Low-Valent Titanium Porphyrin Complexes. Synthesis and Structural Characterization of the First Titanium(II) Porphyrin Complex, ($\eta_2$-Diphenylacetylene)Oitanium Octaethylporphyrin

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Abstract
The anaerobic reduction of the dlchlorotitanium(IV) porphyrins (OEP)TICI2 and (TTP)TICI2 (OEP = octaethylporphyrlnato, TTP = meso-tetra-p-tolylporphyrlnato) with LIAIH4 in the presence of diphenylacetylene in toluene produces the 11"-alkyne T~II) aclducts (OEP)TI(172-Phc==cPh) (1) and (TTP)Ti(172-PhC==cPh) (2). The structure of 1 has been determined by single-crystal X-ray diffraction analysis. Complex 1 crystallizes in the centrosymmetric space group C2/c with a = 49.369 (7) Å, b = 13.734 (9) Å, c = 36.042 (5) Å, α = 136.62 (1)°, V = 16784 (9) Å3, Z = 16, R = 0.061, and Rw = 0.063. The asymmetric unit of 1 contains two molecules. Alkyne C-C distances and Ti-alkyne distances are 1.30 (1) Å (C27-C28), 2.016 (5) Å (Ti 1-C27), 2.015 (5) Å (Ti 1-C8), 1.30 (1) Å (C81-C62), 2.007 (7) Å (T12-C61), and 2.028 (7) Å (Ti2-C62).

Disciplines
Chemistry

Comments
No reaction could be observed between the analogous diorganyl diselenides and sulfur, selenium, or tellurium. Also, no reactions occurred in all investigated systems when mechanical stirring was applied instead of ultrasound.

The solution behavior of 2a, 3a and 2b, 3b is entirely different. 2a, 3a establish equilibria as given in eq 4, whereas 2b, 3b are kinetically stable, most likely for steric reasons. By addition of 1a to the mixture both equilibria

\[ 2a = 1a + \text{PhTeSeSeTePh} \]  \hspace{1cm} (4)

\[ 3a = 1a + \text{PhTeSSTePh} \]

are shifted almost entirely to the left. The $^{129}$Te NMR data for the species involved are given in Table I.

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Low-Valent Titanium Porphyrin Complexes: Synthesis and Structural Characterization of the First Titanium(II) Porphyrin Complex, $\eta^2$-Diphenylacetylene)Titanium Octaethylporphyrin

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Summary: The anaerobic reduction of the dichlorotitanium(IV) porphyrins (OEP)TiCl$_2$ and (TTP)TiCl$_2$ (OEP = octaethylporphyrinate, TTP = meso-tetra-p-tolyloporphyrinato) with LiAlH$_4$ in the presence of diphenylacetylene in toluene produces the $\pi$-alkyne Ti(II) adducts (OEP)Ti(\(\eta^2\)-Ph=CHPh)(1) and (TTP)Ti(\(\eta^2\)-Ph=CHPh)(2). The structure of 1 has been determined by single-crystal X-ray diffraction analysis. Complex 1 crystallizes in the centrosymmetric space group $C2/c$ with $a = 49.369$ (7) Å, $b = 13.734$ (9) Å, $c = 36.042$ (5) Å, $\beta = 136.62$ (1)°, $V = 16784$ (9) Å$^3$, $Z = 16$, $R = 0.061$, and $R_w = 0.063$. The asymmetric unit of 1 contains two molecules. Alkyn C-C distances and Ti-alkyne distances are 1.39 (1) (C$_{27}$-C$_{28}$), 2.016 (5) (Ti$_1$-C$_{27}$), 2.015 (5) (Ti$_2$-C$_{28}$), 1.39 (1) (C$_{27}$-C$_{28}$), 2.007 (7) (Ti$_2$-C$_{61}$), and 2.028 (7) Å (Ti$_2$-C$_{62}$).

Despite the great interest in metalloporphyrins, the chemistry of early-transition metal porphyrin complexes remains in an undeveloped state. A primary reason for this stems from the fact that syntheses of these complexes thermodynamically lead to the formation of high-valent oxo complexes. The M=O groups in these metalloporphyrins are typically $d^0$-$d^2$ and are often extremely difficult to cleave. We have recently examined the metal-centered redox chemistry of titanium oxo and titanium halide porphyrin complexes. As an extension of our work on titanium porphyrins, we have begun to investigate the chemistry of low-valent Ti porphyrin complexes. To date, Ti(III) is the lowest valent state known to exist in a titanium porphyrin complex. We report here the synthesis and structural characterization of the first Ti(III) porphyrin complexes.

As illustrated in eq 1, lithium aluminum hydride reduction of toluene solutions of dichlorotitanium(IV) porphyrins in the presence of diphenylacetylene produces $\eta^2$-alkyne complexes of Ti(II). In a typical reaction, 131 mg of (OEP)TiCl$_2$ (0.201 mmol), 141 mg of LiAlH$_4$ (3.67 mmol), and 41 mg of PhC=CHPh (0.23 mmol) were stirred in toluene (40 mL) under N$_2$ at 22 °C. Over 12 h, the brown solution turned into the ruby red color of the alkynyl adduct 1. Filtering the reaction mixture, concentrating the filtrate to ca. 2 mL, and cooling to −20 °C for 3 days produced 78 mg of purple microcrystals (51% yield) after washing with cold pentane. The TTP analogue 2 can be prepared in a similar manner.

The alkynyl adducts 1 and 2 are diamagnetic complexes that exhibit sharp 1H NMR signals. For example, in C$_6$D$_6$ the diphenylacetylene protons of 1 appear as two multiplets at 6.29 (6 H, $m$ protons) and 4.37 ppm (4 H, $o$ protons). The significant upfield shifts of these resonances are consistent with a structure in which the C-C=C triple bond of the alkynyl binds to titanium, holding the phenyl substituents above the porphyrin ring current. The porphyrin meso protons resonate as a singlet at 10.33 (4 H) ppm. This indicates that rotation of the alkynyl ligand about the axis along the Ti-triple-bond centroid is rapid on the NMR time scale.

Crystals of the OEP complex 1 suitable for single-crystal X-ray diffraction were grown by cooling a toluene solution to −20 °C. Complex 1 crystallizes in the centrosymmetric space group $C2/c$ with two molecules in the asymmetric unit and 16 molecules per unit cell. The large number of non-hydrogen atoms (110) in the asymmetric unit significantly increased the difficulty and complexity of the

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structure determination. Direct methods were attempted but were unsuccessful. A new method was therefore tried, and proved capable of readily determining the structure. Due to the size of this molecule, those positions alone were ineffective at phasing the calculated density. Data were collected at Mo Kα, R(F) = 0.064 (6) A at Cρ. The planarity of the porphyrin core is very likely related to the formation of intermolecular π–π interactions between pairs of porphyrins in the lattice, as shown in Figure 2. The interplanar distance that separates the porphyrins in an associated pair is 3.36 Å. The other structural difference between these two alkyne complexes involves the orientation of the C≡C vector in the molecule. In the Mo case, this vector eclipses two trans pyrrole nitrogens. However, in the Ti complex, the C≡C vector bisects cis pyrrole nitrogens. For example, the torsional angle between the C9-C10-C11-C12 plane and the alkyne C≡C vector, as was proposed for the Mo analogue. A

Figure 2. Crystal-packing diagram for Ti(OEP)(η3-PhC≡CPh).

atom positions were revealed with use of difference Fourier calculations. Further details concerning this method of structure determination will be published elsewhere. The two molecules in the asymmetric unit of I are shown in Figure 1, and both have some features similar to those of a molybdenum analogue (TTTP)Mo(η5-PhC≡CPh), characterized by Weiss. The geometry about each Ti is square pyramidal, with the four pyrrole nitrogens forming the basal plane and the alkyne triple bond at the apical site. The titanium atom is displaced from the mean 24-atom porphyrin core toward the alkyne by 0.54 Å. The Ti1-C27 and Ti1-C38 distances are 2.016 (5) Å, and the C27-C38 distance is 1.30 (1) Å. In the second molecule, Ti2-C61 and Ti2-C62 distances are 2.007 (7) and 2.028 (7) Å, and the C61-C62 distance is 1.30 (1) Å.

Two structural aspects of I differ greatly from those of the Mo analogue. In the Mo complex, the porphyrin ligand is saddle-shaped. The Ti complex 1 possesses a nearly planar porphyrin core. The largest deviation from planarity is 0.064 (6) Å at Cρ. The planarity of the porphyrin core is very likely related to the formation of intermolecular π–π interactions between pairs of porphyrins in the lattice, as shown in Figure 2. The interplanar distance that separates the porphyrins in an associated pair is 3.36 Å. The other structural difference between these two alkyne complexes involves the orientation of the C≡C vector in the molecule. In the Mo case, this vector eclipses two trans pyrrole nitrogens. However, in the Ti complex, the C≡C vector bisects cis pyrrole nitrogens. For example, the torsional angle between the C9-C10-C11-C12 plane and the alkyne C≡C vector, as was proposed for the Mo analogue. A
Cp₂Ti(CO)(η⁵-PhC≡CPh) and a four-electron-donor acetylene (νC≡C = 1701 cm⁻¹) in (OEP)Ti(η⁵-PhC≡CPh). Finally, the ¹³C NMR spectrum for (OEP)Ti(η⁵-PhC≡CPh) provides further support for this bonding interaction. The ¹³C chemical shift for the C≡C carbon occurs at 219.4 ppm. Despite a significant upfield shift due to the porphyrin ring current, this signal falls well within the region expected for a four-electron-donor ligand. In this regard, the alkyne complexes 1 and 2 represent the first metallo-porphyrins that contain Ti(II). Reactivity studies of these novel complexes are also consistent with a Ti(II) formalism.

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Supplementary Material Available: Text detailing the data collection and listings of atomic coordinates, thermal parameters, bond distances and angles, and least-squares planes for I (41 pages); a listing of calculated and observed structure factors for 1 (43 pages). Ordering information is given on any current masthead page.


# Articles

Mechanism of the Photoreaction between (η⁵-C₅H₅)M(CO)₃X (M = Mo, W) and Allylic Halides

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Photolysis of (η⁴-C₅H₄)Mo(CO)₃Cl in the region of 100 K in allyl halide leads to CO loss and the generation of (η⁴-C₅H₄)Mo(CO)₂Cl(η⁴-C₅H₄X)Cl (X = Cl, Br, I). This molecule reacts thermally to produce (η⁴-C₅H₄)Mo(CO)₂Cl(η⁴-C₅H₄X)Cl. The activation barrier to this reaction is 34 kJ/mol (X = Cl). This is contrasted with the results obtained upon photolysis of (η⁴-C₅H₄)Mo(CO)₃ClX with allyl halides (M = Mo, X = Br; M = W, X = Cl, Br, I). Although initial formation of (η⁴-C₅H₄)Mo(CO)₃Cl(η⁴-C₅H₄X)X is observed upon photolysis, the subsequent thermal chemistry differs. Warming results in halogen loss to produce [(η⁴-C₅H₄)Mo(CO)₃Cl](η⁴-C₅H₄X)X. For M = W, X = Cl the activation barrier for the reaction is 69 kJ/mol. When it is warmed further, [(η⁴-C₅H₄)W(CO)₂(η⁴-C₅H₄X)]X decomposes to produce (η⁴-C₅H₄)W(CO)₃X₃. These results are discussed in terms of an electron transfer from the metal to the coordinated allyl halide.

Herein we report a study of the mechanism of the photoreaction between (η⁵-C₅H₅)M(CO)₃X (M = Mo, W) and allylic halides. This reaction was recently reported by Davidson and Vasapollo to generate, in the case of (η⁵-C₅H₅)Mo(CO)₃Cl, good yields of the allylic product according to eq 1. The products obtained for the other met...