Electronic Supplementary Information

Experimental procedures and spectral and elemental analytical data

Amido Pincer Complex of Nickel-Catalyzed Kumada Cross-Coupling Reactions

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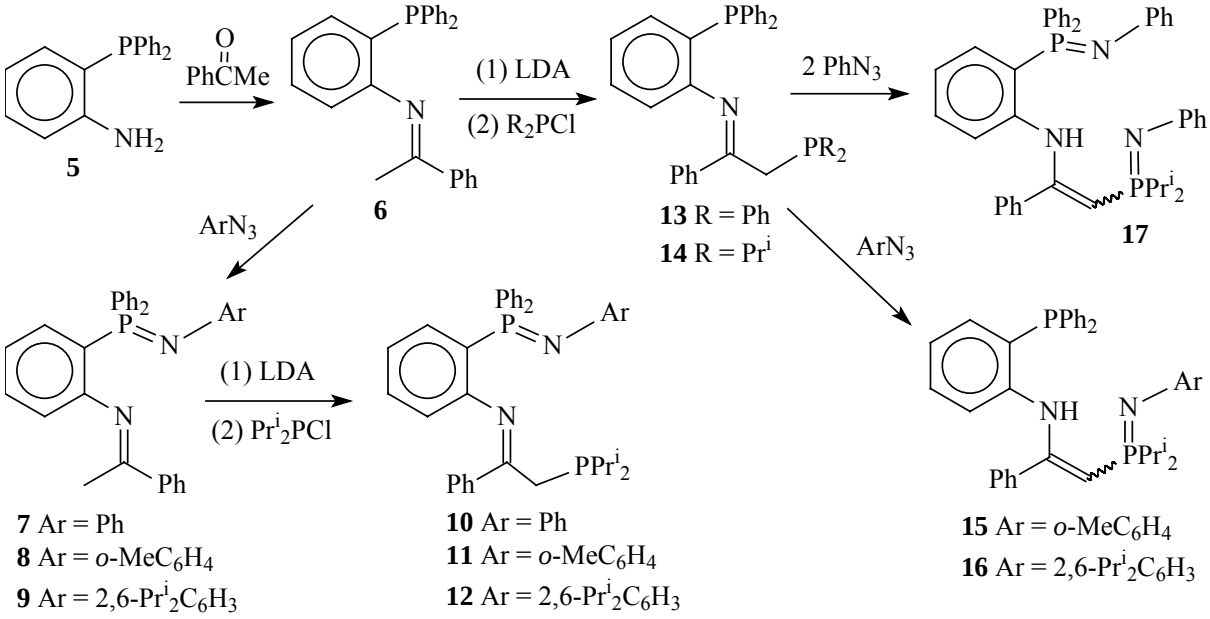
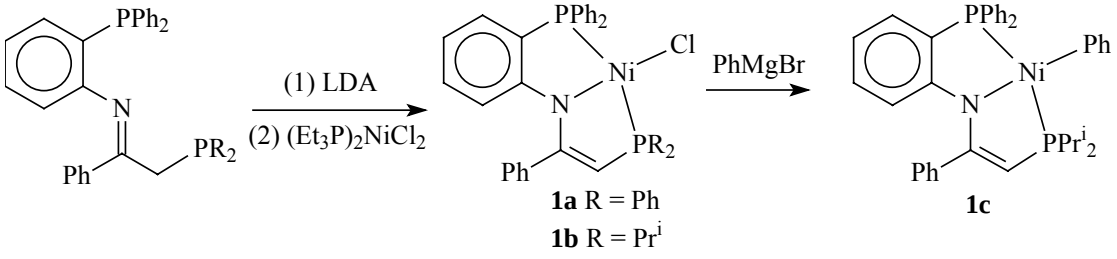
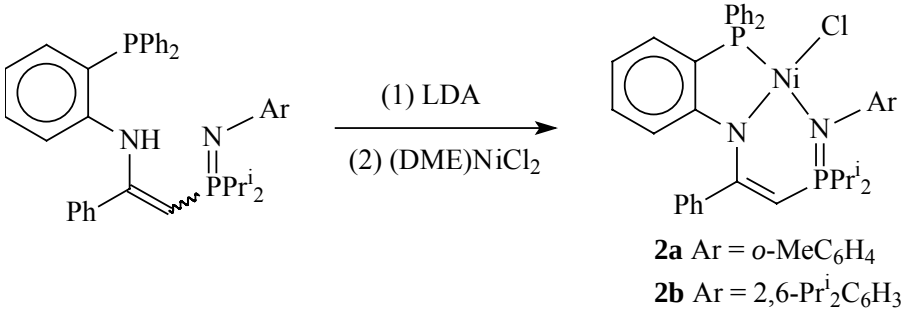
Experimental details



Scheme 1. Synthesis of compounds **5**–**17**

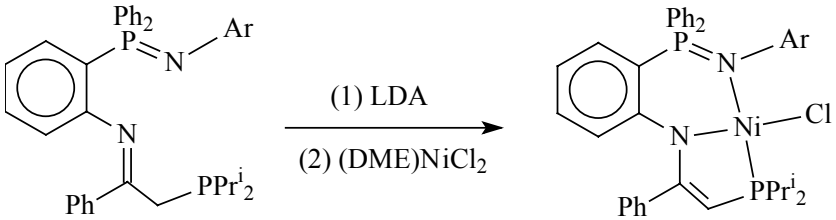


Scheme 2. Synthesis of nickel complexes **1a**–**1c**



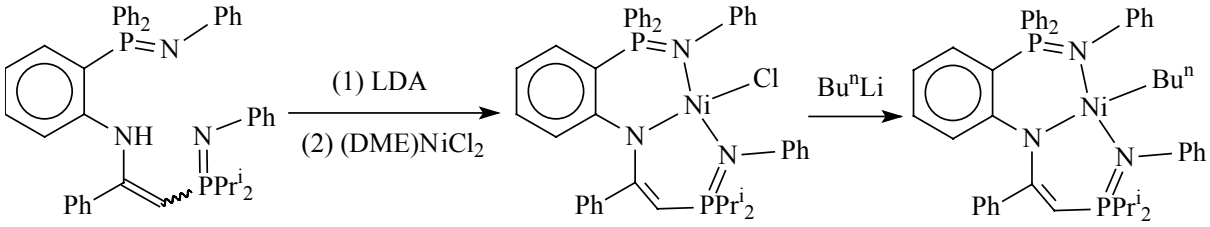
2a Ar = *o*-MeC_6H_4
2b Ar = 2,6-$Pr^i_2C_6H_3$

Scheme 3. Synthesis of nickel complexes **2a** and **2b**



3a Ar = Ph
3b Ar = *o*-MeC_6H_4
3c Ar = 2,6-$Pr^i_2C_6H_3$

Scheme 4. Synthesis of nickel complexes **3a**–**3c**



4a **4b**

Scheme 5. Synthesis of nickel complexes **4a** and **4b**

General procedure

All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (THF, Et_2O and n-hexane) or CaH_2 (CH_2Cl_2) and degassed prior to use. Pr^i_2NH was dried with NaOH and distilled prior to use. *o*-$NH_2C_6H_4PPh_2$,[1] ArN_3,[2] Pr^i_2PCl,[3]

Et_3P,[4] ArMgBr[5] and $(Et_3P)_2NiCl_2$[6] were prepared according to literature methods. Bu^nLi were purchased from Acros Organics and used as received. $CDCl_3$ and C_6D_6, purchased from Acros Organics, were degassed and stored over 4A molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to internal solvent resonances; the ^{31}P NMR spectra were referenced to external 85% H_3PO_4. HRMS was determined on a Agilent6890/Micromass GCT-MS spectrometer. Elemental analyses were performed by the Analytical Center of University of Science and Technology of China.

Synthesis of 6.[7] To a three-necked flask was added toluene (20 ml), 4A molecular sieves (21 g), *o*-$NH_2C_6H_4PPh_2$ (3.0 g, 10.83 mmol), PhC(O)Me (1.47 g, 12.25 mmol) and several drops of HCOOH. The mixture was refluxed under N_2 for 5 days. The mixture was filtered and the molecular sieves were washed with toluene. The toluene solution was combined, washed with water (2 × 20 ml) and dried over Na_2SO_4. Solvent was removed by rotary evaporation and the residue was washed with Et_2O to give white solid (3.5 g, 85%), m.p. 153–154°C. ^1H NMR ($CDCl_3$): δ 1.74 (s, 3H, Me), 6.61 (dd, *J* = 4.2, 7.5 Hz, 1H, Ar), 6.81–6.85 (m, 1H, Ar), 6.94 (t, *J* = 7.8 Hz, 1H, Ar), 7.18–7.33 (m, 14H, Ar), 7.67 (d, *J* = 6.9 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 17.56, 118.73 (d, *J* = 2.3 Hz), 123.49, 127.32, 128.25 (d, *J* = 13.7 Hz), 128.16, 128.39 (d, *J* = 7.2 Hz), 128.66, 129.25, 130.36, 132.53, 134.23, 134.50, 136.45 (d, *J* = 10.8 Hz), 139.23, 153.80 (d, *J* = 20 Hz), 165.84. ^{31}P NMR ($CDCl_3$): δ –19.01.

Anal. Calcd for $C_{26}H_{22}NP$: C, 82.30; H, 5.84; N, 3.69. Found: C, 82.05; H, 5.82; N, 3.72.

Synthesis of 7. To a solution of **6** (1.00 g, 2.64 mmol) in CH_2Cl_2 (10 ml) was added $C_6H_5N_3$ (0.38 g, 3.19 mmol) and the solution was stirred overnight at room temperature. Volatiles were removed *in vacuo* and the residue was washed with hexane (3 × 2 ml) to give yellow crystals of **7** (1.23 g, 99.2%), mp 199–200 °C. ^1H NMR ($CDCl_3$): δ 1.49 (s, 3H, Me), 6.45–6.60 (m, 4H, Ar), 6.80 (t, *J* = 6.9 Hz, 2H, Ar), 7.03–7.13 (m, 3H, Ar), 7.20–7.25 (m, 7H, Ar), 7.31–7.40 (m, 3H, Ar), 7.69–7.79 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$): δ 17.14, 116.84, 120.06 (d, *J* = 7.6 Hz), 123.26 (d, *J* = 11.2 Hz), 123.34 (d, *J* = 18 Hz), 127.51, 127.94, 128.33 (d, *J* = 12.2 Hz), 128.51, 130.50, 130.88, 131.11 (d, *J* = 2.6 Hz), 132.28, 132.54 (d, *J* = 9.7

Hz), 132.91, 135.15 (d, J = 9 Hz), 138.57, 151.95, 154.01 (d, J = 5.4 Hz), 165.74. ^{31}P NMR ($CDCl_3$) : δ –12.29.

Anal. Calcd for $C_{32}H_{27}N_2P$: C, 81.68; H, 5.78; N, 5.95. Found: C, 81.54; H, 5.77; N, 6.09.

Synthesis of 8. To a solution of **6** (0.30 g, 0.79 mmol) in CH_2Cl_2 (10 ml) was added *o*-$MeC_6H_4N_3$ (0.122 g, 0.92 mmol) and the mixture was stirred overnight at room temperature. Volatiles were removed *in vacuo* and the residue was added hexane. The yellow oil turned into yellow crystals after a few days (0.32 g, 83.5%), m.p. 191–192°C. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 3H, Me), 1.95 (s, 3H, Me), 6.23–6.26 (m, 1H, Ar), 6.39–6.44 (m, 1H, Ar), 6.47–6.56 (m, 2H, Ar), 6.84–6.87 (m, 1H, Ar), 7.01–7.09 (m, 5H, Ar), 7.20–7.29 (m, 5H, Ar), 7.32–7.36 (m, 3H, Ar), 7.57–7.64 (m, 1H, Ar), 7.73–7.80 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$): δ 16.72, 19.28, 116.72, 119.98 (d, J = 7.6 Hz), 120.19 (d, J = 10.4 Hz), 120.59, 121.69, 123.08 (d, J = 10.9 Hz), 125.76, 127.51, 127.87, 128.31 (d, J = 12.4 Hz), 129.61, 130.44, 130.96 (d, J = 2.7 Hz), 131.93, 132.29 (d, J = 9.7 Hz), 132.72, 133.38, 135.15 (d, J = 8.8 Hz), 138.38, 150.46, 154.32 (d, J = 5.4 Hz), 165.39. ^{31}P NMR ($CDCl_3$) : δ –4.10.

Anal. Calcd for $C_{33}H_{29}N_2P$: C, 81.80; H, 6.03; N, 5.78. Found: C, 81.76; H, 6.11; N, 5.83.

Synthesis of 9. To a solution of **6** (0.34 g, 0.90 mmol) in CH_2Cl_2 (10ml) was added 2,6-$Pr^i_2C_6H_3N_3$ (0.21 g, 1.04 mmol). The mixture was stirred overnight at room temperature. Volatiles were removed *in vacuo* and the residue was crystallized from Et_2O to give yellow crystals of **9** (0.34 g, 68.4%), m.p. 220–222°C. ^{1}H NMR ($CDCl_3$): δ 0.63 (d, J = 6.6 Hz, 12H, Pr^i), 1.35 (s, 3H, Me), 2.95–3.09 (m, 2H, Pr^i), 6.47–6.51 (m, 1H, Ar), 6.56–6.63 (m, 1H, Ar), 6.73 (d, J = 7.2 Hz, 2H, Ar), 7.01–7.07 (m, 2H, Ar), 7.13–7.19 (m, 8H, Ar), 7.26 (d, J = 7.2 Hz, 2H, Ar), 7.39 (t, J = 7.4 Hz, 1H, Ar), 7.51–7.58 (m, 4H, Ar), 8.01–8.08 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ 16.51, 23.49, 28.68, 118.38 (d, J = 2.4 Hz), 119.72 (d, J = 8.4 Hz), 122.49 (d, J = 1.1 Hz), 123.35 (d, J = 10.7 Hz), 123.61, 127.48, 127.85, 127.99 (d, J = 2.5 Hz), 130.37 (d, J = 2.7 Hz), 130.50, 132.24 (d, J = 9.8 Hz), 132.52 (d, J = 1.8 Hz), 132.95, 134.33, 134.93 (d, J = 7.2 Hz), 138.33, 142.56 (d, J = 7 Hz), 144.99, 153.51 (d, J = 6.9 Hz), 165.06. ^{31}P NMR ($CDCl_3$) : δ –0.69.

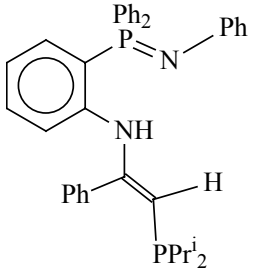
Anal. Calcd for $C_{38}H_{39}N_2P$: C, 82.28; H, 7.09; N, 5.05. Found: C, 82.40; H, 7.14; N,

5.13.

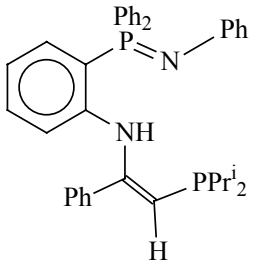
Synthesis of 10. A solution of **7** (0.50 g, 1.06 mmol) in THF (10 ml) was added to a THF solution of LDA [prepared from Pr^i_2NH (0.16 ml, 1.14 mmol) with $LiBu^n$ (0.44 ml, a 2.5 M solution in hexanes, 1.1 mmol) in THF (5ml)] at about −80°C. The resulting solution was warmed to 0°C and stirred at this temperature for 4h. Pr^i_2PCl (0.163 g, 1.07 mmol) in THF (5 ml) was added at about −80°C. The resulting solution was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and Et_2O was added. The solution was filtered and the filtrate concentrated to give pale yellow crystals of **10** (0.56 g, 90%), m.p. 199–201°C. ^{1}H NMR ($CDCl_3$): δ 0.93–1.06 (m, 12H, Pr^i), 1.66–1.80 (m, 2H, Pr^i), 5.19 (d, *J* = 5.4 Hz, 1H, CH), 6.15–6.20 (m, 1H, Ar), 6.54 (d, *J* = 7.2 Hz, 4H, Ar), 6.89–6.92 (m, 7H, Ar), 6.99–7.04 (m, 1H, Ar), 7.37–7.50 (m, 7H, Ar), 7.69–7.75 (m, 4H, Ar), 10.03 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 18.80 (d, *J* = 8.2 Hz), 20.16 (d, *J* = 17.9 Hz), 24.42 (d, *J* = 9.6 Hz), 111.32 (d, *J* = 16.8 Hz), 117.09, 118.14 (d, *J* = 14.4 Hz), 120.49 (d, *J* = 8.7 Hz), 123.70 (dd, *J* = 3.8, 19.6 Hz), 127.14, 127.95, 128.08, 128.76 (d, *J* = 11.4 Hz), 129.13, 130.22, 131.90, 132.93 (d, *J* = 9.6 Hz), 133.35 (d, *J* = 9.6 Hz), 139.51 (d, *J* = 4.8 Hz), 148.45 (d, *J* = 3.1 Hz), 151.16 (d, *J* = 4.2 Hz), 152.66 (d, *J* = 20 Hz). ^{31}P NMR ($CDCl_3$) : δ −22.57, 6.24.

Anal. Calcd for $C_{38}H_{40}N_2P_2$: C, 77.79; H, 6.87; N, 4.77. Found: C, 77.66; H, 6.98; N, 4.89.

^{1}H NMR spectrum showed that this compound exists in an enamine form. However, the enamine exists Z/E isomers (**A** and **B**) and one of the isomers is about 90%, and the other is about 10%.



A



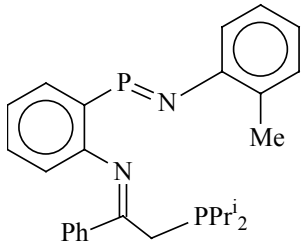
B

Synthesis of 11. A solution of compound **8** (0.54 g, 1.12 mmol) in THF (10 ml) was added to a stirred solution of LDA [prepared from Pr^i_2NH (0.17 ml, 1.21 mmol) with $LiBu^n$ (0.47 ml, a 2.5 M solution in hexanes, 1.17 mmol) in THF (5ml)] at about −80°C. The resulting mixture

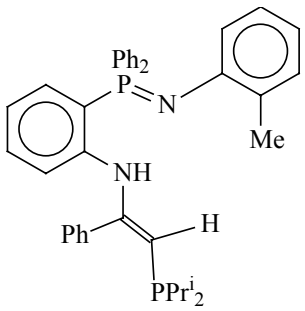
was warmed to 0°C and stirred at this temperature for 4h. The solution was re-cooled to about −80°C and the solution of Pr^i_2PCl (0.179 g, 1.17 mmol) in THF (5 ml) was added. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and Et_2O was added. The solution was filtered and concentrated to about 1 ml. Hexane was added to the solution and cooled at about −30°C to afford pale yellow powder (0.55 g, 82 %), mp 60−65°C. ^{1}H NMR (C_6D_6): δ 0.84−0.93 (m, 6H, Pr^i), 1.07−1.14 (m, 6H, Pr^i), 1.52−1.80 (m, 2H, Pr^i), 2.59 (s, 1H, CH_2), 2.50, 2.69, 2.71 (Me), 5.52 (d, *J* = 4.5 Hz, CH), 5.76 (d, *J* = 6.6 Hz, CH), 6.44−6.64 (Ar), 6,79−7.29 (Ar), 7.34−7.45 (Ar), 7.73−7.91 (Ar), 8.01−8.13 (Ar), 9.87 (d, *J* = 3.9 Hz, NH), 10.34 (s, NH). ^{31}P NMR (C_6D_6): δ −20.56, −15.56, −6.51, 2.36, 5.32, 10.15.

Anal. Calcd for $C_{39}H_{42}N_2P_2$: C, 77.98; H, 7.05; N, 4.66. Found: C, 77.79; H, 6.98; N, 4.74.

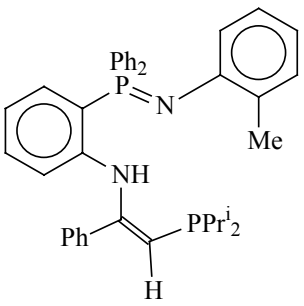
This compound exists in imine and enamine forms, and the enamine form has two isomers (**D** and **E**).



C



D



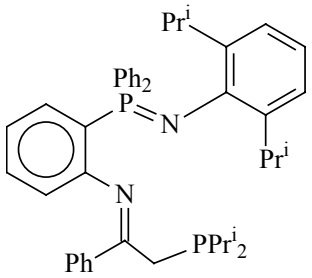
E

Synthesis of 12. Compound **9** (0.34 g, 0.614 mmol) in THF (10 ml) was added to a THF solution of LDA [prepared by reaction of Pr^i_2NH (0.09 ml, 0.64 mmol) with $LiBu^n$ (0.26 ml, a 2.5 M solution in hexanes, 0.65 mmol) in THF (5ml)] at about −80°C. The resulting solution was warmed to 0°C and stirred at this temperature for 4h. To the solution Pr^i_2PCl (0.1 g, 0.656 mmol) in THF (5 ml) was added at about −80°C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was dissolved with Et_2O. The solution was filtered and the filtrate was successively concentrated, added hexane and cooled to −20°C to give pale yellow powders of **12** (0.354 g, 86.1 %), mp 51−55°C. ^{1}H NMR (C_6D_6): δ 0.82−0.92 (m, 9H, Pr^i), 1.00−1.06 (m, 12H, Pr^i), 1.16−1.28 (m, 3H, Pr^i), 1.51−1.63 (m, 2H, CH), 1.99 (s, 2H, CH_2), 3.37−3.56 (m, 2H, CH), 6.77−7.31 (m,

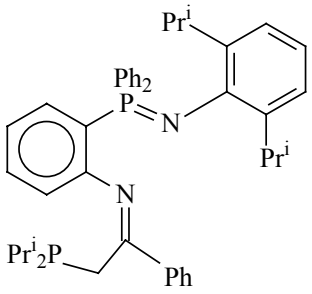
17H, Ar), 7.52–7.97 (m, 5H, Ar). ^{13}C NMR (C_6D_6): δ 14.37, 16.28, 19.25 (d, *J* = 12.9 Hz), 19.56 (d, *J* = 13.8 Hz), 23.07, 23.87, 24.10, 29.21, 31.98, 119.36, 123.24, 123.53 (d, *J* = 10.6 Hz), 127.91, 128.18, 130.30 (d, *J* = 2.6 Hz), 130.58, 132.49 (d, *J* = 9.7 Hz), 133.58, 134.95, 135.46 (d, *J* = 7.1 Hz), 138.22, 142.51 (d, *J* = 5.7 Hz), 145.27, 153.98, 164.90. ^{31}P NMR (C_6D_6): δ –13.58, 10.27.

Anal. Calcd for $C_{44}H_{52}N_2P_2$: C, 78.78; H, 7.81; N, 4.18. Found: C, 78.85; H, 7.76; N, 4.16.

Compound **12** exists in an imine form. No enamine form was observed. A minor component is also existing from the NMR spectra. It seems that two components are:



F (major)



G (minor)

Synthesis of 13. To a stirred THF solution of LDA [prepared by reaction of Pr^i_2NH (0.32 ml, 2.28 mmol) with $LiBu^n$ (0.89 ml, a 2.5 M solution in hexanes, 2.23 mmol) in THF (5 ml)] was added **6** (0.804 g, 2.12 mmol) in THF (10 ml) at 0°C. The mixture was stirred at 0°C for 4h, and then a solution of Ph_2PCl (0.491 g, 2.23 mmol) in THF (10 ml) was added dropwise at about –80°C. The resulting mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was extracted with Et_2O. The extract was filtered and the filtrate was concentrated under vacuum to afford yellow crystals of **13** (1.00 g, 84%), m.p. 152–154°C. ^{1}H NMR ($CDCl_3$): δ 2.73 (s, 2H, CH_2), 5.72–5.75 (m, 1H, Ar), 6.89–6.94 (m, 3H, Ar), 6.88–6.94 (m, 3H, Ar), 7.10–7.13 (m, 3H, Ar), 7.23–7.29 (m, 20H, Ar), 7.54 (d, *J* = 6.9 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 32.40 (d, *J* = 23.6 Hz), 118.79, 123.24, 128.03, 128.24 (d, *J* = 2.8 Hz), 128.39, 128.48, 128.57, 128.68, 128.97, 129.25, 130.22, 132.44, 133.02 (d, *J* = 19.8 Hz), 134.55 (d, *J* = 20.4 Hz), 136.59 (d, *J* = 11.6 Hz), 137.55 (d, *J* = 16.5 Hz), 138.47, 153.50 (d, *J* = 20.9 Hz), 166.47 (d, *J* = 10.7 Hz). ^{31}P NMR (CDCl): δ –19.93, –18.10.

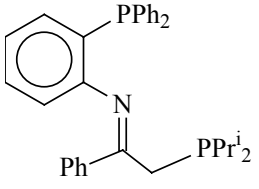
Anal. Calcd for $C_{38}H_{31}NP_2$: C, 80.98; H, 5.54; N, 2.49. Found: C, 80.44; H, 5.53; N,

2.59

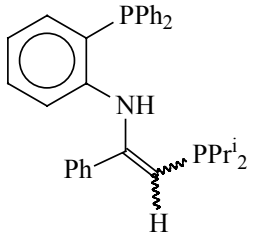
Synthesis of 14. To a THF solution of LDA [prepared from Pr^i_2NH (0.19 ml, 1.35 mmol) and $LiBu^n$ (0.5 ml, a 2.5 M solution in hexanes, 1.25 mmol) in THF (5 ml)] was added **6** (0.45 g, 1.186 mmol) in THF (10 ml) at 0°C. The mixture was stirred at 0°C for 4h, and then Pr^i_2PCl (0.181 g, 1.187 mmol) in THF (5ml) was added dropwise at about −80°C. The resulting mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was extracted with Et_2O. The extract was filtered and the filtrate was concentrated under vacuum to afford yellow microcrystals of **14** (0.53 g, 90.2%), mp: 160–162°C. ^{1}H NMR ($CDCl_3$): Isomer **H**: δ 0.82–0.90 (m, 12H, Pr^i), 1.51–1.65 (m, 2H, Pr^i), 2.36 (s, 2H, CH_2), 6.23–6.28 (m, 1H, Ar), 6.66–6.75 (m, 2H, Ar), 7.30–7.40 (m, 12H, Ar), 7.64 (d, *J* = 6.3 Hz, 4H, Ar). Isomer **I**: δ 0.97–1.07 (m, 12H, Pr^i), 1.68–1.81 (m, 2H, Pr^i), 5.14 (d, *J* = 5.1 Hz, 1H, CH), 6.82–7.00 (m, 3H, Ar), 7.15 (s, 5H, Ar), 7.30–7.40 (m, 11H, Ar). ^{13}C NMR ($CDCl_3$) (isomers **H**+**I**): δ 18.75 (d, *J* = 7.6 Hz), 19.24 (d, *J* = 12.3 Hz), 19.51 (d, *J* = 13.5 Hz), 20.24 (d, *J* = 18 Hz), 23.65 (d, *J* = 16.1 Hz), 24.04 (d, *J* = 7.8 Hz), 26.18 (d, *J* = 25.7 Hz), 106.67 (d, *J* = 13.6 Hz), 119.24, 120.33, 121.05, 123.47, 126.84 (d, *J* = 10 Hz), 127.34, 128.05, 128.23, 128.31, 128.41, 128.50, 128.68, 128.77, 129.04, 129.16, 129.25, 130.14, 133.08, 134.37 (d, *J* = 19.6 Hz), 134.42 (d, *J* = 20.3 Hz), 135.73 (d, *J* = 9.1 Hz), 136.82 (d, *J* = 10.9 Hz), 138.92 (d, *J* = 4.5 Hz), 139.34, 146.33 (d, *J* = 18.3 Hz), 154.38 (d, *J* = 17.7 Hz). ^{31}P NMR (CDCl) (isomers **H**+**I**): δ 6.97 (m), −19.27, −21.33, −21.73.

Anal. Calcd for $C_{32}H_{35}NP_2$: C, 77.56; H, 7.12; N, 2.83. Found: C, 77.06; H, 7.11; N, 2.96.

The ratio of isomer **H** to isomer **I** is about 2:3.



H



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Synthesis of 15. To a stirred solution of **14** (0.70 g, 1.41 mmol) in Et_2O (15 ml) was added *o*-$MeC_6H_4N_3$ (0.19 g, 1.43 mmol) at about −20°C. The resulting solution was warmed to room temperature and stirred overnight to form pale yellow precipitate. The mixture was

filtered to afford pale yellow solid (0.75 g 88.4%), mp: 110–112°C. ^{1}H NMR ($CDCl_3$): δ 1.13–1.26 (m, 12H, Pr^i), 2.34 (s, 3H, Me), 2.41–2.54 (m, 2H, Pr^i), 4.06 (d, *J* = 17.1 Hz, 1H, CH), 6.24–6.28 (m, 1H, Ar), 6.66–6.76 (m, 3H, Ar), 6.91–7.05 (m, 7H, Ar), 7.13–7.21 (m, 11H, Ar), 7.27–7.28 (m, 1H, Ar), 9.79 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 16.32 (d, *J* = 2.6 Hz), 16.59 (d, *J* = 2.6 Hz), 18.41, 25.60 (d, *J* = 54.7 Hz), 77.66, 78.92, 117.09, 123.45, 124.83, 124.95, 125.83, 128.19 (d, *J* = 5.4 Hz), 128.40, 128.49, 128.61, 128.70, 128.89, 129.22, 130.47, 131.02 (d, *J* = 13.1 Hz), 133.00, 133.68, 134.22 (d, *J* = 19.9 Hz), 136.53 (d, *J* = 12.1 Hz), 138.54 (d, *J* = 13.6 Hz), 145.20 (d, *J* = 22 Hz), 150.61, 163.20. ^{31}P NMR (CDCl): δ 43.72 (m), –22.04.

Anal. Calcd for $C_{39}H_{42}N_2P_2$: C, 77.98; H, 7.05; N, 4.66. Found: C, 77.89; H, 7.03; N, 4.73.

Synthesis of 16. To a stirred solution of **14** (0.50 g, 1.01 mmol) in Et_2O (15 ml) was added 2,6-$Pr^i_2C_6H_3N_3$ (0.205 g, 1.01 mmol) at –20°C. The resulting solution was warmed to room temperature and stirred overnight. The mixture was filtered and the filtrate was concentrated to give yellow crystals of **16** (0.58 g, 85.7%), mp: 157–159°C. ^{1}H NMR ($CDCl_3$): δ 0.97 (d, *J* = 5.4 Hz, 12H, Pr^i), 1.05 (dd, *J* = 6, 15.6 Hz, 6H, Pr^i), 1.21 (dd, *J* = 7.2, 14.7 Hz, 6H, Pr^i), 2.15–2.28 (m, 2H, Pr^i), 3.47–3.60 (m, 2H, Pr^i), 4.52 (d, *J* = 21.9 Hz, 1H, CH), 6.20 (t, *J* = 6 Hz, 1H, Ar), 6.58–6.60 (m, 2H, Ar), 6.69–6.80 (m, 2H, Ar), 6.87 (d, *J* = 7.2 Hz, 2H, Ar), 7.02–7.11 (m, 8H, Ar), 7.14–7.18 (m, 8H, Ar), 10.24 (d, *J* = 3.3 Hz, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 17.01 (d, *J* = 2.9 Hz), 17.43 (d, *J* = 1.7 Hz), 24.28, 28.75, 28.88, 29.71, 91.72 (d, *J* = 97.9 Hz), 118.51 (d, *J* = 2.5 Hz), 121.75, 122.38 (d, *J* = 1.6 Hz), 122.62 (d, *J* = 2.5 Hz), 127.62, 128.29, 128.34, 128.38, 128.54, 128.61, 128.86, 134.10, 134.36, 136.72 (d, *J* = 12.3 Hz), 139.52 (d, *J* = 13 Hz), 143.03 (d, *J* = 6.6 Hz), 145.92 (d, *J* = 3.2 Hz), 146.44, 146.73, 158.97. ^{31}P NMR (CDCl): δ –23.18, 9.05.

Anal. Calcd for $C_{44}H_{52}N_2P_2$: C, 78.78; H, 7.81; N, 4.18. Found: C, 78.76; H, 7.87; N, 4.21.

Synthesis of 17. To a solution of **14** (0.60 g, 1.21 mmol) in CH_2Cl_2 (20 ml) was added $C_6H_5N_3$ (0.346 g, 2.90 mmol) at room temperature and the mixture was stirred overnight. Volatiles were removed *in vacuo* and the residue was dissolved in Et_2O. The solution was filtered and the filtrate was concentrated to give yellow crystals of **17** (0.74 g, 90.2%), mp:

162–164°C. ^{1}H NMR ($CDCl_3$): δ 1.12 (dd, *J* = 2.4, 6.9 Hz, 6H, Pr^i), 1.17 (dd, *J* = 3.3, 6.9 Hz, 6H, Pr^i), 2.27–2.42 (m, 2H, Pr^i), 4.76 (d, *J* = 12.6 Hz, 1H, CH), 6.21 (dd, *J* = 5.1, 7.8 Hz, 1H, Ar), 6.45 (t, *J* = 7.2 Hz, 1H, Ar), 6.56 (d, *J* = 7.2 Hz, 2H, Ar), 6.62–6.70 (m, 2H, Ar), 6.76 (t, *J* = 6 Hz, 3H, Ar), 6.85–6.93 (m, 6H, Ar), 7.01–7.09 (m, 3H, Ar), 7.19 (d, *J* = 7.8 Hz, 1H, Ar), 7.32–7.37 (m, 4H, Ar), 7.42 (d, *J* = 7.2 Hz, 2H, Ar), 7.65–7.72 (m, 4H, Ar), 9.78 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 16.66 (d, *J* = 3 Hz), 17.43 (d, *J* = 1.9 Hz), 27.43, 28.32, 116.47, 116.60, 116.87, 117.47, 119.55, 120.48 (d, *J* = 13.3 Hz), 121.08, 123.81 (d, *J* = 2.9 Hz), 123.93, 124.03, 127.90, 128.18, 128.33, 128.53, 128.67, 128.82, 130.25, 131.79 (d, *J* = 2 Hz), 131.93 (d, *J* = 2.6 Hz), 133.16 (d, *J* = 9.6 Hz), 139.03 (d, *J* = 11.7 Hz), 146.98 (d, *J* = 3.5 Hz), 151.09 (d, *J* = 3.6 Hz), 155.70. ^{31}P NMR (CDCl): δ 5.04, 19.94.

Anal. Calcd for $C_{44}H_{45}N_3P_2$: C, 77.97; H, 6.69; N, 6.20. Found: C, 77.85; H, 6.66; N, 6.23.

Synthesis of 1a. Compound **13** (0.428 g, 0.76 mmol) dissolved in THF (10 ml) was added to a THF solution of LDA [prepared from Pr^i_2NH (0.12 ml, 0.85 mmol) and $LiBu^n$ (0.34 ml, a 2.5 M solution in hexanes, 0.85 mmol) in THF (5 ml)] at about –80°C. The resulting solution was warmed to room temperature and stirred for 5h. The solution was added to a stirred solution of $(Et_3P)_2NiCl_2$ (0.276 g, 0.755 mmol) in THF (10 ml) at about –80°C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2. The solution was filtered and solvent was removed from the filtrate. The residue was washed with Et_2O to give brown powder (0.4 g, 80.7%), mp: 247–250°C. ^{1}H NMR ($CDCl_3$): δ 4.76–4.78 (m, 1H, CH), 5.77(dd, *J* = 4.5, 7.8 Hz, 1H, C_6H_4), 6.30 (t, *J* = 7.2 Hz, 1H, C_6H_4), 6.51–6.56 (m, 1H, C_6H_4), 6.84–6.90 (m, 1H, C_6H_4), 7.15 (s, 5H, Ph), 7.30–7.47 (m, 12H, Ph), 7.75–7.87 (m, 8H, Ph). ^{13}C NMR ($CDCl_3$) : δ 95.33 (d, *J* = 51 Hz), 117.79 (d, *J* = 6.7 Hz), 122.01 (d, *J* = 11.2 Hz), 122.28, 122.91, 127.44, 128.28, 128.37, 128.61 (d, *J* = 10.2 Hz), 128.89 (d, *J* = 10.3 Hz), 129.30 (d, *J* = 2.9 Hz), 129.88 (d, *J* = 3 Hz), 130.15 (d, *J* = 2.5 Hz), 130.52 (d, *J* = 2.3 Hz), 130.73 (d, *J* = 2.3 Hz), 132.43 (d, *J* = 3.3 Hz), 132.78 (d, *J* = 1.2 Hz), 132.92 (d, *J* = 1.4 Hz), 133.04 (d, *J* = 3.1 Hz), 133.13, 133.67 (d, *J* = 10.6 Hz), 138.74 (d, *J* = 17.1 Hz), 161.25 (dd, *J* = 3.5, 24 Hz), 174.37 (dd, *J* = 4.2, 23.8 Hz). ^{31}P NMR ($CDCl_3$): δ 7.96 (dm, *J* = 343.6 Hz), 19.04 (d, *J* = 342.1 Hz).

Anal. Calcd for $C_{38}H_{30}NP_2NiCl$: C, 69.50; H, 4.60; N, 2.13. Found: C, 69.02; H, 4.63; N,

1.97.

Synthesis of 1b. Compound **14** (0.38 g, 0.77 mmol) in THF (10 ml) was added to a THF solution of LDA [prepared from Pr^i_2NH (0.12 ml, 0.85 mmol) and $LiBu^n$ (0.34 ml, a 2.5 M solution in hexanes, 0.85 mmol) in THF (5 ml)] at about −80°C. The resulting solution was stirred at room temperature for 5h. This solution was added to a solution of $(Et_3P)_2NiCl_2$ (0.28 g, 0.765 mmol) in THF (10 ml) at about −80°C. The resulting mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was dissolved in CH_2Cl_2. The solution was filtered and solvent was removed from the filtrate. The residue was washed with Et_2O to give green crystals (0.38 g, 84.3%), mp: 267–269°C. ^{1}H NMR ($CDCl_3$): δ 1.31 (dd, *J* = 6.8, 14.4 Hz, 6H, Pr^i), 1.45 (dd, *J* = 6.4, 16.9 Hz, 6H, Pr^i), 2.03–2.17 (m, 2H, Pr^i), 4.23(d, *J* = 3 Hz, 1H, CH), 5.71 (dd, *J* = 4.5, 8.1 Hz, 1H, C_6H_4), 6.26 (t, *J* = 7.2 Hz, 1H, C_6H_4), 6.51 (t, *J* = 7.8 Hz, 1H, C_6H_4), 6.84 (t, *J* = 8.1 Hz, 1H, C_6H_4), 7.06–7.13 (m, 6H, Ph), 7.38–7.40 (m, 5H, Ph), 7.71–7.77 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.98, 18.88(d, *J* = 3.6Hz), 24.23(d, *J* = 23.5 Hz), 91.99 (d, *J* = 43.7 Hz), 117.09 (d, *J* = 6.6 Hz), 121.61 (d, *J* = 11 Hz), 123.02, 127.30, 127.96, 128.33, 128.88 (d, *J* = 10.1 Hz), 129.74, 130.32, 130.39, 130.54 (d, J = 2.2 Hz), 133.18, 133.60 (d, *J* = 110.8 Hz), 138.99 (d, *J* = 15.7 Hz), 161.68 (d, *J* = 24.7 Hz), 174.74 (d, *J* = 20 Hz). ^{31}P NMR ($CDCl_3$) : δ 15.57 (d, *J* = 324.7 Hz), 42.08 (dm, *J* = 339.7 Hz). ^{31}P NMR ($CDCl_3$): δ 17.62 (d, *J* = 265.2 Hz), 31.44 (dm, *J* = 265.7 Hz).

Anal. Calcd for $C_{32}H_{34}NP_2NiCl$: C, 65.29; H, 5.82; N, 2.38. Found: C, 65.17; H, 5.83; N, 2.43.

Synthesis of 1c. To a stirred solution of complex **1b** (0.33 g, 0.56 mmol) in THF (10 ml) was added dropwise C_6H_5MgBr (1.3 ml, a 0.44 M solution in Et_2O, 0.57 mmol) at about −80°C. The resulting solution was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was extracted with Et_2O. The mixture was filtered and the filtrate was concentrated to yield yellow crystals (0.23 g, 65.1%), mp: 178–180°C. ^{1}H NMR (C_6D_6): δ 1.00–1.13 (m, 12H, Pr^i), 1.83–1.96 (m, 2H, Pr^i), 4.35 (s, 1H, CH), 6.25–6.31 (m, 2H, Ar), 6.65 (t, *J* = 7.8 Hz, 1H, Ar), 6.78 (t, *J* = 6.9 Hz, 1H, Ar), 6.92 (t, *J* = 7.2 Hz, 2H, Ar), 7.02–7.07 (m, 10H, Ar), 7.45–7.51 (m, 4H, Ar), 7.56–7.61 (m, 4H, Ar). ^{13}C NMR (C_6D_6): δ 17.63, 18.33 (d, *J* = 4 Hz), 23.32 (dd, *J* = 1.1, 26.3 Hz), 91.72 (d, *J* = 38.8 Hz), 116.38 (d, *J* =

6.1 Hz), 120.59 (d, *J* = 10.4 Hz), 121.48, 123.64, 124.21, 126.26, 128.57, 128.70, 129.95 (d, *J* = 2 Hz), 130.85 (d, *J* = 1.5 Hz), 131.44, 132.02 (d, *J* = 1.6 Hz), 133.54 (d, *J* = 10.9 Hz), 133.87, 138.25 (t, *J* = 3.5 Hz), 141.32 (d, *J* = 14.7 Hz), 150.48, 150.87 (*J* = 3.9 Hz), 151.26, 161.81 (dd, *J* = 3.4, 23.4 Hz), 174.66 (dd, *J* = 4.9, 18.9 Hz). ^{31}P NMR (C_6D_6): δ 17.61 (d, *J* = 265.2 Hz), 31.44 (d, *J* = 265.7 Hz).

Anal. Calcd for $C_{38}H_{39}NP_2Ni$: C, 72.40; H, 6.24; N, 2.22. Found: C, 72.60; H, 6.32, N, 2.18.

Synthesis of 2a. Complex **15** (0.68 g, 1.13 mmol) dissolved in THF (15 ml) was added to a THF solution of LDA [prepared from Pr^i_2NH (0.17 ml, 1.21 mmol) and $LiBu^n$ (0.49 ml, a 2.5 M solution in hexanes, 1.22 mmol) in THF (5 ml)] at about −80°C. The mixture was warmed to room temperature and stirred for 5h. The resulting solution was re-cooled to about −80°C and a solution of $(Et_3P)_2NiCl_2$ (0.39 g, 1.07 mmol) in THF (10 ml) was added. The resulting mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was extracted with CH_2Cl_2. After filtration solvent was removed from the filtrate and the residue was washed with Et_2O to give brown powder (0.58 g, 78%), mp: 238–240°C. ^{1}H NMR ($CDCl_3$): δ 0.74 (dd, *J* = 7.1, 14.9 Hz, 3H, Pr^i), 1.05 (dd, *J* = 7, 15.5 Hz, 3H, Pr^i), 1.53 (dd, *J* = 6.8, 15.7 Hz, 3H, Pr^i), 1.86 (dd, *J* = 6.9, 15.8 Hz, 3H, Pr^i), 2.19–2.40 (m, 2H, Pr^i), 3.52(s, 3H, Me), 3.99 (d, *J* = 23.4 Hz, 1H, CH), 5.82 (d, *J* = 8.1 Hz, 1H, Ar), 6.33−6.38 (m, 1H, Ar), 6.58−6.63 (m, 1H, Ar), 6.72 (b, 2H, Ar), 6.80−6.84 (m, 4H, Ar), 6.92 (t, *J* = 7.5 Hz, 2H, Ar), 7.03 (t, *J* = 7.5 Hz, 1H, Ar), 7.11−7.14 (m, 1H, Ar), 7.23−7.28 (m, 2H, Ar), 7.32−7.37 (m, 1H, Ar), 7.40−7.50 (m, 3H, Ar), 7.62 (b, 2H, Ar), 8.09 (b, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 16.45, 17.08, 22.18, 23.32, 24.10, 29.10 (d, *J* = 56 Hz), 77.37, 118.92, 122.11, 123.79, 125.05 (d, *J* = 1.7 Hz), 127.81, 127.83, 128.50, 128.75, 129.80 (d, *J* = 4 Hz), 130.53, 130.73, 130.86, 130.97, 131.20, 133.60 (d, *J* = 19.7 Hz), 141.59 (d, *J* = 13.2 Hz), 148.02 (d, *J* = 1.7 Hz), 161.71, 169.34. ^{31}P NMR ($CDCl_3$): δ 16.41, 33.11.

Anal. Calcd for $C_{39}H_{41}N_2P_2NiCl$: C, 67.51; H, 5.96; N, 4.04. Found: C, 67.09; H, 6.07; N, 4.08.

Synthesis of 2b. Complex **16** (0.425 g, 0.634 mmol) dissolved in THF (10 ml) was added to a THF solution of LDA [prepared from Pr^i_2NH (0.09 ml, 0.64 mmol) and $LiBu^n$ (0.26 ml, a 2.5 M solution in hexanes, 0.65 mmol) in THF (5 ml)] at about −80°C. The resulting mixture

was warmed to room temperature and stirred for 5h. The solution was re-cooled to about −80°C and a solution of $(Et_3P)_2NiCl_2$ (0.23 g, 0.63 mmol) in THF (10 ml) was added. The resulting mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was extracted with CH_2Cl_2. After filtration solvent was removed from the filtrate and the residue was dissolved in Et_2O. Concentration of the Et_2O solution to give black crystals (0.41 g, 85%), mp: 267–270°C. ^{1}H NMR ($CDCl_3$): δ 0.94 (b, 6H, Pr^i), 1.18 (dd, *J* = 6.9, 16.5 Hz, 6H, Pr^i), 1.24 (d, *J* = 6.6 Hz, 12H, Pr^i), 2.43 (b, 2H, Pr^i), 4.18 (b, 2H, Pr^i), 5.07 (d, *J* = 21.1 Hz, 1H, CH), 6.05 (dd, *J* = 4.5, 7.8 Hz, 1H, Ar), 6.28 (t, *J* = 7.2 Hz, 1H, Ar), 6.64–6.74 (m, 2H, Ar), 6.85 (s, 3H, Ar), 7.04–7.11 (m, 3H, Ar), 7.15–7.17 (m, 2H, Ar), 7.29–7.34 (m, 4H, Ar), 7.38–7.43 (m, 2H, Ar), 7.75–7.81 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$): δ 19.16, 23.93, 26.00, 29.06, 77.36, 117.66 (d, *J* = 6.2 Hz), 122.69, 123.27, 123.32, 123.47, 127.99 (d, *J* = 2.5 Hz), 128.10, 128.49 (d, *J* = 10.6 Hz), 130.45 (d, *J* = 2.6 Hz), 131.30 (d, *J* = 1.8 Hz), 131.87, 133.37 (d, *J* = 9.9 Hz), 141.90 (d, *J* = 12.8 Hz), 144.06 (d, *J* = 5.5 Hz), 146.98 (d, *J* = 4.5 Hz), 163.51 (d, *J* = 26.2 Hz), 166.47. ^{31}P NMR ($CDCl_3$): δ 16.28, 32.93 (m).

Anal. Calcd for $C_{44}H_{51}N_2P_2NiCl$: C, 69.17; H, 6.73; N, 3.67. Found: C, 68.77; H, 6.74 , N, 3.67.

Synthesis of 3a. Compound **10** (0.637 g, 1.09 mmol) dissolved in THF (10 ml) was added to a solution of LDA [prepared from Pr^i_2NH (0.17 ml, 1.21 mmol) and $LiBu^n$ (0.49 ml, a 2.5 M solution in hexanes, 1.22 mmol) in THF (5 ml)] at about −80°C. The mixture was warmed to room temperature and stirred for 4h. The resulting solution was added to a solution of $(Et_3P)_2NiCl_2$ (0.40 g, 1.09 mmol) in THF (10 ml) at about −80°C. The mixture was stirred for 4h at room temperature. Volatiles were removed *in vacuo* and the residue was extracted with Et_2O. The solution was filtered and the filtrate was concentrated to afford dark green crystals (0.66 g, 89%), mp: 222–224°C. ^{1}H NMR ($CDCl_3$): δ 1.21–1.86 (m, 12H, Pr^i), 2.23 (b, 2H, Pr^i), 4.23 (s, 1H, CH), 6.19–6.32 (m, 3H, Ar), 6.55(b, 1H, Ar), 6.70(b, 1H, Ar), 6.76–7.05 (m, 10H, Ar), 7.19–7.71 (m, 8H, Ar), 8.44 (b, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ 17.82 (d, *J* = 1.5 Hz), 19.23, 25.37, 77.36, 94.30 (d, *J* = 43.2 Hz), 117.08 (d, *J* = 14 Hz), 121.22, 122.07 (d, *J* = 2.8 Hz), 122.73, 127.30 (d, *J* = 2 Hz), 127.51, 127.64, 127.87, 127.95, 128.26 (d, *J* = 12 Hz), 130.51 (d, *J* = 10 Hz), 130.71 (d, *J* = 7.4 Hz), 131.79, 132.10 (d, *J* = 1.5 Hz), 134.64 (b),

138.70 (d, J = 14.3 Hz), 148.17 (d, J = 3.5 Hz), 157.71, 157.733, 175.35 (d, J = 20.2 Hz). ^{31}P NMR ($CDCl_3$): δ 22.13, 43.70.

Anal. Calcd for $C_{38}H_{39}N_2P_2NiCl$: C, 67.14; H, 5.78; N, 4.12. Found: C, 66.47; H, 5.88; N, 4.26.

Synthesis of 3b. Compound **11** (1.54 g, 2.56 mmol) dissolved in THF (20 ml) was added to a THF solution of LDA [prepared from Pr^i_2NH (0.38 ml, 2.71 mmol) and $LiBu^n$ (1.08 ml, a 2.5 M solution in hexanes, 2.7 mmol) in THF (5 ml)] at about −80°C. The mixture was warmed to room temperature and stirred for 4h. The resulting solution was added to a solution of $(Et_3P)_2NiCl_2$ (0.94 g, 2.57 mmol) in THF (20 ml) at about −80°C. The mixture was stirred for 8h at room temperature. Volatiles were removed *in vacuo* and the residue was extracted with Et_2O. The solution was filtered and the filtrate was concentrated to afford green powder (1.44 g, 81%), mp: 245–247°C. ^{1}H NMR ($CDCl_3$): δ 1.16–1.63 (m, 12H, Pr^i), 1.75 (b, 1H, Pr^i), 2.20 (b, 1H, Pr^i), 2.66 (s, 3H, Me), 4.03 (s, 1H, CH), 6.22–6.57 (m, 6H, Ar), 6.74–7.69 (m, 15H, Ar), 8.72 (b, 2H, Ar). ^{31}P NMR ($CDCl_3$): δ 21.46, 45.10.

Anal. Calcd for $C_{39}H_{41}N_2P_2NiCl$: C, 67.51; H, 5.96; N, 4.04. Found: C, 67.04; H, 6.15; N, 4.14.

Synthesis of 3c. Compound **12** (1.305 g, 1.95 mmol) dissolved in THF (15 ml) was added to a THF solution of LDA [prepared from Pr^i_2NH (0.28 ml, 1.99 mmol) and $LiBu^n$ (0.8 ml, a 2.5 M solution in hexanes, 2 mmol) in THF (5 ml)] at about −80°C. The mixture was warmed to room temperature and stirred for 5h. The resulting solution was added to a solution of $(Et_3P)_2NiCl_2$ (0.72 g, 1.96 mmol) in THF (15 ml) at about −80°C. The mixture was stirred overnight at room temperature. Volatiles were removed *in vacuo* and the residue was extracted with Et_2O. The solution was filtered and the filtrate was concentrated to give dark green crystals (1.30 g, 87%), mp: 268–271°C. ^{1}H NMR ($CDCl_3$): δ 0.60 (s, 3H, Pr^i), 0.60 (s, 3H, Pr^i), 1.08 (b, 9H, Pr^i), 1.21–1.40 (m, 6H, Pr^i), 1.48–1.70 (m, 6H, Pr^i), 2.21 (b, 1H, Pr^i), 2.67–2.81 (m, 1H, Pr^i), 3.77 (s, 1H, CH), 5.59 (b, 1H, Ar), 6.11–6.42 (m, 4H, Ar), 6.50–7.27 (m, 12H, Ar), 7.48–7.64 (m, 3H, Ar), 8.85 (b, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 17.15 (d, J = 5.4 Hz), 17.91, 19.76 (d, J = 2.5 Hz), 21.89, 22.50, 22.99, 24.30, 24.90, 26.01, 26.03 (d, J = 24.9 Hz), 29.28, 30.34, 77.36, 91.39(d, J = 42.4 Hz), 117.70 (d, J = 13.2 Hz), 122.32 (d, J = 3 Hz), 122.67 (d, J = 2.8 Hz), 123.10 (d, J = 1.1 Hz), 123.16 (d, J = 3.2 Hz), 123.34 (d, J = 2.3 Hz),

123.81 (d, J = 2.9 Hz), 124.45 (d, J = 1 Hz), 127.19, 127.26, 127.83 (d, J = 11.1 Hz), 128.25, 128.42, 128.77 (d, J = 7.9 Hz), 129.06, 129.25 (d, J = 9.4 Hz), 130.59, 131.38 (d, J = 2.1 Hz), 131.86 (d, J = 2.3 Hz), 132.18 (d, J = 2.9 Hz), 134.22 (d, J = 10 Hz), 134.88 (d, J = 8.1 Hz), 139.66 (d, J = 15. 5 Hz), 143.18 (d, J = 4.2 Hz), 145.75 (d, J = 3.7 Hz), 146.74 (d, J = 6.7 Hz), 156.37 (d, J = 2.3 Hz), 175.85 (d, J = 19.8 Hz). ^{31}P NMR ($CDCl_3$): δ 16.37, 43.61.

Anal. Calcd for $C_{44}H_{51}N_2P_2NiCl$: C, 69.17; H, 6.73; N, 3.67. Found: C, 69.01; H, 6.76; N, 3.69.

Synthesis of 4a. Compound **16** (2.13 g, 3.15mmol) dissolved in THF (20 ml) was added dropwise to a solution of LDA [prepared from Pr^i_2NH (0.47 ml, 3.35 mmol) and $LiBu^n$ (1.32 ml, a 2.5 M solution in hexanes, 3.3 mmol) in THF (10 ml)] at about −80°C. The resulting mixture was warmed to room temperature and stirred for 5h. This solution was then added to a solution of $(Et_3P)_2NiCl_2$ (1.15 g, 3.15 mmol) in THF (15 ml) at about −80°C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was extracted with CH_2Cl_2. CH_2Cl_2 was removed from the extract and the residue was washed with Et_2O to give the yellowish green crystals (1.82 g, 75%), mp: 175–179°C. ^{1}H NMR spectral alalysis showed that this complex was paramagnetic.

Anal. Calcd for $C_{44}H_{44}N_3P_2NiCl$: C, 68.55; H, 5.75; N, 5.45. Found: C, 68.02; H, 5.95; N, 5.25. HRMS (EI, m/z): $[M]^+$ ($C_{44}H_{44}N_3P_2Ni^{35}Cl$) calcd. 769.2053; found 769.2059.

Synthesis of 4b. To a stirred solution of **4a** (0.365 g, 0.47 mmol) in THF (10ml) was added dropwise Bu^nLi (0.2 ml, a 2.5M solution in hexanes, 0.5 mmol) at about −80°C. The color of the solution changed gradually from pale-green to red. The solution was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue was dissolved in Et_2O. The solution was filtered and the filtrate was concentrated to afford red crystals (0.30 g, 80%), m.p. 164–168°C. ^{1}H NMR (C_6D_6): δ 0.01–0.15 (m, 2H, Bu^n), 0.7–0.95 (m, 12H, Bu^n+Pr^i), 1.03–1.13 (m, 2H, Bu^n), 1.36 (dd, J = 6.9, 15.9 Hz, 3H, Pr^i), 1.85–2.00 (m, 1H, Pr^i), 2.08 (dd, J = 6.9, 15.3 Hz, 3H, Pr^i), 2.31–2.45 (m, 1H, Pr^i), 4.24 (d, J = 27.3 Hz, 1H, CH), 6.31–6.36 (m, 2H, Ar), 6.79–7.27 (m, 18H, Ar), 7.45–7.55 (m, 3H, Ar), 7.88 (d, J = 7.2 Hz, 2H, Ar), 8.06 (d, J = 7.2 Hz, 2H, Ar), 8.26–8.35 (m, 2H, Ar). ^{13}C NMR (C_6D_6): δ 10.61, 14.32, 16.27 (d, J = 3.2 Hz), 17.04 (d, J = 1.7 Hz), 17.46 (d, J = 1.4 Hz), 18.22 (d, J = 2.5 Hz), 22.01, 22.74, 25.24, 28.36, 29.15, 35.00, 77.78, 79.35, 113.95, 115.22

(d, *J* = 15.2 Hz), 115.58, 120.22, 121.08 (d, *J* = 1.5 Hz), 125.65 (d, *J* = 8.8 Hz), 127.92, 128.15, 128.27, 128.49, 128.88, 129.04, 129.17, 129.31, 129.49 (d, *J* = 7.6 Hz), 129.71, 130.41, 131.37 (d, *J* = 2.7 Hz), 132.08 (d, *J* = 2.2 Hz), 132.40 (d, *J* = 2.3 Hz), 133.36, 133.84, 134.02, 134.09 (d, *J* = 3.6 Hz), 134.22 (d, *J* = 5.4 Hz), 142.74 (d, *J* = 13.3 Hz), 150.86, 151.38, 160.78 (d, *J* = 2.8 Hz), 171.11. ^{31}P NMR ($CDCl_3$): δ 8.05, 31.27.

Anal. Calcd for $C_{48}H_{53}N_3P_2Ni$: C, 72.74; H, 6.74; N, 5.30. Found: C, 72.72; H, 6.76, N, 5.36.

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Molecular structures of complexes 1c, 2b and 4b

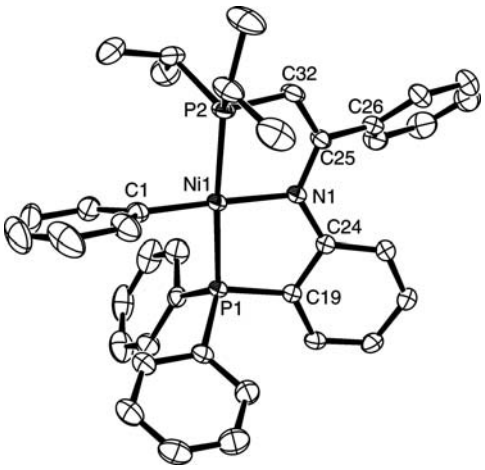

Fig. 1 ORTEP view (30% probability) of complex **1c**.

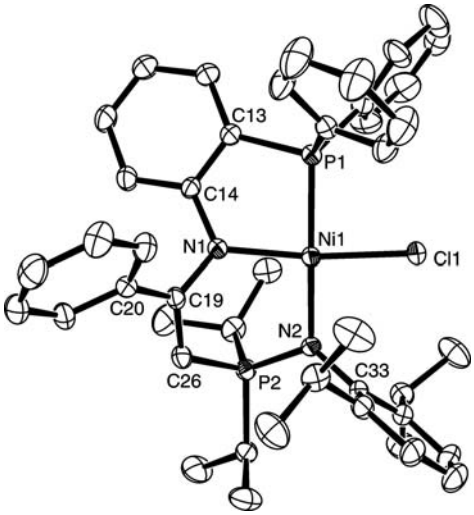

Fig. 2 ORTEP view (20% probability) of complex **2b**.

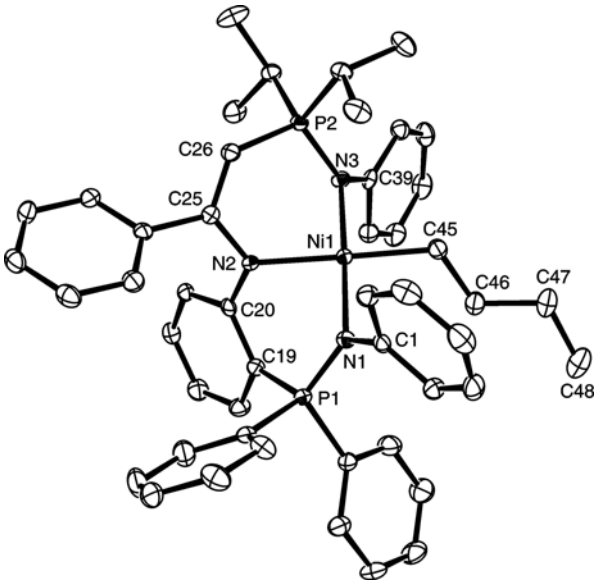

Fig. 3 ORTEP view (30% probability) of complex **4b**.