Supporting Information for Transmethylation of a Four-Coordinate Nickel(I) Monocarbonyl Species with Methyl Iodide

Changho Yoo, Seohee Oh, Jin Kim, Yunho Lee* Department of Chemistry, Korea Advanced Institute of Science and Technology Daejeon 305-701, Republic of Korea

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Optimized coordinates of 2

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under a N₂ atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with Ar gas followed by passage through an activated alumina column. Non-halogenated 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. Compound 1,¹ 6,² (PNP)NiH² and (PNP)NiCl² were prepared according to literature procedures. Elemental analyses were carried out at Columbia Analytical Services, Inc., Tucson, AZ or at KAIST Central Research Instrument Facility on Thermo Scientific FLASH 2000 series. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and Euriso-top, degassed, and dried over activated 4-Å molecular sieves prior to use.

X-ray Crystallography. The diffraction data of 4, 6, (PNP)NiEt, (PNP)NiⁿPr, (PNP)NiCOⁿPr and (PNP)NiCO'Pr were collected on a Bruker SMART APEX II. 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 MoKa radiation ($\lambda = 0.71073$ Å) under a stream of N₂ (g) at 100 or 120 K. Cell parameters were determined and refined by SMART program.³ Data reduction was performed using SAINT software.⁴ An empirical absorption correction was applied using the SADABS program. ⁵ The diffraction data of 2, 3' and (PNP)NiCO'Bu were collected on ADSC Quantum-210 detector at 2D SMC at the Pohang Accelerator Laboratory, Korea. The data were collected with Si(111) double crystal monochromated synchrotron radiation ($\lambda = 0.63000$ Å) at 100 K. The ADSC O210 ADX program⁶ was used for data collection and HKL3000sm (Ver. 703r)⁷ was used for cell refinement, reduction and absorption correction. The structures were solved by direct methods and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F² by using the SHELXTL/PC package.⁸ 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. Bruker 400 spectrometers were used to measure ¹H and ¹³C NMR. The chemical shifts for ¹H and ¹³C NMR spectra were quoted in part per million referenced to residual solvent peaks. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of

¹ C. Yoo, J. Kim and Y. Lee, *Organometallics*, 2013, **32**, 7195-7203.

² O. V. Ozerov, C. Guo, L. Fan and B. M. Foxman, *Organometallics*, 2004, 23, 5573-5580.

³ SMART, Version 5.0; data collection software, Bruker AXS, Inc., Madison, WI, USA, 1998.

⁴ SAINT, Version 5.0; data integration software, Bruker AXS, Inc., Madison, WI, USA, 1998.

⁵ G. M. Sheldrick, SADABS: program for absorption correction with the Bruker SMART system, Universität Göttingen, Göttingen, Germany, 1996.

⁶ A. J. Arvai and C. Nielsen, ADSC Quantum-210 ADX Program, Area Detector System Corporation: Poway, CA, USA, 1983.

⁷ Z. Otwinowski and W. Minor, in Methods in Enzymology, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press: New York, 1997, vol. 276, part A, p 307.

⁸ G. M. Sheldrick, SHELXTL, Version 6.1, Bruker AXS, Inc., Madison, WI, USA, 2000.

doublet, dt = doublet of triplet, br s = broad singlet, br d = broad doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ³¹P NMR spectra were recorded on Bruker 400 spectrometers and were decoupled by broad band proton decoupling. The chemical shifts for ³¹P NMR spectra were quoted in part per million (ppm) referenced to external phosphoric acid as 0.0 ppm. A ³¹P

single-pulse NMR spectrum with continuous wave ¹H decoupling was acquired employing a 30°

excitation pulse of 12 µs and a recycle delay of 30 s, which ensured full return of the ³¹P magnetization to equilibrium in the sample. Solution magnetic moments were determined by the Evans' method.⁹ CW X-band EPR spectrum of 2 was collected on a Bruker EMX plus 6/1 spectrometer equipped with an Oxford Instrument ESR900 liquid He cryostat using an Oxford ITC 503 temperature controller at the division of material science research, Korea Basic Science institute. Spectrum was collected with the following experimental parameters: microwave frequency, 9.6 GHz; microwave power, 0.96 mW; modulation amplitude, 10 G; modulation frequency, 100 kHz; temperature, 20 K. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source using a manual method. Cold spray ionization mass spectra (CSI-MS) were collected on a JEOL JMS-T100CS spectrometer. UV-Vis spectroscopy was measured by Agilent Cary 60 UV-Vis spectrophotometer using a 1-cm twowindow quartz spectrophotometer cell sealed with a screw-cap purchased from Sigma-Aldrich Co. LLC. (Catalog number: Z276820). Infrared spectra were recorded in KBr pellet by Bruker VECTOR 33 and Bruker EQUINOX 55. Frequencies are given in reciprocal centimeters (cm⁻¹) and only selected absorbances were reported.

Electrochemistry. Electrochemical measurements were carried out in a glovebox under a N_2 atmosphere using a 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 0.1 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.

Synthesis of (PNP)NiCO•C₁₀H₈ (2•C₁₀H₈). After sodium (60 mg, 2.6 mmol) was added to the solution of naphthalene (51 mg, 0.40 mmol) in 5 mL of THF, the reaction mixture was stirred for 3 hrs at room temperature. The resulting sodium naphthalide solution was filtered away from remaining sodium and added dropwise to the solution of 1 (250 mg, 0.415 mmol) in 15 mL of THF at -35 °C. The reaction mixture was slowly warmed to room temperature and stirred for 30 min, and the volatiles were removed under vacuum. After dissolved in pentane a green solution was filtered through Celite and volatiles were removed under vacuum. The resulting product (PNP)NiCO•C₁₀H₈ (2•C₁₀H₈, 211 mg, 0.328 mmol, 82%) was isolated as a green solid. Analytically pure material could be obtained by cooling a saturated pentane solution to -35 °C. μ_{eff} : 1.54 μ B (C₆D₆, 25 °C, Evans' method). X-band EPR spectrum in toluene at 20 K; g = [2.08, 2.02, 2.02]; A(P) = [80, 80, 80] G; A(N) = [7, 7, 7] G. CSI-MS {(PNP)NiCO}⁺: calcd, 514.19; found, 514.21. Anal. Calcd. for C₂₇H₄₀NNiOP₂•C₁₀H₈: C, 69.07; H, 7.52; N, 2.18. Found: C, 68.71; H, 7.52; N, 2.00. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 618 (812), ~348 (sh, 15500), 320

⁹ (a) D. F. Evans, J. Chem. Soc., 1959, 2003-2005. (b) S. K. Sur, J. Magn. Reson., 1989, 82, 169-173.

(20500). IR (KBr pellet, cm⁻¹): v_{CO} 1927, v_{Ar} 1593. Crystals suitable for X-ray diffraction were obtained from the concentrated pentane solution at –35 °C.

Synthesis of (PNP)Ni(CO)Na (3). After sodium (21 mg, 0.93 mmol) was added to the solution of naphthalene (21 mg, 0.16 mmol) in 5 mL of THF, the reaction mixture was stirred for 3 hrs at room temperature. The resulting sodium naphthalide solution was filtered away from remaining sodium and added dropwise to the solution of $2 \cdot C_{10}H_8$ (86 mg, 0.13 mmol) in THF of 10 mL at – 35 °C. The reaction mixture was slowly warmed to room temperature resulting in the color changed from green to dark orange. After stirring for 1 hr the solution was filtered through Celite and volatiles were removed under vacuum. The resulting product (PNP)Ni(CO)Na (3, 77 mg, 0.14 mmol, >99%) was isolated as an yellow solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, benzene- d_6 /THF) δ 7.33 (dd, J = 8.4, 4.7 Hz, 2H), 7.21 (d, J = 5.2Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 2.54–2.43 (m, 2H), 2.39 (s, 6H), 2.01–1.84 (m, 2H), 1.26 (dd, J = 15.8, 6.7 Hz, 8H), 1.13 (dd, J = 13.8, 6.8 Hz, 8H), 1.05 (dd, J = 12.5, 7.0 Hz, 8H), 0.97 (dd, J = 12.5, 7.0= 13.7, 6.9 Hz, 8H). ¹³C NMR (101 MHz, benzene- d_6) δ 208.12 (NiC, t, J = 39.5 Hz), 160.40 $(CN_{Ar}, dd, J = 20.9, 3.2 Hz), 131.99 (C_{Ar}), 131.74 (C_{Ar}), 129.00 (C_{Ar}), 122.57 (C_{Ar}, d, J = 2.4 Hz)$ Hz), 114.91 (C_{Ar}), 28.71 (CH_{*i*Pr}), 24.42 (CH_{*i*Pr}, dd, J = 15.2, 7.3 Hz), 20.80 (Me_{Ar}), 20.29–19.58 (Me_{iPr}, m). ³¹P NMR (162 MHz, benzene-d₆/THF) δ 46.59. Anal. Calcd. for C₂₇H₄₀NNaNiOP₂: C, 60.25; H, 7.49; N, 2.60. Found: C, 60.55; H, 7.88; N, 2.33. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 348 (12500), ~313 (sh, 11300). IR (KBr pellet, cm⁻¹): v_{CO} 1821, 1791, v_{Ar} 1594.

Synthesis of {Na(12-crown-4)₂}{(PNP)NiCO} (3'). To the solution of 3 (160 mg, 0.297 mmol) in 5 mL of THF, 12-crown-4 (96 μ L, 0.60 mmol) was added using a micro-syringe. The reaction mixture was stirred for 10 min at room temperature. The solution was filtered through Celite and volatiles were removed under vacuum. The resulting product {Na(12-crown-4)₂} {(PNP)NiCO} (3', 224 mg, 0.252 mmol, 84.6%) was isolated as an orange solid after washing with pentane and drying under vacuum. ¹H NMR (300 MHz, benzene-*d*₆) δ 7.77 (dd, *J* = 8.3, 4.7 Hz, 2H), 7.44 (d, *J* = 5.2 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.16 (s, 32H), 2.87–2.69 (m, 2H), 2.40 (s, 6H), 2.22–2.06 (m, 2H), 1.77–1.56 (m, 12H), 1.42–1.19 (m, 12H). ¹³C NMR (101 MHz, benzene-*d*₆) δ 210.06 (NiC, t, *J* = 39.5 Hz), 159.78 (CN_{Ar}, dd, *J* = 19.7, 3.8 Hz), 132.81 (C_{Ar}, d, *J* = 29.0 Hz), 131.55 (C_{Ar}), 128.48 (C_{Ar}), 119.28 (C_{Ar}, d, *J* = 4.1 Hz), 114.92 (C_{Ar}), 65.68 (12-crown-4), 29.10 (CH_{*i*Pr}), 25.38 (CH_{*i*Pr}), 21.23 (Me_{Ar}), 20.95–20.36 (Me_{*i*Pr}, m). ³¹P NMR (162 MHz, benzene-*d*₆) δ 47.20. IR (KBr pellet, cm⁻¹): *v*_{CO} 1819, *v*_{Ar} 1594, 1583. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated THF solution.

Synthesis of (PNP)NiCO (2) from 3. To a solution of 3 (115 mg, 0.214 mmol) in 10 mL of THF, AgOTf (55 mg, 0.21 mmol) was added at -35 °C. The reaction mixture was stirred for 1.5 hrs at room temperature. All volatiles were removed under vacuum. After dissolved in pentane a green solution was filtered through Celite and volatiles were removed under vacuum. The resulting product (PNP)NiCO (2, 82 mg, 0.16 mmol, 74%) was isolated as a green solid. Analytically pure compound was obtained from the recrystallization of the concentrated pentane solution of 2 at -35 °C. Anal. Calcd. for C₂₇H₄₀NNiOP₂: C, 62.94; H, 7.82; N, 2.72. Found: C, 62.80; H, 8.00; N, 2.71. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 615 (752), ~346 (sh, 15400), 318 (19500). IR (KBr pellet, cm⁻¹): v_{CO} 1928, v_{Ar} 1593. Crystals suitable for X-ray diffraction were obtained from the concentrated pentane solution at -35 °C.

Synthesis of (PNP)NiCOMe (4). In a 50 mL Schlenk tube, 6 (100 mg, 0.199 mmol) was dissolved in 5 mL of benzene. The solution was degassed by three freeze-pump-thaw cycles on the Schlenk line and then exposed to CO gas at ambient pressure. The reaction mixture was stirred for 40 hrs at room temperature, resulting in a slow color change from orange to yellow. The volatiles were removed under vacuum. The resulting product (PNP)NiCOMe (4, 86 mg, 0.16 mmol, 81%) was isolated as a yellow solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, benzene- d_6) δ 7.64 (d, J = 8.6 Hz, 2H), 6.88–6.80 (m, 4H), 2.44 (s, 3H), 2.16–2.10 (m, 8H), 2.06 (br s, 2H), 1.26 (q, *J* = 7.8 Hz, 12H), 1.06 (br d, *J* = 20.4 Hz, 12H). ¹³C NMR (101 MHz, benzene- d_6) δ 259.37 (NiC, t, J = 21.2 Hz), 160.95 (CN_{Ar}, t, J = 12.1 Hz), 132.58 (C_{Ar}), 132.03 (C_{Ar}), 123.83 (C_{Ar} , t, J = 3.2 Hz), 119.20 (C_{Ar} , t, J = 20.2 Hz), 115.27 (C_{Ar} , t, J = 4.7 Hz), 43.87 (Ni(CO)CH₃, t, J = 5.4 Hz), 23.03 (CH_{iPr}), 20.62 (Me_{Ar}), 18.56 (Me_{iPr}), 17.15 (Me_{*i*Pr}). ³¹P NMR (162 MHz, benzene- d_6) δ 35.95. ESI-MS {(PNP)NiCOMe}⁺: calcd, 529.22; found, 528.82. CSI-MS {(PNP)NiCOMe}+: calcd, 529.22; found, 529.17. Anal. Calcd. for C₂₈H₄₃NNiOP₂: C, 63.42; H, 8.17; N, 2.64. Found: C, 63.18; H, 8.22; N, 2.71. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 436 (2910), 343 (18300), 313 (15200). IR (KBr pellet, cm⁻¹): $v_{C=0}$ 1616, v_{Ar} 1595. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated benzene solution.

Reaction of 3 with MeI. To a solution of **3** (31 mg, 0.058 mmol) in 10 mL of THF, MeI (40 μ l, 2.0 M in 'BuOMe, 0.080 mmol) was added using a microsyringe at -35 °C, resulting in an immediate color change from orange to brown. The reaction mixture was stirred for 1 hr at room temperature and volatiles were removed under vacuum. After the residue was dissolved in benzene, the solution was filtered through Celite and volatiles were removed under vacuum. The resulting product (PNP)NiMe (**6**, 28 mg, 0.056 mmol, 97%) was isolated as a red solid after drying under vacuum. The identity of the product was confirmed by its published ¹H and ³¹P NMR spectra.¹² Crystals suitable for X-ray diffraction were obtained from the concentrated THF solution at -35 °C.

Reaction of 3 with EtI. To a solution of **3** (30 mg, 0.056 mmol) in 5 mL of THF, EtI (4.9 μ L, 9.4 mg, 0.060 mmol) was added using a microsyringe was cooled at -35 °C resulting in an immediate color change to brighter orange. The reaction mixture was stirred for 1 hr at room temperature and volatiles were removed under vacuum. After the residue was dissolved in benzene, the solution was filtered through Celite and volatiles were removed under vacuum to yield an orange solid. The formation of two products, (PNP)NiCOEt (73%) and (PNP)NiEt (25%) was confirmed by their ¹H and ³¹P NMR spectra.

Separate synthesis of (PNP)NiEt. To a solution of (PNP)NiCl (101 mg, 0.193 mmol) in 5 mL of THF, EtMgCl (97 μ L, 2.0 M in THF, 0.19 mmol) was added using a microsyringe at -35 °C. The reaction mixture was stirred for 30 min at room temperature resulting in a slow color change from green to reddish orange. After adding 3 mL of 1,4-dioxane, the reaction mixture was stirred for 2 hrs after which time volatiles were removed under vacuum. After the residue was dissolved in benzene, the solution was filtered through Celite and volatiles were removed under vacuum. The resulting product (PNP)NiEt (95 mg, 0.18 mmol, 95%) was isolated as a reddish orange solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, benzene-*d*₆) δ 7.66 (d, *J* = 8.5 Hz, 2H), 6.95 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 2.28–2.15 (m, 10H), 1.34 (q, *J* = 7.4 Hz, 12H), 1.27 (t, *J* = 7.7 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 12H), 0.93-0.79 (m, 2H). ¹³C NMR

(101 MHz, benzene- d_6) δ 161.73 (CN_{Ar}, t, J = 12.4 Hz), 132.16 (C_{Ar}), 131.87 (C_{Ar}), 127.39 (C_{Ar}), 127.37 (C_{Ar}, t, J = 3.5 Hz), 121.11 (C_{Ar}, t, J = 18.4 Hz), 115.37 (C_{Ar}, t, J = 5.1 Hz), 23.70 (CH_{*i*}), t, J = 10.7 Hz), 20.70 (Me_{Ar}), 18.97 (Me_{*i*}), t, J = 2.9 Hz), 17.80 (Me_{*i*}), 16.69 (NiCH₂CH₃), -15.29 (NiCH₂CH₃), -15.51 (NiCH₂CH₃, t, J = 22.7 Hz). ³¹P NMR (162 MHz, benzene- d_6) δ 32.03. ESI-MS {(PNP)NiEt}⁺: calcd, 515.24; found, 515.00. CSI-MS {(PNP)NiEt}⁺: calcd, 515.24; found, 515.20. Anal. Calcd. for C₂₈H₄₅NNiP₂: C, 65.14; H, 8.78; N, 2.71. Found: C, 65.08; H, 8.81; N, 2.60. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: ~484 (sh, 1400), ~362 (sh, 13500), 344 (18200). IR (KBr pellet, cm⁻¹): v_{Ar} 1591. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution.

Separate synthesis of (PNP)NiCOEt. In a 60 mL Schlenk tube, (PNP)NiEt (99 mg, 0.19 mmol) was dissolved in 15 mL of benzene. The solution was degassed by three freeze-pump-thaw cycles on the Schlenk line and then exposed to CO gas at ambient pressure. The reaction mixture was stirred for 32 hrs at room temperature, resulting in a slow color change from orange to yellow. Volatiles were removed under vacuum. The resulting product (PNP)NiCOEt (102 mg, 0.187 mmol, 98%) was isolated as a yellow solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, benzene- d_6) δ 7.64 (dt, J = 9.3, 2.5 Hz, 2H), 6.83 (m, 4H), 2.90 (q, J = 7.2Hz, 2H), 2.23–2.10 (m, 10H), 1.25 (q, J = 7.6 Hz, 12H) 1.16–0.93 (m, 15H). ¹³C NMR (101 MHz, benzene- d_6) δ 259.45 (NiC, t, J = 20.2 Hz), 160.97 (CN_{Ar}, t, J = 11.9 Hz), 132.54 (C_{Ar}), 132.04 (C_{Ar}), 123.78 (C_{Ar}, t, J = 3.3 Hz), 119.32 (C_{Ar}, t, J = 19.7 Hz), 115.30 (C_{Ar}, t, J = 4.9 Hz), 50.93 (Ni(CO)CH₂CH₃, t, J = 5.2 Hz), 22.96 (CH_{*i*Pr}, br), 20.64 (Me_{Ar}), 18.58 (Me_{*i*Pr}), 17.14 (Me_{iPr}), 7.58 (Ni(CO)CH₂CH₃). ³¹P NMR (162 MHz, benzene-d₆) δ 35.56. ESI-MS {(PNP)NiCOEt}⁺: calcd, 543.23; found, 542.80. CSI-MS {(PNP)NiCOEt}⁺: calcd, 543.23; found, 543.20. Anal. Calcd. for C₂₉H₄₅NNiOP₂: C, 63.99; H, 8.33; N, 2.57. Found: C, 63.92; H, 8.44; N, 2.50. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 438 (2760), 345 (18800), 313 (17200). IR (KBr pellet, cm⁻¹): $v_{C=0}$ 1616, v_{Ar} 1593.

Reaction of 3 with "PrI. To a solution of **3** (30 mg, 0.056 mmol) in 5 mL of THF, "PrI (6.1 μ L, 11 mg, 0.062 mmol) was added using a microsyringe at -35 °C resulting in an immediate color change to brighter orange. The reaction mixture was stirred for 1 hr at room temperature and all volatiles were removed under vacuum. After the residue was dissolved in benzene, the solution was filtered through Celite and volatiles were removed under vacuum to yield an orange solid. The formation of two products, (PNP)NiCO"Pr (92%) and (PNP)Ni"Pr (8%) was confirmed by their ¹H and ³¹P NMR spectra.

Separate synthesis of (PNP)Ni^{*n*}Pr. To the solution of (PNP)NiCl (202 mg, 0.386 mmol) and 1,4-dioxane (66 µL, 68 mg, 0.77 mmol) in 5 mL of THF, ^{*n*}PrMgCl (193 µL, 2.0 M in diethylether, 0.39 mmol) was added using a microsyringe at -35 °C. The green reaction mixture was stirred for 1 hr at room temperature resulting in a slow color change to reddish orange. Volatiles were removed under vacuum and the residue was dissolved in benzene. The solution was filtered through Celite and the volatiles were removed under vacuum. The resulting product (PNP)Ni^{*n*}Pr (187 mg, 0.353 mmol, 91.2%) was isolated as a reddish orange solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, benzene-*d*₆) δ 7.67 (dt, *J* = 8.6 2.2 Hz, 2H), 6.94 (s, 2H), 6.82 (dd, *J* = 8.5, 2.0 Hz, 2H), 2.25–2.15 (m, 10H), 1.72–1.61(m, 2H), 1.32 (q, *J* = 7.4 Hz, 12H), 1.14 (m, 15H), 0.81–0.71 (m, 2H). ¹³C NMR (101 MHz, benzene-*d*₆) δ 161.75 (CN_{Ar}, t, *J* = 12.4 Hz), 132.15 (C_{Ar}), 131.87 (C_{Ar}), 123.40 (C_{Ar}, t, *J* = 3.3 Hz), 121.09 (C_{Ar}, t, *J* = 18.4 Hz), 115.37 (C_{Ar}, t, *J* = 4.9 Hz), 25.85 (NiCH₂CH₂CH₃), 23.76 (CH_{*i*Pr}, t, *J* = 10.8 Hz),

20.70 (Me_{Ar}), 19.31 (NiCH₂CH₂CH₃), 18.93 (Me_{*i*Pr}, t, J = 2.9 Hz), 17.78 (Me_{*i*Pr}), -3.58 (NiCH₂CH₂CH₃, t, J = 22.2 Hz). ³¹P NMR (162 MHz, benzene-*d*₆) δ 32.26. ESI-MS {(PNP)NiⁿPr}⁺: calcd, 529.25; found, 529.07. CSI-MS {(PNP)NiⁿPr}⁺: calcd, 529.25; found, 529.26. Anal. Calcd. for C₂₉H₄₇NNiP₂: C, 65.68; H, 8.93; N, 2.64. Found: C, 65.64; H, 9.12; N, 2.41. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: ~485 (sh, 1360), ~362 (sh, 12700), 344 (17700). IR (KBr pellet, cm⁻¹): v_{Ar} 1593. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution.

Separate synthesis of (PNP)NiCO"Pr. In a 40 mL Schlenk tube, (PNP)Ni"Pr (91 mg, 0.17 mmol) was dissolved in 10 mL of benzene. The solution was degassed by three freeze-pumpthaw cycles on the Schlenk line and then exposed to CO gas at ambient pressure. The reaction mixture was stirred for 32 hrs at room temperature resulting in a slow color change from orange to vellow. Volatiles were removed under vacuum. The resulting product (PNP)NiCOⁿPr (95 mg, 0.17 mmol, 99%) was isolated as a yellow solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, benzene- d_6) δ 7.65 (dt, J = 8.4, 2.5 Hz, 2H), 6.90–6.80 (m, 4H), 3.00 (t, J = 7.6 Hz, 2H), 2.19 (m, 10H), 1.77 (m, 2H), 1.29 (q, J = 7.8 Hz, 12H), 1.14 (m, 12H), 0.97 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, benzene- d_6) δ 259.52 (NiC, t, J = 20.2 Hz), 160.94 $(CN_{Ar}, t, J = 11.8 Hz), 132.53 (C_{Ar}), 132.03 (C_{Ar}), 127.92 (C_{Ar}), 123.78 (C_{Ar}, t, J = 3.4 Hz),$ 119.34 (C_{Ar}, t, J = 19.7 Hz), 115.30 (C_{Ar}, t, J = 4.7 Hz), 60.79 (Ni(CO)CH₂CH₂CH₃, t, J = 5.0Hz), 23.15 (CH_{iPr}), 20.65 (Me_{Ar}), 18.63 (Me_{iPr}), 17.16 (Me_{iPr}), 14.53 (Ni(CO)CH₂CH₂CH₃), 1.43 (Ni(CO)CH₂CH₂CH₃). ³¹P NMR (162 MHz, benzene- d_6) δ 35.11. ESI-MS {(PNP)NiCOⁿPr}+: calcd, 557.25; found, 556.87. CSI-MS {(PNP)NiCOⁿPr}⁺: calcd, 557.25; found, 557.24. Anal. Calcd. for C₃₀H₄₇NNiOP₂: C, 64.53; H, 8.48; N, 2.51. Found: C, 64.40; H, 8.57; N, 2.56. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 442 (2330), 345 (16300), 314 (15300). IR (KBr pellet, cm⁻¹): $v_{C=0}$ 1616, v_{Ar} 1594. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution.

Reaction of 3 with 'PrI. To a solution of **3** (100 mg, 0.186 mmol) in 10 mL of THF, 'PrI (21 μ L, 36 mg, 0.21 mmol) was added using a microsyringe at -35 °C resulting in an immediate color change to brighter orange. The reaction mixture was stirred for 1 hr at room temperature and volatiles were removed under vacuum. After the residue was dissolved in benzene, the solution was filtered through Celite and all volatiles were removed under vacuum. The formation of the product (PNP)NiCO^{*i*}Pr (>99%) was confirmed by its ¹H and ³¹P NMR spectra. Analytically pure product (PNP)NiCO'Pr (86 mg, 0.15 mmol, 83%) was isolated as an orange solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, benzene- d_6) δ 7.58 (dt, J = 9.3, 2.4Hz, 2H), 6.87-6.80 (m, 4H), 2.30-2.05 (m, 10H), 2.03-1.94 (m, 1H), 1.53 (s, 3H), 1.51 (s, 3H), 1.33–1.16 (m, 12H), 1.07 (br s, 12H). ¹³C NMR (101 MHz, benzene- d_6) δ 264.24 (NiC, t, J = 20.0 Hz), 160.65 (CN_{Ar}, t, J = 11.7 Hz), 132.45 (C_{Ar}), 131.83 (C_{Ar}), 123.79 (C_{Ar}), 119.76 (C_{Ar}, t, J = 19.7 Hz, 115.46 (C_{Ar}, t, J = 4.5 Hz), 53.42 (Ni(CO)CH(CH₂)₂), 23.05 (CH_{*i*Pr}), 20.68 (Me_{Ar}), 18.62 (Me_{iPr}), 17.07 (Me_{iPr}). One Me_{iPr} could not be found. ³¹P NMR (162 MHz, benzene- d_6) δ 33.97. ESI-MS {(PNP)NiCOⁱPr}⁺: calcd, 557.25; found, 556.80. CSI-MS {(PNP)NiCOⁱPr}⁺: calcd, 557.25; found, 557.24. Anal. Calcd. for C₃₀H₄₇NNiOP₂: C, 64.53; H, 8.48; N, 2.51. Found: C, 64.33; H, 8.70; N, 2.54. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: ~463 (sh, 2090), 340 (21300), 316 (19700). IR (KBr pellet, cm⁻¹): $v_{C=O}$ 1610, v_{Ar} 1597. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution.

Reaction of 3 with 'Bul. To a solution of 3 (100 mg, 0.186 mmol) in 10 mL of THF, 'Bul (27 µL, 42 mg, 0.23 mmol) was added using a microsyringe at -35 °C resulting in an immediate color change to brighter orange. The reaction mixture was stirred for 1 hr at room temperature and all volatiles were removed under vacuum. After the residue was dissolved in pentane, the solution was filtered through Celite and volatiles were removed under vacuum. The formation of (PNP)NiCO'Bu (97%) and a trace amount of (PNP)NiI (3%) was confirmed by their ¹H and ³¹P NMR spectral assignments. Analytically pure product (PNP)NiCO'Bu (69 mg, 0.12 mmol, 65%) was isolated as an orange solid after washing with pentane and drying under vacuum. ¹H NMR (400 MHz, benzene- d_6) δ 7.47 (dt, J = 8.5, 2.3 Hz, 2H), 7.04–6.80 (m, 2H), 6.81 (dd, J = 8.4, 1.4Hz, 2H), 2.29–2.11 (m, 4H), 2.18 (s, 6H), 1.37 (s, 9H), 1.36–1.21 (m, 18H), 1.05 (q, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, benzene- d_6) δ 267.05 (NiC, t, J = 18.9 Hz), 160.12 (C_{Ar}, t, J = 11.3 Hz), 132.34 (C_{Ar}), 131.49 (C_{Ar}), 123.81 (C_{Ar}), 121.23 (C_{Ar}, t, J = 20.0 Hz), 115.75 (C_{Ar}), 51.08 (NiCOC(CH₃)₃), t, J = 3.3 Hz), 28.06 (NiCOC(CH₃)₃), 25.48 (CH_{*i*Pr}, t, J = 11.5 Hz), 23.37 (CH_{*i*Pr}, t, J = 10.6 Hz), 20.76 (Me_{Ar}), 19.11 (Me_{iPr}), 18.50 (Me_{iPr}), 18.29 (Me_{iPr}), 17.32 (Me_{iPr}). ³¹P NMR (162 MHz, benzene-d₆) δ 31.36. ESI-MS {(PNP)NiCO'Bu}⁺: calcd, 571.26; found, 570.73. CSI-MS {(PNP)NiCO'Bu}⁺: calcd, 571.26; found, 571.27. Anal. Calcd. for C₃₁H₄₉NNiOP₂: C, 65.05; H, 8.63; N, 2.45. Found: C, 65.02; H, 8.80; N, 2.52. UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 482 (1760), 340 (25400), 315 (19800). IR (KBr pellet, cm⁻¹): v_{C=O} 1606, v_{Ar} 1599. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a pentane solution.

Synthesis of (PNP)NiI (5).¹³ To a solution of (PNP)NiH (100 mg, 0.205 mmol) in 10 mL of THF, MeI (1.0 mL, 2.0 M in 'BuOMe, 2.0 mmol) was added at room temperature. The orange colored reaction mixture was stirred for 28 hrs resulting in a gradual color change to green. The product (PNP)NiI (5, 101 mg, 0.164 mmol, 80.3%) was isolated as a green solid after washing with pentane and drying under vacuum. The identity of the product was confirmed by comparing newly acquired spectra with previously published ¹H and ³¹P NMR spectral data.¹³ UV-Vis [THF, nm (L mol⁻¹ cm⁻¹)]: 673 (400), ~479 (sh, 765), 344 (30500), 318 (19400).

Reaction of 2 with MeI. To a green solution of **2** (10 mg, 0.019 mmol) in 10 ml of THF, CH₃I (10 μ L, 2.0 M in 'BuOMe, 0.020 mmol) was added using a microsyringe at -35 °C resulting in an immediate color change to dark orange. The reaction mixture was stirred for 30 min at room temperature and volatiles were removed under vacuum. The formation of three products, (PNP)NiI (50%), (PNP)NiCOMe (37%) and (PNP)NiMe (13%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 2 with EtI. To a green solution of **2** (30 mg, 0.058 mmol) in 5 mL of THF, EtI (5.1 μ L, 9.9 mg, 0.064 mmol) was added using a microsyringe at -35 °C resulting in an immediate color change to dark orange. The reaction mixture was stirred for 1 hr at room temperature and volatiles were removed under vacuum. The formation of three products, (PNP)NiI (50%), (PNP)NiCOEt (48%) and (PNP)NiEt (2%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 2 with "PrI. To a green solution of **2** (30 mg, 0.058 mmol) in 5 mL of THF, "PrI (6.0 μ L, 10 mg, 0.062 mmol) was added using a microsyringe at -35 °C resulting in an immediate color change to dark orange. The reaction mixture was stirred for 1 hr at room temperature and all volatiles were removed under vacuum. The formation of three products, (PNP)NiI (50%), (PNP)NiCOⁿPr (49%) and (PNP)NiⁿPr (1%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 2 with 'PrI. To a green solution of **2** (30 mg, 0.058 mmol) in 5 mL of THF, 'PrI (6.5 μ L, 11 mg, 0.065 mmol) was added using a microsyringe at -35 °C resulting in an immediate color change to dark orange. The reaction mixture was stirred for 1 hr at room temperature and volatiles were removed under vacuum. The formation of two products, (PNP)NiI (50%) and (PNP)NiCO'Pr (50%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 2 with 'Bul. To a green solution of **2** (22 mg, 0.043 mmol) in 10 mL of THF, 'Bul (5.2 μ L, 8.0 mg, 0.044 mmol) was added using a microsyringe at -35 °C resulting in an immediate color change to dark orange. The reaction mixture was stirred for 1 hr at room temperature and all volatiles were removed under vacuum. The formation of two products, (PNP)NiI (55%) and (PNP)NiCO'Bu (45%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 2 with MeI for 10 min. To a green solution of **2** (30 mg, 0.058 mmol) in 5 mL of THF, MeI (35 μ L, 2.0 M in 'BuOMe, 70 mmol) was added using a microsyringe at room temperature resulting in an immediate color change from green to dark orange. The reaction mixture was stirred for 10 min at room temperature, and all volatiles were removed under vacuum. The formation of three products, (PNP)NiI (49%), (PNP)NiCOMe (37%) and (PNP)NiMe (12%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 2 with MeI for 1 hr. To a green solution of **2** (30 mg, 0.058 mmol) in 5 mL of THF, MeI (35 μ L, 2.0 M in 'BuOMe, 70 mmol) was added using a microsyringe at room temperature resulting in an immediate color change to orange. The reaction mixture was stirred for 1 hr at room temperature, and all volatiles were removed under vacuum. The formation of three products, (PNP)NiI (48%), (PNP)NiCOMe (37%) and (PNP)NiMe (12%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 6 with 5 equivalent of CO for 10 min. In a 13 mL Schlenk tube, **6** (30 mg, 0.060 mmol) was dissolved in 5 mL of THF. The resulting orange solution was degassed by freezepump-thaw cycles on the Schlenk line and CO gas (~ 8 mL, ~ 0.3 mmol) was charged at ambient pressure. After the reaction mixture was stirred for 10 min at room temperature, all volatiles were removed under vacuum. The formation of (PNP)NiCOMe (3%) with remaining (PNP)NiMe (93%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 6 with 5 eqiv. of CO for 1 hr. In a 13 mL Schlenk tube, **6** (30 mg, 0.060 mmol) was dissolved in 5 mL of THF. The resulting orange solution was degassed by freeze-pump-thaw cycles on the Schlenk line and CO gas (\sim 8 mL, \sim 0.3 mmol) was charged at ambient pressure. After the reaction mixture was stirred for 1 hr at room temperature, the volatiles were removed under vacuum. The formation of (PNP)NiCOMe (10%) with remaining (PNP)NiMe (86%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 6 with 15 eqiv. of CO for 1 hr. In a 17 mL Schlenk tube, **6** (10 mg, 0.020 mmol) was dissolved in 10 mL of THF. The resulting orange solution was degassed by freeze-pump-thaw cycles on the Schlenk line and CO gas (\sim 7 mL, \sim 0.3 mmol) was charged at ambient pressure. After the reaction mixture was stirred for 1 hr at room temperature, all volatiles were removed under vacuum. The formation of (PNP)NiCOMe (10%) with remaining (PNP)NiMe (86%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 2 with MeI in toluene. To a green solution of **2** (30 mg, 0.058 mmol) in 10 mL of toluene, MeI (35 μ L, 2.0 M in 'BuOMe, 0.070 mmol) was added using a microsyringe at -35 °C. The green reaction mixture was stirred for 1 hr at room temperature resulting in a color change to dark orange. The volatiles were removed under vacuum. The formation of three products, (PNP)NiI (49%), (PNP)NiCOMe (36%) and (PNP)NiMe (12%) was confirmed by ¹H and ³¹P NMR spectroscopy.

Reaction of 2 with MeOTf in toluene. To a green solution of **2** (30 mg, 0.058 mmol) in 10 mL of toluene, MeOTf (7.9 μ L, 11 mg, 0.070 mmol) was added using a microsyringe at -35 °C. The green reaction mixture was stirred for 1 hr at room temperature and volatiles were removed under vacuum. Remaining (PNP)NiCO (**2**) was confirmed by IR and UV-Vis spectroscopic methods. The calibration curve was derived from the absorption measurements of 2.5 mM (PNP)NiCO (**2**) stock solution (Supporting Information). The concentration of **2** from the reaction mixture was spectroscopically measured from the absorption at 615 nm and the yield was 93%.







Figure S3. ³¹P NMR spectrum of (PNP)Ni(CO)Na (3) in C₆D₆/THF at room temperature.









Figure S5. ³¹P NMR spectrum of (PNP)Ni(CO)Na (3) in C_6D_6 at room temperature.

Figure S7. ¹³C NMR spectrum of $\{Na(12\text{-}crown-4)_2\}$ {(PNP)NiCO} (3') in C₆D₆ at RT.





Figure S9. ¹H NMR spectrum of (PNP)NiCOMe (4) in C₆D₆ at room temperature.

Figure S10. ¹³C NMR spectrum of (PNP)NiCOMe (4) in C₆D₆ at room temperature.



Figure S11. ³¹P NMR spectrum of (PNP)NiCOMe (4) in C₆D₆ at room temperature.





Figure S12. ¹H NMR spectrum of (PNP)NiEt in C₆D₆ at room temperature.

Figure S13. ¹³C NMR spectrum of (PNP)NiEt in C₆D₆ at room temperature.



Figure S14. ³¹P NMR spectrum of (PNP)NiEt in C₆D₆ at room temperature.







Figure S16. ¹³C NMR spectrum of (PNP)NiCOEt in C₆D₆ at room temperature.



Figure S17. ³¹P NMR spectrum of (PNP)NiCOEt in C₆D₆ at room temperature.







Figure S19. ¹³C NMR spectrum of (PNP)Ni^{*n*}Pr in C₆D₆ at room temperature.



Figure S20. ³¹P NMR spectrum of (PNP)Ni^{*n*}Pr in C₆D₆ at room temperature.





Figure S21. ¹H NMR spectrum of (PNP)NiCO^{*n*}Pr in C₆D₆ at room temperature.

Figure S22. ¹³C NMR spectrum of (PNP)NiCO^{*n*}Pr in C₆D₆ at room temperature.



Figure S23. ³¹P NMR spectrum of (PNP)NiCO^{*n*}Pr in C₆D₆ at room temperature.







Figure S25. ¹³C NMR spectrum of (PNP)NiCO^{*i*}Pr in C₆D₆ at room temperature.



Figure S26. ³¹P NMR spectrum of (PNP)NiCO^{*i*}Pr in C₆D₆ at room temperature.







Figure S28. ¹³C NMR spectrum of (PNP)NiCO'Bu in C₆D₆ at room temperature.



Figure S29. ³¹P NMR spectrum of (PNP)NiCO'Bu in C₆D₆ at room temperature.



Figure S30. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)Ni(CO)Na (3) with MeI.



Figure S31. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)Ni(CO)Na (3) with EtI.



Figure S32. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)Ni(CO)Na (**3**) with "PrI.



Figure S33. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)Ni(CO)Na (3) with ^{*i*}PrI.



Figure S34. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)Ni(CO)Na (3) with 'BuI.





Figure S35. ³¹P NMR spectrum (in C_6D_6 at RT) of the reaction of (PNP)NiCO (2) with MeI.

Figure S40. Experimental (red line) and simulated (black line) EPR spectra of (PNP)NiCO (2) in toluene at 20 K.





Figure S41. Solid-state structure of (PNP)NiCO•C₁₀H₈ ($2 \cdot C_{10}H_8$). Hydrogen atoms are omitted for clarity.

Figure S42. Solid-state structure of $\{Na(12\text{-}crown-4)_2\}$ {(PNP)NiCO} (**3'**). The asymmetric unit cell contains two pairs of **3'**. For clarity, one pair of **3'** is shown. One co-crystallized tetra-hydrofuran solvent and hydrogen atoms are omitted for clarity.



Table S3. Selected bond distances and angles for 1,¹ 2 and 3' (Å and °).

	${Ni^{II}-CO}^+(1)$	Ni ^I -CO (2)	{Ni ⁰ -CO} ⁻ (3')
d _{NiC}	1.746(2)	1.776(2)	1.719(3), 1.713(4)
$d_{ m NiN}$	1.866(1)	1.964(1)	2.039(3), 2.066(3)
d _{NiP}	2.2004(4) 2.2045(4)	2.2131(5) 2.2320(5)	2.162(1), 2.166(1) 2.186(1), 2.169(1)
d _{C=O} d _{C-O}	1.133(2)	1.149(2)	1.174(4), 1.173(4)
∠N-Ni-C	172.36(6)	153.25(8)	128.7(1), 128.7(1)
∠P-Ni-P	168.36(2)	154.82(2)	128.70(4), 130.75(4)
∠N-Ni-P	86.74(4) 85.50(4)	85.28(4) 84.04(4)	82.26(9), 85.28(9) 86.10(9), 85.4(1)
∠0-C-0 ∠Ni-C-0	- 175.8(1)	169.4(2)	172.1(3), 169.5(3)

Figure S43. Solid-state structure of (PNP)NiCOMe (4). One co-crystallized benzene solvent molecule and hydrogen atoms are omitted for clarity.



Table S4. Selected bond distances and angles for (PNP)NiCOMe (Å and °).

Bond distance		Bond a	ngle
d _{Ni1-C1}	1.865(2)	∠N1-Ni1-C1	178.57(6)
d _{Ni1-N1}	1.958(1)	∠P1-Ni1-P2	167.72(2)
d _{Ni1-P1}	2.1780(4)	∠N1-Ni1-P1	85.73(4)
d _{Ni1-P2}	2.1662(4)	∠N1-Ni1-P2	84.95(4)
d _{C1-O1}	1.225(2)	∠C1-Ni1-P1	95.55(5)
d _{C1-C2}	1.510(2)	∠C1-Ni1-P2	93.69(5)
		∠Ni1-C1-O1	123.7(1)
		∠Ni1-C1-C2	116.9(1)
		∠01-C1-C2	119.4(2)

Figure S44. Solid-state structure of (PNP)NiMe (6). One co-crystallized THF solvent molecule and hydrogen atoms are omitted for clarity.



Table S5. Selected bond distances and angles for (PNP)NiMe (6) (Å and °).

Bond distance		Bond angle	
d _{Ni1-C1}	2.004(2)	∠N1-Ni1-C1	176.94(9)
d _{Ni1-N1}	1.947(2)	∠P1-Ni1-P2	170.37(2)
d _{Ni1-P1}	2.1810(5)	∠N1-Ni1-P1	84.73(5)
d _{Ni1-P2}	2.1630(5)	∠N1-Ni1-P2	85.68(5)
		∠C1-Ni1-P1	96.71(6)
		∠C1-Ni1-P2	92.92(6)

Figure S45. Solid-state structure of (PNP)NiEt . Hydrogen atoms are omitted for clarity.



 Table S6. Selected bond distances and angles for (PNP)NiEt (Å and °).

Bond distance		Bond angle	
d _{Ni1-C1}	1.963(5)	∠N1-Ni1-C1	174.9(2)
d _{Ni1-N1}	1.950(4)	∠P1-Ni1-P2	167.58(5)
d _{Ni1-P1}	2.186(1)	∠N1-Ni1-P1	83.9(1)
d _{Ni1-P2}	2.170(1)	∠N1-Ni1-P2	84.5(1)
d _{C1-C2}	1.504(8)	∠C1-Ni1-P1	96.5(2)
		∠C1-Ni1-P2	95.5(2)
		∠Ni1-C1-C2	115.0(4)

Figure S46. Solid-state structure of (PNP)Ni^{*n*}Pr. Hydrogen atoms are omitted for clarity. The *n*-propyl group was disordered over two distinct positions. For clarity, only one component is shown.



Table S7. Selected bond distances and angles for (PNP)Ni^{*n*}Pr (Å and °).

Bond	distance	Bond angle	
d _{Ni1-C1A}	1.980(8)	∠N1-Ni1-C1A	168.6(2)
d _{Ni1-N1}	1.953(1)	∠P1-Ni1-P2	163.57(2)
d _{Ni1-P1}	2.1688(5)	∠N1-Ni1-P1	86.36(4)
d _{Ni1-P2}	2.1917(5)	∠N1-Ni1-P2	83.86(4)
d _{C1A-C2A}	1.507(8)	∠C1A-Ni1-P1	92.6(2)
d _{C2A-C3A}	1.535(6)	∠C1A-Ni1-P2	99.6(2)
		∠Ni1-C1A-C2A	107.7(4)

Figure S47. Solid-state structure of (PNP)NiCO^{*n*}Pr . Hydrogen atoms are omitted for clarity.



Table S8. Selected bond distances and angles for (PNP)NiCO^{*n*}Pr (Å and °).

Bond	distance	Bond an	ngle
d _{Ni1-C1}	1.869(4)	∠N1-Ni1-C1	177.7(2)
d _{Ni1-N1}	1.964(3)	∠P1-Ni1-P2	169.6(4)
d _{Ni1-P1}	2.170(1)	∠N1-Ni1-P1	84.5(1)
d _{Ni1-P2}	2.172(1)	∠N1-Ni1-P2	85.4(1)
d _{C1-O1}	1.215(6)	∠C1-Ni1-P1	95.2(1)
d _{C1-C2}	1.522(7)	∠C1-Ni1-P2	94.9(1)
d _{C2-C3}	1.504(7)	∠Ni1-C1-O1	121.1(4)
d _{C3-C4}	1.505(8)	∠Ni1-C1-C2	118.5(3)
		∠01-C1-C2	120.3(4)

Figure S48. Solid-state structure of (PNP)NiCO'Pr. Hydrogen atoms are omitted for clarity.



Table S9. Selected bond distances and angles for (PNP)NiCO^{*i*}Pr (Å and °).

Bond	distance	Bond angle	
d _{Ni1-C1}	1.873(2)	∠N1-Ni1-C1	174.5(1)
d _{Ni1-N1}	1.949(2)	∠P1-Ni1-P2	164.61(3)
d _{Ni1-P1}	2.1788(6)	∠N1-Ni1-P1	83.72(6)
d _{Ni1-P2}	2.1862(6)	∠N1-Ni1-P2	86.07(6)
d _{C1-O1}	1.221(3)	∠C1-Ni-P1	95.11(7)
d _{C1-C2}	1.506(4)	∠C1-Ni-P2	93.96(7)
d _{C2-C3}	1.493(4)	∠Ni1-C1-O1	119.4(2)
d _{C2-C4}	1.559(3)	∠Ni1-C1-C2	120.5(2)
		∠01-C1-C2	120.0(2)

Figure S49. Solid-state structure of (PNP)NiCO'Bu. Hydrogen atoms are omitted for clarity.



Table S10. Selected bond distances and angles for (PNP)NiCO'Bu (Å and °).

Bond	distance	Bond angle		
d _{Ni1-C1}	1.886(1)	∠N1-Ni1-C1	179.47(4)	
d _{Ni1-N1}	1.962(1)	∠P1-Ni1-P2	161.34(1)	
d _{Ni1-P1}	2.1983(5)	∠N1-Ni1-P1	84.73(4)	
d _{Ni1-P2}	2.1978(5)	∠N1-Ni1-P2	82.66(4)	
d _{C1-O1}	1.217(2)	∠C1-Ni1-P1	95.80(4)	
d _{C1-C2}	1.568(2)	∠C1-Ni1-P2	96.85(4)	
d _{C2-C3}	1.529(2)	∠Ni1-C1-O1	121.90(9)	
d _{C2-C4}	1.531(2)	∠Ni1-C1-C2	120.79(8)	
d _{C2-C5}	1.538(2)	∠01-C1-C2	117.3(1)	

Figure S50. UV-Vis spectra of $\{(PNP)NiCO\}\{BF_4\}$ (1, blue line), (PNP)NiCO (2, red line) and (PNP)Ni(CO)Na (3, green line) in THF at room temperature.



Figure S51. UV-Vis spectra of (PNP)Ni(CO)Na (**3**, blue line) and (PNP)NiMe (**6**, red line) in THF at room temperature.



Figure S52. UV-Vis spectra of (PNP)NiCO (2, blue line), (PNP)NiCOMe (4, red line) and (PNP)NiI (5, green line) and (PNP)NiMe (6, dotted black line) in THF at room temperature.



Figure S53. IR spectra of $\{(PNP)NiCO\}\{BF_4\}$ (1, blue), (PNP)NiCO (2, red) and $\{Na(12-crown-4)_2\}\{(PNP)NiCO\}$ (3', green) (KBr pellet).



Figure S54. IR spectra of (PNP)Ni(CO)Na (3, blue) and (PNP)NiMe (6, red) (KBr pellet).



Figure S55. IR spectra of (PNP)NiCO (2, blue), (PNP)NiCOMe (4, red) and (PNP)NiMe (6, green) (KBr pellet).



Figure S56. Cold-spray ionization mass data of (PNP)NiCO (2); Mass spectra of {(PNP)NiCO}⁺: m/z 514.21. Blue bars represent calculated values and red bars represent experiment values.



Figure S57. ESI (left) and cold-spray ionization (right) mass data of (PNP)NiCOMe (4); Mass spectra of {(PNP)NiCOMe}⁺: m/z 528.82 (ESI), 529.17 (cold-spray ionization). Blue bars represent calculated values and red bars represent experiment values.



Figure S58. ESI (left) and cold-spray ionization (right) mass data of (PNP)NiEt; Mass spectra of {(PNP)NiEt}⁺: m/z 515.00 (ESI), 515.22 (cold-spray ionization). Blue bars represent calculated values and red bars represent experiment values.



Figure S59. ESI (left) and cold-spray ionization (right) mass data of (PNP)NiCOEt; Mass spectra of {(PNP)NiCOEt}⁺: m/z 542.80 (ESI), 543.20 (cold-spray ionization). Blue bars represent calculated values and red bars represent experiment values.



Figure S60. ESI (left) and cold-spray ionization (right) mass data of (PNP)Ni^{*n*}Pr; Mass spectra of {(PNP)Ni^{*n*}Pr}⁺: m/z 529.07 (ESI), 529.26 (cold-spray ionization). Blue bars represent calculated values and red bars represent experiment values.



Figure S61. ESI (left) and cold-spray ionization (right) mass data of (PNP)NiCO^{*n*}Pr; Mass spectra of $\{(PNP)NiCO^{n}Pr\}^+$: m/z 556.87 (ESI), 557.24 (cold-spray ionization). Blue bars represent calculated values and red bars represent experiment values.



Figure S62. ESI (left) and cold-spray ionization (right) mass data of (PNP)NiCO^{*i*}Pr; Mass spectra of {(PNP)NiCO^{*i*}Pr}⁺: m/z 556.80 (ESI), 557.24 (cold-spray ionization). Blue bars represent calculated values and red bars represent experiment values.



Figure S63. ESI (left) and cold-spray ionization (right) mass data of (PNP)NiCO'Bu; Mass spectra of {(PNP)NiCO'Bu}⁺: m/z 570.73 (ESI), 571.27 (cold-spray ionization). Blue bars represent calculated values and red bars represent experiment values.



Figure S64. Cyclic voltammogram of (PNP)NiCO (2) with scan rates: 100, 200, 300, and 400 mV/s. Ni^{II/I} couple at -1.20 V and Ni^{I/0} couple at -1.87 V vs. Fc/Fc⁺ were observed in THF with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as an electrolyte.



Single-pulse experiment

Figure S65. ³¹P NMR spectrum (32 scans in C_6D_6 at room temperature) of the reaction of **2** with MeI.



Figure S66. The single-pulse ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of **2** with MeI.



Control experiments

Figure S67. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)NiCO (2) with MeI. The reaction was conducted for 10 min in THF at room temperature.



Figure S68. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)NiCO (2) with MeI. The reaction was conducted for 1 hr in THF at room temperature.



Figure S69. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)NiMe (6) with CO. The reaction was conducted with 5 equiv. of CO for 10 min in THF at room temperature.



Figure S70. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)NiMe (6) with CO. The reaction was conducted with 5 equiv. of CO for 1 hr in THF at room temperature.



Figure S71. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)NiMe (6) with CO. The reaction was conducted with 15 equiv. of CO for 1 hr in THF at room temperature.



Figure S72. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)NiCO (2) with MeOTf in toluene.



wFigure S73. ³¹P NMR spectrum (in C_6D_6 at room temperature) of the reaction of (PNP)NiCO (2) with MeI in toluene.



Figure S74. IR spectra of (PNP)NiCO (2, blue), the reaction of 2 with MeOTf (red) and the reaction of 2 with MeI (green) (KBr pellet).



Figure S75. UV spectra (in THF) of (PNP)NiCO (**2**, black lines) in four different concentrations (2.46, 2.00, 1.60 and 1.20 mM) and the reaction of **2** with MeOTf (red line). The unknown sample generated from the reaction was prepared by dissolving 10 mg of the crude mixture in 10 mL of THF.



Figure S76. Plot of absorbance vs. concentration of (PNP)NiCO (2, black line) and an unknown sample (red).



Computational details. Geometry optimization and single-point calculation on **2** were run on the Gaussian09¹⁰ with B3LYP¹¹ density functional theory. The lanl2dz basis set¹² associated with effective core potential was used for describing nickel atom and $6-31+G^{**}$ basis set was used for all other atoms. Initial geometry for **2** was obtained from X-ray coordinates. The Mülliken population analysis was performed to examine spin density with SCF method. The spin density contour plot was generated using GaussView.¹³

Figure S77. Mülliken atomic spin density plots derived from the single-point DFT calculation of (PNP)NiCO (2). Lobal representations correspond to the spin density by the number with 0.004 isocontours.



Ni: 71.2%; P1: 2.8%; P2: 4.8%; N: 6.5%; C: 7.8%

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	2		
	(PNP)NiCO cal.	(PNP)NiCO crystal	
$d_{\rm NiC}$	1.830	1.776(2)	
d_{NiN}	2.039	1.964(1)	
$d_{\rm NiP}$	2.374 2.394	2.2131(5) 2.2320(5)	
d _{C-O}	1.154	1.149(2)	
∠N-Ni-C	165.76	153.25(8)	
∠P-Ni-P	155.36	154.82(2)	
∠N-Ni-P	82.18 80.85	85.28(4) 84.04(4)	
∠Ni-C-O	170.22	169.4(2)	

Table S11. Selected bond distances and angles for **2** obtained from XRD data comparing with the calculated data based on the geometry optimization using DFT calculation (Å and °).

Optimized coordinates of 2.

Center	Atomic	A	tomic	Coordinate	s (Angstroms)
Number	Numb	ber	Туре	X Y	Z
			0.0050(0	0.770074	0.051000
1		0	-0.025960	0.//82/4	-0.251890
2	6	0	-1.236419	1.394048	-0.548810
3	6	0	-2.453046	0.743536	-0.188114
4	6	0	-1.351/14	2.60/011	-1.2/4963
5	6	0	-3.690089	1.32/592	-0.505089
6	0	0	-2.590391	3.1539/1	-1.585051
/	l	0	-0.450141	3.104028	-1.61/016
8	6	0	-3.793111	2.537304	-1.19/138
9		0	-4.606463	0.828044	-0.205422
10	l	0	-2.626307	4.081349	-2.154408
	6	0	1.104404	1.493137	0.090028
12	6	0	1.093154	2.841854	0.54/362
13	6	0	2.379782	0.841903	0.086294
14	6	0	2.257190	3.498754	0.919918
15	1	0	0.147761	3.365248	0.631025
16	6	0	3.539418	1.541542	0.461125
17	6	0	3.517458	2.875043	0.873250
18	1	0	2.185081	4.527776	1.268974
19	1	0	4.495846	1.027929	0.434654
20	28	0	-0.013046	-1.260336	-0.222398
21	15	0	-2.221980	-0.881581	0.618892
22	15	0	2.332935	-0.924261	-0.352958
23	6	0	-3.581936	-2.062622	0.052474
24	1	0	-3.176680	-3.027851	0.390233
25	6	0	-2.486988	-0.650072	2.477481
26	1	0	-2.833851	-1.636526	2.817298
27	6	0	3.046284	-1.113262	-2.093252
28	1	0	3.360262	-2.166495	-2.138710
29	6	0	3.458608	-1.919313	0.791112
30	1	0	3.143295	-2.946813	0.558000
31	6	0	-1.142706	-0.354878	3.166440
32	1	0	-0.407953	-1.141729	2.972242
33	1	0	-0.716957	0.591116	2.816211
34	1	0	-1.285243	-0.279340	4.251455
35	6	0	-3.533440	0.408273	2.861732
36	1	0	-3.658339	0.426054	3.951733
37	1	0	-3.211951	1.404921	2.544353
38	1	0	-4.513536	0.218693	2.417394
39	6	0	-4.987611	-1.929730	0.662872
40	1	0	-5.612939	-2.761387	0.314441
41	1	0	-4.973891	-1.969093	1.755685

42	1	0	-5.485024	-1.003456	0.360761
43	6	0	-3.644062	-2.101884	-1.485500
44	1	0	-2.654065	-2.235784	-1.932109
45	1	0	-4.276565	-2.935954	-1.811870
46	1	0	-4.067666	-1.177891	-1.890518
47	6	0	4.981890	-1.859945	0.589201
48	1	0	5.390280	-0.869496	0.810431
49	1	0	5.464004	-2.569303	1.273849
50	1	0	5.278891	-2.136484	-0.425913
51	6	0	3.079341	-1.639374	2.255694
52	1	0	3.369147	-0.626858	2.554333
53	1	0	2.001911	-1.740012	2.420660
54	1	0	3.591021	-2.348102	2.917593
55	6	0	1.928751	-0.898172	-3.131554
56	1	0	1.092064	-1.585911	-2.981705
57	1	0	1.532801	0.121536	-3.075813
58	1	0	2.322354	-1.051464	-4.143856
59	6	0	4.250238	-0.215584	-2.423910
60	1	0	5.094313	-0.360229	-1.745652
61	1	0	4.600900	-0.432290	-3.440773
62	1	0	3.967478	0.840966	-2.385742
63	6	0	-5.132657	3.157941	-1.522878
64	1	0	-5.245613	3.334853	-2.599735
65	1	0	-5.957597	2.511858	-1.205981
66	1	0	-5.262133	4.126487	-1.023214
67	6	0	4.778312	3.616573	1.254633
68	1	0	5.643598	2.945831	1.270531
69	1	0	5.003916	4.425951	0.547995
70	1	0	4.695332	4.073225	2.248785
71	6	0	-0.095552	-3.040750	-0.636992
72	8	0	-0.080664	-4.192705	-0.715880