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Observation of an Unusual Ligand-Induced Rearrangement of a Titanacyclopentadiene Ring

Gary J. Balaich, Phillip E. Fanwick, and Ian P. Rothwell*

Department of Chemistry, Purdue University, 1393 Brown Building,
West Lafayette, Indiana 47907-1393

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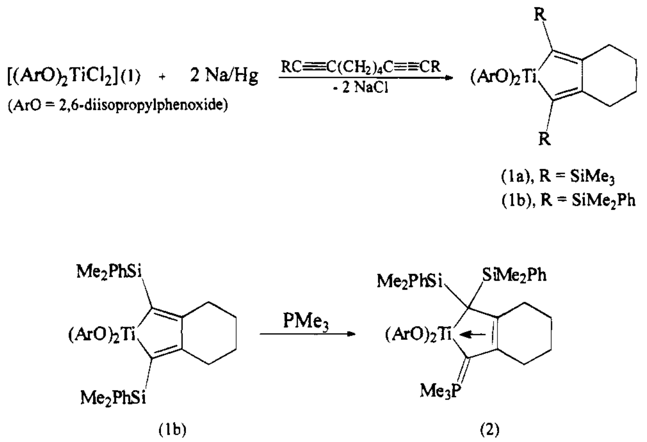
Summary: The sodium amalgam reduction of $[(ArO)_2TiCl_2]$ *(**1**; ArO = 2,6-diisopropylphenoxide) in the presence of the diynes 1,8-bis(trimethylsilyl)-1,7-octadiyne,* $Me_3SiC{\equiv}C(CH_2)_4C{\equiv}CSiMe_3$*, and 1,8-bis(dimethylphenylsilyl)-1,7-octadiyne,* $PhMe_2SiC{\equiv}C(CH_2)_4C{\equiv}CSiMe_2Ph$ *yields the titanacyclopentadiene complexes* $[(ArO)_2Ti\{C_2(R)_2C_6H_8\}]$ *(R =* $SiMe_3$ ***(1a)****, R =* $SiMe_2Ph$ ***(1b)****). Reaction of **1b** with* PMe_3 *results in a ligand-induced rearrangement to form* $[(ArO)_2Ti\{C(SiMe_2Ph)_2C_6H_8C(PMe_3)\}]$ ***(2)****. An X-ray crystallographic analysis has shown that complex **2** is a phosphorus ylide derivative in which migration of a dimethylphenylsilyl substituent has occurred from one α-carbon to the other. The solid-state structure of **2** shows a five-membered titanacycle ring in which the* PMe_3 *group is bound to one α-carbon and both* $SiMe_3Ph$ *substituents are bound to the other α-carbon on the ring. The three carbon−carbon bonds within the ring (C(11)−C(1) = 1.45(1) Å, C(1)−C(2) = 1.39(1) Å, C(2)−C(21) = 1.502(9) Å) are indicative of a titanacyclopent-3-ene structure. The phosphorus−carbon (α) bond distance (1.704(8) Å) is shorter than the other three phosphorus−carbon bond distances (1.771(8), 1.807(8), 1.795(8) Å) and is consistent with a phosphorus−carbon (α) double bond.*

Introduction

Metallacyclopentadiene complexes have been shown to be important intermediates in the catalytic cyclotrimerization of alkynes and other catalytic transformations as well as a number of stoichiometric organometallic reactions.[1] Our group is investigating the reactivity of titanacyclic rings supported by bulky aryloxide ligands. This work has led to the synthesis of various substituted titanacyclopentadiene complexes and has demonstrated that these complexes participate in a wide range of catalytic and stoichiometric reactivity.[2] Recently, we have attempted the synthesis and study of titanacyclopentadienes possessing α-silyl substituents. The reaction chemistry of silyl-substituted titanacyclopentadienes and zirconacyclopentadienes has been reported and involves the use of cyclopentadiene supporting ligands.[3] Herein, we report our observations on an unusual ligand-induced rearrangement of a bis(aryloxide)- and α-silyl-substituted titanacyclopentadiene with PMe_3. This reaction results in the formation of a phosphorus ylide derivative of a bent titanacyclopent-3-ene complex.

Scheme 1



Results and Discussion

A useful method for the synthesis of bis(aryloxide) titanacyclopentadiene complexes is the room-temperature sodium amalgam reduction of the bis(aryloxide) dichloride complexes in the presence of alkynes. Reduction of the bis(2,6-diisopropylphenoxide) dichloride species $[(ArO)_2TiCl_2]$ **(1)** in the presence of the diyne substrates $RC{\equiv}C(CH_2)_4C{\equiv}CR$ (R = $SiMe_3$, $SiMe_2Ph$) results in the formation of the titanacyclopentadiene complexes $[(ArO)_2Ti\{C_2(R)_2C_6H_8\}]$ (R = $SiMe_3$ **(1a)**, R = $SiMe_2Ph$ **(1b)**) (Scheme 1). The lack of crystallinity and the high solubility of **1a,b** in hydrocarbon solvents prevented their purification.

Complexes **1a,b** have been characterized by ^1H and ^{13}C NMR. In the ^{13}C NMR spectra, evidence for the titanacylopentadiene ring is present in the single Ti−C(α) resonances at δ 233.9 **(1a)** and 230.9 **(1b)**.[2a] In addition, the ^1H NMR spectra of **1a,b** show a single resonance for the equivalent methyl groups of the $Si\mathit{Me}_3$ and $Si\mathit{Me}_2Ph$ substituents, respectively.

Exposure of a hexane solution of **1b** to trimethylphosphine at room temperature resulted in the slow formation of the red, crystalline organometallic compound **2**. A single PMe_3 group gives rise to a doublet at δ 0.75 in the ^1H NMR spectrum of the red compound **2**. Four well-resolved singlet resonances for the four nonequiva-

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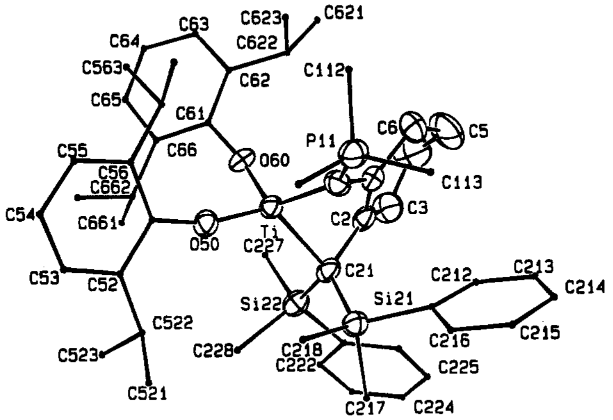

Figure 1. Ortep view of **2**. Selected bond distances (Å) and bond angles (deg): Ti—C(11) = 1.956(7), Ti—C(21) = 2.162(6), C(11)—C(1) = 1.45(1), C(1)—C(2) = 1.39(1), C(2)—C(21) = 1.502(9), Ti—C(1) = 2.424(7), Ti—C(2) = 2.429(7), P(11)—C(11) = 1.704(8), P(11)—C(111) = 1.771(8), P(11)—C(112) = 1.807(8), P(11)—C(113) = 1.795(8); Ti—O(50)—C(51) = 164.2(4), Ti—O(60)—C(61) = 159.1(4).

lent Si*Me*$_2$Ph methyl groups are also observed in the ^{1}H NMR spectrum, a result which is inconsistent with assignment of the red compound as a simple PMe$_3$ adduct of **1b**.

A single-crystal X-ray diffraction analysis of compound **2** revealed the structure to be that shown in Figure 1. In this complex, the PMe$_3$ is bound to one α-carbon and both SiMe$_2$Ph substituents are bound to the remaining α-carbon (Scheme 1). In the central coordination sphere of **2**, the alternating long–short–long carbon–carbon bond distances (C(11)—C(1) = 1.45(1) Å, C(1)—C(2) = 1.39(1) Å, and C(2)—C(21) = 1.502(9) Å) are consistent with a titanacyclopent-3-ene ring structure. The folding of metallacyclopent-3-ene rings is common for group 4 metal diene complexes.[4] Bond distances between P(11) and the carbon atoms of the methyl groups are longer than the P(11)—C(11) bond distance of 1.704(8) Å. This latter distance is consistent with a phosphorus–carbon double bond.

The spectroscopic properties of **2** are consistent with the structure observed in the solid state. In solution, the ^{13}C NMR spectrum of **2** shows the bent titanacyclopent-3-ene structure, giving rise to nonequivalent aryloxide ligands with two distinct Ti—O—*C*(*ipso*) carbon resonances at δ 160.0 and 160.8. The doublet resonance at δ 181.9 in the ^{13}C NMR can be assigned to the olefinic ylide carbon atom and displays a typical phosphorus–carbon coupling of 63.9 Hz. The nonequivalent Si*Me*$_2$Ph and methylene group resonances observed in both the ^{1}H and ^{13}C NMR spectra demonstrate that the solid-state structure of **2** is maintained in solution and that flipping of the titanacyclopent-3-ene ring is slow on the NMR time scale.

Careful analysis of the ^{31}P NMR with time during the reaction of **1b** with PMe$_3$ revealed that complex **2** forms slowly and that two other, unidentified PMe$_3$ complexes are also present in the reaction mixture.

Experimental Section

All reactions were carried out under N$_2$ or vacuum using standard Schlenk techniques. Solvents were dried by distillation over Na/benzophenone under N$_2$. The diynes 1,8-bis(trimethylsilyl)-1,7-octadiyne and 1,8-bis(dimethylphenylsilyl)-1,7-octadiyne were prepared by a modified literature procedure.[5] Proton and ^{13}C NMR spectra were recorded using a Varian Gemini 200-MHz instrument and ^{31}P NMR spectra with a GE QE 300-MHz instrument. Mass spectra and X-ray crystallographic data were acquired through Purdue in-house facilities.

Preparation of [(ArO)$_2$Ti{C$_2$(SiMe$_3$)$_2$C$_6$H$_8$}] (1a; ArO = 2,6-Diisopropylphenoxide). A mixture of [(ArO)$_2$TiCl$_2$] (**1**; 5.0 g, 10.6 mmol) and 1,8-bis(trimethylsilyl)-1,7-octadiyne (4.1 g, 16.4 mmol, 5.0 mL) in diethyl ether was stirred over a sodium amalgam (0.5 g of Na, 21.7 mmol, 0.4%) for 18 h. The initially intensely red solution changed to intensely green within 1 min and then progressively became dark brown. The suspension was decanted from the mercury pool and filtered, and the solvent was removed in vacuo to obtain the dark brown liquid product **1a**. The lack of crystallinity of **1a** prevented its purification. ^{1}H NMR (C$_6$D$_6$, 30 °C; δ): 6.8–7.2 (aromatics); 3.95 (septet, C*H*Me$_2$); 1.36 (d, CH*Me*$_2$, ^3J = 6.9 Hz); 2.42 (m), 1.56 (m, C*H*$_2$); 0.02 (s, Si*Me*$_3$). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C; δ): 233.9 (Ti—*C*); −0.7 (Si*Me*$_3$). MS (+CI; *m/z*): 653 ((M + H)$^+$, 88.3%), 617 (31.7), 616 (33.1), 615 (92.4), 413 (35.5), 341 (13.0), 325 (17.8), 324 (13.3), 323 (55.6), 253 (25.6), 251 (45.6), 179 (85.2), 171 (10.6), 91 (10.2), 73 (26.6). MS (−CI; *m/z*): 652 ((M)$^-$, 100.0%).

Preparation of [(ArO)$_2$Ti{C$_2$(SiMe$_2$Ph)$_2$C$_6$H$_8$}] (1b; ArO = 2,6-Diisopropylphenoxide). A procedure essentially identical with that described for **1a**, except using 1,8-bis(dimethylphenylsilyl)-1,7-octadiyne (2.4 g, 6.3 mmol) with [(OAr)$_2$TiCl$_2$] (3.0 g, 6.3 mmol) over sodium amalgam (0.3 g of Na, 12.6 mmol, 0.2%) yielded **1b** as a dark brown liquid product, which did not crystallize from pentane solution upon cooling. ^{1}H NMR (C$_6$D$_6$, 30 °C; δ): 6.8–7.9 (aromatics); 3.90 (septet, C*H*Me$_2$); 1.31 (d, CH*Me*$_2$, ^3J = 6.8 Hz); 2.40 (m), 1.45 (m, C*H*$_2$); 0.34 (s, Si*Me*$_2$Ph). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C; δ): 230.9 (Ti—*C*); 161.5 (Ti—O—*C*); −0.4 (Si*Me*$_2$Ph).

Preparation of [(ArO)$_2$Ti{C(SiMe$_2$Ph)$_2$C$_6$H$_8$C(PMe$_3$)}] (2; ArO = 2,6-Diisopropylphenoxide). The product **1b** obtained from the above preparation was dissolved in a minimum amount of hexane. Addition of PMe$_3$ to the **1b**/hexane solution was performed with a calibrated gas manifold and resulted in the formation of a dark red-brown solution. Red crystals of **2** formed after a 24-h reaction time at room temperature. Selected ^{1}H NMR (C$_6$D$_6$, 30 °C; δ): 6.7–8.0 (aromatics); 2.39, 2.79, 3.40 (m, C*H*$_2$); 3.93 (septet, C*H*Me$_2$); 0.08, 0.42, 0.50, 0.92 (s, Si*Me*$_2$Ph); 0.75 (d, CP*Me*$_3$); 7.51, 7.77 (m, SiMe$_2$*Ph*). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C; δ): 4.8, 5.8, 6.6, 8.5 (Si*Me*$_2$Ph); 16.3 (d, CP*Me*$_3$, $^1J(^{31}P-^{13}C)$ = 58.9 Hz); 160.0, 160.8 (Ti—O—*C*); 181.9 (d, *C*PMe$_3$, $^1J(^{31}P-^{13}C)$ = 63.9 Hz). ^{31}P NMR (C$_6$D$_6$, 30 °C; δ): −11.7 (C*P*Me$_3$).

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Supplementary Material Available: Text giving details of the data collection and reduction and the structure solution and refinement and tables of crystal data and data collection parameters, positional parameters, general temperature factors, and bond distances and angles for **2** and figures giving proton NMR spectra for **1a,b** and proton and ^{13}C NMR spectra for **2** (27 pages). Ordering information is given on any current masthead page.

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