Di-μ-hydrido-bis(dicyclopentadienyltitanium(III)), a Transition Metal Complex with a Diborane-Like Double Hydrogen Bridge[1]

John E. Bercaw and Hans H. Brintzinger

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104. *Received June 16, 1969*

Abstract: Di-μ-hydrido-bis(di-π-cyclopentadienyltitanium(III)) (**1**) is formed by reaction of solid $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ with gaseous hydrogen. **1** is characterized by its ir spectrum (di-μ-hydridotitanium band at 1450 cm^{-1}) and by the following reactions: thermal decomposition of **1** yields titanocene dimer and 1 mol of H_2; **1** and 1,3-pentadiene give π-(1,3-dimethyl)allyltitanocene; **1** and diborane afford the titanocene borohydride $(\pi\text{-C}_5\text{H}_5)_2\text{TiBH}_4$; reaction of **1** with HCl yields titanocene dichloride and hydrogen; DCl gives largely HD, as expected for a hydride. **1** is a diamagnetic deep violet compound of moderate stability, pyrophoric in air. Tetrahydrofuran at room temperature first cleaves the compound to a monomeric paramagnetic adduct, the epr spectrum of which shows the presence of one hydride ligand, then leads to further degradation. Triphenylphosphine in tetrahydrofuran solution cleaves **1** to a monohydride–monophosphine complex, identified again by its epr spectrum. Like other transition metal compounds with hydrogen bridge bonds, **1** appears to contain a metal–metal bond. In contrast to the acidic character of the bridge hydrogen in other transition metal complexes, however, **1** behaves like a typical hydride.

Hydride derivatives of titanocene such as $(\pi\text{-C}_5\text{H}_5)_2\text{TiH}$ or $[(\pi\text{-C}_5\text{H}_5)_2\text{TiH}]_2$ have been postulated as intermediates in a variety of chemical reactions,[2-4] but no direct evidence for their existence has come forward yet.[5] In fact, no titanium hydride complexes at all have been isolated to the best of our knowledge. In this article we wish to report on the successful synthesis of a first complex of this kind, $[(\pi\text{-C}_5\text{H}_5)_2\text{TiH}]_2$, and on its chemical properties.

Results

Synthesis. Previous experience with titanocene hydride systems in solution had led us to expect that a titanocene monohydride species would not be stable in the presence of solvents.[6] We have tried, therefore, to obtain such a compound in a "dry" process. Indeed we find that the reaction between solid crystalline dimethyl titanocene, $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$, and hydrogen gas yields a titanocene hydride compound. It has long been known that the same reaction, between dimethyltitanocene and hydrogen gas, leads to the dark green compound $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2$, if carried out in hydrocarbon solvents (eq 1).[7] Clauss and Bestian, in their original report on this reaction, have noted the occurrence of a fleeting violet intermediate.[7] This violet material is the main product if the reaction is allowed to proceed in the absence of any solvents. A small amount of dark green titanocene dimer, however, is formed even in our dry reaction. Formation of this side product appears to be enhanced by higher temperatures, or if the rather exothermic reaction proceeds at higher hydrogen pressures. If temperature and hydrogen pressure are kept too low, on the other hand, the reaction is incomplete and substantial amounts of dimethyltitanocene remain in the product. Both contaminants are easily removed, however, from the violet hydride compound. In contrast to the latter, both titanocene dimer and dimethyl titanocene are freely soluble in toluene at −78°; under these conditions the violet hydride is neither dissolved nor decomposed and is obtained, after removal of the solvent, as a residue of analytical purity. Optimal reaction conditions and purification procedures are detailed in the Experimental Section of this report.

$$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2 + \text{H}_2 \xrightarrow[\substack{\text{C}_6\text{H}_{14}\\ \text{as solvent}}]{} {}^1\!/_2[(\text{C}_5\text{H}_5)_2\text{Ti}]_2 + 2\text{CH}_4 \qquad (1)$$

Properties. The violet reaction product is a compound of marginal stability only. On admission of air it oxidizes explosively, and, in contact with even such inert solvents as hexane or toluene, decomposition and formation of brownish solutions are observed at room temperature. As a solid, however, the compound is relatively stable when kept under an atmosphere of pure argon at or below room temperature. On prolonged storage the violet solid tends to convert to a green product; this reaction is almost completely eliminated, however, when the reaction product is thoroughly freed from all contaminants.

When heated to 150–160° *in vacuo* the violet material loses 0.5 mol of hydrogen per titanium and is quantitatively converted to the dark green titanocene dimer.[8] This reaction establishes the composition of the violet compound as $(\text{C}_5\text{H}_5)_2\text{TiH}$ or a multiple thereof (eq 2).

$$2(\text{C}_5\text{H}_5)_2\text{TiH} \longrightarrow [(\text{C}_5\text{H}_5)_2\text{Ti}]_2 + \text{H}_2 \qquad (2)$$

This composition is further corroborated by numerous chemical reactions. In one instance, tetrahydrofuran and 1,3-pentadiene are condensed on the violet solid and the reaction mixture is then warmed to room temperature. From the blue solution thus obtained,

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(1) This work is supported in part by a research grant (GP-8300) from the National Science Foundation to whom we are pleased to acknowledge our thanks.

(2) H. H. Brintzinger, *J. Amer. Chem. Soc.*, **88**, 4305 (1966).

(3) H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, **6**, 293 (1966); *ibid.*, **12**, 149 (1968); H. A. Martin, Thesis, Rijksuniversiteit te Groningen, 1967.

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

(5) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Chem. Commun.*, 849 (1966); *Inorg. Chem.*, **6**, 1979 (1967).

(6) H. H. Brintzinger, *J. Amer. Chem. Soc.*, **89**, 6871 (1967).

(7) K. Clauss and H. Bestian, *Ann.*, **654**, 8 (1962).

(8) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 1138 (1966).

π-(1,3-dimethyl)allyltitanocene[3] is isolated in almost quantitative yield. The stoichiometry for the formation of an allyl ligand from the diolefin requires the presence of one hydride ligand per titanium center (eq 3). Reaction of the violet hydride with an excess of

$$(C_5H_5)_2TiH + C_5H_8 \longrightarrow (\pi\text{-}C_5H_5)_2Ti(\pi\text{-}C_5H_9) \qquad (3)$$

diborane, carried out in tetrahydrofuran in a similar manner, affords a high yield of pure titanocene borohydride.[9] Again, one hydride per titanium is a prerequisite of this reaction.

$$(C_5H_5)_2TiH + {}^1/_2B_2H_6 \longrightarrow (\pi\text{-}C_5H_5)_2TiBH_4 \qquad (4)$$

The reaction with HCl, for which we would expect formation of titanocene dichloride and evolution of $^3/_2$ mol of hydrogen (eq 5), is not quite stoichiometric. Yields of hydrogen range from 1.25 to 1.35 H_2/Ti and, while titanocene dichloride is the main product of the reaction, a small amount of insoluble green material is

$$(C_5H_5)_2TiH + 2HCl \longrightarrow (C_5H_5)_2TiCl_2 + {}^3/_2\ H_2 \qquad (5)$$

consistently observed after extracting the reaction product with chloroform. This green residue is quite reminiscent of the product formed from titanocene dimer and hydrochloric acid.[10] Quite likely, therefore, the reaction with HCl involves two competing reactions: conversion to titanocene dichloride according to eq 5, and a side reaction which leads, probably *via* a titanocene intermediate, to the green polymeric residue.[11]

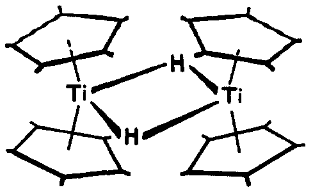
In order to establish whether the hydrogen evolution with HCl is in fact due to the reaction of a hydride (and not just of a reducing agent), we have repeated this reaction with DCl (91.5% isotopic purity). A hydride species should then give rise to HD in the hydrogen evolved (eq 6). For DCl of the given purity the gas should contain 8% H_2, 62% HD, and 30% D_2. In reasonable

$$(C_5H_5)_2TiH + 2DCl \longrightarrow (C_5H_5)_2TiCl_2 + HD + {}^1/_2D_2 \qquad (6)$$

agreement with this expectation, we find 12% H_2, 83% HD, and 6% D_2.[11]

While these reactions do unequivocally prove the presence of titanocene monohydride, we now have to establish which multiple of the $[(C_5H_5)_2TiH]$ unit constitutes the violet compound, and how hydride and cyclopentadienyl ligands are bound to the metal.

The magnetic behavior of the compound gives a first indication: at 79°K as well as at room temperature, the violet solid is diamagnetic. This rules out the possibility that the compound is a monomer, since $(C_5H_5)_2TiH$ contains a formal Ti(III) center and would have one unpaired electron. An obvious explanation for the observed diamagnetism would be the presence of a dimer, $[(C_5H_5)_2TiH]_2$, in which the two spins are antiferromagnetically coupled. Titanocene monochloride is in fact known to exist, in the solid and in nonpolar solvents, as a dimer, $[(C_5H_5)_2TiCl]_2$.[12-14]



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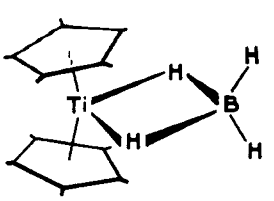

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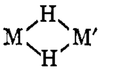
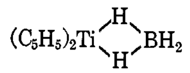
If an analogous dimeric structure is adopted for the titanocene monohydride, a diborane-like double hydrogen bridge bond between the two metal centers has to be postulated (structure **1**). This postulate is supported by infrared spectroscopy. From a large number of ir spectra of substituted diboranes, which have been analyzed by Kapshtal and Sverdlov,[15,16] the following characteristic frequencies of a double hydrogen bridge bond



$$M\overset{H}{\underset{H}{\langle\rangle}}M'$$

can be identified. A very strong band, arising from an antisymmetric stretching mode, occurs at 1600–1500 cm^{-1} in all diboranes. Similarly



$$(C_5H_5)_2Ti\overset{H}{\underset{H}{\langle\rangle}}BH_2$$

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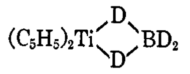
exhibits a strong, broad band at 1350 cm^{-1}.[9] We believe that this band is the same antisymmetric stretching mode of the hydride ring; in the deuterio derivative



$$(C_5H_5)_2Ti\overset{D}{\underset{D}{\langle\rangle}}BD_2$$

we find it shifted to 1000 cm^{-1}, close to the expected isotope shift. In addition to this antisymmetric ring-stretching vibration around 1500 cm^{-1}, some diboranes exhibit an absorption at 2000–2100 cm^{-1}. Since this band arises from a symmetrical ring-stretching mode, it is noticeably strong only in noncentrosymmetrical molecules like 1,1-dimethyldiborane. In the unsymmetric **2** it dominates the spectrum as a very intense band at 1942 cm^{-1} (1420 cm^{-1} for borodeuteride).[9] In centrosymmetrical molecules on the other hand, such as *trans*-dimethyldiborane or tetramethyldiborane, this band is absent. A dimeric hydride with structure **1** should therefore not exhibit a band in the 2000-cm^{-1} region either.

Since the titanocene hydride decomposes on grinding with either KBr or Nujol, we obtained spectra of the compound by preparing it in form of a thin powdery layer directly on NaCl plates. The ir spectrum thus obtained does in fact exhibit a strong, broad absorption at 1450 cm^{-1} (Figure 1), superimposed on several weaker peaks. The small peaks in this region are also present in the air-oxidation product of **1**, and are therefore unrelated to the hydride moiety. The strong, broad band at 1450 cm^{-1}, however, clearly disappears on oxidation. For this reason, and because of its resemblance in width and intensity to the 1350-cm^{-1} band

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

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

[11] The presence of traces of oxygen or chlorine in the large excess of HCl used for reaction 5 would offer an alternative explanation for the low yields of H_2 in this reaction. A direct insert mass spectrum of the titanocene dichloride obtained from reaction 6 showed two contaminants, a high molecular weight titanium derivative and $(C_5H_5)(C_5H_4D)TiCl_2$. The formation of these contaminants might be related to the reduced yields of D_2.

[12] R. L. Martin and G. Winter, *J. Chem. Soc.* 4709 (1965).

[13] H. Nöth and R. Hartwimmer, *Chem. Ber.*, **93**, 2246 (1960).

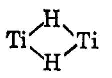
[14] G. Natta, *Angew. Chem.*, 71, 205 (1959).

[15] V. N. Kapshtal, *Zh. Fiz. Khim.*, **40**, 945 (1966); *Russ. J. Phys. Chem.*, 508 (1966).

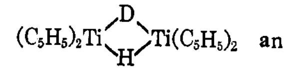
[16] V. N. Kapshtal and L. M. Sverdlov, *Zh. Fiz. Khim.*, **37**, 1275 (1963); **39**, 2193 (1965); **40**, 2818 (1966); *Russ. J. Phys. Chem.*, 680 (1963); 1169 (1965); 1514 (1966).

Figure 1. Infrared spectrum of $[(\pi\text{-}C_5H_5)_2TiH]_2$ (heavy line), prepared as a thin powdery layer on an NaCl plate. The thin line represents the spectrum of the same sample after the slow admission of atmospheric oxygen. Spectra taken on a Perkin-Elmer 337 spectrophotometer.

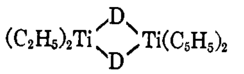
of the borohydride **2**, we attribute this band to the antisymmetric stretching vibration of the


$$\mathrm{Ti}\overset{H}{\underset{H}{\langle\rangle}}\mathrm{Ti}$$

ring. When the preparation of the hydride is carried out with deuterium instead of hydrogen gas, a partially deuterated product is obtained for which we estimate, from epr data given below, a deuterium content of 75% in the metal hydride ring. This material does not exhibit the band at 1450 cm⁻¹; instead, two bands appear at 1260 and 1050 cm⁻¹. A shift of the antisymmetric ring-stretching absorption to these positions should in fact occur in the compounds


$$(C_5H_5)_2\mathrm{Ti}\overset{D}{\underset{H}{\langle\rangle}}\mathrm{Ti}(C_5H_5)_2$$

and


$$(C_2H_5)_2\mathrm{Ti}\overset{D}{\underset{D}{\langle\rangle}}\mathrm{Ti}(C_5H_5)_2$$

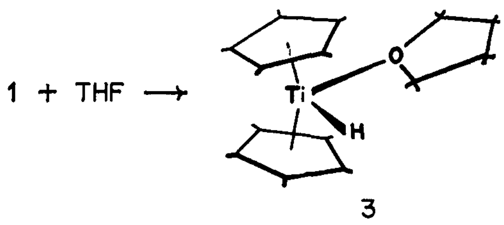
respectively (compare, for example, ref 15 and 16). Unfortunately, the air-oxidation product does also show bands in these regions (although weaker and broader) so that we cannot be absolutely certain about the assignment of the two bands at 1260 and 1050 cm⁻¹ in the deuteride. At any rate, the complete absence of any absorption in the 2000-cm⁻¹ region of the spectrum of the hydride rules out the presence of a terminal Ti–H bond or any unsymmetrical structure, such as $[(C_5H_5)_2TiH_2]^-[Ti(C_5H_5)_2]^+$. As discussed above, the absence of any absorption in this region is in fact quite diagnostic of the centrosymmetric structure **1**.

The other features of the spectrum in Figure 1 are identical in all respects with those of other titanocene derivatives with π-bonded rings.[17] In particular, the spectrum has no resemblance at all to that of the green titanocene dimer, where a multitude of observable splittings suggests the presence of both σ- and π-bonded rings.[8,10] Instead, the spectrum is almost identical, with only minor shifts, with that of $(C_5H_5)_2TiCl_2$, for which π bonding of the two (C_5H_5) rings and a pseudotetrahedral arrangement of the four ligands around the titanium center have been established by an electron diffraction study.[18] We can thus confidently assign structure **1** to our violet titanocene hydride.

An interesting qualitative observation concerns the visible spectrum of the hydride: its violet color is virtually indistinguishable from that of the titanocene borohydride **2**. On the basis of structure **1** such a similarity is indeed to be expected, since it contains each Ti(III) center in a local ligand environment which is identical with that of the borohydride.

Cleavage in Solution. Attempts to investigate the hydride by nuclear magnetic resonance spectroscopy in solution did not yield satisfactory results. Probably due to paramagnetic impurities, only broad and spuriously shifted resonances were observed.

Electron paramagnetic resonance (epr) spectroscopy in solution provided most useful information, however. Solutions of the violet hydride in tetrahydrofuran, prepared and kept at *ca.* −70°, show only weak and unresolved epr signals, which we attribute to impurities, since the hydride is most likely still dimeric and diamagnetic under these conditions. When such a solution is briefly warmed to room temperature, however, its color changes from violet to brown and then in the course of 2–5 min, to brownish green. Simultaneously, a strong epr signal develops and remains unchanged when the solution is cooled again to *ca.* −70° (Figure 2). Prolonged warming to room temperature allows the signal to decay gradually; a peak at higher fields appears to be associated with the product of this decay. The initial epr signal consists of a doublet with a spacing of 11.6 G, centered at $g = 1.992$. Undoubtedly, the dimeric hydride **1** is cleaved by the solvent to form the monomeric paramagnetic species **3**. The origin of the doublet signal from a hydride is confirmed by spectrum b in Figure 2, which we obtained from a partially deuterated sample of the violet hydride. Here, a 1:1:1 triplet with a spacing of 1.8 G dominates the spectrum, superimposed on the doublet spectrum of some undeuterated **3** contained in the sample.



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(7)

Cleavage to the monomeric ether adduct (reaction 7) sets in at approximately −30°. The decay of the monohydride signal appears to be only somewhat slower, however, than its formation by reaction 7.

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(17) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

(18) I. A. Ronova and N. V. Alekseev, *Dokl. Akad. Nauk SSSR*, **174**, 614 (1967).

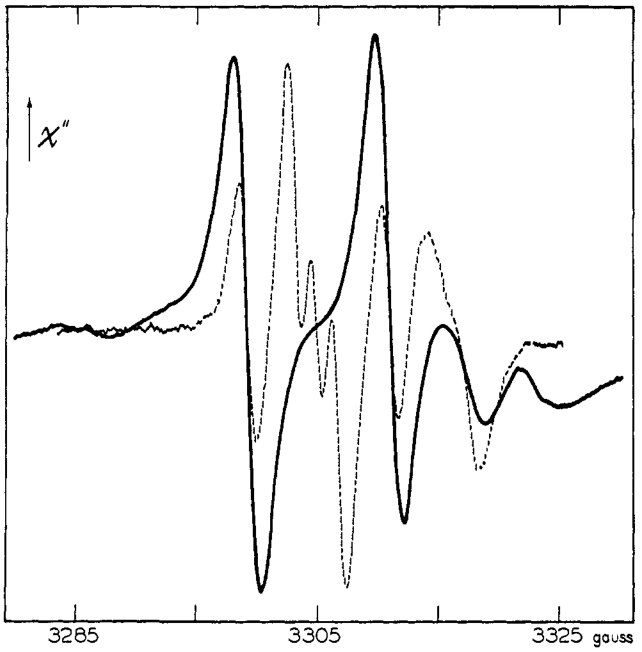
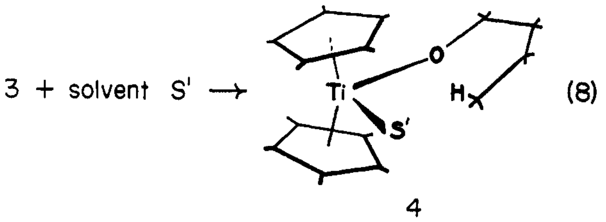


Figure 2. Epr spectrum of **3**, obtained from a *ca.* 0.002 *M* solution of [(π-C_5H_5)$_2$TiH]$_2$ (**1**) in tetrahydrofuran at −68° by brief warming to room temperature (solid line, frequency 9.213 GHz). The dashed curve represents the spectrum obtained from a partially deuterated sample of **1** under identical conditions.

Alkoxide formation by reaction 8 could account for the development of the high-field signal in the decay reaction.[19] Cleavage of ethers to alkoxides by other metal hydrides has been reported in several instances.[20,21]



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Another symmetrical cleavage of the violet hydride **1** is observed in tetrahydrofuran solutions containing triphenylphosphine. Again, the solutions turn brownish green at room temperature, concomitantly with the development of a strong epr signal. In this case however, the signal consists of two doublets with spacings of 10.0 and 24.8 G (Figure 3). The 10.0-G splitting is due to a hydride ligand again, as evidenced by its collapse to an unresolved triplet in the corresponding deuteride (Figure 3b). The larger splitting of 24.8 G however, is undoubtedly due to hyperfine interaction with the ^{31}P nucleus of a phosphine ligand, which in this case appears to fill the fourth coordination site in the monomeric paramagnetic adduct **5**. At higher gain settings weak satellite bands due to ^{47}Ti and ^{49}Ti can be observed in the epr spectra of **3** and **5**. Their intensity distribution is in accord with an interaction of the unpaired electron with one titanium nucleus. The titanium hyperfine coupling constant in the phosphine hydride complex **5** is only 5.8 G; much less than the value of 10–12 G observed in the tetrahydrofuran hydride species **3** and in other comparable complexes.[6] Undoubtedly delocalization to the phosphine ligand causes a reduction of the spin density at the titanium nucleus.

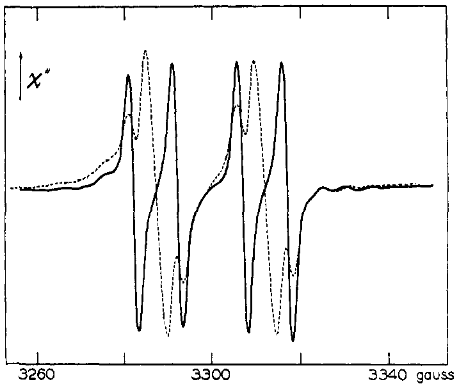
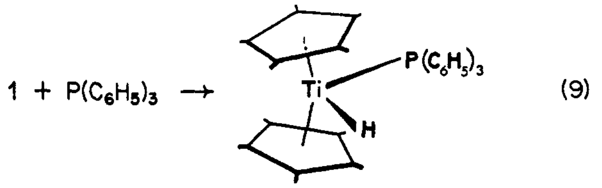


Figure 3. Epr spectrum of **5**; obtained by dissolving [(π-C_5H_5)$_2$TiH]$_2$ (**1**) in a tetrahydrofuran solution of triphenylphosphine (solid line, frequency 9.220 GHz, −68°). The dashed curve is the spectrum obtained from a partially deuterated sample of **1** under identical conditions.



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The symmetrical cleavage of hydride **1** with neutral ligand molecules to monomeric adducts is quite typical for a large number of dihalogen-bridged dinuclear complexes. Diborane on the other hand, while yielding analogous cleavage products with ethers and phosphines, can also be induced to undergo nonsymmetrical cleavage reactions by ligands which stabilize the BH_2^+ ion sufficiently to cause elimination of $[BH_4]^-$ from the dimer.[22] In an attempt to obtain a similar nonsymmetrical cleavage of **1**, we have treated the hydride with tetrahydrofuran solutions of ligands such as sodium acetylacetonate, sodium cyclopentadienide, dimethoxyethane, or 1,2-bis(diphenylphosphine)ethane, which might complex with a $[(C_5H_5)_2Ti]^+$ fragment and eliminate the $[(C_5H_5)_2TiH_2]^-$ anion. In none of these instances, however, have we been able to observe the typical epr spectrum of the dihydride anion.[6,23]

In the epr spectrum of this latter hydride complex, $[(C_5H_5)_2TiH_2]^-$, a hyperfine splitting due to the ten ring protons had been observed,[6,23] the equivalence of all ten protons being strong evidence for the presence of π-bonded, easily rotating ring ligands. This rather small (0.4 G) hyperfine structure is not resolved in the epr spectra of Figure 2. If we assume, however, that the apparent line width of 1.5 G of the gaussian derivative curves in Figure 2 is the envelope of an unresolved hyperfine splitting by ten protons, then we find for the corresponding coupling constant an upper limit of 0.4 G. The close coincidence of this value with those pre-

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[19] The signal of $(C_5H_5)_2TiOCH_3$ occurs, like that of $(C_5H_5)_2TiCl$, at $g = 1.98$ (in tetrahydrofuran solution).

[20] W. J. Bailey and F. Marktscheffel, *J. Org. Chem.*, **25**, 1797 (1960).

[21] E. Wiberg and W. Gösele, *Z. Naturforsch.*, *B*, **11**, 485 (1956).

[22] R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959).

[23] G. Henrici-Olive and S. Olive, *Angew. Chem. Intern. Ed. Engl.*, **7**, 386 (1968).

viously reported justifies the assumption made above and is consistent with the presence of π-bonded cyclopentadienyl ligands.

Discussion

A direct proof of the dimeric nature of our titanocene hydride complex by molecular weight determination would certainly be desirable. However, the instability of its solutions at ambient temperatures appears to preclude such a determination by any of the presently available methods. A conceivable alternative structure would be a polymer, $[(\pi\text{-}C_5H_5)_2TiH]_n$. We do not consider this as very likely, however. One would expect such a compound to be rather insoluble as long as it is not cleaved by a solvent. In fact, the related compound $[(\pi\text{-}C_5H_5)_2ZrH_2]_n$ has been reported to be insoluble in ethers.[5] In contrast to this, the intact violet titanocene hydride is quite soluble at −78° in ethers, particularly in tetrahydrofuran.

As one might expect for a dinuclear compound with a double hydrogen bridge bond, the dimeric hydride **1** imitates many of the reactions of diborane. Apart from the cleavage reactions with ethers and phosphines discussed above, both substances have in common a high reactivity toward oxygen and the rather facile loss of hydrogen when either compound is heated to temperatures above 100°. The details of this hydrogen elimination reaction from the hydride **1** are presently under investigation.

Transfer of a hydride ligand to unsaturated compounds is another common mode of reaction for **1** and for diborane.[24] Addition to an olefin such as in reaction 2 appears to be more facile for the titanocene hydride than for diborane. This could be related to the presence of unoccupied d orbitals in **1**, which are thought to facilitate the ligand transfer step in reactions of this type.[25] Other than that, the reaction chemistry of **1** seems to have more similarity to the main group compound diborane than to that of other hydrogen-bridged transition metal complexes.

Recently, some complexes of group VI–VIII transition metals have been found in which a hydrogen ligand acts as a bridge between two metal centers of a binuclear or polynuclear species.[23–34] However, the hydrogen bridge in these transition metal complexes appears to behave, chemically, rather like a proton embedded in the electron density of a metal–metal bond. In some cases the hydrogen bridge is actually formed by the reversible insertion of a proton into a neutral, metal–metal bonded species;[26–29] in other instances the hydrogen complex is rather easily deprotonated to form the corresponding metal–metal bonded anion in alkaline media.[30] In contrast to this acidic character, the hydrogen ligands in the titanocene hydride **1** are clearly hydridic, as discussed above.

As with these other bridged metal hydride species, however, there is a distinct metal–metal interaction present in compound **1**, as shown by its diamagnetism. The corresponding dimeric titanocene chloride, in which two Cl^- ligands bridge the two metal centers, exhibits a relatively weak antiferromagnetic interaction with a spin–spin coupling constant of only *ca.* 200 cm^{-1}.[12] At room temperature, the chloride does therefore exhibit an almost normal magnetic moment of *ca.* 1.6 BM per titanium.[12] Martin and Winter[12] have ascribed the easy accessibility of the triplet state to a destabilization of a bonding metal–metal δ orbital by the chloride lone pairs. The absence of a similar destabilization in the hydride might explain its stronger metal–metal interaction. On the other hand, the analogous dimer in which two phosphido groups R_2P^- act as bridging ligands has also been reported to be diamagnetic.[35] This almost makes it appear as though "softness" of the ligands introduces itself again as a determining factor here.

From the absence of any observable paramagnetism in compound **1** the strength of the metal–metal interaction can be estimated to be above 1000 cm^{-1} or 3 kcal/mol. Whether it constitutes a metal–metal bond of a strength comparable to that of the bridged hydride compounds of the latter-group transition metals remains to be explored.

At any rate, the presence of the extra electron pair in the metal–metal bond appears to be crucial for some reactions of **1** which do not occur with either diborane or the titanocene borohydride **2**, both of which lack this extra pair. The hydride **1** reacts, for example, with gaseous nitrogen in ethereal solutions to yield a product from which ammonia is liberated on hydrolysis. We plan to report on the details of this and some related reactions in a separate communication, especially with respect to the question whether hydride transfer to N_2, or a previous elimination of H_2 from **1** is the cause of this rather unusual reactivity.

Another open question concerns the mechanism of formation of **1** in the reaction between dimethyltitanocene and hydrogen. While there is no doubt that the stoichiometry is given by eq 10, the possible paths and the nature of the relevant reaction intermediates present an intriguing problem which we hope to report upon at a later date.

$$2(C_5H_5)_2Ti(CH_3)_2 + 3H_2 \longrightarrow [(C_5H_5)_2TiH]_2 + 4CH_4 \quad (10)$$

Experimental Section

Materials. In view of the high air sensitivity of the compounds described in this paper, all manipulations were performed either on a vacuum line or in a glove box with prepurified nitrogen atmosphere, maintained oxygen and water free by continuous exposure to liquid Na–K alloy. Diethyl ether, tetrahydrofuran (THF), hexane, and toluene were stored over calcium hydride under vacuum and distilled under vacuum. Titanocene dichloride was obtained as a gift from Arapahoe Chemicals, Inc., Boulder, Colo., and recrystallized prior to use. Hydrogen and argon were Matheson prepurified grade. Dimethyltitanocene was prepared from titanocene dichloride and methyllithium by a method similar to that described by Clauss and Bestian,[7] with the following modifications: (1) the excess methyllithium was destroyed with methyl alcohol after the

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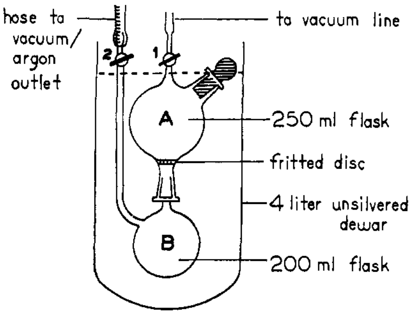

Figure 4. Apparatus used in preparation of $[(\pi\text{-}C_5H_5)_2TiH]_2$.

reaction with titanocene dichloride was complete; (2) the recrystallized dimethyltitanocene was dissolved in hexane and stored as a saturated solution (*ca.* 0.14 *M*) at −60–70°.

Procedures. 1. Preparation of Di-μ-hydrido-bis(di-π-cyclopentadienyltitanium(III)). The apparatus shown in Figure 4 was used in the preparation with good results. Fifty milliliters of (*ca.* 0.14 *M*) $(C_5H_5)_2Ti(CH_3)_2$ solution was syringed into flask A while argon was flushed through the frit *via* stopcock 2. The hexane was then removed under reduced pressure such that the yellow crystals formed on the sides of the flask and on the frit. The dewar was filled with ice water, and hydrogen was introduced to a pressure of 250 Torr. At higher hydrogen pressures (>600 Torr) the reaction becomes almost explosive, yielding $[(C_5H_5)_2Ti]_2$ and thermal decomposition products. The solid changed color from yellow to dull violet after an incubation period of approximately 0.5 hr. The progress of the reaction can be followed by observing the pressure increase of the system. During the course of 3 hr the pressure of the system was gradually increased to 500 Torr by addition of fresh hydrogen. The gas was then removed and the ice–water bath replaced with a Dry Ice–methanol mixture. While pulling a vacuum through stopcock 2, approximately 10 ml of hexane was distilled on the solid in flask A. The hexane was then pushed through the frit by introduction of argon through stopcock 1. This procedure was repeated with toluene until the toluene which passed through the frit, initially green-brown, was colorless or pale violet. The toluene was then washed from flask A with hexane. The dewar was lowered so that only flask B was cooled and the bright violet solid was dried under vacuum. The system was then filled with a positive argon pressure, flask B disconnected, and the ground joint below the frit plugged with a stopper. The flask, evacuated to 10^{-3} Torr, was then transferred to a nitrogen glove box and the violet powder scraped from the frit and the walls of the flask into a storage ampoule; yield 0.90 g (*ca.* 70% based on $(C_5H_5)_2Ti(CH_3)_2$).

2. Thermal Decomposition of Di-μ-hydrido-bis(di-π-cyclopentadienyltitanium(III)). Violet $[(C_5H_5)_2TiH]_2$ (137 mg, 0.382 mmol) was transferred to a 10-ml flask and heated in an oil bath. Gas evolution began at approximately 70° and the powder changed from violet to pale green. Continued heating to 150° resulted in the formation of a dark green powder with further evolution of gas. Further heating to 170° gave no more evolution of gas. The gas was then passed through a series of liquid nitrogen traps and collected *via* a Toepler pump. Noncondensable gas (0.359 mmol, 0.470 mmol/mmol of Ti) was collected. That the evolved gas was hydrogen was determined by its quantitative conversion to water upon passage over CuO at 300°. The green powder was identified as $[(C_5H_5)_2Ti]_2$ by comparison of its infrared spectrum to that of $[(C_5H_5)_2Ti]_2$ prepared by the method described by Salzmann and Mosimann.[10] Additional experiments gave the following H_2/Ti ratios: 0.49, 0.60, and 0.46.

3. Reaction of Di-μ-hydrido-bis(di-π-cyclopentadienyltitanium(III)) with Hydrogen Chloride. Violet $[(C_5H_5)_2TiH]_2$ (387 mg, 1.08 mmol) was transferred to a 10-ml flask. Approximately 5 ml of liquid HCl was condensed into the flask at −196°. A methanol slush at −98° was then placed around the flask and the mixture was stirred for approximately 15 min. The reaction began immediately following liquification of the HCl with vigorous bubbling and a color change from violet to pale green (probably $(C_5H_5)_2TiCl$). Oxidation to $(C_5H_5)_2TiCl_2$ occurred more slowly, being visually complete after approximately 5 min. The gas mixture was then passed through a series of liquid nitrogen traps to remove the HCl and the noncondensable gas was collected *via* a Toepler pump; 2.62 mmol (1.23 mmol/mmol of Ti) of gas was collected. The gas was identified as 99% H_2 by mass spectroscopy. Crude $(C_5H_5)_2TiCl_2$ (530 mg, 2.13 mmol), contaminated with a small amount of green polymeric material, was formed. Other experiments gave the following H_2/Ti ratios: 1.34 and 1.25.

4. Preparation of Deuterium Chloride. Prior to the preparation, all exposed glass in the vacuum line was wetted several times with 38% DCl in D_2O. Twenty milliliters of $POCl_3$ was distilled under nitrogen into a 50-ml flask. Five milliliters of D_2O (99.5% isotopic purity) was distilled into the flask and allowed to react. The evolved DCl was passed through a series of Dry Ice–methyl alcohol traps and condensed into a 2-l. storage bulb. Isotopic purity of the DCl was determined by its infrared spectrum and by mass spectroscopy as 91.5%. This DCl was then allowed to react with $[(C_5H_5)_2TiH]_2$ in the manner described under reaction 3. For results see text.

5. Reaction of Di-μ-hydrido-bis(di-π-cyclopentadienyltitanium(III)) with 1,3-Pentadiene. $[(C_5H_5)_2TiH]_2$ (319 mg, 0.890 mmol) was dissolved in 25 ml of THF at −70°. Approximately 5 ml of 1,3-pentadiene was distilled from CaH_2 into the solution and the mixture was allowed to warm slowly to room temperature. The solution changed from deep violet to blue-violet at approximately −20°. Only 0.006 mmol of H_2 was evolved during the reaction. The THF and excess 1,3-pentadiene were evaporated under reduced pressure and hexane was distilled on the dull blue-violet solid. The solution was filtered and the hexane removed by evaporation. Blue-violet π-(1,3-dimethyl)allyltitanocene (380 mg, 1.53 mmol) was recovered (86% yield). The identity of the blue-violet compound was confirmed by comparison of its infrared spectrum to that given by Martin.[3]

6. Reaction of Di-μ-hydrido-bis(di-π-cyclopentadienyltitanium(III)) with Diborane. $[(C_5H_5)_2TiH]_2$ (180 mg, 0.502 mmol) was dissolved in 20 ml of THF at −70°. B_2H_6 (10.3 mmol) was dissolved in the solution, which was then allowed to warm slowly to room temperature. H_2 (0.086 mmol) was evolved during the reaction. THF–diborane was removed under reduced pressure and the solid was sublimed at 80°, forming long violet needles. Titanocene borohydride (179 mg, 0.925 mmol) was thus recovered (89% yield). The identity of the violet needles was confirmed as $(C_5H_5)_2TiBH_4$ by comparison of its infrared spectrum to that given by Nöth and Hartwimmer.[9]

7. Infrared Spectra. The infrared spectrum of **1** was obtained by preparing the violet solid $[(C_5H_5)_2TiH]_2$ directly on an NaCl plate. A smaller apparatus, similar to that in Figure 4 with a supported NaCl plate replacing the frit, was used with good results. A NaCl window was frosted on one side by rubbing with a grinding compound. The dimethyl titanocene solution was syringed directly on the frosted side of the NaCl plate and the hexane was evaporated such that a film of the yellow solid was formed on the upper side. The violet $[(C_5H_5)TiH]_2$ was prepared and purified by the procedure given in section 1. The window was removed in a nitrogen glove box, and then, together with a second window placed over the sample, assembled in an air-tight holder. Spectra were obtained on a Perkin-Elmer 337 and a Beckman IR-10 spectrophotometer.

8. Electron Paramagnetic Resonance Spectra. A small amount of the violet solid $[(C_5H_5)_2TiH]_2$ is transferred in a nitrogen glove box to an epr tube with ground joint and stopcock. In the experiments involving triphenylphosphine, this compound was added to the tube as a solid prior to addition of the solvent. THF was then distilled into the tube at −80° and the violet solid was dissolved. Spectra were obtained on a Varian Associates 4501 spectrometer. The spectrometer was routinely operated at microwave powers of 0.2–0.5 mW, where no saturation was ever observed with the titanocene systems. Field modulations were kept below 0.2 G, in order to secure full resolution of the spectra. For an analysis of hyperfine coupling constants and relative intensities, an appropriate stick spectrum was calculated, subsequently convoluted with the derivative of a Gaussian function, and plotted out for comparison with the observed spectra, by means of an IBM 360 computer and a Calcomp plotting system.

9. Magnetic Susceptibility Measurements. Magnetic susceptibilities of the violet solid $[(C_5H_5)_2TiH]_2$ were determined at 79 and 300°K with a modified Curie–Cheneveau balance calibrated against $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$. The solid is diamagnetic at both temperatures.