Supporting Information

for

Mechanochemical Synthesis of Cu(I)-N-Heterocyclic Carbene Complexes

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Contents

General information

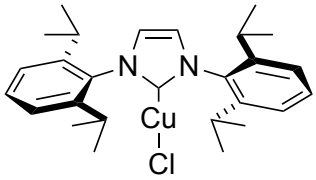
Ball-milling experiments were performed in a planetary mill (Pulverisette 5/4, Fritsch). NMR spectra were recorded on a Bruker ADVANCE 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent residual peak as reference ($CHCl_3$: δ_H = 7.26 ppm) at 298K. $CDCl_3$, K_2CO_3 and CuCl were purchased and used as received. (S)IPr·HCl, (S)IMes·HCl, IPr*·HCl, I^{t}Bu·HCl and MIC·HCl were synthesized following literature procedures.[1-5] Silica gel P60 (230-400 mesh) was used for chromatography.

Synthesis of complexes

General procedure

A 12 mL milling jar (ZrO_2) equipped with 18 balls 5 mm Ø (ZrO_2) was charged with NHC·HCl and CuCl which were ground (400 rpm) for 10 min. K_2CO_3 was added and the reaction mixture was ground for 3 x 30 min (400 rpm). The crude product was extracted (CH_2Cl_2 or acetone) and filtered (SiO_2). After concentration, pentane was added, and the product was collected by filtration. When the product was extracted from the reactor using acetone, filtration through SiO_2 and reducing of the solvent volume by vacuum permits the product to precipitate and alleviates the need for pentane co-solvent use.

[Cu(Cl)(IPr)] - Small scale



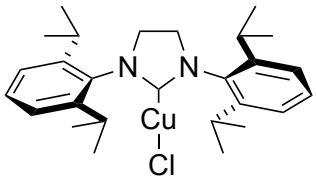
Following the general procedure with IPr·HCl (200 mg, 0.471 mmol), CuCl (47 mg, 0.471 mmol) and K_2CO_3 (195 mg, 1.412 mmol), [Cu(Cl)(IPr)] was obtained as a colourless solid in 78% yield (178 mg, 0.365 mmol). When the product was extracted from the reactor using acetone, filtration through SiO_2 and reducing of the solvent volume by vacuum permits the product to precipitate and alleviates the need for pentane co-solvent use. This acetone extraction/filtration/precipitation leads to yields of 76% yield

[Cu(Cl)(IPr)] - Large scale

A 500 mL milling jar (ZrO_2) equipped with 764 balls 5 mm Ø (ZrO_2) was charged with IPr·HCl (5.0 g, 11.76 mmol), CuCl (1.16 g, 11.76 mmol) and K_2CO_3 (4.88 g, 35.29 mmol). The reaction mixture was ground for 10 min (400 rpm). The crude product was extracted with (CH_2Cl_2) and filtered (SiO_2). After concentration, pentane was added and the product was collected by filtration. [Cu(Cl)(IPr)] was obtained as a colourless solid in 75% yield (4.30 g, 8.82 mol).

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ = 1.24 (d, $^3J_{HH}$ = 8 Hz, 12H, CH-C$\underline{H}_3$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH-C$\underline{H}_3$), 2.58 (spt, $^3J_{HH}$ = 6.9 Hz, 4H, C$\underline{H}$-CH$_3$), 7.14 (s, 2H, NCH=CHN), 7.31 (d, J=7.8 Hz, 4H, ArH), 7.47-7.53 (m, 2 H, ArH). The spectrum matches data from the literature.[6]

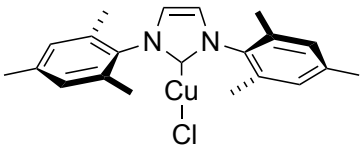
Synthesis of [Cu(Cl)(SIPr)]



Following the general procedure with SIPr·HCl (200 mg, 0.47 mmol), CuCl (46 mg, 0.47 mmol) and K_2CO_3 (194 mg, 1.40 mmol), [Cu(Cl)(SIPr)] was obtained as a colourless solid in 66% yield (151 mg, 0.31 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ = 1.37 (app. t, 24H, CH-C<u>H</u>$_3$), 3.08 (spt, $^3J_{HH}$ = 6.9 Hz, 4H, C<u>H</u>-CH$_3$) 4.03 (s, 4H, NCH_2CH_2N), 7.23-7.29 (m, 4H, ArH), 7.23-7.29 (m, 2H, ArH). The spectrum matches data from the literature.[6]

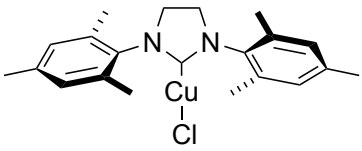
Synthesis of [Cu(Cl)(IMes)]



Following the general procedure with IMes·HCl (200 mg, 0.59 mmol), CuCl (58 mg, 0.59 mmol) and K_2CO_3 (243 mg, 1.76 mmol), [Cu(Cl)(IMes)] was obtained as a colourless solid in 65% yield (154 mg, 0.38 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ= 2.11 (s, 12H, CH_3), 2.36 (s, 6H, CH_3), 7.01 (s, 4H, ArH), 7.06 (s, 2H, NCH=CHN). The spectrum matches data from the literature.[6]

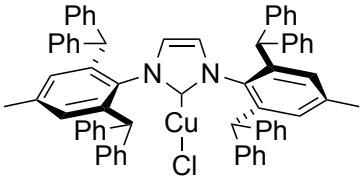
Synthesis of [Cu(Cl)(SIMes)]



Following the general procedure with SIMes·HCl (200 mg, 0.58 mmol), CuCl (58 mg, 0.58 mmol) and K_2CO_3 (242 mg, 1.75 mmol), [Cu(Cl)(SIMes)] was obtained as a colourless solid in 53% yield (124 mg, 0.31 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ= 2.31 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 3.96 (s, 4H, NCH_2CH_2N), 6.96 (s, 4H, ArH). The spectrum matches data from the literature.[6]

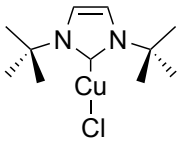
Synthesis of [Cu(Cl)(IPr*)]



Following the general procedure with IPr*·HCl (200 mg, 0.21 mmol), CuCl (21 mg, 0.21 mmol) and K_2CO_3 (87 mg, 0.63 mmol), [Cu(Cl)(IPr*)] was obtained as a colourless solid in 72% yield (152 mg, 0.15 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ= 2.23 (s, 6H, CH_3), 5.20 (s, 4H, CH-Ph_2), 5.82 (s, 2H, NCH=CHN), 6.85 (s, 4H, ArH), 6.87-6.93 (m, 8H, ArH), 7.02 (m, 8H, ArH), 7.12-7.23 (m, 24H, ArH). The spectrum matches data from the literature.[6]

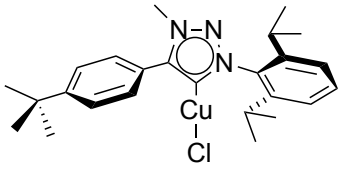
Synthesis of [Cu(Cl)(ItBu)]



Following the general procedure with I^{t}Bu·HCl (200 mg, 0.92 mmol), CuCl (91 mg, 0.92 mmol) and K_2CO_3 (383 mg, 2.77 mmol), [Cu(Cl)(I^{t}Bu)] was obtained as a coloourless solid in 48% yield (124 mg, 0.44 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ= 1.79 (s, 18H, $C(CH_3)_3$), 7.05 (s, 2H, NCH=CHN). The spectrum matches data from the literature.[6]

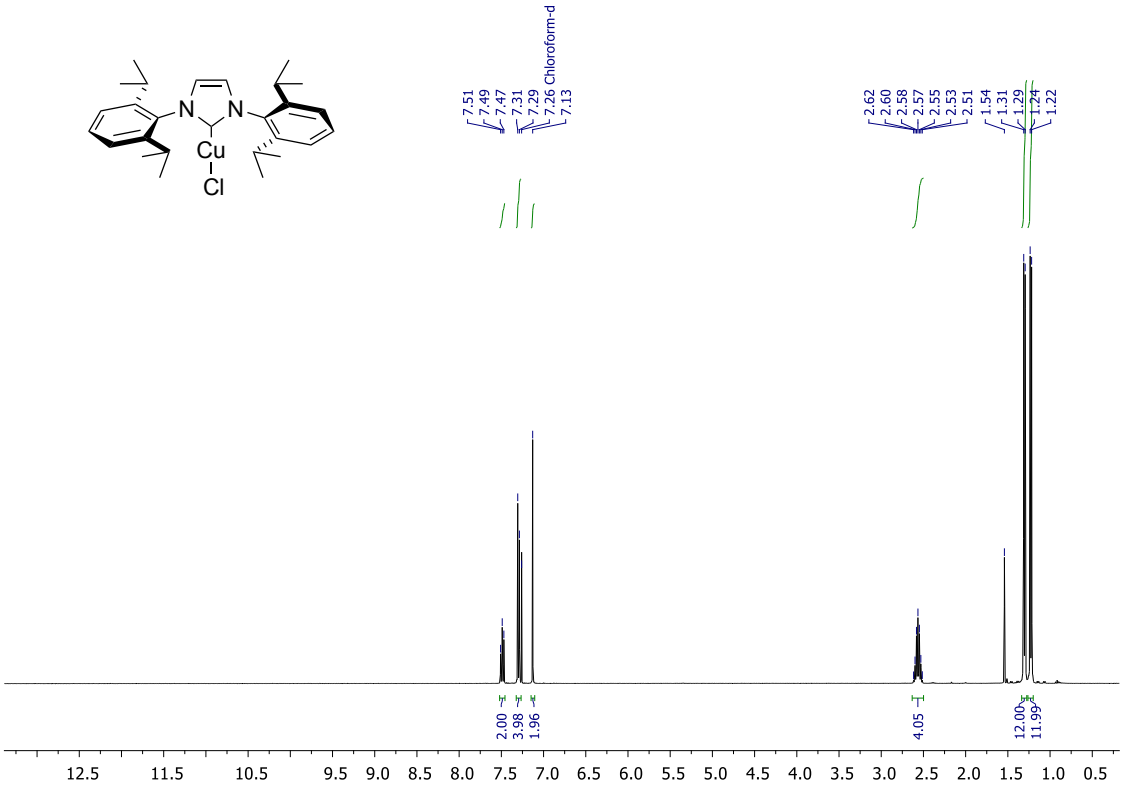
Synthesis of [Cu(Cl)(MIC)]

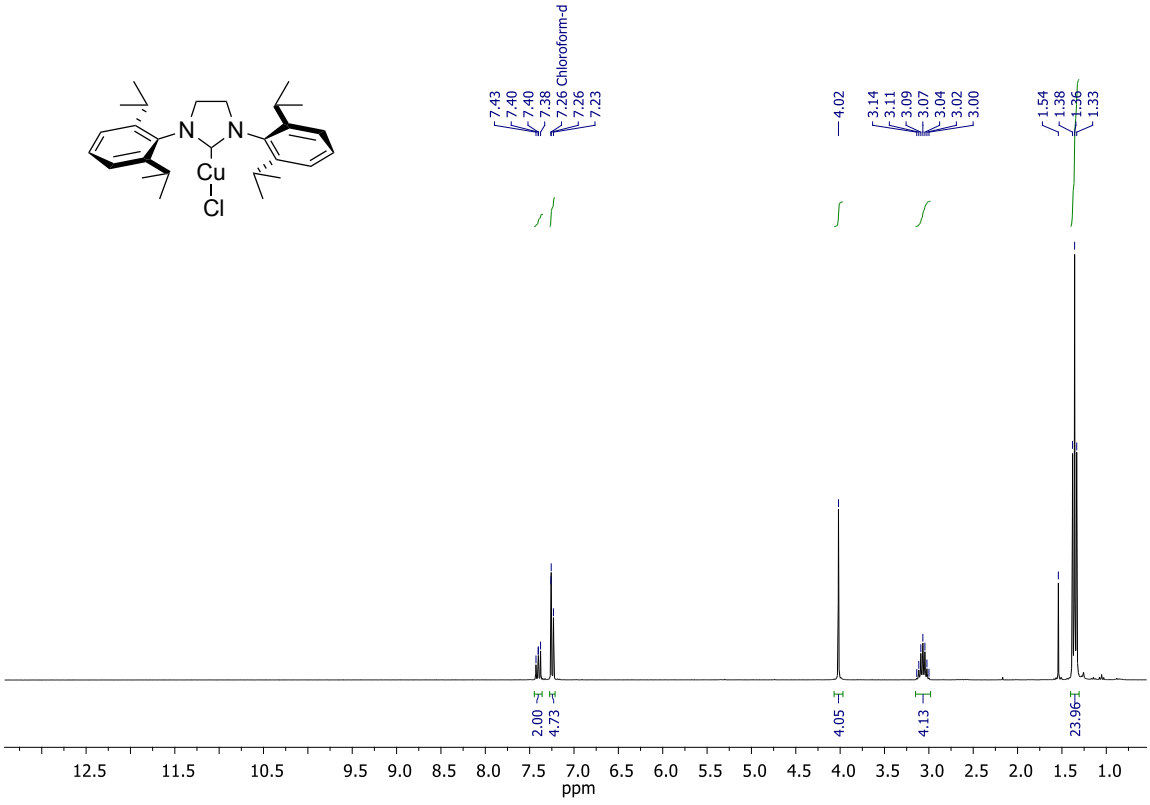


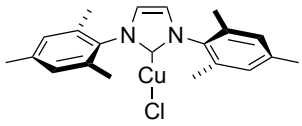
Following the general procedure with MIC·HCl (200 mg, 0.49 mmol), CuCl (48 mg, 0.49 mmol) and K_2CO_3 (201 mg, 1.46 mmol), [Cu(Cl)(MIC)] was obtained as a colourless solid in 36% yield (83 mg, 0.17 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ= 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH-C$\underline{H}_3$), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH-C$\underline{H}_3$), 1.39 (s, 9H, $C(CH_3)_3$), 2.32 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C$\underline{H}(CH_3)_2$), 4.25 (s, 3H, N-CH_3), 7.29-7.30 (m, 2H, ArH), 7.51-7.55 (m, 1H, ArH), 7.55-7.60 (m, 2H, ArH), 7.67-7.73 (m, 2H, ArH). The spectrum matches data from the literature.[5]

NMR spectra of complexes



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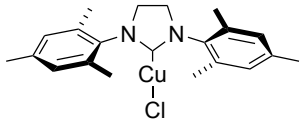
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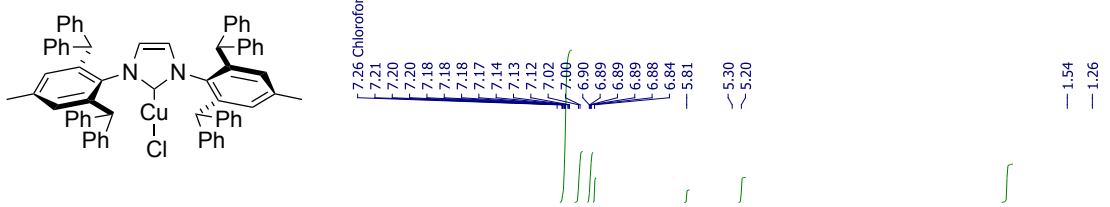
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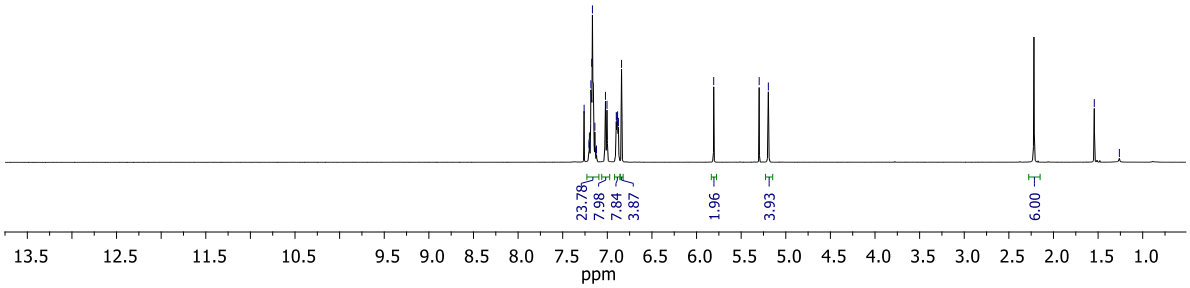
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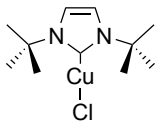
N
N
Cu
Cl

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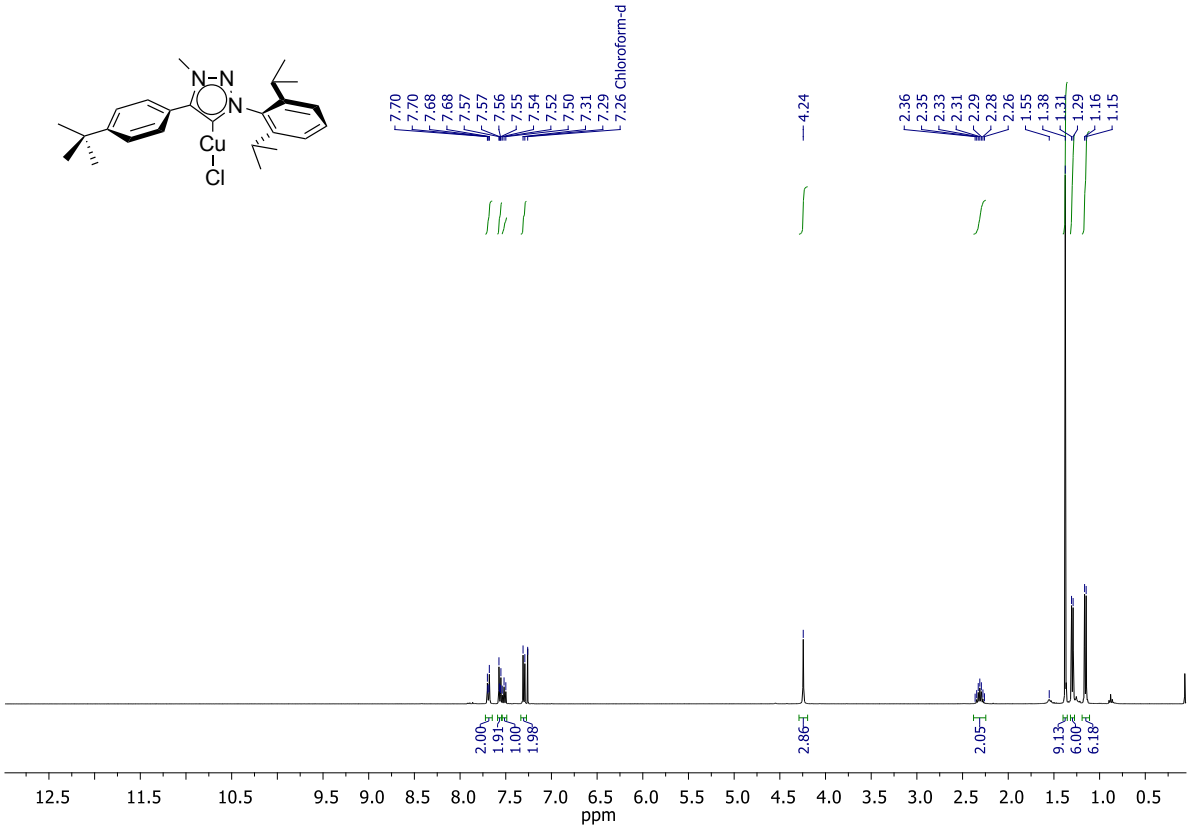

References

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