Supplementary Material (ESI) for Chemical Communications

New ligand platforms for developing the chemistry of the Ti=N-NR_2 functional group and insertion of alkynes into the N-N bond of a Ti=N-NPh_2 ligand

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Supporting information

Data for Ti{MeN($CH_2CH_2NSiMe_3$)$_2$}($NNPh_2$)(py) (2). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 8.68 (2 H, d, ^3J = 6.4 Hz, *o*-NC_5H_5), 7.87 (4 H, d, ^3J = 7.6 Hz, *o*-C_6H_5), 7.31 (4 H, app. t, ^3J = 7.1 Hz and 7.6 Hz, *m*-C_6H_5), 6.91 (2 H, t, ^3J = 7.1 Hz, *p*-C_6H_5), 6.68 (1 H, t, ^3J = 7.6 Hz, *p*-NC_5H_5), 6.38 (2 H, app. t, ^3J = 6.4 Hz and 7.6 Hz, *m*-NC_5H_5), 3.56, 3.39 (2 × 2 H, 2 × m, C$\underline{H}_2$NSiMe$_3$), 2.74, 2.56 (2 × 2 H, 2 × m, C$\underline{H}_2$NMe), 2.62 (3 H, s, NMe), 0.03 (18 H, s, $SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 153.9 (*o*-NC_5H_5), 147.9 (*i*-C_6H_5), 138.7 (*p*-NC_5H_5), 129.3 (*m*-C_6H_5), 124.0 (*m*-NC_5H_5), 122.2 (*p*-C_6H_5), 119.1 (*o*-C_6H_5), 63.6 ($\underline{C}H_2$NMe), 50.7 (NMe), 48.2 ($\underline{C}H_2$NSiMe$_3$), 1.9 ($SiMe_3$). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1600 (m), 1586 (s), 1486 (s), 1445 (s), 1308 (w), 1298 (w), 1240 (s), 1211 (w), 1168 (w), 1078 (m), 1064 (m), 1041 (m), 1012 (w), 989 (w), 919 (s), 841 (s), 799 (m), 745 (s), 697 (s), 636 (w), 621 (w). EI-MS: *m/z* 489 $[M\text{-py}]^+$ (16%), 168 $[NPh_2]^+$ (73%). Anal. Found (calcd. for $C_{28}H_{44}N_6Si_2Ti$): C, 59.0 (59.1); H, 7.7 (7.8); N, 14.7 (14.8) %.

Data for Ti{(2-C_5H_4N)$CH_2N(CH_2CH_2NSiMe_3)_2$}($NNPh_2$) (3). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 8.98 (1 H, d, ^3J = 6.5 Hz , 6-NC_5H_4), 7.75 (4 H, d, ^3J = 8.3 Hz, *o*-C_6H_5), 7.24 (4 H, app. t, ^3J = 8.3 Hz and 7.6 Hz, *m*-C_6H_5), 6.87 (2 H, t, ^3J = 7.6 Hz, *p*-C_6H_5), 6.61 (1 H, app. t, ^3J = 7.6 Hz and 7.7 Hz, 4-NC_5H_4), 6.12 (1 H, app. t, ^3J = 7.7 Hz, 5-NC_5H_4), 6.06 (1 H, d, ^3J = 7.6 Hz, 3-NC_5H_4), 3.66 (2 H, m, C$\underline{H}_2$NSiMe$_3$ inner protons), 3.46 (2 H, m, C$\underline{H}_2$NSiMe$_3$ outer protons), 3.01 (2 H, s, C$\underline{H}_2NC_5H_4$), 2.60 (2 H, m, C$\underline{H}_2$N inner protons), 2.08 (2 H, m, C$\underline{H}_2$N outer protons), 0.45 (18 H, s, $SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 159.3 (2-NC_5H_5), 154.5 (6-NC_5H_5), 147.8 (*i*-C_6H_5), 140.0 (4-NC_5H_5), 129.5 (*m*-C_6H_5), 127.8, 123.5 (3-NC_5H_5 and 5-NC_5H_5), 122.0 (*p*-C_6H_5), 120.5 (o-C_6H_5), 57.3 ($\underline{C}H_2NC_5H_5$), 56.4 (NCH_2), 49.2 ($\underline{C}H_2$NSiMe$_3$), 3.2 ($SiMe_3$). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1593 (m), 1583 (m), 1487 (s), 1312 (w), 1237 (m), 1168 (w), 1156 (w), 1086 (s), 1024 (m), 946 (m), 934 (m), 866 (m), 833 (s), 793 (m), 756 (w), 740 (m), 701 (w), 692 (w), 630 (w), 584 (w). EI-MS: *m/z* 168 $[NPh_2]^+$ (88%), 73 [$SiMe_3$] (88 %). Anal. Found (calcd. for $C_{28}H_{42}N_6Si_2Ti$): C, 59.2 (59.3); H, 7.4 (7.5); N, 14.7 (14.8) %

Data for Ti(NNPh$_2$)(BnCalix) (4). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 8.23 (4 H, d, ^3J = 8.8 Hz, *o*-NC_6H_5), 7.26 (4 H, app. t, ^3J = 7.0 Hz and 8.8 Hz, *m*-NC_6H_5), 7.17 (4 H, s, $OC_6\underline{H_2}^tBu$), 7.02 (10 H, m, CC_6H_5), 6.92 (2 H, t, ^3J = 7.0 Hz, *p*-NC_6H_5), 6.79 (4 H, s, $BnOC_6\underline{H_2}^tBu$), 5.63 (4 H, s, $C\underline{H_2}C_6H_5$), 4.48 (4 H, d, ^2J = 12.4 Hz, $ArC\underline{H_2}Ar$ proximal to Bn), 3.05 (4 H, d, ^2J = 12.4 Hz, $ArC\underline{H_2}Ar$ distal to Bn), 1.43 (18 H, s, $OC_6H_2{}^t\underline{Bu}$), 0.68 (18 H, s, $BnOC_6H_2{}^t\underline{Bu}$). ^{13}C-{^{1}H} NMR ($C_6D_6$, 75.4 MHz, 293 K): δ 160.5 (*i*-$OC_6H_2{}^tBu$), 149.3 (*p*-$BnOC_6H_2{}^tBu$), 148.8 (*i*-$BnOC_6H_5{}^tBu$), 146.9 (*p*-NC_6H_5), 140.8 (*p*-$BnOC_6H_2{}^tBu$), 134.8 (*i*-$CH_2C_6H_5$), 133.9 (*o*-$OC_6H_2{}^tBu$), 131.9 (overlapping 2 × $CH_2\underline{C_6}H_5$), 129.9 (*o*-$BnOC_6H_2{}^tBu$), 128.9 ($CH_2\underline{C_6}H_5$), 127.1 (*m*-$BnOC_6H_2{}^tBu$), 124.9 (*m*-$OC_6H_2{}^tBu$), 123.1 (*m*-NC_6H_5), 118.2 (*o*-NC_6H_5), 89.1 ($\underline{C}H_2C_6H_5$), 34.6 ($Ar\underline{C}H_2Ar$), 34.5 ($OC_6H_2\underline{C}Me_3$), 34.1 ($BnOC_6H_2\underline{C}Me_3$), 32.6 ($OC_6H_2C\underline{Me}_3$), 31.0 ($BnOC_6H_2C\underline{Me}_3$). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1587 (m), 1479 (s, broad), 1393 (w), 1361 (m), 1325 (s), 1314 (s), 1273 (s), 1212 (s),1186 (m), 1168 (m), 1121 (m), 1027 (w), 934 (m), 917 (m), 872 (m), 857 (m), 795 (s), 754 (m), 745 (m), 699 (m), 693 (m), 677 (m), 627 (m), 612 (w), 573 (w). EI-MS: *m/z* 1056 [M$^+$] (26 %). Anal. Found (calcd. for $C_{70}H_{76}N_2O_4Ti$): C, 75.6 (79.5); H, 7.3 (7.3); N, 2.5 (2.7) %.

Data for Ti{MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$}{NC(Me)C(Me)NPh$_2$}(py) (6). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 8.31 (2 H, d, ^3J = 5.2 Hz, *o*-NC_5H_5), 7.60 (4 H, d, ^3J = 8.2 Hz, *o*-C_6H_5), 7.27 (4 H, app. t, ^3J = 8.2 Hz, *m*-C_6H_5), 6.89 (2 H, t, ^3J = 8.2 Hz, *p*-C_6H_5), 6.74 (1 H, t, ^3J = 7.6 Hz, *p*-NC_5H_5), 6.44 (2 H, app. t, ^3J = 7.6 Hz, *m*-NC_5H_5), 3.47 (2 H, m, $C\underline{H_2}NSiMe_3$ inner protons), 3.27 (2 H, m, $C\underline{H_2}NSiMe_3$ outer protons), 2.69 (2 H, m, $C\underline{H_2}NMe$ inner protons), 2.50 (3 H, s, NMe), 2.32 (2 H, m, $C\underline{H_2}NMe$ outer protons), 2.16 (3 H, s, NC($\underline{Me}$)) 1.81 (3 H, s, C($\underline{Me}$)NPh_2), 0.07 (18 H, s, $SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 153.2 (*o*-NC_5H_5), 152.4 (N$\underline{C}$Me), 148.3 (*i*-NC_6H_5), 147.1 (*p*-NC_5H_5), 129.4 (*m*-NC_6H_5), 123.8 (*m*-NC_5H_5), 121.5 (*o*-NC_6H_5), 120.7 (*p*-NC_6H_5), 110.9 ($\underline{C}(NPh_2)Me$), 62.5 ($\underline{C}H_2NMe$), 48.2 ($\underline{C}H_2NSiMe_3$), 48.0 (NMe), 24.1 (NC$\underline{Me}$), 15.7 (C(NPh_2)$\underline{Me}$), 2.0 ($SiMe_3$). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1679 (m), 1589 (s), 1491 (s), 1291 (m), 1247 (s), 926 (w), 837 (s), 750 (m), 699 (m). EI-MS: *m/z* 168 [NPh_2]$^+$ (28%). Elemental analysis was not obtained for this complex, which degrades on handling.

Data for Ti{MeN(CH$_2$CH$_2$NSiMe$_3$)$_2$}{NC(Ph)C(Me)NPh$_2$}(py) (7). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 8.08 (2 H, d, ^3J = 4.7 Hz, *o*-NC_5H_5), 7.69 (6 H, overlapping 2 × d, ^3J = 7.6 Hz and 6.4 Hz, *o*-NC_6H_5 and *o*-CC_6H_5), 7.29 (6 H, overlapping 2 × app. t, ^3J = 7.6 Hz, 7.1 Hz and 6.4 Hz, *m*-NC_6H_5 and *m*-CC_6H_5), 7.12 (1 H, t, ^3J = 7.1 Hz, *p*-CC_6H_5), 6.92 (2 H, t, ^3J = 7.1 Hz, *p*-NC_6H_5), 6.69 (1 H, t, ^3J = 7.6 Hz, *p*-NC_5H_5), 6.39 (2 H, app. t, ^3J = 4.7 Hz and 7.6 Hz, *m*-NC_5H_5), 3.34 (2 H, m, $C\underline{H_2}NSiMe_3$ inner protons), 3.22 (2 H, m, $C\underline{H_2}NSiMe_3$ outer protons), 2.64 (2 H, m, $C\underline{H_2}NMe$ inner protons), 2.13 (2 H, m, $C\underline{H_2}NMe$ outer protons), 2.08 (3 H, s, NMe), 1.69 (3 H, s, CH_3), 0.07 (18 H, s, $SiMe_3$). ^{13}C-{^{1}H} NMR

(C_6D_6, 75.4 MHz, 293 K): δ 158.3 (<u>C</u>C_6H_5), 153.5 (*o*-NC_5H_5), 148.0 (*i*-NC_6H_5), 144.9 (*i*-CC_6H_5), 138.3 (*p*-NC_5H_5), 130.3 (*o*-CC_6H_5), 129.7 (*m*-NC_6H_5), 129.6 (*m*-CC_6H_5) 126.5 (*p*-CC_6H_5), 123.6 (*m*-NC_5H_5), 121.6 (*o*-NC_6H_5), 121.0 (*p*-NC_6H_5), 112.4 (<u>C</u>Me), 61.4 (<u>C</u>H_2NMe), 48.6 (<u>C</u>H_2N$SiMe_3$), 47.0 (NMe), 16.2 (C<u>Me</u>), 2.1 ($SiMe_3$). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1601 (m), 1585 (s), 1489 (s), 1459 (s), 1444 (s), 1324 (s), 1240 (s), 1205 (m), 1082 (m), 1066 (s), 1040 (m), 1013 (m), 993 (w), 943 (m), 923 (s), 832 (s), 803 (s), 748 (s), 703 (s), 694 (s), 637 (w), 601 (m). EI-MS: *m/z* 168 $[NPh_2]^+$ (26 %). Anal. Found (calcd. for $C_{37}H_{52}N_6Si_2Ti$): C,64.8 (64.9); H, 7.6 (7.7); N, 12.2 (12.3) %.

Data for PhC(NH_2)C(Me)NPh_2 (8). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.31 (2 H, dd, ^3J = 7.7 ^4J = 1.7 Hz, *o*-CC_6H_5), 7.23 (4 H, d, ^3J = 7.6 Hz, *o*-NC_6H_5), 7.16-7.05 (7 H, overlapping peaks, *m*-NC_6H_5, *m*-CC_6H_5, *p*-CC_6H_5), 6.83 (2 H, tt, ^3J = 7.1 Hz, ^4J = 1.2, *p*-NC_6H_5), 2.99 (2 H, s, NH_2), 1.73 (3H, s, CH_3). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 146.4 (*i*-NC_6H_5), 140.0 (*i*-CC_6H_5), 139.2 (<u>C</u>C_6H_5), 130.0 *m*-NC_6H_5), 129.4 (*o*-CC_6H_5), 128.7 (*m*-CC_6H_5), 128.2 (*p*-CC_6H_5), 122.0 (*p*-NC_6H_5), 121.0 (*o*-NC_6H_5), 111.9 (<u>C</u>CH_3), 16.3 (C<u>C</u>H_3). IR (NaCl plates, Nujol mull, cm^{-1}): ν 3365 (s, br), 2331 (w, br), 1935 (w), 1653 (m), 1588 (s), 1491 (s), 1307 (m), 1300 (m), 1284 (m), 1150 (s, br), 983 (m), 749 (s), 693 (s). EI-MS: *m/z* 300 $[M^+]$ (100%).

Data for Cp*Ti{MeC(N^iPr)$_2$}($NNPh_2$) (9). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.22 (4 H, d, ^3J = 8.8 Hz, *o*-C_6H_5), 7.13 (4 H, dd, ^3J = 7.5 and 8.8 Hz, *m*-C_6H_5), 6.81 (2 H, t, ^3J = 7.5 Hz, *p*-C_6H_5), 3.60 (2 H, sept., ^3J = 6.3 Hz, NC<u>H</u>MeMe), 1.99 (15 H, s, C_5Me_5), 1.65 (3 H, s, $MeCN_2$), 1.04 (6 H, d, ^3J = 6.3 Hz, NCH<u>Me</u>Me), 1.03 (6 H, d, ^3J = 6.3 Hz, NCHMe<u>Me</u>). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 160.7 (CN_2), 147.1 (*i*-C_6H_5), 129.1 (*m*-C_6H_5), 122.0 (*p*-C_6H_5), 120.6 (*o*-C_6H_5), 120.0 (<u>C</u>$_5Me_5$), 49.5 (N<u>C</u>HMeMe), 26.8 (NCH<u>Me</u>Me), 25.8 (NCHMe<u>Me</u>), 12.7 (C_5<u>Me</u>$_5$), 12.3 (<u>Me</u>CN_2). IR (NaCl plates, Nujol mull, cm^{-1}): ν 2609 (w), 1656 (w), 1595 (s), 1586(s), 1488 (s), 1466 (s), 1378 (s), 1339 (m), 1333 (m), 1319 (m), 1311 (m), 1295 (w), 1277 (w), 1254 (m), 1215 (m), 1169 (m), 1160 (w), 1148 (w), 1119 (w), 1071 (w), 1026 (w), 992 (w), 919 (w), 875 (w), 838 (w), 812 (m), 791 (w), 751 (s), 741 (s), 723 (w), 700 (s), 693 (s), 631 (m). EI-MS: *m/z* 506 $[M^+]$ (70 %), 168 $[NPh_2^+]$ (100 %), 77 $[Ph^+]$ (68 %). Anal. found (calcd. for $C_{30}H_{42}N_4Ti$): C, 71.0 (71.1); H, 8.3 (8.4); N, 11.0 (11.1) %.

Data for Cp*Ti{MeC(N^iPr)$_2$}($NNMe_2$) (10).

^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.22 (4 H, d, ^3J = 8.8 Hz, *o*-C_6H_5), 7.13 (4 H, dd, ^3J = 7.5 and 8.8 Hz, *m*-C_6H_5), 6.81 (2 H, t, ^3J = 7.5 Hz, *p*-C_6H_5), 3.60 (2 H, sept., ^3J = 6.3 Hz, NC<u>H</u>MeMe), 1.99 (15 H, s, C_5Me_5), 1.65 (3 H, s, $MeCN_2$), 1.04 (6 H, d, ^3J = 6.3 Hz, NCH<u>Me</u>Me), 1.03 (6 H, d, ^3J = 6.3 Hz, NCHMe<u>Me</u>). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 160.6 (CN_2), 118.9 (<u>C</u>$_5Me_5$), 49.1

(NCHMeMe), 48.3 (NMe), 26.8 (NCHMeMe), 26.1 (NCHMeMe), 12.6 (C_5Me_5), 11.9 ($MeCN_2$). Anal. found (calcd. for $C_{21}H_{41}N_4Ti$): C, 63.0 (62.8); H, 9.8 (10.0); N, 14.5 (14.7) %.

Data for Cp*Ti(NNPh$_2$)Cl(py) (11). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 8.36 (2 H, d, ^3J = 5.3 Hz, *o*-NC_5H_5), 7.49 (4 H, d, ^3J = 8.8 Hz, *o*-C_6H_5), 7.21 (4 H, app. t, ^3J = 7.1 and 8.8 Hz, *m*-C_6H_5), 6.87 (2 H, t, ^3J = 7.4 Hz, *p*-C_6H_5), 6.75 (1 H, t, ^3J = 7.6 Hz, *p*-NC_5H_5), 6.44 (2 H, app. t, ^3J = 6.5 and 7.1 Hz, *m*-NC_5H_5), 1.88 (15 H, s, C_5Me_5). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 150.8 (*o*-NC_5H_5), 146.7 (*i*-C_6H_5), 138.4 (*p*-NC_5H_5), 129.5 (*m*-C_6H_5), 124.6 (*m*-NC_5H_5), 122.9 (*p*-C_6H_5), 120.4 (*o*-NC_5H_5), 118.5 (C_5Me_5), 12.0 (C_5Me_5). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1603 (m), 1593 (s) 1584 (s) 1486 (s) 1444 (s) 1310 (s) 1281 (m) 1239 (s) 1214 (w) 1169 (m) 1152 (m) 1069 (m) 1014 (m) 989 (m) 875 (w) 746 (s) 692 (s) 640 (w) 518 (s). EI-MS: *m/z* 183 $[NNPh_2]^+$ (100), 168 $[NPh_2]^+$ (95 %), 77 $[C_6H_5]^+$ (85 %). Anal. found (calcd. for $C_{27}H_{31}ClN_3Ti$): C, 67.5 (67.4); H, 6.3 (6.5); N, 8.7 (8.7) %.

Data for Cp$_2$Ti(NNPh$_2$)(py) (12). ^{1}H NMR data (C_6D_6, 299.9 MHz, 293 K): 8.39 (2H, d, ^3J = 6.5 Hz, *o*-NC_5H_5), 7.25 (4H, d, ^3J = 8.8 Hz, *o*-C_6H_5), 7.15 (8H, app. t, ^3J = 7.7 and 8.8 Hz, *m*-C_6H_5, 6.88 (2H, t, ^3J = 7.7, *p*-C_6H_5), 6.66 (1H, t, ^3J = 7.6 Hz, *p*-NC_5H_5), 6.23 (2H, app. t, ^3J = 6.5 and 7.6 Hz, *m*-NC_5H_5), 5.88 (10H, s, C_5H_5). ^{13}C-{^{1}H} NMR data (C_6D_6, 75.4 MHz, 293 K): 155.0 (*o*-NC_5H_5), 146.5 (*i*-C_6H_5), 137.0 (*p*-NC_5H_5), 129.9 (*m*-C_6H_5), 123.8 (*m*-NC_5H_5), 123.3 (*p*-C_6H_5), 120.8 (*o*-C_6H_5), 110.0 (C_5H_5). IR (NaCl plates, Nujol mull, cm^{-1}): ν 1597 (m), 1592 (m), 1584 (m), 1575 (w), 1486 (m), 1440 (s), 1291 (w), 1214 (w), 1151 (w), 1096 (s), 1069 (s), 812 (s), 795 (s), 783 (s), 760 (w), 702 (w), 694 (s), 628 (m). EI-MS: *m/z* 168 $[NPh_2]^+$ (52 %), 77 $[C_6H_5]^+$ (10 %), 65 $[C_5H_5]^+$ (70 %). Anal. Found (Calc.) for $C_{27}H_{25}N_3Ti$: C, 73.8 (73.8); H, 5.6 (5.7); N, 9.5 (9.6).

Data for Cp*Ti(NNPh$_2$)(NHNPh$_2$)(py) (13). ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.85 (2 H, d, ^3J = 6.5 Hz, *o*-NC_5H_5), 7.34 (4 H, d, ^3J = 8.8 Hz, *o*-NNC_6H_5), 7.23 (4 H, d, ^3J = 8.8 Hz, *o*-$NHNC_6H_5$), 7.08 (4 H, app. t, ^3J = 7.1 and 8.8 Hz, *m*-NNC_6H_5), 7.02 (4 H, app. t, ^3J = 7.1 and 8.8 Hz, *m*-$NHNC_6H_5$), 6.96 (1 H, s, $NHNPh_2$), 6.84 (2 H, t, ^3J = 7.1 Hz, *p*-NNC_6H_5), 6.74 (2 H, t, ^3J = 7.5 Hz, *p*-$NHNC_6H_5$), 6.66 (1 H, t, ^3J = 7.7 Hz, *p*-NC_5H_5), 6.24 (2 H, dd, ^3J = 7.7 and 6.5 Hz, *m*-NC_5H_5), 1.88 (15 H, s, C_5Me_5). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 152.1 (*o*-NC_5H_5), 150.9 (*i*-$NHNC_6H_5$), 147.1 (*i*-NNC_6H_5), 137.4 (*p*-NC_5H_5), 129.2 (*m*-NNC_6H_5), 128.9 *m*-$NHNC_6H_5$, 123.6 (*m*-NC_5H_5), 122.0 (*p*-NNC_6H_5), 121.0 (*p*-$NHNC_6H_5$), 120.3 (*o*-NC_5H_5), 116.2 (C_5Me_5), 11.9 (C_5Me_5). IR (NaCl plates, Nujol mull, cm^{-1}): ν 2361 (s), 2338 (s), 1942 (w), 1869 (w), 1844 (w), 1829 (w), 1792 (w), 1772 (w), 1750 (w), 1734 (m), 1717 (m), 1700 (m), 1684 (m), 1670 (w), 1663 (s), 1653 (m), 1647 (m), 1636 (w), 1616 (s), 1594 (s), 1586 (s), 1559 (s), 1541 (s), 1507 (s), 1490 (s), 1444 (s), 1419 (m), 1395 (w), 1376 (s), 1328 (s), 1312 (s), 1277 (m), 1252 (m), 1213 (w), 1167 (m), 1158 (m), 1069 (m), 1044 (m), 1025 (m), 988 (m), 927

(w), 838 (), 791 (s), 744 (s), 697 (m), 640 (w). EI-MS: *m/z* 100 (88 %) $[NPh_2]^+$, 77 $[Ph]^+$ (58 %). Anal. found (calcd. for $C_{39}H_{41}N_5Ti$): C 74.5 (74.6), H 6.8 (6.6), N 11.1 (11.2) %

Computational details. All the calculations have been performed with the Gaussian03 package[1] at the B3PW91 level.[2, 3] The titanium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group (12 valence electrons) and its associated basis set,[4] augmented by an f polarization function (α = 0.869).[5] The remaining atoms (C, H, N) were represented by a 6-31G(d,p) basis set.[6] Full optimizations of geometry without any constraint were performed, followed by analytical computation of the Hessian matrix to confirm the nature of the located extrema as minima on the potential energy surface.

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