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Bis(tetramethylcyclopentadienyl)titanium Chemistry. Molecular Structures of $[(C_5HMe_4)(m-h^1:h^5-C_5Me_4)Ti]_2$ and $[(C_5HMe_4)_2Ti]_2N_2$

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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 $[(C_5HMe_4)(m-h^1:h^5-C_5Me_4)Ti]_2$ (**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 $p(Cp')$ 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 $[(C_5H_3Me_2)_2Ti(m-Cl)]_2$ was found to behave

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(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) Caultletti, 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) Condoireli, 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'_2Ti 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.

analogously.^{10d} The Cp₂TiX compounds with $n = 3-5$ are monomeric.^{5,8,11} Dimeric "titanocene", synthesized by reduction of (C₅H₅)₂TiCl₂ with LiAlH₄, 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 C₅HMe₄ two adjacent methyl groups are metalated and a new cyclopentadienyl-type ligand is formed, resulting in {*m*-h³:h⁴-C₅H(CH₃)₂(CH₂)₂}{(C₅-HMe₄)Ti(*m*-H)}₂ with a bridging *m*-h³:h⁴-1,4-dimethyl-2,3-dimethylenecyclopentadienyl ligand.¹⁴ For the pentamethylcyclopentadienyl derivatives (C₅Me₅)₂TiR, thermolysis ultimately gave analogous dimetalation of a cyclopentadienyl ligand, but here the monomeric compound (C₅Me₅)(h³:h⁴-C₅(CH₃)₃(CH₂)₂)Ti¹⁵ with a trimethyl-1,2-dimethylenecyclopentadienyl ligand was obtained as the main product.¹⁶

In this article we compare reactivity differences of trivalent titanium compounds Cp₂TiR (R = Me, Ph, H) in relation to the stabilizing cyclopentadienyl (C₅HMe₄ vs C₅Me₅) ligand system.

Results and Discussion

Thermolysis of (C₅HMe₄)₂TiMe (2) and (C₅HMe₄)₂-TiPh (3). Compounds **2** and **3** were synthesized by salt metathesis reactions of (C₅HMe₄)₂TiCl (**1**) with MeLi and PhMgBr, respectively, in analogy with the synthesis of (C₅Me₅)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 PbCl₂,¹⁹ yielding the diamagnetic (C₅HMe₄)₂Ti(Me)Cl and (C₅HMe₄)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 CH₄/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 [(C₅HMe₄)(*m*-h¹:h⁵-C₅Me₄)Ti]₂ (**4**) had been formed (eq 1), which is in marked contrast with the monomeric fulvene complex (C₅Me₅)(h¹:h⁵-C₅Me₄-

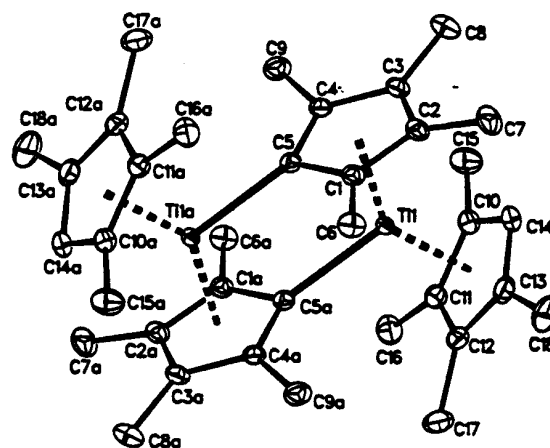


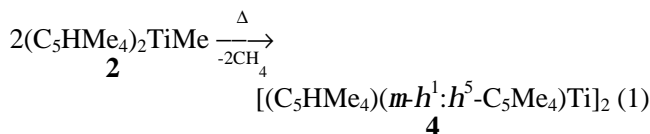
Figure 1. ORTEP drawing (50% probability level) and atom-labeling scheme for [(C₅HMe₄)(*m*-h¹:h⁵-C₅Me₄)Ti]₂ (**4**). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for [(C₅HMe₄)(*m*-h¹:h⁵-C₅Me₄)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.

CH₂)Ti, the product of the thermolysis of the pentamethylcyclopentadienyl analog (C₅Me₅)₂TiMe.^{17,20}



Molecular Structure of [(C₅HMe₄)(*m*-h¹:h⁵-C₅Me₄)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 *p*-bonded to a C₅HMe₄ and a C₅Me₄Ti ligand and *s*-bonded to a neighboring cyclopentadienyl to form a C₅Me₄Ti group.²¹ In fact, the structure of each (C₅HMe₄)(h¹:h⁵-C₅Me₄)Ti(h¹-C₅Me₄) moiety is very similar to that of the monomeric (C₅Me₅)₂TiR compounds.¹⁷ In (C₅-Me₅)₂TiCH₂CMe₃ the Ti-C *s*-bond is 2.235(4) Å, which is comparable to the Ti-C *s*-bond of 2.193(2) Å in **4**. The C₅HMe₄-Ti-C₅Me₄ 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 (C₅Me₅)₂TiCH₂CMe₃. The Ti-CE distances of 2.0231(9) and 2.0515(9) Å for the C₅Me₄ and the C₅HMe₄ ligands, respectively, are also

(20) Luinstra, G. A.; Teuben, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 3361-3367.

(21) A very similar structure has been obtained with C₅H₂Me₃ ligands instead of C₅HMe₄. [(C₅H₂Me₃)(*m*-h¹:h⁵-C₅HMe₃)Ti]₂: (C₁₆H₂₁-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, $\alpha = 102.08(1)^\circ$, $\beta = 101.866(9)^\circ$, $\gamma = 113.353(8)^\circ$, $V = 669.85(14)$ Å³, $Z = 1$, $D_{\text{expt}} = 1.295$ g cm⁻³, $I(\text{Mo K}\alpha) = 0.710$ 73 Å, $m = 6.1$ 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.

(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 [*m*-C₁₆H₂₀][(C₅Me₃H₂)Ti(*m*-H)]₂ derived from 1,2,3-trimethylcyclopentadienyl compounds has recently been determined. Varga, V.; Mach, K.; Polásek, 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.* **1986**, *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.

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 C₅HMe₄ ligand has been observed for other (C₅HMe₄)₂Ti complexes.⁵ The bridging C₅Me₄ ligand displays a somewhat larger ring slippage (0.176 Å, with the shortest Ti-C distance toward the h¹-bonded carbon atom). The Ti-Ti distance (3.5430(6) Å) is significantly longer than the Ti-Ti distance in (C₅H₅)₃(m-h¹:h⁵-C₅H₄)Ti₂(THF) (3.336(4) Å)²² or in [(C₅H₅)(m-h¹:h⁵-C₅H₄)Ti(PMe₃)₂] (3.223(1) Å).²³ The h⁵- and h¹-Ti-C bond lengths of these two complexes are comparable to those in **4**. Similar structures with m-h¹:h⁵-cyclopentadienyl ligands have been found for other metals, e.g. [(C₅H₅)₂Th(m-C₅H₄)₂]²⁴ and [(C₅H₅)₂Nb(H)(m-C₅H₄)₂].²⁵

Formation of [(C₅HMe₄)(m-h¹:h⁵-C₅Me₄)Ti]₂ (4**) vs (C₅Me₅)(h¹:h⁵-C₅Me₄CH₂)Ti.** Both titanocene(III) methyl compounds (C₅HMe₄)₂TiMe (**2**) and (C₅Me₅)₂TiMe decompose upon heating, liberating 1 equiv of CH₄ per Ti. The resulting organometallic products are quite different: the dimeric [(C₅HMe₄)(m-h¹:h⁵-C₅Me₄)Ti]₂ (**4**) for (C₅HMe₄)₂TiMe (**2**) vs the monomeric (C₅Me₅)(h¹:h⁵-C₅Me₄CH₂)Ti for (C₅Me₅)₂TiMe. Since arene C-H bonds (sp² hybridized) are more reactive than aliphatic C-H bonds (sp³ hybridized),²⁶ it is not surprising that upon thermolysis of **2**, activation of an sp²-hybridized ring C-H bond is preferred to activation of an sp³-hybridized methyl C-H. However, thermolysis of (C₅Me₅)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 (C₅Me₅)₂TiMe₂ to (C₅Me₅)(h¹:h⁵-C₅Me₄CH₂)TiMe.²⁷ Another example is the thermolysis of (C₅Me₅)₂TiR compounds to (C₅Me₅)(h¹:h⁵-C₅Me₄CH₂)Ti, which is catalyzed by (C₅Me₅)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 intramolecular activation of the ring C-H bond would lead to a highly constrained monomeric (C₅HMe₄)(h¹:h⁵-C₅Me₄)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 intermolecular activation of ring C-H bonds, which allows the bridging h¹:h⁵-C₅Me₄ ligands to retain their planar geometry.²⁸

(C₅HMe₄)₂TiH (5**) and Reaction with N₂.** Hydrogenolysis of (C₅Me₅)₂TiR produces a monomeric tita-

niium(III) hydride, (C₅Me₅)₂TiH.^{27a,29} Recently the molecular structure of the first monomeric titanocene(III) hydride (C₅PhMe₄)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 (C₅HMe₄)₂TiR (R = Me (**2**), R = Ph (**3**)), the green solution turned red-brown, characteristic for formation of titanocene(III) hydride (C₅HMe₄)₂TiH (**5**). Töpler pump analysis of the gas formed on reaction of **2** with D₂ revealed that 1 equiv of CH₃D/Ti had been liberated. Surprisingly, as soon as N₂ 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 C₅HMe₄ 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 (C₅Me₅)₂TiH^{29a} and (C₅PhMe₄)₂TiH³⁰ reliably allows identification as (C₅HMe₄)₂TiH. Additional proof was obtained from reactivity studies. When 1,3-butadiene was admitted to a solution of **5**, purple (C₅HMe₄)₂Ti(h³-1-methylallyl) (**7**) was formed exclusively, indicating that **5** behaves as a regular titanocene(III) hydride.³² In analogy to (C₅Me₅)₂TiH^{29a} and (C₅PhMe₄)₂TiH,³⁰ oxidation of **5** with PbCl₂¹⁹ yielded the diamagnetic (C₅HMe₄)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 (C₅Me₅)₂TiH and (C₅PhMe₄)₂TiH, because at room temperature crystalline **4** slowly separates from solutions of **5**, accompanied by liberation of H₂.

It is remarkable that **5** immediately reacts with even traces of N₂ at room temperature, whereas (C₅Me₅)₂TiH^{29a} and (C₅PhMe₄)₂TiH³⁰ appear to be completely indifferent toward N₂ at room temperature, even under 1 atm of N₂. The dramatic color change from red-brown to blue upon exposure of a solution of **5** to N₂ gas, followed by the separation of shiny metal-luster crystals, suggests the formation of the dinitrogen complex [(C₅HMe₄)₂TiH]₂N₂, like their regular cyclopentadienyl analogs (Cp₂TiR)₂N₂.³³ However, formation of H₂ during complexation of N₂ indicates a more complicated reaction sequence. An X-ray structure determination of the product showed that instead of the dinuclear titanocene(III) dinitrogen complex [(C₅HMe₄)₂TiH]₂N₂ the dinitrogen complex of titanocene(II) [(C₅HMe₄)₂Ti]₂N₂ (**8**) had been formed.

Molecular Structure of [(C₅HMe₄)₂Ti]₂N₂ (8**).** The molecular structure of **8** is shown in Figure 2, and selected bond distances and angles and details of the

(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 (C₅HMe₄)₂TiMe₂,¹⁶ which decomposes to the monomeric fulvene compound (C₅HMe₄)(C₅HMe₃CH₂)TiMe. Titanium in (C₅HMe₄)₂TiMe₂ is surrounded by four ligands instead of three, which sterically prevent intermolecular activation of ring C-H bonds. Instead, intramolecular activation of a less reactive methyl C-H bond occurs, so that a monomeric fulvene compound is isolated, similar to the decomposition of (C₅Me₅)₂TiMe₂ to (C₅Me₅)(C₅Me₄CH₂)TiMe.²⁶

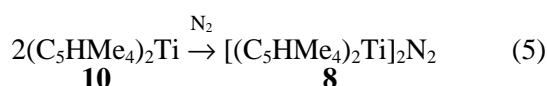
(29) (a) Teuben, J. H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; Reidel: Dordrecht, The Netherlands, 1985; pp 195-227. (b) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087-5094.

(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 N₂ are sufficient to set off the disproportionation of **5** and form the dinitrogen complex [(C₅HMe₄)₂Ti]₂N₂ (**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.



TiH, which are stable under N₂ at room temperature. Unlike the formation of thermolysis product **4**, the difference in reactivity between **5** on one side and (C₅-Me₅)₂TiH and (C₅PhMe₄)₂TiH on the other cannot be explained by the availability of sp² C-H bonds of the C₅HMe₄ ligands, as it is unlikely that they are involved in the reduction of **5** to **8**. Since [(C₅Me₅)₂Ti]₂N₂,³⁴ which is the pentamethylcyclopentadienyl analog of **8**, exists as well, the slightly reduced steric bulk of C₅HMe₄ ligands with respect to C₅Me₅ 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 (C₅Me₅)₂TiH and (C₅PhMe₄)₂TiH.

When a toluene suspension of **8** was stirred under a dynamic vacuum to remove N₂, the blue color disappeared and a brown solution resulted, from which a brown waxy residue was obtained. Admission of N₂ 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 (C₅Me₅)₂Ti upon degassing [(C₅Me₅)₂-Ti]₂N₂,^{29b} this compound was tentatively identified as titanocene (C₅HMe₄)₂Ti (**10**). Admission of H₂ to solutions of **10** resulted in formation of hydride **5**. Presumably the titanocene **10** reacts with H₂ to give the titanocene(IV) dihydride (C₅HMe₄)₂TiH₂ (**9**). Compounds **9** and **10** then subsequently conproportionate to the monohydride **5** (eq 3).

Conclusions

Comparison of bis(cyclopentadienyl)titanium(III) compounds (C₅HMe₄)₂TiR and their permethylcyclopentadienyl analogs (C₅Me₅)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 (C₅HMe₄)₂TiR compounds and the reactivity of the hydride toward N₂. The formation of the dimeric thermolysis product [(C₅HMe₄)(*m*-h¹:h⁵-C₅Me₄)Ti]₂ (**4**) can be explained by the presence of one sp² C-H bond in the tetramethylcyclopentadienyl ligand, which opens up another metalation pattern than in the corresponding pentamethylcyclopentadienyl compounds, in which only sp³ C-H bonds are available. The difference in the reactivity toward N₂ of hydride (C₅HMe₄)₂TiH (**5**), yielding [(C₅HMe₄)₂Ti]₂N₂ (**8**), on one side and homologous hydrides (C₅Me₅)₂TiH and (C₅PhMe₄)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 N₂, using standard Schlenk-line and glovebox or vacuum-line techniques. All solvents were distilled from Na/K alloy or LiAlH₄ prior to use. Tetrameth-

ylcyclopentadiene³⁶ and TiCl₃·3THF³⁷ were prepared according to published procedures. The synthesis of (C₅HMe₄)MgCl was derived from that of (C₅Me₅)MgCl.⁸ H₂ (99.995%, Hoek-Loos) was used without further purification.

Synthesis of (C₅HMe₄)₂TiCl₂.³⁸ A mixture of TiCl₃·3THF (15.9 g, 42.8 mmol) and (C₅HMe₄)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 PbCl₂¹⁹ in THF yielded a red solution, which was filtered, saturated, and cooled to -80 °C. Pure (C₅HMe₄)₂TiCl₂ was isolated as red-brown needles. Yield: 9.25 g, 60% relative to TiCl₃·3THF. ¹H NMR (200 MHz, C₆D₆): *d* 5.37 (s, 2H, C₅HMe₄), 2.06, 1.65 (s, 12H, C₅HMe₂Me₂).

Synthesis of (C₅HMe₄)₂TiCl (1**).**⁵ Compound **1** was made by reduction³⁹ of (C₅HMe₄)₂TiCl₂. To a suspension of (C₅-HMe₄)₂TiCl₂ (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 ¹PrMgCl 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, C₆D₆): *d* 43 (s, 12 H, C₅HMe₂Me₂, WHM (peak width at half maximum height) = 2.75 kHz), 0.3 (s, 12H, C₅HMe₂Me₂, WHM = 160 Hz). IR (KBr/Nujol, cm⁻¹): 3086 (w), 2724 (w), 1500 (w), 1024 (s), 858 (s), 440 (s).

Synthesis of (C₅HMe₄)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): *d* 48 (s, 12 H, C₅HMe₂Me₂, WHM = 3.50 kHz), 3.0 (s, 12 H, C₅HMe₂Me₂, 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, Δ*H* = 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, Δ*H* = 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 PbCl₂¹⁹ in diethyl ether quantitatively yielded red (C₅HMe₄)₂-Ti(Me)Cl. ¹H NMR (200 MHz, C₆D₆): *d* 4.79 (s, 2H, C₅HMe₄), 2.11, 1.99, 1.74, 1.42 (s, 6H, C₅HMe₄), 0.21 (s, 3H, TiMe).

Synthesis of (C₅HMe₄)₂TiPh (3**).** A 1.26 g amount of (C₅-HMe₄)₂TiCl₂ (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): *d* 40 (s, 12H, C₅HMe₂Me₂, 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, C₅HMe₂Me₂, WHM = 200 Hz), -1.0 (m, 2H, *H*_{meta}, WHM = 230 Hz). IR (KBr/Nujol, cm⁻¹): 3042 (w), 2726 (w), 2361

(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.; Schlock, R. R. *Inorg. Synth.* **1982**, *21*, 137.

(38) Mach, K.; Varga, V.; Antropiusová, H.; Poláček, J. *J. Organomet. Chem.* **1987**, *333*, 205-215.

(39) (a) Direct synthesis of **1** via reaction of TiCl₃·3THF with (C₅-HMe₄)MgCl led to contamination of **1** with (C₅HMe₄)₂TiCl₂. (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 $(\text{C}_5\text{HMe}_4)_2\text{Ti}(\text{Ph})\text{Cl}$. ¹H NMR (200 MHz, toluene-*d*₈): *d* 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*₅HMe₄), 1.94, 1.75, 1.62, 1.52 (s, 6H, *C*₅HMe₄).

Synthesis of $[(\text{C}_5\text{HMe}_4)(m\text{-}h^1\text{:}h^5\text{-C}_5\text{Me}_4)\text{Ti}]_2$ (4) by Thermolysis of $(\text{C}_5\text{HMe}_4)_2\text{TiMe}$ (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 $\text{C}_{36}\text{H}_{50}\text{Ti}_2$: 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 H₂ (MS analysis) from a solution of hydride **5** in hexane under a dynamic vacuum.

Thermolysis of $(\text{C}_5\text{HMe}_4)_2\text{TiMe}$ (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 $[(\text{C}_5\text{HMe}_4)(m\text{-}h^1\text{:}h^5\text{-C}_5\text{Me}_4)\text{Ti}]_2$ (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 $13.18^\circ < q < 18.88^\circ$ 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*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 (SHELXS86⁴³). The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (XTAL⁴⁴), 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 $\pm 0.35 \text{ e}/\text{\AA}^3$. Scattering factors were taken from Cromer and Mann.⁴⁶ Anomalous dispersion

factors taken from Cromer and Liberman⁴⁷ 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 EUCLID⁴⁹ (calculation of geometric data), and ORTEP⁵⁰ (preparation of illustrations).

Synthesis of $(\text{C}_5\text{HMe}_4)_2\text{TiH}$ (5). A 0.83 g portion of $(\text{C}_5\text{HMe}_4)_2\text{TiPh}$ (**3**; 2.26 mmol) was dissolved in pentane and degassed thoroughly by several freeze/pump/thaw cycles. H₂ 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 N₂ and small crystals of **4** separated as well. ¹H NMR (200 MHz, C₆D₆): *d* 46.4 (s, 12 H, *C*₅HMe₂Me₂, WHM = 1.68 kHz), 9.6 (s, 12 H, *C*₅HMe₂Me₂, WHM = 160 Hz). ESR (toluene): *g* = 1.9789, $\Delta H = 5 \text{ G}$, *a*(Ti) = 9.3 G. In an identical manner **5** was synthesized by hydrogenolysis of **2**.

Synthesis of $(\text{C}_5\text{HMe}_4)_2\text{Ti}(\text{H})\text{Cl}$ (6). Excess PbCl_2 ¹⁹ was added to a C₆D₆ solution of 30 mg of **5**. After filtration a red-brown solution of $(\text{C}_5\text{HMe}_4)_2\text{Ti}(\text{H})\text{Cl}$ (**6**) was obtained. ¹H NMR (200 MHz, C₆D₆): *d* 4.68 (s, 2H, *C*₅HMe₄), 4.10 (s, 1H, *TiH*), 2.19, 2.09, 1.77, 1.74 (s, 6H, *C*₅HMe₄).

Reaction of $(\text{C}_5\text{HMe}_4)_2\text{TiMe}$ (2) with D₂: 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 D₂ was admitted to the solution, yielding a red-brown solution. The amount of liberated gas and excess of D₂ 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 D₂. D₂O 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 CH₃D (MS).

Reaction of $(\text{C}_5\text{HMe}_4)_2\text{TiH}$ (5) with 1,3-Butadiene: Synthesis of $(\text{C}_5\text{HMe}_4)_2\text{Ti}(h^3\text{-1-methylallyl})$ (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 $(\text{C}_5\text{HMe}_4)_2\text{Ti}(h^3\text{-1-methylallyl})$ (**7**).^{32a} Yield: 0.96 g (93%).

Synthesis of $[(\text{C}_5\text{HMe}_4)_2\text{Ti}]_2\text{N}_2$ (8). To a degassed solution of 1.00 g of **2** (3.28 mmol) in 20 mL of pentane was admitted H₂. The solution was stirred for 2 h, during which time the H₂ atmosphere was refreshed several times. A red-brown solution of **5** had formed, which was cooled to 0 °C. N₂ 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 $\text{C}_{36}\text{H}_{52}\text{N}_2\text{Ti}_2$: 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 $[(\text{C}_5\text{HMe}_4)_2\text{Ti}]_2\text{N}_2$ (8). Suitable single crystals of **8** were grown by slow diffusion of N₂ 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 $10.0^\circ < q < 14.0^\circ$. 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: *s*²-

(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.

$(I) = S_{cs}(I) + (pI)^2$, with $p = 0.01$.⁵¹ An empirical absorption/extinction correction was applied (DIFABS⁵²). 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 (SHELX76⁵⁴). 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 Mann⁴⁶ and anomalous dispersion corrections from Cromer and Liberman.⁴⁷ Geometrical calculations and the ORTEP illustrations were done with PLATON.⁴⁹

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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.

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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