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

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

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(Fc)₂] and [PMDETA.K(μ-Me)₂Zn(Rc)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. 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) involve metals (e.g. Al, Ge, Sn, W and Zr) that have been put there as a solvent(THF)-separated structure in which there are no Li···C(Fc) contacts. Though bimetallic foundations of organometallic chemistry were laid over 150 years ago, their status as versatile chemical reagents has risen remarkably over the past few years with many notable innovations made in organic synthesis, host-guest macrocyclic chemistry, structural science, and polymerisation chemistry. 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. 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. 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. 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.

Scheme 1 Interlocking co-complexation synthesis of the new synergic base [PMDETA.K(μ-TMP)(μ-Me)Zn(Me)] I.

Fig. 1 Molecular structure of one of the four independent molecules of I within the asymmetric unit. Hydrogen atoms have been omitted for clarity.

The molecular structure of I is isostructural to that of its ethyl analogue. 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 (KNZnC) 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(Fc)}∞], 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(Fc) distance, 3.195 Å]. The average K−C(Fc) bond distances compare favourably with those of the monozincated ferrocene compound 2. Thus the Fe···Cp(centroid) distances are found to be 1.635 Å (metallated Cp ring) and 1.634 Å (unsubstituted Cp ring).

Scheme 2 Zincaising reactions of ferrocene and ruthenocene.

distinct metals, generating a new planar KCZnC metallocycle. Trigonal Zn makes three Zn−C bonds, to bridging methyl ligands [bond lengths: Zn(1)−C(11) 2.037(3) Å and Zn(1)−C(12) 2.027(3) Å] and a slightly shorter bond to ferrocene [Zn(1)−C(1) 2.002(3) Å]. The potassium cation has a coordination geometry consisting of two K−C(Me) bonds [lengths, 3.091(3) Å {K(1)−C(11)} and 3.141(3) Å {K(1)−C(12)}] and three shorter K−N donor interactions with the tridentate PMDETA ligand [average K−N bond length, 2.872 Å]. The remainder of the coordination sphere of potassium is made up of intermolecular η5-interactions with the π-surface of a zincaised ferrocene ring from a neighbouring monomer unit to create an unprecedented supramolecular step-ladder [average K−C(Fc) distance, 3.198 Å; K−C(Fc) range, 3.031(3)−3.371(3) Å]. For K to achieve this η5-π-interaction with the metalloccenyl ring the zincaised ferrocene carbon atom has a modestly distorted trigonal environment (mean bond angle around C1, 118.5°). The ligation of ferrocene onto potassium has been seen before in potassium magnesiate chemistry in [[K(ferrocene)2(tol)3]+[Mg(HMDS)5]2−] [HMDS = 1,1,3,3,3-hexamethyldisilazide]. However, in this example

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 KMZnC was used as 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 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 = C8H8RuC8H4), 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 K+ 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) 3.1179(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).

Fig. 2 Asymmetric unit of 2 with hydrogen atoms omitted for clarity.

Fig. 3 Section of the infinite step-ladder of 2. The intermolecular π-interactions are displayed as dashed lines.

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Dimerisation is achieved via the K centre engaging intermonomer with one MeC 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.

Fig. 4 Molecular structure of dimeric 3 with hydrogen atoms omitted for clarity. Intermolecular contacts shown as dashed lines. Symmetry operation A : 2–x, 1–y, –z.

In both cases of monozincation, reagent 1 acts as an amido base with loss of TMPH into the reaction mixture. DFT studies by Uchiyama et al. on zincate chemistry suggest that the free amine generated from the initial metallation step could react onwards, in a second step, with the alkyl substituent, in these cases with a methyl group to eliminate methane and re incorporate a TMPH anion into the structures. In both of the isolated crystalline species 2 and 3, no TMPH is found, indicating possibly that the metals in these structures are so sterically encumbered that there is no room for TMPH to ligate to either K or Zn and to protonate the Me group.

In summary, ferrocene and ruthenocene can be monozincated by potassium-mediated zincation. The role of potassium in the aggregation of the monomer units of the structures produced is crucial. Interacting with the zinccated ferrocene Cp ring in a η¹-π-contact results in a supramolecular step-ladder, whereas dimerisation is the aggregation of choice with the monozincated ruthenocene compound via η¹(Cp) and C(Me) intermolecular contacts to K. The profound influence of potassium on these unique structures calls for a systematic study of how different alkali metals affect the supramolecularity of alkali-metal-mediated metallated (by Zn, Mg, Mn etc) metallocenes.

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 PGA).

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