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PAPER

After-effects of lithium-mediated alumination of 3-iodoanisole: isolation of molecular salt elimination and trapped-benzyne products†

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Gaining a deeper understanding of the *modus operandi* of heterometallic lithium aluminate bases towards deprotonative metallation of substituted aromatic substrates, we have studied the reactions and their aftermath between our recently developed bis-amido base '^{i}Bu$_2$Al(μ-TMP)$_2$Li' **3** and 3-halogenated anisoles. *Ortho*-metallation of 3-iodoanisole with **3** results in a delicately poised heterometallic intermediate whose breakdown into homometallic species and benzyne cannot be suppressed, even at low temperature or in a non-polar solvent (hexane). Homometallic components [LiI·TMP(H)]$_4$ (**5**) and ^{i}Bu$_2$Al(TMP)·THF (**6**) have been isolated while the reactive benzyne intermediate has been trapped *via* Diels–Alder cyclization with 1,3-diphenylisobenzofuran yielding 1-methoxy-9-10-diphenyl-9-10-epoxyanthracene (**7**). In polar THF solution, nucleophilic addition of LiTMP across the benzyne functionality followed by electrophilic quenching with iodine yields the trisubstituted aromatic species 1-(2-iodo-3-methoxyphenyl)-2,2,6,6-tetramethylpiperidide (**8**). Compounds **5–8** have been characterized by single-crystal X-ray diffraction in the solid state and multinuclear NMR spectroscopy in solution. By considering these collated results, a plausible reaction mechanism has been proposed for the breakdown of the aforementioned intermediate bimetallic framework. Interestingly, the metallation reaction can be controlled by changing to 3-chloroanisole with an excess of base **3**, as evidenced by electrophilically trapping the deprotonated aromatic with iodine to give 2-iodo-3-chloroanisole (**9**).

Introduction

Alkali-Metal Mediated Metallation (AMMM) is a recent advance in deprotonative metallation (C–H to C–metal exchange) which shows considerable promise for the synthetic chemistry community.[1] Involving the juxtaposition of a typically powerful, sometimes indiscriminate metallating reagent such as an alkali-metal alkyl or amido compound (R–M^I or R$_2$N–M^I) with a weaker yet more discriminate metallating reagent (R$_x$M^x, x > 1) into a single ligand-shared molecular compound [2] (which seemingly displays the reactivity of the alkali-metal coupled with the selectivity/functional group tolerance of the subordinate metal—see Fig. 1 for a general example where $x = 2$), this method is attractive due to its utility in relatively cheap, non-polar solvents without the need for non-ambient temperature regimes.

Economic advantages aside, AMMM is also attractive from a fundamental chemistry standpoint since not only can it outperform many homometallic reagents, it can also lead to deprotonation of poorly acidic substrates (with high pK_a values) typically considered inert towards metal–hydrogen exchange,[3] or to unusual polydeprotonations of multi-C–H containing substrates.[4] While this field has been dominated largely by Mg^{II} and Zn^{II} as the reactivity enhanced ex-subordinate metal, the concept has been extended recently to include other metals such as Fe^{II},[5] Mn^{II} [6] and Cd^{II},[7] amongst others.[8] One of the key recent advances has involved the extension to a metal which is in the +3 oxidation state, namely Al^{III}.[9] This has resulted in a myriad of novel chemistry being developed, including α-C–*H*-deprotonation of typically unreactive (towards metallation) polyamine Lewis donors such as TMEDA [10] or PMDETA,[10b] α-C–*H*-deprotonation of the cyclic ethers THF and THP,[11] and even the astonishing generation and trapping of a TMP^{2-} dianion from the *C*,*N*-bisdeprotonation of TMP(H).[12] A particularly attractive facet of Alkali-Metal Mediated Alumination (AMM*Al*) is the high halogen tolerance which has been documented by the bases (TMP)$_3$Al·3LiCl (**1**, Knochel),[13] ^{i}Bu$_3$Al(TMP)Li (**2**, Uchiyama—the first reported base of this type),[14] and ^{i}Bu$_2$Al(TMP)$_2$Li (**3**,

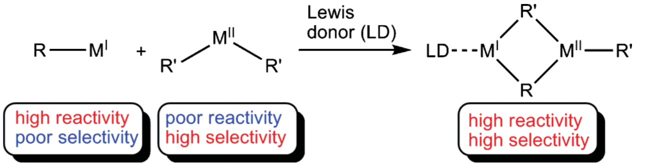

Fig. 1 Generic synthesis of a typical mixed-metal base.

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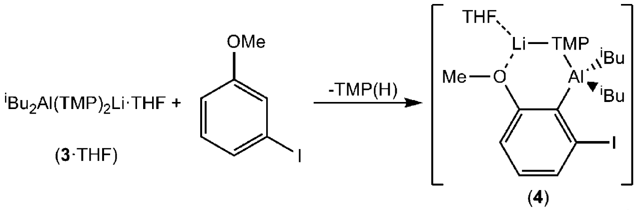
our own group);[15] heterometallic alkali-metal aluminate bases will carry out directed *ortho* metallation (metal–hydrogen exchange) reactions of halo-substituted aromatic molecules in preference to metal–halogen exchange. While alkyl-amido bases **2** and **3** are clearly constitutionally very similar, they can display markedly different reactivity; **2** is stable in THF, a solvent in which it is routinely utilized, while **3** deprotonates a stoichiometric amount of THF in bulk hexane solution. With this in mind and inspired by Uchiyama's recent report of thermally controlled *ortho*-deprotonation of 3-bromo-*N*,*N*-diisopropylbenzamide with mono-TMP base **2**,[16] we investigated whether bis-TMP base **3** can likewise *ortho*-deprotonate 3-halogenated *ortho*-directing substituted aromatics. Focusing on 3-haloanisoles, as reported herein, we learn much about the fate of the different metals and different ligands following their *ortho*-alumination.

Results and discussion

The attempted deprotonation of 3-iodoanisole by THF solvated lithium aluminate base **3** to give complex **4** was carried out in bulk hexane solution as depicted by eqn (1).[17]



(1)

Even at a temperature as low as −78 °C, the mixture instantly precipitated a white solid. This solid was removed by vacuum filtration and the resulting solution was kept overnight at −35 °C, yielding a decent crop of colourless crystals. A single crystal structural determination revealed that this crystalline product was in fact the C_2 symmetric amine solvated lithium iodide cubane $[LiI\cdot TMP(H)]_4$, **5** (Fig. 2, see Table 1 for selected bond parameters).

Since Snaith first reported a HMPA solvated LiCl cubane tetramer in 1984,[18] examples of Lewis donor-solvated (LD) alkali-metal halide cubanes $[(MX\cdot LD)_4]$ have sporadically graced the literature. Surprisingly, only lithium examples with alkali-metal bound Lewis donors are known, including those of Et_2O,[19] Et_3N,[20] $HN=PR_3$ ($R={}^tBu$, Ph)[21] and $O=PH({}^tBu)_2$.[22] While heavier alkali-metal halide cubanes such as those of KF or CsF are known, these are stabilized *via* halide–Lewis acid interactions involving trisalkyl gallium or indium species.[23] Like its predecessors mentioned above, **5** consists of interpenetrating Li_4 and I_4 tetrahedra, with lone pair donation from the TMP(H) nitrogen atoms to the Lewis acidic lithium cations giving Li a distorted tetrahedral environment overall. From the ring-stacking principle developed by Snaith, which is widely applicable throughout lithium structural chemistry, **5** could be alternatively described as a face-to-face stack of two dimeric $(LiI)_2$ rings.[24] Secondary amine TMP(H) is not a common Lewis donor towards electron deficient metals, with most crystallographically authenticated examples involving either late transition metals[25] or group 13 metals.[26] However, TMP(H) solvation of lithium is precedented, with both base **2** [27] and a dilithium zincate[28] having been stabilized *via* a Li···N(TMPH) interaction. The two distinct TMP(H) ligands in **5**, which both reside in the more typical chair conformation, lie tilted towards one of the adjacent iodide anions as displayed by their one smaller (mean 101.7°) and two larger N–Li–I bond angles (mean 125.6°). The NH bond (the H atom was located and independently refined in the crystallographic study) lies almost parallel to the Li–I bond representing the smaller angle (H–N–Li–I torsion angle = 5.8/2.2° for Li1 and Li2 respectively) with an N(H)···I distance of 3.42(3) and 3.34(2) Å for H1–I1 and H2–I2 respectively. The cubane itself is highly distorted [I–Li–I, 97.1(3)–102.3(2)°; Li–I–Li, 77.1(2)–81.8(2)°] with Li–I bond lengths [range 2.799(9)–2.907(7) Å; mean 2.847 Å] in accord with those in previously reported LiI cubanes, as are the dative Li···N distances when compared to those in the tertiary amine solvated $[LiI\cdot NEt_3]_4$.

To the best of our knowledge, somewhat surprisingly complex **5** represents the first example of a secondary amine stabilized alkali-metal halide cubane. Lack of solubility in common non-donating NMR solvents was a problem, precluding us from obtaining such spectra. Polar THF-d_8 was used but this displaced TMP(H) as the donor, giving a spectrum of free secondary amine. Infrared characterization to confirm the presence of the secondary amine functionality was also attempted; however this proved uninformative due to either the hygroscopic nature of the product resulting in peaks masking the region of interest or the inherently weak absorptions of the functionality in question.

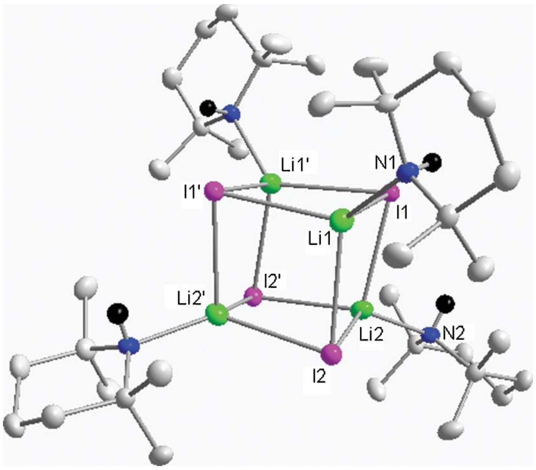


Fig. 2 Molecular structure of tetrameric **5**. Thermal ellipsoids are drawn at the 50% probability level and all carbon bound H atoms have been removed for clarity. Primed atom labels represent symmetry generated atoms *via* symmetry operation −*x*, *y*, 0.5 − *z*.

Table 1 Selected bond lengths (Å) and angles (°) of complex **5**

Li–I				Li–N	
Li1–I1	2.879(8)	Li2–I1	2.843(7)	Li1–N1	2.111(9)
Li1–I1′	2.843(7)	Li2–I2	2.799(9)	Li2–N2	2.097(6)
Li1–I2	2.907(7)	Li2–I2′	2.814(7)		
I–Li–I		**Li–I–Li**		**N–Li–I**	
I1–Li1–I1′	102.3(2)	Li1–I1–Li1′	77.1(2)	N1–Li1–I1	102.4(3)
I1–Li1–I2	98.4(2)	Li1–I1–Li2	79.0(2)	N1–Li1–I1′	126.0(4)
I1′–Li1–I2	97.7(2)	Li1′–I1–Li2	80.4(2)	N1–Li1–I2	124.9(3)
I1–Li2–I2	101.9(2)	Li1–I2–Li2	79.3(2)	N2–Li2–I1	101.1(3)
I1–Li2–I2′	99.9(2)	Li1–I2–Li2′	79.8(2)	N2–Li2–I2	125.1(3)
I2–Li2–I2′	97.1(3)	Li2–I2–Li2′	81.8(2)	N2–Li2–I2′	126.6(3)

Table 2 Crystallographic data and refinement details for compounds **5–8**

	5	**6**·THF	**7**	**8**
Empirical formula	$C_{36}H_{76}I_4Li_4N_4$	$C_{21}H_{44}AlNO$	$C_{27}H_{20}O_2$	$C_{16}H_{24}INO$
M_r	1100.37	353.55	376.43	373.26
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*C2/c*	*Pbca*	*P*21/*n*	*Fdd*2
a/Å	25.5194(9)	10.4710(2)	10.7897(3)	12.8821(5)
b/Å	10.7301(2)	12.1167(2)	17.0361(4)	59.0714(18)
c/Å	19.8807(6)	35.1416(2)	11.4052(3)	8.4330(4)
β (°)	118.682(4)	90	110.652(3)	90
V/Å^3	4775.9(2)	4458.55(14)	1961.72(9)	6417.2(4)
Z	4	8	4	16
ρ_c/g cm^{-3}	1.530	1.053	1.275	1.545
Reflns measured	11422	16838	9138	15680
Unique reflns	5807	5203	4795	4065
Observed reflns	4687	3858	3789	3931
R_{int}	0.0354	0.0294	0.0217	0.0335
GooF	1.082	1.092	1.017	1.083
R [on F , obs rflns only]	0.0409	0.0559	0.0460	0.0212
wR [on F^2,all data]	0.0794	0.1126	0.1044	0.0473
Largest diff. peak/hole/e Å^{-3}	1.070/−0.600	0.308/−0.238	0.327/−0.237	0.444/−0.388

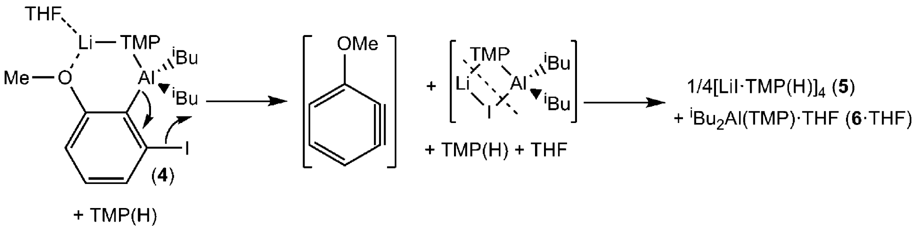
All attempts at a rational synthesis of **5** were unsuccessful. For example, LiI would not dissolve in non-polar solvents in the presence of stoichiometric amounts of TMP(H) or even in neat TMP(H) while *in situ* generated LiI (either from Me_3SiI + MeLi or NH_4I + ^{n}BuLi) immediately precipitated from the mixture. When polar THF was used as a solvent, TMP(H) failed to displace this with the only tangible product identified being the known solvate LiI·3THF.[29]

An NMR spectroscopic study on both the white precipitate isolated initially and the subsequently grown crystals of **5** suggest that these two products are identical. This result implies that the putative metallated product **4** must rapidly decompose, almost certainly *via* a benzyne mechanism, and that unlike Uchiyama's protocol with base **2**, the suppression of this decomposition is not possible since it cannot be stopped even at −78 °C. The fact that a product containing a Li–I fragment is produced, even though it is almost certain that alumination occurs *ortho* to the halide, allows us to propose a potential pathway by which the decomposition of the putative aluminated intermediate occurs (eqn (2)—our recent report of a variety of *ortho*-aluminated substituted aromatics provides us with confidence that it is an alumination, that is, formation of **4**, which first occurs here).

While there are many documented examples of complexes of general formula "Li(μ-anion)$_2$Al(anion)$_2$", from a search of the Cambridge Structural Database[30] surprisingly none involve a mixed organic anion/iodide anion bridging set,[31] perhaps in part due to the appreciably different M–I and M–C/M–N bond lengths which would lead to a severely distorted M–I–M–C/N four atom ring. It is therefore highly likely that putative Li(μ-I)(μ-TMP)Al^{i}Bu$_2$ rapidly disproportionates to **5** and **6**·THF.[32] Since the Lewis donors TMP(H) and THF are only present in stoichiometric quantities it is conceivable that the less sterically bulky donor (THF) will bind preferentially to the more sterically encumbered stronger Lewis acidic metal (in this case Al), leaving only TMP(H) available to solvate the electron-poor lithium.

This pathway was further supported by a ^{1}H NMR spectrum of the residues left over after **5** had been isolated which showed resonances consistent with the neutral dialkylaluminium amide **6**·THF. We recently reported the synthesis of **6** as an oil which was shown by DOSY NMR spectroscopy to exist as a monomer, almost certainly because of the short Al–N$_{TMP}$ distance, coupled with the steric bulk around the TMP nitrogen, which meant that dimerization to give four-coordinate Al centres could not occur.[15,33] Consequently we prepared an authentic sample of **6**·THF by simply adding a molar equivalent of THF to pre-prepared **6** in hexane. Upon cooling to −34 °C, the resultant crystals were confirmed as being the desired product *via* a combination of X-ray crystallography (Fig. 3), and ^{1}H and ^{13}C NMR spectroscopy.

To verify that benzyne formation is a key step during this process, we repeated this reaction and then attempted to trap any benzyne formed *via* a Diels–Alder cyclization by adding a diene (1,3-diphenylisobenzofuran) at −78 °C, before allowing the reaction to naturally warm to room temperature (Fig. 4). After work up and purification (see experimental section for full details) crystals of 1-methoxy-9-10-diphenyl-9-10-epoxyanthracene (**7**) were obtained in near quantitative yield. ^{1}H and ^{13}C NMR spectroscopy (see Fig. 5 for the assigned ^{13}C spectrum) plus elemental analysis established that **7** was the final product. In particular, the ^{13}C NMR spectrum displayed all 23 expected resonances which could be easily assigned to one of five environments—methyl (orange), quaternary aliphatic (red), aromatic C–H (green), *ortho*/*meta*



(2)

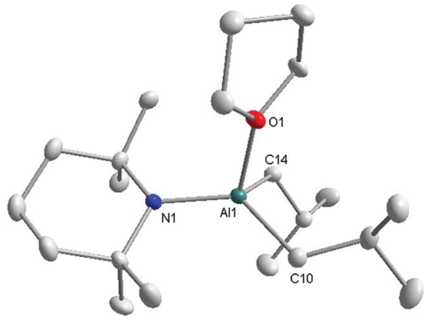
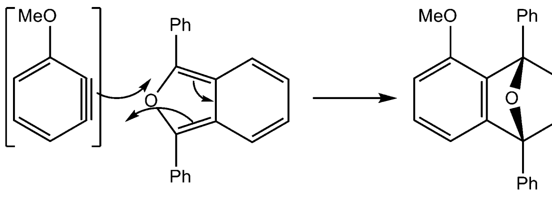


Fig. 3 Molecular structure of **6**·THF. Thermal ellipsoids are drawn at the 50% probability level and all H atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.865(1), Al1–O1 1.951(1), Al1–C10 1.992(2), Al1–C14 2.011(2); N1–Al1–O1 100.99(6), N1–Al1–C10 122.11(7), N1–Al1–C14 119.67(7), O1–Al1–C10 99.45(7), O1–Al1–C14 101.98(7), C10–Al1–C14 107.80(7).



(7)

Fig. 4 Diels–Alder cyclization with the methoxy-substituted benzyne intermediate to give the polycycle **7**.

C–H (blue) and aromatic C (black). The identity of the product was corroborated by a single crystal molecular structure determination (see inset of Fig. 5).

The results described thus far show that bases **2** and **3** display a completely different reactivity towards 3-halogenated substituted aromatic substrates, since Uchiyama *et al.* utilized a low temperature regime to sedate their aluminated product prior to electrophilic quenching.

An interesting parallel can be drawn here with alkali-metal mediated zincations. Bisalkyl TMP zincates formulated as "R_2Zn(TMP)Li"[34] (which are also adept at chemoselective deprotonations in both typical[34a,35] and atypical[36] positions) display contrasting reactivity in the zincation of 3-halogenated substituted aromatic molecules; with the metallated product extruding benzyne when R = Me but not when R = ^{t}Bu, suggesting steric bulk is critical in preventing benzyne formation (Fig. 6a).[37] It is pertinent to note that dual alkyl/amido alkali-metal zincates depend on the identity of the alkali-metal and Lewis donor for their reactivity and can operate *via* a two step mechanism whereby the initial deprotonation occurs *via* TMP basicity [generating TMP(H)]; this amine is subsequently deprotonated by an alkyl group of the deprotonated substrate containing intermediate resulting in re-integration of TMP into the framework and loss of alkane (Fig. 6b).[38] This however relies on the accessibility of the zinc centre by the Lewis donating TMP(H) and is prevalent in lighter alkali-metal congeners (Li, Na) which tend to be monomeric with coordinatively unsaturated 3-coordinate Zn as opposed to heavier potassium zincates which oligomerize and have 4-coordinate inaccessible Zn centres of diminished Lewis acidity.[39]

An analogous two step mechanism can be ruled out for the lithium aluminates **2** and **3** discussed thus far since apart from deprotonated substrate, the only other anions present when **2** executes a deprotonation are ^{i}Bu groups, and if alkyl induced deprotonation were to occur at any stage then volatile ^{i}Bu–H would be permanently lost from the system before it could re-enter. The presence of a TMP anion bound to a coordinatively saturated (4 coordinate) Al centre in our system here would thus appear to be key to the high reactivity of this intermediate and may explain why this breaks down with extrusion of a benzyne. However, while it is tempting at this stage to unequivocally assign the reactivity to anionic effects, it is important to remember that solvent (polar THF *versus* non-polar hexane) in the zincate systems above plays a highly important role. Likewise, **2** is routinely used as a THF solution, while **3** is used in hexane as it α-deprotonates

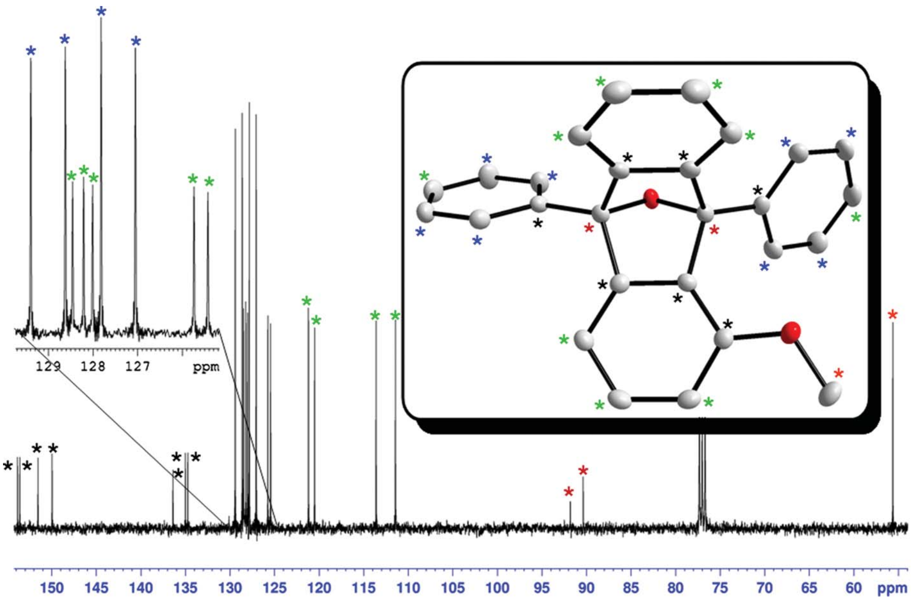


Fig. 5 ^{13}C {^{1}H} NMR spectrum of **7** with molecular structure inset (thermal ellipsoids at 50% probability level and H atoms omitted for clarity. Oxygen atoms are shaded red).

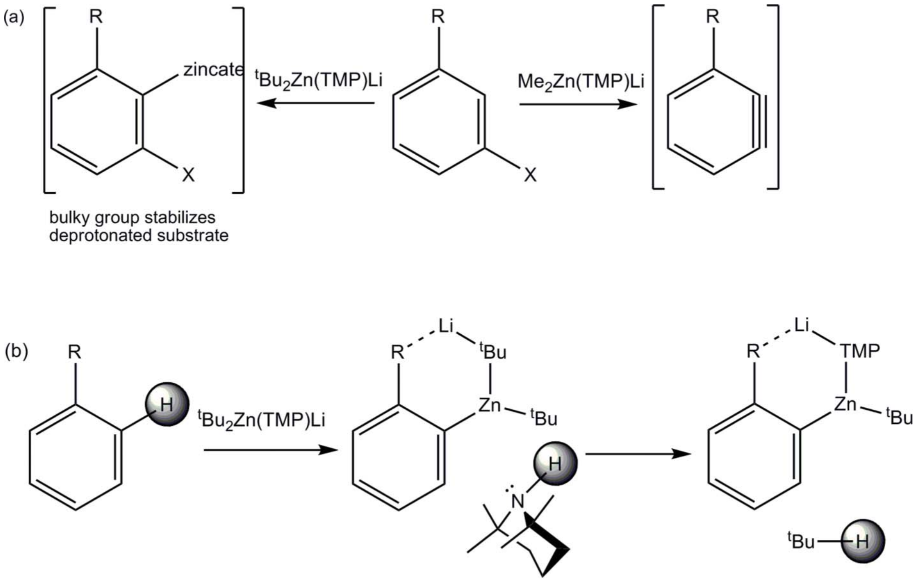


Fig. 6 (a) contrasting reactivity of bisalkyl lithium TMP zincates and (b) two-step mechanism of bisalkyl alkali-metal TMP zincate displaying overall alkyl basicity. R = *ortho* directing group, X = halide.

THF, *vide supra*. Consequently, we decided to repeat the attempted synthesis of complex **4** in THF at −78 °C, anticipating firstly that the low temperature would suppress THF deprotonation and secondly that the more acidic 3-iodoanisole would be preferentially deprotonated. In practice, no white precipitate was witnessed when 3-iodoanisole was introduced to a stirring solution of pre-prepared **3** in THF at −78 °C. After stirring for two hours, a stoichiometric solution of elemental iodine in THF was introduced in an attempt to prepare 2,3-diiodoanisole.[40] After work-up and purification *via* column chromatography, a crystalline product (**8**) was obtained. NMR spectroscopy and a molecular structure determination (Fig. 7) showed the identity of **8** to in fact be the hitherto unknown *N*-substituted TMP compound 1-(2-iodo-3-methoxyphenyl)-2,2,6,6-tetramethylpiperidide.

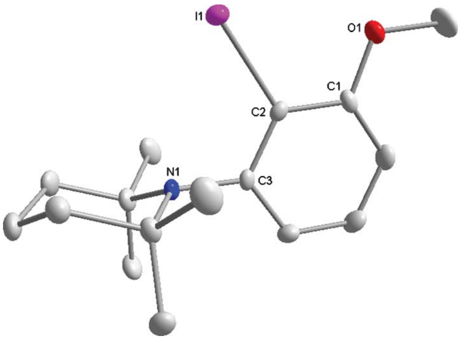
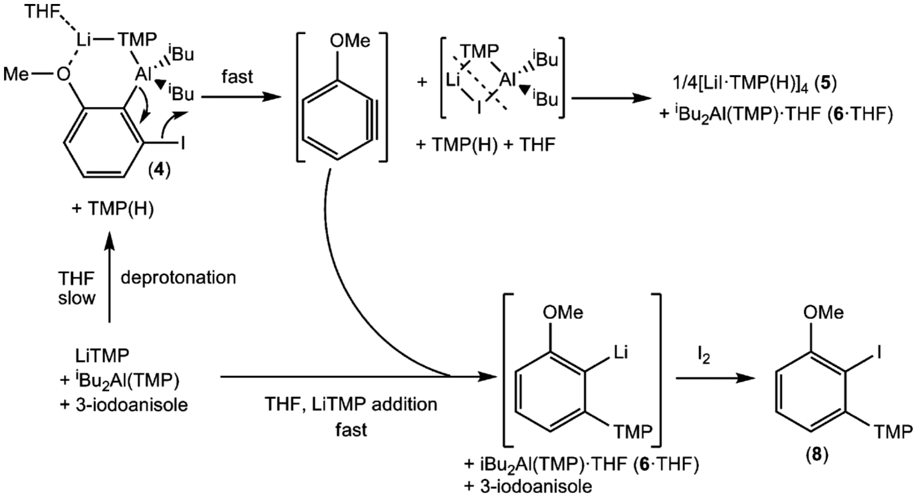


Fig. 7 Molecular structure of *N*-substituted TMP derivative **8**. Thermal ellipsoids are drawn at the 50% probability level and all H atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): C1–O1 13.71(3), C2–I1 2.107(2), C3–N1 1.436(3); O1–C1–C2 116.4(2), C1–C2–I1 117.6(2), C3–C2–I1 120.7(2), C2–C3–N1 119.6(2).

Tri-substituted benzene **8** can be logically considered as the product of Li–TMP addition across the benzyne functionality, followed by replacement of the lithium atom *via* an iodine quench. The ^{1}H NMR spectrum of **8** suggests that the TMP chair is conformationally locked since the methyl, β and γ environments are all resolved into twice the number of resonances typically anticipated for a TMP compound. This cascade of metallation of *meta*-halogenated substituted aromatics, elimination of metal halide/formation of benzyne and then LiTMP addition across the benzynyl functionality has previously been documented by Mortier[41] amongst others.[42]

It should be noted here that prior to column purification, a ^{1}H NMR spectrum of the crude product was obtained whose aromatic region showed product **8** to be present in about an equimolar amount to the starting substrate, 3-iodoanisole. This result allows us to propose a final hypothesis for the fate of the benzyne generated once LiI is expelled from the putative metallated product **4**. If the benzyne reacts with the LiTMP component of the base **3**·THF quicker than the base can deprotonate the remaining substrate, then additional ^{t}Bu$_2$Al(TMP)·THF (**6**·THF) will be generated along with 1-(2-lithio-3-methoxyphenyl)-2,2,6,6-tetramethylpiperidide (which itself is simply quenched with iodine). As a consequence of the base being consumed this way, 50% of the 3-iodoanisole will remain unreacted, as seen here. This allows us to propose a modification of eqn (2) showing the fate of all the intermediate products (eqn (3)).

At this juncture we speculated that perhaps the relatively weak C–I bond was responsible for the failure to *ortho* deprotonate the substrate without causing further decomposition reactions, so consequently we turned our attention to the 3-bromo- and 3-chloroanisole congeners. However, on moving to the bromo congener an analogous reactivity was witnessed. The chloro-substituted derivative however yielded 2-iodo-3-chloroanisole (**9**)[43] in only 25% yield after being subjected to metallation with one molar equivalent of base **3** at −78 °C for 2 h followed by electrophilic quenching with iodine. A longer reaction time (8 h) had no significant effect on the yield, however, using a four fold excess of base **3** furnished a near-quantitative yield of 98% of **9**.



(3)

Conclusion

We have shown that seemingly innocuous changes to a bimetallic framework [in this case switching from the alkyl rich ${}^{i}Bu_3(TMP)AlLi$ to the amide rich ${}^{i}Bu_2(TMP)_2AlLi$] can dramatically alter the pathway that a metallation reaction will follow. While *ortho*-deprotonation at the 2-position of 3-halogenated anisoles is facile with the former, the increased reactivity of the latter (due to the presence of a TMP anion in the deprotonated intermediate not present in the former) causes breakdown of the trapped deprotonated intermediate complex resulting in a series of different homometallic and organic products due to competing reactions. By mapping these products we have shed new light on the processes and potential pitfalls one may encounter when embarking on a deprotonative journey using such heterometallic low-polarity metallators. While factors such as solvent and temperature play an important role in controlling these reactions, what is clear is that aluminium TMP bases are generally highly tolerant of halogeno functionality, preferring metal—hydrogen exchange over metal—halogen exchange.

Experimental

General experimental

All reactions and manipulations were carried out under a protective argon atmosphere using either standard Schlenk techniques or a glove box. All solvents were dried over Na/benzophenone and freshly distilled prior to use. ${}^{i}Bu_2Al(\mu\text{-}TMP)_2Li{\cdot}THF$ (**3**) and ${}^{i}Bu_2Al(TMP)$ were prepared by literature methods.[15] 3-iodoanisole and 1,3-diphenylisobenzofuran were purchased from Aldrich and used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 MHz spectrometer (operating at 400.03 MHz for ^1H and 100.58 MHz for ^{13}C). All ^{13}C NMR spectra were proton decoupled. Elemental (C, H, N) analyses were performed by Denise Gilmour, University of Strathclyde Elemental Analysis Service.

Synthesis of $[LiI{\cdot}TMP(H)]_4$ (5)

A pre-prepared solution of **3** in hexane was cooled to −78 °C and 3-iodoanisole was added *via* syringe. Lithium iodide TMP(H) solvate **5** precipitated immediately as a white powder and was collected by vacuum filtration. The filtrate was left overnight at −35 °C yielding a batch of X-ray quality crystals of **5** (combined yield of powder and crystals 0.45 g, 82%).

El. analysis calc. for $C_{36}H_{76}I_4Li_4N_4$ (M_r = 1100.40) C, 39.29; H, 6.96; N, 5.09; found: C, 39.73; H, 7.22; N, 4.24.

Synthesis of ${}^{i}Bu_2Al(TMP){\cdot}THF$ (6·THF)

Pre-prepared ${}^{i}Bu_2Al(TMP)$ (0.28 g, 1 mmol) was added to hexane (5 mL) and THF (0.08 mL, 1 mmol) was introduced *via* syringe. This solution was left overnight at −34 °C to yield the final product as colourless crystals (0.25 g, 71%).

^1H NMR (400.13 MHz, 298 K, C_6D_6): $\delta = 0.28$ [4H, d, $^3J(H,H) = 6.40$ Hz, Al–CH$_2$], 1.15 [4H, m, THF], 1.25 [12H, d, $^3J(H,H) = 6.40$ Hz, ^{i}Bu CH$_3$], 1.36 [12H, s, TMP CH$_3$], 1.48 [4H, t, $^3J(H,H) = 6.29$ Hz, TMP β], 1.76 [2H, m, TMP γ], 2.08 [2H, sept, $^3J(H,H) = 6.53$ Hz, ^{i}Bu CH], 3.57 ppm [4H, m, THF].

$^{13}C\ \{^1H\}$ (100.62 MHz, 298 K, C_6D_6): $\delta = 18.7$ [TMP γ], 24.9 [THF], 26.8 [^{i}Bu CH], 28.5 [^{i}Bu CH$_2$], 28.9 [^{i}Bu CH$_3$], 34.5 [TMP CH$_3$], 41.6 [TMP β], 51.9 [TMP α], 69.7 ppm [THF].

El. analysis calc. for $AlC_{21}H_{44}NO$ (M_r = 353.56) C, 71.34; H, 12.54, N, 3.96; found: C, 70.98; H, 13.21, N 4.15.

Synthesis of Diels–Alder product (1-methoxy-9-10-diphenyl-9-10-epoxyanthracene) (7)

3-Iodoanisole (0.24 mL, 2 mmol) was added to a prepared solution of **3** in hexane at −78 °C. 1,3-Diphenylisobenzofuran (0.54 g, 2 mmol) was added after a few minutes and the mixture was allowed to stir and to warm to room temperature overnight. Saturated aq. NH_4Cl (40 mL) was added to quench the reaction and the mixture was extracted with $CHCl_3$ (30 mL × 3). The mixture was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The residue was purified by SiO_2 column chromatography using petroleum ether (100%), diethyl ether–petroleum ether (1 : 10) and diethyl ether–petroleum ether (1 : 5) as an eluent to give 1-methoxy-9-10-diphenyl-9-10-epoxyanthracene (0.69 g, 92%).

^1H NMR (400.13 MHz, 298 K, C_6D_{12}): $\delta = 3.66$ [3H, s, OCH$_3$], 6.66 [1H, d, $^3J(H,H) = 7.46$ Hz], 7.02–7.12 [4H, m], 7.37 [1H, d,

^3J(H,H) = 7.05 Hz], 7.47–7.58 [7H, m], 7.92 [2H, m], 8.01 ppm [2H, m].

^{13}C {^{1}H} (100.62 MHz, 298 K, C_6D_{12}): δ = 55.6 [OCH_3], 90.4 [quaternary C], 91.8 [quaternary C], 111.4 [aromatic CH], 113.6 [aromatic CH], 120.5 [aromatic CH], 121.2 [aromatic CH], 125.4 [aromatic CH], 125.7 [aromatic CH], 127.1 [2C, phenyl CH], 127.8 [2C, phenyl CH], 128.0 [aromatic CH], 128.2 [aromatic CH], 128.5 [aromatic CH], 128.6 [2C, phenyl CH], 129.4 [2C, phenyl CH], 134.7 [aromatic C], 135.0 [aromatic C], 136.4 [aromatic C], 150.0 [aromatic C], 151.5 [aromatic C], 153.6 [aromatic C], 153.8 ppm [aromatic C].

El. analysis calc. for $C_{27}H_{20}O_2$ (M_r = 376.46) C, 86.14; H, 5.36; found: C, 85.57; H, 5.33.

Synthesis of 1-(2-iodo-3-methoxyphenyl)-2,2,6,6-tetramethylpiperidide (8)

LiTMP was prepared from TMP(H) (0.17 mL, 1 mmol) and ^{n}BuLi (0.63 mL, 1.6 M in hexanes, 1 mmol) in THF (5 mL) and cooled to −78 °C. A −78 °C solution of ^{i}Bu$_2$Al(TMP) in THF (5 mL) was added *via* cannula to give an *in situ* solution of **3**. 3-Iodoanisole (0.12 mL, 1 mmol) in THF at −78 °C was added and this was stirred for 2 h. I_2 (5 mL of a 1 M solution, 5 mmol) in dry THF was added to the reaction mixture and stirred overnight. The mixture was diluted with saturated aq. $NaHS_2O_3$ (20 mL) and saturated aq. NH_4Cl (40 mL) and extracted with $CHCl_3$ (30 mL × 3). The organic layer was dried over $MgSO_4$ and solvent removed under reduced pressure. The residue was purified by SiO_2 column chromatography using hexane (100%) as an eluent to give 1-(2-iodo-3-methoxyphenyl)-2,2,6,6-tetramethylpiperidide (0.36 g, 48%).

^{1}H NMR (400.13 MHz, 298 K, $CDCl_3$): δ = 0.93 [6H, s, 2 × CH_3 of TMP], 1.30 [6H, s, 2 × CH_3 of TMP], 1.54–1.58 [2H, m, 1 × βCH_2 of TMP], 1.63–1.69 [1H, m, 1 × γCH of TMP], 1.81–1.98 [2H, m, 1 × βCH_2 of TMP] and [1H, m, 1 × γCH of TMP], 3.89 [3H, s, OCH_3], 6.71 [1H, d, ^3J(H,H) = 8.16 Hz, 1 × aromatic C–H], 7.07 [1H, d, ^3J(H,H) = 7.94 Hz, 1 × aromatic C–H], 7.22 ppm [1H, t, ^3J(H,H) = 8.02 Hz, 1 × aromatic C–H].

^{13}C {^{1}H} (100.62 MHz, 298 K, $CDCl_3$): δ = 18.7 [1 × γ*C*H of TMP], 25.7 [1 × *C*H_3 of TMP], 31.4 [1 × *C*H_3 of TMP], 41.2 [1 × β*C*H_2 of TMP], 56.1 [1 × γ*C*H of TMP], 56.5 [1 × O*C*H_3], 106.2 [1 × aromatic C], 108.6 [1 × aromatic *C*H], 124.3 [1 × aromatic *C*H], 127.9 [1 × aromatic *C*H], 150.9 [1 × aromatic C], 159.3 ppm [1 × aromatic C].

El. Analysis calc. for $C_{16}H_{24}NOI$ (M_r = 373.28) C, 51.48; H, 6.48; N, 3.75; found: C, 52.13; H, 6.85; N, 3.76.

X-ray crystallography

Crystallographic data were collected at 123(2) K on Oxford Diffraction Diffractometers with Mo-Kα (λ = 0.71073 Å) radiation. Structures were solved using *SHELXS-97*,[44] and refined to convergence on F^2 against all independent reflections by the full-matrix least-squares method using the *SHELXL-97* program.[44] CCDC 815746 and 847968–847970 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.

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