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Tetrahedron
Tetrahedron 62 (2006) 7583–7588

Reaction of (η^2-arylaldehyde)nickel(0) complexes with Me_3SiX (X=OTf, Cl). Application to catalytic reductive homocoupling reaction of arylaldehyde

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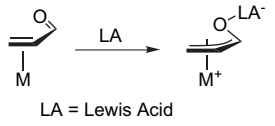
Received 21 November 2005; revised 6 March 2006; accepted 6 March 2006
Available online 19 June 2006

Dedicated to Professor Günther Wilke for his great contribution to the field of organonickel chemistry

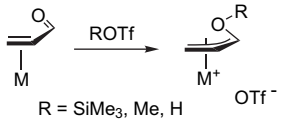
Abstract—Arylaldehydes can coordinate to nickel(0) in η^2-fashion to give η^2-arylaldehydenickel complexes, which react with Me_3SiOTf or Me_3SiCl to give η^1:η^1-siloxybenzylnickel or η^3-siloxybenzyl complex. In the presence of PCy_3 or CO, η^1:η^1-siloxybenzylnickel complex underwent homocoupling reaction to give a pinacol type product. In the presence of zinc dust, the reductive homocoupling reaction of arylaldehyde proceeded catalytically to form pinacol derivatives in 70–99% yield. On the other hand, η^3-siloxybenzylnickel complex regenerated benzaldehyde and Me_3SiOTf under a carbon monoxide pressure.

1. Introduction

The transformation of carbonyl compounds by transition metal catalysts is one of the very efficient methods to introduce oxygen into an organic molecule. However, only scattered studies on the reaction of carbonyl compounds coordinated to late transition metals have been reported. So far, we have reported the reaction of α,β-unsaturated carbonyl compounds coordinated to palladium or platinum in η^2-fashion with Lewis acids or electrophiles to give the corresponding η^3-allyl complexes having oxygen containing substituent at the allyl terminal carbon (Schemes 1 and 2).[1] As the hapticity of the enone coordination changes from η^2 to η^3, the carbonyl carbon–metal covalent bond is formed by the electron donation from palladium or platinum to carbonyl carbon, which is confirmed by the theoretical study.[1a] These results suggest that larger electron donating ability of the metal center is favorable for the formation of a covalent bond between a carbonyl carbon and a transition metal center. We thought η^2-coordination of carbonyl group to an electron rich transition metal center is one of the ideal situations for the formation of carbon–metal covalent bond by the addition of electrophiles. Although the coordination of aldehydes or ketones in η^2-mode is very rare for the late transition metals, several η^2-aldehyde and η^2-ketone complexes of nickel have been reported.[2,3] Moreover, recently, we reported the reaction of η^2-aldehyde complexes with Me_3SiOTf to give η^1:η^1-siloxymethylnickel complexes.[4] However, the reactivity and its application to catalytic reactions have not been studied yet. Here, we report the synthesis and reactivity of both η^3-siloxyarylmethylnickel and η^1:η^1-siloxybenzylnickel complexes generated by the reaction of η^2-aldehyde complex of nickel(0) with Me_3SiOTf or Me_3SiCl. The carbon–carbon bond formation by the homocoupling reactions of these complexes and its application to a catalytic reaction in the presence of zinc dust are also reported.



Scheme 1.



Scheme 2.

2. Results and discussion

η^2-Arylaldehydenickel complexes (**1a**–**1d**) were prepared conveniently in quantitative yield by the reaction of the corresponding arylaldehyde with $Ni(cod)_2$ and PCy_3 or DPPF

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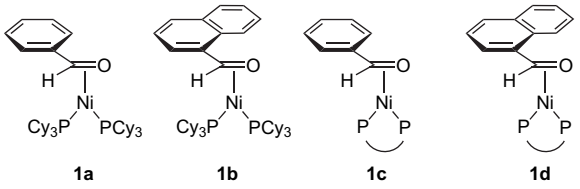
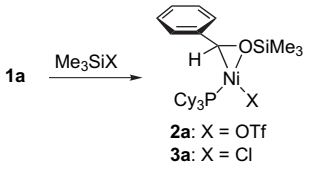
doi:10.1016/j.tet.2006.03.124

(Scheme 3). The X-ray structure analysis on **1a** reported by Walther showed η^2-coordination of benzaldehyde.[2] The formyl hydrogen and carbon in arylaldehyde coordinated to nickel are found far upfield in ^{1}H and ^{13}C NMR spectra compared to those of free arylaldehyde; ArC*H*O in **1a**–**1d** is at ca. δ 6.0–6.7 (δ 9.6–10.0 for free) and Ar*C*HO is at ca. δ 80–90 (δ 180–190 for free), which are consistent with the η^2-coordination of an arylaldehyde to a nickel(0) and the strong back donation from the nickel(0) center to the carbonyl group even in a solution.



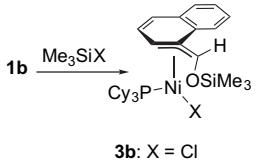
Scheme 3.

The reaction of $(\eta^2$-PhCHO)Ni$(PCy_3)_2$ (**1a**) with Me_3SiOTf gave the corresponding η^1:η^1-siloxybenzylnickel complex (**2a**) (Scheme 4).[4] Similarly, the reaction with Me_3SiCl gave the chloride analog (**3a**). Both resonances of benzyl proton and carbon in ^{1}H and ^{13}C NMR of **3a** are found in higher magnetic field than those for **1a** and were coupled with phosphorus. On the other hand, those of phenyl group are little different from the corresponding resonances of **1a** and free PhCHO in ^{1}H and ^{13}C NMR spectra. These spectral trends are similar to those of **2a**.

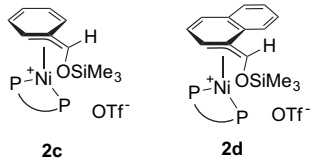


Scheme 4.

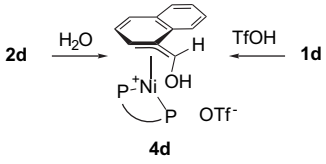
The reaction of $(\eta^2$-(1-NaphCHO))Ni$(PCy_3)_2$ (**1b**) with Me_3SiCl proceeded very rapidly to give $(\eta^3$-1-$Me_3SiOCHC_{10}H_7)$Ni(PCy_3)(Cl) (**3b**) quantitatively (Scheme 5), although **1a** was transformed into η^1:η^1-siloxybenzylnickel under the same condition. The corresponding complex having OTf (**2b**) was generated from **1b** and Me_3SiOTf, but could not be isolated due to the decomposition in the solution. In the spectra of **3b**, both proton and carbon at *ipso*- and β-position of naphthalene ring and Me_3SiOCH- were observed in much higher magnetic field than those in the spectra of **1b**, which indicates that these two carbons of aromatic ring participates in the coordination to nickel. The difference in the coordination mode between **2a**, **3a**, and **3b** might be due to the difference in the number of fused benzene ring. Thus, one benzene ring can remain intact on going from **1b** to **3b**, while **1a** has to lose all of its aromaticity upon forming the corresponding η^3-siloxybenzylnickel complex. The treatment of **1c** or **1d** with Me_3SiOTf led to the corresponding cationic η^3-siloxymethylarylnickel complexes (**2c**, **2d**), which also show higher magnetic field shift of proton and carbon at *ipso*- and β-position of naphthalene ring and Me_3SiOCH– (Scheme 6). These complexes could be the nickel analogs of the proposed intermediate in palladium/Me_3SiOTf-catalyzed bis-silylation of arylaldehyde.[1b] At this moment, we cannot rationalize the different reactivities toward Me_3SiOTf between **1a** and **1c** clearly. However, it may well account for a part of this observation that η^3-coordination of the benzyl ligand may require the softer nature of the nickel center than its η^1-coordination, and this requirement would be better fulfilled by the coordination of more the phosphorus ligands. A similar observation in the equilibrium between η^3-allenyl/propargylpalladium and η^1-propargylpalladium had been reported.[5] η^3-Siloxymethylarylnickel complex **2d** reacted with H_2O to give desilylated complex **4d** (Scheme 7). The X-ray structure analysis on **4d** shows η^3-coordination of hydroxymethylnaphthyl moiety. This complex was also formed by the reaction of **1d** with TfOH very rapidly and quantitatively. A similar reaction, the reaction of η^2-enonepalladium or platinum with TfOH to give η^3-1-hydroxyallylpalladium or platinum, had been reported.[1c]



Scheme 5.



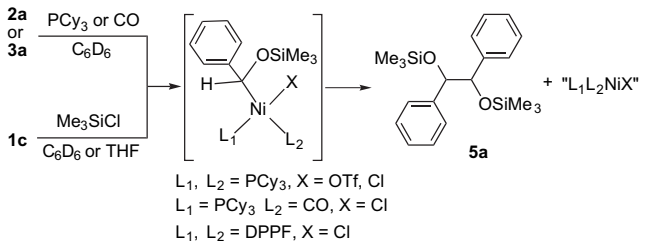
Scheme 6.



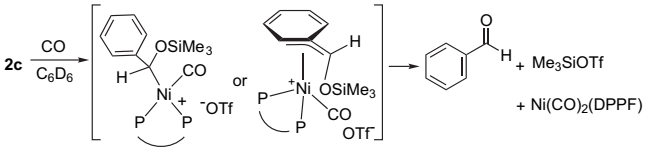
Scheme 7.

The addition of PCy_3 to a solution of **2a** or **3a** led to the formation of 1,2-bis(trimethylsiloxy)-1,2-diphenylethane (**5a**)[6] in 78 or 48% yield concomitant with an unidentified product, probably nickel(I) complex (Scheme 8). Similarly, the treatment of **3a** with carbon monoxide (5 atm) led to the formation of **5a** in 63%. This reaction might have proceeded via neutral nickel(II) intermediate as shown in Scheme 8, in which a radical coupling reaction might be involved. On the other hand, **2c** underwent the regeneration of PhCHO and Me_3SiOTf concomitant with the formation of Ni$(CO)_2$-(DPPF) under the same condition (Scheme 9). The reaction might have proceeded via cationic η^1- or five-coordinated η^3-benzylnickel(II) species generated by the coordination of carbon monoxide to nickel(II) center followed by the nucleophilic attack of TfO^- at Me_3Si group. Similarly, the reaction of **2c** with ^{n}Bu$_4$NCl generated $(\eta^2$-PhCHO)Ni(DPPF) (**1c**) and Me_3SiCl rapidly by the nucleophilic attack of Cl^- at Me_3Si group. The $(\eta^2$-PhCHO)Ni(DPPF) thus generated reacted with Me_3SiCl slowly in situ to give **5a** in

51% yield. In fact, the reaction of **1c** with Me_3SiCl gave **5a** as a sole organic product in 66% yield in C_6D_6 or quantitatively in THF.



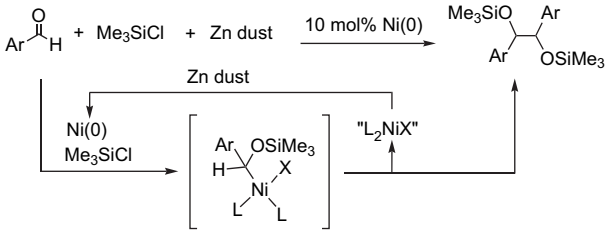
Scheme 8.



Scheme 9.

3. Catalytic reaction

The stoichiometric reaction of **1c** with Me_3SiCl depicted in Scheme 8 prompted us to test a possibility of a catalytic formation of **5a** and analogs by combining Scheme 8 with the reduction of L_1L_2NiX to Ni(0) species.[7] In the presence of 10 mol % of $Ni(cod)_2$ and DPPF or the corresponding (η^2-arylaldehyde)Ni(DPPF) and zinc dust as a reductant, the homocoupling reaction of arylaldehyde moiety proceeded catalytically to give pinacol type products as a mixture of two diastereomers (*threo*/*erythro*=50/50 for all products) (Scheme 10). The results are summarized in Scheme 11. Yields are determined for the diol compounds obtained by the hydrolysis of silylether.[7,8] The substituent group on phenyl group does not affect the yield so much (4-$MeOC_6H_4CHO$ (73%), PhCHO (88%), 4-$CF_3C_6H_4CHO$ (99%)). This reaction can be applied to naphthaldehydes as well (1-NaphCHO (70%), 2-NaphCHO (91%)).



Scheme 10.

4. Conclusion

The reaction of (η^2-PhCHO)$Ni(PCy_3)_2$ with Me_3SiOTf or Me_3SiCl gave neutral η^1:η^1-siloxybenzylnickel complex. This complex underwent the homocoupling reaction to give a pinacol derivative in the presence of PCy_3 or CO. The reaction of (η^2-NaphCHO)$Ni(PCy_3)_2$ with Me_3SiCl gave a neutral η^3-siloxynaphthylmethylnickel complex. Both (η^2-PhCHO)Ni(DPPF) and (η^2-NaphCHO)Ni(DPPF) reacted with Me_3SiOTf to give cationic η^3-siloxyarylmethylnickel complexes. The reaction of (η^2-PhCHO)Ni(DPPF) with Me_3SiCl gave the pinacol derivative and a nickel(I) species. In the presence of Zn dust, the reaction proceeded catalytically by the reduction of the nickel(I) to nickel(0).

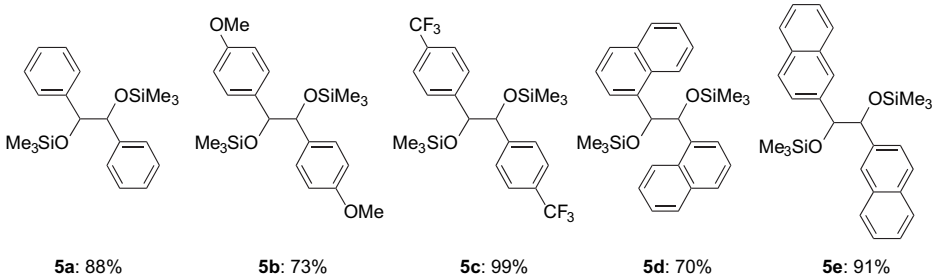
5. Experimental

5.1. General

All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or dry box techniques. ^1H, ^{31}P, and ^{13}C nuclear magnetic resonance spectra were recorded on JEOL GSX-270S and JEOL AL-400 spectrometers. The chemical shifts in ^1H nuclear magnetic resonance spectra were recorded relative to Me_4Si or residual protonated solvent (C_6D_5H (δ 7.16), $CDHCl_2$ (δ 5.32)). The chemical shifts in the ^{13}C spectra were recorded relative to Me_4Si. The chemical shifts in the ^{31}P spectra were recorded using 85% H_3PO_4 as an external standard. Assignment of the resonances in ^1H and ^{13}C NMR spectra was based on ^1H–^1H COSY, HMQC, and HMBC experiments. HMQC and HMBC experiments are inverse detection hetero-correlated NMR experiments recorded at the ^1H frequency of the spectrometer, probing one-bond (CH) and multiple-bond (CCH and CCCH) connectivity. Elemental analyses were performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. For some compounds, accurate elemental analyses were precluded by extreme air or thermal sensitivity and/or systematic problems with elemental analysis of organometallic compounds. X-ray crystal data were collected by using a Rigaku RAXIS-RAPID Imaging Plate diffractometer.

5.2. Materials

The degassed and distilled solvents (THF, toluene, and hexane) used in this work were commercially available. C_6D_6 was distilled from sodium benzophenone ketyl. All commercially available reagents were distilled and degassed prior to use.



Scheme 11.

5.2.1. Isolation of (η^2-(1-NaphCHO))Ni(PCy_3)$_2$ (1b). To a solution of Ni(cod)$_2$ (177 mg, 0.64 mmol) and PCy_3 (362 mg, 0.64 mmol) in 5 mL of toluene was added 88 μL of 1-naphthaldehyde (101 mg, 1.28 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give **1b** (450 mg, dark purple solids) in 95% yield. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.83–2.29 (m, 66H, *Cy*), 6.40 (t, *J*=5.0 Hz, 1H, –C*H*O), 7.27 (dd, *J*=7.2, 7.6 Hz, 1H, 7-*Ar*), 7.39 (dd, *J*=7.2, 8.7 Hz, 1H, 8-*Ar*), 7.44 (dd, *J*=6.9, 8.0 Hz, 1H, 3-*Ar*), 7.67 (d, *J*=8.0 Hz, 1H, 4-*Ar*), 7.75 (d, *J*=7.6 Hz, 1H, 6-*Ar*), 8.29 (d, *J*=6.9 Hz, 1H, 2-*Ar*), 8.81 (d, *J*=8.7 Hz, 1H, 9-*Ar*). ^{31}P NMR (109 MHz, C_6D_6, 25 °C): δ 36.75 (d, J_{PP}=43.3 Hz), 45.13 (d, J_{PP}=43.3 Hz). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 27.02–36.85 (*Cy*), 75.75 (d, J_{CP}=16.7 Hz, –*C*HO), 121.56 (d, J_{CP}=4.6 Hz, 2-*Ar*), 123.57 (d, J_{CP}=3.0 Hz, 4-*Ar*), 124.12 (s, 7-*Ar*), 125.03 (s, 8-*Ar*), 125.36 (s, 6-*Ar*), 126.72 (d, J_{CP}=3.0 Hz, 3-*Ar*), 128.63 (s, 5-*Ar*), 131.26 (d, J_{CP}=2.3 Hz, 9-*Ar*), 135.42 (s, 10-*Ar*), 147.47 (d, J_{CP}=4.6 Hz, 1-*Ar*). Anal. Calcd for $C_{47}H_{74}O_1P_2Ni_1$: C, 72.77; H, 9.62. Found: C, 72.98; H, 9.50.

5.2.2. Isolation of (η^2-PhCHO)Ni(DPPF) (1c). To a solution of Ni(cod)$_2$ (383 mg, 1.39 mmol) and DPPF (771 mg, 1.39 mmol) in 10 mL of toluene was added PhCHO (178 mg, 1.67 mmol) at room temperature. The solution changed from yellow to orange. The reaction mixture was concentrated in vacuo to give orange solids quantitatively. The solids were washed with hexane to give **1c** (988.7 mg, orange solids) in 99% yield. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.82–4.32 (m, 8H, *Cp*), 6.00 (t, *J*=6.1 Hz, 1H, –*CHO*), 7.28–7.35 (m, 15H), 7.28–7.35 (m, 2H), 7.48 (d, *J*=6.8 Hz, 2H), 7.85 (m, 2H), 8.30 (m, 4H). ^{31}P NMR (109 MHz, C_6D_6, 25 °C): δ 20.60 (d, J_{PP}=36.6 Hz), 32.20 (d, J_{PP}=36.6 Hz). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 71.38–86.40 (*Cp*), 86.48 (d, J_{CP}=16.7 Hz, –*C*HO), 124.37–137.49 (*Ph*-CHO), 148.95 (d, J_{CP}=4.6 Hz, *ipso-Ph*-CHO). Anal. Calcd for $C_{41}H_{34}O_1P_2Fe_1Ni_1$: C, 68.47; H, 4.77. Found: C, 67.48; H, 4.67.

5.2.3. Isolation of (η^2-(1-NaphCHO))Ni(DPPF) (1d). To a solution of Ni(cod)$_2$ (179 mg, 0.65 mmol) and DPPF (360 mg, 0.65 mmol) in 5 mL of toluene was added 1-naphthaldehyde (102 mg, 0.65 mmol) at room temperature. The reaction mixture was concentrated in vacuo to give orange solids quantitatively. The solids were washed with hexane to give **1d** (479.2 mg, orange solids) in 96% yield. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.70–4.25 (m, 8H, *Cp*), 6.58 (br s, 2H), 6.70 (s, 2H including –*CHO*), 6.91 (t, *J*=7.1 Hz, 2H), 7.10–7.20 (m, 12H), 7.52 (d, *J*=8.1 Hz, 1H), 7.58 (d, *J*=8.1 Hz, 1H), 7.83 (br s, 2H), 7.96 (d, *J*=6.2 Hz, 1H), 8.24 (br s, 4H), 8.53 (d, *J*=8.4 Hz, 1H). ^{31}P NMR (109 MHz, C_6D_6, 25 °C): δ 20.83 (d, J_{PP}= 35.4 Hz), 31.34 (d, J_{PP}=34.2 Hz). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 70.70–74.39 (*Cp*), 85.99 (d, J_{CP}=16.5 Hz, –*C*HO), 122.20–135.20 (*Ph*), 144.61 (d, J_{CP}=5.5 Hz). Anal. Calcd for $C_{45}H_{36}O_1P_2Fe_1Ni_1$: C, 70.26; H, 4.72. Found: C, 69.73; H, 4.65.

5.2.4. Isolation of (η^1:η^1-$Me_3SiOCHC_6H_5$)Ni(PCy_3)-(OTf) (2a). To a solution of Ni(cod)$_2$ (220 mg, 0.80 mmol), PCy_3 (224 mg, 0.80 mmol), and 81.3 μL of PhCHO (84.8 mg, 0.80 mmol) in 7 mL of THF was added 145 μL of Me_3SiOTf (178 mg, 0.80 mmol) at room temperature. The solution changed from orange to dark purple immediately. The reaction mixture was filtered through a short Celite column followed by concentration in vacuo to give **2a** (368 mg, purple solids) in 69% yield. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.31 (s, 9H, –Si*Me*$_3$), 0.95–1.95 (m, 33H, *Cy*), 4.34 (d, *J*=3.5 Hz, 1H, –C*H*O-SiMe$_3$), 7.02 (d, *J*=7.3, 7.4 Hz, 2H, *m-Ph*), 7.13 (t, *J*=7.4 Hz, 1H, *p-Ph*), 7.47 (d, J_{HP}=7.3 Hz, 2H, *o-Ph*). ^{31}P NMR (109 MHz, C_6D_6, 25 °C): δ 42.0 (s). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 0.5 (s, –Si*Me*$_3$), 27.1 (s, *Cy*), 28.4 (q, J_{CP}=9.9 Hz, *Cy*), 30.6 (d, J_{CP}=30.7 Hz, *Cy*), 33.6 (d, J_{CP}=21.5 Hz, *Cy*), 62.3 (d, J_{CP}=11.4 Hz, –*C*HOSiMe$_3$), 124.0 (s, *o-Ph*), 127.9 (s, *p-Ph*), 130.3 (s, *m-Ph*), 140.9 (s, *ipso-Ph*). Anal. Calcd for $C_{29}H_{48}F_3Ni_1O_4P_1S_1Si_1(H_2O)$: C, 52.18; H, 7.25. Found: C, 50.98; H, 6.71.

5.2.5. Isolation of (η^1:η^1-$Me_3SiOCHC_6H_5$)Ni(PCy_3)(Cl) (3a). To a solution of Ni(cod)$_2$ (220 mg, 0.80 mmol), PCy_3 (224 mg, 0.80 mmol), and 81.3 μL of PhCHO (84.8 mg, 0.80 mmol) in 7 mL of THF was added 101 μL of Me_3SiCl (86.9 mg, 0.80 mmol) at room temperature. The solution changed from orange to dark purple immediately. The reaction mixture was filtered through a short Celite column followed by concentration in vacuo to give **3a** (297 mg, purple solids) in 67% yield. ^{1}H NMR (270 MHz, C_6D_6, 25 °C): δ 0.41 (s, 9H, –Si*Me*$_3$), 0.89–2.20 (m, 33H, *Cy*), 4.54 (d, *J*=3.2 Hz, 1H, –C*H*OSiMe$_3$), 7.03 (m, 3H), 7.49 (d, *J*=6.5 Hz, 2H). ^{31}P NMR (109 MHz, C_6D_6, 25 °C): δ 46.4 (s). ^{13}C NMR (67.5 MHz, C_6D_6, 25 °C): δ 0.6 (s, –Si*Me*$_3$), 27.2 (s, *Cy*), 28.3 (q, J_{CP}=5.5 Hz, *Cy*), 30.4 (d, J_{CP}=17.6 Hz, *Cy*), 34.1 (d, J_{CP}=21.6 Hz, *Cy*), 63.6 (d, J_{CP}=11.5 Hz, –*C*HOSiMe$_3$), 124.1 (s), 126.6 (s), 129.7 (s), 143.2 (s). Anal. Calcd for $C_{28}H_{48}Cl_1Ni_1O_1P_1Si_1$: C, 60.72; H, 8.73. Found: C, 61.00; H, 8.51.

5.2.6. Isolation of (η^3-1-$Me_3SiOCHC_{10}H_7$)Ni(PCy_3)(Cl) (3b). To a solution of Ni(cod)$_2$ (271 mg, 1.0 mmol), PCy_3 (280 mg, 1.0 mmol), and 136 μL of 1-naphthaldehyde (156 mg, 1.0 mmol) in 5 mL of THF was added 127 μL of Me_3SiCl (108 mg, 0.80 mmol) at room temperature. The solution changed from orange to deep red. The reaction mixture was filtered through a short Celite column and reprecipitation from THF/pentane afforded **3b** (383 mg, brown solids) in 63% yield. ^{1}H NMR (400 MHz, toluene-d_8, −30 °C): δ 0.07 (s, 9H, –Si*Me*$_3$), 1.14–1.92 (m, 33H, *Cy*), 5.86 (d, *J*=8.0 Hz, 1H, –C*H*OSiMe$_3$), 6.58 (br s, 1H, 2-*Ar*), 7.29 (dd, *J*=7.4, 7.6 Hz, 1H, 7-*Ar*), 7.36 (dd, *J*=7.4, 8.0 Hz, 1H, 8-*Ar*), 7.48 (d, *J*=7.6 Hz, 1H, 6-*Ar*), 7.51 (dd, *J*=6.5, 8.7 Hz, 1H, 3-*Ar*), 7.62 (d, *J*=8.7 Hz, 1H, 4-*Ar*), 7.70 (d, *J*=8.0 Hz, 1H, 9-*Ar*). ^{31}P NMR (160 MHz, toluene-d_8, −30 °C): δ 37.1 (s). ^{13}C NMR (100 MHz, toluene-d_8, −30 °C): δ 0.10 (s, –Si*Me*$_3$), 14.9–35.0 (*Cy*), 69.7 (s, –*C*HOSiMe$_3$), 92.4 (s, 2-*Ar*), 108.6 (s, 1-*Ar*), 122.4 (s, 8-*Ar*), 126.7 (s, 9-*Ar*), 126.9 (s, 7-*Ar*), 127.60 (6-*Ar*, hidden by toluene-d_8), 127.85 (4-*Ar*, hidden by toluene-d_8), 129.9 (s, 5-*Ar*), 133.3 (s, 3-*Ar*), 136.1 (s, 10-*Ar*). Anal. Calcd for $C_{32}H_{50}Cl_1Ni_1O_1P_1Si_1$: C, 63.64; H, 8.34. Found: C, 63.43; H, 8.35.

5.2.7. Isolation of [(η^3-$Me_3SiOCHC_6H_5$)Ni(DPPF)][OTf] (2c). To a suspension of (η^2-PhCHO)Ni(DPPF) (**1c**) (381 mg, 0.53 mmol) in 5 mL of THF was added 96 μL of Me_3SiOTf (118 mg, 0.53 mmol) at room temperature. The orange

suspension changed to deep red solution. The reaction mixture was concentrated in vacuo. The residue was washed with hexane to give **2c** (492.7 mg, orange solids) in 99% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ −0.11 (s, 9H, –Si*Me*$_3$), 4.16–4.42 (m, 8H, *Cp*), 4.95 (s, 1H, –C*H*OSiMe$_3$), 6.65 (d, J=7.2 Hz, 2H, *o-Ph*), 6.97 (d, J=7.4 Hz, 2H, *m-Ph*), 7.12 (d, J=6.5 Hz, 1H, *p-Ph*), 7.40–7.70 (m, 20H). ^{31}P NMR (160 MHz, CD_2Cl_2, −80 °C): δ 22.66 (d, J_{PP}=2.4 Hz), 27.20 (s). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ −0.35 (s, –Si*Me*$_3$), 74.03–75.68 (m, *Cp*), 86.16 (t, J_{CP}=11.4 Hz, –*C*HOSiMe$_3$), 113.37 (s, *o-PhCHOSiMe*$_3$), 116.67 (s, *ipso-PhCHOSiMe*$_3$), 129.51–134.24 (*Ph*). Anal. Calcd for $C_{45}H_{43}O_4F_3P_2S_1Si_1Fe_1Ni_1$: C, 57.41; H, 4.60. Found: C, 57.46; H, 4.74.

5.2.8. Generation of [(η^3-Me$_3$SiOCHC$_6$H$_5$)Ni(DPPF)][OTf] (2c). To a solution of **1c** (14.4 mg, 0.020 mmol) in 0.5 mL of CD_2Cl_2 was added Me_3SiOTf (4.4 mg, 0.020 mmol) at room temperature. The solution changed from orange to deep red and **2c** was generated quantitatively.

5.2.9. Isolation of [(η^3-1-Me$_3$SiOCHC$_{10}$H$_7$)Ni(DPPF)][OTf] (2d). To a solution of (η^2-(1-NaphCHO))Ni(DPPF) (**1d**) (155.2 mg, 0.20 mmol) in 10 mL of toluene was added 37 μL of Me_3SiOTf (44.8 mg, 0.20 mmol) at room temperature. The solution changed from orange to deep red solution. The reaction mixture was filtered through a short Celite column followed by concentration in vacuo. The residue was washed with hexane to give **2d** (192.4 mg, orange solids) in 96% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, −20 °C): δ −0.02 (s, 9H, –Si*Me*$_3$), 4.00–4.50 (m, 8H, *Cp*), 5.28 (dd, J_{HH}=5.4 Hz, J_{HP}=9.8 Hz, 1H, 2-*Ar*), 6.20 (dd, J=5.4, 7.9 Hz, 1H, 3-*Ar*), 6.44 (dd, J_{HP}=2.9, 10.8 Hz, 1H, –C*H*OSiMe$_3$), 6.74 (d, J=8.3 Hz, 1H, 9-*Ar*), 6.80 (dd, J=7.6, 10.8 Hz, 2H), 7.23–7.90 (m, 22H). ^{31}P NMR (160 MHz, CD_2Cl_2, −20 °C): δ 24.24 (d, J_{PP}=10.3 Hz), 26.81 (d, J_{PP}=10.3 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2, −20 °C): δ −0.42 (s, –Si*Me*$_3$), 73.18–75.25 (m, *Cp*), 83.46 (d, J_{CP}=11.4 Hz, 2-*Ar*), 94.84 (dd, J_{CP}=1.5, 17.5 Hz, –*C*HOSiMe$_3$), 105.95 (s, 1-*Ar*), 121.61 (s, 9-*Ar*), 124.17 (s, 10-*Ar*), 126.15 (s), 126.6 (s), 128.5 (s), 128.82 (d, J_{CP}=3.8 Hz, 3-*Ar*), 129.17–134.71. Anal. Calcd for $C_{45}H_{43}O_4F_3P_2S_1Si_1Fe_1Ni_1$: C, 59.36; H, 4.57. Found: C, 59.70; H, 5.12.

5.2.10. Generation of [(η^3-1-Me$_3$SiOCHC$_{10}$H$_7$)Ni(DPPF)][OTf] (2d). To a suspension of **1d** (11.5 mg, 0.015 mmol) in 0.5 mL of C_6D_6 was added Me_3SiOTf (3.3 mg, 0.15 mmol) at room temperature. The orange suspension changed to deep red solution and **2d** was generated quantitatively.

5.2.11. Isolation of [(η^3-1-HOCHC$_{10}$H$_7$)Ni(DPPF)][OTf] (4d). To a solution of (η^2-(1-NaphCHO))Ni(DPPF) (**1d**) (167.4 mg, 0.22 mmol) in 10 mL of toluene was added 19 μL of HOTf (32.6 mg, 0.22 mmol) at room temperature. The orange solution changed to deep red suspension. The reaction mixture was concentrated in vacuo to give orange solids. The solids were washed with hexane to give **4d** (186.2 mg, orange solids) in 93% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, −30 °C): δ 3.84–4.63 (m, 8H, *Cp*), 5.32 (1H, –C*H*OH, hidden by CD_2Cl_2), 6.38 (s, 1H), 6.49 (s, 1H), 7.12–8.30 (m), 9.34 (s, 1H). ^{31}P NMR (109 MHz, CD_2Cl_2, −80 °C): δ 25.63 (d, J_{PP}=5.0 Hz), 26.07 (d, J_{PP}=5.0 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2, −40 °C): δ 82.32–85.81 (*Cp*), 87.60 (br s), 110.49 (s), 113.02 (br s), 131.52 (s), 133.93 (s), 135.66 (s), 137.06–145.51 (*Ph*). Anal. Calcd for $C_{48}H_{41}O_4F_3P_2S_1Fe_1Ni_1(C_6H_6)$: C, 62.62; H, 4.35. Found: C, 63.18; H, 4.35. X-ray data for **4d**: M=1077.59, brown, triclinic, P-1 (no.2), a=12.448(1) Å, b=13.753(1) Å, c=16.815(1) Å, α=103.833(4)°, β=105.947(3)°, γ=104.314(2)°, V=2532.2(4) Å^3, Z=2, D_{calcd}=1.413 g/cm^3, T=0 °C, R=0.077.

5.2.12. Generation of [(η^3-1-HOCHC$_{10}$H$_7$)Ni(DPPF)][OTf] (4d). To a suspension of (η^2-(1-NaphCHO))Ni(DPPF) **1d** (11.5 mg, 0.015 mmol) in 0.5 mL of C_6D_6 was added Me_3SiOTf (3.3 mg, 0.015 mmol) at room temperature. The orange suspension changed to deep red solution and **2d** was generated quantitatively. To the solution was added 0.5 mg of H_2O (0.028 mmol, 0.5 μL) to give **4d** quantitatively.

5.2.13. Reaction of (η^1:η^1-Me$_3$SiOCHC$_6$H$_5$)Ni(PCy$_3$)(OTf) (2a) with PCy$_3$. To a solution of **2a** (13.4 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added PCy_3 (5.8 mg, 0.02 mmol) at room temperature and the reaction mixture was stirred for 2 days. The pinacol type product (**5a**) was generated in 78% yield.

5.2.14. Reaction of (η^1:η^1-Me$_3$SiOCHC$_6$H$_5$)Ni(PCy$_3$)(Cl) (3a) with PCy$_3$. To a solution of **3a** (11.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added PCy_3 (5.6 mg, 0.02 mmol) at room temperature and the reaction mixture was stirred for 2 days. Compound **5a** was obtained in 48% yield.

5.2.15. Reaction of (η^1:η^1-Me$_3$SiOCHC$_6$H$_5$)Ni(PCy$_3$)(Cl) (3a) with CO. A solution of **3a** (11.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 in a pressure tight NMR tube was treated with CO (5 atm). The solution changed from dark purple to pale blue immediately to give **5a** (63%).

5.2.16. Reaction of (η^1:η^1-Me$_3$SiOCHC$_6$H$_5$)Ni(PCy$_3$)(OTf) (2a) with CO. A solution of **2a** (11.6 mg, 0.02 mmol) in 0.5 mL of C_6D_6 in a pressure tight NMR tube was treated with CO (5 atm). The solution changed from dark purple to colorless solution immediately to give $Ni(PCy_3)(CO)_3$, PhCHO, and Me_3SiOTf quantitatively.

5.2.17. Reaction of [(η^3-Me$_3$SiOCHC$_6$H$_5$)Ni(DPPF)][OTf] (2c) with CO. A solution of **2c** (18.9 mg, 0.02 mmol) in 0.5 mL of C_6D_6 in a pressure tight NMR tube was treated with CO (5 atm). The solution changed from deep red to colorless solution immediately to give $Ni(DPPF)(CO)_2$, PhCHO, and Me_3SiOTf quantitatively.

5.2.18. Reaction of [(η^3-Me$_3$SiOCHC$_6$H$_5$)Ni(DPPF)][OTf] (2c) with Bu$_4$NCl. To a solution of **2c** (18.9 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added Bu_4NCl (5.4 mg, 0.02 mmol) at room temperature and the reaction mixture was stirred for 2 days. Compound **5a** was obtained in 51% yield.

5.2.19. Reaction of (η^2-PhCHO)Ni(DPPF) (1c) with Me$_3$SiCl. To a solution of **1c** (14.5 mg, 0.02 mmol) in 0.5 mL of C_6D_6 was added 2.5 μL of Me_3SiCl (2.3 mg, 0.02 mmol) at room temperature, and the reaction mixture was stirred for 2 days. Pinacol type product was obtained in 66% yield. When the reaction was carried out in THF, **5a** was obtained quantitatively.

5.2.20. Typical procedure for catalytic reaction (PhCHO). Under a nitrogen atmosphere, to a suspension of (η^2-PhCHO)Ni(DPPF) (1.5 mg, 0.002 mmol) and zinc dust (1.2 mg, 0.020 mmol) in 0.5 mL of THF were added 1.8 μL of PhCHO (2.0 mg, 0.018 mmol) and 2.5 μL of Me_3SiCl (2.3 mg, 0.020 mmol) at room temperature. The reaction mixture was stirred for 1 day to give **5a** in 88% yield. The yield was determined by GC as the corresponding diol obtained by the hydrolysis.

5.2.21. Reaction of 4-$MeOC_6H_4CHO$. $Ni(cod)_2$ (10 mol %) and DPPF were employed as a catalyst. Compound **5b** was obtained in 73% yield.

5.2.22. Reaction of 4-$CF_3C_6H_4CHO$. $Ni(cod)_2$ (10 mol %) and DPPF were employed as a catalyst. Compound **5c** was obtained in 99% yield.

5.2.23. Reaction of 1-naphthaldehyde. Compound **2d** (10 mol %) was employed as a catalyst. Compound **5d** was obtained in 70% yield.

5.2.24. Reaction of 2-naphthaldehyde. $Ni(cod)_2$ (10 mol %) and DPPF were employed as a catalyst. Compound **5e** was obtained in 91% yield.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.03.124.

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