

Supporting information for

Synthesis, characterization and isolation of cationic gold(I) *N*-heterocyclic carbene (NHC) complexes†

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Experimental procedure:

[(IPrAu)⁺(CH₃CN)][PF₆⁻]

In a scintillation vial, IPrAuCl (1 eq., 60 mg, 97 μmol) is dissolved in 2 mL of acetonitrile and AgPF₆ (1 eq., 27 mg, 97 μmol) is added. The solution is stirred one minute and filtered over celite to give a colorless solution. After removal of acetonitrile in vacuum, a white powder is isolated which slowly decomposes, turning grey, after a few hours. Attempts to crystallize the complex by slow evaporation from acetonitrile solution gives a small amount of colloidal gold and the desired crystals. It is noteworthy that these crystals, after isolation, do not exhibit any sign of decomposition after a few days. In acetonitrile solution, the complex slowly decomposes within a few days, with appearance of colloidal gold(0).

¹H NMR (400 MHz, CD₃CN) δ 7.66 (s, 2H, *CH*-imidazole), 7.63 (t, *J* = 8.0 Hz, 2H, *CH*-aromatic), 7.45 (d, *J* = 8.0 Hz, 2H, *CH*-aromatic), 2.51 (sept, *J* = 6.8 Hz, 4H, *CH*(CH₃)₂), 1.31 (d, *J* = 6.8 Hz, 12H, *CH*(CH₃)₂), 1.26 (d, *J* = 6.8 Hz, 12H, *CH*(CH₃)₂).

¹³C NMR (100 MHz, CDCl₃) δ 167.6 (s, *C*-carbene), 148.1 (s, *CH*-aromatic), 135.4 (s, *CH*-aromatic), 132.3 (s, *CH*-aromatic), 127.4 (s, *CH*-aromatic), 126.6 (s, *CH*-imidazole), 28.9 (s, *CH*(CH₃)₂), 23.9 (s, *CH*(CH₃)₂), 23.3 (s, *CH*(CH₃)₂).

[(IPrAu)⁺(CH₃CN)][BF₄⁻]

In a scintillation vial, IPrAuCl (1 eq., 200 mg, 322 μmol) is dissolved in 2 mL of acetonitrile and AgBF₄ (1 eq., 62 mg, 322 μmol) is added in the absence of light. The solution is stirred one minute and filtered over celite to give a colorless solution. In acetonitrile the complex slowly decomposes within a few hours, with appearance of

colloidal gold(0). After removal of acetonitrile in vacuum, a white powder is isolated which decomposes, turning grey, after a few minutes. Attempts to crystallize the complex by slow evaporation of acetonitrile lead to the formation of $[\text{Au}^+\text{CH}_3\text{CN}]_4[\text{BF}_4^-]$.

^1H NMR (300 MHz, CD_3CN) δ 7.67 (s, 2H, *CH*-imidazole), 7.63 (t, $J = 8.0$ Hz, 2H, *CH*-aromatic), 7.44 (d, $J = 8.0$ Hz, 2H, *CH*-aromatic), 2.49 (sept, $J = 6.6$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.31 (d, $J = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $J = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$).

^{13}C NMR (75 MHz, CD_3CN) δ 165.9 (s, *C*-carbene), 146.2 (s, *CH*-aromatic), 134.9 (s, *CH*-aromatic), 132.8 (s, *CH*-aromatic), 126.2 (s, *CH*-aromatic), 125.7 (s, *CH*-imidazole), 29.3 (s, $\text{CH}(\text{CH}_3)_2$), 25.6 (s, $\text{CH}(\text{CH}_3)_2$), 24.2 (s, $\text{CH}(\text{CH}_3)_2$).



In a scintillation vial, IPrAuCl (1 eq., 200 mg, 322 μmol) is dissolved in 2 mL of THF and AgPF_6 (1 eq., 81 mg, 322 μmol) is added. The solution is stirred one minute and filtered over celite to give a colorless solution. Overnight, the THF becomes a gel and two extra signals appear for the deuterated THF at 2.7 and 1.0 ppm downfield from the two normal THF signals. Appearance of colloidal gold(0) is observed after 3 days. After removal of THF in vacuum, a white powder is isolated and decomposes turning grey after a few hours.

^1H NMR (300 MHz, THF_{d8}) δ 7.82 (s, 2H, *CH*-imidazole), 7.59 (t, $J = 8.0$ Hz, 2H, *CH*-aromatic), 7.42 (d, $J = 8.0$ Hz, 2H, *CH*-aromatic), 2.57 (sept, $J = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.33 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$).

^{13}C NMR (75 MHz, THF_{d8}) δ 159.7 (s, *C*-carbene), 146.7 (s, *CH*-aromatic), 134.8 (s, *CH*-aromatic), 131.7 (s, *CH*-aromatic), 126.3 (s, *CH*-aromatic), 125.1 (s, *CH*-imidazole), 29.7 (s, $\text{CH}(\text{CH}_3)_2$), 25.8 (s, $\text{CH}(\text{CH}_3)_2$), 24.7 (s, $\text{CH}(\text{CH}_3)_2$).



In a scintillation vial, I^tBuAuCl (1 eq., 50 mg, 121 μmol) is dissolved in 2 mL of acetonitrile and AgPF_6 (1 eq., 31 mg, 121 μmol) is added. The solution is stirred one minute and filtered over celite to give a colorless solution. In acetonitrile, the complex slowly decomposes within a few days, with appearance of colloidal gold(0). After

removal of acetonitrile in vacuum, a white powder is isolated which decomposes, turning grey, after a few minutes.

^1H NMR (300 MHz, CD_3CN) δ 7.38 (s, 2H, *CH*-imidazole), 1.83 (s, 18H, $\text{C}(\text{CH}_3)_3$).

^{13}C NMR (75 MHz, CD_3CN) δ 159.7 (s, *C*-carbene), 60.6 (s, $\text{NC}(\text{CH}_3)_3$), 32.7 (s, $\text{NC}(\text{CH}_3)_3$).

$[(\text{IMesAu})^+(\text{CH}_3\text{CN})][\text{BF}_4^-]$

In a scintillation vial, IMesAuCl (1 eq., 50 mg, 93 μmol) is dissolved in 2 mL of acetonitrile and AgPF_6 (1 eq., 24 mg, 93 μmol) is added. The solution is stirred one minute and filtered over celite to give a colorless solution. After one day in acetonitrile, extra signals appear in the ^{13}C NMR spectrum and are attributed to $[(\text{IMes})_2\text{Au}^+][\text{PF}_6^-]$. After removal of acetonitrile in vacuum, a white powder is isolated which decomposes, turning purple, after few hours.

^1H NMR (300 MHz, CD_3CN) δ 7.50 (s, 2H, *CH*-imidazole), 7.15 (s, 4H, *CH*-aromatic), 2.38 (s, 6H, CH_3), 1.31 (s, 12H, CH_3).

^{13}C NMR (75 MHz, CD_3CN) δ 165.3 (s, *C*-carbene), 141.9 (s, *CH*-aromatic), 136.4 (s, *CH*-aromatic), 135.6 (s, *CH*-aromatic), 130.6 (s, *CH*-aromatic), 125.6 (s, *CH*-imidazole), 21.5 (s, $\text{CH}(\text{CH}_3)_2$), 18.2 (s, $\text{CH}(\text{CH}_3)_2$), 25.1 (s, $\text{CH}(\text{CH}_3)_2$).

Catalysis Protocol:

0.01 mmol of $\text{IPrAu}(\text{NCMe})\text{PF}_6$ were dissolved in 3 mL of the neat substrate in the case of alcohols, styrene, benzene or in a mixture of the substrate (5 mL) and dichloromethane (5 mL) for amines or 2,3-dimethylbutane. EDA (0.25 mmol) was added in one portion (or with a syringe pump for 6 h in the case of the alkane). Reactions were monitored by GC, at time intervals shown in Table 1, and also the product identity confirmed by NMR spectroscopy. Yields were obtained following procedures described in previous work from this laboratory (see reference 17).