

Phosphine-Scavenging Cationic Gold(I) Complexes: Alternative Applications of Gold Cocatalysis in Fundamental Palladium-Catalyzed Cross-Couplings

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Supporting Information

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I. General

Unless otherwise specified all reactants and reagents were purchased and used as received. Stock solutions were made with degassed anhydrous solvents (THF, acetonitrile and 1,4-dioxane) and stored in an N₂ atmosphere glovebox. Ethyl acrylate and tributylphenylstannane were degassed, stored in a nitrogen-filled glovebox.

¹H, ¹³C NMR and ³¹P spectra were recorded on a Bruker NMR spectrometer operating at 400 MHz for proton, 100 MHz for carbon, and 162 MHz for phosphorus nuclei. ³¹P spectra were referenced against H₃PO₄ (internal standard). GC data were obtained on an Agilent 6850 Network GC System using an Agilent HP-5 ms capillary column (30 m x 0.25 mm x 0.25 mm): injection temp = 250 °C, oven temp = 45 °C (1 min) → 250 °C @ 10 °C per min. All Suzuki–Miyaura, Stille, and Mizoroki–Heck cross-coupling reactions were performed in Schlenk flasks under an atmosphere of N₂.

II. General Procedures

Pd-Catalyzed Suzuki–Miyaura Cross-Couplings General Procedure (Figure 2):

Reactions Employing 1% [Pd{P(*t*-Bu)₃]₂] and 1% [Au{P(*t*-Bu)₃}(NTf₂)]. In a nitrogen-filled glovebox, phenylboronic acid (200 μmol; 1.00 mL of a 200 mM solution in THF), 4-bromotoluene (220 μmol; 1.00 mL of a 220 mM solution in THF),[†] and Na₂CO₃ (800 μL of a 1 M aqueous solution) were added to a Schlenk flask (containing a stir bar). This Schlenk flask was removed from the glovebox and placed in a preheated oil bath (50 °C). A THF solution (1.00 mL) containing [Pd{P(*t*-Bu)₃]₂] (2.00 μmol) and [Au{P(*t*-Bu)₃}(NTf₂)] (2.00 μmol), maintained at 35 °C, was added to the Schlenk flask.[‡] The ensuing mixture was then magnetically stirred at 50 °C under N₂. Aliquots were obtained from the reaction mixture at the specified times and were added directly to Pasteur pipettes containing MgSO₄ (~0.5 cm), eluted with Et₂O, and analyzed by GC.

Reactions Employing 1% [Pd{P(*t*-Bu)₃]₂]. In a nitrogen-filled glovebox, phenylboronic acid (200 μmol; 1.00 mL of a 200 mM solution in THF), 4-bromotoluene (220 μmol; 1.00 mL of a 220 mM solution in THF),[†] and Na₂CO₃ (800 μL of a 1 M aqueous solution) were added to a Schlenk flask (containing a stir bar). This Schlenk flask was removed from the glovebox and placed in a preheated oil bath (50 °C). A THF solution (1.00 mL) containing [Pd{P(*t*-Bu)₃]₂] (2.00 μmol), maintained at 35 °C, was added to the Schlenk flask.[‡] The ensuing mixture was then magnetically stirred at 50 °C under N₂. Aliquots were obtained from the reaction mixture at the specified times and were added directly to Pasteur pipettes containing MgSO₄ (~0.5 cm), eluted with Et₂O, and analyzed by GC.

Pd-Catalyzed Suzuki–Miyaura Cross-Couplings General Procedure (Scheme 3C):

Reactions Employing 1% [Pd(PPh₃)₄] and 2% [Au(PPh₃)(NTf₂)]. In a nitrogen-filled glovebox, phenylboronic acid (200 μmol; 1.00 mL of a 200 mM solution in *n*-PrOH), 4-iodotoluene (220 μmol; 1.00 mL of a 220 mM solution in *n*-PrOH),[§] and Na₂CO₃ (800 μL of a 1 M aqueous solution) were added to a Schlenk flask (containing a stir bar). This Schlenk flask was removed from the glovebox and placed in a preheated oil bath (50 °C). A THF solution (1.00 mL) containing [Pd(PPh₃)₄] (2.00 μmol) and [Au(PPh₃)(NTf₂)] (4.00 μmol), maintained at 35 °C, was added to the Schlenk flask.[‡] The ensuing mixture was then magnetically stirred at 50 °C under N₂. Aliquots were obtained from the reaction mixture at the specified times and were added directly to Pasteur pipettes containing MgSO₄ (~0.5 cm), eluted with Et₂O, and analyzed by GC.

Reactions Employing 1% [Pd(PPh₃)₄]. In a nitrogen-filled glovebox, phenylboronic acid (200 μmol; 1.00 mL of a 200 mM solution in *n*-PrOH), 4-iodotoluene (220 μmol; 1.00 mL of a 220 mM solution in *n*-PrOH),[§] and Na₂CO₃ (800 μL of a 1 M aqueous solution) were added to a Schlenk flask (containing a stir bar). This Schlenk flask was removed from the glovebox and placed in a preheated oil bath (50 °C). A THF solution (1.00 mL) containing [Pd(PPh₃)₄] (2.00 μmol), maintained at 35 °C, was added to the Schlenk flask.[‡] The ensuing mixture was then magnetically stirred at 50 °C under N₂. Aliquots were obtained from the reaction mixture at the specified times and were added directly to Pasteur pipettes containing MgSO₄ (~0.5 cm), eluted with Et₂O, and analyzed by GC.

[†] This 4-bromotoluene solution also contained 1,4-dimethoxybenzene (50 μmol, 50 mM) as an internal standard.

[‡] This THF solution was magnetically stirred for 0.25 h at 35 °C prior to addition to the mixture in the Schlenk flask.

[§] This 4-iodotoluene solution also contained 1,4-dimethoxybenzene (50 μmol, 50 mM) as an internal standard.

Pd-Catalyzed Stille Cross-Couplings General Procedure (Figure 3):

Reactions Employing 1% [Pd{P(*t*-Bu)₃]₂] and 1% [Au{P(*t*-Bu)₃}(NTf₂)]. In a nitrogen-filled glovebox, tributylphenylstannane (220 μmol; 1.00 mL of a 220 mM solution in MeCN), 4-iodotoluene (200 μmol; 1.00 mL of a 200 mM solution in MeCN)[§] were added to a Schlenk flask (containing a stir bar). This Schlenk flask was removed from the glovebox and placed in a preheated oil bath (35 °C). A THF solution (1.00 mL) containing [Pd{P(*t*-Bu)₃]₂] (2.00 μmol) and [Au{P(*t*-Bu)₃}(NTf₂)] (2.00 μmol), maintained at 35 °C, was added to the Schlenk flask.[‡] The ensuing mixture was then magnetically stirred at 35 °C under N₂. Aliquots were obtained from the reaction mixture at the specified times and were added directly to Pasteur pipettes containing MgSO₄ (~0.5 cm), eluted with Et₂O, and analyzed by GC.

Reactions Employing 1% [Pd{P(*t*-Bu)₃]₂]. In a nitrogen-filled glovebox, tributylphenylstannane (220 μmol; 1.00 mL of a 220 mM solution in MeCN), 4-iodotoluene (200 μmol; 1.00 mL of a 200 mM solution in MeCN)[§] were added to a Schlenk flask (containing a stir bar). This Schlenk flask was removed from the glovebox and placed in a preheated oil bath (35 °C). A THF solution (1.00 mL) containing [Pd{P(*t*-Bu)₃]₂] (2.00 μmol), maintained at 35 °C, was added to the Schlenk flask.[‡] The ensuing mixture was then magnetically stirred at 35 °C under N₂. Aliquots were obtained from the reaction mixture at the specified times and were added directly to Pasteur pipettes containing MgSO₄ (~0.5 cm), eluted with Et₂O, and analyzed by GC.

Pd-Catalyzed Mizoroki–Heck Cross-Couplings General Procedure (Figure 4):

Reactions Employing 2% [Pd{P(*t*-Bu)₃]₂] and 2% [Au{P(*t*-Bu)₃}(NTf₂)]. In a nitrogen-filled glovebox, ethyl acrylate (800 μmol, neat), 4-iodotoluene (200 μmol; 2.00 mL of a 200 mM solution in dioxane),[§] and Cs₂CO₃ (85 mg, 260 μmol) were added to a Schlenk flask (containing a stir bar). This Schlenk flask was removed from the glovebox and placed in a preheated oil bath (50 °C). A THF solution (1.00 mL) containing [Pd{P(*t*-Bu)₃]₂] (4.00 μmol) and [Au{P(*t*-Bu)₃}(NTf₂)] (4.00 μmol), maintained at 35 °C, was added to the Schlenk flask.[‡] The ensuing mixture was then magnetically stirred at 50 °C under N₂. Aliquots were obtained from the reaction mixture at the specified times and were added directly to Pasteur pipettes containing MgSO₄ (~0.5 cm), eluted with Et₂O, and analyzed by GC.

Reactions Employing 2% [Pd{P(*t*-Bu)₃]₂]. In a nitrogen-filled glovebox, ethyl acrylate (800 μmol, neat), 4-iodotoluene (200 μmol; 2.00 mL of a 200 mM solution in dioxane),[§] and Cs₂CO₃ (85 mg, 260 μmol) were added to a Schlenk flask (containing a stir bar). This Schlenk flask was removed from the glovebox and placed in a preheated oil bath (50 °C). A THF solution (1.00 mL) containing [Pd{P(*t*-Bu)₃]₂] (4.00 μmol), maintained at 35 °C, was added to the Schlenk flask.[‡] The ensuing mixture was then magnetically stirred at 50 °C under N₂. Aliquots were obtained from the reaction mixture at the specified times and were added directly to Pasteur pipettes containing MgSO₄ (~0.5 cm), eluted with Et₂O, and analyzed by GC.

III. All Results from Time Course Experiments

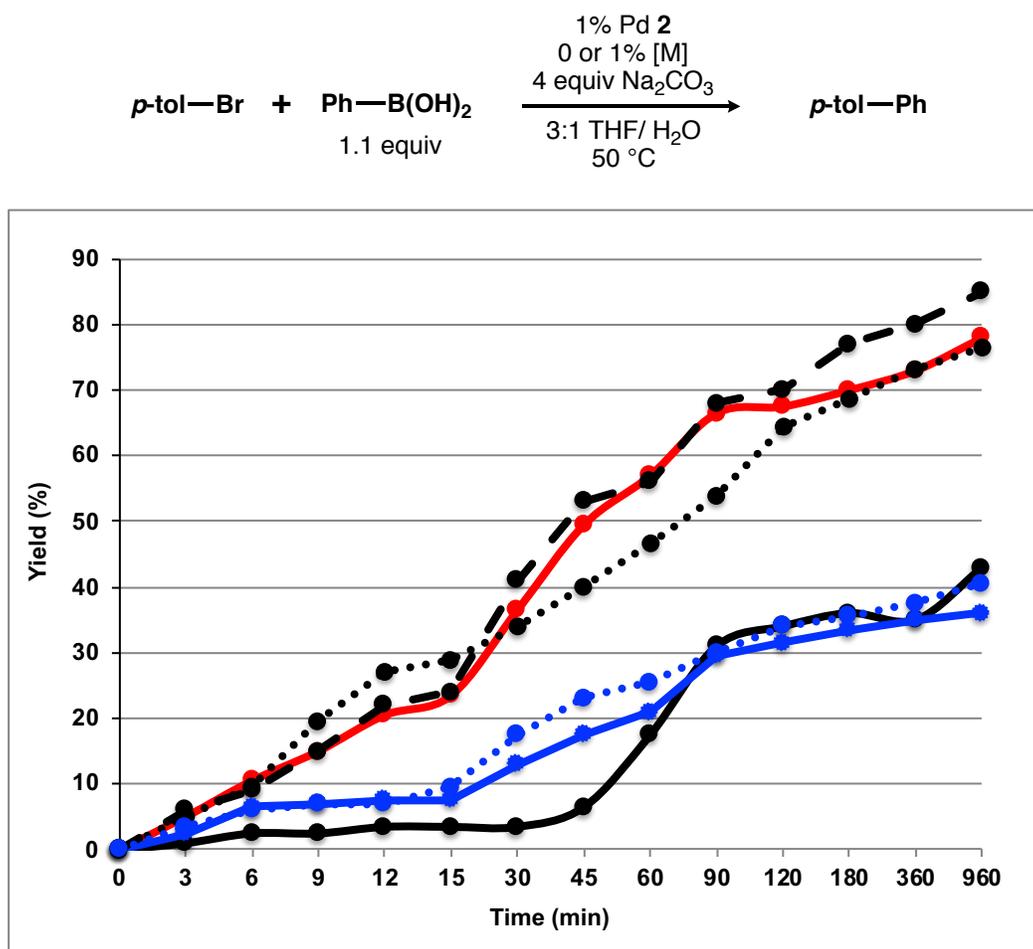


Figure S1. Suzuki–Miyaura reactions. Investigating the respective effects of cocatalysts 1% [Au{P(*t*-Bu)₃}(NTf₂)] (**1**) (solid red line) 3% [Au{P(*t*-Bu)₃}(NTf₂)] (dashed black line), 1% [Cu(MeCN)₄]PF₆ (**8**) (solid blue line), 1% [Pd(*dba*)₂]/ 1% [HP(*t*-Bu)₃]BF₄ (dotted black line) and 1% CuI (dotted blue line) on the efficiency of Pd-mediated Suzuki–Miyaura cross-couplings with *p*-bromotoluene. The experiment employing 1% [Pd{P(*t*-Bu)₃}₂] (**2**) is represented with a solid black line. Each data point represents the average of two experiments with yields determined via GC with the aid of a calibrated internal standard.

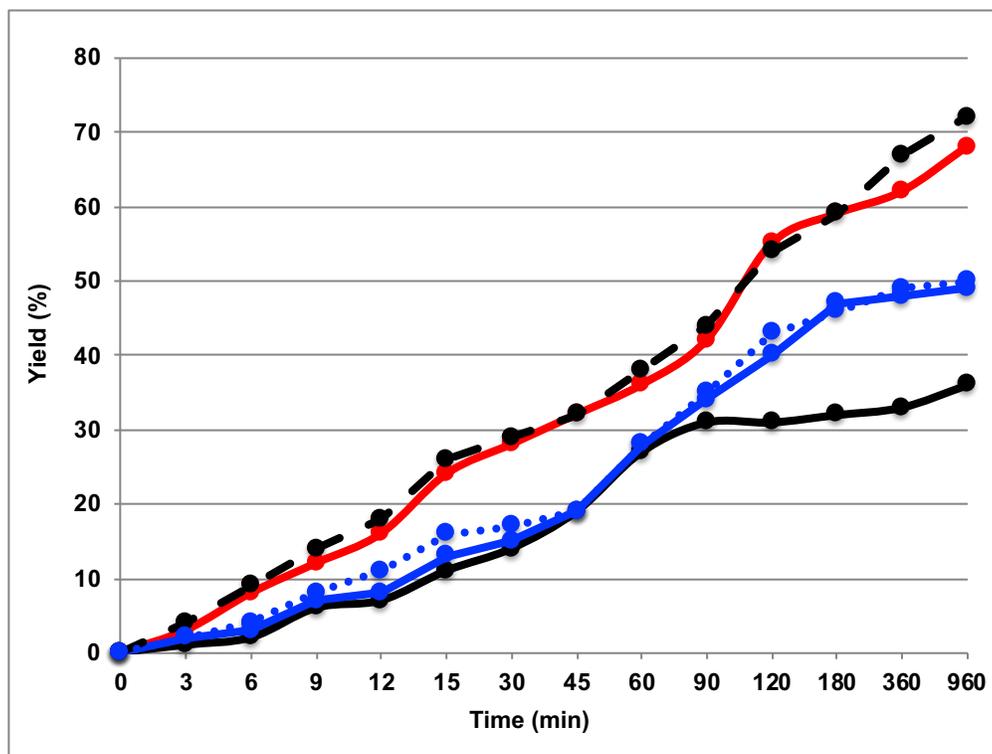
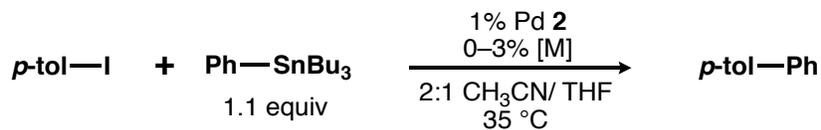


Figure S2. Stille reactions. Investigating the respective effects of cocatalysts 1% [Au{P(*t*-Bu)₃}(NTf₂)] (**1**) (solid red line) 3% [Au{P(*t*-Bu)₃}(NTf₂)] (dashed black line), 1% [Cu(MeCN)₄]PF₆ (**8**) (solid blue line), and 1% CuI (dotted blue line) on the efficiency of Pd-mediated Stille cross-couplings with *p*-iodotoluene. The experiment employing 1% [Pd{P(*t*-Bu)₃]₂] (**2**) is represented with a solid black line. Each data point represents the average of two experiments with yields determined via GC with the aid of a calibrated internal standard.

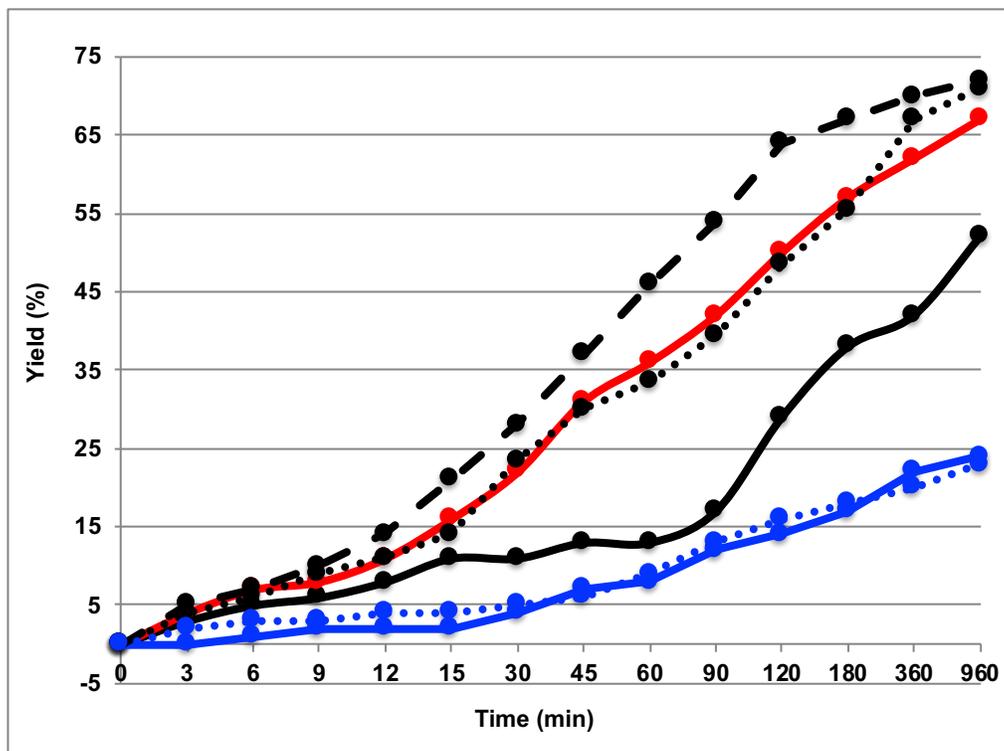
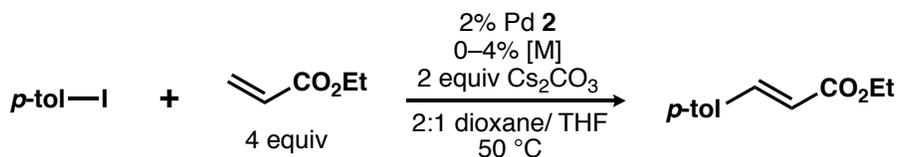


Figure S3 Heck reactions. Investigating the respective effects of cocatalysts 2% [Au{P(*t*-Bu)₃}(NTf₂)] (**1**) (solid red line) 4% [Au{P(*t*-Bu)₃}(NTf₂)] (dashed black line), 2% [Cu(MeCN)₄]PF₆ (**8**) (solid blue line), 2% [Pd(*dba*)₂]/ 2% [HP(*t*-Bu)₃]BF₄ (dotted black line), and 2% CuI (dotted blue line) on the efficiency of Pd-mediated Mizoroki–Heck cross-couplings with *p*-iodotoluene. The experiment employing 2% [Pd{P(*t*-Bu)₃}]₂ (**2**) is represented with a dashed black line. Each data point represents the average of two experiments with yields determined via GC with the aid of a calibrated internal standard.

IV. X-Ray Crystallographic Data

Data for complexes **3** and **9** were collected at $-173\text{ }^{\circ}\text{C}$ on crystals mounted on a Hampton Scientific cryoloop at the MX2 beamline of the Australian Synchrotron.¹ The structures were solved by direct methods with SHELXT-2014, refined using full-matrix least-squares routines against F^2 with SHELXT-2014,² and visualized using OLEX2.³ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined using a riding model with fixed C–H distances of 0.95 \AA ($sp^2\text{CH}$), 1.00 \AA ($sp^3\text{CH}$), 0.99 \AA (CH_2), 0.98 \AA (CH_3). The thermal parameters of all hydrogen atoms were estimated as $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ except for CH_3 where $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

$[\text{Au}\{\text{P}(t\text{-Bu})_3\}_2]^+$ is a known complex.⁴ Crystal data for complex **3**: $\text{C}_{26}\text{H}_{55}\text{AuF}_6\text{NO}_4\text{P}_2\text{S}_2$, $M = 882.73$, triclinic, $a = 13.081(3)$, $b = 14.761(4)$, $c = 19.576(4)\text{ \AA}$, $\alpha = 86.57(3)^{\circ}$, $\beta = 80.94(3)^{\circ}$, $\gamma = 73.87(3)^{\circ}$, $U = 3585.3(14)\text{ \AA}^3$, $T = 100\text{ K}$, space group P-1 (no 2), $Z = 4$, 32084 reflections measured, 18105 unique ($R_{\text{int}} = 0.0649$), 10064 $> 4\sigma(F)$, $R = 0.0662$ (observed), $R_w = 0.2320$ (all data). CCDC Number: 1875862

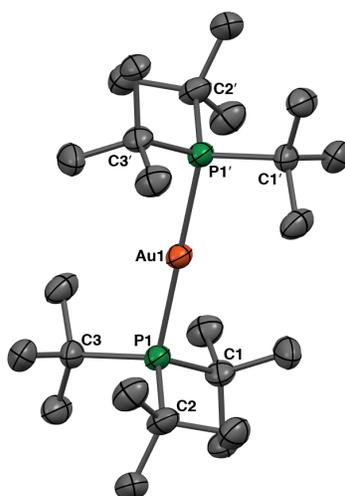


Figure S4. Structural representation of complex **3**, (' denotes symmetry operator: $-x, -y, -z$). Thermal ellipsoids are shown at 50% probability level. $[\text{NTf}_2]^-$ counteranion and hydrogen atoms have been omitted for clarity. Selected bond lengths (\AA) and angles ($^{\circ}$): Au1-P1 2.331(14), P1-C1 1.905(6), P1-C2 1.891(6), P1-C3 1.896(7), P1-Au1-P1' 180.0, C1-P1-Au1 107.10(18), C2-P1-Au1 110.05(17), C3-P1-Au1 107.3(2).

$[\text{Cu}\{\text{P}(t\text{-Bu})_3\}_2]^+$ is a known complex (CCDC Number: 1453515). Crystal data for complex **9**: $\text{C}_{32}\text{H}_{70}\text{CuF}_6\text{O}_2\text{P}_3$, $M = 757.31$, trigonal, $a = 11.5107(16)$, $c = 51.641(10)\text{ \AA}$, $U = 5926(2)\text{ \AA}^3$, $T = 100\text{ K}$, space group R-3c (no. 167), $Z = 6$, 16925 reflections measured, 1951 unique ($R_{\text{int}} = 0.0347$), 1818 $> 4\sigma(F)$, $R = 0.0344$ (observed), $R_w = 0.1147$ (all data). CCDC Number: 1875861.

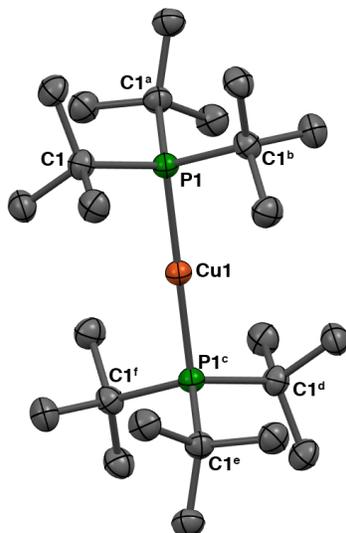


Figure S5. Structural representation of complex **9** (a, b, c, d, e, f denotes symmetry operators: $2-y, x-y, z$; $1+y-x, 2-x, z$; $2-x, 2-y, 1-z$; $2-x, 2-z, 1-z$; $y, 1-x, 1-z$; $1-y+x, x, 1-z$). Thermal ellipsoids are shown at 50% probability level. $[\text{PF}_6]^-$ counteranion, hydrogen atoms and THF solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Cu1-P1 2.2187(6)(14), P1-C1 1.9022(11), P1-Cu1-P1^c 180.0, C1-P1-Cu1 108.37(4).

V. References

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