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

Sensuke Ogoshi,* Tomoya Arai, Masato Ohashi, and Hideo Kurosawa

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
ogoshi@chem.eng.osaka-u.ac.jp

General: All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. $^1$H, $^{31}$P and $^{13}$C nuclear magnetic resonance spectra were recorded on JEOL GSX-270S and JEOL AL-400 and Bruker DPX-400 spectrometers. The chemical shifts in $^1$H nuclear magnetic resonance (NMR) spectra were recorded relative to Me$_4$Si or residual protiated solvent (C$_6$D$_5$H (δ 7.16) or THF-d$_7$ (δ 3.58)). The chemical shifts in the $^{13}$C spectra were recorded relative to Me$_4$Si. The chemical shifts in the $^{31}$P spectra were recorded using 85% H$_3$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, C$_6$D$_6$ and 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 Ni(CO)$_4$ (extremely toxic) due to the addition of insufficient amounts of PR$_3$, careless handling or an accident. The reaction mixture must be handled in a well-ventilated fume hood.

Generation of [Ni(μ-$\eta^1$-$\eta^1$-C(CH$_3$)=C(CH$_3$)C(Ph)O)(PCy$_3$)]$_2$ (1): To a solution of Ni(cod)$_2$ (5.5 mg, 0.02 mmol), PCy$_3$ (5.6 mg, 0.02 mmol), PhCHO (2.0 μL, 0.02 mmol) in 0.5 mL of C$_6$D$_6$ was added 2-butyne (4.0 μL, 0.05 mmol) at room temperature. The reaction was followed by $^1$H and $^{31}$P NMR spectra. After 1 h, 1 and $\eta^2$-(PhCHO)Ni(PCy$_3$)$_2$ were generated in 48%, 25% respectively. The formation of $\eta^2$-(PhCHO)Ni(PCy$_3$)$_2$ was confirmed by comparison of $^1$H and $^{31}$P NMR spectra with that of the authentic sample.$^1$
Isolation of $[\text{Ni}(\mu-\eta^1:1-C(\text{CH}_3)=C(\text{CH}_3)\text{C(Ph)O})(\text{PCy}_3)]_2$ (1): To a solution of Ni(cod)$_2$ (275 mg, 1.0 mmol), PCy$_3$ (280 mg, 1.0 mmol), PhCHO (101.6 μL, 1.0 mmol) in 25 mL of C$_6$H$_6$ was added 2-butyne (196 μL, 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 °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°C. $^1$H NMR (400 MHz, THF-$d_8$, -20 °C): δ 0.81 (s, 6H, -NiC(\text{CH}_3)=C(\text{CH}_3)-), 1.09 (s, 6H, -NiC(\text{CH}_3)=C(CH_3)-), 1.1-2.4 (m, 66H, Cy), 4.23 (s, 2H, -NiOC\text{H}Ph-), 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). $^{31}$P NMR (109 MHz, THF-$d_8$): 31.9 (s). 13C NMR (100 MHz, THF-$d_8$, -20 °C): δ 12.7 (s, -NiC(\text{CH}_3)=C(CH_3)-), 14.7 (s, Cy), 21.6 (s, Cy), 23.6 (s, Cy), 23.7 (-NiC(CH$_3$)=C(CH$_3$)-), 27.5 (brs, Cy), 29.0 (brs, Cy), 32.7 (s, Cy), 90.4 (s, -NiOC\text{CH}Ph-), 126.2 (d, $J$ = 27.0 Hz, -NiC(CH$_3$)=C(CH$_3$)-), 128.7 (s, p-Ph), 129.0 (s, m-Ph), 129.7 (s, o-Ph), 148.6 (s, ipso-Ph), 150.7 (s, -NiC(CH$_3$)=C(CH$_3$)-). Anal. Calcd for C$_{58}$H$_{90}$NiO$_2$P$_2$: C, 69.75; H, 9.08. Found: C, 69.32; H, 9.08. X-ray data for 1·(C$_5$H$_{12}$)·(C$_4$H$_8$O): M = 1142.91, black, monoclinic, $C_2/c$ (No. 15), $a$ = 49.179(3) Å, $b$ = 13.9696(8) Å, $c$ = 20.1131(11) Å, $\beta$ = 110.2380 (15)°, $V$ = 12964.8 (13) Å$^3$, $D_{\text{calcd}}$ = 1.171 g/cm$^3$, $T$ = 0 °C, $R_1$ = 0.0585 [$\text{I}$$>$2σ(I)], w$R_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 C$_6$D$_6$ was treated with carbon monoxide (5 atm). The solution changed from purple to pale yellow immediately. The corresponding lactone 2 and Ni(CO)$_3$(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%). $^1$H NMR (270 MHz, CDCl$_3$): δ 2.02 (s, 3H, -COOC(\text{CH}_3)=C(\text{CH}_3)-), 2.04 (s, 3H, -COC(\text{CH}_3)=C(\text{CH}_3)-), 5.60 (s, 1H, -COOC\text{H}Ph-), 7.20 (dd, $J$ = 6.1, 2.9 Hz, 2H, Ph), 7.30-7.40 (m, 3H, Ph). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 88.33 (-COOC(CH$_3$)=C(CH$_3$)-), 12.34 (-COOC(CH$_3$)=C(CH$_3$)-), 85.33 (-COOC\text{H}Ph-), 123.339 (-COOC(CH$_3$)=C(CH$_3$)-), 127.05 (Ph), 129.16 (Ph), 129.44 (Ph), 135.22 (Ph), 159.31 (-COOC(CH$_3$)=C(CH$_3$)-), 174.22 (-COOC(CH$_3$)=C(CH$_3$)-). HRMS Calcd for C$_{12}$H$_{12}$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 $^{31}$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%). $^1$H NMR (270 MHz, 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). $^{13}$C NMR (100 MHz, 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 $^1$H and $^{31}$C NMR spectra with those of the authentic sample.

**Reaction of 1 with ZnMe$_2$:** To a solution of 1 (10.0 mg, 0.01 mmol) in 2 mL of THF was added ZnMe$_2$ (0.02 mmol, 20 $\mu$L, 1M/hexane) at -20 °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 NaHCO$_3$ aqueous solution and extracted with three portions of 3 mL of Et$_2$O. The combined organic extracts were dried over MgSO$_4$. The solvent was removed in vacuo to give a trace amount of 4.

**Reaction of 1 with ZnMe$_2$ in the presence of PhCHO and PCy$_3$:** To a solution of 1 (99.8 mg, 0.1 mmol), PhCHO (202 $\mu$L, 2.0 mmol) and PCy$_3$ (55.4 mg, 0.2 mmol) in 8 mL of THF was added ZnMe$_2$ (0.2 mmol, 200 $\mu$L, 1M/hexane) at -20 °C. The solution was allowed to warm up to room temperature. Then the solution changed from purple to dark red. The quantitative formation of $\eta^2$-(PhCHO)Ni(PCy$_3$)$_2$ was confirmed by $^{31}$P NMR spectrum. The reaction mixture was poured into 1 mL of 1 M HCl aqueous solution. The solution was treated with a saturated NaHCO$_3$ aqueous solution and extracted with three portions of 3 mL of Et$_2$O. The combined organic extracts were dried over 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 Ni(cod)$_2$ (27.5 mg, 0.1 mmol), PCy$_3$ (56 mg, 0.1 mmol), PhCHO (159 $\mu$L, 1.0 mmol) and 2-butyne (94 $\mu$L, 1.0 mmol) in 2 mL of THF was added 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 Et$_2$O and combined organic extracts were dried over MgSO$_4$ and concentrated in vacuo. The residue was separated by a short column (silica gel) to give the corresponding alcohol (169 mg, 96%). $^1$H NMR (400 MHz, 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). $^{13}$C NMR (100 MHz, 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$_3$)$_2$C=C(CH$_3$)-), 143.4 ((CH$_3$)$_2$C=C(CH$_3$)-). HRMS Calcd for C$_{12}$H$_{12}$O$_2$ 176.1201, Found m/z 176.1205.

References