

**Supplementary information**  
**for**  
**Nickeladihydrofuran. Key Intermediate for Nickel-catalyzed**  
**Reaction of Alkyne and Aldehyde**

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**General:** All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques.  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectra were recorded on JEOL GSX-270S and JEOL AL-400 and Bruker DPX-400 spectrometers. The chemical shifts in  $^1\text{H}$  nuclear magnetic resonance (NMR) spectra were recorded relative to  $\text{Me}_4\text{Si}$  or residual protiated solvent ( $\text{C}_6\text{D}_5\text{H}$  ( $\delta$  7.16) or  $\text{THF-d}_7$  ( $\delta$  3.58)). The chemical shifts in the  $^{13}\text{C}$  spectra were recorded relative to  $\text{Me}_4\text{Si}$ . The chemical shifts in the  $^{31}\text{P}$  spectra were recorded using 85%  $\text{H}_3\text{PO}_4$  as external standard. Elemental analyses were performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected by a Rigaku RAXIS-RAPID Imaging Plate diffractometer.

**Materials:** Unless indicated otherwise, solvents and reagents were purchased from commercial vendors, distilled and degassed prior to use. Tetrahydrofuran, pentane, hexane,  $\text{C}_6\text{D}_6$  and  $\text{THF-d}_8$  were purified by distillation from sodium benzophenone ketyl. Celite filtrations were performed using a plug of Hyflo Super Gel (Fisher) over glass wool in disposal pipettes or alone on fritted glass funnels under vacuum.

**Caution:** The treatment of nickel compounds with carbon monoxide can yield  $\text{Ni}(\text{CO})_4$  (extremely toxic) due to the addition of insufficient amounts of  $\text{PR}_3$ , careless handling or an accident. The reaction mixture must be handled in a well-ventilated fume hood.

**Generation of  $[\text{Ni}(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{C}(\text{Ph})\text{O})(\text{PCy}_3)]_2$  (**1**):** To a solution of  $\text{Ni}(\text{cod})_2$  (5.5 mg, 0.02 mmol),  $\text{PCy}_3$  (5.6 mg, 0.02 mmol),  $\text{PhCHO}$  (2.0  $\mu\text{L}$ , 0.02 mmol) in 0.5 mL of  $\text{C}_6\text{D}_6$  was added 2-butyne (4.0  $\mu\text{L}$ , 0.05 mmol) at room temperature. The reaction was followed by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra. After 1 h, **1** and  $\eta^2\text{-(PhCHO)Ni(PCy}_3)_2$  were generated in 48%, 25% respectively. The formation of  $\eta^2\text{-(PhCHO)Ni(PCy}_3)_2$  was confirmed by comparison of  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra with that of the authentic sample.<sup>1</sup>

**Isolation of  $[\text{Ni}(\mu\text{-}\eta^1\text{:}\eta^1\text{-C(CH}_3\text{)=C(CH}_3\text{)C(Ph)O)(PCy}_3\text{)}]_2$  (**1**):** To a solution of  $\text{Ni(cod)}_2$  (275 mg, 1.0 mmol),  $\text{PCy}_3$  (280 mg, 1.0 mmol),  $\text{PhCHO}$  (101.6  $\mu\text{L}$ , 1.0 mmol) in 25 mL of  $\text{C}_6\text{H}_6$  was added 2-butyne (196  $\mu\text{L}$ , 2.5 mmol) at room temperature and stirred for 1 h. The solution changed from red to dark red. The reaction mixture was filtered through a short celite column, followed by concentration *in vacuo*. The residue was dissolved in 4 mL of toluene/hexane (1/3). Reprecipitation at  $-20^\circ\text{C}$  for 24 h gave a purple solid. The solid was washed with cold hexane to give **1** (201 mg, 40%). Analytical sample and a single crystal for X-ray diffraction analysis were prepared by recrystallization from THF/pentane at  $-20^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ,  $-20^\circ\text{C}$ ):  $\delta$  0.81 (s, 6H,  $-\text{NiC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 1.09 (s, 6H,  $-\text{NiC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 1.1-2.4 (m, 66H, **Cy**), 4.23 (s, 2H,  $-\text{NiOCHPh-}$ ), 7.20 (t,  $J = 6.8$  Hz, 2H, *p-Ph*), 7.28 (t,  $J = 6.8$  Hz, 4H, *m-Ph*), 7.85 (t,  $J = 7.2$  Hz, 4H, *o-Ph*).  $^{31}\text{P}$  NMR (109 MHz,  $\text{THF-}d_8$ ): 31.9 (s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF-}d_8$ ,  $-20^\circ\text{C}$ ):  $\delta$  12.7 (s,  $-\text{NiC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 14.7 (s, **Cy**), 21.6 (s, **Cy**), 23.6 (s, **Cy**), 23.7 ( $-\text{NiC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 27.5 (brs, **Cy**), 29.0 (brs, **Cy**), 32.7 (s, **Cy**), 90.4 (s,  $-\text{NiOCHPh-}$ ), 126.2 (d,  $J = 27.0$  Hz,  $-\text{NiC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 128.7 (s, *p-Ph*), 129.0 (s, *m-Ph*), 129.7 (s, *o-Ph*), 148.6 (s, *ipso-Ph*), 150.7 (s,  $-\text{NiC(CH}_3\text{)=C(CH}_3\text{)-}$ ). Anal. Calcd for  $\text{C}_{58}\text{H}_{90}\text{NiO}_2\text{P}_2$ : C, 69.75; H, 9.08. Found: C, 69.32; H, 9.08. X-ray data for **1**·( $\text{C}_5\text{H}_{12}$ )·( $\text{C}_4\text{H}_8\text{O}$ ):  $M = 1142.91$ , black, monoclinic,  $C2/c$  (No. 15),  $a = 49.179(3)$  Å,  $b = 13.9696(8)$  Å,  $c = 20.1131(11)$  Å,  $\beta = 110.2380(15)^\circ$ ,  $V = 12964.8(13)$  Å<sup>3</sup>,  $D_{\text{calcd}} = 1.171$  g/cm<sup>3</sup>,  $T = 0^\circ\text{C}$ ,  $R_1 = 0.0585$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1712$  (all data).

**Carbonylation of **1**:** In a pressure tight NMR tube, a solution of **1** (10.0 mg, 0.01 mmol) in 0.5 mL of  $\text{C}_6\text{D}_6$  was treated with carbon monoxide (5 atm). The solution changed from purple to pale yellow immediately. The corresponding lactone **2** and  $\text{Ni(CO)}_3(\text{PCy}_3)$  was generated quantitatively. The solution was concentration *in vacuo* and separated by short column (silica gel) to give **2** (3.6 mg, 95%).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.02 (s, 3H,  $-\text{COC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 2.04 (s, 3H,  $-\text{COC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 5.60 (s, 1H,  $-\text{COOCHPh-}$ ), 7.20 (dd,  $J = 6.1, 2.9$  Hz, 2H, **Ph**), 7.30-7.40 (m, 3H, **Ph**).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.83 ( $-\text{COC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 12.34 ( $-\text{COC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 85.33 ( $-\text{COOCHPh-}$ ), 123.339 ( $-\text{COC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 127.05 (**Ph**), 129.16 (**Ph**), 129.44 (**Ph**), 135.22 (**Ph**), 159.31 ( $-\text{COC(CH}_3\text{)=C(CH}_3\text{)-}$ ), 174.22 ( $-\text{COC(CH}_3\text{)=C(CH}_3\text{)-}$ ). HRMS Calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$  188.0837, Found  $m/z$  188.0835.

#### Isolation of (*E*)-2-Methyl-1-phenylbut-2-en-1-one (**3**)

A solution of **1** (15 mg, 0.015 mmol) in 0.5 mL of THF was stirred for 48 h at room

temperature. The reaction mixture changed from purple to dark red. The decomposition of **1** was confirmed by  $^{31}\text{P}$  NMR spectrum. The reaction mixture was concentrated *in vacuo* and separated by short column (silica gel) to give (*E*)-2-Methyl-1-phenylbut-2-en-1-one (**3**) (3.3 mg, 70%).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.88 (dq,  $J = 7.0$  Hz, 1.4 Hz), 1.98 (m, 3H), 6.41 (qq,  $J = 6.8$  Hz, 1.4 Hz), 7.25-7.63 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.3, 14.9, 127.9, 129.4, 131.4, 137.9, 139.1, 141.6, 199.1. The structure of **3** was confirmed by comparison of  $^1\text{H}$  and  $^{31}\text{C}$  NMR spectra with those of the authentic sample.<sup>2</sup>

**Reaction of 1 with  $\text{ZnMe}_2$ :** To a solution of **1** (10.0 mg, 0.01 mmol) in 2 mL of THF was added  $\text{ZnMe}_2$  (0.02 mmol, 20  $\mu\text{L}$ , 1M/hexane) at  $-20^\circ\text{C}$ . The solution was allowed to warm up to room temperature. Then the solution changed from purple to black. The reaction mixture was poured into 1 mL of 1 M HCl aqueous solution. The mixture was treated with a saturated  $\text{NaHCO}_3$  aqueous solution and extracted with three portions of 3 mL of  $\text{Et}_2\text{O}$ . The combined organic extracts were dried over  $\text{MgSO}_4$ . The solvent was removed *in vacuo* to give a trace amount of **4**.

**Reaction of 1 with  $\text{ZnMe}_2$  in the presence of PhCHO and  $\text{PCy}_3$ :** To a solution of **1** (99.8 mg, 0.1 mmol), PhCHO (202  $\mu\text{L}$ , 2.0 mmol) and  $\text{PCy}_3$  (55.4 mg, 0.2 mmol) in 8 mL of THF was added  $\text{ZnMe}_2$  (0.2 mmol, 200  $\mu\text{L}$ , 1M/hexane) at  $-20^\circ\text{C}$ . The solution was allowed to warm up to room temperature. Then the solution changed from purple to dark red. The quantitative formation of  $\eta^2\text{-(PhCHO)Ni(PCy}_3)_2$  was confirmed by  $^{31}\text{P}$  NMR spectrum. The reaction mixture was poured into 1 mL of 1 M HCl aqueous solution. The solution was treated with a saturated  $\text{NaHCO}_3$  aqueous solution and extracted with three portions of 3 mL of  $\text{Et}_2\text{O}$ . The combined organic extracts were dried over  $\text{MgSO}_4$  and concentrated *in vacuo* to give **4** in 70% NMR yield.

**Synthesis of 2,3-Dimethyl-1-phenyl-but-2-en-1-ol (catalytic reaction):** To a solution of  $\text{Ni(cod)}_2$  (27.5 mg, 0.1 mmol),  $\text{PCy}_3$  (56 mg, 0.1 mmol), PhCHO (159  $\mu\text{L}$ , 1.0 mmol) and 2-butyne (94  $\mu\text{L}$ , 1.0 mmol) in 2 mL of THF was added  $\text{ZnMe}_2$  (2.0 mmol, 2.0 mL, 1 M/hexane) at room temperature. The reaction mixture was stirred for 24 h and then poured into 2 mL of 1 M HCl aqueous solution. The aqueous layer was extracted with three portions of 3 mL of  $\text{Et}_2\text{O}$  and combined organic extracts were dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. The residue was separated by a short column (silica gel) to give the corresponding alcohol (169 mg, 96%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.43 (s, 3H, *Me*), 1.66 (s, 3H, *Me*), 1.83 (s, 3H, *Me*), 5.79 (dd,  $J = 6.1, 2.9$  Hz, 2H, *Ph*),

7.10-7.25 (m, 5H, *Ph*).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.4 (*Me*), 20.5 (*Me*), 21.4 (*Me*), 72.3 (-CH(*Ph*)OH), 125.7 (*Ph*), 126.9 (*Ph*), 128.3 (*Ph*), 128.8 (*Ph*), 129.6 ((CH<sub>3</sub>)<sub>2</sub>C=C(CH<sub>3</sub>)-), 143.4 ((CH<sub>3</sub>)<sub>2</sub>C=C(CH<sub>3</sub>)-). HRMS Calcd for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub> 176.1201, Found *m/z* 176.1205.

## References

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