Inorganic Chemistry

Synthesis and Reactivity of Low-Coordinate Titanium Synthons Supported by a Reduced Redox-Active Ligand

Kensha Marie Clark*^{,†}

Department of Chemistry, University of California, Irvine, California 92697

Supporting Information

ABSTRACT: To further explore the reactivity and redox capability of the bisarylimino acenaphthylene ligand (BIAN) in early transition metal complexes, the coordinatively unsaturated titanium synthons, $[(dpp-BAAN)Ti(R)_2]$ ($[dpp-BAAN]^{2^-} = N,N'$ -bis(2,6-diisopropylphenylamido)acenaphthylene and $R = O^tBu$ (2) or $CH_2C(CH_3)_3$ (3)), in which the BAAN ligand is reduced by two electrons, were isolated in good yields via sterically induced radical elimination reactions. Addition of *p*-tolyl azide to complex 3 initiated reductive elimination of the neopentyl ligands to generate a putative imido species. The imido species was trapped by a second oxidative addition of chloride ligands to yield the titanium imido complex, $[(dpp-BIAN)Ti[=N(4-C_6H_4Me)]Cl_2$ (4). These reactions demonstrate that the BAAN ligand can provide redox equivalents for enhanced reactivity that includes oxidative addition and reductive elimination at d^0 metal centers.



Bis-arylimino acenaphthylenes (BIANs), as a class of α -diimine ligands, have rapidly gained increased attention because of their easily tunable steric and electronic properties.¹ These ligands, which are stable in multiple oxidation states (Scheme 1), 2 have the ability to act as electron reservoirs by facilitating the transfer of electrons to and from metal centers.³ The result of strong mixing between ligand frontier $p(\pi)$ and metal orbitals, this noninnocent behavior makes BIANs particularly attractive for a variety of applications, including catalysis,⁴ whereby the electronic flexibility of the ligand can enable unusual reactivity at metal centers. The use of such ligands in low-coordinate early transition metal synthons is particularly appealing, as the combination would create a juncture between the inherent reactivity of coordinatively unsaturated d^0 complexes⁵ and the availability of redox equivalents that can be redistributed within the complex.⁶ Synthetic routes that afford transition-metal complexes featuring reduced redox-active ligands often require the independent reduction of the ligand prior to metalation.⁷ This process can be arduous and yield limiting, making a more direct, high-yielding path to such reduced complexes desirable.

The phenomenon of intramolecular electron transfer (IET) has been investigated for numerous main group and lanthanide metal complexes supported by various α -diimine ligands, including BIAN ligands.⁸ Complexes supported by this ligand have been found to be particularly susceptible to ligand reduction.^{9,10} These ligand-mediated reductive events are commonly induced thermally, by irradiation into the charge-transfer band,¹⁰ or by using the combination of a sterically encumbering redox-active ligand and bulky nucleophilic ligands.³ Considering the noninnocence observed in early transition metal BIAN complexes,¹¹ it seemed feasible that similar reductive paths could be accessed at d^0 metal centers.



Choosing the steric approach, there was a desire to determine if reduction by bulky nucleophilic ligands could be induced at a Ti⁴⁺ metal center equipped with the sterically encumbering dpp-BIAN ligand (where dpp-BIAN = N,N'-bis(2,6-diisopropylphenylimino)acenaphthylene) to generate low-coordinate dpp-BAAN-titanium complexes. Furthermore, if these complexes could be isolated, demonstration of enhanced reactivity at titanium, facilitated by ligand-supplied redox equivalents, would be paramount in illustrating the utility of the BIAN ligand. Herein, the results of these efforts are reported.

RESULTS AND DISCUSSION

Initially, complex (dpp-BIAN)TiCl₄ (1), which can be isolated quantitatively from TiCl₄ and dpp-BIAN, was treated with 4 equiv of the bulky base, potassium *tert*-butoxide in benzene (Scheme 2). This reaction yielded the brick red colored product, (dpp-BAAN)Ti(O^tBu)₂ (2), in 77% yield. The composition of **2** was confirmed by elemental analysis and NMR spectroscopy.

Single crystals of **2** were precipitated from a concentrated solution in pentane at -35 °C; however, the high solubility of these crystals in Paratone oil used for protection resulted in weak data that was sufficient only for establishing the connectivity of the tetrahedral complex (Figure 1). From the connectivity, it becomes apparent that the bulky alkoxide ligands can enforce approximate C_s symmetry around the titanium metal center, an arrangement that is confirmed by NMR spectroscopy. Notably, there is a loss of symmetry observed for the ¹H NMR resonances of the ligand

Received: February 23, 2016

Scheme 1. Reversible 2 e⁻ Reduction of the BIAN Ligand



Scheme 2. Syntheses of Complexes 2 and 3



Figure 1. Structural depiction of **2** on the basis of connectivity from X-ray diffraction data.

diisopropylphenyl substituents in benzene- d_6 , whereby four isopropyl methyl peaks at 1.01, 1.21, 1.39, and 1.63 ppm, as well as two isopropyl methine peaks at 3.21 and 4.09 ppm, are visible (Figure SI1). These peaks are indicative of hindered rotation about the ligand N–C_{aryl} bond. The sharp ¹H NMR signals and the connectivity provide support that the ligand has been reduced to the closed-shell, dianionic BAAN form.

In an attempt to better understand the formation of **2**, the reaction was performed in benzene- d_6 solution, and the reaction volatiles were analyzed by ¹H and ¹³C NMR for byproducts. Two ¹³C signals at 31.0 and 68.1 ppm confirm the formation of *tert*-butanol (Figure SI2); however, the ¹H NMR experiment revealed only one proton resonance at 1.05 ppm consistent with *tert*-butanol (Figure SI3). The absence of the hydroxyl proton resonance suggests that the O^tBu⁻ radical was generated in the reaction and was quenched by H atom abstraction from the solvent, benzene- d_6 .¹² The formation of ^tBuOD was confirmed by ²H NMR (Figure SI4).¹³

Expanding the reagent scope of this reaction to metal alkyls, complex 1 was treated with 4 equiv of the alkylating reagent neopentyl lithium to yield the diamagnetic complex, (dpp-BAAN)Ti(CH₂C(CH₃)₃)₂ (3) in 85% yield. Similar to 2, ¹H NMR spectroscopy confirms C_s local symmetry about the titanium metal center, which yields a loss of symmetry for the ¹H NMR resonances of the BIAN diisopropylphenyl substituents and the neopentyl ligands in benzene- d_6 . Furthermore, when these reactions were performed in benzene- d_6 , analysis of the reaction volatiles by ¹H and ²H NMR confirmed both the formation of neopentane and H atom abstraction from the solvent (Figure SI5), providing further support that radicals are eliminated in this process.

Single crystals of 3 suitable for X-ray diffraction studies were precipitated from pentane by slow evaporation. Selected metrical parameters are listed in Table 1. The molecular

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3 and 4

	3	4
Ti-N(1)	1.9389(14)	2.2676(14)
Ti-N(2)	1.9363(14)	2.2510(14)
Ti-N(3)		1.6987(15)
Ti-C(1)	2.4052(17)	
Ti-C(2)	2.4166(17)	
Ti-C(3)	2.098(2)	
Ti-C(4)	2.0834(18)	
C(1) - N(1)	1.393(2)	1.283(2)
C(2) - N(2)	1.389(2)	1.281(2)
C(1) - C(2)	1.401(2)	1.501(2)
N(1)—Ti– $N(2)$	93.27(6)	72.33(5)
N(1)— Ti – $C(3)$	115.32(8)	
N(1)— Ti – $C(4)$	116.98(7)	
N(2)—Ti–C(3)	112.57(7)	
N(2)— Ti – $C(4)$	114.81(7)	
$Ti-N(3)-C_{aryl}$		165.32(13)

structure of 3 (Figure 2) provides further evidence of ligandenforced, local C_s symmetry at titanium in the apparent tetrahedral complex. Inspection of the bond angles in this complex, however, reveals significant deviations from an idealized tetrahedron. For example, the average N–Ti–C(3) and N–Ti–C(4) bond angles were found to be ~114° and ~116°, respectively, while the C(3)–Ti–C(4) angle is approximately 104°. Also, the N(1)–Ti–N(2) bite angle of the five-membered Ti–N–C–C–N chelate ring has widened to 93.27(6)° from ~70–80° observed in titanium BIAN¹⁴ and BIAN^{isq} complexes.^{11a} Diagnostic C(1)–N(1), C(2)–N(2), and C(1)–C(2) bond lengths of this chelate ring (1.393(2), 1.389(2), and 1.401(2) Å, respectively) unambiguously indicate that the ligand has been reduced to the BAAN form,² while the short average Ti–N bond length (~1.94 Å) confirms a Ti⁴⁺



Figure 2. Oak Ridge thermal ellipsoid plot (ORTEP) of 3, as determined by single-crystal X-ray diffraction studies. Thermal ellipsoids are shown at 50% probability. Isopropyl groups and hydrogen atoms have been omitted for clarity. (See the Supporting Information for more details.)

Scheme 3. Synthesis of $(dpp-BIAN)Ti[=N(4-C_6H_4Me)]Cl_2$ (4)



metal center.^{11a} Contracted Ti–C(1) and Ti–C(2) bond distances suggest that the ethylene bridge of the acenaphthyl backbone is π -bonded to the metal center in a prone, η^2 -coordination mode.¹⁵ This prone coordination is a likely contributor to the severe distortion of the N–Ti–C(3) and N–Ti–C(4) bond angles. From this assessment of the metrical parameters, **3** is best described as (*prone-* η^4 -dpp-BAAN)Ti(CH₂C(CH₃)₃)₂.

While the syntheses of 2 and 3 demonstrate ligand-enabled reactivity, they fail to illustrate whether the steric encumbrance provided by the dpp-BIAN ligand is necessary or if a bulky nucleophile alone is sufficient to induce the observed radical eliminations. With this in mind, preliminary experiments using a starting material analogous to 1, (dmp-BIAN)TiCl₄ (dmp = 3,5-dimethylphenyl), in which the BIAN ligand has reduced steric bulk, were also conducted.¹⁶ In these experiments, bulky

nucleophiles could only induce one radical elimination, confirming that there are certain steric requirements that the ligand must meet to enable this reactivity.

To probe the availability of reducing equivalents in the dpp-BAAN ligand, 3 was oxidized by *p*-tolyl azide, which generated 2,2,5,5-tetramethylhexane (bineopentyl), dinitrogen, and a paramagnetic species. Multiple attempts to isolate the paramagnetic species were unsuccessful; however, when this reaction mixture was treated with the oxidant, PhICl₂, the titanium-imdo complex, (dpp-BIAN)TiCl₂[=N(4-C₆H₄Me)] (4), was isolated in 58% yield (Scheme 3). This result strongly suggests that the oxidation of 3 by the azide putatively produced an imido species and initiated the reductive elimination of the neopentyl ligands. The formation of a paramagnetic species in these reactions, likely a bridged imido, is a strong indicator that electronic delocalization or charge redistribution between the metal and the BAAN ligand is occurring.¹⁶ These coupled events regenerated the twoelectron-reduced dpp-BAAN ligand, making reducing equivalents available for the subsequent oxidation by PhICl₂. It is noteworthy that **2** is inert to oxidation by *p*-tolyl azide, which suggests that the oxidative addition of azide illustrated in Scheme 3 requires reductive elimination rather than a radical elimination pathway to proceed. Namely, the elimination of di*t*-butyl peroxide from **2** is thermodynamically unfavorable, and thus, oxidative addition to **2** is precluded. While it is feasible that this inertness can be attributed to π -donation from the *t*butoxy ligands, which may raise the barrier for binding of *p*tolyl azide, oxidative addition of this azide to form **4** occurs rapidly with an analogous complex containing less bulky, π donating chloride ligands.¹⁶

It was expected that protonolysis of 3 by 1 equiv of *p*-toluidine would yield the identical putative imido species (Scheme 3), and indeed, this reaction also generated a paramagnetic species, which upon oxidation by PhICl₂, afforded 4 in 43% yield. This reactivity provides further support for the formation of an imido species and the sterically induced regeneration of the dpp-BAAN ligand.

The molecular structure of 4 was probed using single-crystal X-ray diffraction (Figure 3). Much like analogous complexes,¹⁴ the local geometry about the titanium center is square pyramidal having approximate C_s symmetry, whereby the BIAN and chloride ligands comprise the basal plane of the molecule and the aryl-imido ligand occupies the apical position. Metrical parameters for the BIAN ligand confirm that the



Figure 3. ORTEP of **4**, as determined by single-crystal X-ray diffraction studies. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity. (See the Supporting Information for more details.)

ligand is in the neutral dpp-BIAN form. Specifically, the average BIAN C–N bond length was found to be 1.28 Å, which is indicative of a carbon–nitrogen double bond.^{2,14} The elongated BIAN C(1)—C(2) bond length of 1.501(2) Å, which is consistent with a carbon–carbon single bond, provides additional support for the ligand oxidation state. The very short Ti–N bond length (1.6987(15) Å) and the nearly linear Ti–N–C_{aryl} bond angle (165.32(13)°) of the imido ligand indicate that the imido is acting as a six electron donor to titanium.¹⁵ These parameters fully confirm that the species isolated from the aforementioned reactions contains the oxidized, neutral dpp-BIAN ligand coordinated to a Ti⁴⁺ metal center.

In summary, sterically induced reductive events were used to generate the coordinatively unsaturated titanium complexes supported by the reduced, dpp-BAAN ligand in good yields. Oxidation of complex 3 by p-tolylazide and PhICl₂ demonstrates that the BIAN ligand platform supports both oxidative addition and reductive elimination, which were directly coupled to yield 4. These reactions not only display the electronic utility of this ligand set, they also highlight that the electron-transfer mechanism that yields 2 and 3 is different from that which affords 4. Specifically, the reaction that forms 2 and 3 generates byproducts that suggest the elimination of respective alkoxide and alkyl radicals from the metal center. Contrarily, the oxidative addition of *p*-tolyl azide to sterically encumbered 3 induces extrusion of bineopentyl, but no reaction occurs in the case of similarly encumbered 2. Overall, sterically induced reduction can be used strategically as a more direct route to low-coordinate complexes supported by redox-active ligands, whereby the reduced ligand is available to provide redox equivalents at the metal center. Future studies will seek to understand the mechanistic details of the apparent radical and reductive eliminations, as well as nucleophile scope and the effects of steric modifications to the BIAN ligand.

EXPERIMENTAL SECTION

General Procedures. All complexes described herein are highly air- and moisture-sensitive, requiring that all manipulations be carried out under an inert atmosphere of argon or nitrogen gas using Schlenk, vacuum-line, and glovebox techniques. Hydrocarbon solvents were dried and deoxygenated by sparging with argon, followed by passage through Q5 and activated alumina columns. Similarly, ethereal solvents were sparged with argon and were passed through two activated alumina columns. A few drops of sodium benzophenone ketyl in tetrahydrofuran (THF) were used to test nonchlorinated solvents for effective oxygen and water removal. TiCl₄ (Aldrich), boric acid (Fisher), and sodium borohydride (Fluka) were used as received. The ligand N,N'-bis(2,6diisopropylphenylimino)acenaphthylene (dpp-BIAN),¹⁷ neopentyl lithium,¹⁸ and the metal complex (dpp-BIAN)TiCl₄ $(1)^{14}$ were prepared according to published procedures. Potassium tert-butoxide was prepared fresh prior to use from tert-butanol and excess potassium hydride in THF.

Physical Measurements. NMR spectra were collected on Bruker Avance 300, 500, and 600 MHz spectrometers in dry, degassed benzene- d_6 at 298 K, unless otherwise stated. ¹H NMR and ¹³C NMR spectra were both referenced to tetramethylsilane (TMS) using residual proteo impurities and the natural abundance ¹³C of the solvent, respectively. Chemical shifts were reported using the standard notation in parts-per-million. Bio-Rad Merlin and PerkinElmer Spectrum One Fourier transform infrared (FTIR) spectrophotometers were used to record infrared spectra as KBr pellets.

Synthesis of (dpp-BAAN)Ti(O^tBu)₂ (2). In a scintillation vial equipped with a stir bar, 100 mg of 1 (0.15 μ mol, 1 equiv) was suspended in 5 mL of benzene. The suspension was cooled to -35 °C, and a solution of KO^tBu (0.65 mmol, 4.5 equiv) in benzene (5 mL) was added. The mixture was allowed to warm to room temperature and was stirred an additional 1.5 h. The solvent then was removed from the mixture under reduced pressure, and the product was extracted from the residual solid in pentane. The mixture was then filtered, followed by the removal of the solvent under reduced pressure to yield 2 as a dark red solid in 77% yield. Anal. Calcd for C44H58N2O2Ti: C 76.06%, H 8.41%, N 4.03%. Found: C 75.85%, H 8.39%, N 3.86%. ¹H NMR (C_6D_6 500 MHz) δ /ppm: 0.82 (s, C(CH₃)₃, 9H), 1.01 (d, ${}^{3}J$ = 6.5 Hz, CH(CH₃)₂, 6H), 1.21 (s, C(CH₃)₃, 9H), 1.21 (d, ³J = 7.0 Hz, CH(CH₃)₂, 6H), 1.39 (d, ³J = 7.0 Hz, $CH(CH_3)_2$, 6H), 1.61 (d, ³J = 7.0 Hz, $CH(CH_3)_2$), 3.21 (m, $CH(CH_3)_2$, 2H), 4.09 (m, $CH(CH_3)_2$, 2H), 6.78 (dd, J = 7.0, 0.5 Hz, aryl-H, 2H), 6.90 (t, ³J = 7.0 Hz, aryl-H, 2H), 7.18 (dd, J = 8.5, 0.5 Hz aryl-H, 2H), 7.20 (dd, J = 8.0, 1.5 Hz, 1.5 Hz)aryl-H, 2H), 7.27 (t, ³I = 7.5 Hz, aryl-H, 2H), 7.35 (dd, I = 7.5, 1.5 Hz, aryl-H, 2H). ¹³C NMR (C_6D_{61} 125.7 MHz) $\delta/$ ppm: 25.1 (CH(CH₃)₂), 26.4(CH(CH₃)₂), 27.5 (C(CH₃)₃), 28.2 (C(CH₃)₃), 32.0 (CH(CH₃)₂), 32.8 (CH(CH₃)₂), 80.1 (C(CH₃)₃), 82.7 (C(CH₃)₃), 115.9 (aryl-C), 121.7 (aryl-C), 123.9 (aryl-C), 124.0 (aryl-C), 124.5 (aryl-C), 126.0 (aryl-C), 126.2 (aryl-C), 128.7 (aryl-C), 134.9 (aryl-C), 136.5 (aryl-C), 142.4 (aryl-C), 143.7 (aryl-C), 146.4 (aryl-C). IR (KBr) ν/cm^{-1} : 3043 (w), 2961 (s), 2917 (m), 2868 (m), 1583 (m), 1451 (s), 1382 (s), 1360 (s), 1256 (m), 1015 (s), 814 (s), 795 (s), 765 (m), 749 (m).

Synthesis of (dpp-BAAN)Ti(CH₂C(CH₃)₃)₂ (3). A suspension of 1 (1.0 g, 1.4 mmol, 1.0 equiv) in 20 mL of pentane was frozen in a liquid nitrogen cold well. Upon thawing, a solution of (CH₃)₃CH₂Li (488 mg, 6.2 mmol, 4.3 equiv) in 10 mL of pentane was added. The reaction mixture was allowed to warm to room temperature with stirring and was stirred an additional hour. The mixture was then filtered, and the filtrate was concentrated to ~4 mL under reduced pressure. The solution was cooled to -35 °C to yield crystals of 3 in 85% yield (820 mg). Several attempts to acquire composition data via elemental analysis and mass spectrometry of this highly air sensitive complex were unsuccessful. Sample ¹H and ¹³C spectra are reported in Figure SI8 and SI9. ¹H NMR (C₆D₆ 500 MHz) δ/ppm: 0.73 (s, C(CH₃)₃, 9H), 0.86 (s, C(CH₃)₃, 9H), 0.93 $(d, {}^{3}J = 6.0 \text{ Hz}, \text{ CH}(\text{CH}_{3})_{2}, 6\text{H}), 1.13 (d, {}^{3}J = 6.0 \text{ Hz},$ $CH(CH_3)_{2}$, 6H), 1.22 (s, $CH_2C(CH_3)_3$, 2H), 1.45 (d, ${}^{3}J = 5.5$ Hz, $CH(CH_3)_2$), 1.72 (d, ${}^{3}J = 5.5$ Hz, $CH(CH_3)_2$), 2.79 (s, $CH_2C(CH_3)_3$, 2H), 3.09 (m, $CH(CH_3)_2$, 2H), 4.82 (m, $CH(CH_3)_2$, 2H), 6.71 (d, ³J = 5.5 Hz, aryl-H, 2H), 6.85 (t, ³J = 6.0 Hz, aryl-H, 2H), 7.12 (t, ³J = 7.0 Hz, aryl-H, 2H), 7.19 (*dd*, ${}^{3}J$ = 6.5, 1.0 Hz, aryl-H, 2H), 7.26 (*t*, ${}^{3}J$ = 6.5 Hz, aryl–H, 2H), 7.40 (*dd*, ³*J* = 6.5, 1.0 Hz, aryl–H, 2H). ¹³C NMR $(CDCl_3, 125.7 \text{ MHz}) \delta/\text{ppm:} 24.5 (CH(CH_3)_2), 25.2$ (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 26.1 (CH(CH₃)₂), 28.5 $(CH(CH_3)_2)$, 29.5 $(CH(CH_3)_2)$, 33.9 $(C(CH_3)_3)$, 34.0 $(C-1)^{-1}$ (CH₃)₃), 37.0 (C(CH₃)₃), 38.5 (C(CH₃)₃), 109.5 (aryl-C), 114.0 (aryl-C), 122.3 (aryl-C), 124.5 (aryl-C), 125.3 (aryl-C), 126.4 (aryl-C), 126.6 (aryl-C), 128.3 (aryl-C), 134.2 (aryl-C), 136.0 (aryl-C), 142.7 (aryl-C), 142.8 (aryl-C), 147.2 (aryl-C). IR (KBr) ν/cm^{-1} : 3049 (w), 2945 (s), 2868

(m), 1456 (m), 1434 (m), 1360 (m), 1251 (w), 792 (m), 757 (m).

Syntheses of (dppBIAN)TiCl₂[=N(4-C₆H₄Me)] (4). *Ni*trene Addition to (dpp-BAAN)Ti(CH₂C(CH₃)₃)₂ (**3**). In 5 mL of benzene, 8.0 mg of *p*-tolyl azide (60 μ mol, 1 equiv) was added to 40 mg of 3 (60 μ mol, 1 equiv). The solution immediately changed in color from violet to dark red-brown. The solution was allowed to stir for an additional 5 min, and 16 mg of PhICl₂ (60 μ mol, 1 equiv) dissolved in 2 mL of benzene was added to the reaction mixture. The solution immediately turned a brownish-green color accompanied by the formation of a green precipitate. The reaction mixture was allowed to stir for an additional 5 min, after which the reaction volatiles were removed under reduced pressure. The residual solid was washed with pentane to afford **4** as a green solid (24 mg, 58% yield).

Protonolysis of (dpp-BAAN)Ti(CH₂C(CH₃)₃)₂. To a violet solution of 3 (52 μ mol, 1 equiv) dissolved in 5 mL of benzene was added *p*-toluidine (5.0 mg, 53 μ mol, 1 equiv). Upon addition, the reaction mixture immediately changed to redbrown in color. The reaction mixture was stirred for 5 min followed by the addition of 16 mg of $PhICl_2$ (60 μ mol, 1.1 equiv). The solution immediately turned a brownish-green color, and a green precipitate formed. The reaction mixture was stirred for an additional 5 min. The solvent was removed from the reaction mixture under reduced pressure, and the residual solid was washed with pentane. Complex 4 was isolated as a green solid in 43% yield (16 mg). Anal. Calcd for C43H49Cl2N3Ti: C 71.08%, H 6.80%, N 5.78%. Found: C 71.21%, H 6.42%, N 5.66%. ¹H NMR (CDCl₃, 500 MHz) $\delta/$ ppm: 0.85 ($d_1^{3}J = 5.5$ Hz, CH(CH₃)₂, 12H), 1.14 ($d_1^{3}J = 5.5$ Hz, CH(CH₃)₂, 12H), 2.20 (s, aryl-CH₃, 3H), 3.22 (m, $CH(CH_3)_2$, 4H), 6.54 (*d*, ³*J* = 6.0 Hz, aryl-H, 2H), 6.72 (*d*, ³*J* = 7.0 Hz, aryl-H, 2H), 6.76 (*d*, ³*J* = 7.0 Hz, aryl-H, 2H), 7.35 $(d, {}^{3}J = 7.0 \text{ Hz}, \text{ aryl}-\text{H}, 4\text{H}), 7.47 (t, {}^{3}J = 6.0, \text{ aryl}-\text{H}, 2\text{H}),$ 7.55 (t, ${}^{3}J$ = 7.0, aryl-H, 2H), 8.13 (d, ${}^{3}J$ = 7.0, aryl-H, 2H). ¹³C NMR (CDCl₃, 125.7 MHz) δ /ppm: 23.8 (CH(CH₃)₂), 24.4 (CH(CH₃)₂, 28.6 (aryl-CH₃), 29.5 (CH(CH₃)₂), 122.4 (aryl-C), 123.3 (aryl-C), 123.4 (aryl-C), 124.6 (aryl-C), 125.9 (aryl-C), 126.8 (aryl-C), 127.8 (aryl-C), 128.3 (aryl-C), 128.9 (aryl-C), 131.1 (aryl-C), 131.4 (aryl-C), 132.6 (aryl-C), 138.8 (aryl-C), 145.4 (aryl-C), 169.3 (aryl-C). IR (KBr) ν/cm^{-1} : 3054(w), 2967 (s), 2928 (m), 2868 (w), 1621(s), 1580 (s), 1489(s), 1382(m), 1182 (w), 1100(m), 1086(m), 1053(m), 1034(w), 812(s), 795 (s), 779(s), 754(s), 491(w).

General Details of X-ray Data Collection and Reduction. Single-crystal X-ray diffraction studies of 3 and 4 were carried out at 200(2) K and 100(2) K, respectively, following previously described protocols.¹⁹ For complex 3, the crystal-to-detector distance was 30 mm and the exposure time was 5 s per frame using a scan width of 0.75° . The crystal-todetector distance was 60 mm and the exposure time was 1 s per frame using a scan width of 0.5° in the case of 4. Data collection was 99.9% and 100% complete to 25.00° in θ , for 3 and 4, respectively. All nonhydrogen atoms in both complexes were refined anisotropically by full-matrix least-squares (SHELXL-2014). Using a riding model, all hydrogen atoms were placed, and their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table 2.

Table 2. Crystallographic Data for 3 and 4

	3	4
empirical formula	C46H62N2Ti	$C_{43}H_{47}Cl_2N_3Ti$
formula weight	690.87	724.63
crystal system	triclinic	tetragonal
space group	P-1	$P4_2/n$
a/Å	11.4606(12)	29.0005(11)
b/Å	13.0568(12)	29.0005(11)
c/Å	14.1283(15)	9.0398(4)
α/deg	93.342(4)	90
β /deg	96.771(4)	90
γ/deg	14.1283(15)	90
$V/\text{\AA}^3$	2051.1(4)	7602.7(7)
Z	2	8
refl. collected	47 580	55 095
indep. reflec (R_{int})	7513 (0.0506)	6999 (0.0579)
data/restraints/parameters	7513/36/487	6999/0/451
goodness-of-fit on F ²	1.015	1.031
R1 $(I \ge 2\sigma_I)$	0.0398	0.0324
wR2 (all data)	0.1085	0.0759

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00404.

NMR spectra

(PDF)

X-ray crystallographic data for C₄₆H₆₂N₂Ti (CIF)

(CIF)

X-ray crystallographic data for $C_{43}H_{47}Cl_2N_3Ti$ (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: kmclark@uci.edu.

Present Address

[†]Chevron Phillips Chemical Company, LP, Building 94-E, PRC, Highway 60 and 123, Bartlesville, OK 74004.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

K. M. C. thanks Prof. Alan F. Heyduk (UCI) for support through grants from the NSF (NSF CAREER Grant CHE-0645685) and Prof. Daniel J. Mindiola (UPenn) for introducing this ligand reactivity. K. M. C. also thanks Dr. Curtis Moore (UCSD) for the crystallographic data.

REFERENCES

(1) Hill, N. J.; Vargas-Baca, L.; Cowley, A. H. Dalton Trans. 2009, 240.

(2) Fedushkin, I. L.; Skatova, A. A.; Chudakova, V. A.; Fukin, G. K. Angew. Chem., Int. Ed. 2003, 42, 3294.

(3) Vasudevan, K.; Cowley, A. H. Chem. Commun. 2007, 3464.

(4) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. J. Am. Chem. Soc. **2000**, 122, 6686.

(5) Mindiola, D. J. Acc. Chem. Res. 2006, 39, 813.

(6) Heyduk, A. F.; Zarkesh, R. A.; Nguyen, A. I. Inorg. Chem. 2011, 50, 9849.

(7) (a) Fedushkin, I. L.; Makarov, V. M.; Sokolov, V. G.; Fukin, G. K.; Maslov, M. O.; Ketkov, S. Y. *Russ. Chem. Bull.* **2014**, *63*, 870–882.

(b) Anga, S.; Naktode, K.; Adimulam, H.; Panda, T. K. Dalton Trans.
2014, 43, 14876. (c) Nguyen, A. I.; Blackmore, K. J.; Carter, S. M.; Zarkesh, R. A.; Heyduk, A. F. J. Am. Chem. Soc. 2009, 131, 3307.
(d) Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. Inorg. Chem. 2005, 44, 5559.

(8) (a) Ren, W.; Zi, G.; Walter, M. D. Organometallics 2012, 31, 672.
(b) Walter, M. D.; Berg, D. J.; Andersen, R. A. Organometallics 2007, 26, 2296. (c) Schelter, E. J.; Wu, R.; Scott, B. L.; Thompson, J. D.; Cantat, T.; John, K. D.; Batista, E. R.; Morris, D. E.; Kiplinger, J. L. Inorg. Chem. 2010, 49, 924. (d) Bailey, P. J.; Dick, C. M.; Fabre, S.; Parsons, S.; Yellowlees, L. J. Dalton Trans. 2006, 1602. (e) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Parsons, S.; Yellowlees, L. J. Chem. Commun. 2005, 4563. (f) Fedushkin, I. L.; Maslova, O. V.; Baranov, E. V.; Shavyrin, A. S. Inorg. Chem. 2009, 48, 2355. (g) Fedushkin, I. L.; Maslova, O. V.; Morozov, A. G.; Dechert, S.; Demeshko, S.; Meyer, F. Angew. Chem., Int. Ed. 2012, 51, 10584.

(9) (a) Jastrzebski, J.T.B.H; Klerks, J. M.; van Koten, G.; Vrieze, K. J. Organomet. Chem. 1981, 210, C49. (b) Klerks, J. M.; Stufkens, D. J.; van Koten, G.; Vrieze, K. J. Organomet. Chem. 1979, 181, 271.

(10) Kaim, W. Acc. Chem. Res. 1985, 18, 160.

(11) (a) Clark, K. M.; Bendix, J.; Heyduk, A. F.; Ziller, J. W. Inorg. Chem. 2012, 51, 7457. (b) Fedushkin, I. L.; Makarov, V. M.; Sokolov, V. G.; Fukin, G. K. Dalton Trans. 2009, 38, 8047. (c) Bendix, J.; Clark, K. M. Angew. Chem., Int. Ed. 2016, 55, 2748.

(12) Brook, J. H. T.; Snedden, W. Tetrahedron 1964, 20, 1043.

(13) The reaction was executed in toluene-d₈ to facilitate the separation of the volatiles from the deuterated solvent. The volatiles were dissolved in C_6H_6 for ²H NMR experiments.

(14) Clark, K. M.; Heyduk, A. F.; Ziller, J. W. Inorg. Chem. 2010, 49, 2222.

(15) Nakamura, A.; Mashima, K. J. Organomet. Chem. 2001, 621, 224.
(16) Clark, K. M. University of California, Irvine, CA. Unpublished work, 2010.

(17) Paulovicova, A.; El-Ayaan, U.; Shibayama, K.; Morita, T.; Fukuda, Y. *Eur. J. Inorg. Chem.* **2001**, 2001, 2641.

(18) Shrock, R. R.; Fellmann, J. D. J. Am. Chem. Soc. 1978, 100, 3359.
(19) Nelson, K.; DiPasquale, A. G.; Rheingold, A. L.; Daniels, M. C.; Miller, J. S. Inorg. Chem. 2008, 47, 7768.