IMes-acac: hybrid combination of diaminocarbene and acetylacetonato sub-units into a new anionic ambidentate NHC ligand

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Supporting Information

Contents

Materials and methods

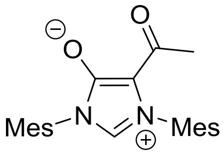
All manipulations were performed under an inert atmosphere of dry nitrogen by using standard vacuum line and Schlenk tube techniques. Glassware was dried at 120°C in an oven for at least three hours. Toluene, CH_2Cl_2, pentane, Et_2O and THF were dried using an SPS system from Innovative Technology and water content was quantified by Karl Fischer titration. DMF was deoxygenated by bubbling N_2 for 15 min and was stored over activated 4Å molecular sieves.

NMR spectra were recorded on Bruker AV300 or AV400 spectrometers. Chemical shifts are reported in ppm (δ) compared to TMS (^{1}H and ^{13}C) using the residual peak of deuterated solvent as internal standard.[1] Infrared spectra were obtained on a Perkin-Elmer Spectrum 100 FT-IR spectrometer using the ATR mode. Microanalyses were performed by the Microanalytical Services of the LCC and MS spectra by the mass spectrometry service of the "Institut de Chimie de Toulouse".

1,3-dimesityl-4-hydroxyimidazolium chloride,[2] and (IPr)CuCl[3] were synthesized according to literature procedures. Et_3N was distilled over CaH_2 prior to use. All other reagents were commercially available and used as received.

Synthetic procedures

1,3-dimesityl-5-acetylimidazolium-4-olate [(acac-IMes)·H] (1·H)



1,3-dimesityl-4-hydroxyimidazolium chloride (**IMes$^{\mathbf{OH}}$**)·HCl (3.73 g, 10.45 mmol) was suspended in toluene (100 mL) and Et_3N (1.75 mL, 12.5 mmol, 1.2 eq.) was added at room temperature. After 15 minutes, the mixture was heated at 110°C and acetyl chloride (0.89 mL, 12.5 mmol, 1.2 eq.) was added dropwise resulting in a color change of the solution to yellow. After 1.5 hours at that temperature, the reaction mixture was cooled to room temperature and Et_2O (150 mL) was added. The mixture was filtered through a Büchner funnel to remove the salts and the filtrate was evaporated. The brown residue was purified by flash chromatography (SiO_2, hexane/ethyl acetate: 1/2) to afford a yellow solid, which was further washed with small quantities of Et_2O until the yellow color disappeared. After drying, an off-white powder was obtained (2.1 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (s, 1H, $N_2C\mathit{H}$), 6.96 (s, 2H, $C\mathit{H}_{\mathrm{Mes}}$), 6.90 (s, 2H, $C\mathit{H}_{\mathrm{Mes}}$), 2.41 (s, 3H, $C\mathit{H}_3CO$), 2.31 (s, 3H, $C\mathit{H}_{3\ \mathrm{para}}$), 2.29 (s, 3H, $C\mathit{H}_{3\ \mathrm{para}}$), 2.12 (s, 6H, $C\mathit{H}_3$

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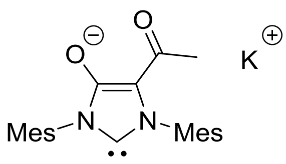
[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.

[2] L. Benhamou, V. César, H. Gornitzka, N. Lugan, G. Lavigne, *Chem. Commun.* **2009**, 4720.

[3] O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan, C. S. J. Cazin, *Chem. Commun.* **2013**, *49*, 10483.

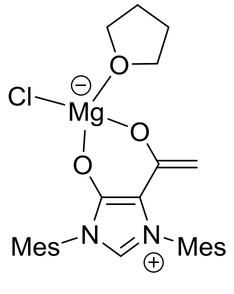
$_{ortho}$), 2.05 (s, 6H, C$H_{3\ ortho}$); $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 184.6 (CH_3*C*O), 157.5 (C_{Im}-O^-), 139.7 139.2, 135.5, 134.0, 133.8 (C_{Mes}), 129.3 (CH_{Mes}), 128.8 (CH_{Mes}), 128.7 (N_2*C*H), 108.4 ($C_{Im\text{-}5}$), 27.0 (*C*H_3CO), 21.1 ($CH_{3\ para}$), 17.8 ($CH_{3\ ortho}$), 17.3 ($CH_{3\ ortho}$); IR (ATR): ν= 3023 (w), 2920 (w), 2859 (w), 1670 (s), 1597 (vs), 1553 (s), 1486 (w), 1423 (m), 1397 (m), 1375 (w), 1351 (w), 1227 (s), 1011 (w), 951 (w), 916 (m), 856 (m), 795 (m), 743 (w) cm^{-1}; MS (ESI): m/z (%): 363 (100) $[M + H]^+$; HRMS (ESI): m/z calcd. for $C_{23}H_{27}N_2O_2$: 363.2073; found: 363.2071, ε_r = 0.6 ppm; elemental analysis *calcd* (%) for $C_{23}H_{26}N_2O_2$ (MW = 362.47): C 76.21, H 7.23, N 7.73, *found*: C 75.92, H 7.20, N 7.62.

Potassium 1,3-dimesityl-5-acetyl-2*H*-imidazol-2-ylidene-4-olate [(acac-IMes)·K] (1·K)



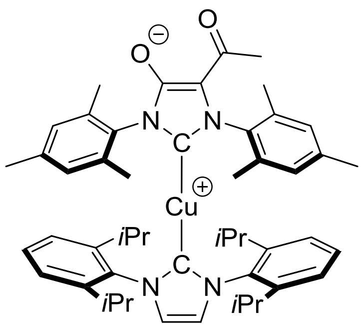
At room temperature, a solution of KHMDS (0.5 M in toluene, 365 μL, 0.182 mmol, 1.1 eq.) was added to a solution of **1**·H (60 mg, 0.166 mmol) in THF (2 mL). After 15 minutes, all volatiles were removed in vacuo and the crude residue was analyzed by NMR spectroscopy after dissolution in THF-d8 (0.7 mL). ^1H NMR (400 MHz, THF-d8): δ = 6.90 (s, 2H, CH_{Mes}), 6.86 (s, 2H, CH_{Mes}), 2.30 (s, 3H, C$H_{3\ para}$), 2.27 (s, 3H, C$H_{3\ para}$), 2.12 (s, 6H, C$H_{3\ ortho}$), 2.05 (s, 6H, C$H_{3\ ortho}$), 1.30 (s, 3H, CH_3CO), $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d8): δ = 220.3 (N_2*C*), 179.3 (CH_3*C*O), 164.0 (C_{Im}-O^-), 141.9, 138.1, 137.2, 137.1, 136.8 (C_{Mes}), 129.3 (CH_{Mes}), 129.1 (CH_{Mes}), 112.1 ($C_{Im\text{-}5}$), 27.2 (*C*H_3CO), 21.4 ($CH_{3\ para}$), 21.3 ($CH_{3\ para}$), 19.0 ($CH_{3\ ortho}$), 18.5 ($CH_{3\ ortho}$).

Compound 2: (thf)ClMg(acac'-IMes)H



Isopropylmagnesium chloride (2M in Et_2O, 100 μL, 0.20 mmol, 1.2 eq.) was added dropwise to a solution of **1**·H (60 mg, 0.166 mmol) in THF (2 mL) at – 30°C. The reaction mixture turned orange during addition. The cooling bath was removed and after return to room temperature, all volatiles were removed under vacuum. The crude residue was taken up in THf-d8 (0.7 mL) and analyzed by ^1H and ^{13}C NMR spectroscopy. ^1H NMR (400 MHz, THF-d8): δ = 7.77 (s, 1H, N_2C*H*), 7.03 (s, 2H, CH_{Mes}), 6.77 (s, 2H, CH_{Mes}), 3.97 (br s, 1H, C(-O)=CH_2), 3.63-3.60 (m, 4H, O-C$H_{2\ THF}$), 2.79 (br s, 1H, C(-O)=CH_2), 2.34 (s, 3H, C$H_{3\ para}$), 2.15 (s, 6H, C$H_{3\ ortho}$), 2.08 (s, 6H, C$H_{3\ ortho}$), 2.07 (s, 3H, C$H_{3\ para}$), 1.79-1.76 (m, 4H, O-CH_2-C$H_{2\ THF}$); $^{13}C\{^1H\}$ NMR (100.5 MHz, THF-d8): δ = 153.1, 153.0 (C_{Im}-O + *C*(-O)=CH_2), 140.7, 140.1, 136.1, 135.9, 134.7, 130.9 (C_{Mes}), 130.2 (CH_{Mes}), 129.9 (CH_{Mes}), 123.1 (N_2*C*H), 108.9 ($C_{Im\text{-}5}$), 80.8 (C(-O)=*C*H_2)), 68.4 (O-*C*$H_{2\ THF}$), 26.5 (O-CH_2-*C*$H_{2\ THF}$), 21.4 ($CH_{3\ para}$), 21.3 ($CH_{3\ para}$), 18.3 ($CH_{3\ ortho}$), 17.9 ($CH_{3\ ortho}$).

Complex 3: (acac-IMes)Cu(IPr)



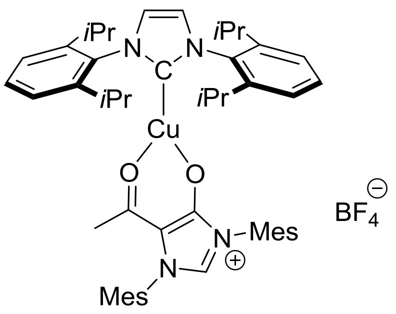
A solution of KHMDS (0.5 M in toluene, 2.4 mL, 1.2 mmol, 1.2 equiv.) was added dropwise to a solution of **1**·H (398 mg, 1.1 mmol, 1.1 eq.) in THF (20 mL) at room temperature. After 15 minutes, (IPr)CuCl (487 mg, 1.0 mmol, 1.0 equiv.) was added as a solid to the solution, and the mixture was stirred for 20 hours. All volatiles were removed under vacuum and the crude residue was purified by flash chromatography (neutral Al_2O_3, Brockmann type 3, pure CH_2Cl_2 then CH_2Cl_2/MeOH: 98/2) to yield the title compound as a white powder (747 mg, 92%). Single crystals suitable fro an X-Ray diffraction analysis were grown by layering a solution of **3** in CH_2Cl_2 with pentane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (t, *J* = 7.8 Hz, 2H, C$H_{\text{Dipp-p}}$), 7.15 (d, *J* = 7.8 Hz, 4H, C$H_{\text{Dipp-m}}$), 6.98 (s, 2H, CH_{Im}), 6.64 (s, 2H, CH_{Mes}), 6.54 (s, 2H, CH_{Mes}), 2.34-2.19 (m, 4H, CH_{iPr}), 2.29 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.70 (s, 6H, C$H_{3\ \text{ortho}}$), 1.64 (s, 6H, C$H_{3\ \text{ortho}}$), 1.03 (d, *J* = 6.8 Hz, 12H, C$H_{3\ iPr}$), 0.82 (d, *J* = 6.9 Hz, 12H, C$H_{3\ iPr}$); $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 182.1, 180.7 ($N_2C_{\text{“IMes-acac”}}$ + *C*=O), 170.6 (N_2C_{IPr}), 161.3 (C_{Im}-O^-), 144.7, 138.0, 136.6, 135.9, 135.7, 134.4, 134.3, 133.1 (C_{Ar}), 130.3 (*C*$H_{\text{Dipp-p}}$), 129.0 (*C*H_{Mes}), 128.5 (*C*H_{Mes}), 124.1 (*C*$H_{\text{Dipp-m}}$), 123.3 (*C*H_{Im}), 108.5 ($C_{\text{Im-5}}$), 28.5 (*C*H_{iPr}), 26.1 (*C*H_3-C=O), 24.0 (*C*$H_{3\ iPr}$), 23.5 (*C*$H_{3\ iPr}$), 21.3 (*C*$H_{3\ \text{para}}$), 21.2 (*C*$H_{3\ \text{para}}$), 17.9 (*C*$H_{3\ \text{ortho}}$), 17.4 (*C*$H_{3\ \text{ortho}}$); IR (ATR): ν = 2966 (w), 2918 (w), 2870 (w), 1645 (s), 1594 (vs), 1557 (m), 1459 (m), 1424 (s), 1405 (s), 1291 (m), 1235 (w), 1032 (w), 927 (m), 849 (m), 811 (s), 804 (m), 762 (s) cm^{-1}; MS (ESI): m/z (%): 835 (27) $[M + Na]^+$, 813 (100) $[M + H]^+$; elemental analysis *calcd* (%) for $C_{50}H_{61}CuN_4O_2$ (MW = 813.61): C 73.81, H 7.56, N 6.89, *found*: C 73.50, H 7.53, N 6.66.

From 4

A solution of KHMDS (0.5 M in toluene, 240 μL, 0.12 mmol, 1.1 equiv.) was added dropwise to a solution of complex **4** (98.5 mg, 0.109 mmol) in THF (6 mL) at – 80°C. The reaction mixture was allowed to warm up to room temperature overnight, and all volatiles were removed in vacuo. The crude residue was purified by flash chromatography (neutral Al_2O_3, Brockmann type 3, CH_2Cl_2/MeOH: 98/2 then 95/5) to yield an off-white powder (61 mg, 69%).

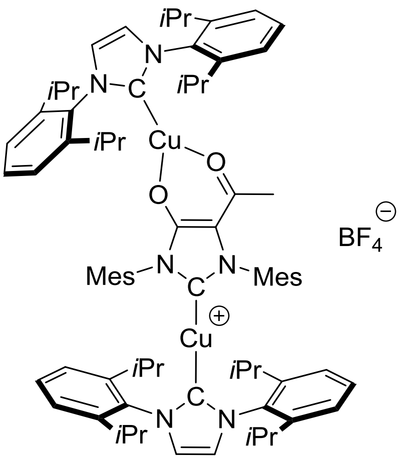
Complex 4: [(IPr)Cu(acac-IMes)H](BF_4)

CH_3CN (6 mL) was syringed on a mixture of (IPr)CuCl (250 mg, 0.513 mmol, 1.0 eq.) and $AgBF_4$ (100 mg, 0.513 mmol, 1.0 eq.) at room temperature. The solution was colorless with a white precipitate. After 5 minutes, **1**·H (186 mg, 0.513 mmol, 1.0 eq.) was added as a solid and the reaction mixture was stirred for 40 min. All volatiles were removed under vacuum and the residue was taken up with CH_2Cl_2 (5 mL) and filtered through Celite. After evaporation, the crude mixture was washed with Et_2O (2 x 3



mL) and dried under vacuum to yield a light yellow powder (420 mg, 91%). Yellow single crystals suitable for an X-Ray diffraction experiment were grown by layering Et_2O over a solution of **4** in CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1H, N_2C*H*), 7.44 (t, *J* = 7.8 Hz, 2H, C*H*$_{\text{Dipp-p}}$), 7.23 (d, *J* = 7.8 Hz, 4H, C*H*$_{\text{Dipp-m}}$), 7.10 (s, 2H, C*H*$_{\text{Im}}$), 6.97 (s, 2H, C*H*$_{\text{Mes}}$), 6.92 (s, 2H, C*H*$_{\text{Mes}}$), 2.58 (sept, *J* = 6.8 Hz, 4H, C*H*$_{i\text{Pr}}$), 2.32 (s, 3H, C*H*$_{3\ \text{para}}$), 2.31 (s, 3H, C*H*$_{3\ \text{para}}$), 2.06 (s, 6H, C*H*$_{3\ \text{ortho}}$), 1.92 (s, 6H, C*H*$_{3\ \text{ortho}}$), 1.47 (br s, 3H, C*H*$_3$CO), 1.19 (d, *J* = 6.9 Hz, 12H, C*H*$_{3\ i\text{Pr}}$), 1.10 (d, *J* = 6.8 Hz, 12H, C*H*$_{3\ i\text{Pr}}$); ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ = 185.2 (*C*=O), 158.2 (*C*$_{\text{Im}}$-O$^-$), 146.0, 141.2, 140.2, 135.2, 135.2, 134.8 (*C*$_{\text{Ar}}$), 133.3 (N_2*C*H), 131.2 (*C*$_{\text{Ar}}$), 130.2 (*C*H$_{\text{Dipp-p}}$), 129.9 (*C*H$_{\text{Mes}}$), 129.3 (*C*H$_{\text{Mes}}$), 127.3 (*C*$_{\text{Ar}}$), 124.0 (*C*H$_{\text{Dipp-m}}$), 122.9 (*C*H$_{\text{Im}}$), 110.0 (*C*$_{\text{Im-5}}$), 28.8 (*C*H$_{i\text{Pr}}$), 26.0 (*C*H$_3$CO), 24.2 (*C*H$_{3\ i\text{Pr}}$), 24.1 (*C*H$_{3\ i\text{Pr}}$), 21.4 (*C*H$_{3\ \text{para}}$), 21.3 (*C*H$_{3\ \text{para}}$), 17.7 (*C*H$_{3\ \text{ortho}}$), 17.2 (*C*H$_{3\ \text{ortho}}$), N_2*C*$_{\text{IPr}}$ was not detected though concentrated sample and high number of scans; IR (ATR): ν = 2962 (m), 2926 (w), 2869 (w), 1657 (s), 1610 (m), 1562 (m), 1469 (s), 1406 (m), 1385 (m), 1329 (w), 1226 (m), 1055 (vs), 1033(vs), 946 (m), 929 (m), 852 (m), 804 (s), 759 (s) cm^{-1}; MS (ESI): m/z (%): 813 (12) [M − BF_4]$^+$, 492 (100) [(IPr)Cu(CH_3CN)]$^+$, 363 (76) [(acac-IMes)H]$^+$; HRMS (ESI): m/z calcd. for $C_{50}H_{62}CuN_4O_2$: 813.4169; found: 813.4150, ε_r = 2.3 ppm; Despite drying under vacuum for several days, residual dichloromethane could not be removed for elemental analysis: elemental analysis *calcd* (%) for $C_{50}H_{62}BCuF_4N_4O_2$ (MW = 901.42) + 0.15 CH_2Cl_2: C 65.89, H 6.87, N 6.13, *found*: C 65.93, H 6.70, N 6.04.

Complex 5: [(IPr)Cu(acac-IMes)Cu(IPr)](BF_4)



$AgBF_4$ (44.9 mg, 0.230 mmol, 1.05 eq.) and (IPr)CuCl (107 mg, 0.219 mmol, 1.0 eq.) were stirred together in CH_3CN (5 mL) for 5 min under exclusion of light. The mixture was evaporated and complex **3** (178 mg, 0.219 mmol, 1.0 eq.) was added as a solid. CH_2Cl_2 (7 mL) was syringed into the Schlenk tube and the mixture was stirred for 25 min at room temperature and filtered through celite. Additional CH_2Cl_2 (3 mL) was used to rinse the celite plug. Evaporation of all volatiles left a light orange foam as crude product, which was purified by washing with Et_2O (3 x 3 mL) to yield after drying an off-white powder (260 mg, 88%). Yellow crystals of $5\cdot2CH_2Cl_2$ could be obtained by layering a solution of **5** in CH_2Cl_2 with pentane. An X-Ray diffraction experiment could be performed but the poor quality of the crystals prevented a proper determination of the structure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, *J* = 7.8 Hz, 2H, C*H*$_{\text{Dipp-p}}$), 7.36 (t, *J* = 7.8 Hz, 2H, C*H*$_{\text{Dipp-p}}$), 7.15-7.13 (m, 8H, C*H*$_{\text{Dipp-m}}$), 7.10 (s, 2H, C*H*

$_{\mathrm{Im}}$), 7.00 (s, 2H, $\mathrm{C}H_{\mathrm{Im}}$), 6.65 (s, 2H, $\mathrm{C}H_{\mathrm{Mes}}$), 6.60 (s, 2H, $\mathrm{C}H_{\mathrm{Mes}}$), 2.51 (sept, *J* = 6.9 Hz, 4H, $\mathrm{C}H_{i\mathrm{Pr}}$), 2.35 (s, 3H, $\mathrm{C}H_{3\ \mathrm{para}}$), 2.32 (s, 3H, $\mathrm{C}H_{3\ \mathrm{para}}$), 2.28 (sept, *J* = 6.9 Hz, 4H, $\mathrm{C}H_{i\mathrm{Pr}}$), 1.58 (s, 6H, $\mathrm{C}H_{3\ \mathrm{ortho}}$), 1.38 (s, 6H, $\mathrm{C}H_{3\ \mathrm{ortho}}$), 1.11 (d, *J* = 6.9 Hz, 12H, $\mathrm{C}H_{3\ i\mathrm{Pr}}$), 1.06 (d, *J* = 6.8 Hz, 12H, $\mathrm{C}H_{3\ i\mathrm{Pr}}$), 0.97 (d, *J* = 6.8 Hz, 12H, $\mathrm{C}H_{3\ i\mathrm{Pr}}$), 0.94 (s, 3H, $\mathrm{C}H_3\mathrm{CO}$), 0.76 (d, *J* = 6.9 Hz, 12H, $\mathrm{C}H_{3\ i\mathrm{Pr}}$), $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.5 MHz, $\mathrm{CDCl_3}$): δ = 183.7 ($\mathrm{N_2}C_{\mathrm{IPr\ on\ Cu}}$), 182.1 ($C$=O), 179.2 ($\mathrm{N_2}C_{\mathrm{IPr\ on\ Cu+}}$), 172.8 ($\mathrm{N_2}C_{\text{“IMes-acac”}}$), 160.6 ($C_{\mathrm{Im}}$-$\mathrm{O^-}$), 146.0, 145.0 ($C_{\mathrm{Dipp}}$), 139.0, 137.7 ($C_{\mathrm{Mes}}$), 135.4 ($C_{\mathrm{Mes}}$), 135.3 ($C_{\mathrm{Dipp}}$), 135.2 ($C_{\mathrm{Mes}}$), 134.4 ($C_{\mathrm{Dipp}}$), 131.2 ($C_{\mathrm{Mes}}$), 130.5 ($C\mathrm{H}_{\mathrm{Dipp\text{-}p}}$), 129.7 ($C\mathrm{H}_{\mathrm{Dipp\text{-}p}}$ + $C\mathrm{H}_{\mathrm{Mes}}$), 129.1 ($C\mathrm{H}_{\mathrm{Mes}}$), 124.2 ($C\mathrm{H}_{\mathrm{Dipp\text{-}m}}$), 124.1 ($C\mathrm{H}_{\mathrm{Im\text{-}IPr}}$), 123.7 ($C\mathrm{H}_{\mathrm{Dipp\text{-}m}}$), 122.4 ($C\mathrm{H}_{\mathrm{Im\text{-}IPr}}$), 111.0 ($C_{\mathrm{Im\text{-}5}}$), 28.6, 28.5 ($C\mathrm{H}_{i\mathrm{Pr}}$), 24.3 ($C\mathrm{H}_{3\ i\mathrm{Pr}}$), 24.2 ($C\mathrm{H}_{3\ i\mathrm{Pr}}$), 23.7 ($C\mathrm{H_3CO}$), 23.6 ($C\mathrm{H}_{3\ i\mathrm{Pr}}$), 21.4 ($C\mathrm{H}_{3\ \mathrm{para}}$), 21.3 ($C\mathrm{H}_{3\ \mathrm{para}}$), 17.6 ($C\mathrm{H}_{3\ \mathrm{ortho}}$), 17.1 ($C\mathrm{H}_{3\ \mathrm{ortho}}$); IR (ATR): ν = 2963 (m), 2927 (w), 2869 (w), 1635 (s), 1469 (s), 1403 (m), 1329 (w), 1049 (vs), 943 (m), 937 (m), 802 (m), 757 (s) $\mathrm{cm^{-1}}$; MS (ESI): m/z (%): 1265 (3) $[\mathrm{M - BF_4}]^+$, 813 (100) $[\mathrm{(acac\text{-}IMes)Cu(IPr) + H}]^+$, 492 (31) $[\mathrm{(IPr)Cu(CH_3CN)}]^+$, HRMS (ESI): m/z calcd. for $\mathrm{C_{77}H_{97}{}^{63}Cu_2N_6O_2}$: 1263.6265; found: 1263.6277, ε_r = 0.9 ppm; Despite drying under vacuum for several days, residual dichloromethane could not be removed for elemental analysis: elemental analysis *calcd* (%) for $\mathrm{C_{77}H_{97}BCu_2F_4N_6O_2}$ (MW = 1352.56) + 0.3 $\mathrm{CH_2Cl_2}$: C 67.38, H 7.14, N 6.10, *found*: C 67.50, H 7.01, N 6.07.

X-Ray diffraction studies

Crystals of complexes **3** and **4** suitable for X-ray diffraction were obtained by crystallization from $\mathrm{CH_2Cl_2}$/pentane and from $\mathrm{CH_2Cl_2/Et_2O}$ at room temperature, respectively; data were collected at 173 K on a Bruker D8 / Apex II diffractometer. All calculations were performed on a PC-compatible computer using the WinGX system.[4] The structures were solved using the SIR92 program,[5] which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXL97 program.[6] Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Cu atoms were included in Fc. All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealised position ($\mathrm{R_3CH}$, C–H = 0.96 Å; $\mathrm{R_2CH_2}$, C–H = 0.97 Å; $\mathrm{RCH_3}$, C–H = 0.98 Å; C(sp^2) –H = 0.93 Å; U_{iso} 1.2 or 1.5 time greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and their position were

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[4] A. L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849.

[5] B. A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.

[6] C. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

refined as “riding” atoms. Complex **4** crystallizes with two independent molecules per unit cell. The tetrafluoroborate anions were found to be heavily disordered and the disorder could not be accurately resolved; they were thus both refined whithin constrained tetrahedral models. CCDC-1031661 (**3**) and CCDC-1031662 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The structure of **5** has been tentatively determined by single-crystal X-ray diffraction. Despite all our efforts, only in one occasion a crystal barely suitable for X-ray diffraction could be obtained. Its diffraction power was nevertheless extremely low (Smax » 0.45 Å^{-1}) and the structure could not be properly refined.[7] However, the connectivity scheme, shown in Figure S1, could be determined without any ambiguity.

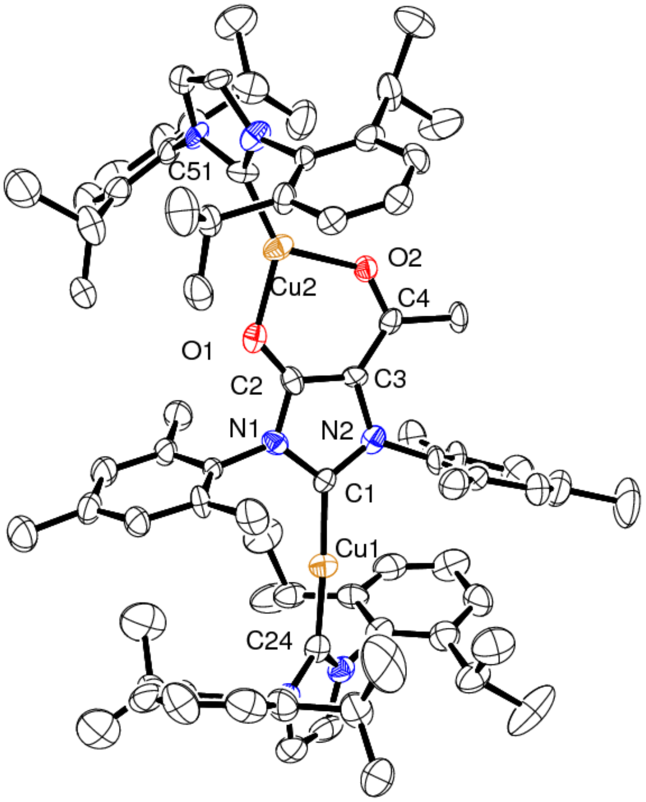

Figure S1. Molecular structure of complex **5** (Ellipsoids drawn at 30% probability level). Tetrafluoroborate anion, solvent molecules and all hydrogen atoms were removed for clarity.

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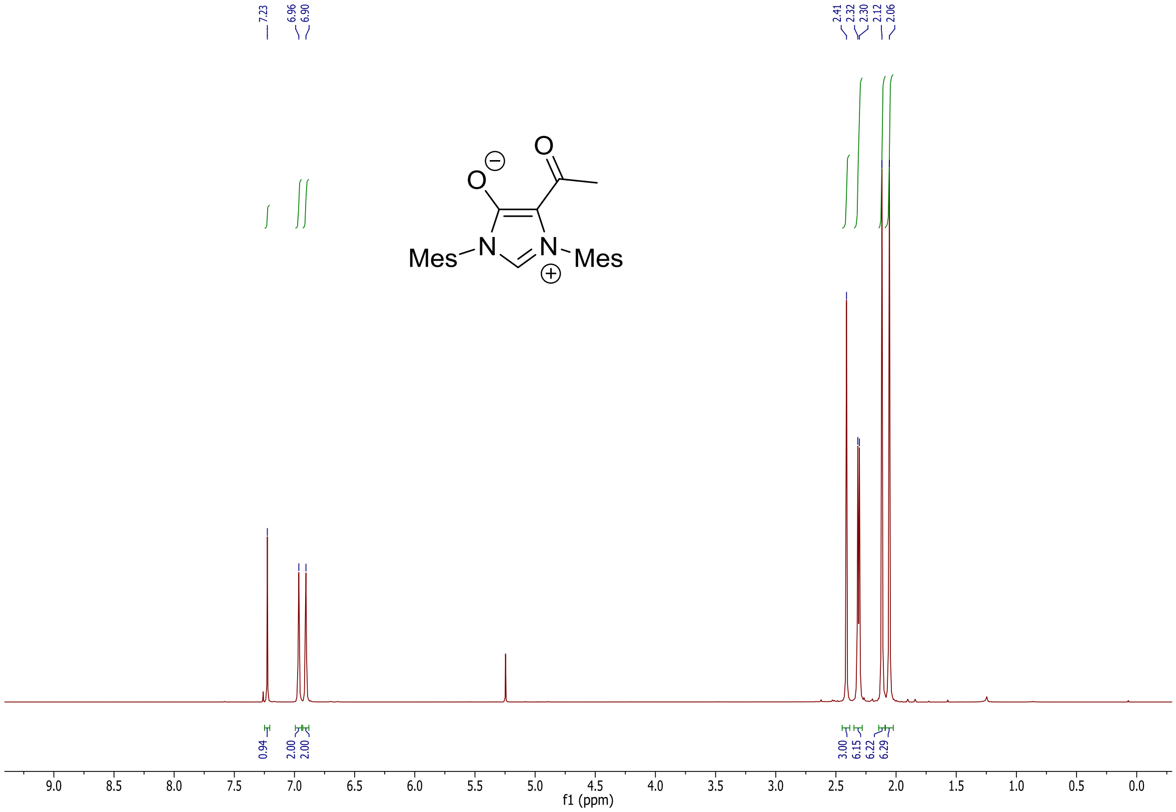
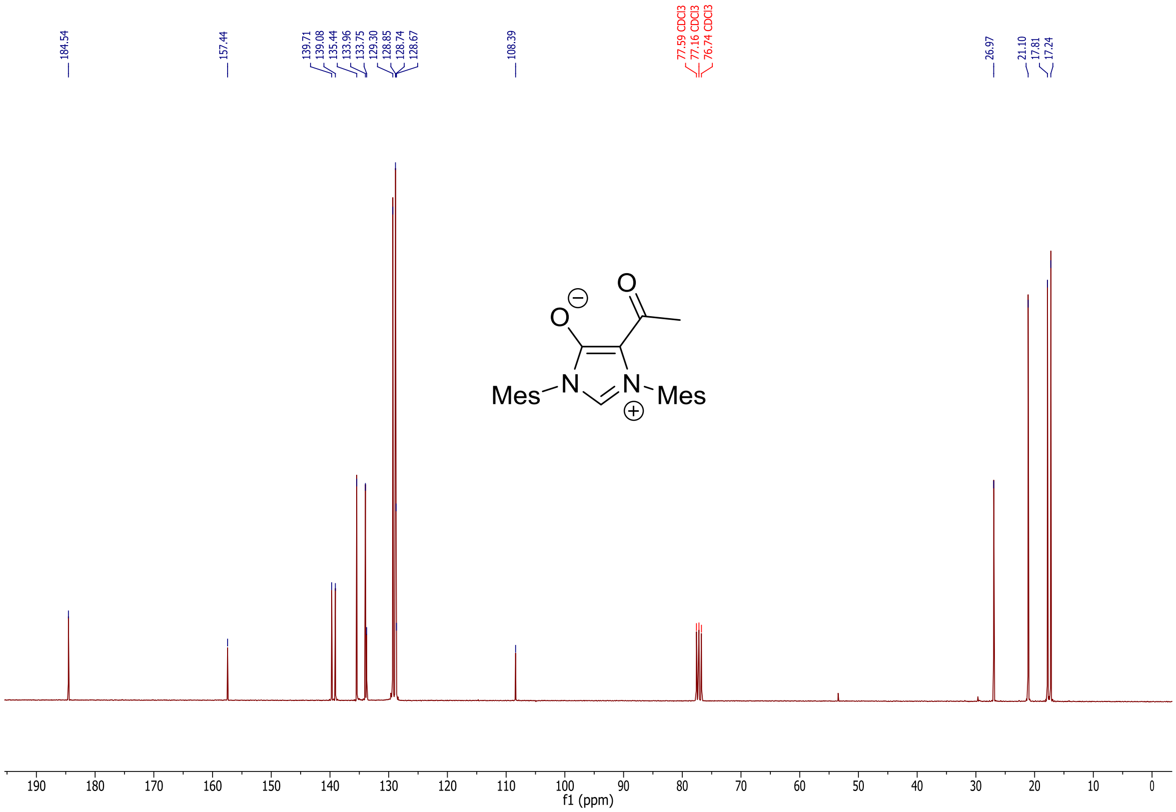
[7] **5**.2CH$_2$Cl$_2$: triclinic P-1, a = 14.351(4) Å, b = 16.176(4) Å, c = 22.172(5) Å, a = 88.921(7)°, b = 85.783(7)°, g = 65.117(6)°, V = 4656(2) Å^3, T = 173(1) K, Z = 4, F000 = 1600, Dc = 1.086 g/cm^3, μ = 0.62 mm^{-1}. 36061 reflections collected up to S$_{max}$ » 0.45 Å^{-1}, 9061 unique (R$_{int}$ = 0.0736), final wR(F$_2$) was 0.2079 (all data).

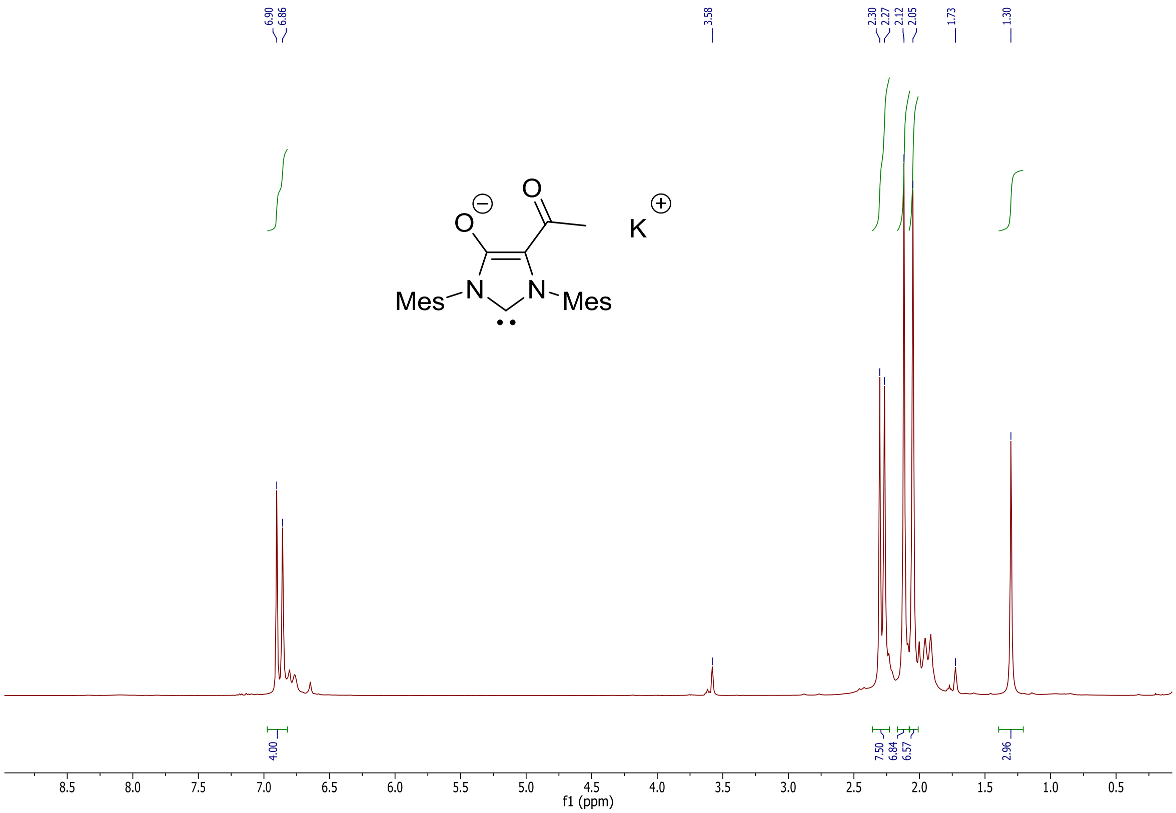
^{1}H NMR spectrum of (acac-IMes)H (300 MHz, $CDCl_3$)



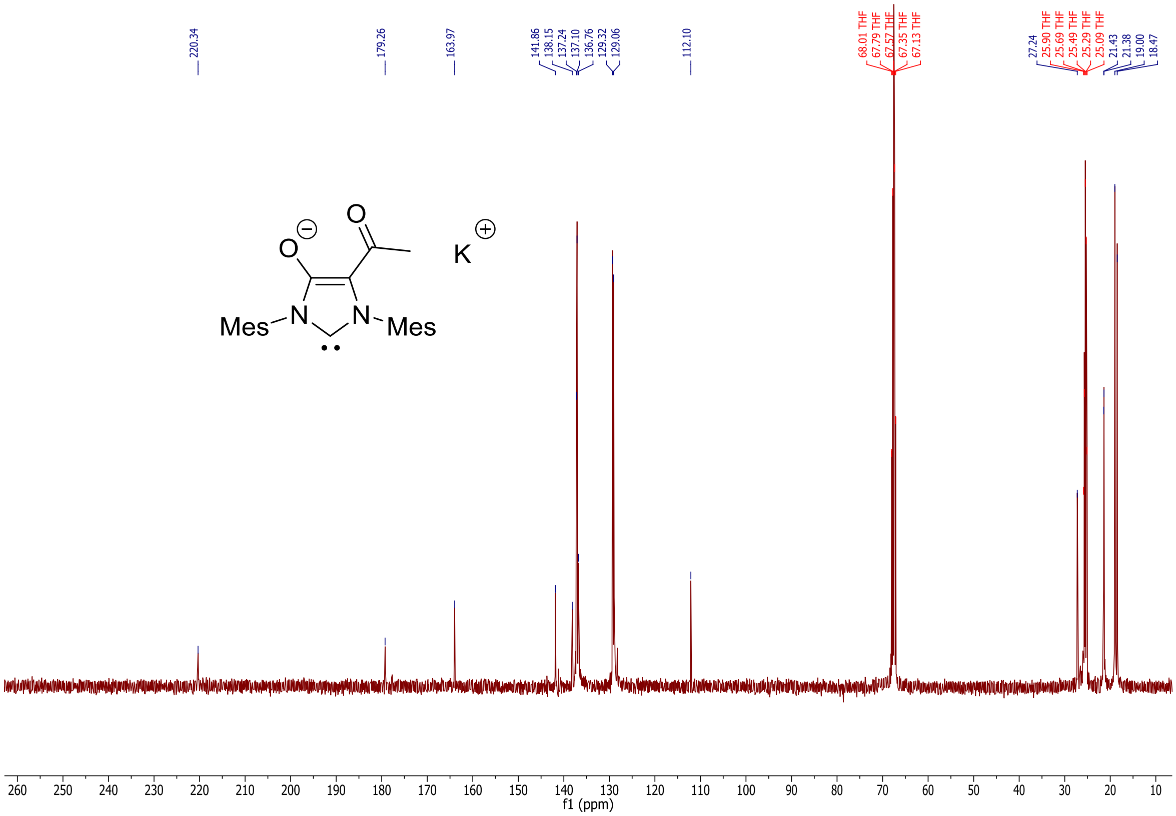
$^{13}C\{^{1}H\}$ NMR spectrum of (acac-IMes)H (75.5 MHz, $CDCl_3$)



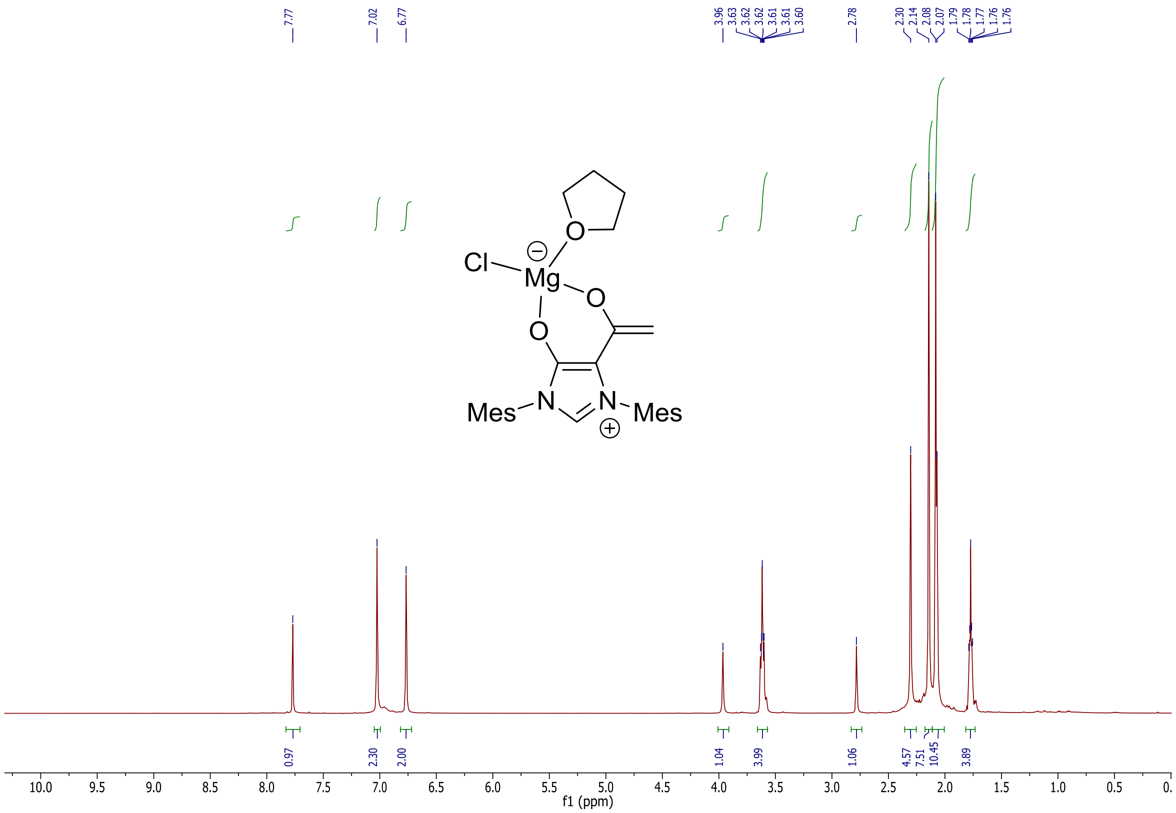
^{1}H NMR spectrum of (acac-IMes)K (300 MHz, THF-d8)



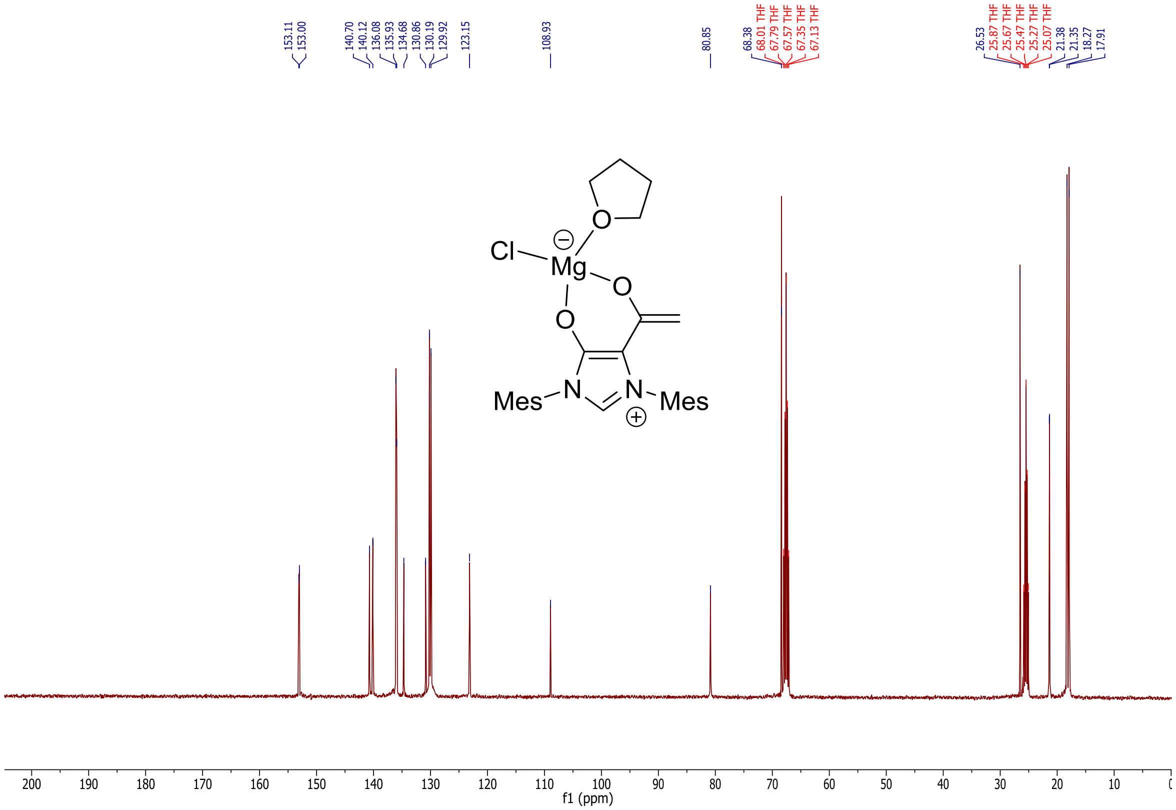
^{13}C{^{1}H} NMR spectrum of (acac-IMes)K (75.5 MHz, THF-d8)



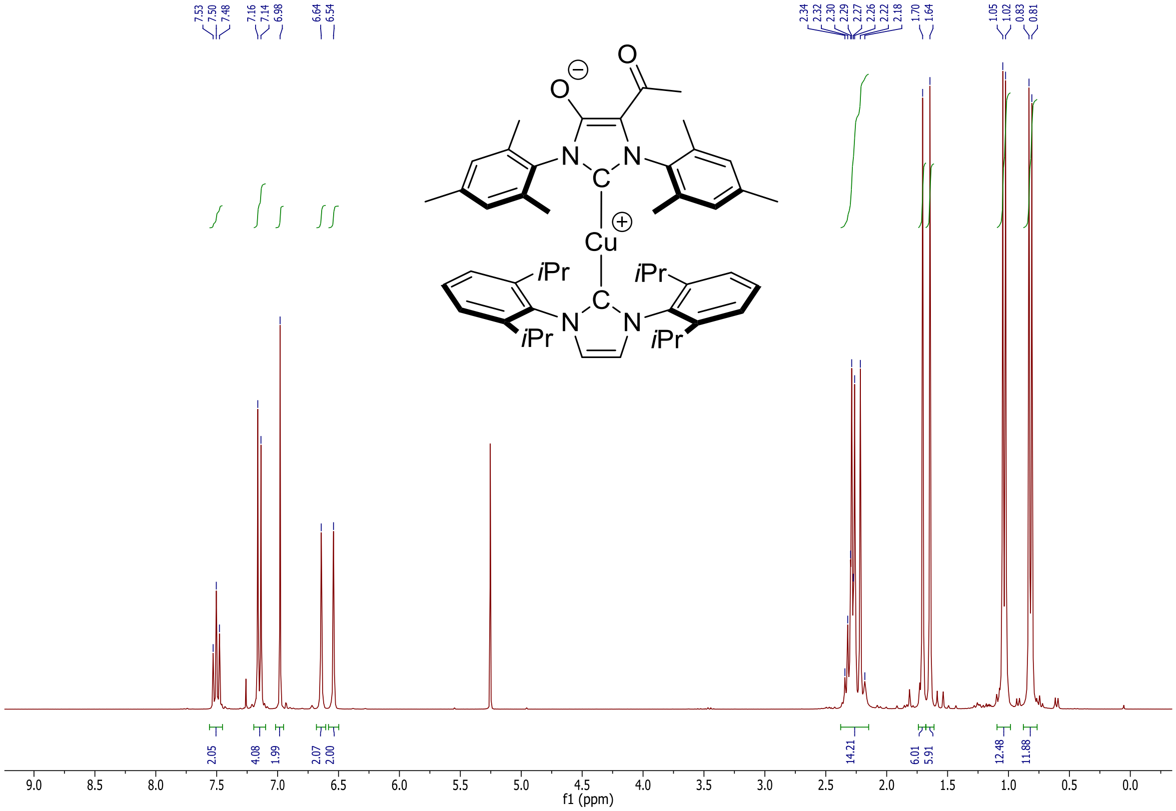
^{1}H NMR spectrum of (thf)ClMg(acac’-IMes)H (300 MHz, THF-d8)



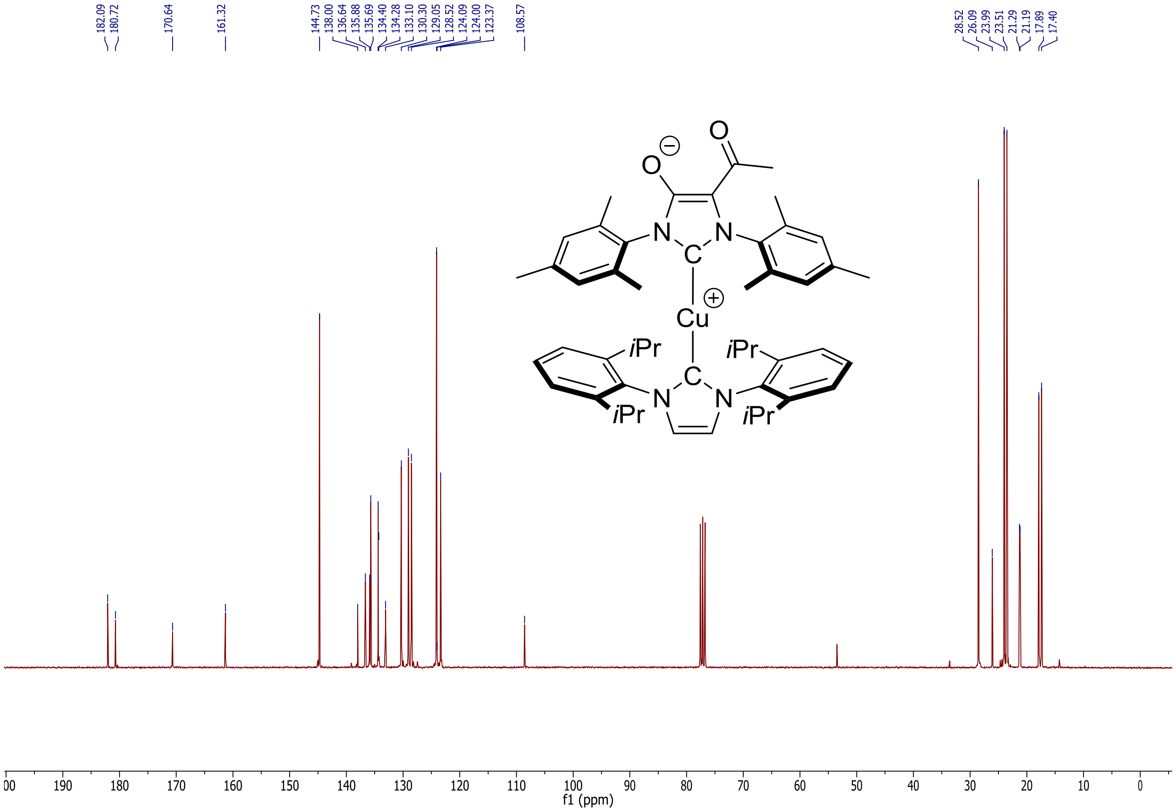
^{13}C{^{1}H} NMR spectrum of (thf)ClMg(acac’-IMes)H (75.5 MHz, THF-d8)



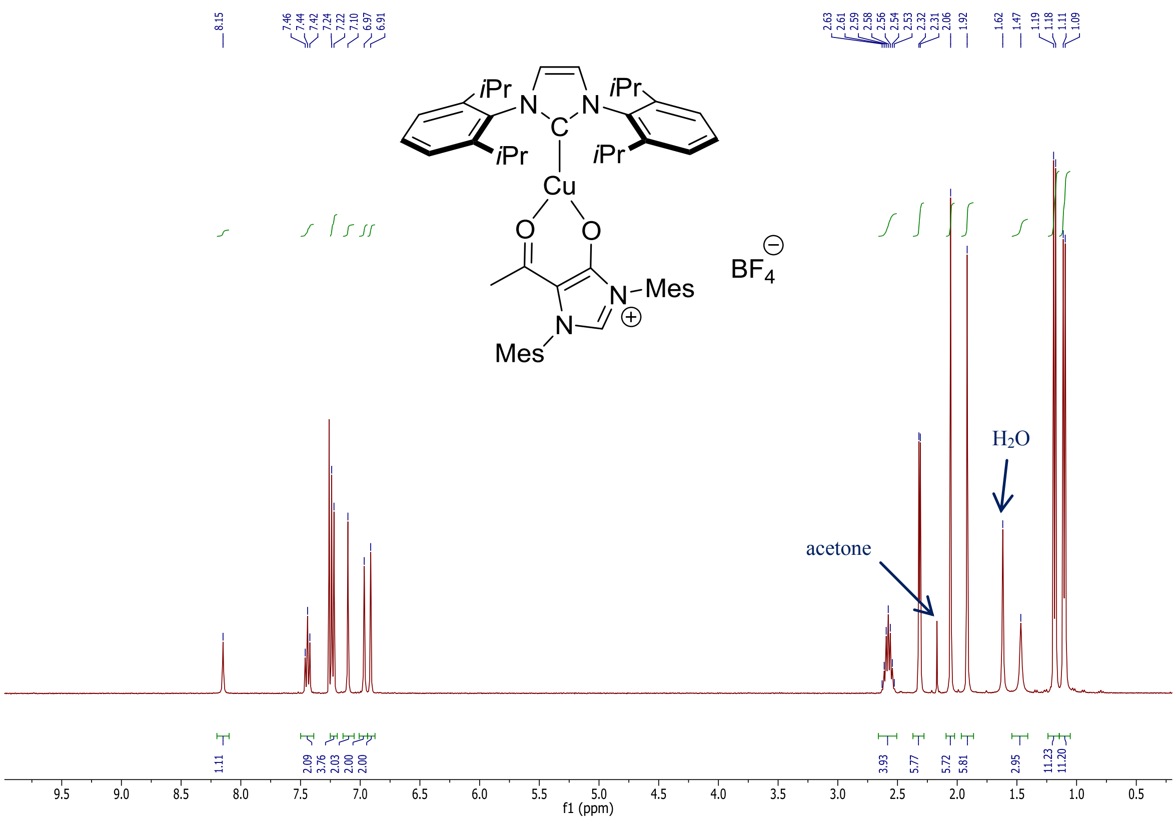
^{1}H NMR spectrum of (acac-IMes)Cu(IPr) (400 MHz, $CDCl_3$)



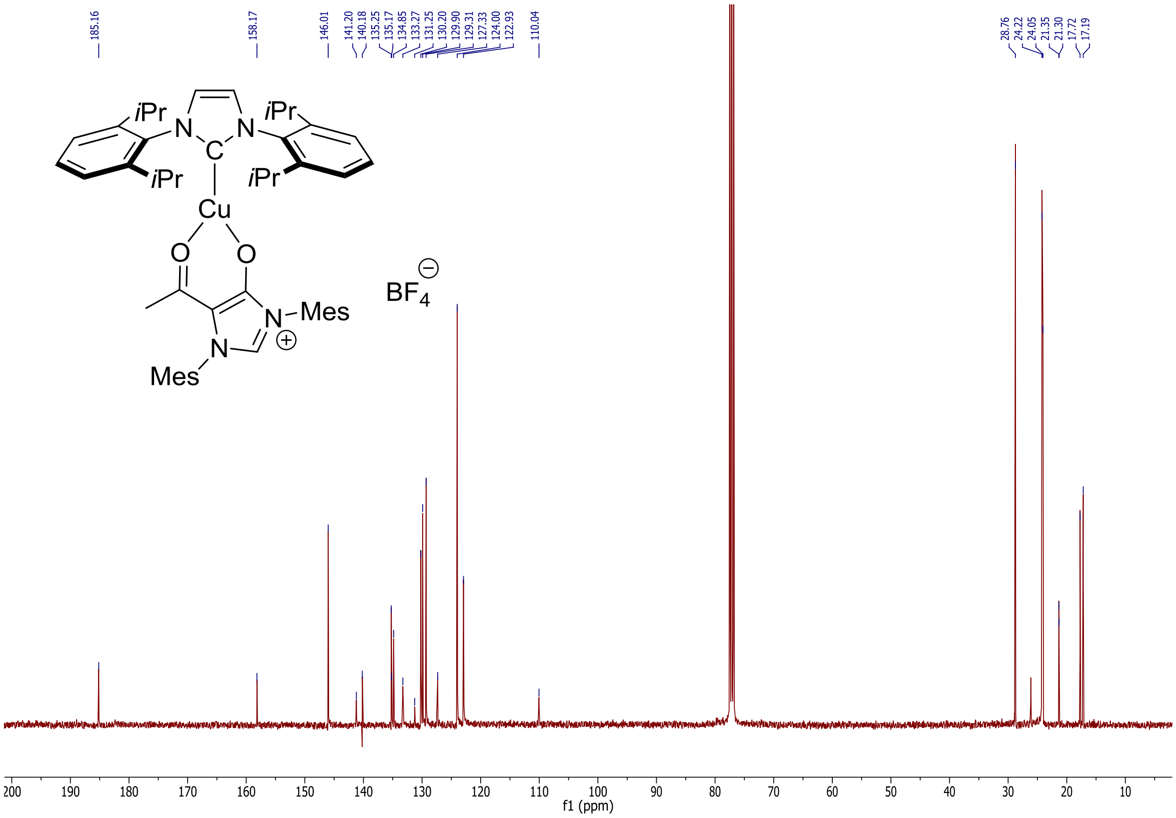
^{13}C{^{1}H} NMR spectrum of (acac-IMes)Cu(IPr) (100.5 MHz, $CDCl_3$)



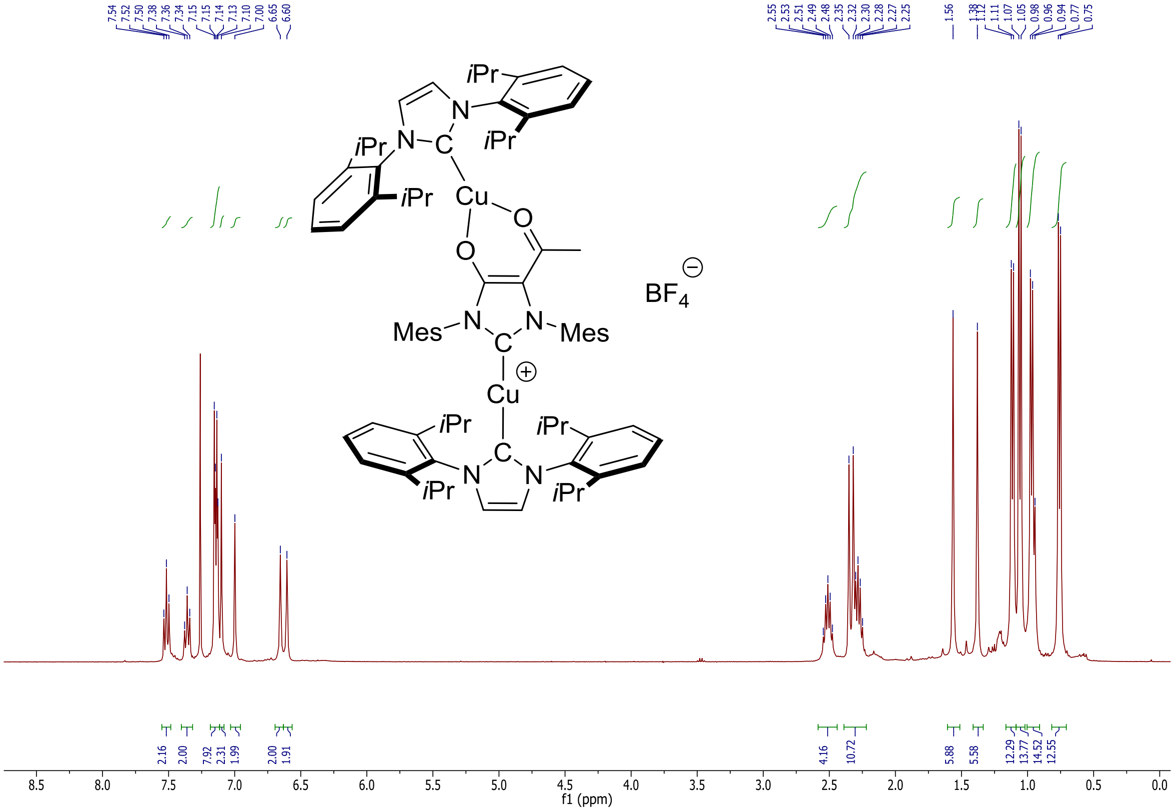
^1H NMR spectrum of [(IPr)Cu(acac-IMes)H](BF_4) (400 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR spectrum of [(IPr)Cu(acac-IMes)H](BF_4) (100.5 MHz, $CDCl_3$)



^{1}H NMR spectrum of [(IPr)Cu(acac-IMes)Cu(IPr)](BF$_4$) (400 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR spectrum of [(IPr)Cu(acac-IMes)Cu(IPr)](BF$_4$) (100.5 MHz, CDCl$_3$)