

General Considerations: Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen. Anhydrous diethyl ether was purchased from Mallinckrodt; pentane, n-hexane, and tetrahydrofuran (THF) were purchased from EM Science. Diethyl ether, toluene, benzene, pentane, and n-hexane were dried and deoxygenated by the method of Grubbs.¹ THF was distilled under nitrogen from purple sodium benzophenone ketyl. Distilled solvents were transferred under vacuum into vacuum-tight glass vessels before being pumped into a Vacuum Atmospheres drybox. C₆D₆ was purchased from Cambridge Isotopes and were degassed and dried over 4 Å sieves. The 4 Å sieves, alumina, and Celite were dried in vacuo overnight at a temperature just above 200° C. Compound **1** was prepared as reported in reference 12 in the main text. *t*-Butyl formate was passed through alumina and stored over molecular sieves. All other compounds were used as received. ¹H and ¹³C NMR spectra were recorded on Unity 300, Mercury 300 or Varian INOVA501 spectrometers at room temperature, unless indicated otherwise. Chemical shifts are reported with respect to internal solvent: 7.15 ppm and 128.38 (t) ppm (C₆D₆). CHN analyses were performed by H. Kolbe Mikroanalytisches Laboratorium (Mülheim, Germany).

Synthesis of (Ar[*t*-Bu]N)₃TiOC(O)H (2**):** Ti(N[*t*-Bu]Ar)₃ (700 mg, 1.21 mmol) was dissolved in 50 mL of pentane. To the green solution was added *t*-butyl formate (124 mg, 1.21 mmol) in 5 mL of pentane resulting in an immediate darkening. The solution was allowed to stir for 30 m, and then volatiles were removed in vacuo. The resulting bright yellow solid was transferred to a fine frit and washed with pentane until the washings were clear. Yield: 614 mg, 81%. ¹H NMR, 500 MHz (C₆D₆): 1.26 (s, 27H, *t*-Bu); 2.16 (s, 18H, Ar-CH₃); 6.22 (br s, 6H, *o*-ArH); 6.69 (s, 3H, *p*-ArH); 8.36 (br s, 1H, OC(O)-H) ppm. ¹³C NMR, 125 MHz (C₆D₆): 21.95 (C(CH₃)₃); 30.94 (Ar-CH₃); 62.69 (C(CH₃)₃); 127.36; 128.10; 137.14; 151.75; 162.05 (OC(O)H) ppm. IR (C₆D₆, 25 °C): 2783 (w), 1685 (s), 1231 (s), 1206 (s) cm⁻¹. Anal Calcd. for C₃₇H₅₅N₃O₂Ti: C, 71.48; H, 8.92; N, 6.76. Found: C, 71.28; H, 8.96; N, 6.68.

¹ Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J. *Organometallics* 1996, **15**, 1518.

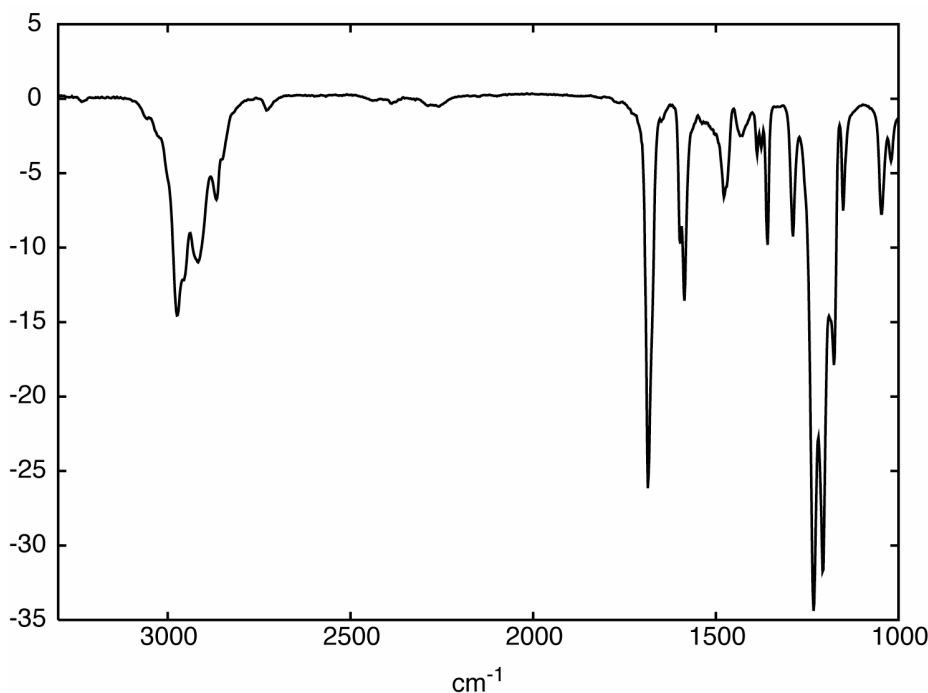


Figure 1: IR spectrum of **2** in C₆D₆.

Synthesis of (Ar[*t*-Bu]N)₃TiOLi(Et₂O)₂ (3**):** Titanium formate **2** (420 mg, 0.68 mmol) was slurried in 20 mL of Et₂O in a 100 mL round-bottom flask and frozen in the glovebox coldwell. In a 20 mL scintillation vial, LiN(*i*-Pr)₂ was dissolved in 5 mL Et₂O and similarly frozen. The thawing solutions were combined and allowed to warm to room temperature. After 1 h, the reaction mixture was orange and nearly homogenous. The solution was filtered through Celite, concentrated to a volume of 10 mL, and stored at -35 °C. Large block-shaped crystals grew within hours and could be isolated simply by decanting off the mother liquor. Yield: 302 mg, 60% (three crops). ¹H NMR, 300 MHz (C₆D₆): 1.39 (s, 27H, *t*-Bu); 2.32 (s, 18H, Ar-CH₃); 6.70 (s, 6H, *o*-ArH); 6.76 (s, 3H, *p*-ArH) ppm. ¹³C NMR, 125 MHz (C₆D₆): 22.19 (C(CH₃)₃); 32.78 (Ar-CH₃); 58.28 (C(CH₃)₃); 126.01; 129.28; 137.41; 153.68 ppm. Anal Calcd. for C₄₄H₇₄N₃O₃TiLi: C, 70.66; H, 9.97; N, 5.62. Found: C, 70.23; H, 9.89; N, 5.72.

Quantification of CO evolution in the synthesis of **3:** In the glovebox, a 25 mL Schlenk tube (**A**) fitted with Teflon stopcock was charged with **2** and LiN(*i*-Pr)₂ and sealed. A 50 mL round-bottom flask (**B**) was charged with (PPh₃)₃RhCl and 10 mL of toluene, fitted with a 180° degree adapter, and sealed. Both flasks were removed from the glovebox, attached to a high vacuum manifold, and thoroughly evacuated. The Et₂O from flask **B** was condensed into flask **A** at -196° C. Flask **A** was sealed and allowed to warm to room temperature. After 1h, flask **B** was cooled to -196° C and the volatiles from flask **A** were allowed to condense into flask **B**. Flask **B** was sealed and allowed to warm to room temperature, whereupon it turned purple. ³¹P NMR analysis of the contents of flask **B** revealed the formation of (PPh₃)₂Rh(CO)Cl.