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Synthesis, Electrochemistry, and Imido Transfer Reactions of (TTP)Ti(η^2-PhN═NPh)

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Treatment of (TTP)Ti(η^2-RC≡CR) (R = Et or Ph) with PhN═NPh results in formation of the azobenzene adduct (TTP)Ti(η^2-PhN═NPh) (**1**) in good isolated yield. Complex **1** reacts with (TTP)Ti(η^2-RC≡CR) at elevated temperatures to cleanly afford 2 equiv of the phenylimido compound, (TTP)Ti═NPh (**2**). The azobenzene complex, **1**, is also formed in low yields by the reaction of the (TTP)Ti═NPh (**2**) with excess 1,2-diphenylhydrazine. The electrochemistry of the azobenzene adduct (**1**) and the phenylimido complex (**2**) is investigated by cyclic voltammetry experiments.

Introduction

Reactions which result in the transfer of imido [NR^{2-}] fragments are still relatively rare and have generated much interest with respect to their potential in aziridine synthesis as well as other organic transformations involving the formation of nitrogen−carbon bonds.[2] Recently we reported that the reaction of (TTP)Ti(η^2-RC≡CR) (TTP = *meso*-tetra-*p*-tolylporphyrinato, R = Et or Ph) with 0.5 equiv of azobenzene resulted in the formation of 1 equiv of the phenylimido complex, (TTP)Ti═NPh.[3] On the basis of our previous studies involving atom transfers from the perchalcogenido complexes (TTP)Ti^{IV}(η^2-X_2) (X = O, S, Se) to (TTP)Ti^{II}(η^2-EtC≡CEt),[4] we believe that this transformation most likely occurred via an azobenzene adduct, (TTP)Ti(η^2-PhN═NPh). A related thermal conversion of $(ArO)_2(py')_2$Ti(η^2-PhN═NPh) to an imido complex was reported by Rothwell.[5] Here we report the full characterization of (TTP)Ti(η^2-PhN═NPh) as well as our studies of its reactivity and ability to engage in intermetal imido transfer reactions.

Experimental Section

General Methods. All manipulations were performed under an inert atmosphere of nitrogen using a Vacuum Atmospheres glovebox equipped with a Model MO40−1 Dri-Train gas purifier. The glovebox atmosphere was continuously monitored with an Illinois Instrument Model 2550 trace oxygen analyzer. The concentration of O_2 in the glovebox was kept at less than 5 ppm at all times. All solvents were rigorously degassed and dried prior to use. Benzene-d_6, toluene, and hexane were freshly distilled from purple solutions of sodium benzophenone and brought into the glovebox without exposure to air. (TTP)$TiCl_2$ and (TTP)Ti(η^2-RC≡CR) (R = Et or Ph) were prepared according to published procedures and recrystallized prior to use.[6] Azobenzene was purchased from Aldrich and used without purification.

NMR experiments were performed by charging NMR tubes with the appropriate complexes and Ph_3CH as an internal standard and sealed with a high-vacuum Teflon stopcock in the glovebox. The tube was attached to a Schlenk line, evacuated, and cooled with liquid nitrogen, and approximately 0.5 mL of C_6D_6 was added to the tube by vapor transfer. The solution was degassed by three freeze−pump−thaw cycles and finally flame sealed. Thermolysis experiments were

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performed in a controlled temperature oil bath, and the NMR spectra was recorded periodically.

^{1}H NMR data were recorded at 20 °C on either a Varian VXR (300 MHz) or a Bruker DXR (400 MHz) spectrometer. Chemical shifts are referenced to the residual protonated solvent peak (d 7.15, C_6D_5H). UV−vis data were recorded on a HP8452A diode array spectrophotometer. Elemental analyses (C, H, N) were performed by Atlantic Microlab of Norcross, GA. All samples were handled under nitrogen, and WO_3 was used as a combustion aid.

Electrochemical measurements were carried out with an EG&G 280 voltammetric analyzer. A three-electrode system was used which consisted of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The SCE was separated from the bulk of the solution by a fritted-glass bridge which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE. Electrochemical studies were performed in a glovebox. Anhydrous dichloromethane (Aldrich) was used as a solvent, and 0.2 M tetrabutylammonium perchlorate (TBAP), as a supporting electrolyte. TBAP was purchased from Sigma Chemical Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least 1 week prior to use.

(TTP)Ti(η^2-PhN=NPh). In a glovebox, (TTP)Ti(η^2-PhC≡CPh) (101 mg, 0.113 mmol) and a slight excess of azobenzene (21 mg, 0.12 mmol, 1.03 equiv) were dissolved in toluene (ca. 15 mL) to afford immediately a dark red solution. Over the course of 23 h, the solution was rapidly stirred and no additional color change was observed. Subsequently, the reaction mixture was filtered and the solvent was removed from the dark red filtrate under reduced pressure. The resultant purple solid was dissolved in a minimum of toluene (ca. 5 mL), and the solution was layered with hexanes (ca. 15 mL). The sample was cooled to −20 °C for 16 h, which resulted in the formation of large purple crystals. The resultant crystals were collected via filtration, washed with hexanes (ca. 10 mL), and dried in vacuo to afford (TTP)Ti(η^2-PhN=NPh) (80 mg, 0.090 mmol, 80%) as a crystalline solid. The initial solid consistently contained trace amounts of (TTP)Ti=NPh and (TTP)Ti(η^2-PhC≡CPh), but analytically pure samples could be obtained by recrystallizing the solid twice from toluene/hexanes. ^{1}H NMR (C_6D_6, room temperature, 300 MHz): 9.12 (s, 8 H, β-H), 8.06 (d, $^3J_{HH}$ = 6.9 Hz, 4 H, $-C_6H_4Me$), 7.96 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, $-C_6H_4$-Me), 7.28 (m, 8 H, $-C_6H_4Me$), 6.32 (t, J_{HH} = 7 Hz, 4 H, H_m, PhN=NPh); 6.24 (t, J_{HH} = 7 Hz, 2 H, H_p, PhN=NPh); 4.15 (d, J_{HH} = 7 Hz, 2 H, H_o, PhN=NPh); 2.39 (s, 12 H, $-C_6H_4Me$). UV−vis (toluene): 428 (Soret), 548 nm. Anal. Calcd for $C_{60}H_{46}N_6Ti$: C, 80.17; H, 5.16; N, 9.35. Found: C, 79.91; H, 5.06; N, 9.22.

Reaction of (TTP)Ti=NPh with PhNH−NHPh. In a glovebox, an NMR tube was charged with (TTP)Ti=NPh (13 mg, 16 μmol), PhNH−NHPh (4 mg, 21 mmol), and Ph_3CH (7 mg, 29 μmol, internal standard) and sealed with a high-vacuum Teflon stopcock. The tube was attached to a high-vacuum line, evacuated, cooled with liquid nitrogen, filled with 0.5 mL of C_6D_6 by vapor transfer, and flame sealed. The NMR tube was heated in an oil bath at 85 °C and monitored periodically by ^{1}H NMR. After 7 h, no further reaction was observed. ^{1}H NMR for (TTP)Ti(η^2-PhN=NPh) in C_6D_6: 9.13 (s, 8H, β-H), 8.06 (d, partially obscured by (TTP)Ti=NPh signals), 7.96 (d, partially obscured by (TTP)Ti=NPh signals), 7.28 (completely obscured by (TTP)Ti−NPh signals), 6.32 (t, partially obscured by (TTP)Ti=NPh signals), 6.24 (t, partially obscured by (TTP)Ti=NPh signals), 4.15 (d, 2H, H_2, PhN=NPh), 2.39 (s, CH_3, overlapped with (TTP)Ti=NPh signal). ^{1}H NMR for aniline: 7.06 (t, 2H, *m*-H), 6.72 (t, 1H, *p*-H), 2.74 (s, 2H, NH).

Reaction of (TTP)Ti(η^2-PhN=NPh) with (TTP)Ti(η^2-EtC≡CEt). In a glovebox, an NMR tube was charged with (TTP)Ti(η^2-PhN=NPh) (7.1 mg, 7.9 mmol), (TTP)Ti(η^2-EtC≡CEt) (7.8 mg, 9.7 μmol), and 0.68 mL of C_6D_6 and sealed with a high-vacuum Teflon stopcock. The tube was heated to 80 °C and monitored daily by ^{1}H NMR spectroscopy. After 237 h, all of the azobenzene complex was gone and quantitative formation of (TTP)Ti=NPh was observed (15.4 μmol, 97%). ^{1}H NMR for (TTP)Ti=NPh: 9.21 (s, 8H, β-H), 8.14 (d, 4H, *o*-$C_6H_4CH_3$), 8.03 (d, 4H, *o′*-$C_6H_4CH_3$), 7.30 (d, 8H, *m*-$C_6H_4CH_3$), 5.72 (m, 3H, *m*-, *p*-NC_6H_5), 3.85 (d, 2H, *o*-NC_6H_5), 2.41 (s, 12H, CH_3). ^{1}H NMR for EtC≡CEt: 2.02 (q, 4H), 0.99 (t, 6H).

Reaction of (TTP)Ti(η^2-PhN=NPh) with Water. In a glovebox, an NMR tube was loaded with (TTP)Ti(η^2-PhN=NPh) (8 mg, 9 mmol) and 0.5 mL of C_6D_6, capped with a septum, and removed from the box. Degassed water (0.8 mL, 44 mmol) was added via syringe. ^{1}H NMR spectroscopy indicated quantitative formation of (TTP)Ti=O and PhNH−NHPh in a 1:1 ratio. ^{1}H NMR for (TTP)Ti=O: 9.24 (s, 8H, β-H), 8.00 (d, 8H, *o*-H), 7.28 (d, 8H, *m*-H), 2.42 (s, 12H, CH_3). ^{1}H NMR for PhNH-NHPh: 7.08 (t, 4H, *m*-H), 6.75 (t, 2H, *p*-H), 6.60 (d, 4H, *o*-H), 4.68 (s, 2H, NH).

Results

Treatment of the known Ti(II)−alkyne complexes, (TTP)Ti(η^2-RC≡CR) (R = Et or Ph) with 1 equiv of azobenzene affords the azobenzene complex, (TTP)Ti(η^2-PhN=NPh) (**1**), which was isolated in ca. 80% yield as a purple crystalline complex by recrystallization from toluene (eq 1). ^{1}H NMR

$$\begin{gathered}(TTP)Ti(\eta^2\text{-}RC{\equiv}CR) + PhN{=}NPh \rightarrow \\ \underset{\mathbf{1}}{(TTP)Ti(\eta^2\text{-}PhN{=}NPh)} + RC{\equiv}CR \qquad (1) \\ R = Et,\ Ph\end{gathered}$$

experiments show that the reaction of (TTP)Ti(η^2-EtC≡CEt) with azobenzene occurs quantitatively (greater than 95%, Ph_3-CH internal standard) with the only spectroscopically observable products being (TTP)Ti(η^2-PhN=NPh) (**1**) and free alkyne. The ^{1}H NMR spectrum (C_6D_6) of **1** resembles that of (TTP)Ti(η^2-X_2) (X = O, S, Se) complexes with the exception of new resonances for the phenyl rings of the ligated azobenzene which are significantly upfield shifted from the free ligand. Thus the H_o, H_m, and H_p protons of the coordinated azobenzene ligand appear at 4.14 (d), 6.32 (t), and 6.24 (t) ppm, respectively. Similar upfield shifts have been previously noted for the alkyne starting materials and are attributed to the proximity of these ligands to the strong ring current of the porphyrin. We have also observed that the azobenzene complex, **1**, can be produced, albeit in low yields, by the reaction of the known phenylimido complex, (TTP)Ti=NPh (**2**), with 1,2-diphenylhydrazine (eq 2).

$$\begin{gathered}(TTP)Ti{=}NPh + 1,2\text{-}PhNH\text{-}NHPh \rightleftharpoons \\ (TTP)Ti(\eta^2\text{-}PhN{=}NPh) + H_2NPh \qquad (2)\end{gathered}$$

Thus, treatment of **2** with 1 equiv of 1,2-diphenylhydrazine (C_6D_6, 85 °C) results in less than 1% conversion of **2** to the azobenzene complex, **1**, along with the aniline byproduct. The conversion is incomplete, indicating that the reaction reaches an equilibrium. On the basis of NMR data, the K_{eq} for eq 2 is calculated as 4.8×10^{-3}.

Complex **1** expands the set of known (TTP)Ti(η^2-X_2) (X = O, S, Se) complexes and should exhibit similar chemistry. Previously, we noted that (TTP)Ti(η^2-X_2) (X = O, S, Se) rapidly oxidizes (TTP)Ti(η^2-RC≡CR) (R = Et or Ph) to afford 2 equiv of (TTP)Ti=X and free RC≡CR. In addition, we recently reported that the reaction of (TTP)Ti(η^2-EtC≡CEt) with 0.5 equiv of azobenzene results in the formation of (TTP)Ti=NPh. Given the above observations, complex **1** appears to be a reasonable intermediate for this process. Accordingly, the reaction of (TTP)Ti(η^2-PhN=NPh), **1,** with (TTP)Ti(η^2-EtC≡CEt) in benzene quantitatively affords the known imido complex (TTP)Ti=NPh after 10 d at 80 °C (eq 3). Unlike the

$$\begin{gathered}(TTP)Ti(\eta^2\text{-}PhN{=}NPh) + (TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt) \rightarrow \\ 2(TTP)Ti{=}NPh + EtC{\equiv}CEt \qquad (3)\end{gathered}$$

reactions of (TTP)Ti(η^2-X_2) (X = O, S, Se) complexes with

(TTP)Ti(η^2-RC≡CR) (R = Et or Ph) which occur rapidly, the reaction of (TTP)Ti(η^2-PhN=NPh) with (TTP)Ti(η^2-EtC≡CEt) occurs much more slowly and requires heating for the imido transfer to be driven to completion. This feature may be attributed to the greater steric bulk of the $[NPh]^{2-}$ fragment.

The azobenzene complex is hydrolytically sensitive. Thus, treatment of a C_6D_6 solution of (TTP)Ti(η^2-PhN=NPh) with 5 equiv of water results in a the rapid formation of a 1:1 mixture of (TTP)Ti=O and PhNH-NHPh at 22 °C (eq 4). Product

$$\text{(TTP)Ti}(\eta^2\text{-PhN=NPh}) + H_2O \rightarrow \text{(TTP)Ti=O} + \text{PhNH}-\text{NHPh} \quad (4)$$

identities and quantities were readily determined by ^1H NMR. For example, a ^1H NMR spectrum of the final reaction mixture shows the absence of a β-pyrrole proton signal at 9.12 ppm for (TTP)Ti(η^2-PhN=NPh) and the appearance of a new singlet at 9.24 ppm which is diagnostic for the oxo complex, (TTP)Ti=O. In addition, the formation of 1,2-diphenylhydrazine is clearly indicated by the appearance of the NH signal at 4.68 ppm.

Discussion

Kharasch and Ashford proposed in 1936 that diazene compounds (RN=NR) should form coordination complexes similar to those observed for olefins.[7] However, the first η^2-diazene complexes did not appear until 1971.[8,9] The first titanium η^2-diazene complex, $Cp_2Ti(\eta^2\text{-PhN=NPh})$, was reported by Floriani and co-workers in 1973.[10] Synthesis of group IV η^2-diazene complexes has involved displacement reactions[10,11] or methane elimination from a methylzirconium η^2-hydrazido(1−) complex (eq 5).[12] In general, η^2-diazene complexes are still relatively rare.[13]

$$Cp_2ZrMe(\eta^2\text{-PhN}-\text{NHPh}) \rightarrow Cp_2Zr(\eta^2\text{-PhN=NPh}) + CH_4 \quad (5)$$

Our recent synthesis of labile Ti(II) porphyrin complexes provided the opportunity to explore further the chemisty of new η^2-diazene complexes. For example, treatment of (TTP)Ti(η^2-EtC≡CEt) with azobenzene readily produces the η^2-diazene complex (TTP)Ti(η^2-PhN=NPh). The ^1H NMR spectrum of this new complex reveals that the two phenyl groups of the azobenzene ligand are equivalent, consistent with an η^2 binding mode. In addition, the porphyrin tolyl methyl proton singlet at 2.41 ppm and the single resonance for the β-pyrrole protons at 9.21 ppm indicate that the porphyrin ligand maintains 4-fold symmetry on the NMR time scale. Thus, the η^2-azobenzene ligand rotates rapidly about the C_4 symmetry axis.

An alternative method for the preparation of the η^2-azobenzene complex involves the acid/base reaction between (TTP)Ti=NPh and 1,2-diphenylhydrazine (eq 2). However, this reaction does not proceed to completion. Although Brønsted acid/base arguments would predict that eq 2 would favor the formation of aniline, the strong multiple bonding in the imido complex [(TTP)Ti=NPh ↔ (TTP)Ti$^-$≡N$^+$−Ph] appears to favor reactants over the products.

Table 1. Half-Wave Potentials for Reduction and Peak Potentials for Oxidation (V vs SCE) of (TTP)TiL in CH_2Cl_2, 0.1 M TBAP

	redn ($E_{1/2}$)		oxidn (E_{pa})[a]		
	1st	2nd	1st	2nd	ref
η-$(NPh)_2$	−1.18	−1.59	0.35	1.19	this work
η-Se_2	−1.06	−1.39	0.80		14a
η-S_2	−1.04	−1.38	0.98		14a
NPh	−1.20	−1.59	1.04		this work
O[b]	−1.04	−1.43	1.20[c]	1.42[c]	14b
Se	−1.07	−1.46	0.83	1.17	14c
S	−1.08	−1.48	0.97	1.17	14c

[a] Measured with scan rates of 0.1 V/s. [b] Data in the table are for the tetraphenylporphyrinato complex, (TPP)TiO. [c] Reversible ring-centered oxidations.

Electrochemistry of (TTP)Ti(η^2-PhN=NPh) and (TTP)Ti=NPh. Half-wave and peak potentials for (TTP)Ti(η^2-PhN=NPh), **1**, and (TTP)Ti=NPh, **2**, in CH_2Cl_2 with 0.1 M TBAP are summarized in Table 1 along with literature data for the related chalco- and perchalcogenido analogues, (TTP)Ti=X and (TTP)Ti(η^2-X_2), X = S, Se, and O.[14] The azobenzene complex **1** undergoes two reversible one-electron reductions (see Table 1). The potential difference between the two reductions is ~0.40 V. This difference is typical for the consecutive reductions of the porphyrin macrocycle[15] and is similar to $\Delta E_{1/2}$ values found for other related complexes in Table 1.

Overall, the η^2-azobenzene complex shows electrochemistry which is similar to that of the perchalcogenide analogues. The only significant difference involves the cathodic shift of the two reductions of (TTP)Ti(η^2-PhN=NPh) by ~0.12 V with respect to $E_{1/2}$ for the reduction of the perchalcogenido complexes. This difference in potentials for macrocycle-based reductions of porphyrins with the same central metal ion reflects different electron-withdrawing powers of the η^2-ligands. The more positive reduction potentials for the perchalcogenido complexes indicate that the η^2-S_2 and η^2-Se_2 ligands are more electron withdrawing than the η^2-azobenzene ligand. Presumably, a similar effect takes place in the axial ligand centered oxidation; i.e., the η^2-azobenzene complex is the easiest to oxidize (E_{pa} = 0.35 V), followed by the η^2-Se_2 (E_{pa} = 0.77 V) and the η^2-S_2 complexes (E_{pa} = 0.98 V).

The electrochemistry of the imido complex **2** is also similar to that of the sulfido and selenido analogues. The imido complex **2** exhibits two reversible single-electron reductions at −1.20 and −1.59 V. The $\Delta E_{1/2}$ for these reductions is consistent with macrocycle-centered processes. The electrooxidation of (TTP)Ti=NPh is irreversible and occurs at E_{pa} = 1.04 V. Note that the electrooxidation of (TPP)Ti=O is a reversible, macrocycle-centered process which occurs at 1.20 V.[14b] Thus, the irreversible nature of the (TTP)Ti=NPh oxidation and the cathodic shift of E_{pa} relative to that of (TPP)Ti=O suggest that the imido ligand is involved in the oxidation process and not the porphyrin π system.

The formation of (TTP)Ti=NPh in eq 3 represents a novel example of intermetal imido transfer mediating a net two-

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electron redox process. Nonredox processes such as the intermetal pairwise exchange of oxo and imido groups have been reported by Gibson[16] and Schrock.[17] Although mechanistic studies for eq 3 have not yet been undertaken, some insight into the nature of the imido transfer can be derived from our electrochemical studies on (TTP)Ti(η^2-PhN═NPh). Since the first two reductions of complex **1** are porphyrin-ring based, it is unlikely that the imido transfer involves prior outer-sphere electron transfer. Cleavage of the azobenzene adduct to a bis(imido) complex, (TTP)Ti(═NPh)$_2$, as observed by Rothwell for a Mo system,[18] is not possible since this would require a formal Ti(VI) oxidation state. Moreover, our electrochemical studies do not indicate that the η^2-azobenzene ligand is reduced in an outer-sphere process. The most feasible mechanism for eq 3 is likely to be a pathway which involves a bridging azobenzene ligand in an activated dinuclear complex.

Concluding Remarks

The labile alkyne complexes (TTP)Ti(η^2-RC≡CR) provide a convenient starting material for the synthesis of new Ti(II) porphyrin complexes. Thus, a simple substitution reaction using azobenzene (eq 1) allows for the preparation of (TTP)Ti(η^2-PhN═NPh). This complex formally consists of Ti(IV) as indicated by the hydrolysis reaction (eq 4) which produces (TTP)Ti═O and 1 equiv of PhNH−NPhH. The electrochemical behavior of the η^2-azobenzene complex is also consistent with a formal Ti(IV) oxidation state.

The hydrazine/amine exchange reaction in eq 2 represents an alternative method of preparing the η^2-azobenzene complex. This process, coupled with the imido transfer in eq 3, formally involves the net disproportionation of hydrazine to diazene and amine and subsequent N═N bond activation. Further work to examine the scope of this process is underway.

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