# Synthesis and Reactivity of Titanium and Zirconium Complexes Supported by a Multidentate Monoanionic [N<sub>2</sub>P<sub>2</sub>] Ligand

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The coordination chemistry of titanium and zirconium complexes supported by the monoanionic multidentate ligand  $[N_2P_2]$  (where  $[N_2P_2] = {}^{B}UN^{-S}iMe_2N(CH_2CH_2P^{i}Pr_2)_2)$  is presented. The zirconium(IV) halide complex  $[N_2P_2]ZrCl_3$  (1) serves as a precursor to the alkyl species  $[N_2P_2]Zr(CH_2SiMe_3)_3$  (2) and  $[N_2P_2]ZrMe_3$  (3). The coordination behavior of the  $[N_2P_2]$  ligand in compound 3 is determined using NMR and X-ray diffraction data, and protonation of 3 results in the formation of the cationic species  $\{[N_2P_2]ZrMe_2\}\{B(C_6H_5)_4\}$  (4). The reduction of 1 in the presence of various traps leads to the isolation of  $([N_2P_2]ZrCl)_2(\mu-\eta^2:\eta^2-N_2)$  (5),  $([N_2P_2]ZrCl)_2(\mu-Cl)_2$  (6), and  $[N_2P_2]ZrAr^*$  (9). The titanium(III) halide complex  $[N_2P_2]TiCl_2$  (10) also serves as a precursor to alkyl and reduced species  $[N_2P_2]TiMe_2$  (11) and  $([N_2P_2]TiCl)_2(\mu-N_2)$  (12). Alkylation of 12 results in the formation of  $([N_2P_2]TiCH_2SiMe_3)_2(\mu-N_2)$  (13), and the degree of reduction of the  $N_2$  moiety in 12 and 13 is examined using X-ray crystallography and Raman spectroscopy. A series of titanium(IV) imido complexes  $[N_2P_2]TiCl(N^{*}Bu)$  (14),  $[N_2P_2]TiMe(N^{*}Bu)$  (15), and  $\{[N_2P_2]Ti(N^{*}Bu)\}\{MeB(C_6F_5)_3)\}$  (16) are synthesized, and the coordination behavior of the  $[N_2P_2]$  ligand is presented.

#### Introduction

The seminal work of Fryzuk et al.<sup>1–3</sup> and the work of Mindiola et al.<sup>4,5</sup> and Ozerov et al.<sup>6,7</sup> demonstrated that "mixeddonor" ligands (containing N and P donors) can stabilize earlymetal alkyl, alkylidene, and alkylidyne complexes as well as low-oxidation-state early-metal species. We recently reported the synthesis of the new multidentate monoanionic ligand [N<sub>2</sub>P<sub>2</sub>] and demonstrated the versatility of its coordination geometry through the synthesis and structural characterization of a series of first-row transition-metal halide complexes. We extended this work to include main-group coordination compounds where an additional coordination mode ( $\kappa^2$ -NP) was observed.<sup>8</sup> These initial results are promising for the application of this ligand to support a variety of metal-based reactivities because of the ability of this ligand to adapt to the steric and electronic preferences of the metal center.

This paper focuses on early-transition-metal derivatives of the  $[N_2P_2]$  ligand, with the aim of exploring the scope of reactivity supported by this ligand set. Intramolecular C–H bond activation has been reported with other TDMA ligand systems examined by our group and others when reactive metal centers

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are involved.<sup>9–11</sup> We therefore undertook the synthesis of a range of early-metal alkyl and reduced-metal complexes to establish the stability of the  $[N_2P_2]$  ligand framework under related conditions. The utility of the metal alkyl compounds as precursors to alkylidene complexes was examined, as was the synthesis and substitution chemistry of a series of titanium imido complexes. A portion of this work has been communicated.<sup>12–14</sup>

## **Experimental Section**

All reactions were performed using standard Schlenk-line techniques or in an MBraun drybox (<1 ppm  $O_2/H_2O$ ) unless noted otherwise. All glassware, cannulae, and Celite were stored in an oven at >425 K. Pentane, toluene, diethyl ether, and tetrahydrofuran (THF) were purified by passage through a column of activated alumina and degassed with nitrogen prior to use.<sup>15</sup> Hexamethyld-isiloxane was distilled from sodium and degassed with nitrogen prior to use. Deuterated solvents ( $C_6D_6$ , Tol- $d_8$ ) were vacuum transferred from sodium/benzophenone. NMR spectra were recorded at ambient temperature on Bruker AV-300, AVQ-400, AVB-400, and DRX-500 spectrometers. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are given relative to residual solvent peaks, and coupling constants (*J*) are given in hertz (Hz). <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are referenced to an external standard of P(OMe)<sub>3</sub> set to 1.67 ppm. IR

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<sup>(12)</sup> As we reported with main-group derivatives of the  $[N_2P_2]$  ligand, fluxional behavior with "hard" metals is common. Accordingly, we have found that assessing the solution structures of these compounds by <sup>1</sup>H NMR spectroscopy is complicated. In contrast, <sup>31</sup>P NMR spectroscopy is a useful diagnostic tool, and a good deal of structural information on the reported compounds is based on these data.

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compound no.	compound name	color	mp (°C)	yield (%)	coordination mode of [N <sub>2</sub> P <sub>2</sub> ]
1	$[N_2P_2]ZrCl_3$	colorless	137-138	82	$\kappa^3$ -N <sub>2</sub> P
2	$[N_2P_2]Zr(CH_2SiMe_3)_3$	colorless		quant.	
3	$[N_2P_2]ZrMe_3$	colorless	64-65	46	$\kappa^3$ -N <sub>2</sub> P
4	$\{[N_2P_2]ZrMe_2\}\{B(C_6H_5)_4\}$	yellow		82	$\kappa^4$ -N <sub>2</sub> P <sub>2</sub>
5	$([N_2P_2]ZrCl)_2(\mu - \eta^2 \cdot \eta^2 - N_2)$	purple	175-176	17	$\kappa^3$ -N <sub>2</sub> P
6	$([N_2P_2]ZrCl)_2(\mu-Cl)_2$	green	82-83 (dec)	20	$\kappa^3$ -N <sub>2</sub> P
8	$[N_2P_2]Zr^{II}(Cl)C \equiv N(2,6-Mes_2)C_6H_3$	forest green		quant.	$\kappa^3$ -N <sub>2</sub> P
9	[N <sub>2</sub> P <sub>2</sub> ]ZrAr*	orange	74-75	18	$\kappa^3$ -N <sub>2</sub> P
11	$[N_2P_2]TiMe_2$	blue	114-115	58	$\kappa^3$ -N <sub>2</sub> P
12	$([N_2P_2]TiCl)_2(\mu-N_2)$	purple	124-126	57	$\kappa^3$ -N <sub>2</sub> P
13	$([N_2P_2]TiCH_2SiMe_3)_2(\mu-N_2)$	orange	135-136	34	$\kappa^3$ -N <sub>2</sub> P
14	$[N_2P_2]TiCl(N'Bu)$	orange	107-108	76	$\kappa^3$ -N <sub>2</sub> P
15	$[N_2P_2]$ TiMe(N <sup>t</sup> Bu)	yellow	73-75	62	$\kappa^3$ -N <sub>2</sub> P
16	$\{[N_2P_2]Ti(N^tBu)\}\{MeB(C_6F_5)_3\}$	orange		quant.	$\kappa^4$ -N <sub>2</sub> P <sub>2</sub>

samples were prepared as Nujol mulls and taken between KBr disks. Magnetic susceptibility ( $\mu_{eff}$ ) values were determined using the solution Evans method at ambient temperature (22 °C).<sup>16</sup> Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected. Li[N<sub>2</sub>P<sub>2</sub>],<sup>17</sup> ZrCl<sub>4</sub>(THF)<sub>2</sub>,<sup>18</sup> [PhNMe<sub>2</sub>H][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>],<sup>19</sup> TiCl<sub>3</sub>(THF)<sub>3</sub>,<sup>20</sup> [N<sub>2</sub>P<sub>2</sub>]TiCl<sub>2</sub> (**10**),<sup>17</sup> 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>,<sup>21</sup> and Cl<sub>2</sub>(py)<sub>3</sub>Ti(N'Bu)<sup>22</sup> were prepared following the literature procedures, and unless otherwise noted, all reagents were acquired from commercial sources. Elemental analyses and mass spectral data were determined at the College of Chemistry, University of California, Berkeley. X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley. A full list of compounds and their physical properties is provided in Table 1.

[N<sub>2</sub>P<sub>2</sub>]ZrCl<sub>3</sub> (1). A solution of Li[N<sub>2</sub>P<sub>2</sub>] (1.5 g, 3.4 mmol) in 20 mL of toluene was added dropwise to a suspension of ZrCl<sub>4</sub>(THF)<sub>2</sub> (1.3 g, 3.4 mmol) in 20 mL of toluene, and the reaction mixture was stirred overnight. The solution was filtered, and the solvent was removed under vacuum. The crude product was washed with pentane and dried under vacuum to afford analytically pure 1 as a colorless solid (1.8 g, 82% yield). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 0.46 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.52 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 1.03 (m, 20 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.37 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.48 (s, 9 H, <sup>t</sup>Bu); 1.53 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.65 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.34 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.87 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.21 (m, 1 H, -CH<sub>2</sub>-CH<sub>2</sub>-); 3.52 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.77 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.85 (s); 5.25 (s); 19.12 (d); 19.23 (d); 19.54 (d); 20.01 (d); 20.26 (d); 20.38 (d); 20.57 (d); 20.70 (d); 21.16 (d); 21.53 (d); 23.65 (d); 23.96 (d); 27.01 (d); 27.40 (d); 34.60 (s); 44.94 (d); 51.72 (s); 51.97 (s); 56.17 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 2.59 (s, 1 P); 16.38 (s, 1 P). IR  $(cm^{-1})$ : 1308 (w); 1259 (s); 1226 (m); 1181 (s); 1095 (w); 1061 (m); 1036 (w); 1011 (w); 984 (s); 954 (m); 919 (m); 883 (m); 845 (s); 798 (m); 755 (s); 644 (m); 584 (m); 547 (m); 503 (m); 471 (m); 446 (m). Anal. Calcd for H<sub>51</sub>C<sub>22</sub>Cl<sub>3</sub>N<sub>2</sub>P<sub>2</sub>SiZr: C, 41.85; H, 8.16; N, 4.44. Found: C, 42.21; H, 8.22; N, 4.28. Mp: 137-138 °C

**Generation of**  $[N_2P_2]Zr(CH_2SiMe_3)_3$  (2). A solution of LiCH<sub>2</sub>SiMe<sub>3</sub> (0.14 g, 1.4 mmol) was added to a solution of 1 (0.30 g, 0.48 mmol) in 5 mL of toluene at -40 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The volatile material was removed under vacuum, and the product was

extracted with pentane. Following the removal of solvent under vacuum, analytically pure **2** (as determined by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy) was isolated as a colorless oil in quantitative yield. <sup>1</sup>H NMR (500 MHz, Tol- $d_8$ ):  $\delta$  0.22 (s, 27 H, -CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>); 0.48 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.92 (s, 6 H, -CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>); 1.02 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.42 (s, 9 H, <sup>1</sup>Bu); 1.58 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.72 (m, 4 H, -CH<sub>2</sub>CH<sub>2</sub>--); 3.31 (m, 4 H, -CH<sub>2</sub>CH<sub>2</sub>--). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, Tol- $d_8$ ):  $\delta$  3.16 (s); 18.84 (d); 19.87 (d); 20.01 (d); 23.30 (d); 34.67 (s); 50.17 (d); 54.28 (s); 65.08 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (500 MHz, Tol- $d_8$ ):  $\delta$  8.11 (s).

[N<sub>2</sub>P<sub>2</sub>]ZrMe<sub>3</sub> (3). Methyllithium (1.6 M in Et<sub>2</sub>O, 3.2 mL, 4.8 mmol) was added via syringe to a suspension of 1 (1.0 g, 1.6 mmol) in 20 mL of Et<sub>2</sub>O at -40 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The volatiles were removed under vacuum, and the crude product was extracted with pentane. Colorless crystals of 3 were collected in 46% yield (0.42 g) following cooling of a pentane solution at -40 °C overnight. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  0.48 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.90 (s, 9 H, -CH<sub>3</sub>); 1.08 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.25 (m, 2 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.50 (s, 9 H, <sup>t</sup>Bu); 1.68 (m, 6 H, -CH<sub>2</sub>CH<sub>2</sub>-, PCH(CH<sub>3</sub>)<sub>2</sub>); 2.99 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.16 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ 5.02 (s); 19.74 (d); 20.21 (d); 20.72 (d); 24.20 (d); 34.79 (s); 45.32 (d); 46.28 (d); 54.69 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (400 MHz,  $C_6D_6$ ):  $\delta$  2.75 (s). IR (cm<sup>-1</sup>): 1357 (m); 1297 (w); 1248 (s); 1194 (s); 1123 (m); 1065 (m); 1036 (s); 1017 (s); 965 (w); 939 (m); 923 (w); 894 (s); 883 (m); 821 (m); 802 (m); 744 (m); 720 (m); 688 (w); 674 (w); 627 (w); 614 (w); 539 (m); 502 (m); 463 (w). Anal. Calcd for C<sub>25</sub>H<sub>60</sub>N<sub>2</sub>P<sub>2</sub>SiZr: C, 52.66; H, 10.63; N, 4.91. Found: C, 53.02; H, 10.77; N, 5.21. Mp: 64-65 °C.

**Generation of {**[N<sub>2</sub>P<sub>2</sub>]**ZrMe**<sub>2</sub>}**{**B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>} (4). A solution of [PhNMe<sub>2</sub>H][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] (0.16 g, 0.35 mmol) in 5 mL of THF was added to a solution of **3** (0.20 g, 0.35 mmol) in 10 mL of THF at -40 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed under vacuum, and the product was washed with pentane (3 × 10 mL). The remaining solid was dried under vacuum and isolated as a yellow solid in 80% yield (0.24 g). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.13 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.26 (s, 6 H,  $-CH_3$ ); 0.91 (m, 28 H, PC*H*(CH<sub>3</sub>)<sub>2</sub> and PCH(CH<sub>3</sub>)<sub>2</sub>); 1.17 (s, 9 H, <sup>1</sup>Bu); 1.43 (m, 2 H,  $-CH_2CH_2-$ ); 1.62 (m, 2 H,  $-CH_2CH_2-$ ); 1.76 (m, 2 H,  $-CH_2CH_2-$ ); 2.51 (m, 2 H,  $-CH_2CH_2-$ ); 7.34 (m, 8 H, Ar–H); 7.68 (d, J<sub>HH</sub> = 6.8 Hz, 4 H, Ar–H); 7.95 (d, J<sub>HH</sub> = 6 Hz, 8 H, Ar–H). <sup>31</sup>P{<sup>1</sup>H} NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  15.61 (s).

 $([N_2P_2]ZrCl)_2(\mu - \eta^2:\eta^2-N_2)$  (5). A suspension of KC<sub>8</sub> (0.14 g, 1.0 mmol) in 10 mL of THF was added to a thick-walled reaction flask containing a solution of 1 (0.30 g, 0.48 mmol) in 5 mL of THF at -70 °C. The reaction mixture was stirred at -70 °C under nitrogen for 3 h, and the vessel was sealed. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was transferred to a new reaction flask, and the solvent was removed under vacuum. The crude product was extracted with

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pentane, and the solution was cooled at -40 °C overnight. Purple crystals of 5 were isolated in 17% yield (0.045 g). A 3:2 mixture of isomers was determined by <sup>31</sup>P{<sup>1</sup>H} NMR. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  0.36 (s, 9 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.85 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.92 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 1.12 (m, 45 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.28 (m, 12 H,  $PCH(CH_3)_2$  and  $-CH_2CH_2-$ ; 1.51 (m, 15 H,  $PCH(CH_3)_2$ ); 1.61-1.71 (m, 8 H, PCH(CH<sub>3</sub>)<sub>2</sub> and -CH<sub>2</sub>CH<sub>2</sub>-); 1.74 (s, 13.5 H, <sup>t</sup>Bu); 1.75 (s, 9 H, <sup>t</sup>Bu); 2.11 (m, 4 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.26 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.71 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.11 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.75 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 4.05 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-). <sup>31</sup>P{<sup>1</sup>H} NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 17.08 (s, 2 P); 14.46 (s, 3 P); 1.54 (s, 2 P); 0.07 (s, 3 P). IR (cm<sup>-1</sup>): 1297 (w); 1247 (m); 1197 (m); 1046 (s); 969 (w); 930 (w); 880 (m); 848 (s); 818 (m); 762 (s); 704 (s); 676 (w); 611 (w); 530 (m); 493 (w). Anal. Calcd for C<sub>44</sub>H<sub>102</sub>Cl<sub>2</sub>N<sub>6</sub>P<sub>4</sub>Si<sub>2</sub>Zr<sub>2</sub>: C, 45.99; H, 8.97; N, 7.32. Found: C, 46.35; H, 9.25; N, 6.97. Mp: 175-176 °C.

 $([N_2P_2]ZrCl)_2(\mu-Cl)_2$  (6). A suspension of KC<sub>8</sub> (0.12 g, 0.87) mmol) in 10 mL of Et<sub>2</sub>O was added to a suspension of 1 (0.30 g, 0.79 mmol) in 10 mL of Et<sub>2</sub>O at -40 °C. The reaction mixture was allowed to warm to room temperature. Over the course of 1 h, the reaction mixture turned green. The solution was filtered and concentrated. Green crystals of 6 were collected in 20% (0.047 g) yield following cooling at -40 °C overnight. A 4:1 mixture of isomers was determined by <sup>31</sup>P{<sup>1</sup>H} NMR. <sup>1</sup>H NMR integrations are reported relative to an assignment of 1.00 H for the peak at 5.17 ppm. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.43 (s, 3.2 H); 0.88 (m, 4.16 H); 0.97 (s, 3.16 H); 1.06 (s, 14.40 H); 1.21 (m, 20.99 H); 1.41 (m, 3.34 H); 1.47 (s, 0.64 H); 1.63 (m, 1.35 H); 1.76 (m, 5.51 H); 1.93 (m, 2.13 H); 2.21 (m, 1.05 H); 2.36 (m, 1.34 H); 2.46 (m, 0.83 H); 2.93 (m, 1.03 H); 3.75 (m, 1.06 H); 4.02 (m, 1.00 H); 5.17 (m, 1.00 H). <sup>31</sup>P{<sup>1</sup>H} NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.09 (s, 1 P); 0.88 (s, 4 P); 14.19 (s, 1 P); 15.93 (s, 4 P). IR (cm<sup>-1</sup>): 1336 (m); 1253 (s); 1191 (m); 1100 (m); 1015 (s); 921 (w); 885 (w); 849 (s); 809 (m); 767 (m); 721 (s); 610 (m). Anal. Calcd for  $C_{44}H_{102}$ -Cl<sub>4</sub>N<sub>4</sub>P<sub>4</sub>Si<sub>2</sub>Zr<sub>2</sub>: C, 44.34; H, 8.64; N, 4.70. Found: C, 44.55; H, 8.83; N, 4.91. Mp: 82-83 °C (dec).

**2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C** (7). A modified literature procedure was used.<sup>23</sup> A solution of 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> (5.0 g, 15 mmol) in 30 mL of methylene chloride was added to a mixture of 50% aqueous sodium hydroxide (40 mL), chloroform (6 mL), and benzyltriethylammonium chloride (0.30 g, 1.3 mmol), and the resulting solution was refluxed for 2 h. The reaction mixture was allowed to cool to room temperature before the organic layer was separated and washed with (1) water and (2) a saturated sodium chloride solution before being dried over K<sub>2</sub>CO<sub>3</sub>. The solvent was removed under vacuum, yielding a white solid. Washing with pentane removed excess aniline. The remaining solid was crystallized from methylene chloride at -40 °C to afford colorless crystals of 7 (2.9 g, 57%) yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.05 (s, 12 H, *o*-Me); 2.26 (s, 6 H, p-Me); 6.99 (s, 4 H, Mes-H); 7.24 (d, 2 H, o-H); 7.53 (t, 1 H, p-H). <sup>13</sup>C{<sup>1</sup>H} NMR: 20.40 (s, o-Me); 21.45 (s, p-Me); 128.71 (s); 129.57 (s); 129.73 (s); 134.44 (s); 135.87 (s); 138.03 (s); 139.68 (s); 167.11 (s, N=C). IR (cm<sup>-1</sup>): 2119 (s,  $\nu_{C=N}$ ), 1612 (m), 1272 (m), 1032 (m), 852 (m), 806 (m), 759 (m), 737 (m), 608 (w). Anal. Calcd for C<sub>25</sub>H<sub>25</sub>N: C, 88.50; H, 7.36; N, 4.12. Found: C, 88.20; H, 7.56; N, 4.08.

Generation of  $[N_2P_2]Zr^{II}CI[C=N(2,6-Mes_2)C_6H_3]$  (8). A 1:1 mixture of 6 and 7 was added to an NMR tube and dissolved in C<sub>6</sub>D<sub>6</sub> at room temperature. The solution immediately turned dark forest green, indicating the presence of 8. The <sup>1</sup>H and <sup>31</sup>P NMR spectra display resonance peaks suggestive of a 1:1 mixture of 1 and 8. Because of a high degree of overlap in the <sup>1</sup>H NMR spectrum, only some signals could be assigned. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.02 (s, 9 H, <sup>1</sup>Bu); 0.25 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.58 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 1.00 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 2.20 (s, 6 H, Ar–CH<sub>3</sub>);

2.27 (s, 6 H, Ar–CH<sub>3</sub>); 2.35 (s, 6 H, Ar–CH<sub>3</sub>).  ${}^{31}P{}^{1}H{}$  NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –2.96 (s, 1 P); 22.40 (s, 1 P). IR (cm<sup>-1</sup>): 1872 (C–N).

 $[N_2P_2]ZrAr^*$  (9). A suspension of KC<sub>8</sub> (0.14 g, 1.0 mmol) in 10 mL of Et<sub>2</sub>O was added to a suspension of 1 (0.30 g, 0.48 mmol) and 7 (0.16 g, 0.48 mmol) in 10 mL of Et<sub>2</sub>O at -40 °C. The colorless solution turned dark green, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting yellow/green solution was filtered, concentrated, and stored at -40 °C overnight. Orange crystals of 9 were collected in 18% yield (0.075 g). The -CH<sub>2</sub>CH<sub>2</sub>- hydrogens were not visible in the <sup>1</sup>H NMR spectrum at room temperature and are not reported. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.32 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.39 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.97 (br s, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.16 (s, 9 H, <sup>t</sup>Bu); 2.02 (s, 3 H, Ar-CH<sub>3</sub>); 2.19 (s, 3 H, Ar-CH<sub>3</sub>); 2.33 (s, 3 H, Ar-CH<sub>3</sub>); 2.56 (s, 3 H, Ar-CH<sub>3</sub>); 2.63 (s, 3 H, Ar-CH<sub>3</sub>); 4.90 (s, 1 H, Ar-H); 5.00 (s, 1 H, Ar-H); 6.59 (s, 1 H, Ar-H); 6.89 (s, 1 H, Ar-H); 6.99 (m, 1 H, Ar-H); 7.02 (m, 1 H, Ar-H); 8.29 (d, 1 H,  $J_{\text{HH}} = 8$  Hz, Ar–H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 6.37 (d); 19.14 (s); 20.02 (s); 21.12 (d); 23.93 (s); 29.59 (d); 35.17 (s); 54.44 (s); 66.94 (s); 74.16 (s); 83.73 (s); 89.68 (s); 90.67 (s); 91.89 (s); 115.01 (s); 118.29 (s); 120.02 (s); 121.82 (s); 135.80 (s); 136.56 (s); 136.64 (s); 137.40 (s); 137.97 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (400 MHz,  $C_6D_6$ ):  $\delta$  2.70 (br s); 3.58 (br s). IR (cm<sup>-1</sup>): 3471 (w); 1311 (m); 1249 (s); 1227 (m); 1191 (m); 1090 (m); 1051 (w); 1018 (m); 926 (m); 880 (m); 844 (s); 793 (m); 767 (m); 739 (s); 690 (w); 496 (w). Anal. Calcd for C<sub>47</sub>H<sub>77</sub>N<sub>3</sub>P<sub>2</sub>SiZr: C, 65.23; H, 8.99; N, 4.86. Found: C, 64.84; H, 9.37; N, 5.17. Mp: 74-75 °C.

[N<sub>2</sub>P<sub>2</sub>]TiMe<sub>2</sub> (11). Methylmagnesium bromide (3.0 M in Et<sub>2</sub>O, 0.36 mL, 1.1 mmol) was added via syringe to a suspension of 10 (0.30 g, 0.54 mmol) in 10 mL of Et<sub>2</sub>O at -40 °C. The resulting deep-blue solution was stirred for 3 h at room temperature. Solvent was removed under vacuum, and the crude product was extracted with Et<sub>2</sub>O. Following concentration and cooling at -40 °C, brightblue crystals of 11 were isolated in 58% yield (0.27 g). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -4.11 (br s); -0.42 (br s); 1.07 (br s); 1.17 (br s); 3.25 (s); 3.74 (br s). IR (cm<sup>-1</sup>): 1354 (s); 1290 (w); 1247 (s); 1204 (s); 1099 (m); 1050 (s); 1020 (s); 941 (w); 880 (m); 850 (s); 825 (m); 801 (m); 770 (s); 697 (m); 662 (m); 640 (w); 611 (m); 543 (m); 483 (m). Anal. Calcd for C<sub>24</sub>H<sub>57</sub>N<sub>2</sub>P<sub>2</sub>SiTi: C, 56.32; H, 11.25; N, 5.48. Found: C, 54.83; H, 11.05; N, 5.34. Mp: 114–115 °C.  $\mu_{eff}$ : 1.7  $\mu_{B}$ .

([N<sub>2</sub>P<sub>2</sub>]TiCl)<sub>2</sub>(µ-N<sub>2</sub>) (12). A suspension of KC<sub>8</sub> (0.26 g, 1.9 mmol) in 15 mL of Et<sub>2</sub>O was added to a solution of 10 (0.95 g, 1.7 mmol) in 15 mL of Et<sub>2</sub>O at -40 °C. The reaction mixture was warmed to room temperature and stirred overnight. The solution was filtered, and the remaining solid was washed with Et<sub>2</sub>O (20 mL). Concentration of the solution followed by cooling at -40 °C overnight resulted in the formation of purple crystals of 12 (0.52 g, 57% yield). <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$  0.23 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.68 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 1.05 (m, 20 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.16 (s, 9 H, <sup>t</sup>Bu); 1.40 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.55 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 2.24 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.47 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.57 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.74 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.03 (m, 1 H, -CH<sub>2</sub>-CH<sub>2</sub>-); 3.21 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.48 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.69 (m, 1 H,  $-CH_2CH_2-$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 1.76 (s); 3.49 (s); 5.38 (s); 18.31 (s); 19.28 (m); 20.53 (s); 20.70 (d); 20.86 (s); 21.29 (d); 23.43 (d); 23.60 (s); 23.75 (s); 23.84 (d); 24.01 (d); 34.07 (s); 36.17 (s); 37.69 (s); 38.02 (s); 49.44 (s); 56.79 (s).  ${}^{31}P{}^{1}H{}$  NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.92 (s, 1 P); 32.56 (s, 1 P). IR (cm<sup>-1</sup>): 1301 (m); 1251 (s); 1200 (m); 1154 (m); 1109 (m); 1054 (s); 1021 (s); 964 (m); 933 (m); 892 (m); 847 (s); 820 (m); 771 (m); 614 (w); 546 (w); 506 (w). Raman (cm<sup>-1</sup>): 1300 ( $\nu_{N-N}$ ). Anal. Calcd for C44H102Cl2N6P4Ti2: C, 49.75; H, 9.69; N, 7.91. Found: C, 49.87; H, 9.90; N, 7.94. Mp: 124-126 °C.

 $([N_2P_2]TiCH_2SiMe_3)_2(\mu-N_2)$  (13). A solution of LiCH<sub>2</sub>SiMe<sub>3</sub> (0.071 g, 0.75 mmol) in 10 mL of pentane was added to a

<sup>(23)</sup> Weber, W. P.; Ugi, I. K.; Gokel, G. W. Angew. Chem., Int. Ed. Engl. 1972, 11, 530.

suspension of 12 (0.40 g, 0.38 mmol) in 10 mL at -40 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was filtered and concentrated until a crystalline material began to precipitate. Cooling at -40 °C overnight led to the isolation of orange bladelike crystals of 13 in 34% yield (0.15 g). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -0.62 (d, J<sub>SiH</sub> = 10 Hz, 1 H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>); 0.39 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.48 (s, 9 H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>); 0.77 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.98-1.25 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.59 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.71 (m, 4 H, -CH<sub>2</sub>-CH<sub>2</sub>-); 1.78 (s, 9 H, <sup>t</sup>Bu); 2.30 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.44 (d,  $J_{\text{SiH}} = 10$  Hz, 1 H,  $CH_2\text{Si}(CH_3)_3$ ; 2.61 (m, 1 H,  $-CH_2CH_2-$ ); 3.06 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.41 (m, 1 H, -CH<sub>2</sub>CH<sub>2</sub>-). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz,  $C_6D_6$ ):  $\delta$  5.98 (s); 6.36 (s); 13.81 (d); 17.49 (d); 18.90 (d0; 19.19 (d); 19.41 (d); 19.66 (d); 20.45 (d); 20.86 (d); 21.16 (m); 21.72 (m); 22.97 (d); 23.91 (d); 37.89 (s); 45.14 (d); 45.67 (s); 45.92 (s); 50.26 (s); 56.33 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (500 MHz,  $C_6D_6$ ):  $\delta$  22.45 (s, 1 P); 0.73 (s, 1 P). IR (cm<sup>-1</sup>): 1664 (w); 1589 (w); 1254 (s); 1227 (m); 1177 (m); 1109 (m); 1053 (m); 1020 (s); 985 (m); 927 (m); 882 (m); 857 (m); 796 (s); 477 (m). Raman (cm<sup>-1</sup>): 1270 ( $\nu_{N-N}$ ). Anal. Calcd for C<sub>52</sub>H<sub>124</sub>N<sub>6</sub>P<sub>4</sub>Si<sub>4</sub>Ti<sub>2</sub>: C, 53.57; H, 10.74; N, 7.21. Found: C, 51.46; H, 10.75; N, 7.11. Mp: 135-136 °C.

 $[N_2P_2]$ TiCl(N<sup>t</sup>Bu) (14). A solution of Li[N\_2P\_2] (0.30 g, 0.68) mmol) in 5 mL of Et<sub>2</sub>O was added to a suspension of Cl<sub>2</sub>(py)<sub>3</sub>Ti(N<sup>t</sup>Bu) (0.30 g, 0.68 mmol) in 5 mL of Et<sub>2</sub>O at -40 °C. The reaction mixture was allowed to warm and stirred for 5 h. Solvent was removed under vacuum, and the crude product was extracted with pentane. Following concentration and cooling at -40°C, orange crystals of 14 were isolated in 76% yield (0.30 g). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  0.24 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.77 (m, 3 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 0.82 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 1.06 (m, 16 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.31 (m, 5 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.38 (s, 9 H, 'Bu); 1.49 (m, 2 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.62 (m, 3 H, -CH<sub>2</sub>CH<sub>2</sub>-); 1.67 (s, 9 H, <sup>t</sup>Bu); 1.78 (m, 2 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 2.32 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.02 (m, 1 H,  $-CH_2CH_2-$ ; 3.32 (m, 1 H,  $-CH_2CH_2-$ ); 4.10 (m, 1 H,  $-CH_2CH_2-$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.50 (s); 4.91(s); 15.44 (d); 16.19 (d); 18.57 (m); 19.19 (m); 21.90 (d); 23.27 (m); 32.82 (s); 35.60 (s); 46.47 (d); 50.69 (s); 51.02 (s); 53.70 (s); 69.01 (s); 96.96 (s); 99.94 (s).  $^{31}P\{^{1}H\}$  NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.61 (s, 1 P); 27.53 (s, 1 P). IR (cm<sup>-1</sup>): 1245 (s); 1204 (m); 1123 (w); 1056 (s); 1019 (m); 941 (w); 886 (m); 849 (s); 821 (m); 801 (w); 772 (m); 749 (m). Anal. Calcd for C<sub>26</sub>H<sub>60</sub>ClN<sub>3</sub>P<sub>2</sub>SiTi: C, 53.08; H, 10.30; N, 7.14. Found: C, 53.28; H, 10.55; N, 7.22. Mp: 107-108 °C.

Generation of [N<sub>2</sub>P<sub>2</sub>]TiMe(N<sup>t</sup>Bu) (15). Methylmagnesium bromide (3.0 M in Et<sub>2</sub>O, 0.60 mL, 1.7 mmol) was added via syringe to a solution of 14 (1.0 g, 1.7 mmol) in 15 mL of  $Et_2O$  at -40 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. Solvent was removed under vacuum, and the crude product was extracted with pentane. Following the removal of solvent under vacuum, a pale-yellow oil was obtained. Two species appear to be present, as evidenced by <sup>31</sup>P{<sup>1</sup>H} NMR in a 9:2 ratio, and the vast majority of the peaks are coincident. The material was used without further purification (see 16 below). <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$  0.31 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.73 (s, 3 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.86 (2 s, 3 H, Ti-CH<sub>3</sub>); 1.03 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.23 (m, 2 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.36 (m, 2 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.59 (s, 9 H, <sup>t</sup>Bu); 1.64 (s, 9 H, <sup>t</sup>Bu); 1.92 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.45 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.00 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 3.23 (m, 1 H,  $-CH_2CH_2-$ ); 3.89 (m, 1 H,  $-CH_2CH_2-$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (125) MHz, C<sub>6</sub>D<sub>6</sub>): δ 5.59 (s); 5.75 (s); 16.72 (d); 17.08 (d); 19.17 (d); 19.38 (d); 19.80 (d); 20.13 (d); 20.48 (d); 20.61 (d); 22.50 (d); 22.75 (d); 23.78 (d); 24.13 (d); 34.08 (s); 35.84 (s); 36.92 (s); 46.14 (d); 49.60 (d); 49.86 (s); 53.50 (s); 67.52 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 2.18 (s, 2 P); 3.48 (s, 9 H); 19.24 (s, 2 P); 24.98 (s, 9 P). IR (cm<sup>-1</sup>): 1406 (w); 1353 (m); 1246 (s); 1204 (s); 1122 (w); 1096 (w); 1061 (s); 1018 (m); 940 (m); 889 (m); 848 (s); 821 (m); 798 (m); 770 (m); 746 (m); 694 (w); 624 (w); 539 (w); 512 (m); 438 (w).

**Generation of {[N<sub>2</sub>P<sub>2</sub>]Ti(N'Bu)}{MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>} (16).** Et<sub>2</sub>O (10 mL) was added to a flask containing crude **15** (0.27 g, 0.48 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.24 g, 0.48 mmol). The reaction mixture quickly changed color from yellow to orange. The solution was stirred for 1 h before the solvent was removed under vacuum, leaving a thick orange oil. The resonance peaks for both species present in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **15** have vanished and have been replaced by one major resonance peak at 23.90 ppm. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.08 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.71 (s, 3 H, H<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>); 0.85 (m, 24 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.06 (m, 4 H, PCH(CH<sub>3</sub>)<sub>2</sub>); 1.19 (s, 9 H, <sup>1</sup>Bu); 1.29 (s, 9 H, <sup>1</sup>Bu); 1.68 (m, 4 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.31 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); 2.95 (m, 2 H, -CH<sub>2</sub>CH<sub>2</sub>-); <sup>31</sup>P{<sup>1</sup>H} NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 23.90 (s, 1 P). <sup>19</sup>F NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): -130.83 (d, *J*<sub>FF</sub> = 20 Hz, 2 F, *o*-F); -163.44 (t, *J*<sub>FF</sub> = 24 Hz, 1 F, *p*-F); -165.92 (m, 2 F, *m*-F).

Crystallographic Analysis. Single crystals of 3, 5, 6, 9-11, 13, and 14 were coated in Paratone-N oil, mounted on a Kaptan loop, transferred to a Siemens SMART diffractometer or a Bruker APEX CCD area detector,<sup>24</sup> centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by the collection of 60 30-s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected, and the raw data were integrated using SAINT.<sup>25</sup> Cell dimensions reported were calculated from all reflections with  $I > 10\sigma$ . The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Data were analyzed for agreement and possible absorption using XPREP.26 An empirical absorption correction based on a comparison of redundant and equivalent reflections was applied using SADABS.<sup>27</sup> The structures were solved using SHELXS<sup>28</sup> and refined on all data by full-matrix least squares with SHELXL-97.29 ORTEP diagrams were created using ORTEP-3. A summary of the X-ray diffraction data is presented in Table 2.

#### **Results and Discussion**

The reaction of Li[N<sub>2</sub>P<sub>2</sub>] and ZrCl<sub>4</sub>(THF)<sub>2</sub> in toluene at -40 °C resulted in the formation of **1**, which was isolated as a colorless solid in 82% yield following filtration, removal of the solvent under vacuum, and washing with pentane. The <sup>1</sup>H NMR spectrum displays resonances suggestive of a low-symmetry molecule in solution with two SiMe<sub>2</sub> and six  $-CH_2CH_2-$  resonance peaks. This is further supported by the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, which contains two resonances at 2.59 and 16.38 ppm, indicating that only one phosphine donor is coordinated (16.38 ppm) and the ligand is bound  $\kappa^3$ -N<sub>2</sub>P. We propose that the structure of **1** is similar to that of the related titanium(III) complex [N<sub>2</sub>P<sub>2</sub>]TiCl<sub>2</sub>, with the addition of a chloride atom in

<sup>(24)</sup> *SMART: Area-Detector Software Package*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1995–1999.

<sup>(25)</sup> SAINT: SAX Area-Detector Integration Program, version 7.06; Siemens Industrial Automation, Inc.: Madison, WI, 2005.

<sup>(26)</sup> XPREP (v6.12): Part of the SHELXTL Crystal Structure Determination Package; Bruker AXS Inc.: Madison, WI, 1995.

<sup>(27)</sup> Sheldrick, G. SADABS (v2.10): Siemens Area Detector ABSorption correction program; Bruker Analytical X-ray Systems Inc.: Madison, WI, 2005.

<sup>(28)</sup> XS: Program for the Refinement of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination Package; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1995–1999.

<sup>(29)</sup> XL: Program for the Refinement of X-ray Crystal Structures, Part of the SHELXT Crystal Structure Determination Package; Bruker Analytical Systems Inc.: Madison, WI: 1995–1999.

Table 2. Crystal Data and Structure Refinement for 3, 5, 6, 9, 11, 13, and 14

Chomitz.	et	al.
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	3	5	6	9	11	13	14
compound name	[N <sub>2</sub> P <sub>2</sub> ]ZrMe <sub>3</sub>	$([N_2P_2]ZrCl)_2(\mu-\eta^2:\eta^2-N_2)$	([N <sub>2</sub> P <sub>2</sub> ]ZrCl) <sub>2</sub> (µ-Cl) <sub>2</sub>	[N <sub>2</sub> P <sub>2</sub> ]ZrAr*	[N <sub>2</sub> P <sub>2</sub> ]TiMe <sub>2</sub>	([N <sub>2</sub> P <sub>2</sub> ]TiCH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> (µ-N <sub>2</sub> )	[N <sub>2</sub> P <sub>2</sub> ]TiCl(N <sup>t</sup> Bu)
empirical formula	$C_{25}H_{60}N_2P_2SiZr$	$C_{44}H_{102}Cl_2N_6P_4Si_2Zr_2$	$C_{44}H_{102}Cl_4N_4P_4Si_2Zr_2$	$C_{47}H_{77}N_3P_2SiZr$	$C_{24}H_{57}N_2P_2SiTi$	$C_{59.5}H_{142}N_6P_4Si_4Ti_2$	C26H60ClN3P2SiTi
fw	570.00	574.36	1191.63	865.39	511.65	1274.84	588.15
temperature (K)	155(2)	151(2)	155(2)	151(2)	133(2)	148(2)	160(2)
cryst syst	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P\overline{1}$	$P\overline{1}$	$P2_1/n$	$P2_1/n$	Pbcn	$P2_{1}/c$	$Pca2_1$
a (Å)	8.0482(17)	11.956(2)	11.0595(12)	18.455(7)	32.287(4)	19.224(4)	18.935(3)
b (Å)	9.626(2)	12.070(3)	25.137(3)	18.696(7)	8.8785(11)	18.899(4)	17.017(2)
c (Å)	23.012(5)	12.438(2)	13.1081(14)	16.811(6)	21.700(3)	23.297(5)	21.658(3)
α (deg)	94.477(3)	111.752(4)	90	90	90	90	90
$\beta$ (deg)	96.876(3)	110.138(3)	91.4150(10)	115.02(5)	90	109.599(2)	90
$\gamma$ (deg)	111.824(3)	100.111(3)	90	90	90	90	90
$V(Å^3)$	1628.5(6)	1467.6(5)	3642.9(7)	5255.9(3)	6220.7(13)	7974(3)	6979.0(17)
Ζ	2	2	4	4	8	4	8
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
$\mu  (\rm cm^{-1})$	0.487	0.630	0.580	0.328	0.430	0.380	0.466
no. of rflns	4833	3736	5636	5725	4756	3235	7887
R(int)	0.0336	0.1337	0.0319	0.0720	0.0313	0.0856	0.0588
$R_{\rm obs}$ (%)	3.17	6.51	3.60	5.35	3.95	5.83	4.33
$R_{\rm wobs}$ (%)	8.08	13.36	10.08	13.65	10.25	11.87	9.43

## Scheme 1. Synthesis of [N<sub>2</sub>P<sub>2</sub>]ZrR<sub>3</sub> Complexes

$$[N_2P_2]ZrCl_3 + 3LiR \xrightarrow{Et_2O} [N_2P_2]ZrR_3 \xrightarrow{N_2P_2}]ZrR_3$$

the open coordination site in the zirconium case.<sup>17</sup> The solid-state structure is unknown at this time.

Given the success that "mixed-donor" ligands have had at supporting species containing metal-ligand multiple bonds, alkyl derivatives of 1 were pursued as potential precursors to alkylidene and alkylidyne complexes. The reaction of 1 with 3 equiv of LiCH<sub>2</sub>SiMe<sub>3</sub> led cleanly to the highly soluble trialkyl compound 2 in quantitative yield (Scheme 1a). The <sup>1</sup>H NMR spectrum displays resonances suggestive of a C2-symmetric molecule in solution with equivalent -CH<sub>2</sub>SiMe<sub>3</sub> moieties, likely because of fast exchange on the NMR time scale. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displays one resonance at 8.11 ppm, and the relatively high-field nature of this resonance suggests that both phosphine donors are uncoordinated or are exchanging quickly through a fluxional process. A variable-temperature NMR experiment was undertaken to determine the nature of the fluxional process; however, even at -70 °C, only moderate line broadening is observed, indicating that the exchange process is still too fast to be resolved on the NMR time scale at this temperature.

The reaction of **1** with 3 equiv of methyllithium (1.6 M in  $Et_2O$ ) led to the isolation of **3** following crystallization from pentane as colorless crystals in 46% yield (Scheme 1b). The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **3** are similar to those observed for 2 with equivalent alkyl groups and only one <sup>31</sup>P NMR resonance peak (2.75 ppm). Again, a fluxional process that cannot be resolved by low-temperature NMR spectroscopy is operative. An ORTEP diagram of 3 is shown in Figure 1 with selected bond lengths and angles provided in Table 3. In the solid state, the [N<sub>2</sub>P<sub>2</sub>] ligand is coordinated  $\kappa^3$ -N<sub>2</sub>P, and the zirconium center is six-coordinate. This differs from the solution NMR data, where both phosphines are equivalent and appear to be unbound. The  $Zr-CH_3$  bond distances of 2.278(3), 2.277(3), and 2.297(3) Å are similar to values observed in (PNP)ZrMe<sub>3</sub> [2.255(7), 2.285(7), and 2.253(7) Å]<sup>7</sup> and <sup>t</sup>Bu<sub>2</sub>(2-C<sub>6</sub>H<sub>4</sub>Ph)PNZrMe<sub>3</sub> [2.233(6), 2.239(5), and 2.247(6) Å].<sup>30</sup> The anionic Zr-N [2.111(2) Å] and Zr-P [2.8909(9) Å] distances are also comparable to the values observed in the related

Table 3. Selected Bond Lengths (A) and Angles (deg) for 3					
Zr1-N1	2.111(2)	Zr1-C23	2.297(3)		
Zr1-C24	2.277(3)	Zr1-C25	2.278(3)		
Zr1-N2	2.660(2)	Zr1-P1	2.8909(9)		
N1-Zr1-C24	94.26(10)	N1-Zr1-C25	116.25(11)		
C24-Zr1-C25	90.56(13)	N1-Zr1-C23	136.61(10)		
C24-Zr1-C23	81.67(11)	C25-Zr1-C23	107.00(12)		
N1-Zr1-N2	65.00(7)	C24-Zr1-N2	121.94(11)		
C25-Zr1-N2	147.50(10)	C23-Zr1-N2	80.64(8)		
N1-Zr1-P1	108.79(6)	C24-Zr1-P1	156.94(9)		
C25-Zr1-P1	79.51(9)	C23-Zr1-P1	81.45(8)		
N2-Zr1-P1	70.31(5)				

compound (PNP)ZrMe<sub>3</sub> [Zr–N = 2.223(4) Å; Zr–P = 2.7549(17) and 2.7984(18) Å].<sup>7</sup>

Metal-ligand multiple bonds are of significant interest given their role in many catalytic cycles,<sup>31</sup> and although numerous stable complexes possessing metal-ligand multiple bonds exist, they are primarily located in the middle of the transition-metal series and in the second and third rows.<sup>32</sup> C-H bond activation and group-transfer reactions have been observed with early and late transition metals,<sup>4,33-41</sup> and the development of oxo, imido, and carbene/alkylidene functionalities with these metals is of



**Figure 1.** Thermal ellipsoid (50%) plot of **3**. Hydrogen atoms and isopropylmethyl and *tert*-butylmethyl groups have been omitted for clarity.

<sup>(30)</sup> Ghesner, I.; Fenwick, A.; Stephan, D. W. Organometallics 2006, 25, 4985–4995.



**Figure 2.** (PNP) and  $[N_2P_2]$  ligand sets.

interest. To gain access to these reactive metal-ligand fragments, proper electronic and steric conditions must be met through a prudent choice of ligand. Attempts to generate an alkylidene complex from 3 or 4 either by thermolysis or photolysis were unsuccessful and resulted in gradual decomposition. This contrasts with the recent results of Ozerov et al., who found that the formation of the tribenzyl complex (PNP)Zr(CH<sub>2</sub>Ph)<sub>3</sub> was quickly followed by the elimination of toluene and the formation of the alkylidene species  $(PNP)Zr(=CHPh)(CH_2Ph)$ .<sup>7</sup> One possible reason for the difference in reactivity is the flexible nature of the [N<sub>2</sub>P<sub>2</sub>] ligand, which has been shown to change coordination modes to accommodate the geometric and electronic preferences of the metal center. In contrast, the pincer ligand (PNP) used by Ozerov et al. (Figure 2) has a strong chelate effect due to the phenyl linker bridges that enforce rigid coordination of the ligand.

Full  $\kappa^4$ -coordination of the [N<sub>2</sub>P<sub>2</sub>] ligand in a derivative of **3** was achieved by lowering of the coordination number at the zirconium center via protonation of a methyl group. The reaction of **3** and [PhNMe<sub>2</sub>H][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] led cleanly to the cationic species **4** in quantitative yield on the basis of NMR spectroscopy (Scheme 2). The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra indicate a *C*<sub>2</sub>-symmetric molecule in solution. The <sup>31</sup>P{<sup>1</sup>H} NMR resonance peak shifts downfield from 2.75 to 15.64 ppm. The downfield shift of the <sup>31</sup>P NMR resonance suggests coordination of both phosphine donors and a change in the coordination mode of the [N<sub>2</sub>P<sub>2</sub>] ligand to  $\kappa^4$ -N<sub>2</sub>P<sub>2</sub>.

**Reduction Chemistry of 1.** Encouraged by the stability of the zirconium alkyl compounds, low-valent zirconium species were targeted. Though only a limited number of side-on-bound  $N_2$  complexes of zirconium have been isolated,<sup>42</sup> a number of these compounds have shown remarkable reactivity in which

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 $N_2$  functionalization has been achieved with  $H_2,$  silanes, and alkynes.  $^{43-45}$ 

The reduction of 1 with 2 equiv of KC<sub>8</sub> in THF under an atmosphere of N<sub>2</sub> resulted in a color change of colorless to purple. Following crystallization from pentane, **5** was isolated as purple crystals in 17% yield. The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **5** display resonances suggesting the presence of two isomers (3:2 ratio) in solution, but attempts to further characterize these species in solution have been hampered by the complexity of the data because of overlap of the <sup>1</sup>H NMR resonance peaks. In the solid state, we have evidence for only one isomer upon crystallization, as judged by X-ray diffraction.

To determine the coordination mode of the N<sub>2</sub> moiety in **5**, an X-ray diffraction study was undertaken. The ORTEP diagram is shown in Figure 3 with selected bond lengths and angles provided in Table 4. The solid-state structure of **5** reveals a six-coordinate zirconium complex with the [N<sub>2</sub>P<sub>2</sub>] ligand bound  $\kappa^3$ -N<sub>2</sub>P and a side-on-bound bridging N<sub>2</sub> moiety. Although the Zr1–N3 and Zr1–N3' distances are on the short end of typical at 2.084(5) and 1.975(5) Å, the N–N bond distance is extremely long at 1.576(9) Å<sup>13,43</sup> and is longer than the single N–N bond in hydrazine (1.45 Å). The distance is comparable, however, to the N–N bond lengths observed in the related compounds {[N(SiMe<sub>2</sub>CH<sub>2</sub>P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]Zr}<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -N<sub>2</sub>)<sup>46</sup> [1.503(3) Å], and {[PhP(CH<sub>2</sub>SiMe<sub>2</sub>NSiMe<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh]Zr}( $\mu$ - $\eta^2$ : $\eta^2$ -N<sub>2</sub>)<sup>44</sup> [1.43(1) Å]. The low yield of **5** has hindered further reactivity studies.

In an attempt to increase the yield of **5**, the reduction of **1** under different reaction conditions was explored. When a less polar solvent such as pentane, Et<sub>2</sub>O, or toluene was used, the reaction mixture turned green prior to turning dark purple (suggestive of the presence of **5**). We were interested in the nature of the green intermediate, which led to the examination of the reaction of **1** with 1 equiv of KC<sub>8</sub> in Et<sub>2</sub>O. The addition of a suspension of KC<sub>8</sub> to a suspension of **1** in Et<sub>2</sub>O at  $-40 \,^{\circ}$ C resulted in a green solution. Removal of the solvent under vacuum, extraction with pentane, and cooling at  $-40 \,^{\circ}$ C led to the isolation of bright-green crystals of **6** in 20% yield.

Although the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **6** indicate the presence of a new diamagnetic compound, the assignment of resonances from the <sup>1</sup>H NMR spectrum of **6** is complicated by the presence of two non-interchanging isomers (mirror and inversion symmetry), similar to the results obtained for 5. More informative is the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, which displays two sets (4:1 ratio) of two <sup>31</sup>P NMR resonance peaks at 0.09 and 14.19 ppm and at 0.88 and 15.93 ppm and is suggestive of  $\kappa^3$ -N<sub>2</sub>P coordination of the [N<sub>2</sub>P<sub>2</sub>] ligand. These chemical shifts are similar to those previously observed from spectra of 1 and 5, which possessed  $\kappa^3$ -N<sub>2</sub>P-bound [N<sub>2</sub>P<sub>2</sub>] ligands. An ORTEP diagram of 6 is shown in Figure 4 with selected bond lengths and angles provided in Table 5. Compound 6 is a chloridebridged zirconium(III) dimer with a Zr-Zr distance of 3.2190(5) Å, which falls in the expected range of 3.20–3.48 Å for a typical Zr-Zr single bond.<sup>47</sup> Each zirconium atom lies in a distorted octahedral geometry with the  $[N_2P_2]$  ligand-bound  $\kappa^3$ -N<sub>2</sub>P, and

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Table 4. Selected Bond Lengths $({\rm \AA})$ and Angles (deg) for 5					
Zr1-N3	2.084(5)	Zr1-N3'	1.975(5)		
Zr1-N1	2.179(4)	Zr1-N2	2.456(4)		
Zr1-P1	2.7976(15)	Zr1-Cl1	2.4757(16)		
N3'-N3	1.576(9)				
N3'-Zr1-N3	45.6(2)	N3'-Zr1-N1	104.06(18)		
N3-Zr1-N1	142.87(18)	N3'-Zr1-N2	98.53(19)		
N3-Zr1-N2	92.54(17)	N1-Zr1-N2	68.30(15)		
N3'-Zr1-Cl1	108.56(16)	N3-Zr1-Cl1	104.74(15)		
N1-Zr1-Cl1	105.93(12)	N2-Zr1-Cl1	152.83(11)		
N3'-Zr1-P1	136.42(14)	N3-Zr1-P1	91.29(13)		
N1-Zr1-P1	111.53(12)	N2-Zr1-P1	73.27(10)		
Cl1-Zr1-P1	85.34(5)				
		0			
Table 5. Selected Bond Lengths (Å) and Angles (deg) for 6					
Zr1-N1	2.145(2)	Zr1-Zr1	3.2190(5)		
Zr1-N2	2.478(2)	Zr1-Cl2	2.5401(7)		
Zr1-Cl1	2.4928(7)	Zr1-P1	2.7366(8)		
N1-Zr1-N2	68.99(8)	N1-Zr1-Cl1	148.90(6)		
N1-Zr1-Cl2	111.44(6)	N2-Zr1-Cl2	169.06(6)		
Cl1-Zr1-Cl2	90.13(2)	N1-Zr1-P1	84.79(6)		
N1-Zr1-Cl2	97.36(6)	N2-Zr1-Cl2	88.50(6)		

a center of inversion relates the two " $[N_2P_2]ZrCl_2$ " fragments. The bridging Zr–Cl bond distance of 2.5401(7) Å is typical<sup>48,49</sup> as is the terminal Zr–Cl bond [2.4928(7) Å].<sup>48,49</sup> The Zr1–N1, Zr1–N2, and Zr1–P1 distances are also similar to those observed in **5**. A related compound reported by Schrock et al., [ZrCl<sub>3</sub>(PBu<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, has structural parameters comparable with a Zr–Zr bond distance of 3.182(1) Å, terminal Zr–Cl distances of 2.433(2) and 2.429(2) Å, and bridging Zr–Cl distances of 2.546(1) and 2.542(2) Å.<sup>50</sup> The Zr–P bond distance of 2.7366(8) Å in **6** is shorter than the ones observed in [ZrCl<sub>3</sub>(PBu<sub>3</sub>)<sub>2</sub>]<sub>2</sub>

Cl1-Zr1-P1

80.87(2)

78.55(6)

165.18(2)

N2-Zr1-P1

Cl2-Zr1-P1



**Figure 3.** Thermal ellipsoid (50%) plot of **5**. Hydrogen atoms and isopropylmethyl and *tert*-butylmethyl groups have been omitted for clarity.

[2.830(2) and 2.839(2) Å], possibly because of greater steric congestion at the metal center.

The diamagnetism of **6** indicates either a Zr–Zr two-electron bond or antiferromagnetic coupling between the metal centers.<sup>50</sup> To clarify this point, B3LYP<sup>51</sup>/LACVP\*<sup>52–56</sup> hybrid density functional theory optimizations<sup>57</sup> were performed on a closedshell singlet model of **6** (**Zr**<sub>d,model</sub>) and its hypothetical d<sub>0</sub>, yttrium(III) analogue (**Y**<sub>d,model</sub>). The constraint of inversion symmetry was imposed during the initial optimization of each structure and then removed for a final, nonconstrained optimization. The gas-phase structure of **Zr**<sub>d,model</sub> is shown in Figure 5 (top). The overall geometry is reproduced fairly well, although the Zr–Zr bond distance of 3.13 Å is somewhat too short. By contrast, the analogous Y–Y distance of 4.17 Å in **Y**<sub>d,model</sub> (Figure 5, bottom) clearly shows that a significant metal–metal bonding contribution must be present for the geometric parameters of **6** to be realized.

The frontier orbitals (HOMO and LUMO, bottom and top, respectively) of  $\mathbf{Zr}_{d,model}$  are depicted in Figure 6. As expected, the HOMO consists of two d-type zirconium orbitals forming an s bond, with almost no orbital contribution from neighboring atoms. The calculated LUMO is localized, and bonding, and thus the electron density resulting from a one- or two-electron reduction, might be centered in a stabilizing d-d p bond; however, accessible decomposition pathways appear to render such a complex nonisolable.

As with **5**, we have been unable to isolate **6** in yields greater than 20%. We attribute this problem to the instability of the " $[N_2P_2]Zr^{III}Cl_2$ " fragment, which, unless it can dimerize to form **6**, decomposes. Substitution of KC<sub>8</sub> with stronger reductants, such as sodium naphthalide, results in over-reduction to give **5**, and the use of milder reducing reagents (Na/Hg and Mg) leads to slower reactions that result in decomposition (see below). Compound **6** is stable in the solid state: samples stored in the glovebox at room temperature showed no decomposition after 1 month. In solution, monitoring of the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of a sample of **6** in C<sub>6</sub>D<sub>6</sub> showed that disproportionation to **1** and an unknown, NMR-silent product occurs over 12 h.

The reactivity of **6** with neutral ligands was probed in attempts to determine the propensity for homolytic or heterolytic Zr-Zr

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**Figure 4.** Thermal ellipsoid (50%) plot of **6**. Hydrogen atoms and isopropylmethyl and *tert*-butylmethyl groups have been omitted for clarity.



Figure 5. Diagrams<sup>58</sup> of optimized  $Zr_{d,model}$  (top) and  $Y_{d,model}$  (bottom) at the B3LYP/LACVP\* level of theory. Hydrogen atoms have been removed for clarity.  $Zr_{d,model}$  bond lengths (Å):  $Zr-Cl_{term}$ , 2.54;  $Zr-Cl_{bridge}$ , 2.59, 2.66;  $Zr-N_{amide}$ , 2.12;  $Zr-N_{amine}$ , 2.59; Zr-P, 2.72; Zr-Zr, 3.13.  $Y_{d,model}$  bond lengths (Å):  $Y-Cl_{term}$ , 2.60;  $Y-Cl_{bridge}$ , 2.73, 2.76;  $Y-N_{amide}$ , 2.21;  $Y-N_{amine}$ , 2.70; Y-P, 2.90; Y-Y, 4.17. Legend: C, black; Cl, green; N, blue; P, purple; Si, yellow; Y, red; Zr, slate.

bond cleavage. The reaction of **6** with carbon monoxide, 2,6dimethylphenyl isocyanide, diphenylacetylene, and trimethylphosphine resulted in either no reaction or the re-formation of **1** and other intractable, paramagnetic products. Alkylation of **6** with LiCH<sub>2</sub>SiMe<sub>3</sub> led cleanly to the formation of **2** as well as uncharacterized, NMR-silent products. To obtain **2**, compound **6** could disproportionate to **1** (which is then alkylated) and "[N<sub>2</sub>P<sub>2</sub>]Zr<sup>II</sup>Cl", which decomposes.

The addition of the terphenylisocyanide<sup>59</sup> **7** to a solution of **6** resulted in an immediate color change from bright lime green to dark forest green. The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the resulting reaction mixture revealed a 1:1 mixture of **1** and what we postulate to be the zirconium(II) species **8** (Scheme 3). Compound **8** displays two <sup>31</sup>P NMR resonances at -2.96 and



**Figure 6.** HOMO (bottom) and LUMO (top) diagrams for  $Zr_{d,model}$ . Only the zirconium centers, chlorides, and ligand backbones are shown. Legend: C, black; Cl, green; N, blue; P, purple; Si, yellow; Zr, slate.



**Figure 7.** Thermal ellipsoid (50%) plot of **9**. Hydrogen atoms and isopropylmethyl and *tert*-butylmethyl groups have been omitted for clarity.

22.40 ppm, indicative of  $\kappa^3$ -N<sub>2</sub>P coordination of the [N<sub>2</sub>P<sub>2</sub>] ligand. The IR spectrum revealed a C–N absorption at 1872 cm<sup>-1</sup> (free isocyanide  $\nu_{\rm CN} = 2119$  cm<sup>-1</sup>), suggesting significant back-bonding into the C–N  $\pi^*$  orbitals. Isolation of **8** was complicated by the presence of **1** and its decomposition within hours of its generation in solution at room temperature.

The isolation of **8** was attempted through an alternative synthetic route. The addition of 2 equiv of KC<sub>8</sub> to a colorless solution of **1** and **7** resulted in an immediate color change of the solution to dark forest green. The reaction mixture was allowed to warm to room temperature before the solvent was removed under vacuum. Extraction with pentane gave a dark-green solution, which, following concentration and cooling at -40 °C overnight, yielded bright-orange crystals of **9** in 18% yield. An ORTEP diagram of **9** is shown in Figure 7, with selected bond lengths and angles provided in Table 6. The [N<sub>2</sub>P<sub>2</sub>] ligand is coordinated  $\kappa^3$ -N<sub>2</sub>P, and the new aryl ligand, Ar\*, appears to be coordinated in a distorted  $\eta^7$  fashion. Five of the Zr–C bonds are shorter than the other two, with an average distance of 2.377(33) Å. The remaining two Zr–C bonds are significantly longer (>3 $\sigma$ ), with bond distances of 2.576(4) and

<sup>(59)</sup> For recent work with terphenylisocyanides, see: Fox, B. J.; Sun, Q. Y.; DiPasquale, A. G.; Fox, A. R.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2008**, *47*, 9010–9020.

Scheme 3. Formation of a Transient Zirconium(II) Isocyanide Complex



Table 6. Selected Bond Lengths (Å) and Angles (deg) for 9

Zr1-N1	2.151(3)	Zr1-C25	2.334(4)
Zr1-C27	2.358(4)	Zr1-C28	2.373(4)
Zr1-C26	2.406(4)	Zr1-C24	2.412(4)
Zr1-C23	2.576(4)	Zr1-C29	2.612(4)
Zr1-N2	2.652(3)	Zr1-P1	2.7943(11)
N1-Zr1-C25	115.93(13)	N1-Zr1-C27	104.15(13)
C25-Zr1-C27	64.81(14)	N1-Zr1-C28	121.22(13)
C25-Zr1-C28	86.04(14)	C27-Zr1-C28	34.92(14)
N1-Zr1-C26	101.31(13)	C25-Zr1-C26	34.62(13)
C27-Zr1-C26	34.49(14)	C28-Zr1-C26	65.90(14)
N1-Zr1-C24	143.21(13)	C25-Zr1-C24	35.07(13)
C27-Zr1-C24	83.50(13)	C28-Zr1-C24	85.63(13)
C26-Zr1-C24	64.87(13)	N1-Zr1-C23	175.79(13)
C25-Zr1-C23	61.03(13)	C27-Zr1-C23	77.44(13)
C28-Zr1-C23	62.25(13)	C26-Zr1-C23	77.73(12)
C24-Zr1-C23	32.72(12)	N1-Zr1-C29	152.27(13)
C25-Zr1-C29	80.14(13)	C27-Zr1-C29	60.59(13)
C28-Zr1-C29	33.43(12)	C26-Zr1-C29	78.97(13)
C24-Zr1-C29	62.24(12)	C23-Zr1-C29	31.80(12)
N1-Zr1-N2	65.16(11)	C25-Zr1-N2	96.70(12)
C27-Zr1-N2	153.20(13)	C28-Zr1-N2	171.04(12)
C26-Zr1-N2	120.53(12)	C24-Zr1-N2	91.71(11)
C23-Zr1-N2	111.69(11)	C29-Zr1-N2	138.61(11)
N1-Zr1-P1	93.61(9)	C25-Zr1-P1	140.97(10)
C27-Zr1-P1	134.54(11)	C28-Zr1-P1	100.44(10)
C26-Zr1-P1	163.56(10)	C24-Zr1-P1	106.51(9)
C23-Zr1-P1	87.88(8)	C29-Zr1-P1	84.62(8)
N2-Zr1-P1	72.09(7)		

2.612(4) Å. Although this suggests  $\eta^5$  coordination, the C–C distances of the new seven-membered ring do not deviate significantly from one another [ave 1.423(14) Å, min 1.412(5) Å, and max 1.452(5) Å], thus suggesting a closed  $\pi$  system and  $\eta^7$  coordination. While no N–H bond was located in the difference Fourier map, the IR spectrum reveals a moderate N-H stretch at 3471 cm<sup>-1</sup>. Though the aforementioned reaction does produce a small quantity of 8, as seen by NMR spectroscopy of the crude reaction mixture, the primary product observed is 9 along with some other uncharacterized side-products.

We believe the reason the reduction of 1 in the presence of 7 yields 9 primarily instead of 8 is due to a precoordination event, which lowers the reduction potential of the zirconium center, making the reduction of the proposed intermediate  $[N_2P_2]ZrCl_3CN(2,6-Mes_2)C_6H_3$  to  $[N_2P_2]Zr^{I}CN(2,6-Mes_2)C_6H_3$ more facile than that of 1 to "[N<sub>2</sub>P<sub>2</sub>]Zr<sup>J</sup>". Although no intermediates have been observed along the reaction coordinate of 1 to 9, the mechanism likely involves (i) the reduction of  $[N_2P_2]ZrCl_3CN(2,6-Mes_2)C_6H_3$  to  $[N_2P_2]ZrCN(2,6-Mes_2)C_6H_3$ as the first step. This is followed by (ii) the metal-assisted insertion of the isocyanide carbon into the C-C bond of the mesityl group of the terphenyl ligand. Finally, (iii) reduction of the resulting aromatic system by the zirconium(I) center (returning Zr to a 4+ oxidation state) and protonation of the anionic nitrogen atom (by solvent or adventitious water) gives 9 (Scheme 4). A conceptually related insertion reaction by a ruthenium carbene complex was recently reported.<sup>60</sup> In addition, reactions involving photolytically induced isocyanide insertion into an adjacent aromatic ring have been known for many years.<sup>61</sup> Our efforts to shed light on the mechanism of this



unusual reaction have been hampered by the low yields and complexity of the products formed.

As described previously,<sup>17</sup> 10 is monomeric and paramagnetic in contrast to the zirconium(III) analogue 6, which is dimeric and diamagnetic. We were therefore curious to explore potential reactivity differences between the two congeners. In contrast to the synthesis of 2 and 3, attempts to synthesize organometallic titanium(III) species with alkyllithium reagents failed to yield isolable products. Nonetheless, milder reagents proved to be more effective: the reaction of 10 with 2 equiv of methylmagnesium bromide in Et<sub>2</sub>O at -40 °C resulted in a color change from purple to bright blue. Following removal of the solvent under vacuum, extraction with  $Et_2O$ , and cooling at -40 °C, bright-blue crystals of 11 were isolated in 58% yield (Scheme 5). The results of an X-ray diffraction study are shown in Figure 8, with selected bond lengths and angles provided in Table 7. As with compound 10, the  $[N_2P_2]$  ligand is bound  $\kappa^3$ -N<sub>2</sub>P. The Ti-CH<sub>3</sub> bond distances were found to be 2.168(2) and 2.139(2) Å. These values are similar to those reported for other titanium(III) methyl complexes such as  $[TiMe(\eta^5-C_5Me_4-$ (SiMe<sub>3</sub>)<sub>2</sub>] [2.213(2) Å],<sup>62</sup> [PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>TiMe [2.120(5) Å],<sup>63</sup> and  $\{HC[C(Me)NAr]_2\}TiMe_2$  (Ar = mesityl) [2.131(3) and 2.123(3) Å].<sup>64</sup> The solution magnetic susceptibility is 1.7  $\mu_{\rm B}$ , in agreement with an  $S = \frac{1}{2}$  spin state.

The reduction chemistry of 10 was explored to see how it compared to that of 1. The reduction of 10 with  $KC_8$  in  $Et_2O$ under an atmosphere of N2 resulted in a color change of purple to brown (Scheme 5). Following crystallization from the same solvent, 12 was isolated as fluffy purple crystals in 57% yield. Raman spectroscopy is consistent with a high degree of reduction of the N–N bond, with  $\nu_{N-N}$  at 1300 cm<sup>-1</sup>. The reaction of 12 with 2 equiv of LiCH<sub>2</sub>SiMe<sub>3</sub> in pentane, followed by filtration and crystallization from pentane, yielded orangebrown crystals of the diamagnetic compound 13 in 34% yield. An ORTEP diagram is shown in Figure 9 with selected bond lengths and angles provided in Table 8. The solid-state structure of 13 reveals a five-coordinate titanium in a square-based pyramidal geometry with an end-on bridging N2 moiety. The  $[N_2P_2]$  ligand is bound  $\kappa^3$ -N<sub>2</sub>P to the metal center, and because of steric constraints, the second phosphine is unable to coordinate to the titanium center. To the best of our knowledge, this is the first report of alkylation at the metal center of a dinitrogen complex.<sup>65</sup> The short Ti-µ-N<sub>2</sub> bond distances [1.783(4) and 1.782(3) Å] and the elongated N–N bond length [1.286(4) Å] are similar to those of related non-cyclopentadienvl-supported diamagnetic titanium dinitrogen compounds such as {[PhC(NSiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Ti}<sub>2</sub>( $\mu$ -N<sub>2</sub>)<sup>63</sup> [1.771(5) and 1.759(5) Å

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Scheme 4. Proposed Reaction Pathway to the Formation of 9



Scheme 5. Substitution Chemistry of 10



Table 7. Selected Bond Lengths (Å) and Angles (deg) for 11

Ti1-N1 Ti1-C23 Ti1-P1	2.0024(16) 2.168(2) 2.6215(6)	Ti1-C24 Ti1-N2	2.139(2) 2.4441(16)
N1-Ti1-C24 C24-Ti1-C23 C24-Ti1-N2 N1-Ti1-P1 C23-Ti1-P1	109.70(8) 100.71(9) 98.56(7) 125.20(5) 85.75(6)	N1-Ti1-C23 N1-Ti1-N2 C23-Ti1-N2 C24-Ti1-P1 N2-Ti1-P1	113.92(8) 71.00(6) 156.68(7) 116.15(6) 73.98(4)

 $(Ti-\mu-N_2)$  and 1.275(6) Å (N-N)], {[(Me\_3Si)\_2N]TiCl(C\_6H\_5N)\_2}\_2(\mu-N\_2)^{66} [1.759(3) Å  $(Ti-\mu-N_2)$  and 1.263(7) Å (N-N)], and



Figure 8. Thermal ellipsoid (50%) plot of 11. Hydrogen atoms and isopropylmethyl and *tert*-butylmethyl groups have been omitted for clarity.

{[PhP(CH<sub>2</sub>SiMe<sub>2</sub>NSiMe<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh]Ti}( $\mu$ -N<sub>2</sub>)<sup>46</sup> [1.783(4) Å (Ti- $\mu$ -N<sub>2</sub>) and 1.255(7) Å (N-N)]. The  $\nu_{N-N}$  value at 1270 cm<sup>-1</sup> indicates a high degree of activation of the N<sub>2</sub> moiety and agrees well with the value observed in the spectrum of **12** as well as the previously reported literature value of 1284 cm<sup>-1</sup> for [(Me<sub>3</sub>Si)<sub>2</sub>NTiCl(TMEDA)]<sub>2</sub>( $\mu$ -N<sub>2</sub>)].<sup>67</sup>

The Ti- $\mu$ -N<sub>2</sub> bond distances in **13** [1.783(4) and 1.782(3) Å] are closer in length to Ti-N double bonds (1.709 Å) than Ti-N single bonds (1.932 Å),<sup>47</sup> suggesting that the Ti-N bond may have some double-bond character. This observation prompted the synthesis of monomeric [N<sub>2</sub>P<sub>2</sub>]-supported titanium imido species to determine how the coordination mode of the ligand would change when going from a dimer to a monomer and how the [N<sub>2</sub>P<sub>2</sub>] ligand would affect the Ti-N<sub>imido</sub> bond. Titanium imido complexes are also of interest because they have proven to be competent hydroamination catalysts<sup>68</sup> and have shown interesting reactivity with small molecules such as CO<sub>2</sub>.<sup>69-71</sup> We were therefore interested in exploring imido complexes in our [N<sub>2</sub>P<sub>2</sub>] systems. The reaction of Li[N<sub>2</sub>P<sub>2</sub>] and Cl<sub>2</sub>(py)<sub>3</sub>Ti(N<sup>t</sup>Bu) in toluene at -40 °C resulted in the formation



**Figure 9.** Thermal ellipsoid (50%) plot of **13**. Hydrogen atoms and isopropylmethyl and *tert*-butylmethyl groups have been omitted for clarity.



of 14, which was isolated as bright-orange crystals in 76% yield following crystallization from pentane at -40 °C. The solidstate structure of 14 was determined by X-ray crystallography. An ORTEP diagram is shown in Figure 10, with selected bond lengths and angles provided in Table 9. The ligand is bound  $\kappa^3$ -N<sub>2</sub>P, and the imido group occupies the axial position of the square-based pyramid surrounding the titanium atom. Two nonsymmetry-related molecules are present in the asymmetric unit. The two Ti-N<sub>imido</sub> bond distances are identical [1.698(4) and 1.700(4) Å] as are the Ti-N-C<sub>bu</sub> angles [166.3(3)° and 166.9(4)°], which moderately deviate from 180°. The Ti $-N_{imido}$ bond distance is close to the mean value of 1.708 Å of all structurally characterized titanium(IV) imidos recorded (>70 compounds) in the Cambridge Structural Database. The coordination number does appear to have a slight affect on Ti-N<sub>imido</sub> bond lengths. The six-coordinate complex Ti(O2tBuNN')- $(N^{t}Bu)(py)$  has a Ti-N<sub>imido</sub> bond of 1.719(2) Å,<sup>72</sup> whereas the five-coordinate compounds [Ti(N<sup>t</sup>Bu){PhC(NSiMe<sub>3</sub>)<sub>2</sub>}(CH<sub>2</sub>Si-Me<sub>3</sub>)(py)] [1.690(2) Å]<sup>73</sup> and [Ti( $\eta^{8}$ -C<sub>8</sub>H<sub>8</sub>)(N<sup>t</sup>Bu)] [1.699(6) Å]<sup>74</sup> have shorter Ti-N<sub>imido</sub> bond distances and are closer to the values observed in 14. The remaining structural features are similar to those of related complexes.

As demonstrated in the case of compound 4, the coordination mode of the  $[N_2P_2]$  ligand can be altered to accommodate a change at the metal center (see above). With this in mind, the synthesis of a cationic titanium imido species was examined. The reaction of 14 with 1 equiv of methylmagnesium bromide (3.0 M in Et<sub>2</sub>O) in Et<sub>2</sub>O resulted in a slight color change from orange to yellow. Following removal of the solvent under vacuum, extraction with pentane, and evaporation of the volatile material, 15 was isolated as a yellow oil. Because of the high solubility of 15, a solid material could not be obtained; however, further reaction of 15 with 1 equiv of  $B(C_6F_5)_3$  in Et<sub>2</sub>O resulted in the formation



Figure 10. Thermal ellipsoid (50%) plot of 14. Hydrogen atoms and isopropylmethyl and *tert*-butylmethyl groups of the  $[N_2P_2]$  ligand have been omitted for clarity.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for 13					
Ti1-N5	1.783(4)	Ti1-N1	2.012(3)		
Ti1-C23	2.166(4)	Ti1-N2	2.497(3)		
Ti1-P1	2.5875(14)	Ti2-N6	1.782(3)		
Ti2-N3	2.018(3)	Ti2-C49	2.161(4)		
Ti2-N4	2.520(3)	Ti2-P3	2.6227(15)		
N5-N6	1.286(4)				
N5-Ti1-N1	110.14(14)	N5-Ti1-C23	102.08(15)		
N1-T1-C23	118.12(15)	N5-Ti1-N2	158.80(13)		
N1-Ti1-N2	70.50(12)	C23-Ti1-N2	95.59(13)		
N5-Ti1-P1	89.01(11)	N1-Ti1-P1	123.55(10)		
C23-Ti1-P1	107.89(12)	N2-Ti1-P1	74.36(8)		
N6-Ti2-N3	107.44(14)	N6-Ti2-C49	107.13(16)		
N3-Ti2-C49	116.36(15)	N6-Ti2-N4	155.69(14)		
N3-Ti2-N4	69.77(12)	C49-Ti2-N4	95.04(15)		
N6-Ti2-P3	90.51(11)	N3-Ti2-P3	126.46(11)		
C49-Ti2-P3	104.68(13)	N4-Ti2-P3	73.98(9)		
Table 9. Selected Bond Lengths (Å) and Angles (deg) for 14					
Ti1-N3	1.701(4)	Ti1-N1	2.011(4)		
Ti1-N2	2.332(3)	Ti1-Cl1	2.3646(13)		
Ti1-P1	2.6067(14)				
N3-Ti1-N1	118.22(16)	N3-Ti1-N2	99.81(14)		
N1-Ti1-N2	73.19(13)	N3-Ti1-Cl1	103.47(12)		
N1-Ti1-Cl1	105.25(11)	N2-Ti1-Cl1	153.89(10)		
N3-Ti1-P1	106.63(13)	N1-Ti1-P1	128.73(10)		
N2-Ti1-P1	76.04(9)	Cl1-Ti1-P1	86.03(5)		

of the cationic species **16** (Scheme 6). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **16** displays one major resonance at 23.90 ppm, in the region associated with coordinated phosphine. Additional evidence for phosphine coordination and ion-pair formation was obtained by <sup>19</sup>F NMR spectroscopy using Horton's criteria: the separation between the *m*- and *p*-fluorine resonance peaks is 2.47 ppm, indicating complete abstraction of a methyl ligand.<sup>75</sup>

#### Conclusions

The  $[N_2P_2]$  ligand has proven to be stable and capable of supporting early-metal alkyl, imido, and reduced early-metal species. A range of coordination modes and geometries were

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### Titanium and Zirconium Complexes

observed, including *fac* and *mer* coordination. With electropositive metals, the  $[N_2P_2]$  ligand appears to prefer a  $\kappa^3$ -N<sub>2</sub>P binding mode; however, upon abstraction of an alkyl group, the ligand binds  $\kappa^4$ -N<sub>2</sub>P<sub>2</sub>, as was seen in the cases of **4** and **16**. The reduction of **1** led to isolation of a zirconium(III) dimer and a formal zirconium(IV) side-on-bound bridging dinitrogen complex. Compound **6** could be observed to cleave heterolytically to **1** and a transient zirconium(II) center if the appropriate trapping reagent was used. The reduction of **1** in the presence of a terphenylisocyanide resulted in the isolation of an unusual insertion product involving the cleavage of an aromatic C–C bond. The substitution and reduction chemistry of related Ti  $[N_2P_2]$  complexes was also explored, and many differences between the two congeners were seen. The reduction of **10** resulted in the isolation of an end-on bridging dinitrogen compound, which was stable to substitution reactions with strongly alkylating reagents. In addition, a series of titanium imido complexes were synthesized, and no decomposition of the  $[N_2P_2]$  ligand was observed. The reactivity of **14–16** with small molecules will be the focus of future work.

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**Supporting Information Available:** Crystallographic information files (CIFs). This material is available free of charge via the Internet at http://pubs.acs.org.

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