Supplementary Material (ESI) for Chemical Communications

Transition Metal Dinitrogen Complexes Supported by a Versatile Monoanionic [N_2P_2] Ligand†

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SUPPORTING INFORMATION

Experimental Section

All reactions were performed using standard Schlenk-line techniques or in an MBraun dry box (<1 ppm O_2/H_2O) unless noted otherwise. All glassware, cannulae and Celite® were stored in an oven at >425 K. Pentane, toluene, methylene chloride, diethyl ether, THF, and DME were purified by passage through a column of activated alumina and degassed with nitrogen prior to use.[1] Deuterated solvents were vacuum transferred from sodium/benzophenone (benzene, toluene and THF) or calcium hydride (chloroform and pyridine). NMR spectra were recorded at ambient temperature on Bruker AV-300, AVQ-400, AVB-400 and DRX-500 spectrometers. ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts are given relative to residual solvent peaks and coupling constants (J) are given in Hz. $^{31}P\{^{1}H\}$ chemical shifts are referenced to an external standard of $P(OMe)_3$ set to 1.67 ppm. Infra-red samples were prepared as Nujol mulls and taken between KBr disks. Raman samples were taken as toluene solutions on a DeltaNu Advantage 200A Raman Spectrometer with a 633 nm HeNe laser. Magnetic susceptibility (μ_{eff}) values were determined using the solution Evans' method.[2] Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected. $TiCl_3(THF)_3$,[3], $ZrCl_4(THF)_2$,[4] H[PNP][5], Li[PNP][6], and $ClSiMe_2NHtBu$[7] were prepared using the literature procedures and unless otherwise noted all reagents were acquired from commercial sources. Elemental analyses and mass spectral data were determined at the College of Chemistry, University of California, Berkeley. The X-ray structural determination was performed at CHEXRAY, University of California, Berkeley.

H[N_2P_2] (1). To a solution of $ClSiMe_2NHtBu$ (3.4 g, 21 mmol) in 70 mL pentane was added a solution of Li[PNP] (6.1 g, 20 mmol) in 50 mL pentane dropwise at room temperature. The solution was stirred for 12 h, filtered, and the remaining solid washed with pentane (30 mL). Volatiles were removed *in vacuo* leaving spectroscopically pure product as a colorless oil (7.8 g, 91% yield). H[N_2P_2] thus prepared was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.028 (s, 6 H, $Si(CH_3)_2$), 1.05 (m, 24 H, $PCH(CH_3)_2$), 1.15 (s, 9 H, ^{t}Bu), 1.43 (m, 4 H, $PCH(CH_3)_2$), 1.68 (m, 4 H, NCH_2CH_2P), 2.89 (m, 4 H, NCH_2CH_2P). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.92 (s), 18.67 (m), 20.08 (d), 22.34 (m), 23.01 (d), 33.53 (d), 45.09 (m), 48.91 (d). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ -1.0 (s). IR (cm^{-1}): 1363 (s); 1297 (w); 1250 (s); 1227 (s); 1198 (w); 1108 (m); 1054 (m); 1019 (m); 920 (m); 879 (w); 833 (s); 774 (s); 681 (m); 487 (w); 412 (m).

Li[N_2P_2] (2). To a solution of **1** (11 g, 25 mmol) in 50 mL pentane was added 2.9 M BuLi (9.3 mL, 27 mmol) at -40 °C. The solution was allowed to warm to room temperature and stirred for 4 h. The solution was concentrated under vacuum until precipiration of crystalline material was observed. Cooling to -40 °C resulted in the isolation of colorless crystals (9.2 g, 83% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 0.50 (s, 6 H, $Si(CH_3)_2$), 1.09 (m, 24 H, $PCH(CH_3)_2$), 1.55 (s, 9 H, ^{t}Bu), 1.64 (m, 8 H, $PCH(CH_3)_2$ and NCH_2CH_2P), 3.25 (m, 4 H, NCH_2CH_2P). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 6.39 (s), 19.53 (d), 19.94 (d), 20.63 (d), 24.00 (d), 38.31 (s), 44.23 (d), 52.22 (s). $^{31}P\{^1H\}$ NMR (200 MHz, C_6D_6): δ -3.40 (s). IR (cm^{-1}): 1412 (w); 1354 (m); 1297 (m); 1247 (s); 1220 (m); 1192 (s); 1152 (w); 1096 (m); 1076 (m); 1056 (s); 1020 (m); 994 (w); 967 (w); 909 (m); 879 (w); 842 (s); 825 (s); 794 (m); 761 9s); 700 (m); 649 (m); 605 (w); 514 (w); 496 (m). $H_{51}C_{22}N_2P_2SiLi$: C, 59.95; H, 11.69; N, 6.36. Found: C, 60.14; H, 11.67; N, 6.67. m.p. = 115-116 °C.

[N_2P_2]$TiCl_2$ (3). To a suspension of $TiCl_3(THF)_3$ (0.25 g, 0.68 mmol) in 10 mL toluene was added a solution of **2** (0.30 g, 0.68 mmol) in 5 mL toluene dropwise at room temperature. The solution was stirred for 4 h. The reaction mixture was filtered and concentrated until precipitation of crystalline material was observed. Storage at -40 °C resulted in the formation of turquoise crystals (0.21 g, 56% yield). IR (cm^{-1}): 1359 (s); 1296 (m); 1251 (s); 1225 (m); 1200 (s); 1104 (m); 1040 (s); 1016 (s); 944 (w); 924 (w); 891 (s); 850 (s); 822 (m); 802 (m); 775 (s); 750 (s); 666 (m); 640 (m); 615 (m); 546 (m); 525 (m); 502 (m); 463 (m); 424 (m). Anal. calcd. for $H_{51}C_{22}N_2P_2SiTiCl_2$: C, 47.82; H, 9.32; N, 5.07. Found: C, 47.68; H, 9.33; N, 5.42. m.p. = 146-147 °C. $\mu_{eff} = 1.3\ \mu_B$

[N_2P_2]MnCl (4). To a suspension of $MnCl_2$ (0.086 g, 0.68 mmol) in 10 mL DME was added a solution of **2** (0.30 g, 0.68 mmol) in 5 mL DME dropwise at room temperature. The solution was stirred for 12 h. Following the removal of solvent under vacuum, the product was extracted with toluene, and the resulting solution was concentrated and cooled to -40 °C resulting in the formation of colorless crystalline material (0.20 g, 56% yield). IR (cm^{-1}): 1348 (m); 1242 (m); 1224 (m); 1202 (m); 1056 (s); 1036 (m); 938 (w); 903 (m); 846 (s); 818 (m); 793 (w); 761 (m); 735 (m); 657 (w); 608 (w); 528 (w); 499 (w); 476 (w). Anal. calcd for $H_{51}C_{22}N_2P_2SiMnCl$: C, 50.41; H, 9.83; N, 5.35. Found: C, 50.02; H, 10.06; N, 5.06. m.p. = 153-154 °C. $\mu_{eff} = 5.8\ \mu_B$

[N_2P_2]FeCl (5). To a suspension of $FeCl_2$ (0.086 g, 0.68 mmol) in 5 mL DME was added a solution of **2** (0.30 g, 0.68 mmol) in 5 mL DME dropwise at room temperature. The solution was stirred for 12 h. Following the removal of solvent under vacuum, the product was extracted with toluene, and the resulting solution was concentrated and cooled to -40 °C resulting in the formation of yellow needles (0.22 g, 61% yield). IR (cm^{-1}): 1349 (m); 1309 (w); 1240 (s); 1200 (s); 1095 (s); 1050 (s); 1017 (m); 917 (w); 929 (w); 884 (w); 848 (s); 798 (m); 757 (m); 739 (m); 685 (w); 657 (w); 603 (w); 528 (w). Anal. calcd for $H_{51}C_{22}N_2P_2SiFeCl$: C, 50.32; H, 9.81; N, 5.34. Found: C, 50.03; H, 9.90; N, 5.63. m.p. = 221-223 °C. $\mu_{eff} = 4.9\ \mu_B$

[N_2P_2]$ZrCl_3$ (6): To a suspension of $ZrCl_4(THF)_2$ (1.3 g, 3.4 mmol) in 20 mL toluene was added a solution of **2** in 20 mL toluene dropwise. The reaction mixture was stirred overnight. The solution was filtered, and the solvent was removed under vacuum. The crude product was washed with pentane and dried under vacuum. An analytically pure colorless powder of **6** was collected (1.8 g, 82% yield). ^1H (500 MHz, C_6D_6): δ 0.46 (s, 3 H, $Si(CH_3)_2$); 0.52 (s, 3 H, $Si(CH_3)_2$); 1.03 (m, 20 H, $PCH(C\mathit{H}_3)_2$); 1.37 (m, 4 H, $PCH(C\mathit{H}_3)_2$); 1.48 (s, 9 H, ^{t}Bu); 1.53 (m, 4 H, $PC\mathit{H}(CH_3)_2$); 1.65 (m, 2 H, $-CH_2-$); 2.34 (m, 2 H, $-CH_2-$); 2.87 (m, 1 H, $-CH_2-$); 3.21 (m, 1 H, $-CH_2-$); 3.52 (m, 1 H, $-CH_2-$); 3.77 (m, 1 H, $-CH_2-$). $^{13}C\{^1H\}$ (125 MHz, C_6D_6): δ 1.85; 5.25; 19.12; 19.23; 19.54; 20.01; 20.26; 20.38; 20.57; 20.70; 21.16; 21.53; 23.65; 23.96; 27.01; 27.40; 34.60; 44.94; 51.85; 56.17. $^{31}P\{^1H\}$ (200 MHz, C_6D_6): δ 2.59 (s, 1 P); 16.38 (s, 1 P). IR (cm^{-1}): 1308 (w); 1259 (s); 1226 (m); 1181 (s); 1095 (w); 1061 (m); 1036 (w); 1011 (w); 984 (s); 954 (m); 919 (m); 883 (m); 845 (s); 798 (m); 755 (s); 644 (m); 584 (m); 547 (m); 503 (m); 471 (m); 446 (m). Anal. Calc. for $H_{51}C_{22}Cl_3N_2P_2SiZr$: C, 41.85: H, 8.16; N, 4.44. Found: C, 42.21; H, 8.22; N, 4.28. m.p. = 137-138 °C.

([N_2P_2]$TiCl)_2(\mu$-N_2) (7): To a solution of **3** (950 mg, 1.70 mmol) in 15 mL Et_2O was added a suspension of KC_8 (260 mg, 1.90 mmol) in 15 mL Et_2O at -40 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solution was filtered, and the remaining solid was washed with Et_2O (20 mL). Concentration of the solution followed by cooling at -40 °C overnight lead to the formation of purple crystals of **7** (520 mg, 57% yield). ^1H (500 MHz, C_6D_6): δ 0.23 (s, 3 H, $Si(CH_3)_2$); 0.68 (s, 3 H, $Si(CH_3)_2$); 1.05 (m, 20 H, $PCH(C\mathit{H}_3)_2$); 1.16 (s, 9 H, ^{t}Bu); 1.40 (m, 4 H, $PCH(C\mathit{H}_3)_2$); 1.55 (m, 4 H, $PC\mathit{H}(CH_3)_2$); 2.24 (m, 1 H, $-CH_2-$); 2.47 (m, 1 H, $-CH_2-$); 2.57 (m, 1 H, $-CH_2-$); 2.74 (m, 1 H, $-CH_2-$); 3.03 (m, 1 H, $-CH_2-$); 3.21 (m, 1 H, $-CH_2-$); 3.48 (m, 1 H, $-CH_2-$); 3.69 (m, 1 H, $-CH_2-$). $^{13}C\{^1H\}$ (125 MHz, C_6D_6): δ 1.76; 3.49; 5.38; 18.31; 19.28; 20.53; 20.70; 20.86; 21.29; 23.43; 23.60; 23.75; 23.84; 24.01; 34.07; 36.17; 37.69; 38.02; 49.44; 56.79. $^{31}P\{^1H\}$ (200 MHz, C_6D_6): δ 0.92 (s, 1 P); 32.56 (s, 1 P). IR (cm^{-1}): 1301 (m); 1251 (s); 1200 (m); 1154 (m); 1109 (m); 1054 (s); 1021 (s); 964 (m); 933 (m); 892 (m); 847 (s); 820 (m); 771 (m); 614 (w); 546 (w); 506

(w). Raman (ν_{N-N}): 1300 (cm^{-1}). Anal. Calc. for $H_{102}C_{44}Cl_2N_6P_4Ti_2$: C, 49.75; H, 9.69; N, 7.91. Found: C, 49.87; H, 9.90; N, 7.94. m.p. = 124-126 °C.

($[N_2P_2]TiCH_2Si(CH_3)_3)_2(\mu-N_2)$ (8): To a suspension of **7** (400 mg, 0.38 mmol) in 10 mL of pentane was added a solution of $LiCH_2Si(CH_3)_3$ (71 mg, 0.75 mmol) in 10 mL of pentane at -40 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solution was filtered and concentrated until crystalline material was observed on the side of the flask. Cooling at -40 oC overnight led to the isolation of 150 mg (34% yield) of orange blade-like crystals of **8**. ^{1}H NMR (500 MHz, C_6D_6): δ -0.62 (d, J_{SiH} = 10 Hz, 1 H, $CH_2Si(CH_3)_3$); 0.39 (s, 3 H, $Si(CH_3)_2$); 0.48 (s, 9 H, $CH_2Si(CH_3)_3$); 0.77 (s, 3 H, $Si(CH_3)_2$); 0.98-1.25 (m, 24 H, $PCH(CH_3)_2$); 1.59 (m, 4 H, $PCH(CH_3)_2$); 1.71 (m, 4 H, $-CH_2-$); 1.78 (s, 9 H, ^{t}Bu); 2.30 (m, 1 H, $-CH_2-$); 2.44 (d, J_{SiH} = 10 Hz, 1 H, $CH_2Si(CH_3)_3$); 2.61 (m, 1 H, $-CH_2-$); 3.06 (m, 1 H, $-CH_2-$); 3.41 (m, 1 H, $-CH_2-$). $^{13}C\{^1H\}$ (125 MHz, C_6D_6): δ 5.98; 6.36; 13.81; 17.49; 18.90; 19.19; 19.41; 19.66; 20.45; 20.86; 21.16; 21.72; 22.97; 23.91; 37.89; 45.14; 45.67; 45.92; 50.26; 56.33. $^{31}P\{^1H\}$ (200 MHz, C_6D_6): δ 22.45 (s, 1 P); 0.73 (s, 1 P). IR (cm^{-1}): 1664 (w); 1589 (w); 1254 (s); 1227 (m); 1177 (m); 1109 (m); 1053 (m); 1020 (s); 985 (m); 927 (m); 882 (m); 857 (m); 796 (s); 477 (m). Raman (ν_{N-N}): 1270 (cm^{-1}).Anal. Calc. for $H_{124}C_{52}N_6P_4Si_4Ti_2$: C, 53.57; H, 10.74; N, 7.21. Found: C, 51.46; H, 10.75; N, 7.11. m.p. = 135-136 °C.

($[N_2P_2]Mn)_2(\mu-N_2)$ (9): To a suspension of **4** (mg, mmol) in 5 mL THF was added a solution of sodium naphthalide (mmol) in 5 mL THF at –40 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed under vacuum. Naphthalene was removed by sublimation, and the crude product was extracted with pentane (10 mL). The solution was concentrated until the precipitation of crystalline material was observed. Cooling at -40 °C resulting in the isolation of large dark red blocks of **9** (mg, % yield). IR (cm^{-1}): 1298 (w); 1229 (s); 1196 (m); 1111 (m); 1050 (s); 1017 (s); 927 (m); 833 (s); 776 (m); 689 (m); 646 (m); 490 (m). Raman (ν_{N-N}): 1685 (cm^{-1}). Anal. Calc. for $H_{102}C_{44}N_6P_2Si_2Mn_2$: C, 52.56; H, 10.25; N, 8.36. Found: C, 52.68; H, 10.55; N, 8.31. m.p. (dec) = 108-111 °C. $\mu_{eff} = 8.7\ \mu_B$

($[N_2P_2]Fe)_2(\mu$-$N_2)$ (10): To a suspension of **5** (1.4 g, 2.7 mmol) in 15 mL THF was added a suspension of KC_8 (360 mg, 2.7 mmol) in 10 mL THF at -40 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed under vacuum, and the crude product was extracted with pentane. Following concentration and cooling at -40 °C, large dark red block of **10** were isolated (1.1 g, 80% yield). IR (cm^{-1}): 1417 (w); 1349 (m); 1300 (w); 1239 (m); 1201 (m); 1105 (m); 1077 (w); 1047 (s); 1015 (m); 921 (s); 885 (m); 839 (s); 802 (w); 730 (s); 689 (w); 652 (w); 603 (w); 511 (w); 487 (s). Raman ($\nu_{N\text{-}N}$): 1760 (cm^{-1}). Anal. Calc. for $H_{102}C_{44}N_6P_4Si_2Fe_2$: C, 52.46; H, 10.23; N, 8.35. Found: C, 52.74; H, 10.50; N, 7.97. m.p. = 115-116 °C. μ_{eff} = 7.0 μ_B

($[N_2P_2]ZrCl)_2(\mu$-η^2:η^2-$N_2)$ (11): To reaction bomb containing a solution of **6** (300 mg, 0.48 mmol) in 5 mL THF was added a suspension of KC_8 (140 mg, 1.0 mmol) in 10 mL THF at -70 °C. The reaction mixture was stirred at -70 °C for 3 h and the bomb was sealed. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solution was transferred to a new reaction flask and solvent was removed under vacuum. The crude product was extracted with pentane, and the solution was cooled at -40 °C overnight. Purple crystals of **11** were isolated (45 mg, 17% yield). 3:2 mixture of isomers as determined by $^{31}P\{^1H\}$ NMR. ^1H NMR (400 MHz, C_6D_6): δ 0.36 (s, 9 H, $SiMe_2$); 0.85 (s, 3 H, $SiMe_2$); 0.92 (s, 3 H, $SiMe_2$); 1.12 (m, 45 H, $PCH(CH_3)_2$); 1.28 (m, 12 H, $PCH(CH_3)_2$ and –CH_2-); 1.51 (m, 15 H, $PCH(CH_3)_2$); 1.61-1.71 (m, 8 H, $PCH(CH_3)_2$ and –CH_2-); 1.74 (s, 13.5 H, ^{t}Bu); 1.75 (s, 9 H, ^{t}Bu); 2.11 (m, 4 H, -CH_2-); 2.26 (m, 1 H, -CH_2-); 2.71 (m, 2 H, -CH_2-); 3.11 (m, 1 H, -CH_2-); 3.75 (m, 1 H, -CH_2-); 4.05 (m, 1 H, -CH_2-). $^{31}P\{^1H\}$ (200 MHz, C_6D_6): δ 17.08 (s, 2 P); 14.46 (s, 3 P); 1.54 (s, 2 P); 0.07 (s, 3 P). IR (cm^{-1}): 1297 (w); 1247 (m); 1197 (m); 1046 (s); 969 (w); 930 (w); 880 (m); 848 (s); 818 (m); 762 (s); 704 (s); 676 (w); 611 (w); 530 (m); 493 (w). Anal. Calc. for $H_{102}C_{44}Cl_2N_6P_4Si_2Zr_2$: C, 45.99; H, 8.97; N, 7.32. Found: C, 46.35; H, 9.25; N, 6.97. m.p. = 175-176 °C.

Crystallographic Analysis. Single crystals of **8-11** were coated in Paratone-N oil, mounted on a Kaptan loop, transferred to a Siemens SMART diffractometer or a Bruker APEX CCD area detector,[8] centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that has been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 30-second frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected and the raw data were integrated using SAINT.[9] Cell dimensions reported were calculated from all reflections with $I > 10\sigma$. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Data were analyzed for agreement and possible absorption using XPREP.[10] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[11] The structures were solved using SHELXS[12] and refined on all data by full-matrix least squares with SHELXL-97.[13] Thermal parameters for all non-hydrogen atoms were refined anisotropically. ORTEP diagrams were created using ORTEP-3. A summary of the X-ray diffraction data is presented in Table S1.

Table S1. Summary of crystallographic data collection and refinement for ([N$_2$P$_2$]TiCH$_2$SiMe$_3$)(μ-N$_2$) **8**, ([N$_2$P$_2$]Mn)(N$_2$) **9**, ([N$_2$P$_2$]Fe)$_2$(μ-N$_2$) **10**, and ([N$_2$P$_2$]ZrCl)$_2$(μ-η^2:η^2-N$_2$) **11**

	8	**9**	**10**	**11**
	([N$_2$P$_2$]TiCH$_2$SiMe$_3$)(μ-N$_2$)	([N$_2$P$_2$]Mn)(μ-N$_2$)	([N$_2$P$_2$]Fe)$_2$(μ-N$_2$)	([N$_2$P$_2$]ZrCl)$_2$(μ-η^2:η^2-N
empirical formula	$C_{59.5}H_{142}N_6P_4Si_4Ti_2$	$C_{22}H_{51}MnN_3P_2Si$	$C_{22}H_{51}FeN_3P_2Si$	$C_{22}H_{51}ClN_3P_2SiZr$
formula weight	1274.84	502.63	503.54	574.36
crystal size	0.18 x 0.18 x 0.06 mm	0.15 x 0.08 x 0.08 mm	0.52 x 0.37 x 0.15 mm	0.18 x 0.15 x 0.06 mm
color, habit	orange, block	red, block	red, block	orange, block

temp (K)	148(2)	151(2)	154(2)	151(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/c$	Pbca	$P2_1/c$	P-1
a (Å)	19.224(4)	18.381(2)	11.648(1)	11.956(2)
b (Å)	18.899(4)	15.461(2)	18.056(2)	12.070(3)
c (Å)	23.297(5)	19.772(2)	13.382(1)	12.438(2)
α	90^o	90^o	90^o	$111.753(4)^o$
β	$109.599(2)^o$	90^o	$102.055(1)^o$	$110.138(3)^o$
γ	90^o	90^o	90^o	$100.111(3)^o$
Volume (Å^3)	7974(3)	5619.0(11)	2752.3(5)	1467.6(5)
Z	4	8	4	2
d_c (g/cm^3)	1.062	1.188	1.215	1.300
μ(MoKα) (cm^{-1})	0.38	0.64	0.72	0.63
F(000)	2808	2184	1096	610
no. of reflns collected	35244	26856	13059	9536
no. of unique reflns	13477	4787	5248	5812
R_{int}	0.0856	0.1055	0.0162	0.0556
no. of reflns with $Fo \geq 10\sigma$	3235	1333	5424	750
Reflection/parameters ratio	9.6	12.5	15.5	13.8
GOF	0.987	1.190	1.311	1.081
R, wR_2, R_{all}	0.0583, 0.1187, 0.1509	0.0534, 0.1263, 0.0907	0.0319, 0.0883, 0.0403	0.0651, 0.1336, 0.1144
Max, min (e$^-$/Å^3)	0.393 / -0.316	0.568 / -0.364	0.625 / -0.230	1.166 / -0.639

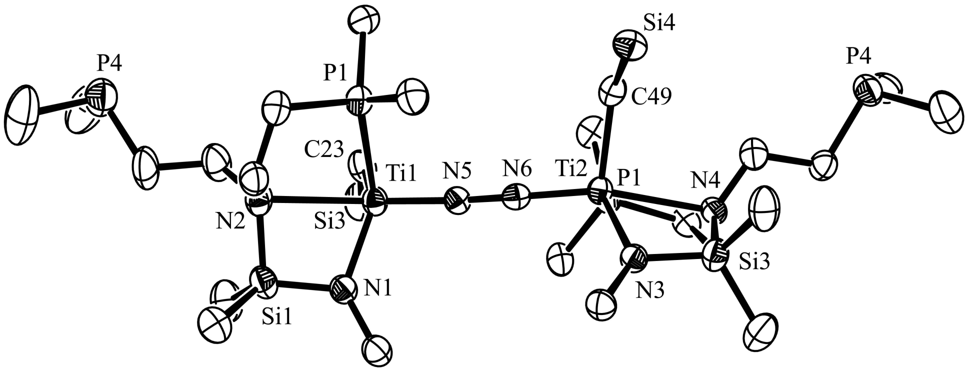

Figure S1. Thermal ellipsoid (50 %) plot of **8**. Hydrogen atoms, *iso*-propyl methyl, *tert*-butyl methyl, and methyl from trimethylsilyl groups have been omitted for clarity.

Table S2. Selected bond lengths (Å) and angles (dec) for ([N_2P_2]$TiCH_2Si(CH_3)_3$)$_2$(μ-N_2) (**8**)

Ti(1)-N(5)	1.783(4)	Ti(1)-N(1)	2.012(3)
Ti(1)-C(23)	2.166(4)	Ti(1)-N(2)	2.497(3)
Ti(1)-P(1)	2.5875(14)	Ti(2)-N(6)	1.782(3)
Ti(2)-N(3)	2.018(3)	Ti(2)-C(49)	2.161(4)
Ti(2)-N(4)	2.520(3)	Ti(2)-P(3)	2.6227(15)
N(5)-N(6)	1.286(4)		
N(5)-Ti(1)-N(1)	110.14(14)	N(5)-Ti(1)-C(23)	102.08(15)
N(1)-T(1)-C(23)	118.12(15)	N(5)-Ti(1)-N(2)	158.80(13)
N(1)-Ti(1)-N(2)	70.50(12)	C(23)-Ti(1)-N(2)	95.59(13)
N(5)-Ti(1)-P(1)	89.01(11)	N(1)-Ti(1)-P(1)	123.55(10)

C(23)-Ti(1)-P(1)	107.89(12)	N(2)-Ti(1)-P(1)	74.36(8)
N(6)-Ti(2)-N(3)	107.44(14)	N(6)-Ti(2)-C(49)	107.13(16)
N(3)-Ti(2)-C(49)	116.36(15)	N(6)-Ti(2)-N(4)	155.69(14)
N(3)-Ti(2)-N(4)	69.77(12)	C(49)-Ti(2)-N(4)	95.04(15)
N(6)-Ti(2)-P(3)	90.51(11)	N(3)-Ti(2)-P(3)	126.46(11)
C(49)-Ti(2)-P(3)	104.68(13)	N(4)-Ti(2)-P(3)	73.98(9)

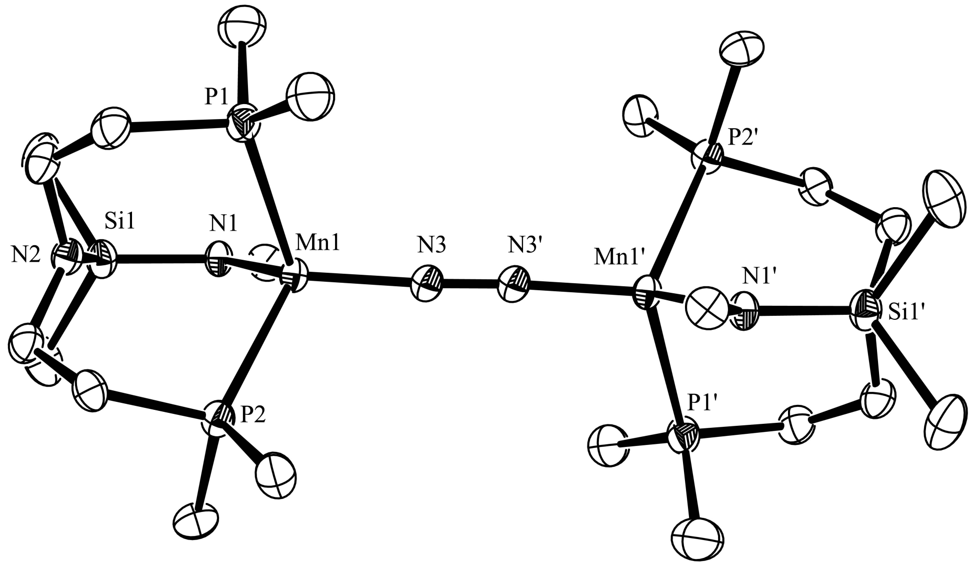

Figure S2. Thermal ellipsoid (50 %) plot of **9**. Hydrogen atoms, *iso*-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity.

Table S3. Selected bond lengths (Å) and angles (dec) for $([N_2P_2]Mn)_2(\mu\text{-}N_2)$ (**9**)

Mn(1)-N(3)	1.860(3)	Mn(1)-N(1)	2.066(3)
Mn(1)-P(1)	2.5514(12)	Mn(1)-P(2)	2.5543(12)
N(3)-N(3’)	1.208(6)		
N(3)-Mn(1)-N(1)	128.21(13)	N(3)-Mn(1)-P(1)	105.07(10)
N(1)-Mn(1)-P(1)	102.08(9)	N(3)-Mn(1)-P(2)	107.33(10)
N(1)-Mn(1)-P(2)	107.91(9)	P(1)-Mn(1)-P(2)	103.61(4)

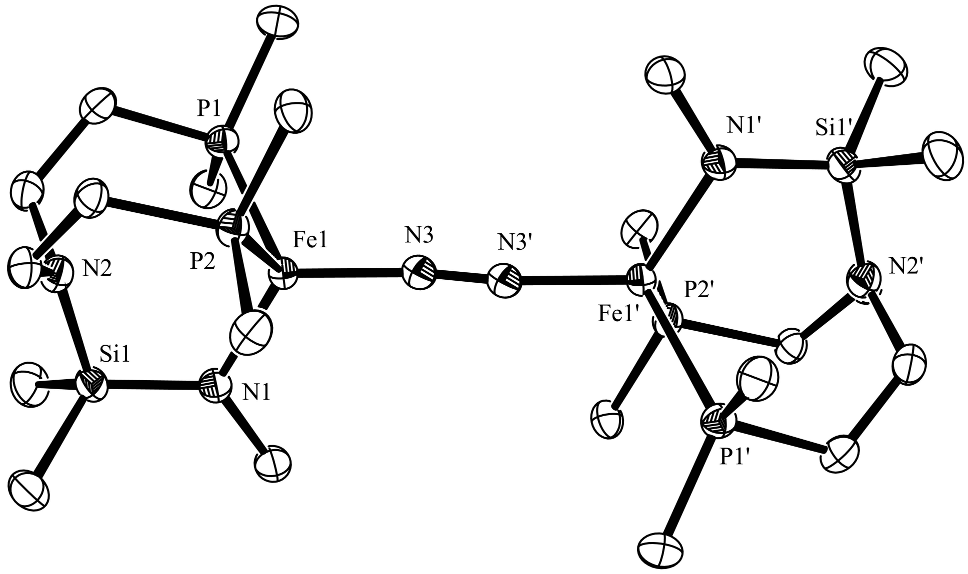

Figure S3. Thermal ellipsoid (50 %) plot of **10**. Hydrogen atoms, *iso*-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity.

Table S4. Selected bond lengths (Å) and angles (dec) for ([N_2P_2]Fe)$_2$(μ-N_2) (**10**)

Fe(1)-N(3)	1.8510(15)	Fe(1)-N(1)	1.9983(15)
Fe(1)-P(1)	2.4465(6)	Fe(1)-P(2)	2.3958(5)
N(3)-N(3’)	1.166(3)		
N(3)-Fe(1)-N(1)	120.99(6)	N(3)-Fe(1)-P(1)	113.64(5)
N(1)-Fe(1)-P(1)	101.34(5)	N(3)-Fe(1)-P(2)	99.97(5)
N(1)-Fe(1)-P(2)	116.41(5)	P(1)-Fe(1)-P(2)	103.756(19)

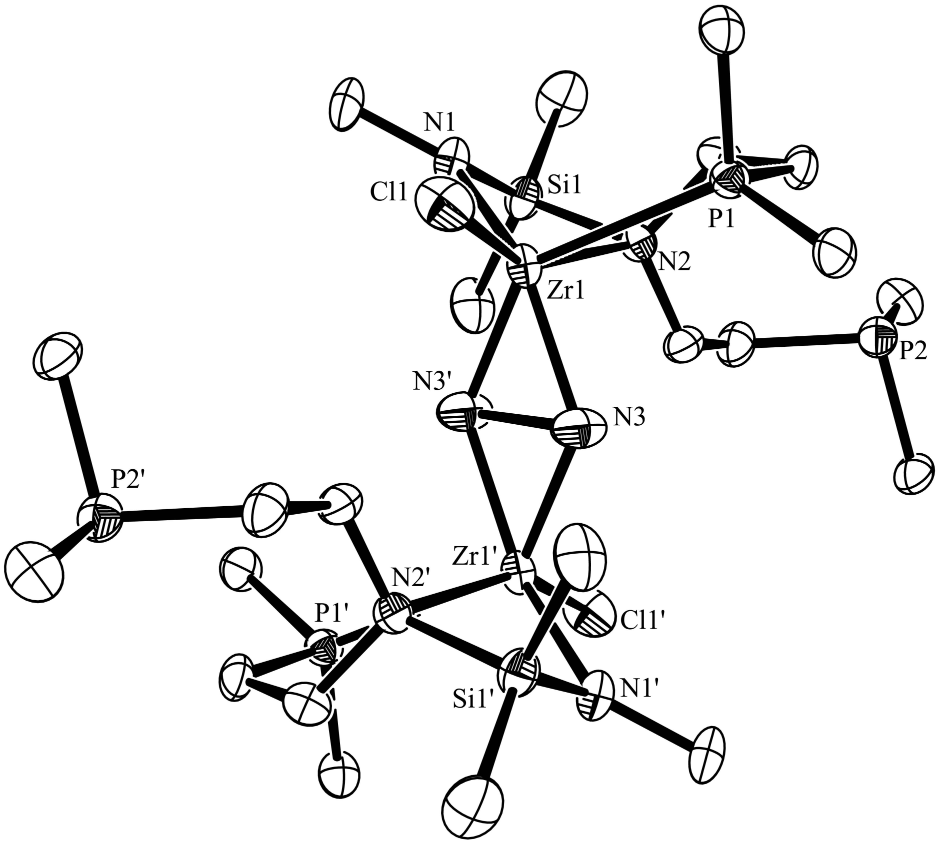

Figure S4. Thermal ellipsoid (50 %) plot of **3**. Hydrogen atoms, *iso*-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity.

Table S5. Selected bond lengths (Å) and angles (dec) for ([N_2P_2]ZrCl)$_2$(μ-η^2:η^2-N_2) (**11**)

Zr(1)-N(3)	2.084(5)	Zr(1)-N(3’)	1.975(5)
Zr(1)-N(1)	2.179(4)	Zr(1)-N(2)	2.456(4)
Zr(1)-P(1)	2.7976(15)	Zr(1)-Cl(1)	2.4757(16)
N(3’)-N(3)	1.576(9)		
N(3’)-Zr(1)-N(3)	45.6(2)	N(3’)-Zr(1)-N(1)	104.06(18)
N(3)-Zr(1)-N(1)	142.87(18)	N(3’)-Zr(1)-N(2)	98.53(19)
N(3)-Zr(1)-N(2)	92.54(17)	N(1)-Zr(1)-N(2)	68.30(15)
N(3’)-Zr(1)-Cl(1)	108.56(16)	N(3)-Zr(1)-Cl(1)	104.74(15)

N(1)-Zr(1)-Cl(1)	105.93(12)	N(2)-Zr(1)-Cl(1)	152.83(11)
N(3')-Zr(1)-P(1)	136.42(14)	N(3)-Zr(1)-P(1)	91.29(13)
N(1)-Zr(1)-P(1)	111.53(12)	N(2)-Zr(1)-P(1)	73.27(10)
Cl(1)-Zr(1)-P(1)	85.34(5)		

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