Organometallics **1996,** *15,* 4977−4983

Bis(tetramethylcyclopentadienyl)titanium Chemistry. Molecular Structures of $[(C_5HMe_4)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5Me_4)Ti]_2$ and $[(C_5HMe_4)_2Ti]_2N_2$

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Received June 25, 1996[⊗]

Thermolysis of bis(tetramethylcyclopentadienyl)-stabilized titanium(III) compounds $(C_5HMe_4)_2TiR$ (R = Me (**2**), Ph (**3**)) yields, in marked contrast with the bis(pentamethylcyclopentadienyl) analog, the dimeric product $[(C_5HMe_4)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (**4**), with a bridging metalated tetramethylcyclopentadienyl ligand. The hydride $(C_5HMe_4)_2TiH$ (**5**), synthesized by hydrogenolysis of **2** or **3**, reacts with N_2 to form the dinuclear Ti(II) dinitrogen compound $[(C_5HMe_4)_2Ti]_2N_2$ (**8**). Under a dynamic vacuum, the dinitrogen complex **8** loses the N_2 ligand to give the titanocene $(C_5HMe_4)_2Ti$ (**10**). The molecular structures of both **4** and **8** were determined by X-ray diffraction methods.

Introduction

Methyl substituents at cyclopentadienyl ligands influence the reactivity of metallocene derivatives by their electron-donating effect and by steric shielding of the central atom.[1] The electron-donating effect leads to an increased electron density at the cyclopentadienyl ligand and, consequently, at the metal atom.[2] Experimentally, this is observed as a decreased ionization potential of both the dominantly Cp′ ($Cp' = C_5H_{5-n}Me_n$, $n = 0-5$) molecular orbitals and the dominantly metal orbitals.[3] UPS spectra of the titanocene dihalides Cp'_2TiX_2 and monohalides Cp'_2TiX (X = Cl, Br) show an approximately constant increase in energy of the π(Cp′) and d(Ti) orbitals per methyl group.[3e,f] The additivity of the effect of methylation on the ionization energies does not extend to the pentamethylcyclopentadienyl derivatives of the dihalide compounds,[3e] probably as a result of the larger CE−Ti−CE (CE = Cp ring centroid) angle affecting the orbital energies.[4] Structure data show that the difference in this angle between $(C_5HMe_4)_2TiCl_2$[5] and $(C_5Me_5)_2TiCl_2$[6] (4.0°) is larger than between the former and unsubstituted $(C_5H_5)_2TiCl_2$[7] (2.4°). In the Ti(III) series Cp'_2TiCl, the difference in the CE−Ti−CE angle between the C_5Me_5[8] and the C_5HMe_4[5] compound is 4.5°.[9] The molecular structures of $(C_5HMe_4)_2TiX_n$ ($n = 1$, X = Cl, I and $n = 2$, X = Cl) compounds show that the C_5HMe_4 ligands are staggered with the unsubstituted carbon atoms of each Cp ring in hinge positions.[5] With five instead of four methyl substituents on the Cp ring, steric repulsion between the methyl groups in hinge positions is relieved by opening up the Cp'_2Ti wedge, leading to the above-mentioned increase in the CE−Ti−CE angle.

The number of methyl substituents on the cyclopentadienyl rings of titanocene compounds has a profound effect on their reactivity. In the series Cp'_2TiX (X = Cl, Br, I), the number of methyl substituents determines whether the compound is monomeric or dimeric. The C_5H_5 and C_5H_4Me derivatives form dimers with bridging halide ligands, both in the solid state[10a] and in solution.[10b] In polar solvents they split to give monomeric solvates.[10c,11] Recently, the 1,3-dimethylcyclopentadienyl complex $[(C_5H_3Me_2)_2Ti(\mu\text{-}Cl)]_2$ was found to behave

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) (a) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1−11. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−56. (c) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839−6846.

(2) (a) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882−1893 and references therein. (b) Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* **1985**, *4*, 533−538.

(3) (a) Lichtenberger, D. L.; Kellogg, G. E. *Acc. Chem. Res.* **1987**, *20*, 379−387. (b) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433−6441. (c) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragala, I. L.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 61−73. (d) Condoreli, G.; Fragala, I. L.; Centineo, A.; Tondello, E. *J. Organomet. Chem.* **1975**, *87*, 311−315. (e) Vondrák, T.; Mach, K.; Varga, V. *J. Organomet. Chem.* **1989**, *367*, 69−76. (f) Vondrák, T.; Mach, K.; Varga, V. *Organometallics* **1992**, *11*, 2030−2034.

(4) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742.

(5) Troyanov, S. I.; Rybakov, V. B.; Thewalt, U.; Varga, V.; Mach, K. *J. Organomet. Chem.* **1993**, *447*, 221−225.

(6) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457−466.

(7) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622−1629.

(8) Pattiasina, J. W.; Heeres, H. J.; Van Bolhuis, F.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *Organometallics* **1987**, *6*, 1004−1010.

(9) Comparison of the CE−Ti−CE angles for bis(cyclopentadienyl)-derivatives Cp'_2TiCl ($Cp' = C_5H_{5-n}Me_n$) with various degrees of methyl substitution is hampered by the fact that for $n = 0$, 1 the compounds are dimers,[10a] thus adding the steric interaction between the two Cp'_2-Ti fragments as a new variable to determine the CE−Ti−CE angle.

(10) (a) Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645−1655. (b) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *47*, 375−382. (c) Samuel, E.; Vedel, J. *Organometallics* **1989**, *8*, 237−241. (d) Mach, K.; Varga, V.; Schmid, G.; Hiller, J.; Thewalt, U. *Collect. Czech. Chem. Commun.*, in press.

S0276-7333(96)00509-2 CCC: $12.00

analogously.[10d] The Cp'_2TiX compounds with $n = 3-5$ are monomeric.[5,8,11] Dimeric "titanocene", synthesized by reduction of $(C_5H_5)_2TiCl_2$ with $LiAlH_4$, contains two bridging hydrides and a bridging fulvalene ligand.[12] Similar compounds can be obtained for cyclopentadienyl ligands up to a maximum of three methyl substituents,[13] whereas for C_5HMe_4 two adjacent methyl groups are metalated and a new cyclopentadienyl-type ligand is formed, resulting in $\{\mu\text{-}\eta^3{:}\eta^4\text{-}C_5H(CH_3)_2(CH_2)_2\}\{(C_5HMe_4)Ti(\mu\text{-}H)\}_2$ with a bridging $\mu\text{-}\eta^3{:}\eta^4$-1,4-dimethyl-2,3-dimethylenecyclopentadienyl ligand.[14] For the pentamethylcyclopentadienyl derivatives $(C_5Me_5)_2TiR$, thermolysis ultimately gave analogous dimetalation of a cyclopentadienyl ligand, but here the monomeric compound $(C_5Me_5)(\eta^3{:}\eta^4\text{-}C_5(CH_3)_3(CH_2)_2)Ti$[15] with a trimethyl-1,2-dimethylenecyclopentadienyl ligand was obtained as the main product.[16]

In this article we compare reactivity differences of tervalent titanium compounds Cp'_2TiR (R = Me, Ph, H) in relation to the stabilizing cyclopentadienyl (C_5HMe_4 *vs* C_5Me_5) ligand system.

Results and Discussion

Thermolysis of $(C_5HMe_4)_2TiMe$ (2) and $(C_5HMe_4)_2TiPh$ (3). Compounds **2** and **3** were synthesized by salt metathesis reactions of $(C_5HMe_4)_2TiCl$ (**1**) with MeLi and PhMgBr, respectively, in analogy with the synthesis of $(C_5Me_5)_2TiR$ compounds.[17] The compounds are paramagnetic, which complicates NMR spectroscopic characterization. ^1H NMR spectroscopy shows two resonances for the ring methyl groups, one very broad signal at 48 ppm for **2** and at 40 ppm for **3** and a much narrower resonance (3.0 ppm (**2**) and 4.1 ppm (**3**)). The Ti−Me group of compound **2** appears at −26 ppm.[18] To facilitate identification, **2** and **3** were oxidized with $PbCl_2$,[19] yielding the diamagnetic $(C_5HMe_4)_2Ti(Me)Cl$ and $(C_5HMe_4)_2Ti(Ph)Cl$, respectively. Thermolysis of **2** or **3** in toluene at 130 °C led to formation of a green-brown crystalline compound, which is poorly soluble in organic solvents, thereby precluding proper characterization by NMR spectroscopy. Töpler pump experiments revealed that 1 equiv of CH_4/Ti is released during thermolysis of **2**. Evolution of benzene was observed during thermolysis of the phenyl complex **3** (GC). An X-ray crystal structure determination showed that the dimeric product $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (**4**) had been formed (eq 1), which is in marked contrast with the monomeric fulvene complex $(C_5Me_5)(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)Ti$, the product of the thermolysis of the pentamethylcyclopentadienyl analog $(C_5Me_5)_2TiMe$.[17,20]

$$\underset{\mathbf{2}}{2(C_5HMe_4)_2TiMe} \xrightarrow[-2CH_4]{\Delta} \underset{\mathbf{4}}{[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2} \quad (1)$$

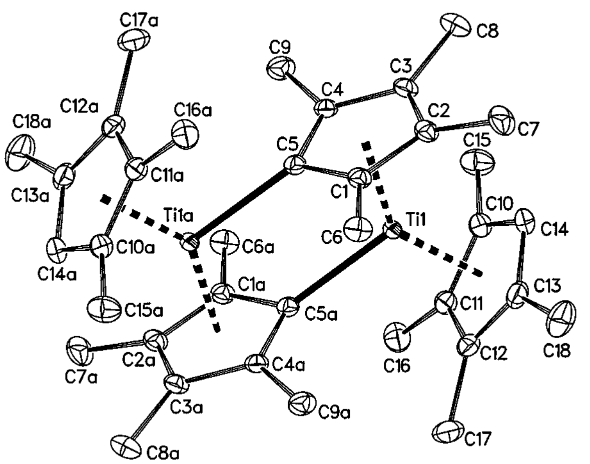

Figure 1. ORTEP drawing (50% probability level) and atom-labeling scheme for $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (**4**). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (4)

Ti1−C1	2.320(2)	Ti1−C10	2.360(2)
Ti1−C2	2.435(2)	Ti1−C11	2.431(2)
Ti1−C3	2.434(2)	Ti1−C12	2.430(2)
Ti1−C4	2.325(2)	Ti1−C13	2.365(2)
Ti1−C5	2.284(2)	Ti1−C14	2.311(2)
Ti1−CE1[a]	2.0231(9)	Ti1−CE2[a]	2.0515(9)
Ti1−C5a	2.193(2)		
Ti1−C5−Ti1a	104.62(8)	C5−Ti1−C5a	75.38(7)
CE1−Ti1−CE2	141.43(2)		

[a] CE1 = C1−C5 ring centroid; CE2 = C10−C14 ring centroid.

Molecular Structure of $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (4). The molecular structure of **4** is shown in Figure 1. Selected bond distances and angles are shown in Table 1 and details of the X-ray structure determination in Table 3. Compound **4** possesses a crystallographically imposed C_i symmetry. Each titanium atom is π-bonded to a C_5HMe_4 and a C_5Me_4Ti ligand and σ-bonded to a neighboring cyclopentadienyl to form a C_5Me_4Ti group.[21] In fact, the structure of each $(C_5HMe_4)(\eta^5\text{-}C_5Me_4)Ti(\eta^1\text{-}C_5Me_4)$ moiety is very similar to that of the monomeric $(C_5Me_5)_2TiR$ compounds.[17] In $(C_5Me_5)_2TiCH_2CMe_3$ the Ti−C σ-bond is 2.235(4) Å, which is comparable to the Ti−C σ-bond of 2.193(2) Å in **4**. The C_5HMe_4−Ti−C_5Me_4 angle is 141.43(2)°, which is only slightly larger than the CE−Ti−CE (CE = Cp ring centroid) angle of 139.4(3)° in $(C_5Me_5)_2TiCH_2CMe_3$. The Ti−CE distances of 2.0231(9) and 2.0515(9) Å for the C_5Me_4 and the C_5HMe_4 ligands, respectively, are also

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[11] Mach, K.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1992**, 683−688.

[12] (a) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182−6185. (b) Davison, A.; Wreford, S. S. *J. Am. Chem. Soc.* **1974**, *96*, 3017−3018. (c) Troyanov, S. I.; Antropiusová, H.; Mach, K. *J. Organomet. Chem.* **1992**, *427*, 48−55.

[13] The X-ray structure of $[\mu\text{-}C_{16}H_{20}][(C_5Me_3H_2)Ti(\mu\text{-}H)]_2$ derived from 1,2,3-trimethylcyclopentadienyl compounds has recently been determined. Varga, V.; Mach, K.; Polášek, M.; Sedmera, P.; Hiller, J.; Thewalt, U.; Troyanov, S. I. *J. Organomet. Chem.* **1996**, *506*, 241−251.

[14] Troyanov, S. I.; Mach, K.; Varga, V. *Organometallics* **1993**, *12*, 3387−3389.

[15] Pattiasina, J. W.; Hissink, C. E.; De Boer, J. L.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 7758−7759.

[16] Mach, K.; Varga, V.; Hanuš, V.; Sedmera, P. *J. Organomet. Chem.* **1991**, *415*, 87−95.

[17] Luinstra, G. A.; Ten Cate, L. C.; Heeres, H. J.; Pattiasina, J. W.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3227−3237.

[18] The resonances are integrated according to the expected intensities.

[19] Luinstra, G. A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1470−1471.

[20] Luinstra, G. A.; Teuben, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 3361−3367.

[21] A very similar structure has been obtained with $C_5H_2Me_3$ ligands instead of C_5HMe_4. $[(C_5H_2Me_3)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5HMe_3)Ti]_2$: $(C_{16}H_{21}Ti)_2$, M_r = 522.44, triclinic, $P\bar{1}$, a = 8.819(1) Å, b = 9.026(1) Å, c = 9.899(1) Å, α = 102.08(1)°, β = 101.866(9)°, γ = 113.353(8)°, V = 669.85(14) Å^3, Z = 1, D_{exptl} = 1.295 g cm^{-3}, λ(Mo K$\bar{\alpha}$) = 0.710 73 Å, μ = 6.1 cm^{-1}, T = 130 K, R_F = 0.039 for 2830 unique observed reflections with $I \geq 2.5\sigma(I)$ and 238 parameters. Mach, K.; Teuben, J. H.; Meetsma, A. Unpublished results.

in the range normally observed.[5] The ring slippage (0.129 Å, with the shortest Ti−C distance toward the unsubstituted carbon atom) of the C_5HMe_4 ligand has been observed for other $(C_5HMe_4)_2Ti$ complexes.[5] The bridging C_5Me_4 ligand displays a somewhat larger ring slippage (0.176 Å, with the shortest Ti−C distance toward the η^1-bonded carbon atom). The Ti−Ti distance (3.5430(6) Å) is significantly longer than the Ti−Ti distance in $(C_5H_5)_3(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)Ti_2(THF)$ (3.336(4) Å)[22] or in $[(C_5H_5)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)Ti(PMe_3)]_2$ (3.223(1) Å).[23] The η^5- and η^1-Ti−C bond lengths of these two complexes are comparable to those in **4**. Similar structures with μ-η^1:η^5-cyclopentadienyl ligands have been found for other metals, *e.g.* $[(C_5H_5)_2Th(\mu\text{-}C_5H_4)]_2$[24] and $[(C_5H_5)_2Nb(H)(\mu\text{-}C_5H_4)]_2$.[25]

Formation of $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (4) *vs* $(C_5Me_5)(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)Ti$. Both titanocene(III) methyl compounds $(C_5HMe_4)_2TiMe$ (**2**) and $(C_5Me_5)_2TiMe$ decompose upon heating, liberating 1 equiv of CH_4 per Ti. The resulting organometallic products are quite different: the dimeric $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (**4**) for $(C_5HMe_4)_2TiMe$ (**2**) *vs* the monomeric $(C_5Me_5)(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)Ti$ for $(C_5Me_5)_2TiMe$. Since arene C−H bonds (sp^2 hybridized) are more reactive than aliphatic C−H bonds (sp^3 hybridized),[26] it is not surprising that upon thermolysis of **2**, activation of an sp^2-hybridized ring C−H bond is preferred to activation of an sp^3-hybridized methyl C−H. However, thermolysis of $(C_5Me_5)_2TiR_n$ (n = 1, 2) compounds is known to proceed via complicated mechanisms such as the formation of a carbene intermediate during the thermolysis of $(C_5Me_5)_2TiMe_2$ to $(C_5Me_5)(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)TiMe$.[27] Another example is the thermolysis of $(C_5Me_5)_2TiR$ compounds to $(C_5Me_5)(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)Ti$, which is catalyzed by $(C_5Me_5)_2TiH$, formed during the reaction itself.[20] A similar autocatalytic mechanism, including the activation of the ring C−H bond, may well take place in the decomposition of **2** to **4**, but the actual thermolysis mechanism was not studied. An *intra*molecular activation of the ring C−H bond would lead to a highly constrained monomeric $(C_5HMe_4)(\eta^1{:}\eta^5\text{-}C_5Me_4)Ti$ compound, which is considered unlikely. Though the intermediacy of such a product cannot be excluded, the formation of stable dimeric **4** presumably occurs via *inter*molecular activation of ring C−H bonds, which allows the bridging η^1:η^5-C_5Me_4 ligands to retain their planar geometry.[28]

$(C_5HMe_4)_2TiH$ (5) and Reaction with N_2. Hydrogenolysis of $(C_5Me_5)_2TiR$ produces a monomeric titanium(III) hydride, $(C_5Me_5)_2TiH$.[27a,29] Recently the molecular structure of the first monomeric titanocene(III) hydride $(C_5PhMe_4)_2TiH$ has been determined.[30] These titanocene(III) hydrides are intriguing compounds, because of their key role in the "titanocene enigma" and their activity as catalysts for many organic reactions.[30]

Upon hydrogenolysis of $(C_5HMe_4)_2TiR$ (R = Me (**2**), R = Ph (**3**)), the green solution turned red-brown, characteristic for formation of titanocene(III) hydride $(C_5HMe_4)_2TiH$ (**5**). Töpler pump analysis of the gas formed on reaction of **2** with D_2 revealed that 1 equiv of CH_3D/Ti had been liberated. Surprisingly, as soon as N_2 was admitted to a solution of **5**, a blue precipitate formed, which prevented isolation and characterization of the pure hydride.[31] However, the close similarity between the NMR (broad resonances for the methyl substituents of the C_5HMe_4 ligands are at 46.4 and 9.6 ppm; no resonances for the hydride proton or the ring protons are observed) and ESR (singlet at g = 1.9789, with a(Ti) = 9.3 G) solution spectra of the red-brown **5** with those of $(C_5Me_5)_2TiH$[29a] and $(C_5PhMe_4)_2TiH$[30] reliably allows identification as $(C_5HMe_4)_2TiH$. Additional proof was obtained from reactivity studies. When 1,3-butadiene was admitted to a solution of **5**, purple $(C_5HMe_4)_2Ti(\eta^3\text{-}$1-methylallyl) (**7**) was formed exclusively, indicating that **5** behaves as a regular titanocene(III) hydride.[32] In analogy to $(C_5Me_5)_2TiH$[29a] and $(C_5PhMe_4)_2TiH$,[30] oxidation of **5** with $PbCl_2$[19] yielded the diamagnetic $(C_5HMe_4)_2Ti(H)Cl$ (**6**), in which the hydride resonance appears at 4.10 ppm in the ^1H NMR spectrum. The hydride **5** is not as stable as the corresponding hydrides of $(C_5Me_5)_2TiH$ and $(C_5PhMe_4)_2TiH$, because at room temperature crystalline **4** slowly separates from solutions of **5**, accompanied by liberation of H_2.

It is remarkable that **5** immediately reacts with even traces of N_2 at room temperature, whereas $(C_5Me_5)_2TiH$[29a] and $(C_5PhMe_4)_2TiH$[30] appear to be completely indifferent toward N_2 at room temperature, even under 1 atm of N_2. The dramatic color change from red-brown to blue upon exposure of a solution of **5** to N_2 gas, followed by the separation of shiny metal-luster crystals, suggests the formation of the dinitrogen complex $[(C_5HMe_4)_2TiH]_2N_2$, like their regular cyclopentadienyl analogs $(Cp_2TiR)_2N_2$.[33] However, formation of H_2 during complexation of N_2 indicates a more complicated reaction sequence. An X-ray structure determination of the product showed that instead of the dinuclear titanocene(III) dinitrogen complex $[(C_5HMe_4)_2TiH]_2N_2$ the dinitrogen complex of titanocene(II) $[(C_5HMe_4)_2Ti]_2N_2$ (**8**) had been formed.

Molecular Structure of $[(C_5HMe_4)_2Ti]_2N_2$ (8). The molecular structure of **8** is shown in Figure 2, and selected bond distances and angles and details of the

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(22) Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072−8078.

(23) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Honold, B. *J. Organomet. Chem.* **1986**, *310*, 27−34.

(24) Baker, E. C.; Raymond, K. N.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 7586−7588.

(25) Guggenberger, L. J. *Inorg. Chem.* **1973**, *12*, 294−301.

(26) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203−219.

(27) (a) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219−1238. (b) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046−2048. (c) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629−1634.

(28) The situation is different for the thermolysis of the titanocene(IV) dimethyl compound $(C_5HMe_4)_2TiMe_2$,[16] which decomposes to the monomeric fulvene compound $(C_5HMe_4)(C_5HMe_3CH_2)TiMe$. Titanium in $(C_5HMe_4)_2TiMe_2$ is surrounded by four ligands instead of three, which sterically prevent *inter*molecular activation of ring C−H bonds. Instead, *intra*molecular activation of a less reactive methyl C−H bond occurs, so that a monomeric fulvene compound is isolated, similar to the decomposition of $(C_5Me_5)_2TiMe_2$ to $(C_5Me_5)(C_5Me_4CH_2)TiMe$.[26]

(29) (a) Teuben, J. H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; Reidel: Dordrecht, The Netherlands, 1985; pp 195−227. (b) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087−5094.

(30) De Wolf, J. M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1995**, *14*, 5466−5468 and references therein.

(31) Even under Ar, formation of an intensely blue solution was observed. Apparently traces of N_2 are sufficient to set off the disproportionation of **5** and form the dinitrogen complex $[(C_5HMe_4)_2Ti]_2N_2$ (**8**).

(32) (a) Mach, K.; Antropiusová, H.; Varga, V.; Hanuš, V. *J. Organomet. Chem.* **1988**, *358*, 123−133. (b) Gao, Y.; Iijima, S.; Urabe, H.; Sato, F. *Inorg. Chim. Acta* **1994**, *222*, 145−153.

(33) (a) Teuben, J. H.; De Liefde Meijer, H. J. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 360−363. (b) Zeinstra, J. D.; Teuben, J. H.; Jellinek, F. *J. Organomet. Chem.* **1979**, *170*, 39−50.

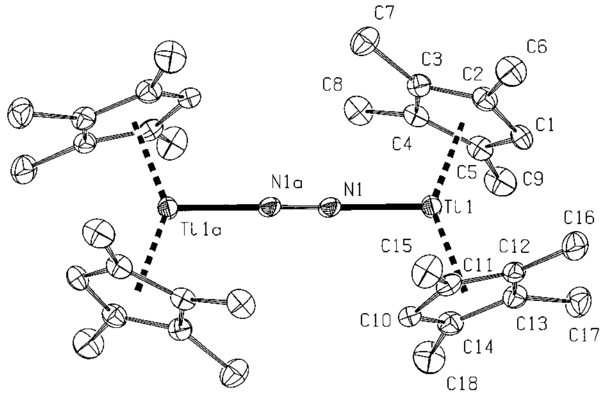

Figure 2. ORTEP drawing (50% probability level) and atom-labeling scheme for $[(C_5HMe_4)_2Ti]_2N_2$ (**8**). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[(C_5HMe_4)_2Ti]_2N_2$ (8)

Ti1−N1	1.987(3)	N1−N1a	1.170(4)
Ti1−CE1[a]	2.0338(6)	Ti1−CE2[a]	2.0348(7)
Ti1−C1	2.327(3)	Ti1−C10	2.312(4)
Ti1−C2	2.355(3)	Ti1−C11	2.360(3)
Ti1−C3	2.388(3)	Ti1−C12	2.397(3)
Ti1−C4	2.394(3)	Ti1−C13	2.399(3)
Ti1−C5	2.356(4)	Ti1−C14	2.342(4)
Ti1−N1−N1a	178.5(3)	CE1−Ti1−CE2	140.99(3)
N1−Ti1−CE1	108.11(9)	N1−Ti1−CE2	110.33(9)

[a] CE1 = C1−C5 ring centroid; CE2 = C10−C14 ring centroid.

Table 3. Details of the X-ray Structure Determinations of $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (4) and $[(C_5HMe_4)_2Ti]_2N_2$ (8)

	$C_{36}H_{50}Ti_2$ (**4**)	$C_{36}H_{52}N_2Ti_2$ (**8**)
mol wt	578.55	608.58
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	8.583(1)	8.4661(9)
b, Å	9.249(1)	10.3254(12)
c, Å	11.085(1)	20.3205(17)
α, deg	68.766(6)	
β, deg	88.553(6)	114.541(8)
γ, deg	69.285(4)	
V, Å	761.9(2)	1615.9(3)
Z	1	2
D_{calcd}, g cm^{-3}	1.261	1.251
F(000), e	310	652
μ(Mo K$\bar{\alpha}$), cm^{-1}	5.4	5.1
cryst size, mm	0.25 × 0.37 × 0.50	0.25 × 0.25 × 0.25
radiation, Å	Mo K$\bar{\alpha}$, 0.710 73	Mo K$\bar{\alpha}$, 0.710 73
monochromator	graphite	graphite
temp, K	130	150
total no. of data	3920	6191
no. of unique data	3678	3712
no. of obsd data ($I \geq 2.5\sigma(I)$)	3397	2296
no. of refined params	273	214
R_F[a]	0.029	0.053
R_w[b]	0.039	0.054
w	1	$1/[\sigma^2(F) + 0.000413F^2]$
S[c]	0.625	1.32
residual density, e Å^{-3}	−0.33, 0.35	−0.51, 0.48

[a] $R_F = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma(w(|F_o| - |F_c|)^2)/\Sigma w|F_o|^2]^{1/2}$. [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$; *m* = number of observations, *n* = number of variables.

X-ray structure determination are shown in Tables 2 and 3. Compound **8** is a dinuclear complex, in which two $(C_5HMe_4)_2Ti$ moieties are bridged by N_2 in an essentially linear arrangement. It is a centrosymmetric molecule with the center of inversion in the middle of the N−N bond. No hydride ligands are present. The CE(1)−Ti−CE(2) angle of 140.99(3)° and the CE(1)−Ti−N(1) and CE(2)−Ti−N(1) angles of 108.11(9) and 110.33(9)° add up to 359.4°, which illustrates a planar triangular coordination around titanium. The distance between the nitrogen atoms is 1.170(4) Å, which compares well with the N−N distances in $[(C_5Me_5)_2Ti]_2N_2$ (1.160(14) Å)[34] and $[(C_5H_5)_2Ti(4\text{-}CH_3C_6H_4)]_2N_2$ (1.162(12) Å).[33b] The Ti−N distance of 1.987(3) Å is between those found for $[(C_5Me_5)_2Ti]_2N_2$ (2.017(12) Å) and $[(C_5H_5)_2Ti(4\text{-}CH_3C_6H_4)]_2N_2$ (1.962(6) Å). The Ti−N−N−Ti skeleton is almost linear (Ti(1)−N(1)−N(2) = 178.5(3)°), as in $[(C_5Me_5)_2Ti]_2N_2$ (177.4(4)°) and $[(C_5H_5)_2Ti(4\text{-}CH_3C_6H_4)]_2N_2$ (176.5(5)°). Within each $(C_5HMe_4)_2Ti$ unit a staggered conformation is adopted with the sp^2 C−H bond of one C_5HMe_4 ligand pointing between two methyl groups of the other. Other dinuclear $(C_5HMe_4)_2Ti$ complexes display the same orientation of the C_5HMe_4 ligands.[35] In mononuclear $(C_5HMe_4)_2Ti$ complexes such as $(C_5HMe_4)_2TiCl$ and $(C_5HMe_4)_2TiCl_2$[5] the ligands are staggered too, but with the sp^2 C-H bonds of each C_5HMe_4 ligand pointing toward each other, thereby minimizing the steric hindrance between the ligands. In dinuclear $(C_5HMe_4)_2Ti$ complexes such as **8**, such an orientation would produce more steric hindrance between the methyl substituents of the two different $(C_5HMe_4)_2Ti$ moieties on each side of the bridging N_2 ligand.

Reduction of $(C_5HMe_4)_2TiH$ (5) to $[(C_5HMe_4)_2Ti]_2N_2$ (8). Surprisingly, the Ti(III) hydride **5** is reduced to the dinuclear Ti(II) N_2 complex $[(C_5HMe_4)_2Ti]_2N_2$ (**8**) upon reaction with N_2, under liberation of H_2 (eq 2).

$$\underset{\mathbf{5}}{2(C_5HMe_4)_2TiH} \xrightarrow[-H_2]{N_2} \underset{\mathbf{8}}{[(C_5HMe_4)_2Ti]_2N_2} \qquad (2)$$

The question arises how titanium is reduced from the 3+ to the 2+ oxidation state. Most likely, equilibria are involved in which the Ti(III) hydride **5** disproportionates to the Ti(IV) dihydride $(C_5HMe_4)_2TiH_2$ (**9**) and a Ti(II) compound, $(C_5HMe_4)_2Ti$ (**10**) (eq 3). The dihydride **9** can lose dihydrogen in a subsequent equilibrium reaction to form the titanocene **10** (eq 4). Such equilibria have been proposed by Bercaw to explain the decomposition of $(C_5Me_5)_2TiH_2$.[29b]

$$\underset{\mathbf{5}}{2(C_5HMe_4)_2TiH} \rightleftharpoons \underset{\mathbf{9}}{(C_5HMe_4)_2TiH_2} + \underset{\mathbf{10}}{(C_5HMe_4)_2Ti} \qquad (3)$$

$$\underset{\mathbf{9}}{(C_5HMe_4)_2TiH_2} \xrightleftharpoons{-H_2} \underset{\mathbf{10}}{(C_5HMe_4)_2Ti} \qquad (4)$$

Next, the titanocene **10** reacts with N_2 to form the dinuclear N_2 complex $[(C_5HMe_4)_2Ti]_2N_2$ (**8**) (eq 5). Because of the consumption of **10** by reaction with N_2, the equilibria 3 and 4 are shifted to the right and eventually all Ti(III) hydride **5** is converted into **8**.

The reactivity of $(C_5HMe_4)_2TiH$ (**5**) is in contrast with the related Ti(III) hydrides $(C_5Me_5)_2TiH$ and $(C_5PhMe_4)_2$-

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[34] Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 8358−8365.

[35] (a) Gyepes, R.; Mach, K.; Císarová, I.; Loub, J.; Hiller, J.; Šindelář, P. *J. Organomet. Chem.* **1995**, *497*, 33−41. (b) Troyanov, S. I.; Varga, V.; Mach, K. *J. Organomet. Chem.* **1993**, *461*, 85−90.

$$2\underset{\mathbf{10}}{(C_5HMe_4)_2Ti} \xrightarrow{N_2} \underset{\mathbf{8}}{[(C_5HMe_4)_2Ti]_2N_2} \qquad (5)$$

TiH, which are stable under N_2 at room temperature. Unlike the formation of thermolysis product **4**, the difference in reactivity between **5** on one side and $(C_5Me_5)_2TiH$ and $(C_5PhMe_4)_2TiH$ on the other cannot be explained by the availability of sp^2 C−H bonds of the C_5HMe_4 ligands, as it is unlikely that they are involved in the reduction of **5** to **8**. Since $[(C_5Me_5)_2Ti]_2N_2$,[34] which is the pentamethylcyclopentadienyl analog of **8**, exists as well, the slightly reduced steric bulk of C_5HMe_4 ligands with respect to C_5Me_5 ligands is unlikely to be responsible either. The reason for the different reactivity seems to be electronic. The electron-donating capacity of tetramethylcyclopentadienyl ligands to the titanium(III) center is less than that of pentamethylcyclopentadienyl ligands, which probably causes **5** to be more susceptible to reduction than $(C_5Me_5)_2TiH$ and $(C_5PhMe_4)_2TiH$.

When a toluene suspension of **8** was stirred under a dynamic vacuum to remove N_2, the blue color disappeared and a brown solution resulted, from which a brown waxy residue was obtained. Admission of N_2 to the brown solution restored **8** quantitatively. The brown product showed no reaction with 1,3-butadiene; therefore, it cannot be hydride **5**.[32a] In analogy with the formation of $(C_5Me_5)_2Ti$ upon degassing $[(C_5Me_5)_2Ti]_2N_2$,[29b] this compound was tentatively identified as titanocene $(C_5HMe_4)_2Ti$ (**10**). Admission of H_2 to solutions of **10** resulted in formation of hydride **5**. Presumably the titanocene **10** reacts with H_2 to give the titanocene(IV) dihydride $(C_5HMe_4)_2TiH_2$ (**9**). Compounds **9** and **10** then subsequently conproportionate to the monohydride **5** (eq 3).

Conclusions

Comparison of bis(cyclopentadienyl)titanium(III) compounds $(C_5HMe_4)_2TiR$ and their permethylcyclopentadienyl analogs $(C_5Me_5)_2TiR$ shows that replacement of one methyl group of the pentamethylcyclopentadienyl ligands by hydrogen has a dramatic effect on the reactivity, as follows from a study of the thermolysis of $(C_5HMe_4)_2TiR$ compounds and the reactivity of the hydride toward N_2. The formation of the dimeric thermolysis product $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (**4**) can be explained by the presence of one sp^2 C−H bond in the tetramethylcyclopentadienyl ligand, which opens up another metalation pattern than in the corresponding pentamethylcyclopentadienyl compounds, in which only sp^3 C−H bonds are available. The difference in the reactivity toward N_2 of hydride $(C_5HMe_4)_2TiH$ (**5**), yielding $[(C_5HMe_4)_2Ti]_2N_2$ (**8**), on one side and homologous hydrides $(C_5Me_5)_2TiH$ and $(C_5PhMe_4)_2TiH$ on the other, is ascribed to a subtle variation of electronic properties induced by these ligands, resulting in a slightly higher Lewis acidity of the metal center in hydride **5**.

Experimental Section

General Comments. All manipulations of air-sensitive compounds were carried out under N_2, using standard Schlenk-line and glovebox or vacuum-line techniques. All solvents were distilled from Na/K alloy or $LiAlH_4$ prior to use. Tetramethylcyclopentadiene[36] and $TiCl_3{\cdot}3THF$[37] were prepared according to published procedures. The synthesis of $(C_5HMe_4)MgCl$ was derived from that of $(C_5Me_5)MgCl$.[8] H_2 (99.995%, Hoek-Loos) was used without further purification.

Synthesis of $(C_5HMe_4)_2TiCl_2$.[38] A mixture of $TiCl_3{\cdot}3THF$ (15.9 g, 42.8 mmol) and $(C_5HMe_4)MgCl$ (21.7 g, 86.0 mmol) in 300 mL of THF was stirred at room temperature for 46 h. A dark brown solution formed, from which the solvent was removed by evaporation. The residue was continuously extracted with pentane. The purple-brown extract was concentrated to saturation and cooled to −30 °C. Dark purple needles of crude **1** separated, which were isolated after washing with pentane. Oxidation of crude **1** with excess $PbCl_2$[19] in THF yielded a red solution, which was filtered, saturated, and cooled to −80 °C. Pure $(C_5HMe_4)_2TiCl_2$ was isolated as red-brown needles. Yield: 9.25 g, 60% relative to $TiCl_3{\cdot}3THF$. ^1H NMR (200 MHz, C_6D_6): δ 5.37 (s, 2H, $C_5\mathit{H}Me_4$), 2.06, 1.65 (s, 12H, $C_5H\mathit{Me}_2Me_2$).

Synthesis of $(C_5HMe_4)_2TiCl$ (1).[5] Compound **1** was made by reduction[39] of $(C_5HMe_4)_2TiCl_2$. To a suspension of $(C_5HMe_4)_2TiCl_2$ (1.51 g, 4.18 mmol) in 30 mL of diethyl ether were added 0.4 mL of 1,4-dioxane (4.7 mmol) and 3.4 mL of a solution of ^iPrMgCl in diethyl ether (1.23 M, 4.2 mmol). After this mixture was stirred for 2 h, a blue solution had formed. The volatiles were removed by evaporation, and the residue was extracted with pentane. Concentration and cooling to −80 °C afforded 1.23 g (90%) of **1** as dark blue needles. ^1H NMR (200 MHz, C_6D_6): δ 43 (s, 12 H, $C_5H\mathit{Me_2Me_2}$, WHM (peak width at half maximum height) = 2.75 kHz), 0.3 (s, 12H, $C_5HMe_2\mathit{Me}_2$, WHM = 160 Hz). IR (KBr/Nujol, cm^{-1}): 3086 (w), 2724 (w), 1500 (w), 1024 (s), 858 (s), 440 (s).

Synthesis of $(C_5HMe_4)_2TiMe$ (2). To 1.24 g of **1** (3.81 mmol) dissolved in 30 mL of diethyl ether was added 2.3 mL of a solution of MeLi in diethyl ether (1.64 M, 3.8 mmol). After it was stirred for 1 h, the reaction mixture had turned dark green. It was evaporated to dryness, and the residue was extracted with pentane. Evaporation of solvent gave 0.92 g of **2** (79%) as a green powder. ^1H NMR (200 MHz, toluene-d_8): δ 48 (s, 12 H, $C_5H\mathit{Me_2Me_2}$, WHM = 3.50 kHz), 3.0 (s, 12 H, $C_5HMe_2\mathit{Me}_2$, WHM = 115 Hz), −26 (s, 3 H, TiMe, WHM = 1.19 kHz). IR (KBr/Nujol, cm^{-1}): 3081 (w), 2724 (w), 1501 (w), 1024 (s), 835 (s), 692 (s), 606 (s), 432 (m). UV/vis (toluene, nm): 313, 350 (sh), 450, 585. ESR (toluene, 23 °C): g_{iso} = 1.9637, ΔH = 14 G. ESR (toluene, −130 °C): g_1 = 1.9983, g_2 = 1.9831, g_3 = 1.9137, g_{av} = 1.9650. ESR (MTHF, 23 °C): g_{iso} = 1.9633, ΔH = 17 G. ESR (MTHF, −150 °C): g_1 = 1.9982, g_2 = 1.9822, g_3 = 1.9153, g_{av} = 1.9652. Oxidation of **2** with $PbCl_2$[19] in diethyl ether quantitatively yielded red $(C_5HMe_4)_2Ti(Me)Cl$. ^1H NMR (200 MHz, C_6D_6): δ 4.79 (s, 2H, $C_5\mathit{H}Me_4$), 2.11, 1.99, 1.74, 1.42 (s, 6H, $C_5H\mathit{Me}_4$), 0.21 (s, 3H, TiMe).

Synthesis of $(C_5HMe_4)_2TiPh$ (3). A 1.26 g amount of $(C_5HMe_4)_2TiCl_2$ (3.50 mmol) was reduced to **1** (*vide supra*). To the diethyl ether suspension of **1** was added 3.8 mL of a diethyl ether solution of PhMgBr (1.0 M, 3.8 mmol), after which the reaction mixture was stirred for 1 h. A dark green solution had formed. The solvent was removed by evaporation, and the residue was extracted with pentane. Concentration and cooling to −80 °C gave two crops of dark green crystals. Yield: 1.21 g of **3** (94%). ^1H NMR (200 MHz, toluene-d_8): δ 40 (s, 12H, $C_5H\mathit{Me}_2Me_2$, WHM = 5.2 kHz), 23 (s, 2 H, H_{ortho}, WHM = 1.8 kHz), 13.6 (s, 1 H, H_{para}, WHM = 240 Hz), 4.1 (s, 12 H, $C_5HMe_2\mathit{Me}_2$, WHM = 200 Hz), −1.0 (m, 2H, H_{meta}, WHM = 230 Hz). IR (KBr/Nujol, cm^{-1}): 3042 (w), 2726 (w), 2361

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[36] (a) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828−1838. (b) Szymoniak, J.; Besançon, J.; Dormond, A.; Moïse, C. *J. Org. Chem.* **1990**, *55*, 1429−1432.

[37] Manzer, L. E.; Deaton, J.; Sharp, P.; Schrock, R. R. *Inorg. Synth.* **1982**, *21*, 137.

[38] Mach, K.; Varga, V.; Antropiusová, H.; Polácek, J. *J. Organomet. Chem.* **1987**, *333*, 205−215.

[39] (a) Direct synthesis of **1** via reaction of $TiCl_3{\cdot}3THF$ with $(C_5HMe_4)MgCl$ led to contamination of **1** with $(C_5HMe_4)_2TiCl_2$. (b) Martin, H. A.; Jellinek, F. *J. Organomet. Chem.* **1967**, *8*, 115−128.

(w), 1562 (w), 1412 (w), 1233 (w), 1173 (w), 1150 (w), 1113 (w), 1049 (w), 1022 (s), 824 (vs), 721 (vs), 704 (vs), 610 (m), 473 (s), 428 (s). Oxidation with $PbCl_2$[19] quantitatively yielded red $(C_5HMe_4)_2Ti(Ph)Cl$. ^1H NMR (200 MHz, toluene-d_8): δ 7.36 (d, 1H, H_{ortho}, $J = 6.4$ Hz), 7.01 (m, 2H, H_{meta}), 6.90 (m, 1H, H_{para}), 6.20 (d, 1H, H_{ortho}), 4.95 (s, 2H, C_5HMe_4), 1.94, 1.75, 1.62, 1.52 (s, 6H, C_5HMe_4).

Synthesis of $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (4) by Thermolysis of $(C_5HMe_4)_2TiMe$ (2). A solution of **2** (1.23 g, 4.03 mmol) in 20 mL of toluene in a sealed ampule was heated to 130 °C for 4 h. The green-brown solution was cooled to room temperature slowly, and dark green-brown crystals separated, which were isolated and washed with pentane. Yield: 0.78 g of **4** (67%). MS (75 eV, *m/e*): 578 (M^+). UV/vis (toluene, nm): 295, 360 (sh), 435, 525, 610 (sh). Anal. Calcd for $C_{36}H_{50}Ti_2$: C, 74.74; H, 8.71; Ti, 16.55. Found: C, 74.65; H, 8.67; Ti, 16.63. In an identical manner **4** was synthesized by thermolysis of **3**; GC analysis showed the formation of benzene during the thermolysis. The thermolysis product **4** was also synthesized by removing H_2 (MS analysis) from a solution of hydride **5** in hexane under a dynamic vacuum.

Thermolysis of $(C_5HMe_4)_2TiMe$ (2): Gas Analysis. On a vacuum line a solution of 0.069 g of **2** (0.226 mmol) in 5 mL of toluene was heated to 130 °C for 4 h. The amount of liberated gas was measured using a Töpler pump: 0.224 mmol (0.99 mol/mol of Ti). It was analyzed as methane (MS).

X-ray Structure Determination of $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (4). Single crystals of **4** were grown by slow cooling of a hot toluene solution of **4**. A green-brown parallelepiped crystal was selected, glued on a glass fiber in a drybox, transferred to the goniostat, and cooled to 130 K using an on-line liquid nitrogen cooling system mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer. Unit cell parameters were determined from a least-squares treatment of the setting angles of 22 reflections in the range $13.18° < \theta < 18.88°$ in four alternate settings.[40] A search of a limited hemisphere of reciprocal space yielded a set of reflections that showed no evidence of symmetry or systematic extinction. The unit cell was identified as triclinic, space group $P\bar{1}$. This choice was confirmed by the solution and the successful refinement in this space group of the structure. Reduced cell calculations did not indicate any higher metrical lattice symmetry,[41] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[42] The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86[43]). The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (XTAL[44]), minimizing the function $Q = \sum_h[w|F_o| - |F_c|)^2]$. A subsequent difference Fourier synthesis gave all the hydrogen atoms, whose coordinates and isotropic thermal parameters were refined. Final full-matrix least-squares refinement (based on F_o) with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged at $R_F = 0.029$ ($R_w = 0.039$, $w = 1$). The crystal exhibited some secondary extinction, for which the F values were corrected by refinement of an empirical isotropic extinction parameter.[45] A final difference Fourier map did not show residual peaks outside the range ±0.35 e/Å^3. Scattering factors were taken from Cromer and Mann.[46] Anomalous dispersion factors taken from Cromer and Liberman[47] were included in F_c. All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL,[48] EUCLID[49] (calculation of geometric data), and ORTEP[50] (preparation of illustrations).

Synthesis of $(C_5HMe_4)_2TiH$ (5). A 0.83 g portion of $(C_5HMe_4)_2TiPh$ (**3**; 2.26 mmol) was dissolved in pentane and degassed thoroughly by several freeze/pump/thaw cycles. H_2 was admitted to the frozen solution, which was warmed to room temperature with stirring. The color of the solution changed to red-brown. It proved impossible to isolate pure **5** from this solution, since it reacted immediately with the slightest trace of N_2 and small crystals of **4** separated as well. ^1H NMR (200 MHz, C_6D_6): δ 46.4 (s, 12 H, $C_5HMe_2Me_2$, WHM = 1.68 kHz), 9.6 (s, 12 H, $C_5HMe_2Me_2$, WHM = 160 Hz). ESR (toluene): $g = 1.9789$, $\Delta H = 5$ G, a(Ti) = 9.3 G. In an identical manner **5** was synthesized by hydrogenolysis of **2**.

Synthesis of $(C_5HMe_4)_2Ti(H)Cl$ (6). Excess $PbCl_2$[19] was added to a C_6D_6 solution of 30 mg of **5**. After filtration a red-brown solution of $(C_5HMe_4)_2Ti(H)Cl$ (**6**) was obtained. ^1H NMR (200 MHz, C_6D_6): δ 4.68 (s, 2H, C_5HMe_4), 4.10 (s, 1H, Ti*H*), 2.19, 2.09, 1.77, 1.74 (s, 6H, C_5HMe_4).

Reaction of $(C_5HMe_4)_2TiMe$ (2) with D_2: Gas Analysis. A solution of 0.114 g of **2** (0.374 mmol) in pentane was degassed by three freeze/pump/thaw cycles. A 0.692 mmol amount of D_2 was admitted to the solution, yielding a red-brown solution. The amount of liberated gas and excess of D_2 were measured using a Töpler pump (0.710 mmol). The gas mixture was cycled over a CuO column at 300 °C in order to burn D_2. D_2O was collected in a trap cooled with liquid nitrogen, leaving 0.391 mmol of gas (1.05 mol/mol of Ti), which was analyzed as CH_3D (MS).

Reaction of $(C_5HMe_4)_2TiH$ (5) with 1,3-Butadiene: Synthesis of $(C_5HMe_4)_2Ti(\eta^3\text{-1-methylallyl})$ (7). To a stirred solution of 0.87 g of **5** (3.0 mmol) in 20 mL of hexane was admitted 1,3-butadiene. The red-brown solution turned intensely purple immediately. After evaporation of the solvent a purple solid was isolated, which was characterized spectroscopically as $(C_5HMe_4)_2Ti(\eta^3\text{-1-methylallyl})$ (**7**).[32a] Yield: 0.96 g (93%).

Synthesis of $[(C_5HMe_4)_2Ti]_2N_2$ (8). To a degassed solution of 1.00 g of **2** (3.28 mmol) in 20 mL of pentane was admitted H_2. The solution was stirred for 2 h, during which time the H_2 atmosphere was refreshed several times. A red-brown solution of **5** had formed, which was cooled to 0 °C. N_2 was allowed to slowly diffuse into the solution. Beautiful shiny metal-luster crystals formed, which were isolated from the dark blue solution by filtration and washed with pentane. Yield: 0.73 g of **8** (73%). UV/vis (toluene, nm): 310 (sh), 350 (sh), 592. Anal. Calcd for $C_{36}H_{52}N_2Ti_2$: C, 71.04; H, 8.61; N, 4.60; Ti, 15.74. Found: C, 70.94; H, 8.65; N, 4.43; Ti, 15.62.

X-ray Structure Determination of $[(C_5HMe_4)_2Ti]_2N_2$ (8). Suitable single crystals of **8** were grown by slow diffusion of N_2 into a pentane solution of **5**. A crystal sealed in a Lindemann-glass capillary was mounted on an Enraf-Nonius CAD4-T diffractometer on a rotating anode and was held under a cold nitrogen stream. Accurate unit-cell parameters and an orientation matrix were determined from the setting angles of 25 well-centered reflections (SET4)[40] in the range $10.0° < \theta < 14.0°$. The unit-cell parameters were checked for the presence of higher lattice symmetry.[41] Data were corrected for Lp effects. Standard deviations of the intensities as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: σ^2-

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(40) De Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410.

(41) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578−579.

(42) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264−269.

(43) Sheldrick G. M. SHELXS86, Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1986.

(44) Olthof-Hazekamp, R. In "CRYLSQ", XTAL2.6 User's Manual; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1989.

(45) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558−564.

(46) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321−324.

(47) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891−1898.

(48) Hall, S. R.; Stewart, J. M. XTAL2.6 User's Manual; Universities of Western Australia and Maryland, 1989.

(49) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, D., Ed.; Oxford University Press (Clarendon): London, New York, 1982; p 528.

(50) Johnson, C. K. ORTEP; Report ORNL-3794; Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

$(I) = \sigma_{cs}(I) + (pI)^2$, with $p = 0.01$.[51] An empirical absorption/extinction correction was applied (DIFABS[52]). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).[53] Refinement on F was carried out by full-matrix least-squares techniques (SHELX76[54]). Hydrogen atoms (except the Cp-ring hydrogens) were included in the refinement on calculated positions (C−H = 0.98 Å), riding on their carrier atoms. Weights were optimized in the final refinement cycles. The final difference map was inspected for possible hydride atoms. The largest peaks are within 1.5 Å from Ti but were rejected, being artifacts. Neutral atom scattering factors were taken from Cromer and Mann[46] and anomalous dispersion corrections from Cromer and Liberman.[47] Geometrical calculations and the ORTEP illustrations were done with PLATON.[49]

Acknowledgment. This work was supported in part (N.V. and A.L.S.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Foundation for Scientific Research (NWO).

Supporting Information Available: Further details of the structure determinations, including tables of atomic coordinates, bond lengths and angles, and thermal parameters for **4** and **8** (20 pages). Ordering information is given on any current masthead page.

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(51) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245−249.

(52) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.

(53) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System, Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.

(54) Sheldrick, G. M. SHELX76, Program for Crystal Structure Determination; University of Cambridge, Cambridge, U.K., 1976.