



Supporting Information

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Making the True “CP” ligand

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Part A: General techniques

All experiments were performed using standard Schlenk and vacuum line techniques or in a Braun glovebox under an inert atmosphere of Ar in 20-mL scintillation vials unless otherwise noted. Glassware was dried at 120 °C overnight prior to use. All reagents were used as received from commercial suppliers unless otherwise noted. THF, diethyl ether, hexane, and toluene were distilled from a sodium/benzophenone ketyl-tetraglyme mixture under Ar and stored over 3 Å molecular sieves prior to use. Dichloromethane and acetonitrile were distilled from CaH₂ under Ar prior to use and stored over 3 Å molecular sieves. Deuterated solvents were purchased from Euriso-top, degassed and distilled from the proper drying agent, and stored over 3 Å sieves. Silica gel, Alumina, and diatomaceous-earth (Celite) used for chromatography or filtrations were dried under vacuum at 240 °C for 2 days and stored in the glovebox.

All NMR spectra were recorded on Bruker Avance spectrometers. Chemical shifts (δ) are expressed in parts per million (ppm). ¹H NMR spectra were recorded at 500, 400, 300, or 250 MHz and chemical shifts were referenced to the residual protiated solvent peak. ¹³C NMR spectra are proton decoupled and were recorded at 75.5 MHz; chemical shifts were referenced to the solvent. ¹⁹F NMR spectra were recorded at 188 MHz and chemical shifts are

reported relative to an external standard of CFCl_3 . ^{31}P NMR spectra were recorded at 121.5 or 101.3; chemical shifts were referenced to an external standard of H_3PO_4 . Coupling constants J are given in Hertz [Hz] as absolute values, unless specifically stated. Where a first order analysis is appropriate, the multiplicity of the signals is indicated as s, d, t, q, qnt or m for singlets, doublets, triplets, quartets, quintets, or multiplets, unless otherwise specified. IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with KBr beam splitter (range $500 - 4000 \text{ cm}^{-1}$) using the ATR technique. The absorption bands are described as follows: very strong (vs), strong (s), medium (m), weak (w), or broad (br). Mass spectra were recorded on a Finnigan MAT SSQ 7000 mass spectrometer. Melting points were determined with a Büchi melting point apparatus and are not corrected. Samples were prepared in open glass capillaries.

NaOPh was synthesized from PhOH and Na in THF. The isolated salt was dried under vacuum at $200 \text{ }^\circ\text{C}$. $\text{Ph}_3\text{SiCH}_2\text{Cl}^{[1]}$ and $[\text{RuH}(\text{dppe})_2]\text{OTf}^{[2]}$ were prepared according to literature procedures.

Part B: Syntheses and spectroscopic data

$\text{Ph}_3\text{SiCH}_2\text{PCl}_2$ (2). A 250-mL Schlenk flask equipped with a stir bar was charged with freshly ground Mg turnings (10 g, 0.411 mol) and THF (50 mL). In a separate Schlenk flask $\text{Ph}_3\text{SiCH}_2\text{Cl}^{[1]}$ (13.0 g, 0.042 mol) was dissolved in THF (50 mL). The alkyl chloride was slowly added to the Mg turnings in 10-mL portions over 1h, at which time the Grignard initiated. An additional 50 mL

of THF was used to rinse the remaining alkyl chloride into the reaction mixture. The Grignard was mixed for 3h and then transferred via cannula to a solution of PCl_3 (11 mL, 0.126 mol) in THF (100 mL) cooled to $-78\text{ }^\circ\text{C}$. The mixture was stirred and allowed to warm to room temperature over 18h. After removal of the volatile materials the gray solid was extracted with toluene (ca. 200 mL) and filtered through diatomaceous earth on a medium-pore fitted glass filter frit. The volatile materials were removed under reduced pressure to furnish a white solid. Crystallization from THF/hexane at $-30\text{ }^\circ\text{C}$ afforded analytically pure material. Yield 13.8 g (87.6%). M.p. $96 - 97\text{ }^\circ\text{C}$. ^1H NMR (300 MHz, C_6D_6 , $23\text{ }^\circ\text{C}$): d 7.46 (m, 5H), 7.14 (m, 10H), 2.60 (d, $^2J_{\text{H-P}} = 14.3$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6 , $23\text{ }^\circ\text{C}$): d 136.2 (d, $J_{\text{C-P}} = 2.0$ Hz), 133.1 (d, $J_{\text{C-P}} = 2.7$ Hz), 130.4, 32.5 (d, $J_{\text{C-P}} = 64.6$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6 , $23\text{ }^\circ\text{C}$): d 199.7. IR (Solid ATR): 3055 (w), 3019 (w), 1491 (s), 1444 (s), 1406 (m), 1189 (m), 1158 (m), 1112 (m), 1033 (m), 1001 (m), 789 (m), 768 (s), 752 (s), 692 (vs). Anal. Calcd. for $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{PSi}$: C, 60.80; H, 4.57. Found: C, 60.72; H, 4.70. EI HRMS: m/z calc. for $\text{C}_{19}\text{H}_{16}\text{Cl}_2\text{PSi}$ 373.01305 $[\text{M-H}]^+$, found 373.0132.

$\text{Ph}_3\text{Si-C=P}$ (3). A 20-mL scintillation vial equipped with a stir bar was charged with $\text{Ph}_3\text{SiCH}_2\text{PCl}_2$ (**2**) (0.375 g, 1.00 mmol), AgOTf (0.564 g, 2.20 mmol), and toluene (18 mL). The suspension was protected from light and vigorously stirred. After 5 min DABCO (0.248 g, 2.20 mmol) was added to the vial and the stirring was continued. After an additional 60 min. the mixture was filtered through a pad of diatomaceous earth on a medium-pore fitted glass filter frit eluting with toluene (ca. 10 mL). The resulting yellow solution was used immediately. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, Et_2O , $23\text{ }^\circ\text{C}$): d 193.3 (d, $^1J_{\text{C-P}} = 16.4$

Hz), 135.7, 133.4 (d, $^3J_{C-P} = 3.1$ Hz), 130.1, 128.2. $^{31}P\{^1H\}$ NMR (121.5 MHz, Et₂O, 23 °C): d 111.3.

[RuH(dppe)₂(Ph₃SiC=P)]OTf (4). A 250-mL Schlenk flask equipped with a stir bar was charged with [RuH(dppe)₂]OTf^[2] (0.524 g, 0.500 mmol) and CH₂Cl₂ (80 mL). The silyl substituted phosphalkyne **3** (1.0 mmol, 2 equiv) synthesized above was added via cannula transfer resulting in a red to light orange color change. After 1h the solution was concentrated to ca. 40 mL under reduced pressure resulting in copious amounts of white precipitate. The suspension was mixed for 2h then allowed to settle. The mother liquor was removed via cannula filtration and the faint yellow solid washed with diethyl ether (3 x 10 mL). Excess solvent was removed under reduced pressure to furnish a white solid. Yield 0.576 g (84.5%). Crystals suitable for X-ray analysis were grown from a solution of **3** in CH₂Cl₂ layered with hexane at room temperature. Analytically pure material was obtained via crystallization from THF/toluene. M.p. 185 °C (dec). 1H NMR (300 MHz, [d₈]THF, 23 °C): d 7.48 (m, 11H), 7.40 (m, 19H), 7.22 (9H), 7.10 (m, 8H), 7.00 (t, $J_{H-H} = 7.5$ Hz, 8H), 2.76 (br, 4H), 2.42 (br, 4H), -8.13 (dqnt, $trans\text{-}^2J_{P-H} = 122.1$ Hz, $cis\text{-}^2J_{P-H} = 17.0$ Hz, 1H). $^{13}C\{^1H\}$ NMR (75.5 MHz, [d₈]THF, 23 °C): d 175.1 (d, $^1J_{C-P} = 71.4$ Hz), 135.5, 135.1 (m), 134.7 (br), 133.3, 132.8 (m), 132.6, 130.1, 130.1, 129.5, 128.5, 128.2, 127.6, 31.9 (m, $^1J_{C-P} \sim 12$ Hz). ^{19}F NMR (188 MHz, [d₈]THF, 23 °C): d -78.4. $^{31}P\{^1H\}$ NMR (121.5 MHz, [d₈]THF, 23 °C): d 143.8 (qnt, $^2J_{P-P} = 27.8$ Hz, 1P), 60.1 (d, $^2J_{P-P} = 27.3$ Hz, 4P). IR (Solid ATR): 3053 (w), 1586 (w), 1571 (w), 1484 (m), 1434 (s), 1266 (vs), 1223 (m), 1146 (s), 1092 (s), 1030 (s), 1000 (m), 879 (m), 827 (m), 742 (s),

692 (vs), 674 (s), 636 (s). Anal. Calcd. for $C_{78}H_{76}F_3O_{4.5}P_5RuSSi$ (1.5 equiv THF): C, 64.23; H, 5.25. Found: C, 64.44; H, 5.29.

$RuH(dppe)_2(C=P)$ (5). A 20-mL vial equipped with a stir bar was charged with **4** (0.270 g, 0.20 mmol) and THF (18 mL). After stirring for 5 min the solid dissolved. The solution was then cooled to $-30\text{ }^\circ\text{C}$ and NaOPh (0.032 g, 0.276 mmol) in THF (2 mL) was added. The solution was warmed to $23\text{ }^\circ\text{C}$ over 30 min. After mixing for 14h the yellow-orange solution was filtered through a pad of silica gel eluting with THF (5 mL). After removal of the volatile materials, the solid was washed with CH_3CN (2 x 10 mL) then re-dissolved in THF (ca. 15 mL) and filtered through diatomaceous earth in a Pasteur filter pipette. Excess solvent was removed under reduced pressure to furnish a yellow solid. Yield: 0.135 g (71.8%) By NMR spectroscopy this product was >95% pure. Crystallization from THF/hexane furnished analytically pure material also suitable for X-ray analysis (0.60 g, 31.9%). M. p. $>198\text{ }^\circ\text{C}$ (dec). 1H NMR (300MHz, $[d_8]$ THF, $23\text{ }^\circ\text{C}$): δ 7.49 (br, 8H), 7.42 (br, 8H), 7.17 – 7.07 (m, 10H), 6.99 (m, 14H), 2.04 (br, 4H), 1.97 (br, 4H), – 11.22 (dqnt, $cis\text{-}^2J_{H-P} = 20.7\text{ Hz}$, $trans\text{-}^3J_{H-P} = 20.4\text{ Hz}$, 1H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $[d_8]$ THF, $23\text{ }^\circ\text{C}$): δ 287.1 (m), 139.2 (m), 136.4 (m), 134.2 (br), 133.5 (d, $J_{C-P} = 2.9\text{ Hz}$), 128.3, 128.3, 126.8 (d, $J_{C-P} = 2.1\text{ Hz}$), 126.4 (d, $J_{C-P} = 2.1\text{ Hz}$), 32.4 (m, $J_{C-P} \sim 13\text{ Hz}$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $[d_8]$ THF, $23\text{ }^\circ\text{C}$): δ 165.0 (br, 1H), 65.2 (br, 4P). IR (Solid ATR): 3053 (w), 1485 (m), 1432 (s), 1307 (w), 1263 (w), 1229 (s), 1187 (w), 1154 (w), 1089 (s), 1028 (w), 1001 (w), 884 (m), 823 (s), 738 (s), 691 (vs), 672 (s), 652 (s). Raman: 3052 (s), 1885 (w, Ru-H), 1585 (m), 1570 (m), 1228 (vs, C=P), 1096 (m), 1028 (m), 999 (m). Anal. Calcd. for $C_{53}H_{49}P_5Ru$: C, 67.58; H, 5.24. Found: C, 67.43; H, 5.42.

[1] J. J. Eisch, C. C. S. Chiu, *Heteroat. Chem.* **1994**, 5, 265.

[2] $[\text{RuH}(\text{dppe})_2][\text{OTf}]$ was made via anion metathesis of $[\text{RuH}(\text{dppe})_2][\text{BF}_4]$ in THF using KOTf (1.2 mol eq.) followed by filtration through Celite to remove the precipitated KBF_4 ; for $[\text{RuH}(\text{dppe})_2][\text{BF}_4]$ see: S.P. Nolan, T.R. Belderrain, R. H. Grubbs, *Organometallics* **1997**, 16, 5569.