

Cycloaddition reactions of transition metal hydrazides with alkynes and heteroalkynes: coupling of Ti=NNPh₂ with PhCCMe, PhCCH, MeCN and ^tBuCP

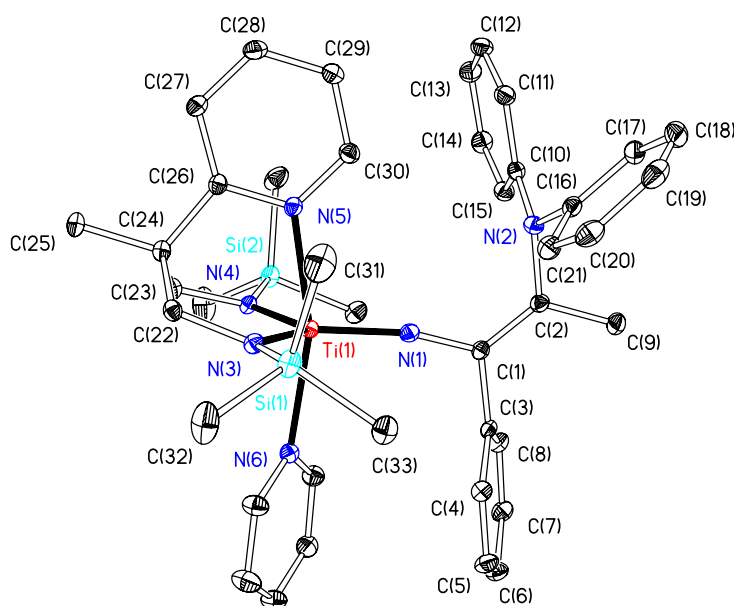
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Characterising data and details of the DFT calculations

Data for Ti(N₂N^{py}){N(NPh₂)C(Me)CPh} (2). ¹H NMR (500.3 MHz, C₆D₆, 298 K): δ 9.06 (1 H, d, ³J = 4.4 Hz, py-H⁶), 7.56 (4 H, d, ³J = 7.8 Hz, *o*-NC₆H₅), 7.40 (2 H, app. t, ³J = 7.8 and 7.3 Hz, *m*-CC₆H₅, app. t), 7.36 (2 H, dd, ³J = 8.3 Hz, ⁴J = 1.6 Hz, *o*-CC₆H₅), 7.20 (4 H, app. t, ³J = 8.8 and 7.8 Hz, *m*-NC₆H₅), 6.96 (1 H, t, ³J = 7.0 Hz, *p*-CC₆H₅), 6.90 (1 H, app. t, app. ³J = 7.2 Hz, py-H⁴), 6.81 (2 H, t, ³J = 7.3 Hz, *p*-NC₆H₅), 6.71 (1 H, d, ³J = 7.9 Hz, py-H³), 6.34 (1 H, app. t, app. ³J = 6.3 Hz, py-H⁵), 4.07 (2 H, d, ²J = 12.7 Hz, CH_aH_bNSiMe₃), 3.26 (2 H, d, ²J = 12.7 Hz, CH_aH_bNSiMe₃), 2.35 (3 H, s, TiC=CMe), 1.13 (3 H, s, CH₂Me), 0.12 (18 H, s, SiMe₃). ¹³C-{¹H} NMR (125.8 MHz, C₆D₆, 298 K): δ 216.1 (TiC=CMe), 161.5 (py-C²), 149.2 (*i*-NC₆H₅), 147.7 (py-C⁶), 146.3 (TiC=CMe), 139.5 (py-C⁴), 129.9 (*m*-NC₆H₅), 128.9 (*i*-CC₆H₅), 128.7 (*m*-CC₆H₅), 126.7 (*o*-CC₆H₅), 122.4 (*p*-CC₆H₅), 121.5 (py-C⁵), 120.0 (*p*-NC₆H₅), 119.5 (*o*-NC₆H₅), 118.5 (py-C³), 63.4 (CH₂NSiMe₃), 51.2 (CH₂Me), 24.2 (CH₂Me), 15.1 (TiC=CMe), 1.3 (SiMe₃). IR (NaCl plates, Nujol mull, cm⁻¹): ν 1589 (s), 1541 (w), 1492 (s), 1458 (m), 1377 (s), 1308 (m), 1245 (m), 1230 (m), 1245 (m), 1200 (w), 1155 (w), 1140 (w), 1087 (w), 1029 (w), 997 (w), 953 (w), 920 (w), 836 (w), 805 (w), 748 (m), 693 (m), 666(m), 589 (w). Anal. found (calcd. for C₃₆H₄₇N₅Si₂Ti): C, 66.19 (66.13); H, 7.32 (7.25); N, 10.65 (10.71) %.

Data for Ti(N₂N^{py}){NC(Ph)C(Me)NPh₂}(py) (3). ¹H NMR (C₆D₆, 299.9 MHz, 293 K): δ 9.31 (1 H, d, ³J = 5.4 Hz, py-H⁶), 8.72 (2 H, d, ³J = 4.7 Hz, *o*-NC₅H₅), 7.65 (4 H, d, ³J = 8.3 Hz, *o*-NC₆H₅), 7.53 (2 H, d, ³J = 7.1 Hz, *o*-CC₆H₅), 7.29 (4 H, overlapping 2 × app. t, *m*-NC₆H₅ and *m*-CC₆H₅), 7.08 (1 H, t, ³J = 7.1 Hz, *p*-CC₆H₅), 7.01 (1 H, t, ³J = 7.1 Hz, *p*-NC₅H₅), 6.93 - 6.82 (3 H, m, overlapping peaks, *p*-NC₆H₅ and py-H⁴), 6.71 (1 H, d, ³J = 8.2 Hz, py-H³), 6.54 (app. t, overlapping peaks, *m*-NC₅H₅ and py-H⁵), 3.52 (2 H, d, ³J = 12.3 Hz, CH_aH_bNSiMe₃), 3.13 (2 H, d, ³J = 12.3 Hz, CH_aH_bNSiMe₃), 1.77 (3 H, s, NC=CMe), 0.96 (3 H, s, CH₂Me), 0.07 (18 H, s, SiMe₃). ¹³C-{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): δ 159.7 (py-C²), 158.2 (NC=CMe), 151.4 (*o*-NC₅H₅), 148.0 (*i*-NC₆H₅), 144.4 (py-C⁶), 137.5 (*p*-NC₅H₅), 137.0 (py-C⁴),

130.0 (*m*-NC₆H₅), 129.6 (*o*-CC₆H₅), 129.5 (*i*-CC₆H₅), 129.4 (*m*-CC₆H₅), 126.0 (*o*-CC₆H₅), 123.7 (*m*-NC₅H₅), 122.0 (*o*-NC₆H₅), 121.5 (py-C⁵), 121.1 (*p*-NC₆H₅), 119.9 (py-C³), 112.3 (NC=CMe), 64.3 (CH₂NSiMe₃), 45.5 (CH₂CMe), 24.2 (NC=CMe), 16.4 (CH₂CMe), 1.24 (SiMe₃). IR (NaCl plates, Nujol mull, cm⁻¹): ν 1772 (w), 1734 (w), 1717 (w), 1700 (w), 1684 (w), 1670 (w), 1653 (s), 1636 (s), 1616 (w), 1600 (w), 1586 (w), 1570 (m), 1559 (m), 1521 (w), 1488 (s), 1456 (w), 1420 (w), 1311 (s), 1242 (s), 1199 (m), 1157 (w), 1139 (w), 1087 (w), 1057 (s), 998 (w), 970 (w), 950 (w), 896 (s), 875 (s), 830 (w), 798 (w), 746 (m), 695 (m), 667 (w), 600 (w), 588 (w). Anal. found (calcd. for C₄₁H₅₂N₆Si₂Ti): C, 67.15 (67.19); H, 7.27 (7.15); N, 11.39 (11.47) %.



Displacement ellipsoid plot (20%) of Ti(N₂N^{py}){NC(Ph)C(Me)NPh₂}(py) (**3**). H atoms and Et₂O of crystallization omitted for clarity. Further details are given in the CIF supporting information.

Data for Ti(N₂N^{py}){N(NPh₂)C(H)CPh} (4**).** ¹H NMR (500.3 MHz, C₆D₆, 298 K): δ 9.47 (1 H, s, TiC=CH), 9.20 (1 H, d, ³J = 4.8 Hz, py-H⁶), 7.43 (4 H, d, ³J = 7.6 Hz, *o*-NC₆H₅), 7.38 (2 H, d, ³J = 7.3 Hz, *o*-CC₆H₅), 7.34 (2 H, app. t, app. ³J = 7.3 and 6.9 Hz, *m*-CC₆H₅), 7.18 (4 H, app. t, app. ³J = 7.6 Hz, *m*-NC₆H₅), 6.96 (1 H, t, ³J = 6.9 Hz, *p*-CC₆H₅), 6.87 – 6.82 (3 H, m, overlapping peaks, py-H⁴ and *p*-NC₆H₅), 6.76 (1 H, d, ³J = 7.9 Hz, py-H³), 6.38 (1 H, app. t, app. ³J = 6.3 Hz, py-H⁵), 4.06 (2 H, d, ²J = 12.4 Hz, CH_aH_bNSiMe₃), 3.29 (2 H, d, ²J = 12.4 Hz, CH_aH_bNSiMe₃), 1.15 (3 H, s, CMe), 0.06 (18 H, s, SiMe₃). ¹³C-{¹H} NMR (125.8 MHz, C₆D₆, 298 K): δ 214.7 (TiC=CH), 162.7 (py-C²), 149.5 (*i*-NC₆H₅), 147.4 (py-C⁶), 145.7 (TiC=CMe), 139.7 (py-C⁴), 130.0 (*m*-NC₆H₅), 128.9 (*i*-CC₆H₅), 128.7 (*m*-CC₆H₅), 125.2 (*o*-CC₆H₅), 123.5 (*p*-CC₆H₅), 122.9 (py-C⁵), 122.1 (*p*-NC₆H₅), 121.7 (*o*-NC₆H₅), 120.2 (py-C³), 63.7 (CH₂NSiMe₃), 51.1 (CMe), 24.2 (CMe), 1.4 (SiMe₃). IR (NaCl plates, Nujol mull, cm⁻¹): ν 1653 (w),

1586 (m), 1559 (w), 1540 (w), 1507 (m), 1487 (s), 1312 (w), 1245 (m), 1141 (w), 1088 (w), 1064 (w), 1030 (w), 919(w), 908 (w), 890 (w), 862 (s), 836 (m), 781 (w), 752 (w), 696 (w), 666 (w), 602 (w). Because of the lability of this compound, an accurate elemental analysis has not yet been obtained.

Data for $\text{Ti}_2(\text{N}_2\text{N}^{\text{py}})_2\{\mu\text{-N}(\text{NPh}_2)\text{C}(\text{Me})\text{N}\}_2$ (5). ^1H NMR (C_6D_6 , 299.9 MHz, 293 K): δ 8.41 (2 H, d, $^3J = 4.7$ Hz, py- H^6), 7.47 (8 H, d, $^3J = 8.2$ Hz, o- C_6H_5), 7.22 (8 H, app. t, app. $^3J = 8.0$ Hz, m- C_6H_5), 6.99 (2 H, td, $^3J = 7.7$ Hz, $^4J = 1.7$ Hz, py- H^3), 6.84 (4 H and 2 H, overlapping peaks, p- C_6H_6 and py- H^3), 6.57 (2 H, dd, $^3J = 8.0$ and 4.7 Hz, py- H^5) 4.71 (4 H, d, $^2J = 14.1$ Hz, $\text{CH}_a\text{H}_b\text{NSiMe}_3$), 3.28 (4 H, d, $^2J = 13.5$ Hz, $\text{CH}_a\text{H}_b\text{NSiMe}_3$), 1.94 (6 H, s, NCMe), 1.48 (6 H, s, CH_2CMe), 0.33 (36 H, s, SiMe_3). $^{13}\text{C}\{-^1\text{H}\}$ NMR (C_6D_6 , 75.4 MHz, 293 K): δ 185.3 (NCMe), 166.3 (py- C^2), 149.4 (py- C^6), 146.8 (i- C_6H_5), 136.0 (py- C^4), 129.6 (m- C_6H_5), 122.0 (p- C_6H_5), 121.6 (py- C^5), 121.0 (py- C^3), 120.1 (o- C_6H_5), 62.8 (CH_2CMe), 54.6 ($\text{CH}_2\text{NSiMe}_3$), 24.1 (NCMe), 21.1 (CH_2CMe), 3.5 (SiMe_3). IR (NaCl plates, Nujol mull, cm^{-1}): ν 3069 (w), 1587 (s), 1492 (s), 1385 (s), 1335 (w), 1315 (m), 1277 (w), 1246 (s), 1175 (w), 1144 (w), 1079 (w), 1006 (s), 962 (w), 950 (w), 922 (m), 845 (s), 785 (m), 744 (m), 700 (m), 691 (m), 684 (m), 666 (w), 622 (w), 582 (w), 554 (w). EI-MS: m/z 168 (13%) $[\text{NPh}_2]^+$, 78 (5%) $[\text{Ph}]^+$. Anal. found (calcd. For $\text{C}_{58}\text{H}_{86}\text{N}_{12}\text{Si}_4\text{Ti}_2$): C, 59.93 (60.08); H, 7.45 (7.48); N, 14.56 (14.50) %.

Data for $\text{Cp}_2\text{Ti}\{\text{N}(\text{NPh}_2)\text{PC}^t\text{Bu}\}$ (7). ^1H NMR (300 MHz, C_6D_6 , 303 K): δ 1.48 (d, $^4J_{\text{PH}} = 1.2$ Hz, 9 H, Bu t), 5.45 (s, 10 H, Cp), 6.83-7.10 (m, 10H, Ar-H); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 303 K): δ -28.9; $^{13}\text{C}\{^1\text{H}\}$ NMR (74.4 MHz, C_6D_6 , 303 K): 36.6 (d, $^3J_{\text{PC}} = 12$ Hz, $\text{C}(\text{CH}_3)_3$), 45.6 (d, $^2J_{\text{PC}} = 14$ Hz, $\text{C}(\text{CH}_3)_3$), 110.4 (Cp), 121.4 (o- C_6H_5), 122.6 (p- C_6H_5), 129.6 (m- C_6H_5) 148.8 (ipso- C_6H_5), PC not observed; IR (NaCl plates, Nujol mull, cm^{-1}): ν 1586 (m), 1489 (m), 1352 (m), 1321 (m), 1296 (m), 1237 (m), 1074 (m), 843 (m); acc. MS/EI m/z (%): 461 [M^+ , 4], 403 [$\text{M}^+ - \text{Bu}$, 12], 178 [Cp_2Ti^+ , 100]; MS (EI) calc. for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{P}_1\text{Ti}_1$: 460.1542, found: 60.152; Anal. calcd. for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{P}_1\text{Ti}_1$: C 70.44, H 6.35, N 6.08 %; found: C 70.59, H 6.46, N 6.18 %.

DETAILS OF THE DFT STUDIES

Calculations have been performed with the Gaussian03 package¹ using the hybrid functional B3PW91.^{2,3} The Ti atom was represented by the pseudo-potential of Dolg et al. and the associated basis set,⁴ augmented by an f polarization function.⁵ The other atoms (C, H, N, and P) were treated with the 6-31G(d,p) basis set.⁶ Full optimizations without any symmetry constraint were performed followed by analytical computations of the Hessian matrix to characterize the extrema located as minimum or transition state. The NMR calculations were performed in the GIAO approximation^{7,8} using IGLOO-II basis sets for C, N, H, and P and the Ahlrichs TZP basis set for Ti.⁹ The ^{31}P chemical shifts were expressed assuming a value of -69 ppm for the calculated free $^t\text{BuCP}$.

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