Inorg. Chem. **2007**, *46*, 6373–6381

Synthesis, Structure, and LLCT Transitions in Terminal Hydrazido(2–) Bipyridine Complexes of Titanium

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Received March 5, 2007

Addition of 2,2′-bipyridine and its derivatives to $Ti(NMe_2)_2$(dpma), where dpma is *N*,*N*-di(pyrrolyl-α-methyl)-*N*-methylamine, followed by various hydrazine derivatives was used to generate a series of terminal hydrazido(2–) complexes. Among the new complexes is Ti[═NN(H)Ph](Bu^t-bpy)(dpma), which was structurally characterized, where Bu^t-bpy is 4,4′-*tert*-butyl-2,2′-bipyridine. Other new complexes reported are $Ti(NNMe_2)$(Me-bpy)(dpma), $Ti(NNMe_2)$(bpy)(dpma), $Ti(NNMe_2)$(Ph-bpy)(dpma), Ti[NN(Me)Ph](Bu^t-bpy)(dpma), Ti[NN(Me)*p*-tolyl](Bu^t-bpy)(dpma), and Ti[NN(Me)4-FC_6H_4](Bu^t-bpy)(dpma). Titanium hydrazido(2–) complexes bearing bpy substituents possess a low-energy transition, leading them to have blue or green colors, which is somewhat unusual for titanium(IV) species. Through absorption studies on the derivatives, it was determined that the low-energy transition is the result of an unusual ligand-to-ligand charge transfer where electron density residing on the hydrazido(2–) is transferred to the bpy π^* orbitals.

Introduction

Hydrazido(2−) complexes are largely of interest due to their intermediacy in dinitrogen reduction. For example, they are known intermediates in the reductive cleavage of dinitrogen to produce ammonia in the catalytic system of Schrock.[1] They are believed to be involved in the natural nitrogenase[2] enzymatic cycle as well, e.g., in the E_4 and E_5 states of the FeMo cofactor.[3] In other applications, terminal hydrazido(2−) ligands are believed to participate in alkyne hydrohydrazination[4] and iminohydrazination[5] catalysis.

While hydrazido(2−) complexes have a role in several important catalytic cycles and are known for many transition metals,[6] only a few terminal hydrazido(2−) complexes of the Group 4 elements have been reported until quite recently. The first report was that of $(Me_3Si)_2N{-}N{=}TiCp_2$ by Wiberg.[7] With the Schiff-base ligand TMTAA, Mountford and co-workers synthesized $Ph_2N{-}N{=}$Ti(TMTAA).[8] Woo and Thorman prepared the porphyrin complexes $R_2N{-}N{=}$Ti(TPP).[9] The synthesis and structure of $Ph_2N{-}N{=}$Zr(DMAP)Cp_2 was reported by Bergman and co-workers.[10]

The first structurally characterized example of a terminal titanium hydrazido(2−) complex appeared in 2004 with the report of $Me_2N{-}N{=}$Ti(dpma)(Bu^t-bpy) (**1**).[11] This complex is readily prepared (Scheme 1) by addition of Bu^t-bpy (4,4′-di-*tert*-butyl-2,2′-bipyridine) to $Ti(NMe_2)_2$(dpma), where dpma is *N*,*N*-di(pyrrolyl-α-methyl)-*N*-methylamine. To this solution is then added H_2NNMe_2 to generate **1**. Since the structure of this complex has appeared, Mountford and co-workers have reported $Ph_2N{-}N{=}TiCl_2(L)_x$ complexes, where

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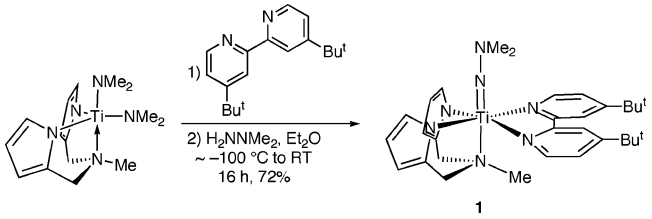
10.1021/ic700426s CCC: $37.00
Published on Web 07/11/2007

Scheme 1. Synthesis of Ti(NNMe$_2$)(Bu^t-bpy)(dpma) (**1**)



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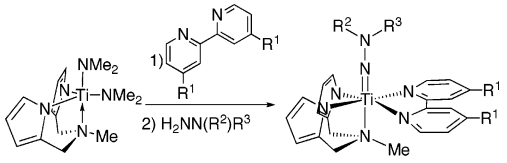
Scheme 2. Preparation of Ti[NN(R^2)R^3](R^1-bpy)(dpma) Complexes



2: R^1= Me, R^2 = R^3 = Me, 33%
3: R^1= H, R^2 = R^3 = Me, 66%
4: R^1= Ph, R^2 = R^3 = Me, 68%
5: R^1= Bu^t, R^2 = Me, R^3 = Ph, 63%
6: R^1= Bu^t, R^2 = Me, R^3 = *p*-tolyl, 83 %
7: R^1= Bu^t, R^2 = Me, R^3 = *p*-FC$_6$H$_4$, 85 %
8: R^1= Bu^t, R^2 = H, R^3 = Ph, 68%

L is a donor ligand and $x = 2-3$.[12] In the same report, DFT was used to study the bonding of titanium hydrazido(2−) complexes relative to the better known imido.

The hydrazido pyrrolyl complex **1** has an optical transition leading to the complex appearing blue, an unusual color for a Ti(IV) complex. Here, we report a study on the nature of that transition and the synthesis of several related terminal hydrazido(2−) complexes of titanium and discuss what may be gleaned from the electronic structure of these compounds from these electronic transitions. There are multiple signs of the hydrazido(2−) π system being strongly delocalized with a pendant β-aryl group. In addition to explaining some of the transition energy effects below, this delocalization is likely the cause for the planarity of aryl-containing hydrazido(2−) ligands on titanium and zirconium complexes as opposed to the dimethylhydrazido(2−) titanium complexes, which are usually strongly pyramidalized.

Results and Discussion

Synthesis and Structure. For this study, we prepared a series of 2,2′-bipyridine complexes with various substituents (R^1) in the 4,4′ positions (R^1-bpy). The substituents on the β-nitrogen were also altered to observe the effects on the electronic structure. To this end, complexes containing a variety of groups R^2 and R^3 such as methyl, aryl, and hydrogen groups on the β-nitrogen were all prepared and characterized. The syntheses were all analogous to that shown in Scheme 1 for **1**. The variety of complexes Ti[NN(R^2)R^3](R^1-bpy)(dpma) prepared is shown in Scheme 2.

The β-nitrogen in all the structurally characterized titanium dimethylhydrazido(2−) complexes[11,13] are pyramidalized to typical angles for an sp^3-hybridized nitrogen.[14] This type of pyramidalization is unusual in terminal hydrazido(2−) complexes as a whole, where the angles around the uncoordinated nitrogen are typically more indicative of sp^2 hybridization.[6,15] A planar geometry in dialkylhydrazido(2−) complexes can be attributed, in some cases, to significant participation by the isodiazene resonance form, which can be considered the result of β-N lone pair donation into the M=N double bond. The resulting electronic structure at one extreme can be drawn as shown in Figure 1 where the ligand becomes a neutral donor and the formal oxidation state is reduced by 2 relative to the hydrazido(2−) resonance form. This isodiazene form is the major contributor for many complexes. For example, Mansuy, Weiss, and co-workers reported an isodiazene iron porphyrin complex with an N−N bond distance of 1.232(5) Å,[16] indicating a bond order of ~2.0.[17] Mössbauer and other techniques indicated the complex was best described as iron(II).

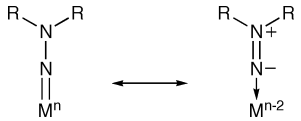


Figure 1. Hydrazido(2−) (left) and isodiazene (right) resonance forms for metal center M.

In the case of the titanium complexes, there is some indication that the isodiazene resonance form participates. For example, the N−N distance in **1** was determined to be 1.388(4) Å by X-ray diffraction. Hydrazido **1** reacts with methyliodide to methylate the β-nitrogen forming [Ti(NNMe$_3$)(Bu^t-bpy)(dpma)]I (**1-MeI**),[11] which removes the possibility of the isodiazene resonance form. The N−N distance in this complex was determined as 1.429(13) Å, similar to a typical N−N single bond distance of 1.451 ± 0.05 Å in hydrazine.[14] Consequently, some small participation of the isodiazene resonance form in **1** is suggested by the experimental data for these complexes, but the participation is quite small. By the strongly pyramidalized β-nitrogen angles, typical Ti−N double to triple bond distances, and only slightly shortened N−N distances, the hydrazido(2−) form is the major contributor in these titanium derivatives.

By contrast, β-nitrogen pyramidalization is not observed in titanium and zirconium complexes where the β-nitrogen bears aromatic groups.[10,12] This suggests that the nitrogen lone pair is delocalized by pendant aromatic groups in these systems, a suggestion consistent with the DFT calculations of Mountford and Green[12] and consistent with the experimental work in this study (vide infra).

Synthesized in the course of this work was a hydrazido(2−) complex of titanium bearing a hydrogen on the β-nitrogen, Ti[NN(H)Ph](Bu^t-bpy)(dpma) (**8**). While these types of protio complexes are known for other groups, they have not been previously reported in Group 4. Their synthesis

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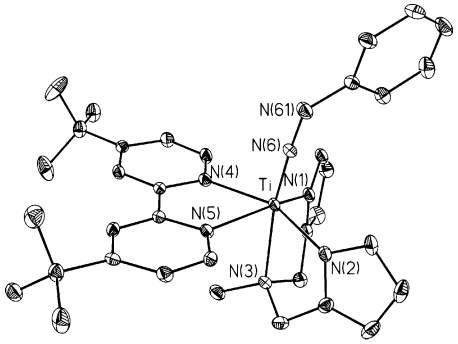
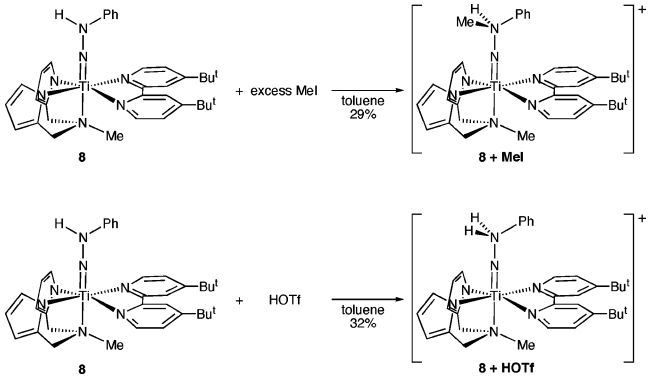


Figure 2. ORTEP structural drawing of Ti[NN(H)Ph](Bu^t-bpy)(dpma) (**8**). Selected bond lengths (Å) and angles (deg): Ti−N(6) 1.712(4), Ti−N(1) 2.079(4), Ti−N(2) 2.073(4), Ti−N(3) 2.396(4), Ti−N(4) 2.237(4), Ti−N(5) 2.251(4), N(6)−N(61) 1.350(5), N(6)−Ti−N(2) 95.68(17), N(6)−Ti−N(1) 103.82(18), N(2)−Ti−N(1) 101.94(15), N(6)−Ti−N(4) 100.13-(16), N(2)−Ti−N(4) 157.97(14), N(1)−Ti−N(4) 89.13(14), N(6)−Ti−N(5) 97.39(17), N(2)−Ti−N(5) 91.60(15), N(1)−Ti−N(5) 153.41(14), N(4)−Ti−N(5) 71.30(14), N(6)−Ti−N(3) 170.20(16), N(2)−Ti−N(3) 74.60(15), N(1)−Ti−N(3) 77.49(16), N(4)−Ti−N(3) 89.58(13), N(5)−Ti−N(3) 84.35-(15).

Scheme 3. Reactions of Ti[NN(H)Ph](Bu^t-bpy)(dpma) (**8**) with MeI and HOTf



was sought because current catalysts for hydrohydrazination have not been reported to be effective with monosubstituted hydrazines such as phenylhydrazine. However, the synthesis of **8** suggests that the cause for these problematic reactions is not pandemic instability across all titanium complexes, and catalysts for these monosubstituted hydrazine transformations may yet be accessible.[18]

The complex prepared from phenylhydrazine has been structurally characterized (Figure 2). This complex, like the others described, has a Ti−N(hydrazido) distance typical of a double to triple bond at 1.712(4) Å. The N−N distance is indicative of a small amount of double-bond character at 1.350(5) Å.

The β-nitrogen in **8** is also nucleophilic, and adducts with methyl iodide (**8** + **MeI**) and triflic acid (**8** + **HOTf**) have been prepared (Scheme 3).

Structural Effects and the Nature of the Electronic Transition. The absorption transitions for compounds **1**−**8** are shown in Table 1. All the complexes exhibit a single

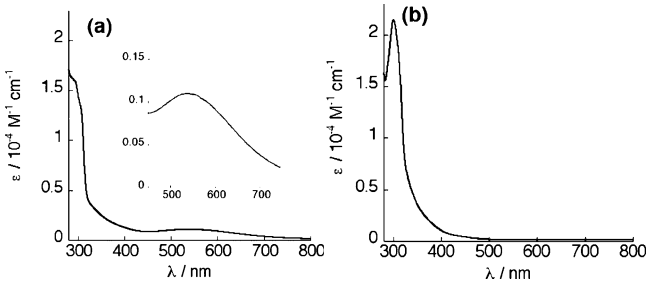


Figure 3. Absorption spectra for (a) Ti(NNMe$_2$)(Bu^t-bpy)(dpma) (**1**) with expansion of the 450−800 nm region and (b) [Ti(NNMe$_3$)(Bu^t-bpy)(dpma)]I (**1** + **MeI**).

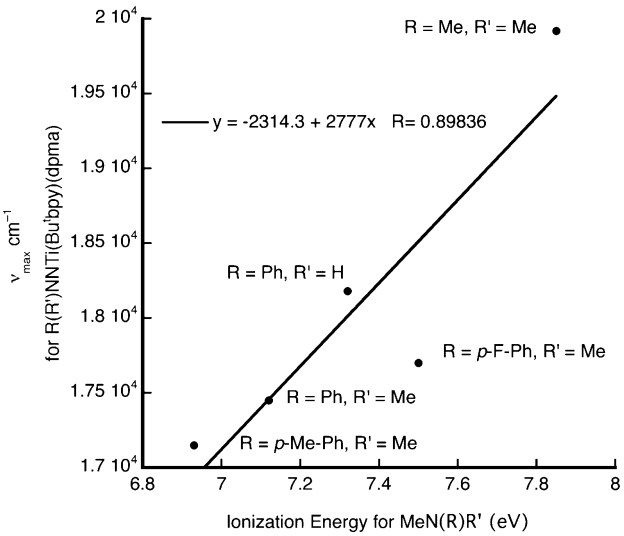


Figure 4. Plot of the low-energy transition energy versus the ionization energy of the corresponding tertiary amine derivatives, MeN(R′)R.

low-energy band in the 400−800 nm region leading to their blue or green colors in solution with extinction coefficients from about 900 to 2200 M^{-1} cm^{-1}.[19] As shown, there are solvent effects on the energy of the transition, which are discussed in a later section.

Several of these compounds were also examined for emission both at room temperature and in liquid-nitrogen-cooled toluene glasses. However, the emission is either too weak to observe or shifted outside of our observation window.

To discover the nature of the transition, the effect on the energy of the band caused by changing the structure in several ways was observed—methylation of the β-nitrogen lone pair, altering the substituents R^1 on the bpy, and altering the substituents R^2 and R^3 on the β-nitrogen.

Methylation of the β-nitrogen extinguishes the low-energy transition of the complex. For example, blue **1** exhibits a band in the absorption spectrum at 550 nm (Figure 3a). On methylation of the β-nitrogen, the complex becomes yellow with the low-energy absorption no longer present (Figure 3b). Consequently, the low-energy band is likely related to the lone pair on the β-nitrogen.

(18) The authors' research group has recently developed a 6-coordinate precatalyst effective for hydrohydrazination with monosubstituted hydrazines. Banerjee, S.; Barnea, E.; Odom, A. L. Manuscript in preparation.

(19) During data analysis, the oscillator strengths (*f*) for compounds **1**, **5**, **6**, and **7** were calculated from Gaussian fits to the peak shapes in benzene. The values varied from 0.02 to 0.04, as would be expected for compounds with extinction coefficients of this order. Figgis, B. N.; Hitchman, M. A. *Ligand Field Theory and its Applications*; Wiley-VCH: New York 2000; Chapter 8.

Table 1. Absorption Spectra Data for Complexes **1**−**8**

complex	$\bar{\nu}_{max} \times 10^{-3}$ (cm^{-1}) [$\epsilon \times 10^{-2}$ ($M^{-1}\,cm^{-1}$)]			
	C_6H_5CN	CH_3CN	THF	C_6H_6
$Ti(NNMe_2)(Bu^t\text{-bpy})dpma$ (**1**)	19.23 [9.60]	19.92 [8.57]	18.28 [10.9]	17.27 [9.44]
$Ti(NNMe_2)$(Me-bpy)dpma (**2**)	19.01 [11.1]	19.88 [6.44]	18.28 [10.4]	17.69 [9.18]
$Ti(NNMe_2)$(bpy)dpma (**3**)	18.18 [9.90]	19.05 [7.26]	17.76 [11.3]	16.64[a]
$Ti(NNMe_2)$(Ph-bpy)dpma (**4**)	17.27 [12.4]	18.08 [13.3]	16.70 [12.1]	15.87 [14.2]
Ti[NN(Me)Ph](Bu^t-bpy)dpma (**5**)	16.89 [16.8]	17.45 [13.5]	16.18 [14.0]	15.02 [14.4]
Ti[NN(Me)(*p*-tolyl)](Bu^t-bpy)dpma (**6**)	16.53 [21.5]	17.15 [11.8]	15.82 [15.3]	14.66 [19.6]
Ti[NN(Me)(*p*-FC_6H_4)](Bu^t-bpy)dpma (**7**)	17.06 [10.4]	17.70 [10.2]	16.53 [12.4]	15.20 [16.0]
Ti[NN(H)Ph](Bu^t-bpy)dpma (**8**)	17.70 [12.6]	18.18 [10.8]	16.52 [15.5]	16.13 [10.2]

[a] Low solubility limited ability to get an accurate measurement of the extinction coefficient.

Changing the substituents on the bpy ligand, R^1, has a dramatic effect on the energy of the transition. As the substituents are made more electron donating, the energy of the absorption increases. That the energy of the transition changes significantly on altering the bpy suggests that the bipyridine is also involved in the transition. The increasing energy with greater electron-donating ability indicates that the ligand is acting as an acceptor of electron density.

The substituents on the β-nitrogen greatly alter the energy of the transition as well. The dimethylhydrazido complexes have the highest energy bands. If an aromatic group is added to the β-nitrogen, the transition red-shifts significantly. If an electron-donating group is added to the aromatic group, like in the *p*-tolyl complex **6**, the absorption red-shifts relative to the phenyl containing **5**. In other words, a donor on the β-nitrogen makes the transition more energetically accessible, which is consistent with this group acting as an electron donor. Consistent with this, addition of an electron-withdrawing group, as in *p*-fluoro-containing **7**, causes the transition to blue-shift relative to the phenyl derviative.

That the energy of the absorption is strongly affected by the inductive effects of substituents as far away from the β-nitrogen as a *p*-methyl on a phenyl group indicates that the important nitrogen lone pair is delocalized with the arene π system. Consistent with this, the β-nitrogens of hydrazido(2−) ligands bearing aromatic groups are generally planar regardless of the metal center.[10,12,15] Naturally, this is consistent with the structures usually obtained for simple aniline derivatives, which are often near planar at nitrogen due to delocalization.

For the donor in the charge transfer, the ionization energy of the fragment should correlate with the transition energy if the donor is kept constant.[20] For the donor fragment, which we believe to be the hydrazido(2−), we used the ionization energies[21] for the aniline derivatives of the hydrazido(2−) complexes essentially replacing the "Ti(dpma)(Bu^t-bpy)" fragment with Me, e.g., using the ionization energy of Me_2-NPh for Ti(NN(Me)Ph)(Bu^t-bpy)(dpma) in the plot (Figure 4). The trend observed is consistent with the electron density for the charge transfer originating with the hydrazido(2−) unit in these complexes (Figure 4). The most anomalous point is for the *p*-fluoro derivative, which is unique as a potential π donor among this small set of compounds. The direction the fluoro derivative is off the line is consistent with it acting as a better donor in the charge transfer than anticipated from its ionization potential. The equation for the line not including the fluoro data, albeit with only four points, is $y = -4565 + 3113x$ with $R = 0.995$.

The red-shift on addition of aromatic rings to the β-nitrogen is readily explained using the one-electron argument given above. In this explanation, the HOMO is shifted upward in energy relatively to the LUMO by the presence of the aromatic ring as indicated by the ionization energies of the corresponding aniline derivatives. An alternative and perhaps more appealing resonance explanation for the red-shifting of the transition on addition of an aromatic ring involves stabilization of the transition state, which will have a positive or partial positive charge on the hydrazido(2−) ligand. In other words, the stabilization of the incipient cationic charge on the β-nitrogen by the aromatic ring would lower the transition energy associated with the LLCT. This delocalization between the β-nitrogen and the aromatic ring is supported by the planar structure of the aryl-substituted derivatives and the calculations (vide infra).

From the results above, we suggest that the low-energy transition is assignable to a ligand-to-ligand charge transfer (LLCT), where the donor is located on the hydrazido(2−) ligand and the acceptor is the π^* orbital of the bipyridine. LLCT transitions[22] have been extensively explored since their early observation in beryllium complexes by Coates and Green.[23] In only a couple of instances have absorption bands for Group 4 complexes been assigned to LLCT bands, and these systems involved zirconium.[24]

One could argue that the transition could be assigned as an MLCT with the metal acting as the donor being attenuated by the hydrazido ligand, which would depend on the metal having electron density (formally titanium is d^0) through the isodiazene resonance form (Figure 1). However, the authors prefer the LLCT assignment because the structural data suggest that the hydrazido(2−) resonance form is strongly favored and because the presence of the transition is dependent upon the existence of a β-nitrogen lone pair (vide supra). This having been said, the transfer of electron density is mediated by the metal, as it often will be in LLCT

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(22) For recent reviews see (a) Vogler, A.; Kunkely, H. *Top. Curr. Chem.* **2001**, *213*, 143. (b) Vogler, A.; Kunkely, H. *Comment. Inorg. Chem.* **1997**, *19*, 283.
(23) Coates, Y. E.; Green, S. I. E. *J. Chem. Soc.* **1962**, 3340.
(24) (a) Kunkely, H.; Vogler, A. *Inorg. Chem. Commun.* **2004**, *7*, 35. (b) Kunkely, H.; Vogler, A. *Eur. J. Inorg. Chem.* **1998**, 1863.

transitions, and the best description is probably one that involves the Ti═N−N(R^2)R^3 delocalized system acting as the donor with the π^* orbital of the bipyridine acting as the acceptor.

Another possible interpretation of the above data would be to assign the transition to an LMCT transition from the hydrazido(2−) ligand to the titanium metal center. In this interpretation, the hydrazido again acts as electron donor to the metal where the electron density at the metal is attenuated by electronics of the bpy. However, the electron would not interact strongly with the π system of the bpy. While this is difficult to exclude completely, there are several results that make it seem unlikely. First, other hydrazido(2−)-terminal titanium(IV) complexes not bearing bpy co-ligands and even bearing pyrrolyl ancillaries do not have this low-energy transition. For example, the recently reported[13] Ti($NNMe_2$)(nacnac)(dap), where dap is dimethylaminomethylpyrrolyl, is a more typical red color associated with LMCT transitions to titanium(IV). Second, the transition is strongly effected by substituents on the bpy.[25] If the LMCT transition occurs from the hydrazido(2−) to titanium in such a way that it strongly interacts with the bpy π system, it again becomes a semantic issue as to whether it is better to call it an LMCT with some interaction with a bpy π system or an LLCT mediated by the metal center. The calculations suggest the LUMO (the most likely acceptor) is largely bpy-based (vide infra), again favoring the LLCT designator.

DFT Calculations on Titanium Hydrazido(2−) Complexes. The experimental results may be explained by transitions resulting in electron transfer from hydrazido(2−) to bpy π^*.[26] Calculations at the B3LYP/6-31G(d/p) level on the dimethylhydrazido bpy containing **3** provide evidence that the transition is one from HOMO to LUMO, which have hydrazido and bpy π^* character, respectively (Figure 5). The HOMO is comprised largely of hydrazido(2−) character, with the Ti−N_α π bonding and N_α−N_β π antibonding. Also in the HOMO are found some minor mixing with the bpy and pyrrolyl π systems. The LUMO is largely bpy π^* in character with some mixing of the hydrazido π system.

Similar calculations were carried out on Ti[NN(Me)Ph](Bu^t-bpy)(dpma) (**5**). The overall character of the HOMO and LUMO between this complex bearing a phenyl-substituted β-nitrogen and the dimethylhydrazido(2−) complexes were similar except for the expected contributions of the aromatic group to the hydrazido(2−) electronic structure

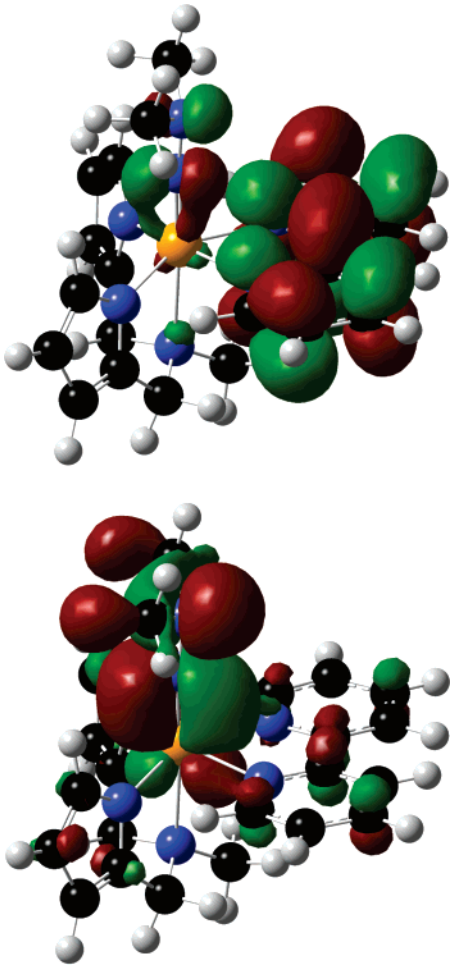

Figure 5. Kohn−Sham orbitals for the LUMO (top) and HOMO (bottom) of Ti($NNMe_2$)(bpy)(dpma) (**3**).

(Figure 6). In other words, the HOMO in this case is largely hydrazido(2−)-based with significant delocalization in the π system of the phenyl group and some mixing with other ligands on the metal as well. The LUMO is largely bpy π^* in character with some smaller contributions from other ligands, most notably the hydrazido(2−). The HOMO of the phenyl-substituted hydrazido, not surprisingly, is the apparent combination of the HOMO of an aniline fragment and a hydrazido(2−) orbital of similar character to the HOMO of **3**. There are other subtle differences between the dialkylhydrazido and the phenyl-substituted derivative, e.g., rotation around the Ti═N vector which alters the nature of the [Ph(Me)N−N═Ti]−N(bpy) interactions in the HOMO. The LUMO exhibits modest participation of the phenyl ring.

The overall effect of the arene π system's participation in both the HOMO and the LUMO of **5** is to decrease the energy of the HOMO−LUMO gap (E_{HL}^{calc}) relative to the dimethylhydrazido derivatives. This is consistent with the red-shift found experimentally. For **3**, E_{HL}^{calc} was 15 810 cm^{-1} versus the experimental energy for the transition in benzene of 16 640 cm^{-1}. For **5**, E_{HL}^{calc} was 14 549 cm^{-1} versus the experimental energy of 15 020 cm^{-1} for the transition in benzene. The agreement is remarkable considering the lack of consideration for solvent effects and the one-electron nature of this transition energy calculation. This

(25) If one plots the energy of the transition in Pt(R-bpy)Cl_2 versus the one in the titanium complexes in this paper with various R (unfortunately only three overlapping examples), one gets a straight line (R = 0.983) with a slope of 0.56 for the two systems. In other words, the effect of the substituents in the titanium system is to change the energy of the absorbance by about 1.8× more than in this known platinum system, where the transition is a well-established MLCT with the bpy as the acceptor. McInnes, E. J. L.; Farley, R. D.; Rowlands, C. C.; Welch, A. J.; Rovatti, L.; Yellowless, L. J. *Dalton Trans.* **1999**, 4203.

(26) TD-DFT calculations on **3** have been carried out using Gaussian at the B3LYP/6-31G** level. However, the number, intensity, and energy of the bands at this level did not seem to match well with experiment. A full TD-DFT study on the entire series would be interesting and may be enlightening as to the nature of the transitions. However, limitations of this technique have been noted. (a) Neese, F. *J. Biol. Inorg. Chem.* **2006**, *11*, 702. (b) Deeth, R. J. *Faraday Discuss.* **2003**, *124*, 378.

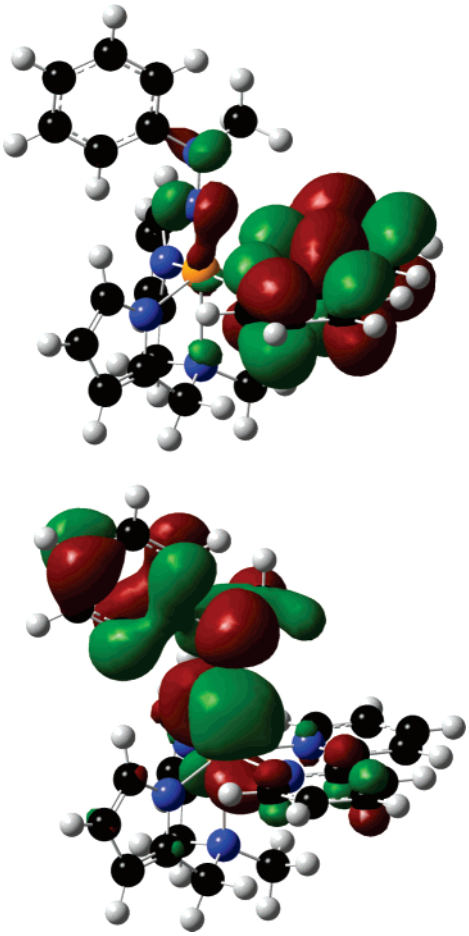

Figure 6. Kohn−Sham orbitals for the LUMO (top) and HOMO (bottom) of Ph(Me)NN═Ti(Bu^t-bpy)dpma (**5**). (Derivative without *tert*-butyl groups shown.)

seems consistent with the assertion of the HOMO−LUMO nature of the transition.

Solvent Effects. As shown in Table 1, changing the solvent has a dramatic effect on the energy of the transition. The energy of the band blue-shifts over 2000 cm^{-1} on moving from low-dielectric benzene to high-dielectric acetonitrile for all of the complexes. The increase in energy of the transition tracks roughly with the increasing dielectric constant of the medium consistent with the above arguments on the nature of the excited state. In this case, there is no apparent correlation with acceptor number of the solvents, which has been noted for other systems, e.g., cyano complexes of ruthenium(II).[27]

In the ground state, the hydrazido(2−) ligand will be negatively charged.[28] On excitation some of that electron density will shift to the bpy ligand. If the medium is polar, it is aligned to interact with the negatively charged hydrazido ligand in the ground state. On excitation, the charge density shifts to the bpy, leaving the solvent "out of position" to stabilize the molecular charge density. Consequently, the more polar solvents that were better organized by the charges of the ground state lead to a higher-energy transition by being poorly organized to support the charges of the excited state. As a result, the energy of transition correlates fairly well to the static dielectric constant of the solvent (Figure 7).[29]

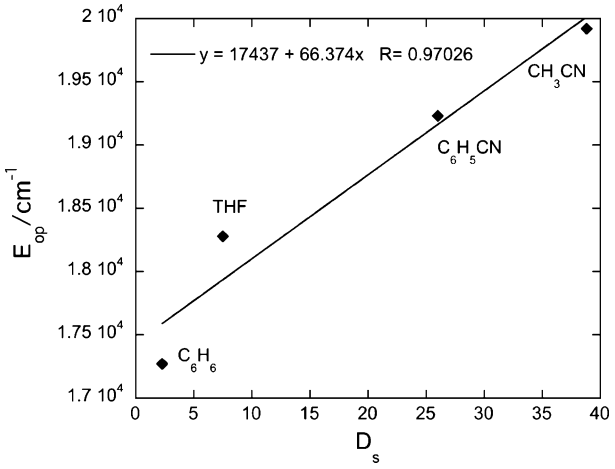

Figure 7. Plot of transition energy versus dielectric constant of the solvent for **1**.

Concluding Remarks

Titanium hydrazido(2−) complexes can be readily prepared in circumstances where the dimerization processes can be avoided, and we have prepared a series varying in structure and electronics. The delocalization along the Ti−N−N bonding vector leads to some unique electronic features. In the presence of a bpy co-ligand, a rare example of a Group 4 LLCT band results, which stretches well into the visible absorption region and leads to observed colors in solution from green to blue. Using structural modifications, it was also possible to discern that the charge transfer likely occurs with electron density moving from the hydrazido(2−) to the bpy π^* orbitals.

The dramatic effects on the energy of the transition with changing the para substituent of a phenyl group on the hydrazido(2−) indicate the electronics of the system are very sensitive to the nitrogen substituents and may suggest delocalization from the metal−ligand multiple-bond π system through the aromatic ring π system.[12] The planarity of terminal Group 4 hydrazido(2−) complexes bearing aryl groups[10,12] is likely due to this delocalization, and this explains the disparity with pyrrolyl-bearing dimethylhydrazido(2−) complexes, which have been uniformly pyramidalized.[11,13]

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(28) This charge distribution is certainly what would be expected for nitrogen bound to titanium considering the differences in anticipated electronegativities for the two fragments. For further conformation, see ref 12, especially footnote 28.

(29) An attempt at a more thorough analysis on the complexes using the Marcus−Hush equations gave results that were unreliable due to incompatibilities between the model and the system being studied. Namely, the "two sphere" model for the electron transfer may be breaking down due to interpenetration of the spheres describing the donor and acceptor. See the Supporting Information for more details. Attempts to access additional information through electrochemical measurements in these systems were thwarted by a consistent lack of reversibility on oxidation. For some relevant references see the following and references therein. (a) Goldsby, K. A.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3002. (b) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439. (c) Blackbourn, R. L.; Hupp, J. T. *J. Phys. Chem.* **1990**, *94*, 1788. (d) Hupp, J. T.; Dong, Y.; Blackbourn, R. L.; Lu, H. *J. Phys. Chem.* **1993**, *97*, 3278.

Experimental

General Considerations. All manipulations of air-sensitive compounds were carried out in an MBraun drybox under a purified nitrogen atmosphere. Anhydrous ether, pentane, and tetrahydrofuran were purchased from Jade Scientific. Toluene was purchased from Spectrum Chemical Mfg. Corp. Benzene was purchased from EMD chemicals. Acetonitrile was purchased from Fischer chemicals. Solvents were purified by sparging with dry N_2; then, water was removed by running through activated alumina systems purchased from Solv-Tek. Benzonitrile was purchased from ACROS and distilled over P_2O_5. Solvents were transferred under vacuum or N_2 to vacuum tight glass vessels and stored in the glove box.

Deuterated solvents were dried over purple sodium benzophenone ketyl (C_6D_6) or phosphoric anhydride ($CDCl_3$) and distilled under nitrogen. ^1H and ^{13}C spectra were recorded on Inova-300 or VXR-500 spectrometers. ^1H and ^{13}C assignments were confirmed when necessary with the use of 2-dimensional $^1H-^1H$ and $^{13}C-^1H$ correlation NMR experiments. All spectra were referenced internally to residual protiosolvent (^1H) or solvent (^{13}C) resonances. Chemical shifts are quoted in ppm and coupling constants in Hz. Typical coupling constants in ^{13}C NMR are not listed. H_2dpma,[30] Ti(NMe_2)$_2$(dpma),[31] and Ti($NNMe_2$)(Bu^t-bpy)(dpma)[11] were prepared as previously described. The hydrazines $H_2NN(Me)(4\text{-}CH_3C_6H_4)$ and $H_2NN(Me)(4\text{-}FC_6H_4)$ were prepared using the published procedure[32] (except that the final extraction was done with ethyl acetate in place of diisopropylether) from the arylhydrazine hydrochloride salts, which were purchased from Aldrich Chemical Co. The arylhydrazine hydrochloride salts were converted to the free base form by addition of NaOH.[33]

General Considerations for X-ray Diffraction. Crystals grown from concentrated solutions at −35 °C quickly were moved from a scintillation vial to a microscope slide containing Paratone N. Samples were selected and mounted on a glass fiber in wax and Paratone. The data collections were carried out at a sample temperature of 173 K on a Bruker AXS platform three-circle goniometer with a CCD detector. The data were processed and reduced utilizing the program SAINTPLUS supplied by Bruker AXS. The structures were solved by direct methods (SHELXTL v5.1, Bruker AXS) in conjunction with standard difference Fourier techniques.

Collection of UV−Vis Absorption Spectra. The room-temperature absorption spectra were recorded on a Shimadzu UV 3101 PC. The extinction coefficients were obtained from Beer's law studies and were determined from at least four points. Solutions for all the complexes were made in the dry box using freshly distilled solvents. Determination of the absorption maxima for the LLCT transition was accomplished by fitting the spectral data to a Gaussian function. The details for the fits and plots are found in the Supporting Information.

Computational Details. The calculated molecular structure of **3** was obtained by geometry optimizations using DFT with the B3LYP functional and Gaussian's "Ultrafine" grid size.[34] The 6-31G(p,d) basis set was used on all atoms, and the calculation was done in restricted mode. All calculations used the Gaussian-03M program[35] as implemented on a G5 Macintosh desktop with dual processors.

Synthesis and Characterization. Ti(dpma)(4,4′-dimethyl-2,2′-bipyridine)($NNMe_2$) (2). To a mixture of Ti(dpma)(NMe_2)$_2$ (85 mg, 0.26 mmol) and 4,4′-dimethyl-2,2′-bipyridine (48 mg, 0.26 mmol) in Et_2O (5 mL) cooled to −100 °C was added a colorless solution of H_2NNMe_2 (16 mg, 0.26 mol) in Et_2O (1 mL) dropwise. After stirring at room temperature overnight, the color of the mixture changed from yellow to purple. The volatiles of the reaction mixture were removed in vacuo, resulting in a purple solid that was washed with pentane. The solid was dried under reduced pressure to yield 42 mg of product (33%). ^1H NMR (300 MHz, $CDCl_3$): 7.91 (2 H, s, 3.3′-[4,4′-dimethyl-2,2′-bipyridine]), 7.70 (2 H, s, 5-C_4H_3N), 7.62 (2 H, m, 6,6′-[4,4′-dimethyl-2,2′-bipyridine]), 7.19 (2 H, m, 5,5′-[4,4′-dimethyl-2,2′-bipyridine]), 6.26 (2 H, dd, 4-C_4H_3N), 5.94 (2 H, s, 3-C_4H_3N), 3.68 (2 H, d, $C_4H_3NCH_2N$), 3.00 (2 H, d, $C_4H_3NCH_2N$), 2.55 (6 H, s, TiNN(CH_3)$_2$), 2.51 (6 H, s, 4,4′-dimethyl), 1.36 (3 H, s, $C_4H_3NCH_2N(CH_3)$). ^{13}C NMR ($CDCl_3$): 151.9 (2,2′-[4,4′-dimethyl-2,2′-bipyridine]), 151.2 (4,4′-[4,4′-dimethyl-2,2′-bipyridine]), 150.7 (6,6′-[4,4′-dimethyl-2,2′-bipyridine]), 137.0 (2-C_4H_3N), 131.5 (5,5′-[4,4′-dimethyl-2,2′-bipyridine]), 126.7 (5-C_4H_3N), 121.3 (3,3′-[4,4′-dimethyl-2,2′-bipyridine]), 107.0 (4-C_4H_3N), 102.2 (3-C_4H_3N), 58.4 ($C_4H_3NCH_2N$), 48.0 (TiNN(CH_3)$_2$), 44.1 ($C_4H_3NCH_2N(CH_3)$), 21.4 (4,4′-dimethyl). Anal. Found for $C_{25}H_{31}N_7Ti$ (Calcd): C, 62.64 (62.89); H, 6.63 (6.54); N, 20.42 (20.53).

Ti(dpma)(2,2′-bipyridine)($NNMe_2$) (3). To a mixture of Ti(dpma)(NMe_2)$_2$ (345 mg, 1.07 mmol) and 2,2′-bipyridine (167 mg, 1.07 mmol) in Et_2O (10 mL) cooled to −100 °C was added a colorless solution of H_2NNMe_2 (64 mg, 1.07 mol) in Et_2O (5 mL) dropwise. After stirring at room temperature overnight, the color of the mixture changed from yellow to purple. The volatiles of the reaction mixture were removed in vacuo, and the resulting purple powder was washed with pentane. The powder was dried under reduced pressure to yield 316 mg of product (66%). ^1H NMR (300 MHz, $CDCl_3$): 8.10 (2 H, d, 3,3′-[2,2′-bipyridine]), 7.95 (2 H, m, 4,4′-[2,2′-bipyridine]), 7.81 (2 H, d, 6,6′-[2,2′-bipyridine]), 7.70 (2 H, s, 5-C_4H_3N), 7.39 (2 H, m, 5,5′-[2,2′-bipyridine]), 6.26 (2 H, s, 4-C_4H_3N), 5.93 (2 H, s, 3-C_4H_3N), 3.79 (2 H, d, ^2J = 13.7 Hz, $C_4H_3NCH_2N$), 2.98 (2 H, d, ^2J = 13.5 Hz, $C_4H_3NCH_2N$), 2.56 (6 H, s, TiNN(CH_3)$_2$, 1.34 (3 H, s, $C_4H_3NCH_2N(CH_3)$). ^{13}C NMR ($CDCl_3$): 151.9 (2,2′-[2,2′-bipyridine]), 138.8 (3,3′, 5,5′-[2,2′-bipyridine]), 136.9 (2-C_4H_3N), 131.6 (4,4′-[2,2′-bipyridine]), 125.9 (5-C_4H_3N), 120.6.0 (6,6′-[2,2′-bipyridine]), 107.2 (4-C_4H_3N), 102.4 (3-C_4H_3N), 58.4 ($C_4H_3NCH_2N$), 47.9 (TiNN(CH_3)$_2$), 44.1 ($C_4H_3NCH_2N(CH_3)$). EI MS low res.; found (calcd): 449 (449). Anal. Found for $C_{23}H_{27}N_7Ti$ (Calcd): C, 61.60 (61.47); H, 6.19 (6.06); N, 21.57 (21.82).

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Ti(dpma)(4,4′-diphenyl-2,2′-bipyridine)(NNMe$_2$) (4). To a mixture of Ti(dpma)(NMe$_2$)$_2$ (73 mg, 0.23 mmol) and 4,4′-diphenyl-2,2′-bipyridine (70 mg, 0.23 mmol) in toluene (8 mL) cooled to −100 °C was added a colorless solution of H_2NNMe_2 (16 mg, 0.26 mmol) in toluene (1 mL) dropwise. After stirring at room temperature overnight, the color of mixture changed from yellow to dark blue. The volatiles of the reaction mixture were removed in vacuo, and the resulting dark blue solid was washed with pentane. The solid was dried under reduced pressure to yield 92 mg of product (68%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.36 (2 H, s, 3,3′-[2,2′-bipyridine]), 7.88 (2 H, s, 5-C_4H_3N), 7.77 (6 H, m, 6,6′, 4,4′-[2,2′-bipyridine]) and [4,4′-diphenyl), 7.60 (8 H, m, [4,4′-diphenyl]), 6.26 (2 H, dd, 4-C_4H_3N), 5.94 (2 H, s, 3-C_4H_3N), 3.76 (2 H, d, ^2J = 13.4 Hz, $C_4H_3NCH_2N$), 3.08 (2 H, d, ^2J = 13.7 Hz, $C_4H_3NCH_2N$), 2.64 (6 H, s, TiNN(CH_3)$_2$, 1.48 (3 H, s, $C_4H_3NCH_2N(CH_3)$). ^{13}C NMR ($CDCl_3$): 152.4 (2,2′-[4,4′-diphenyl-2,2′-bipyridine]), 152.1 (4,4′-[4,4′-diphenyl-2,2′-bipyridine]), 151.4 (6,6′-[4,4′-diphenyl-2,2′-bipyridine]), 136.9 (2-C_4H_3N), 131.6 (5,5′-[4,4′-diphenyl-2.2′-bipyridine]), 130.3 (1,1′-diphenyl), 129.5 (2,2′-diphenyl), 129.0 (3,3′-diphenyl), 127.1 (4,4′-diphenyl), 123.7 (5-C_4H_3N), 118.4 (3,3′-[4,4′-diphenyl-2,2′-bipyridine]), 107.2 (4-C_4H_3N), 102.4 (3-C_4H_3N), 58.4 ($C_4H_3NCH_2N$), 48.0 (TiNN(CH_3)$_2$), 44.3 ($C_4H_3NCH_2N(CH_3)$). Anal. Found for $C_{35}H_{35}N_7Ti$ (Calcd): C, 69.73 (69.88); H, 5.72 (5.86); N, 16.44 (16.30).

Ti(dpma)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(NNMePh) (5). To a mixture of Ti(dpma)(NMe$_2$)$_2$ (413 mg, 1.28 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (343 mg, 1.28 mmol) in Et_2O (10 mL) cooled to −100 °C was added a colorless solution of H_2NN(Me)-(Ph) (156 mg, 1.28 mol) in Et_2O (5 mL) dropwise. After stirring at room temperature overnight, the color of mixture changed from yellow to dark green. The volatiles of the reaction mixture were removed in vacuo, and the resulting dark green solid was washed with pentane three times. The solid was dried under reduced pressure to yield 501 mg of product (63%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.03 (2 H, s, 3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 7.59 (2 H, m, 5-C_4H_3N), 7.59 (2 H, m, 6,6′-[4,4′-di-*tert*-butyl-2.2′-bipyridine]), 7.39 (2 H, m, 5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 6.88 (2 H, m, 3-C_6H_5), 6.57 (2 H, d, 2-C_6H_5), 6.46 (1 H, m, 4-C_6H_5), 6.22 (2 H, dd, 4-C_4H_3N), 5.96 (2 H, s, 3-C_4H_3N), 3.77 (2 H, d, ^2J = 13.5 Hz, $C_4H_3NCH_2N$), 3.37 (3 H, s, TiNNCH_3Ph), 3.11 (2 H, d, ^2J = 13.5 Hz, $C_4H_3NCH_2N$), 1.49 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 1.41 (18 H, s, 4,4′-di-*tert*-butyl). ^{13}C NMR ($CDCl_3$): 163.9 (2,2′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 152.4 (4,4′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 151.5 (6.6′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 136.9 (2-C_4H_3N), 130.6 (5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 128.1 (3-C_6H_5), 123.5 (5-C_4H_3N), 117.0 (3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 116.2 (2-C_6H_5), 110.2 (4-C_6H_5), 107.3 (4-C_4H_3N), 102.4 (3-C_4H_3N), 58.7 ($C_4H_3NCH_2N$), 44.6 (TiNNCH_3), 40.2 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 35.4 ($C_4H_3NCH_2N$-(CH_3)), 30.3 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]). EI MS low res.; found (calcd): 623 (623). Anal. Found for $C_{36}H_{45}N_7Ti$ (Calcd): C, 69.53 (69.27); H, 7.12 (7.20); N, 15.49 (15.71).

Ti(dpma)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(NN(Me)(4-CH$_3$C$_6$H$_4$)) (6). To a mixture of Ti(dpma)(NMe$_2$)$_2$ (112 mg, 0.347 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (93 mg, 0.347 mmol) in Et_2O (5 mL) cooled to −100 °C was added dropwise to a solution of H_2N-N(Me)(4-$CH_3C_6H_4$) (47 mg, 0.346 mmol) in Et_2O (2 mL). After stirring at room temperature overnight, the color of mixture changed from yellow to green. The volatiles of the reaction mixture were removed under reduced pressure, and the resulting green solid was washed with pentane (3 × 3 mL). The solid was dried under reduced pressure to yield 0.18 g of product (82.6%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.01 (2 H, s, 3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 7.60 (2 H, d, 5-C_4H_3N), 7.57 (2 H, m, 6,6′-[4,4′-di-*tert*-butyl-2.2′-bipyridine]), 7.38 (2 H, m, 5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 6.68 (2 H, d, ^2J = 7.7 Hz, 3-[4-$CH_3C_6H_4$]), 6.50(2 H, d, ^2J = 7.7 Hz, 2-[4-$CH_3C_6H_4$]), 6.20(2 H, m, 4-C_4H_3N), 5.94 (2 H, s, 3-C_4H_3N), 3.74 (2 H, d, ^2J = 13.5 Hz, $C_4H_3NCH_2N$), 3.32 (3 H, s, TiNN(CH_3)(4-$CH_3C_6H_4$)), 3.08 (2 H, d, ^2J = 13.5 Hz, $C_4H_3NCH_2N$), 2.12 (3 H, s, TiNN(CH_3)(4-$CH_3C_6H_4$)); 1.47 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 1.40 (18 H, s, 4,4′-di-*tert*-butyl). ^{13}C NMR ($CDCl_3$): 164.0, (2,2′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 152.6 (4,4′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 151.8 (6,6′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 137.2 (2-C_4H_3N), 130.9 (5,5′-[4,4′-di-*tert*-butyl-2.2′-bipyridine]), 128.9 (2,3,4,5,6-(4-$CH_3C_6H_4$), 123.6 (5-C_4H_3N), 117.0 (3,3′-[4,4′-di-*tert*-butyl-2.2′-bipyridine]), 110.7 (1-(4-$CH_3C_6H_4$), (107.5 (4-C_4H_3N), 102.6 (3-C_4H_3N), 58.9 ($C_4H_3NCH_2N$), 44.8 ($C_4H_3NCH_2N(CH_3)$), 40.7 (TiNN(CH_3)(4-$CH_3C_6H_4$)), 35.6 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′bipyridine]), 30.6 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 20.5 (4-$CH_3C_6H_4$). Anal. Found for $C_{37}H_{47}N_7Ti$ (Calcd): C, 69.80 (69.69); H, 7.34 (7.43); N, 15.49 (15.39).

Ti(dpma)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(NN(Me)(4-FC$_6$H$_4$)) (7). To a mixture of Ti(dpma)(NMe$_2$)$_2$ (200 mg, 0.619 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (169 mg, 0.63 mmol) in Et_2O (5 mL) cooled to −100 °C was added dropwise a solution of H_2N-N(Me)(4-FC_6H_4) (90 mg, 0.642 mmol) in Et_2O (2 mL). After stirring at room temperature overnight, the color of the reaction mixture changed from yellow to green. The volatiles of the reaction mixture were removed under reduced pressure, and the resulting green solid was washed with pentane (3 × 3 mL). The solid was dried under reduced pressure to yield 0.34 g of product (85.4%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.02 (2 H, s, 3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 7.57 (2 H, d, 5-C_4H_3N), 7.52 (2 H, m, 6,6′-[4,4′-di-*tert*-butyl-2.2′-bipyridine]), 7.38 (2 H, m, 5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 6.60−6.55 (4H, m, 4-$CH_3C_6H_4$), 6.20 (2 H, m, 4-C_4H_3N), 5.94 (2 H, s, 3-C_4H_3N), 3.76 (2 H, d, ^2J = 13.5 Hz, $C_4H_3NCH_2N$), 3.30 (3 H, s, TiNN(CH_3)(4-FC_6H_4)), 3.09 (2 H, d, ^2J = 13.5 Hz, $C_4H_3NCH_2N$), 1.47 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 1.40 (18 H, s, 4,4′-di-*tert*-butyl). ^{13}C NMR ($CDCl_3$): 164.3, (2,2′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 152.6 (4,4′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 151.8 (6,6′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 137.2 (2-C_4H_3N), 130.8 (5,5′-[4,4′-di-*tert*-butyl-2.2′-bipyridine]), 123.6 (5-C_4H_3N), 117.4 (3,3′-[4,4′-di-*tert*-butyl-2.2′-bipyridine]), 114.7 (splitting, 2,3,5,6-(4-FC_6H_4), 111.7 (splitting, 1-(4-FC_6H_4)), 107.6 (4-C_4H_3N), 102.8 (3-C_4H_3N), 58.9 ($C_4H_3NCH_2N$), 44.8 ($C_4H_3NCH_2N(CH_3)$), 41.0 (TiNN(CH_3)(4-FC_6H_4), 35.6 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 30.6 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]). ^{19}F NMR (300 MHz, $CDCl_3$): −130.5 (1F, s, 4-FC_6H_4). GC-MS direct probe found (calcd): 641 (641). Anal. Found for $C_{36}H_{44}N_7FTi$ (Calcd): C, 67.18 (67.36); H, 6.82 (6.86); N, 14.56 (15.28).

Ti(dpma)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(NNHPh) (8). To a mixture of Ti(dpma)(NMe$_2$)$_2$ (539 mg, 1.67 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (447.4 mg, 1.67 mmol) in Et_2O (10 mL) cooled to −100 °C was added a colorless solution of H_2NN(H)Ph (180 mg, 1.67mmol) in Et_2O (5 mL) dropwise. After stirring at room temperature overnight, the color of mixture changed from yellow to dark green. The volatiles of the reaction mixture were removed in vacuo, and the resulting dark green solid was washed with pentane three times. The solid was dried under reduced pressure to yield 691 mg of product (68%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.22 (1 H, s, Ti(NN*H*Ph), 8.04 (2 H, s, 3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 7.61 (2 H, m, 5-C_4H_3N), 7.59 (2 H, m, 6,6′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 7.42 (2 H, m, 5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 6.94 (2 H, m, 3-C_6H_5), 6.54 (3 H, m, 2-C_6H_5

Table 2. Structural Parameters for the X-ray Diffraction Studies of **8**·CH_2Cl_2

	8
empirical formula	$C_{36}H_{45}Cl_2N_7Ti$
fw	694.59
space group	$P\bar{1}$
a (Å)	11.467(12)
b (Å)	12.308(13)
c (Å)	15.270(16)
β (deg)	95.438(17)
V (Å^3)	1794(3)
Z	2
μ (mm^{-1})	0.423
D_{calcd} (g cm^{-3})	1.286
total reflns	15 167
uniq. reflns (R_{int})	5182 (0.0656)
extinction	0.0014
$R(F_0)(I > 2\sigma)$	0.0560
$R_w(F_0^2)(I > 2\sigma)$	0.1365

and 4-C_6H_5), 6.24 (2 H, dd, 4-C_4H_3N), 5.98 (2 H, s, 3-C_4H_3N), 3.79 (2 H, d, ^2J = 13.6 Hz, $C_4H_3NCH_2N$), 3.14 (2 H, d, ^2J = 13.6 Hz, $C_4H_3NCH_2N$), 1.52 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 1.43 (18 H, s, 4,4′-di-*tert*-butyl). ^{13}C NMR ($CDCl_3$): 164.1 (2,2′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 152.6 (4,4′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 151.8 (6.6′-[4,4′-di-tert-butyl-2.2′-bipyridine]), 137.2 (2-C_4H_3N), 130.5 (5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 128.8 (3-C_6H_5), 123.8 (5-C_4H_3N), 117.9 (3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 117.5 (2-C_6H_5), 109.8 (4-C_6H_5), 107.6 (4-C_4H_3N), 102.6 (3-C_4H_3N), 58.9 ($C_4H_3NCH_2N$), 44.9 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 35.7 ($C_4H_3NCH_2N(CH_3)$), 30.6 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]). Satisfactory analysis on this complex was not obtained after multiple attempts. However, the salts derived from the compound were readily obtained as analytically pure compounds, and the compound's composition has been confirmed by X-ray diffraction and NMR spectroscopy.

Ti(dpma)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(NNHMePh)I (8 + MeI). To dark green Ti(dpma)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(NNHPh) (207 mg, 0.34 mmol) in toluene (10 mL) cooled to near frozen in a liquid nitrogen cold well was added a colorless solution of MeI (100 mg, 0.70 mmol) in toluene (5 mL) dropwise. After stirring at room temperature overnight, the color of the mixture changed from dark green to brown. The volatiles of the reaction mixture were removed in vacuo, and the resulting brown solid was recrystallized from dichloromethane/pentane to yield 74 mg of red product (29%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.24 (2 H, s, 3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 7.33 (6 H, m, 5-C_4H_3N; 6,6′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]; 5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 6.97 (3 H, m, TiNNMe*H*Ph and 3-C_6H_5), 6.78 (2 H, d, 2-C_6H_5), 6.01 (6 H, m, 4-C_6H_5, 4-C_4H_3N, and 3-C_4H_3N), 4.23 (2 H, d, ^2J = 13.9 Hz, $C_4H_3NCH_2N$), 3.59 (2 H, d, ^2J = 13.9 Hz, $C_4H_3NCH_2N$), 2.00 (3 H, s, Ti(NN*Me*HPh)), 1.43 (18 H, s, 4.4′-di-*tert*-butyl), 1.39 (3 H, s, $C_4H_3NCH_2N(CH_3)$). ^{13}C NMR ($CDCl_3$): 166.7 (2,2′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 153.1 (4,4′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 151.0 (6,6′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 137.3 (2-C_4H_3N), 129.2 (5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 128.0 (3-C_6H_5), 125.3 (5-C_4H_3N), 124.5 (3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 120.9 (2-C_6H_5), 120.1 (4-C_6H_5), 109.1 (4-C_4H_3N), 103.0 (3-C_4H_3N), 60.8 ($C_4H_3NCH_2N$), 46.9 ($TiNNCH_3$), 36.1 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 30.5 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]). Anal. Found for $C_{36}H_{46}IN_7Ti$ (Calcd): C, 57.26 (57.54); H, 6.02 (6.13); N, 13.16 (13.05).

Ti(dpma)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(NNH$_2$Ph)(CF$_3$SO$_3$) (8 + HOTf). To dark green Ti(dpma)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(NNHPh) (256 mg, 0.42 mmol) in toluene (10 mL) cooled to near frozen in a liquid nitrogen cold well was added a yellow solution of CF_3SO_3H (63 mg, 0.42 mmol) in toluene (5 mL) dropwise. The color of the mixture changed from green to red after addition. The reaction was stirred at room temperature for 2 h, and the volatiles were removed in vacuo. The resulting red solid was recrystallized from dichloromethane/pentane, and 74 mg of product was obtained (32%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.28 (2 H, s, 3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 7.35 (6 H, m, 5-C_4H_3N, 6,6′-[4,4′-di-*tert*-butyl-2,2′-bipyridine] and Ti(NNH_2Ph)), 7.03 (1 H, m, 4-C_6H_5), 6.92 (2 H, d, 3-C_6H_5), 6.76 (2 H, m, 2-C_6H_5), 6.01 (2 H, m, 5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 5.98 (2 H, dd, 4-C_4H_3N), 5.67 (2 H, s, 3-C_4H_3N), 4.25 (2 H, d, ^2J = 13.9 Hz, $C_4H_3NCH_2N$), 3.62 (2 H, d, ^2J = 13.7 Hz, $C_4H_3NCH_2N$), 2.02 (3 H, s, $C_4H_3NCH_2N(CH_3)$), 1.43 (18 H, s, 4.4′-di-*tert*-butyl). ^{13}C NMR ($CDCl_3$): 163.0 (2,2′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 153.1 (4,4′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 150.6 (6,6′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 137.3 (2-C_4H_3N), 129.3 (5,5′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 128.0 (3-C_6H_5), 125.1 (5-C_4H_3N), 124.6 (3,3′-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 120.3 (2-C_6H_5), 109.2 (4-C_6H_5), 104.0 (4-C_4H_3N), 102.4 (3-C_4H_3N), 60.8 ($C_4H_3NCH_2N$), 40.2 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]), 36.1 ($C_4H_3NCH_2N(CH_3)$), 30.6 ($C(CH_3)_3$-[4,4′-di-*tert*-butyl-2,2′-bipyridine]). Anal. Found for $C_{36}H_{44}N_7F_3SO_3Ti$ (Calcd): C, 56.73 (56.89); H, 5.88 (5.79); N, 12.74 (12.91).

Acknowledgment. The authors greatly appreciate the financial support of the National Science Foundation, Department of Energy−Defense Programs, and Michigan State University. A.L.O. is an Alfred P. Sloan Fellow. A.L.O. thanks Jim McCusker, Ned Jackson, Tom Meyer, and Richie Eisenberg for helpful discussions.

Supporting Information Available: Crystallographic details and tabular material on positional and displacement parameters, bond length, and angles are available for compound **8** in CIF format. Gaussian fits, fitting parameters, tabular material for $\Delta E°$ calculations and plots of $E_{op} - \Delta E°$ vs $1/D_{op} - 1/D_s$ are available in pdf format. ^{1}H NMR spectra for **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700426S