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Steric Control of Coordination Geometry in Titanium-Imido Complexes of *N,N′*-bis(arylimino)acenaphthylene Ligands

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Titanium complexes of *N,N′*-bis(arylimino)acenaphthylene (BIAN) α-diimine ligands with varied steric profiles have been prepared. Coordination of the BIAN ligand derivatives to $TiCl_4$ afforded the adducts (dpp-BIAN)$TiCl_4$ (**1a**), (tmp-BIAN)-$TiCl_4$ (**1b**), and (dmp-BIAN)$TiCl_4$ (**1c**) (dpp = 2,6-diisopropylphenyl; tmp = 2,4,6-trimethylphenyl; dmp = 3,5-dimethylphenyl). While the least sterically crowded complex **1c** is robust toward loss of the diimine ligand, the dpp-BIAN and tmp-BIAN ligands are readily displaced by pyridine from the more crowded derivatives **1a** and **1b**, respectively. The crowded profiles engendered by the tmp-BIAN and dpp-BIAN ligands result in the formation of five-coordinate titanium-imide complexes, (dpp-BIAN)$TiCl_2$(=N^{t}Bu) (**2a**) and (tmp-BIAN)$TiCl_2$(=N^{t}Bu) (**2b**), upon addition of ^{t}BuNH$_2$ to solutions of **1a** or **1b**, respectively. Single-crystal X-ray diffraction studies reveal a square pyramidal coordination environment with an apical imide ligand and a short Ti−N distance, consistent with a Ti−N triple bond. Conversely, the less crowded dmp-BIAN ligand affords a six-coordinate titanium imido complex, (dmp-BIAN)$TiCl_2$(=N^{t}Bu)($NH_2{}^t$Bu) (**4**), upon treatment of **1c** with ^{t}BuNH$_2$. Surprisingly the imido ligand is coordinated trans to one arm of the diimine. This six coordinate species is fluxional in solution, and exchange and variable temperature ^{1}H NMR experiments suggest dissociation of the coordinated ^{t}BuNH$_2$ ligand to generate a five-coordinate imido intermediate analogous to **2a** and **2b**.

Introduction

Transition metal complexes with terminal imido ligands have attracted interest owing to their varied reactivity.[1−3] In mid- and late transition metal complexes, terminal imido ligands can access many reactivity pathways, including H-atom abstraction, [2 + 2] cycloaddition, and insertion.[4−28] There are also many transition metal complexes in which a terminal imido ligand acts as a robust spectator ligand while reactions such as metathesis occur at a more reactive alkylidene or alkylidyne functionality within the complex.[14,29−33] In the case of the early transition metal imido complexes, especially of the Group IV

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metals titanium and zirconium, the imido ligand dominates the reactivity of the complex. Facile room-temperature C−H bond activation of hydrocarbons by $(silox)_2Ti(=NSi^tBu_3)$ (silox = $^tBu_3SiO^-$) and $Cp^*_2Ti(=N^tBu)$ ($Cp^* = C_5Me_5^-$) intermediates highlight the enhanced reactivity of the $M^{IV}=NR$ fragment (M = Ti or Zr) deriving from strong polarization of the metal−nitrogen multiple bond.[34−38] Examples of the reactivity of Group IV imidos with unsaturated substrates are legion, including stoichiometric and catalytic imine metathesis, and 1,2-addition reactions like hydroamination.[38−73] Manipulation of the coordination geometry and steric and electronic environment of the metal complex has been shown to play a pivotal role in controlling the selectivity of these reactions.[41,53,74−79]

Owing to the dependence of imido reactivity on the sterics and electronics of auxiliary ligand platforms, the synthesis and structural characterization of Group IV imido complexes with new supporting ligands continues to be of interest. The synthon, $Ti^{IV}(=N^tBu)Cl_2(py)_n$ (n = 2, 3), has been used to prepare a variety of new titanium imido complexes, including anilido derivatives and complexes with multidentate nitrogen donor ligands such as amidinates,[80] pyridylamines,[81] and tetraazamacrocycles.[82] Formally reduced, titanium(II) complexes react with azobenzene, resulting in the transfer of a nitrene and formation of $Ti^{IV}=NPh$ complexes with simple alkoxide or halide ligands.[38,69] More recently, one-electron oxidation and deprotonation of a titanium(III) diamido complex have been employed to prepare an imidotitanium(IV) complex supported β-diketiminate ligand.[48,83−85] An attractive feature of the latter system is that the steric profile of β-diketiminate ligand can be easily modified; however, the ligand backbone itself is prone to nucleophilic attack and often reacts with metal−ligand multiple-bond functionalities.[84−86]

This paper reports recent efforts to support the titanium imido functionality with α-diimine ligands containing an acenaphthylene backbone. The coordination chemistry of *N*,*N*′-bis(arylimino)acenaphthylene (BIAN) ligands with mid- and late transition metals is well established, and the ligand is noted for its stability, particularly in supporting electrophilic catalysts for olefin polymerization.[87−96] Moreover, the ligand is prepared by a condensation reaction from acenaphthenequinone and virtually any aniline derivative, so the steric profile of the ligand can be tailored to control the metal coordination environment. Three different BIAN derivatives, shown in Chart 1, were used herein to prepare

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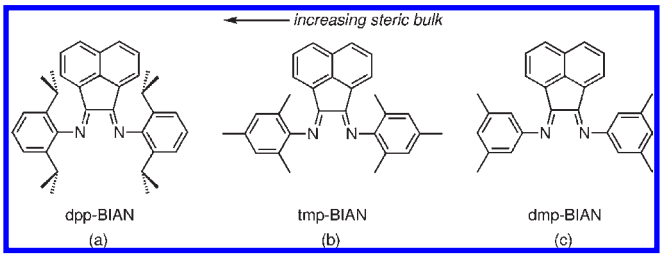
Chart 1



new titanium imido complexes. Whereas BIAN ligands with sterically demanding substituents afford five-coordinate complexes with apical imido ligands, the BIAN ligand with the smallest aryl substituent affords an unusual six-coordinate complex with an imido ligand cis to a primary amine ligand. This paper reports the synthesis and characterization in solution and the solid state of titanium imido complexes supported by chelating BIAN ligands.

Experimental Section

General Procedures. The complexes described below are air- and moisture-sensitive necessitating that manipulations be carried out under an inert atmosphere of argon or nitrogen gas using standard Schlenk, vacuum-line, and glovebox techniques. Hydrocarbon solvents were sparged with argon, then deoxygenated and dried by passage through Q5 and activated alumina columns, respectively. Ethereal and halogenated solvents were sparged with argon and then dried by passage through two activated alumina columns. To test for effective oxygen and water removal, non-chlorinated solvents were treated with a few drops of a purple solution of sodium benzophenone ketyl in tetrahydrofuran (THF). The metal salt $TiCl_4$ was purchased from Alfa-Aesar and used as received. $^tBuNH_2$ and pyridine (Aldrich) were dried by refluxing over CaH_2 and distilling under argon. The ligands *N*,*N*′-bis(2,6-diisopropylphenylimino)acenaphthylene (dpp-BIAN), *N*,*N*′-bis(2,4,6-trimethylphenylimino)-acenaphthylene (tmp-BIAN), and *N*,*N*′-bis(3,5-dimethylphenylimino)acenaphthylene (dmp-BIAN) were prepared according to published procedures.[95,97,98]

Physical Measurements. NMR spectra were collected on Bruker Avance 500 MHz spectrometers in dry, degassed chloroform-d_1 at 298 K. ^{1}H NMR spectra were referenced to TMS using the residual proteo impurities of the solvent; ^{13}C NMR spectra were referenced to TMS using the natural abundance ^{13}C impurities of the solvent. All chemical shifts are reported using the standard notation in parts-per-million; positive chemical shifts are to a higher frequency from the given reference. Infrared spectra were recorded as KBr pellets with a PerkinElmer Spectrum One FTIR spectrophotometer.

Synthesis of (dpp-BIAN)$TiCl_4$ (1a). In a typical preparation, 5.0 g of dpp-BIAN (10.0 mmol, 1 equiv) was added to 75 mL of CH_2Cl_2 and frozen in a liquid nitrogen cold well. Upon thawing the mixture, neat $TiCl_4$ (1.9 g, 10.0 mmol, 1 equiv) was added, and the mixture was allowed to warm slowly to 25 °C with constant stirring. After 1 h, the solvent was removed under reduced pressure, and the red-orange residue was washed several times with pentane to afford 6.19 g of pure **1a** (90% yield). Anal. Calcd for $C_{36}H_{40}N_2Cl_4Ti$: C 62.63%, H 5.86%, N 4.06%. Found: C 62.89%, H 6.21%, N 3.86%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 0.81 (*d*, ^3J = 6.8 Hz, $CH(CH_3)_2$, 12H), 1.43 (*d*, ^3J = 6.6 Hz, $CH(CH_3)_2$, 12H), 3.90 (*m*, $CH(CH_3)_2$, 4H), 6.49 (*d*, ^3J = 7.4 Hz, aryl−H, 2H), 7.43 (*d*, ^3J = 7.7 Hz, aryl−H, 4H), 7.53 (*t*, ^3J = 6.5, aryl−H, 4H), 8.12 (*d*, ^3J = 8.3, aryl−H, 2H). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ/ppm: 25.11 ($CH(CH_3)_2$), 25.12 ($CH(CH_3)_2$, 29.3 ($CH(CH_3)_2$), 125. Seven (aryl−C), 126.0 (aryl−C), 127.8 (aryl−C), 128.7 (aryl−C), 129.1 (aryl−C), 130.9 (aryl−C), 132.9 (aryl−C), 140.4 (aryl−C), 145. One (aryl−C), 170.8 (aryl−C). IR (KBr) ν/cm^{-1}: 3061(w), 2964 (s), 1615(s), 1579 (s), 1290 (m), 1179 (m), 936 (m br), 780 (m).

Synthesis of (tmp-BIAN)$TiCl_4$ (1b). Using the same conditions reported for **1a**, tmp-BIAN derivative **1b** was isolated as a brick-red solid in 98% yield from 5.0 g of tmp-BIAN (8.2 mmol) and 1.7 g of $TiCl_4$ (9.0 mmol). Anal. Calcd for $C_{30}H_{28}N_2Cl_4Ti \cdot 1/2CH_2Cl_2$: C 56.47%, H 4.51%, N 4.32%. Found: C 56.83%, H 4.77%, N 4.38%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 2.42 (*s*, *p*-CH_3, 6H), 2.52 (*s*, *o*-CH_3, 12H), 6.12 (*d*, ^3J = 7.3 Hz, aryl−H, 2H), 7.09 (*s*, aryl−H, 4H), 7.58 (*t*, ^3J = 7.5, aryl−H, 2H), 8.14 (*d*, ^3J = 8.3, aryl−H, 2H). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ/ppm: 14.1 (CH_3), 20.9 (CH_3), 126.0 (aryl−C), 126.2 (aryl−C), 129.4(aryl−C), 129.5 (aryl−C), 130.5 (aryl−C), 131.0, 132.6 (aryl−C), 138.0 (aryl−C), 145.0 (aryl−C), 146.7 (aryl−C), 169.5 (aryl−C). IR (KBr) ν/cm^{-1}: 2961 (s), 2917(s), 1619 (m), 1582 (s), 1436 (w), 1295 (s), 1198 (w), 854 (s), 833 (s), 778 (s).

Synthesis of (dmp-BIAN)$TiCl_4$ (1c). Using the same conditions reported for **1a**, dmp-BIAN derivative **1c** was isolated as an orange solid in 84% yield from 3.0 g of tmp-BIAN (6.2 mmol) and 1.3 g of $TiCl_4$ (6.8 mmol). Anal. Calcd for $C_{28}H_{24}N_2Cl_4Ti$: C 58.16%, H 4.18%, N 4.85%. Found: C 58.16%, H 4.24%, N 4.87%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 2.46 (*s*, *m*-CH_3, 12H), 6.82 (*d*, ^3J = 7.3 Hz, aryl−H, 2H), 7.16 (*s*, aryl−H, 2H), 7.22 (*s*, aryl−H, 4H), 7.57 (*t*, ^3J = 8.4, aryl−H, 2H), 8.13 (*d*, ^3J = 8.4, aryl−H, 2H). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ/ppm: 21.5 (CH_3), 118.3 (aryl−C), 125.2 (aryl−C), 126.7 (aryl−C), 128.9 (aryl−C), 130.1 (aryl−C), 131.1 (aryl−C), 132.4 (aryl−C), 139.9 (aryl−C), 145.7 (aryl−C), 150.1 (aryl−C), 167.9 (aryl−C). IR (KBr) ν/cm^{-1}: 2926(s), 1608 (m), 1298 (s), 848 (m), 830 (m), 777 (s), 669(m).

Synthesis of (dpp-BIAN)$TiCl_2$(=N^{t}Bu) (2a). In a typical experiment, 1.0 g of **1a** (1.5 mmol, 1 equiv) was added to 50 mL of CH_2Cl_2 and then frozen in a liquid nitrogen cold well. Upon thawing, $^tBuNH_2$ (318 mg, 1.47 mmol, 3.0 equiv) was added to the mixture portion-wise over 30 min. The reaction mixture was allowed to warm slowly to 25 °C with constant stirring, which was continued overnight. The reaction mixture was filtered, and the solvent was removed under reduced pressure to yield 970 mg of pure **2a** as an orange solid (71% yield). Anal. Calcd for $C_{40}H_{49}N_3Cl_2Ti$: C 69.57%, H 7.15%, N 6.08%. Found: C 69.84%, H 6.79%, N 5.60%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 0.80 (*d*, ^3J = 6.8 Hz, $CH(CH_3)_2$, 12H), 1.22 (*s*, $C(CH_3)_3$, 9H), 1.41 (*d*, ^3J = 6.6 Hz, $CH(CH_3)_2$, 12H), 3.40 (*m*, $CH(CH_3)_2$, 4H), 6.27 (*d*, ^3J = 7.3 Hz, aryl−H, 2H), 7.41 (*d*, ^3J = 7.8 Hz, aryl−H, 4H), 7.51 (*m*, aryl−H, 4H), 8.08 (*d*, ^3J = 8.2, aryl−H, 2H). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ/ppm: 24.0 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 30.5 ($C(CH_3)_3$), 73.4 ($C(CH_3)_3$), 123.5 (aryl−C), 124.9 (aryl−C), 127.2 (aryl−C), 128.2 (aryl−C), 128.4 (aryl−C), 128.7 (aryl−C), 132.2 (aryl−C), 135.4 (aryl−C), 138.9 (aryl−C), 169.7(aryl−C). IR (KBr) ν/cm^{-1}: 2806 (m), 1964 (s), 1622 (s), 1232 (s), 836 (s), 798 (m), 783 (s), 757 (s), 610 (w), 504 (m).

Synthesis of (tmp-BIAN)$TiCl_2$(=N^{t}Bu) (2b). Using the same conditions reported for the preparation of **2a**, tmp-BIAN derivative **2b** was isolated as a brick-red solid in 89% yield from 720 mg of $^tBuNH_2$ (9.8 mmol, 3 equiv) and 2.0 g of **1b** (3.2 mmol, 1 equiv). Anal. Calcd for $C_{34}H_{37}N_3Cl_2Ti \cdot 1/2CH_2Cl_2$: C 63.86%, H 5.90%, N 6.48%. Found: C 64.28%, H 6.55%, N 6.34%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 1.16 (*s*, $C(CH_3)_3$, 9H), 2.32 (*s*, *o*-C H_3, 12H), 2.42 (*s*, *p*-CH_3, 6H), 6.68 (*d*, ^3J = 7.0 Hz, aryl−H, 2H), 7.09 (*s*, aryl−H, 4H), 7.59 (*t*, ^3J = 7.4, aryl−H, 2H), 8.19 (*d*, ^3J = 8.3, aryl−H, 2H). ^{13}C NMR

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($CDCl_3$, 125.7 MHz) δ/ppm: 18.7 (aryl-CH_3), 21.2 (aryl-CH_3), 31.0 ($C(CH_3)_3$), 73.8 ($C(CH_3)_3$), 125.6 (aryl−C), 126.0 (aryl−C), 127.8 (aryl−C), 129.0 (aryl−C), 129.3 (aryl−C), 130.6 (aryl−C), 132.3 (aryl−C), 137.1 (aryl−C), 145.0 (aryl−C), 168.7 (aryl−C). IR (KBr) ν/cm^{-1}: 2967 (s), 2917 (s), 1624 (m), 1584 (s), 1470 (s), 1380 (m), 1223 (s), 1026 (m), 850(m), 829 (m), 775(s).

Synthesis of (dpp-BIAN)TiCl$_2$[=N(2,6-C$_6$H$_3$Me$_2$)] (3a). 2,6-Dimethylaniline (106 mg, 0.876 mmol, 1 equiv) was added dropwise to a stirred solution of **2a** (576 mg, 0.834 mmol, 1 equiv) in 20 mL of CH_2Cl_2. After 2 h the solvent was removed under reduced pressure. The residue was recrystallized by layering a CH_2Cl_2 solution with pentane for 250 mg of dark green crystalline **3a** (43% yield). Anal. Calcd for $C_{44}H_{49}N_3Cl_2Ti\cdot 1/4CH_2Cl_2$: C 69.94%, H 6.67%, N 5.53%. Found: C 71.0%, H 6.60%, N 5.78%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 0.88 (*d*, ^3J = 6.5 Hz, CH(CH_3)$_2$, 12H), 1.17 (*d*, ^3J = 6.5 Hz, CH(CH_3)$_2$, 12H), 2.46 (*s*, aryl−C H_3, 6H), 3.24 (*m*, C*H*-(CH_3)$_2$, 4H), 6.54 (*t*, ^3J = 7.4 Hz, aryl−H, 1H), 6.71 (*t*, ^3J = 9.0 Hz, aryl−H, 2H), 7.36 (*d*, ^3J = 8 Hz, aryl−H, 4H), 7.49 (*t*, ^3J = 8 Hz, aryl−H, 2H), 7.60 (*t*, ^3J = 7.5 Hz, aryl−H, 2H), 8.16 (*d*, ^3J = 8, aryl−H, 2H). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ/ppm: 19.4 (aryl-CH_3), 23.7 (CH(CH_3)$_2$, 24.4(CH(CH_3)$_2$, 29.6($CH(CH_3)_2$), 121.1 (aryl−C), 123.5 (aryl−C), 124.8 (aryl−C), 126.0 (aryl−C), 126.7 (aryl−C), 126.9 (aryl−C), 128.3 (aryl−C), 128.4 (aryl−C), 128.5 (aryl−C), 128.9 (aryl−C), 129.0 (aryl−C), 132.7 (aryl−C), 138.9 (aryl−C), 145.1 (aryl−C), 145.8 (aryl−C). IR (KBr) ν/cm^{-1}: 3061(w), 2961 (s), 2926 (m), 1622 (s), 1582 (s), 1565 (m), 1437 (m), 1300 (s), 800 (m), 785 (m), 758 (m).

Synthesis of (tmp-BIAN)TiCl$_2$[=N(2,6-C$_6$H$_3$Me$_2$)] (3b). Using the same conditions reported for the preparation of **3a**, tmp-BIAN derivative **3b** was isolated as a green solid in 21% yield from 31 mg of 2,6-dimethylaniline (0.25 mmol, 1.1 equiv) and 140 mg of **2b** (0.23 mmol, 1 equiv). Anal. Calcd for $C_{38}H_{37}N_3Cl_2Ti\cdot 1/4CH_2Cl_2$: C 67.99%, H 5.59%, N 6.22%. Found: C 67.93%, H 5.99%, N 6.25%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 2.12 (*s*, Ar−CH_3, 12H), 2.31(*s*, Ar−CH_3, 6H), 2.33 (*s*, Ar−CH_3, 6H), 6.43 (*t*, ^3J = 7.5 Hz, Ar-*H*, 1H), 6.60 (*d*, ^3J = 7.5 Hz, Ar-*H*, 2H), 6.62 (*d*, ^3J = 7.5 Hz, Ar-*H*, 2H), 6.95 (*s*, Ar-*H*, 4H), 7.48 (*t*, ^3J = 7.5 Hz, Ar-*H*, 2H), 8.05 (*d*, ^3J = 8.5 Hz, Ar-*H*, 2H). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ/ppm: 18.8 (aryl-CH_3), 19.8 (aryl-CH_3), 21.2 (aryl-CH_3), 121.8 (aryl-C), 125.8 (aryl-C), 126.9 (aryl-C), 128.1 (aryl-C), 128.3 (aryl-C), 129.0 (aryl-C), 129.5 (aryl-C), 130.0 (aryl-C), 131.1 (aryl-C), 132.7 (aryl-C), 133.4 (aryl-C), 137.3 (aryl-C), 145.5(aryl-C), 161.5-(aryl-C). IR (KBr) ν/cm^{-1}: 2953 (s), 2896 (s), 1613 (s), 1577 (s), 1473 (s), 1280 (m), 1094 (m), 1029 (m), 850 (m), 772 (m), 736 (m).

Synthesis of (dmp-BIAN)TiCl$_2$(=N^{t}Bu)(NH$_2$^{t}Bu) (4). A solution of 1.0 g of **1c** (1.7 mmol, 1 equiv) dissolved in 50 mL of CH_2Cl_2 was frozen in a liquid nitrogen cold well. Upon thawing, ^{t}BuNH$_2$ (760 mg, 10.4 mmol, 6 equiv) was added to the mixture in aliquots over 30 min. The reaction mixture was allowed to warm slowly to 25 °C with constant stirring, which was continued overnight. The reaction mixture was filtered, and the solvent was removed under reduced pressure to yield 710 mg of pure **3** as a golden solid (64% yield). Anal. Calcd for $C_{36}H_{44}N_4Cl_2Ti\cdot 1/4CH_2Cl_2$: C 64.72%, H 6.67%, N 8.33%. Found: C 65.10%, H 7.06%, N 8.36%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 0.64 (s, Ti=NC(CH_3)$_3$, 9H), 1.20 (s, Ti−NH$_2$-C(CH_3)$_3$, 9H), 2.37 (*s*, *m*-CH_3, 6H), 2.42 (*s*, *m*-CH_3, 6H), 2.82 (*s*, Ti−NH_2C(CH_3)$_3$, 2H), 6.65 (*d*, ^3J = 7.2 Hz, aryl−H, 1H), 6.66 (*d*, ^3J = 7.8 Hz, aryl−H, 1H), 6.99 (*s*, aryl−H, 2H), 7.00 (*s*, aryl−H, 1H), 7.06 (*s*, aryl−H, 1H), 7.35 (*s*, aryl−H, 2H), 7.37 (*t*, ^3J = 7.2, aryl−H, 1H), 7.40 (*t*, ^3J = 7.8, aryl−H, 1H), 7.91 (*d*, ^3J = 8.4, aryl−H, 1H), 7.96 (*d*, ^3J = 7.8, aryl−H, 1H). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ/ppm: 21.4 (aryl-CH_3), 30.1 (C(CH_3)$_3$), 31.1 (C(CH_3)$_3$), 51.4 (Ti−NH$_2$C(CH_3)$_3$), 70.4 (Ti=NC(CH_3)$_3$), 116.8 (aryl−C), 118.4 (aryl−C), 124.7 (aryl−C), 126.2 (aryl−C), 126.7 (aryl−C), 126.9 (aryl−C), 128.0 (aryl−C), 128.2 (aryl−C), 128.25 (aryl−C), 128.3 (aryl−C), 130.1 (aryl−C), 130.7 (aryl−C), 130.9 (aryl−C), 139.7 (aryl−C), 140.1 (aryl−C), 147.3 (aryl−C), 150.7 (aryl−C), 162.6 (aryl−C), 166.0 (aryl−C). IR (KBr) ν/cm^{-1}: 3283 (m), 3192 (m), 3107(w), 2960 (s), 1633 (s), 1591 (s), 1372 (m), 1247 (s), 1121 (s), 846 (s), 774 (s), 659 (s), 533 (m).

Synthesis of (dmp-BIAN)TiCl$_2$[=N(2,6-C$_6$H$_3$Me$_2$)](NH$_2$^{t}Bu) (5). 2,6-Dimethylaniline (97 mg, 0.81 mmol, 1.5 equiv) was added to a scintillation vial containing 400 mg of **4** (0.61 mmol, 1 equiv) in 20 mL of CH_2Cl_2. After 2.5 h at 25 °C the solvent was removed from the mixture under reduced pressure. The residual solid was redissolved in 20 mL of CH_2Cl_2, and an additional 97 mg of 2,6-dimethylaniline (0.81 mmol, 1.5 equiv) was added to the solution. After stirring overnight at 25 °C, the solvent was again removed from the mixture under reduced pressure. The residual solid was washed with pentane to afford 300 mg of **5**, as a yellow solid (71% yield). Anal. Calcd for $C_{40}H_{44}N_4Cl_2Ti\cdot 1/4CH_2Cl_2$: C 67.07%, H 6.22%, N 7.77%. Found: C 67.33%, H 6.13%, N 7.55%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ/ppm: 1.24 (s, Ti−NH$_2$C(CH_3)$_3$, 9H), 2.11 (s, *m*-CH_3, 6H), 2.42 (*s*, Ti=N-(C_6H_3(*m*-CH_3)$_2$), 6H), 2.55 (*s*, *m*-CH_3, 6H), 2.87 (*s*, Ti−NH_2-C(CH_3)$_3$, 2H), 6.42 (*t*, ^3J = 7.5, aryl-H, 1H), 6.56 (*d*, ^3J = 7.5 Hz, aryl−H, 2H), 6.62 (*s*, aryl−H, 1H), 6.85 (d, aryl-H, ^3J = 7.5 Hz, 1H), 7.05 (*s*, aryl−H, 1H), 7.08 (*s*, aryl−H, 2H), 7.13 (*d*, ^3J = 7.5 Hz, aryl−H, 1H), 7.17 (*s*, aryl−H, 2H), 7.43 (*t*, ^3J = 7.5, aryl−H, 1H), 7.45 (*t*, ^3J = 7.5, aryl−H, 1H), 7.96 (*d*, ^3J = 8.5, aryl−H, 1H), 8.00 (*d*, ^3J = 8.5, aryl−H, 1H). ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ/ppm: 20.0 (aryl-CH_3), 20.5 (aryl-CH_3), 21.0 (aryl-CH_3), 30.5 (C(CH_3)$_3$), 51.5 (Ti−NH$_2$C(CH_3)$_3$), 116.7 (aryl−C), 117.6 (aryl−C), 120.3 (aryl−C), 124.2 (aryl−C), 125.6 (aryl−C), 125.7 (aryl−C), 126.0 (aryl−C), 126.1 (aryl−C), 127.7 (aryl−C), 127.8 (aryl−C), 128.0 (aryl−C), 129.8 (aryl−C), 130.4 (aryl−C), 130.8 (aryl−C), 136.4 (aryl−C), 138.3 (aryl−C), 139.4 (aryl−C), 144.0 (aryl−C), 146.3 (aryl−C), 147.6 (aryl−C), 156.9 (aryl−C), 161.7 (aryl−C), 164.6 (aryl−C). IR (KBr) ν/cm^{-1}: 3302 (w), 3347 (w), 2956 (s), 2917(s), 1629 (s), 1585 (s), 1467 (s), 1371 (m), 1283 (s), 1207 (m), 1111(m), 845 (m), 773 (s), 661 (s).

VT NMR studies of 4. Variable-temperature ^{1}H NMR spectroscopy (600 MHz) was used to extract activation parameters for the fluxionality of **4** in both the presence and absence of added ^{t}BuNH$_2$. An NMR tube fitted with a J. Young Teflon valve was charged with 20 mg of **4**. The sample was dissolved in $CDCl_3$ and subjected to three freeze−pump−thaw cycles. ^{1}H NMR spectra were collected in the temperature range 328−380 K, allowing the sample to equilibrate for 5 min at each temperature. The shape and position of the two methyl resonances for the dmp-BIAN ligand were fitted using the Complete Band Shapes Method to acquire the rate constants for exchange at each temperature. Activation parameters were subsequently calculated using an Eyring plot over the temperature range.

General Details of X-ray Data Collection and Reduction. X-ray diffraction data were collected on a Bruker CCD platform diffractometer equipped with a CCD detector. Measurements were carried out at 163 K using Mo Kα (λ = 0.71073 Å) radiation, which was wavelength selected with a single-crystal graphite monochromator. The SMART program package was used to determine unit-cell parameters and for data collection. The raw frame data were processed using SAINT and SADABS to yield the reflection data files. Subsequent calculations were carried out using the SHELXTL program suite. Analytical scattering factors for neutral atoms were used throughout the analyses. Thermal ellipsoid plots were generated using ORTEP-3 for Windows. Diffraction data for **1b**, **2b**, **3b**, and **4** are shown in Table 1.

Results and Discussion

Synthesis and Characterization of (BIAN)TiCl$_4$ Complexes. Lewis acidic $TiCl_4$ readily coordinates neutral BIAN donor ligands to afford six-coordinate adduct complexes. The BIAN ligand derivatives that will be

Table 1. X-ray Diffraction Data-Collection and Refinement Parameters for [tmp-BIAN]$TiCl_4$ (**1b**), [tmp-BIAN]Ti(=N^{t}Bu)Cl_2 (**2b**), (tmp-BIAN)$TiCl_2$[=N(2,6-$C_6H_3Me_2$)] (**3b**), and [dmp-BIAN]Ti(=N^{t}Bu)Cl_2($NH_2{}^t$Bu) (**4**)

	1b·CH_2Cl_2	**2b**·$2CH_2Cl_2$	**3b**·$2CH_2Cl_2$	**4**·CH_2Cl_2
empirical formula	$C_{31}H_{30}Cl_6N_2Ti$	$C_{36}H_{41}Cl_6N_3Ti$	$C_{40}H_{41}Cl_6N_3Ti$	$C_{37}H_{46}Cl_4N_4Ti$
formula weight	691.17	776.32	824.36	736.48
crystal system	orthorhombic	monoclinic	monoclinic	triclinic
space group	$Pna2_1$	$P2_1$	Cc	$P\bar{1}$
a/Å	19.5926(16)	10.7937(14)	12.249(5)	12.1324(17)
b/Å	18.4456(15)	12.3268(16)	21.633(8)	13.1859(18)
c/Å	8.7253(7)	15.0167(19)	15.987(6)	13.2874(19)
α/deg	90	90	90	104.719(3)
β/deg	90	105.631(2)	110.581(5)	112.632(2)
γ/deg	90	90	90	92.344(3)
V/Å^3	3153.3(4)	1924.1(4)	3966(3)	1874.6(5)
Z	4	2	4	2
refl. collected	33904	11717	33004	16242
indep. refl. (R_{int})	7786 (0.0276)	7061 (0.0303)	8846 (0.0325)	6398 (0.0262)
$R1$ ($I \geq 2\sigma_I$)	0.0290	0.0557	0.0364	0.0588
w$R2$ (all data)	0.0788	0.1421	0.0958	0.1548

discussed here present substantially different steric profiles when coordinated to a metal center. As shown in Chart 1, the most crowded metal environment is expected for the dpp-BIAN ligand, which directs four *iso*-propyl substituents above and below the metal binding site. Conversely, dmp-BIAN should afford the least crowded metal environment since the methyl groups of the 3,5-dimethylphenyl substituents point away from the metal binding site. The reactions of dpp-BIAN, tmp-BIAN, and dmp-BIAN with $TiCl_4$ proceeded smoothly, forming the six coordinate adducts **1a**−**c** in high overall yields (**1a**, (dpp-BIAN)$TiCl_4$, 90%; **1b**, (tmp-BIAN)$TiCl_4$, 98%; **1c**, (dmp-BIAN)$TiCl_4$, 84%;). Reaction progress was indicated by darkening of the reaction solutions from the orange color of the free BIAN ligands to the dark red color of the titanium(IV) adducts. In the infrared spectrum, coordination of the BIAN ligands to titanium resulted in small but characteristic red-shifts in the C=N stretching frequencies (ca. 30 cm^{-1}). Similarly, coordination of the BIAN ligands to titanium induces diagnostic shifts in the ^{1}H NMR resonances of the acenaphthylene ring. Downfield shifts of ∼0.17 and ∼0.27 ppm were observed for the 3,3′ and 4,4′ resonances of the naphthyl moiety, respectively, while an upfield shift of 0.26 ppm was observed for the 5,5′ resonances. Additionally, the ^{1}H NMR resonances in the aryl imine functionalities each shifted downfield upon coordination to the titanium metal center.

Single crystal X-ray diffraction studies were used to probe the solid-state structure of **1b**. Layering CH_2Cl_2 solutions of **1b** with pentane resulted in the precipitation of deep red crystals suitable for X-ray diffraction studies. Figure 1 shows the molecular structure of the six-coordinate titanium complex and Table 2 highlights metrical data for the titanium coordination sphere. The titanium center of **1b** is best described as octahedral; however, there is significant distortion resulting from the small bite angle of the tmp-BIAN ligand (N(1)−Ti(1)−N(2) 73.53°). This small bite angle results in a strained five-membered chelate ring, as evidenced by N−C−C bond angles that are smaller in **1b** (∼118°) than in free BIAN ligands (∼133°).[95] Titanium-chloride bond lengths vary between 2.23 and 2.29 Å, with the shorter distances observed for chloride ligands located *trans* to the tmp-BIAN ligand. Long Ti−N bonds are consistent with the

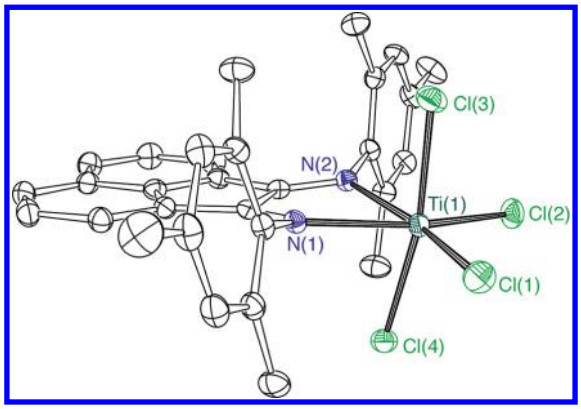


Figure 1. ORTEP for (tmp-BIAN)$TiCl_4$·CH_2Cl_2 (**1b**·CH_2Cl_2). Ellipsoids are drawn at 50% probability. Solvent and hydrogen atoms have been omitted for clarity.

tmp-BIAN ligand acting as a neutral diimine toward titanium. This is further supported by the observed N−C and C−C distances, which are normal for an acenaphthylenediimine.[91,95]

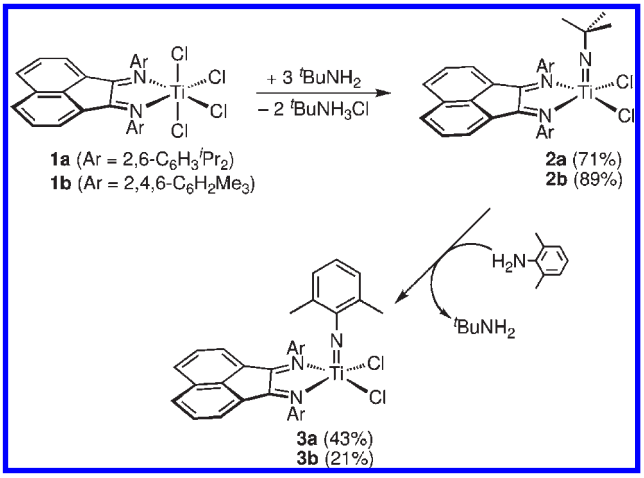
The addition of 2 equiv of pyridine to CH_2Cl_2 solutions of **1a** or **1b** results in loss of BIAN ligand and precipitation of the bis(pyridine) adduct, $TiCl_4(py)_2$. Similarly, the addition of dpp-BIAN or tmp-BIAN to $TiCl_4(py)_2$ did not result in the formation of **1a** or **1b**. In contrast, complex **1c**, with the smaller dmp-BIAN ligand, is stable in the presence of pyridine, and **1c** could be prepared by the addition of dmp-BIAN to $TiCl_4(py)_2$. Since the three BIAN ligands and pyridine all offer similar imine nitrogen donor atoms to the Lewis-acidic metal center, the displacement of dpp-BIAN and tmp-BIAN from **1a** and **1b**, respectively, suggests that steric crowding around the BIAN ligands overrides any stabilizing effect associated with a chelate effect. This idea is supported further by the stability of **1c** to pyridine. While the displacement of BIAN from **1a** and **1b** by pyridine is rapid and complete, all three complexes, **1a**−**c**, appear to be stable to weaker donor ligand such as Et_2O and THF.[97]

Synthesis and Characterization of Five-Coordinate Alkyl- and Aryl-Imido Complexes. Titanium complexes **1a** and **1b** with sterically demanding dpp-BIAN and tmp-BIAN ligands readily react with ^{t}BuNH_2 to afford five-coordinate titanium imido complexes. In a typical

Table 2. Selected Bond Distances and Angles for [tmp-BIAN]$TiCl_4$ (**1b**)

Bond Distances/Å			
Ti−Cl(1)	2.2280(6)	Ti−N(1)	2.2654(16)
Ti−Cl(2)	2.2430(6)	Ti−N(2)	2.2717(16)
Ti−Cl(3)	2.2875(6)		
Ti−Cl(4)	2.2986(6)		
Bond Angles/deg			
N(1)−Ti−Cl(1)	96.04(4)	N(1)−Ti−N(2)	73.53(2)
N(2)−Ti−Cl(1)	169.60(4)	Cl(1)−Ti−Cl(2)	103.59(2)
N(1)−Ti−Cl(2)	160.33(4)	Cl(1)−Ti−Cl(3)	90.91(2)
N(2)−Ti−Cl(2)	86.80(4)	Cl(2)−Ti−Cl(3)	90.91(2)
N(1)−Ti−Cl(3)	85.95(4)	Cl(1)−Ti−Cl(4)	93.20(2)
N(2)−Ti−Cl(3)	88.61(4)	Cl(2)−Ti−Cl(4)	94.18(2)
N(1)−Ti−Cl(4)	84.07(4)	Cl(3)−Ti−Cl(4)	169.55(2)
N(2)−Ti−Cl(4)	85.62(4)		

Scheme 1



experiment, cold CH_2Cl_2 solutions of **1a** or **1b** were treated portion-wise with 3 equiv of $^tBuNH_2$, resulting in an exothermic reaction and the precipitation of 2 equiv of $^tBuNH_3Cl$ as a white solid. From the resulting dark red solutions, the five-coordinate complexes (dpp-BIAN)$TiCl_2$(=N^{t}Bu) (**2a**) and (tmp-BIAN)$TiCl_2$(=N^{t}Bu) (**2b**), respectively, could be obtained in high yields (Scheme 1). Crude samples of **2a** and **2b** are always contaminated with some free BIAN ligand, which could be removed by recrystallization of the crude product from dichloromethane.

Alkyl-imido ligands coordinated to titanium(IV) typically are reactive toward imide exchange with anilines.[80,99] Despite a crowded coordination environment at titanium, complexes **2a** and **2b** react with the hindered aniline, 2,6-dimethylaniline, at room temperature to afford (dpp-BIAN)$TiCl_2$[=N(2,6-$C_6H_3Me_2$)] (**3a**) and (tmp-BIAN)$TiCl_2$[=N(2,6-$C_6H_3Me_2$)] (**3b**), respectively. Reaction yields for these imide metathesis reactions were lowered by competitive displacement of the BIAN ligand with $^tBuNH_2$, which is liberated during the reaction. Attempts to increase the overall yield of **3a** and **3b** by introducing the aniline as the anilinium chloride (and trap the $^tBuNH_2$ as $^tBuNH_3Cl$) resulted in lower yields of the desired aryl imido products and more free BIAN ligand.

The coordination environments about the titanium(IV) centers of **2b** and **3b** were elucidated by single crystal X-ray diffraction experiments. The molecular structure of **2b** is shown as a thermal ellipsoid plot in Figure 2a, and selected metrical parameters can be found in Table 3. The titanium center of **2b** is square pyramidal with approximate C_s symmetry. The apical position is occupied by the *tert*-butyl-imido ligand. The imido displays a short Ti−N bond length of 1.69 Å and a nearly linear Ti−N−C bond angle of 167°. These metrical parameters fall in the ranges normally assigned to Ti≡N triple bonds.[1] Simple molecular-orbital and symmetry arguments suggest that an apical imido ligand in a square pyramid can act as a six-electron donor ($\sigma^2 + \pi^4$) to a d^0 Ti^{IV} center to form a Ti≡NR triple bond.[3,100,101] The impact of this strong N→Ti π donation is noticeable in the bond lengths of the chloride ligands as well, which are elongated by nearly 0.1 Å relative to the equatorial chloride ligands of **1b**. Since five-coordinate **2b** should have less steric repulsion than six-coordinate **1b**, this elongation in Ti−Cl bond lengths can be ascribed to a decrease in the Cl→Ti π donation in **2b**. In contrast to the lengthening of the Ti−Cl bonds, the dpp-BIAN Ti−N bonds are slightly shorter than the tmp-BIAN Ti−N bonds of **1b**. Finally, the titanium center of **2b** is displaced from the basal plane of the square pyramid by 0.594 Å, resulting in an average angle of 104° between the apical and equatorial donor atoms.

The solid-state structure for aryl imido complex **3b** is analogous to that of *tert*-butyl imido complex **2b**. Dark green crystals suitable for X-ray diffraction provided the molecular structure shown in Figure 2b and the metrical data presented in Table 3. The titanium center in **3b** is square pyramidal with the aryl imido ligand occupying the apical position. As observed for **2b**, a short Ti−N bond distance (1.718(2) Å) and a nearly linear Ti−N−C bond angle (165.27(19)°) are consistent with significant Ti≡N triple bond character in **3b**. The aryl group of the imido ligand is rotated into the mirror plane of the approximately C_s-symmetric structure to minimize steric interactions with the methyl groups of the tmp-BIAN ligand. Other bond distances and angles are consistent with those observed for **2b**.

(99) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. J. *Polyhedron* **1995**, *14*, 2455.

(100) Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 7879.

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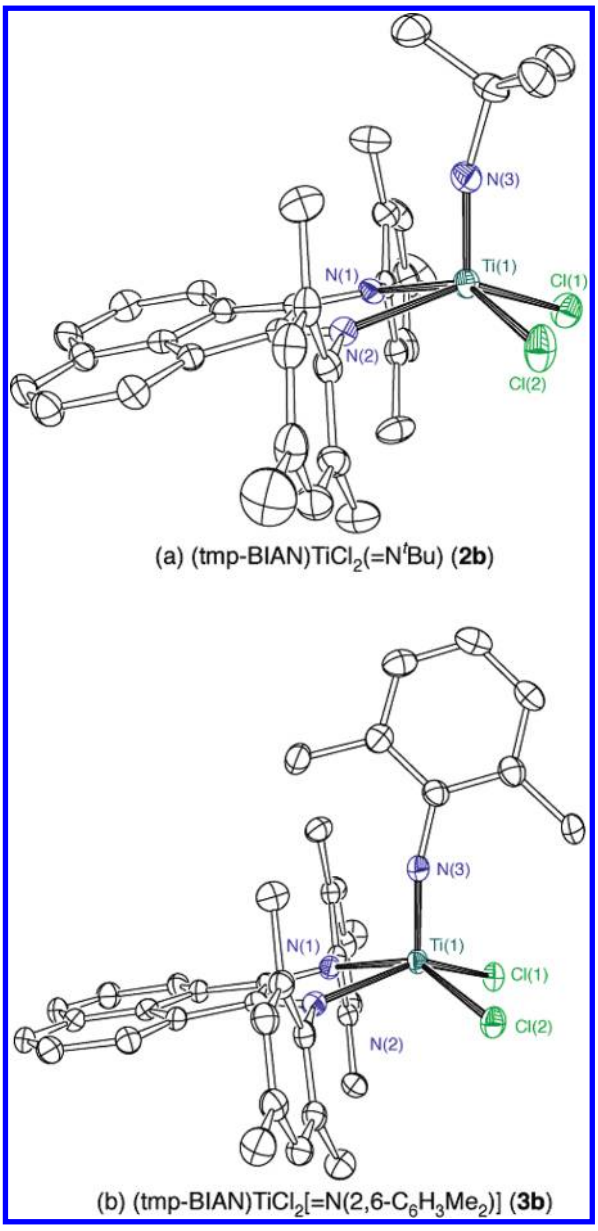


Figure 2. ORTEP of (a) (tmp-BIAN)$TiCl_2$(=N^{t}Bu)·$2CH_2Cl_2$ (**2b**·$2CH_2Cl_2$) and (b) (tmp-BIAN)$TiCl_2$[=N(2,6-$C_6H_3Me_2$)]·$2CH_2Cl_2$ (**3b**·$2CH_2Cl_2$) as determined by single crystal X-ray diffraction studies. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

NMR spectroscopic data for **2a,b** and **3a,b** are consistent with the observed solid-state X-ray structures. A singlet ^{1}H NMR resonance, attributable to the *tert*-butyl imido ligand of complexes **2a** and **2b**, was observed at 1.22 and 1.16 ppm, respectively. The ^{1}H and ^{13}C NMR signatures for the acenaphthylene backbone of **2a** and **2b** are consistent with C_s symmetric geometry. The *N*-aryl groups also appeared symmetric in solution at room temperature; notably, only one ^{1}H NMR resonance was observed for the *ortho*-methyl groups of the 2,4,6-trimethylphenyl groups of **2b**, indicating fast rotation about the N−C_{ipso} bond. Similarly, in the case of **2a**, only one methine resonance and two isopropyl methyl resonances (at 0.80 and 1.41 ppm) were observed. Variable temperature NMR studies of **2a,b** did not reveal significant changes to the ^{1}H NMR spectra upon cooling, suggesting that any fluxional behavior in the titanium coordination environment is significantly faster than the NMR time scale. Conversion of *tert*-butylimido derivatives **2a**−**b** to arylimido derivatives **3a**−**b** is readily observed in the ^{1}H NMR resonances for the ortho substituents of the dpp-BIAN and tmp-BIAN ligands. In complex **3b**, an upfield shift of 0.1 ppm is observed for the ortho-methyl resonances of the tmp-BIAN ligand. In the case of **3a**, the isopropyl methyl resonances shift closer together by ∼0.3 ppm. The methine resonance shifts slightly, from 3.37 ppm in **2a**, to 3.25 ppm in complex **3a**. This methine resonance also is broadened, indicating hindered rotation about the N−C_{ipso} bond as a result of increased steric constraints imposed by the 2,6-dimethylphenylimido ligand.

Six-Coordinate Imido Amine Complexes. In contrast to the reactions used to prepare **2a** and **2b**, complex **1c** reacts with ^{t}BuNH_2 to afford an octahedral imido-amine complex, (dmp-BIAN)$TiCl_2$(=N^{t}Bu)(NH_2^tBu) (**4**), as shown in Scheme 2. As discussed above, the dmp-BIAN ligand is expected to provide a more open coordination environment around the metal center since the methyl substituents of the *N*-aryl groups are oriented away from the metal-binding pocket of the diimine. Using the same reaction conditions employed for the preparation of **2a** and **2b** (i.e., 3 equiv of ^{t}BuNH_2), the conversion of **1c** to an imido complex was incomplete; however, the addition of a fourth equivalent of ^{t}BuNH_2 afforded the six coordinate complex, **4**, as the major product. Further increasing the quantity ^{t}BuNH_2 to 6 equiv produced high yields of spectroscopically pure **4**, without any contamination by free dmp-BIAN ligand.

The solid-state structure of **4** differs substantially from the structures of five-coordinate imido complexes **2b** and **3b**. Single-crystal X-ray diffraction studies were conducted on brown crystals of **4** grown by layering a saturated CH_2Cl_2 solution of **4** with heptane. The molecular structure of **4** is shown in Figure 3, and selected metrical parameters are given in Table 3. Crystals of **4** are triclinic with $P\bar{1}$ symmetry. The imido and amine ligands occupy cis positions of a six-coordinate titanium center. These two ligands were disordered so that the imido and amino ligands had to be modeled at 50% occupancy for each position (see Supporting Information). While reasonably accurate Ti−N (2.156(4) Å) and Ti═N (1.787(4) Å) bond distances could be obtained for amino and imido ligands, respectively, we could not observe asymmetry in the binding of the titanium center to the dmp-BIAN ligand. It is worth noting that the Ti═N bond distance observed in **4** is elongated by 0.19 Å relative to the titanium-imido distance observed for **2b**, consistent with the imido ligand being trans to the BIAN ligand in **4**. While the Ti−N−C bond angle for the imido ligand of **4** is still close to linear (179.1(4)°), the longer Ti═N bond length suggests an effective decrease in N→Ti π donation, though the imido group can still be considered an overall six-electron donor. The titanium coordination sphere is completed by two trans chloride ligands that bond at lengths of 2.4545(11) Å and 2.3734(11) Å. These halide distances are considerably longer than the distances observed for the trans chloride ligands in **1b** and are comparable to the equatorial chloride ligand distances observed in **2b**.

Table 3. Selected Bond Distances and Angles for [tmp-BIAN]Ti(=N^{t}Bu)Cl$_2$ (**2b**), (tmp-BIAN)TiCl$_2$[=N(2,6-C$_6$H$_3$Me$_2$)] (**3b**), and [dmp-BIAN]Ti(=N^{t}Bu)Cl$_2$(NH$_2$^{t}Bu) (**4**)

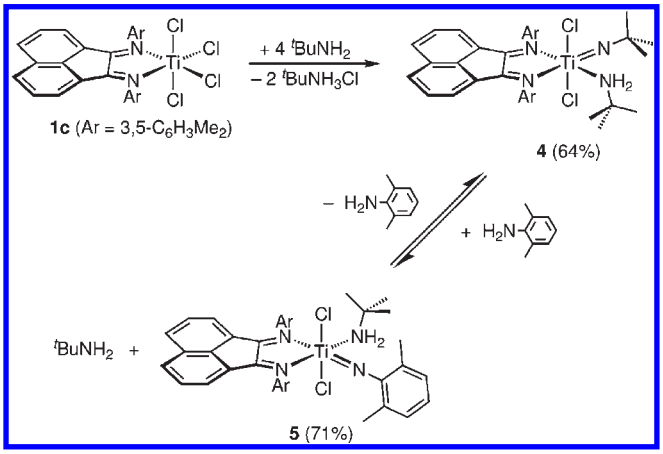
Bond Distances/Å

	2b	**3b**	**4**
Ti−N(1)	2.254(4)	2.257(2)	2.398(3)
Ti−N(2)	2.259(4)	2.258(2)	2.288(3)
Ti−N(3)	1.690(4)	1.718(2)	1.787(4)
Ti−N(4)			2.156(4)
Ti−Cl(1)	2.3208(14)	2.3366(9)	2.4545(11)
Ti−Cl(2)	2.3360(13)	2.3241(10)	2.3734(11)

Bond Angles/deg

	2b	**3b**	**4**
Ti−N(3)−C(31)	164.1(4)	165.27(19)	179.1(4)
Ti−N(4)−C(33)			132.2(3)
N(1)−Ti−N(2)	73.30(12)	73.45(8)	71.73(10)
N(1)−Ti−Cl(1)	89.98(10)	85.50(6)	80.39(7)
N(2)−Ti−Cl(1)	145.38(10)	146.24(6)	82.12(7)
N(1)−Ti−Cl(2)	149.38(10)	148.82(6)	84.48(7)
N(2)−Ti−Cl(2)	85.01(9)	88.64(6)	85.15(8)
N(1)−Ti−N(3)	100.03(16)	101.75(9)	168.16(16)
N(2)−Ti−N(3)	104.23(17)	103.39(9)	96.43(16)
N(1)−Ti−N(4)			90.36(13)
N(2)−Ti−N(4)			157.67(14)
N(3)−Ti−Cl(1)	107.85(14)	106.60(8)	98.64(17)
N(3)−Ti−Cl(2)	106.19(14)	107.21(8)	94.43(17)
N(4)−Ti−Cl(1)			81.79(13)
N(4)−Ti−Cl(2)			106.84(13)
Cl(1)−Ti−Cl(2)	96.68(5)	96.90(3)	162.66(4)

Scheme 2



NMR data suggest that the imido-amine functionalities of **4** are preserved in solution. Unlike the spectra obtained for five-coordinate imido complexes **2a** and **2b**, which show only three ^{1}H NMR resonances for the acenaphthylenediimine backbone, six sharp ^{1}H NMR resonances are observed for the BIAN backbone of **4** in the room-temperature spectrum. This data is consistent with the molecular structure shown in Figure 3, which has the imido ligand trans to one nitrogen donor of the BIAN ligand and the amino ligand trans to the other nitrogen donor of the BIAN ligand. The proton signatures for the *tert*-butyl groups of the imido and amino ligands are well resolved as singlets at 0.64 and 1.20 ppm, respectively, indicating that these ligands do not exchange on the NMR time scale. Moreover, the coordinated ^{t}BuNH$_2$ ligand does not exchange rapidly with free ^{t}BuNH$_2$ at

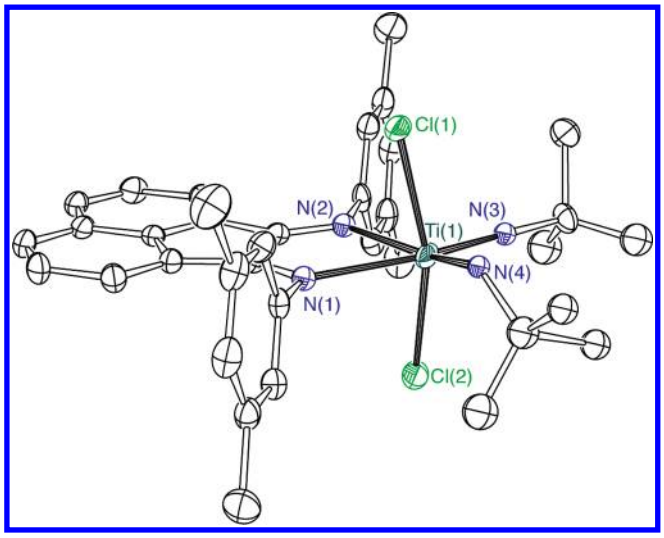


Figure 3. ORTEP of (dmp-BIAN)TiCl$_2$(=N^{t}Bu)(NH$_2$^{t}Bu)·CH$_2$Cl$_2$ (**4**·CH$_2$Cl$_2$) as determined by single crystal X-ray diffraction studies. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and the solvent molecule are omitted for clarity.

room temperature. The ^{1}H NMR spectrum of **4** in CDCl$_3$ containing one equiv of ^{t}BuNH$_2$ showed separate sharp resonances for free and coordinated amine ligand at 1.18 and 1.20 ppm, respectively. The chemical shift of the *tert*-butyl imido resonance is well upfield of the chemical shift for the *tert*-butyl imido resonances observed for **2a** and **2b**, consistent with decreased N→Ti π donation. Two singlets were observed for the 3,5-dimethylaryl substituents of the dmp-BIAN in the ^{1}H NMR spectrum, consistent with the arylimine arms of the dmp-BIAN ligand being located trans to different groups. Complex

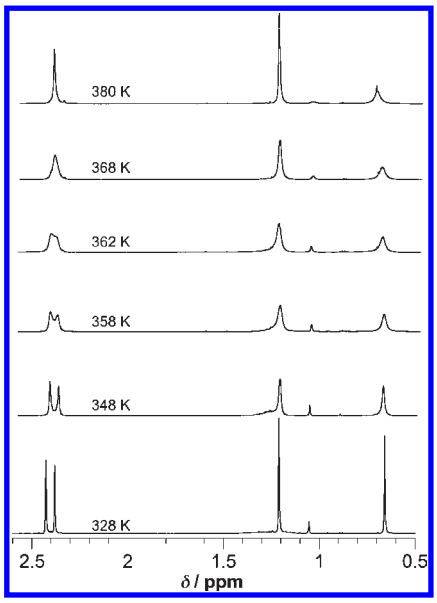


Figure 4. Partial ^{1}H NMR spectra (600 MHz) in $CDCl_3$ of **4** in the temperature range 328−380 K showing the dmp-BIAN methyl resonances (2.4 ppm), the *tert*-butylamino resonance (1.2 ppm), and the *tert*-butylimido resonance (0.65 ppm).

4 maintains overall C_s symmetry in solution at room temperature.

Variable-temperature ^{1}H NMR experiments on **4** in the presence and absence of added ^{t}BuNH$_2$ suggest that the coordinated amine ligand does dissociate at elevated temperatures to access a fluxional five-coordinate species. Monitoring samples of pure **4** in $CDCl_3$ by ^{1}H NMR spectroscopy at elevated temperatures revealed broadening of the two methyl resonances at 2.37 and 2.42 ppm for the dmp-BIAN ligand, eventually coalescing into a singlet at 2.42 ppm at approximately 362 K as shown in Figure 4. Similarly, the six unique BIAN resonances in the aryl region of the ^{1}H NMR spectrum of **4** coalesced to three resonances at elevated temperatures. These observations are consistent with the two sides of the dmp-BIAN ligand of **4** becoming equivalent on the NMR time scale at elevated temperatures. Rate constants were estimated in the temperature range 328−380 K for the process that exchanges the two methyl environments in **4** (trans to amino and trans to imido ligands, respectively). Figure 5 shows the Eyring plot used to extract activation parameters of $\Delta H^{\ddagger} = 19.7 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.0 \pm 4.8$ eu. Similar VT NMR experiments carried out in the presence of 1 equiv of ^{t}BuNH$_2$ showed the same coalescence behavior for the dmp-BIAN ^{1}H NMR resonances. In this experiment, the ^{1}H NMR resonances for the coordinated and free ^{t}BuNH$_2$, which are separate and sharp at 298 K, broaden and merge into a singlet with a coalescence temperature of 360 K. These exchange data and activation parameters are consistent with the dissociation of the neutral ^{t}BuNH$_2$ ligand from **4** at elevated temperature to afford a five-coordinate intermediate. By analogy to the five-coordinate geometries of **2a** and **2b**, this putative intermediate is likely a square-pyramidal (dmp-BIAN)TiCl$_2$(=N^{t}Bu) species.

The *tert*-butyl imido ligand could be exchanged with 2,6-dimethylaniline to form a six-coordinate arylimido-amine complex, **5**, as shown in Scheme 2. Unlike the

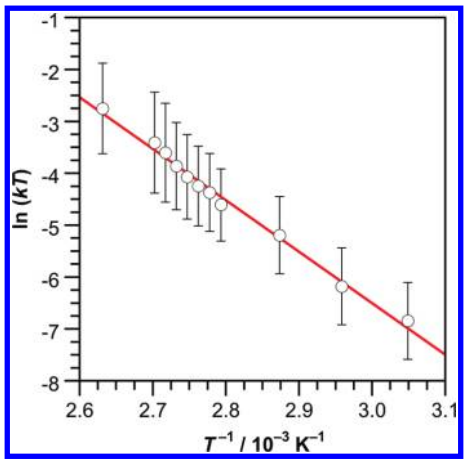


Figure 5. Eyring plot of the rate constants for the isomerization of **4** in $CDCl_3$ (328−378 K).

analogous reactions to form **3a** and **3b**, the formation of **5** must be driven to completion by the removal of free ^{t}BuNH$_2$ liberated during the reaction. Hence the formation of **5** is in equilibrium as long as free ^{t}BuNH$_2$ is present, and NMR-scale reactions provided an estimate for K_{eq} of ~0.37 at 298 K.

Changes in the ^{1}H NMR spectrum of **5** relative to complex **4** are consistent with the formation of the six-coordinate arylimido-amine complex. Namely, the disappearance of the *tert*-butylimido resonance at 0.65 ppm, and the appearance of the arylimido *ortho*-methyl resonance at 2.43 ppm were observed. The downfield shift of the *ortho*-methyl substituents from those found in free 2,6-dimethylaniline (2.16 ppm), which is consistent with the chemical shifts observed for complexes **3a** and **3b**, is indicative of the delocalization of electron density about the titanium-imido bond and the aryl moiety. As observed for **4** the backbone of the dmp-BIAN ligand in **5** is asymmetric showing six resonances, while two resonances are observed for the dimethylaryl groups on the imine nitrogens. These spectroscopic signatures are consistent with **5** having C_s symmetry with trans chloride ligands and cis imido and amino ligands.

Conclusions

Steric profiles of the BIAN ligands examined herein have an impact on the observed coordination geometry and stability of titanium halide and titanium imido complexes. In the case of the (BIAN)TiCl$_4$ derivatives, the smallest BIAN ligand, dmp-BIAN, stays coordinated to the titanium center in the presence of excess pyridine. Furthermore, dmp-BIAN displaces pyridine from TiCl$_4$(py)$_2$ to form (dmp-BIAN)-TiCl$_4$, indicating that the stability of the titanium complex with the smallest BIAN ligand is not derived from a kinetic barrier but rather from thermodynamic preference. On the other hand, the larger BIAN derivatives, tmp-BIAN and dpp-BIAN, which have 2,6-disubstituted arylimine donors, were readily displaced by pyridine from (tmp-BIAN)TiCl$_4$ and (dpp-BIAN)TiCl$_4$, respectively. The instability of these two complexes relative to TiCl$_4$(py)$_2$ indicates that unfavorable steric interactions between the BIAN substituents and the chloride ligands must offset the thermodynamic preference for chelating a ligand to the titanium center.[63,80,82]

In the case of the titanium imido complexes, increased BIAN ligand sterics enforce low-coordinate and more reactive

geometries at the metal center. The smallest dmp-BIAN ligand affords pseudo-octahedral titanium imido complexes that retain a neutral amine donor ligand in the sixth coordination site. The imido and amine ligands orient themselves trans to the BIAN imine donors leaving the chloride ligands in mutually trans positions. While the neutral ^{t}BuNH$_2$ ligand does dissociate from **4** to give access to a more reactive five-coordinate intermediate, even in thermodynamically favorable aryl-for-alkyl imide aminolysis reactions, binding of the alkylamine to the metal center strongly inhibits the reaction. In contrast, the larger tmp-BIAN and dmp-BIAN ligands enforce five-coordinate geometries by precluding the binding of a neutral amine ligand, and as such the aminolysis reaction proceeds readily. While the neutral ^{t}BuNH$_2$ ligand does dissociate from **4** to give access to a more reactive five-coordinate intermediate, even in thermodynamically favorable aryl-for-alkyl imide aminolysis reactions, binding of the alkylamine to the metal center strongly inhibits the reaction. In contrast, the larger tmp-BIAN and dmp-BIAN ligands enforce five-coordinate geometries by precluding the binding of a neutral amine ligand, and as such the aminolysis reaction proceeds readily.

The strong impact of BIAN ligand sterics on the coordination geometry and the stability of titanium imido complexes has implications for future ligand and molecule designs. To exploit the full reactivity of early transition metal imido complexes, low-coordinate environments must be generated for the metal center.[34−38] While the larger steric profiles of tmp-BIAN and dpp-BIAN did afford lower coordinate titanium-imido complexes, these steric parameters also turn on a decomposition pathway that expels the BIAN ligand from the metal coordination sphere. Thus, future efforts to design low-coordinate titanium imido complexes with sterically demanding, chelating ligands must avoid this type of decomposition. One strategy to avoid this path would be to keep the sterically demanding groups on formally anionic ligands, so that ligand loss is inhibited by both covalent and ionic bonding contributions.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.