

Assessing the reactivity of sodium zincate [(TMEDA)Na(TMP)Zn⁺Bu₂] towards benzoylferrocene: deprotonative metalation vs. alkylation reactions†

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Received 3rd August 2011, Accepted 9th September 2011

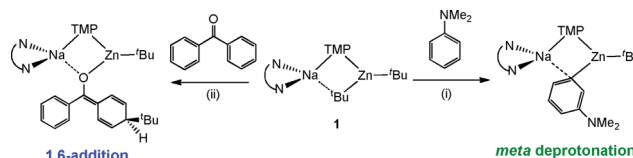
DOI: 10.1039/c1dt11465d

Exploring the reactivity of the mixed-metal reagent [(TMEDA)Na(TMP)Zn⁺Bu₂] (**1**) towards substituted metallocene benzoylferrocene **2**, this study has found that two competing reactivity pathways are available for the sodium TMP-zincate, namely (i) remote 1,6-nucleophilic addition of a *tert*-butyl group to the phenyl ring of **2**, and (ii) simultaneous *alpha*-deprotonation of the substituted cyclopentadienyl ring of the metallocene and alkylation (1,2-addition) across the C=O bond of the carbonyl group. A key organometallic intermediate [(TMEDA)Na(μ-TMP)Zn{OC(^{*t*}Bu)(Ph)(η⁵-C₅H₃)-Fe(η⁵-C₅H₅)}] (**3**), resulting from the latter reaction has been trapped and characterised by X-ray crystallography and multinuclear (¹H and ¹³C) NMR spectroscopy. Its molecular structure revealed a unique two-fold activation of the *tert*-butyl groups bonded to zinc in the bimetallic base **1**, showing for the first time that each alkyl group can exhibit markedly different reactivities (deprotonation vs. 1,2-addition) towards the same substrate molecule. Iodine interception of the organometallic intermediates of the reaction between **1** and **2** allowed the isolation and characterization (¹H, ¹³C NMR and X-ray crystallography) of the ferrocenyl derivatives [PhC(OH)(^{*t*}Bu)(η⁵-C₅H₃I)Fe(η⁵-C₅H₅)] (**4**) and [4-^{*t*}Bu-C₆H₄C(=O)(η⁵-C₅H₄)Fe(η⁵-C₅H₅)] (**5**) in a 29% and 24% isolated yield respectively. The low yield observed for the formation of **5** (resulting from the 1,6-addition reaction followed by spontaneous aerobic oxidation during aqueous workup) could be increased to 41% when the reaction mixture was hydrolysed in the presence of the radical oxidant TEMPO.

Introduction

Alkali-metal zincates have recently emerged as an important family of organometallic reagents which can efficiently be applied to a broad range of fundamental organic transformations including metal-halogen exchange,¹ deprotonative metalation,² nucleophilic addition³ or Negishi cross-coupling reactions.⁴ Amongst this family of mixed-metal reagents, sodium TMP-dialkyl zincate [(TMEDA)Na(TMP)Zn⁺Bu₂] (**1**)⁵ (TMP = 2,2,6,6-tetramethylpiperidide, TMEDA = *N,N,N',N'*-tetramethylethylenediamine) stands out as an especially effective and versatile base for executing direct zincation (C–H to C–Zn exchange) on several different aromatic molecules (such as benzene,^{5,6} toluene,⁷ benzonitriles,⁸ benzamides,^{2,9} naphthalene,¹⁰ aromatic ethers,¹¹ carbamates,¹² *etc.*) which are usually inert towards conventional organozinc reagents. Outperforming existing single-metal reagents, this bimetallic (alkali metal-zinc) approach not only allows the use of milder reaction conditions (generally room temperature) but also can enable unique synergic regioselectivities which cannot be replicated by classical metallating champi-

ons such as organolithiums or lithium amides.¹³ An example of this special regioselectivity is illustrated in Scheme 1(i) depicting the *meta*-deprotonation of *N,N*-dimethylaniline by **1**,¹⁴ contrasting with conventional *ortho*-regioselectivity observed when ^{*n*}BuLi is employed.¹⁵ As they require the presence of an alkali-metal to proceed, although the departing hydrogen of the aromatic molecule is replaced by a zinc atom, these deprotonations have been designated as alkali-metal-mediated-zincations (AMMZn).¹⁶



Scheme 1

Structural elucidation of key organometallic intermediates prior to any electrophilic interception have demonstrated that these deprotonations are genuine examples of zincations, where the heteroleptic zincate **1** has displayed an overall alkyl basicity (Scheme 1, i). Shedding new light on the mechanisms involved, recent reactivity (in solution)¹⁷ and computational (in the gas

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† Electronic supplementary information (ESI) available: Full experimental details and NMR spectra. CCDC reference numbers 838243–838246. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c1dt11465d

phase)¹⁸ studies have established that these TMP-dialkyl zincates operate *via* a stepwise mechanism, where the mixed-metal reagent acts first as an amide base (favoured by the greater kinetic reactivity of the Zn–N bonds in comparison with Zn–C bonds), metallating the aromatic substrate to generate a bisalkyl(aryl) zincate [NaZn(arenide)Bu₂] intermediate, with the concomitant formation of TMP(H). In a second step, the acidic amine reacts with this kinetic intermediate, to afford the final organometallic product of the reaction containing the TMP anion releasing isobutane.

Adding to this intriguing metallating ability, Mulvey has shown that zincate **1** can also promote the remote addition of a *t*Bu group to benzophenone in a highly unusual 1,6-fashion (Scheme 1, *ii*).¹⁹ This alternative nucleophilic reactivity has recently been extended to other ketones such as fluorenone and 2-benzoylpyridine, demonstrating the versatility of **1** to prepare alkyl-substituted arylketones.²⁰

Herein, we extend for the first time our studies on sodium zincate **1** to their application in the area of metallocene functionalisation, using metallocenyl-ketone benzoylferrocene (**2**) as a case study. In general, the synthesis of functionalised ferrocene derivatives attracts widespread interest from the synthetic community due to their important applications in catalysis,²¹ materials science²² and bioorganometallic chemistry.²³ An invaluable synthetic tool which facilitates the incorporation of ferrocenyl units into more complex molecular scaffolds is deprotonative metalation, usually accomplished by polar organolithium reagents.²⁴ Recent advances in mixed-metal chemistry have revealed the selective deprotonation of ferrocene can also be achieved using alkali-metal magnesiates,²⁵ zincates,²⁶ cadmates,^{26b,27} manganates,²⁸ and cuprates.²⁹ Furthermore, in certain cases, these bimetallic reagents can promote unique polymetalations (as for example the spectacular four-fold regioselective magnesiation of ferrocene performed by the sodium tris(amido)magnesiate [NaMg(NⁱPr)₃])^{25b} as well as the efficient functionalisation of substituted ferrocenes bearing sensitive organic functional groups (such as nitriles, esters or carboxylic acids)^{25c,26b} which are not compatible with traditional organolithium reagents. Building on these precedents, the molecule chosen for our study, benzoylferrocene (**2**), combines relatively acidic hydrogen atoms of the Cp rings (therefore susceptible towards C–H deprotonation) with an electrophilic benzoyl fragment (which can undergo 1,2- or 1,6-addition reactions) (Fig. 1). By trapping and structurally defining a new organometallic intermediate from the reaction of **1** and **2** coupled with ¹H NMR monitoring of this reaction and carrying out subsequent electrophilic interceptions, we provide new insights into the reactivity of TMP-zincate **1**, assessing its metallating power against its ability to promote remote nucleophilic additions.

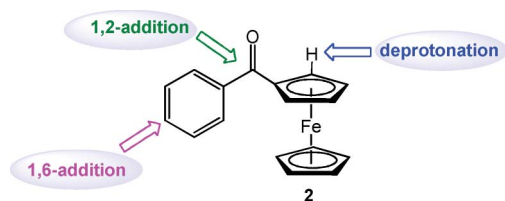
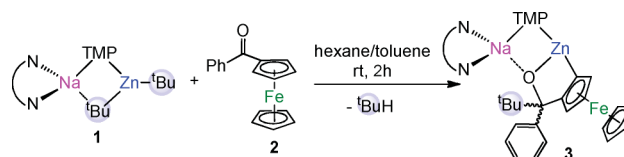


Fig. 1 Potential reactivity sites of benzoylferrocene (**2**).

Results and discussion

In the experimental work a hexane solution of sodium zincate [(TMEDA)Na(TMP)Zn^{*t*}Bu₂] (**1**) was mixed with one molar equivalent of commercial benzoylferrocene (**2**) at room temperature to afford a deep red suspension. Removal of hexane *in vacuo* and addition of toluene gave a red solution which on cooling deposited a batch of deep orange crystals of [(TMEDA)Na(μ-TMP)Zn{OC(*t*Bu)(Ph)(η⁵-C₅H₅)Fe(η⁵-C₅H₅)}] (**3**) as determined by X-ray crystallography and NMR spectroscopy in a modest isolated yield of 12% (Scheme 2).



Scheme 2

The composition and molecular structure of **3** (Fig. 2)³⁰ established by X-ray crystallographic studies revealed an unprecedented double activation of the *tert*-butyl groups bonded to Zn in the bimetallic base **1** had taken place. Thus the benzoylferrocene starting material has been simultaneously deprotonated (zincated) at the *alpha* carbon position on the substituted Cp ring (concomitantly releasing isobutane) and undergone a 1,2-addition of the second *t*Bu group across the C=O bond of the carbonyl group (Scheme 2 and Fig. 2). To the best of our knowledge, **3** constitutes not only the first structurally defined organometallic intermediate resulting from the reaction of **1** with

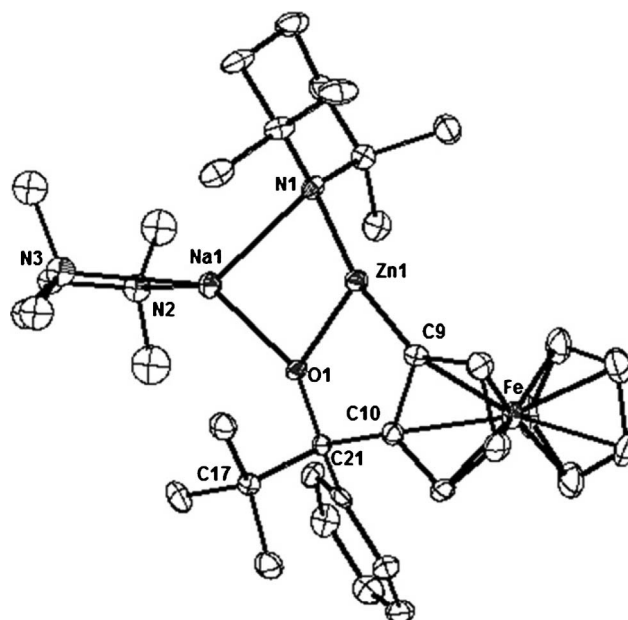


Fig. 2 Molecular structure of **3** with selective atom labelling and 40% probability ellipsoids. Hydrogen atoms and minor disordered component of TMEDA have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 1.926(2), Zn(1)–C(9) 1.930(3), Zn(1)–O(1) 1.9827(17), Na(1)–O(1) 2.229(2), Na(1)–N(1) 2.527(2), O(1)–C(21) 1.415(3), N(1)–Zn(1)–C(9) 166.66(11), N(1)–Zn(1)–O(1) 104.30(8), C(9)–Zn(1)–O(1) 89.03(10), O(1)–Na(1)–N(1) 80.66(7), Zn(1)–O(1)–Na(1) 90.26(7).

a metallocene but also the first example where two alkyl groups of a dialkylamidozincate exhibit strikingly different reactivities (deprotonation vs. alkylation) towards a substrate.³¹ This double activation is even more remarkable when compared with the lack of reactivity of the homoleptic neutral zinc bis-alkyl ^tBu₂Zn when treated with **2**, where neither addition nor deprotonation reactions of the metallocene occur to any measurable extent.

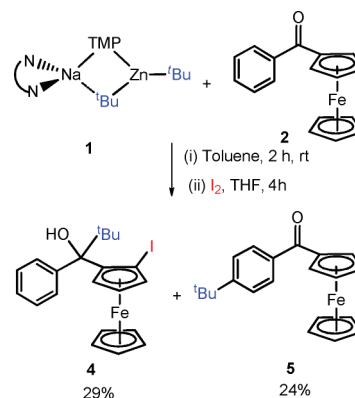
Retaining the “[TMEDA)-Na-(μ-TMP)-Zn]²⁺” backbone of reactant **1**, the contacted ion pair structure of **3** (Fig. 2) is completed by a dianionic ferrocenyl fragment {OC(^tBu)(Ph)(η⁵-C₅H₅)Fe(η⁵-C₅H₅)}²⁻ which coordinates asymmetrically to the bimetallic system, bridging Na and Zn through the oxygen (O1) of the newly generated tertiary alkoxide and bonding exclusively to Zn through ferrocenyl C9 (the carbon that has experienced the deprotonation, which defines the reaction as a direct zincation). This unique coordination mode led to the formation of two fused metallocycles, a four-membered {NaNZnO} ring and a five-membered {ZnOCCC} ring, with the latter subsequently fused (through C9 and C10, Fig. 2) to the cyclopentadienyl ring of the metallocene. The five-membered {ZnOCCC} ring lies essentially co-planar with the C₅H₅ ring (maximum deviation from the mean plane is 0.55 Å for C10) whereas the {NaNZnO} ring is slightly puckered (sum of internal angles, 358.38°, torsion N1NaO1Zn1, 8.49(7)°). As a consequence of this rigid ring-fused framework, Zn and O atoms adopt highly distorted trigonal planar geometries (with angles ranging from 166.66(11) to 89.03(10)° and from 154.80(16) to 90.26(7)° for Zn1 and O1 respectively). Despite this distortion the Zn–C_{ferrocenyl} distance in **3** (1.930(3) Å) is similar to those found in other related zincated ferrocenyl compounds such as [(TMEDA)Zn{(η⁵-C₅H₄)Fe(η⁵-C₅H₅)}₂] (1.9814(11) Å)^{26a} and [{C,N-[Fe(η⁵-C₅H₃-CH₂NMe₂)(η⁵-C₅H₅)]₂Zn] (1.948(2) and 1.945(2) Å).³² Similarly the Na–O (2.229(2) Å) and Zn–O (1.9827(17) Å) distances are within the same range as those reported in the structurally elucidated compounds resulting from 1,6-addition reactions of **1** to aromatic ketones.^{19,20} Consistent with the formation of a tertiary alkoxide resulting from a 1,2 addition process, C21 (which originally in **2** had an sp² hybridisation) exhibits a distorted sp³ tetrahedral geometry (average bond angle 108.9°), bonded to a *tert*-butyl group, a phenyl group and the cyclopentadienyl fragment as well as forming a single C–O bond with O1 (C21–O1, 1.415(3) Å).³³

Being soluble in deuterated benzene, **3** was also characterized in solution using ¹H and ¹³C NMR spectroscopy (see Experimental section and ESI† for full details). The most diagnostic resonances in the ¹H NMR spectrum were three broad singlets at 4.33, 4.63 and 4.70 ppm in a 1:1:1 ratio which can be assigned to the three distinct hydrogens on the metallated cyclopentadienyl ring,³⁴ and that differ significantly from the two multiplets present on the mono-functionalised Cp ring of **2** (at 4.14 and 4.84 ppm).³⁵ In addition, a sharp singlet at 1.07 ppm was observed for the *tert*-butyl group of **3** which has added nucleophilically to the electrophilic carbonyl group of **2**. In the solid state structure of **3**, the bulky amido group TMP acts as a bridge between the two metals; this coordination mode must be retained in deuterated benzene solution as evidenced by the inequivalence of the α-Me groups of the TMP fragment in the ¹H NMR spectrum (at 1.44 and 1.52 ppm). A comparison of the ¹³C NMR spectra of compounds **2** and **3** revealed large changes in the chemical shifts observed for the distinct carbon atoms that have experienced the metalation or

the addition reactions (111.9 ppm for Zn–C_α and 81.3 ppm for C–O in **3** vs. 72.3 ppm for C_α and 197.4 ppm for C=O in **2**).³⁵

As mentioned above, **3** can only be isolated as a crystalline solid in modest yields. Therefore in order to assess the selectivity and the overall conversion of the reaction we then analysed by ¹H and ¹³C NMR spectroscopy the constitution of the remaining filtrate solution. To our surprise, we found that although no starting material **2** was present in solution, the ¹H NMR spectrum only showed trace amounts of **3** along with a series of broad resonances (ranging from 7.5 to 3.0 ppm) which were found to belong to the same single species as evidenced by a 2D-[¹H–¹H] COSY NMR experiment. Furthermore, it appears that this unknown compound is the major product of the reaction of **1** with **2**. Despite several attempts this second intermediate could not be isolated as a crystalline solid or any solid.

In order to shed some light on the overall outcome of the reaction and the constitution of this species, we next probed the electrophilic interception of the organometallic intermediates of the reaction with iodine, an electrophile which has been previously successfully used to trap magnesiated and zincated ferrocenyl species.^{25c,26b} Thus benzoylferrocene (**2**) was treated with one molar equivalent of Na/Zn base **1** in toluene at room temperature for 2 h and subsequently reacted with a THF-solution of iodine to afford a mixture of the ferrocenyl derivatives [PhC(OH)(^tBu)(η⁵-C₅H₅)Fe(η⁵-C₅H₅)] (**4**) and [4-^tBu-C₆H₄C(=O)(η⁵-C₅H₄)Fe(η⁵-C₅H₅)] (**5**) in a 29% and 24% isolated yield respectively (Scheme 3).



Scheme 3

The composition and structures of **4** and **5** were confirmed by X-ray crystallographic studies (Fig. 3 and 4 respectively) and ¹H and ¹³C NMR spectroscopy (see Experimental section for

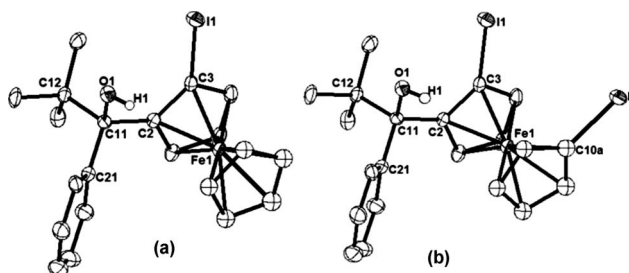


Fig. 3 Molecular structures of **4** (a) and **6** (b) (present as a mixture in the crystalline lattice in a relative ratio of 95:5) with selective atom labelling and 40% probability ellipsoids. Hydrogen atoms (apart from in the OH group) have been omitted for clarity.

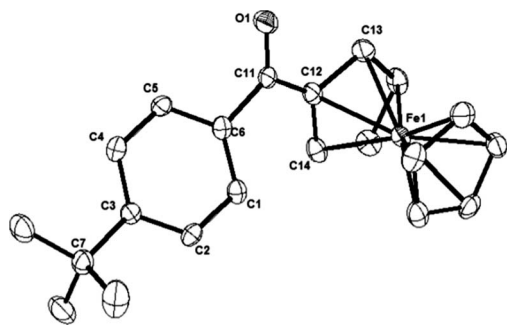
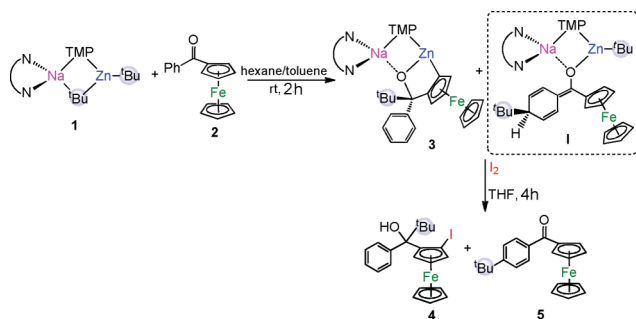


Fig. 4 Molecular structure of **5** with selective atom labelling and 40% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

full details). Disubstituted ferrocene **4** is the expected iodinated species resulting from the electrophilic quenching of **3** with I_2 , where the position previously filled by a Zn center in the substituted pentadienyl ring in **3** is now occupied by an iodine atom and the alkoxide group has been hydrolysed to a tertiary alcohol (Fig. 3a). X-Ray crystallographic analysis revealed that a mixture of compound **4** and the di-iodo analog $[PhC(OH)(^tBu)(\eta^5-C_5H_3I)Fe(\eta^5-C_5H_3I)]$ (**6**) (Fig. 3b) in a respective ratio of 95:5% was found in the crystal lattice. Initially the formation of **6** could be attributed to a putative double zincation of **2**, however considering that the reaction when performed using D_2O as an electrophile (see below) does not show the formation of a related double deuterated species and that the yield of **6** is extremely small, it seems more plausible that **6** is the result of a side reaction of iodine (used in excess) with compound **3**. In this regard, selectivity problems using I_2 as a quenching agent for organometallic intermediates which can lead to polysubstituted products have already been flagged up in the literature.³⁶

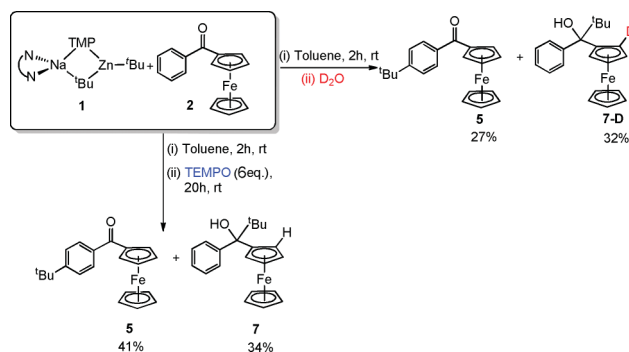
Turning to compound **5** (Fig. 4) its formation must proceed *via* a different organometallic intermediate to **3**. Featuring a *tert*-butyl substituent at the C3(*para*) position of the phenyl ring, **5** appears to be the oxidised product of an unusual 1,6-addition of a *t*-Bu group from **1** to substrate **2** (Scheme 4). This unique addition pattern has been previously reported for the reaction of **1** with other aromatic ketones,¹⁹ for which the relevant enolate intermediates have been structurally characterized (Scheme 1, *ii*). Contrasting with **2**, when these substrates are examined no products of aromatic metalation or 1,2-addition are observed. This difference in reactivity can probably be explained in terms of the enhanced acidity of the α -H's on the (electron withdrawing group)-substituted cyclopentadienyl ring, which must switch on a competing reaction pathway promoting the *alpha*-zincation of **2**



Scheme 4

leading to **4** after iodine interception. The close proximity between the electrophilic $C=O$ group and the remaining *t*-Bu group on the zincate must subsequently favour the 1,2-addition process to form **3**. Based on the previously structurally characterized 1,6-addition products,^{19,20} **1** (Scheme 4) can be proposed as the second organometallic intermediate of the reaction which, when treated with I_2 followed by an aqueous workup, is oxidised to **5**.

The relatively modest yields obtained for **4** and **5** were somewhat surprising considering that 1H NMR analysis of the reaction solution prior to the I_2 quenching step showed no unreacted **2** present in solution. Similar results were observed when the crude reaction was treated with D_2O (Scheme 5) which yielded **5** (1,6-addition product) and $[PhC(OH)(^tBu)(\eta^5-C_5H_3D)Fe(\eta^5-C_5H_3)]$ (**7D**) (zincation, 1,2-addition product) in 27% and 32%, respectively, along with the recovery of 41% of starting material **2**. Previous studies on the ring alkylation of benzophenone with *t*-BuLi have revealed that aqueous workups decompose the 1,6-addition intermediate to regenerate benzophenone whilst if a strong oxidising agent such as $SOCl_2$ is used, it is possible to minimise this degradation route and significantly increase the yield of *tert*-butylbenzophenone.³⁷ A similar process could be taking place in the 1,6-alkylation of **2**. In fact, supporting this hypothesis we found that when the reaction mixture was quenched using radical oxidant TEMPO $[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]$ ³⁸ followed by an aqueous work-up we could isolate **5** in an increased 41% yield, along with the 1,2-adduct $[C_6H_5C(OH)^tBu(\eta^5-C_5H_4)Fe(\eta^5-C_5H_3)]$ (**7**) (34%) yield, and with the recovery of only 7% of unreacted **2** (Scheme 5).



Scheme 5

Conclusions

By combining the trapping of a key organometallic intermediate with subsequent electrophilic interceptions we have provided new insights into the reactivity of sodium zincate **1** towards substituted metallocene benzoylferrocene (**2**). Our study shows that at room temperature two different reactivity pathways are available for the bimetallic reagent: (i) remote 1,6-nucleophilic addition of a *tert*-butyl group to the phenyl ring of **2** and (ii) simultaneous *alpha*-deprotonation of the substituted cyclopentadienyl ring of the metallocene and 1,2-addition of a *tert*-butyl anion to the electrophilic carbonyl group of the ketone. The latter, involving two-fold activation of the *tert*-butyl groups of bimetallic base **1** where the two alkyl groups react strikingly differently (deprotonation *vs.* alkylation) towards a substrate, is unprecedented in AMMZN chemistry and it is in sharp contrast to the lack of reaction

observed when **2** is treated with homometallic Zn'Bu₂. NMR analysis of the reaction mixture prior to electrophilic interception suggests that the 1,6-addition product is the major product of the reaction. Electrophilic interception of these species using I₂ and D₂O as quenching agents revealed that although the yield of the deprotonated/1,2-addition product remains constant (29–34%), the amounts of co-product resulting from the competing 1,6-addition reaction [which can only be isolated in its oxidised form [^tBu-C₆H₄CO(η⁵-C₅H₄)Fe(η⁵-C₅H₅)] (**5**)] seem to vary considerably (from 24% to 41%) depending on the reaction conditions employed. These variations can be due to a competing degradation route taking place in the aqueous workup (previously reported for the 1,6-addition of ^tBuLi to benzophenone) which regenerates starting material **2**. In our study we found that this process can be minimised when the reaction is performed in the presence of the radical oxidant TEMPO.

Overall we believe these findings highlight some of the complexity of the organometallic species and the mechanisms involved in the reactions of activated ferrocenes with alkali-metal zincates as well as unveiling new reactivity patterns for these molecules which are not available to any significant extent using more conventional monometallic systems.

Experimental section

General conditions

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Toluene and hexane, purchased from Sigma Aldrich, were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ¹H, and 100.62 MHz for ¹³C{¹H}. Sodium zincate **1** was prepared following the previously published procedure.⁵

General crystallography

All data was collected at 123 K on Oxford-Diffraction CCD diffractometers using Mo-Kα radiation, λ = 0.71073 Å. All refinements were to convergence on F² and used all unique reflections and the program SHELXL-97.^{39†} Selected crystallographic

parameters are given in the ESI† and full data has been deposited, see CCDC reference numbers 838243–838246.

[(TMEDA)Na(μ-TMP)Zn{OC(^tBu)(Ph)(η⁵-C₅H₃)Fe(η⁵-C₅H₅)}](**3**)

To a hexane solution of **1** (2 mmol scale, prepared as described above) was added one molar equivalent of benzoylferrocene (0.580 g, 2 mmol). The resulting deep red suspension was stirred for 2 h at room temperature, after which time the solvent was removed *in vacuo*, and toluene (5 mL) added to give a dark red solution. After 48 h in the freezer (−30 °C) a batch of orange, cubic crystals of **3** were obtained (0.172 g, 12%). ¹H NMR (400.13 MHz, 298 K, [D₆]-benzene) δ 8.19 (2H, doublet, CH_{ortho}), 7.38 (2H, triplet, CH_{meta}), 7.26 (1H, triplet, CH_{para}), 4.71 (1H, broad singlet, C₅H₃), 4.65 (1H, broad singlet, C₅H₃), 4.34 (1H, broad singlet, C₅H₃), 3.85 (5H, singlet, C₅H₅), 1.94 (12H, singlet, CH₃, TMEDA), 1.84 (2H, multiplet, γ-CH₂, TMP), 1.78 (4H, singlet, CH₂, TMEDA), 1.53 (6H, singlet, α-CH₃, TMP), 1.44 (6H, singlet, α-CH₃, TMP), 1.40 (4H, multiplet, β-CH₂, TMP), 1.07 (9H, singlet, C(CH₃)₃, ^tBu). ¹³C{¹H} NMR (100.62 MHz, 298 K, [D₆]-benzene) δ 154.5 (C_{ipso}), 128.7 (C_{ortho}), 126.0 (C_{meta}), 125.9 (C_{para}), 111.9 (Zn-C_a), 81.3 (C-O), 75.3 (OC-C₅H₃), 73.0 (C₅H₃), 70.9 (C₅H₃), 70.1 (C₅H₃), 68.0 (C₅H₅), 57.5 (CH₂, TMEDA), 53.1 (α-TMP), 46.6 (CH₃, TMEDA), 41.2 (β-CH₂, TMP), 40.6 (C(CH₃)₃, ^tBu), 36.8 and 36.1 (α-CH₃, TMP), 28.2 (C(CH₃)₃, ^tBu), 19.8 (γ-CH₂, TMP).

[PhC(OH)(^tBu)(η⁵-C₅H₃I)Fe(η⁵-C₅H₅)] (**4**) and [4-^tBu-C₆H₄C(O)(η⁵-C₅H₄)Fe(η⁵-C₅H₅)] (**5**)

Benzoylferrocene (0.290 g, 1 mmol) was dissolved in toluene (7 mL) and added *via* cannula to a second Schlenk tube containing isolated crystals of **1** (0.460 g, 1 mmol, prepared as described above). The resulting deep red solution was stirred for 2 h at room temperature, after which time I₂ solution (1 M in THF, 3 mL, 3 mmol) was added, and the reaction stirred for a further 4 h at room temperature. The reaction was then quenched with saturated Na₂S₂O₃ solution (5 mL) and saturated NH₄Cl solution (5 mL) and then extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried over MgSO₄ and concentrated *in vacuo*. The crude residue was purified by column chromatography (eluent: hexane/diethyl ether, 1 : 0 to 9 : 1) affording **4** (0.1380 g, 29%) as an orange solid and **5** (0.0845 g, 24%) as a red solid. NMR data for **4**: ¹H NMR (400.13 MHz, 298 K, CDCl₃) δ 7.90 (2H, doublet, CH_{ortho}), 7.42 (2H, triplet, CH_{meta}), 7.33 (1H, triplet, CH_{para}), 4.45 (2H, multiplet, C₅H₃), 4.30 (1H, triplet, C₅H₃), 3.74 (5H, singlet, C₅H₅), 2.63 (1H, singlet, OH), 0.97 (9H, singlet, C(CH₃)₃, ^tBu). ¹³C{¹H} NMR (100.62 MHz, 298 K, CDCl₃) δ 146.4 (C_{ipso}), 127.2 (C_{ortho}), 126.6 (C_{meta}), 89.9 (C-O), 81.1 (OC-C₅H₃), 77.4 (C₅H₃), 71.7 (C₅H₅), 70.8 (C₅H₃), 69.2 (C₅H₃), 41.2 (C-I), 40.0 (C(CH₃)₃, ^tBu), 27.0 (C(CH₃)₃, ^tBu). NMR data for **5**: ¹H NMR (400.13 MHz, 298 K, CDCl₃) δ 7.88 (2H, doublet, CH_{ortho}), 7.49 (2H, doublet, CH_{meta}), 4.93 (2H, triplet, C₅H₄), 4.58 (2H, triplet, C₅H₄), 4.23 (5H, singlet, C₅H₅), 1.38 (9H, singlet, C(CH₃)₃, ^tBu). ¹³C{¹H} NMR (100.62 MHz, 298 K, CDCl₃) δ 198.7 (C-O), 155.1 (C_{ipso}), 137.0 (C_{para}), 128.2 (C_{ortho}), 125.2 (C_{meta}), 78.6 (C₅H₅), 72.3 (C₅H₄), 71.6 (C₅H₄), 70.2 (OC-C₅H₃), 35.0 (C(CH₃)₃, ^tBu), 31.2 (C(CH₃)₃, ^tBu).

† Crystal data for **3**: C₃₆H₄₆FeN₃NaOZn, M_r = 691.05, monoclinic, space group P2₁/c, a = 16.5928(8), b = 11.8192(4), c = 19.0005(8) Å, β = 111.772(5)°, V = 3460.5(3) Å³, Z = 4, ρ_c = 1.326 g cm^{−3}, μ = 1.157 mm^{−1}; Final refinement gave R = 0.0464 (F, 4235 obs. data only) and R_w = 0.0771 (F², 8165 unique data), GOF = 0.788, 395 refined parameters. Residual electron density max. and min. 0.818 and −0.479 e Å^{−3}. Crystal data for cocrystal of **4** and **6**: C₂₁H_{22.95}FeI_{0.5}O, M_r = 480.44, monoclinic, space group P2₁/c, a = 9.6150(3), b = 11.7549(4), c = 17.2226(5) Å, β = 105.283(3)°, V = 1877.72(10) Å³, Z = 4, ρ_c = 1.699 g cm^{−3}, μ = 2.534 mm^{−1}; Final refinement gave R = 0.0505 (F, 4244 obs. data only) and R_w = 0.1161 (F², 5212 unique data), GOF = 1.129, 206 refined parameters. Residual electron density max. and min. 1.336 and −0.621 e Å^{−3}. The ratio of **4** to **6** was measured by refining occupancies of separate C₅H₃ and C₅H₄I fragments and setting their total occupancy to 1. This gave 5.03(8)% for the di-iodo species. Crystal data for **5**: C₂₁H₂₂FeO, M_r = 346.24, monoclinic, space group P2₁/n, a = 10.9164(6), b = 25.1685(13), c = 18.3340(11) Å, β = 91.060(5)°, V = 5036.4(5) Å³, Z = 12, ρ_c = 1.370 g cm^{−3}, μ = 0.900 mm^{−1}; Final refinement gave R = 0.0580 (F, 6409 obs. data only) and R_w = 0.1252 (F², 10967 unique data), GOF = 0.990, 631 refined parameters. Residual electron density max. and min. 0.502 and −0.618 e Å^{−3}.

Acknowledgements

We thank the Royal Society (University Research Fellowship to E. H.), and the EPSRC for their generous sponsorship of this research.

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- Although there are no examples of double activation of the *tert*-butyl groups of **1**, related lithium-zincate [(THF)Li(μ-TMP)Zn'Bu₂] can exhibit polybasicity when reacted with two or three equivalents of substituted aromatic molecules such as anisole or *N,N*-diisopropyl benzamide, see ref. 9 and: (a) W. Clegg, S. H. Dale, A. M. Drummond, E. Hevia, G. W. Honeyman and R. E. Mulvey, *J. Am. Chem. Soc.*, 2006, **128**, 7434; (b) Y. Kondo, J. V. Morey, J. C. Morgan, H. Naka, D. Nobuto, P. R. Raithby, M. Uchiyama and A. E. H. Wheatley, *J. Am. Chem. Soc.*, 2007, **129**, 12734.
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