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Synthesis and Molecular Structure of (TTP)Ti(1,2- η^2 -PhC \equiv C-C \equiv CPh)

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Synthesis and Molecular Structure of $(\text{TTP})\text{Ti}(1,2-\eta^2\text{-PhC}\equiv\text{C}-\text{C}\equiv\text{CPh})$

Abstract

The tetratolylporphyrinato complex, $(\text{TTP})\text{TiCl}_2$, oxidatively couples lithium acetylide reagents ($\text{LiC}\equiv\text{CR}$; $\text{R} = \text{Ph}, \text{SiMe}_3$) to 1,3-butadiyne products. The reduced $\text{Ti}(\text{II})$ fragment scavenges the diyne to form an η^2 -complex involving π -bonding to only one of the alkyne units, $(\text{TTP})\text{Ti}(1,2-\eta^2\text{-RC}\equiv\text{C}-\text{C}\equiv\text{CR})$. Independent syntheses of the diyne complex starting from $(\text{TTP})\text{TiCl}$ and $(\text{TTP})\text{Ti}(\eta^2\text{-EtC}\equiv\text{CEt})$ confirm the composition of the π -adduct. The lability of the butadiyne ligand in these Ti porphyrin complexes is readily demonstrated by displacement with pyridine.

Disciplines

Chemistry

Comments

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Synthesis and Molecular Structure of (TTP)- Ti(1,2- η^2 -PhC \equiv C–C \equiv CPh)

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Introduction

Titanium porphyrin complexes of the general formula Ti(por) L_1L_2 or Ti(por) L_1 (por = general porphyrin dianion; L_1 , L_2 = halide, NR, NHR, NR $_2$, OR, O, O $_2$, S, S $_2$, RC \equiv CR, THF, RN=NR, etc.)^{1–8} are well-known. However, metalloporphyrin complexes with titanium–carbon σ -bonded axial ligands are still rare. The only reported examples are monoalkyl metalloporphyrin complexes, Ti(TPP)R (TPP = *meso*-5,10,15,20-tetraphenylporphyrinato dianion; R = C $_6$ H $_5$, *o*-CH $_3$ C $_6$ H $_4$, and CH $_2$ C $_6$ H $_5$).⁹ In contrast, Zr(IV) and Hf(IV) porphyrin complexes with two alkyl ligands are well characterized.^{1,10} In this work, synthesis of dialkyl titanium metalloporphyrin complexes was attempted.

Experimental Section

General Methods. The synthesis and handling of air-sensitive porphyrin complexes and treatment of solvents were performed as described previously.¹¹ Literature procedures were used to synthesize (TTP)TiCl $_2$,² (TTP)TiCl $_2$,² and (TTP)Ti(η^2 -EtC \equiv CEt).⁶ Lithium phenylacetylide was synthesized by the reaction of phenylacetylene with *n*-butyllithium (1.6 M in hexane) in Et $_2$ O. LiC \equiv CSi(CH $_3$) $_3$ was prepared from (CH $_3$) $_3$ SiC \equiv CH and BuLi in hexane. Other chemicals were reagent grade and used without further purification.

Proton NMR spectra were obtained on a Varian VXR-300 spectrometer (300 MHz). UV–visible spectra were obtained using a Hewlett-Packard HP 8452A diode-array spectrophotometer. X-ray crystallographic analysis was performed on a Bruker CCD-1000 diffractometer. MS analysis was performed on a Finnigan TSQ 700 mass spectrometer.

(TTP)Ti(1,2- η^2 -PhC \equiv C–C \equiv CPh), 1. Method A. To a stirred solution of (TTP)TiCl $_2$ (0.043 g, 0.055 mmol) in approximately 12 mL of a toluene:THF mixture (10:1 v:v) at –25 °C was added 0.014 g of PhC \equiv CLi (0.13 mmol). The solution was then kept at –25 °C in a glovebox. After 20 h, the solution was taken to dryness in vacuo at ambient temperature. The residue was then redissolved in ca. 2 mL of toluene and filtered off. The filtrate was layered with 4–5 mL of hexane

and cooled to –25 °C. After 1 day, a dark blue precipitate was isolated by filtration, washed with hexanes, and dried in vacuo (17 mg, 34% yield). ¹H NMR (C $_6$ D $_6$, ppm): 9.14 (s, 8H, β -H), 8.12 (d, 4H, –C $_6$ H $_4$ -Me), 7.99 (d, 4H, –C $_6$ H $_4$ Me), 7.25 (pseudo t, 8H, –C $_6$ H $_4$ Me), 6.82 (m, 5H, –C $_6$ H $_5$), 6.40 (m, 3H, –C $_6$ H $_5$), 5.14 (dd, 2H, –C $_6$ H $_5$), 2.38 (s, 12H, –C $_6$ H $_4$ Me). UV–vis (toluene): 426 (Soret), and 551 nm.

Method B. To a stirred solution of (TTP)TiCl (0.146 g, 0.194 mmol) and 1,4-diphenylbutadiyne (0.153 g, 0.758 mmol) in ca. 18 mL of toluene was added dropwise 0.218 mL of NaBEt $_3$ H solution (1.0 M in toluene) at ambient temperature. After stirring for 24 h, the solution was filtered and the filtrate was concentrated to 3 mL and mixed with 5 mL of hexanes. The solution was then cooled to –25 °C to deposit dark blue microcrystals. The product was then isolated by filtration, washed with hexanes, and dried in vacuo (80 mg, 44%). The ¹H NMR and UV–vis spectra were identical to those reported in method A.

Method C. After dissolving 0.004 g of (TTP)Ti(η^2 -EtC \equiv CEt) (0.005 mmol) into 0.7 mL of C $_6$ D $_6$ in an NMR tube fitted with a high-vacuum Teflon stopcock, 0.004 g of 1,4-diphenylbutadiyne (0.02 mmol) was added to the solution at ambient temperature. After 1 h, (TTP)Ti(η^2 -EtC \equiv CEt) was completely converted to (TTP)Ti(PhC \equiv CC \equiv CPh) as monitored by ¹H NMR. The ¹H NMR of **1** in C $_6$ D $_6$ was identical to the data reported in method A. ¹H NMR of free EtC \equiv CEt (C $_6$ D $_6$, ppm): 2.03 (m, 4H), 0.99 (t, 6H), identical to the NMR spectrum of authentic compound.

(TTP)Ti(η^2 -TMSC \equiv CC \equiv CTMS), 2. To a stirred solution of (TTP)TiCl $_2$ (0.033 g, 0.041 mmol) in ca. 10 mL of toluene/THF(10:1) at –25 °C was added TMSC \equiv CLi (0.012 g, 0.12 mmol). After 22 h at –25 °C, the solution was taken to dryness in vacuo. The ¹H NMR spectrum of the residue showed that (TTP)Ti(η^2 -TMSC \equiv CC \equiv CTMS) was the main product. Further purification by following a similar route to purify **1** failed due to the oxidation of **2** in the glovebox to form (TTP)Ti=O. ¹H NMR of (TTP)Ti(η^2 -TMSC \equiv CC \equiv CTMS) (C $_6$ D $_6$, ppm): 9.07 (s, 8H, β -H), 8.34 (d, 4H, –C $_6$ H $_4$ Me), 7.95 (d, 4H, –C $_6$ H $_4$ -Me), 7.36 (d, 4H, –C $_6$ H $_4$ Me), 7.26 (d, 4H, –C $_6$ H $_4$ Me), 2.40 (s, 12H, –C $_6$ H $_4$ Me), –0.15 (s, 9H, –Si(CH $_3$) $_3$), –1.22 (s, 9H, –Si(CH $_3$) $_3$).

Reaction of (TTP)Ti(η^2 -PhC \equiv CC \equiv CPh) with Air. After ca. 3 mg of **1** was dissolved into 0.7 mL of C $_6$ D $_6$ at ambient temperature, the solution was opened in the air for approximately 1 h. The ¹H NMR spectrum showed that **1** was cleanly converted to (TTP)Ti=O and PhC \equiv CC \equiv CPh. The mass spectrum (EI) of the solution showed a *m/e* peak at 202.1, corresponding to the molecular weight of 1,4-diphenylbutadiyne (MW: 202.261). ¹H NMR spectrum of PhC \equiv CC \equiv CPh (C $_6$ D $_6$, ppm): 7.34 (dd, 4H), 6.87 (m, 6H), identical to that of the authentic compound.

Reaction of (TTP)Ti(η^2 -PhC \equiv CC \equiv CPh) with Pyridine. After dissolving ca. 4 mg of **1** into 0.7 mL of C $_6$ D $_6$ at ambient temperature, excess pyridine was added to the solution. A ¹H NMR spectrum taken immediately showed that **1** was completely converted to (TTP)Ti(py) $_2$ and PhC \equiv CC \equiv CPh. ¹H NMR of (TTP)Ti(py) $_2$ (C $_6$ D $_6$, ppm): 22.95 (s, 4H, *o*-py), 13.78 (s, 4H, *m*-py), 6.26 (d, 8H, –C $_6$ H $_4$ Me), 4.30 (d, 8H, –C $_6$ H $_4$ Me), 1.61 (s, 12H, –C $_6$ H $_4$ Me), –11.79 (s, 8H, β -H), experimentally similar to the data reported in the literature.¹²

X-ray Structure Determination of 1. Selected crystallographic data for the crystal structure determination of complex **1** are shown in Table 1. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer.

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/c$, which yielded chemically reasonable and computationally stable results of refinement.¹³ The structure was solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic

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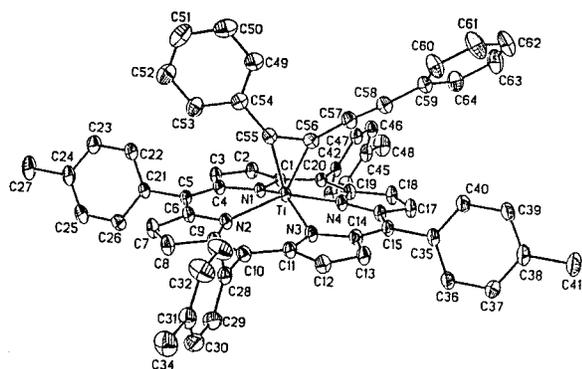
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- All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).

Table 1. Selected Crystallographic Data and Structure Refinement for the Structure Determination of (TTP)Ti(η^2 -PhC \equiv C \equiv CPh)

empirical formula	C ₆₄ H ₄₈ N ₄ Ti
fw	920.96
temp, K	173(2)
λ , Å	0.71073
space group	<i>P2₁/c</i>
<i>a</i> , Å	14.1665(7)
<i>b</i> , Å	24.7743(12)
<i>c</i> , Å	16.2716(8)
β , deg	97.994(1)
vol, Å ³	5655.3(5)
Z	4
density (calcd), Mg/m ³	1.082
abs coeff, μ	0.191
goodness-of-fit on F^2	1.037
final <i>R</i> indices [$I > 2\sigma(I)$] ^a	<i>R</i> 1 = 0.0634, <i>wR</i> 2 = 0.1535

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|, wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]]^{0.5}.$$

**Figure 1.** Molecular structure of (TTP)Ti(η^2 -PhC \equiv C \equiv CPh). Thermal ellipsoids are drawn at the 30% probability level.

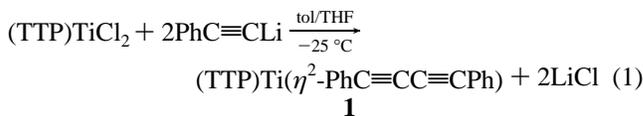
displacement coefficients. All hydrogen atoms were treated as idealized contributions. The refinement of the structure of **1** revealed the presence of severely disordered solvent molecules. The SQUEEZE filter of the program PLATON¹⁴ was applied to identify and account for six solvent molecules of toluene present in the unit cell along with four molecules of the complex.

A significant amount of time was invested in identifying and refining these solvates as toluene molecules. Bond length restraints were applied to model these molecules, but the resulting isotropic displacement coefficients suggested that the molecules were mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecules. PLATON calculated the upper limit of volume that can be occupied by the solvent to be 1182.7 Å³, or 20.9% of the unit cell volume. The program calculated 312 electrons in the unit cell for the diffuse species. This approximately corresponds to six toluene molecules in the unit cell (300 electrons). No data are given for the diffusely scattering species (solvent molecules).

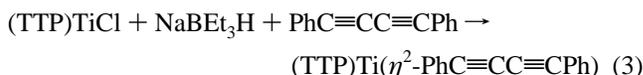
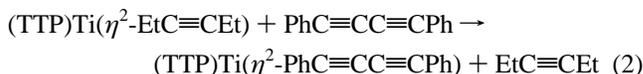
Results and Discussion

(TTP)Ti(1,2- η^2 -PhC \equiv CC \equiv CPh), **1**. Lithium phenylacetylidyde was successfully used to synthesize robust tin metalloporphyrin complexes containing one or two metal-carbon σ -bonded axial ligands.¹¹ Because Sn and Ti have similar valence states and sizes, analogous Ti complexes were expected. However, the desired target complex was not obtained. When (TTP)TiCl₂ was treated with more than 2 equiv of LiC \equiv CPh in toluene/THF at low temperature (−25 °C), (TTP)TiCl₂ was reduced to form a Ti(II) complex. Two phenylacetylidyde anions were

concomitantly oxidized and coupled to form a π -bonded 1,4-diphenylbutadiyne (eq 1).

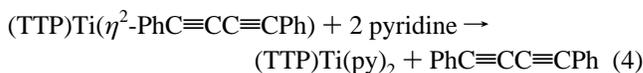


To verify the formulation of this product, two independent routes to synthesize complex **1** were used. The reaction of (TTP)Ti(η^2 -EtC \equiv CEt) with excess PhC \equiv CC \equiv CPh resulted in ligand exchange (eq 2). An alternate route was homogeneous reduction of Ti(III) with NaBEt₃H in the presence of PhC \equiv CC \equiv CPh (reaction 3).



The five-coordinate geometry of complex **1** was shown by the nonequivalent ortho protons of the tolyl groups on the macrocycle (8.12 (d) and 7.99 (d) ppm). The singlet due to the eight β -pyrrole protons indicated that the π -bound ligand PhC \equiv CC \equiv CPh rotates rapidly about the axial position. The phenyl substituents of the bound diyne ligand are clearly inequivalent. The protons of one phenyl group appear at 6.82 ppm (m, 5H), while the other phenyl group gives rise to signals at 6.40 (m, 3H) and 5.14 (dd, 2H) ppm. These data are consistent with a 1,2- η^2 coordination mode of 1,4-diphenylbutadiyne. An X-ray molecular structure of complex **1** verified this coordination geometry (vide infra).

Complex **1** was easily oxidized in air to form (TTP)Ti=O. The pyridine exchange reaction of **1** to form (TTP)Ti(py)₂ (eq 4) also indicated that the ligand binding strength of PhC \equiv CC \equiv CPh to (TTP)Ti(II) is similar to that of PhC \equiv CPh.



A recent article reported that the treatment of (por)ZrCl₂ with excess LiC \equiv CR produced (por)Zr(η^1 -C \equiv CR)₃Li(THF) (por = octaethylporphyrinato or tetraphenylporphyrinato dianion; R = Ph, SiMe₃).¹⁵ The greater size and electropositivity of Zr rationalizes this difference in chemistry.

(TTP)Ti(η^2 -TMSC \equiv CC \equiv CTMS), **2**. Complex **2** was synthesized from (TTP)TiCl₂ and excess TMSC \equiv CLi in toluene/THF(10:1) at −25 °C. The ¹H NMR spectrum of complex **2** indicated that its coordination geometry is quite similar to that of complex **1**. Complex **2** failed to be purified, as the workup process always resulted in partial decomposition to (TTP)Ti=O.

The reactivity differences between **1** and **2** are possibly due to the π -acceptor differences between 1,4-diphenylbutadiyne and TMSC \equiv CC \equiv CTMS. A related study¹⁶ showed that the mode of reaction of titanocene "Cp₂Ti" with disubstituted butadiynes RC \equiv CC \equiv CR depended strongly on the nature of the substituent. For R = SiMe₃ the starting butadiyne was cleaved by titanocene to yield the dinuclear complex [Cp₂Ti(C \equiv CSiMe₃)₂]₂. In contrast,

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in Complex **1**

Ti–C(56)	2.018(3)	Ti–C(55)	2.019(3)
Ti–N(1)	2.1003(19)	Ti–N(3)	2.103(2)
Ti–N(4)	2.109(2)	Ti–N(2)	2.122(2)
C(54)–C(55)	1.462(4)	C(55)–C(56)	1.316(4)
C(56)–C(57)	1.396(4)	C(57)–C(58)	1.210(4)
C(58)–C(59)	1.428(4)	C(55)–Ti–N(1)	99.11(9)
C(56)–Ti–C(55)	38.06(10)	C(55)–Ti–N(3)	111.48(9)
C(56)–Ti–N(1)	116.61(9)	C(56)–Ti–N(4)	86.37(10)
C(56)–Ti–N(3)	92.98(9)	N(1)–Ti–N(4)	85.02(7)
C(55)–Ti–N(4)	119.55(10)	C(56)–Ti–N(2)	125.39(10)
C(55)–Ti–N(2)	92.90(9)	C(56)–C(55)–C(54)	134.1(3)
C(56)–C(55)–Ti	70.91(17)	C(54)–C(55)–Ti	154.9(2)
C(55)–C(56)–C(57)	143.5(3)	C(55)–C(56)–Ti	71.03(17)
C(57)–C(56)–Ti	145.5(2)	C(58)–C(57)–C(56)	175.1(3)

for R = Ph only a dinuclear complex with a central 1,4-disubstituted μ - η (1,3), η (2,4)-*trans,trans*-butadiene unit (“zigzag-butadiyne”) between the two titanium centers was formed. Such differences are likely due to the electronic effect of the substituents on the diyne.¹⁵

X-ray Structure of 1. The coordination geometry of (TTP)-Ti(η^2 -PhC \equiv CC \equiv CPh) is shown in Figure 1. Only one C \equiv C bond of the axial ligand is bound to Ti in a 1,2- η^2 coordination

mode. Selected bond lengths and bond angles of this molecule are listed in Table 2. The Ti–N bond distances range from 2.1003(19) to 2.109(2) Å, similar to the Ti–N bond distances [2.094(7)–2.099(7) Å] in (OEP)Ti(η^2 -PhC \equiv CPh).⁶ The Ti–C distances are 2.018(3) and 2.019(3) Å and are also quite similar to those in (OEP)Ti(η^2 -PhC \equiv CPh) [2.016(5) and 2.015(5) Å].⁶ In complex **1**, the C55–C56 bond distance is 1.316(4) Å. The uncomplexed C \equiv C bond distance is 1.210(4) Å (C57–C58). In (OEP)Ti(η^2 -PhC \equiv CPh), the C \equiv C bond distance is 1.30(1) Å. As in (OEP)Ti(η^2 -PhC \equiv CPh), the butadiyne ligand in complex **1** can be regarded as a 4e[−] donor to the titanium center. The bond angles of C55–C56–C57 and C56–C57–C58 are 143.5(3)° and 175.1(3)°, respectively.

Acknowledgment. We thank the Camille and Henry Dreyfus Foundation for partial support of this work.

Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of (TTP)Ti(1,2- η^2 -PhC \equiv C–C \equiv CPh). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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