

## Novel Addition Reactions of 2,2,7,7-Tetramethyl-3,5-octadiyne to the Methyl Groups of a $\eta^5$ -Pentamethylcyclopentadienyl Ligand

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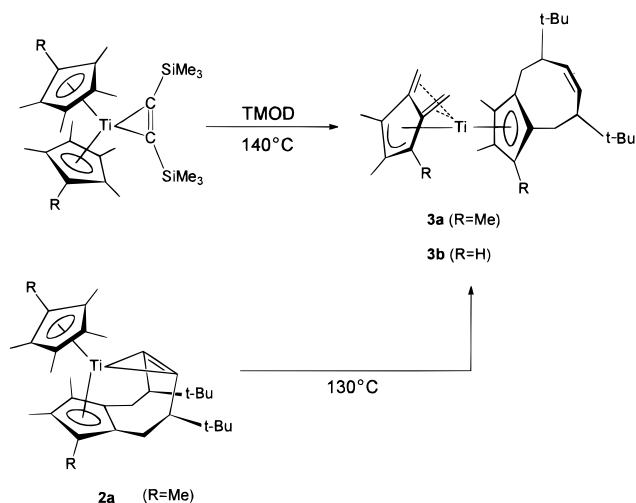
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In situ generated metallocenes of electron-deficient early transition metals easily undergo various rearrangements to increase the number of valence electrons.<sup>1</sup> This is usually achieved by a primary abstraction of hydrogen atoms from the cyclopentadienyl ligands or their substituents, with the subsequent steps depending on the nature of the substituents and the metal.<sup>2</sup> Brintzinger and Bercaw found for permethyltitanocene, which is stable at low temperatures, an intramolecular hydrogen abstraction affording a “tucked-in” hydride complex,  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-}\eta^4\text{-C}_5\text{Me}_4\text{CH}_2)\text{-TiH}]$ ,<sup>3</sup> which sublimates in a vacuum with a loss of hydrogen to give the paramagnetic  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^1\text{-}\eta^5\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ti}]$ .<sup>4</sup> The doubly “tucked-in” ( $\eta^3\text{-}\eta^4$ -allyldiene) complex  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^3\text{-}\eta^4\text{-C}_5\text{Me}_3(\text{CH}_2)_2)\text{Ti}]$  (**1a**)<sup>5</sup> is also readily accessible. The reactivity of these and similar complexes<sup>6</sup> has only scarcely been investigated. Complex  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^1\text{-}\eta^5\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ti}]$  reacts cleanly with alcohols ROH to give  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{OR})]$  and with 2-methylpyridine<sup>7a</sup> or isonitriles<sup>7b</sup> yielding products of insertion into the Ti–CH<sub>2</sub> bond. An insertion of acetophenone into the Ti–CH<sub>2</sub> bond of **1a** has also been described.<sup>5</sup>

We have reported very recently that the reduction of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiCl}_2]$  with magnesium in the presence of  $\text{Me}_3\text{Si-C}\equiv\text{C-C}\equiv\text{CSiMe}_3$  resulted in a  $\eta^2$ -complex  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{-C}\equiv\text{CSiMe}_3)]$ .<sup>8a</sup> For 2,2,7,7-tetramethyl-3,5-octadiyne (TMOD) a coupling product of the diyne with two methyl groups

Scheme 1



of one pentamethylcyclopentadienyl ring system  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}\{\eta^5\text{-C}_5\text{Me}_3(\text{CH}_2\text{CH}(\text{tBu})\text{-}\eta^2\text{-C}_2\text{-CH}(\text{tBu})\text{CH}_2)\}]$  (**2a**) was obtained, in which the triple bond of an annelated cyclooctyne moiety is coordinated to the titanium center.<sup>8b</sup> We also found that thermolysis of the  $\eta^2$ -bis(trimethylsilyl)acetylene (BTMSA) complex of permethyltitanocene  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta^2\text{-BTMSA})]$ <sup>9</sup> gives **1a** in nearly quantitative yield.<sup>9c</sup> Now, we report that thermolysis of equimolar amounts of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta^2\text{-BTMSA})]$  and 2,2,7,7-tetramethyl-3,5-octadiyne (TMOD) in  $m$ -xylene (130 °C/5 h) gives rise to a blue complex of the overall composition “ $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{-TMOD}]\text{Ti}$ ” (85% isolated yield) which was identified as the product of an insertion of TMOD into the C–H bonds of two adjacent methyl groups of the pentamethylcyclopentadienyl ligand,  $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{CH}(\text{tBu})\text{CH}=\text{CHCH}(\text{tBu})\text{CH}_2)\{\eta^3\text{-}\eta^4\text{-C}_5\text{Me}_3(\text{CH}_2)_2\}\text{Ti}(\text{II})]$  (**3a**; Scheme 1). The same complex **3a** was also obtained (80% yield) by heating the above-mentioned alkylne complex **2a** in  $m$ -xylene (130 °C/48 h) as a product of a 2-fold hydrogen transfer from methyl groups to the triple bond (Scheme 1). A similar thermolysis of a  $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\eta^2\text{-BTMSA})]$ –TMOD mixture (140 °C/2 h) gave the blue olefinic complex  $[(\eta^5\text{-C}_5\text{HMe}_2(\text{CH}_2\text{CH}(\text{tBu})\text{CH}=\text{CHCH}(\text{tBu})\text{CH}_2)\{\eta^3\text{-}\eta^4\text{-C}_5\text{HMe}_2(\text{CH}_2)_2\}\text{Ti}(\text{II})]$  (**3b**), but only in 8% yield.<sup>10</sup>

The molecular structures of complexes **3a**<sup>11a</sup> and **3b**<sup>11b</sup> determined by X-ray diffraction (Figure 1) represent novel examples of structurally characterized titanocene-derived complexes with doubly “tucked-in” ligands.<sup>12</sup> They show one allyldiene ligand and one pentamethylcyclopentadienyl ligand modified by the

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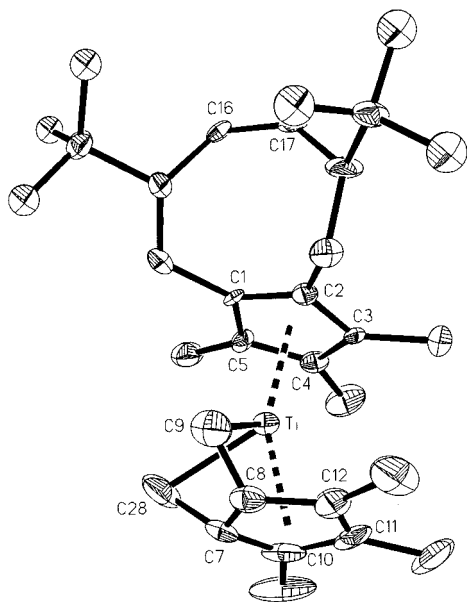
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(10) All experimental details and characterization data for **3a** and **3b** are given in the Supporting Information.

(11) (a) Crystal data for **3a**: blue prism, triclinic, space group  $P\bar{1}$ ,  $a = 9.389(2)$  Å,  $b = 12.069(2)$  Å,  $c = 13.328(3)$  Å,  $\alpha = 79.82(3)^\circ$ ,  $\beta = 83.11(3)^\circ$ ,  $\gamma = 75.82(3)^\circ$ ,  $V = 1436.5(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 200$  K,  $R(F) = 6.2\%$ ,  $wR(F^2) = 12.2\%$  (for all 2929 diffractions),  $\text{GOF}(F^2) = 1.095$ . (b) Crystal data for **3b**: blue prism, monoclinic, space group  $P2_1/n$ ,  $a = 12.390(2)$  Å,  $b = 11.8747(8)$  Å,  $c = 18.655(2)$  Å;  $\beta = 91.79(1)^\circ$ ,  $V = 2743.3(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 293(2)$  K;  $R(F) = 4.1\%$ ,  $wR(F^2) = 11.8\%$  (for all 4300 diffractions),  $\text{GOF}(F^2) = 1.03$ .

(12) (a) For an example of a doubly “tucked-in” ligand in a dimeric zirconocene complex see: Spek, A. L.; Pattiasina, J. W.; Teuben, J. H. *Z. Kristallogr.* **1996**, *211*, 643–644. (b) The structure of a doubly “tucked-in” ligand in half-metallocene  $[(\eta^3\text{-}\eta^4\text{-C}_5\text{Me}_3(\text{CH}_2)_2)\text{Ta}(\text{H})_2(\text{PMe}_2)_2]$  was also reported: Carter, S. T.; Clegg, W.; Gibson, V. C.; Kee, T. P.; Sanner, R. D. *Organometallics* **1989**, *8*, 253–255.



**Figure 1.** Molecular structure of **3a** (hydrogen atoms and disordered groups are omitted for clarity). Selected bond distances (Å): Ti–C7 2.057(7), Ti–C8 2.067(8), Ti–C10 2.344(8), Ti–C11 2.515(9), Ti–C12 2.327(9), Ti–C9 2.232(8), Ti–C28 2.222(8), Ti–CE1 1.926, Ti–CE2 2.018, C16–C17 1.330(9). CE1 and CE2 denote the centroids of the rings C7, C8, C10, C11, C12, and C1–C5, respectively.

cycloaddition of TMOD to its two vicinal methyl groups with concurrent 4-fold hydrogen transfer. The allyldiene ring in **3a/3b** is planar (the ring carbon atoms deviate from their least-squares plane by less than 0.009/0.007 Å) with the ring C–C bond lengths between 1.373(11)/1.385(3) Å and 1.451(11)/1.443(3) Å, and the *C-exo*CH<sub>2</sub> bond lengths of 1.452(11)/1.442(5) Å and 1.409(10)/1.422(5) Å. The diene moiety is inclined to the titanium atom. The dihedral angle subtended by the diene {C=CH<sub>2</sub>}<sub>2</sub> moiety and its parent ring plane is 42.5/43.9(2)°. The least-squares plane of the annelated cyclopentadienyl is perpendicular to the Ti-centroid line (89° both), the in-ring C–C bond lengths varying in the range 1.387(9)/1.406(3)–1.419(9)/1.417(3) Å. The dihedral angle between both C<sub>5</sub>-planes (10.7/12.9(2)°) opens to the side of the *exo*-methylene groups and the titanium atom is shifted toward the allyldiene moiety so that the distances of the Ti atom from the allyldiene ring and {C=CH<sub>2</sub>}<sub>2</sub> planes are 1.865(4)/1.863(2) and 1.706(4)/1.722(2) Å, respectively.

In the NMR spectra of **3a** and **3b**, the signals of the annelated cyclopentadienyl rings are grouped in the usual region when compared to, e.g., [(η<sup>5</sup>-C<sub>5</sub>H<sub>5-*n*</sub>Me<sub>*n*</sub>)<sub>2</sub>Ti(η<sup>2</sup>-BTMSA)] (*n* = 0–5).<sup>9c</sup> Therefore, the most striking features are due to the newly formed cyclooctene ring (HC≡; δ<sub>H</sub> ca. 5.6, δ<sub>C</sub> ca. 132) and those of the η<sup>3</sup>:η<sup>4</sup>-allyldiene ligand. Similar to **1a**<sup>6,13</sup> and **1b**,<sup>13</sup> the signals of Ti-coordinated *exo*-methylenes are observed at δ<sub>H</sub> ca. 1.0 and δ<sub>C</sub> ca. 65. The complete nonequivalence<sup>10</sup> of signals due to CH<sub>*n*</sub> groups (*n* = 0–3) results from the chirality of the complexes **3a** and **3b**, which was also found and discussed for the precursor complex **2a**.<sup>8b</sup> The NMR spectra also revealed that only one of four possible isomers of **3b** was isolated, which bears the *exo*-methylene groups asymmetrically with respect to the cyclopentadienyl

tadienyl proton. Such a tendency to form asymmetric allyldiene ligands was reported for **1b** in which case the asym/sym isomers were obtained in an 8:1 ratio.<sup>8,13</sup>

The electronic absorption spectra of **3a** and **3b** are similar to those of **1a** and **1b**. The presence of a single absorption band in the range 500–600 nm (ε ≈ 200 cm<sup>2</sup> mmol<sup>-1</sup>) and the absence of d electrons in UPS spectra previously led to a conclusion that d<sup>2</sup> electrons in **1a** and **1b** occupy low-lying empty orbitals of the η<sup>3</sup>:η<sup>4</sup>-allyldiene ligand.<sup>14</sup>

Unlike thermolysis of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(η<sup>2</sup>-BTMSA)] in the absence of TMOD, which affords **1a** and a mixture of (*E*)- and (*Z*)-1,2-bis(trimethylsilyl)ethene,<sup>9c</sup> thermolysis in the presence of TMOD leads exclusively to **3a** under evolution of BTMSA. This indicates that the coordinated TMOD plays the role of a proton acceptor instead of BTMSA. A primary formation of **1a** is excluded by the inertness of **1a** toward TMOD.<sup>15</sup> It should be concluded that permethyltitanocene and not **1a** is the first reacting intermediate. Hence, the formation of **3a** is very likely initiated by a thermally induced BTMSA-TMOD ligand exchange in [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(η<sup>2</sup>-BTMSA)] leading to, e.g., a titanacyclocumulene [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti{η(1-4)-(tBu)C=C=C(tBu)}]<sup>16</sup> or, more likely, a titanacyclopentadiene<sup>8a</sup> [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti{η<sup>2</sup>-(tBu)C<sub>2</sub>-C≡C(tBu)}] intermediate similar to the above mentioned Me<sub>3</sub>Si analogue.<sup>8a</sup> Then, a transfer of two protons to the coordinated TMOD at the onset of permethyltitanocene formation takes place followed by addition of (TMOD + 2 H) to the methylene carbon atoms giving the alkyne complex **2a** as a plausible intermediate for the formation of **3a**. In the thermolysis, the restored titanocene eliminates two hydrogen atoms from the unperturbed η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> ligand, which are transferred to the triple bond in the eight-membered ring to give **3a**. The tendency of transiently formed titanocene to eliminate two hydrogen atoms is the driving force of the addition of TMOD to the methyl groups of pentamethylcyclopentadienyl ligand. The formation of **3b** proceeds in the same way; however, the efficacy of the transfer of the first two protons is much lower, similarly to the formation of **1b** from the thermolysis of [(η<sup>5</sup>-C<sub>5</sub>HMe<sub>4</sub>)<sub>2</sub>Ti(η<sup>2</sup>-BTMSA)]<sup>9c</sup> or from the reaction of [(η<sup>5</sup>-C<sub>5</sub>HMe<sub>4</sub>)<sub>2</sub>TiCl<sub>2</sub>] with LiAlH<sub>4</sub> in boiling toluene.<sup>13</sup> Further derivatizations of **3a** at the double bond and at the methylene groups of the doubly “tucked-in” ligand are being investigated.

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**Supporting Information Available:** Synthetic procedures and characterization data for complexes **3a** and **3b**, tables of crystallographic data, atomic coordinates, bond lengths, anisotropic displacement parameters and hydrogen coordinates for **3a** and **3b**, and for **3b** additionally dihedral angles of least-squares planes, intermolecular contacts, and packing diagrams (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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