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°. In very concentrated solutions of $[(C_5H_5)_2Ti]_2$ in toluene, the blue complex 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°, filtering, washing with butane, and drying in vacuum, all operations carried out at −80°, 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 1 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 $(C_5H_5)_2TiN_2Ti(C_5H_5)_2$. 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.*[7] When ether solutions of $(C_5H_5)_2TiCl_2$ are treated with 2 equiv of C_3H_7MgBr at −70° in a nitrogen atmosphere, a transient intensely blue species (λ_{max} 600 nm) appears in solution.

The blue complex $[(C_5H_5)_2Ti]_2N_2$ is easily reduced to some ammonia derivative of titanocene. When a diethyl ether solution of $[(C_5H_5)_2Ti]_2N_2$ is treated with 2 equiv of lithium naphthalide at −80° and then warmed to room temperature under a pressure of *ca.* 150 atm of N_2, most of the coordinated nitrogen is reduced and, upon subsequent hydrolysis, released as NH_3.

(5) A Phosphine Complex of Titanocene, Characterization and Reactions with H_2 and N_2. Still another highly reactive derivative of titanocene is obtained in reaction systems containing triphenylphosphine. In a variety of such systems, discussed in detail below, an intensely purple phosphine complex is obtained. Shilov, *et al.*, have reported similar observations.[7] However, these authors have interpreted their results in terms of the formation of an 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. This complex reacts reversibly with hydrogen to yield the previously described complex $(C_5H_5)_2Ti(H)P(C_6H_5)_3$.[21] In addition, it also reacts, in a somewhat nonstoichiometric and irreversible manner, with molecular nitrogen.

A particularly clean and mechanistically transparent mode of preparation utilizes the violet titanocene hydride, $[(C_5H_5)_2TiH]_2$,[21] as a starting material. When THF solutions of $[(C_5H_5)_2TiH]_2$ are treated with triphenylphosphine at −20°, cleavage to $(C_5H_5)_2Ti(H)P(C_6H_5)_3$ occurs, giving rise to a characteristic epr spectrum. Upon warming to room temperature *in vacuo*, hydrogen (1 mmol/2 mmol of Ti) is evolved, concurrent with the formation of a green-brown, diamagnetic solution. When the THF solvent is removed under reduced pressure, an intensely purple compound of stoichiometry $C_{10}H_{10}TiP(C_6H_5)_3$ is obtained. When the sequence is carried out in toluene, the purple compound is formed in solution concurrent with the evolution of hydrogen, with no evidence of the green-brown intermediate. These results imply that this green-brown intermediate formed in tetrahydrofuran solution is a tetrahydrofuran adduct of the purple phosphine complex. A completely analogous reaction sequence is observed when the gray-green polymeric hydride, $[(C_5H_5)_2TiH]_x$, is substituted for the dimeric hydride. 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 treatment of $(C_5H_5)_2Ti(CH_3)_2$ with hydrogen and triphenylphosphine in hexane at 0°; under these conditions the compound precipitates cleanly from the reaction mixture.

The elemental composition, in satisfactory agreement with the stoichiometry $[C_{10}H_{10}TiP(C_6H_5)_3]_2$, rules out a conceivable identity of the compound described here with $[(C_5H_5)_2TiP(C_6H_5)_2]_2$, another deep purple complex invoked by Issleib, *et al.*,[30] as the reaction product formed from $(C_5H_5)_2TiCl_2$ and sodium diphenylphosphide.

The compound is only moderately stable in solution at room temperature, possessing much greater stability in solutions which contain excess triphenylphosphine. It is slightly soluble in toluene (to *ca.* 10^{-2} *M*) and benzene, insoluble in aliphatic hydrocarbons, and slightly soluble in THF and diethyl ether, showing a tendency to cleave to green-brown ether adducts, especially when slightly impure. The phosphine complex is diamagnetic in toluene solution and as a solid.

Treatment of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with HCl yields triphenylphosphine and the magenta chloride $[(C_5H_5)(C_5H_4)TiCl]_2$. Heating $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ to 110° yields triphenylphosphine and $[(C_5H_5)(C_5H_4)TiH]_2$. The strong ir absorption at 1230 cm^{-1}, characteristic of $[(C_5H_5)(C_5H_4)TiH]_2$, is completely absent in the phosphine complex, however. The possibility that the phosphine complex is simply a triphenylphosphine adduct of $[(C_5H_5)(C_5H_4)TiH]_2$ is also ruled out by the fact that upon stirring the dark green $[(C_5H_5)(C_5H_4)TiH]_2$ and excess triphenylphosphine in toluene solution for 3 days, formation of the purple compound was not observed. Rather it appears that a more reactive form of titanocene is preserved in the phosphine complex, $[C_{10}H_{10}TiP(C_6H_5)_3]_2$; this supposition is supported by its observed reactivity toward carbon monoxide, molecular hydrogen, and nitrogen.

Upon exposure to 1 atm of CO, a toluene solution of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ changes color from purple to the red-brown characteristic of $(C_5H_5)_2Ti(CO)_2$; this dicarbonyl complex can be sublimed from the residue after removal of the solvent.

When solid samples of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ are exposed to a nitrogen atmosphere, up to 0.4 mmol of N_2/mmol of Ti is absorbed, which is evolved only upon destruction of the complex by reaction with HCl. This reactivity toward molecular nitrogen is also observed when toluene solutions are stirred at room temperature with nitrogen. Under these conditions up to 0.33 mmol of N_2/mmol of Ti is absorbed, concurrent with the formation of a pale yellow-brown precipitate. When the resulting mixture is heated to 110°, approximately half of the complexed nitrogen is reduced to some ammonia derivative, the remainder being evolved as N_2. The degree of complexation with nitrogen depends on the concentration of excess triphenylphosphine; essentially no activity toward N_2 is observed at very high $P(C_6H_5)_3$ concentrations.

In addition to its reactivity toward molecular nitrogen, $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ reversibly absorbs 1 mmol of H_2/2 mmol of Ti to form $(C_5H_5)_2Ti(H)P(C_6H_5)_3$. Uv-visible spectral studies of this equilibrium were undertaken to determine whether a monomeric or a dimeric species is in equilibrium with the hydride (eq 11 and 12, respectively).

$$2C_{10}H_{10}TiP(C_6H_5)_3 + H_2 \rightleftharpoons 2(C_5H_5)_2Ti(H)P(C_6H_5)_3 \quad (11)$$

$$[C_{10}H_{10}TiP(C_6H_5)_3]_2 + H_2 \rightleftharpoons 2(C_5H_5)_2Ti(H)P(C_6H_5)_3 \quad (12)$$

The absorbance *A* at 521 nm was measured at various hydrogen pressures, and analyzed in the following way. The concentration of the hydride is proportional to ΔA, the change in absorption; since the absorbance of the hydride at 521 nm is small compared to that of the phosphine complex, the concentration of the latter is closely proportional to *A*. Substitution into the appropriate equilibrium expressions gives $\Delta A/A = c_1 \cdot \sqrt{p(H_2)}$ for a monomer, and $\Delta A/A = c_2\sqrt{p(H_2)}/\sqrt{A}$ for a dimer, where c_1 and c_2 are constants. The nonlinearity of a plot of $\Delta A/A$ *vs.* $\sqrt{p(H_2)}$ and the close linearity of a plot of $\Delta A/A$ *vs.* $\sqrt{p(H_2)}/\sqrt{A}$ (Figure 4) leave little doubt that the species in equilibrium with the hydride is dimeric. Based on this evidence, only eq 12 correctly describes the equilibrium between toluene solutions of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$, $(C_5H_5)_2Ti(H)P(C_6H_5)_3$, and H_2.

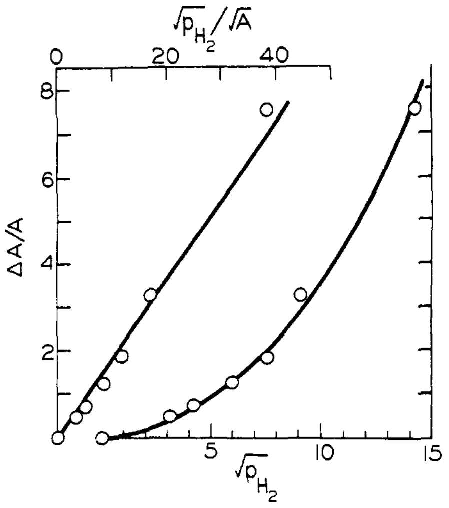

Figure 4. Plots of $\Delta A/A$ *vs.* $\sqrt{p(H_2)}/\sqrt{A}$ (top) and of $\Delta A/A$ *vs.* $\sqrt{p(H_2)}$ (bottom) for a toluene solution of the purple titanocene triphenylphosphine complex (λ_{max} 520 nm) in equilibrium with hydrogen gas: $[Ti]_{total} = 9.6 \times 10^{-3}$ *M*; the linear $\Delta A/A$ *vs.* $\sqrt{p(H_2)}/\sqrt{A}$ plot indicates that the purple triphenylphosphine complex is dimeric.

If D_2 is substituted for H_2 in equilibrium 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 deuterated complex. (3) Thermal decomposition of the resulting phosphine 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–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,[31] indicates that the reactive species involved in the exchange is void of triphenylphosphine. Therefore, we favor the hypothesis, suggested by the close 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 $P(C_6H_5)_3$ and by its reaction with CO to form $(C_5H_5)_2Ti(CO)_2$, as discussed above.

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(30) K. Issleib and H. Hackert, *Z. Naturforsch. B*, 21, 19 (1966).

(31) G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

(6) 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 dichloride is allowed to react with excess Grignard reagent in an ethereal solvent.[4,32] In an effort to identify intermediates in these systems, we have reported, in an earlier publication, the electron paramagnetic (epr) spectra of several alkyl and hydride complexes of titanocene, which form in these reaction mixtures.[33] More recently, we have found that on addition of ethylmagnesium chloride to a suspension of $(C_5H_5)_2TiCl_2$ in ether, the reactive ingredient of this reaction mixture can be isolated as a yellow, microcrystalline powder.

The yellow precipitate begins to snow out from solutions containing a six–eightfold excess of C_2H_5MgCl after about 10–15 min. 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°, and dried *in vacuo*, as described in the Experimental Section of this paper.

The stoichiometry of a number of reactions of the yellow solid establishes its formulation as a titanocene ethyl complex with a composition $[(C_5H_5)_2TiC_2H_5]_2\cdot 6MgCl_2\cdot 7(C_2H_5)_2O$. Upon heating to 125°, 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 TiC_2H_5 units in the complex, to yield 1 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 1.0–1.1 mmol of C_2H_6 and 0.5 mmol of H_2 per mmol of Ti. 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 recovered 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 compound contains a small admixture of C_2H_5MgCl. The determination of magnesium, chloride, and ether content of the compound is 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 $(C_5H_5)_2TiC_2H_5$ 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 $[(C_5H_5)_2TiH]_2$, 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 titanocene moiety. In principle, the yellow solid could also be formulated as $[(C_5H_5)_2TiCl]_2\cdot 2C_2H_5MgCl\cdot 4MgCl_2\cdot 7(C_2H_5)_2O$. The ease with which the ethyl groups are lost as C_2H_4 and C_2H_6 upon moderate warming is much more indicative, however, of a titanium alkyl structure than of a Grignard compound.

Upon dissolution in THF at room temperature, the yellow solid disintegrates to form a titanocene species like $[(C_5H_5)_2Ti]_2$ as an intermediate. 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 (eq 13); 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 (eq 14).[34]

$$[(C_5H_5)_2TiC_2H_5]_2 \longrightarrow (2/x)[(C_5H_5)_2TiH]_x + 2C_2H_4 \qquad (13)$$

$$[(C_5H_5)_2TiC_2H_5]_2 \longrightarrow [(C_5H_5)_2Ti]_2 + C_2H_4 + C_2H_6 \qquad (14)$$

The availability of a hydride species is evident in the following reactions of the yellow complex which are uniquely characteristic of a $(C_5H_5)_2TiH$ intermediate. The complex reacts with diborane in THF to give, in about 20% yield, the violet titanocene borohydride complex[35] (eq 15). Similarly, the complex reacts with

$$[(C_5H_5)_2TiC_2H_5]_2 + B_2H_6 \longrightarrow 2(C_5H_5)_2TiBH_4 + 2C_2H_4 \qquad (15)$$

1,3-pentadiene to form, although in low yield, the blue allyl complex[36] (eq 16). The epr spectrum of a mixture

$$[(C_5H_5)_2TiC_2H_5]_2 + 2C_5H_8 \longrightarrow 2(C_5H_5)_2Ti(\pi\text{-}C_5H_9) + 2C_2H_4 \qquad (16)$$

of the yellow ethyl compound and triphenylphosphine in 2-methyltetrahydrofuran exhibits two doublets identical with those observed for a mixture of $[(C_5H_5)_2TiH]_2$ and $P(C_6H_5)_3$, and assigned to the complex $(C_5H_5)_2Ti(H)P(C_6H_5)_3$.[21] 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.[37] When evacuated, these solutions turn intensely purple upon loss of H_2 to form $[C_{10}H_{10}TiP(C_6H_5)_3]_2$.

Decomposition to $[(C_5H_5)_2Ti]_2$ according to eq 14 appears to be the favored process in the presence of CO and N_2. When $[(C_5H_5)_2TiC_2H_5]_2\cdot 6MgCl_2\cdot 7(C_2H_5)_2O$ is suspended and stirred in ether under a pressure of 150 atm of carbon monoxide a gas mixture containing about 88% C_2H_6 and 12% C_2H_4 can be condensed at −200° from the autoclave exhaust. The evolution of C_2H_6[38] and the subsequent isolation of $(C_5H_5)_2Ti(CO)_2$

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[32] G. N. Nechiporenko, G. M. Tabrina, A. K. Shilova, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **164**, 1062 (1965).

[33] H. H. Brintzinger, *J. Amer. Chem. Soc.*, **89**, 6871 (1967).

[34] Throughout this discussion the 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.

[35] H. Nöth and R. Hartwimmer, *Chem. Ber.*, **93**, 2238 (1960).

[36] (a) H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, **6**, 293 (1966); **12**, 149 (1968); (b) H. A. Martin, Thesis, Rijksuniversiteit te Groningen, 1967.

[37] S. Wreford and H. H. Brintzinger, unpublished results.

[38] Due to the limited solubility of the ethyl complex in diethyl ether, this reaction had to be run for 24 hr at room temperature. It seems likely that some C_2H_4 might have polymerized under the conditions of this reaction, leaving a gas mixture with predominantly C_2H_6.

in about 70% yield from the reaction mixture clearly establishes the occurrence of a $(C_5H_5)_2Ti$ intermediate in this reaction.[37]

Even more interesting is the observation that $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ 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 toward molecular nitrogen results from its ability to act as a source of the reactive species $[(C_5H_5)_2Ti]_2$.[34]

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

The presence of excess ethylmagnesium chloride enhances the 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 tenfold excess raised the yield only slightly to 72.6%. Since C_2H_5MgCl is only slightly soluble in DME, a 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 of Ti) and ethylene (0.36 mmol/mmol of Ti) are liberated when the yellow complex reacts with N_2. By analogy to 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 (eq 14). Furthermore, when the yellow solid is treated with 100 atm of CO in DME under conditions identical with those used in the N_2 reduction, $(C_5H_5)_2Ti(CO)_2$ is formed, supporting again 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 $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ in an atmosphere 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 N_2 reduction (see sections 2 and 4), and eliminates the possibility that a hydride species like $[(C_5H_5)_2TiH]_x$ is responsible for the N_2 reduction, since the occurrence of such a species could only be favored by the presence of excess H_2.

From the crude product mixture of the reaction of the yellow complex with N_2 in 1,2-dimethoxyethane, a black powdery solid containing the reduced nitrogen has been isolated. 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 $2NH_3$ per 3Ti, thus establishing the stoichiometry of the product as a titanocene nitride derivative.

The black material contains, in addition, $MgCl_2$ and coordinated ethers, complicating the complete characterization of this reaction product. However, the virtually complete absence of H_2 evolution upon hydrolysis establishes a formal oxidation state of 4+ for the Ti center in the N_2 reduction product, in accord with the following formulation (eq 17). While the

$$[(C_5H_5)_2Ti^{2+}]_3[N^{3-}]_2 + 6HCl \longrightarrow 3(C_5H_5)_2TiCl_2 + 2NH_3 \quad (17)$$

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° *in vacuo*.

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 two of the three reduction equivalents required for the formation of a N^{3-} species, the formation of 0.67 NH_3 per titanium is the theoretical maximum yield, if $(C_5H_5)_2Ti(II)$ is in fact the sole reducing agent in this reaction system. Maximum yields of 60–64% NH_3 obtained in the N_2 reductions with $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ in the absence of additional reducing agents and the 3:2 stoichiometry of the titanocene nitride product therefore provide further evidence that a $(C_5H_5)_2Ti(II)$ species not only coordinates, but, in fact, also reduces the N_2 molecule in this system.

(7) Electrochemical Generation of a $(C_5H_5)_2Ti(II)$ Species. Numerous studies have been published on the electrochemical reduction of $(C_5H_5)_2Ti(IV)X_2$ derivatives.[39–47] There is essentially complete agreement that a first, one-electron reduction step at a voltage of *ca.* −1.4 V *vs.* Ag–AgClO₄ leads to a $(C_5H_5)_2Ti(III)$ derivative in solution. In addition however, several authors[44,46,47] have observed a second one-electron reduction wave occurring at voltages of about −2.7 V *vs.* $Ag\text{–}AgClO_4$ and have postulated the occurrence of $(C_5H_5)_2Ti$ as the final product of this electrochemical reduction. Dessy, *et al.*,[44] for example, have reported on the controlled-potential reduction of $(C_5H_5)_2TiCl_2$ in dimethoxyethane (DME) which yields, after uptake of 2 electrons, a deep-blue species claimed to be $(C_5H_5)_2Ti$. More recently, Doisneau and Marchon[46] reported that the blue color appears upon uptake of 2 electrons only in an atmosphere of N_2, but not under He. These observations would suggest that the blue nitrogen

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The formation of C_2H_6 in reactions of the yellow complex with aprotic reagents, however, is clearly indicative of a disproportionation like that shown in eq 14.

(39) G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, **76**, 4281 (1954).

(40) H. S. Hsiung and G. H. Brown, *J. Electrochem. Soc.*, **110**, 1085 (1963).

(41) I. A. Korshunov and N. I. Malyugina, *Zh. Obshch. Khim.*, **34**, 734 (1964).

(42) V. Gutmann and M. Michmayr, *Monatsh. Chem.*, **99**, 316 (1968), and earlier references quoted there.

(43) K. Andra, *J. Organometal. Chem.*, **11**, 567 (1968).

(44) R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, **88**, 5112 (1966).

(45) S. Valcher and M. Mastragostino, *J. Electroanal. Chem.*, **14**, 219 (1967).

(46) R. G. Doisneau and J. C. Marchon, *ibid.*, **30**, 487 (1971).

(47) S. P. Gubin and S. A. Smirnova, *J. Organometal. Chem.*, **20**, 229, 241 (1969); *Izv. Akad. Nauk SSSR*, 1890 (1969).

complex $[(C_5H_5)_2Ti]_2N_2$ might be generated in these electrolytic reductions. In order to investigate this point, we have repeated experiments of this kind. In accord with Dessy, *et al.*,[44] we find that controlled-potential reduction of $(C_5H_5)_2TiCl_2$ solutions in DME with tetrabutylammonium perchlorate as supporting electrolyte leads to uptake of exactly 2 electrons at -2.7 V *vs.* Ag–0.01 *M* $AgClO_4$. We were not able, however, to repeat the experiments described by Doisneau and Marchon[46]; under rigorously anhydrous conditions, the electrolyte used by these authors, tetrabutylammonium chloride, is not sufficiently soluble to give conducting solutions. Only after addition of small amounts of water (*ca.* 0.05 *M*) are conducting solutions obtained. Under these conditions, however, hydroxy species such as the blue complex $(C_5H_5)_2TiOH$ are to be expected.

The blue solutions obtained under the conditions described by Dessy, *et al.*,[44] invariably turned brown after about 1–2 hr at room temperature. We were not able to isolate the blue material initially formed. Several experiments indicate, however, that this blue compound is *not* the nitrogen complex $[(C_5H_5)_2Ti]_2N_2$. (1) Blue solutions are obtained under argon as well as in a nitrogen atmosphere. (2) The blue solutions do not react with CO to form the dicarbonyl complex $(C_5H_5)_2Ti(CO)_2$. (3) Treatment with HCl, while regenerating $(C_5H_5)_2TiCl_2$, does not liberate H_2. (4) In independent experiments, we find that the blue nitrogen complex is too unstable to form in DME solutions at room temperature.

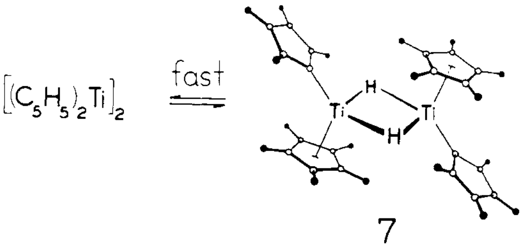
At the present time the identity of the blue species generated in these electrolytic reductions remains unclear; we favor the hypothesis that it is a secondary product formed by reaction of a primarily generated $(C_5H_5)_2Ti(II)$, either with the solvent or with the electrolyte. We have obtained evidence that this intermediate, $(C_5H_5)_2Ti(II)$, does in fact occur during these electrolytic reductions. In the presence of a CO atmosphere it is trapped and stabilized as $(C_5H_5)_2Ti(CO)_2$. This stabilization is apparent in voltammetry experiments by an enhancement of the second reduction wave. In controlled-potential reductions of $(C_5H_5)_2TiCl_2$ in DME under a CO atmosphere, the dicarbonyl complex $(C_5H_5)_2Ti(CO)_2$ is formed in high yield. In addition, electrolysis at -3.0 V in DME–sodium tetraphenylborate in an atmosphere of N_2 leads to reduction of molecular nitrogen; 0.33–0.35 mmol of NH_3/mmol of Ti are reproducibly obtained upon hydrolysis of these solutions. The blue intermediate was not observed in these reductions.

Discussion

In sections 1 and 3 of this paper, we have reported the isolation of highly reactive titanocene species, formed under mild conditions. A number of characteristic reactions of these species have been observed by which these reaction intermediates can be identified even in those reaction systems in which their actual isolation is not feasible. The formation of $(h^5\text{-}C_5H_5)_2Ti(CO)_2$ in the presence of carbon monoxide, of titanocene hydride complexes in the presence of hydrogen, of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ in the presence of triphenylphosphine, and of $(C_5H_5)_2TiN_2Ti(C_5H_5)_2$ in the presence of gaseous nitrogen may be considered as diagnostic of the intermediate existence of such a $(h^5\text{-}C_5H_5)_2Ti(II)$ species. In addition, a facile hydrogen exchange between the C_5H_5 rings and a D_2 atmosphere is also highly indicative of the occurrence of a $[(C_5H_5)_2Ti]$ intermediate. In the absence of suitable reaction partners, this titanocene intermediate deactivates *via* an α-hydrogen shift from one of the cyclopentadienyl ligands to the titanium center, forming the green $[(C_5H_5)(C_5H_4)TiH]_2$. The presence of a $(h^5\text{-}C_5H_5)_2Ti(II)$ intermediate may be suspected therefore in any reaction system from which one of these characteristic products is obtained, or in which $[(C_5H_5)(C_5H_4)TiH]_2$ is formed from a titanocene derivative with normal $(h^5\text{-}C_5H_5)$ rings.

Direct evidence for the unique reactivity of titanocene is provided by the investigation of the metastable species $[(C_5H_5)_2Ti]_2$. 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 $(C_5H_5)_2Ti$, it is indeed surprising to find that a dimeric, yet highly reactive form of this compound, $[(C_5H_5)_2Ti]_2$, is fairly stable in solution at room temperature. The normally occurring rearrangement to $[(C_5H_5)(C_5H_4)TiH]_2$ *via* a ring–titanium hydrogen shift is apparently suppressed under reaction conditions where $[(C_5H_5)_2Ti]_2$ is formed from (and presumably still in equilibrium with) titanocene–hydride complexes.

For the deuterium exchange which occurs between D_2 gas and all the hydrogen positions in the C_5H_5 rings, a *reversible* ring–titanium hydrogen shift must be invoked. The structure resulting from this reversible hydrogen shift could for instance be **7**, or the corresponding monomer.[9,48] The concentration of such a species must be rather small, however, since ir spectra of $[(C_5H_5)_2Ti]_2$ solutions do not exhibit any absorption attributable to a titanium–hydride moiety. Judging from the isotope exchange rate, the reversible conversion to a hydride structure like **7** is much faster than the final rearrangement to the green dimer, $[(C_5H_5)(C_5H_4)TiH]_2$. The higher activation energy of this latter rearrangement could be associated either with a coupling of two C_5H_4 units to a $C_{10}H_8$ ligand, or with



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(48) This exchange between D_2 and all the ring hydrogen positions has been observed before by H. A. Martin and R. O. de Jongh (*Chem. Commun.*, 1366 (1969)), when solutions of the grayish hydrogenation product of 1-methylallyltitanocene are exposed to D_2; this material is most likely identical with the gray-green $[(C_5H_5)_2TiH]_x$ described here. For the actual exchange mechanism several pathways can be envisioned; one possibility is the formation of a mixed dimer, $(C_5H_5)(C_5H_4)TiHDTi(C_5H_5)_2$, formed from the monomeric moieties of structure 7 and $[(C_5H_5)_2TiD]_2$ arising from the D_2 addition. This mixed dimer can then revert to $(C_5H_5)(C_5H_4D)Ti$, etc. In any event, however, the D_2 exchange with the ring protons requires a ring–metal hydrogen shift of the kind represented in structure 7. We find that the gas mixture obtained by exposure of D_2 to toluene solutions of $[(C_5H_5)_2Ti]_2$ contains significantly more ^1H than predicted by a random scrambling between these two reagents (see Experimental Section, B-9). While this might be due to an isotope effect, it is also quite conceivable that $[(C_5H_5)_2Ti]_2$ or one of its hydrides catalyzes an isotope exchange between D_2 and the aromatic solvent, as has been observed with tantalocene and niobocene hydrides (E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, 92, 5235 (1970); and, also, ref 27.)

the conversion to a structure containing bridging C_5H_4 ligands, similar to that recently reported for the dimer of niobocene.[27b]

While $[C_5(CH_3)_5]_2Ti$ and $[(C_5H_5)_2Ti]_2$ resemble each other in many of their reaction patterns, they do exhibit some interesting differences of behavior which are related to the steric crowding of the decamethyltitanocene sandwich. Whereas the unsubstituted titanocene is preponderantly dimeric in solution, a monomer–dimer equilibrium is observed in solutions of decamethyltitanocene. In 0.1 *M* solutions, monomeric and dimeric decamethyltitanocene are present in almost equal concentrations. Whereas a titanium–titanium bond of appreciable strength appears to exist in both $(C_5H_5)_2Ti\text{–}Ti(C_5H_5)_2$ and $[C_5(CH_3)_5]_2Ti\text{–}Ti[C_5(CH_3)_5]_2$, the steric crowding of the methylated ring ligands undoubtedly favors the mononuclear species $[C_5(CH_3)_5]_2Ti$.

Just as with $[(C_5H_5)_2Ti]_2$, a high reactivity toward H_2 is also displayed by $[C_5(CH_3)_5]_2Ti$. However, instead of a hydrogen-bridged bi- or polynuclear Ti(III) hydride complex, such as $[(C_5H_5)_2TiH]_2$ or $[(C_5H_5)_2TiH]_x$, the mononuclear titanium(IV) dihydride complex, $[C_5(CH_3)_5]_2TiH_2$, is the product of H_2 uptake by $[C_5(CH_3)_5]_2Ti$. The steric crowding and the concomitant preference for monomeric complexes thus appear to make for a rather clear-cut mechanism in this case. Obviously, the d^2 species $[C_5(CH_3)_5]_2Ti$ just inserts into, or oxidatively adds an H_2 molecule.

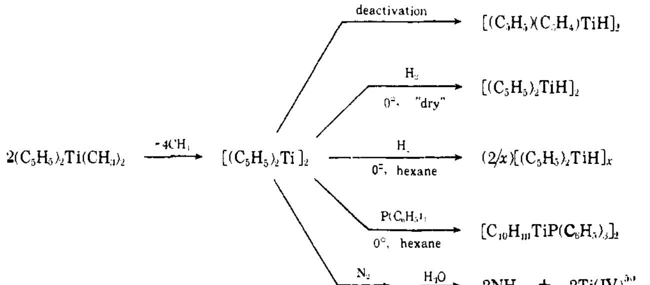
Although no detailed equilibrium studies of the reaction were undertaken, an estimate of the enthalpy of this reaction can be made from our data; the equilibrium constant, K_{eq}, for reaction 18 is *ca.* 10^2 atm^{-1} at

$$[C_5(CH_3)_5]_2Ti + H_2 \rightleftharpoons [C_5(CH_3)_5]_2TiH_2 \qquad (18)$$

300°K; the entropy change, $\Delta S°$, is essentially equal to $-S°(H_2)$. Therefore, we can estimate a value of $\Delta H° = -12 \pm 2$ kcal mol^{-1} for reaction 18. Using this value, a Ti–H bond energy of *ca.* 58 kcal is calculated for $[C_5(CH_3)_5]_2TiH_2$. As one would expect, the Ti–H bond energy is much less than that of a C–H bond (*ca.* 100 kcal) but rather close to the average Si–H bond energy in SiH_4 (76 kcal).[49] Both the mobility and the moderate enthalpy of the equilibrium reaction **18** are important factors for the participation of titanocene in catalytic reactions involving molecular hydrogen (see below).

Based on the diagnostic criteria discussed above, the occurrence of titanocene as an intermediate can be established for a number of reaction systems. Many reactions with dimethyltitanocene, $(C_5H_5)_2Ti(CH_3)_2$, for instance, exhibit virtually all the characteristic features mentioned above. The reactions of $(C_5H_5)_2Ti(CH_3)_2$, in which titanocene appears to occur as an intermediate, are summarized in Scheme I. The dimethyl derivative is relatively unstable at room temperature, decomposing in the course of 1 or 2 hr. This decomposition most likely involves the loss of two methyl radicals[51] as a primary reaction step, thus generating a titanocene intermediate. The mass spectrum of $(C_5H_5)_2Ti(CH_3)_2$[9] demonstrates the lability of the Ti–CH_3 bonds; the parent ion is completely absent and the ion $C_{10}H_{10}Ti^+$ is in fact a major species present.

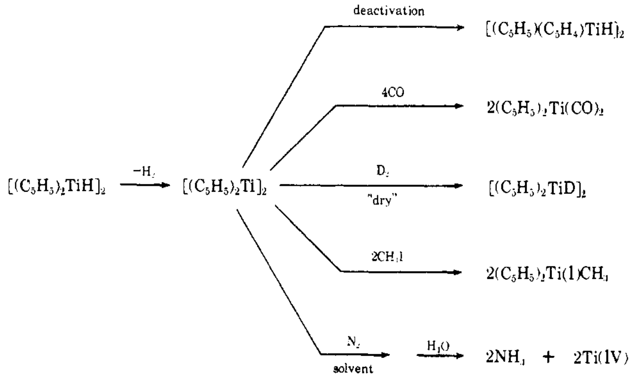
Scheme I. Reactions of $(C_5H_5)_2Ti(CH_3)_2$ in Which Titanocene Occurs as an Intermediate



In the presence of gaseous hydrogen, $(C_5H_5)_2Ti(CH_3)_2$ yields a variety of products, depending upon the reaction conditions. If the rather exothermic reaction is allowed to proceed at room temperature in hydrocarbon solvents, $[(C_5H_5)(C_5H_4)TiH]_2$ is the exclusive product.[14] If solid crystalline $(C_5H_5)_2Ti(CH_3)_2$ is exposed to *ca.* 0.5 atm of H_2 at 0°, the violet hydride, $[(C_5H_5)_2TiH]_2$, is formed in high yield. When the reaction is allowed to proceed at 0° in hexane, the grayish polymeric hydride, $[(C_5H_5)_2TiH]_x$, is precipitated from solution. Presumably, $(h^5\text{-}C_5H_5)_2Ti(II)$ is an intermediate in these reactions of $(h^5\text{-}C_5H_5)_2Ti(CH_3)_2$ with hydrogen. This initially formed, highly reactive titanocene species may then either undergo a deactivation to $[(C_5H_5)(C_5H_4)TiH]_2$ or, under more carefully controlled conditions, be induced to react with excess H_2 in the system, yielding one of the hydride derivatives.

Like $(C_5H_5)_2Ti(CH_3)_2$, $[(C_5H_5)_2TiH]_2$ undergoes a series of reactions in which titanocene appears to occur as an intermediate, which are summarized in Scheme II. This hydride is again somewhat unstable; it loses hydrogen rather easily on mild heating.

Scheme II. Reactions of $[(C_5H_5)_2TiH]_2$ in Which Titanocene Occurs as an Intermediate



Deuterium studies indicate the existence of the following equilibrium for solid $[(C_5H_5)_2TiH]_x$, solid $(C_5H_5)_2Ti$, and gaseous H_2 at 100° (eq 19). Solid samples of

$$2[(C_5H_5)_2TiH]_x \rightleftharpoons 2(C_5H_5)_2Ti + H_2 \qquad (19)$$

$[(C_5H_5)_2TiD]_2$, prepared from $(C_5H_5)_2Ti(CH_3)_2$ and D_2, were treated with 1700 psi of H_2 at 100°. Essentially pure $[(C_5H_5)_2TiH]_x$ was recovered, in agreement with equilibrium 19.

Solid $[(C_5H_5)_2TiH]_2$ reacts with 1 atm of carbon monoxide at room temperature to yield $(C_5H_5)_2Ti(CO)_2$, concurrent with the evolution of the stoichiometric amount of H_2. Since $[(C_5H_5)(C_5H_4)TiH]_2$ shows little

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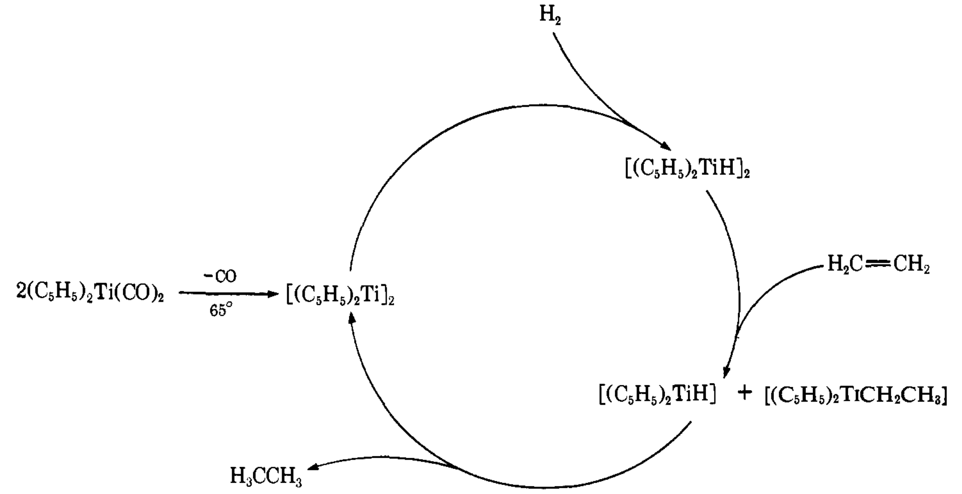
(49) S. R. Gunn, *J. Phys. Chem.*, **68**, 949 (1964).

(50) M. E. Vol'pin, V. B. Shur, V. N. Latyaeva, L. I. Vyshinskaya, and L. A. Shul'gaitser, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2, 385 (1966).

(51) G. A. Razuvaev, V. N. Latyaeva, and L. I. Vyshinskaya, *Dokl. Akad. Nauk SSSR*, **159**, 382 (1964).

Scheme III



or no reactivity toward CO,[20] (h^5-C_5H_5)$_2$Ti(II) must be assumed to be the species responsible for the coordination of the two carbon monoxide molecules.

[(C$_5$H$_5$)$_2$TiH]$_2$ readily reacts with methyl iodide under evolution of both H_2 and CH_4. The evolution of hydrogen at first appears to be surprising, since hydrides generally react with CH_3I to yield only CH_4. This result is understandable in view of the ease with which [(C$_5$H$_5$)$_2$TiH]$_2$ loses its coordinated H_2. The relative amounts of H_2 and CH_4 formed in this reaction indicate that loss of H_2 and subsequent oxidative addition of CH_3I to (h^5-C_5H_5)$_2$Ti is in fact the preferred reaction (eq 20 and 21).

$$[(C_5H_5)_2TiH]_2 + 2CH_3I \xrightarrow{66\%} 2(C_5H_5)_2Ti(I)CH_3 + H_2 \quad (20)$$

$$[(C_5H_5)_2TiH]_2 + 2CH_3I \xrightarrow{34\%} 2(C_5H_5)_2TiI + 2CH_4 \quad (21)$$

Reactions of [(C$_5$H$_5$)$_2$TiH]$_2$ with N_2, and the intermediacy of [(C$_5$H$_5$)$_2$Ti]$_2$ in this reaction, will be discussed later.

In addition to the reaction systems encountered during the course of this research, (h^5-C_5H_5)$_2$Ti(II) may be postulated as an intermediate in other reaction systems. Titanocene dicarbonyl, (h^5-C_5H_5)$_2$Ti(CO)$_2$, was found to generate a catalyst for the homogeneous hydrogenation of alkenes and alkynes.[2] At the temperatures used in the hydrogenations, *viz.*, 50–65°, the formation of (h^5-C_5H_5)$_2$Ti(II) as an intermediate is quite likely; (C$_5$H$_5$)$_2$Ti(CO)$_2$ is known to decompose *via* loss of carbon monoxide at a temperature of 90°.[52] The (h^5-C_5H_5)$_2$Ti(II) intermediate, generated by such a loss of 2CO, will react with H_2 in the system to yield a titanocene hydride complex as discussed above. The reaction of [(C$_5$H$_5$)$_2$TiH]$_2$ with 1,3-pentadiene has been shown to yield 1,3-dimethylallyltitanocene,[21] (h^5-C_5H_5)$_2$-Ti(h^3-C_5H_9), which in turn may be hydrogenated to *n*-pentane upon subsequent treatment with 1 atm of H_2.[36] With the assumption that alkenes and alkynes react with a titanocene hydride in essentially the same way as a diolefin, almost every reaction step of the following scheme is therefore independently established (Scheme III). The liberation of C_2H_6 from a titanocene ethyl complex by treatment with H_2 is in fact observed with the yellow compound [(C$_5$H$_5$)$_2$Ti-C$_2$H$_5$]$_2$·6MgCl$_2$·7(C$_2$H$_5$)$_2$O.[37]

It is interesting to note that if 1-pentyne or 1-hexyne are substrates in catalytic hydrogenation according to Scheme III, the corresponding alkenes are formed almost exclusively.[2] 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,[53,54] and even considered by some[55] as a necessary criterion for an acceptable nitrogenase model system.

It has been known for some time that reaction systems obtained from various titanocene derivatives do in fact promote reduction of molecular nitrogen.[4–8] The results presented here, particularly those in section 6, rule out earlier postulates that a titanocene hydride species is responsible for the N_2 reduction.[4,5,56] The violet hydride, [(C$_5$H$_5$)$_2$TiH]$_2$, will reduce gaseous nitrogen when solvents are added to the solid material under N_2 pressures of *ca.* 150 atm. However, under these conditions the hydride was found to eliminate H_2. No reduction was observed when a gas mixture of *ca.* 20% H_2 and 80% N_2 (at 150 atm) was substituted for pure nitrogen. The presence of excess hydrogen in this reaction system, just as in the [(C$_5$H$_5$)$_2$TiC$_2$H$_5$]$_2$·6MgCl$_2$·7(C$_2$H$_5$)$_2$O system, can only favor a hydride species. The deleterious effect of hydrogen on the N_2 reduction must therefore mean that, rather than a titanocene–hydride, an H_2 elimination product, presumably [(C$_5$H$_5$)$_2$Ti]$_2$, is the reactive species. The involvement of titanocene in N_2-reducing systems has been postulated before.[57 58]

We can now offer direct evidence concerning the mode of interaction between titanocene and molecular nitrogen. Both [(C$_5$H$_5$)$_2$Ti]$_2$ and [C$_5$(CH$_3$)$_5$]$_2$Ti are found to coordinate N_2, in a rapid and reversible reaction. In both cases binuclear complexes, (C$_5$H$_5$)$_2$-TiN$_2$Ti(C$_5$H$_5$)$_2$ and [C$_5$(CH$_3$)$_5$]$_2$TiN$_2$Ti[C$_5$(CH$_3$)$_5$]$_2$, respectively, are formed. Although the complete structural assignment of these complexes will have to await

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(52) J. G. Murray, *J. Amer. Chem. Soc.*, **83**, 1287 (1961).

(53) R. W. F. Hardy and R. C. Burns, *Annu. Rev. Biochem.*, 37, 331 (1968).

(54) K. Kuchynka, *Catal. Rev.*, 3, 111 (1969).

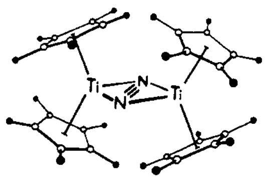
(55) G. N. Schrauzer and G. Schlesinger, *J. Amer. Chem. Soc.*, **92**, 1808 (1970).

(56) H. H. Brintzinger, *ibid.*, **88**, 4305 (1966).

(57) E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *ibid.*, **92**, 5251 (1970).

(58) V. Schurig (Thesis, University of Tübingen, 1968) discusses the possible intermediacy of titanocene in reactions with H_2 and in the reduction of molecular nitrogen.

an X-ray diffraction study, some inferences concerning their structures can be made. The absence of any observable infrared absorption attributable to a N_2-stretching mode indicates a centrosymmetric TiN_2Ti 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 fashion, $TiN{\equiv}NTi$, as in $(NH_3)_5RuN{\equiv}NRu(NH_3)_5$,[59] or else be coordinated edge-on between the two titanium centers (structure **8**).



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Of these two possibilities we favor the latter (structure **8**) 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 pseudotetrahedral 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 **8** is in accord with this requirement for a pseudotetrahedral coordination. In all of the previously described mononuclear and binuclear transition metal–N_2 complexes, an end-on coordination has either been established[59–62] or inferred from infrared data.[63,64] However, in most 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 system and would, therefore, require *two* electron pairs to complete its valence shell. An edge-on coordination of the N_2 molecule does allow such a four-electron donation.[65]

It remains to be clarified in which way this N_2 complex enters into reduction reactions; that is, which intermediates and reaction products are obtained in these reductions and why, in some of the systems studied, *viz.* $[(C_5H_5)_2TiH]_2$, $[C_{10}H_{10}TiP(C_6H_5)_3]_2$, and $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$, reduction to a nitride occurs without further reducing agents, whereas, in other cases, the reduction is incomplete and either hydrazine is recovered,[7] or N_2 remains unreduced.

Experimental Section

Procedures for the handling of the gases and air-sensitive materials used were as outlined in earlier publications.[9,21] An improved glovebox, which can be evacuated to 5×10^{-2} Torr and filled just prior to use with either prepurified nitrogen or argon, was used for the majority of this work.

Magnetic susceptibilities were measured either on a modified Curie-Cheneveau magnetic balance or by the nmr method described by Evans.[16] Uv-visible spectra were run on a Cary 14 spectrophotometer. Nmr spectra were obtained on a Varian T-60 and a modified Varian HR-100 spectrometer, using tetramethylsilane (TMS) as reference at 0 ppm. Elemental analyses were determined by Spang Microanalytical Laboratories, Inc., Ann Arbor, Mich., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Titanocene dichloride and methyllithium were obtained from Alfa Inorganics, Beverly, Mass. Titanocene dichloride was further purified by recrystallization from dry chloroform. Tiglaldehyde was Eastman practical grade. 2-Bromo-2-butene was obtained from J. T. Baker Chemical Co., Phillipsburg, N. J., or by treatment of 2,3-dibromobutane (Eastman practical grade) with KOH in ethylene glycol by the method described by Dreiding and Pratt.[66]

A. **Bis(pentamethylcyclopentadienyl)titanium(II), $[C_5(CH_3)_5]_2Ti$. (1) Preparation of 1,2,3,4,5-Pentamethylcyclopentadiene, $C_5(CH_3)_5H$.** 1,2,3,4,5-Pentamethylcyclopentadiene was prepared by the method described by deVries[67] with some modifications suggested by Dr. A. J. Ashe III.[68] In particular, oxidation of di-*sec*-2-butenylcarbinol to di-*sec*-2-butenyl ketone was carried out with CrO_3 in pyridine.

(2) Preparation of Bis(pentamethylcyclopentadienyl)dichlorotitanium(IV), $[C_5(CH_3)_5]_2TiCl_2$. Cut-up sodium (2.3 g; 100 mmol) and a small crystal of $Fe(NO_3)_3 \cdot 9H_2O$ were placed in a 1000-ml flask under argon. Liquid ammonia (500 ml) was condensed into the flask at −78°. The solution was warmed slowly to −33° and stirred until the initial blue color changed to light gray. 1,2,3,4,5-Pentamethylcyclopentadiene (11.5 g; 85 mmol) was syringed into the sodium amide–liquid ammonia suspension, and the mixture was stirred at −33° for 2 hr. The ammonia was then removed *in vacuo* and pale yellow crystals of $NaC_5(CH_3)_5$ precipitated. The crystals were freed of ammonia by evacuation to 10^{-3} Torr at room temperature. THF (200 ml) was distilled onto the crystals; the sodium pentamethylcyclopentadienide was dissolved. The solution was filtered under argon and syringed onto 4.38 g (28.4 mmol) of anhydrous $TiCl_3$ at *ca.* −30°. The mixture was allowed to warm slowly and stirred for 24 hr at room temperature. Concentrated aqueous hydrochloric acid (50 ml) was added to the green-brown suspension at −20° whereupon red-brown crystals precipitated from the mixture. Chloroform (250 ml) was added and the dark red-brown chloroform–THF layer was separated and dried over anhydrous sodium sulfate. The chloroform and THF were removed under reduced pressure and the residue was transferred to the extraction thimble of a Soxhlet extractor. The $[C_5(CH_3)_5]TiCl_3$ contaminant was removed by extracting the red-orange compound from the residue with petroleum ether (30–60°) saturated with HCl; the product, $[C_5(CH_3)_5]_2TiCl_2$, is only slightly soluble in petroleum ether. The collection flask was then replaced, and the residue was extracted with CCl_4 saturated with HCl. The purple-brown $[C_5(CH_3)_5]_2TiCl_2$ crystallized as long needles from the cooled CCl_4 solution. Large, well-formed dark purple crystals were obtained by recrystallization from a small amount of chloroform saturated with HCl: mp 273° dec; yields, 3.4 g (31%) for $[C_5(CH_3)_5]_2TiCl_2$; 1.7 g (21%) for $[C_5(CH_3)_5]TiCl_3$.

Anal. Calcd for $[C_5(CH_3)_5]_2TiCl_2$: C, 61.71; H, 7.77; Ti, 12.31; Cl, 18.22. Found: C, 61.81; H, 7.92; Ti, 12.16; Cl, 18.09. Calcd for $[C_5(CH_3)_5]TiCl_3$: C, 41.6; H, 5.19; Ti, 16.7; Cl, 36.7. Found: C, 41.8; H, 5.16; Ti, 14.7; Cl, 35.0.

(3) Preparation of Bis(pentamethylcyclopentadienyl)dimethyltitanium(IV), $[C_5(CH_3)_5]_2Ti(CH_3)_2$. Freshly powdered bis(pentamethylcyclopentadienyl)dichlorotitanium(IV) (3.1 g; 8.0 mmol) was slurried in 75 ml of diethyl ether at −78°. 2 *M* methyllithium (9 ml; 18 mmol) in ether was syringed into the mixture. The mixture was allowed to warm slowly to room temperature and stirred for 3 hr; its color changed from purple-brown to yellow. The mixture was then cooled to −30° and 1 ml of CH_3OH was added to destroy any excess methyllithium. The ether and CH_3OH

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(59) I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 6512 (1969).

(60) B. R. Davis, N. C. Payne, and J. A. Ibers, *ibid.*, **91**, 1240 (1969).

(61) B. R. Davis and J. A. Ibers, *Inorg. Chem.*, **9**, 2768 (1970); **10**, 578 (1971).

(62) F. Bottomley and S. C. Nyburg, *Acta. Crystallogr., Sect. B*, **24**, 1298 (1968).

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

(64) For a recent review see A. D. Allen, *Advan. Chem. Ser.*, No. **100**, 79 (1971).

(65) The resulting bonding situation is then comparable to that 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 red-shift of the C≡C stretching vibration is several times larger than in those alkyne complexes where the acetylene is coordinated to a species with 16 valence electrons (E. O. Graves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968)).

(66) A. S. Dreiding and R. F. Pratt, *J. Amer. Chem. Soc.*, **76**, 1902 (1954).

(67) L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

(68) A. J. Ashe III, personal communication.

were removed *in vacuo*, and the yellow $[C_5(CH_3)_5]_2Ti(CH_3)_2$ was dissolved from the residue with *ca.* 140 ml of petroleum ether and filtered. The filtrate was cooled to −100°, and the yellow needles filtered off, dried *in vacuo*, and stored at −60° (yield *ca.* 80%).

Analysis. The yellow crystals (215 mg; 0.612 mmol) were treated with *ca.* 40 mmol of HCl in toluene. The evolved noncondensable gas consisted of 1.218 mmol of CH_4 (1.224 mmol calculated for 215 mg of $[C_5(CH_3)_5]_2Ti(CH_3)_2$). The residue consisted of $[C_5(CH_3)_5]_2TiCl_2$.

(4) Preparation of the Turquoise Intermediate, $C_{10}(CH_3)_{10}CH_2Ti$. *Ca.* 0.05 *M* $[C_5(CH_3)_5]_2Ti(CH_3)_2$ (60 ml) in petroleum ether (30–60°) was syringed under argon into a reaction vessel equipped with a sublimation probe. The petroleum ether was removed *in vacuo*, and toluene (*ca.* 25 ml) was distilled onto the yellow crystals. The toluene solution was heated under argon for 4 hr at 110°, whereupon the color gradually changed from yellow to turquoise. The solution was then cooled and the toluene was removed *in vacuo*. The residue was heated to 75° at 10^{-3} Torr to sublime the product as small turquoise needles. The evacuated apparatus was then transferred to a nitrogen-filled glovebox and the crystals were scraped from the probe into a storage ampoule (yield 450 mg, *ca.* 50%).

In one experiment the reaction was carried out under isobutane instead of argon, so that any evolved gas could be fractionated from the inert atmosphere. $[C_5(CH_3)_5]_2Ti(CH_3)_2$ (566 mg; 1.63 mmol) yielded 1.01 mmol of noncondensable gas, identified as methane by its ir spectrum. $C_{10}(CH_3)_{10}CH_2Ti$ (330 mg; 1.0 mmol) was sublimed from the residue so that 1.0 mmol of CH_4 was evolved per mmol of $C_{10}(CH_3)_{10}CH_2Ti$ formed.

(5) Preparation of Bis(pentamethylcyclopentadienyl)dihydridotitanium(IV), $[C_5(CH_3)_5]_2TiH_2$. $C_{10}(CH_3)_{10}CH_2Ti$ (900 mg; 2.7 mmol) was transferred to a swivel filtration–reaction vessel complete with a fritted disc in a nitrogen-filled glovebox. The apparatus was connected to the vacuum line, and approximately 10 ml of pentane was distilled onto the turquoise crystals at −50°. Hydrogen (1 atm) was introduced, and the slurry was allowed to warm slowly to 5°. The mixture was stirred at 5° for 2 hr, fresh hydrogen being occasionally introduced. The resulting bright orange solution was then cooled slowly to −90° under hydrogen, and orange crystalline $[C_5(CH_3)_5]_2TiH_2$ was precipitated. The apparatus was then quickly inverted, and the receiving flask was evacuated to collect the filtrate. The filtrate and crystals were dried *in vacuo*, the evacuated apparatus was transferred to an argon-filled glovebox, and the crystalline $[C_5(CH_3)_5]_2TiH_2$ was placed in a storage ampoule (yield *ca.* 50%).

(6) Preparation of Bis(pentamethylcyclopentadienyl)titanium(II), $[C_5(CH_3)_5]_2Ti$. A pentane solution of $[C_5(CH_3)_5]_2TiH_2$ was prepared as described above, but then stirred at room temperature *in vacuo* for 3 hr whereupon the orange solution gradually darkened, concurrent with the evolution of hydrogen. The solution was then cooled slowly to −90° under argon, and the red-brown crystalline $[C_5(CH_3)_5]_2Ti$ was precipitated. The crystalline slurry was then filtered and dried (yield *ca.* 50%).

(7) Reaction of $C_{10}(CH_3)_{10}CH_2Ti$ with Hydrogen. $C_{10}(CH_3)_{10}CH_2Ti$ (68.0 mg; 0.204 mmol) was dissolved in 3.0 ml of toluene at −80°. H_2 (1.140 mmol) (determined with a blank solution) was introduced, and the solution was allowed to warm slowly to room temperature. After 1.5 hr the gas mixture above the bright orange solution was passed through a series of liquid-nitrogen-cooled traps and collected *via* a Toepler pump. The hydrogen–methane mixture amounted to 1.137 mmol. The gas mixture was then cycled over CuO at 300° to convert the H_2 to H_2O, which was removed in a liquid-nitrogen-cooled trap. CH_4 (0.181 mmol; 0.89 mmol/mmol of Ti) remained. Net hydrogen consumed in the reaction was therefore 0.184 mmol (0.90 mmol/mmol of Ti), consistent with the overall reaction of eq 22–24. The stoichiometry of

$$C_{10}(CH_3)_{10}CH_2Ti + 2H_2 \longrightarrow [C_5(CH_3)_5]_2TiH_2 + CH_4 \qquad (22)$$

$$\underline{[C_5(CH_3)_5]_2TiH_2 \longrightarrow [C_5(CH_3)_5]_2Ti + H_2} \qquad (23)$$

$$C_{10}(CH_3)_{10}CH_2Ti + H_2 \longrightarrow [C_5(CH_3)_5]_2Ti + CH_4 \qquad (24)$$

reaction 22 was confirmed as follows: 86 mg (0.259 mmol) of $C_{10}(CH_3)_{10}CH_2Ti$ was stirred in pentane with 3.210 mmol of H_2 at 0° for 1 hr. The solution was then cooled to −80° (at this temperature the orange hydride, $[C_5(CH_3)_5]_2TiH_2$, is stable to H_2 loss, even *in vacuo*) and the hydrogen–methane mixture was collected and analyzed as before. The evolved methane amounted to 0.224 mmol (0.865 mmol/mmol of Ti) and the hydrogen consumed in the production of $[C_5(CH_3)_5]_2TiH_2$ was 0.495 mmol (1.91 mmol/mmol of Ti).

In one case the reaction of $C_{10}(CH_3)_{10}CH_2Ti$ was carried out with D_2 instead of H_2 following the procedure described above. $C_{10}(CH_3)_{10}CH_2Ti$ (47 mg; 0.14 mmol) yielded 0.13 mmol of essentially pure CH_3D, identified by its mass spectrum.

(8) Nitrogen Complexation Reactions of $[C_5(CH_3)_5]_2Ti$. $[C_5(CH_3)_5]_2Ti$ (115 mg; 0.362 mmol) was dissolved in 10 ml of pentane at −100°. An atmosphere of nitrogen was introduced, and the red-orange solution immediately changed color to dark green-gray. The solution was allowed to warm slowly to room temperature whereupon the color changed from green-gray to purple-blue at −80°, and finally returned to red-orange on stirring at room temperature for several minutes.

The solution was then cooled to −80° and 1 atm of nitrogen was introduced. The resulting purple-blue solution was stirred for 15 min, then the excess nitrogen was removed *in vacuo*. The solution became intensely purple-blue when the excess nitrogen was removed at −80°. Fresh nitrogen was introduced and the solution was again stirred for 15 min. This cycle was repeated an additional three times at −80°. Finally the excess nitrogen was removed *in vacuo*, and the flask was closed off. The resulting intensely purple-blue solution was allowed to warm slowly to room temperature, concurrent with a color change to red-orange. The evolved nitrogen (0.176 mmol, 0.487 mmol/mmol of Ti) was passed through a series of liquid-nitrogen-cooled traps and collected *via* a Toepler pump.

In a separate experiment *ca.* 0.10 mmol of $[C_5(CH_3)_5]_2Ti$ was prepared by treating $C_{10}(CH_3)_{10}CH_2Ti$ with hydrogen in toluene and then stirring for 2 hr *in vacuo*. In order to determine the stoichiometry of the green-gray nitrogen complex, 1 atm of nitrogen was added, and the solution was cooled slowly to −196°. The excess nitrogen was removed from the resulting gray glassy solid, the flask was closed off, and the system warmed slowly to room temperature. The nitrogen evolved upon warming amounted to 0.158 mmol (1.58 mmol/mmol of Ti). The nitrogen retained at −196° in an equal volume of pure toluene was found to be negligible. The solution was finally treated with CO as described below. The CO consumed in the formation of $[C_5(CH_3)_5]_2Ti(CO)_2$ amounted to 0.20 mmol (2.0 mmol/mmol of Ti). These results indicate that the green-gray complex may be formulated as $[C_5(CH_3)_5]_2Ti(N_2)_2$.

(9) Reaction of $[C_5(CH_3)_5]_2Ti$ with Carbon Monoxide. $[C_5(CH_3)_5]_2Ti$ (70 mg; 0.220 mmol) was dissolved in 5 ml of pentane at −80°. CO (1.080 mmol) was introduced and the reaction mixture was allowed to warm slowly to room temperature. After stirring for 1 hr at room temperature, the residual CO (0.783 mmol) was passed through a series of liquid nitrogen cold traps and collected *via* a Toepler pump. The CO consumed amounted to 0.297 mmol (1.35 mmol/mmol of Ti). The pentane was removed *in vacuo* from the yellow brown solution and $[C_5(CH_3)_5]_2Ti(CO)_2$ was sublimed from the residue at 80–85°, 10^{-3} Torr.

B. Metastable Form of Titanocene, $[(C_5H_5)_2Ti]_2$. (1) Preparation of $[(C_5H_5)_2TiH]_x$. *Ca.* 0.14 *M* $(C_5H_5)_2Ti(CH_3)_2$ (50 ml) 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°. After several minutes of incubation, the reaction proceeded smoothly, beginning with the film of crystalline $(C_5H_5)_2Ti(CH_3)_2$ on the sides of the flask and spreading rapidly throughout 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 ensure removal of the 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 min. The mixture was filtered and the solid was 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 25-ml flask in a glovebox under prepurified Ar. The flask was attached to the vacuum line and the green-gray solid heated with an oil bath. The evolution of noncondensable gas began at about 60° and was essentially complete after heating for 2 hr at 100°. The green-gray solid slowly turned dark green as the reaction proceeded. The noncondensable gas (0.26 mmol, 0.55 mmol/mmol of Ti) was identified as pure H_2 by its quantitative conversion to H_2O upon passage over CuO at 320°. The dark green product was identified as $[(C_5H_5)(C_5H_4)TiH]_2$ by comparison of its ir spectrum to that of an authentic sample, prepared by the method of Salzmann and Mosimann.[69]

(3) Reaction of $[(C_5H_5)_2TiH]_x$ with Deuterium Chloride. All exposed glass surfaces in the vacuum line were wetted with several portions of 38% DCl in D_2O, and then with two 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° 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 −50°. Noncondensable gas (1.07 mmol; 1.19 mmol/mmol of Ti) 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 eq 10. A similar and undoubtedly related observation was made previously in the reaction of violet $[(C_5H_5)_2TiH]_2$ with DCl.[21]

(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° and 1 atm of CO was introduced at this temperature. Upon slowly warming to room temperature, the mixture changed in color from greenish 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° (10^{-2} Torr) for 3 hr and an additional hour at 90°. Bright red crystals of $(C_5H_5)_2Ti(CO)_2$ (133 mg, 0.64 mmol), identified by its ir spectrum, 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 *ca.* 10 ml of toluene at room temperature for about 2 hr. The solid hydride slowly dissolved yielding a dark, slightly greenish solution. Hydrogen (0.64 mmol, 0.47 mmol/mmol of Ti) was evolved during the reaction and identified by its quantitative conversion to H_2O upon reaction with CuO at 320°. 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 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°. The toluene solution was refluxed for about 2 hr. 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.[69]

(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 2 hr at room temperature until all the hydride had dissolved. The hydrogen evolved (0.32 mmol) was removed, and the toluene solution cooled to −80°. Excess HCl gas 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 ensure complete reaction and the evolved H_2 (0.55 mmol) was collected and identified as described 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 by 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 *ca.* 10 ml of diethyl ether at room temperature for 2 hr to form $[(C_2H_5)_2Ti]_2$. The evolved H_2 (0.44 mmol, 0.52 mmol/mmol of Ti) was collected and analyzed as described above. The $[(C_5H_5)_2Ti]_2$ solution was cooled to −80° and CO (1 atm) was 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 was distilled in at −80°. Noncondensable gas (2.53 mmol), a mixture of CO and H_2, was evolved upon warming the mixture to room temperature. The gas mixture was recycled over CuO at 320° for 2 hr to form CO_2 and H_2O, which were then quantitatively separated by passage through a −80° trap. The composition of the gas mixture determined by this procedure was 1.65 mmol of CO (1.94 mmol/mmol of Ti) and 0.87 mmol of H_2 (1.04 mmol/mmol of Ti).

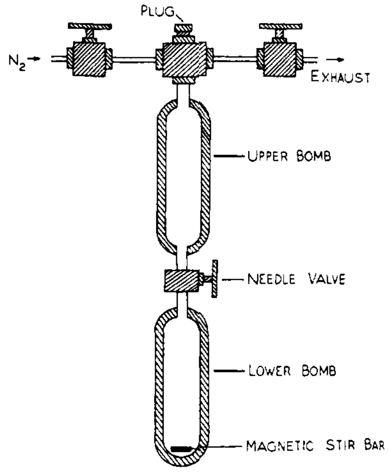

Figure 5. Double bomb apparatus used in high-pressure reactions.

(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 noncondensable gas was collected *via* a Toepler pump and its composition determined by mass spectroscopy: found, 89.0% H_2, 10.5% HD, and 0.5% D_2; expected for 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 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° and N_2 (1 atm) was introduced at this temperature. The solution immediately turned intensely blue. After stirring for about 20 min at −80°, the excess N_2 was removed and the blue solution allowed to warm slowly. At *ca.* −20° 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 temperature and all the N_2 was removed *via* a Toepler pump. The N_2 collected (0.43 mmol, 0.47 mmol/mmol of Ti) was identified by its mass spectrum. Upon readmission of N_2 to the solution, and cooling to −80°, 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 hr at room temperature until a homogeneous solution of $[(C_5H_5)_2Ti]_2$ was obtained. The solution was cooled to −80° and N_2 (1 atm) was introduced. After stirring for about 10 min at −80°, a small amount of blue solid was observed. Approximately 10 ml of hexane was distilled in at −80° and the mixture became quite thick with the formation of a dark blue precipitate. The mixture was filtered cold and the dark blue complex was washed with an additional 10 ml of hexane at −80°. The blue material was slurried with 10 ml of fresh hexane at −80° under 1 atm of N_2. The slurry was filtered and the solid was washed with about 5 ml of isobutane at −80°, and dried *in vacuo* while cold. The blue solid (*ca.* 200 mg) was transferred to a storage ampoule in a glovebox 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 *ca.* 10 ml of toluene at −80° and allowed to warm slowly. The initially bright blue solution bubbled vigorously upon warming to *ca.* −20°, changing color to a dark, slightly greenish hue characteristic of $[(C_5H_5)_2Ti]_2$ solutions. Passage of the evolved gas through several liquid nitrogen traps, and collection *via* a Toepler pump, yielded 0.20 mmol (0.47 mmol/mmol of Ti) of N_2.

(12) Reduction of $[(C_5H_5)_2Ti]_2N_2$. $[(C_5H_5)_2TiH]_x$ (362 mg, 2.02 mequiv based on Ti) was stirred with 15 ml of diethyl ether for about 2 hr at room temperature until all the gray-green hydride dissolved.

The resulting $[(C_5H_5)_2Ti]_2$ solution was syringed under N_2 into the lower cylinder of the double bomb apparatus (Figure 5) containing a magnetic stir bar, then pressurized to 2500 psi with pre-

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[69] J. J. Salzmann and P. Mosimann, *Helv. Chim. Acta*, **50**, 1831 (1967).

purified N_2, and cooled to −80° to ensure complete formation of $[(C_5H_5)_2Ti]_2N_2$. The pressure in the top cylinder released and 12 ml of a 0.194 *M* solution of lithium naphthalide (LiNp) in THF (2.33 mmol, 1.15 mmol/mmol of Ti) was syringed into the top cylinder. After pressurizing to 3000 psi with N_2, the LiNp was added to the $[(C_5H_5)_2Ti]_2N_2$ solution at −80°. The mixture was stirred at −80° for 1 hr, warmed slowly to room temperature over a 2-hr period, and then hydrolyzed with 10 ml of 2.5 *M* H_2SO_4. The NH_3 formed (1.92 mmol, 95% based on Ti) was determined by the Kjeldahl method. Occasionally, lower yields of only *ca.* 0.5 mmol of NH_3/mmol of Ti were obtained. A negative spot test with *p*-dimethylaminobenzaldehyde indicated that no N_2H_4 was formed in the reduction.

C. Titanocene Triphenylphosphine Complex, $[C_{10}H_{10}TiP(C_6H_5)_3]_2$. (1) Preparation of $[(C_{10}H_{10}TiP(C_6H_5)_3]_2$. (a) From Di-μ-hydridobis(dicyclopentadienyltitanium(III)), $[(C_5H_5)_2TiH]_2$. Toluene (25 ml) was distilled onto 125 mg (0.350 mmol) of $[(C_5H_5)_2TiH]_2$ and 185 mg (0.707 mmol) of $P(C_6H_5)_3$ at −78°. The slurry was allowed to warm slowly. At *ca.* 5° the mixture turned brown with no evolution of gas. At *ca.* 25° the solution turned purple, concurrent with the evolution of hydrogen. The hydrogen (0.40 mmol, 0.57 mmol/mmol of Ti) was passed through a liquid nitrogen cold trap and collected *via* a Toepler pump. The gas was identified as hydrogen by its quantitative conversion to H_2O on passage through CuO at 300°.

(b) From Dicyclopentadienyldimethyltitanium(IV), $(C_5H_5)_2Ti(CH_3)_2$. Triphenylphosphine (5.2 g; 20 mmol) and 80 ml (*ca.* 10 mmol) of $(C_5H_5)_2Ti(CH_3)_2$ in hexane were placed in a flask equipped with a swivel filtration apparatus and cooling cup. Hexane (30 ml) was removed under vacuum and a hydrogen atmosphere was introduced. The reaction was initiated by local warming with a hot-air gun, and immediately after the reaction started, the solution was cooled to 0° with an ice bath. The mixture was stirred for 3 hr at 0°, fresh hydrogen being introduced occasionally. The hydrogen and methane were then removed and the mixture was stirred at room temperature under vacuum for 1 hr to convert any $(C_5H_5)_2Ti(H)P(C_6H_5)_3$ to $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ and H_2. The mixture was then filtered and the precipitate washed at −70° with *ca.* 40 ml of hexane, with five or six 10-ml portions of toluene until the filtrate was bright purple, and finally with another 40 ml of hexane. The cooling bath was removed and the bright purple precipitate was dried under vacuum, and then transferred to a storage ampoule in an inert atmosphere of argon (yield *ca.* 70%).

Anal. Calcd for $C_{28}H_{25}PTi$: C, 76.4; H, 5.67; P, 7.02; Ti, 10.9. Found: C, 76.3; H, 5.73; P, 6.99; Ti, 11.0.

(2) Thermal Decomposition of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$. $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ (357 mg; 0.405 mmol) was heated at 110° in toluene under Ar for 20 hr. The solution changed color from purple to green. The toluene was then removed under vacuum and the green residue was washed with hexane. White crystalline material (168 mg; 0.64 mmol), identified as $P(C_6H_5)_3$ by its ir spectrum, was recovered from the hexane washings. The green residue was identified as $[(C_5H_5)(C_5H_4)TiH]_2$ by its ir spectrum.

(3) Reaction of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with Hydrogen Chloride. On the vacuum line *ca.* 5 ml of liquid HCl was condensed onto 366 mg (0.383 mmol) of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ at −100° and stirred for about 30 min. The H_2 formed (0.727 mmol, 0.947 mmol/mmol of Ti) was collected *via* a Toepler pump. The greenish residue was washed with ether (in air), and a white crystalline material was obtained from the ether washings. The ir spectrum of this material was virtually identical with that of $P(C_6H_5)_3$, except for an absorption at 535 cm^{-1} (possibly a P–Cl stretch) which, however, lost intensity upon recrystallization. The green insoluble residue was identified as the polymeric dichloride, $(C_{10}H_{10}TiCl_2)_n$, identical with that obtained by treatment of $[(C_5H_5)(C_5H_4)TiH]_2$ with excess HCl.[69]

(4) Reaction of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with Hydrogen. 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 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° and removing the excess H_2, the yellow-brown color persisted. The absorbed H_2 was released upon warming the solution to room temperature *in vacuo* and the purple color of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ reappeared. The evolved H_2 (0.43 mmol, 0.52 mmol/mmol of Ti) was collected and analyzed as described above.

(5) 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 about 25 ml of toluene containing 240 mg (0.92 mmol) of $P(C_6H_5)_3$ in a 400-ml flask. The solution was stirred under 1 atm of D_2 (*ca.* 20 mmol) for 4 hr at room temperature. After this period the D_2 atmosphere was renewed and the yellow-brown solution was stirred for an additional 4 hr. 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 phosphine complex. The purple complex was then thermally decomposed by heating the solution with an oil bath to 110° for 3 hr 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 a D_2 giving rise to large peaks at *m/e* 374 and 372 confirmed that complete deuteration of the cyclopentadienyl rings had occurred. The nmr spectrum of the phosphine oxide prepared from the triphenylphosphine 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.

(6) 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° 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 hr, it appeared dark red-brown. The solution was cooled to −80° and the noncondensable material collected *via* a Toepler pump. Analysis of this mixture 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°, 10^{-2} Torr, yielded $(C_5H_5)_2Ti(CO)_2$ (49 mg, 0.21 mmol).

(7) Reactions of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ with Molecular Nitrogen. $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ (626 mg, 0.71 mmol) was stirred at room temperature with *ca.* 5 ml of toluene under 1 atm of N_2. After about 30 min the solution began to turn brown. After 2 hr the mixture looked uniformly green-brown, and the formation of a yellow precipitate was observed. The mixture was cooled to −80° and the excess N_2 was removed. Upon warming again, no N_2 was released into the vacuum. The solution was then heated with an oil bath at 110° for 1 hr. Noncondensable gas was evolved upon heating and identified as N_2 (0.104 mmol, 0.07 mmol/mmol of Ti) by its mass spectrum. The solution was hydrolyzed with 10 ml of 2.5 *N* H_2SO_4 and extracted with about 20 ml of H_2O. A subsequent Kjeldahl determination yielded 0.18 mmol of NH_3 (0.13 mmol/mmol of Ti). An analogous experiment, conducted in an autoclave at 95° and 150 atm of N_2, yielded 0.26 mmol of NH_3/mmol of Ti after hydrolysis.

When a mixture of 285 mg (0.32 mmol) of $[C_{10}H_{10}TiP(C_6H_5)_3]_2$ and 842 mg (3.2 mmol) of $P(C_6H_5)_3$ was stirred with 10 ml of toluene, no reaction with N_2 was observed after 24 hr at room temperature. The solution remained bright purple.

D. Intermediate in the Volpin–Shur System, $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$. (1) Preparation of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$. Eight milliliters of *ca.* 1.5 *M* (12 mmol) C_2H_5MgCl in diethyl 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° 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° to prevent the gradual decomposition which is observed upon prolonged storage at room temperature.

(2) Analyses. (a) Titanium was determined colorimetrically as the Ti(IV)–H_2O_2 complex, using standard solutions prepared from potassium titanyl oxalate, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, as a reference. A weighed sample of the yellow solid was slowly air oxidized and digested in hot concentrated 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 for Ti 6.29%; found, 6.31%, corresponding to an equivalent weight of 749 (calcd, 752).

(b) Magnesium was determined volumetrically by titration with standard EDTA using Eriochromeblack T indicator. The solution obtained for the Ti(IV) determinations was used for the magnesium analyses: calcd, 3.00 mmol of Mg/mmol of Ti; found, 2.98 mmol of Mg/mmol of Ti.

(c) Chloride was determined by the Mohr method. A weighed sample of the yellow solid was oxidized slowly and extracted with hot concentrated KOH. The resulting solution was filtered, neutralized with HNO_3, and quantitatively diluted: calcd, 6.00 mmol of Cl^-/mmol of Ti; found, 5.97 mmol of Cl^-/mmol of Ti.

(d) Coordinated diethyl ether was determined by treatment of the yellow solid with ethylene glycol. On the vacuum line, 841 mg (1.12 mequiv based on Ti) of the yellow solid was treated with *ca.* 5 ml of ethylene glycol. The $(C_2H_5)_2O$ liberated was collected, fractionated, and identified by its ir spectrum: calcd, 3.50 mmol of $(C_2H_5)_2O$/mmol of Ti; found, 3.52 mmol of $(C_2H_5)_2O$/mmol of Ti.

(3) Thermal Decomposition of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$. The yellow solid (948 mg, 1.27 mequiv) was heated slowly under vacuum with an oil bath. The evolution of ethylene and ethane began at 60°, and was complete after heating for 1 hr at 125°. The coordinated $(C_2H_5)_2O$ was evolved continuously upon heating but liberation was not complete even on heating to 200°. The yellow complex darkened upon warming and appeared brownish black at 125°. Ethylene and ethane were fractionated from the evolved ether on the vacuum line by repeated passage through a trap in a −130° pentane slush. 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 of C_2H_4 (0.49 mmol/mmol of Ti), 0.60 mmol of C_2H_6 (0.47 mmol/mmol of Ti).

No green $[(C_5H_5(C_5H_4)TiH]_2$ was observed upon extraction of the brownish black residue with toluene. Treatment of the residue with HCl gas gave an intense green solution upon evolution of 1.43 mmol of H_2 (1.13 mmol of H_2/mmol of Ti).

(4) Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ with Oxygen. Yellow $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ (995 mg, 1.28 mequiv) was treated 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 reaction proceeded. The ethylene and ethane evolved in the reaction were collected and analyzed as described above: found, 0.68 mmol of C_2H_4 (0.53 mmol/mmol of Ti), 0.68 mmol of C_2H_6 (0.53 mmol/mmol of Ti).

(5) Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ with H_2O. Yellow $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ (879 mg, 1.17 mequiv based on Ti) was treated 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 hr 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 mmol/mmol of Ti) was collected and its purity confirmed by its quantitative conversion to H_2O upon passage over CuO at 300°. Ethane (1.19 mmol, 1.02 mmol/mmol of Ti) was collected by the fractionation procedure described above, and its purity was confirmed by a comparison of its ir spectrum to that of pure C_2H_6.

(6) Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ with Hydrogen Chloride. Excess HCl was recycled over a solid sample of $[(C_5H_5)_2TiC_5H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ (780 mg, 1.04 mequiv) *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 hr. 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 mmol of C_2H_6 (1.20 mmol/mmol of Ti), 0.5 mmol of H_2 (0.51 mmol/mmol of Ti).

Extraction of the dark red solid residue with $CHCl_3$ yielded a bright red solution. Removal of the solvent, and drying *in vacuo*, gave 232 mg (0.92 mmol) of $(C_5H_5)_2TiCl_2$ 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 $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ with Diborane. Diborane (2.04 mmol) and 15 ml of THF were distilled onto the yellow solid (751 mg, 1.00 mequiv based on Ti) at −80°. The mixture was allowed to warm slowly to room temperature. After stirring for 30 min at room temperature, the solvent was removed from the brownish violet solution leaving a dark brown residue. Sublimation of this residue at 80° (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.[35] Fractionation and analysis of the evolution products showed that predominantly ethylene was formed in the reaction.

(8) Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ with 1,3-Pentadiene. 1,3-Pentadiene (5 ml) and THF (5 ml) were distilled onto the yellow solid (*ca.* 1.0 mequiv) at −80°, and the mixture was allowed to warm to room temperature. After stirring for *ca.* 30 min, the mixture was evaporated to dryness and the dark residue was filtered, and the solvent was removed *in vacuo* leaving dark blue needles of π-(1,3-dimethyl)allyltitanocene, identified by comparison of its ir spectrum with that given by Martin.[36]

(9) Reaction of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ with Nitrogen. Reactions of the yellow solid with nitrogen were carried out at high pressure in an autoclave. The apparatus used allowed solvents to be added at high nitrogen pressures, thus minimizing the competitive decomposition reactions of the complex in solution (Figure 5). In a glovebox, the yellow solid was transferred from a tared storage ampoule to the lower cylinder, and the needle valve was attached. The apparatus was assembled on the high-pressure line and the upper cylinder was flushed with N_2. Both cylinders were then pressurized to 130 atm with prepurified N_2. The pressure was then released from the upper cylinder and the solvent was 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, $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ (741 mg, 0.99 mequiv) was treated 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 was hydrolyzed with 10 ml of *ca.* 2.5 *N* H_2SO_4, and the ammonia liberated was determined by the Kjeldahl method: found, 0.63 mmol of NH_3 (0.6 mmol/mmol of 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 (0.95 mequiv) of the yellow complex was treated with N_2 at 230 atm in DME and the evolution products were trapped out by releasing the pressure slowly through a cooling coil at −196°. The cold trap was attached to the vacuum line and the condensed material was fractionated and analyzed as previously described: found, 0.51 mmol of C_2H_6 (0.54 mmol/mmol of Ti), 0.34 mmol of C_2H_4 (0.36 mmol/mmol of Ti). A subsequent Kjeldahl determination on the autoclave mixture yielded 0.56 mmol of NH_3 (0.59 mmol/mmol of Ti).

(10) Characterization of the N_2 Reduction Product. The crude product from the reaction of *ca.* 750 mg (1 mequiv) of $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$ 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° 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 a nitrogen glovebox.

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 with a mixture of $CHCl_3$ and dilute HCl yielded a bright red $CHCl_3$ solution from which 75 mg (0.30 mmol) of $(C_5H_5)_2TiCl_2$ was obtained upon removal of 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) was collected and analyzed as described above. The residue from the reaction was extracted with boiling concentrated H_2SO_4, and the [Ti] determined colorimetrically as previously described: found, 0.236 mmol of Ti (3.08 mmol of Ti/1.0 mmol of N_2).

E. Reactions of Di-μ-hydridobis[di-π-cyclopentadienyltitanium(III)], $[(C_5H_5)_2TiH]_2$. $[(C_5H_5)_2TiH]_2$ was prepared by the procedure presented in an earlier publication.[21]

(1) Reaction with Carbon Monoxide. $[(C_5H_5)_2TiH]_2$ (106 mg, 0.296 mmol) was placed in a flask with a volume of 52.0 ml, 742 Torr (corrresponding to 2.06 mmol) of carbon monoxide was added to the evacuated flask, and the flask was closed off. The solid slowly changed from violet to brown. Analysis of the gas mixture showed that the evolved H_2 amounted to 0.20 mmol and the consumed CO to 0.79 mmol, indicating 68% conversion of $[(C_5H_5)_2$-

Table III. Nitrogen Reduction by $[(C_5H_5)_2TiH]_2$ in Various Solvents

Solvent	Solvent addition temp, °C	Maximum reaction temp, °C	Reaction time, hr	Nitrogen pressure, atm, at addition	Yield of NH_3/Ti
THF	25	25	0.25	120	0.33
Toluene	25	25	0.50	120	0.17
DME[a]	25	25	0.50	120	0.42
DME	30	30	0.50	220	0.20
Ether[b]	25	25	0.25	150	0.05
THF	−30	−30	3	75	0.03
DME	−60	25	1	150	0.12
THF	−70	20	1	200	0.17
Hexane	0	25	0.50	200	0.00
None		170	2.0	160	0.10

[a] 1,2-Dimethoxyethane. [b] Diethyl ether.

Table IV. Nitrogen Reduction by $[(C_5H_5)_2TiH]_2$ in Lithium Naphthalide Solutions

Solvent	LiNp/Ti molar ratio	Solvent addition temp, °C	Maximum reaction temp, °C	Reaction time, hr	Nitrogen pressure, atm, at addition	Yield of NH_3/Ti
THF	1.50	−10	25	1	150	0.18
DME	1.50	25	25	1	150	0.32
DME	1.50	−60	25	1	150	0.52
DME	2.0	−60	25	2.5	150	0.58
THF	30	25	25	1	200	0.99

$TiH]_2$ to $(C_5H_5)_2Ti(CO)_2$ according to $[(C_5H_5)_2TiH]_2 + 4CO \rightarrow 2(C_5H_5)_2Ti(CO)_2 + H_2$. The titanocene dicarbonyl was sublimed at 45° (10^{-3} Torr) and identity confirmed by its ir spectrum.[20]

(2) Reaction with Methyl Iodide. Approximately 5 ml of methyl iodide was distilled onto 206 mg (0.580 mmol) of $[(C_5H_5)_2TiH]_2$ at −60°. The mixture was allowed to warm slowly and was stirred at room temperature for 2 hr, whereupon the color changed from violet to red brown. The gaseous products contained 0.221 mmol of CH_4 and 0.421 mmol of H_2. The total H evolved (as H_2 and CH_4) was 1.06 mmol (0.92 H/Ti). These results indicate that reactions 20 and 21 took place.

(3) Hydrogen Exchange with $[(C_5H_5)_2TiD]_2$. A sample of $[(C_5H_5)_2TiD]_2$ was prepared by treatment of solid $(C_5H_5)_2Ti(CH_3)_2$ with D_2 following the procedure described earlier.[21] This deuteride (91 mg, 0.255 mmol) was thermally decomposed *in vacuo* to $[(C_5H_5)(C_5H_4)TiH]_2$. The evolved gas (0.32 mmol, 0.61 mmol/mmol of Ti) contained 92.3% H_2, 7.6% HD, and 0.1% D_2, which corresponds to a D content of 7.8%. A small portion of the deuteride was also cleaved to the triphenylphosphine adduct by treatment with $P(C_6H_5)_3$ in THF at −20°. The epr spectrum of this adduct indicated *ca.* 75% $(C_5H_5)_2Ti(D)P(C_6H_5)_3$ and *ca.* 25% $(C_5H_5)_2Ti(H)P(C_6H_5)_3$ by comparison of the observed spectrum to a computer-simulated one.

Another portion of the deuteride was heated at 100° under 1700 psi of hydrogen for 1 hr in an autoclave. This treated sample (114 mg; 0.318 mmol) was then thermally decomposed to $[(C_5H_5)(C_5H_4)TiH]_2$. The evolved gas (0.40 mmol, 0.63 mmol/mmol of Ti) contained 99.3% H_2, 0.66% HD, and 0.03% D_2 which corresponds to 0.72% D. Another portion of this treated sample was cleaved to the triphenylphosphine adduct by treatment with $P(C_6H_5)_3$ as before. The epr spectrum of this adduct showed only the doublet of doublets attributable to $(C_5H_5)_2Ti(H)P(C_6H_5)_3$.

(4) Reactions of $[(C_5H_5)_2TiH]_2$ with Molecular Nitrogen. (a) N_2 Reduction without Additional Reducing Agents. A solvent was added to dry $[(C_5H_5)_2TiH]_2$ under high nitrogen pressure in these experiments by the procedure described for $[(C_5H_5)_2TiC_2H_5]_2 \cdot 6MgCl_2 \cdot 7(C_2H_5)_2O$, using the double bomb apparatus shown in Figure 5. Typically, 1 mmol of $[(C_5H_5)_2TiH]_2$ and 5 ml of solvent were used. The results of these experiments are summarized in Table III.

(b) N_2 Reduction in the Presence of Lithium Naphthalide. Standardized lithium naphthalide (LiNp) solutions were added to dry $[(C_5H_5)_2TiH]_2$ by the procedure described above. The results of these experiments are summarized in Table IV.

F. Electrochemical Experiments. Supporting Electrolyte. Tetrabutylammonium perchlorate, TBAP (Southwestern Analytical Inc., Austin, Tex., polarographic grade), was used as the supporting electrolyte in 1,2-dimethoxyethane solutions. The material was dried *in vacuo* at 60° for 24 hr prior to use. Sodium tetraphenylborate (Aldrich Chemical Co., Milwaukee, Wis., Puriss) was used without further purification.

Solvent. 1,2-Dimethoxyethane was first distilled from $LiAlH_4$ and then distilled on a vacuum line, from a blue solution containing Na–K alloy, directly into the electrolysis cell.

Cell Description. A three-electrode cell fitted with the appropriate adapters was employed for controlled potential electrolysis experiments. The reference electrode, a silver wire in a solution consisting of 0.01 M $AgClO_4$ in 1,2-dimethoxyethane, was separated from the sample solution by a fine-porosity frit. The counterelectrode consisted of a coiled Pt wire immersed in 0.1 M TBAP solution which was separated from the Pt gauze working electrode by a 20 mm medium frit. Standard vacuum techniques were used in all operations.

Instrumental. Electrochemical reductions were conducted with an operational amplifier potentiostat ("adder" configuration)[70] with suitable Hewlett Packard Model 6824A power supplies.

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