Synthesis of titanium borylimido compounds supported by diamide-amine ligands and their reactions with alkynes

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Figure S2. Displacement ellipsoid plot (25% probability) of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Tol})\}$ (**14**). H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ti(1)–N(1) 1.9833(13), Ti(1)–N(4) 2.2530(14), Ti(1)–N(5) 1.9944(15), Ti(1)–N(6) 1.9882(15), Ti(1)–C(44) 1.9522(17), N(1)–B(1) 1.443(2), N(1)–C(45) 1.402(2), C(44)–C(45) 1.389(2), N(1)–Ti(1)–C(44) 77.19(6), Ti(1)–N(1)–B(1) 161.16(11), Ti(1)–C(44)–C(45) 80.31(10), N(1)–C(45)–C(44) 123.18(15) ($\tau = 0.69$).

Figure S3. Displacement ellipsoid plot (20% probability) of $\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Ar}^{\text{F}})\text{CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (**15**). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–N(1) 1.9300(17), Ti(1)–N(4) 2.2667(19), Ti(1)–N(5) 1.9759(18), Ti(1)–N(6) 1.9466(18), Ti(1)–F(1) 1.8016(12), N(1)–B(1) 1.479(3), N(1)–C(45) 1.405(2), C(44)–C(45) 1.343(3), Ti(1)–N(1)–B(1) 127.01(13) ($\tau = 0.93$).

Figure S4. Top: first order semi-logarithmic plots for the conversion of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Tol})\}$ (**14**) to $\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Tol})\text{CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (**17**) in C_6D_6 . (avg. $r^2 = 0.998$, range 0.995 – 0.999). Bottom: Eyring plot for the conversion of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Tol})\}$ (**14**) to $\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Tol})\text{CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (**17**) in C_6D_6 . Activation parameters derived from linear regression analysis ($r^2 = 0.969$): $\Delta H^\ddagger = 14.1(1.5) \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -34.3(4.4) \text{ cal mol}^{-1} \text{ K}^{-1}$; $\Delta G_{333}^\ddagger = 25.5(1.5) \text{ kcal mol}^{-1}$. The experiment at 333 K was repeated with double $[\mathbf{14}]_0$, giving $\ln(k/T) = -14.8$ ($1/T = 3.00 \times 10^{-3} \text{ K}^{-1}$).

Figure S5. Top: first order semi-logarithmic plots for the conversion of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Ar}^{\text{F}})\}$ (**16**) to $\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Ar}^{\text{F}})\text{CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (**15**) in C_6D_6 . (avg. $r^2 = 0.996$, range 0.990 – 0.999). Bottom: Eyring plot for the conversion of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Ar}^{\text{F}})\}$ (**16**) to $\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Ar}^{\text{F}})\text{CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (**15**) in C_6D_6 . Activation parameters derived from linear regression analysis ($r^2 = 0.985$): $\Delta H^\ddagger = 13.9(1.0) \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -35.3(2.9) \text{ cal mol}^{-1} \text{ K}^{-1}$; $\Delta G_{333}^\ddagger = 25.7(1.0) \text{ kcal mol}^{-1}$. The experiment at 336 K was repeated with double $[\textbf{16}]_0$, giving $\ln(k/T) = -14.8$ ($1/T = 2.98 \times 10^{-3} \text{ K}^{-1}$).

Table S1. First order rate constants obtained for the conversion of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Tol})\}$ (**14**) to $\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Tol})\text{-CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (**17**). Unless otherwise stated, $[\mathbf{14}]_0 = 0.026 \text{ mol dm}^{-3}$.

Temperature / K	Notes	$k_{\text{obs}} / 10^{-5} \text{ s}^{-1}$
327		8.15(2)
330		10.34(1)
333		11.04(3)
333	$[\mathbf{14}]_0 = 0.052 \text{ mol dm}^{-3}$	12.72(2)
336		15.18(2)
339		18.41(6)

Table S2. First order rate constants obtained for the conversion of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Ar}^{\text{F}})\}$ (**16**) to $\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Ar}^{\text{F}})\text{-CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (**15**). Unless otherwise stated, $[\mathbf{16}]_0 = 0.026 \text{ mol dm}^{-3}$.

Temperature / K	Notes	$k_{\text{obs}} / 10^{-5} \text{ s}^{-1}$
327		6.60(2)
330		8.35(2)
333		9.32(3)
336		11.82(1)
336	$[\mathbf{16}]_0 = 0.052 \text{ mol dm}^{-3}$	12.63(2)
339		14.97(1)

Figure S6. Displacement ellipsoid plot (25% probability) of *cis*-Ti(N₂^{iPr}N^{Me}){N{B(NAr'CH)₂}C(H)C(Tol)} (*cis*-**18**). H atoms are omitted for clarity. Selected bond distances (Å) and angles (°) Ti(1)–N(1) 1.999(2) [1.996(2)], Ti(1)–N(4) 2.294(2) [2.301(2)], Ti(1)–N(5) 1.963(3) [1.943(3)], Ti(1)–N(6) 1.957(2) [1.953(3)], Ti(1)–C(38) 1.998(3) [2.007(3)], N(1)–B(1) 1.432(4) [1.426(4)], N(1)–C(39) 1.433(3) [1.424(4)], C(38)–C(39) 1.358(4) [1.357(4)], N(1)–Ti(1)–C(38) 75.34(10) [75.13(10)], Ti(1)–N(1)–B(1) 160.17(18) [159.24(19)], Ti(1)–C(38)–C(39), 82.13(17) [81.65(18)], N(1)–C(39)–C(38) 122.1(2) [122.6(3)]. Values in brackets are for the second crystallographically independent molecule ($\tau = 0.58$ [0.63]).

Figure S7. Left: plot of the sum of $[\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NHB}(\text{NAr}'\text{CH})_2\}(\text{CCAr}^{\text{F}})]$ (**[23]**) and $[\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Tol})\}]$ (**[24]**) vs time. $[\mathbf{21}]_0 = [\text{Ar}^{\text{F}}\text{CCH}]_0 = 0.0299 \text{ mol dm}^{-3}$ and $T = 298 \text{ K}$. The best-fit line ($r^2 = 0.9928$) shown gave an initial rate of $19.2(1) \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$. Right: plot of the sum of $[\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NDB}(\text{NAr}'\text{CH})_2\}(\text{CCAr}^{\text{F}})]$ (**[23-d₁]**) and $[\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{D})\text{C}(\text{Tol})\}]$ (**[24-d₁]**) vs time. The best-fit line ($r^2 = 0.9847$) shown gave an initial rate of $3.9(1) \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Note: In order to avoid the effects of the build-up of the released pyridine as the reaction progressed, the initial rates method was used to effectively measure the rate of the reaction, $d[\mathbf{23}]/dt$ at time = 0, t_0 . The reaction of $\text{Ar}^{\text{F}}\text{CCH}$ with **21** was monitored by a ^1H NMR array at 298 K. A small (<10 molar%) amount of the thermodynamic metallacycle product **24** was also observed to form, though remaining as a constant proportion of the product mixture as the reaction proceeded. It was shown independently that **23** does not itself convert to **24** under these conditions and so $d[\mathbf{23}]/dt$ is independent of $d[\mathbf{24}]/dt$. Therefore, a composite initial rate was measured, and was then scaled to the correct proportion of the acetylide complex **23** in the mixture, to give an initial rate reflecting only the formation of **23**. The graph of $([\mathbf{23}] + [\mathbf{24}])$ vs time gave the non-linear plot drawn above in Fig. S7 Graphical software (*Origin*) was used to fit a curve to all of the data points, thus describing the evolution of product throughout the kinetic study.

Figure S8. First order semi-logarithmic plots for the conversion of $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NHB}(\text{NAr}'\text{CH})_2\}(\text{CCAr}^{\text{F}})$ (**23**) to $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Ar}^{\text{F}})\}$ (**24**), and **23-*d*₁** to **24-*d*₁**, at 343 K in C_6D_6 ($r^2 = 0.991$ and 0.982).

Figure S9. Relative Gibbs free energies (G_{rel} , kcal mol⁻¹) at 298 K (G_{rel} values at 343 K in parentheses) for the DFT computed, gas phase reactions of $\text{Ti}(\text{N}_2^{\text{SiH}_3}\text{N}^{\text{py}})\{\text{NB}(\text{NMeCH})_2\}(\text{py})$ (**1Q**) with $\text{Ar}^{\text{F}}\text{CCH}$ and $\text{Ar}^{\text{F}}\text{CCD}$.

Experimental Details

General methods and instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were either degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent¹ or refluxed over sodium (toluene), potassium (THF), Na/K alloy (Et₂O) or CaH₂ (pyridine) and distilled. Deuterated solvents were dried over potassium (C₆D₆) or CaH₂ (pyridine-*d*₅), distilled under reduced pressure and stored under argon in Teflon valve ampoules. Unless otherwise stated NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H, ¹³C{¹H}, ¹¹B{¹H} and ²H spectra were recorded on a Bruker Ascend 400 NMR spectrometer, a Bruker Avance III 500 NMR spectrometer or on a Bruker AVC 500 spectrometer fitted with a ¹³C cryoprobe. Unless otherwise stated, all NMR spectra were recorded at 298 K. ¹H and ¹³C{¹H} and spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ²H NMR spectra were referenced to the natural abundance deuterium resonance of the protio solvent. ¹¹B and ¹⁹F NMR spectra were referenced externally to Et₂O·BF₃ and CFC₃ respectively. Assignments were confirmed as necessary with the use of two dimensional ¹H–¹H, ¹³C–¹H and ¹⁹F–¹⁹F correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FTIR spectrometer and samples prepared in a dry-box using NaCl plates as a Nujol mull. The data are quoted in wavenumbers (cm⁻¹). Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry. Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University.

Starting materials. Ti{NB(NAr'CH)₂}Cl₂(py)₃ (**3**),² Li₂N₂^{SiMe₃N^{Me}},³ H₂N₂^{Ar^FN^{Me}},⁴ Li₂N₂^{iPrN^{Me}},⁵ Li₂N₂^{N^{Py}},⁶ Ar^FCCH,⁷ Ti(N₂^{pyrN^{Me}}){NB(NAr'CH)₂}(py)₂ (**4**)² and H₂NB(NAr'CH)₂⁸ were synthesised according to literature procedures. All other reagents were purchased from commercial suppliers, and (for liquid reagents) degassed before use. TolCCH, MeCCMe and PhCCMe were dried over CaH₂ and distilled (trap-to-trap under static vacuum) before use.

Li₂N₂^{Ar^FN^{Me}}. To a slurry of H₂N₂^{Ar^FN^{Me}} (1.00 g, 2.20 mmol) in hexane at –78°C was added dropwise ⁿBuLi (1.6 M in hexane, 3.03 ml, 4.8 mmol) over 10 minutes. The solution was allowed to warm to room temperature, where upon a white precipitate formed, and the solid product was then filtered and washed with hexane (3 × 10 ml) and dried *in vacuo*. Yield: 0.730 g (72%). ¹H NMR (pyridine-*d*₅, 299.9 MHz): 4.18 (4H, br. s, CH₂), 2.75 (4H, br. s, CH₂), 2.01 (3H, s, NMe). ¹³C{¹H}

(pyridine-*d*₅, 75.4 MHz): 140.0 (*o*-C₆F₅), 139.3 (*m*-C₆F₅), 124.3 (*p*-C₆F₅), 122.8 (*i*-C₆F₅), 58.1 (CH₂), 47.4 (CH₂), 42.1 (NMe). ¹⁹F NMR (pyridine-*d*₅, 282.1 MHz): −170.89 (4F, br. s, *o*-C₆F₅), −171.50 (4F, t, ³*J* = 23.8 Hz, *m*-C₆F₅), −200.30 (2F, m, *p*-C₆F₅). IR (NaCl plates, Nujol mull, cm^{−1}): 2725 (w), 2678 (w), 2608 (w), 1662 (w), 1648 (m), 1589 (w), 1515 (s), 1360 (s), 1343 (s), 1304 (w), 1207 (w), 1174 (m), 1137 (w), 1062 (m), 1045 (m), 973 (s), 904 (w), 861 (w), 762 (w), 655 (w), 606 (w), 529(w). Anal. found (calcd. for C₁₇H₁₁N₃F₁₀Li₂); C, 44.10 (44.28); H, 2.60 (2.40); N, 9.00 (9.11) %.

Procedure for deuteration of Ar^FCCH. To a stirred CH₂Cl₂ (5 mL) solution of Ar^FCCH (1.00 g, 5.21 mmol) was added D₂O (30 mL) and NaOD (40 % solution in D₂O, 0.020 mL, 0.27 mmol). The resultant mixture was left to stir for 3 days and then quenched with DCl (45 % solution in D₂O, 0.028 mL). The two layers were then separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layers were dried over Na₂SO₄ and then the CH₂Cl₂ was removed under reduced pressure. Yield: 0.800 g (79%). ¹H NMR analysis indicated ≥98% deuteration.

Ti(N₂^{ArF}N^{Me}){NB(NAr'^FCH)₂}(py) (10). To a Schlenk flask containing Ti{NB(NAr'^FCH)₂}Cl₂(py)₃ (**3**, 1.50 g, 1.98 mmol) and Li₂N₂^{ArF}N^{Me} (0.913 g, 1.98 mmol), was added toluene (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and then stirred for 1 hour, after which it had become a dark red suspension. The volatiles were removed under reduced pressure, and the product extracted into pentane (3 × 15 mL). The solvent was removed from the combined extracts under reduced pressure, yielding **10** as a deep red solid, which was then dried *in vacuo*. Yield: 1.51 g (78%). Diffraction-quality crystals were grown from a concentrated pentane solution at 5 °C. ¹H NMR (C₆D₆, 400.1 MHz): δ 7.88 (2 H, m, 2,6-py), 7.18 – 7.10 (6 H, overlapping 2 × m with residual protio solvent resonance, *m*- and *p*-C₆H₃ⁱPr₂), 6.46 (1 H, m, 3,5-py), 6.09 (2 H, m, 4-py), 5.79 (2 H, s, NCH), 3.60 (4 H, sept., ³*J* = 6.9 Hz, CHMeMe), 3.47 (2 H, m, CH₂NAr^F), 3.20 (2 H, m, CH₂NAr^F), 2.49 (2 H, m, CH₂NMe), 2.28 (2 H, m, CH₂NMe), 1.96 (3 H, s, NMe), 1.28 (12 H, d, ³*J* = 6.9 Hz, CHMeMe), 1.26 (12 H, d, ³*J* = 6.9 Hz, CHMeMe) ppm. ¹³C{¹H} NMR (C₆D₆, 100.6 MHz): δ 151.4 (2,6-py), 147.6 (*i*-C₆H₃ⁱPr₂), 144.4 (*o*-C₆F₅), 141.4 (*o*-C₆H₃ⁱPr₂), 139.5 (*m*-C₆F₅), 138.3 (4-py), 137.0 (*i*-C₆F₅), 133.7 (*p*-C₆F₅), 126.9 (*p*-C₆H₃ⁱPr₂), 123.7 (3,5-py), 123.6 (*m*-C₆H₃ⁱPr₂), 116.8 (NCH), 56.7 (CH₂NMe), 52.4 (CH₂NC₆F₅), 46.2 (NMe), 28.6 (CHMeMe), 25.6 (CHMeMe), 23.2 (CHMeMe) ppm. ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): δ 14.7 ppm. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): δ −149.4 (2 F, d, ³*J* = 22.4 Hz, *o*-C₆F₅), −166.0 (2 F, app. t, app. ³*J* = 22.4 Hz, *m*-C₆F₅), −169.9 (1 F, t, ³*J* = 22.4 Hz, *p*-C₆F₅) ppm. IR (NaCl plates, Nujol mull, cm^{−1}): 3084 (w), 2608 (w), 2459 (w), 1997 (w), 1605 (w), 1583 (m), 1507 (m), 1491 (m), 1446 (w), 1406 (m), 1368 (s), 1303 (m), 1259 (m), 1157 (m), 1114 (w), 1086 (w), 1065 (m), 982 (s), 931 (w), 897 (w), 862 (m), 806 (w), 765 (m), 752 (w), 702

(m), 668 (w), 640 (w). EI-MS: $m/z = 896 [M - \text{py}]^+$ (4%). Anal. found (calcd. for $\text{C}_{48}\text{H}_{52}\text{BF}_{10}\text{N}_7\text{Ti}$): C, 59.17 (59.09); H, 5.36 (5.37); N, 9.98 (10.05)%.

Ti(N₂^{iPr}N^{Me}){NB(NAr'CH)₂}(py) (11**).** To a Schlenk flask containing Ti{NB(NAr'CH)₂}Cl₂(py)₃ (**3**, 1.50 g, 1.98 mmol) and Li₂N₂^{iPr}N^{Me} (0.422 g, 1.98 mmol) was added toluene (30 mL) at -78°C . The mixture was allowed to warm to RT, and then stirred for 3 h, after which time it had become a deep red suspension. The volatiles were removed under reduced pressure, and the product extracted into pentane (4 × 15 mL). The solvent was removed from the combined extracts under reduced pressure, resulting in **11** as a red solid, which was then dried *in vacuo*. Yield: 1.27 g (88%). Diffraction-quality crystals were grown from a concentrated pentane solution at 5°C . ¹H NMR (C₆D₆, 400.1 MHz): δ 8.01 (2 H, m, 2,6-py), 7.25 (6 H, overlapping 2 × m, *m*- and *p*-C₆H₃^{iPr}Pr₂), 6.76 (1 H, m, 4-py), 6.40 (2 H, m, 3,5-py), 5.90 (2 H, s, NCH), 3.87 (4 H, sept., ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 3.76 (2 H, sept., ³*J* = 6.5 Hz, NCHMeMe) 3.29 (2 H, m, CH₂N^{iPr}), 3.08 (2 H, m, CH₂N^{iPr}), 2.77 (2 H, m, CH₂NMe), 2.29 (2 H, m, CH₂NMe), 1.55 (3 H, s, NMe), 1.50 (12 H, d, ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 1.41 (6 H, d, ³*J* = 6.5 Hz, NCHMeMe), 1.37 (12 H, d, ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 0.66 (6 H, d, ³*J* = 6.5 Hz, NCHMeMe) ppm. ¹³C{¹H} NMR (C₆D₆, 100.6 MHz): δ 152.9 (2,6-py), 148.1 (*o*-C₆H₃^{iPr}Pr₂), 143.8 (*i*-C₆H₃^{iPr}Pr₂), 137.1 (4-py), 126.4 (*p*-C₆H₃^{iPr}Pr₂), 123.3 (overlapping *m*-C₆H₃^{iPr}Pr₂ and 3,5-py), 116.8 (NCH), 58.7 (CH₂NMe), 51.4 (NCHMeMe), 45.1 (CH₂N^{iPr}), 45.0 (NMe), 28.7 (C₆H₃(CHMeMe)₂), 25.2 (C₆H₃(CHMeMe)₂), 24.3 (C₆H₃(CHMeMe)₂), 21.5 (NCHMeMe), 21.1 (NCHMeMe) ppm. ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): δ 15.2 ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 2777 (w), 2653 (w), 1601 (s), 1543 (w), 1443 (w), 1422 (m), 1359 (s), 1350 (m), 1337 (s), 1308 (m), 1287 (w), 1272 (w), 1239 (w), 1210 (m), 1179 (w), 1139 (w), 1065 (m), 1040 (w), 1013 (w), 999 (m), 930 (w), 895 (w), 879 (w), 814 (w), 763 (m), 755 (w), 699 (m), 668 (m), 640 (m). Anal. found (calcd. for C₄₂H₆₆BN₇Ti): C, 69.23 (69.32); H, 9.31 (9.14); N, 13.55 (13.47)%.

Ti(N₂^{SiMe₃}N^{Me}){N{B(NAr'CH)₂}C(H)C(Ar^F)} (13**).** To a solution of Ti(N₂^{SiMe₃}N^{Me}){NB(NAr'CH)₂}(py) (**9**, 0.261 g, 0.331 mmol) in hexane (15 mL) was added Ar^FCCH (44 μL , 0.331 mmol) at RT, giving an immediate color change to deep red/brown. The reaction mixture was stirred at RT for 1 h, after which the volatiles were removed under reduced pressure, giving **13** as a deep brown waxy solid. Yield: 0.198 g (66%). ¹H NMR (C₆D₆, 400.1 MHz): δ 10.43 (br. s overlapping with minor isomer, TiC=CH), 7.22 – 7.11 (overlapping 2 × m with minor isomer and residual protio solvent resonance, *m*- and *p*-C₆H₃^{iPr}Pr₂), 6.11 (2 H, s, NCH), 3.39 (4 H, sept., ³*J* = 6.9 Hz, CHMeMe), 3.02 (2 H, m, CH₂NSiMe₃), 2.62 (2 H, m, CH₂NMe), 1.97 (3 H, s, NMe), 1.89 (2 H, m, CH₂NMe), 1.29 (12 H, d, ³*J* = 6.9 Hz, CHMeMe), 1.20 (12 H, d, ³*J* = 6.9 Hz, CHMeMe) 0.02

(18 H, s, SiMe₃) ppm. A second resonance assigned to CH₂NSiMe₃ is found to be obscured by the CHMeMe resonance at 3.39 ppm, as observed by HSQC and HMBC spectra. ¹³C{¹H} NMR (C₆D₆, 125.7 MHz): δ 179.4 (TiC=CH), 161.8 (TiC=CH), 147.2 (*o*-C₆H₃ⁱPr₂), 143.7 (m, *o*-C₆F₅), 141.8 (m, *m*-C₆F₅), 139.5 (*i*-C₆H₃ⁱPr₂), 136.5 (m, *p*-C₆F₅), 124.2 (*m*-C₆H₃ⁱPr₂), 121.2 (m, *i*-C₆F₅), 119.2 (NCH), 57.8 (CH₂NMe), 51.0 (CH₂NSiMe₃), 43.3 (NMe), 29.0 (CHMeMe), 26.3 (CHMeMe), 23.7 (CHMeMe), 1.9 (SiMe₃) ppm. The *p*-C₆H₃ⁱPr₂ resonance is obscured by the solvent resonance. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): -140.4 (2 F, d, ³J = 21.6 Hz, *o*-C₆F₅), -163.1 (1 F, t, ³J = 21.5 Hz, *p*-C₆F₅), -165.4 (2 F, m, *m*-C₆F₅) ppm. ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): δ 23.4 ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 3522 (w), 3391 (m), 1832 (w), 1866 (w), 1797 (w), 1655 (m), 1637 (m), 1586 (m), 1510 (m), 1201 (m), 1180 (m), 1117 (s), 1031 (s), 960 (s), 909 (s), 837 (s), 759 (m), 674 (m), 651 (m), 604 (m), 556 (m). EI-MS: *m/z* = 595 [Ar^FC(H)C(H)N(H)B(NAr'^FCH)₂]⁺ (100%). Anal. found (calcd. for C₄₅H₆₆BF₅N₆Si₂Ti): C, 59.71 (59.99); H, 7.13 (7.38); N, 9.32 (9.33)%.

Ti(N₂^{ArF}N^{Me}){N{B(NAr'^FCH)₂}C(H)C(Tol)} (**14**). To a solution of Ti(N₂^{ArF}N^{Me}){NB(NAr'^FCH)₂}(py) (**10**, 0.499 g, 0.511 mmol) in toluene (10 mL) was added TolCCH (65 μL, 0.511 mmol) at RT, giving an immediate color change to deep red. The reaction mixture was stirred for 20 minutes, after which the volatiles were removed under reduced pressure, to yield **14** as a deep red solid, which was then dried *in vacuo*. Yield: 0.395 g (76%). Diffraction-quality crystals were grown from a concentrated hexane solution at 5 °C. ¹H NMR (C₆D₆, 400.1 MHz): δ 11.61 (1 H, s, TiC=CH), 7.27 – 7.19 (6 H, overlapping 2 × m, *m*- and *p*-C₆H₃ⁱPr₂), 6.65 (2 H, d, ³J = 7.9 Hz, *o*-C₆H₄Me), 6.12 (2 H, d, ³J = 7.9 Hz, *m*-C₆H₄Me), 6.01 (2 H, s, NCH), 3.67 (2 H, m, CH₂NAr^F), 3.49 (4 H, sept., ³J = 6.9 Hz, CHMeMe), 3.10 (2 H, m, CH₂NAr^F), 2.95 (2 H, m, CH₂NMe), 2.19 (2 H, m, CH₂NMe), 1.86 (3 H, s, C₆H₄Me), 1.28 (24 H, app. t, app. ³J = 7.5 Hz, CHMeMe), 1.27 (3 H, s, NMe) ppm. ¹³C{¹H} NMR (C₆D₆, 125.8 MHz): δ 217.2 (TiC=CH), 163.8 (TiC=CH), 147.5 (*o*-C₆H₃ⁱPr₂), 143.3 (m, *o*-C₆F₅), 141.4 (m, *p*-C₆F₅), 140.8 (*i*-C₆H₃ⁱPr₂), 137.2 (*i*-C₆H₄Me), 136.7 (m, *m*-C₆F₅), 135.7 (*p*-C₆H₄Me), 133.3 (td, ²J_{C-F} = 14.3 Hz, ³J_{C-F} = 3.7 Hz, *i*-C₆F₅), 129.3 (*p*-C₆H₃ⁱPr₂), 128.6 (*m*-C₆H₄Me), 126.3 (*o*-C₆H₄Me), 124.5 (*m*-C₆H₃ⁱPr₂), 119.2 (NCH), 56.8 (CH₂NAr^F), 55.9 (CH₂NMe), 41.4 (NMe), 29.0 (CHMeMe), 25.0 (CHMeMe), 23.4 (CHMeMe), 20.8 (C₆H₄Me) ppm. ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): δ 21.9 ppm. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): -150.1 (2 F, m, *o*-C₆F₅), -166.1 (2 F, m, *m*-C₆F₅), -167.0 (1 F, t, ³J = 21.9 Hz, *p*-C₆F₅). IR (NaCl plates, Nujol mull, cm⁻¹): 3407 (w), 3067 (w), 1942 (w), 1658 (m), 1625 (w), 1583 (m), 1496 (s), 1408 (w), 1391 (m), 1349 (w), 1278 (w), 1207 (m), 1118 (w), 1065 (w), 982 (s), 937 (w), 901 (m), 861 (m), 816 (w), 769 (m), 694 (w), 650 (m). EI-MS: *m/z* = 1012 [*M*]⁺ (10%). Anal. found (calcd. for C₅₂H₅₅BF₁₀N₆Ti): C, 61.54 (61.67); H, 5.65 (5.47); N, 8.12 (8.30)%.

NMR tube scale synthesis of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Ar}^{\text{F}})\}$ (16**).** To an NMR tube fitted with a J. Youngs valve was added a solution of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{NB}(\text{NAr}'\text{CH})_2\}(\text{py})$ (**10**, 0.0150 g, 0.0153 mmol) and $\text{B}(\text{Ar}^{\text{F}})_3$ (0.0078 g, 0.0153 mmol) in C_6D_6 (0.6 mL). $\text{Ar}^{\text{F}}\text{CCH}$ (2.0 μL , 0.0153 mmol) was added *via* microsyringe, followed by an immediate color change to very deep brown. Conversion to **16** and $[\text{py}-\text{B}(\text{Ar}^{\text{F}})_3]$ was found to be quantitative. *Major isomer*: ^1H NMR (C_6D_6 , 400.1 MHz): δ 11.51 (1 H, s, $\text{TiC}=\text{CH}$), 7.26 – 7.17 (multiple m overlapping with minor isomer, *m*- and *p*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 5.98 (2 H, s, NCH), 3.46 (4 H, sept. overlapping with minor isomer, CHMeMe), 2.91 (multiple m overlapping with minor isomer, $\text{CH}_2\text{NAr}^{\text{F}}$ and CH_2NMe), 2.12 (2 H, m, CH_2NMe), 1.26 (multiple m overlapping with minor isomer, NMe and CHMeMe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.7 MHz): δ 194.1 ($\text{TiC}=\text{CH}$), 162.6 ($\text{TiC}=\text{CH}$), 147.2 (*o*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 140.1 (*i*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 128.4 (*p*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 124.9 (*m*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 119.6 (NCH), 56.4 (CH_2NMe), 55.8 ($\text{CH}_2\text{NAr}^{\text{F}}$), 41.6 (NMe), 28.9 (CHMeMe), 25.3 (CHMeMe), 23.2 (CHMeMe) ppm. Those resonances belonging to the NAr^{F} and $\text{TiC}(\text{Ar}^{\text{F}})=\text{CH}$ rings could not be satisfactorily assigned. *Minor isomer*: ^1H NMR (C_6D_6 , 400.1 MHz): δ 11.30 (1 H, s, $\text{TiC}=\text{CH}$), 7.26 – 7.17 (multiple m overlapping with major isomer, *m*- and *p*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 6.10 (2 H, s, NCH), 3.76 (4 H, m, $\text{CH}_2\text{NAr}^{\text{F}}$), 3.46 (4 H, sept. overlapping with major isomer, CHMeMe), 2.91 (m overlapping with major isomer, CH_2NMe), 2.74 (3 H, s, NMe) 1.93 (2 H, m, CH_2NMe), 1.26 (multiple m overlapping with major isomer, CHMeMe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.7 MHz): δ 201.1 ($\text{TiC}=\text{CH}$), 160.2 ($\text{TiC}=\text{CH}$), 146.0 (*o*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 124.3 (*m*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 118.8 (NCH), 56.9 (CH_2NMe), 55.4 ($\text{CH}_2\text{NAr}^{\text{F}}$), 37.8 (NMe), 29.0 (CHMeMe), 25.9 (CHMeMe), 23.1 (CHMeMe) ppm. Those resonances belonging to the NAr^{F} and $\text{TiC}(\text{Ar}^{\text{F}})=\text{CH}$ rings, and the *i*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$ resonance could not be satisfactorily assigned. The *p*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$ resonance is obscured by the solvent resonance. *Common data*: $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 128.4 MHz): δ 22.6 ppm.

$\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Tol})=\text{CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (17**).** To a solution of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{NB}(\text{NAr}'\text{CH})_2\}(\text{py})$ (**10**, 0.290 g, 0.297 mmol) in toluene (10 mL) was added TolCCH (38 μL , 0.297 mmol) at RT, giving an immediate color change to deep red. The reaction mixture was heated to 70 °C and stirred for 3.5 h, after which the volatiles were removed under reduced pressure, resulting in an orange waxy solid. Washing with hexane (3×10 mL) gave **17** as a yellow-orange solid. Yield: 0.141 g (47%). Diffraction-quality crystals were grown from a concentrated hexane solution at RT. ^1H NMR (C_6D_6 , 400.1 MHz): δ 7.31 (2 H, t, $^3J = 7.7$ Hz, *p*- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 7.15 (2 H, d, $^3J = 7.7$ Hz, *m*_a- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 7.10 (2 H, d, $^3J = 7.7$ Hz, *m*_b- $\text{C}_6\text{H}_3^{\text{iPr}_2}$), 6.93 (4 H, m, $\text{C}_6\text{H}_4\text{Me}$), 6.59 (1 H, s, $\text{NC}(\text{H})=\text{CTol}$), 5.98 (2 H, s, BNCH), 4.28 (1 H, m, $\text{MeNCH}_2\text{CH}_2\text{NC}_6\text{F}_4$), 3.51 (2 H, sept., $^3J = 6.9$ Hz, CH_aMeMe), 3.34 (2 H, sept., $^3J = 6.9$ Hz, CH_bMeMe), 3.14 (2 H, overlapping $2 \times$ m, $\text{MeNCH}_2\text{CH}_2\text{NC}_6\text{F}_4$ and $\text{MeNCH}_2\text{CH}_2\text{NC}_6\text{F}_5$), 2.82 (3 H, overlapping $2 \times$ m, $\text{MeNCH}_2\text{CH}_2\text{NC}_6\text{F}_4$

and MeNCH₂CH₂NC₆F₅), 2.37 (3 H, s, NMe), 2.17 (3 H, s, C₆H₄Me), 2.03 (1 H, m, MeNCH₂CH₂NC₆F₅), 1.76 (1 H, m, MeNCH₂CH₂NC₆F₄), 1.40 (12 H, d, ³J = 6.9 Hz, overlapped CHMe_aMe and CHMe_bMe), 1.18 (6 H, d, ³J = 6.9 Hz, CHMe_bMe), 1.13 (6 H, d, ³J = 6.9 Hz, CHMe_aMe). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz): δ 146.9 (*o*_a-C₆H₃ⁱPr₂), 145.9 (*o*_b-C₆H₃ⁱPr₂), 138.7 (*i*_a-C₆H₃ⁱPr₂), 138.0 (*i*-C₆H₄Me), 137.9 (*i*_b-C₆H₃ⁱPr₂), 130.2 (NC(H)=CTol), 129.4 (*o*-C₆H₄Me), 129.3 (*p*-C₆H₄Me), 126.4 (*m*-C₆H₄Me), 124.0 (*m*_a-C₆H₃ⁱPr₂), 123.0 (*m*_b-C₆H₃ⁱPr₂), 119.4 (NCH), 114.6 (NC(H)=CTol), 55.1 (MeNCH₂CH₂NC₆F₅), 55.5 (MeNCH₂CH₂NC₆F₅), 54.0 (MeNCH₂CH₂NC₆F₄), 51.7 (MeNCH₂CH₂NC₆F₄), 43.2 (NMe), 28.6 (CH_aMeMe), 28.3 (CH_bMeMe), 26.7 (CHMe_aMe), 26.2 (CHMe_bMe), 23.9 (CHMe_aMe), 22.9 (CHMe_bMe), 21.0 (C₆H₄Me) ppm. Those resonances belonging to the NAr^F and C₆F₄ rings could not be satisfactorily assigned. ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): δ 22.9 ppm. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): -102.5 (s, TiF), -128.9 (1 F, m, δ-C₆F₄), -146.4 (1 F, dd, ³J = 20.2 Hz, ⁴J = 7.8 Hz, β-C₆F₄), -147.0 (2 F, d, ³J = 23.4 Hz, *o*-C₆F₅), -158.1 (1 F, app. t, app. ³J = 21.0 Hz, α-C₆F₄), -163.0 (1 F, m, *p*-C₆F₅), -163.3 (2 F, m, *m*-C₆F₅), -164.8 (1 F, app. t, *J* = 23.1 Hz, γ-C₆F₄) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 1634 (w), 1607 (w), 1586 (w), 1557 (w), 1502 (s), 1363 (s), 1335 (s), 1289 (m), 1203 (w), 1115 (m), 1060 (s), 997 (s), 989 (s), 951 (w), 899 (m), 858 (m), 821 (w), 786 (w), 758 (m), 690 (w), 656 (m), 623 (m), 601 (m). EI-MS: *m/z* = 1012 [*M*]⁺ (100%). Anal. found (calcd. for C₅₂H₅₅BF₁₀N₆Ti): C, 61.47 (61.67); H, 5.61 (5.47); N, 8.11 (8.30)%.

NMR tube scale synthesis of Ti{MeN(CH₂CH₂NAr^F){CH₂CH₂NC₆F₄C(Tol)-CHNB(NAr'^FCH)₂}}(F) (17). To an NMR tube fitted with a J. Youngs valve was added a solution of Ti(N₂^{ArF}N^{Me}){N{B(NAr'^FCH)₂}C(H)C(Tol)} (14, 0.0150 g, 0.0148 mmol) in C₆D₆ (0.6 mL), and the tube heated to 60 °C for 16 h, after which time the ¹H NMR spectrum indicated quantitative conversion to 17.

Kinetic measurements for the conversion of Ti(N₂^{ArF}N^{Me}){N{B(NAr'^FCH)₂}C(H)C(Tol)} (14) to Ti{MeN(CH₂CH₂NAr^F){CH₂CH₂NC₆F₄C(Tol)CHNB(NAr'^FCH)₂}}(F) (17). The general procedure is as follows. In a dry-box, a C₆D₆ solution (0.6 mL) of Ti(N₂^{ArF}N^{Me}){N{B(NAr'^FCH)₂}C(H)C(Tol)} (14, 0.0156 g, 0.0154 mmol) was transferred to an NMR tube fitted with a J. Youngs valve. A blank C₆D₆ sample was added to the NMR probe at RT, locked and shimmed, and the probe heated to the relevant temperature (327, 330, 333, 336 or 339 K). After thermal equilibration, the experimental sample replaced the blank sample, the shimming was checked and an array was set up to record a ¹H NMR spectrum (4 scans) every 120 s. The formation

of **17** was calculated by measuring the integral of NMe. First order rate constants were obtained from linear plots of $-\ln(1-([\mathbf{17}]/[\mathbf{17}]_{\text{final}}))$ vs time.

Kinetic measurements for the conversion of $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Ar}^{\text{F}})\}$ (16**) to $\text{Ti}\{\text{MeN}(\text{CH}_2\text{CH}_2\text{NAr}^{\text{F}})\{\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_4\text{C}(\text{Ar}^{\text{F}})=\text{CHNB}(\text{NAr}'\text{CH})_2\}\}(\text{F})$ (**15**).** The general procedure is as follows. In a dry-box, $\text{Ti}(\text{N}_2^{\text{ArF}}\text{N}^{\text{Me}})\{\text{NB}(\text{NAr}'\text{CH})_2\}(\text{py})$ (**10**, 0.0150 g, 0.0154 mmol) and $\text{B}(\text{Ar}^{\text{F}})_3$ (0.0079 g, 0.0154 mmol) were mixed in C_6D_6 (0.6 mL), and the mixture transferred to an NMR tube fitted with a J. Youngs valve. Next, $\text{Ar}^{\text{F}}\text{CCH}$ (2.0 μL , 0.0154 mmol) was added *via* microsyringe, giving immediate conversion to **16**. A blank C_6D_6 sample was added to the NMR probe at RT, locked and shimmed, and the probe heated to the relevant temperature (327, 330, 333, 336 or 339 K). After thermal equilibration, the experimental sample replaced the blank sample, the shimming was checked and an array was set up to record a ^1H NMR spectrum (4 scans) every 120 s. The formation of **15** was calculated by measuring the integral of NMe. First order rate constants were obtained from linear plots of $-\ln(1-([\mathbf{15}]/[\mathbf{15}]_{\text{final}}))$ vs time.

$\text{Ti}(\text{N}_2^{\text{iPr}}\text{N}^{\text{Me}})\{\text{N}\{\text{B}(\text{NAr}'\text{CH})_2\}\text{C}(\text{H})\text{C}(\text{Tol})\}$ (18**).** To a solution of $\text{Ti}(\text{N}_2^{\text{iPr}}\text{N}^{\text{Me}})\{\text{NB}(\text{NAr}'\text{CH})_2\}(\text{py})$ (**11**, 0.500 g, 0.687 mmol) in toluene (15 mL) was added TolCCH (87 μL , 0.686 mmol) at RT, giving an immediate color change to deep brown. The mixture was stirred for 1 h, then the volatiles removed under reduced pressure. The product was dissolved in hexane (5 mL), concentrated to 2 mL then cooled to $-30\text{ }^\circ\text{C}$, resulting in large, deep brown crystals of **18**. Yield: 0.228 g (43%). Diffraction-quality crystals were grown from a concentrated hexane solution at $5\text{ }^\circ\text{C}$. *Major isomer (cis-18)*: ^1H NMR (C_6D_6 , 400.1 MHz): δ 10.32 (1 H, s, $\text{TiC}=\text{CH}$), 7.32 – 7.20 (6 H, overlapping 2 $\times$ m with minor isomer, *m*- and *p*- $\text{C}_6\text{H}_3^{\text{iPr}}\text{Pr}_2$), 7.04 (2 H, d, $^3J = 8.0\text{ Hz}$, *o*- $\text{C}_6\text{H}_4\text{Me}$), 6.93 (2 H, d, $^3J = 8.0\text{ Hz}$, *m*- $\text{C}_6\text{H}_4\text{Me}$), 5.99 (2 H, s, BNCH), 4.26 (2 H, sept., $^3J = 6.7\text{ Hz}$, NCHMeMe), 3.56 (4 H, sept. overlapping with minor isomer, $^3J = 6.9\text{ Hz}$, $\text{C}_6\text{H}_3(\text{CHMe}_2)_2$), 3.40 (2 H, m, $\text{CH}_2\text{N}^{\text{iPr}}$), 2.99 (4 H, overlapping 2 $\times$ m with minor isomer, $\text{CH}_2\text{N}^{\text{iPr}}$ and CH_2NMe), 2.21 (2 H, m, CH_2NMe), 2.14 (3 H, s, $\text{C}_6\text{H}_4\text{Me}$), 1.29 (12 H, d overlapping with minor isomer, $^3J = 6.9\text{ Hz}$, $\text{C}_6\text{H}_3(\text{CHMeMe})_2$), 1.08 (3 H, s, NMe), 1.00 (6 H, d, $^3J = 6.7\text{ Hz}$, NCHMeMe), 0.91 (6 H, d, $^3J = 6.7\text{ Hz}$, NCHMeMe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.6 MHz): δ 209.5 ($\text{TiC}=\text{CH}$), 148.9 ($\text{TiC}=\text{CH}$), 147.3 (*o*- $\text{C}_6\text{H}_3^{\text{iPr}}\text{Pr}_2$), 142.0 (*i*- $\text{C}_6\text{H}_3^{\text{iPr}}\text{Pr}_2$), 139.7 (*i*- $\text{C}_6\text{H}_4\text{Me}$), 133.5 (*p*- $\text{C}_6\text{H}_4\text{Me}$), 129.2 (*o*- $\text{C}_6\text{H}_4\text{Me}$), 127.5 (*p*- $\text{C}_6\text{H}_3^{\text{iPr}}\text{Pr}_2$), 127.0 (*m*- $\text{C}_6\text{H}_4\text{Me}$), 124.1 (*m*- $\text{C}_6\text{H}_3^{\text{iPr}}\text{Pr}_2$), 118.6 (BNCH), 57.2 (NCHMeMe), 56.9 (CH_2NMe), 47.2 ($\text{CH}_2\text{N}^{\text{iPr}}$), 41.5 (NMe), 28.9 ($\text{C}_6\text{H}_3(\text{CHMeMe})_2$), 24.6 ($\text{C}_6\text{H}_3(\text{CHMeMe})_2$), 23.9 ($\text{C}_6\text{H}_3(\text{CHMeMe})_2$), 23.6 (NCHMeMe), 22.2 (NCHMeMe), 21.2 ($\text{C}_6\text{H}_4\text{Me}$) ppm. *Minor isomer (trans-18)*: ^1H NMR (C_6D_6 , 400.1 MHz): δ 9.35 (1 H, s, $\text{TiC}=\text{CH}$), 7.32 – 7.20 (6 H, overlapping 2 $\times$ m with major isomer, *m*-

and *p*-C₆H₃ⁱPr₂), 6.94 (2 H, overlapping with major isomer, *o*-C₆H₄Me), 6.71 (2 H, d, ³*J* = 8.0 Hz, *m*-C₆H₄Me), 6.02 (2 H, s, BNCH), 4.18 (2 H, sept., ³*J* = 6.7 Hz, NCHMeMe), 3.56 (2 H, sept. overlapping with major isomer, ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 3.25 (2 H, m, CH₂NⁱPr), 2.99 (4 H, overlapping 2 × m with major isomer, CH₂NⁱPr and CH₂NMe), 2.42 (2 H, m, CH₂NMe), 2.09 (3 H, s, C₆H₄Me), 1.35 (12 H, d, ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 1.30 (3 H, s, NMe), 1.29 (12 H, d overlapping with major isomer, ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 0.95 (6 H, d, ³*J* = 6.7 Hz, NCHMeMe), 0.76 (6 H, d, ³*J* = 6.7 Hz, NCHMeMe) ppm. ¹³C{¹H} NMR (C₆D₆, 100.6 MHz): δ 196.7 (TiC=CH), 147.2 (*o*-C₆H₃ⁱPr₂), 144.8 (*i*-C₆H₄Me), 143.5 (TiC=CH), 141.3 (*i*-C₆H₃ⁱPr₂), 132.6 (*p*-C₆H₄Me), 129.0 (*o*-C₆H₄Me), 127.5 (*p*-C₆H₃ⁱPr₂), 125.7 (*m*-C₆H₄Me), 123.9 (*m*-C₆H₃ⁱPr₂), 119.6 (BNCH), 57.1 (CH₂NMe), 54.4 (NCHMeMe), 46.7 (CH₂NⁱPr), 43.8 (NMe), 25.9 (C₆H₃(CHMeMe)₂), 23.7 (C₆H₃(CHMeMe)₂), 23.7 (NCHMeMe), 21.6 (NCHMeMe), 21.0 (C₆H₄Me) ppm. *Common data*: ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): 22.1 ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 2078 (w), 1930 (w), 1867 (w), 1656 (s), 1585 (m), 1568 (w), 1504 (m), 1487 (m), 1361 (m), 1276 (m), 1227 (w), 1116 (m), 1104 (m), 1042 (w), 994 (w), 944 (m), 898 (w), 762 (m), 648 (m). EI-MS: *m/z* = 519 [TolC(H)C(H)N(H)B(NAr'CH)₂]⁺ (95%). Anal. found (calcd. for C₄₆H₆₉BN₆Ti): C, 72.12 (72.24); H, 9.09 (9.09); N, 10.88 (10.99)%.

Ti(N₂ⁱPrN^{Me})₂{N{B(NAr'CH)₂}C(H)C(Ar^F)} (**20**). To a solution of Ti(N₂ⁱPrN^{Me})₂{NB(NAr'CH)₂}(py) (**11**, 0.300 g, 0.412 mmol) in toluene (10 mL) was added Ar^FCCH (55 μL, 0.412 mmol) at RT. The mixture was heated to 60 °C, stirred for 16 h and then the volatiles removed under reduced pressure to yield **20** as a brown, waxy solid. Yield: 0.253 g (73%). *Major isomer (trans-20)*: ¹H NMR (C₆D₆, 500.3 MHz): δ 9.29 (1 H, s, TiC=CH), 7.28 – 7.17 (multiple m overlapping with minor isomer, *m*- and *p*-C₆H₃ⁱPr₂), 5.97 (2 H, s, BNCH), 4.27 (2 H, sept. overlapping with minor isomer, ³*J* = 6.5 Hz, NCHMeMe), 3.50 (4 H, sept. overlapping with minor isomer, ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 3.22 (2 H, m, CH₂NⁱPr), 2.89 (4 H, overlapping 2 × m, CH₂NMe and CH₂NⁱPr), 2.40 (2 H, m, CH₂NMe), 1.89 (3 H, s, NMe), 1.37 (12 H, d, ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 1.29 – 1.25 (12 H, d overlapping with minor isomer, C₆H₃(CHMeMe)₂), 0.97 (6 H, d, ³*J* = 6.5 Hz, NCHMeMe), 0.71 (6 H, d, ³*J* = 6.5 Hz, NCHMeMe) ppm. ¹³C{¹H} NMR (C₆D₆, 125.7 MHz): δ 168.7 (TiC=CH), 147.6 (TiC=CH), 147.0 (*o*-C₆H₃ⁱPr₂), 142.7 (m, *o*-C₆F₅), 140.8 (*i*-C₆H₃ⁱPr₂), 140.4 (m, *m*-C₆F₅), 136.9 (m, *p*-C₆F₅), 127.8 (*p*-C₆H₃ⁱPr₂), 124.0 (*m*-C₆H₃ⁱPr₂), 122.2 (td, ²*J*_{C-F} = 17.9 Hz, ³*J*_{C-F} = 3.5 Hz, *i*-C₆F₅), 119.9 (BNCH), 56.8 (CH₂NMe), 54.7 (NCHMeMe), 46.8 (CH₂NⁱPr), 43.4 (NMe), 28.9 (C₆H₃(CHMeMe)₂), 25.9 (C₆H₃(CHMeMe)₂), 23.7 (C₆H₃(CHMeMe)₂), 23.0 (NCHMeMe), 21.5 (NCHMeMe) ppm. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): -144.1 (2 F, m, *o*-C₆F₅), -164.5 (1 F, t, ³*J* = 21.5 Hz, *p*-C₆F₅), -165.6 (2 F, m, *m*-C₆F₅). *Minor isomer (cis-20)*: ¹H NMR (C₆D₆, 500.3 MHz): δ

10.32 (1 H, s, TiC=CH), 7.28 – 7.17 (multiple m overlapping with major isomer, *m*- and *p*-C₆H₃ⁱPr₂), 6.17 (2 H, s, BNCH), 4.27 (2 H, sept. overlapping with major isomer, ³*J* = 6.5 Hz, NCHMeMe), 3.50 (4 H, sept. overlapping with major isomer, ³*J* = 6.9 Hz, C₆H₃(CHMeMe)₂), 3.31 (2 H, m, CH₂NⁱPr), 2.95 (2 H, m, CH₂NⁱPr), 2.75 (2 H, m, CH₂NMe), 2.17 (2 H, m, CH₂NMe), 1.29 – 1.25 (24 H, 2 × d overlapping with major isomer, C₆H₃(CHMeMe)₂), 1.10 (3 H, s, NMe), 0.94 (6 H, d, ³*J* = 6.5 Hz, NCHMeMe), 0.90 (6 H, d, ³*J* = 6.5 Hz, NCHMeMe) ppm. ¹³C{¹H} NMR (C₆D₆, 125.7 MHz): δ 183.3 (TiC=CH), 149.7 (TiC=CH), 146.9 (*o*-C₆H₃ⁱPr₂), 141.2 (*i*-C₆H₃ⁱPr₂), 127.7 (*p*-C₆H₃ⁱPr₂), 124.1 (*m*-C₆H₃ⁱPr₂), 120.2 (NCH), 57.1 (NCHMeMe), 57.0 (CH₂NMe), 47.3 (CH₂NⁱPr), 41.3 (NMe), 28.9 (C₆H₃(CHMeMe)₂), 24.9 (C₆H₃(CHMeMe)₂), 23.9 (C₆H₃(CHMeMe)₂), 22.2 (NCHMeMe), 22.1 (NCHMeMe) ppm. Those resonances belonging to the Ar^F ring could not be satisfactorily assigned. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): δ -141.7 (2 F, m, *o*-C₆F₅), -164.9 (1 F, t, ³*J* = 21.5 Hz, *p*-C₆F₅), -166.2 (2 F, m, *m*-C₆F₅) ppm. *Common data*: ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): 22.7 ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 3438 (w), 3065 (w), 1929 (w), 1655 (m), 1638 (m), 1585 (m), 1512 (s), 1415 (s), 1288 (w), 1228 (w), 1203 (w), 1176 (w), 1117 (m), 1007 (m), 989 (m), 976 (m), 960 (s), 940 (w), 898 (w), 888 (w), 865 (w), 823 (s), 759 (s), 674 (w), 649 (w), 620 (w), 606 (m), 566 (w). EI-MS: *m/z* = 595 [Ar^FC(H)C(H)N(H)B(NAr'CH)₂]⁺ (100%). Anal. found (calcd. for C₄₅H₆₂BF₅N₆Ti): C, 64.09 (64.29); H, 7.59 (7.43); N, 9.90 (10.00)%.

NMR tube scale synthesis of Ti(N₂ⁱPrN^{Me}){N{B(NAr'CH)₂}C(H)C(Ar^F)} (20). To an NMR tube fitted with a J. Youngs valve was added a solution of Ti(N₂ⁱPrN^{Me}){NHB(NAr'CH)₂}(CCAr^F) (**19**, 0.0150 g, 0.0178 mmol) in C₆D₆ (0.6 mL). The tube was heated at 70 °C for 16 h, after which time the ¹H NMR spectrum indicated quantitative conversion to **20**.

Ti(N₂N^{py}){NB(NAr'CH)₂}(py) (21). To a Schlenk flask containing Ti{NB(NAr'CH)₂}Cl₂(py)₃ (**3**, 1.50 g, 1.98 mmol) and Li₂N₂N^{py} (0.668 g, 2.08 mmol) was added toluene (25 mL) at -78 °C. The mixture was allowed to warm to room temperature and then stirred for 3 h, after which it had become a dark orange suspension. The volatiles were removed under reduced pressure, and the product extracted into hexane (2 × 20 mL). The solvent was removed from the combined extracts under reduced pressure, resulting in **21** as an orange solid, which was dried *in vacuo*. Yield: 1.38 g (83%). Diffraction-quality crystals were grown from a concentrated pentane solution cooled to 5 °C. ¹H NMR (C₆D₆, 400.1 MHz): δ 8.70 (2 H, d, ³*J* = 4.6 Hz, 2,6-py), 8.05 (1 H, br. m, 6-C₅H₄N), 7.18 (6 H, overlapping 2 × m, *m*- and *p*-C₆H₃ⁱPr₂), 7.03 (1 H, m, 4-py), 6.88 (1 H, m, 4-C₅H₄N), 6.70 (1 H, d, ³*J* = 8.0 Hz, 3-C₅H₄N), 6.53 (3 H, m, overlapping 3,5-py and 5-C₅H₄N), 5.89 (2 H, s, NCH), 3.90 (4 H, sept., ³*J* = 6.9 Hz, CHMeMe), 3.36 (2 H, d, ²*J* = 12.4 Hz, NCH₂), 3.09 (2 H, d, ²*J* = 12.4 Hz,

NCH₂), 1.40 (12 H, d, ³J = 6.9 Hz, CHMeMe), 1.34 (12 H, d, ³J = 6.9 Hz, CHMeMe), 0.94 (3 H, s, CMe), 0.09 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR (C₆D₆, 100.6 MHz): δ 159.6 (2-C₅H₄N), 150.9 (2,6-py), 150.6 (6-C₅H₄N), 147.6 (*o*-C₆H₃ⁱPr₂), 143.2 (*i*-C₆H₃ⁱPr₂), 137.1 (4-py), 136.6 (4-C₅H₄N), 126.6 (*p*-C₆H₃ⁱPr₂), 123.7 (*m*-C₆H₃ⁱPr₂), 123.3 (3,5-py), 121.2 (5-C₅H₄N), 119.9 (3-C₅H₄N), 117.3 (NCH), 63.9 (NCH₂), 45.3 (CMe), 28.5 (CHMeMe), 26.2 (CHMeMe), 24.4 (CHMeMe), 24.0 (CMe), 1.0 (SiMe₃) ppm. ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): δ 14.5 ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 2781 (w), 1601 (s), 1570 (m), 1240 (m), 1209 (w), 1177 (w), 1113 (m), 1053 (s), 994 (m), 952 (w), 892 (m), 875 (w), 829 (m), 775 (w), 762 (m), 701 (m), 668 (m), 643 (m), 560 (w). EI-MS: *m/z* = 756 [*M* – py]⁺ (38%). Anal. found (calcd. for C₄₆H₇₀BN₇Si₂Ti): C, 65.95 (66.09); H, 8.58 (8.44); N, 11.88 (11.73)%.

Ti(N₂N^{py}){N{B(NAr'CH)₂}C(H)C(Tol)} (**22**). To a solution of Ti(N₂N^{py}){NB(NAr'CH)₂}(py) (**21**, 0.300 g, 0.359 mmol) in toluene (10 mL) was added TolCCH (46 μL, 0.359 mmol) at RT. The mixture was heated to 60 °C and stirred for 2 h, then the volatiles removed under reduced pressure. The dark brown waxy solid was then dissolved in hexane (10 mL), concentrated to ~5 mL and cooled to 5 °C, resulting in deep brown, diffraction-quality crystals of **22**. Yield: 0.076 g (24%). ¹H NMR (C₆D₆, 400.1 MHz): δ 9.56 (1 H, s, TiC=CH), 9.07 (1 H, d, ³J = 4.3 Hz, 6-C₅H₄N), 7.35 (2 H, d, ³J = 8.0 Hz, *m*-C₆H₄Me), 7.20 – 7.09 (9 H, 5 × m overlapping with residual protio solvent resonance, *m*- and *p*-C₆H₃ⁱPr₂ and 3,4,5-C₅H₄N), 6.88 (2 H, d, ³J = 8.0 Hz, *o*-C₆H₄Me), 6.21 (2 H, s, NCH), 4.07 (2 H, d, ²J = 12.3 Hz, NCH₂), 3.55 (4 H, sept., ³J = 6.9 Hz, CHMeMe), 3.22 (2 H, d, ²J = 12.3 Hz, NCH₂), 2.18 (3 H, s, C₆H₄Me), 1.29 (12 H, d, ³J = 6.9 Hz, CHMeMe), 1.15 (3 H, s, CMe), 1.12 (12 H, d, ³J = 6.9 Hz, CHMeMe), -0.26 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR (C₆D₆, 125.7 MHz): δ 210.6 (TiC=CH), 162.0 (2-C₅H₄N), 154.9 (TiC=CH), 146.9 (*o*-C₆H₃ⁱPr₂), 146.7 (6-C₅H₄N), 143.0 (5-C₅H₄N), 140.0 (*i*-C₆H₃ⁱPr₂), 138.5 (4-C₅H₄N), 132.1 (*p*-C₆H₄Me), 129.2 (*p*-C₆H₃ⁱPr₂), 127.6 (3-C₅H₄N), 124.9 (*m*-C₆H₄Me), 123.9 (*m*-C₆H₃ⁱPr₂), 121.1 (*i*-C₆H₄Me), 120.0 (*o*-C₆H₄Me), 119.2 (NCH), 63.4 (NCH₂), 51.0 (CMe), 29.0 (CHMeMe), 26.5 (CHMeMe), 23.8 (CHMeMe), 22.7 (CMe), 21.3 (C₆H₄Me), 0.44 (SiMe₃) ppm. ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): 25.5 ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 3437 (w), 1656 (m), 1601 (w), 1587 (m), 1571 (w), 1403 (s), 1246 (s), 1179 (w), 1159 (w), 1140 (w), 1115 (w), 1059 (m), 915 (m), 856 (s), 837 (s), 806 (m), 780 (w), 762 (m), 683 (w), 645 (m). EI-MS: *m/z* = 519 [TolC(H)C(H)N(H)B(NAr'CH)₂]⁺ (8%). Anal. found (calcd. for C₅₀H₇₃BN₆Si₂Ti): C, 68.66 (68.79); H, 8.52 (8.43); N, 9.51 (9.63)%.

Ti(N₂N^{py}){NHB(NAr'CH)₂}(CCAr^F) (**23**). To a solution of Ti(N₂N^{py}){NB(NAr'CH)₂}(py) (**21**, 0.300 g, 0.359 mmol) in toluene (10 mL) was added Ar^FCCH (47.5 μL, 0.359 mmol) at RT, then the

mixture left to stir for 24 h, resulting in a deep red-brown solution. The volatiles were then removed under reduced pressure, and the crude product dissolved in hexane (10 mL). This solution was concentrated to ~5 mL and cooled to 5 °C, resulting in orange, diffraction-quality crystals of **23**. Yield: 0.075 g (22%). ^1H NMR (C_6D_6 , 400.1 MHz): δ 9.11 (1 H, d, $^3J = 5.3$ Hz, 6- $\text{C}_5\text{H}_4\text{N}$), 7.25 – 7.18 (6 H, overlapping 2 $\times$ m, *m*- and *p*- $\text{C}_6\text{H}_3^i\text{Pr}_2$), 7.13 (1 H, m, 4- $\text{C}_5\text{H}_4\text{N}$), 6.88 (1 H, m, 5- $\text{C}_5\text{H}_4\text{N}$), 6.82 (1 H, d, $^3J = 7.9$ Hz, 3- $\text{C}_5\text{H}_4\text{N}$), 6.08 (1 H, s, $\text{NHB}(\text{NAr}'\text{CH})_2$), 6.01 (2 H, s, NCH), 3.99 (2 H, d, $^2J = 12.8$ Hz, NCH_2), 3.44 (4 H, sept., $^3J = 6.9$ Hz, CHMeMe), 3.16 (2 H, d, $^2J = 12.8$ Hz, NCH_2), 1.28 (12 H, d, $^3J = 6.9$ Hz, CHMeMe), 1.26 (6 H, d, $^3J = 6.9$ Hz, CHMeMe_a), 1.19 (6 H, br. m, CHMeMe_b), 1.06 (3 H, s, CMe), 0.01 (18 H, s, SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.6 MHz): δ 162.0 (2- $\text{C}_5\text{H}_4\text{N}$), 161.1 (TiCCAr^F), 148.7 (m, *o*- C_6F_5), 147.6 (*o*- $\text{C}_6\text{H}_3^i\text{Pr}_2$), 147.5 (6- $\text{C}_5\text{H}_4\text{N}$), 147.2 (*o*- $\text{C}_6\text{H}_3^i\text{Pr}_2$), 139.7 (*i*- $\text{C}_6\text{H}_3^i\text{Pr}_2$), 138.8 (m, *p*- C_6F_5), 138.5 (4- $\text{C}_5\text{H}_4\text{N}$), 136.9 (m, *m*- C_6F_5), 127.6 (*p*- $\text{C}_6\text{H}_3^i\text{Pr}_2$), 124.3 (*m*- $\text{C}_6\text{H}_3^i\text{Pr}_2$), 123.9 (*m*- $\text{C}_6\text{H}_3^i\text{Pr}_2$), 121.2 (5- $\text{C}_5\text{H}_4\text{N}$), 119.5 (3- $\text{C}_5\text{H}_4\text{N}$), 118.0 (NCH), 103.6 (td, $^2J_{\text{C-F}} = 19.0$ Hz, $^3J_{\text{C-F}} = 3.7$ Hz, *i*- C_6F_5), 87.6 (TiCCAr^F), 64.5 (NCH_2), 49.7 (CMe), 28.7 (CHMeMe), 25.7 (CHMeMe), 24.4 (CHMeMe_b), 24.3 (CHMeMe_a), 22.8 (CMe), -0.34 (SiMe_3) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 128.4 MHz): 23.0 ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 376.5 MHz): -138.8 (2 F, m, *o*- C_6F_5), -159.8 (1 F, t, $^3J = 21.4$ Hz, *p*- C_6F_5), -164.7 (2 F, m, *m*- C_6F_5) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 3484 (w), 3409 (w), 3213 (w), 2096 (m, $\nu(\text{C}\equiv\text{C})$), 1604 (m), 1575 (w), 1512 (s), 1492 (s), 1354 (s), 1326 (w), 1289 (w), 1275 (w), 1184 (w), 1141 (m), 1112 (m), 1059 (m), 1047 (m), 989 (s), 958 (s), 913 (s), 890 (w), 839 (s), 808 (m), 754 (m), 688 (w), 657 (m), 645 (w), 611 (m). EI-MS: $m/z = 595$ [$\text{Ar}^F\text{C}(\text{H})\text{C}(\text{H})\text{N}(\text{H})\text{B}(\text{NAr}'\text{CH})_2$] $^+$ (56%). Anal. found (calcd. for $\text{C}_{49}\text{H}_{66}\text{BF}_5\text{N}_6\text{Si}_2\text{Ti}$): C, 61.89 (62.02); H, 7.13 (7.01); N, 9.01 (8.86)%.

Kinetic isotope effect measurements for the reaction of $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NB}(\text{NAr}'\text{CH})_2\}$ (21**) with Ar^FCCH to form $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NHB}(\text{NAr}'\text{CH})_2\}(\text{CCAr}^F)$ (**23**).** To a C_6D_6 solution (0.6 mL) of $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NB}(\text{NAr}'\text{CH})_2\}(\text{py})$ (**21**, 0.0150 g, 0.0179 mmol) in an NMR tube equipped with a J. Youngs valve was added Ar^FCCH or Ar^FCCD (2.4 μL , 0.0179 mmol) *via* microsyringe. The NMR tube was transferred to a temperature-regulated (298 K) probe, and the reaction monitored by ^1H NMR spectroscopy using an array which recorded spectra (4 scans) every 120 s. The formation of **23** (or **23-d1**) was calculated by measuring the integral of an NCH_2 resonance. Initial rate constants were obtained from plots of [**23**] *vs* time.

Competition reaction of $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NB}(\text{NAr}'\text{CH})_2\}(\text{py})$ (21**) with Ar^FCCH and Ar^FCCD .** To a C_6D_6 solution (0.3 mL) of $\text{Ti}(\text{N}_2\text{N}^{\text{py}})\{\text{NB}(\text{NAr}'\text{CH})_2\}(\text{py})$ (**21**, 0.0100 g, 0.0120 mmol) in an NMR tube fitted with a J. Youngs valve was added a C_6D_6 solution (0.3 mL) of Ar^FCCH (7.9 μL , 0.0598

mmol) and Ar^FCCD (8.0 μL, 0.0598 mmol). The mixture was then left at RT for 16 h, with ¹H NMR integration showing the products to be 87% **23** and 13% **23-d₁**.

Ti(N₂N^{py}){N{B(NAr'^FCH)₂}C(H)C(Ar^F)} (24**).** To a solution of Ti(N₂N^{py}){NB(NAr'^FCH)₂}(py) (**21**, 0.267 g, 0.319 mmol) in toluene (10 mL) was added Ar^FCCH (42.5 μL, 0.359 mmol) at RT, then the mixture heated to 60 °C and stirred for 40 h, resulting in a deep brown solution. The volatiles were then removed under reduced pressure, and **24** isolated as a deep brown, waxy solid. Yield: 0.195 g (64%). ¹H NMR (C₆D₆, 500.3 MHz): δ 10.05 (1 H, s, TiC=CH), 9.04 (1 H, d, ³J = 5.2 Hz, 6-C₅H₄N), 7.25 – 7.17 (6 H, overlapping 2 × m, *m*- and *p*-C₆H₃ⁱPr₂), 7.10 (1 H, m, 4-C₅H₄N), 6.89 (1 H, m, 5-C₅H₄N), 6.85 (1 H, d, ³J = 8.1 Hz, 3-C₅H₄N), 6.20 (2 H, s, NCH), 4.09 (2 H, d, ²J = 12.4 Hz, NCH₂), 3.46 (4 H, sept., ³J = 6.9 Hz, CHMeMe), 3.12 (2 H, d, ²J = 6.9 Hz, NCH₂), 1.28 (6 H, d, ³J = 6.9 Hz, CHMe_aMe), 1.26 (12 H, d, ³J = 6.9 Hz, CHMe_bMe), 1.10 (3 H, s, CMe), 1.08 (6 H, br. m, CHMe_bMe), -0.28 (18 H, s, SiMe₃) ppm. ¹³C{¹H} NMR (C₆D₆, 125.7 MHz): δ 177.9 (TiC=CH), 161.4 (TiC=CH), 161.2 (2-C₅H₄N), 147.6 (*o*-C₆H₃ⁱPr₂), 146.4 (6-C₅H₄N), 142.9 (m, *o*-C₆F₅), 140.9 (m, *m*-C₆F₅), 139.5 (*i*-C₆H₃ⁱPr₂), 138.9 (4-C₅H₄N), 137.4 (m, *p*-C₆F₅), 127.6 (*p*-C₆H₃ⁱPr₂), 124.0 (*m*-C₆H₃ⁱPr₂), 121.4 (5-C₅H₄N), 120.2 (3-C₅H₄N), 119.5 (td, ²J_{C-F} = 14.5 Hz, ³J_{C-F} = 4.5 Hz, *i*-C₆F₅), 119.3 (NCH), 63.4 (NCH₂), 50.4 (CMe), 28.6 (CHMeMe), 26.6 (CHMe_aMe), 24.4 (CHMe_bMe), 23.4 (CMe), 0.01 (SiMe₃) ppm. ¹¹B{¹H} NMR (C₆D₆, 128.4 MHz): 25.0 ppm. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): -141.5 (2 F, m, *o*-C₆F₅), -166.9 (2 F, m, *m*-C₆F₅), -168.5 (1 F, tt, ³J = 21.6 Hz, ⁴J 4.1 Hz, *p*-C₆F₅) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 3522 (w), 3436 (w), 3391 (w), 1931 (w), 1865 (w), 1655 (m), 1638 (m), 1602 (m), 1587 (s), 1506 (s), 1327 (m), 1209 (m), 1180 (w), 1116 (m), 1059 (s), 959 (s), 913 (s), 856 (s), 780 (m), 758 (s), 675 (m), 646 (m), 604 (m). EI-MS: *m/z* = 595 [Ar^FC(H)C(H)N(H)B(NAr'^FCH)₂]⁺ (4%). Anal. found (calcd. for C₄₉H₆₆BF₅N₆Si₂Ti): C, 61.88 (62.02); H, 7.10 (7.01); N, 9.02 (8.86)%.

NMR tube scale synthesis of Ti(N₂N^{py}){N{B(NAr'^FCH)₂}C(H)C(Ar^F)} (24**).** To an NMR tube fitted with a J. Youngs valve was added a solution of Ti(N₂N^{py}){NHB(NAr'^FCH)₂}(CCAr^F) (**23**, 0.0150 g, 0.0158 mmol) in C₆D₆ (0.6 mL). The tube was heated at 70 °C for 18 h, after which time the ¹H NMR spectrum indicated quantitative conversion to **24**.

Kinetic isotope effect measurements for the conversion of Ti(N₂N^{py}){NHB(NAr'^FCH)₂}(CCAr^F) (23**) to Ti(N₂N^{py}){N{B(NAr'^FCH)₂}C(H)C(Ar^F)} (**24**).** A C₆D₆ solution (0.6 mL) of Ti(N₂N^{py}){NHB(NAr'^FCH)₂}(CCAr^F) (**23**, 0.0150 g, 0.0158 mmol) or **23-d₁** was transferred to an NMR tube equipped with a J. Youngs valve. A blank C₆D₆ sample was added to the NMR probe at RT, locked and shimmed, and the probe heated to 343 K. After thermal equilibration, the

experimental sample replaced the blank sample, the shimming was checked and an array was set up to record a ^1H NMR spectrum (4 scans) every 120 s (or every 600 s for **23-d**₁). The decay of **23** was calculated by measuring the integral of an NCH₂ doublet. First order rate constants were obtained from linear plots of $-\ln([\mathbf{23}]/[\mathbf{23}]_0)$ vs time.

X-ray data collection and processing procedures. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N₂ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using either an Enraf-Nonius KappaCCD or Agilent Technologies Supernova diffractometer using Mo- K_α or Cu- K_α radiation, respectively. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.⁹ The structures were solved with SIR92¹⁰ or Superflip,¹¹ and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.¹² The CIF supporting information file contains specific details for the refinements of the individual structures. The CCDC codes for the structures in this paper are: CCDC 1575707 – 1575717.

Computational Details. Geometry optimizations for all systems were performed with the Gaussian09 package (rev. D.01)¹³ at the B3PW91 level of hybrid density functional theory in the gas phase with all atoms represented by the def2-svp basis set.¹⁴ For the sterically pruned systems additional single point calculations were carried out on the optimised geometry using the def2-tzvp basis set also in the gas phase, and dispersion was not accounted for in either the optimisation or single point calculations. For the sterically more realistic models dispersion was taken into account both at the optimization and single point stages using Grimme's d3(bj) corrections¹⁵ as implemented in Gaussian09. In addition, the solvent (benzene) influence was taken into consideration in the single point calculations on the gas-phase optimised geometry with SCRF calculations within the SMD model. Gibbs free energies and enthalpies were obtained by summing the SCF or (where appropriate) SMD energy, the gas-phase Gibbs or enthalpy contribution at 298.15 K obtained from the geometry optimisations, and the d3(bj) correction. NMR chemical shifts were computed using the GIAO method¹⁶ as implemented in Gaussian09 at the B3PW91 level. All atoms were described with the pcSseg-2 NMR basis sets of Jensen.¹⁷ The ^{11}B NMR shifts are referenced with respect to the experimental value of 0.0 ppm for BF₃(Et₂O). The Cartesian coordinates for the following structures are provided as a separate file. The total SCF and other energies (Hartree) are given below after each compound or transition state.

Table S3. Total SCF Energies, thermal corrections to enthalpies, thermal corrections to Gibbs free energies (Hartree, at 298.15 K except for values in brackets which are for 343 K) for the species depicted in Figure 8 of the main text or Figure S9 of the SI (gas phase reactions).

Compound or transition state	Total SCF Energy	Thermal correction to H	Thermal correction to G
PhCCH	-308.38073	0.116805	0.07901
Pyridine	-248.27671	0.093032 [0.095377]	0.061356 [0.056351]
Ar ^F CCH	-804.56489	0.080977 [0.084088]	0.032663 [0.084088]
Ar ^F CCD	-804.56489	0.078311 [0.081483]	0.029601 [0.022021]
1Q	-2540.66384	0.499618 [0.508877]	0.39978 [0.38411]
2Q	-2292.35998	0.403413 [0.411025]	0.31716 [0.30365]
3Q_Ar^F	-3096.95878	0.487667 [0.498616]	0.37285 [0.35481]
3Q_Ar^F-d₁	-3096.95878	0.484676 [0.495714]	0.36959 [0.35143]
3Q_Ph	-2600.76993	0.523481	0.41858
4Q_Ph	-2600.74784	0.522475	0.41657
5Q_Ar^F	-3096.97777	0.488148 [0.498957]	0.37596 [0.35833]
5Q_Ar^F-d₁	-3096.97777	0.485035 [0.496028]	0.37265 [0.35502]
5Q_Ar^F_2,1-addition (Markovnikov)	-3096.96477	0.487737	0.37470
5Q_Ph	-2600.78435	0.523855	0.42190
5Q_Ph_2,1-addition (Markovnikov)	-2600.77906	0.523657	0.42212
TS1_Ar^F	-3096.91467	0.482017 [0.492872]	0.36632 [0.34815]
TS1_Ar^F-d₁	-3096.91467	0.480385 [0.491325]	0.36457 [0.34631]
TS1_Ph	-2600.72897	0.517934	0.41286
TS2_Ar^F	-3096.92298	0.485431 [0.496254]	0.37441 [0.35695]

TS2_Ar^F-d₁	-3096.92298	0.482323 [0.493471]	0.37110 [0.35372]
TS2_Ph	-2600.73842	0.521502	0.42005
TS3_2Q_6Q_Ar^F	-3096.90635	0.482583	0.36677
TS3_2Q_6Q_Ph	-2600.72141	0.518427	0.41308
6Q_Ar^F	-3096.93225	0.488928	0.37294
6Q_Ph	-2600.74324	0.524831	0.41995

Table S4. Total SCF energies (E(B3PW91/SMD) + D3(bj), Hartree) and sums of SCF energy and thermal corrections to enthalpies or Gibbs free energies (kcal mol⁻¹ at 298.15 K) for the full experimental compounds.

Compound	Total SCF Energy	SCF Energy + Thermal correction to G	SCF Energy + Thermal correction to H
^t BuNH ₂	-213.83786	-134110.4	-134087.5
XylNH ₂	-366.28228	-229758.0	-229731.2
H ₂ NB(NAr'CH) ₂	-1203.04531	-754589.1	-754527.1
Pyridine	-248.30109	-155772.6	-155752.2
PhCCH			
TolCCH	-347.73761	-218142.7	-218117.4
Ar ^F CCH	-804.59442	-504870.1	-504839.6
Ar ^F CCD	-804.59442	-504872.0	-504841.3
MeCCMe	-155.99220	-97850.9	-97829.8
PhCCMe	-347.74565	-218149.4	-218121.3
^t BuNH ₂ _PhCCH_amination (26)	-522.31858	-327619.4	-327586.4
Borylamine_TolCCH_amination (27a)	-1550.85337	-972759.4	-972685.3
^t BuNH ₂ _TolCCH_amination (27b)	-561.64129	-352279.9	-352243.6
XylNH ₂ _TolCCH_amination (27c)	-714.07979	-447923.7	-447883.4
9	-3479.80015	-2182996.9	-2182900.6
9 _Ar ^F CCH_CH_activation	-4036.09471	-2532094.7	-2531988.6
9 _Ar ^F CCH_cycloaddition	-4036.11985	-2532107.0	-2532004.2
9 _TolCCH_CH_activation	-3579.23021	-2245364.1	-2245260.8
9 _TolCCH_cycloaddition	-3579.25050	-2245374.0	-2245273.8

10	-4116.90231	-2582866.2	-2582763.0
10_Ar^FCCH_cycloaddition	-4673.21769	-2645247.0	-2645139.8
10_TolCCH_cycloaddition	-4216.35856	-2645247.7	-2645139.0
11	-2898.28855	-1818112.1	-1818022.9
11_Ar^FCH_activation	-3454.58750	-2167211.9	-2167113.1
11_Ar^FCCH_cycloaddition	-3454.60858	-2167223.2	-2167126.9
11_TolCCH_CH_activation	-2997.71909	-1880481.8	-1880384.1
11_TolCCH_cycloaddition	-2997.74380	-1880493.7	-1880398.4
21	-3632.25490	-2278653.8	-2278552.6
21_py-free	-3383.91930	-2122876.2	-2122781.2
21_Ar^FCCH_CH_activation	-4188.55543	-2627755.1	-2627643.9
21_Ar^FCCD_CD_activation	-4188.55543	-2627757.2	-2627645.8
21_Ar^FCCH_cycloaddition	-4188.57781	-2627766.2	-2627657.2
21_MeCCMe	-3539.93946	-2220726.2	-2220625.6
21_PhCCMe	-3731.70442	-2341028.9	-2340924.0
21_TolCCH_CH_activation	-3731.69194	-2341022.5	-2340918.1
21_TolCCH_cycloaddition	-3731.70870	-2341022.5	-2340918.1
<i>trans</i> -Ti(N ₂ N ^{py}){N(^t Bu)C(H)C(Ph)} (25)	-2703.16808	-1695896.9	-1695825.1
Ti(N ₂ N ^{py})(N ^t Bu)(py)	-2643.02566	-1658170.0	-1658101.2

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