Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Copper *N*-Heterocyclic Carbene (NHC) Complexes as Carbene Transfer Reagents

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1. Generalities

All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line and glovebox techniques. Solvents were dispensed from a solvent purification system. All other reagents were used without further purification. ^{1}H and ^{13}C-{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 300 spectrometer using the residual solvent peak as reference ($CHCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm) at 298K. Elemental analyses were performed by the University of St Andrews Analytical Service. All complexes of type **1** -[CuCl(NHC)]- were prepared by reaction of Cu_2O with the chloride imidazolium salt.[1]

2. Carbene transfer reactions leading to

[AuCl(IMes)] 2a

A mixture of [AuCl(SMe_2)] (137.2 mg, 0.47 mmol) and [CuCl(IMes)] **1a** (187.9 mg, 0.47 mmol) in dichloromethane (5 mL) was stirred at 40°C for 1 h. The mixture was filtered through celite and the solvent was removed *in vacuo*. Dichloromethane (3 mL) and petroleum ether (10 mL) were added, resulting in the precipitation of an off-white solid. The product was collected by filtration, washed with petroleum ether (3 x 5 mL) and obtained as a colourless solid in 71% yield (178 mg, 0.33 mmol). NMR spectra were compared to published data.[2]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.10 (s, 2H, H^4 and H^5), 7.00 (s, 4H, CH mesityl), 2.36 (s, 6H, CH_3), 2.11 (s, 12H, CH_3). **^{13}C-{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ = 173.6 (s, C^2 carbene), 140.05 (s, CH mesityl), 135.0 (s, CH mesityl), 134.9 (s, CH mesityl), 129.8 (s, CH mesityl), 122.4 (s, C^4H and C^5H carbene), 21.4 (s, CH_3), 18.0 (s, CH_3). **Elem. Anal**.: Calcd for $C_{21}H_{24}ClN_2Au$: C, 46.98; H, 4.51; N, 5.22. Found: C, 47.09; H, 4.33; N, 5.03.

[AuCl(SIMes)] 2b

A mixture of [AuCl(SMe_2)] (136.7 mg, 0.46 mmol) and [CuCl(SIMes)] **1b** (188.1 mg, 0.46 mmol) in dichloromethane (5 mL) was stirred at 40°C for 1 h. The mixture was filtered through celite and the solvent was removed *in vacuo*. Dichloromethane (3 mL) and petroleum ether (10mL) were added, resulting in the precipitation of an off-white solid. The product was collected by filtration, washed with petroleum ether (3 x 5 mL) and obtained as a colourless solid in 90% yield (225 mg, 0.42 mmol). NMR spectra were compared to published data.[2]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.95 (s, 4H, CH mesityl), 3.99 (s, 4H, H^4 and H^5), 2.32 (s, 12H, CH_3), 2.30 (s, 6H, CH_3). **^{13}C-{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ = 195.4 (s, carbene C^2), 139.2 (s, CH mesityl), 135.8 (s, CH mesityl), 134.85 (s, CH mesityl), 130.1 (s, CH mesityl), 51.0 (s, C^4H and C^5H), 21.35 (s, CH_3), 18.3 (s, CH_3). **Elem. Anal**.: Calcd for $C_{21}H_{26}ClN_2Au$: C, 46.81; H, 4.86; N, 5.20. Found: C, 46.32; H, 4.77; N, 4.89.

[AuCl(IPr)] 2c

A mixture of [AuCl(SMe_2)] (118.6 mg, 0.40 mmol) and [CuCl(IPr)] **1c** (196.3 mg, 0.40 mmol) in dichloromethane (5 mL) was stirred at 40°C for 2 h. The mixture was filtered through celite and the solvent was removed *in vacuo*. Dichloromethane (3 mL) and petroleum ether (10mL) were added, resulting in the precipitation of an off-white solid. The product was

collected by filtration, washed with petroleum ether (3 x 5 mL) and obtained as a colourless solid in 84% yield (209 mg, 0.34 mmol). NMR spectra were compared to published data.[2]

^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.57 (t, 2H, CH phenyl), 7.34 (d, 4H, CH phenyl), 7.23 (s, 2H, H^4 and H^5), 2.57 (pseudo-septuplet, 4H, CH isopropyl), 1.33 (d, 12H, CH_3 isopropyl), 1.23 (d, 12H, CH_3 isopropyl). **^{13}C-{^{1}H} NMR** (CD_2Cl_2, 75 MHz): δ = 146.6 (s, CH phenyl), 131.55 (s, CH phenyl), 125.1 (s, CH phenyl), 124.2 (s, C^4H and C^5H), 29.7 (s, CH isopropyl), 25.0 (s, CH_3 isopropyl), 24.60 (s, CH_3 isopropyl). **Elem. Anal**.: Calcd for $C_{27}H_{36}ClN_2Au$: C, 52.22; H, 5.84; N, 4.51. Found: C, 51.76; H, 5.83; N, 4.23.

[Pd(μ-Cl)Cl(IMes)]$_2$ 3a

A mixture of [$PdCl_2(NCPh)_2$] (199 mg, 0.52 mmol) and [CuCl(IMes)] **1a** (209.4 mg, 0.52 mmol) in dichloromethane (5 mL) was stirred at 40°C for 1 h. The mixture was filtered through celite and the solvent was removed *in vacuo*. Dichloromethane (3 mL) and petroleum ether (10 mL) were added, resulting in the precipitation of a yellow solid. The product was collected by filtration, washed with petroleum ether (3 x 5 mL) and obtained as a yellow solid in 79% yield (196 mg, 0.20 mmol). NMR spectra were compared to published data.[3]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33 (s, broad, 8H, CH mesityl), 6.95 (s, 4H, H^4 and H^5), 2.45 (s, 12H, CH_3), 2.24 (s, 12H, CH_3), 2.09 (s, 12H, CH_3). **^{13}C-{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ = 139.5 (s, CH mesityl), 135.9 (s, CH mesityl), 134.75 (s, CH mesityl), 129.7 (s, CH mesityl), 124.8 (s, C^4H and C^5H), 21.6 (s, CH_3), 19.3 (s, CH_3, 19.0 (s, CH_3). **Elem. Anal**.: Calcd for $C_{42}H_{48}Cl_4N_4Pd_2$: C, 52.36; H, 5.02; N, 5.81. Found: C, 52.67; H, 5.12; N, 5.71.

[Pd(μ-Cl)Cl(SIMes)]$_2$ 3b

A mixture of [$PdCl_2(NCPh)_2$] (198.2 mg, 0.52 mmol) and [CuCl(SIMes)] **1b** (209.5 mg, 0.52 mmol) in dichloromethane (5 mL) was stirred at 40°C for 1 h. The mixture was filtered through celite and the solvent was removed *in vacuo*. Dichloromethane (3 mL) and petroleum ether (10 mL) were added, resulting in the precipitation of a yellow solid. The product was collected by filtration, washed with petroleum ether (3 x 5 mL) and obtained as a yellow solid in 82% yield (205 mg, 0.21 mmol). NMR spectra were compared to published data.[3]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.00 (s, broad, 8H, CH mesityl), 3.86 (s, broad, 8H, H^4 and H^5), 2.45 (s, 12H, CH_3), 2.41 (s, 12H, CH_3), 2.26 (s, 12H, CH_3). **^{13}C-{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ = 138.7 (s, CH mesityl), 134.6 (s, CH mesityl), 129.9 (s, CH mesityl), 129.9 (s, CH

mesityl), 51.5 (s, C^4H and C^5H), 21.6 (s, CH_3), 19.4 (s, CH_3). **Elem. Anal**.: Calcd for $C_{42}H_{52}Cl_4N_4Pd_2$: C, 52.14; H, 5.42; N, 5.79. Found: C, 52.12; H, 5.49; N, 5.56.

[Pd(μ-Cl)Cl(IPr)]$_2$ 3c

A mixture of $[PdCl_2(NCPh)_2]$ (169.4 mg, 0.44 mmol) and [CuCl(IPr)] **1c** (215.4 mg, 0.44 mmol) in dichloromethane (5 mL) was stirred at 40°C for 2 h. The mixture was filtered through celite and the solvent was removed *in vacuo*. Dichloromethane (3 mL) and petroleum ether (10 mL) were added, resulting in the precipitation of a yellow solid. The product was collected by filtration, washed with petroleum ether (3 x 5 mL) and obtained as an ochre yellow solid in 82% yield (206 mg, 0.18 mmol). NMR spectra were compared to published data.[4]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.55 (t, 4H, CH phenyl), 7.30 (d, 8H, CH phenyl), 6.99 (s, 4H, H^4 and H^5), 2.87 (br. s, 2H, CH isopropyl), 2.61 (br. s, 2H, CH isopropyl), 1.31 (d, broad, 24H, CH_3 isopropyl), 0.99 (d, broad, 24H, CH_3 isopropyl). **^{13}C-{^{1}H} NMR** ($CDCl_3$, 75 MHz): δ = 148.14 (s, CH phenyl), 146.53 (s, CH phenyl), 134.54 (s, CH phenyl), 130.6 (s, CH phenyl), 125.5 (s, CH phenyl), 124.5 (s, C^4H and C^5H), 28.9 (s, CH isopropyl), 26.5 (s, CH_3 isopropyl), 23.5 (s, CH_3 isopropyl). **Elem. Anal**.: Calcd for $C_{54}H_{72}Cl_4N_4Pd_2$: C, 57.30; H, 6.41; N, 4.95. Found: C, 57.09; H, 6.41; N, 4.66.

References

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