Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

Potassium-mediated zincation of ferrocene and ruthenocene: potassium, the architect behind supramolecular structural variations

William Clegg,[a] Ben Conway,*[b] Pablo García-Álvarez,[b] Alan R. Kennedy,[b] Jan Klett,[b] Robert E. Mulvey,*[b] and Luca Russo[a]

[a] School of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK.

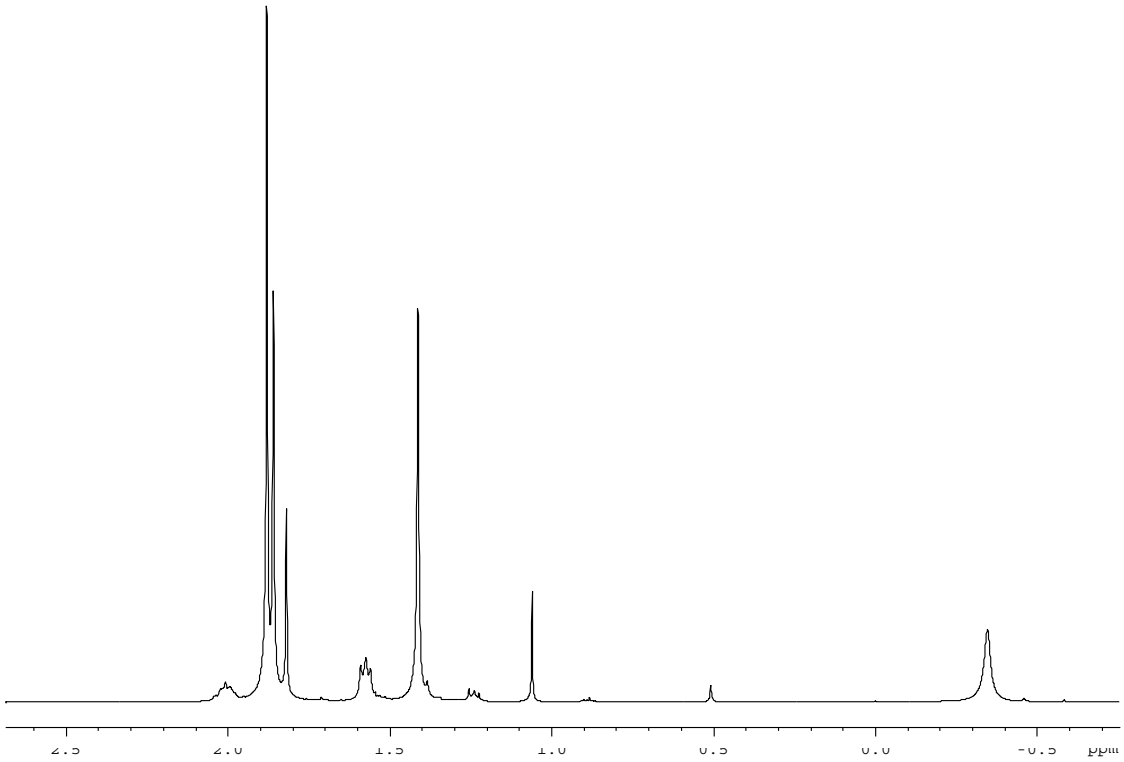
[b] WestChem, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK. E-mail: r.e.mulvey@strath.ac.uk

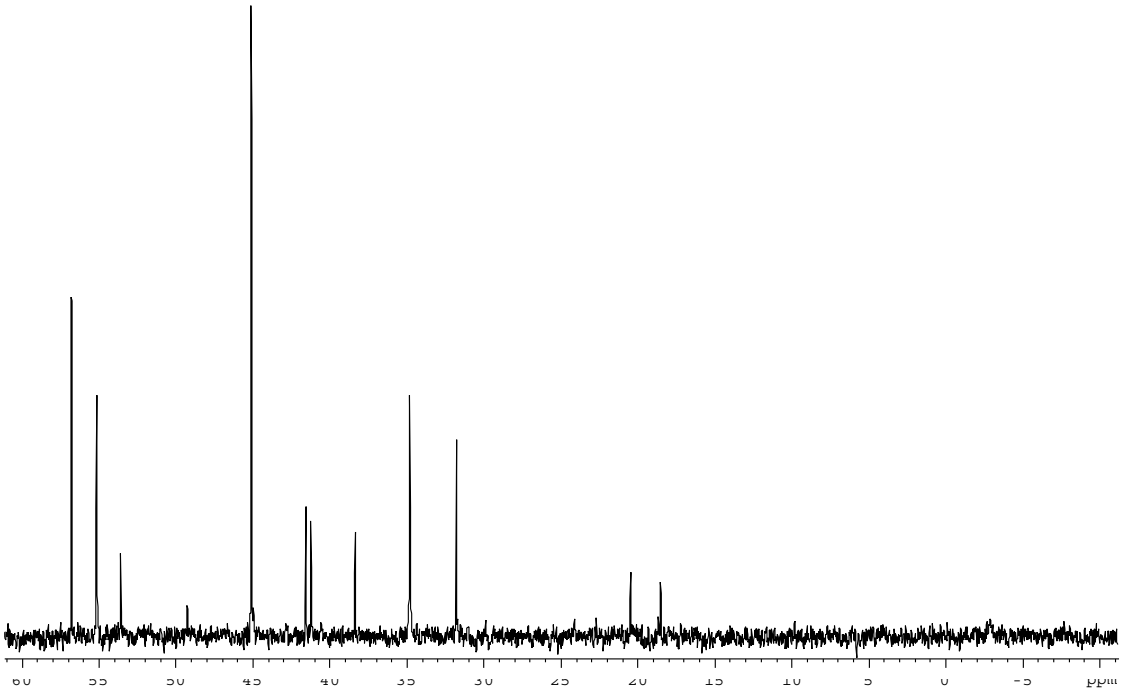
Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DPX 400 MHz or a Bruker AV 500 MHz spectrometer. All ^{13}C NMR spectra were proton decoupled. All solvents were distilled from sodium-benzophenone. Crystal structure **1** was measured at 150 K and structures **2** and **3** were measured at 123 K. All structures were measured on Oxford Diffraction Gemini A Ultra and Gemini S diffractometers with graphite-monochromated Mo Kα radiation (λ =0.71073 Å). Structures were solved by direct methods (SHELX program family or SIR) and refined to convergence on F^2 using SHELXL. Full details are given in the associated CIFs. All synthetic work was carried out under an inert argon atmosphere.

Synthesis of [PMDETA.K(μ-TMP)(μ-Me)Zn(Me)] (1)

0.24 g (2 mmol) of $KCH_2Si(CH_3)_3$ was suspended in 10 mL of hexane. 0.42 mL (2 mmol) of PMDETA was added, followed by 0.34 mL (2 mmol) of TMPH to afford a clear orange solution. Next, 2 mL (2 mmol) of 1M Me_2Zn (in heptanes) was added to the reaction mixture. The Schlenk tube was next placed in the freezer (–28°C) overnight to afford colourless crystals (0.54 g, 60 % yield).





^{1}H NMR (400.13 MHz, 298K, C_6D_6):

δ 2.01 [2H, m, γH of TMP], 1.88 [12H, s, 4 × CH_3 of PMDETA], 1.86 [8H, s, 4 × CH_2 of PMDETA], 1.82 [3H, s, 1 × CH_3 of PMDETA], 1.57 [4H, t, 2 × βCH_2 of TMP, J = 6.0 Hz], 1.41 [12H, s, 4 × CH_3 of TMP], −0.35 [6H, s, 2 × Zn−CH_3]. Some traces of free TMPH were found at δ 1.53, 1.22 and 1.06.

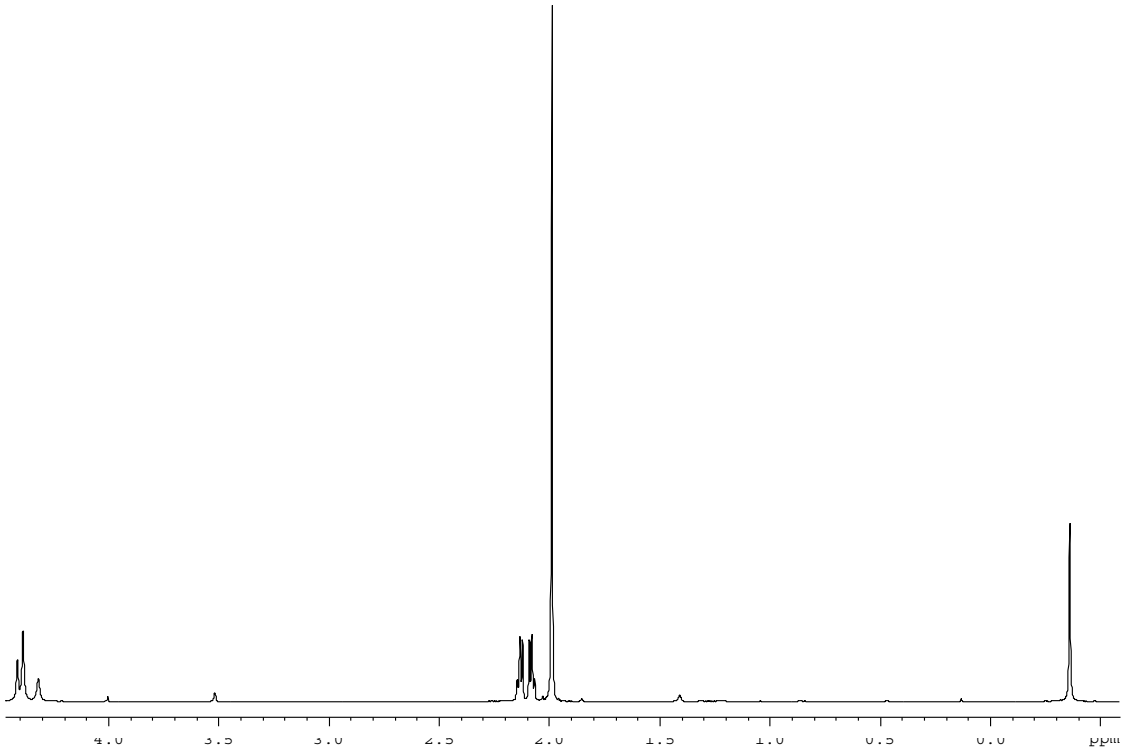
^{13}C{^{1}H} NMR (100.62 MHz, 298K, C_6D_6):

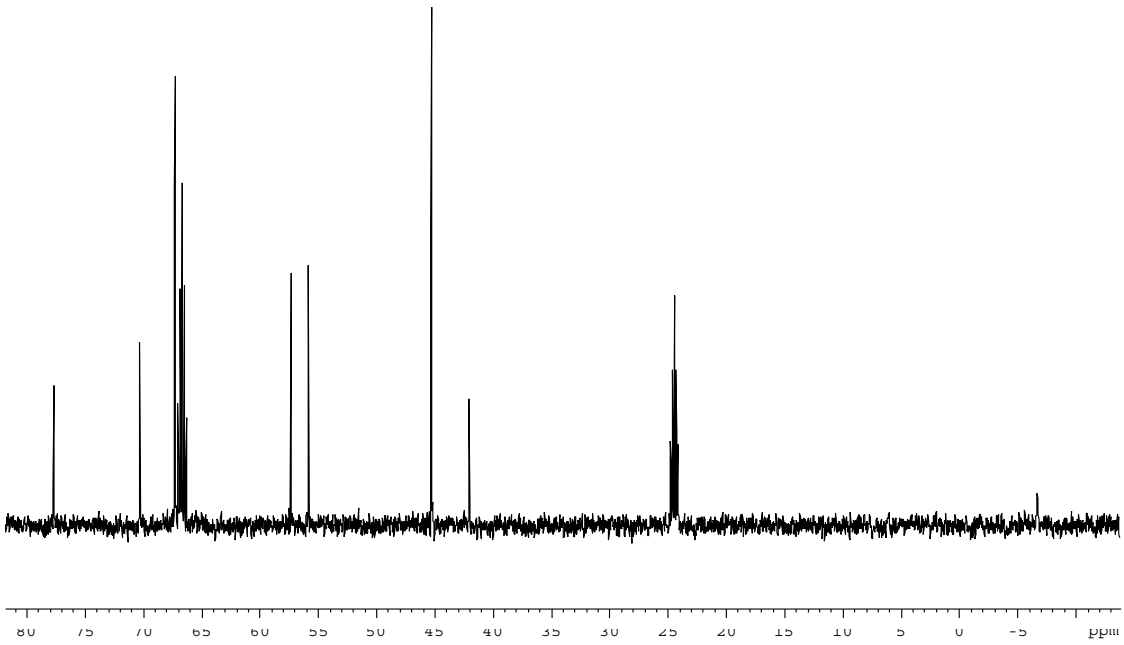
δ 56.5 [2 × CH_2 of PMDETA at ^{H}δ 1.86], 54.9 [2 × CH_2 of PMDETA at ^{H}δ 1.86], 45.1 [4 × CH_3 of PMDETA at ^{H}δ 1.88], 41.5 [1 × CH_3 of PMDETA at ^{H}δ 1.82], 41.2 [2 × βCH_2 at ^{H}δ 1.57], 34.8 [4 × CH3 of TMP at ^{H}δ 1.41], 20.4 [1 × δCH_2 of TMP at ^{H}δ 2.01], −2.9 [2 × Zn−CH_3 at ^{H}δ −0.35]. Some traces of free TMPH were found at δ 38.2, 31.8 and 18.8.

Synthesis of [{PMDETA.K(μ-Me)$_2$Zn(Fc)}$_\infty$] (2)

0.24 g (2 mmol) of $KCH_2Si(CH_3)_3$ was suspended in 10 mL of hexane. 0.42 mL (2 mmol) of PMDETA was added, followed by 0.34 mL (2 mmol) of TMPH to afford a transparent orange solution. Next, 2 mL (2 mmol) of 1M Me_2Zn (in heptanes) was added to the reaction mixture. In

a separate Schlenk tube, 0.37 g (2 mmol) of ferrocene was dissolved in 10 mL of hexane. The base mixture was then transferred to the ferrocene-containing Schlenk tube *via* a canula and stirred overnight. An orange suspension was formed and was isolated as an orange crystalline solid (0.45 g, 46% yield).





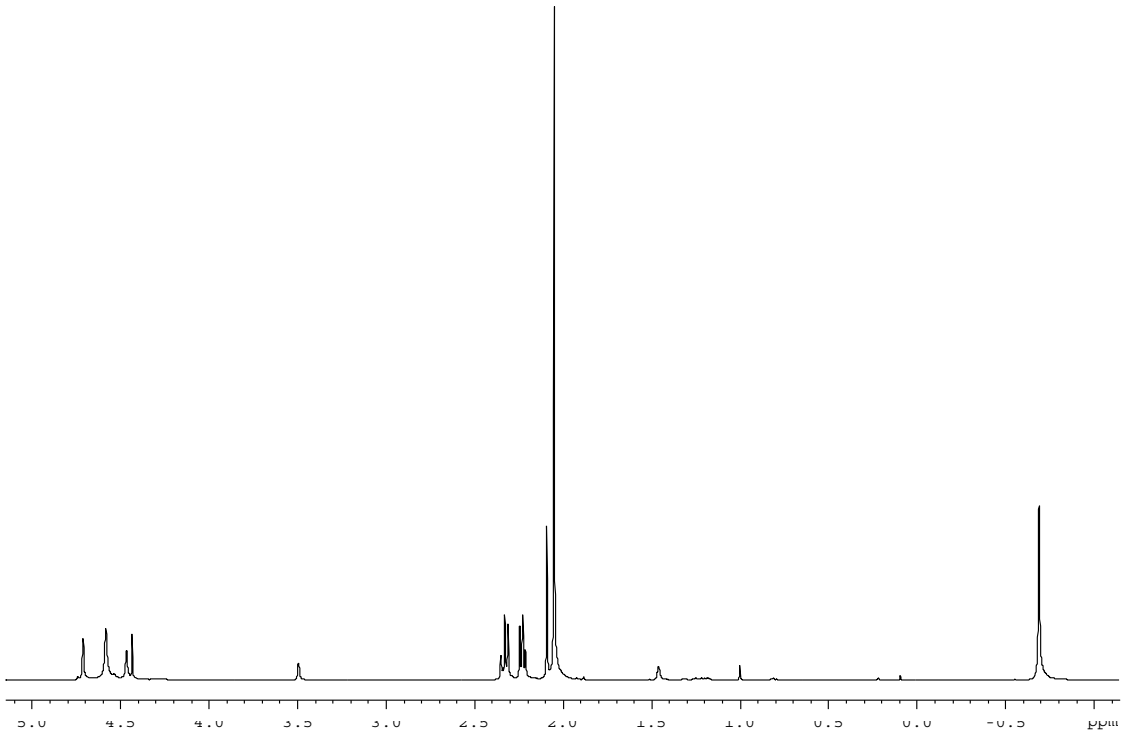
^{1}H NMR (500.13 MHz, 298K, C_6D_6 plus a few drops of deuterated THF to aid solubility): δ 4.41 [2H, broad s, 2 × CH of metallated Cp ring], 4.38 [5H, broad s, 5 × CH of unsubstituted Cp ring], 4.31 [2H, broad s, 2 × CH of metallated Cp ring], 2.13 [4H, m, 2 × CH_2 of PMDETA], 2.08 [4H, m, 2 × CH_2 of PMDETA], 2.00 [15H, s, 5 × CH_3 of PMDETA], –0.36 [6H, s, 2 × Zn–CH_3]. THF signals can be seen at δ 3.52 and 1.41. A very small amount of free ferrocene can be seen at δ 4.00.

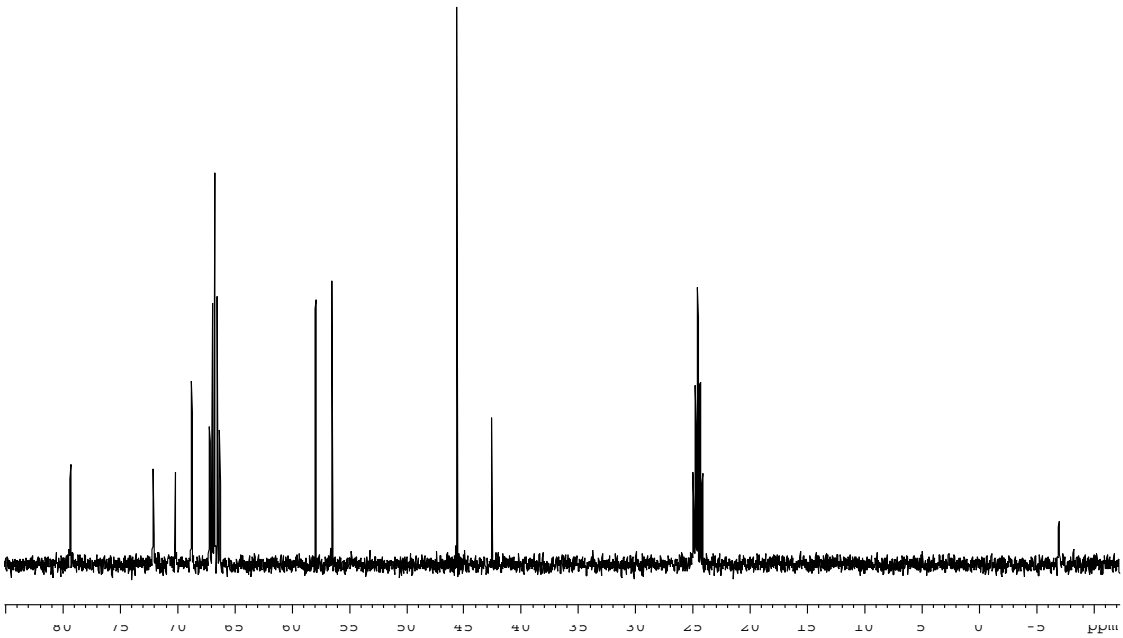
^{13}C{^{1}H} NMR (100.62 MHz, 298K, C_6D_6 plus a few drops of deuterated THF to aid solubility): δ 77.6 [2 × CH from metallated Cp at ^{H}δ 4.31], 70.4 [2 × CH from metallated Cp at ^{H}δ 4.41], 67.3 [5 × CH of unsubstituted Cp at ^{H}δ 4.38], 57.4 [2 × CH_2 of PMDETA at ^{H}δ 2.08], 55.9 [2 × CH_2 of PMDETA at ^{H}δ 2.13], 45.3 [4 × CH_3 of PMDETA at ^{H}δ 2.00], 42.1 [1 × CH_3 of PMDETA at ^{H}δ 2.00], –6.6 [2 × Zn−CH_3 at ^{H}δ –0.36]. Solvent THF signals can be seen at δ 66.7 and 24.5.

Filtrate: Only free ferrocene can be seen, no metallated ferrocene resonances are present. PMDETA, TMP and peaks from the Me groups are also present. Free TMPH is also not present as the filtrate was put under vacuum for several hours.

Synthesis of [{PMDETA.K(μ-Me)$_2$Zn(Ru)}$_2$] (3)

0.24 g (2 mmol) of $KCH_2Si(CH_3)_3$ was suspended in 10 mL of hexane. 0.42 mL (2 mmol) of PMDETA was added, followed by 0.34 mL (2 mmol) of TMPH to afford a transparent orange solution. Next, 2 mL (2 mmol) of 1M Me_2Zn (in heptanes) was added to the reaction mixture. In a separate Schlenk tube, 0.46 g (2 mmol) of ruthenocene was dissolved in 20 mL of hexane. The base mixture was then transferred to the ruthenocene-containing Schlenk tube *via* a canula and stirred overnight. An pale yellow suspension was formed and was isolated as a pale yellow crystalline solid (0.42 g, 39% yield).





^{1}H NMR (500.13 MHz, 298K, C_6D_6 plus a few drops of deuterated THF to aid solubility): δ 4.71 [2H, broad s, 2 × CH of metallated Cp ring], 4.58 [5H, broad s, 5 × CH of unsubstituted Cp ring], 4.46 [2H, broad s, 2 × CH of metallated Cp ring], 2.33 [4H, m, 2 × CH_2 of PMDETA], 2.23 [4H, m, 2 × CH_2 of PMDETA], 2.10 [3H, s, 1 × CH_3 of PMDETA], 2.05 [12H, s, 4 × CH_3 of PMDETA], –0.69 [6H, s, 2 × Zn–CH_3]. THF signals can be seen at δ 3.49 and 1.46. A very small amount of free ruthenocene (from slight hydrolysis) can be seen at δ 4.43.

^{13}C{^{1}H} NMR (100.62 MHz, 298K, C_6D_6 plus a few drops of deuterated THF to aid solubility): δ 79.3 [2 × CH from metallated Cp at ^{H}δ 4.46], 72.1 [2 × CH from metallated Cp at ^{H}δ 4.71], 68.8 [5 × CH of unsubstituted Cp at ^{H}δ 4.58], 58.0 [2 × CH_2 of PMDETA at ^{H}δ 2.23], 56.6 [2 × CH_2 of PMDETA at ^{H}δ 2.33], 45.6 [4 × CH_3 of PMDETA at ^{H}δ 2.05], 42.6 [1 × CH_3 of PMDETA at ^{H}δ 2.10], –6.9 [2 × Zn–CH_3 at ^{H}δ –0.69]. THF signals can be seen at δ 66.8 and 24.6. A very small amount of ruthenocene can be seen at δ 70.1.

Filtrate: Small amount of monometallated ruthenocene can be seen, mostly free ruthenocene is observed. PMDETA, TMP and Me groups can also be seen. Free TMPH is also not present as the filtrate was put under vacuum for several hours.