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**Structurally defined zincated and aluminated complexes of ferrocene made by
alkali-metal-synergistic syntheses**

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Abstract

Reaction of ferrocene with 1 or 2 molar equivalents of the synergistic-operative bimetallic sodium zincate base TMEDA·Na(μ-TMP)(μ-*t*Bu)Zn(*t*Bu) yields mainly mono- or di-zincated complexes TMEDA·Na(μ-TMP)[μ-(C₅H₄)Fe(C₅H₅)]Zn*t*Bu (**1**) and [TMEDA·Na(μ-TMP)Zn(*t*Bu)]₂(C₅H₄)₂Fe (**2**). Likewise, the separated pairing of Li(TMP) and (TMP)Al(*i*Bu)₂ in the presence of THF can mono- or dimetalate ferrocene in a synergistic two step lithiation/trans-metal-trapping protocol to give THF·Li(μ-TMP)[μ-(C₅H₄)Fe(C₅H₅)]Al(*i*Bu)₂ (**4**) or [THF·Li(μ-TMP)Al(*i*Bu)₂]₂(C₅H₄)₂Fe (**5**). In the absence of Lewis donating co-solvents, a four-fold excess of the sodium zincate appears to produce an unprecedented four-fold zincated ferrocene of formula Na₄(TMP)₄Zn₄(*t*Bu)₄[(C₅H₃)₂Fe] (**3**); whereas when donor solvent is withheld from the lithium/aluminium pairing only dimetalation of ferrocene is possible.

Tetrametalation seems to be inhibited by the *in situ* generation of TMP(H) via amido basicity which then acts as a Lewis donor towards lithium, preventing inverse-crown formation and preferentially forming the Lewis acid – Lewis base adduct [TMP(H)·Li(μ-TMP)Al(*i*Bu)₂]₂(C₅H₄)₂Fe (**6**). With the exception of **3**, all aforementioned complexes have been characterized by X-ray crystallography, while **1** - **6** have also been studied by solution NMR spectroscopic studies.

Introduction

Alkali Metal Mediated Metallation (AMMM) is a term coined to reflect the positive mediating influence that an alkali metal can have on the metalating power of a less electropositive secondary metal, most notably magnesium, zinc or aluminium, which generally form low polarity metal-carbon bonds of low basicity.¹ This frequently occurs through the formation of metallate ('ate') complexes which have various formulas of which [(AM)⁺(M^xR_{x+1})⁻] (AM = alkali metal, M = secondary metal, R = anion) is typical.² Although such a cooperative effect has been recognized for over 60 years since seminal observations of Wittig,³ a deeper understanding of this cooperativity and its wider exploitation has only really come to light in the past decade through the studies a number of researchers of whom Knochel,⁴ Mongin,⁵ Uchiyama and Wheatley,⁶ and ourselves have been particularly prominent.⁷ In the best cases the result of combining two distinct organometallic compounds, AM(R) and M(R')₂ together into a single bimetallic compound is a reagent which in combining the higher reactivity of the alkali metal component with the better selectivity and functional group tolerance of the secondary metal can execute deprotometalation reactions at room temperature (contrast the sub-ambient protocols

necessary in many organolithium reactions) in non-polar solvents; an improvement on either of the homometallic reagents operating independently. However, not only can AMMM improve on existing homo-metalation protocols it also can bring about novel metalation reactions; for example metalation at typically unreactive or remote sites; or polymetalation of substrates typically strongly resistant to more than one metalation event. The most significant examples of the former reactivity are the recently reported directed *ortho-meta*' and *meta-meta*' dimetalations of a range of substituted arenes⁸ by the template ate base $[\text{Na}_2\text{Mg}(\text{TMP})_3(n\text{Bu})]_2$, which the authors refer to as pre-inverse crowns.⁹ The latter polymetalations are normally manifested in the form of a supramolecular 'inverse crown' structure, that is a polymetallic cationic ring with the single polyanionic substrate¹⁰ or multiple monoanionic substrates encapsulated within the core of the cationic ring;⁹ the name inverse crown being derived from the antithetical nature of the positive and negative moieties with respect to the cation-dipole sites in a conventional crown ether complex.¹¹ One of the most extraordinary examples of this type of chemistry was the unprecedented 1,1',3,3'-tetramagnesiumation of ferrocene¹² along with that of its heavier group 8 congeners ruthenocene and osmocene,¹³ with the resulting tetraanions being captured within a $[\text{Mg}_4\text{Na}_4(\text{NiPr}_2)_8]^{4+}$ 16-membered inverse-crown ring (figure 1). The formation of this tetramagnesiumated ferrocene product was dependent on the identity of the secondary amido component within the ate base since substitution of diisopropylamide, NiPr_2 by TMP (2,2,6,6-tetramethylpiperidide) resulted in an alternative trinuclear ferrocenophane product in which the three ferrocene molecules were only 1,1'-dimetalated.¹⁴

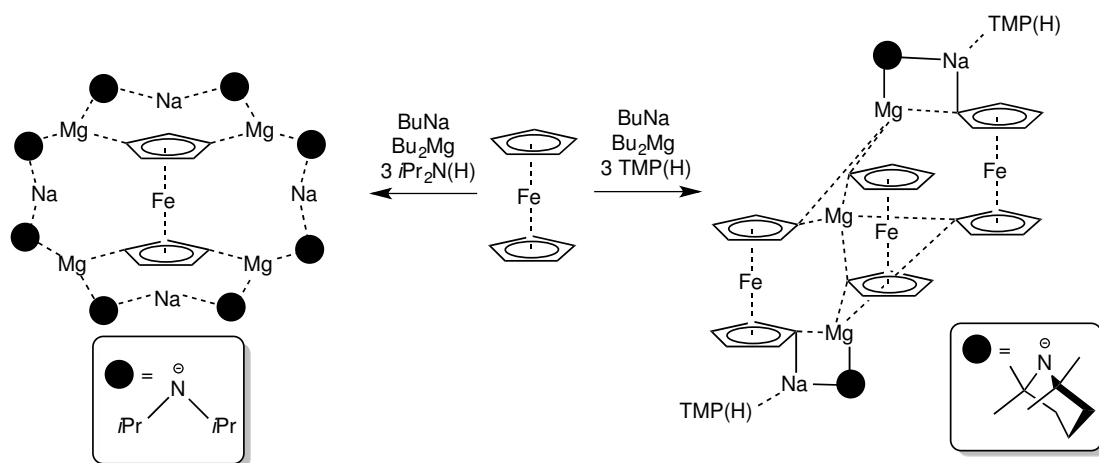


Figure 1 Amide-dependent reactivity of ferrocene with a sodium magnesiate base

Prior to these ate-based direct (i.e., magnesium-hydrogen) metalations, lower-polarity-metalated ferrocenes have generally been made via salt metathesis approaches often using metal halide starting materials. Figures 2 and 3 show examples of some zincated and aluminated ferrocene complexes, many of which were prepared by such salt metathesis. Zinc species **A**, **B** and **C** are dinuclear ferrocenophanes either mono or dizincated, **E** and **F** are mononuclear monozincated ferrocenes, while **D** is a trinuclear ferrocenophane held together by a single zinc atom. Mononuclear, dinuclear and trinuclear ferrocenophane examples are also shown for the aluminium species, with **H** catching the eye with the deprotonated C atom of the mononuclear ferrocene binding to two Al centers in a AlCAI ring. Salt metathesis has been one of the most widely utilized synthetic methodologies for transforming numerous polar organometallic compounds (especially those of Li, Na and K) into derivatives of other metals all across the periodic table. Aside from his many other achievements, Lappert has been probably the World's leading exponent of this approach, having exploited it to synthesize a huge variety of organometallic compounds including alkyl,¹⁵ amido,¹⁶ azaallyl¹⁷ and metallocenyl examples.¹⁸

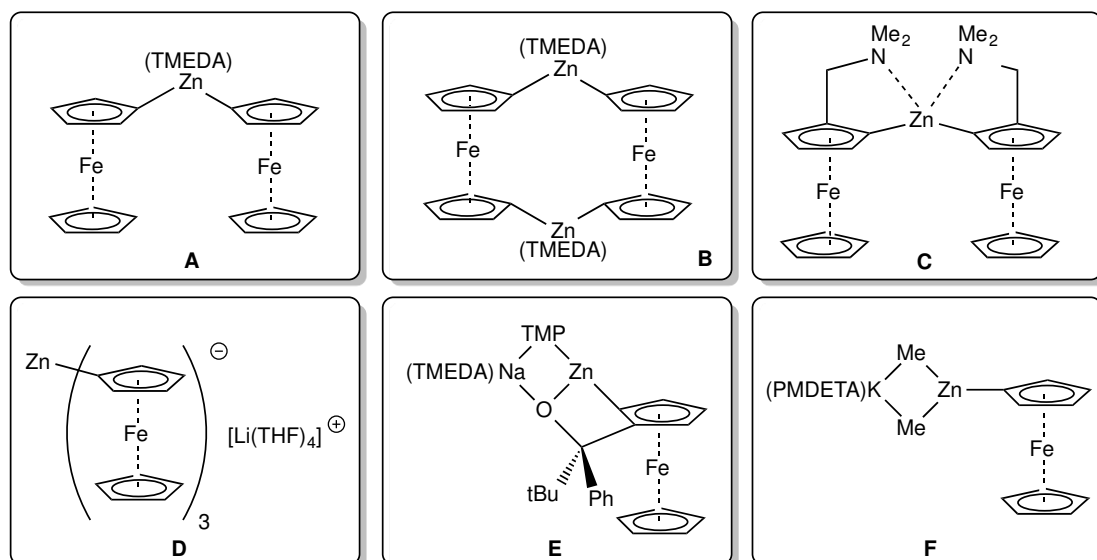


Figure 2 ChemDraw representations of a selection of crystallographically characterized zincated ferrocene molecules. References: **A**,¹⁹ **B**,²⁰ **C**,²¹ **D**,¹⁹ **E**,²² **F**.²³

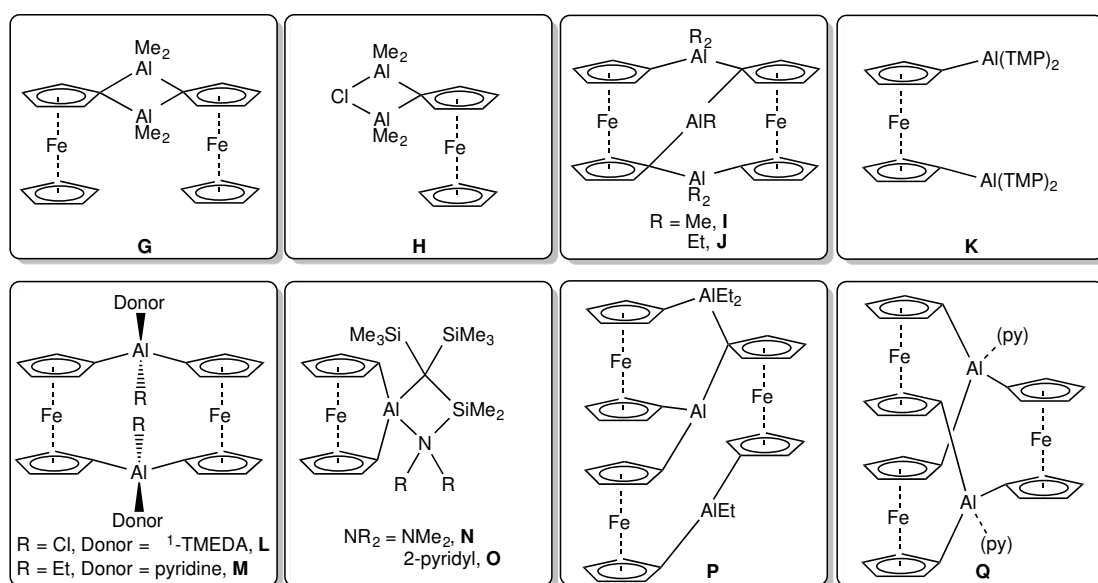


Figure 3 ChemDraw representations of a selection of crystallographically characterized aluminated ferrocene molecules. References: **G**,²⁴ **H**,²⁵ **I**,²⁶ **J**,²⁷ **K**,²⁸ **L**,²⁹ **M**,³⁰ **N**,³¹ **O**,³² **P**,³³ **Q**.³⁰

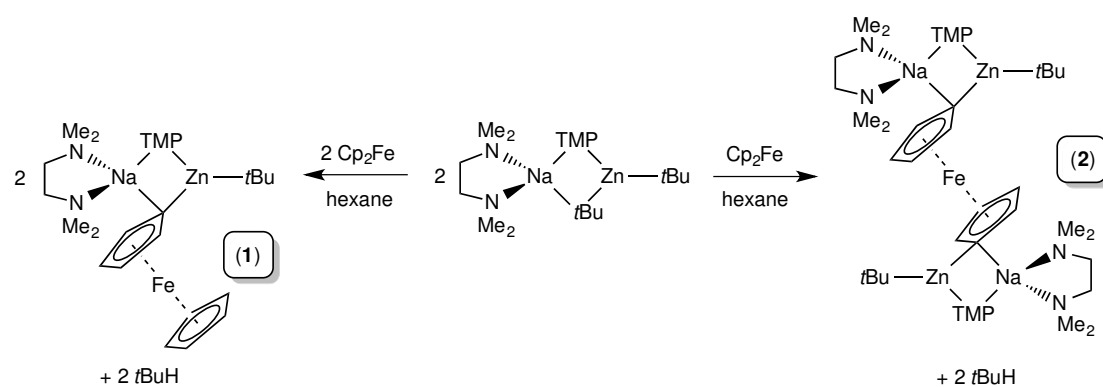
AMMM has the advantage that generally reaction mixtures are homogeneous unlike those in salt metathesis and more importantly, provides access to compounds

inaccessible via salt metathesis (e.g., the aforementioned tetramagnesiated Group 8 metallocenes). Of course, functionalized ferrocene derivatives are particularly interesting due to their myriad of uses in diverse areas such as materials,³⁴ medicinal chemistry,³⁵ bioorganometallic chemistry³⁶ and as specialty ligands for asymmetric catalysis³⁷ amongst others.³⁸ We were therefore keen to examine if these discussed precedented metalation patterns, or indeed any others, could be achievable through application of other common bimetallic ate bases at our disposal and now report our findings herein.

Results and Discussion

Studies of sodium zincate TMEDA·Na(μ-TMP)(μ-*t*Bu)Zn(*t*Bu)

We commenced our ferrocene ate base studies by investigating the sodium monoamido-bisalkylzincate reagent TMEDA·Na(μ-TMP)(μ-*t*Bu)Zn(*t*Bu).³⁹ Its constituent parts, namely *t*Bu₂Zn, NaTMP and TMEDA are simply mixed together in equimolar quantities (a cocomplexation reaction) to generate it *in situ* in hexane solution, to which a molar equivalent of ferrocene was introduced (scheme 1).



Scheme 1

After some gentle heating of the solution, a crystalline material was deposited upon bench cooling which was subjected to an X-ray crystallographic structure determination (Figure 4 shows one of the two independent molecules found in the unit cell). This study showed that the bimetallic base had mono-deprotonated ferrocene to give a discrete molecular product of formula $\text{TMEDA} \cdot \text{Na}(\mu\text{-TMP})[\mu\text{-}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)]\text{Zn}(t\text{Bu})$ (**1**). The spirocyclic structure consists of a central NaNZnC core with a terminal $t\text{Bu}$ group plus a TMP anion and a monodeprotonated ferrocene bridging between the metals. TMEDA chelation of sodium completes the structure. This could also be viewed as a trapezium NaNZnC ring with four distinct TMEDA, TMP, $t\text{Bu}$ and ferrocenyl $[(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)]$ corners. The zinc and sodium atoms lie in distorted trigonal planar and distorted tetrahedral environments respectively with the sum of the three angles at zinc being exactly 360° and the τ_4 value of sodium being 0.69, where a value of 1 is perfectly tetrahedral and 0 is perfectly square planar as described by Houser and co-workers.⁴⁰ Such distortion from perfect tetrahedral symmetry is enforced since the sodium atom is the common atom of a spirocycle, resulting in tightening of these angles, with non-cyclic angles being consequently much larger than 109.5° . The central NaNZnC ring is heavily distorted due to the mismatch of longer Na-C [$2.652(7)\text{\AA}$] and Na-N [$2.487(5)\text{\AA}$] bonds and shorter Zn-C [$2.057(7)\text{\AA}$] and Zn-N [$2.041(5)\text{\AA}$] bonds. There is possibly a degree of coordination between the sodium cation and the π system of the deprotonated ferrocene with the distance of sodium to the centroid of the C_5 ring being 2.817\AA . This value reflects the ‘donor’ nature of the C_5H_4 ring to the Lewis acidic sodium and is marginally longer than that seen in the ferrocene-solvated hexamethyldisilazide dimer $[\{\text{NaN}(\text{SiMe}_3)_2\}_2 \cdot (\text{Cp}_2\text{Fe})]_\infty$ which has a corresponding distance of 2.791\AA ,⁴¹ perhaps due to the increased coordination number of **1** (4) with respect to that of the

NaN(SiMe₃)₂ complex (3). Definite cation-anion interactions between a cyclopentadienyl ring and a sodium cation are noticeably shorter, for example only 2.357Å for unsolvated [NaCp]_∞.⁴² Solvated NaCp derivatives display understandably longer interactions, such as in dimethoxyethane (2.55Å),⁴³ 15-crown-5 (2.563Å),⁴³ THF (2.455Å),⁴⁴ ammonia (2.502Å)⁴⁵ and TMEDA (2.667Å) complexes,⁴⁶ although these are still understandably shorter than that in **1**. The Na-Cp interaction has virtually no corresponding effect on the Cp-Fe distance.⁴⁷

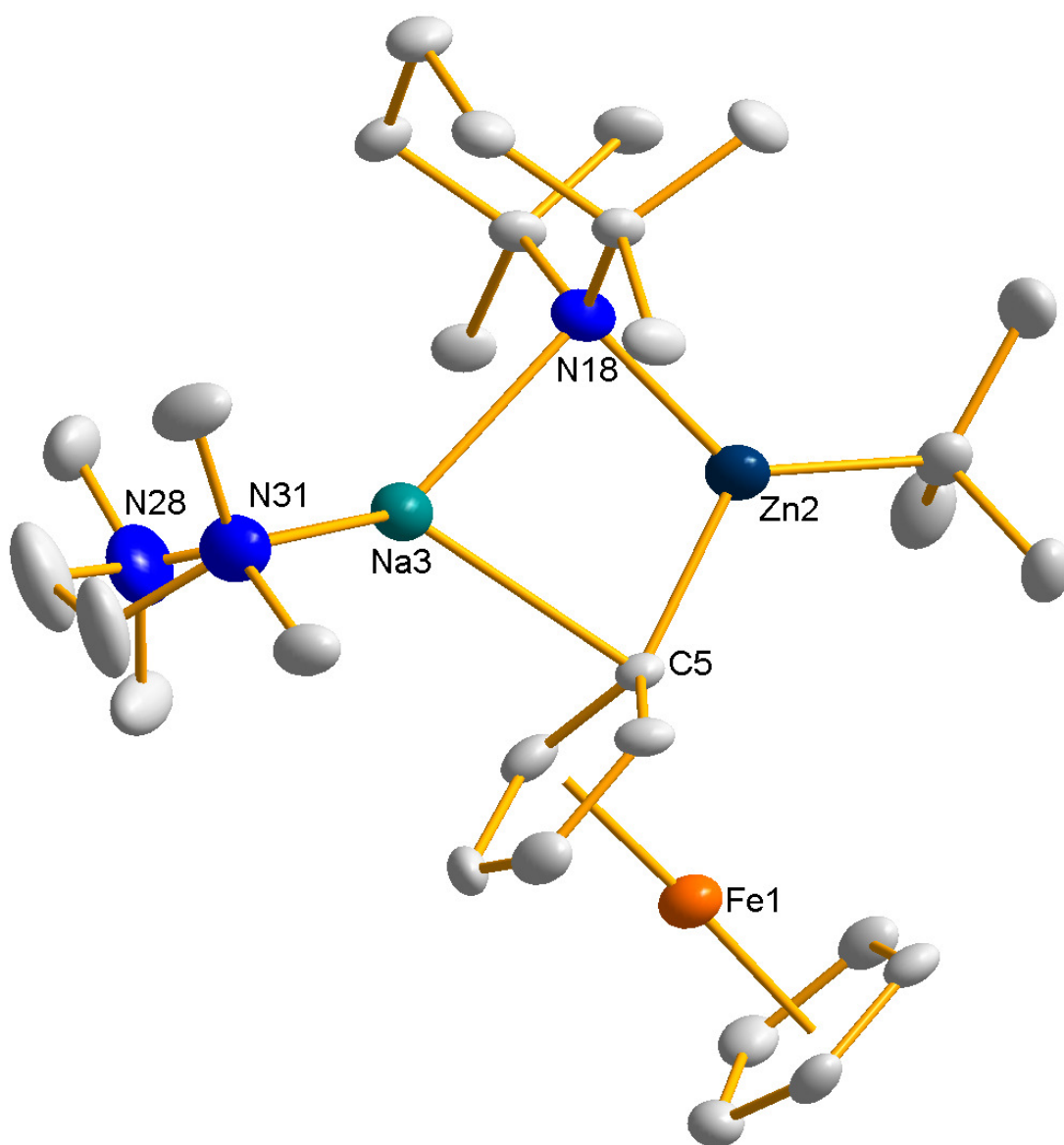


Figure 4 Molecular structure of one of the independent molecules of TMEDA·Na(μ -TMP)[μ -(C₅H₄)Fe(C₅H₅)]Zn*t*Bu (**1**). Ellipsoids are shown at 50% probability level and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Zn2-C5 2.057(7), Zn2-N18 2.041(5), Na3-C5 2.652(7), Na3-N18 2.487(5), Na3-N28 2.587(7), Na3-N31 2.525(6); C5-Zn2-N18 104.5(2), Zn2-N18-Na3 91.0(2), N18-Na3-C5 78.1(2), Na3-C5-Zn2 86.2(2).

The same reaction was then repeated but this time only 0.5 molar equivalents of ferrocene per mole of bimetallic base was introduced (scheme 1). This second reaction produced a different crystalline product in [TMEDA·Na(μ -TMP)Zn(*t*Bu)]₂(C₅H₄)₂Fe (**2**). Though having a similar structure to **1**, now both cyclopentadienyl rings in **2** have been monodeprotonated by the sodium zincate such that the ferrocendiyl molecule acts as a metal-containing bridge between the two bimetallic units (figure 5). The positions of deprotonation on each ring are staggered such that they are almost orthogonal [the dihedral angle formed between the two Zn-C₅centroid planes is 84.28(2)^o] to minimize the steric clashing of the bulky bimetallic frameworks. This product can formally be considered as that obtained when complex **1** is metalated at its intact cyclopentadienyl ring by a further equivalent of the active bimetallic base. The distance of the C₅ centroid to sodium is elongated with respect to that in **1** at 2.975 Å (c.f. 2.791 Å in **1**) although in this complex the Na-C₅H₄ interaction is probably better defined as η^2 since the distance from sodium to a carbon atom adjacent to the metalated carbon [2.704(6) Å] is virtually identical to that of the Na-C_{metalated} distance [2.703(6) Å; indeed on the other metalated ring the distance to

the adjacent carbon atom, 2.635(6)Å, is actually shorter than the Na-C_{metalated} distance, 2.762(6)Å].

Due in part to steric clashing between the top and bottom ferrocene appendages, the sodium atom of the second deprotonated ring is noticeably displaced compared to that of the first, with a longer bond to the metalated carbon atom [2.762(6) versus 2.703(6)Å for Na3-C4] and to the C₅ centroid [3.190Å].

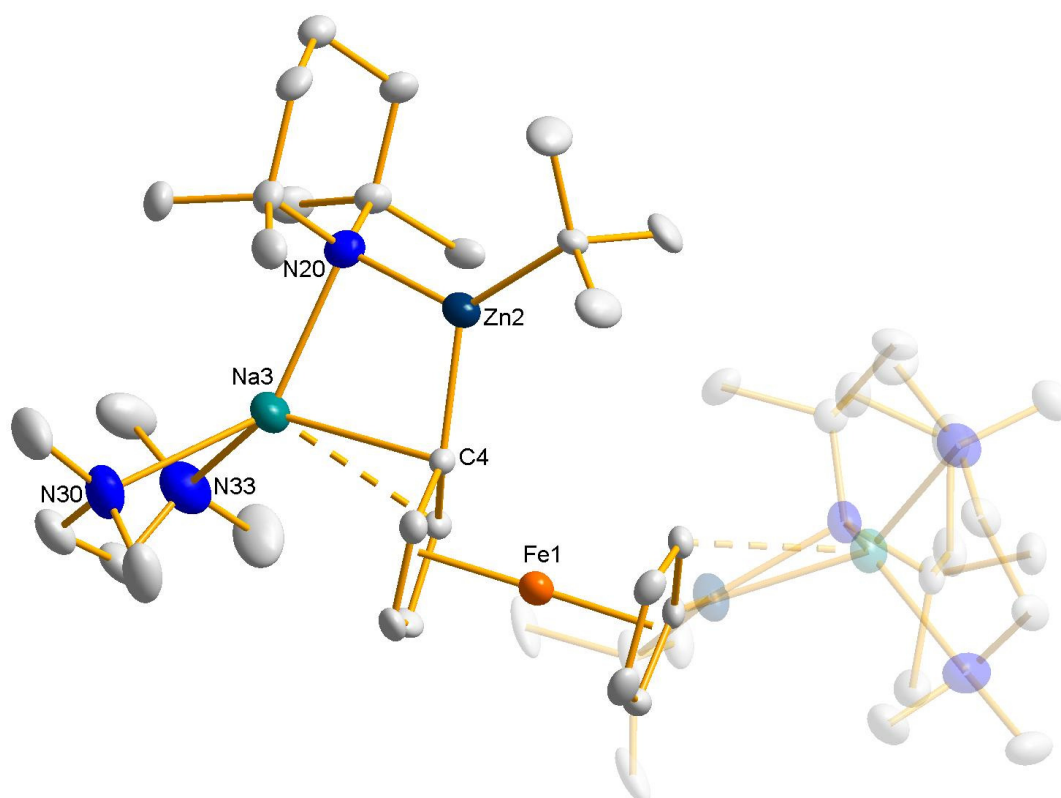


Figure 5 Molecular structure of [TMEDA·Na(μ-TMP)Zn(*t*Bu)]₂(C₅H₄)₂Fe (**2**). Ellipsoids are shown at 50% probability level and all hydrogen atoms and minor disordered components of TMP and *t*Bu groups have been removed for clarity. Selected bond lengths (Å) and angles (°) [values in parentheses represent equivalent parameters on the opposite (transparent) side of molecule]: Zn2-C4 2.045(5) [2.052(5)], Zn2-N20 2.047(4) [2.052(4)], Na3-C4 2.703(6) [2.762(6)], Na3-N20 2.432(4) [2.434(5)], Na3-N30 2.602(5) [2.536(6)], Na3-N33 2.530(5) [2.537(5)]; C4-

Zn₂-N₂O 105.2(2) [107.2(2)], Zn₂-N₂O-Na₃ 91.7(2) [90.2(2)], N₂O-Na₃-C₄ 78.4(2) [78.7(2)], Na₃-C₄-Zn₂ 84.3(2) [81.6(2)].

Notably, the molecular structure shows no evidence of ligand redistribution to give either higher order zincate species or homometallic complexes such as seen previously when utilising the related zincate base TMEDA·Li(μ-TMP)(μ-*n*Bu)Zn(*n*Bu);¹⁹ or intermolecular aggregation (via K-π-arene interactions) as witnessed when ferrocene was metalated using a related potassium zincate base.²³

Next, complexes **1** and **2** were probed in C₆D₁₂ solution via NMR spectroscopy. Comparing the ¹H NMR spectra of the two complexes, it was clear that neither product was pure but contained traces of the other, meaning that final yields are not absolute. We note that complex mixtures of products when metalating ferrocene have been obtained previously, for example by Lerner and co-workers when metalating a diaminoborylferrocene with more than one molar equivalent of homometallic Mg(TMP)₂, which contains the same active amido anion as in our zinc and aluminum bases.⁴⁸ The aliphatic region of the spectra of **1** and **2** was complicated in each case due to the overlapping multiplets of the TMP resonances. However, the region around 4 ppm was indicative of the outcome of the reaction with the mono-zincated species **1** displaying three singlets (resonances were slightly broadened with mutual coupling not noticed) in a 2:2:5 ratio at 3.86, 4.21 and 4.02 ppm respectively, while the di-zincated complex **2** displayed two broad singlets in a 4:4 ratio at 3.84 and 4.29 ppm. The ¹³C NMR spectra of these complexes were in agreement although despite repeated attempts with multiple scans we were unable to discern a resonance for the metalated carbon atom of the cyclopentadienyl rings.

In an attempt to ascertain whether more than twofold zincation of ferrocene could be accessed the reaction stoichiometry was altered to four moles of base per mole of ferrocene. This time no donor solvent (TMEDA) was added since the preceded tetramagnesiated inverse crown complex (*vide supra*) does not contain any neutral Lewis donor molecules. This reaction mixture precipitated a fine red powder (complex **3**), which was collected by filtration and washed. Unfortunately despite several attempts, this powder could not be recrystallized in a quality suitable enough for X-ray crystallographic study. A ^1H NMR spectrum of this sparingly soluble product was obtained in C_6D_6 , which crucially revealed two sets of three equal integration singlets in the diagnostic region of the spectrum around 4 ppm, in a ratio of 2.5:1 (figure 6). Resolving three different resonances rather than two tenuously suggests that tetrametalation could have taken place as in tetramagnesiato $[\text{Fe}(\text{C}_5\text{H}_3)_2]^{4-}$ complex.¹²⁻¹³ To the best of our knowledge no other reaction involving four zinc-hydrogen exchanges has been described in the literature. The fact that there are two sets of these resonances suggests that there are two isomers present in solution, which could be speculated as being an eclipsed and a staggered isomer. Due to the poor solubility of this compound, a useful ^{13}C NMR spectrum of it (and thus a ^1H - ^{13}C HSQC spectrum) could not be obtained, precluding definitive assignment of the many overlapping resonances in the aliphatic region.

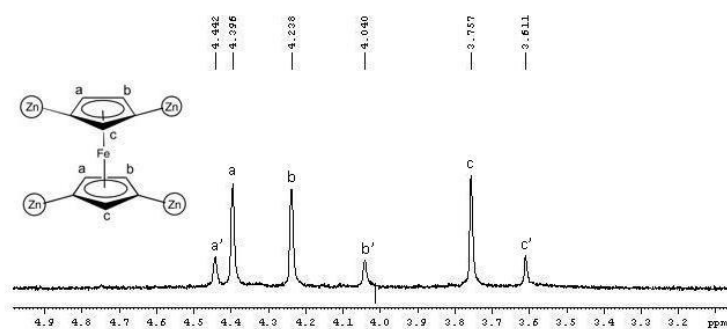
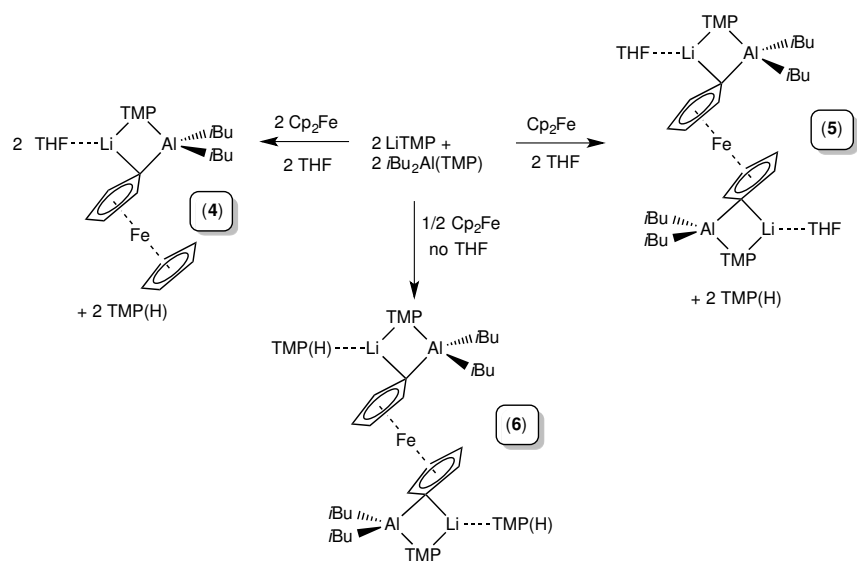


Figure 6 Section of ^1H NMR spectrum of putative tetrazincated ferrocene complex **3**
in C_6D_6 solution

Studies of lithium aluminate “ $\text{LiAl}(\text{TMP})_2i\text{Bu}_2$ ”

Following our sodium zincate studies, we moved to another combination with which we have considerable experience, namely the putative lithium/aluminium pairing previously written as “ $\text{LiAl}(\text{TMP})_2i\text{Bu}_2$ ”. Originally thought likely to be a highly reactive contacted ion pair primed for direct aluminations,⁴⁹ in a parallel study⁵⁰ we recently established it actually exists as a sterically-dictated, non-interacting mixture of its component homometallic compounds, $\text{Li}(\text{TMP})$ and $i\text{Bu}_2\text{Al}(\text{TMP})$, which in proton abstraction applications operates via a two step lithiation/aluminium trans-metal trapping protocol. The first two reactions (scheme 2) of this bimetallic mixture with one or 0.5 molar equivalents of ferrocene, respectively, in the presence of stoichiometric THF produced crystalline mono and di-deprotonated ferrocene complexes of formula $\text{THF}\cdot\text{Li}(\mu\text{-TMP})[\mu\text{-}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)]\text{Al}(i\text{Bu})_2$ (**4**, figure 7) and $[\text{THF}\cdot\text{Li}(\mu\text{-TMP})\text{Al}(i\text{Bu})_2]_2(\text{C}_5\text{H}_4)_2\text{Fe}$ (**5**, figure 8) respectively. As is the case with complexes **1** and **2**, the secondary metal of lower electropositivity than lithium has replaced the abstracted hydrogen atom with the alkali-metal lying outside the plane of the C_5H_4 ring, although as the smaller alkali-metal in these cases is less π -philic, it is best described as a η^1 interaction. In both cases, the lithium atoms occupy a three-coordinate (1x C ; 1x N ; 1x O) environment with a bridging TMP and a neutral THF completing their coordination spheres.



Scheme 2

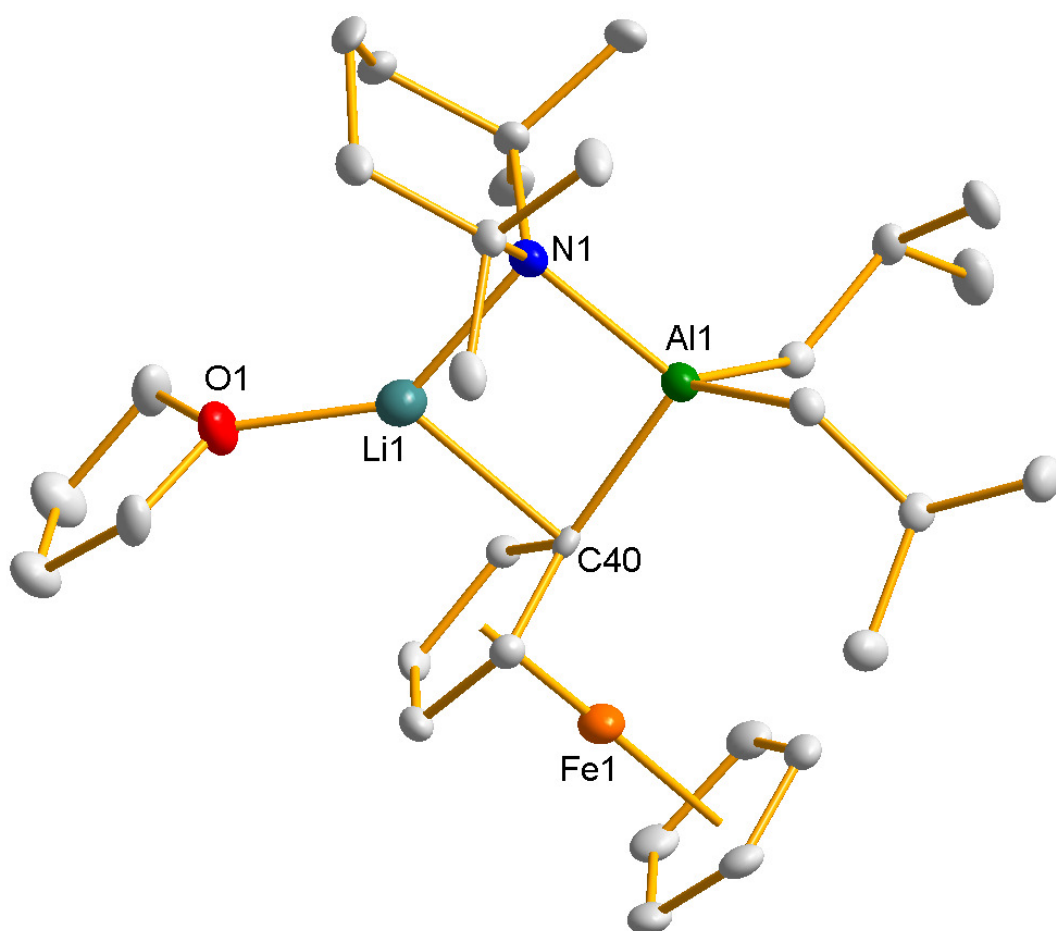


Figure 7 Molecular structure of the monoaluminated ferrocene THF·Li(μ -TMP)[μ -(C₅H₄)Fe(C₅H₅)]Al(*i*Bu)₂ (**4**). Ellipsoids are shown at 50% probability level and all hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1-C40 2.039(3), Al1-N1 1.994(2), Li1-C40 2.188(6), Li1-N1 2.005(5), Li1-O1 1.866(6); C40-Al1-N1 96.1(1), Al1-N1-Li1 89.3(2), N1-Li1-C40 91.2(2), Li1-C40-Al1 83.3(2).

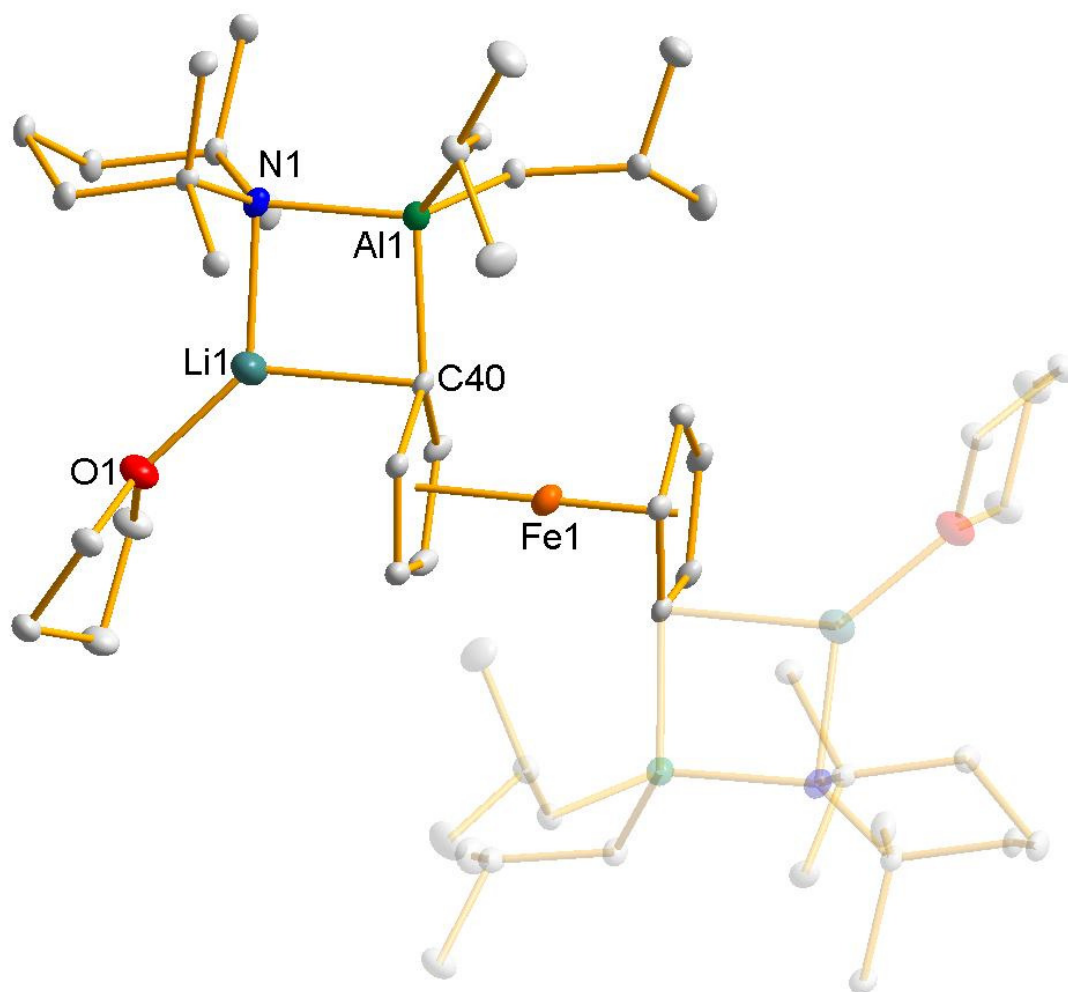


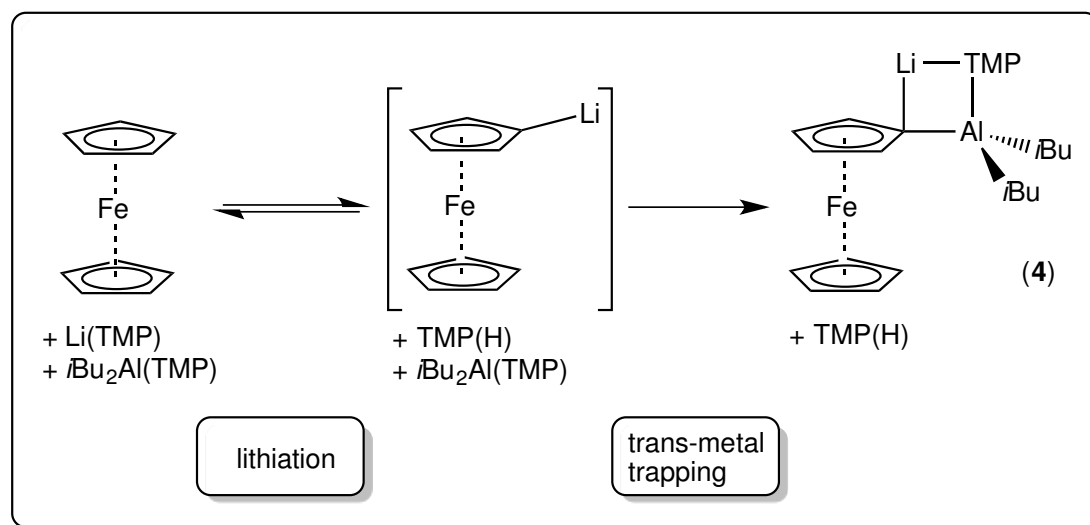
Figure 8 Molecular structure of the dialuminated ferrocene [THF·Li(μ -TMP)Al(*i*Bu)₂]₂(C₅H₄)₂Fe (**5**). Ellipsoids are shown at 50% probability level and all hydrogen atoms have been removed for clarity. Symmetry operation to generate second half of structure: 2.5-x, y, 2-z. Selected bond lengths (Å) and angles (°): Al1-

C40 2.053(1), Al1-N1 1.996(1), Li1-C40 2.194(3), Li11-N1 2.032(2), Li1-O1 1.884(2); C40-Al1-N1 97.3(4), Al1-N1-Li1 88.2(1), N1-Li1-C40 91.9(1), Li1-C40-Al1 82.5(1).

The local environments around the deprotonated ferrocene molecules are unsurprisingly similar in complexes **4** and **5**. Specifically, there is very little difference in the dimensions of the four-membered, four-element Li-N-Al-C rings of each as demonstrated by comparison of their Al-C [2.039(1) and 2.053(1) Å respectively], Al-N [1.994(2)/1.996(1) Å], Li-N [2.005(5)/2.032(2) Å] and Li-C [2.188(6)/2.194(3) Å] bond distances. In complex **5**, the position of deprotonation of the cyclopentadienyl rings (that is the newly formed Al-C bonds) are perfectly staggered due to its centrosymmetric nature.

Taking complex **4** as an example (although the same principle applies to the second Cp ring to yield **5**) the mechanism is, as mentioned earlier, likely to involve a two step process of lithiation, which occurs in only a poor yield using Li(TMP) as a metalating agent, followed by trans-metal trapping with the soluble monomer (TMP)Al*i*Bu₂ (scheme 3). Although not directly involved in the first step as it cannot cocomplex with LiTMP nor deprotonate ferrocene, the presence of the aluminium reagent is necessary for the reaction to proceed by mopping up the product on the right hand side of the equilibrium and thus this can be considered a synergistic reaction. Indeed this process is likely at play in other metalations of functionalized ferrocene with bimetallic combinations⁵¹ which are sterically prevented (through the use of bulky amides such as TMP) from combining into a contacted molecular bimetallic ate type base.⁵² This contrasts with TMEDA·Na(μ-TMP)(μ-*t*Bu)Zn(*t*Bu), which has been

proven to be a contacted ion pair zincate that generally deprotonates aromatic substrates intramolecularly with sodium acting as a Lewis acidic coordination point.



Scheme 3 Proposed two-step lithiation/trans-metal-trapping mechanism for monoalumination of ferrocene.

Finally, we attempted to prepare a tetra-aluminated ferrocene complex by adding 0.25 molar equivalents of ferrocene to the synergistic lithium/aluminium mixture (scheme 2). Following the preparation of **3**, no donor solvent was included as this could potentially cap the Lewis acidic metal and prevent formation of the inverse crown ring. However, the crystalline material $[\text{TMP(H)} \cdot \text{Li}(\mu\text{-TMP})\text{Al}(i\text{Bu})_2]_2(\text{C}_5\text{H}_4)_2\text{Fe}$ **6** (figure 9) resulting from this reaction turned out to be only a di-aluminated derivative (akin to **5**). Interestingly, in the absence of THF the non-volatile, bulky amine TMP(H) , liberated as a co-product from the deprotonation reaction due to amine basicity, acts as a Lewis donor, capping the lithium and preventing the bimetallic units from linking up further into a ring as seen in the sodium magnesiate inverse crown in Figure 1. Dative $\text{TMP(H)} \cdots \text{Li}$ contacts are relatively rare in the literature

with the bond length in complex **6** [mean, 2.229Å] being longer than those previously reported in $\text{TMP(H)}\cdot\text{LiN}(t\text{Bu})\text{B(Ph)}(\text{TMP})$ [2.155(5)Å],⁵³ $\text{TMP(H)}\cdot\text{Li}(\mu\text{-}i\text{Bu})(\mu\text{-TMP})\text{Al}i\text{Bu}_2$ [2.165(5)Å]⁵⁴ or $[\text{TMP(H)}\cdot\text{Li}]_4$ [mean, 2.104Å].^{49f}

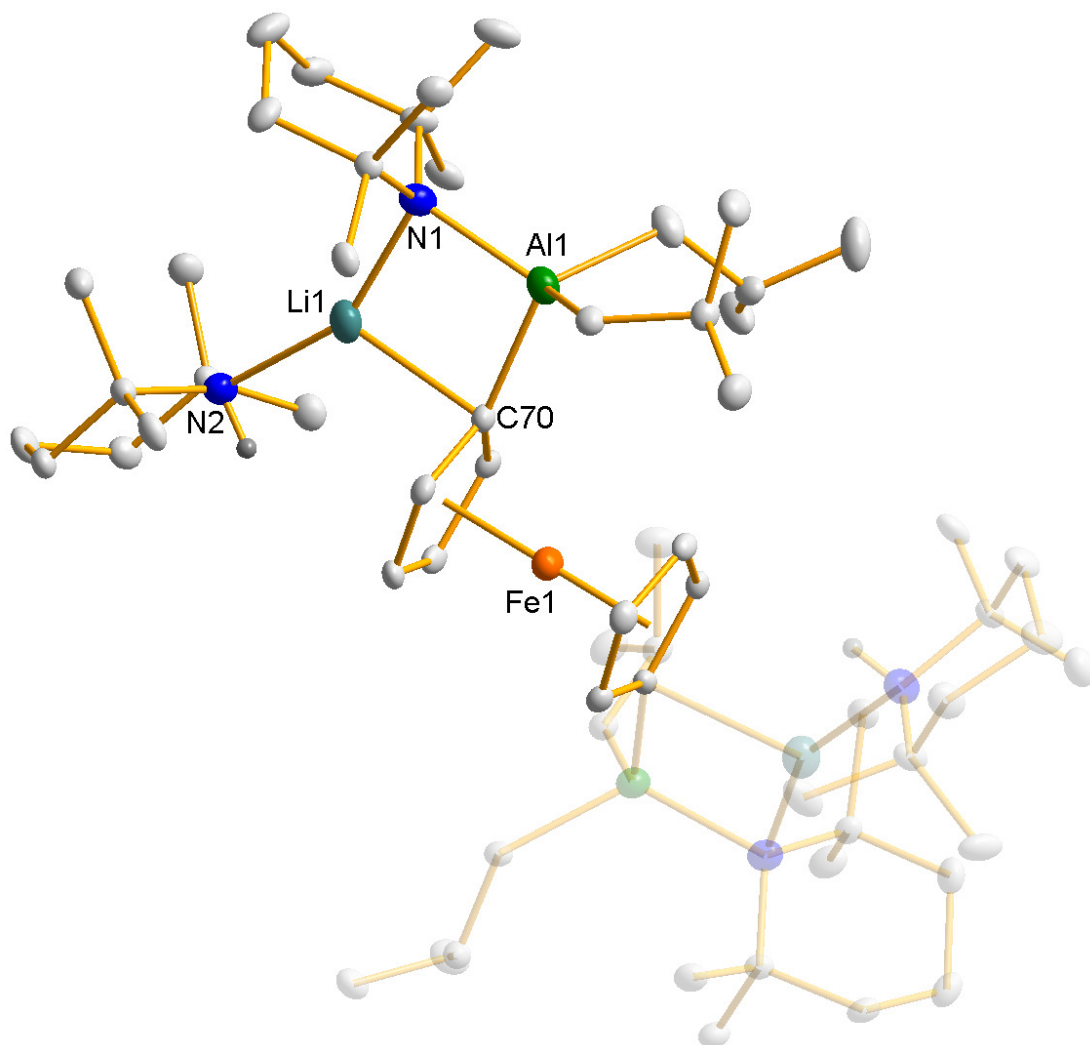
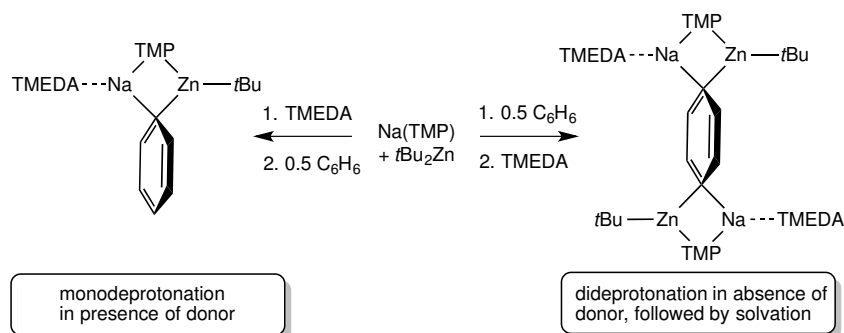


Figure 9 Molecular structure of the dialuminated ferrocene $[\text{TMP(H)}\cdot\text{Li}(\mu\text{-TMP})\text{Al}(i\text{Bu})_2]_2(\text{C}_5\text{H}_4)_2\text{Fe}$ (**6**). Ellipsoids are shown at 50% probability level and all hydrogen atoms [except on TMP(H)] have been removed for clarity. Selected bond lengths (Å) and angles (°) [values in parentheses represent equivalent parameters on the opposite (transparent) side of molecule]: Al1-C70 2.043(3) [2.030(3)], Al1-N1 1.996(2) [1.993(2)], Li1-C70 2.248(6) [2.297(5)], Li11-N1 2.106(5) [2.095(6)], Li1-

N2 2.223(5) [2.236(6)]; C70-A11-N1 97.5(1) [97.8(1)], A11-N1-Li1 89.2(2) [90.7(2)], N1-Li1-C70 88.4(2) [87.2(2)], Li1-C70-A11 84.3(2) [84.3(2)].

The inability of this synergistic lithium-aluminium base mixture to effect a dual deprotonation of each ring due to the presence of (in this case *in situ* generated) donor is reminiscent of the alkali-metal mediated metalation of other simple arenes such as benzene or toluene. While the donor free base NaMgnBu(TMP)₂ can smoothly dideprotonate these aromatic rings (note that in the toluene case the most acidic methyl substituent is left untouched),⁵⁵ solvation of the base with TMEDA prior to introducing the substrate results in only monodeprotonation.⁵⁶ Likewise, and more directly related to this work, the NaTMP/*t*Bu₂Zn combination will dideprotonate benzene prior to TMEDA addition but only monodeprotonate it if TMEDA is in the reaction mixture at the onset (scheme 4).⁵⁷ We note here that it is extremely challenging to doubly deprotonate a non-metallocenic cyclopentadiene ring with to the best of our knowledge the only example being the *n*BuLi induced deprotonation of Cp⁻ in the molecular square complex [Li(μ-TMP)Li(μ-Cp)]₄ to generate [Li(μ-TMP)Li(μ-Cp)]₄Li₆(*n*Bu)₂] as reported by Klett and coworkers.⁵⁸



Scheme 4

Unlike in complex **5**, the deprotonated rings in **6** are not perfectly staggered, with the Al-C bonds lying at $145.65(2)^\circ$ to one another. The larger steric bulk of the TMP(H) donor ligand with respect to THF may be a factor in the elongation of the Li-N and Li-C bonds within the four membered ring to 2.106(5) and 2.248(6)Å respectively (c.f. Li-N [2.005(5)/2.032(2) Å] and Li-C [2.188(6)/2.194(3) Å] in THF solvated complexes **4** and **5** respectively).

Complexes **4** (in C_6D_{12} solution) and **6** (in C_6D_6 solution, as the resonances in C_6D_{12} were very broad) proved to be of higher purity than the aforementioned zinc complexes with only resonances corresponding to their molecular structures being seen in their solution 1H spectra. This was further corroborated through the 7Li NMR spectra, which showed only one sharp resonance. In the case of **5**, a small amount of complex **4** was evidently present in C_6D_{12} solution as seen in both the 1H and 7Li spectra. Again, the 1H spectra were very cluttered in the aliphatic region although the region around 4 ppm was particularly diagnostic due to the lucid resolution of the cyclopentadienyl resonances of ferrocene. Monodeprotonated complex **4** displayed three characteristic singlets in a 2:2:5 ratio at 4.00, 4.25 and 4.09 ppm while the dideprotonated complexes gave a pair of equal intensity singlets at 3.97/4.47 ppm (**5**) and 4.15/4.29 ppm (**6**). Interestingly, the lower field resonance in complex **6** is considerably broadened. Once again, a resonance for the metalated carbon atom could not be identified in the ^{13}C spectra.

Conclusion

This study has revealed that the sodium zincate reagent $TMEDA \cdot Na(\mu-TMP)(\mu-tBu)Zn(tBu)$ can successfully perform one or two zinc-hydrogen exchange reactions

with ferrocene to afford TMEDA·Na(μ -TMP)[μ -(C₅H₄)Fe(C₅H₅)]Zn(*t*Bu) **1** or [TMEDA·Na(μ -TMP)Zn(*t*Bu)]₂(C₅H₄)₂Fe **2**, respectively. Though the number of C-H deprotonations essentially matches the stoichiometry of the base used in the reaction (1 or 2 equivalents respectively), the reactions are not clean in that there are always trace amounts of **2** found in solid samples of **1** and *vice versa*. The crystal structures obtained are similar to those previously observed using other metal bases. Where a sodium zincate could be unique is in generating the suspected tetradeprotonated ferrocene **3**. Zinc ate reagents are not generally known for multiple (more than two) zinc-hydrogen exchanges within the same molecule nor generating inverse crown architectures unlike their magnesium counterparts (the best example being the aforementioned tetra-magnesiated ferrocene) so the full formulation and structural characterization of such a polyzincated species would be a particularly intriguing finding though this has proved elusive in this study. The aluminum reactions appear to be cleaner giving rise to the monodeprotonated ferrocene THF·Li(μ -TMP)[μ -(C₅H₄)Fe(C₅H₅)]Al(*i*Bu)₂ **4**, and the dideprotonated ferrocene [THF·Li(μ -TMP)Al(*i*Bu)₂]₂(C₅H₄)₂Fe **5**, though unlike the aforementioned zincate reactions which are direct zinc-hydrogen exchange processes these reactions are two step lithiation, trans-metal(aluminum)-trapping (or indirect aluminations) akin to salt metathesis processes but with the advantage that the trapping agent, *i*Bu₂Al(TMP), is hydrocarbon soluble. Unlike from the zincation (or magnesiation) reaction, a tetra-aluminated ferrocene has remained elusive, even in the total absence of neutral Lewis donating solvent, with only a di-aluminated product solvated by the *in situ* generated secondary amine, [TMP(H)·Li(μ -TMP)Al(*i*Bu)₂]₂(C₅H₄)₂Fe **6**, being identified. Tentatively (as only a few reactions have been considered for this effect), this suggests that multiple deprotonations of a substrate, often manifested as the guest of

an inverse-crown type structure, cannot be obtained when a non-volatile Lewis donating secondary amine is generated as a part of the original deprotonation reaction and that overall alkyl basicity (that is, in the sense that the alkyl group deprotonates TMP(H) to enable TMP to re-enter the coordination sphere of the deprotonated substrate as discussed in several papers⁵⁹) with its concomitant generation of non-donating, volatile alkanes is more suited for such polymetalation reactions. Work is ongoing to prove or disprove this hypothesis.

Experimental

General experimental

All reactions and manipulations were performed under a protective argon atmosphere using either standard Schlenk techniques or a glove box. Hexane and THF were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. TMEDA was distilled over CaH₂ and stored over 4Å molecular sieves. TMP(H) was stored over 4Å molecular sieves. *n*BuLi solution (1.6 M in hexanes), *t*Bu₂AlCl and ferrocene were purchased commercially from Sigma-Aldrich and used as received. *t*Bu₂Zn was prepared by a literature method.⁶⁰ NMR spectra were recorded on a Bruker AV 400 MHz spectrometer operating at 400.13 MHz for ¹H, 155.47 MHz for ⁷Li and 100.62 MHz for ¹³C. All ¹³C spectra were proton decoupled. ¹H and ¹³C spectra were referenced to the residual solvent signal while ⁷Li spectra were referenced to an external sample of LiCl in D₂O. Satisfactory elemental analyses of the air sensitive products **1** (co-crystallized with **2**), **2** (co-crystallized with **1**), **3** (too air sensitive) and **6** (decomposed on balance due to increased lability of donor amine) could not be obtained.

X-ray crystallography

Crystallographic data were collected on Nonius KappaCCD or Oxford Diffraction instruments with Mo K α radiation ($\lambda = 0.71073\text{\AA}$). Structures were solved using *SHELXS-97*,⁶¹ while refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method using the *SHELXL-97* program.⁶¹ All non-hydrogen atoms were refined using anisotropic thermal parameters. Selected crystallographic details and refinement details are given in table S1 of supplementary information. CCDC-1036678 to CCDC-1036682 contain the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of TMEDA·Na(μ -TMP)[μ -(C₅H₄)Fe(C₅H₅)]Zn*t*Bu (**1**)

A Schlenk flask was charged with *t*Bu₂Zn (0.358g, 2 mmol) which was dissolved in hexane (10 mL). In a separate Schlenk flask BuNa (0.160g, 2 mmol) was suspended in hexane (10 mL) and TMP(H) (0.34 mL, 2 mmol) was added via syringe to give a creamy white suspension which was allowed to stir for an hour. After this time the *t*Bu₂Zn solution was introduced to the mixture via syringe to give a yellow suspension. TMEDA (0.30 mL, 2 mmol) was added via syringe and the reaction mixture was heated gently to form a yellow solution. Once this mixture had returned to ambient temperature ferrocene (0.372, 2 mmol) was added via solid addition tube and this was heated gently to give a transparent solution. Upon cooling the solution at -35°C a crop of orange crystals of **1** formed (0.22g, not an absolute yield due to traces of **2** also being present).

¹H NMR (400.13 MHz, C₆D₁₂, 300K): δ 1.06 [6H, s, TMP Me], 1.20 [6H, s, TMP Me], 1.21 [9H, s, *t*Bu], 1.23 [2H, m, TMP β -CH₂], 1.54 [2H, m, TMP β -CH₂], 1.71 [2H, m, TMP γ -CH₂], 2.06 [12H, s, TMEDA Me], 2.16 [4H, s, TMEDA CH₂], 3.86 [2H, s, C₅H₄Fe], 4.02 [5H, s, C₅H₅Fe], 4.21 [2H, s, C₅H₄Fe].

¹³C NMR (100.63 MHz, C₆D₁₂, 300K): δ 19.4 [CMe₃], 20.5 [TMP γ], 35.4 [TMP Me], 35.5 [CMe₃], 35.7 [TMP Me], 40.5 [TMP β], 46.6 [TMEDA Me], 53.2 [TMP α], 58.0 [TMEDA CH₂], 68.5 [C₅H₅Fe], 70.4 [C₅H₄Fe], 76.1 [C₅H₄Fe].

Synthesis of [TMEDA·Na(μ -TMP)Zn(*t*Bu)]₂(C₅H₄)₂Fe (**2**)

A Schlenk flask was charged with *t*Bu₂Zn (0.358g, 2 mmol) which was dissolved in hexane (10 mL). In a separate Schlenk flask BuNa (0.160g, 2 mmol) was suspended in hexane (10 mL) and TMP(H) (0.34 mL, 2 mmol) was introduced via syringe. The

resulting creamy white suspension was then stirred for an hour. After this time the $t\text{Bu}_2\text{Zn}$ solution was added via syringe to give a yellow suspension to which TMEDA (0.30 mL, 2 mmol) was also added. This mixture was then heated gently to form a yellow solution. Once this solution had cooled to ambient temperature ferrocene (0.186, 1 mmol) was added via solid addition tube and this was heated gently to give a transparent solution. Upon cooling this solution at -35°C a crop of orange crystals formed of **2** (0.98g, not an absolute yield due to traces of **1** also being present) were obtained.

^1H NMR (400.13 MHz, C_6D_{12} , 300K): δ 1.02 [6H, s, TMP Me], 1.18 [6H, s, TMP Me], 1.22 [9H, s, $t\text{Bu}$], 1.24 [2H, m, TMP β - CH_2], 1.55 [2H, m, TMP β - CH_2], 1.71 [2H, m, TMP γ - CH_2], 2.13 [12H, s, TMEDA Me], 2.22 [4H, s, TMEDA CH_2], 3.84 [4H, s, $\text{C}_5\text{H}_4\text{Fe}$], 4.29 [4H, s, $\text{C}_5\text{H}_4\text{Fe}$].

^{13}C NMR (100.63 MHz, C_6D_{12} , 300K): δ 20.5 [TMP γ], 17.6 [$\underline{\text{C}}\text{Me}_3$], 35.2 [TMP Me], 35.7 [TMP Me], 35.8 [$\underline{\text{C}}\text{Me}_3$], 40.4 [TMP β], 46.7 [TMEDA Me], 53.2 [TMP α], 58.1 [TMEDA CH_2], 71.4 [$\text{C}_5\text{H}_4\text{Fe}$], 75.9 [$\text{C}_5\text{H}_4\text{Fe}$].

Synthesis of $\text{Na}_4(\text{TMP})_4\text{Zn}_4(t\text{Bu})_4[(\text{C}_5\text{H}_3)_2\text{Fe}]$ (**3**)

A Schlenk flask was charged with $t\text{Bu}_2\text{Zn}$ (0.358g, 2 mmol) which was dissolved in hexane (10 mL). In a separate Schlenk flask BuNa (0.160g, 2 mmol) was suspended in hexane (10 mL) and TMP(H) (0.34 mL, 2 mmol) was added via syringe, the resulting creamy white suspension being allowed to stir for an hour. Next the $t\text{Bu}_2\text{Zn}$ solution was added via syringe followed by ferrocene (0.09g, 0.5 mmol) via a solid addition tube. This mixture was stirred for 2 hours during which time the suspension changed from yellow to orange to red. The resulting red powder of **3** was collected

via filtration, washed with hexane and dried in vacuo (0.08 g, 10%, based on the above formula being correct).

Synthesis of THF·Li(μ-TMP)[μ-(C₅H₄)Fe(C₅H₅)]Al(*i*Bu)₂ (**4**)

In a Schlenk flask, *n*BuLi (1.25 mL, 1.6 M in hexanes, 2 mmol) was suspended in hexane (10 mL) and TMP(H) (0.34 mL, 2 mmol) was added via syringe, before *i*Bu₂AlCl (0.38 mL, 2 mmol) was introduced via syringe producing a white suspension almost immediately. This suspension was stirred for one hour and then filtered through Celite and glass wool to remove solid LiCl. In a separate Schlenk flask LiTMP was prepared in hexane (10 mL) from a mixture of *n*BuLi (1.25 mL, 2 mmol) and TMP(H) (0.34 mL, 2 mmol). The *i*Bu₂AlTMP solution was added to the LiTMP solution via cannula to give a colourless solution. THF (0.16 mL, 2 mmol) and ferrocene (0.372 g, 2 mmol) were added producing an orange solution which was stirred overnight at room temperature and then allowed to stand until a crop of orange needles of **4** formed (0.52 g, 48%).

¹H NMR (400.13 MHz, C₆D₁₂, 300K): δ 0.37 [4H, d, ³J(H,H) = 5.03 Hz, 2 x CH₂ of *i*Bu], 0.75 [2H, t, ³J(H,H) = 12.44 Hz, 2 x βCH₂ of TMP], 1.09 [12H, 2 x overlapping d, ³J(H,H) = 6.49 Hz, 4 x CH₃ of *i*Bu], 1.27 [7H, s, 2 x TMP Me + 1 x γCH₂ of TMP (confirmed by HSQC)], 1.33 [6H, s, 2 x TMP Me], 1.48 [2H, d, ³J(H,H) = 12.43 Hz, 2 x βCH₂ of TMP], 1.73 [4H, s, 2 x βCH₂ of THF], 1.84 [1H, m, 1 x γCH₂ of TMP], 2.14 [2H, sept, ³J(H,H) = 6.42 Hz, 2 x CH of *i*Bu], 3.50 [4H, m, 2 x αCH₂ of THF], 4.00 [2H, s, C₅H₄Fe], 4.09 [5H, s, C₅H₅Fe], 4.25 [2H, s, C₅H₄Fe].

¹³C NMR (100.63 MHz, C₆D₁₂, 300K): δ 18.7 [TMP γ], 25.3 [THF βCH₂], 28.0 [CH₂CHMe₂], 29.2 [CH₂CHMe₂], 29.8 [TMP Me], 31.0 [CH₂CHMe₂], 36.8 [TMP

Me], 45.2 [TMP β], 53.1 [TMP α], 69.1 [THF α CH₂], 69.5 [C₅H₅Fe], 71.7 [C₅H₄Fe], 77.1 [C₅H₄Fe].

⁷Li NMR (155.46 MHz, C₆D₁₂, 300K): δ -0.56 ppm.

Calculated (%) for Al₁C₃₁Fe₁H₅₃Li₁N₁O₁: C, 68.25; H, 9.79; N, 2.57; found: C, 67.99; H, 10.06; N, 3.11.

Synthesis of [THF·Li(μ -TMP)Al(*i*Bu)₂]₂(C₅H₄)₂Fe (**5**)

In a Schlenk flask, *n*BuLi (1.25 mL, 1.6 M in hexanes, 2 mmol) was suspended in hexane (10 mL) and TMP(H) (0.34 mL, 2 mmol) was added via syringe, before *i*Bu₂AlCl (0.38 mL, 2 mmol) was introduced via syringe producing a white suspension almost immediately. This was stirred for one hour and then filtered through Celite and glass wool to remove LiCl. In a separate Schlenk flask LiTMP was prepared in hexane (10 mL) from a mixture of *n*BuLi (1.25 mL, 2 mmol) and TMP(H) (0.34 mL, 2 mmol). The *i*Bu₂AlTMP solution was added to the LiTMP solution via cannula to give a colourless solution. THF (0.16 mL, 2 mmol) and ferrocene (0.186 g, 1 mmol) were added producing an orange solution which was stirred for 2 hours at reflux and then stored at -30°C until a crop of orange crystals formed (0.50 g, not an absolute yield due to traces of **4** also being present).

¹H NMR (400.13 MHz, C₆D₁₂, 300K): δ 0.38 [8H, m, 4 x CH₂ of *i*Bu], 0.75 [4H, t, ³*J*(H,H) = 12.29 Hz, 2 x β CH₂ of TMP], 1.10 [24H, t, ³*J*(H,H) = 7.55 Hz, 8 x CH₃ of *i*Bu], 1.25 [12H, s, 4 x TMP Me], 1.29 [2H, m, 2 x γ CH of TMP], 1.32 [12H, s, 4 x TMP Me], 1.47 [4H, d, ³*J*(H,H) = 12.38 Hz, 2 x β CH₂ of TMP], 1.78 [8H, s, 4 x β CH₂ of THF], 1.84 [2H, m, 2 x γ CH of TMP], 2.15 [4H, sept, ³*J*(H,H) = 6.37 Hz, 4 x

CH of *i*Bu], 3.53 [8H, s, 4 x α CH₂ of THF], 3.97 [4H, s, C₅H₄Fe], 4.47 [4H, s, C₅H₄Fe].

¹³C NMR (100.63 MHz, C₆D₁₂, 300K): δ 18.7 [TMP γ], 25.9 [THF β CH₂], 28.1 [CH₂CHMe₂], 29.4 [CH₂CHMe₂], 29.7 [TMP Me], 30.8 [CH₂CHMe₂], 36.8 [TMP Me], 45.1 [TMP β], 53.0 [TMP α], 69.2 [THF α CH₂], 74.7 [C₅H₄Fe], 77.4 [C₅H₄Fe].

⁷Li NMR (155.46 MHz, C₆D₁₂, 300K): δ -0.69 ppm.

Calculated (%) for Al₂C₅₂Fe₁H₉₆Li₂N₂O₂: C, 69.01; H, 10.69; N, 3.10; found: C, 68.54; H, 10.60; N, 3.39.

Synthesis of [TMP(H)·Li(μ -TMP)Al(*i*Bu)₂]₂(C₅H₄)₂Fe (**6**)

In a Schlenk flask, *n*BuLi (2.50 mL, 1.6 M in hexanes, 4 mmol) was suspended in more hexane (10 mL) and TMP(H) (0.68 mL, 4 mmol) was added via syringe, before *i*Bu₂AlCl (0.76 mL, 4 mmol) was introduced via syringe producing a white suspension almost immediately. This suspension was stirred for one hour and then filtered through Celite and glass wool to remove solid LiCl. In a separate Schlenk flask LiTMP was prepared in hexane (10 mL) from a mixture of *n*BuLi (2.50 mL, 4 mmol) and TMP(H) (0.68 mL, 4 mmol). Next, ferrocene (0.186 g, 1 mmol) was added to the LiTMP solution followed immediately by the *i*Bu₂AlTMP solution via cannula. This mixture was gently heated to give an orange solution and then stored at room temperature until a crop of orange crystals of **6** formed (0.50 g, 48%).

¹H NMR (400.13 MHz, C₆D₆, 300K): δ 0.58 [8H, m, 4 x CH₂ of *i*Bu], 0.66 [4H, br m, 2 x β CH₂ of TMP], 1.04 [24H, s, 8 x TMP(H) Me], 1.20 [8H, t, ³*J*(H,H) = 6.46 Hz, 4 x β CH₂ of TMP(H)], 1.34 [24H, m, 8 x CH₃ of *i*Bu], 1.43 [24H, s, 8 x TMP Me], 1.49 [4H, m, 2 x γ CH of TMP], 1.50 [4H, br m, 2 x β CH₂ of TMP], 1.77 [4H, br m, 2 x

γ CH of TMP(H)], 2.30 [4H, m, 4 x CH of *i*Bu], 4.15 [4H, s, C₅H₄Fe], 4.29 [4H, br s, C₅H₄Fe].

¹³C NMR (100.63 MHz, C₆D₆, 300K): δ 18.2 [TMP γ], 18.6 [TMP(H) γ], 27.7 [CH₂CHMe₂], 28.3 [CH₂CHMe₂], 29.6 [TMP Me], 30.0 [CH₂CHMe₂], 30.6 [CH₂CHMe₂], 32.0 [TMP(H) Me], 37.1 [TMP Me], 38.6 [TMP(H) β], 45.5 [TMP β], 49.9 [TMP(H) α], 52.5 [TMP α], 72.6 [C₅H₄Fe], 77.5 [C₅H₄Fe].

⁷Li NMR (155.46 MHz, C₆D₁₂, 300K): δ 2.27 ppm.

Associated Content

Supporting Information

NMR spectra, X-ray collection data table and X-ray data in crystallographic file (CIF) format for compounds **1**, **2**, **4**, **5** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Dedication

In memory of Mike Lappert. The landscape of modern inorganic/organometallic chemistry is much richer due to his phenomenal seminal output.

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