# Heterobimetallic Ti/Co Complexes That Promote Catalytic N–N Bond Cleavage

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**Supporting Information** 

**ABSTRACT:** Treatment of the tris(phosphinoamide) titanium precursor ClTi(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub> (1) with CoI<sub>2</sub> leads to the heterobimetallic complex ( $\eta^{2}$ -<sup>i</sup>Pr<sub>2</sub>PNXyl)Ti(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>( $\mu$ -Cl)CoI (2). One-electron reduction of 2 affords ( $\eta^{2}$ -<sup>i</sup>Pr<sub>2</sub>PNXyl)-Ti(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>CoI (3), which can be reduced by another electron under dinitrogen to generate the reduced diamagnetic complex (THF)Ti(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub> (4). The removal of the dinitrogen ligand from 4 under vacuum affords (THF)Ti-(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>Co (5), which features a Ti–Co triple bond. Treatment of 4 with hydrazine or methyl hydrazine results in N–N bond cleavage and affords the new diamagnetic complexes



 $(L)Ti(XylNP^{i}Pr_{2})_{3}CoN_{2}$  (L = NH<sub>3</sub> (6), MeNH<sub>2</sub> (7)). Complexes 4, 5, and 6 have been shown to catalyze the disproportionation of hydrazine into ammonia and dinitrogen gas through a mechanism involving a diazene intermediate.

### INTRODUCTION

The transition metal-catalyzed production of ammonia from dinitrogen under mild conditions remains one of the greatest challenges in small molecule activation chemistry.<sup>1</sup> Extensive studies have been carried out in efforts to understand the mechanisms of the two well-established nitrogen fixation processes, namely, the Haber-Bosch process and the biological fixation of dinitrogen by nitrogenase enzymes. Several recent reports have elegantly demonstrated the catalytic production of ammonia from dinitrogen using well-defined iron and molybdenum complexes.<sup>2</sup> The operative catalytic cycles are thought to involve a Chatt-type "distal" mechanism in which one transition metal atom coordinates N2, and subsequent reduction and protonation steps first occur at the distal nitrogen atom  $(M^n N \equiv N \rightarrow M^{n+3} \equiv N + NH_3 \rightarrow M^n + NH_3)$ . However, detailed spectroscopic studies of the nitrogenase enzyme have revealed intermediates involving N2H2 and N2H4 bound to the FeMo cofactor in the middle or late stages of the catalytic cycle in the N2-fixation process (M<sup>n</sup>N $\equiv$ N  $\rightarrow$  $M^{n}HN=NH \rightarrow M^{n}H_{2}N=NH_{2} \rightarrow M^{n} + NH_{3}$ , and both hydrazine and diazene are substrates for nitrogenase.<sup>3</sup> Within this context, reductive cleavage of the N-N bonds in hydrazine to form ammonia is of considerable importance and there are a number of transition metal complexes known to promote the transformation stoichiometrically4 or catalytically.5 In some cases, the transition metal species mediate the disproportionation of hydrazine into ammonia and dinitrogen.

Our group has been investigating heterobimetallic complexes featuring polar metal-metal multiple bonds in an effort to promote multielectron redox processes and/or uncover new stoichiometric and catalytic transformations of small molecules facilitated by cooperative reactivity involving both transition metals.<sup>6</sup> The zwitterionic Zr<sup>IV</sup>Co<sup>-I</sup> heterobimetallic complexes (THF)Zr(MesNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub> (Mes = 2,4,6-trimethylphenyl) and (THF)Zr(MesNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>Co feature metal-metal double and triple bonds, respectively,<sup>6b,7</sup> and have been shown to activate alkyl halides,<sup>8</sup> CO<sub>2</sub>,<sup>9</sup> diaryl ketones,<sup>10</sup> and organic azides<sup>11</sup> via one-, two-, or four-electron transformations. In addition, the reaction of hydrazine and its derivatives with (THF)Zr(MesNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub> results in cleavage of an N–H bond via a one-electron dissociative electron transfer process (Scheme 1).<sup>12</sup>





From both a steric and an electronic perspective, zirconium and its lighter congener titanium are quite different. In light of titanium's ability to undergo one-electron redox processes, we have recently extended our studies to heterobimetallic Ti/M complexes. A series of bis(phosphinoamide) Ti–Co complexes featuring Ti/Co multiple bonds was recently reported, and the reduced complex  $ClTi(XylNP^iPr_2)_2CoPMe_3$  (Xyl = 3,5-

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dimethylphenyl) was shown to promote the reductive coupling of aryl ketones into alkenes.<sup>13</sup> Herein, we build upon this work by synthesizing a series of heterobimetallic Ti/Co complexes featuring metal–metal bonds. To showcase the enhanced reactivity of the Ti/Co combination compared to Zr/Co, we explore the reactivity of reduced Ti/Co complexes toward hydrazine, demonstrating the ability of these complexes to cleave N–N bonds and catalytically disproportionate hydrazine to ammonia and dinitrogen.

#### RESULTS AND DISCUSSION

**Synthesis and Spectroscopic Characterization of 1–5.** We previous reported the inability to install three [MesN-P<sup>i</sup>Pr<sub>2</sub>]<sup>-</sup> ligands around a Ti center, presumably due to the steric hindrance of the mesityl group.<sup>13</sup> However, changing the *N*-aryl group from 2,4,6-trimethylphenyl to 3,5-dimethylphenyl permits the formation of the desired tris(phosphinoamide) precursor ClTi(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub> (1) via treatment of TiCl<sub>4</sub> with three equivalents of *in situ*-generated Li[XylNP<sup>i</sup>Pr<sub>2</sub>] (Scheme 2).

#### Scheme 2



Treatment of **1** with 1 equiv of CoI<sub>2</sub> afforded a heterobimetallic paramagnetic Ti/Co complex  $(\eta^{2-i}Pr_2PNXyI)$ -Ti(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>( $\mu$ -Cl)CoI (**2**). The <sup>1</sup>H NMR spectrum of complex **2** displays ten distinct broad paramagnetically shifted resonances between 23 and -10 ppm, suggesting an asymmetric structure similar to the previously reported Zr/Co analogue  $(\eta^2$ -XylNP<sup>i</sup>Pr<sub>2</sub>)Zr(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>( $\mu$ -I)CoI.<sup>14</sup> The solution magnetic moment of **2** is 3.20  $\mu_{\rm B}$ , consistent with an S = 1 ground state. Cyclic voltammetry of complex **2** reveals a quasi-reversible reduction at -1.7 V and an irreversible reductive features were well-separated, bulk chemical reductions of **2** 

were carried out to investigate both the one- and two-electron reduced products.

One-electron reduction of 2 with KC<sub>8</sub> led to the formation of a new paramagnetic complex  $(\eta^2 - i Pr_2 PNXyl)Ti$ - $(XyINP'Pr_2)_2CoI$  (3) shown in Scheme 2. Complex 3 adopts an asymmetric geometry in which one of the phosphinoamide ligands is bound  $\eta^2$  to the titanium center in the solid state (vide infra). However, the <sup>1</sup>H NMR spectrum of complex 3 in THF $d_8$  shows six broad resonances, which is more consistent with a  $C_3$ -symmetric geometry in solution (Figure S6). The <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub> displays fewer and broader resonances (Figure S5). We hypothesize that weak THF binding to the Ti center of 3 favors a  $C_3$ -symmetric structure in solution, but that the phosphinoamide ligands are rapidly exchanging on the NMR time scale in benzene via reversible phosphine dissociation, resulting in coalescence behavior.<sup>15</sup> Measurement of the solution magnetic moment of 3 reveals an S = 1/2ground state ( $\mu_{eff} = 1.98 \ \mu_{B_l} C_6 D_6$ ). An analogous one-electron reduced product has not been isolated for tris-(phosphinoamide) Zr/Co complexes, which favor two electron reductions.<sup>7a,14,16</sup>

Complex 3 can be further reduced using additional KC8 under a dinitrogen atmosphere, and from this reaction the diamagnetic complex  $(THF)Ti(XylNP^{i}Pr_{2})_{3}CoN_{2}$  (4) was isolated. Alternatively, complex 4 can be synthesized directly by reducing 2 with 2.5 equiv of Na/Hg under dinitrogen (Scheme 2). The <sup>31</sup>P NMR spectrum of 4 shows one broad resonance at 45.5 ppm, consistent with a  $C_3$ -symmetric environment. The  $\nu(N_2)$  stretch at 2084 cm<sup>-1</sup> in the IR spectrum of 4 is considerably higher in energy than the N<sub>2</sub> vibrational frequency of the Zr/Co analogue (THF)Zr- $(XyINP^{i}Pr_{2})_{3}CoN_{2}$  ( $\nu(N_{2}) = 2045 \text{ cm}^{-1}$ ).<sup>14</sup> This indication of less  $\pi$  back-bonding from cobalt to dinitrogen suggests a less electron rich cobalt center in 4 and, in turn, a stronger donation from Co to the more Lewis acidic early metal. The N2 molecule is so weakly bound to cobalt that it easily dissociates upon exposure to vacuum or argon atmosphere to generate a new coordinatively unsaturated product, (THF)Ti(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>Co (5) (Scheme 2), as indicated by a dramatic color change from red to green. The <sup>31</sup>P NMR resonance of 5 is also diagnostic and shifts from 45.5 to 39.6 ppm upon removal of the N2 ligand. Consistent with the weak binding of  $N_2$  to Co in 4, a related heterobimetallic Ti/Co complex, CoTi[N(o-(NCH<sub>2</sub>P- $({}^{t}Pr)_{2}C_{6}H_{4})_{3}$ , was recently reported to not bind N<sub>2</sub> at all.<sup>1</sup>

Structural Characterization of Complexes 2-5. Complexes 1-5 were characterized in the solid state using single crystal X-ray diffraction. The solid state structure of monometallic complex 1 was determined and is shown in Figure S21. Consistent with the <sup>1</sup>H NMR data, the solid state structure of 2 features two bridging phosphinoamide ligands, a terminal iodide ligand bound to cobalt, and one chloride ligand bridging titanium and cobalt. The third phosphinoamide ligand is bound  $\eta^2$  to titanium (Figure 1). The Ti–Co intermetallic distance in 2 is 2.6530(4) Å, which corresponds to a "formal shortness ratio" (the ratio of the metal-metal interatomic distance to the sum of the single bond atomic radii of the two metal ions, FSR<sup>18</sup>) of 1.07 and suggests a weak metal-metal dative interaction (Table 1). One-electron reduction significantly decreases the Ti–Co intermetallic distance to 2.2735(8) Å and 2.2734(8) Å in the two independent molecules in the asymmetric unit of complex 3, indicative of a metal-metal double bond (FSR = 0.92). The Ti-Co bond length in complex 3 is slightly longer than that in the previously reported



Figure 1. Displacement ellipsoid (50%) representations of 2 and 3. For clarity, all hydrogen atoms and solvate molecules are omitted. Only one of two independent molecules in the asymmetric unit of 3 is shown.

bis(phosphinoamide) complex  $[(\mu-Cl)Ti(XylNP^{i}Pr_{2})_{2}CoI]_{2}$ (2.2051(4) Å, FSR = 0.89), which was described as having a Ti–Co double bond (Table 1).

Both 4 and 5 are  $C_3$ -symmetric in the solid state with trigonal bipyramidal geometries at the Ti centers if the metal-metal bond is taken into consideration (Figure 2). The Co center in complex 4 has a distorted trigonal bipyramidal geometry with Co 0.60 Å above the plane of the three phosphorus atoms. In the absence of the dinitrogen ligand in complex 5, the Co atom moves 0.2 Å closer to the plane of phosphine donors but is likely restricted from adopting a true trigonal monopyramidal geometry by the orientation of the phosphorus lone pairs. The Ti–Co distances in complex 4 are 2.2371(3) Å and 2.2268(3) Å in the two molecules in the asymmetric unit, corresponding to an FSR of 0.90 that is in line with the previously reported Zr/Co analogue (THF)Zr(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub> (Table 1).<sup>14</sup> The



Figure 2. Displacement ellipsoid (50%) representations of 4 and 5. For clarity, all hydrogen atoms and solvate molecules are omitted. Only one of two independent molecules in the asymmetric unit of 4 and 5 is shown.

decrease in the distance between the two metal centers in 5 to 2.0252(5) Å and 2.0271(5) Å (FSR = 0.81) indicates an increase in Ti–Co bond order upon removal of the N<sub>2</sub> ligand. The FSR of complex 5 compares well with other heterobimetallic complexes from our group that have been assigned as having a metal–metal triple bond, including (THF)Zr-(MesNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>Co (FSR = 0.82)<sup>7 a</sup> and ClTi-(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>CoPMe<sub>3</sub> (FSR = 0.81).<sup>13</sup> However, the Ti–Co distance in 5 is significantly shorter than that of Lu's recently reported C<sub>3</sub>-symmetric CoTi[N(o-(NCH<sub>2</sub>P(<sup>i</sup>Pr)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>] complex (2.1979(8) Å, FSR = 0.88), which was assigned a Ti=Co double bond.<sup>17</sup>

Upon examining the metal-ligand distances in complexes 2-5, a general trend emerges. With each sequential reduction event, the Co-P distances contract and the Ti-N distances elongate (Table 1). This trend is consistent with increased Co $\rightarrow$ P back-bonding and decreased N $\rightarrow$ Ti  $\pi$  donation as the

Table 1. Metal–Cobalt and Metal–Ligand Distances and  $FSRs^a$  of Complexes 2–7 and a Selection of Similar Heterobimetallic M/Co Complexes (M = Ti, Zr)

				distance <sup>®</sup> (av)	
compound	core	M–Co distance	FSR	Co-P	M–N
$(\eta^{2-i} Pr_2 PNXyl) Ti(XylNP^i Pr_2)_2(\mu-Cl) CoI$ (2)	(TiCo) <sup>5+</sup>	2.6530(4) Å	1.07	2.27 Å	1.96 Å <sup>c</sup>
$(\eta^2$ -XylNP <sup>i</sup> Pr <sub>2</sub> )Zr(XylNP <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> ( $\mu$ -Br)CoBr <sup>14</sup>	(ZrCo) <sup>5+</sup>	2.7602(3) Å	1.06	2.28 Å	2.10 Å <sup>c</sup>
$(\eta^2 - Pr_2 PNXyl)Ti(XylNP'Pr_2)_2CoI$ (3)	(TiCo) <sup>4+</sup>	2.2735(8) Å	0.92	2.25 Å	1.98 Å <sup>c</sup>
		2.2734(8) Å			
$[(\mu-Cl)Ti(XylNP^{i}Pr_{2})_{2}CoI]_{2}^{13}$	(TiCo) <sup>4+</sup>	2.2051(4) Å	0.89	2.24 Å	1.96 Å
$(THF)Ti(XylNP^{i}Pr_{2})_{3}CoN_{2}$ (4)	(TiCo) <sup>3+</sup>	2.2371(3) Å	0.90	2.21 Å	2.00 Å
		2.2268(3) Å			
$(H_3N)Ti(XyINP^iPr_2)_3CoN_2$ (6)	(TiCo) <sup>3+</sup>	2.2461(3) Å	0.90	2.22 Å	1.99 Å
$(MeH_2N)Ti(XylNP'Pr_2)_3CoN_2$ (7)	(TiCo) <sup>3+</sup>	2.2703(5) Å	0.91	2.21 Å	1.99 Å
(THF)Zr(MesNP <sup>i</sup> Pr <sub>2</sub> ) <sub>3</sub> CoN <sub>2</sub> <sup>7a</sup>	$(ZrCo)^{3+}$	2.3683(9) Å	0.90	2.22 Å	2.15 Å
		2.3615(9) Å			
(THF)Zr(XylNP <sup>i</sup> Pr <sub>2</sub> ) <sub>3</sub> CoN <sub>2</sub> <sup>14</sup>	(ZrCo) <sup>3+</sup>	2.3778(5) Å	0.91	2.23 Å	2.12 Å
		2.3854(5) Å			
$(THF)Ti(XylNP^{i}Pr_{2})_{3}Co$ (5)	(TiCo) <sup>3+</sup>	2.0252(5) Å	0.81	2.24 Å	2.03 Å
		2.0271(5) Å			
ClTi(XylNP <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> CoPMe <sub>3</sub> <sup>13</sup>	(TiCo) <sup>3+</sup>	2.0234(9) Å	0.81	2.24 Å	1.99 Å
$CoTi[N(o-(NCH_2P(^iPr)_2C_6H_4)_3]^{17}$	(TiCo) <sup>3+</sup>	2.1979(8) Å	0.88	2.26 Å	1.95 Å
(THF)Zr(MesNP <sup>i</sup> Pr <sub>2</sub> ) <sub>3</sub> Co <sup>7a</sup>	(ZrCo) <sup>3+</sup>	2.1468(6) Å	0.82	2.22 Å	2.19 Å
		2,1395(7) Å			

<sup>*a*</sup>FSR =  $D^{MCo}/(R_1^M + R_1^{Co})$ .<sup>18</sup> <sup>*b*</sup>Average distances are within 0.01 Å of the individual Co–P and Ti–N distances in all molecules in the asymmetric units. <sup>*c*</sup>Only Ti–N distances associated with the bridging phosphinoamide ligands are included in the average value.

complexes become more reduced. The notable outlier is the N<sub>2</sub>-free complex **5**, whose average Co–P distance (2.24 Å) is 0.03 Å longer than N<sub>2</sub>-bound complex **4**. This phenomenon could possibly result from attenuation of the electron density at Co by stronger metal–metal bonding or from the geometric constraints that could weaken the overlap of the sp<sup>3</sup>-hybridized phosphine lone pair with the Co center as it moves into the plane of the three phosphorus atoms; however, it should be noted that a similar phenomenon was not observed for the Zr/Co analogues (Table 1).<sup>7a</sup>

**EPR Spectroscopy.** In contrast to previously reported Zr/Co complexes, both metals in the series of Ti/Co complexes are potentially redox active. Therefore, EPR spectroscopy was used to evaluate the localization of the unpaired electron in the S = 1/2 complex 3. The X-band EPR spectrum of complex 3 was collected in toluene glass at 3 K. An axial signal is observed with  $g_{\parallel} = 2.12$  and  $g_{\perp} = 2.01$  (Figure 3) that can be simulated



**Figure 3.** Experimental (black) and simulated (red) X-band EPR spectra for **3** (A) and  $Ti(XyINP^{i}Pr_{2})_{3}$  (B) in toluene glass obtained at 3 K (frequency = 9.43 GHz, modulation to 5 G, power = 0.6325 mW).

with both hyperfine coupling to the I = 7/2 <sup>59</sup>Co nucleus ( $A_{\parallel} = 442$  MHz) and superhyperfine coupling to the I = 5/2 <sup>127</sup>I nucleus ( $A_{\perp} = 150$  MHz) (Figure 3A). The large hyperfine coupling to <sup>59</sup>Co suggests that the unpaired electron in 3 is localized on the Co atom, consistent with a Ti<sup>IV</sup>Co<sup>0</sup> assignment. The *g* values and hyperfine coupling values are consistent with similar phosphine-ligated S = 1/2 cobalt iodide complexes in which the unpaired electron is cobalt-centered.<sup>19</sup> For comparison, an EPR spectrum of the monometallic tris(phosphinoamide) Ti<sup>III</sup> complex, Ti(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>,<sup>13</sup> was also collected. The EPR signal of Ti(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub> is isotropic with much weaker coupling that is simulated as superhyperfine coupling to three equivalent <sup>14</sup>N nuclei (I = 1), resulting in a seven-line splitting pattern (g = 1.98, A = 47 MHz) (Figure 3B).

**Computational Studies of 3–5.** To better understand the metal-metal bonding in complexes 3-5, a theoretical investigation was carried out using density functional theory (DFT). The BP86 functional and a mixed LANL2TZ(f)/6-311+G(d)/D95 V basis set were chosen based on the previous success of this method in accurately predicting the structural

features of related heterobimetallic compounds.<sup>7,13</sup> A table comparing selected calculated interatomic distances and angles derived from DFT geometry optimizations with those determined crystallographically is provided in Table S2, showing good agreement.

Consistent with the Co–Ti multiple bond character insinuated by the short metal–metal distance in 3, the calculated frontier molecular orbital diagram of 3 reveals a Co→Ti  $\sigma$  bond along with two polarized  $\pi$  bonds involving the Co and Ti  $d_{xz}$  and  $d_{yz}$  orbitals (Figure S30). Further, as suggested by the hyperfine coupling in the EPR spectrum of 3, Mulliken population analysis predicts that significantly more of the unpaired spin density resides on the Co atom (Mulliken spin densities: 1.20 (Co), -0.44 (Ti), Figure 4B), consistent with a Ti<sup>IV</sup>Co<sup>0</sup> formulation.



Figure 4. (A) Depictions and energies of the frontier molecular orbitals of 5 derived from DFT calculations (BP86/LANL2TZ(f)/6-311+G(d)/D95 V). (B) Calculated unpaired spin density surface of complex 3. Mulliken spin densities: 1.20 (Co); -0.44 (Ti).

The calculated frontier molecular orbital diagrams of complexes 4 and 5 are shown in Figures S31 and 4A, respectively. In addition to a  $\sigma$  bond between the Co and Ti  $d_{z^2}$  orbitals, two  $\pi$  bonds involving the Co and Ti  $d_{xz}$  and  $d_{yz}$  orbitals are predicted to contribute to the metal-metal bonding in both complexes. Similar to 5, the previously reported b is (ph os ph in o am id e) Ti - Co complex ClTi - (XylNP'Pr\_2)\_2CoPMe\_3^{13} adopts a  $(\sigma)^2(\pi)^4(Co_{nb})^4$  electronic configuration, which corresponds to a formal bond order of 3. In the case of complex 4, competitive  $\pi$  back-bonding from Co to the N<sub>2</sub> ligand partially disrupts the metal-metal  $\pi$  bonding, leading to a longer Ti-Co distance and estimated bond order closer to 2.

Natural bond orbital (NBO) calculations were used to assess the electronic structure of complexes **3–5**. Wiberg bond indices (WBIs) were also calculated and used to assess trends in metal-metal bonding, although we have found that the WBIs calculated for metal-ligand and metal-metal bonds are always lower than the formal bond orders we would predict based on structural parameters and idealized molecular orbital considerations.<sup>20</sup> As expected based on their similar Ti–Co bond distances, the calculated WBIs of complexes **3** and **4** are similar (1.14 and 1.18, respectively), which confirms that the additional electron in complex **4** occupies a Co-based orbital that is nonbonding with respect to Ti. Natural population analysis (NPA) also reveals a decrease in the natural charge on the Co atom upon reduction from **3** to **4**, suggesting that the redox event is cobalt-centered and that complex **4** is best described using a zwitterionic  $Ti^{IV}Co^{-I}$  formalism. The Ti–Co WBI increases upon removal of the N<sub>2</sub> ligand in complex **5** (WBI = 1.60), and becomes nearly identical to that reported for  $CITi(XyINP^{i}Pr_{2})_{2}CoPMe_{3}$  (WBI = 1.59) (Table 2), consistent

# Table 2. Computed Natural Charges and Wiberg Bond Indices (WBIs) of Heterobimetallic Complexes

	natural charges		
	Ti/Zr	Со	WBI
$(\eta^{2-i}Pr_2PNXyl)Ti(XylNP^iPr_2)_2CoI$ (3)	0.38	-0.38	1.14
$(THF)Ti(XylNP^{i}Pr_{2})_{3}CoN_{2}$ (4)	0.45	-1.14	1.18
$(THF)Ti(XylNP'Pr_2)_3Co$ (5)	0.44	-0.66	1.60
$[(\mu-Cl)Ti(XylNP^{i}Pr_{2})_{2}CoI]_{2}^{13}$	0.26	-0.25	1.26
ClTi(XylNP <sup>i</sup> Pr <sub>2</sub> ) <sub>2</sub> CoPMe <sub>3</sub> <sup>13</sup>	0.40	-0.64	1.59
(THF)Zr(MesNP <sup>i</sup> Pr <sub>2</sub> ) <sub>3</sub> CoN <sub>2</sub> <sup>7b</sup>	1.39	-1.22	0.95

with the complexes having the same Ti $\equiv$ Co triple bond order. The natural charges on Ti and Co in **5** and ClTi-(XylNP<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>CoPMe<sub>3</sub> are similar, and in both cases the difference in the natural charge between the two metal atoms is significantly smaller than in the Zr<sup>IV</sup>/Co<sup>-1</sup> complex (THF)Zr(MesNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub>, suggesting a more covalent metal-metal bond between the two first row transition metals, Ti and Co (Table 2). While we have assigned formal oxidation states here that are consistent with spectroscopic and computational data, a more detailed spectroscopic study will be needed to confirm these assignments.

Stoichiometric Reactions of 4 with Hydrazine and Methylhydrazine. We previously reported that the activation of the N-H bonds of hydrazine and its derivatives by  $(THF)Zr(MesNP'Pr_2)_3CoN_2$  affords a series of S = 1/2zirconium hydrazido complexes (RNNH<sub>2</sub>)Zr- $(MesNP'Pr_2)_3CoN_2$  (R = H, Me, and Ph) via one-electron dissociative electron transfer processes (Scheme 1).<sup>12</sup> In contrast, addition of hydrazine to 4 quantitatively generates a new diamagnetic complex 6 (Scheme 3). Both the  ${}^{1}$ H and  ${}^{31}$ P NMR spectra are indicative of a symmetric complex similar to 4, with an additional broad signal at -1.01 ppm and the notable absence of the resonances corresponding to the bound THF protons in the <sup>1</sup>H NMR spectrum of 6. The presence of an  $N_2$ vibration in the IR spectrum of 6 ( $\nu(N_2) = 2062 \text{ cm}^{-1}$ ) confirms that dinitrogen remains bound to Co and the 22 cm<sup>-1</sup> decrease compared to 4 ( $\nu(N_2) = 2084 \text{ cm}^{-1}$ ) suggests a more electron rich cobalt center in 6, as would result from weaker bonding to a less Lewis acidic titanium center. Taken together, these data indicate that the Ti-bound THF molecule has been replaced by a more basic neutral ligand. As expected from the spectroscopic results, the solid-state structure of 6 reveals that the THF ligand in 4 was replaced by an ammonia molecule to give  $(H_3N)Ti(XylNP'Pr_2)_3CoN_2$  (6) (Figure 5). Since the oxidation state of the two metal centers remains unchanged in this reaction, we speculate that hydrazine disproportionates to form the bound ammonia molecule with concomitant elimination of N2, based on the balanced equation depicted in Scheme 3. While the N<sub>2</sub> released from the reaction was not quantified, its formation was verified via a control reaction between N<sub>2</sub>-free complex 5 and N<sub>2</sub>H<sub>4</sub> (vide infra). Similarly, methylhydrazine is disproportionated by 4 to afford a 1:3 mixture of 6 and (MeH<sub>2</sub>N)Ti(XylNP'Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub> (7) (Scheme 3, Figure S20). As an alternative synthetic method, addition of





**Figure 5.** Displacement ellipsoid (50%) representation of **6**. For clarity, all solvate molecules and hydrogen atoms, with the exception of those bound to ammonia, are omitted. The cobalt-bound dinitrogen ligand is disordered over two positions, and only one is shown for clarity.

ammonia or methylamine to 4 cleanly generates 6 or 7, respectively, via displacement of THF.

The structures of complexes 6 and 7 have been confirmed by X-ray crystallographic structure determination, and the structures of 6 and 7 are shown in Figures 5 and S27, respectively. As predicted by the <sup>1</sup>H and <sup>31</sup>P NMR spectra, complex 6 is  $C_3$ -symmetric in the solid state with an NH<sub>3</sub> ligand bound to titanium in place of THF. The hydrogen atoms of the ammonia and methylamine ligands in 6 and 7 were located and refined and are shown in Figures 5 and S27. The Ti–Co interatomic distances in complexes 6 and 7 are slightly longer than that of the THF-bound precursor 4 (2.2461(3) Å for 6 and 2.2703(5) Å for 7), suggesting similar metal–metal multiple bonding (Table 1).

**Catalytic Disproportionation of Hydrazine.** Inspired by the stoichiometric reactions of 4 with hydrazines, we investigated the activity of 4 as a catalyst for the disproportionation of hydrazine at ambient temperature without the addition of a reductant or proton source. In a typical reaction, complex 4 was dissolved in Et<sub>2</sub>O followed by the addition of N<sub>2</sub>H<sub>4</sub>. After 30 min, the solution was quenched by HCl, and the product was quantified using the indophenol assay.<sup>21</sup> The product yields summarized in Table 3 clearly

Table 3. Catalytic Disproportionation of Hydrazine b	y
Heterobimetallic Ti/Co Complexes 4–6	

	3	$N_2H_4 \xrightarrow{0.1}{Et}$	02 mmol catalyst <sub>2</sub> O, 30 min	4 NH <sub>3</sub> + N <sub>2</sub>	
entry	catalyst	N <sub>2</sub> H <sub>4</sub> (equiv)	NH <sub>3</sub> yield <sup>a</sup> (mmol)	NH <sub>3</sub> yield (equiv) [theor]	turnover
1	4	1	0.026	1.3 [1.3]	1.0
2	4	5	0.13	6.6 [6.7]	5.0
3	4	10	0.26	13 [13]	10
4	4	20	0.42	21 [27]	16
5	4	50	0.47	22 [67]	18
6	5 <sup>b</sup>	20	0.38	19 [27]	14
7	6	20	0.46	23 [27]	17
			21 4		

<sup>*a*</sup>Determined by colorimetry.<sup>21</sup> <sup>*b*</sup>The reaction was carried out in an argon filled glovebox.

suggest that a maximum of 16-18 turnovers can be reached. The N<sub>2</sub>-free complex **5** and the ammonia coordinated complex **6** show comparable activity to complex **4** (entries 4, 6, and 7), implying that product inhibition with either NH<sub>3</sub> or N<sub>2</sub> is not problematic. However, the efficiency of **4** as a catalyst for this reaction and the limited number of turnovers are most likely hampered by the degradation of **4** under the reaction conditions. Analysis of the reaction mixture by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy upon the completion of the reaction reveals that most of the catalyst has decomposed to free XylNHP<sup>*i*</sup>Pr<sub>2</sub> ligand. In fact, when 20 equiv of NH<sub>3</sub> are added to complex **4**, a substantial quantity of XylNHP<sup>*i*</sup>Pr<sub>2</sub> is formed along with the NH<sub>3</sub> complex **6**, suggesting that the buildup of NH<sub>3</sub> in the catalyst mixture is responsible for catalyst deactivation.

A series of control reactions demonstrated that monometallic complexes including the monometallic  $Ti^{IV}$  complex 1, a monometallic  $Ti^{III}$  complex  $Ti(XylNP^iPr_2)_3$ , and a monometallic  $Co^I$  complex  $ICo(Ph_2PNH^iPr)_3$  were inactive catalysts and produced no ammonia upon treatment with hydrazine. Furthermore, a 1:1 mixture of  $Ti(XylNP^iPr_2)_3$  and ICo- $(Ph_2PNH^iPr)_3$  showed no catalytic activity for hydrazine disproportionation.

While the ammonia formed via hydrazine disproportionation could be easily quantified, the formation of dinitrogen in these reactions was confirmed qualitatively via the reaction of N<sub>2</sub>-free complex **5** with hydrazine. Addition of 3 equiv of hydrazine to a  $C_6D_6$  solution of **5** in a J. Young NMR tube under an argon atmosphere resulted in the quantitative generation of **6**, as confirmed by NMR spectroscopy and IR spectroscopy ( $\nu(N_2)$ = 2062 cm<sup>-1</sup>).

A number of transition metal complexes promote hydrazine disproportionation reactions to generate diazene,  $^{4c,5a,b,d}$  which can be considered the first step in the disproportionation of hydrazine to ammonia and dinitrogen. Based on this precedent, we propose a reaction mechanism for the disproportionation of hydrazine by 4-6, in which the heterobimetallic Ti/Co

complex first reacts with two molecules of hydrazine, affording two ammonia molecules and a diazene-coordinated adduct. In the following step, the diazene complex can further react with another molecule of hydrazine to generate  $N_2$  and  $NH_3$  (Scheme 4). The isolation or spectroscopic observation of

Scheme 4



any intermediate complexes was unsuccessful. Furthermore, the 3:1 mixture of 6 and 7 observed when MeNHNH<sub>2</sub> was used is difficult to explain, although similar product distributions have been observed in dispoportionation reactions of substituted hydrazines that proceed through diazene intermediates in the literature.<sup>Sb</sup>

Since diazene itself, HN=NH, is not stable, we attempted to access a related intermediate using a stoichiometric reaction of 4 with azobenzene, PhN=NPh (Scheme 5). Treatment of 4



with stoichiometric azobenzene cleanly generates a paramagnetic complex 8, rather than the expected diamagnetic azobenzene adduct. The same paramagnetic complex 8 was identified by <sup>1</sup>H NMR spectroscopy as a product of the reaction of 4 with 1,2-diphenylhydrazine. We were able to determine the formulation and connectivity of complex 8 as  $[(\kappa^2 - Xy lNP^i Pr_2 NPh)Ti(Xy lNP^i Pr_2)_2(\mu - NPh)Co]_2(\mu - N_2)$  using single crystal X-ray diffraction (Figure S28); its formation in both reactions suggests that azobenzene is an intermediate in the reaction of 4 with 1,2-diphenylhydrazine, supporting the mechanistic hypothesis shown in Scheme 4. The exact role of Ti and Co in each N-H and N-N bond activation step and the binding mode of hydrazine or diazene intermediates is unknown, and given that one of the phosphinoamide ligands has been oxidized in complex 8, this complex is likely an offcycle byproduct and not an intermediate in the hydrazine disproportionation reaction. However, it is clear that both metals play an essential role in substrate binding during the catalytic disproportionation process.

### CONCLUSION

In conclusion, we have prepared a series of tris-(phosphinoamide) heterobimetallic Ti/Co complexes featuring

metal-metal multiple bonds. Several notable differences between these complexes and their Zr/Co analogues have emerged from this study:

- (1) The metal-metal distances are substantially shorter in the Ti/Co series; however, the difference is relatively small when corrected for the smaller atomic radius of Ti. DFT calculations suggest that the metal-metal bonds in the Ti/Co series are generally more covalent.
- (2) A comparison of the infrared  $\nu(N_2)$  stretches of the  $(THF)M(XyINP^iPr_2)_3CoN_2$  (M = Zr, Ti (4)) complexes suggests substantially more Co $\rightarrow$ N<sub>2</sub>  $\pi$  back-bonding in the Zr/Co case, which, in turn, is consistent with weaker Co $\rightarrow$ M donation. The more weakly bound N<sub>2</sub> ligand in the Co/Ti complex may permit more facile small molecule activation processes involving the Co center.
- (3) The reduced C<sub>3</sub>-symmetric heterobimetallic Ti/Co complex 4 reacts with hydrazine and its derivatives quite differently from the Zr/Co analogue (THF)Zr-(MesNP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub>. While the Zr/Co complex undergoes a one-electron dissociative electron transfer process to form a metal-bound N<sub>2</sub>H<sub>3</sub><sup>-</sup> hydrazido species and NH<sub>3</sub>, the Ti/Co complex proceeds further down the N–H and N–N bond cleavage pathway to disproportionate hydrazine into ammonia and dinitrogen catalytically.

Several mechanistic questions regarding the latter catalytic transformation remain unanswered, including the binding mode of the diazene molecule in the purported diazene intermediate, which could be either terminal at Ti or bridging between the Ti and Co centers. However, it is clear that both Ti and Co play an important role in the reaction mechanism and, more importantly, are a more reactive pair than Zr and Co in the tris(phosphinoamide) heterobimetallic scaffold.

#### EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques unless otherwise noted. All glassware was oven or flame-dried immediately prior to use. Diethyl ether and THF were obtained as HPLC grade without inhibitors; pentane and benzene were obtained as ACS reagent grade. All protio solvents were degassed by sparging with ultrahigh purity argon and dried via passage through columns of drying agents using a Seca solvent purification system from Pure Process Technologies. THF- $d_8$  and dichloromethane- $d_2$  were dried with CaH2 and degassed before use. All NMR spectra were obtained using a Varian Inova or MR 400 MHz instrument, and all chemical shifts are reported in ppm. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to residual solvent, and <sup>31</sup>P NMR chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub>. For the paramagnetic molecules (2 and 3), the <sup>1</sup>H NMR data are reported with the chemical shift, followed by the peak width at half-height in parentheses. <sup>i</sup>Pr<sub>2</sub>PNHXyl,<sup>1</sup> (<sup>i</sup>Pr<sub>2</sub>PNXyl)<sub>3</sub>Ti,<sup>13</sup> and ICo(Ph<sub>2</sub>PNH<sup>i</sup>Pr)<sub>3</sub><sup>16</sup> were synthesized using literature procedures. All other reagents and solvents were obtained from commercial sources and used without further purification. IR spectra were recorded on a Varian 640-IR spectrometer controlled by Resolutions Pro software. UV-vis spectra were recorded on a Cary 50 UV-vis spectrophotometer using Cary WinUV software. Elemental microanalyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ. Caution! Anhydrous hydrazine is a highly toxic, volatile, and flammable liquid. While we did not encounter any issues, proper precautions were taken.

*Synthesis of*  $({}^{P}PNXyl)_{3}TiCl$  (1). A solution of  ${}^{i}Pr_{2}PNHXyl$  (1.42 g, 6.0 mmol) in Et<sub>2</sub>O (150 mL) was cooled to -78 °C. To this was added "BuLi (3.7 mL, 1.6 M in hexanes, 6.0 mmol) dropwise over 10 min. The resulting yellow solution was warmed to room temperature and stirred for 2 h. The solution was then cooled again to -78 °C, and

TiCl<sub>4</sub> (220 μL, 2.0 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 12 h to ensure completion of the reaction. LiCl was removed by filtration, and the volatiles were removed from the filtrate in vacuo. The crude red material was extracted with pentane, and slow evaporation of a concentrated pentane solution of 1 at room temperature yielded orange crystals of 1 (1.01 g, 64%). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 293 K, 162 MHz):  $\delta$  –1.6 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 293 K, 400 MHz):  $\delta$  6.90 (s, 6H, *o*-Ar), 6.46 (s, 3H, *p*-Ar), 2.61 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.23 (s, 18H, Ar–CH<sub>3</sub>), 1.25 (m, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (m, 18H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 293 K, 100.63 MHz):  $\delta$  152.8, 137.6, 125.8, 120.8, 29.0, 21.3, 20.1, 19.5. UV–vis (Et<sub>2</sub>O,  $\lambda_{max}$  nm ( $\varepsilon$ , mol<sup>-1</sup> cm<sup>-1</sup>)): 250 (5100), 292 (2300), 605 (310). Anal. Calcd for C<sub>42</sub>H<sub>69</sub>N<sub>3</sub>P<sub>3</sub>TiCl: C, 63.67; H, 8.78; N, 5.30. Found: C, 63.59; H, 8.71; N, 5.19.

Synthesis of  $(\eta^{2-i}Pr_2PNXyl)Ti(XylNP^iPr_2)_2(\mu-Cl)Col$  (2). Solid 1 (0.792 g, 1.00 mmol) and solid CoI<sub>2</sub> (0.313 g, 1.00 mmol) were combined in THF (15 mL) and stirred for 4 h at room temperature. The resulting brown solution was filtered through Celite, and solvent was removed from the filtrate in vacuo. The crude dark material was extracted with Et<sub>2</sub>O, and slow evaporation of a concentrated Et<sub>2</sub>O solution of **2** at room temperature yielded brown crystals of **2** (0.802 g, 82%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  22.0 (323 Hz), 11.9 (101 Hz), 8.3 (11 Hz), 7.5 (8 Hz), 3.3 (16 Hz), 2.2 (12 Hz), 1.3 (9 Hz), -1.5 (195 Hz), -6.0 (214 Hz), -9.8 (258 Hz). Evans method (C<sub>6</sub>D<sub>6</sub>): 3.20  $\mu_{\rm B}$ . UV–vis (Et<sub>2</sub>O,  $\lambda_{\rm max}$ , nm ( $\varepsilon$ , mol<sup>-1</sup> cm<sup>-1</sup>)): 255, (27000), 296 (12000), 370 (4100), 578 (670). Anal. Calcd for C<sub>42</sub>H<sub>69</sub>N<sub>3</sub>P<sub>3</sub>TiCoICI: C, 51.57; H, 7.11; N, 4.30. Found: C, 51.52; H, 7.03; N, 4.19.

Synthesis of  $(\eta^{2-i}Pr_2PNXyl)Ti(XylNPiPr_2)_2Col$  (3). A solution of 2 (0.978 g, 1.00 mmol) in THF (15 mL) was added to solid KC<sub>8</sub> (0.128 g, 0.95 mmol). The reaction mixture was stirred at room temperature for 2 h to ensure completion of the reaction. The insoluble byproducts were removed by filtration. The volatiles were removed from the filtrate in vacuo, and the remaining dark solid was washed with pentane. Slow evaporation of a concentrated Et<sub>2</sub>O solution of 3 at room temperature yielded brown crystals of 3 (0.790 g, 84%). <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>):  $\delta$  33.7 (1600 Hz), 7.22 (129 Hz), 6.69 (14 Hz), 3.82 (193 Hz), 2.28 (12 Hz), -0.17 (396 Hz); <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.05 (1600 Hz), 6.48 (1360 Hz), 2.31 (41 Hz), -0.06 (595 Hz). Evans method (C<sub>6</sub>D<sub>6</sub>): 1.98  $\mu_{\rm B}$ . UV–vis (Et<sub>2</sub>O,  $\lambda_{\rm max}$  nm ( $\varepsilon$ , mol<sup>-1</sup> cm<sup>-1</sup>)): 259 (39000), 291 (15860), 411 (5620), 627 (740). Anal. Calcd for C<sub>42</sub>H<sub>69</sub>N<sub>3</sub>P<sub>3</sub>TiCoI: C, 53.51; H, 7.38; N, 4.46. Found: C, 53.38; H, 7.51; N, 4.40.

Synthesis of (THF)Ti(XyINP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>CoN<sub>2</sub> (4). A 0.5% Na/Hg amalgam was prepared from 0.057 g of Na (2.5 mmol) and 11.0 g of Hg. To this vigorously stirred amalgam in 10 mL of THF was added a solution of 2 (0.978 g, 1.00 mmol) in THF (50 mL). The solution immediately began to change color from brown to red. After 2 h, the resulting red solution was filtered away from the amalgam, and the solvent was removed from the filtrate in vacuo. The resulting solid was extracted back into Et<sub>2</sub>O and filtered through Celite. Slow evaporation of the concentrated Et<sub>2</sub>O solution of 4 at -35 °C yielded pure red crystals of 4 (0.750 g, 82%). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 293 K, 162 MHz):  $\delta$  45.5 (br s). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.71 (s, 6H, o-Ar), 6.46 (s, 3H, p-Ar), 3.32 (br, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.79 (br m, 4H, THF), 2.15 (s, 18H, Ar-CH<sub>3</sub>), 1.64 (br m, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.51 (br m, 18H,  $CH(CH_3)_2$ ), 0.72 (br, 4H, THF). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.63 MHz): δ 152.6, 138.2, 124.0, 123.8, 69.5, 35.8, 25.3, 22.2, 21.9, 21.4. UV-vis (Et<sub>2</sub>O,  $\lambda_{max}$ , nm ( $\epsilon$ , mol<sup>-1</sup> cm<sup>-1</sup>)): 250 (9100), 299 (2200), 443 (300), 680 (150). IR: 2084 cm<sup>-1</sup> (KBr solution cell,  $C_6D_6$ ). Anal. Calcd for C46H77N5P3TiCoO: C, 60.33; H, 8.47; N, 7.65. Found: C, 60.17; H, 8.46, N, 7.42.

Synthesis of (THF)Ti(XyINP<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>Co (5). The solvent was removed from a Et<sub>2</sub>O solution of 4 (0.091 g, 0.10 mmol) in vacuo, and the solution began to change color from red to green under vacuum. The resulting green solid was extracted back into Et<sub>2</sub>O under argon atmosphere. Slow evaporation of the concentrated Et<sub>2</sub>O solution of **5** at room temperature yielded pure green crystals of **5** (0.074 g, 83%). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz):  $\delta$  39.6 (br s). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.86 (s, 6H, o-Ar), 6.49 (s, 3H, p-Ar), 3.47 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.71 (br m, 4H, THF), 2.22 (s, 18H, Ar–CH<sub>3</sub>), 1.67 (br, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.52 (br, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.69 (br, 4H, THF). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 293 K, 100.63 MHz): δ 154.3, 138.0, 124.5, 123.2, 69.1, 32.7, 25.4, 22.9, 22.3, 20.5. UV–vis (Et<sub>2</sub>O,  $\lambda_{max}$ , nm ( $\varepsilon$ , mol<sup>-1</sup> cm<sup>-1</sup>)): 250 (3100), 291 (910), 499 (170). Owing to the oxygen sensitivity of this complex, repeated elemental analysis samples analyzed as the oxidized compound (THF)Ti(XylNP(=O)<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>Co. Anal. Calcd for C<sub>46</sub>H<sub>77</sub>N<sub>5</sub>P<sub>3</sub>TiCoO<sub>4</sub>: C, 59.04; H, 8.29; N, 4.49. Found: C, 59.11; H, 8.19, N, 4.70.

Synthesis of  $(H_3N)Ti(XyINP^iPr_2)_3CoN_2$  (6). In a 20 mL scintillation vial containing a stir bar, complex 4 (91 mg, 0.10 mmol) was dissolved in 5 mL of Et<sub>2</sub>O. To this solution was added H<sub>2</sub>NNH<sub>2</sub> (2.4  $\mu$ L, 0.075 mmol). The reaction mixture was stirred at room temperature for 10 min, and then the volatiles were removed in vacuo. The remaining red solid was extracted with benzene and filtered through Celite. The solvent was removed in vacuo to yield spectroscopically pure product as a red solid (75 mg, 88% yield). Crystals suitable for X-ray diffraction were grown from a concentrated Et<sub>2</sub>O solution at room temperature.  $^{31}P{^{1}H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz):  $\delta$  39.6 (br s). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.83 (s, 6H, o-Ar), 6.47 (s, 3H, p-Ar), 3.20 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.15 (s, 18H, Ar-CH<sub>3</sub>), 1.71 (br, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.47 (br, 18H,  $CH(CH_3)_2$ ), -1.01 (s, 3H, NH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.63 MHz): δ 153.7, 137.5, 123.8, 123.3, 35.7, 21.1, 21.0, 19.9. UVvis (Et<sub>2</sub>O,  $\lambda_{max}$  nm ( $\epsilon$ , mol<sup>-1</sup> cm<sup>-1</sup>)): 252 (33000), 298 (12000), 443 (1500), 688 (170). IR: 2062 cm<sup>-1</sup> (KBr solution cell,  $C_6H_6$ ). Mutilple elemental analysis samples failed owing to the oxygen sensitivity of complex 6 and the lability of the dinitrogen ligand.

Synthesis of  $(MeH_2N)Ti(XyINP^iPr_2)_3CoN_2$  (7). In a 20 mL scintillation vial containing a stir bar, complex 4 (91 mg, 0.10 mmol) was dissolved in 5 mL of Et<sub>2</sub>O. To this solution was added a THF solution of MeNH $_2$  (50  $\mu$ L, 2 M THF solution, 0.1 mmol). The reaction mixture was stirred at room temperature for 10 min, and then the volatiles were removed in vacuo. The remaining red solid was extracted with benzene and filtered through Celite. The solvent was removed from the filtrate in vacuo to yield spectroscopically pure product as a red solid (74 mg, 84% yield). Crystals suitable for X-ray diffraction were grown from a concentrated  $Et_2O$  solution at room temperature. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz):  $\delta$  39.6 (br s). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.92 (s, 6H, o-Ar), 6.50 (s, 3H, p-Ar), 3.21 (br m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.17 (s, 18H, Ar-CH<sub>3</sub>), 1.72 (br, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.47 (br, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.5 (br, 3H, CH<sub>3</sub>), -0.31 (br, 2H, NH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.63 MHz):  $\delta$  152.4, 137.8, 123.5, 123.3, 35.3, 21.5, 21.3, 20.6. UV-vis (Et<sub>2</sub>O,  $\lambda_{max}$  nm ( $\epsilon$ , mol<sup>-1</sup>  $cm^{-1}$ ): 250 (14000), 297 (6100), 518 (1100), 483 (580), 681 (83). IR: 2061 cm<sup>-1</sup> (KBr solution cell,  $C_6D_6$ ). Anal. Calcd for C43H74N6P3TiCo: C, 59.04; H, 8.53; N, 9.61. Multiple elemental analysis samples failed owing to the oxygen sensitivity of complex 7 and the lability of the dinitrogen ligand.

Synthesis of  $[(\kappa^2-XyINP^i)Pr_2NPh)Ti(XyINP^iPr_2)_2(\mu-NPh)Co]_2(\mu-N_2)$ (8). In a 20 mL scintillation vial containing a stir bar, complex 4 (91 mg, 0.10 mmol) was dissolved in 5 mL of Et<sub>2</sub>O. To this solution was added azobenzene (18.2 mg, 0.10 mmol). The reaction mixture was stirred at room temperature for 10 min, and then the volatiles were removed in vacuo. The remaining red solid was extracted with benzene and filtered through Celite. The solvent was removed in vacuo to yield analytically pure product as a red solid (80 mg, 79% yield). Crystals suitable for X-ray diffraction were grown from a concentrated Et<sub>2</sub>O solution at room temperature. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  36.28, 18.59, 16.06, 10.14, 8.73, 8.00, 6.94, 6.77, 4.63, 4.31, 3.77, 2.59, -0.12, -1.59, -2.98, -3.24, -3.63, -7.17, -62.13, -69.72. Evans method (CD<sub>2</sub>Cl<sub>2</sub>): 5.10  $\mu_{\rm B}$ . UV–vis (Et<sub>2</sub>O,  $\lambda_{\rm max}$ , nm ( $\varepsilon$ , mol<sup>-1</sup> cm<sup>-1</sup>)): 250 (8500), 300 (2000), 650(300). Anal. Calcd for: C, 64.09; H, 7.87; N, 8.30. Found: C, 64.24; H, 7.70; N, 8.17.

**Catalytic Disproportionation of Hydrazine.** To a solution of 4 (18.2 mg, 0.0200 mmol) in diethyl ether (5 mL) in a 20 mL scintillation vial was added anhydrous hydrazine, and the mixture was stirred for 30 min at room temperature. 200  $\mu$ L of concentrated HCl was added to the reaction mixture by syringe. The solvent was then immediately removed in vacuo, and the residue was extracted with distilled H<sub>2</sub>O (30 mL). Aliquots of this solution, diluted if necessary,

were tested quantitatively for ammonia by using the indophenol test.<sup>21</sup> *Caution!* The generation of dinitrogen gas may lead to the buildup of positive pressure. All the catalytic hydrazine disproportionation reactions were performed on very small scales. Large scale reactions would require the appropriate venting equipment or pressure resistant containers.

**X-ray Crystallography.** All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo K $\alpha$  radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections, were carried out using the Bruker Apex2 software.<sup>22</sup> Fully labeled diagrams and data collection and refinement details are included in Table S1 and on pages S14–S22 of the Supporting Information.

**Computational Details.** All calculations were performed using Gaussian09, Revision A.02 for the Linux operating system.<sup>23</sup> Density functional theory calculations were carried out using a combination of Becke's 1988 gradient-corrected exchange functional<sup>24</sup> and Perdew's 1986 electron correlation functional<sup>25</sup> (BP86). A mixed-basis set was employed, using the LANL2TZ(f) triple- $\zeta$  basis set with effective core potentials for cobalt, iodine, and titanium,<sup>26</sup> Gaussian09's internal 6-311+G(d) for heteroatoms (nitrogen, phosphorus, oxygen), and Gaussian09's internal LANL2DZ basis set (equivalent to D95 V<sup>27</sup>) for carbon and hydrogen. Using crystallographically determined geometries as a starting point, the geometries were optimized to a minimum, followed by analytical frequency calculations to confirm that no imaginary frequencies were present. *XYZ* coordinates of optimized geometries are provided on Supporting Information pages S25–S32.

**EPR Spectroscopy.** X-band EPR spectra were obtained on a Bruker ElexSys E500 EPR spectrometer (fitted with a cryostat for measurements at 3 K). EPR samples were crystalline samples, and spectra were measured as frozen toluene glasses at 3 K. The spectra were referenced to diphenylpicrylhydrazyl (DPPH; g = 2.0037) and modeled using EasySpin for MATLAB.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b01962.

Computational and spectral data and crystallographic details (PDF)

Crystallographic data (CIF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) (a) Hazari, N. Chem. Soc. Rev. **2010**, 39, 4044–4056. (b) Hidai, M.; Mizobe, Y. Chem. Rev. **1995**, 95, 1115–1133. (c) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. Science **2011**, 334, 780–783.

(2) (a) Schrock, R. R. Acc. Chem. Res. 2005, 38, 955–962.
(b) Yandulov, D. V.; Schrock, R. R. Science 2003, 301, 76–78.
(c) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. Nat. Chem. 2011, 3,

120–125. (d) Tian, Y.-H.; Pierpont, A. W.; Batista, E. R. *Inorg. Chem.* 2014, 53, 4177–4183. (e) Kuriyama, S.; Arashiba, K.; Nakajima, K.; Tanaka, H.; Kamaru, N.; Yoshizawa, K.; Nishibayashi, Y. *J. Am. Chem. Soc.* 2014, 136, 9719–9731. (f) Anderson, J. S.; Rittle, J.; Peters, J. C. *Nature* 2013, 501, 84–87.

(3) (a) Hoffman, B. M.; Dean, D. R.; Seefeldt, L. C. Acc. Chem. Res. **2009**, 42, 609–619. (b) Hoffman, B. M.; Lukoyanov, D.; Dean, D. R.; Seefeldt, L. C. Acc. Chem. Res. **2013**, 46, 587–595.

(4) (a) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. J. Am. Chem. Soc. 1993, 115, 1760–1772. (b) Powers, T. M.; Betley, T. A. J. Am. Chem. Soc. 2013, 135, 12289–12296. (c) Sellmann, D.; Hille, A.; Rösler, A.; Heinemann, F. W.; Moll, M.; Brehm, G.; Schneider, S.; Reiher, M.; Hess, B. A.; Bauer, W. Chem. - Eur. J. 2004, 10, 819–830.
(d) Saouma, C. T.; Lu, C. C.; Peters, J. C. Inorg. Chem. 2012, 51, 10043–10054. (e) Nakajima, Y.; Inagaki, A.; Suzuki, H. Organometallics 2004, 23, 4040–4046.

(5) (a) Umehara, K.; Kuwata, S.; Ikariya, T. J. Am. Chem. Soc. 2013, 135, 6754–6757. (b) Kuwata, S.; Mizobe, Y.; Hidai, M. Inorg. Chem. 1994, 33, 3619–3620. (c) Rozenel, S. S.; Arnold, J. Inorg. Chem. 2012, 51, 9730–9739. (d) Saouma, C. T.; Moore, C. E.; Rheingold, A. L.; Peters, J. C. Inorg. Chem. 2011, 50, 11285–11287. (e) Chen, Y.; Zhou, Y.; Chen, P.; Tao, Y.; Li, Y.; Qu, J. J. Am. Chem. Soc. 2008, 130, 15250–15251. (f) Chang, Y.-H.; Chan, P.-M.; Tsai, Y.-F.; Lee, G.-H.; Hsu, H.-F. Inorg. Chem. 2014, 53, 664–666. (g) Szklarzewicz, J.; Matoga, D.; Kłyś, A.; Łasocha, W. Inorg. Chem. 2008, 47, 5464–5472. (h) Chu, W.-C.; Wu, C.-C.; Hsu, H.-F. Inorg. Chem. 2006, 45, 3164–3166. (i) Demadis, K. D.; Malinak, S. M.; Coucouvanis, D. Inorg. Chem. 1996, 35, 4038–4046.

(6) (a) Thomas, C. M. Comments Inorg. Chem. 2011, 32, 14–38.
(b) Krogman, J. P.; Thomas, C. M. Chem. Commun. 2014, 50, 5115–5127.

(7) (a) Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. J. Am. Chem. Soc. **2010**, 132, 44–45. (b) Krogman, J. P.; Gallagher, J. R.; Zhang, G.; Hock, A. S.; Miller, J. T.; Thomas, C. M. Dalton Trans. **2014**, 43, 13852–13857.

(8) (a) Thomas, C. M.; Napoline, J. W.; Rowe, G. T.; Foxman, B. M. *Chem. Commun.* **2010**, *46*, 5790–5792. (b) Zhou, W.; Napoline, J. W.; Thomas, C. M. *Eur. J. Inorg. Chem.* **2011**, *2011*, 2029–2033.

(9) Krogman, J. P.; Foxman, B. M.; Thomas, C. M. J. Am. Chem. Soc. 2011, 133, 14582-14585.

(10) (a) Zhou, W.; Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Organometallics 2013, 32, 1766–1772.
(b) Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. J. Am. Chem. Soc. 2013, 135, 6018–6021. (c) Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Organometallics 2014, 33, 2071–2079.

(11) Wu, B.; Hernández Sánchez, R.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. *Inorg. Chem.* **2014**, *53*, 10021–10023.

(12) Napoline, J. W.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Chem. Commun. 2013, 49, 4388-4390.

(13) Wu, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Chem. Sci. 2015, 6, 2044–2049.

(14) Zhou, W.; Saper, N. I.; Krogman, J. P.; Foxman, B. M.; Thomas, C. M. Dalton Trans. **2014**, *43*, 1984–1989.

(15) Attempts to collect meaningful <sup>1</sup>H NMR data at low temperature using toluene- $d_8$  were unsuccessful, as complex 3 decomposes over time in toluene- $d_8$ .

(16) Greenwood, B. P.; Forman, S. I.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. *Inorg. Chem.* **2009**, *48*, 6251–6260.

(17) Clouston, L. J.; Bernales, V.; Carlson, R. K.; Gagliardi, L.; Lu, C. C. *Inorg. Chem.* **2015**, *54*, 9263–9270.

(18) Cotton, F. A.; Murillo, C. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Springer Science and Business Media, Inc.: New York, 2005.

(19) Jenkins, D. M.; Di Bilio, A. J.; Allen, M. J.; Betley, T. A.; Peters, J. C. J. Am. Chem. Soc. **2002**, 124, 15336–15350.

(20) For example, the average Co-P and Ti-N WBIs calculated for complex 4 are 0.61 and 0.78, respectively.

(21) Chaney, A. L.; Marbach, E. P. Clin. Chem. 1962, 8, 130-132.

(22) Apex 2, Version 2 User Manual, M86-E01078; Bruker Analytical X-ray Systems: Madison, WI, 2006.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09, Revision A. 2*; Gaussian, Inc.:

Wallingford, CT (see Supporting Information for full reference), 2009. (24) Becke, A. D. Phys. Rev. A: At. Mol. Opt. Phys. 1988, 38, 3098–3100.

(25) Perdew, J. P. Phys. Rev. B: Condens. Matter 1986, 33, 8822–8824.

(26) (a) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299-310.
(b) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 270-283.

(27) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaeffer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3.