

## SUPPORTING INFORMATION

### STRUCTURE AND REACTIVITY OF A NEW ANIONIC N-HETEROCYCLIC CARBENE SILVER(I) COMPLEX.

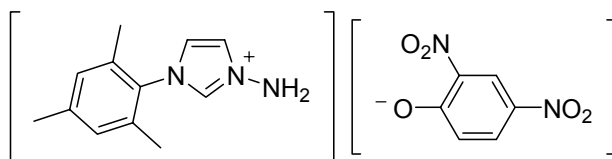
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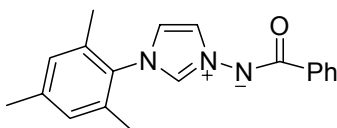
**General:** All non-aqueous reactions were run under an inert atmosphere (argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. All glassware was stored in the oven and/or was flame-dried prior to use. Anhydrous solvents (THF, Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, benzene, MeCN) were obtained by filtration through drying columns on a GlassContour system (Irvine, CA). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel (Merck 60 F<sub>254</sub>). Visualization of the developed chromatogram was performed by UV absorbance and/or aqueous KMnO<sub>4</sub>. Flash column chromatography was performed using 230-400 mesh silica (EM Science or Silicycle) of the indicated solvent system according to standard technique.

Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin Elmer Spectrum One FTIR and are reported in reciprocal centimeters (cm<sup>-1</sup>). Nuclear magnetic resonance spectra (<sup>1</sup>H, <sup>13</sup>C) were recorded either on a Bruker AV 300 or AV 400 spectrometer. Chemical shifts for <sup>1</sup>H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), integration, and coupling constant in Hz. Chemical shifts for <sup>13</sup>C NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard. All spectra were obtained with complete proton decoupling. Low resolution mass spectra were obtained using an Agilent 1100 Series LC system equipped with a electrospray (ES) or APCI mass detector with simultaneous diode array UV detection. Combustion analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal.

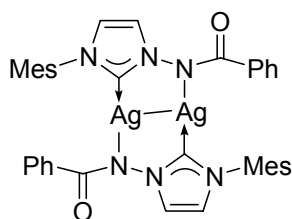
The residual electron density peak in the X-ray structure of compound **7** is located within 1 Å of the Cu atom.



**3-Amino-1-mesityl-1H-imidazolium 2,4-dinitrophenolate (4).** A solution of 2.05 g (11.0 mmol) of 1-mesityl-1H-imidazole and 2.41 g (12.1 mmol) of *O*-(2,4-dinitrophenyl)hydroxylamine in 20 mL of MeCN was stirred for 16 h at 40 °C. The reaction was cooled to room temperature, diluted with 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, and concentrated to dryness. The residue was suspended in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>, diluted dropwise with 200 mL of Et<sub>2</sub>O, and filtered. The filter cake was rinsed with Et<sub>2</sub>O and dried *in vacuo* to afford 3.41 g (80%) of **4** as a mustard yellow solid: IR (neat) 1603, 1553, 1537, 1467, 1426, 1372, 1316, 1252, 1127, 1046, 921, 828, 753, 709 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO) δ 9.44 (t, 1 H, *J* = 1.5 Hz), 8.57 (d, 1 H, *J* = 3.3 Hz), 7.93 (t, 1 H, *J* = 1.7), 7.84 (t, 1 H, *J* = 1.8 Hz), 7.76 (dd, 1 H, *J* = 9.8, 3.1 Hz), 7.10 (s, 2 H), 7.04 (s, 2 H), 6.29 (d, 1 H, *J* = 9.6 Hz), 2.29 (s, 3 H), 1.99 (s, 6 H); <sup>13</sup>C NMR (100 MHz, DMSO) δ 170.3, 140.3, 136.6, 136.1, 134.4 (2 C), 131.4, 129.3 (2 C), 127.5, 127.5, 126.7, 125.1, 124.8, 122.6, 20.6, 16.9 (2 C).

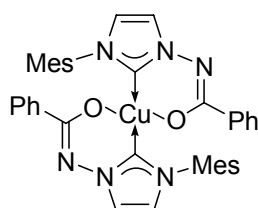


**3-Benzoylimino-1-mesityl-1H-imidazolium ylide (5).** A solution of 1.04 g (2.69 mmol) of imidazolium salt **4** in 7 mL of benzoyl chloride was stirred for 12 h at 90 °C. The reaction was cooled to 60 °C and the excess benzoyl chloride was removed under reduced pressure. The residue was cooled to room temperature, dissolved in 25 mL of CH<sub>2</sub>Cl<sub>2</sub>, treated with 1.00 g (7.24 mmol) of K<sub>2</sub>CO<sub>3</sub>, stirred for 30 min at room temperature, filtered and concentrated to dryness. The residue was purified on SiO<sub>2</sub> (99:1, CH<sub>2</sub>Cl<sub>2</sub>/MeOH then 95:5, CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to afford 799 mg (97%) of **5** as a pale brown solid: IR (neat) 1685, 1596, 1544, 1484, 1328, 1276, 1222, 1090, 1060, 1026, 906, 855, 802, 710, 658 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.82 (s, 1 H), 8.20-8.15 (m, 2 H), 7.75 (t, 1 H, *J* = 1.6 Hz), 7.44-7.41 (m, 3 H), 7.03 (s, 2 H), 6.98 (t, 1 H, *J* = 1.8 Hz), 2.37 (s, 3 H), 2.11 (s, 6 H); <sup>13</sup>C NMR (76 MHz, CDCl<sub>3</sub>) δ 167.6, 141.3, 134.9, 134.5 (2 C), 132.4, 132.0, 130.8, 129.8 (2 C), 128.4 (2 C), 128.3 (2 C), 123.9, 120.1, 21.1, 17.4 (2 C).

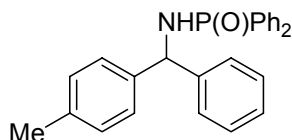


**Silver(I) Complex (6).** A suspension of 411 mg (1.35 mmol) of ylide **5**, 247 mg (1.48 mmol) of AgOAc, and 157 mg (1.48 mmol) of Na<sub>2</sub>CO<sub>3</sub> in 7 mL of THF was stirred for 16 h at 60 °C in the dark. The reaction was cooled to room temperature, diluted with 10 mL of benzene, filtered through Celite, and concentrated to dryness to afford 529 mg

(95%) of **6** as a pale brown solid: IR (neat) 1615, 1576, 1488, 1317, 1304, 1289, 1134, 941, 851, 724, 716, 697, 674, 658  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.94 (s, 2 H), 7.67 (d, 4 H,  $J = 7.2$  Hz), 7.35 (t, 2 H,  $J = 7.2$  Hz), 7.09 (t, 4 H,  $J = 7.6$  Hz), 7.00 (s, 4 H), 6.83 (s, 2 H), 2.48 (s, 6 H), 1.88 (s, 12 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  172.4 (2 C), 138.8 (2 C), 138.2 (2 C), 135.8 (2 C), 134.7 (4 C), 129.2 (2 C), 128.8 (4 C), 127.8 (4 C), 125.8 (2 C), 122.8 (2 C), 118.9 (2 C), 20.5 (2 C), 17.0 (4 C); APCI MS (+ve, 120 eV) 825 ( $[\text{M}+\text{H}]^+$ , 12), 306 (18), 187 (100); Anal. calcd (found) for  $\text{C}_{38}\text{H}_{36}\text{Ag}_2\text{N}_6\text{O}_2$ : C 55.36 (55.96), H 4.40 (4.46), N 10.19 (9.95).



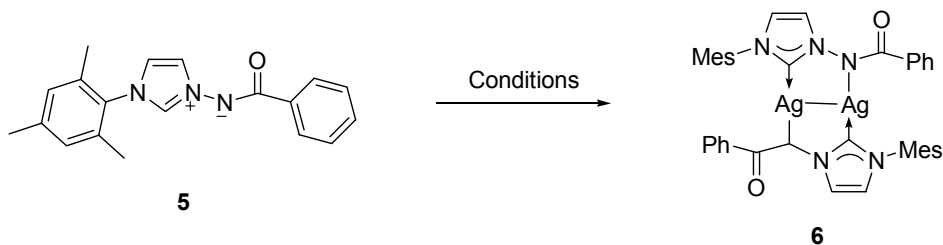
**Copper(II) complex (7).** A solution of 12.0 mg (0.0704 mmol) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 1 mL of THF was treated with a solution of 60.0 mg (0.0728 mmol) of silver carbene **6** in 2 mL of THF, at which point a white precipitate was rapidly formed. The reaction was stirred at room temperature for 45 minutes, diluted with 5 mL of benzene, filtered through Celite and concentrated to dryness. The residue was dissolved in 2 mL of dry benzene and lyophilized to afford 41 mg (87%) of **7** as a green-brown solid: APCI MS (+ve, 120 eV) 673 ( $[\text{M}+\text{H}]^+$ , 32), 306 (100), 187 (21); Anal. calcd (found) for  $\text{C}_{38}\text{H}_{36}\text{CuN}_6\text{O}_2$ : C 67.89 (68.11), H 5.40 (5.52), N 12.50 (11.95).



**P,P-Diphenyl-N-[phenyl(p-tolyl)methyl]phosphinamide (9).** A suspension of 251 mg (0.786 mmol) of imine **8**, 143 mg (1.17 mmol) of phenylboronic acid, 16.3 mg (0.0197 mmol) of Ag(I) complex **6**, and 10.9 mg (0.0221 mmol) of  $[\text{RhCl}(\text{cod})]_2$  in 8 mL of dioxane was stirred at 50  $^\circ\text{C}$  for 36 h. The reaction was poured into  $\text{H}_2\text{O}$  and extracted with  $3 \times \text{CH}_2\text{Cl}_2$ . The combined extracts were washed with brine, dried ( $\text{MgSO}_4$ ) and concentrated to dryness. The residue was purified on  $\text{SiO}_2$  (EtOAc) to afford 241 mg (77%) of **9** as a colourless solid:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88-7.82 (m, 4 H), 7.48-7.10 (m, 15 H), 5.44 (t, 1 H,  $J = 10.8$  Hz), 3.77 (dd, 1 H,  $J = 10.4, 6.8$  Hz), 2.33 (s, 3 H).

# Supplementary Material (ESI) for Chemical Communications  
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**Silver(I) Complex (6) reaction optimization**  
(conversion = ratio of Ag(I) complex 6 to ylide 5)



Entry	Conditions	Solvent	T (°C)	Time (h)	Conversion (%)
1	1.1 equiv AgOAc	Toluene	90	14	73
2	1.1 equiv AgOAc	Toluene	50	14	58
3	2.0 equiv AgOAc	Toluene	50	14	57
4	1.1 equiv AgOAc	THF	25	15	63
5	1.1 equiv AgOAc	THF	60	16	85 (48% yield)
6	2.0 equiv AgOAc	THF	60	15	85
7	1.1 equiv AgOAc and 1.1 equiv Na <sub>2</sub> CO <sub>3</sub>	THF	60	15	> 95 (85% yield)
8	1.1 equiv Ag <sub>2</sub> CO <sub>3</sub>	THF	60	16	76
9	2.0 equiv Ag <sub>2</sub> CO <sub>3</sub>	THF	60	16	84