

Experimental Section

All reactions were performed using standard Schlenk-line techniques or in an MBraun drybox (<1 ppm O₂/H₂O) unless noted otherwise. All glassware, cannulae, and Celite® were stored in an oven at >425 K. Pentane, toluene, diethyl ether, and tetrahydrofuran 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). NMR spectra were recorded at ambient temperature on Bruker AV-300, AVQ-400, AVB-400, and DRX-500 spectrometers. ¹H and ¹³C{¹H} chemical shifts are given relative to residual solvent peaks, and coupling constants (*J*) are given in hertz. ³¹P{¹H} chemical shifts are referenced to an external standard of P(OMe)₃ set to 1.67 ppm. Infrared samples were prepared as Nujol mulls and taken between KBr disks. Magnetic susceptibility (μ_{eff}) values were determined using the solution Evans method at ambient temperature (22 °C).² Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected. Li[N₂P₂],³ phenylazide,⁴ and *p*-tosylazide⁴ 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.

[N₂P₂]CoI (1). To a suspension of CoI₂ (2.83 g, 9.07 mmol) in 50 mL toluene at -70 °C was added a solution of Li[N₂P₂] (4.00 g, 9.08 mmol) in 50 mL toluene *via* cannula. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The dark green solution was filtered, and the remaining solid was washed with 30 mL toluene. The combined filtrates were concentrated and stored at -40 °C overnight, resulting in the formation of dark green crystals (4.66 g, 7.53 mmol) in 83 % yield. ¹H NMR (C₆D₆): δ 23.27 (br s); 8.74 (br s); 4.78 (br s); 4.13 (s); 3.25 (s); 3.09 (s); 2.12 (s); 1.18 (s); 1.09 (s); 0.25 (s). IR (cm⁻¹): 1410 (w); 1350 (w); 1306 (w); 1245 (s); 1198 (s); 1105 (m); 969 (w); 926 (m); 884 (w); 845 (s); 797 (m); 760 (m); 738 (s); 696 (w); 655

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(s); 602 (w); 532 (w); 478 (m). Anal. Calc. for $C_{22}H_{51}CoIN_2P_2Si$: C: 42.64; H: 8.31; N: 4.52. Found. C: 42.86; H: 8.37; N, 4.85. mp - 173-174 °C. $\mu_{eff} = 4.0 \mu_B$.

[N₂P₂]Co (2). To a solution of **1** (2.00 g, 3.23 mmol) in 15 mL of THF at -40 °C was added a suspension of KC₈ (0.460 g, 3.39 mmol) in 15 mL THF *via* cannula. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. After removal of the volatile materials under vacuum, the product was extracted with Et₂O (40 mL) and the filtrate was passed through a bed of Celite®. The solution was concentrated and stored at -40 °C overnight, resulting in the formation of large dark blue needles (1.34 g, 2.72 mmol) in 84 % yield. ¹H NMR (C₆D₆): δ 42.02 (br s); 35.33 (br s); 31.38 (br s); 18.01 (br s); 12.12 (br s); 10.62 (br s); 5.75 (s); 2.10 (s); 0.35 (s); -0.72 (br s); -30.61 (br s). IR (cm⁻¹): 1345 (s); 1321 (w); 1225 (s); 1170 (m); 1093 (s); 1036 (s); 986 (w); 968 (w); 923 (w); 884 (s); 845 (s); 818 (m); 787 (m); 753 (s); 733 (s); 664 (m); 594 (s); 536 (w); 511 (w); 475 (w); 455 (w). Anal. Calc. for $C_{22}H_{51}CoN_2P_2Si$. C: 53.71; H: 10.47; N: 5.70. Found. C: 53.96; H: 10.37; N: 5.80. mp – 126-128 °C. $\mu_{eff} = 3.0 \mu_B$.

[N₂P₂]CoNHC₆H₅ (3). Method A. To a solution of **1** (0.30 g, 0.48 mmol) in 5 mL of THF at -40 °C was added a solution of LiNHC₆H₅ (0.048 g, 0.48 mmol) in 5 mL THF *via* cannula. The color changed from dark green to dark red instantly. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The volatile materials were removed under vacuum and the product was extracted with pentane. The filtrate was concentrated, then stored at -40 °C overnight, resulting in the formation of red-orange blade-like crystals (0.20 g, 0.35 mmol) in 72 % yield.

Method B. To a solution of **2** (0.25 g, 0.51 mmol) in 5 mL of pentane at -40 °C was added a solution of phenylazide (0.061 g, 0.51 mmol) in 5 mL pentane. The solution changed from blue to dark red instantly upon addition of azide. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solution was filtered and concentrated until crystals began to precipitate. The solution was stored at -40 °C overnight, resulting in the formation of red-orange crystals (170 mg, 57 %). Repeating the above in THF yielded 102 mg (34 %); in toluene 70 mg (23 %). ¹H NMR (C₆D₆): δ 39.39 (br s); 30.04 (br s); 4.14 (s); 3.25 (s); 1.66 (s); 1.49 (s); 1.18 (s); 1.09 (s); 0.25 (s); -

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0.82 (s); -3.20 (br s); -87.12 (s). IR (cm^{-1}): 3320 (w); 1585 (s); 1486 (m); 1352 (w); 1295 (s); 1243 (m); 1218 (m); 1169 (w); 1073 (m); 1054 (w); 1023 (w); 986 (w); 900 (m); 848 (s); 816 (w); 796 (w); 767 (m); 745 (s); 688 (m); 661 (w); 568 (w); 506 (w). Anal. Calc. for $\text{C}_{28}\text{H}_{57}\text{CoN}_3\text{P}_2\text{Si}$. C: 57.5; H: 9.84; N: 7.19. Found. C: 57.28; H: 10.06; N: 7.13. mp – 99–101 °C. $\mu_{\text{eff}} = 3.8 \mu_B$. High Resolution MS (EI): 129.5 (M+, $\text{Me}_2\text{SiN}^t\text{Bu}$); 304.6 (M+, $\text{N}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$); 491.6 (M+, $^t\text{BuNSiMe}_2\text{N}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$). For the product of the reaction carried out in C_6D_6 : 130.1 (M+, $\text{Me}_2\text{SiN}^t\text{Bu}$); 304.2 (M+, $\text{N}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$); 493.2 (M+, $^t\text{BuNSiMe}_2\text{N}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$).

[PhN=PⁱPr₂(CH₂)₂NPh][^tBuNSiMe₂N(CH₂)₂PⁱPr₂]Co (5). The compound was isolated by fractional crystallization from the above reaction. Solvent = pentane (< 1 %); THF (0.025 g, 7.3 %); toluene (0.050 g, 15 %). ¹H NMR (C_6D_6): δ 54.74 (s); 49.38 (s); 41.91 (s); 19.33 (s); 15.06 (s); 10.23 (s); 1.40 (s); 0.88 (s); -0.76 (s); -5.29 (s); -6.76 (d); -15.49 (s); -1604 (s); -25.95 (s); -28.92 (s); -59.05 (s). IR (cm^{-1}): 3386 (w); 1586 (s); 1301 (m); 1279 (m); 1241 (s); 1179 (m); 1069 (s); 1033 (m); 1005 (s); 984 (m); 922 (w); 903 (s); 837 (m); 815 (m); 778 (m); 741 (m); 700 (m); 663 (w); 621 (w); 601 (w); 526 (w); 494 (w); 466 (w). Anal. Calc. for $\text{C}_{34}\text{H}_{62}\text{CoN}_4\text{P}_2\text{Si}$. C: 60.41; H: 9.26; N: 8.29. Found. C: 60.34; H: 8.94; N: 8.57. mp – 132–135 °C. $\mu_{\text{eff}} = 4.1 \mu_B$.

[N₂P₂]CoNHC₆H₅CH₃ (4). Method A. To a solution of **1** (0.30 g, 0.48 mmol) in 5 mL of THF at -40 °C was added a solution of LiNHC₆H₅CH₃ (0.073 g, 0.48 mmol) in 5 mL THF *via* cannula. The color changed from dark green to dark red instantly. The reaction mixture was allowed to warm to room temperature and stirred overnight. The volatile materials were removed under vacuum. The product was extracted with pentane, and the filtrate was concentrated and stored at -40 °C overnight, resulting in the formation of dark red blade-like crystals (0.21 g, 0.35 mmol) in 73 % yield.

Method B. To a solution of **2** (0.25 g, 0.51 mmol) in 5 mL of pentane at -40 °C was added a solution of *p*-toslyazide (0.068 g, 0.51 mmol) in 5 mL pentane. The solution changed from blue to dark red instantly upon addition of azide. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The solution was filtered and concentrated until crystals began to precipitate. The solution was stored at -40 °C

overnight, resulting in the formation of dark red crystals (0.095 g, 0.16 mmol) in 32 % yield. ^1H NMR (C_6D_6): δ 102.05 (s); 42.19 (s); 29.61 (br s); 3.24 (s); 1.67 (s); 1.10 (s); 0.25 (s); -3.09 (s); -113.03 (br s). IR (cm^{-1}): 3325 (w); 1605 (s); 1501 (s); 1347 (m); 1289 (s); 1246 (s); 1223 (s); 1173 (m); 1071 (s); 1052 (m); 1036 (m); 933 (w); 899 (m); 846 (s); 809 (s); 771 (s); 758 (m); 741 (s); 691 (w); 666 (w); 608 (w); 579 (w); 546 (m); 505 (m). Anal. Calc. for $\text{C}_{29}\text{H}_{59}\text{CoN}_3\text{P}_2\text{Si}$. C: 58.23; H: 9.96; N: 7.03. Found. C: 57.91; H: 9.86; N: 6.72. mp – 105-107 °C. $\mu_{\text{eff}} = 4.1 \mu_{\text{B}}$.

[$^t\text{BuN}(\text{C}=\text{O})\text{SiMe}_2\text{N}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2\text{]Co(CO)}_2$ (**6**). **Method A.** To a solution of **2** (0.15 g, 0.30 mmol) in 5 mL pentane at -116 °C was added a solution of phenylazide (0.036 g, 0.30 mmol) in 5 mL pentane. A green precipitate formed instantly. The flask was filled with an atmosphere of CO and was sealed using a Teflon stopcock. The reaction mixture was allowed to warm to room temperature, during which time the green color faded to yellow. The volatile materials were vacuum transferred for analysis by GCMS. The remaining solid was extracted with toluene, and the resulting solution was stored at -40 °C overnight. Yellow crystals of **6** were collected (0.13 g, 0.23 mmol) in 78 % yield.

Method B. To a flask containing a solution of **2** (0.20 g, 0.41 mmol) in 10 mL pentane at -70 °C was added an atmosphere of CO. The flask was sealed off, and the reaction mixture was allowed to warm to room temperature. As the reaction warmed, a yellow precipitate formed. The reaction was allowed to stir for 1 h. The solvent was removed under vacuum, and the product was extracted with toluene. The solution was stored overnight at -40 °C, resulting in the formation of large yellow crystals (0.19 g, 0.33 mmol) in 80 % yield. ^1H NMR (C_6D_6): δ 0.28 (s, 3 H, SiMe₂); 0.53 (s, 3 H, SiMe₂); 0.86-1.25 (m, 26 H, PCH(CH₃)₂, PCH(CH₃)₂); 1.55 (s, 9 H, ^tBu); 1.67-1.74 (m, 4 H, -CH₂CH₂- , PCH(CH₃)₂); 1.96 (m, 1 H, -CH₂CH₂-); 2.30-2.48 (m, 3 H, -CH₂CH₂-); 2.68-2.76 (m, 2 H, -CH₂CH₂-). ^{13}C NMR (C_6D_6): δ 3.33; 18.00; 18.38; 18.53; 18.77; 19.44; 20.05; 20.65; 22.54; 22.79; 24.09; 24.54; 25.55; 53.70; 56.71; 59.19; 197.98. ^{31}P NMR (C_6D_6): δ 5.80 (s, 1 P); 77.26 (s, 1 P). IR (cm^{-1}): 1952 (s); 1893 (s); 1583 (s); 1359 (m); 1289 (w); 1251 (m); 1197 (m); 1095 (s); 1069 (s); 1033 (m); 990 (m); 924 (w); 884 (w); 840 (w); 824 (w); 804 (w); 778 (w); 726 (w). mp (dec) – 115-117 °C. Anal. Calc. for $\text{C}_{25}\text{H}_{51}\text{CoN}_2\text{O}_3\text{P}_2\text{Si}$. C: 52.06; H, 8.93; N, 4.86. Found. C: 51.85; H, 9.01; N: 4.75.

Crystallographic Analysis. Single crystals of **1-3**, and **5-6** were coated in Paratone-N oil, mounted on a Kaptan loop, transferred to a Siemens SMART diffractometer or a Bruker APEX CCD area detector,⁵ 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.⁶ 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.⁷ An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.⁸ The structures were solved using SHELXS⁹ and refined on all data by full-matrix least squares with SHELXL-97.¹⁰ 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. Crystal Data and Structure Refinement for **1**, **2**, **3**, **5**, and **6**

	1	2	3	5	6
empirical formula	C ₂₂ H ₅₁ CoIN ₂ P ₂ Si	C ₂₂ H ₅₁ CoN ₂ P ₂ Si	C ₂₈ H ₅₇ CoN ₃ P ₂ Si	C ₃₄ H ₆₂ CoN ₄ P ₂ Si	C ₂₅ H ₅₁ CoN ₂ O ₃ P ₂ Si
fw	619.51	492.61	584.73	675.84	576.64
T (K)	168(2)	244(2)	151(2)	167(2)	160(2)
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /c	Pnma	P2 ₁ /n	P2 ₁ /n	P2 ₁
<i>a</i> (Å)	9.356(2)	14.742(4)	13.154(5)	11.044(3)	8.3023(11)
<i>b</i> (Å)	34.812(8)	11.265(3)	15.801(6)	14.324(4)	12.2795(17)
<i>c</i> (Å)	9.299(2)	17.148(5)	16.304(6)	23.454(6)	15.354(2)
α (°)	90	90	90	90	90
β (°)	105.015(4)	90	102.657(5)	93.105(4)	93.718(2)
γ (°)	90	90	90	90	90
<i>V</i> (Å ³)	2925.4(11)	2847.6(13)	3307(2)	3704.7(16)	1562.1(4)
<i>Z</i>	4	4	4	4	2
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (cm ⁻¹)	1.804	0.768	0.672	0.610	0.716
Num of Ref	5914	2931	4423	7547	5638
R(int)	0.0457	0.0423	0.0745	0.0455	0.0336
R _{obs} (%)	0.0396	0.0528	0.0531	0.0436	0.0417
R _{wobs} (%)	0.0881	0.1429	0.1122	0.1056	0.0889

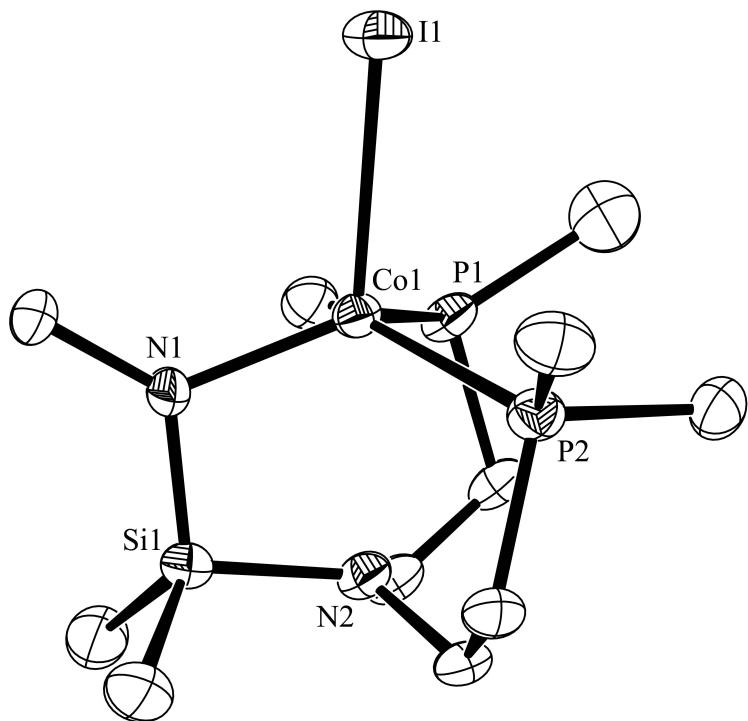


Figure S1. Thermal ellipsoid (50 %) plot of **1**. Hydrogen atoms, *iso*-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity.

Table S2. Selected bond lengths (\AA) and angles (deg) for $[\text{N}_2\text{P}_2]\text{CoI 1}$

Co(1)-I(1)	2.7229(7)	Co(1)-P(1)	2.3947(12)
Co(1)-N(1)	1.957(3)	Co(1)-P(2)	2.3993(13)
N(1)-Co(1)-P(1)	119.01(10)	N(1)-Co(1)-P(2)	112.20(10)
P(1)-Co(1)-P(2)	107.43(4)	N(1)-Co(1)-I(1)	114.58(9)
P(1)-Co(1)-I(1)	96.55(3)	P(2)-Co(1)-I(1)	105.30(4)

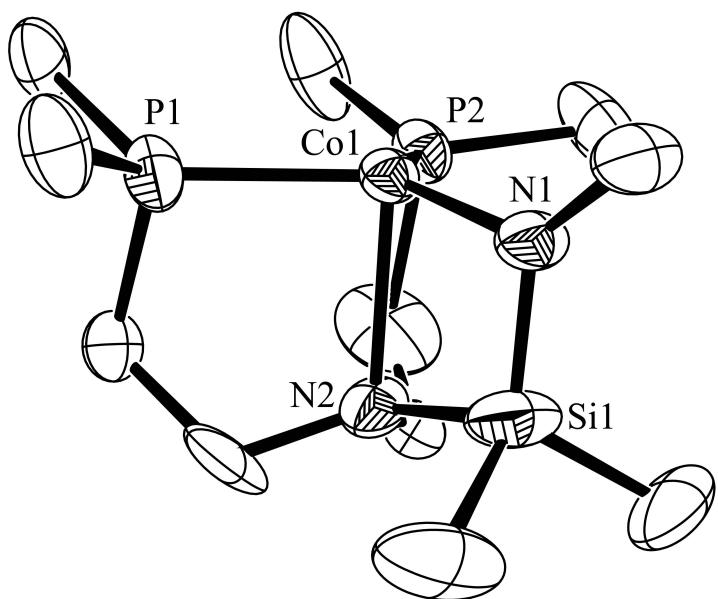


Figure S2. Thermal ellipsoid (30 %) plot of **2**. Hydrogen atoms, *iso*-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity.

Table S3. Selected bond lengths (\AA) and angles (deg) for $[\text{N}_2\text{P}_2]\text{Co}$ **2**

Co(1)-N(1)	1.917(4)	Co(1)-P(1)	2.2124(11)
Co(1)-N(2)	2.207(4)	Co(1)-P(2)	2.2124(11)
N(1)-Co(1)-P(1)	126.46(4)	N(1)-Co(1)-P(2)	126.46(4)
P(1)-Co(1)-P(2)	105.17(6)	N(1)-Co(1)-N(2)	79.76(18)
P(2)-Co(1)-N(2)	88.91(8)	P(1)-Co(1)-N(2)	88.91(8)

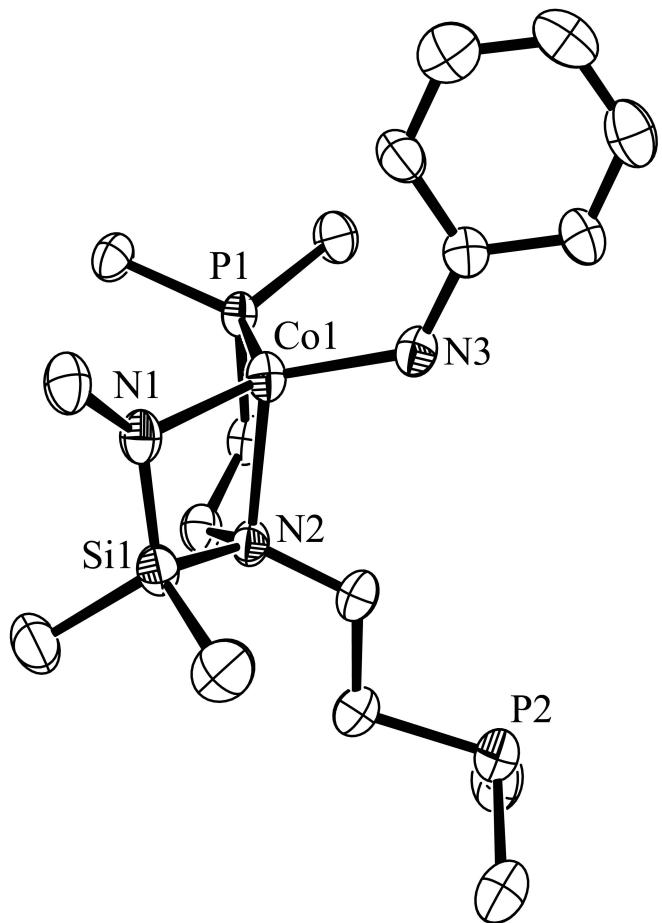


Figure S3. Thermal ellipsoid (50 %) plot of **3**. Hydrogen atoms, *iso*-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity.

Table S4. Selected bond lengths (\AA) and angles (deg) for $[\text{N}_2\text{P}_2]\text{CoNHPh}$ **3**

Co(1)-N(1)	1.908(4)	Co(1)-N(2)	2.241(4)
Co(1)-N(3)	1.906(4)	Co(1)-P(1)	2.3826(17)
N(3)-Co(1)-N(1)	131.49(17)	N(3)-Co(1)-N(2)	109.77(16)
N(1)-Co(1)-N(2)	77.03(16)	N(3)-Co(1)-P(1)	110.18(13)
N(1)-Co(1)-P(1)	118.24(13)	N(2)-Co(1)-P(1)	86.61(11)

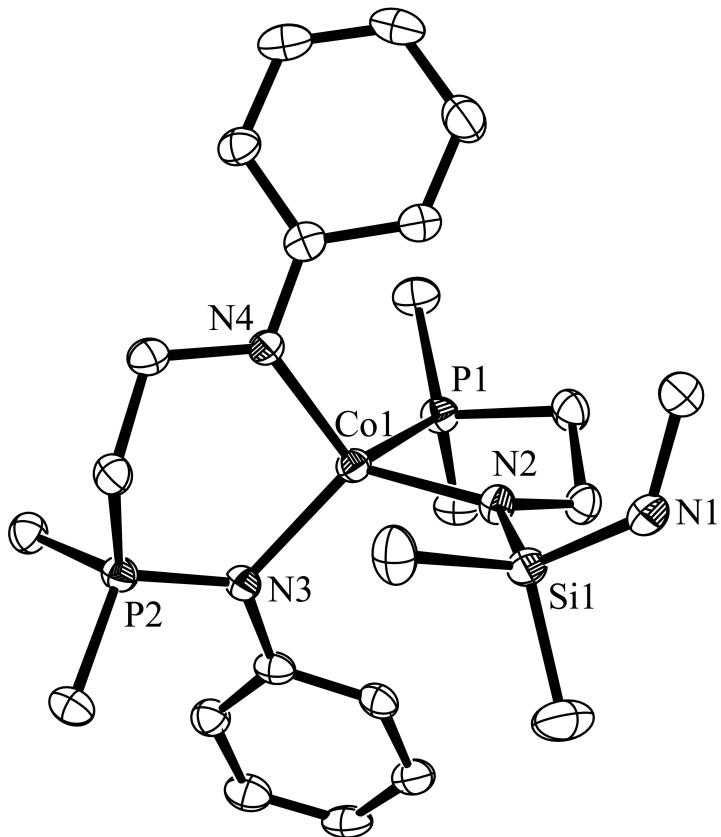


Figure S4. Thermal ellipsoid (50 %) plot of **5**. Hydrogen atoms, *iso*-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity.

Table S5. Selected bond lengths (Å) and angles (deg) for [PhN=PⁱPr₂(CH₂)₂NPh][^tBuN(H)SiMe₂N(CH₂)₂PⁱPr₂]Co **5**

Co(1)-N(2)	1.950(2)	Co(1)-N(4)	1.9779(19)
Co(1)-N(3)	2.0694(19)	Co(1)-P(1)	2.4248(8)
P(2)-N(3)	1.619(2)		
N(2)-Co(1)-N(4)	121.02(9)	N(2)-Co(1)-N(3)	119.95(8)
N(4)-Co(1)-N(3)	103.59(8)	N(2)-Co(1)-P(1)	86.90(6)
N(4)-Co(1)-P(1)	114.26(6)	N(3)-Co(1)-P(1)	110.47(6)

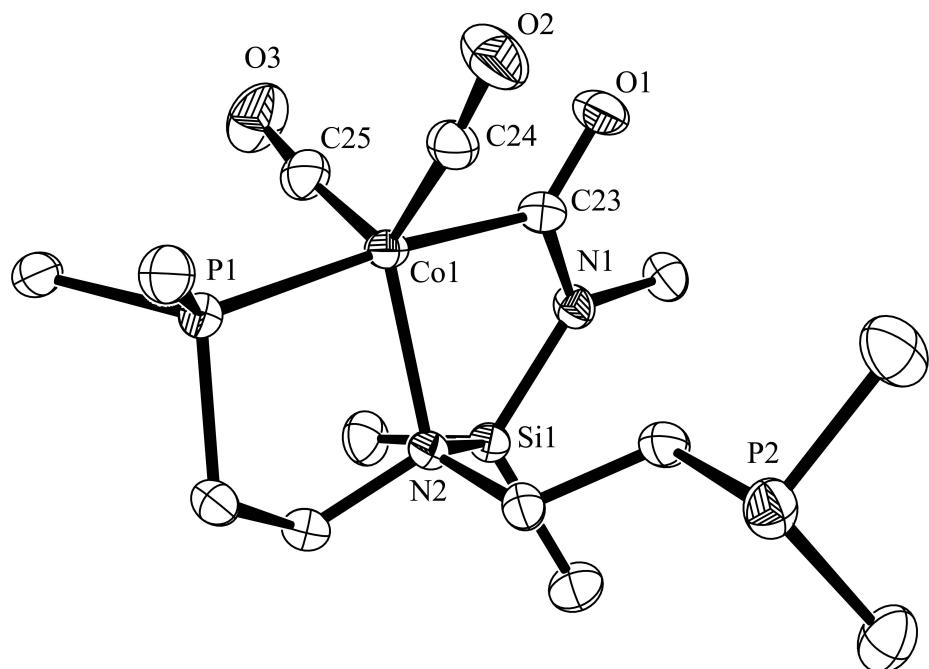


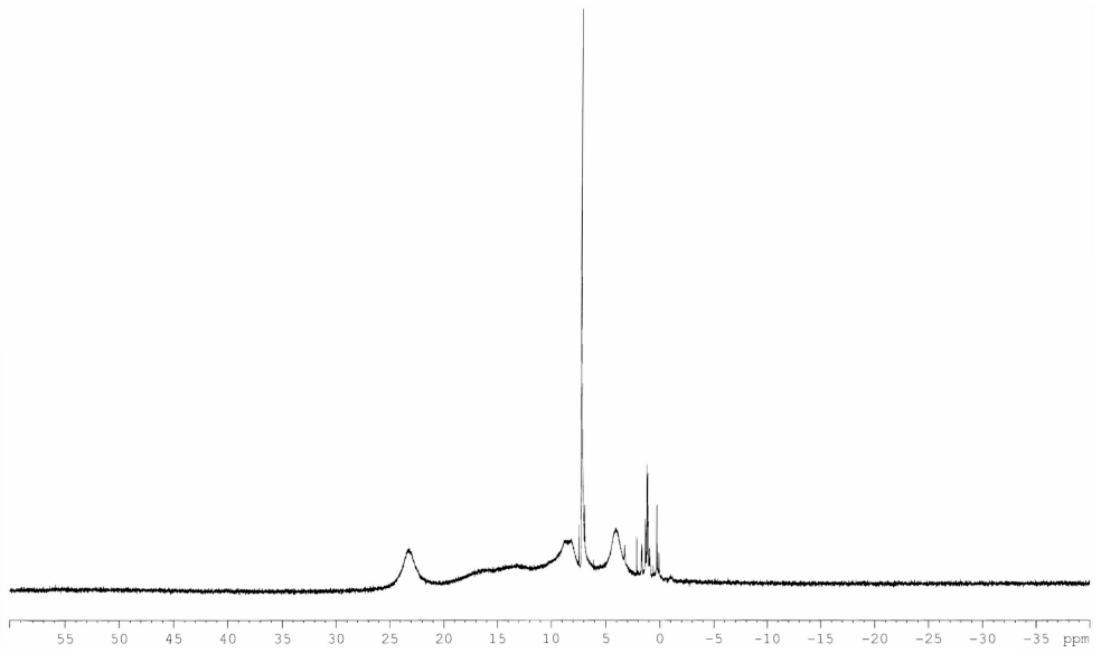
Figure S5. Thermal ellipsoid (50 %) plot of **6**. Hydrogen atoms, *iso*-propyl methyl and *tert*-butyl methyl groups have been omitted for clarity.

Table S6. Selected bond lengths (Å) and angles (deg) for [^tBuN(C=O)SiMe₂N(CH₂CH₂)P(ⁱPr)₂]Co **6**

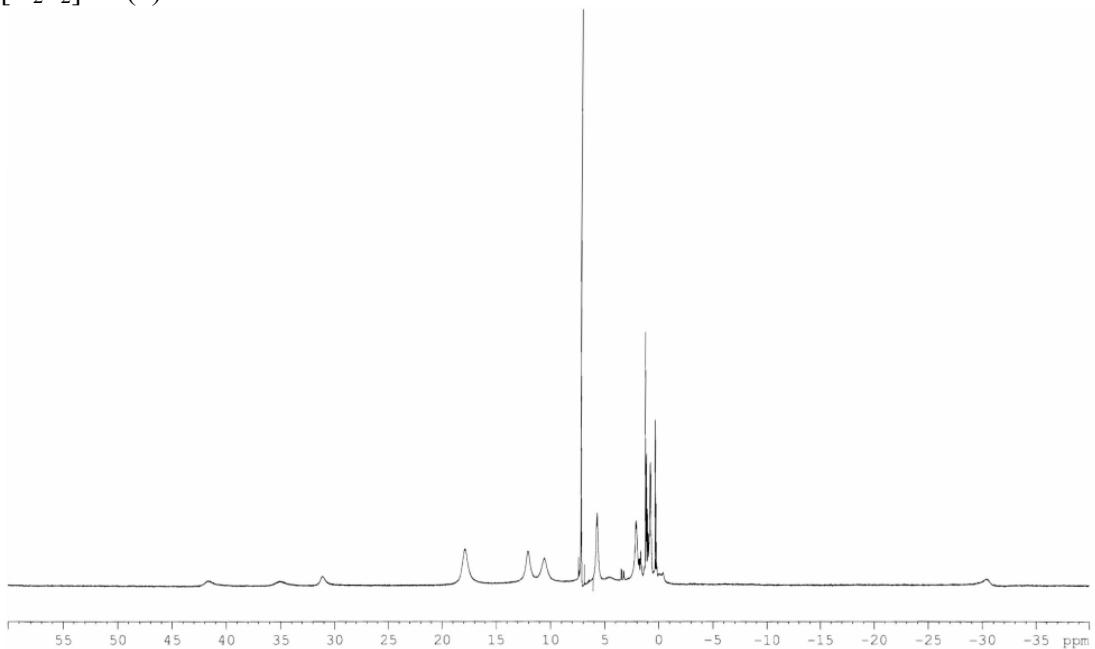
Co(1)-C(23)	1.983(4)	Co(1)-C(24)	1.765(4)
Co(1)-C(25)	1.740(4)	Co(1)-N(2)	2.114(3)
Co(1)-P(1)	2.2379(10)		
C(25)-Co(1)-C(24)	117.5(2)	C(25)-Co(1)-C(23)	86.45(16)
C(24)-Co(1)-C(23)	88.13(15)	C(25)-Co(1)-N(2)	119.16(15)
C(24)-Co(1)-N(2)	122.92(17)	C(23)-Co(1)-N(2)	88.88(13)
C(25)-Co(1)-P(1)	95.78(13)	C(24)-Co(1)-P(1)	95.34(11)
C(23)-Co(1)-P(1)	174.42(11)	N(2)-Co(1)-P(1)	85.57(8)

NMR Spectra

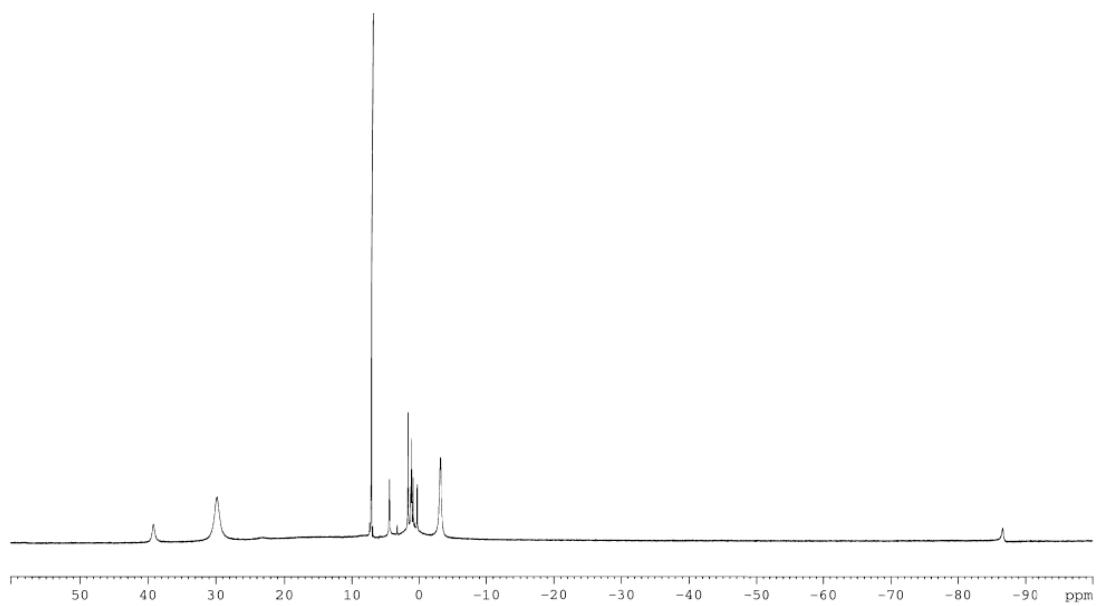
[N₂P₂]CoI (**1**)



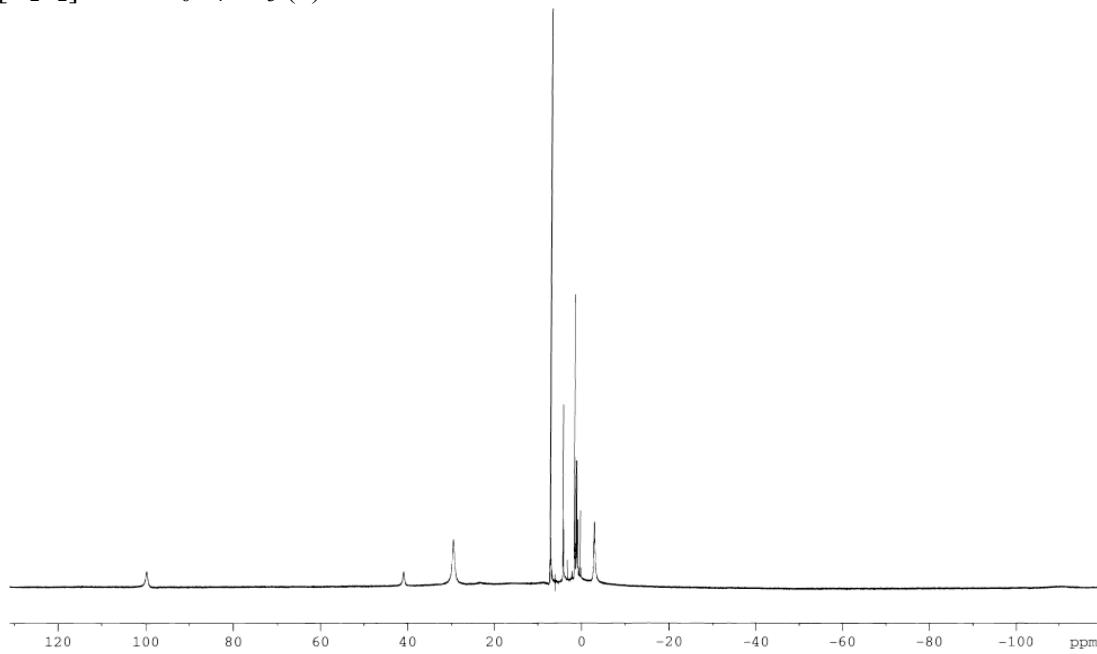
[N₂P₂]Co (**2**)



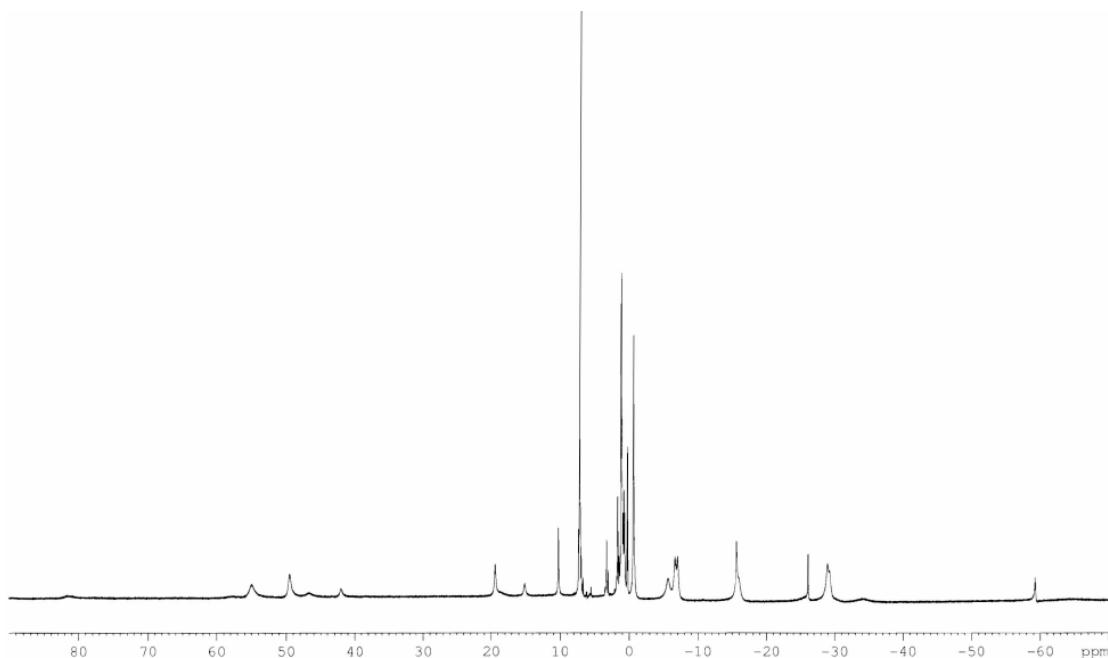
[N₂P₂]CoNHC₆H₅ (**3**)



[N₂P₂]CoNHC₆H₄CH₃ (**4**)



[PhN=PⁱPr₂(CH₂)₂NPh][^tBuNHSiMe₂N(CH₂)₂PⁱPr₂]Co (**5**)



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