A Polymer-Supported Rhodium Catalyst That Can Function in Polar Protic Solvents

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Supporting Information

General Procedures: All reactions were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques or in an MBraun Lab-Master 100 glovebox. All solvents, except methanol and THF, were dried by passing through a column of activated alumina[1] and stored under argon prior to use. Methanol was distilled from $Mg(OCH_3)_2$ and stored over 4Å molecular sieves. THF was distilled from sodium benzophenone ketyl. $CDCl_3$ was stored over K_2CO_3 and 4Å molecular sieves. CD_2Cl_2 was distilled from CaH_2. Both protiated and deuterated solvents except $CDCl_3$ and $(CD_3)_2CO$ were freeze-pump-thaw degassed before use.

Methyl-(*Z*)-α-acetamidocinnamate (entry 1),[2] 3-acryloyloxazolidin-2-one (entry 3),[3] *exo*-*N*-(norborn-5-en-2-carboxy)oxazolidi-2-one (entry 4),[4] $[(nbd)RhCl]_2$[5] and [dppeRh(nbd)]BF_4[6] were prepared by literature procedures. All reagents were purchased from Aldrich except the following: tetrachlorodiphosphine (Strem) and rhodium trichloride hydrate (Next Chimica). α-Acetamidocinnamic acid was used as received. Geraniol and 3-methyl-2-cyclohexen-1-ol were freeze-pump-thaw degassed prior to use. Methyl cinnamate was purified by sublimation before use. Styrene was distilled from CaH_2 and freeze-pump-thaw degassed before use. Catecholborane was vacuum transferred and freeze-pump-thaw degassed before use. Ethylene glycol dimethacrylate (EGDMA)[7] and dimethylformamide (DMF)[8] were purified according to the literature procedure and freeze-pump-thaw degassed before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under vacuum.

High pressure hydrogenations (>15 psi) were performed in a high pressure glass reactor vessel purchased from Andrews Glass Company, Inc., Vineland, NJ. Gas chromatography was performed on a Hewlett-Packard 6890 series instrument, using an HP-5 (30.0 m x 250 μm x 0.50 μm) or a DB-1 capillary column (30.0 m x 320 μm x 0.25 μm). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or $(CD_3)_2CO$ at ambient temperature on a Bruker AMX300 or Avance 400 spectrometer. Elemental

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[1] Pangborn, .B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

[2] Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946-5952.

[3] Ho, G. J.; Mathre, D. J. *J. Org. Chem.* **1995**, *60*, 2271-2273.

[4] Jaquith, J. B.; Levy, C. J.; Bondar, G. V.; Wang, S.; Collins, S. *Organometallics* **1998**, *17*, 914-925.

[5] Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178-3182.

[6] Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397-2407.

[7] Gilmore, M. A.; Spivak, D.; Shea, K. J. *J. Am. Chem. Soc.* **1997**, *119*, 4388-4393.

[8] Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966-3968.

analyses of the ligands, solution catalysts, and the hydrogenated analogs of **2** and **3** (Table 1) were performed by E&R Microanalytical Laboratory, Inc., Parsippany, NJ. Polymer analysis and trace Rh analysis was performed using ICP by Robertson Microlit Laboratories, Inc., Madison, NJ.

Isopropenyl dppe (2)[9]: A 1.0 M THF solution of methyl iodide (1.09 mL, 17.7 mmol) was prepared and added to Mg shavings (3.45 g, 140 mmol) to activate the Mg. The milky solution was cannula transferred off and the Mg was rinsed several times with dry THF. A 3.5 M THF solution of 4-chloro-α-methylstyrene (5.00 mL, 34.9 mmol) was prepared and approximately half of the solution was added to cover the Mg shavings. Heating of this mixture resulted in a color change from white to brown. The remaining 4-chloro-α-methylstyrene solution was diluted to 1.0 M in THF and added to the Mg, heating the reaction mixture until reflux occurred. The reaction was stirred for 12 h at room temperature and transferred via cannula to a cold solution (0˚C) of tetrachlorodiphosphine (1.14 mL, 2.69 mmol). All solvents used in the workup were sparged with dinitrogen or argon for at least 20 minutes prior to use.

The inhibitor 4-*t*-butylcatechol was added to each step of the workup procedure. The isopropenyl dppe solution was added to a cold solution (0˚C) of 3 M NH_4Cl and extracted 3x with THF. The THF layers were washed with brine, dried over $MgSO_4$, and the solvent removed i*n vacuo*. The white solid was dissolved in THF, hexanes were added, and the solution was filtered through Celite. The crude phosphine was recrystallized from THF/95% EtOH (2.35 g, 56% yield). ^{31}P NMR (162 MHz, $CDCl_3$): δ –13.7; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 8H), 7.27 (m, 8H), 5.38 (s, 4H), 5.08 (s, 4H), 2.10 (m, 16H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 126.1, 113.4, 68.4, 26.0, 24.3, 22.1; Anal. calcd. for $C_{38}H_{40}P_2$: C, 81.70%; H, 7.22%. Found: C, 80.52%; H, 7.81%. Due to 3-5% monooxidized phosphorus in the sample, the calculated analysis is off slightly from the experimental analysis.

Rhodium Metallomonomer (3)[6]: A slurry of bis(rhodium chloronorbornadiene) (90 mg, 0.196 mmol) in 5 mL of acetone was prepared. Addition of silver tetrafluoroborate (76.0 mg, 0.39 mmol) resulted in a yellow precipitate which was filtered off. A solution of the isopropenyl ligand (**2**) (218 mg, 0.389 mmol) was prepared in acetone and added dropwise to the yellow acetone solution of the rhodium cation, resulting in an orange-red solution. The solution was pumped down to dryness to give a brown-red solid. Recrystallization in CH_2Cl_2/Et_2O resulted in 233.7 mg of analytically pure material (71% yield). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 55.3 (d, $J_{P\text{-}Rh}$ = 157 Hz); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.62 (m, 8H), 7.49 (m, 8H), 5.51 (s, 4H), 5.37 (s, 4H), 5.25 (s, 4H), 4.20 (s, 2H), 2.32 (d, 4H, $J_{H\text{-}P}$ = 19 Hz), 2.18 (s, 12H), 1.85 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ 145.0, 142.5, 132.8, 128.9, 115.2, 91.2, 72.3, 56.3, 26.8, 26.5, 21.6; Anal. calcd. for $C_{45}H_{48}BF_4P_2Rh \cdot 1/4\ Et_2O$: C, 64.30%; H, 5.59%. Found: C, 63.98%; H, 5.69%.

[9] The synthesis of **2** was inspired by: Rabinovich, R.; Marcus, R. *J. Org. Chem.* **1961**, *26*, 4157-4158, and reference 2 therein.

***tert*-Butyl dppe:** This procedure is analogous to the synthesis of isopropenyl dppe. 4-Bromo-*tert*-butyl-benzene (10.0 mL, 57.7 mmol) in 5 mL THF was added dropwise to Mg shavings (1.41 g, 57.8 mmol). Reflux occurred due to the exothermic nature of the reaction. An additional 35 mL THF was added after all of the 4-bromo-*tert*-butyl-benzene had been added and the mixture was heated at reflux for 1.5 h until most of the Mg had reacted. The brown-green mixture was cooled to room temperature and placed in an ice bath. 1,2-Bis(dichlorophosphino)ethane (1.95 mL, 12.92 mmol) was added, producing a white precipitate. The reaction mixture was stirred for an additional 30 min. All solvents used in the workup were sparged with dinitrogen or argon for at least 20 min prior to use.

The mixture was poured into a solution of 3 M NH_4Cl and extracted three times with THF. The THF layers were washed with brine, dried over $MgSO_4$, and the solution removed i*n vacuo*. The solid was taken up in hexanes, filtered through Celite, and reduced i*n vacuo*. The crude solid was recrystallized from 95% ethanol (5.66, 70% yield). ^{31}P NMR (162 MHz, $CDCl_3$): δ –15.0; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 16H), 2.08 (t, 4H), 1.29 (s, 16H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 152.0, 135.0, 133.0, 126.0, 35.0, 31.5, 26.0, 24.4; Anal. calcd. for $C_{42}H_{56}P_2$: C, 80.99%; H, 9.06%. Found: C, 80.49%; H, 9.35%.

Precatalyst 5[6]: This procedure is analogous to the synthesis of the rhodium metallomonomer **1**, using the following stoichiometries: $[Rh(nbd)Cl]_2$ (96.6 mg, 0.21 mmol), *tert*-butyl dppe (262 mg, 0.421 mmol) and $AgBF_4$ (81.5 mg, 0.418 mmol). The orange solid was isolated in 61% yield (312 mg) after recrystallization. ^{31}P NMR (162 MHz, CD_2Cl_2): δ 54.29 (d, $J_{P\text{-}Rh}$ = 158 Hz); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.53 (m, 8H), 7.44 (m, 8H), 5.33 (s, 4H), 4.18 (s, 2H), 2.26 (d, 4H, $J_{H\text{-}P}$ = 19 Hz), 1.84 (s, 2H), 1.35 (s, 36H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ 155.8, 132.6, 127.0, 126.5, 90.5, 72.0, 56.2, 35.4, 31.2, 26.5. Anal. calcd. for $C_{42}H_{56}BF_4P_2Rh \cdot 1/4\ CH_2Cl_2$: C, 64.49%; H, 6.14%. Found: C, 64.07%; H, 6.51%.

P_{Rh}: Under a dinitrogen atmosphere, the rhodium metallomonomer **2** (153.1 mg, 0.178 mmol), AIBN (14.8 mg, 0.089 mmol), EGDMA (1.74 g), and DMF (1.79 g) were added to a 20 mL scintillation vial and sealed with a Teflon-lined cap. The vial was heated at 60°C for 24 h and the resulting insoluble orange polymer was rinsed with dichloromethane in a Soxhlet extractor for 12 h. Drying of the polymer at high vacuum (<1 mTorr) for 12 h gave 1.87 g of dried polymer. Anal. calcd for P_{Rh}: Rh, 0.93%; P, 0.56%. Found: Rh, 0.82%, P, 0.50%.

Typical Low Pressure Hydrogenation Experiment (<15psi): Under an inert atmosphere, substrate, solvent (reactions performed in 1-2 mL), and catalyst were loaded in a flask. A balloon filled with dihydrogen was placed overhead and bubbled through the solution in order to saturate the flask with dihydrogen. After bubbling, a new balloon of dihydrogen was placed overhead. Reactions were monitored by GC. After each GC aliquot was taken, dihydrogen was bubbled through the reaction mixture. After complete conversion to product, the polymer was filtered from the product solution and rinsed at least 3 times with solvent to remove any residual product within the polymer. Products were obtained by solvent removal *in vacuo*.

Typical High Pressure Hydrogenation Experiment (>15psi): Under an inert atmosphere, substrate, solvent (reactions performed in 1-2 mL), and catalyst were loaded into a 90 mL glass pressure reactor vessel (PRV). The PRV was charged and evacuated at least three times with dihydrogen to the desired pressure. Reactions were monitored by GC with aliquots taken by venting the PRV of dihydrogen and placing the vessel under dinitrogen or argon. Once the aliquot was taken, the PRV was refilled with dihydrogen, and venting the vessel with dihydrogen three times. Once complete, the polymer was filtered from the product and rinsed at least 3 times with solvent to remove any residual product within the polymer. Products were obtained by solvent removal *in vacuo*.

Typical Hydroboration Experiment: Experimental details of the hydroboration of styrene were followed by literature precedence with a few minor changes.[10] After aqueous workup, solvents were reduced *in vacuo*. In the case of the two rhodium solution catalysts, removal of the catalyst was performed after aqueous workup by running the product through a plug of silica with ethyl acetate. In the case of P_{Rh}, the catalyst was easily filtered from the reaction solution before the aqueous workup.

Typical Recycling Experiment: Upon full conversion to product, the solution was filtered from the polymer and the polymer was rinsed three to five times with dry solvent. New substrate and fresh solvent were added to the polymer to perform a new reaction. Care was taken to be sure the polymer was never exposed to the atmosphere.

Typical Leaching Experiment: Once the hydrogenation of MAC reached 50% conversion, the reaction solution was transferred via cannula from the polymer into a new reaction vessel. Stirring of the solution under a balloon of dihydrogen continued for one additional hour. GC analysis of the product solution after one hour revealed no additional product formation, indicating no catalytically active rhodium in the solution.

Methyl *N*-Carbomethoxyphenylalaninate: ^{1}H and ^{13}C NMR data match that as seen in the literature.[11]

2-((Methoxycarbonyl)amino)-3-phenylpropanoic Acid: : ^{1}H NMR data match that as seen in the literature.[12] ^{13}C NMR (76 MHz, $(CD_3)_2CO$): δ 172.5, 169.6, 137.7, 129.5, 128.4, 126.7, 53.7, 53.6, 37.5, 22.0, 21.9.

***N*-Propionyloxazolidin-2-one:** ^{1}H and ^{13}C NMR data match that observed in the literature.[13] GC conditions: HP-5 capillary; T = 150°C; 3-acryloyloxazolidin-2one, 2.86

[10] (a) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron: Asym.* **1991**, *2*, 601-612. (b) Doucet, H.; Fernandez, E.; Layzell, T. P.; Brown, J. M. *Chem. Eur. J.* **1999**, *5*, 1320-1330.

[11] (a) Versleijen, J. P.;Sanders-Hovens, M. S.; Vanhommerig, S. A.; Vekemans, J. A.; Meijer, E. M. *Tetrahedron* **1993**, *49*, 7793-7802. (b) Fadnavis, N. W.; Reddy, N. P.; Bhalerao, U. T. *J. Org. Chem.* **1989**, *54*, 3218-3221.

[12] Romero, A. G.; Darlington, W. H.; McMillan, M. W. *J. Org.Chem.* **1997**, *62*, 6582-6587.

[13] Bull, S. D.; Davies, S. G.; Jones, S.; Sanganee, H. J. *J. Chem. Soc., Perkin Trans. 1* **1999**, *4*, 387-398.

min; *N*-propionyloxazolidin-2-one, 2.79 min. Anal. calcd for $C_6H_9NO_3$: C, 50.36%; H, 6.34%; N, 9.79%. Found: C, 50.61%; H, 6.18%; N, 9.86%.

***exo-N*-(Norbornan-2-carboxy)oxazolidin-2-one:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.40 (m, 2H), 4.05 (m, 2H), 3.84 (m, 1H), 2.71 (br t, 1H), 2.30 (br t, 1H), 1.82 (m, 1H), 1.65-1.19 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 175.4, 153.6, 62.3, 46.1, 43.4, 42.0, 41.2, 37.6, 31.9, 29.5, 25.0. GC conditions: DB-1 capillary; T = 200°C; dienophile, 3.58 min; product, 3.83 min. Anal. calcd for $C_{11}H_{15}NO_3$: C, 63.16%; H, 7.18%; N, 6.70%. Found: C, 63.21%; H, 7.32%; N, 6.61%.

Methyl 3-Phenylpropanoate: ^{1}H and ^{13}C NMR data match that observed in the literature.[14] GC conditions: DB-1 capillary; T = 200°C; methyl cinnamate, 1.97 min; methyl 3-phenylpropanoate, 2.15 min.

α-Citronellol: ^{1}H and ^{13}C NMR data match that of authentic sample from Aldrich. GC conditions: DB-1 capillary; T = 150°C; geraniol, 2.63 min; α-citronellol, 2.47 min; 3,7-dimethyl-1-octanol, 2.35 min.

***trans*- and *cis*- 3-Methylcyclohexanol:** The ^{1}H NMR spectrum of a mixture of *cis* and *trans* 3-methylcyclohexanol is incorrectly assigned in the Aldrich Library of NMR Spectra. Correct assignments for the key carbinol proton are as follows: *cis* ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (m, 1H); ^{13}C NMR δ 67.1; *trans* ^{1}H NMR δ 3.52 (m, 1H); ^{13}C NMR δ 71.0.[15]

Mixture of 1-Phenylethanol and 2-Phenylethanol: ^{1}H and ^{13}C NMR data match that of authentic samples from Aldrich. GC conditions: DB-1 capillary; T = 75°C (5 min); 1-phenylethanol, 8.12 min; 2-phenylethanol, 6.03 min.

[14] Shipman, M; Thorpe, H. R.; Clemens, I. R. *Tetrahedron* **1998**, *54*, 14265-14282.
[15] ^{1}H NMR; Musher J. I *J. Chem. Phys.* **1961**, *35*, 1159-1168. ^{13}C NMR; Roberts, J. D.; Weigart, F. J.; Kroschwitz, J. I.; Reich, H. J. *J. Am. Chem. Soc.* **1970**, *92*, 1338-1347.