Supplementary Information for

Metal-Ligand Cooperative Transformation of Alkyl Azide to Isocyanate Occurring at a Co-Si Moiety

Jongho So,^a Seji Kim,^b Kyung-Bin Cho,^c and Yunho Lee^{b*}

^aDepartment of Chemistry, KAIST, Daejeon 34141, Republic of Korea ^bDepartment of Chemistry, Seoul National University, Seoul 08826, Republic of Korea ^cDepartment of Chemistry, Jeonbuk National University, Jeonju 54896, Republic of Korea

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EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an N_2 atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with Ar gas followed by passage through an activated alumina column. Solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. MeSiHP₂¹ and (MeSiP₂)CoBr² were prepared according to the literature procedures. Elemental analyses were carried out at the KAIST Research Analysis Center on a Thermo Scientific FLASH 2000 series instrument. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. or Euriso-top, degassed, and dried over activated 4 Å molecular sieves prior to use.

X-ray Crystallography. The diffraction data of **1**, **2**, **3-CN'Bu**, **5** and **6** were collected on a Bruker D8 QUEST. A suitable size and quality of crystal was coated with Paratone-*N* oil and mounted on a Dual-Thickness MicroLoops LD purchased from MiTeGen. The data were collected with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) under a stream of N₂ (g) at 120 K. Cell parameters were determined and refined by the SMART program.³ Data reduction was performed using SAINT software.⁴ An empirical absorption correction was applied using the SADABS program.⁵ The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 by using the SHELXTL/PC package.⁶ Unless otherwise noted, hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters.

Spectroscopic Measurements. A Bruker AVHD-400 spectrometer was used to measure ¹H, ¹³C, ²⁹Si and ³¹P NMR spectra. The chemical shifts for ¹H NMR spectra were quoted in part per million (ppm) referenced to residual solvent peaks. ¹³C NMR chemical shifts were quoted in part per million (ppm) referenced to internal solvent peaks. The N values corresponding to $1/2(J_{AX} +$ $J_{A'X}$) were provided when virtual couplings were observed in the ¹³C NMR spectra. ²⁹Si NMR spectra were recorded on Bruker 400 spectrometers and were decoupled by broad band proton decoupling. The chemical shifts for ²⁹Si NMR spectra are quoted in parts per million (ppm) referenced to external tetramethylsilane. The chemical shifts for ³¹P NMR spectra were quoted in parts per million (ppm) referenced to external phosphoric acid. Coupling constants, J, were reported in hertz unit (Hz). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dt =doublet of triplet, br s = broad singlet. Solution magnetic moments were determined by the Evans' method.⁷ UV-Vis spectra were measured by an Agilent Cary 60 UV-Vis spectrophotometer using a 1 cm two-window quartz spectrophotometer cell sealed with a screwcap purchased from Hellma Analytics (117.100-QS). Low temperature UV-Vis spectra were measured by an Agilent Cary 8454 UV-Vis spectrophotometer equipped with a UNISOKU Scientific Instruments cryostat. Air sensitive solution were prepared in a glove box (N₂ filled, Korea Kiyon) and carried out in custom-made Schlenk tubes designed for the dip probe. Infrared spectra were recorded in KBr pellets by Agilent 660-IR. Frequencies are given in reciprocal centimeters (cm⁻¹) and only selected absorbances were reported. GC-MS data was measured by Agilent 7890A (GC), 5977B and 6890 (GC), 5973N (MSD).

Electrochemistry. Electrochemical measurements were carried out in a glovebox under a N_2 atmosphere using an Autolab PGSTAT12 potentiostat. A glassy carbon electrode was used as the working electrode and a platinum wire was used as the auxiliary electrode. The reference electrode was Ag/AgNO₃ in an electrolyte solution. Solution of 0.5 M tetra-*n*-butylammonium hexafluorophosphate in THF was used as an electrolyte solution. The solutions of reference electrode, electrolyte and analyte were also prepared under an inert atmosphere. The ferrocene couple FeCp₂/FeCp₂⁺ was used as an external reference.

Computational details. Density Functional Theory (DFT)⁸ geometry optimizations and frequency calculations were performed at the B3LYP/Def2-SVP level⁹ of theory using the Gaussian 16 package. Single point energy evaluations were done at the B3LYP/Def2-TZVPP level^{9b,c} including the solvent (benzene) implemented through the CPCM scheme.¹⁰ It is this electronic energy value that is discussed in the main text, as experience has shown that B3LYP/Def2-TZVPP electronic energy is quite frequently more accurate than the calculated Gibb's free energy in this kind of systems. For geometry optimizations for 1, 2, 3-CO and 6, the initial geometries were obtained from their corresponding X-ray crystal structures. The initial geometry for (MeSiP₂)Co(CO)(N₃Ad) (Int) computational model was obtained from X-ray crystal structure of (MeSiP₂)Co(CO)(PMe₃) (5). The optimized geometry coordinates are provided at the end of this SI.

DATA AVAILABILITY

Full crystallographic details can be obtained free of charge from the Cambridge Crystallographic

Data Center via www.ccdc.cam.ac.uk/data request/cif (CCDC 1954680-1954686 for 1-6). All

other data are available within its Supplementary Information.

Synthesis of {(MeSiP₂)Co}₂(μ -N₂) (1). After sodium (147 mg, 6.39 mmol) was added to a solution of naphthalene (86 mg, 0.67 mmol) in 5 mL THF, the reaction mixture was stirred for 3 hrs at room temperature. The resulting sodium naphthalenide solution was filtered away from remaining sodium and added dropwise to a solution of (MeSiP₂)CoBr (383 mg, 0.674 mmol) in 10 mL THF at -35 °C. The color of solution was changed from dark brown to dark green within 10 min. The reaction mixture was stirred for 1 hr at room temperature. All volatiles were removed under vacuum and the resulting mixture was washed with additional portions of pentane. The resulting product {(MeSiP₂)Co}₂(μ -N₂) (1, 159 mg, 0.158 mmol, 47%) was isolated as a green solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, THF-*d*₈, ppm, *under vacuum*): δ 7.95 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.53 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.32 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 7.24 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 2.69 – 2.57 (m,

2H, CH(CH₃)₂), 2.52 – 2.41 (m, 2H, CH(CH₃)₂), 1.43 – 1.33 (m, 6H, CH(CH₃)₂), 1.26 – 1.18 (m, 6H, CH(CH₃)₂), 1.15 – 1.02 (m, 12H, CH(CH₃)₂), 0.47 (s, 3H, SiCH₃). ¹³C NMR (101 MHz, THF-*d*₈, ppm, *under vacuum*) δ 160.2 (virtual t, N = 27.9 Hz, Ar-C), 145.4 (virtual t, N = 23.7 Hz, Ar-C), 131.8 (virtual t, N = 10.4 Hz, Ar-C), 129.3 (s, Ar-C), 129.1 (s, Ar-C), 128.8 (s, Ar-C), 127.5 (virtual t, N = 2.7 Hz, Ar-C), 29.8 (virtual t, N = 8.6 Hz, CH(CH₃)), 26.8 (virtual t, N = 9.6 Hz, CH(CH₃)), 21.8 (virtual t, N = 2.9 Hz, CH(CH₃)), 20.6 (virtual t, N = 1.9 Hz, CH(CH₃)), 19.5 (s, CH(CH₃)), 5.6 (t, J = 4.9 Hz, SiCH₃). ²⁹Si NMR (79 MHz, THF-*d*₈, ppm, *under vacuum*) δ 62.9 (t, J = 44.4 Hz). ³¹P NMR (162 MHz, THF-*d*₈, ppm, *under vacuum*) δ 79.2 (s). UV–Vis [THF, nm (L mol⁻¹ cm⁻¹), *under vacuum*]: 381 (12000), 725 (6200). IR (KBr pellet, cm⁻¹): $v_{N=N} = 2129$, 2077. Anal. Calcd. for C₅₀H₇₈Co₂N₂P₄Si₂: C, 59.75; H, 7.82; N, 2.79. Found: C, 59.49; H, 7.44; N, 1.07. Combustion analysis data were reproducibly low in nitrogen, likely due to modest lability of the N₂ ligand under vacuum. Dark green crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated benzene solution of **1** at room temperature.

Synthesis of {(^{MeSi}N^{Ad}P₂)Co}₂(μ -N₂) (2). At -78 °C, to a yellow solution of 1 (121 mg, 0.120 mmol) in 15 mL of THF, the solution of 1-azidoadamantane (43.9 mg, 0.240 mmol) in 3 mL THF was added dropwise. The color of solution was immediately changed to dark green upon addition of azide. The reaction mixture was stirred for additional 1 hr at -78 °C and slowly warmed to room temperature. After volatiles were removed by vacuum, the brown solid was dissolved in benzene. The resulting solution was filtered through Celite and all volatiles were removed under vacuum. The product {(^{MeSi}N^{Ad}P₂)Co}₂(μ -N₂) (2, 145 mg, 0.111 mmol, 92%) was isolated as a dark brown powder. ¹H NMR (400 MHz, benzene-*d*₆, ppm): δ 19.79, 18.32, 11.28, 10.49, 5.54, 4.19, 3.32, 1.48, -0.08, -0.58, -2.09, -2.27. μ_{eff} : 4.56 μ_{B} (benzene-*d*₆, 25 °C, Evans' method). UV–Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 350 (sh, 10000), 530 (710), 790 (470), 950 (350). IR (KBr pellet, cm⁻¹): $v_{N=N} = 2060$. Anal. Calcd. for C₇₀H₁₀₈Co₂N₄P₄Si₂: C, 64.50; H, 8.35; N, 4.30. Found: C, 64.39; H, 8.71; N, 3.59. Combustion analysis data were reproducibly low in nitrogen, likely due to modest lability of the N₂ ligand under vacuum. Dark red crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated benzene solution of **2** at room temperature.

Alternative synthesis of 2. To a green solution of 1 (55 mg, 0.055 mmol) in 10 mL of THF, the solution of 1-azidoadamantane (20 mg, 0.11 mmol) in 3 mL THF was added dropwise at room temperature causing an immediate color change to dark brown. The reaction mixture was stirred for additional 30 min and all volatiles were removed by vacuum. After dissolving in benzene, the resulting solution was filtered through Celite and drying under vacuum. The product ${(^{MeSi}N^{Ad}P_2)Co}_2(\mu-N_2)$ (2, 62 mg, 0.048 mmol, 87%) was isolated as a dark brown powder. The identity of the product was confirmed by comparison of its ¹H NMR data with those of an authentic sample.

Synthesis of $(MeSiP_2)Co(CO)_2$ (3-CO). A solution of 1 (109 mg, 0.108 mmol) in 10 mL of THF in a 100 mL Schlenk tube was degassed by three freeze-pump-thaw cycles. At room temperature, CO (g) was charged under ambient pressure resulting in an immediate color change from dark green to yellow. The solution was stirred for additional 10 min and all volatiles were removed under vacuum. After dissolving in pentane, the resulting solution was filtered through Celite and drying under vacuum. The resulting product (MeSiP_2)Co(CO)_2 (3-CO, 116 mg, 0.213 mmol, 98%) was isolated as a yellow powder. Analytically pure material was obtained from the recrystallization of a saturated pentane solution of 3-CO at -35 °C. ¹H NMR (400 MHz,

benzene-*d*₆, ppm): δ 7.84 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.29 – 7.19 (m, 4H, Ar-*H*), 7.10 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 2.39 – 2.15 (m, 4H, *CH*(CH₃)₂), 1.34 – 1.22 (m, 6H, *CH*(*CH*₃)₂), 1.03 (s, 3H, SiC*H*₃), 0.99 – 0.88 (m, 12H, *CH*(*CH*₃)₂), 0.87 – 0.79 (m, 6H, *CH*(*CH*₃)₂). ¹³C NMR (101 MHz, benzene-*d*₆, ppm) δ 207.4 (s, Co-CO), 157.9 – 156.7 (m, Ar-*C*), 145.8 – 144.7 (m, Ar-*C*), 132.5 (virtual t, *N* = 11.8 Hz, Ar-*C*), 129.8 (s, Ar-*C*), 128.6 (s, Ar-*C*), 32.5 (virtual t, *N* = 15.2 Hz, *CH*(*CH*₃)), 30.0 (virtual t, *N* = 8.5 Hz, *CH*(*CH*₃)), 19.7 (virtual t, *N* = 2.5 Hz, *CH*(*CH*₃)), 19.4 (s, *CH*(*CH*₃)), 19.1 (virtual t, *N* = 2.2 Hz, *CH*(*CH*₃)), 18.9 (virtual t, *N* = 2.0 Hz, *CH*(*CH*₃)), 7.5 (s, Si*CH*₃). ²⁹Si NMR (79 MHz, benzene-*d*₆, ppm) δ 69.6 (t, *J* = 23.6 Hz). ³¹P NMR (162 MHz, benzene-*d*₆, ppm) δ 94.3 (br s). UV–Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 316 (sh, 3300). IR (KBr pellet, cm⁻¹): v_{CO} = 1907, 1957. Anal. Calcd. for C₂₇H₃₉CoO₂P₂Si: C, 59.55; H, 7.22. Found: C, 59.65; H, 7.31. Yellow crystals suitable for X-ray diffraction were obtained by cooling a saturated pentane solution of **3-CO** at –35 °C.

Synthesis of (MeSiP₂)Co(CN'Bu)₂ (3-CN'Bu). To a solution of 1 (31 mg, 0.031 mmol) in 10 mL of benzene, 'BuNC (10 µL, 0.087 mmol) was added using a microsyringe resulting an immediate color change from dark green to yellow at room temperature. The solution was stirred for 10 min and all volatiles were removed under vacuum. The resulting solid was dissolved in pentane and filtered through Celite. After all volatiles were removed under vacuum, the resulting product (MeSiP₂)Co(CN'Bu)₂ (**3-CN'Bu**, 39 mg, 0.060 mmol, 95%) was isolated as an orange powder. Analytically pure material could be obtained from the recrystallization of a saturated pentane solution of **3-CN'Bu** at -35 °C. ¹H NMR (400 MHz, benzene- d_6 , ppm): δ 8.14 – 8.09 (m, 2H, Ar-H), 7.54 – 7.49 (m, 2H, Ar-H), 7.35 – 7.29 (m, 2H, Ar-H), 7.23 – 7.19 (m, 2H, Ar-H), 2.60 - 2.41 (m, 4H, CH(CH₃)₂), 1.47 - 1.40 (m, 6H, CH(CH₃)₂), 1.29 - 1.23 (m, 6H, CH(CH₃)₂), 1.21 (d, J = 12.3 Hz, 18H, C(CH₃)₃), 1.04 – 0.97 (m, 12H, CH(CH₃)₂), 0.98 (s, 3H, SiCH₃). ¹³C NMR (101 MHz, benzene- d_6 , ppm) δ 161.0 – 159.5 (m, Ar-C), 149.4 –149.1 (m, Ar-C), 132.1 (virtual t, N = 11.5 Hz, Ar-C), 128.7 (s, Ar-C), 126.9 (virtual t, N = 2.0 Hz, Ar-C), 55.1 (s, $C(CH_3)_3$, 54.0 (s, $C(CH_3)_3$), 34.3 (virtual t, N = 14.1 Hz, $CH(CH_3)$), 31.6 (s, $C(CH_3)_3$), 31.1 (virtual t, N = 5.2 Hz, $CH(CH_3)$), 30.9 (s, $C(CH_3)_3$), 21.1 (virtual t, N = 3.4 Hz, $CH(CH_3)$), 20.5 (m, C(CH₃)₃), 19.8 (virtual t, N = 2.0 Hz, CH(CH₃)), 6.9 (s, SiCH₃). ²⁹Si NMR (79 MHz, benzene- d_6 , ppm) δ 69.2 (t, J = 28.6 Hz). ³¹P NMR (162 MHz, benzene- d_6 , ppm) δ 92.3 (br s). UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 380 (sh, 3900). IR (KBr pellet, cm⁻¹): $v_{CN} = 2058$, 2004. Anal. Calcd. for C₃₅H₅₇CoN₂P₂Si: C, 64.20; H, 8.77; N, 4.28. Found: C, 64.45; H, 8.89; N, 3.90. Orange crystals suitable for X-ray diffraction were obtained by cooling a saturated pentane solution of **3-CN^tBu** at -35 °C.

Synthesis of (MeSiP₂)Co(N₂)(PMe₃) (4). To a solution of 1 (115 mg, 0.114 mmol) in 10 mL of benzene, PMe₃ (1.0 M solution in THF, 1.0 mL, 1.0 mmol) was added using a syringe resulting an immediate color change from dark green to orange. The solution was stirred for 10 min at room temperature and all volatiles were removed under vacuum. The resulting solid was dissolved in pentane and filtered through Celite. After all volatiles were removed under vacuum, the resulting product (MeSiP₂)Co(N₂)(PMe₃) (4, 133 mg, 0.224 mmol, 98%) was isolated as an orange solid. Analytically pure material could be obtained from the recrystallization of a saturated pentane solution of 4 at -35 °C. ¹H NMR (400 MHz, benzene-*d*₆, ppm): δ 7.72 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.36 (d, *J* = 6.6 Hz, 2H, Ar-*H*), 7.20 (t, *J* = 8.0 Hz, 2H, Ar-*H*), 7.10 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 2.56 – 2.42 (m, 4H, CH(CH₃)₂), 1.33 – 1.25 (m, 6H, CH(CH₃)₂), 1.25 (d, *J* = 6.1 Hz, 9H, P(CH₃)₃), 1.17 – 1.08 (m, 12H, CH(CH₃)₂), 0.78 – 0.69 (m, 6H, CH(CH₃)₂), 0.72 (s, 3H, SiCH₃). ¹³C NMR (101 MHz, benzene-*d*₆, ppm) δ 159.5 (virtual t, *N* = 30.7 Hz, Ar-*C*), 145.8

(virtual t, N = 18.1 Hz, Ar-*C*), 132.0 (virtual t, N = 10.8 Hz, Ar-*C*), 128.8 (s, Ar-*C*), 126.7 (s, Ar-*C*), 30.6 (virtual t, N = 12.8 Hz, *C*H(CH₃)), 29.5 (dt, J = 10.5, 4.8 Hz, *C*H(CH₃)), 22.6 (dt, J = 19.0, 4.0 Hz, P(*C*H₃)₃), 20.4 (virtual t, N = 3.3 Hz, CH(*C*H₃)), 20.0 (s, CH(*C*H₃)), 19.5 (s, CH(*C*H₃)), 19.1 (s, CH(*C*H₃)), 7.3 (d, J = 13.0 Hz, Si*C*H₃). ²⁹Si NMR (79 MHz, benzene-*d*₆, ppm) δ 56.6 (dt, J = 44.7, 25.4 Hz). ³¹P NMR (162 MHz, benzene-*d*₆, ppm) δ 73.2 (d, J = 79.4 Hz, 2P), -15.2 (t, J = 79.4 Hz, 1P). UV–Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 268 (16000), 380 (4200). IR (KBr pellet, cm⁻¹): $v_{N\equiv N} = 2062$. Anal. Calcd. for C₂₈H₄₈CoN₂P₃Si: C, 56.75; H, 8.16; N, 4.73. Found: C, 56.57; H, 7.99; N, 4.45. Orange crystals suitable for X-ray diffraction were obtained by cooling a saturated pentane solution of **4** at –35 °C.

Synthesis of 3-CO from 4. In an NMR tube with a J-Young valve, the orange solution of **4** (10 mg, 0.017 mmol) in 1 mL of C_6D_6 was taken out of the dry-box and degassed by three freezepump-thaw cycles on the Schlenk line. After CO(g) was added at ambient pressure, the solution was heated at 100 °C for 2 hr. After the volatiles were removed under vacuum, the resulting solid was dissolved in pentane and filtered through Celite. After all volatiles were removed under vacuum, the resulting product (MeSiP₂)Co(CO)₂ (**3-CO**, 8 mg, 0.02 mmol, 87%) was isolated as a yellow powder after drying under vacuum. The identity of the product was confirmed by comparison of its ¹H and ³¹P NMR data with those of an authentic sample.

Synthesis of (MeSiP₂)Co(CO)(PMe₃) (5). To a solution of 3-CO (42 mg, 0.077 mmol) in 20 mL of benzene in a 100 mL Schlenk tube, excess amount of PMe₃ (1.0 M solution in THF, 2.0 mL, 2.0 mmol) was added. The reaction tube was taken out of the dry-box and the reaction mixture was stirred under light conditions by using irradiation with a 365 nm light for 3 hr. After all volatiles were removed under vacuum, the resulting solid was dissolved in pentane and filtered through Celite. The resulting product (MeSiP₂)Co(CO)(PMe₃) (5, 43 mg, 0.072 mmol, 93%) was isolated an yellow powder after all volatiles were removed and dried under vacuum. Analytically pure material could be obtained from the recrystallization of a saturated pentane solution of 5 at -35 °C. ¹H NMR (400 MHz, benzene- d_6 , ppm): δ 7.82 (d, J = 7.2 Hz, 2H, Ar-H), 7.30 (d, J = 7.0 Hz, 2H, Ar-H), 7.23 (t, J = 7.3 Hz, 2H, Ar-H), 7.09 (t, J = 7.3 Hz, 2H, Ar-H), 2.37 - 2.32 (m, 4H, CH(CH₃)₂), 1.28 - 1.22 (m, 6H, CH(CH₃)₂), 1.25 (d, J = 6.5 Hz, 9H, $P(CH_3)_3$, 1.11 – 0.98 (m, 12H, CH(CH_3)_2), 0.85 (s, 3H, SiCH_3), 0.73 – 0.65 (m, 6H, CH(CH_3)_2). ¹³C NMR (101 MHz, benzene- d_6 , ppm) δ 225.1 (s, Co-CO), 159.4 (virtual t, N = 30.3 Hz, Ar-C), 146.6 (virtual t, N = 17.8 Hz, Ar-C), 132.2 (virtual t, N = 11.2 Hz, Ar-C), 129.0 (s, Ar-C), 126.8 (s, Ar-C), 30.9 - 30.5 (m, CH(CH₃)), 24.7 (dt, J = 24.7, 3.7 Hz, P(CH₃)₃), 19.7 (virtual t, N =73.8 Hz, CH(CH₃)), 19.5 (s, CH(CH₃)), 7.9 (d, J = 12.6 Hz, SiCH₃). ²⁹Si NMR (79 MHz, benzene- d_6 , ppm) δ 65.9 (dt, J = 26.9 Hz). ³¹P NMR (162 MHz, benzene- d_6 , ppm) δ 85.8 (br s, 2P), -9.4 (br s, 1P). UV–Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 360 (3800). IR (KBr pellet, cm⁻¹): $v_{CO} =$ 1894. Anal. Calcd. for C₂₉H₄₈CoOP₃Si: C, 58.77; H, 8.16. Found: C, 59.19; H, 7.87. Orange crystals suitable for X-ray diffraction were obtained by cooling a saturated pentane solution of 5 at −35 °C.

Synthesis of $(^{MeSi}N^{Ad}P_2)Co(CO)$ (6). In a 3 mL NMR tube equipped with a J-Young valve, the solution of 2 (20 mg, 0.016 mmol) in 2.25 mL of C_6D_6 was degassed by freeze-pump-thaw cycles on the Schlenk line. CO(g) was charged under ambient conditions resulting in an immediate color change from dark brown to green. After shaking for 30 min at room temperature, all volatiles were removed under vacuum. After dissolved in pentane a green solution was filtered through Celite and all volatiles were removed. The resulting product ($^{MeSi}N^{Ad}P_2$)Co(CO)

(6, 14 mg, 0.021 mmol, 69%) was isolated as a dark green crystalline solid obtained from the recrystallization of a cold pentane solution of 6 at –35 °C. ¹H NMR (400 MHz, benzene- d_6 , ppm): δ 98.59, 57.18, 24.86, 22.99, 11.06, 9.36, 5.31, 3.22, 2.07, 1.25, 0.91, 0.30, 0.10, –0.96. μ_{eff} : 2.41 μ_B (benzene- d_6 , 25 °C, Evans' method). UV–Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 390 (1900), 680 (230), 950 (260). IR (KBr pellet, cm⁻¹): v_{CO} = 1913. Anal. Calcd. for C₃₆H₅₄CoNOP₂Si: C, 64.94; H, 8.18; N, 2.10. Found: C, 65.29; H, 8.49; N, 1.72. Green crystals suitable for X-ray diffraction were obtained by cooling a saturated pentane solution of 6 at –35 °C.

Reaction of 2 with CO followed by NMR experiments. In an NMR tube with a J-Young valve, the brown solution of **2** (8 mg, 0.005 mmol) in 0.7 mL of C_6D_6 was taken out of the dry-box and degassed by three freeze-pump-thaw cycles on the Schlenk line. After CO(g) was added at ambient pressure, the solution was shaken for 5 min. The identity of **3-CO** was confirmed by comparisons of its ¹H and ³¹P NMR data with those of an authentic sample of **3-CO**. Adamantyl isocyanate was determined by GC-MS and ¹H NMR spectrum. The yield of adamantylisocyanate (3.0 mg, 92%) was determined by the integration of a peak at 1.69 ppm in ¹H NMR spectrum using mesitylene (5.0 μ L, 0.035 mmol, 2.16 ppm) as an internal standard.

Reaction of 2 with 'BuNC followed by NMR experiments. To a solution of **2** (9 mg, 0.007 mmol) in 3 mL of C_6D_6 , 'BuNC (10 µL, 0.09 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 30 min and all volatiles were removed under vacuum. The identity of **3-CN'Bu** was confirmed by comparisons of its ¹H and ³¹P NMR data with those of an authentic sample of **3-CN'Bu**. AdN=C=N'Bu was determined by GC-MS and ¹H NMR spectrum, which was previously reported.¹

Catalytic formation of AdNCO. In a quartz NMR tube with a J-Young valve, the yellow solution of **3-CO** (8.6 mg, 0.016 mmol) and AdN_3 (56 mg, 0.18 mmol) in 1 mL of C_6D_6 was taken out of the dry-box and degassed by three freeze-pump-thaw cycles on the Schlenk line. After CO(g) was added at ambient pressure, the solution was irradiated for 3, 6 or 9 hr. During photolysis, the color of a reaction mixture was changed from yellow to brown. The resulting mixture was analyzed by GC-MS. The resulting product, AdNCO (m/z = 177.1) was authenticated and quantified by GC-MS against an internal standard (eicosane). A similarly prepared control reactions in the absence of **3-CO** revealed no conversion and the resulting data are listed in Table S9.

Figure S1. ¹H NMR spectrum of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) under vacuum in THF-*d*₈ at room temperature.



Figure S2. ¹³C NMR spectrum of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) under vacuum in THF-*d*₈ at room temperature.



Figure S3. ²⁹Si NMR spectrum of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) under vacuum in THF-*d*₈ at room temperature.



Figure S4. ³¹P NMR spectrum of {(MeSiP₂)Co}₂(μ -N₂) (1) under vacuum in THF- d_8 at room temperature.



Figure S5. Variable-temperature (VT) ³¹P NMR spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) under vacuum in THF-*d*₈.



Figure S6. Variable-temperature (VT) ³¹P NMR spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) under N₂ in THF-*d*₈.







Figure S8. ¹H NMR spectrum of $(MeSiP_2)Co(CO)_2$ (3-CO) in C_6D_6 at room temperature.





Figure S9. ¹³C NMR spectrum of $(MeSiP_2)Co(CO)_2$ (3-CO) in C_6D_6 at room temperature.





Figure S12. ¹H NMR spectrum of (MeSiP₂)Co('BuNC)₂ (**3-**CN'Bu) in C₆D₆ at room temperature.

Figure S13. ¹³C NMR spectrum of $(MeSiP_2)Co('BuNC)_2$ (3-CN'Bu) in C_6D_6 at room temperature.



f1 (ppm)



Figure S14. ²⁹Si NMR spectrum of $(MeSiP_2)Co('BuNC)_2$ (3-CN'Bu) in C₆D₆ at room temperature.

Figure S15. ³¹P NMR spectrum of $(MeSiP_2)Co('BuNC)_2$ (3-CN'Bu) in C₆D₆ at room temperature.





Figure S16. ¹H NMR spectrum of $(MeSiP_2)Co(N_2)(PMe_3)$ (4) in C_6D_6 at room temperature.

Figure S17. ¹³C NMR spectrum of $(MeSiP_2)Co(N_2)(PMe_3)$ (4) in C_6D_6 at room temperature.





Figure S18. ²⁹Si NMR spectrum of $(MeSiP_2)Co(N_2)(PMe_3)$ (4) in C_6D_6 at room temperature.

Figure S19. ³¹P NMR spectrum of $(MeSiP_2)Co(N_2)(PMe_3)$ (4) in C_6D_6 at room temperature.





Figure S20. ¹H NMR spectrum of $(MeSiP_2)Co(CO)(PMe_3)$ (5) in C_6D_6 at room temperature.

Figure S21. ¹³C NMR spectrum of (MeSiP₂)Co(CO)(PMe₃) (5) in C₆D₆ at room temperature.



f1 (ppm)



Figure S22. ²⁹Si NMR spectrum of $(MeSiP_2)Co(CO)(PMe_3)$ (5) in C_6D_6 at room temperature.





Figure S24. ¹H NMR spectrum of $(^{MeSi}N^{Ad}P_2)Co(CO)$ (6) in C_6D_6 at room temperature.



Figure S25. ¹H NMR spectra of (a) the reaction of **2** with excess CO(g), (b) **3-CO** and (c) AdNCO in C_6D_6 at room temperature. (•:**3-CO**, •:AdNCO)



Figure S26. Solid-state molecular structure of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1). Hydrogen atoms are omitted for clarity.



 $\label{eq:constraint} \textbf{Table S1.} Selected bond distances and angles for $$ (MeSiP_2)Co$_2($\mu$-N_2)(1)(Å and °).$$ }$

Bon	d distance	Bond angle			
$\begin{array}{c} d_{Co1-Si1} \\ d_{Co2-Si2} \end{array}$	2.2391(4) 2.2354(4)	\angle Si1-Co1-N1 151.31(3) \angle Si2-Co2-N2 146.39(3)			
$\begin{array}{c} d_{Co1-P1} \\ d_{Co2-P3} \end{array}$	2.1713(3) 2.1849(3)	∠Si1–Co1–P1 ∠Si2–Co2–P3 ∠Si1–Co1–P2 ∠Si2–Co2–P4	83.13(1) 83.00(1) 83.64(1) 83.25(1)		
$d_{Co1-P2} \\ d_{Co2-P4}$	2.1701(3) 2.1737(3)	∠P1–Co1–P2 ∠P3–Co2–P4	143.48(1) 142.35(1)		
$\begin{array}{c} d_{Co1-N1} \\ d_{Co2-N2} \end{array}$	1.803(1) 1.811(1)	∠P1–Co1–N1 ∠P3–Co2–N2 ∠P2–Co1–N1 ∠P4–Co2–N2	102.83(3) 107.23(3) 105.04(3) 103.56(3)		
d _{N1-N2}	1.147(1)	∠Co1-N1-N2 ∠Co2-N2-N1	169.17(9) 167.68(9)		

 $\tau_4 = 0.46$ and 0.51^{12}

Figure S27. Solid state molecular structure of $\{({}^{MeSi}N^{Ad}P_2)Co\}_2(\mu-N_2)$ (2). Hydrogen atoms are omitted for clarity.



Table S2. Selected bond distances and angles for $\{({}^{MeSi}N^{Ad}P_2)Co\}_2(\mu-N_2)$ (2) (Å and °).

Bond distance		Bond angle		
d _{Co1-N1}	1.951(2)	∠N1–Co1–N2	134.05(8)	
d _{Co1-N2}	1.895(2)	∠N1–Co1–P1 ∠N1–Co1–P2	96.91(7) 103.04(7)	
d _{Co1-P1}	2.3006(8)	∠P1–Co1–P2	114.26(3)	
d _{Co1-P2}	2.3290(8)	∠P1–Co1–N2 ∠P2–Co1–N2	104.83(6) 103.96(6)	
d _{N1-Si1}	1.695(2)	∠Co1–N2–N2'	170.9(3)	
d _{Co1-Si1}	2.9504(8)	∠Si1–N1–Co1	107.9(1)	
d _{N2-N2} ,	1.138(4)			

Figure S28. Solid state molecular structure of $(MeSiP_2)Co(CO)_2$ (3-CO). Hydrogen atoms are omitted for clarity.



Table S3. Selected bond distances and angles for (MeSiP₂)Co(CO)₂ (3-CO) (Å and °).

Bon	nd distance	Bond angle		
d _{Co1-Si1}	2.2898(8)	∠Si1–Co1–C1 ∠Si1–Co1–C2	172.99(9) 87.6(1)	
d _{Co1-P1}	2.2160(8)	∠Si1–Co1–P1 ∠Si1–Co1–P2	83.68(3) 83.43(3)	
d _{Co1-P2}	2.2046(8)	∠P1–Co1–P2	132.23(3)	
d _{Co1-C1}	1.830(4)	∠P1–Co1–C1 ∠P2–Co1–C1	94.21(9) 93.15(9)	
d _{Co1-C2}	1.747(3)	∠P1–Co1–C2 ∠P2–Co1–C2	115.2(1) 110.0(1)	
d _{C1-O1}	1.027(4)	∠C1–Co1–C2	99.3(1)	
d _{C2-O2}	1.158(4)			
$\tau_5 = 0.68^{13}$				

Figure S29. Solid state molecular structure of $(MeSiP_2)Co('BuNC)_2$ (3-CN'Bu). Hydrogen atoms are omitted for clarity.



Table S4. Selected bond distances and angles for (MeSiP₂)Co('BuNC)₂ (3-CN'Bu) (Å and °).

Bond distance		Bond angle		
d _{Co1-Si1}	2.2591(7)	∠Si1–Co1–C26 ∠Si1–Co1–C31	176.81(7) 85.25(8)	
d _{Co1-P1}	2.1846(7)	∠Si1–Co1–P1 ∠Si1–Co1–P2	84.98(3) 84.25(3)	
d _{Co1-P2}	2.1832(7)	∠P1–Co1–P2	131.05(3)	
d _{Co1-C26}	1.830(2)	∠P1–Co1–C26 ∠P2–Co1–C26	96.95(7) 96.31(7)	
d _{C01-C31}	1.793(2)	∠P1–Co1–C31 ∠P2–Co1–C31	111.12(7) 115.33(7)	
d _{C26–N1}	1.172(3)	∠C26–Co1–C31	91.7(1)	
d _{C31-N2}	1.168(3)			

Figure S30. Solid state molecular structure of $(MeSiP_2)Co(N_2)(PMe_3)$ (4). Hydrogen atoms are omitted for clarity.



Table S5. Selected bond distances and angles for (MeSiP₂)Co(N₂)(PMe₃) (4) (Å and °).

2.2722(8)	∠Si1–Co1–N1	177 60(7)
		177.00(7)
2.2069(8)	∠Si1–Co1–P1 ∠Si1–Co1–P2	82.82(3) 83.65(2)
2.2351(7)	∠Si1–Co1–P3	87.52(3)
2.1902(8)	∠P1–Co1–N1 ∠P2–Co1–N1	95.06(7) 98.42(7)
1.836(2)	∠P1–Co1–P2	120.42(3)
1.020(3)	∠P1–Co1–P3 ∠P2–Co1–P3	124.50(3) 112.47(3)
	∠Co1–N1–N2	176.4(2)
	2.2351(7) 2.1902(8) 1.836(2) 1.020(3)	$\angle S11-Co1-P2$ 2.2351(7) $\angle S11-Co1-P3$ 2.1902(8) $\angle P1-Co1-N1$ $\angle P2-Co1-N1$ 1.836(2) $\angle P1-Co1-P2$ 1.020(3) $\angle P1-Co1-P3$ $\angle Co1-N1-N2$

Figure S31. Solid state molecular structure of $(MeSiP_2)Co(CO)(PMe_3)$ (5). Hydrogen atoms are omitted for clarity.



Table S6. Selected bond distances and angles for (MeSiP₂)Co(CO)(PMe₃) (5) (Å and °).

Bond distance		Bond angle		
d _{Co1-Si1}	2.296(1)	∠Si1–Co1–C1	177.6(2)	
d _{Co1-P1}	2.192(1)	∠Si1–Co1–P1 ∠Si1–Co1–P2	82.65(5) 83.55(4)	
d _{Co1-P2}	2.216(1)	∠Si1–Co1–P3	87.68(5)	
d _{Co1-P3}	2.177(1)	∠P1–Co1–C1 ∠P2–Co1–C1	95.5(2) 98.7(2)	
d _{Co1-C1}	1.738(5)	∠P1–Co1–P2	121.00(5)	
d _{C1-O1}	1.170(5)	∠P1–Co1–P3 ∠P2–Co1–P3	123.40(5) 112.94(5)	
		∠Co1–C1–O1	177.4(4)	

Figure S32. Solid state molecular structure of $(^{MeSi}N^{Ad}P_2)Co(CO)$ (6). Hydrogen atoms are omitted for clarity.



Table S7. Selected bond distances and angles for $(^{MeSi}N^{Ad}P_2)Co(CO)$ (6) (Å and °).

Bond distance		Bond angle		
d _{Co1-N1}	1.928(4)	∠Si1–N1–Co1	106.1(2)	
d _{Co1-P1}	2.348(1)	∠N1–Co1–P1 ∠N1–Co1–P2	105.3(1) 99.0(1)	
d _{Co1-P2}	2.270(2)	∠N1–Co1–C26	135.0(3)	
d _{N1-Si1}	1.687(5)	∠P1–Co1–C26 ∠P2–Co1–C26	103.6(2) 101.1(2)	
d _{Co1-C26}	1.798(7)	∠P1–Co1–P2	112.28(6)	
d _{C26-O1}	1.131(9)	∠Co1–C26–O1	174.3(7)	

Figure S33. Plots of the normalized signal intensities (I/I_o) versus gradient strength (G) (top) and plots of $\ln(I/I_o)$ versus G² (bottom). The corresponding data obtained from pulsed gradient spin echo experiments for {(MeSiP₂)Co}₂(μ -N₂) (1, blue), (MeSiP₂)Co(CO)₂ (3-CO, red), (MeSiP₂)Co(N₂)(PMe₃) (4, green) and {(PP^{Me}P)Ni}₂(μ -N₂) (orange) in benzene- d_6 at room temperature.



Compound	Diffusion constant (×10 ⁻¹⁰ m ² /s)	R _{solution} (Å)
1	5.015	5.440
3	6.651	4.102
5	7.021	3.891
${(PP^{Me}P)Ni}_{2}(\mu-N_{2})$	5.040	5.413
(PP ^{Me} P)Ni(N ₂)	6.884	3.963

Table S8. Diffusion constants, hydrodynamic radii ($R_{solution}$) for 1, 3-CO, 4 and {($PP^{Me}P$)Ni}₂(μ -N₂).¹⁴

Figure S34. UV-Vis spectra of $(MeSiP_2)CoBr$ (blue) and $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1, red) in THF at room temperature.



Figure S35. UV-Vis spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1, blue) and $\{(^{MeSi}N^{Ad}P_2)(Co)\}_2(\mu-N_2)$ (2, red) in THF at room temperature.



Figure S36. UV-Vis spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1, blue), $(MeSiP_2)Co(CO)_2$ (3-CO, red) and $(MeSiP_2)Co(^{t}BuNC)_2$ (3-CN^tBu, black) in THF at room temperature.



Figure S37. UV-Vis spectra of $(MeSiP_2)Co(CO)_2$ (**3-CO**, blue), $(MeSiP_2)Co(N_2)(PMe_3)$ (**4**, red) and $(MeSiP_2)Co(CO)(PMe_3)$ (**5**, black) in THF at room temperature.



Figure S38. UV-Vis spectrum of (MeSiNAdP₂)Co(CO) (6, blue) in THF at room temperature.



Figure S39. UV-Vis spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) in THF measured at room temperature (blue) and -80 °C (red).



Figure S40. UV-Vis spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) in low concentration (0.14 mM) in THF under N₂ measured at room temperature (blue), under vacuum at room temperature (red) and under vacuum at -80 °C (green).



Figure S41. Variable temperature UV-Vis spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) measured at room temperature (solid lines) and -80 °C (dotted lines) in THF; five cycles by lowering/raising temperature.



Figure S42. Time stacked UV-Vis spectra of (a) the reaction of **1** with adamantyl azide (blue) in THF revealing the formation of an intermediate species (**A**, red, 3 sec intervals), (b) formation of an intermediate species (**B**, green, 5 min intervals) at -80 °C and (c) comparison of **B** with $\{(^{MeSi}N^{Ad}P_2)(Co)\}_2(\mu-N_2)$ (**2**, black) measured at room temperature.



Figure S43. IR spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1, blue) and $\{(MeSiN^{Ad}P_2)Co\}_2(\mu-N_2)$ (2, red) (KBr pellet).



Figure S44. IR spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1, blue), $(MeSiP_2)Co(CO)_2$ (3-CO, red) and $(MeSiP_2)Co('BuNC)_2$ (3-CN'Bu, green) (KBr pellet).



Figure S45. IR spectra of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1, blue) and $(MeSiP_2)Co(N_2)(PMe_3)$ (4, red) (KBr pellet).



Figure S46. IR spectra of $(MeSiP_2)Co(CO)_2$ (**3-CO**, blue), $(MeSiP_2)Co(N_2)(PMe_3)$ (**4**, red) and $(MeSiP_2)Co(CO)(PMe_3)$ (**5**, green) (KBr pellet).





Figure S47. IR spectrum of (MeSiNAdP2)Co(CO) (6, blue) (KBr pellet).

Figure S48. IR spectra of $(MeSiP_2)Co(CO)_2$ (**3-CO**, blue), AdNCO (black) and the product mixture obtained from the reaction of $\{(^{MeSi}N^{Ad}P_2)Co\}_2(\mu-N_2)$ (**2**) and CO (red) (KBr pellet).



Figure S49. IR spectra of $(MeSiP_2)Co({}^{t}BuNC)_2$ (**3-CN'Bu**, blue) and the product mixture obtained from the reaction of $\{({}^{MeSi}N^{Ad}P_2)Co\}_2(\mu-N_2)$ (**2**) and ${}^{t}BuNC$ (red) (KBr pellet).



Figure S50. Solution IR spectrum of $\{(MeSiP_2)Co\}_2(\mu-N_2)$ (1) under N_2 in THF at room temperature (KBr window).



Figure S51. Cyclic voltammogram of $(MeSiP_2)CoBr$ with scan rates: 100, 200, 300, and 400 mV/s. Co^{II/I} couple at -1.98 V and Co^{I/0} couple at -2.32 V vs. Fc/Fc⁺ were observed in THF with 0.5 M tetra-*n*-butylammonium hexafluorophosphate as an electrolyte.



Figure S52. GC-MS data of the product mixture obtained from reaction of $\{(M^{eSi}N^{Ad}P_2)Co\}_2(\mu N_2)$ (2) and CO.



Figure S53. GC-MS data of the product mixture obtained from reaction of $\{(^{MeSi}N^{Ad}P_2)Co\}_2(\mu N_2)$ (2) and 'BuNC.



Figure S54. GC-MS data of (a) the mixture of AdN_3 and CO(g) with $(MeSiP_2)Co(CO)_2$ (**3-CO**) with eicosane, (b) authentic adamantly isocyanate with eicosane and (c) the mixture of AdN_3 and CO(g) without **3-CO** after 6 h under 365 nm UV lamp.



$CO + AdN_3 \xrightarrow{3-CO} AdNCO + N_2$							
Entry	3-CO (mmol)	C ₆ H ₆ (mL)	CO(g) (mmol) ^a	AdN ₃ (mmol)	Remained AdN ₃ (mmol)	hr	AdNCO (mmol)
1	0.016 1 eq	1	0.08 5 eq	0.24 15 eq	0.20 13 eq	3	0.032 2.0 eq
2	0.016 1 eq	1	0.08 5 eq	0.24 15 eq	0.13 8.1 eq	6	0.051 3.2 eq
3	0.016 1 eq	1	0.08 5 eq	0.24 15 eq	0.14 8.7 eq	9	0.079 5.0 eq
4	0.016 1 eq	1	0.08 5 eq	0.32 20 eq	0.19 12 eq	3	0.034 2.1 eq
5	0.016 1 eq	1	0.08 5 eq	0.32 20 eq	0.23 14 eq	6	0.077 4.8 eq
6	0.016 1 eq	1	0.08 5 eq	0.32 20 eq	0.19 12 eq	9	0.065 4.1 eq
7	0	1	0.08 5 eq	0.32 20 eq	0.30 19 eq	6	0
8	0.016 1 eq	0.5	0.10 6 eq	0.32 20 eq	0.19 12 eq	6	0.033 2.1 eq
9	0.008 1 eq	0.5	0.10 12 eq	0.16 20 eq	0.13 16 eq	6	0.003 0.4 eq

Table S9. Catalytic isocyanate generation by using 3-CO, AdN_3 and CO.



Figure S55. Electronic structures for 1 derived from the single point DFT calculations; energies in cm⁻¹.

Figure S56. Frontier orbitals of 1.



Figure S57. Electronic structures of (a) alpha and (b) beta spin for **2** derived from the single point DFT calculations; energies in cm^{-1} .





Figure S58. Optimized molecular structures for (MeSiP₂)Co(CO)(N₃Ad) (Int). Hydrogen atoms are omitted for clarity.



Table S10. Computed energies (kcal/mol) of $(MeSiP_2)Co(CO)_2$ (**3-CO**, S = 0), $(MeSiP_2)Co(CO)(N_3Ad)$ (**Int**, S = 0), and $(^{MeSi}N^{Ad}P_2)Co(CO)$ (**6**, S = 1) with reagents of the catalytic reaction.

	$\Delta \mathbf{E}$	Dispersion	Complexation	$\Delta \mathbf{G}$
$3-CO + AdN_3 + CO$	0.00	0.00	0.00	0.00
Int + 2CO	30.63	-2.94	0.00	26.27
$6 + 2CO + N_2$	-26.77	-5.98	2.49	-42.71
$AdNCO + N_2 + 3-CO$	-68.92	-0.03	0.00	-68.93

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