
This version is available at https://strathprints.strath.ac.uk/27630/

Strathprints is designed to allow users to access the research output of the University of Strathclyde. Unless otherwise explicitly stated on the manuscript, Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Please check the manuscript for details of any other licences that may have been applied. You may not engage in further distribution of the material for any profitmaking activities or any commercial gain. You may freely distribute both the url (https://strathprints.strath.ac.uk/) and the content of this paper for research or private study, educational, or not-for-profit purposes without prior permission or charge.

Any correspondence concerning this service should be sent to the Strathprints administrator: strathprints@strath.ac.uk

The Strathprints institutional repository (https://strathprints.strath.ac.uk) is a digital archive of University of Strathclyde research outputs. It has been developed to disseminate open access research outputs, expose data about those outputs, and enable the management and persistent access to Strathclyde's intellectual output.

http://strathprints.strath.ac.uk/27630/

Strathprints is designed to allow users to access the research output of the University of Strathclyde. Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. You may not engage in further distribution of the material for any profitmaking activities or any commercial gain. You may freely distribute both the url (http://strathprints.strath.ac.uk) and the content of this paper for research or study, educational, or not-for-profit purposes without prior permission or charge. You may freely distribute the url (http://strathprints.strath.ac.uk) of the Strathprints website.

Any correspondence concerning this service should be sent to The Strathprints Administrator: eprints@cis.strath.ac.uk
Potassium-mediated zincation of ferrocene and ruthenocene: potassium, the architect behind supramolecular structural variations

William Clegg,² Ben Conway,³b Pablo García-Álvarez,² Alan R. Kennedy,² Jan Klett,² Robert E. Mulvey,³b and Luca Russo³

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

Direct zincation of ferrocene and ruthenocene by the synergic base [PMDETA.K(µ-TMP)(µ-Me)Zn(Me)] produces the monozincated complexes [PMDETA.K(µ-Me)Zn(Fe)₂] and [PMDETA.K(µ-Me)₂Zn(FeC)₃] respectively, having similar monomeric (dinuclear) units but aggregating supramolecularly in very different polymeric and dimeric forms.

Ferrocene, and to a much lesser extent, its Group 8 homologue, ruthenocene, have a very rich metallation chemistry, which includes a large variety of structural types.¹ Poorly represented in this category are synthetically useful polar monometallated derivatives which can be subsequently utilised for framework functionalization. Many monometallated ferrocenes and ruthenocenes in the Cambridge Structural Database (CSD)² involve metals (e.g. Al, Ge, Sn, W and Zr) that have been put there via reaction of a preformed polar intermediate and a metal salt via an indirect metathetical approach.³ Such is the sparse volume of definitive structural data available on these types of monometallated compounds, there are no examples at all of structurally defined molecules where an alkali metal or alkaline-earth metal is directly attached to the Cp ring. Earlier we reported the lithium triferrocenylzincate [Li(THF)₃][Zn(FeC)₃] (where Fe = C₅H₅FeC₆H₄), but this has a solvent(THF)-separated structure in which there are no Li···C(Fe) contacts.⁴ Though bimetallic foundations of organometallic chemistry were laid over 150 years ago,⁵ their status as versatile chemical reagents has risen remarkably over the past few years with many notable innovations made in organic synthesis,⁶ host-guest macrocyclic chemistry,⁷ structural science,⁸ and polymerisation chemistry.⁹ Applying bimetallic formulations to metallocene chemistry, we previously reported the application of lithium-mediated zincation to ferrocene metallation and although, as mentioned above, lithium ferrocenylzincate compounds were produced, no examples were obtained in which both metals (lithium and zinc) are involved in the coordination of the ferrocenyl anion. In his masterwork on “Organometallics in Synthesis” Schlosser reminds us that “the individuality of the metal is the most critical parameter for designing tailor-made organometallic reactions”, so by extrapolation this must be even more significant in the context of bimetallic formulations.¹² Therefore in this paper we introduce “potassium-mediated zincation (KMZn)” to metallocene chemistry and, echoing Schlosser’s comments, find that the reactions yield potassium ferrocenylzincate and potassium ruthenocenylzincate products with unique structures different from each other and from the aforementioned lithium ferrocenylzincate.

To perform the KMZn reactions we developed a new synergic base [PMDETA.K(µ-TMP)(µ-Me)Zn(Me)], I, using an established co-complexation approach (Scheme 1) [PMDETA = N,N,N',N'',N''-pentamethyldiethylenetriamine; TMPh = 2,2,6,6-tetramethylpiperidine]. Previously we have employed the diethyl homologue of I in KMZn reactions of substituted pyridines.¹³ Base I (Fig. 1) can be prepared as colourless crystals in a yield of 60% and was characterised in solution by ¹H and ¹³C NMR spectroscopy and in the solid state by X-ray crystallography.¹ The Me groups appear equivalent in the ¹H NMR spectrum of I, as the resonance associated with them comes as a broad peak at –0.35 ppm, which represents a downfield shift of 0.17 ppm compared to the spectrum of the homometallic reagent Me₂Zn (δ = –0.52 ppm) in deuterated benzene solution.

![Fig. 1 Molecular structure of one of the four independent molecules of I within the asymmetric unit. Hydrogen atoms have been omitted for clarity.](Image)

The molecular structure of I is isostructural to that of its ethyl analogue.¹³ Note that there are four, nearly identical,
independent molecules of 1 in the asymmetric unit of the crystal structure. Though the precision of 1 is relatively low as a result of imperfectly resolved twinning, limiting any detailed comparison of bond lengths and angles, the molecular connectivity within 1 is unambiguous. Possessing one terminal methyl group on zinc, bridging TMP and methyl ligands to the potassium and zinc centres generating a four-element (K\nZnC) ring, the base is completed by a tridentate PMDETA ligand coordinated to the alkali metal via its three N donor atoms.

Base 1 was first tested with ferrocene to assess its ability as a zincaising reagent (Scheme 2). A set of orange crystals was isolated and characterised by 1H and 13C NMR spectroscopy and also by X-ray crystallography as the polymeric compound [{PMDETA.K(μ-Me)2Zn(Fe)}2], 2 (Figs. 2 and 3), obtained in an isolated yield of 46%. In the monomer unit, unlike 1 where the TMP is bridging the potassium and zinc metal centres, the mono-zincated ferrocene in 2 is now at the terminal position with two smaller methyl groups bridging the ferrocene has not been metallated but instead acts as a neutral π-donating ligand to the potassium cation to form the discrete ion-pair compound [mean K–C(Fe) distance, 3.195Å]. The average K–C(Fe) bond distances compare favourably with those of the monozincated ferrocene compound 2. Thus the Fe···Cp(centroid) distances are found to be 1.635Å (metallated Cp ring) and 1.634Å (unsubstituted Cp ring).

Scheme 2 Zincaising reactions of ferrocene and ruthenocene.

Scheme 2 Zincaising reactions of ferrocene and ruthenocene.

Currently there is a dearth of solid-state structures of metallated ruthenocenes within the CSD. There are only four examples of monometallated ruthenocene structures, two of which were prelithiated and reacted onwards with metal salts to make platinum derivatives. Therefore KMZn seemed an ideal vehicle from which to add to the number of informative crystal structures of this type. Carried out with the purpose of obtaining crystalline material as opposed to informative crystal structures of this type. Carried out with the purpose of obtaining crystalline material as opposed to reaction optimisation, base 1 was reacted with one molar equivalent of ruthenocene in hexane solution. Crystallisation was duly realised in the form of the pale yellow product [{PMDETA.K(μ-Me)2Zn(Rc)}2], 3 (Rc = C5H7RuC(C5H5)), isolated in a clean first batch yield of 39%. Mono-zincated ruthenocene 3 was characterised by a combination of 1H,13C NMR spectroscopic and X-ray crystallographic studies. To the best of our knowledge 3 represents the first crystallographically-characterised ruthenocene structure containing zinc made via any synthetic procedure (indirect metathesis or direct zincaisation). It is a centrosymmetric molecular dimer. The monomer unit of 3 closely matches that of 2, comprising a PMDETA-chelated K2 cation bridged through two Me ligands to Zn [K–C(Me) bond lengths: K(1)–C(2) {3.2546(18)Å} and K(1)–C(3) {3.1747(19)Å}; Zn–C(Me) bond distances, 2.0174(16)Å {Zn(1)–C(2)} and 2.0358(17)Å {Zn(1)–C(3)}], which has the largest anion, the monodeprotonated ruthenocene, in a terminal position [Zn(1)–C(18) bond length, 2.0192(15)Å] (Fig. 4).
Dimerisation is achieved via the K centre engaging intermonomer with one Me C atom, C(3A) [3.3226(19)Å] and η1° with the deprotonated C atom of the ruthenocene, C(18A) [3.2775(15)Å]. The average K–C bond length to the rest of the carbon atoms of the zinccated Cp ring [average distance, 4.559Å, range, 3.6162(15)–5.2830(16)Å] highlights this η1° interaction. For this type of interaction to occur, the zinccated ruthenocene carbon atom deviates from planarity with an average bond angle of 116.8°, resulting in a distorted trigonal arrangement. The Ru···Cp(centroid) distances in 3 [1.807Å (metallated Cp ring) and 1.818Å (unsubstituted Cp ring)] are larger than those for Fe in 2.

In summary, ferrocene and ruthenocene can be dimerized, and the crystallographic data support this. The interaction involved in this dimerization is complex, involving both η1° and η2° interactions, with the ruthenocene carbon atom deviating from planarity to form a distorted trigonal arrangement. The Ru···Cp(centroid) distances in 3 are larger than those in 2, suggesting that the metallated Cp ring is less sterically encumbered.

We thank the UK EPSRC for their generous sponsorship through the grant awards EP/D076889/1 and EP/F03637X/1 and the Royal Society/Wolfson Foundation for a research merit award to REM. This research was also supported by a Marie Curie Intra European Fellowship within the 7th European Community Framework Programme (for PQA).

Notes and references
1 School of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK.
2 WestCHEM Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XH, UK; E-mail: r.e.mulvey@strath.ac.uk

† Electronic Supplementary Information (ESI) available: experimental details of 1–3, including 1H and 13C NMR spectra. See DOI: 10.1039/b000000x/

‡ Crystal data for 1: C18H12K4Zn, M = 448.09, monoclinic, space group P21/c, a = 24.7840(7), b = 8.4806(2), c = 48.933(2) Å, β = 93.929(3)°, V = 10260.7(6)Å³, Z = 16, T = 150 K; 48234 reflections, 17948 unique, Rint 0.0786; R = 0.0959 (F, F2 > 2σ), Rw = 0.2332 (F2, all data), GoF = 1.023. The crystal was twinned with approximately 9% of a minor component and disorder was modelled for two CH3CH3 segments.

Crystal data for 2: C18H12FeK4Zn, M = 492.86, orthorhombic, space group Pca21, a = 18.2193(7), b = 7.5981(4), c = 17.7793(7) Å, V = 2461.23(19)Å³, Z = 4, T = 123 K; 14510 reflections, 6300 unique, Rint 0.0517; R = 0.0374 (F, F2 > 2σ), Rw = 0.0486 (F2, all data), GoF = 0.799.

Crystal data for 3: C18H12K4NiRu2Zn, M = 1076.17, triclinic, space group P1, a = 8.18155(3), b = 11.9380(4), c = 12.9284(5) Å, α = 114.673(4), β = 95.400(3), γ = 99.969(3)°, V = 1196.61(7)Å³, Z = 1, T = 123 K; 21909 reflections, 6756 unique, Rint 0.0246; R = 0.0213 (F, F2 > 2σ), Rw = 0.0485 (F2, all data), GoF = 0.990.

CCDC reference numbers ?????.

1 P. Štěpnička, Ferrocenes: Ligands, Materials and Biomolecules; VCH: Weinheim, Germany, 2008.


This journal is © The Royal Society of Chemistry [year]