

Phosphine-Olefin Ligands: A Facile Dehydrogenative Route to Catalytically Active Rhodium Complexes

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Fig. S.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **(dppe)RhCl(P(C₅H₉)₃)Cl** and **1**.

Fig. S.2. ^1H and ^{31}P NMR spectra for **3**.

Fig. S.3. ^1H NMR spectra of **5** (298 K and 220 K).

Experimental details for compound synthesis, characterisation and catalytic studies.

Crystal structure data for **1**, **2** and **3**.

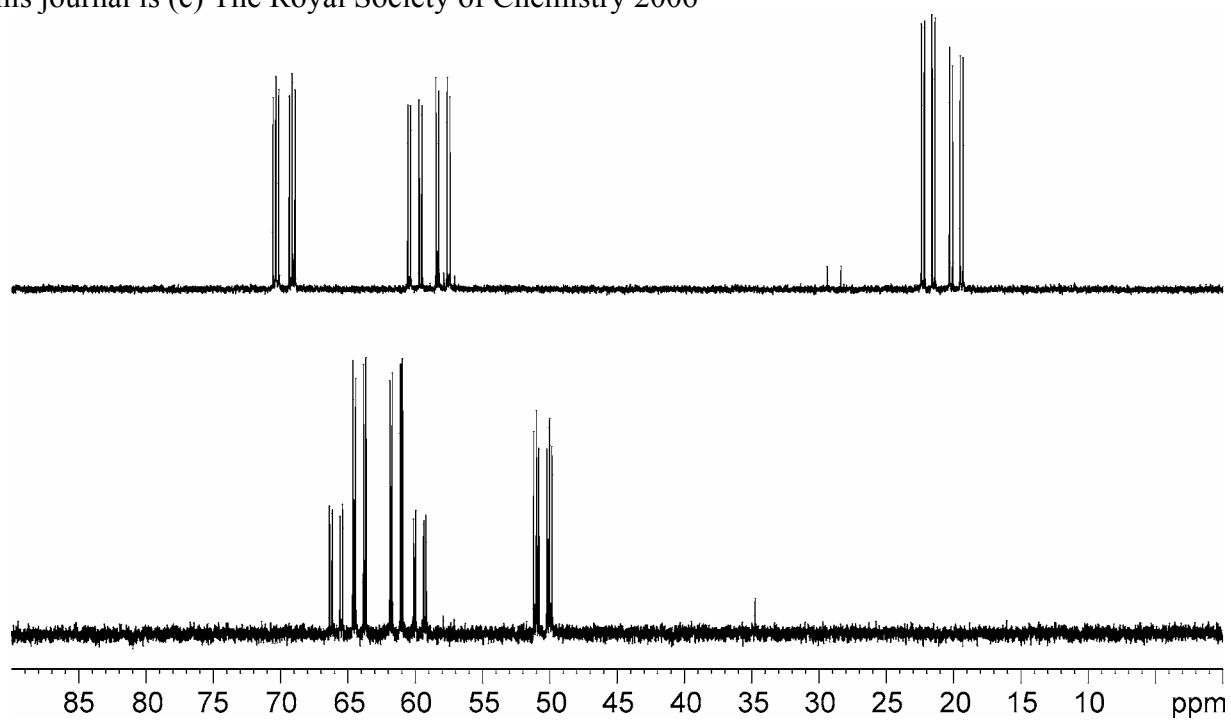


Fig. S.1 ^{13}P $\{^1\text{H}\}$ NMR spectra of $(\text{dppe})\text{Rh}(\text{P}(\text{C}_5\text{H}_9)_3)\text{Cl}$ (upper) and **1** (lower).

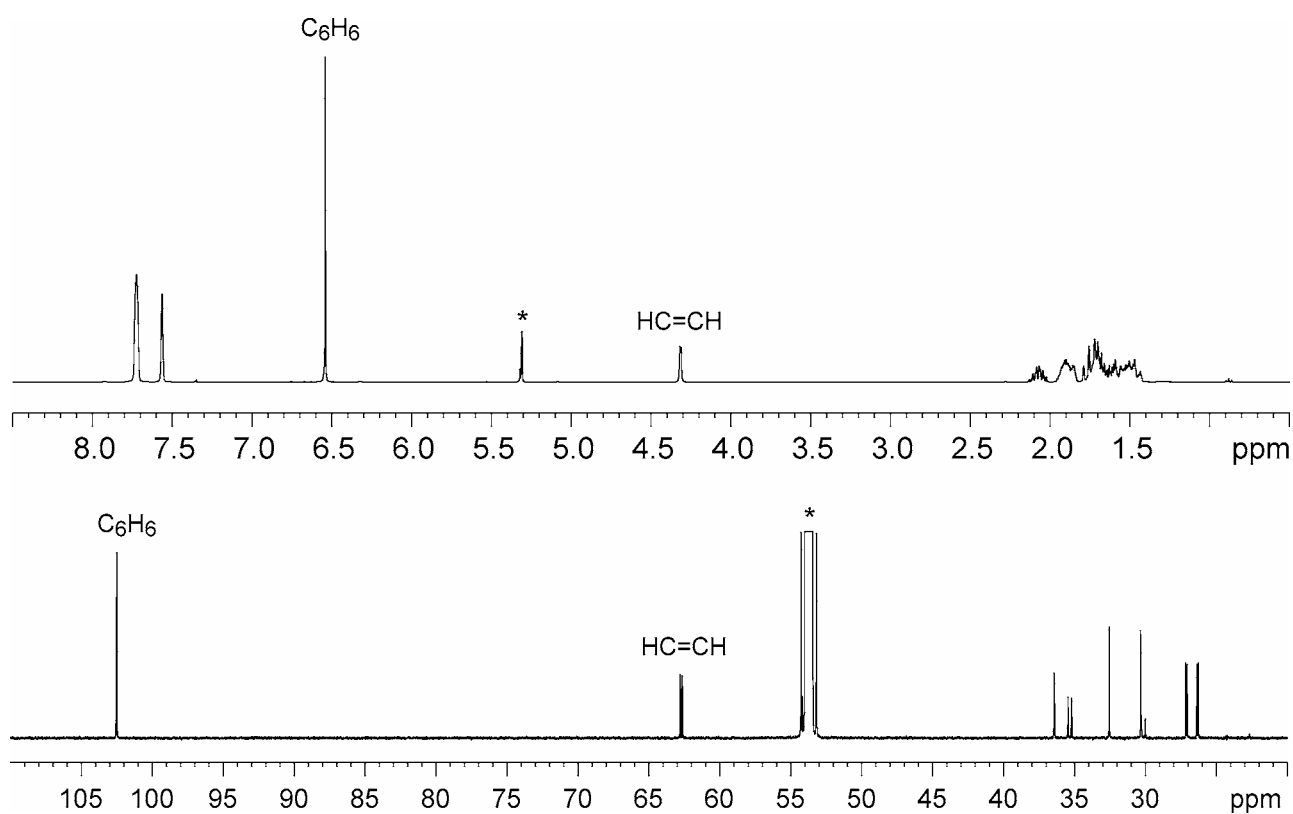
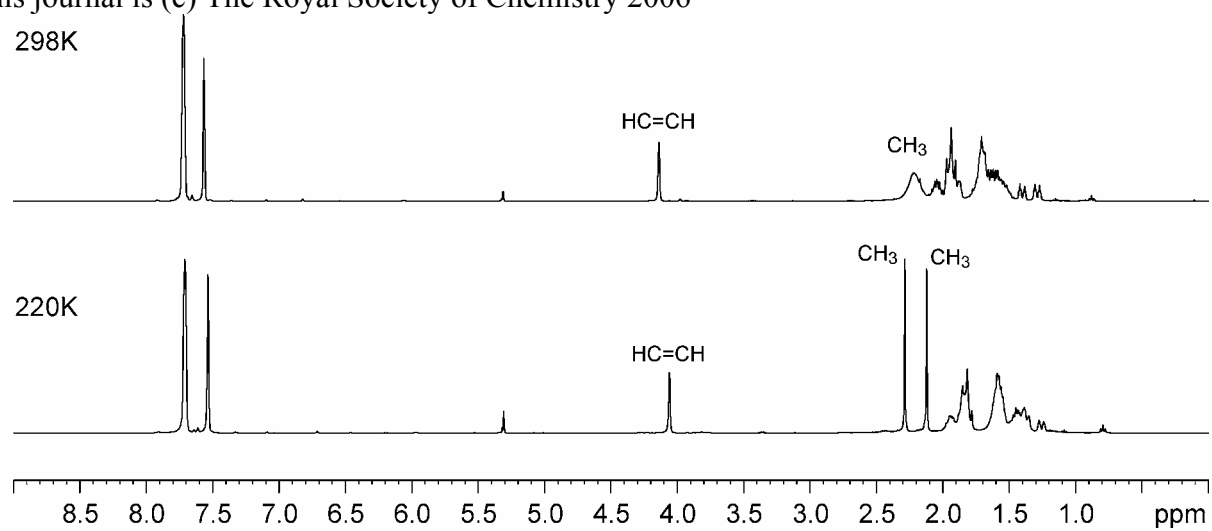


Fig. S.2 ^1H (upper) and ^{13}C $\{^1\text{H}\}$ (lower) NMR spectra of **3**.



^1H NMR spectra of **5** at 298K (upper) and 220K (lower).

General

All manipulations were carried out under an atmosphere of argon, using standard Schlenk line and glove box techniques, unless otherwise stated. Glassware was pre-dried in an oven at 130°C and flamed with a blowtorch under vacuum prior to use. Solvents were dried over activated alumina, copper or molecular sieve columns using a MBraun solvent purification system and stored under argon in ampoules equipped with Young's taps. CD₂Cl₂ and fluorobenzene was distilled under vacuum from CaH₂. Flash chromatography was carried out using Fisher silica 60A (35-70 micron). TLC was performed using Alugram® silica G/UV₂₅₄ coated plates. [Rh(nbd)Cl]₂¹ and Rh(nbd)(P(C₅H₉)₃)Cl² were prepared using literature methods. All other chemicals were used as received from Aldrich, Strem, Fisher Scientific (Acros), Lancaster. Microanalyses were performed by Elemental Microanalysis Ltd, Devon, UK.

NMR spectroscopy

¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectra were recorded on Brüker Avance 300MHz or 400MHz spectrometers. Residual protio solvent was used as reference for ¹H NMR spectra. ¹³C spectra were referenced to the perdeuterio-solvent resonance. ¹H and ¹³C spectra in C₆H₅F were referenced against the solvent signal which was in turn referenced to an external sample of tetramethylsilane. ³¹P{¹H} spectra were referenced against 85% H₃PO₄ (external). Values are quoted in ppm. Coupling constants are quoted in Hz.

X-Ray crystallography

Hemispheres of data for **1**, **2** and **3** were collected at 150K a Nonius KappaCCD diffractometer at 150 K, using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Data were processed using the supplied Nonius software. Structure solution, followed by full-matrix least squares refinement, was performed using the WinGX-1.70 suite of programs throughout. In each structure, several of the CF₃ groups in the anion were disordered in the ratios:

Rh(dppe)(P(C₅H₉)₃)Cl

A solution of 1,2-bis(diphenylphosphino)ethane (42.5 mg, 0.11 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a J.Youngs flask containing a stirred solution of Rh(NBD)(P(C₅H₉)₃)Cl (50 mg, 0.11mmol) in CH₂Cl₂ (5 mL). The resulting yellow solution was stirred for 30 minutes after which

the solvent was removed *in vacuo*. The residue was washed with pentane (5 mL) to give (dppe)Rh(P(C₅H₉)₃)Cl as a yellow powder (60 mg, 72%).

¹H NMR (400.13 MHz, CD₂Cl₂): δ 7.96-7.88 (m, 4H, ArH), 7.85-7.77 (m, 4H, ArH), 7.44-7.29 (m, 12H ArH), 2.2-1.2 (m, 31H, CH/CH₂).

³¹P{¹H} NMR (161.98 MHz, CD₂Cl₂): δ 69.80 [ddd, *J*(RhP) 196 Hz, *J*(PP) 36 Hz, *J*(PP) 33 Hz], 59.03 [ddd, *J*(PP) 338 Hz, *J*(RhP) 134, *J*(PP) 33 Hz], 20.87 [ddd, *J*(PP) 338 Hz, *J*(RhP) 128 Hz, *J*(PP) 36 Hz].

Microanalysis: C₄₁H₅₁ClP₃Rh·0.2 CH₂Cl₂ requires: C, 62.47; H, 6.54. Found: C, 62.45; H, 6.50.

[Rh(dppe)-η²-(P(C₅H₉)₂(C₅H₇))][BAr^F₄] (1)

A mixture of Rh(dppe)(P(C₅H₉)₃)Cl (30 mg, 3.87 x 10⁻² mmol) and Na(BAr^F₄) (34 mg, 3.87 x 10⁻² mmol) in CH₂Cl₂ (5 mL) was stirred for 15 minutes. The resulting orange mixture was filtered and the solvent was removed *in vacuo*. Diffusion of pentane into a solution of the residue in C₆H₅F gave **1** as orange crystals (38 mg, 61%).

¹H NMR (400.13 MHz, CD₂Cl₂): δ 7.72 (m, 8H, BAr^F₄), 7.55 (s, 4H, BAr^F₄), 7.70-7.45 (m, 20H, ArH), 4.89 (m, 2H, HC=CH), 2.2-1.2 (m, 27H, CH/CH₂).

³¹P{¹H} NMR (161.98 MHz, CD₂Cl₂): δ 65.03 [ddd, *J*(PP) 283 Hz, *J*(RhP) 125, *J*(PP) 31 Hz], 60.55 [ddd, *J*(PP) 283 Hz, *J*(RhP) 125 Hz, *J*(PP) 28 Hz], 50.53 [ddd, *J*(RhP) 158 Hz, *J*(PP) 31 Hz, *J*(PP) 28 Hz].

¹³C{¹H} NMR (100.61, CD₂Cl₂): δ 162.10 [q, *J*(BC) 50 Hz, BAr^F₄], 135.14 (s, BAr^F₄), 133.44 [d, *J*(PC) 12 Hz, Ar CH], 133.24 [d, *J*(PC) 11 Hz, Ar CH], 133.23 [d, *J*(PC) 41 Hz, Ar CH], 131.87 [d, *J*(PC) 11 Hz, Ar CH], 131.85 [d, *J*(PC) 11 Hz, Ar CH], 131.33 [dd, *J*(PC) 37 Hz, *J*(RhC) 3.5 Hz, Ar CH], 129.71 [d, *J*(PC) 9.3 Hz, Ar CH], 129.46 [d, *J*(PC) 10 Hz, Ar CH], [q, *J*(FC) 31 Hz, BAr^F₄], 124.94 [q, *J*(FC) 272 Hz, BAr^F₄], 117.79 (s, BAr^F₄), 96.21 [t, *J* 9.7 Hz, HC=CH], 37.75 [d, *J*(PC) 7.5 Hz, CH₂], 35.52 [d, *J*(PC) 19 Hz, CH], 31.27 (s, CH₂), 29.91 (s, CH₂), 29.48 [dd, *J*(PC) 19 Hz, *J*(RhC) 3.3 Hz, CH], 26.43 [d, *J*(PC) 7.9 Hz, CH₂], 25.60 [d, *J*(PC) 8.4 Hz, CH₂].

Microanalysis: C₇₁H₆₁BF₂₄P₃Rh requires: C, 54.77; H, 3.84. Found: C, 54.73; H, 3.78.

[Rh(C₆H₅F)-η²-(P(C₅H₉)₂(C₅H₇))][BAr^F₄] (2)

A mixture Rh(NBD)(P(C₅H₉)₃)Cl (50.0 mg, 0.11 mmol) and Na(BAr^F₄) (94.75 mg, 0.11 mmol) in C₆H₅F (5 mL) was stirred for 1 hour. The mixture was filtered and the solution was layered with pentanes. Slow diffusion gave **2** as pale yellow crystals (84 mg, 61%).

¹H NMR (400.13 MHz, C₆H₅F): δ 8.29 (s, 8H, BAr^F₄), 7.63 (s, 4H, BAr^F₄), 6.07 (m, 4H, ArH), 5.45 (m, 1H, *p*ArH), 3.89 [d, *J* 3.0 Hz, 2H, HC=CH], 1.70-1.05 (m, 23H, CH/CH₂).

$^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, $\text{C}_6\text{H}_5\text{F}$): δ 109.67 [dd, $J(\text{RhP})$ 178 Hz, $J(\text{FP})$ 3.9 Hz].

Selected $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61, $\text{C}_6\text{H}_5\text{F}$): δ 145.55 [dt, $J(\text{FC})$ 275 Hz, J 2.6 Hz, $\text{C}_5\text{H}_5\text{CF}$], 103.32 [ddd, $J(\text{FC})$ 7.1 Hz, J 2.7 Hz, J 1.5 Hz, $\text{C}_6\text{H}_5\text{F}$], 96.30 [ddd, J 3.7 Hz, J 2.7 Hz, J 1.1 Hz, $\text{C}_6\text{H}_5\text{F}$], 92.23 [dt, $J(\text{FC})$ 20 Hz, J 2.0 Hz, $\text{C}_6\text{H}_5\text{F}$], 65.04 [d, $J(\text{RhC})$ 16 Hz, $\text{HC}=\text{CH}$], 36.15 [d, $J(\text{PC})$ 3.7 Hz, CH_2], 35.20 [dd, $J(\text{PC})$ 26 Hz, $J(\text{RhC})$ 1.1 Hz, CH], 32.22 (s, CH_2), 30.08 [dd, $J(\text{PC})$ 29 Hz, $J(\text{RhC})$ 2.2 Hz, CH], 30.06 (s, CH_2), 27.23 [d, $J(\text{PC})$ 8.4 Hz, CH_2], 26.32 [d, $J(\text{PC})$ 9.3 Hz, CH_2].

$[\text{Rh}(\text{C}_6\text{H}_6)-\eta^2\text{-(P(C}_5\text{H}_9)_2(\text{C}_5\text{H}_7))][\text{BAr}^{\text{F}}_4]$ (3)

A mixture of benzene (0.2 ml, 2.9×10^{-3} mol), $\text{Rh}(\text{NBD})(\text{P}(\text{C}_5\text{H}_9)_3)\text{Cl}$ (20.0 mg, 4.2×10^{-2} mmol) and $\text{Na}(\text{BAr}^{\text{F}}_4)$ (37.9 mg, 4.2×10^{-2} mmol) in CH_2Cl_2 (5 mL) was stirred for 1 hour. The mixture was filtered and the solvent was removed *in vacuo*. Diffusion of pentane into a solution of the residue in CH_2Cl_2 gave **3** as pale yellow crystals (28 mg, 52%).

^1H NMR (400.13 MHz, CD_2Cl_2): δ 7.70 (s, 8H, BAr^{F}_4), 7.55 (s, 4H, BAr^{F}_4), 6.55 (s, 6H, C_6H_6), 4.30 (d, J 2.7 Hz, 2H, $\text{HC}=\text{CH}$), 2.15-1.35 (m, 23H, CH/CH_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CD_2Cl_2): δ 111.45 [d, $J(\text{RhP})$ 178 Hz].

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.61, CD_2Cl_2): δ 162.10 [q, $J(\text{BC})$ 50 Hz, BAr^{F}_4], 135.14 (s, BAr^{F}_4), 129.21 [qq, $J(\text{FC})$ 31 Hz, $J(\text{BC})$ 2.9 Hz, BAr^{F}_4], 124.94 [q, $J(\text{FC})$ 272 Hz, BAr^{F}_4], 117.81 (s, BAr^{F}_4), 102.53 (s, C_6H_6), 62.72 [d, $J(\text{RhC})$ 16 Hz, $\text{HC}=\text{CH}$], 36.44 [d, $J(\text{PC})$ 4.0 Hz, CH_2], 35.33 [d, $J(\text{PC})$ 26 Hz, PCH], 32.55 (s, CH_2), 30.33 (s, CH_2), 30.15 [dd, $J(\text{PC})$ 28 Hz, $J(\text{RhC})$ 2.2 Hz, PCH], 27.10 [d, $J(\text{PC})$ 8.8 Hz, CH_2], 26.32 [d, $J(\text{PC})$ 9.5 Hz, CH_2].

Microanalysis: $\text{C}_{53}\text{H}_{43}\text{BF}_{24}\text{PRh}$ requires: C, 49.71; H, 3.38. Found: C, 49.58; H, 3.34.

$[\text{Rh}-\eta^2\text{-(P(C}_5\text{H}_9)_2(\text{C}_5\text{H}_7))(\text{C}_4\text{H}_8\text{O})_2][\text{BAr}^{\text{F}}_4]$ (4)

A solution of $[\text{Rh}(\text{C}_6\text{H}_5\text{F})-\eta^2\text{-(P(C}_5\text{H}_9)_2(\text{C}_5\text{H}_7))][\text{BAr}^{\text{F}}_4]$ (30 mg, 2.3×10^{-5} mol) in THF (2 mL) was stirred for 1 hour. Diffusion of pentanes into the solution to gave **4** as yellow crystals (22 mg, 71%).

^1H NMR (400.13 MHz, $\text{D}^8\text{-THF}$): δ 7.79 (m, 8H, BAr^{F}_4), 7.57 (s, 4H, BAr^{F}_4), 3.66 (br s, 2H, $\text{HC}=\text{CH}$), 2.29-0.83 (m, 23H, CH/CH_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, $\text{D}^8\text{-THF}$): δ 102.95 [d, $J(\text{RhP})$ 196 Hz].

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.61, $\text{D}^8\text{-THF}$): δ 162.77 [q, $J(\text{BC})$ 50 Hz, BAr^{F}_4], 135.56 (s, BAr^{F}_4), 129.97 [qq, $J(\text{FC})$ 31 Hz, $J(\text{BC})$ 2.9 Hz, BAr^{F}_4], 125.48 [q, $J(\text{FC})$ 272 Hz, BAr^{F}_4], 118.13 (m, BAr^{F}_4), 63.80 [br d, $J(\text{RhC})$ 21 Hz, $\text{HC}=\text{CH}$], 36.95 [d, $J(\text{PC})$ 3.1 Hz, CH_2], 34.71 [d, $J(\text{PC})$ 25 Hz, CH], 32.25 (s,

CH₂), 31.59 [d, *J*(PC) 28 Hz, CH], 30.20 (s, CH₂), 27.66 [d, *J*(PC) 8.2 Hz, CH₂], 26.64 [d, *J*(PC) 8.8 Hz, CH₂].

[Rh- η^2 -(P(C₅H₉)₂(C₅H₇))(CH₃CN)₂][BAr^F₄] (5)

A solution of CH₃CN (25 μ L, 4.8 x 10⁻⁴ mol) and [Rh(C₆H₅F)- η^2 -(P(C₅H₉)₂(C₅H₇))][BAr^F₄] (30 mg, 2.3 x 10⁻⁵ mol) in C₆H₅F (2 mL) was stirred for 1 hour. The solution was layered with pentanes and left for 3 days, giving an orange oil. The oil was washed with pentane and dried *in vacuo* to give **5** as a yellow solid (27 mg, 91%).

¹H NMR (400.13 MHz, CD₂Cl₂, 220 K): δ 7.71 (s, 8H, BAr^F₄), 7.53 (s, 4H, BAr^F₄), 4.06 (s, 2H, HC=CH), 2.29 (s, 3H, CH₃), 2.12 (s, 3H, CH₃), 2.01-1.20 (m, 23H, CH/CH₂).

³¹P{¹H} NMR (161.98 MHz, CD₂Cl₂, 220 K): δ 93.33 [d, *J*(RhP) 163 Hz].

¹³C{¹H} NMR (100.61, CD₂Cl₂, 220 K): δ 161.36 [q, *J*(BC) 50 Hz, BAr^F₄], 134.24 (s, BAr^F₄), 128.22 [q, *J*(FC) 31 Hz, BAr^F₄], 124.03 [q, *J*(FC) 273 Hz, BAr^F₄], 123.17 (s, CN), 119.8 (d, *J* 5.5 Hz, CN), 117.15 (s, BAr^F₄), 73.43 [d, *J*(RhC) 16 Hz, HC=CH], 36.34 [d, *J*(PC) 3.7 Hz, CH₂], 31.42 (s, CH₂), 31.27 [d, *J*(PC) 26 Hz, CH], 28.56 [d, *J*(PC) 27 Hz, CH], 28.41 (s, CH₂), 26.01 [d, *J*(PC) 8.4 Hz, CH₂], 25.67 [d, *J*(PC) 9.5 Hz, CH₂], 3.40 (s, 2 x CH₃).

Procedure for the 1,4-addition of Phenylboronic acid to 2-cyclohexenone (I).³ To a solution of catalyst (**2**) (6.43 mg, 1 mol%) in THF (1 mL) and degassed water (0.1 mL) were added potassium hydroxide (2.8 mg, 10 mol%), 2-cyclohexenone (**I**) (0.048 mL, 0.5 mmol) and phenylboronic acid (122 mg, 1 mmol). The reaction mixture was heated for 16 h at 70°C. After cooling to room temperature the reaction was quenched with brine, extracted twice with EtOAc and the combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by silica gel chromatography using EtOAc/Petrol (1/10) as eluent to afford 3-phenylcyclohexanone (**II**)³ as a colorless oil (81 mg, 93%): **¹H NMR** (300 MHz, CDCl₃): δ 1.61-1.82 (m, 2 H), 1.96-2.17 (m, 2 H), 2.23-2.57 (m, 4 H), 2.85-3.03 (m, 1 H), 7.09-7.19 (m, 3 H), 7.21-7.30 (m, 2 H). **¹³C NMR** (75 MHz, CDCl₃): δ 25.5, 32.7, 41.1, 44.7, 48.9, 126.5, 126.6, 128.6, 144.3, 211.0.

General procedure for the preparation of Phenylzinc Chloride solution in tetrahydrofuran:⁴ *t*-*n*-BuLi (26.7 mL, 1.5 M solution in pentane, 40 mmol) was added dropwise to a solution of iodobenzene (2.24 mL, 20 mmol) in THF (40 mL) at -78 °C. The reaction mixture was stirred 30 min at -78 °C, and then 15 min at room temperature. The phenyllithium solution was then added to a solution of ZnCl₂ (42.0 mL, 0.5 M solution in tetrahydrofuran, 21 mmol) at 0 °C and the resulting

solution was stirred for 30 min, warmed to room temperature and stirred for a further 2 hours. The pale yellow solution was concentrated *in vacuo* to 40 mL to afford a 0.5 M solution of phenylzinc chloride in tetrahydrofuran.

General procedure for the 1,4-addition of Phenylzinc Chlorides.⁴ To a solution of catalyst (**2**) (6.43 mg, 1 mol%) in THF (1 mL) were added the enone (0.5 mmol), chlorotrimethylsilane (0.095 mL, 0.75 mmol) and phenylzinc chloride (1.5 mL, 0.5 M in tetrahydrofuran, 0.75 mmol) and the reaction mixture was stirred for 2 h. The reaction was quenched with brine, extracted twice with EtOAc and the combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude material was purified by silica gel chromatography using EtOAc/Petrol (1/10) as eluent to afford the 1,4-addition product.

3-Phenylcyclohexanone (II)³ (77.5 mg, 89%) was obtained as a colorless oil by following the general procedure described above with 2-cyclohexenone (**I**) (0.048 mL, 0.5 mmol).

Dimethyl 2-benzylsuccinate⁵ (111 mg, 94%) was obtained as a colorless oil by following the procedure described above with dimethyl itaconate (79 mg, 0.5 mmol). ¹H NMR (300 MHz, CDCl₃): δ 2.30 (dd, J = 5.0 Hz, 17.0 Hz, 1H), 2.51-2.72 (m, 2 H), 2.92-3.11 (m, 2 H), 3.53 (s, 3 H), 3.58 (s, 3H), 7.01-7.24 (m, 5 H). ¹³C NMR (75 MHz, CDCl₃): δ 34.8, 37.7, 43.0, 51.7, 51.9, 126.6, 128.5, 128.9, 138.1, 172.2, 174.6.

1,3,3-Triphenylpropan-1-one⁶ (89 mg, 85%) was obtained as a white powder by following the procedure described above with dimethyl itaconate (104 mg, 0.5 mmol). ¹H NMR (300 MHz, CDCl₃): δ 3.63 (d, J = 7.3 Hz, 2H), 4.72 (t, J = 7.3 Hz, 1H), 7.02-7.20(m, 10 H), 7.27-7.37 (m, 2 H), 7.39-7.50 (m, 1 H), 7.80-7.91 (m, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ 44.7, 45.9, 126.3, 127.8, 128.0, 128.2, 128.51, 128.54, 133.0, 137.0, 144.1, 198.0.

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