Neutral, cationic and anionic organonickel and -palladium complexes supported by iminophosphine/phosphinoenaminato ligands.

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Electronic Supporting Information (ESI)

CONTENTS

Specific synthetic Procedures and characterization data.

General Considerations

All manipulations were carried out under inert atmosphere, either using standard vacuum line operating with purified argon (previously passed through two consecutive drying and O_2-scavenging columns, filled with activated molecular sieves and reduced Cr oxide supported on silica, respectively), or a nitrogen-filled glove box equipped with a pump for solvent evaporation, an externally cooled (with liquid N_2) cavity, a freezer and an analytical balance. The glassware was oven-dried for at least 1 h prior to use. Solvents were kept refluxing under N_2 over suitable drying agents and distilled immediately prior to use. Hexane and toluene were dried over Na pieces, Et_2O and THF over sodium-benzophenone ketyl and CH_2Cl_2 over calcium hydride. Likewise, small amounts of deuterated solvents (25 mL) were dried over the corresponding drying agents (C_6D_6 and THF-d_8, over sodium-benzophenone ketyl; and CD_2Cl_2 over $LiAlH_4$) and vacuum transferred to PTFE-valve glass ampoules, in which these were stored until needed. NMR spectra were recorded using Bruker DPX-300, DRX-400, Avance^{III}-400/R and DRX-500 spectrometers. NMR sample tubes with gastight PTFE valves have been systematically used for sensitive organometallic compounds. All NMR signals have been assigned with the routine assistance of gated-^{13}C and broadband ^{31}P decoupling, as well as a complete ensemble of 2D homonuclear (^{1}H-^{1}H COSY and NOESY) and heteronuclear correlations (^{1}H-^{13}C HSQC and HMQC). Non-conventional multiplicity abbreviations: *sept:* septet, *d-sept*: doublet of septets. Diastereotopic signals (e. g. CH*Me*Me and CHMe*Me*) are marked in italics only to facilitate signal codification and do not mean explicit/consistent stereochemical assignments. Multiplicities in the ^{13}C{^{1}H} listings are indicated only if different of singlet. For characterization purposes, spectra were recorded in solution using the chemical shifts of the residual ^{1}H and the ^{13}C resonances of the solvents as internal standards[30] and referenced with respect to TMS. ^{31}P{^{1}H} NMR spectra for reaction monitoring were measured directly from the reaction mixtures in normal solvents, using NMR sample tubes containing a sealed glass capillary filled with a solution of PPh_3 (-6.0 ppm) in C_6D_6 that provides ^{31}P and deuterium resonances as external references for chemical shift and for lock signals, respectively. Transmission FT-IR spectra were recorded in nujol emulsion in a Bruker Tensor 2 spectrometer. Gas chromatography analyses of reaction mixtures were carried out in a Shimadzu GCMS-QP20plus gas chromatograph with mass spectrometry detector equipped with a 10 m, 0.18 mm I. D. HP2 capillary column. ESI-MS spectra and elemental analysis were performed by Instrumentation Services of the IIQ (Mass Spectrometry and Analytical Services) in a Bruker ion trap Esquire 6000 and LECO True-Spec elemental analyzer, respectively. The starting materials chlorodiphenyl phosphine, chlorodiisopropylphos-phine, 2-bromoanisole, and [Pd(DBA)$_2$] were purchased from commercial sources and used as received. The complexes [Ni(CH_2SiMe_3)$_2$(Py)$_2$] (**1**),[1] [Pd(CH_2SiMe_3)$_2$(COD)] (**2**),[2] and [Ni(COD)$_2$][3] were synthesized according to methods reported in the literature. [Ni(COD)$_2$] was purified by recrystallization from THF prior to use.

Ligands and Ligand Precursors

***N*-(2,6-diisopropylphenyl)-1-phenylethan-1-imine (Ph(Me)C=N(DiPP)):** This was synthesized following a standard procedure by condensation of acetophenone and 2,6-diisopropylaniline in the presence of small amount of *p*-toluensulfonic acid in boiling toluene in a Dean-Stark apparatus with azeotropic removal of water, and was recrystallized from methanol. ^{1}H NMR (400 MHz, 25 ^{o}C, C_6D_6): δ 1.10 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, Ar-CH*Me*Me), 1.16 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, Ar-CHMe*Me*), 1.79 (s, 3 H, -C*H*$_3$), 2.85 (sept, 2 H, $^3J_{HH}$ = 7.0 Hz, Ar-C*H*Me$_2$), 7.13 (m, 2 H, *m*-Ph), 7.16 (m, 1 H, *p*-Ph), 7.16 (m, 2 H, *m*-C$_6$*H*$_3$), 7.18 (m, 1 H, *p*-C$_6$*H*$_3$), 8.00 (m, 2 H, *o*-Ph). ^{13}C{^{1}H} NMR (100.6 MHz, 25 ^{o}C, C_6D_6): δ 17.9 (-*C*H$_3$), 23.0 (Ar-CH*Me*Me), 23.5 (Ar-CHMe*Me*), 28.8 (Ar-*C*HMe$_2$), 123.4 (*m*-*C*$_6$H$_3$), 124.0 (*p*-*C*$_6$H$_3$), 127.5 (*o*-Ph), 128.6 (*m*-Ph), 130.6 (s, *p*-Ph), 136.4 (C$_q$, *o*-*C*$_6$H$_3$), 139.5 (C$_q$, *ipso*-Ph), 147.4 (C$_q$, *ipso*-C$_6$H$_3$), 164.5 (s, *C*=N). IR (nujol, cm^{-1}): 1632 (*ν*(C=N)), 1577 (arom. C=C).

Chlorodi(*o*-anisyl)phosphine: This chlorophosphine was synthesized according to the method reported by Jordan,[32] but starting from ClP(NEt$_2$)$_2$ instead of ClP(NMe$_2$). ^{31}P{^{1}H} NMR (202.4 MHz, 25 ^{o}C, C_6D_6) δ 63.4 (s, minor isomer), 70.6 (s, major isomer). ^{1}H NMR (500 MHz, 25 ^{o}C, C_6D_6): δ 3.17 (s, 6 H, -O*Me*), 6.39 (dd, 2 H, $^3J_{HP}$ = 5.0 Hz, $^3J_{HH}$ = 8.2 Hz, 3-C*H*, P(Anis.)$_2$), 6.79 (t, 2 H, $^3J_{HH}$ = 7.4 Hz, 5-C*H*, P(Anis.)$_2$), 7.07 (t, 2 H, $^3J_{HH}$ = 7.4 Hz, 4-C*H*, P(Anis.)$_2$), 7.66 (m, 2 H, 6-C*H*, P(Anis.)$_2$).

^{i}Pr)$_2$PCH$_2$(Ph)C=N(dipp) (La): The general procedure gave 0.759 g (97 % yield) of the titled compound as a yellow oil. The compound was obtained as a mixture of two geometric isomers in 4:1 ratio. ^{31}P{^{1}H} NMR (161.9 MHz, 25 ^{o}C, C_6D_6) δ 5.2 (minor isomer), 8.1 (major isomer). ^{1}H NMR (C 400 MHz, 25 °C, C_6D_6): Major isomer, δ 0.70 (dd, 6 H, $^3J_{HP}$ = 12.1 Hz, $^3J_{HH}$ = 6.9 Hz, P-CH*Me*Me), 0.75 (dd, 6 H, $^3J_{HP}$ = 12.4 Hz, $^3J_{HH}$ = 6.8 Hz, P-CHMe*Me*), 1.25 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 1.36 (m, 2 H, P-C*H*Me$_2$), 1.36 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, Ar-CHMe*Me*), 2.76 (d, 2 H, $^2J_{HP}$ = 1.5 Hz, P-C*H*$_2$),

3.12 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, Ar-C*H*Me$_2$), 6.82 – 7.28 (m, 6 H, C*H$_{arom}$*), 8.05 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, *o*-Ph). Minor isomer: δ 0.99 – 1.10 (overlapped, 6H, (PCH*Me*Me), 1.22 – 1.37 (overlapped, 12 H, CH*Me$_2$*), 1.77 (m, 2 H, PC*H*Me$_2$), 2.95 (d, 2 H, $^2J_{HP}$ = 1.4 Hz, P-C*H$_2$*), 3.21 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, ArC*H*Me$_2$), 6.82 – 7.28 (m, 8H C*H$_{arom}$*). ^{13}C {^{1}H}NMR (100.6 MHz, 25 °C, C_6D_6): Major isomer, δ 19.1 (d, $^2J_{CP}$ = 13.0 Hz, P-CH*Me*Me), 19.6 (d, $^2J_{CP}$ = 14.7 Hz, P-CHMe*Me*), 21.7 (Ar-CH*Me*Me), 24.1 (d, $^2J_{CP}$ = 18.1 Hz, P-*C*HMe$_2$), 24.3 (Ar-CHMe*Me*), 25.9 (d, $^1J_{CP}$ = 30.6 Hz, P-*C*H$_2$), 29.1 (Ar-*C*HMe$_2$), 123.3 (*m*-*C*H, *N*-Ar), 124.1 (*p*-*C*H, *N*-Ar), 128.4 (*o*-Ph), 128.5 (*m*-Ph), 130.3 (*p*-Ph), 136.3 (*o*-*C*$_q$, *N*-Ar), 140.7 (*ipso*-*C$_q$*, Ph), 146.7 (*ipso*-*C$_q$*, *N*-Ar), 167.3 (d, $^2J_{CP}$ = 9.1 Hz, *C*=N). Minor isomer, δ 19.5 (d, $^2J_{CP}$ = 13.0 Hz, P-CH*Me*Me), 19.7 (d, $^2J_{CP}$ = 14.7 Hz, P-CHMe*Me*), 22.5 (Ar-CH*Me*Me), 24.1 (d, $^2J_{CP}$ = 18.1 Hz, P-*C*HMe$_2$), 24.6 (Ar-CHMe*Me*), 28.6 (Ar-*C*HMe$_2$), 35.7 (d, $^1J_{CP}$ = 26.2 Hz, P-*C*H$_2$), 136.3 (*o*-*C$_q$*, *N*-Ar), 138.5 (*ipso*-*C$_q$*, Ph), 146.3 (*ipso*-*C$_q$*, *N*-Ar), 168.5 (d, $^2J_{CP}$ = 11.0 Hz, *C*=N).

(Ph)$_2$PCH$_2$(Ph)C=N(dipp) (Lb):[9b] 0.917 g (97 % yield) of the title compound as yellow oil. Two geometric isomers in 3.3:1 ratio. ^{31}P{^{1}H} NMR (161.9 MHz, 25 °C, C_6D_6) δ -21.0 (s, minor isomer), -14.6 (s, major isomer). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): Major isomer, δ 1.23 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CH*Me*Me), 1.25 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, Ar-CHMe*Me*), 3.14 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, Ar-C*H*Me$_2$), 3.56 (d, 2 H, $^2J_{HP}$ = 1.8 Hz, P-C*H$_2$*), 6.81 – 7.27 (m, 8 H, C*H$_{arom}$*), 7.07 (m, 4 H, *m*-*CH*, PPh$_2$), 7.52 (m, 4 H, *o*-C*H*, PPh$_2$), 7.84 (d, 2 H, $^3J_{HH}$ = 7.3 Hz, *o*-Ph); Minor isomer: δ 0.9 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, Ar-CH*Me*Me), 1.12 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, Ar-CHMe*Me*), 2.83 (sept, 2 H, $^3J_{HH}$ = 6.9 Hz, Ar-C*H*Me$_2$), 3.68 (m, 2 H, P-C*H$_2$*), 6.81 – 7.27 (m, C*H$_{arom}$*). ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, C_6D_6): Major isomer, δ 22.0 (CH*Me*Me), 23.9 (CHMe*Me*), 29.2 (*C*HMe$_2$), 32.7 (d, $^1J_{CP}$ = 26.0 Hz, P-*C*H$_2$), 123.6 (*m*-*C*H, *N*-Ar), 124.1 (*p*-*C*H, *N*-Ar), 128.2 (*m*-*C*H, Ph), 128.7 (*o*-*C*H, Ph), 128.8 (d, $^2J_{CP}$ = 5.5 Hz, *m*-*C*H, PPh$_2$), 130.4 (*p*-*C*H, Ph), 133.2 (d, $^2J_{CP}$ = 19.9 Hz, *o*-*C*H, PPh$_2$), 136.2 (*o*-*C*$_q$, *N*-Ar), 139.0 (d, $^1J_{CP}$ = 14.7 Hz, *ipso*-*C$_q$*, PPh$_2$), 139.4 (*ipso*-*C*$_q$, Ph), 147.4 (*ipso*-*C*$_q$, *N*-Ar), 165.8 (d, $^2J_{CP}$ = 14.0 Hz, *C*=N). Minor Isomer: δ 22.5 (Ar-CH*Me*Me), 23.9 (Ar-CHMe*Me*), 28.6 (Ar-*C*HMe$_2$), 41.7 (d, $^1J_{CP}$ = 15.3 Hz, P-*C*H$_2$), 128.7 (*o*-*C*H, Ph), 130.4 (*m*-*C*H, Ph), 133.3 (d, $^2J_{CP}$ = 20.0 Hz, *o*-*C*H, PPh$_2$), 139.4 (*ipso*-*C$_q$*, Ph), 139.7 (d, $^1J_{CP}$ = 14.7 Hz, *ipso*-*C$_q$*, PPh$_2$), 146.4 (*ipso*-*C$_q$*, *N*-Ar).

(*o*-*anisyl*)$_2$PCH$_2$(Ph)C=N(dipp) (Lc): 0.576 g (55 % yield) of a microcrystalline pale-yellow solid after crystallization from *n*-pentane at -25 °C. 3:1 mixture of geometric isomers ^{31}P{^{1}H}NMR (161.9 MHz, 25 °C, C_6D_6): δ -31.9 (minor isomer), -27.7 (s, major isomer). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): Major isomer, δ 1.26 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, Ar-CH*Me$_2$*), 3.02 (s, 6 H, -O*Me*), 3.16 (sept, 2 H, $^3J_{HH}$ = 6.9 Hz, Ar-C*H*Me$_2$), 3.56 (d, 2 H, $^2J_{HP}$ = 1.8 Hz, P-C*H$_2$*), 6.26 (dd, 2 H, $^3J_{HP}$ = 3.1 Hz, $^3J_{HH}$ = 8.0 Hz, 3-C*H*, P(Anis.)$_2$), 6.65 (t, 2 H, $^3J_{HH}$ = 7.3 Hz, 5-C*H*, P(Anis.)$_2$), 6.98 (t, 2 H, $^3J_{HH}$ = 7.3 Hz, 4-C*H*, P(Anis.)$_2$), 6.98 – 7.20 (m, 6H, C*H$_{arom}$*), 7.16 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, 6-C*H,* P(Anis.)$_2$), 8.05 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, *o*-C*H*, Ph). Minor isomer, δ 0.9 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, Ar-CH*Me*Me), 1.15 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, ArCHMe*Me*), 2.96 (sept, 2 H, $^3J_{HH}$ = 6.5 Hz, Ar-C*H*Me$_2$), 3.12 (s, 6 H, -O*Me*), 4.03 (m, 2 H, P-C*H$_2$*), 6.46 (d, 2 H, $^3J_{HH}$ = 6.2, 3-C*H*, P(Anis.)$_2$), 6.85 (m, 5-C*H*, P(Anis.)$_2$), 6.98 – 7.20 (m, C*H$_{arom}$*),7.26 (t, 2 H, $^3J_{HH}$ = 6.0, 4-C*H*, P(Anis.)$_2$), 7.6 (d, 2 H, $^3J_{HH}$ = 6.2, 6-C*H*, P(Anis.)$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, C_6D_6): Major isomer, δ 22.1 (Ar-CH*Me*Me), 24.0 (Ar-CHMe*Me*), 28.1 (d, $^1J_{CP}$ = 25.9 Hz, P-*C*H$_2$), 29.1 (s, Ar-*C*HMe$_2$), 54.7 (s, -O*Me*), 110.6 (3-*C*H, P(Anis.)$_2$), 121.0 (5-*C*H, P(Anis.)$_2$), 123.3 (*m*-*C*H, *N*-Ar), 123.7 (*p*-*C*H, *N*-Ar), 125.6 (d, $^1J_{CP}$ = 22.3 Hz, *ipso*-*C*$_q$, P(Anis.)$_2$), 128.7 (*o*-*C*H, Ph), 130.4 (s, 4-*C*H, P(Anis.)$_2$), 134.1 (6-*C*H, P(Anis.)$_2$), 136.2 (*o*-*C*$_q$ *N*-Ar), 140.3 (*ipso*-*C$_q$*, *N*-Ar), 140.7 (*ipso*-*C*$_q$, Ph), 160.9 (2-*C*$_q$, P(Anis.)$_2$), 161.7 (d, $^2J_{CP}$ = 11.1 Hz, *C*=N). Minor Isomer, δ 22.5 (Ar-CH*Me*Me), 24.5 (Ar-CHMe*Me*), 27.7 (d, $^1J_{CP}$ = 16.4 Hz, P-*C*H$_2$), 28.6 (Ar-*C*HMe$_2$), 55.1 (s, -O*Me*), 110.6 (s, 3-*C*H, P(Anis.)$_2$), 121.2 (5-*C*H, P(Anis.)$_2$), 130.1 (4-*C*H, P(Anis.)$_2$), 134.3 (6-*C*H, P(Anis.)$_2$), 138.0 (*ipso*-*C*$_q$, Ph), 166.6 (d, $^2J_{CP}$ = 12.8 Hz, *C*=N).

Palladium dialkyl complexes 4a-4c

[Pd(CH$_2$SiMe$_3$)$_2$(La)], (4a): Crystallized from pentane. Starting from 0.339 g (0.870 mmol) of **2**, and an equimolar amount of **La** (0.324 g) the procedure gives 0.316 g (0.468 mmol, 57 % yield) of dark-yellow crystals. ^{31}P{^{1}H} NMR (161.9 MHz, 25 °C, C_6D_6): δ 37.3 (s). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.04 (d, 2 H, $^3J_{HP}$ = 9.5 Hz, C*H$_2$*SiMe$_3$ (P-*cis*)), 0.38 (s, 9 H, CH$_2$Si*Me$_3$* (P-*trans*)), 0.49 (s, 9 H, CH$_2$Si*Me$_3$* (P-*cis*)), 0.76 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, Ar-CH*Me*Me), 0.91 (d, 2 H, $^3J_{HP}$ = 11.7 Hz, C*H$_2$*SiMe$_3$ (P-*trans*)), 0.97 (dd, 6 H, $^3J_{HP}$ = 12.2 Hz, $^3J_{HH}$ = 7.0 Hz, P-CH*Me*Me), 1.17 (dd, 6 H, $^3J_{HP}$ = 15.4 Hz, $^3J_{HH}$ = 7.0 Hz, P-CHMe*Me*), 1.46 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CHMe*Me*), 1.78 (d-sept, 2 H, $^2J_{HP}$ = 6.8 Hz, $^3J_{HH}$ = 7.4 Hz, P-C*H*Me$_2$), 2.81 (d, 2 H, $^2J_{HP}$ = 7.7 Hz, P-C*H$_2$*), 3.50 (m, 2 H, Ar-C*H*Me$_2$), 6.75 (m, 1 H, *p* -Ph), 6.77 (t, 2 H, $^3J_{HH}$ = 7.5 Hz, *m*-Ph), 6.92 (d, 2 H, $^3J_{HH}$ = 6.6 Hz, *o*-Ph), 7.02 (m, 2 H, *m*-*N*-Ar), 7.06 (m, 1 H, *p*-*N*-Ar). ^{13}C{^{1}H}NMR (100.6 MHz, 25 °C, C_6D_6): δ -10.1 (d, $^2J_{CP}$ = 4.3 Hz, *C*H$_2$SiMe$_3$ (P-*cis*)), 4.3 (CH$_2$Si*Me$_3$* (P-*trans*)), 5.7 (CH$_2$Si*Me$_3$* (P-*cis*)), 10.9 (d, $^2J_{CP}$ = 101.1 Hz, *C*H$_2$SiMe$_3$ (P-*trans*)), 18.8 (P-CH*Me*Me), 22.9 (P-CHMe*Me*), 23.7 (d, $^1J_{CP}$ = 49.3 Hz, P-*C*HMe$_2$), 23.8 (ArCH*Me*Me), 25.3 (ArCHMe*Me*), 28.6 (Ar*C*HMe$_2$), 37.3 (d, $^1J_{CP}$ = 10.9 Hz, P-*C*H$_2$), 124.3 (*m*-*C*H, N-*Ar*), 126.7 (s, *p*-*C*H, *N*-Ar), 129.3 (*p*-*C*H, Ph), 128.6 (*m*-*C*H, Ph), 129.3 (*o*-*C*H, Ph), 136.7 (d, $^3J_{CP}$ = 4.5 Hz, *ipso*-*C*$_q$, Ph), 139.3 (*o*-*C*$_q$, N-Ar), 144.8 (*ipso*-*C*$_q$, *N*-Ar), 176.6 (d, $^2J_{CP}$ = 10.0 Hz, *C*=N). IR (Nujol mull, cm^{-1}): 1588, 1566 (Arom C-C and C=N), 1237 (SiMe$_3$), 846, 815 (SiMe$_3$). Anal. Calcd for $C_{34}H_{60}NPPdSi_2$: C, 60.37; H, 8.94; N, 2.07. Found: C, 60.50; H, 8.65; N, 2.27.

[Pd(CH$_2$SiMe$_3$)$_2$(Lb)], (4b): Crystallized from CH_2Cl_2/*n*-hexane. Starting from 0.300 g (0.771 mmol) of complex **2** and an equimolar amount of **Lb** (0.357 g, 0.771 mmol), the general procedure gave 0.521 g (0.702 mmol, 91% yield) of dark yellow crystals of the product. ^{31}P{^{1}H} NMR (161.9 MHz, 25 °C, C_6D_6): δ 19.9 (s). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.12 (d, 2 H, $^3J_{HP}$ =

9.9 Hz, CH_2SiMe$_3$ (P-*cis*)), 0.35 (s, 9 H, CH$_2$SiMe_3 (*P-trans*)), 0.51 (s, 9 H, CH$_2$SiMe_3 (P-*cis*)), 0.52 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 1.19 (d, 2 H, $^3J_{HP}$ = 12.6 Hz, CH_2SiMe$_3$ (P-*trans*)), 1.44 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CHMe*Me*), 3.29 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, Ar-C*H*Me$_2$), 3.67 (d, 2 H, $^2J_{HP}$ = 7.8 Hz, CH_2), 6.69 (m, 1 H, *p*-Ph), 6.70 (t, 2 H, $^3J_{HH}$ = 8 Hz, *m*-Ph), 6.75 (d, 2 H, $^3J_{HH}$ = 6.7 Hz, *o*-Ph), 7.04 (m, 2 H, *m-N*-Ar), 7.05 (m, 4 H, *m*-C*H,* PPh$_2$), 7.08 (m, 1 H, *p-N*-Ar), 7.19 (m, 2 H, *p*-C*H*, PPh$_2$), 7.64 (dd, 4 H, $^3J_{HP}$ = 9.7 Hz, $^3J_{HH}$ = 7.8 Hz, *o*-C*H*, PPh$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, C$_6$D$_6$): δ - 4.9 (d, $^2J_{CP}$ = 3.9 Hz, *C*H$_2$SiMe$_3$ (P-*cis*)), 3.8 (CH$_2$SiMe_3 (P-*trans*)), 5.6 (CH$_2$SiMe_3(P-*cis*)), 11.4 (d, $^2J_{CP}$ = 101.1 Hz, *C*H$_2$SiMe$_3$ (P-*trans*)), 23.4 (Ar-CH*Me*Me), 24.8 (Ar-CHMe*Me*), 28.6 (Ar-*C*HMe$_2$), 45.0 (d, $^1J_{CP}$ = 18.3 Hz, P-*C*H$_2$), 124.2 (*m-C*H, *N*-Ar), 126.7 (*p- C*H, *N*-Ar), 128.8 (*p*-C*H*, Ph), 128.8 (d, $^3J_{CP}$ = 8.7 Hz, *m*-*C*H, PPh$_2$), 129.3 (*m*-*C*H, Ph), 130.2 (*o*-*C*H, Ph), 130.3 (*p*-*C*H, PPh$_2$), 133.3 (d, $^2J_{CP}$ = 13.2 Hz, *o*-*C*H, PPh$_2$), 134.1 (d, $^1J_{CP}$ = 23.4 Hz, *ipso*-C_q, PPh$_2$), 136.2 (d, $^3J_{CP}$ = 4.5 Hz, *ipso*-C_q, Ph), 138.6 (*o*-C_q, *N*-Ar), 144.6 (*ipso*-C_q *N*-Ar), 173.7 (d, $^2J_{CP}$ = 9.9 Hz, *C*=N). IR (Nujol mull, cm^{-1}): 1587, 1560 (Arom C-C and C=N), 1235 (SiMe$_3$), 844, 821 (P-C). Anal. Calcd. for $C_{40}H_{56}NPPdSi_2$: C, 64.54; H, 7.58; N, 1.88. Found: C, 64.40; H, 7.65; N, 1.96.

[Pd(CH$_2$SiMe$_3$)$_2$(Lc)], (4c): Crystallized from CH$_2$Cl$_2$/*n*-hexane. Starting from 0.100 g (0.257 mmol) of complex **2** and an equimolar amount of **Lc** (0.134 g, 0.257 mmol), the general procedure gave 0.188 g (0.234 mmol, 91% yield) of dark yellow crystals of the product. ^{31}P{^{1}H} NMR (161.9 MHz, 25 °C, C$_6$D$_6$): δ 15.1 (s). ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ 0.05 (d, 2 H, $^3J_{HP}$ = 10.0 Hz, CH_2SiMe$_3$ (P-*cis*)), 0.25 (s, 9 H, CH$_2$SiMe_3 (P-*trans*)), 0.51 (s, 9 H, CH$_2$SiMe_3 (P-*cis*)), 0.62 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 1.07 (d, 2 H, $^3J_{HP}$ = 12.7 Hz, CH_2SiMe$_3$ (P-*trans*)), 1.52 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CHMe*Me*), 3.11 (s, 6 H, -O*Me*), 3.31 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, Ar-C*H*Me$_2$), 4.39 (d, 2 H, $^2J_{HP}$ = 9.1 Hz, P-CH_2), 6.40 (dd, 2 H, $^4J_{HP}$ = 3.0 Hz, $^3J_{HH}$ = 8.3 Hz, 3-C*H*, P(Anis.)$_2$), 6.70 (m, 1 H, *p*-Ph), 6.72 (m, 2 H, *m*-Ph), 6.92 (t, 2 H, $^3J_{HH}$ = 7.5 Hz, 5-C*H*, P(Anis.)$_2$), 6.97 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, *o*-Ph), 7.08 (d, 2 H, $^3J_{HH}$ = 4.3 Hz, *m-N*-Ar), 7.11 (m, 1 H, *p-N*-Ar), 7.11 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, 4-C*H*, P(Anis.)$_2$), 8.20 (dd, 2 H, $^3J_{HP}$ = 8.3 Hz, $^3J_{HH}$ = 7.5 Hz, 6-C*H*, P(Anis.)$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, C$_6$D$_6$): δ - 6.1 (d, $^2J_{CP}$ = 3.8 Hz, *C*H$_2$SiMe$_3$ (P-*cis*)), 3.7 (CH$_2$SiMe_3 (P-*trans*)), 5.7 (CH$_2$SiMe_3 (P-*cis*)), 10.4 (d, $^2J_{CP}$ = 103.1 Hz, *C*H$_2$SiMe$_3$ (P-*trans*)), 23.4 (Ar-CH*Me*Me), 24.7 (Ar-CHMe*Me*), 28.4 (Ar*C*HMe$_2$), 42.2 (d, $^1J_{CP}$ = 21.6 Hz, P-*C*H$_2$), 55.1 (-O*Me*), 111.3 (3-*C*H, P(Anis.)$_2$), 120.7 (d, $^3J_{CP}$ = 11.0 Hz, 5-*C*H, P(Anis.)$_2$), 121.2 (d, $^1J_{CP}$ = 24.8 Hz, 1-C_q, P(Anis.)$_2$), 124.0 (*m-C*H *N*-Ar), 126.3 (*p-C*H,N-*Ar*), 128.0 (*m-C*H Ph), 129.1 (*o-C*H*,* Ph), 129.9 (*p-C*H, Ph), 132.0 (4-*C*H, P(Anis.)$_2$), 136.9 (d, $^3J_{CP}$ = 6 Hz, *ipso*-C_q, Ph), 137.1 (d, $^2J_{CP}$ = 19.0 Hz, 6-*C*H, P(Anis.)$_2$), 138.5 (*o*-C_q, *N*-Ar), 144.9 (*ipso*-C_q, *N-Ar*), 160.9 (2-C_q, P(Anis.)$_2$), 175.4 (d, $^2J_{CP}$ = 12.0 Hz, *C*=N). IR (Nujol mull, cm^{-1}): 1588, 1572 (Arom C-C and C=N), 1247 (ν as, C-O-C), 1236 (SiMe$_3$), 842, 846 (SiMe$_3$). Anal. Calcd. for $C_{42}H_{60}NO_2PPdSi_2$: C, 62.70; H, 7.52; N, 1.74. Found: C, 62.50; H, 7.55; N, 1.84.

Cationic Alkylnickel complexes and their precursors.

Dipyridinium Triflate, [Py$_2$H]+ [TfO]-: To a stirred solution of pyridine (0.162 ml, 2 mmol) in Et$_2$O (10 mL) at – 40 °C, 3.22 mL of a 0.31 M solution of triflic acid (1 mmol) in Et$_2$O, was added dropwise. A white precipitate was immediately formed as the acid was added. The cold bath was removed and the stirring was continued for 30 min. at the room temperature. The resulting suspension was decanted, the remaining solvent was filtered off and the solid was dried under vacuum. The compound was isolated as a pure white solid without further purification with a yield of 59 % (0.181 g, 0.587 mmol). The product was stored in the globe box freezer at – 25 °C. ^{1}H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$): δ 8.05 (t, 4 H, $^3J_{HH}$ = 6.8 Hz, β-C*H*, Py), 8.56 (t, 2 H, $^3J_{HH}$ = 7.9 Hz, γ-*C*H, Py), 8.86 (d, 4 H, $^3J_{HH}$ = 5.4 Hz, α-C*H*, Py), 13.9 (br s, 1 H, N-H···N).

[Ni(CH$_2$SiMe$_3$)(Py)$_3$]$^+$ [TfO]$^-$ (5): In the glove box, a solution of [Py$_2$H]$^+$ [TfO]$^-$ (0.036 g, 0.117 mmol) in 3 mL of THF was added to a pre-cooled (frozen at the liquid N$_2$ temperature) scintillation vial containing a small magnetic stir bar and 3 ml of solution of Ni(CH$_2$SiMe$_3$)$_2$Py$_2$ (0.088 g, 0.226 mmol) in the same solvent (THF). The mixture was shaken and stirred for 1 h at the room temperature. The solvent was evaporated under reduced pressure. The oily residue solidified when it was stirred with 3 mL of hexane at – 80 °C. The suspension was filtered and the solid dried under vacuum to afford **5** as a greenish yellow powder in a 99 % yield. ^{1}H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$): δ -0.24 (s, 2 H, CH_2SiMe$_3$), -0.11 (s, 9 H, CH$_2$SiMe_3), 7.31 (t, 4 H, $^2J_{HH}$ =6.6 Hz, β-Py (C-*cis*)), 7.35 (br, partially hidden, 2 H, β-Py (C-*trans*), 7.69 (br, partially hidden, 1 H, γ-Py (C-*trans*)), 7.71 (t, 2 H, $^2J_{HH}$ = 7.5 Hz, γ-Py (C-*cis*)), 8.73 (br, 2 H, α-Py (C-*trans*)), 9.05 (d, 4 H, $^2J_{HH}$ = 5.2 Hz, α-Py (C-*cis*)). ^{1}H NMR (400 MHz, -20 °C, CD$_2$Cl$_2$): δ -0.32 (s, 2 H, CH_2SiMe$_3$), -0.17 (s, 9 H, CH$_2$SiMe_3), 7.25 (partially hidden t, 2 H, $^2J_{HH}$ =6.7 Hz, β-Py (C-*trans*), 7.30 (t, 4 H, $^2J_{HH}$ =6.3 Hz, β-Py (C-*cis*)), 7.67 (partially hidden t, 1 H, $^2J_{HH}$ = 7.5 Hz, γ-Py (C-*trans*)), 7.70 (t, 2 H, $^2J_{HH}$ = 7.0 Hz, γ-Py (C-*cis*)), 8.62 (d, 2 H, $^2J_{HH}$ = 4.3 Hz, α-Py (C-*trans*)), 8.97 (d, 4 H, $^2J_{HH}$ = 4.7 Hz, α-Py (C-*cis*)). ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, C$_6$D$_6$): δ 1.3 (CH$_2$SiMe_3), 5.6 (*C*H$_2$SiMe$_3$), 125.6 (β-*C*H, Py (C-*cis*)), 126.1 (br, partially hidden, β-*C*H, Py (C-*trans*)), 138.2 (γ-*C*H, Py (C-*cis*)), 138.5, (br, partially hidden, γ-*C*H, Py (C-*trans*)), 148.9 (br, α-*C*H, Py (C-*trans*)), 151.6 (α-*C*H, Py (C-*cis*)). ^{19}F NMR (376.5 MHz, 25 °C, CD$_2$Cl$_2$), δ -77.5 (OTf). ESI-MS (THF): Positive m/z: 382.1 (M$^+$, very low intensity); 303.1 (M$^+$-Py, I = 100 %); 224.1 (M$^+$- 2 Py, I = 66 %). Negative m/z: 148.8 (OTf$^-$). IR (nujol mull): 1605 (sh, ν(C=C) Py), 1409 (sh, δ C-H, Py), 1222 (doublet split, Si-C-H, SiMe$_3$), 1180 (st, br, ν S=O, OTf), 1069 (sh, ν_{as} CF$_3$), 849 (ν_s SiMe$_3$), 765 (ν_{as} SiMe$_3$). Anal. Calcd. for $C_{20}H_{26}F_3N_3NiO_3SSi$: C, 45.13; H, 4.92; N, 7.89; S, 6.02. Found: C, 45.01; H, 4.59; N, 8.29; S, 6.18.

[Ni(CH$_2$SiMe$_3$)(La)(Py)]$^+$[OTf]$^-$, 6a: Starting from 0.116 g (0.3 mmol) of **1**, 0.092 g of [Py$_2$H]$^+$[TfO]$^-$ (0.3 mmol) and 3.0 mL of a 0.1 M solution of **La** in THF, the above procedure afforded 0.19 g (0.247 mmol) of the product (82 % yield) as a yellow oil that solidified as a yellow powder upon drying under vacuum. ^{31}P{^{1}H} NMR (161.9 MHz, 25 °C, CD$_2$Cl$_2$): δ 51.5 (s). ^{1}H NMR

(400 MHz, 25 °C, CD_2Cl_2): δ -0.56 (d, 2 H, $^3J_{HP}$ = 9.1 Hz, CH_2SiMe$_3$), -0.32 (s, 9 H, CH_2SiMe_3), 0.60 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CHMeMe), 1.11 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CHMeMe), 1.54 (dd, 6 H, $^3J_{HP}$ = 15.4 Hz, $^3J_{HH}$ = 7.3 Hz, P-CHMeMe), 1.61 (dd, 6 H, $^3J_{HP}$ = 16.7 Hz, $^3J_{HH}$ = 7.0 Hz, P-CHMeMe), 2.43 (d sept, 2 H, $^2J_{HP}$ = 9.5 Hz, $^3J_{HH}$ = 7.2 Hz, P-CHMe$_2$), 3.20 (sept, $^3J_{HH}$ = 6.6 Hz, 2 H, Ar-CHMe$_2$), 3.59 (d, 2 H, $^2J_{HP}$ = 9.6 Hz, P-CH_2), 6.92 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, *m-N*-Ar), 7.08 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, *o*-Ph), 7.12 (t, 2 H, $^3J_{HH}$ = 7.3 Hz, β-Py), 7.12 (m, 1 H, *p-N*-Ar), 7.18 (t, 2 H, $^3J_{HH}$ = 8 Hz, *m*-Ph), 7.34 (m, 1 H, *p*-Ph), 7.63 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, γ-Py), 8.30 (d, 2 H, $^3J_{HH}$ = 6.3 Hz, α-Py). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ -7.7 (d, $^2J_{CP}$ = 35.4 Hz, CH_2SiMe$_3$), 1.7 (CH_2SiMe_3), 17.9 (P-CHMeMe), 18.9 (P-CHMeMe), 23.8 (Ar-CHMeMe), 24.0 (Ar-CHMeMe_2), 24.5 (d, $^1J_{CP}$ = 29.3 Hz, P-CHMe$_2$), 28.9 (Ar-CHMe$_2$), 38.4 (d, $^1J_{CP}$ = 20.2 Hz, P-CH_2), 124.8 (*m-C*H, *N*-Ar), 125.0 (β-*C*H, Py), 128.1 (*p-C*H, *N*-Ar), 128.8 (*m-C*H, Ph), 130.3 (*o-C*H Ph), 132.2 (*p-C*H Ph), 133.3 (d, $^3J_{CP}$ = 6.5 Hz, *ipso*-C_q Ph), 138.3 (γ-*C*H Py), 138.6 (*o*-C_q, *N*-Ar), 142.7 (s, *ipso*-C_q, *N*-Ar), 150.5 (α-*C*H, Py), 179.5 (d, $^2J_{CP}$ = 7.1 Hz, *C*=N). ^{19}F NMR (376.5 MHz, 25 °C, CD_2Cl_2): δ -78.1 (br, OTf). ESI-MS (THF): Positive m/z: 542.3 (M^+-Py + 2H). Negative m/z: 148.8 (OTf^-). IR (nujol mull, cm^{-1}): 1634 (sh, m, Py), 1554 (m, sh, C=C Arom), 1223 (m, $SiMe_3$) 1153 (st, br, ν(S=O) OTf), 849, 827 (st, $SiMe_3$). Anal. Calcd for $C_{36}H_{54}F_3N_2NiO_3PSSi$: C, 56.18; H, 7.07; N, 3.64; S, 4.17. Found: C, 56.02; H, 6.87; N, 3.85; S, 4.41.

$[Ni(CH_2SiMe_3)(Lb)(Py)]^+[OTf]^-$, 6b: Starting from 0.098 g (0.254 mmol) of **1**, 0.078 g of $[Py_2H]^+[TfO]^-$ (0.254 mmol) and 1.0 mL of a 0.253 M solution of **Lb** in THF, the above procedure afforded 0.19 g (0.247 mmol) of the product (82 % yield) as a yellow solid, that crystallized by layering hexane over a dichloromethane solution at -25 °C. $^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 39.3 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ -0.55 (s, 9 H, CH_2SiMe_3), -0.33 (d, 2 H, $^3J_{HP}$ = 9.8 Hz, CH_2SiMe$_3$), 0.30 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, Ar-CHMeMe), 1.10 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, Ar-CHMeMe), 3.51 (sept, 2 H, $^3J_{HH}$ = 6.2 Hz, Ar-CHMe$_2$), 4.56 (d, 2 H, $^2J_{HP}$ = 11.6 Hz, P-CH_2), 6.85 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, *m-N*-Ar), 7.04 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, *p-N*-Ar), 7.07 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, *o*-Ph), 7.17 (m, 2 H, β -Py), 7.17 (m, 2 H, *m*-Ph), 7.31 (m, 1 H, *p*-Ph), 7.62 (m, 1 H, γ -Py), 7.62 (m, 4 H, (*m-C*H PPh$_2$), 7.70 (m, 2 H, *p-C*H PPh$_2$), 7.91 (dd, 4 H, $^3J_{HP}$ = 11.3 Hz, $^3J_{HH}$ = 7.8 Hz, *o-C*H PPh$_2$), 8.52 (d, 2 H, $^3J_{HH}$ = 4.9 Hz, α-Py). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ 1.2 (d, $^2J_{CP}$ = 31.4 Hz, *C*H_2SiMe$_3$), 1.2 (CH_2SiMe_3), 23.1 (s, Ar-CHMeMe), 23.7 (Ar-CHMeMe), 28.8 (s, Ar-*C*HMe$_2$), 45.6 (d, $^1J_{CP}$ = 25.3 Hz, P-*C*H_2), 124.5 (*m-C*H *N*-Ar), 124.9 (β-*C*H Py), 127.7 (*p-C*H *N*-Ar), 127.9 (d, $^1J_{CP}$ = 53.8 Hz, *ipso*-C_q PPh$_2$), 128.6 (*m-C*H Ph), 128.6 (*p-C*H PPh$_2$), 129.6 (d, $^3J_{CP}$ = 10.5 Hz, *m-C*H PPh$_2$), 130.1 (*o-C*H Ph), 132.1 (*p-C*H Ph), 133.3 (d, $^2J_{CP}$ = 10.5 Hz, *o-C*H PPh$_2$), 133.7 (d, $^3J_{CP}$ = 5.9 Hz, *ipso*-C_q Ph), 138.2 (γ-*C*H Py), 138.6 (*o*-C_q *N*-Ar), 142.2 (*ipso*-C_q N-*Ar*), 150.8 (α-*C*H Py), 177.3 (d, $^2J_{CP}$ = 7.2 Hz, *C*=N). ^{19}F NMR (376.5 MHz, 25 °C, CD_2Cl_2): δ 78.3 (s) (OTf^-). ESI-MS (THF). Positive, m/z: 542.3 (M^+- Py). Negative, m/z: 148.8 (OTf^-). IR (nujol mull, cm^{-1}): 1605 (sh, m, Py), 1560 (m, C=C Arom.), 1223 (m, $SiMe_3$) 1153 (st, br ν S=O, OTf), 849, 827 (st, $SiMe_3$). Although the NMR spectra indicate that the samples of this complex were spectroscopically pure, elemental analyses were unsuccessful possibly due to combustion problems.

$[Ni(CH_2SiMe_3)(Lc)(Py)]^+[OTf]^-$, 6c: The general procedure for the preparation of the cationic monoalkyl Ni(II) complex starting from **Lc** ligand (0.100 g, 0.191 mmol), $Ni(CH_2SiMe_3)_2Py_2$ (0.074 g, 0.191 mmol) and Py_2H^+ TfO^- (0.076 g, 0.191 mmol) gave a yellow solid with an 84 % (0.145 g, 0.161 mmol) yield. This compound is formed as a mixture of geometric isomers in variable ratio. ^{31}P $\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 25.5 (s, major) 29.9 (s, minor). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): Major isomer, δ -0.61 (s, 9 H, CH_2SiMe_3), -0.58 (d, 2 H, $^3J_{HP}$ = 10 Hz, CH_2SiMe$_3$), 0.43 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CHMeMe), 1.22 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CHMeMe), 3.58 (m, 2 H, Ar-CHMe$_2$), 4.01 (s, 6 H, -OMe), 4.41 (d, 2 H, $^2J_{HP}$ = 12.0 Hz, P-CH_2), 6.88 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, *m-N*-Ar), 6.95 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, *o*-Ph), 7.06 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, *p-N*-Ar), 7.16 (m, 2 H, *m*-Ph), 7.18 (m, 2 H, 3-C*H*, P(Anis.)$_2$), 7.19 (m, 2 H, 5-C*H*, P(Anis.)$_2$), 7.20 (m, 2 H, β-Py), 7.30 (t, 1 H, $^3J_{HH}$ = 7.4 Hz, *p*-Ph), 7.64 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, γ-Py), 7.69 (t, 2 H, $^3J_{HH}$ = 7.9 Hz, 4-C*H*, P(Anis.)$_2$), 7.84 (m, 2 H, 6-C*H*, P(Anis.)$_2$), 8.45 (d, 2 H, $^3J_{HH}$ = 4.8 Hz, α-Py). Minor isomer: δ -0.49 (d, 2H, $^3J_{HP}$ = 11.6 Hz, CH_2SiMe$_3$), -0.27 (s, 9H, CH_2SiMe_3), 0.69 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, Ar-CHMeMe, 1.49, (d, 6H, $^3J_{HH}$ = 6.8 Hz, Ar-CHMeMe, 3.30 (sept, 2 H , $^3J_{HH}$ = Ar-CHMe_2), 3.91 (s, 6 H, -OMe), 4.15 (d, 2 H, $^2J_{HP}$ = 11.4 Hz, P-CH_2). ^{13}C $\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): Major isomer, δ 0.2 (*C*H_2SiMe$_3$), 0.9 (CH_2SiMe_3), 23.2 (Ar-CHMeMe), 23.7 (Ar-CHMeMe), 29.0 (Ar-*C*HMe$_2$), 45.0 (d, $^1J_{CP}$ = 30.5 Hz, P-*C*H_2), 56.1 (-OMe), 112.1 (3-*C*H P(Anis.)$_2$), 114.7 (d, $^1J_{CP}$ = 57.0 Hz, *ipso*-C_q P(Anis.)$_2$), 121.4 (d, $^3J_{CP}$ = 12.0 Hz, 5-*C*H, P(Anis.)$_2$), 124.6 (*m-C*H, *N*-Ar), 124.9 (β-*C*H, Py), 127.8 (*p-C*H *N*-Ar), 128.7 (*m-C*H, Ph), 129.6 (*o-C*H, Ph), 131.8 (*p-C*H, Ph), 134.0 (d, $^3J_{CP}$ = 8.4 Hz, *ipso*-C_q Ph), 134.6 (4-*C*H P(Anis.)$_2$), 136.6 (d, $^2J_{CP}$ = 12.6 Hz, 6-*C*H P(Anis.)$_2$), 138.2 (*o*-C_q, *N*-Ar), 138.3 (γ-CH Py), 142.5 (*ipso*-C_q N-Ar), 150.6 (α-*C*H Py), 160.1 (2-C_q P(Anis.)$_2$), 178.7 (d, $^2J_{CP}$ = 9.1 Hz, *C*=N). ESI-MS (THF): Positive, m/z: 668.3 (M^+-Py). Negative, m/z: 148.8 (OTf^-). IR (nujol mull, cm^{-1}): 1605 (sh, m, Py), 1587, 1575, 1559 (m, C=N or C=C Arom), 1246 (st, as Ar-O-Me) 1222 ($SiMe_3$), 1153 (st, br ν S=O, OTf), 847, 827 (st, $SiMe_3$). Anal. Calcd. for $C_{44}H_{54}F_3N_2NiO_5PSSi$: C, 58.87; H, 6.06; N, 3.12; S, 3.57. Found: C, 58.88; H, 3.99; N, 3.39; S, 3.63.

Neutral Alkylnickel Complexes $[Ni(CH_2SiMe_3)(L')(Py)]$ (L' = deprotonated L), 3a-c.

$[Ni(CH_2SiMe_3)(L'a)(Py)]$, 3a: Starting from 0.089 g (0.23 mmol) of **1**, and equimolar amounts of $[HPy_2]^+[OTf]^-$ (0.071 g) and **La** (0.120 g), the reaction with NaH (0.055 g, 2.30 mmol) conducted as described above, and evaporation of the THF solvent gave a yellow solid. The remaining NaOTf was removed by extraction with a 1:1 Et_2O/hexane mixture. The product precipitated when extract was slowly evaporated under reduced pressure to some less than ca. 50 % of the initial volume. The resulting yellow microcrystalline solvent was filtrated, washed with a small amount of hexane and dried under vacuum. Yield, 0.100 g (0.161 mmol), 65 %. $^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 47.9 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ -0.40 (s, 9 H,

$CH_2Si\mathit{Me}_3$), -1.13 (d, 2 H, $^3J_{HP}$ = 7.6 Hz, CH_2SiMe_3), 0.60 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 1.02 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, Ar-CHMe*Me*), 1.43 (dd, 6 H, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 6.9 Hz, P-CH*Me*Me), 1.55 (dd, 6 H, $^3J_{HP}$ = 15.8 Hz, $^3J_{HH}$ = 7.0 Hz, P-CHMe*Me*), 2.05 (d sept, 2 H, $^2J_{HP}$ = 8.9 Hz, $^3J_{HH}$ = 7.0 Hz, P-C*H*Me$_2$), 3.22 (s, 1 H, P-C*H*=), 3.69 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, Ar-C*H*Me$_2$), 6.61 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-*N*-Ar), 6.73 (t, 1 H, $^3J_{HH}$ = 6.8 Hz, *p*-*N*-Ar), 6.87 (m, 2 H, β-Py), 6.88 (m, 2 H, *m*-Ph), 6.94 (m, 1 H, *p*-Ph), 6.97 (d, 2 H, $^3J_{HH}$ = 6.8 Hz, *o*-Ph), 7.38 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, γ-Py), 8.35 (d, 2 H, $^3J_{HH}$ = 4.2 Hz, α-Py). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ -13.1 (d, $^2J_{CP}$ = 36.3 Hz, *C*H_2SiMe_3), 2.5 ($CH_2Si\mathit{Me}_3$), 18.4 (P-CH*Me*Me), 20.0 (P-CHMe*Me*), 24.1 (Ar-CH*Me*Me), 24.4 (s, Ar-CHMe*Me*), 25.2 (d, $^1J_{CP}$ = 32.0 Hz, P-*C*HMe$_2$), 28.3 (Ar*C*HMe$_2$), 69.8 (d, $^1J_{CP}$ = 47.0 Hz, P-*C*H=), 122.7 (*m*-*C*H *N*-Ar), 123.1 (*p*-*C*H *N*-Ar), 123.4 (β-*C*H Py), 126.8 (*m*-*C*H Ph), 126.8 (*p*-*C*H Ph), 129.6 (*o*-*C*H Ph), 135.8 (γ-*C*H Py), 141.2 (d, $^3J_{CP}$ = 16.1 Hz, *ipso*-C_q Ph), 144.9 (*o*-C_q *N*-Ar), 149.1 (*ipso*-C_q *N*-Ar), 151.4 (α-*C*H Py), 175.3 (d, $^2J_{CP}$ = 21.4 Hz, *C*=N). IR (nujol mull, cm^{-1}): 1634 (ν C=C, Py), 1621 (ν C=C arom.), 1236 ($SiMe_3$), 849, 820 (C-H arom, $SiMe_3$). Anal. Calcd for $C_{35}H_{53}N_2NiPSi$: C, 67.85; H, 8.62; N, 4.52. Found: C, 68.03; H, 8.81; N, 4.39.

[Ni(CH_2SiMe_3)(L'b)(Py)], 3b: *This complex can also be prepared directly from **1** and **Lb** as described in the main text.* Starting from 0.023 g (0.060 mmol) of **1**, and equimolar amounts of $[HPy_2]^+[OTf]^-$ (0.018 g) and **Lb** (0.237 □L of a 0.253 M solution in THF)), the reaction with NaH (0.014 g, 0.6 mmol) conducted as described above, and evaporation of the THF solvent gave a yellow solid. The remaining NaOTf was removed by extraction with a 1:1 toluene/hexane mixture. The extract was evaporated to dryness and the residue was crystallized by slow diffusion of hexane into a CH_2Cl_2 solution at -25 °C. The yellow crystals were filtrated, and dried under vacuum. Yield, 0.020 g (0.029 mmol), 50 %. $^{31}P\{^1H\}$NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 32.4 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ -0.82 (d, 2 H, $^3J_{HP}$ = 7.8 Hz, CH_2SiMe_3), -0.63 (s, 9 H, $CH_2Si\mathit{Me}_3$), 0.50 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 1.07 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CHMe*Me*), 3.78 (s, 1 H, PC*H*=), 3.97 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, Ar-C*H*Me$_2$), 6.63 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, *m*-*N*-Ar), 6.73 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, *p*-N-Ar), 6.93 (m, 2 H, β -Py), 6.93 (m, 2 H, *m*-Ph), 6.95 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, *p*-Ph), 6.99 (d, 2 H, $^3J_{HH}$ = 7.4 Hz, *o*-Ph), 7.42 (m, 1 H, γ -Py), 7.45 (m, 2 H, *p*-C*H*, PPh_2), 7.46 (m, 4 H, *m*-C*H* PPh_2), 7.99 (dd, 4 H, $^3J_{HP}$ = 10.7 Hz, $^3J_{HH}$ = 8.0 Hz, *o*-C*H*, PPh_2), 8.50 (d, 2 H, $^3J_{HH}$ = 5.0 Hz, α-Py). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ -3.9 (d, $^2J_{CP}$ = 34.2 Hz, *C*H_2SiMe_3), 1.7 ($CH_2Si\mathit{Me}_3$), 23.9 (Ar-CH*Me*Me), 24.2 (Ar-CHMe*Me*), 28.7 (Ar-*C*HMe$_2$), 76.4 (d, $^1J_{CP}$ = 54.8 Hz, P-*C*H=), 122.3 (β-*C*H Py), 122.8 (*m*-*C*H *N*-Ar), 123.4 (*p*-*C*H *N*-Ar), 123.4 (*p*-*C*H Ph), 127.1 (*m*-*C*H Ph), 128.4 (d, $^3J_{CP}$ = 10.0 Hz, *m*-*C*H PPh_2), 129.3 (*o*-*C*H Ph), 129.4 (d, $^4J_{CP}$ = 2.3 Hz, *p*-*C*H PPh_2), 133.7 (d, $^2J_{CP}$ = 10.2 Hz, *o*-*C*H, PPh_2), 136.2 (γ-*C*H Py), 137.6 (d, $^1J_{CP}$ = 53.4 Hz, *ipso*-C_q PPh_2), 140.8 (d, $^3J_{CP}$ = 17.3 Hz, *ipso*-C_q Ph), 144.3 (*o*-C_q *N*-Ar), 148.3 (*ipso*-C_q N-Ar), 151.5 (α-*C*H Py), 175.0 (d, $^2J_{CP}$ = 24.4 Hz, *C*=N). IR (nujol, cm^{-1}): 1606 (ν C=C, Py), 1574 (ν C=C arom.), 1238 ($SiMe_3$), 849, 820 (C-H arom, $SiMe_3$). Anal. Calcd. for $C_{41}H_{48}N_2NiPSi$: C, 71.72; H, 7.05; N, 4.08. Found: C, 71.50; H, 7.39; N, 4.13.

[Ni(CH_2SiMe_3)(L'c)(Py)], 3c: Starting from 0.089 g (0.230 mmol) of **1**, and equimolar amounts of $[HPy_2]^+[OTf]^-$ (0.071 g) and **Lc** (0.120 g), the reaction with NaH (0.055 g, 2.3 mmol) conducted as described above, and evaporation of the THF solvent gave a yellow solid. The remaining NaOTf was removed by extraction with a 1:1 toluene/hexane mixture. The extract was evaporated to dryness and the residue was crystallized by slow diffusion of hexane into a CH_2Cl_2 solution at -25 °C. An oil precipitated out, which was decanted. Upon vacuum drying the oil solidified affording a yellow powder. Yield, 0.130 g (0.174 mmol), 76 %. $^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 27.6 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ -0.92 (d, 2 H, $^3J_{HP}$ = 7.2 Hz, C*H*$_2$SiMe$_3$), -0.66 (s, 9 H, $CH_2Si\mathit{Me}_3$), 0.46 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, ArCH*Me*Me), 1.11 (d, 6 H, $^3J_{HH}$ = 6.5 Hz, CHMe*Me*), 3.68 (s, 6 H,-O*Me*), 3.93 (s, 1 H, P-C*H*=), 4.11 (m, 2 H, ArC*H*Me$_2$), 6.60 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, *m*-*N*-Ar), 6.69 (t, 1 H, $^3J_{HH}$ = 7.6 Hz, *p*-*N*-Ar), 6.89 (m, 2 H, 3-C*H* P(Anis.)$_2$), 6.90 (m, 2 H, β-Py), 6.93 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, *o*-Ph), 6.95 (m, 2 H, *m*-Ph), 6.97 (m, 1 H, *p*-Ph), 7.07 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, 5-C*H* P(Anis.)$_2$), 7.37 (m, 1 H, γ-Py), 7.42 (t, 2 H, $^3J_{HH}$ = 7.9 Hz, 4-C*H* P(Anis.)$_2$), 8.26 (m, 2 H, 6-C*H* P(Anis.)$_2$), 8.53 (d, 2 H, $^3J_{HH}$ = 4.3 Hz, α-Py). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 ºC, CD_2Cl_2): δ -7.5 (CH_2SiMe_3), 1.7 ($CH_2Si\mathit{Me}_3$), 23.9 (Ar-CH*Me*Me), 24.3 (Ar-CHMe*Me*), 28.6 (Ar-*C*HMe$_2$), 55.4 (-O*Me*), 77.5 (d, $^1J_{CP}$ = 56.5 Hz, P-*C*H=), 111.1 (d, $^3J_{CP}$ = 3.9 Hz, 3-*C*H P(Anis.)$_2$), 115.0 (d, $^1J_{CP}$ = 56.7 Hz, 1-C_q P(Anis.)$_2$), 120.4 (d, $^3J_{CP}$ = 10.5 Hz, 5-*C*H P(Anis.)$_2$), 122.7 (*m*-*C*H *N*-Ar), 122.8 (*p*-*C*H *N*-Ar), 123.3 (β-*C*H Py), 126.6 (*p*-*C*H Ph), 126.9 (*m*-*C*H Ph), 129.2 (*o*-*C*H Ph), 130.1 (4-*C*H P(Anis.)$_2$), 135.6 (d, $^2J_{CP}$ = 14.0 Hz, 6-*C*H P(Anis.)$_2$), 135.9 (γ-*C*H Py), 141.5 (d, $^3J_{CP}$ = 18.1 Hz, *ipso*-C_q Ph), 144.5 (*o*-C_q *N*-Ar), 148.6 (*ipso*-C_q N-Ar), 151.6 (α-*C*H Py), 161.0 (2-C_q P(Anis.)$_2$), 173.0 (d, $^2J_{CP}$ = 24.9 Hz, *C*=N). IR (nujol, cm^{-1}): 1601 (ν C=C, Py), 1576 (ν C=C arom.), 1252 (ν_{as} Ar-O-Me), 1236, (δ SiCH, $SiMe_3$), 849, 820 (γ C-H arom, $SiMe_3$). Anal. Calcd. for $C_{43}H_{53}N_2NiO_2PSi$: C, 69.08; H, 7.15; N, 3.75. Found: C, 69.37; H, 7.21; N, 3.49.

Nickel aryl derivatives 7a-c (X = Br) and 8a-c (X = Cl)

[Ni(C_6H_4-*p*-$COCH_3$)(Br)(La)], 7a: Starting from 1.04 mmol of $Ni(COD)_2$ (0.287 g), and equimolar amounts of ligand **La** (5.5 mL of a 0.19 M solution in THF) in, and 4-bromoacetophenone (0.212 g), the general procedure gave the title product as off-yellow crystals in 74 % yield (0.505 g, 0.775 mmol). $^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 47.1 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 0.84 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 1.26 (dd, 6 H, $^3J_{HP}$ = 15.1 Hz, $^3J_{HH}$ = 7.0 Hz, P-CH*Me*Me), 1.38 (dd, 6 H, $^3J_{HP}$ = 15.4 Hz, $^3J_{HH}$ = 7.0 Hz, P-CHMe*Me*), 1.52 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CHMe*Me*), 2.20 (d sept, 2 H, $^2J_{HP}$ = 9.8 Hz, $^3J_{HH}$ = 7.0 Hz, P-C*H*Me$_2$), 2.44 (s, 3 H, -COC*H*$_3$), 3.38 (d, 2 H, $^2J_{HP}$ = 8.6 Hz, P-C*H*$_2$), 3.60 (sept, 2 H, $^3J_{HH}$ = 7.0 Hz, Ar-C*H*Me$_2$), 7.01 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, *m*-*N*-Ar), 7.05 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 7.12 (t, 1 H, $^3J_{HH}$ = 7.7 Hz, *p*-*N*-Ar), 7.18 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-Ph), 7.30 (t, 1 H, $^3J_{HH}$ = 7.4 Hz, *p*-Ph), 7.40 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-C*H*, Ni-Ar), 7.60 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, *o*-C*H*, Ni-Ar). $^{13}C\{^1H\}$ NMR (100.6

MHz, 25 °C, CD_2Cl_2): δ 17.1 (P-CH*Me*Me), 17.7 (P-CHMe*Me*), 23.4 (Ar-CH*Me*Me), 23.6 (d, $^1J_{CP}$ = 41.4 Hz, P-*C*HMe$_2$), 24.3 (s, Ar-CHMe*Me*), 26.4 (s, -CO*C*H$_3$), 29.6 (s, Ar-*C*HMe$_2$), 38.4 (d, $^1J_{CP}$ = 17.1 Hz, P-*C*H$_2$), 123.6 (*m*-*C*H, *N*-Ar), 124.3 (*m*-*C*H, Ni-Ar), 127.0 (*p*-*C*H *N*-Ar), 128.5 (*m*-*C*H, Ph), 129.1 (*o*-*C*H, Ph), 131.1 (*p*-*C*H, Ph), 132.2 (*ipso*-*C*$_q$, *Ni*-Ar), 134.7 (*ipso*-*C*$_q$, Ph), 137.9 (*o*-*C*H, Ni-Ar), 139.4 (*o*-*C*$_q$, N-*Ar*), 144.9 (*ipso*-*C*$_q$, N*Ar*), 156.2 (d, $^2J_{CP}$ = 41.3 Hz, *ipso*-*C*$_q$, Ni*Ar*), 177.7 (d, $^2J_{CP}$ = 5.2 Hz, *C*=N), 198.5 (-*C*OMe). IR (nujol mull, cm^{-1}): 1664 (*ν* C=O), 1563 (*ν* C=N). Anal. Calcd for $C_{34}H_{45}BrNNiOP$: C, 62.51; H, 6.94; N, 2.14. Found: C, 62.37; H, 7.29; N, 2.03.

[Ni(C$_6$H$_4$-*p*-COCH$_3$)(Br)(Lb)], 7b: Starting from 0.82 mmol of Ni(COD)$_2$ (0.225 g), and equimolar amounts of **Lb** ligand (4.3 mL of a 0.19 M solution in THF), and 4-bromoacetophenone (0.163 g), the general procedure gave the title product as off-yellow crystals in 76 % yield (0.450 g, 0.626 mmol). $^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 35.6 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 0.61 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CH*Me*Me), 1.53 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, Ar-CHMe*Me*), 2.37 (s, 3 H, -COC*H*$_3$), 3.57 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, Ar-*C*HMe$_2$), 4.31 (d, 2 H, $^2J_{HP}$ = 10.6 Hz, P-C*H*$_2$), 7.04 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-*N*-Ar), 7.05 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, *o*-Ph), 7.18 (m, 1 H, *p*-*N*-Ar), 7.19 (m, 2 H, *m*-C*H*, Ni-Ar), 7.20 (m, 2 H, *m*-Ph), 7.32 (m, 1 H, *p*-Ph), 7.35 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, *o*-C*H*, Ni-Ar), 7.47 (t, 4 H, $^3J_{HH}$ = 7.3 Hz, *m*-C*H*, PPh$_2$), 7.55 (m, 2 H, *p*-C*H*, P*Ph*$_2$), 7.61 (dd, 4 H, $^3J_{HP}$ = 10.7 Hz, $^3J_{HH}$ = 7.9 Hz, *o*-C*H*, PPh$_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ 23.3 (Ar-CH*Me*Me), 24.7 (Ar-CHMe*Me*), 26.3 (-COC*H*$_3$), 29.4 (Ar-*C*HMe$_2$), 46.1 (d, $^1J_{CP}$ = 23.3 Hz, P-*C*H$_2$), 123.9 (*m*-*C*H, -*N*Ar), 124.2 (*m*-*C*H, Ni-Ar), 127.3 (*p*-*C*H, *N*-Ar), 128.2 (*p*-*C*$_q$, Ni-Ar), 128.4 (d, $^1J_{CP}$ = 49.7 Hz, *ipso*-*C*$_q$, PPh$_2$), 128.6 (*m*-*C*H, Ph), 129.3 (*o*-*C*H, Ph), 129.4 (*m*-C*H*, PPh$_2$), 131.6 (*p*-*C*H, Ph), 131.8 (*p*-*C*H, PPh$_2$), 132.8 (d, $^2J_{CP}$ = 10.2 Hz, *o*-C*H*, PPh$_2$), 134.6 ($^3J_{CP}$ = 6.5 Hz, *ipso*-*C*$_q$, Ph), 138.0 (d, $^3J_{CP}$ = 3.7 Hz, *o*-*C*H, Ni-*Ar*), 139.7 (*o*-*C*$_q$, *N*-Ar), 144.2 (*ipso*_*C*$_q$-N*Ar*), 157.4 (d, $^2J_{CP}$ = 41.3 Hz, *ipso*-*C*$_q$, Ni*Ar*), 175.5 (d, $^2J_{CP}$ = 7.7 Hz, *C*=N), 198.6 (-*C*OMe). IR (nujol mull, cm^{-1}): 1666 (*ν* C=O), 1564 (*ν* -C=N). Anal. Calcd for $C_{40}H_{41}BrNNiOP$: C, 66.60; H, 5.73; N, 1.94. Found: C, 66.50; H, 5.73; N, 1.99.

[Ni(C$_6$H$_4$-*p*-COCH$_3$)(Br)(Lc)], 7c: Starting from 1.00 mmol of Ni(COD)$_2$ (0.275 g), and equimolar amounts of **Lc** ligand (0.520 g), and 4-bromoacetophenone (0.199 g), the general procedure gave the title product as off-yellow crystals in 69 % yield (0.537 g, 0.687 mmol).$^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, 161.9 MHz, CD_2Cl_2,): 26.7 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 0.71 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CHMe*Me*), 1.64 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 2.27 (s, 3 H, COC*H*$_3$), 3.61 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, Ar-*C*HMe$_2$), 3.98 (s, 6 H, -O*Me*), 4.75 (d, 2 H, $^2J_{HP}$ = 11.9 Hz, P-C*H*$_2$), 6.97 (m, 2 H, 5-C*H*, P(Anis.)$_2$), 6.97 (m, 2 H, *o*-C*H*, Ph), 6.99 (m, 2 H, *m*-C*H*, Ni-Ar), 7.03 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, *m*-*N*-Ar), 7.06 (m, 2 H, 3-C*H*, P(*Anis.*)$_2$), 7.13 (m, 2 H, *m*-Ph), 7.15 (m, 1 H, *p*-*N*-Ar), 7.19 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, *o*-C*H*, Ni-Ar), 7.25 (t, 1 H, $^3J_{HH}$ = 7.4 Hz, *p*-Ph), 7.55 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, 4-C*H*, P(Anis.)$_2$), 7.79 (dd, 2 H, $^2J_{HP}$ = 7.6 Hz, $^3J_{HH}$ = 14.1 Hz, 6-C*H*, P(Anis.)$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 100.6 MHz): 23.1 (Ar-CHMe*Me*), 24.3 (Ar-CH*Me*Me), 26.1 (CO*C*H$_3$), 29.1 (Ar-*C*HMe$_2$), 44.4 (d, $^1J_{CP}$ = 23.3 Hz, P-*C*H$_2$), 56.1 (-O*C*H$_3$), 111.5 (d, $^3J_{CP}$ = 4.3 Hz, 3-*C*H, P(Anis.)$_2$), 115.1 (d, $^1J_{CP}$ = 53.7 Hz, 1-*C*$_q$ P(Anis.)$_2$), 120.9 (d, $^3J_{CP}$ = 12.1 Hz, 5-*C*H, P(Anis.)$_2$), 123.3 (*m*-*C*H, Ni-Ar), 123.6 (*m*-*C*H, *N*-Ar), 126.6 (*p*-*C*H, *N*-Ar), 128.1 (*m*-*C*H, Ph), 128.9 (*o*-*C*H, Ph), 130.7 (*p*-*C*H, Ph), 130.8 (*p*-*C*$_q$, Ni-Ar), 133.8 (4-*C*H, P(Anis.)$_2$), 135.0 (d, $^3J_{CP}$ = 8.3 Hz, *ipso*-*C*$_q$, Ph), 136.2 (d, $^2J_{CP}$ = 12.7 Hz, 6-*C*$_q$, P(Anis.)$_2$), 136.7 (d, $^3J_{CP}$ = 3.1 Hz, *o*-*C*H, NiAr), 139.2 (*o*-*C*$_q$, *N*-Ar), 144.6 (*ipso*-*C*$_q$, *N*-Ar), 160.0 (d, $^2J_{CP}$ = 41.0 Hz, *ipso*-*C*$_q$, Ni*Ar*), 160.1 (2-*C*$_q$, P(Anis.)$_2$), 177.3 (d, $^2J_{CP}$ = 9.7 Hz, *C*=N), 198.3 (*C*=O). IR (nujol mull, cm^{-1}): 1662 (*ν* C=O), 1561 (*ν* C=N).

[Ni(C$_6$H$_4$-*p*-COCH$_3$)(Cl)(La)], 8a: Starting from 1.00 mmol of Ni(COD)$_2$ (0.275 g), and equimolar amounts of ligand **La** (5.6 mL of a 0.18 M solution in THF), and 4-chloroacetophenone (0.129 mL), the general procedure gave the title product as off-yellow crystals in 49 % yield (0.300 g, 0.493 mmol).$^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 46.4 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 0.89 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 1.24 (dd, 6 H, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 7.4 Hz, P-CH*Me*Me), 1.40 (dd, 6 H, $^3J_{HP}$ = 15.2 Hz, $^3J_{HH}$ = 7.0 Hz, P-CHMe*Me*), 1.52 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CHMe*Me*), 2.19 (d sept, 2 H, $^2J_{HP}$ = 9.4 Hz, $^3J_{HH}$ = 6.7 Hz, P-C*H*Me$_2$), 2.45 (s, 3 H, -COC*H*$_3$), 3.35 (d, 2 H, $^2J_{HP}$ = 8.9 Hz, P-C*H*$_2$), 3.52 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, Ar-C*H*Me$_2$), 6.99 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-*N*-Ar), 7.04 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, *o*-Ph), 7.13 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, *p*-*N*-Ar), 7.18 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-Ph), 7.30 (t, 1 H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 7.42 (d, 2 H, $^3J_{HH}$ = 8.0 Hz, *m*-C*H*, Ni-Ar), 7.59 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, *o*-C*H*, NiAr). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ 17.1 (P-CH*Me*Me), 17.7 (P-CHMe*Me*), 23.2 (Ar-CH*Me*Me), 23.4 (d, $^1J_{CP}$ = 27.8 Hz, P-*C*HMe$_2$), 24.3 (Ar-CHMe*Me*), 26.4 (-CO*C*H$_3$), 29.5 (Ar-*C*HMe$_2$), 38.1 (d, $^1J_{CP}$ = 18.0 Hz, P-*C*H$_2$), 123.4 (*m*-*C*H, *N*-Ar), 124.5 (*m*-*C*H, Ni-Ar), 126.8 (*p*-*C*H, *N*-Ar), 128.4 (*m*-*C*H, Ph), 128.7 (*o*-*C*H, Ph), 131.0 (*p*-*C*H, Ph), 132.3 (*p*-*C*$_q$, Ni*Ar*), 134.7 (d, $^3J_{CP}$ = 8.0 Hz, *ipso*-*C*$_q$, Ph), 137.7 (*o*-*C*H, NiAr), 139.6 (*o*-*C*$_q$, *N*Ar), 144.1 (*ipso*-*C*$_q$ *N*-Ar), 157.4 (d, $^2J_{CP}$ = 45.4 Hz, *ipso*-*C*$_q$, Ni*Ar*), 177.9 (d, $^2J_{CP}$ = 8.0 Hz, *C*=N), 198.5 (-*C*OMe). IR (nujol mull, cm^{-1}): 1659 (*ν* C=O), 1561 (*ν* C=N).Anal. Calcd for $C_{34}H_{45}ClNNiOP$: C, 67.07; H, 7.45; N, 2.30. Found: C, 67.36; H, 7.36; N, 2.38.

[Ni(C$_6$H$_4$-*p*-COCH$_3$)(Cl)(Lb)], 8b: Starting from 0.8 mmol of Ni(COD)$_2$ (0.226 g), and equimolar amounts of **Lb** ligand (4.2 mL of a 0.19 M solution in THF), and 4-chloroacetophenone (107 µL), the general procedure gave the title product as off-yellow crystals in 64 % yield (0.345 g, 0.510 mmol). $^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): δ 33.9 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 0.66 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CH*Me*Me), 1.51 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Ar-CHMe*Me*), 2.37 (s, 3 H, -COC*H*$_3$), 3.51 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, Ar-C*H*Me$_2$), 4.27 (d, 2 H, $^2J_{HP}$ = 10.5 Hz, P-C*H*$_2$), 7.04 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-*N*-Ar), 7.05 (d, 2 H, $^3J_{HH}$ = 8.4 Hz, *o*-Ph), 7.17 (t, 1 H, $^3J_{HH}$= 7.4 Hz, *p*-*N*-Ar), 7.19 (t, 2 H, $^3J_{HH}$= 8.1 Hz, *m*-Ph), 7.21 (d, 2 H, $^3J_{HH}$= 8.3 Hz, *m*-C*H*, Ni-Ar), 7.32 (t, 1 H, $^3J_{HH}$= 7.2 Hz, *p*-Ph), 7.34 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, *o*-C*H*, NiAr), 7.47 (t, 4 H, $^3J_{HH}$ = 7.7 Hz, *m*-PPh$_2$), 7.56 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, *p*-PPh$_2$), 7.62 (dd, 4 H, $^3J_{HP}$ = 11.3 Hz, $^3J_{HH}$ = 8.1 Hz, *o*-PPh$_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ 23.1 (Ar-CH*Me*Me), 24.7 (Ar-CHMe*Me*), 26.3 (-COC*H*$_3$), 29.4 (Ar-*C*HMe$_2$), 46.1 (d, $^1J_{CP}$ = 24.3 Hz, P-*C*H$_2$), 123.7 (*m*-*C*H, *N*-Ar), 124.4 (*m*-*C*H, Ni-Ar), 127.2 (*p*-*C*H, *N*-Ar), 128.5 (*p*-*C*$_q$, Ni-Ar), 128.5 (d, $^1J_{CP}$ = 50.4 Hz, *ipso*-*C*$_q$, PPh$_2$), 128.6 (*m*-*C*H, Ph), 129.2 (*o*-Ph), 129.3 (d, $^3J_{CP}$ = 50.4 Hz,

m-C**H**), 131.5 (*p*-C**H**, Ph), 131.8 (d, $^4J_{CP}$ = 2.6 Hz, *p*-C**H**, PPh_2), 132.9 (d, $^2J_{CP}$ = 10.3 Hz, *o*-C**H**, PPh_2), 134.6 (d, $^3J_{CP}$ = 6.3 Hz, *ipso*-C_q, Ph), 137.6 (d, $^3J_{CP}$ = 3.4 Hz, *o*-C**H**, Ni-Ar), 139.8 (*o*-C_q -N*Ar*), 143.4 (*ipso*-C_q, *N*-Ar), 158.0 (d, $^2J_{CP}$ = 42.2 Hz, *ipso*-C_q, Ni-Ar), 175.4 (d, $^2J_{CP}$ = 7.7 Hz, *C*=N), 198.6 (-*C*OMe). IR (nujol mull, cm^{-1}): 1663 (ν C=O), 1562 (ν C=N).Anal. Calcd for $C_{40}H_{41}ClNNiOP$: C, 70.98; H, 6.11; N, 2.07. Found: C, 70.82; H, 6.12; N, 1.73.

[Ni(C_6H_4-*p*-$COCH_3$)(Cl)(Lc)], 8c: Starting from 1.00 mmol of $Ni(COD)_2$ (0.275 g), and equimolar amounts of **Lc** ligand (0.523 g), and 4-chloroacetophenone (0.129 mL), the general procedure gave the title product as golden crystals in 46 % yield (0.340 g, 0.461 mmol). $^{31}P\{^1H\}$ NMR (161.9 MHz, 25 °C, CD_2Cl_2): 25.6 (s). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 0.76 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CHMe*Me*), 1.64 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, Ar-CH*Me*Me), 2.28 (s, 3 H, COCH_3), 3.53 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, Ar-C*H*Me_2), 3.99 (s, 6 H, -O*Me*), 4.34 (d, 2 H, $^2J_{HP}$ = 11.9 Hz, P-CH_2), 6.97 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, *o*-Ph), 7.00 (m, 2 H, 5-C*H*, P(*Anis.*)$_2$), 7.02 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-C*H*, Ni-Ar), 7.03 (m, 2 H, *m*-C*H*, *N*-Ar), 7.05 (m, 2 H, 3-C*H*, P(Anis.)$_2$), 7.13 (m, 2 H, *m*-Ph), 7.15 (m, 1 H, *p*-C*H*, *N*-Ar), 7.20 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, *o*-C*H*, Ni*Ar*), 7.25 (t, 1 H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 7.55 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, 4-C*H*, P(Anis.)$_2$), 7.83 (dd, 2 H, $^2J_{HP}$ = 13.8 Hz, $^3J_{HH}$ = 7.5 Hz, 6-C*H*, P(Anis.)$_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ 23.1 (Ar-CH*Me*Me), 24.5 (s, Ar-CHMe*Me*), 26.2 (COCH_3), 29.1 (Ar-*C*HMe_2), 44.3 (d, $^1J_{CP}$ = 28.9 Hz, P-*C*H_2), 56.1 (OCH_3), 111.5 (s, 3-C*H*, P(Anis.)$_2$), 115.2 (d, $^1J_{CP}$ = 53.7 Hz, *ipso*-C_q, P(Anis.)$_2$), 121.0 (d, $^3J_{CP}$ = 11.5 Hz, 5-*C*H, P(Anis.)$_2$), 123.3 (*m*-*C*H, NiAr), 123.8 (*m*-*C*H, *N*-Ar), 126.6 (*p*-*C*H, *N*-Ar), 128.2 (*m*-*C*H, Ph), 128.7 (*o*-*C*H, Ph), 130.7 (*p*-*C*H, Ph), 131.2 (s, *p*-C_q, Ni-Ar), 133.9 (s, 4-C*H*, P(Anis.)$_2$), 135.2 (d, $^3J_{CP}$ = 7.5 Hz, *ipso*-C_q, Ph), 136.4 (*o*-*C*H, Ni-Ar), 136.5 (d, $^2J_{CP}$ = 11.2 Hz, 6-*C*H, P(Anis.)$_2$), 139.5 (*o*-C_q, *N*-Ar), 143.9 (*ipso*-C_q, *N*-Ar), 160.1 (2-C_q, P(Anis.)$_2$), 160.8 (d, $^2J_{CP}$ = 43.5 Hz, *ipso*-C_q, Ni-Ar), 177.3 (d, $^2J_{CP}$ = 8.4 Hz, *C*=N), 198.5 (*C*=O). IR (nujol mull, cm^{-1}): 1666 (ν C=O), 1568 (ν C=N).Anal. Calcd for $C_{42}H_{45}ClNNiO_3P$: C, 68.45; H, 6.16; N, 1.90. Found: C, 68.45; H, 6.38; N, 1.77.

Spectroscopic data for mixtures of palladium aryl complexes.

10a/13a: $^{31}P\{^1H\}$ NMR (THF, 161.9 MHz, 25 °C): 47.1 (**10a**), 56.9 (**13a**).

10b/13b: $^{31}P\{^1H\}$ NMR (THF, 161.9 MHz, 25 °C): 30.5 (**10b**), 38.3 (**13b**). ^{31}P NMR (C_6D_6, 25 °C, 161.9 MHz): 29.0 (**10b**), 36.4 (**13b**). ^1H NMR (C_6D_6, 25 °C, 400 MHz): Signals assigned to **10b**: 0.68 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, ArCHMe*Me*), 1.78 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, ArCH*Me*Me), 2.11 (s, 3 H, COCH_3), 3.26 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, C*H*Me_2), 3.82 (d, 2 H, $^2J_{HP}$ = 11.2 Hz, P-CH_2); Signals assigned to **13b**: δ 0.39 (s, 9 H, CH_2SiMe_3), 0.64 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, ArCH*Me*Me), 1.59 (d, 2 H, $^3J_{HP}$ = 6.0 Hz, C$H_2$$SiMe_3$), 1.71 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, ArCHMe*Me*), 3.15 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, C*H*MeMe), 3.71 (d, 2 H, $^2J_{HP}$ = 10.9 Hz, P-CH_2).

10c/13c: $^{31}P\{^1H\}$ NMR (THF, 161.9 MHz, 25 °C): 25.2 (**10c**), 30.3 (**13c**). ^{31}P NMR (CD_2Cl_2, 25 °C, 161.9 MHz): 25.9 (**10c**), 30.9 (**13c**). ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz): Signals assigned to **10c** (a complete signal list is given below): δ 0.75 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, ArCH*Me*Me), 1.59 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CHMe*Me*), 2.35 (s, 3 H, COCH_3), 3.13 (sept, 2 H, $^3J_{HH}$ = 6.8 Hnalz, C*H*Me_2), 3.93 (s, 6 H, O*Me*), 4.61 (d, 2 H, $^2J_{HP}$ = 12.5 Hz, P-CH_2). Signals assigned to **13c**: δ -0.25 (s, 9 H, CH_2SiMe_3), 0.69 (d, 2 H, $^3J_{HP}$ = 5.5 Hz, C$H_2$$SiMe_3$), 0.75 (overlapped signal, 6 H, CH*Me*Me), 1.45 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CHMe*Me*), 3.05 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, C*H*MeMe), 3.89 (s, 6 H, O*Me*), 4.47 (d, 2 H, $^2J_{HP}$ = 12.1 Hz, P-CH_2).

Isolation of [Pd(C_6H_4-*p*-$COCH_3$)(Br)(Lc)], 10c: A solution of **Lc** (0.114 g, 0.217 mmol) in dry THF (2 mL) was dropwise added over a cooled solution of precursor complex **2** (0.085 g, 0.217 mmol) in dry THF (3 mL). After the addition, the reaction mixture was a. stirred for 1 h at the room temperature. The dark orange mixture was transferred to a PTFE-valve glass ampoule charged with a magnetic bar, and 4-acetylphenyltrifluoromethanesulfonare (0.041 ml, 0.217 mmol) was added. The mixture was stirred at 60 °C for 1 h, after which time it was transferred to the glove box, where the contents were poured on a scintillation vial charged with solid LiBr (0.037 g, 0.435 mmol, 2 equiv.) and stirred overnight. The reaction mixture was filtered and the solvent was evaporated under reduced pressure. The residual oil was washed with 20 ml of n-hexane, then with 20 mL of Et_2O. The solid residue was recrystallized by slow diffusion of hexane in a concentrated solution of CH_2Cl_2 at – 25 °C. Yield, 64 % (0.115 g, 0.138 mmol). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 161.9 MHz): 25.8 (s). ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ 0.75 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, ArCH*Me*Me), 1.59 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, CHMe*Me*), 2.34 (s, 3 H, COCH_3), 3.13 (sept, 2 H, $^3J_{HH}$ = 6.9 Hz, C*H*Me_2), 3.92 (s, 6 H, O*Me*), 4.61 (d, 2 H, $^2J_{HP}$ = 12.7 Hz, P-CH_2), 6.99 (t, 2 H, $^3J_{HH}$ = 7.9 Hz, 5-C*H* P(Anis.)$_2$), 7.06 (m, 2 H, 3-C*H*, P(Anis.)$_2$), 7.07 (d, 2 H, $^3J_{HH}$ = 6.9 Hz, *o*-Ph), , 7.08 (m, 2 H, *m*-*N*-Ar), 7.13 (m, 2 H, *m*-Ph), 7.15 (d, 2 H, $^3J_{HH}$ = 8.7 Hz, *m*-C*H*, Ni*Ar*), 7.19 (m, 1 H, *p*-*N*-Ar), 7.20 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, *o*-C*H*, Ni-Ar), 7.30 (t, 1 H, $^3J_{HH}$ = 7.6 Hz, *p*-Ph), 7.57 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, 4-C*H*, P(Anis.)$_2$), 7.60 (m, 2 H, 6-C*H*, P(Anis)$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 100.6 MHz): 23.2 (ArCH*Me*Me), 24.5 (ArCHMe*Me*), 26.3 (COCH_3), 28.9 (Ar*C*HMe_2), 44.6 (d, $^1J_{CP}$ = 33.1 Hz, P-*C*H_2), 56.2 (s, OCH_3), 115.2 (d, $^1J_{CP}$ = 53.6 Hz, *ipso*-C_q, P(Anis.)$_2$), 116.9 (d, $^3J_{CP}$ = 4.3 Hz, 3-*C*H, P(Anis.)$_2$), 121.3 (d, $^3J_{CP}$ = 12.9 Hz, 5-*C*H, P(Anis.)$_2$), 123.6 (*m*-*C*H, *N*-Ar), 125.3 (*m*-*C*H, Ni-Ar), 126.6 (*p*-*C*H, *N*-Ar), 128.4 (*m*-*C*H, Ph), 128.8 (*o*-*C*H, Ph), 130.9 (*p*-*C*H, Ph), 132.1 (*p*-C_q, Ni-Ar), 134.3 (4-*C*H, P(Anis.)$_2$), 135.1 (d, $^3J_{CP}$ = 9.1 Hz, *ipso*-C_q, Ph), 136.5 (*o*-*C*H, Ni-Ar), 136.7 (d, $^2J_{CP}$ = 6.0 Hz, 6-*C*H, P(Anis.)$_2$), 138.8 (*o*-C_q *N*-Ar), 144.4 (*ipso*-C_q *N*-Ar), 157.2 (d, $^2J_{CP}$ = 2.5 Hz, *ipso*-C_q, Ni-Ar), 160.6 (2-C_q, P(Anis.)$_2$), 177.3 (d, $^2J_{CP}$ = 7.8 Hz, *C*=N), 198.7 (s, *C*=O). Anal. Calcd. for $C_{42}H_{45}BrNO_3PPdS$: C, 60.84; H, 5.47; N, 1.69. Found: C, 60.87; H, 5.59; N, 1.70.

Deprotonation of complex 7a with NaH or NaOH: Syntheses of [Ni(*p*-C_6H_4COMe)(OH)(L'a)]$^-$$Na^+$ 16: In the globe box, NaH (0.037 g, 1.53 mmol) was placed in a 7 mL scintillation vial, with a small magnetic sitting bar. Then, a solution of complex **7a** (0.100 g, 0.153 mmol) in 4.5 mL of THF was added dropwise over the NaH reagent at r.t. The reaction mixture was stirred for 1 h, during which time its colour changed from yellow to dark orange. Once the prescribed time was over, the mixture was

filtered through a PTFE 0.45 μM HPLC syringe filter and dried under reduced pressure, to obtain a dark orange oily residue. This was washed with *n*-hexane (3 mL), and dried under vacuum giving a fine yellow powder. The latter was purified by subsequent crystallization by slow diffusion of a hexane layer on a THF solution in the box freezer (-25 °C). The compound (**16**) was obtained as clear orange crystals in 33% yield (0.030 g, 0.048 mmol). X-ray quality crystals were obtained by slow diffusion of hexane on a THF/Et_2O mixture of **16**. The same product **16** was obtained in 97 % yield (0.091 g, 0.15 mmol) using finely grounded NaOH (0.061 g, 1.53 mmol) instead of NaH, and following exactly the same protocol. In this case, the colour of the reaction mixture remained clear orange, no darkening was observed as with NaH. $^{31}P\{^1H\}$ NMR (161.9 MHz, 25ºC, THF-d_8): δ 47.7 (s). ^1H NMR (400 MHz, 25ºC, THF-d_8): δ -2.79 (s, 1 H, -O*H*), 0.96 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, ArCH*Me*Me), 1.11 (dd, 6 H, $^3J_{HP}$ = 15.1 Hz, $^3J_{HH}$ = 7.3 Hz, P-CH*Me*Me), 1.29 (dd, 6 H, $^3J_{HP}$ = 13.3 Hz, $^3J_{HH}$ = 7.0 Hz, P-CHMe*Me*), 1.55 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, ArCHMe*Me*), 1.82 (d sept, 2 H, $^2J_{HP}$ = 9.2 Hz, $^3J_{HH}$ = 6.9 Hz, P-C*H*Me_2), 2.33 (s, 3 H, -COCH_3), 3.03 (d, 1 H, $^2J_{HP}$ = 1.7 Hz, P-C*H*), 3.86 (sept, 2 H, $^3J_{HH}$ = 7.2 Hz, C*H*Me_2), 6.73 (m, 2 H, *m*-*N*-Ar), 6.75 (m, 1 H, *p*-*N*-Ar), 6.87 (m, 2 H, *m*-Ph), 6.87 (m, 1 H, *p*-Ph), 7.02 (m, 2 H, *o*-Ph), 7.31 (d, 2 H, $^3J_{HH}$ = 8.1 Hz, *m*-Ni-Ar), 7.88 (dd, 2 H, $^4J_{HP}$ = 1.1 Hz, $^3J_{HH}$ = 8.1 Hz, *o*-Ni-Ar). $^{13}C\{^1H\}$ NMR (100.6 MHz, 25ºC, THF-d_8): δ 17.7 (P-CH*Me*Me), 18.5 (P-CHMe*Me*), 23.4 (ArCH*Me*Me), 23.8 (d, $^1J_{CP}$ = 30.3 Hz, P*C*HMe_2), 25.8 (ArCHMe*Me*), 25.8 (-CO*C*H_3), 28.8 (Ar*C*HMe_2), 67.9 (hidden under the solvent residual signal, P-*C*H), 122.7 (*m*-*C*H, *N*-Ar), 123.2 (*p*-*C*H, *N*-Ar), 123.7 (*m*-*C*H, Ni-Ar), 126.5 (*p*-*C*H, Ph), 126.8 (*m*-*C*H, Ph), 129.3 (*o*-*C*H, Ph), 131.8 (*p*-C_q, Ni-*Ar*), 139.1 (*o*-*C*H, Ni*Ar*), 142.7 (d, $^3J_{CP}$ = 16.2 Hz, *ipso*-C_q, Ph), 147.2 (*o*-C_q, N-Ar), 148.3 (*ipso*-C_q N-*Ar*), 175.8 (d, $^2J_{CP}$ = 22.5 Hz, =*C*-N), 182.4 (d, $^2J_{CP}$ = 43.0 Hz, *ipso*-C_q, Ni-*Ar*), 197.2 (-*C*OMe). IR (nujol mull, cm^{-1}): 3584 (sh, w, ν(O-H)), 3422 (br, st, ν(O-H)), 3053 (sh, w, ν(C-H arom.), 1669, 1657 (ν(C=O, νC=C). Anal. Calcd for $C_{34}H_{45}NNaNiO_2P$: C, 66.68; H, 7.41; N, 2.29. Found: C, 66.93; H, 7.68; N, 1.96.

X-Ray structure analysis of complexes 3b, 4c, 6b, 7b and 16

Crystal and refinement data for these structures are shown on Table S1. Crystals suitable for X-ray diffraction analysis were coated with dry perfluoropolyether, mounted on glass fibers, and fixed in a cold nitrogen stream to the goniometer head. Data collections were performed on a Bruker-Nonius X8 Apex-II CCD diffractometer, using graphite monochromatized Mo radiation (λ(Mo Kα) = 0.71073 Å) and fine-sliced ω and φ scans (scan widths 0.30° to 0.50°).[4] The data were reduced (*SAINT*) and corrected for absorption effects by the multiscan method (*SADABS*).[5] The structures were solved by direct methods (*SIR2002*, *SHELXS*) and refined against all F^2 data by full-matrix least-squares techniques (*SHELXL*-2018/3) minimizing $w[F_o^2-F_c^2]^2$.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and allowed to ride on their carrier atoms with the isotropic temperature factors U_{iso} fixed at 1.2 times (1.5 times for methyl groups) of the U_{eq} values of the respective carrier atoms. In the crystalline structure of salt 6b the fluorine atoms of the anion appear disordered, so these fluorine atoms were modeled in two sets of sites. At the end of the refinement the occupancy coefficients were set at 0.55 and 0.45. Moreover, a dichloromethane molecule as a crystallization solvent appears also disordered and was modeled in two sites with occupancy coefficients set at 0.58 and 0.42. In the crystalline structure of **16**, both ligands of tetrahydrofuran and diethyl ether appear disordered, so both were modeled in two sites with occupancy coefficients set at 0.68:0.32 and 0.52:0.48 respectively. A search for solvent accessible voids in the crystal structures **4c** and **6b** using *PLATON*,[7] showed some small volumes of potential solvents less than 187 Å^3 and 187 Å^3 respectively, impossible to model even with the most severe restraints. The corresponding CIF data represent SQUEEZE[8] treated structures with the solvent molecules handling as a diffuse contribution to the overall scattering, without specific atom position and excluded from the structural model. The *SQUEEZE* results were appended to the CIF. The modeling of the observed disorders described above required some geometric restraints (DFIX instruction), the ADP restraint SIMU and the rigid bond restraint DELU were used in order to obtain more reasonable geometric and ADP values of the disordered atoms. It was also useful to restraint the anisotropic U-values of these atoms to behave more isotropically (ISOR instruction). A summary of cell parameters, data collection, structures solution, and the refinement of crystal structures are provided below (Table 1). The corresponding crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publications. CCDC 1944621 (**3b**), 1944622 (**4c)**, 1944623 (**6b**), 1944624 (**7b**) and 1944625 (**16**). The data can be obtained free of charge *via:* https://www.ccdc.cam.ac.uk/structures/

Table S1. Crystal data and refinement details for complexes 3b, 4c, 6b, 7b and 16

	3b	4c	6b	7b	16
Empirical formula	$C_{41}H_{49}N_2NiPSi$	$C_{42}H_{60}NO_2PPdSi_2$	$C_{42}H_{50}F_3N_2NiO_3PSSi\cdot\cdot CH_2Cl_2$	$C_{40}H_{41}BrNNiOP$	$C_{84}H_{126}N_2Na_2Ni_2O_8P_2$
Formula weight	687.59	840.46	922.59	721.33	1517.2
Temperature (K)	193(2)	193(2)	193(2)	193(2)	253(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1$	$P\bar{1}$
Unit cell dimensions:					
a (Å)	12.7840(5)	12.8081(15)	10.8549(5)	9.9701(2)	11.604(6)
b (Å)	18.6105(8)	22.863(3)	12.2040(6)	14.6823(3)	12.092(7)
c (Å)	16.2525(6)	14.9029(18)	18.5076(9)	12.4003(3)	18.006(10)
α (deg)	90	90	96.275(2)	90	82.74(3)
β (deg)	103.625(2)	98.384(3)	94.927(2)	108.9940(10)	75.53(2)
γ (deg)	90	90	94.771(2)	90	64.70(3)
Volume (Å^3)	3757.9(3)	4317.4(9)	2417.4(2)	1716.37(7)	2211(2)
Z	4	4	2	2	1
Density (Mg·m^{-3}, calcd.)	1.215	1.238	1.267	1.396	1.139
Absorption coeff. (mm^{-1})	0.621	0.555	0.662	1.808	0.522
F(000)	1464	1696	964	748	816
Crystal size, mm	0.30 x 0.25 x 0.20	0.20 x 0.1 x 0.05	0.50 x 0.40 x 0.15	0.25 x 0.20 x 0.18	0.20 x 0.15 x 0.10
θ range (deg)	2.133 to 25.248	1.643 to 25.250	1.112 to 25.248	2.160 to 25.244	1.863 to 25.249
Index ranges	-15 ≤ h ≤ 10, -22 ≤ k ≤ 22, -19 ≤ l ≤ 19	-15 ≤ h ≤ 15, 27 ≤ k ≤ 27, -8 ≤ l ≤ 17	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14 -22 ≤ l ≤ 22	-8 ≤ h ≤ 11 -17 ≤ k ≤ 14 -14 ≤ l ≤ 14	-13 ≤ h ≤ 13 -14 ≤ k ≤ 14 -21 ≤ l ≤ 21
Reflections collected	66822	62440	49159	24230	31181
Independent reflns. [R(int)]	10664[0.0259]	12943 [0.0787]	14773 [0.0276]	8272 [0.0191]	13268 [0.0396]
Completeness to θ = 25.242°	99.0%	98.6%	100%	99.7 %	99.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7461, 0.6809	0.7461, 0.4598	0.7461, 0.6607	0.7461, 0.6436	0.7461, 0.7002
Data / restraints / parameters	10664 / 0 / 422	12943 / 0 / 454	14773 / 147 / 577	8272 / 1 / 412	13268 / 473 / 559
Goodness-of-fit on F^2	1.021	1.086	1.057	1.010	0.979
Final R indices [I>2σ(I)]	R1 = 0.0327, wR2 = 0.0796	R1 = 0.0951, wR2 = 0.2490	R1 = 0.0426, wR2 = 0.1171	R1 = 0.0236, wR2 = 0.0549	R1 = 0.0512, wR2 = 0.1307
R indices (all data)	R1 = 0.0463, wR2 = 0.0869	R1 = 0.1306, wR2 = 0.2801	R1 = 0.0591, wR2 = 0.1268	R1 = 0.0269, wR2 = 0.0560	R1 = 0.1043, wR2 = 0.1564
Largest diff. peak and hole (e·Å^{-3})	0.321, -0.205	3.127, -3.406	0.684, -0.582	0.386, -0.193	0.528, -0.417

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