Supplementary Material (ESI) for Chemical Communications

Supporting Information

Structurally-defined direct C-magnesiation and C-zincation of N-heterocyclic aromatic compounds using alkali-metal-mediated metallation†

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Experimental Section

General Methods.

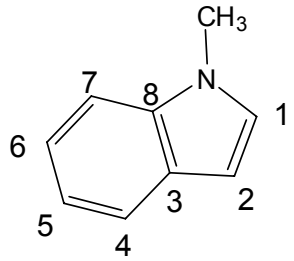
General: All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. *n*,*s*-Dibutylmagnesium and *n*BuLi were purchased from Aldrich Chemicals as solutions in heptane and hexane respectively. Butylsodium[1] and tBu$_2$Zn[2] were prepared according to literature methods. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C.

1 Schade, C.; Bauer, W.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, *295*, C25.

2 P. C. Andrikopoulos, D. R. Armstrong, H. R. L. Barley, W. Clegg, S. H. Dale, E. Hevia, G. W. Honeyman, A. R. Kennedy, R. E. Mulvey, *J. Am. Chem. Soc.* **2005**, *127*, 6184.

Synthesis of $[(TMEDA)_2Na_2Mg(C_8H_5NCH_3)_4]$ (2)

In an oven-dried Schlenk tube 2 mmol (0.16 g) of freshly prepared n-butylsodium were suspended in 10 mL of hexane, and placed in an ultrasonic bath for 10 minutes. To this suspension, 1 mmol of a commercial n,s-dibutylmagnesium solution in heptane (1 mL, 1.0 M) was added to produce a white precipitate. This was then dissolved by the addition of 2 molar equivalents of TMEDA (2 mmol, 0.3 mL) and rigorous stirring for 15 minutes. 4 mmol of *N*-methylindole (0.508 mL) was then injected into the reaction mixture. The mixture was then subjected to reflux conditions for 30 minutes and allowed to cool to room temperature, and left to stir vigorously overnight. A pale yellow suspension was formed. Toluene (2 mL) was added to help to dissolve this solid. The resulting pale yellow solution was placed in a refrigerator at 0°C. A crop of colourless crystals was obtained overnight. Yield: 0.56 g (68 %).

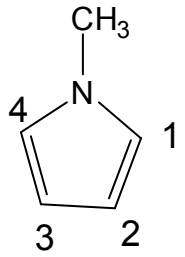


^{1}H NMR (C_6D_6): 7.63 [4H, d, H_4], 7.26 [4H, d, H_7], 7.18 [8H, m, H_5 and H_6], 6.94 [4H, s, H_2], 4.14 [12H, s, indol-yl CH_3], 1.37 [24H, s, CH_3, TMEDA], 1.29 [8H, s, CH_2, TMEDA].

$^{13}C\{^1H\}$ NMR (C_6D_6): 181.11 (C_1), 141.91 (C_8), 132.52 (C_3), 119.24 (C_5 or C_6), 118.67 (C_4), 118.36 (C_5 or C_6), 110.47 (C_2), 109.34 (C_7), 55.87 (CH_2, TMEDA), 45.38 (CH_3, TMEDA), 37.12 (CH_3, indol-yl).

Synthesis of [(TMEDA)Na(μ-TMP)(μ-$C_4H_3NCH_3$)Zn(*t*Bu)] (4)

A solution of tBu_2Zn in hexane (2mmol) was added via canula to a solution of NaTMP in hexane [prepared *in situ* by reaction of BuNa(0.16 g, 2mmol) and TMP(H) (0.34 mL, 2 mmol)]. TMEDA (0.30 mL, 2mmol) was then introduced and the resulting pale yellow solution was allowed to stir for 15 minutes. N-methyl pyrrole (0.17 mL, 2mmol) was added and the mixture was allow to stir at room temperature for 45 minutes. The resulting pale yellow solution was placed in the refrigerator at -4°C. A crop of colourless crystals was deposited overnight; one of them was employed in an X-ray diffraction experiment. Yield: 0.64 g, 67%.

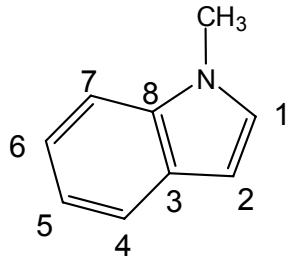


^{1}H NMR (C_6D_6): 6.87 (d, 1H, *H*$_4$), 6.45 (m, 1H, H$_3$), 6.18 (d, 1H, H$_2$), 3.66 (s, 3H, CH_3), 1.88 (s, 16H, CH_3 and CH_2, TMEDA), 1.81 (m, 2H, Hγ, TMP), 1.75 (s, 9H, *t*Bu), 1.32 (m, 4H, H$_\beta$, TMP), 1.20 (s, 6H, CH_3, TMP), 1.17 (s, 6H, CH_3, TMP).

^{13}C{^{1}H} NMR (C_6D_6):144.27 (Zn-C_1), 123.44 (C_4), 115.01 (C_3), 108.58 (C_2), 57.22 (CH_2, TMEDA), 52.96 (C_α, TMP), 45.74 (CH_3, TMEDA), 40.78 (C_β, TMP), 38.97 (CH_3, N-CH_3), 37.71 (C(*C*H$_3$)$_3$, *t*Bu), 35.58 (Me, TMP), 32.06 (Me, TMP), 20.77 (Cγ, TMP), 20.33 (*C*(CH$_3$)$_3$, *t*Bu).

Synthesis of [(TMEDA)Zn($C_8H_5NCH_3$)$_2$] (6)

A solution of *t*Bu_2Zn in hexane (2mmol) was added via canula to a solution of NaTMP in hexane [prepared *in situ* by reaction of BuNa (0.16 g, 2mmol) and TMP(H) (0.34 mL, 2 mmol)]. TMEDA (0.30 mL, 2mmol) was then introduced and the resulting pale yellow solution was allowed to stir for 15 minutes. N-methyl indole (0.25 mL, 2mmol) was added and the mixture was allowed to stir at room temperature for 45 minutes. The resulting pale yellow solution was placed in the refrigerator at -4^{o}C. A crop of colourless crystals was deposited after 48hours; one of them was employed in an X-ray diffraction experiment. Yield: 0.30 g, 34% (maximum yield possible, 50%).



^{1}H NMR (C_6D_6): 7.64 (d, 2H, *H*$_4$), 7.33 (d, 2H, H_7), 7.23 (m, 4H, H_5 and H_6), 6.70 (s, 2H, H_2), 4.11 (s, 6H, CH_3), 1.23 (s, 12H, CH_3, TMEDA), 1.21 (s, 4H, CH_2, TMEDA).

^{13}C{^{1}H} NMR (C_6D_6):177.23 (Zn-C_1), 142.33 (C_8), 132.57 (C_3), 119.60 (C_5 or C_6), 118.82 (C_4), 118.44 (C_5 or C_6), 109.61 (C_7), 109.18 (C_2), 55.88 (CH_2, TMEDA), 45.29 (CH_3, TMEDA), 37.13 (CH_3, N-CH_3, indol-yl).