

# SUPPORTING INFORMATION FOR

Rhenium-Containing Phosphorus Donor Ligands for Palladium-Catalyzed Suzuki  
Cross-Coupling Reactions; A New Strategy for High-Activity Systems

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**Additional General Data.** Solvents were freshly dried before use: ether, THF, pentane and toluene, distilled from sodium/benzophenone; benzene (99.5%, Grüssing) and CH<sub>2</sub>Cl<sub>2</sub>, distilled from CaH<sub>2</sub>; chlorobenzene, distilled from P<sub>2</sub>O<sub>5</sub>; CD<sub>2</sub>Cl<sub>2</sub> (99.6%, Deutero GmbH), CDCl<sub>3</sub> (99.8%, Deutero GmbH), stored over molecular sieves; C<sub>6</sub>D<sub>6</sub> (99.5%, Deutero GmbH) freeze-pump-thaw degassed and stored over molecular sieves.

The following materials were used as received: TfOH (99%, Acros), HBF<sub>4</sub> (7.4 M in ether), P(*t*-Bu)<sub>2</sub>H (97%, Fluka), PPh<sub>2</sub>H (99%, Strem), Ph<sub>3</sub>C<sup>+</sup> PF<sub>6</sub><sup>-</sup> (≥95.0%, Fluka; see however note in text), Ph<sub>3</sub>C<sup>+</sup> BF<sub>4</sub><sup>-</sup> (>98%, Fluka; see however note in text), *t*-BuOK (1.0 M in THF, Aldrich), phenylboronic acid (97%, Aldrich), K<sub>3</sub>PO<sub>4</sub> (97%, Aldrich), Pd(OAc)<sub>2</sub> (99%, Lancaster), bromobenzene (99%, Aldrich), tridecane (99%, Aldrich), biphenyl (99%, Aldrich), PPh<sub>3</sub> (99%, Acros), P(*t*-Bu)<sub>3</sub> (99%, Strem), 4-bromoacetophenone (98%, Aldrich), hexadecane (99%, Aldrich), 4-acetylbiphenyl (99%, Aldrich), 4-bromotoluene (98%, Aldrich), 4-methylbiphenyl (98%, Aldrich), 4-bromoanisole (99%, Aldrich), 4-methoxybiphenyl (97%, Aldrich), 6-methoxy-2-bromonaphthalene (97%, Aldrich), NaOH (99%, Grüssing), MgSO<sub>4</sub> (≥98%, Riedel-de Haën), eicosane (99%, Aldrich), 4-chloroacetophenone (97%, Aldrich), Pd<sub>2</sub>(dba)<sub>3</sub> (ABCR), KF (98%, Aldrich), *N*-benzylbenzamide (99%, Lancaster), P(*t*-Bu)<sub>2</sub>Cl (96% or 98%, Acros), silica gel 60M (Macherey-Nagel), Celite®535 (Fluka).

$[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{P}(\textit{t}\text{-Bu})_2\text{H})]^+ \text{TfO}^-$  (**2b**).<sup>7,20</sup> A Schlenk flask was charged with **1** (4.033 g, 7.219 mmol)<sup>19,35</sup> and dry degassed CH<sub>2</sub>Cl<sub>2</sub> (100 mL), and cooled to 0 °C. Then TfOH (0.94 mL, 1.6 g, 11 mmol) was slowly added with stirring. After 20 min, the mixture was filtered through a medium frit containing 1 cm of silica gel. The silica gel was eluted with dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and then dry CH<sub>2</sub>Cl<sub>2</sub>/acetone (95:5 v/v; 50 mL). Solvent was removed from the eluate via oil pump vacuum. The red powder was dissolved in dry benzene (150 mL), and P(*t*-Bu)<sub>2</sub>H (4.00 mL, 3.16 g, 21.6 mmol) was added with stirring. The red solution was refluxed for 24 h. The precipitate was collected by filtration (medium frit), washed with benzene, and dried by oil pump vacuum to give **2b** (3.369 g, 4.016 mmol, 56%) as a yellow powder, M.p. 166-169 °C.

IR (thin film, cm<sup>-1</sup>):  $\tilde{\nu}$  = 2436 (w, PH), 1698 (s, NO), 1266 (vs, CF); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): PPh<sub>3</sub> at  $\delta$  = 7.49-7.48 (m, 9H), 7.22-7.18 (m, 6H); 5.70 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.31 (dd, 1H,

$^1J(\text{H,P}) = 356.8$  Hz,  $^3J(\text{H,P}) = 3.6$  Hz, PH), 1.25 (d, 9H,  $^3J(\text{H,P}) = 15.2$  Hz, CH<sub>3</sub>), 1.08 (d, 9H,  $^3J(\text{H,P}) = 15.2$  Hz, C'H<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz, CDCl<sub>3</sub>): PPh<sub>3</sub> at  $\delta = 133.2$  (d,  $^2J(\text{C,P}) = 10.2$  Hz, o), 132.1 (d,  $^1J(\text{C,P}) = 55.4$  Hz, i), 131.6 (d,  $^4J(\text{C,P}) = 1.8$  Hz, p), 129.2 (d,  $^3J(\text{C,P}) = 11.1$  Hz, m); 120.4 (q,  $^1J(\text{C,F}) = 259.6$  Hz, CF<sub>3</sub>), 91.1 (s, C<sub>5</sub>H<sub>5</sub>), 39.4 (d,  $^1J(\text{C,P}) = 28.6$  Hz, PC), 35.5 (d,  $^1J(\text{C,P}) = 23.1$  Hz, PC'), 32.1 (d,  $^2J(\text{C,P}) = 3.7$  Hz, CH<sub>3</sub>), 31.1 (d,  $^2J(\text{C,P}) = 2.7$  Hz, C'H<sub>3</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.8 MHz, CDCl<sub>3</sub>):  $\delta = 41.0$  (br s, P(*t*-Bu)<sub>2</sub>H), 8.0 (d,  $^2J(\text{P,P}) = 11.3$  Hz, PPh<sub>3</sub>).

**( $\eta^5\text{-C}_5\text{H}_5$ )Re(NO)(PPh<sub>3</sub>)(PPh<sub>2</sub>) (3a).**<sup>7,20,S1</sup> An oven-dried Schlenk flask was charged with **2a** (1.582 g, 1.800 mmol) and dry THF (70 mL). Then *t*-BuOK (1.0 M in THF; 2.2 mL, 2.2 mmol) was added by syringe with stirring. The yellow suspension turned deep red. After 3 h, the mixture was filtered. The frit was rinsed with dry THF (2 × 10 mL). The combined filtrates were concentrated in vacuo to *ca.* 10 mL. Dry ether (40 mL) was added. The precipitate was collected by filtration and dried by oil pump vacuum to give **3a** (1.122 g, 1.540 mmol, 86%) as an orange-red powder.

$^1\text{H}$  NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): PPh<sub>3</sub> and PPh<sub>2</sub> at  $\delta = 7.57\text{--}6.98$  (m, 25H); 5.14 (s, 5H, C<sub>5</sub>H<sub>5</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz, C<sub>6</sub>D<sub>6</sub>): PPh<sub>3</sub> at  $\delta = 134.9$  (d,  $^1J(\text{C,P}) = 50.7$  Hz, i), 134.3 (d,  $^2J(\text{C,P}) = 10.2$  Hz, o), 130.6 (s, p), 128.8 (d,  $^3J(\text{C,P}) = 10.2$  Hz, m), PPhPh<sup>S2</sup> at 132.8 (d,  $^2J(\text{C,P}) = 9.1$  Hz, o), 132.1 (d,  $^2J(\text{C,P}) = 9.2$  Hz, o'), 130.1 (s, p), 129.7 (s, p'); 90.9 (s, C<sub>5</sub>H<sub>5</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.8 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 20.3$  (d,  $^3J(\text{P,P}) = 16.3$  Hz, PPh<sub>3</sub>),  $-44.6$  (d,  $^3J(\text{P,P}) = 16.3$  Hz, PPh<sub>2</sub>).

**( $\eta^5\text{-C}_5\text{H}_5$ )Re(NO)(PPh<sub>3</sub>)(P(*t*-Bu)<sub>2</sub>) (3b).**<sup>7,20</sup> An oven-dried Schlenk flask was charged with **2b** (0.839 g, 1.00 mmol) and dry THF (50 mL). Then *t*-BuOK (1.0 M in THF; 1.2 mL, 1.2 mmol) was added by syringe with stirring. The yellow-orange suspension turned deep red. After 30 min, all volatiles were removed by oil pump vacuum. Dry benzene (20 mL) was added, and the mixture was filtered through a medium frit containing degassed Celite (4 × 2 cm, oven-dried at 120 °C, cooled to room temperature under vacuum, and washed with dry benzene (10 mL)). The Celite was rinsed with dry benzene (3 × 5 mL). Solvent was removed from the combined filtrates by oil pump vacuum to give **3b** (0.635 g, 0.922 mmol, 92%) as a red-brown powder.

$^1\text{H}$  NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): PPh<sub>3</sub> at  $\delta = 7.63\text{--}6.59$  (m, 6H), 7.10–6.97 (m, 9H); 4.91 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 1.34 (d, 9H,  $^3J(\text{H,P}) = 9.2$  Hz, CH<sub>3</sub>), 1.31 (d, 9H,  $^3J(\text{H,P}) = 9.2$  Hz, CH'<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR

(100.5 MHz, C<sub>6</sub>D<sub>6</sub>): PPh<sub>3</sub> at  $\delta$  = 136.9 (d,  $^1J(\text{C,P})$  = 50.7 Hz, i), 134.5 (d,  $^2J(\text{C,P})$  = 9.7 Hz, o), 130.0 (d,  $^4J(\text{C,P})$  = 1.9 Hz, p), 128.5<sup>S3</sup> (d, m); 88.1 (s, C<sub>5</sub>H<sub>5</sub>), 35.2 (d,  $^2J(\text{C,P})$  = 14.8 Hz, CH<sub>3</sub>);<sup>S4</sup>  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.8 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 20.6 (d,  $^2J(\text{P,P})$  = 13.3 Hz, PPh<sub>3</sub>), 10.5 (d,  $^2J(\text{P,P})$  = 12.3 Hz, P(*t*-Bu)<sub>2</sub>).

$[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{P}(\text{t-Bu})_2\text{H})]^+ \text{PF}_6^-$  (**4b** with an alternative counter-anion).<sup>20</sup> A Schlenk flask was charged with **1** (4.500 g, 8.055 mmol)<sup>19,35</sup> and dry CH<sub>2</sub>Cl<sub>2</sub> (200 mL), and cooled to -60 °C. Then Ph<sub>3</sub>C<sup>+</sup> PF<sub>6</sub><sup>-</sup> (3.441 g, 8.862 mmol) was added with stirring. Within 30 min, the orange suspension became light yellow. Then P(*t*-Bu)<sub>2</sub>H (1.79 mL, 1.41 g, 9.64 mmol) was added dropwise with stirring. The cold bath was removed, and the mixture turned red. After 1 h, the sample was concentrated to *ca.* 50 mL by oil pump vacuum. Dry pentane (150 mL) was added. After 3 h, the precipitate was collected by filtration, washed with dry pentane (2 × 25 mL), and dried by oil pump vacuum to give  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{P}(\text{t-Bu})_2\text{H})]^+ \text{PF}_6^-$  (6.510 g, 7.670 mmol, 95%) as an orange powder, M.p. 192-193 °C dec; calcd (%) for C<sub>32</sub>H<sub>41</sub>F<sub>6</sub>NOP<sub>3</sub>Re (848.80): C 45.28, H 4.87, N 1.65; found C 44.97, H 4.95, N 1.60.

IR (thin film, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1652 (m, NO), 834 (vs, PF<sub>6</sub>);  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>): PPh<sub>3</sub> at  $\delta$  = 7.45 (m, 9H), 7.33-7.28 (m, 6H); 5.55 (dd, 1H,  $^1J(\text{H,P})$  = 451.0 Hz,  $^3J(\text{H,H})$  = 8.2 Hz, PH), 5.18 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 1.70-1.55 (m, 2H, CHH'), 1.30 (d, 9H,  $^3J(\text{H,P})$  = 14.9 Hz, CH<sub>3</sub>), 1.28 (d, 9H,  $^3J(\text{H,P})$  = 15.3 Hz, CH'<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz, CDCl<sub>3</sub>): PPh<sub>3</sub> at  $\delta$  = 134.0 (d,  $^1J(\text{C,P})$  = 53.6 Hz, i), 133.4 (d,  $^2J(\text{C,P})$  = 10.2 Hz, o), 131.0 (d,  $^4J(\text{C,P})$  = 2.7 Hz p), 129.0 (d,  $^3J(\text{C,P})$  = 10.2 Hz, m); 91.1 (s, C<sub>5</sub>H<sub>5</sub>), 33.6 (d,  $^1J(\text{C,P})$  = 32.4 Hz, PC), 32.4 (d,  $^1J(\text{C,P})$  = 36.0 Hz, PC'), 28.3 (s, CH<sub>3</sub>), 27.4 (s, C'H<sub>3</sub>), -44.5 (d,  $^1J(\text{C,P})$  = 24.8 Hz, CH<sub>2</sub>);  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.8 MHz, CDCl<sub>3</sub>):  $\delta$  = 75.0 (d,  $^3J(\text{P,P})$  = 17.8 Hz, P(*t*-Bu)<sub>2</sub>H), 20.0 (d,  $^3J(\text{P,P})$  = 22.2 Hz, PPh<sub>3</sub>), -142.8 (sep,  $^1J(\text{P,F})$  = 709.6 Hz, PF<sub>6</sub>).

$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{PPh}_2)$  (**5a**).<sup>18a,20</sup> An oven-dried Schlenk flask was charged with **4a** (1.333 g, 1.500 mmol) and dry THF (50 mL). Then *t*-BuOK (1.0 M in THF; 1.8 mL, 1.8 mmol) was added with stirring. After 1 h, the solvent was removed by oil pump vacuum. Dry benzene (20 mL) was added. The mixture was filtered through a Celite plug (4 × 2 cm, oven-dried at 120 °C, cooled to room temperature under vacuum, and washed with dry benzene (10 mL)). The

Celite was rinsed with dry benzene (3 × 10 mL). The combined filtrates were concentrated to *ca.* 10 mL, and layered with dry pentane (40 mL). After 18 h, the supernatant was decanted from a precipitate, which was dried by oil pump vacuum to give **5a** (1.045 g, 1.407 mmol, 94%) as an orange powder.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): PPh<sub>3</sub> and PPh<sub>2</sub> at δ = 7.83-7.79, 7.71-7.68, 7.54-7.50, 7.25-6.95 (m, 25H); 4.49 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 2.82 (m, 1H, CHH'), 2.07 (dd, 1H, <sup>2</sup>J(H',P) = 2.4 Hz, <sup>2</sup>J(H',H) = 11.6 Hz, CHH'); <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, C<sub>6</sub>D<sub>6</sub>): PPh<sub>3</sub> at δ = 136.5 (d, <sup>1</sup>J(C,P) = 50.8 Hz, i), 134.0 (d, <sup>2</sup>J(C,P) = 11.1 Hz, o), 130.1 (d, <sup>4</sup>J(C,P) = 2.8 Hz, p), 128.5 (d, <sup>3</sup>J(C,P) = 9.2 Hz, m); PPhPh' at 147.7 (d, <sup>1</sup>J(C,P) = 21.3 Hz, i), 146.9 (d, <sup>1</sup>J(C,P) = 20.3 Hz, i'), 133.8 (d, <sup>2</sup>J(C,P) = 18.5 Hz, o), 133.0 (d, <sup>2</sup>J(C,P) = 17.5 Hz, o'), 127.7 (s, p), 127.2 (s, p'); <sup>89.9</sup> (s, C<sub>5</sub>H<sub>5</sub>), -18.7 (dd, <sup>1</sup>J(C,P) = 37.4 Hz, <sup>2</sup>J(C,P) = 5.1 Hz, CH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 27.2 (d, <sup>3</sup>J(P,P) = 7.1 Hz, PPh<sub>3</sub>), 8.6 (d, <sup>3</sup>J(P,P) = 6.1 Hz, PPh<sub>2</sub>).

( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>2</sub>P(*t*-Bu)<sub>2</sub>) (**5b**).<sup>S6</sup> An oven-dried Schlenk flask was charged with [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(NO)(PPh<sub>3</sub>)(CH<sub>2</sub>P(*t*-Bu)<sub>2</sub>H)]<sup>+</sup> PF<sub>6</sub><sup>-</sup> (1.273 g, 1.500 mmol) and dry THF (50 mL). Then *t*-BuOK (1.0 M in THF; 1.8 mL, 1.8 mmol) was added with stirring. The orange mixture turned red. After 1 h, the THF was removed by oil pump vacuum. Dry benzene (20 mL) was added. The mixture was filtered through a Celite plug (4 × 2 cm, oven-dried at 120 °C, cooled to room temperature under vacuum, and washed with dry benzene (15 mL)). The Celite was rinsed with dry benzene (15 mL). The combined filtrates were concentrated to *ca.* 5 mL, and layered with dry pentane (30 mL). After 18 h, the supernatant was decanted from a precipitate, which was dried by oil vacuum to give **5b** (0.889 g, 1.26 mmol, 84%) as an orange powder, M.p. 196-198 °C dec.

IR (thin film, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1637 (s, NO); <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): PPh<sub>3</sub> at δ = 7.56-7.44 (m, 6H), 7.05-6.96 (m, 9H); 4.92 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 1.90-1.85 (dd, <sup>2</sup>J(H,P) = 14.0 Hz, <sup>3</sup>J(H,P) = 4.4 Hz, 1H, CHH'), 1.65-1.63 (m, 1H, CHH'), 1.49 (d, 9H, <sup>3</sup>J(H,P) = 12.0 Hz, CH<sub>3</sub>), 1.16 (d, 9H, <sup>3</sup>J(H,P) = 10.0 Hz, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, C<sub>6</sub>D<sub>6</sub>): PPh<sub>3</sub> at δ = 136.3 (d, <sup>1</sup>J(C,P) = 50.9 Hz, i), 133.9 (d, <sup>2</sup>J(C,P) = 11.1 Hz, o), 130.1 (s, p), 128.5 (d, <sup>3</sup>J(C,P) = 11.0 Hz, m); 91.3 (s, C<sub>5</sub>H<sub>5</sub>), 32.0 (d, <sup>1</sup>J(C,P) = 20.4 Hz, PC), 30.0 (d, <sup>1</sup>J(C,P) = 23.1 Hz, PC'), 28.6 (s, CH<sub>3</sub>), 27.9 (s, C'H<sub>3</sub>), -25.2 (d, <sup>1</sup>J(C,P) = 45.3 Hz, CH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 53.3 (d, <sup>3</sup>J(P,P) = 6.1

Hz, P(*t*-Bu)<sub>2</sub>), 23.5 (d, <sup>3</sup>*J*(P,P) = 6.1 Hz, PPh<sub>3</sub>).

### Additional References

(S1) The enantiomerically pure complex,<sup>18a</sup> and racemic and enantiomerically pure P(*p*-tol)<sub>2</sub> analogs,<sup>7</sup> have also been reported.

(S2) The PPhPh' *ipso* signals were not observed, and the *meta* signals were obscured by C<sub>6</sub>D<sub>6</sub>.

(S3) This represents the chemical shift of the downfield line of the doublet; the other line was obscured by C<sub>6</sub>D<sub>6</sub>.

(S4) The *t*-butyl PC signals were not observed.

(S5) The PPhPh' *meta* signals were obscured by C<sub>6</sub>D<sub>6</sub>.

(S6) This independent preparation differs from that in the text only in the counter-anion of the starting material.