

Tuning the Basicity of Synergic Bimetallic Reagents: Switching the Regioselectivity of the Direct Dimetalation of Toluene from 2,5- to 3,5-Positions**

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Organolithium reagents have long enjoyed iconic status amongst synthetic chemists, in part because of their unrivaled ability to affect directed metalation (lithiation, lithium–hydrogen exchange) reactions on arenes, heteroarenes, and related compounds.^[1] If the objective is to generate non-lithium metal–carbon bonds with subordinate metals having lower reactivity than lithium, then usually these bonds must be made indirectly by first forming a lithium–carbon bond and subsequently carrying out a metathesis reaction with a subordinate metal salt.^[2] Recently, however, there is increasing realization that direct (subordinate) metalation with low-polarity metals magnesium,^[3] zinc,^[4] aluminum,^[5] or manganese(II)^[6] is now achievable with imaginatively composed bases. Bimetallic cooperativity (mixed-metal synergy) within the base molecule/mixture^[7] is a major contributory factor in this surprising turnaround. For example, sodium–magnesium cooperativity in the *n*-butyl-based compound {Na(*n*Bu)(tmp)Mg(tmp)} (tmp = 2,2,6,6-tetramethylpiperidide) resulted in direct regioselective 2, 5-dimagnesiation of toluene, manifested in the inverse-crown product [(tmp)₆Na₄(2,5-Mg₂C₆H₃CH₃)] (**1**).^[8] The tmeda-supported complex of this base, [(tmeda)Na(*n*Bu)(tmp)Mg(tmp)], monomagnesiates toluene at the 3-position to give [(tmeda)Na(tmp)₂(3-MgC₆H₄CH₃)] (tmeda = *N,N,N',N'*-tetramethylethylenediamine).^[9] The bimetallic cooperativity operating in these reactions prompted their description as alkali-metal-mediated magnesiations (AMMM).^[2a] Knochel also recently reported^[10] direct magnesiation reactions of a series of polyfunctionalized arenes and heteroarenes using the related bimetallic base (tmp)₂Mg·2LiCl. We recently employed the

sodium manganate base {Na₄Mn₂(tmp)₆(CH₂SiMe₃)₂} to 1,4-dimanganate benzene to afford the inverse crown [(tmp)₆Na₄(1,4-Mn₂C₆H₄)] (**2**).^[11] This result demonstrates that the concepts of direct metalation and inverse crown complexation also extend to open-shell transition elements.

Given that the active deprotonating alkyl ligand of our magnesiate and manganate bases are different (*n*-butyl and trimethylsilylmethyl, respectively), for completeness we have further investigated the reaction of the manganese(II) bases with toluene. Remarkably, the regioselectivity of the dimetalation (in this case, dimanganation) switches to the 3,5-(*meta,meta*) positions. Preparing a new trimethylsilylmethyl-based magnesiate base and reacting it with toluene reveals the same surprising 3,5-regioselectivity. Thus, as disclosed herein, these synergic bases can be tuned to metalate arenes selectively at different positions depending on the identity of the basic alkyl component. Furthermore, X-ray crystallographic studies establish that these unique 3,5-dimetalations are manifested in a new type of inverse crown, which undergo electrophilic interception reactions with iodine to give 3, 5-diiodotoluene.

Previously, we found no metal dependency in the reactions of the magnesiate base {Na(*n*Bu)(tmp)Mg(tmp)} or manganate base {Na₄Mn₂(tmp)₆(CH₂SiMe₃)₂} with benzene: both produce benzene-1,4-diide inverse crowns [(tmp)₆Na₄(1,4-M^{II}C₆H₄)] (M^{II} = Mg or Mn). Therefore, one would expect the manganate base to also replicate the magnesiate base in its reaction with toluene to afford [(tmp)₆Na₄(2,5-Mn₂C₆H₃CH₃)]. Therefore, we applied the same manganate reaction mixture as that used to dimanganate benzene, BuNa/Htmp/Mn(CH₂SiMe₃)₂ in a 4:6:2 stoichiometry in hexane solution, to one molar equivalent of toluene (Scheme 1).

The isolated product, in the form of yellow crystalline needles, was not the one expected, but its 3,5-isomer [(tmp)₆Na₄(3,5-Mn₂C₆H₃CH₃)] (**3**). Compound **3** is paramagnetic, and thus not conducive to a diagnostic NMR spectroscopic study, but has been characterized directly by X-ray crystallography^[12] and indirectly by electrophilic interception (see below). It has a different type of molecular structure from that of **1**: There are two crystallographically distinct but essentially chemically equivalent molecules in the crystal structure of **3**, so for brevity only one (Figure 1) is discussed herein. Key features of **1** and **2** are still mimicked in **3**. For example, a severely puckered twelve-atom [(NaN–NaNMnN)₂] host ring encapsulates a toluenediide guest. However, a major distinction is in how the host ring and guest

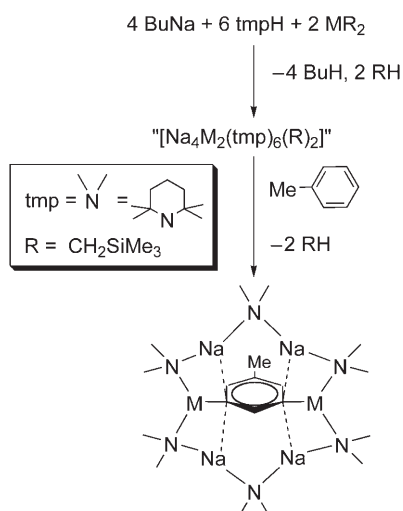
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Scheme 1. Synthesis of the new inverse crowns **3** ($\text{M} = \text{Mn}$) and **4** ($\text{M} = \text{Mg}$).

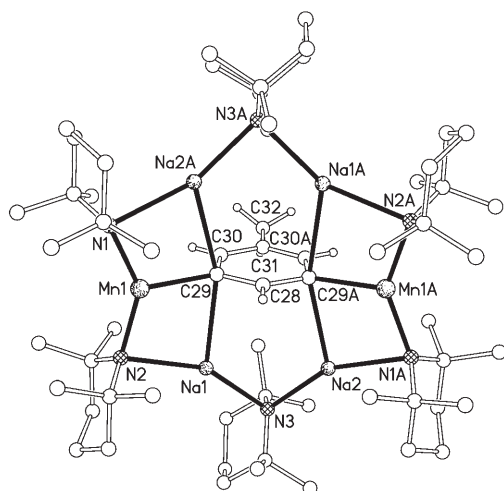


Figure 1. Molecular structure of one of the two independent molecules of **3**, with tmp hydrogen atoms omitted for clarity. Symmetry operator (C_2 axis) A: $2-x, y, 1/2-z$. Selected bond lengths [Å] and angles[°]: Mn1–N1 2.072(5), Mn1–N2 2.082(5), Na1–N2 2.544(5), Na1–N3 2.416(5), Na2–N1A 2.566(6), Na2–N3 2.360(5), Mn1–C29 2.220(6), Na1–C29 2.803(6), Na2–C29A 2.782(6); N1–Mn1–N2 141.70(19), N1–Mn1–C29 110.7(2), N2–Mn1–C29 107.45(19), N2–Na1–N3 155.28(19), N2–Na1–C29 80.75(17), N3–Na1–C29 123.93(18), N1A–Na2–N3 156.6(2), N1A–Na2–C29A 82.50(17), N3–Na2–C29A 119.41(18).

fit together. This can clearly be seen from a superimposition of **1** and **3** (Figure 2). More of the substituted end of the tolyl ring is exposed in **3**, whereas the host ring adopts a curved, convex-like posture over the unsubstituted end, in contrast to its more planar appearance in **1**. Chemically this change in morphology is a consequence of the manganese atoms in **3** bonding to C29/C29A (note the exact molecular C_2 axis running through C28/C31/C32) in place of the hydrogen atoms abstracted from these 3,5-positions. The manganese atoms sit coplanar with the arene ring plane (deviations ± 0.126 Å) with a Mn1–C29 bond length of 2.220(6) Å.

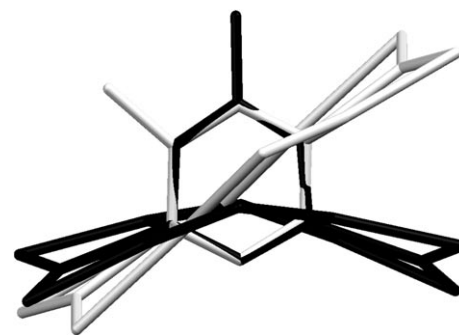


Figure 2. Superposition of the molecular structures of **1** (gray) and **3** (black), with a least-squares fit of the two aryl rings, showing their metal–nitrogen host rings around the carbon atoms of their arenediide guests.

Comparison with **2** shows remarkably similar corresponding values of ± 0.085 Å and 2.201(2) Å, despite the different (1,4) metal substitution pattern on the benzenediide ring, suggesting these inverse crown structures organize about the optimization of Mn–C σ bonds. In contrast, the sodium atoms are situated almost orthogonal to the arene ring plane (at 84.3 and 75.8°, cf. 79.6 and 85.2° in **2**) and their interaction with the π system appears to be compromised slightly (Na1–C29 2.803(6) Å, Na2–C29A 2.782(6) Å; cf in **2** 2.710(2) Å and 2.715(2) Å).

Can the synergic magnesiate base system also be modified so that it similarly affects 3,5-dideprotonation instead of the 2,5-dideprotonation achieved with the butyl-active base? Following the recipe that was successful for manganese, we reacted a 4:2:6 stoichiometric mixture of BuNa/Mg-(CH₂SiMe₃)₂/Htmp (equating to Na₄Mg₂(tmp)₆(CH₂SiMe₃)₂ after evolution of 4 BuH and 2 Me₄Si) with one molar equivalent of toluene (Scheme 1). In this case, as hoped, the isolated yellow crystalline product was not **1**, but its regioisomer [(tmp)₆Na₄(3,5-Mg₂C₆H₃CH₃)] (**4**). The 3,5-aromatic substitution pattern was immediately discernible from a ¹H NMR spectrum, as *meta* H resonances were absent, but *ortho* H and *para* H resonances in a ratio of 2:1, shifted downfield (at $\delta = 7.57$ and 8.06 ppm, respectively) relative to those of toluene, were present. X-ray crystallographic studies^[12] established that the molecular structure of **4** (Figure 3) is analogous to that of **3**, though the two crystal structures are not isomorphous, **4** having only one independent molecule with exact C_2 symmetry. This strong resemblance between magnesiate **4** and manganate **3** extends to molecular dimensions (corresponding values in **4** to those discussed for **3**: deviation of magnesium atom from arene ring plane ± 0.247 Å; Mg1–C2, 2.217(3) Å; angles between Na–C bonds and arene ring plane, 86.1 and 73.0°; Na1–C2, 2.801(3) Å, Na2–C2, 2.749(3) Å). Dimetalation of the toluene ring leads to a noticeable narrowing of the angle at the metalated, *meta* carbon atoms (C1–C2–C3, 112.6(3)°; cf 114.1(6)° in **3**) and concomitant widening at the *ortho* (C2–C3–C4, 125.3(3)°; cf 123.5(6)° in **3**) and *para* carbon atoms (C2–C1–C2A, 127.1(4)°; 125.9(9)°). A comparison between the two magnesiate regioisomers **4** and **1** also reveals dimensional similarities (for example, Mg–C in **1**, 2.200(2) Å), but

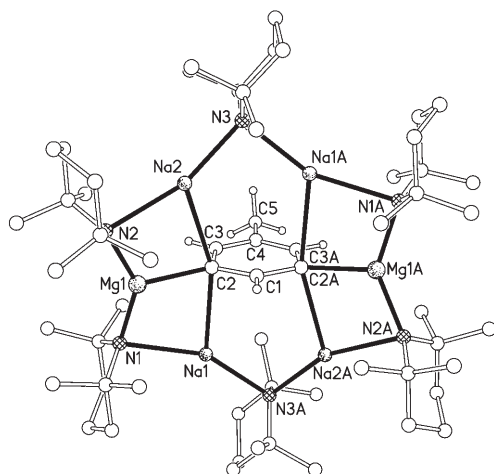


Figure 3. Molecular structure of **4**, with tmp hydrogen atoms omitted for clarity. Symmetry operator (C_2 axis) A: $-x, y, 1/2 - z$. Selected bond lengths [Å] and angles[°]: Mg1–N1 2.058(3), Mg1–N2 2.053(3), Na1–N1 2.599(3), Na1–N3A 2.400(3), Na2–N2 2.570(2), Na2–N3 2.361(3), Mg1–C2 2.217(3), Na1–C2 2.801(3), Na2–C2 2.749(3); N1–Mg1–N2 101.09(10), N1–Mg1–C2 108.45(11), N2–Mg1–C2 111.07(11), N1–Na1–N3A 155.55(10), N1–Na1–C2 79.86(9), N3A–Na1–C2 123.88(9), N2–Na2–N3 159.88(9), N2–Na2–C2 82.84(9), N3–Na2–C2 117.06(9).

as in the comparison between **2** and **3**, the interaction of the sodium atom with the arene π system appears marginally more efficient in the 2,5-isomer (mean Na–C bond length: 2.686 Å; in **4**, 2.775 Å; angles between Na–C bonds and arene ring plane: in **1**, 87.4 and 76.7°; in **4** 86.1 and 73.0°).

Both **3** and **4** were subjected to electrophilic quenching reactions with iodine. Their 3,5-metal substitution patterns were confirmed by the formation of 3,5-diiodotoluene after aqueous workup, with yields of isolated product of 55% and 30%, respectively.

Whereas **4** is diamagnetic, **3** is paramagnetic, and so its magnetic properties have been explored by variable-temperature magnetization measurements on a powdered sample.^[13] The room temperature value for χT is 8.4 emu K mol^{−1}, which is only slightly lower than the theoretical expectation value of 8.75 emu K mol^{−1} for two uncoupled $S = 5/2$ centers. With lowering temperature a decrease in χT is observed only below 50 K, indicating very weak antiferromagnetic exchange interaction between the two manganese ions. Using the spin Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$ the susceptibility data were simulated satisfactorily, with $\hat{S}_1 = \hat{S}_2 = 5/2$, $J = -0.1$ cm^{−1} and $g = 1.97$.

In summary, unprecedented polymetalation reactions have been uncovered in which toluene is directly dimagnated or dimagnesiased at 3,5-positions in a new type of inverse crown product.^[14] The key to unlocking this 3,5-regioselectivity appears to lie with the trimethylsilylmethyl ligand,^[15] in combination with tmp ligands, in the synergic bimetallic sodium–manganese or sodium–magnesium bases employed. This surprising finding calls for a screening of a wide range of bimetallic compounds with different combinations/permutations of ligands as potential synergic bases.

Experimental Section

All reactions were carried out under a protective argon atmosphere. The compound $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ was prepared from the Grignard reagent $(\text{Me}_3\text{SiCH}_2)\text{MgCl}$ by manipulation of the Schlenk equilibrium by the dioxane precipitation method. The resultant off-white solid was purified by sublimation at 175 °C (10^{-2} torr) to furnish pure $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$.

3: Htmp (1.2 mL, 6 mmol) was added to a suspension of BuNa (0.32 g, 4 mmol) in dry *n*-hexane (45 mL), and the resultant mixture was allowed to stir at room temperature for 1 h. $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (0.46 g, 2 mmol) was added to give a yellow/orange solution. Toluene (0.22 mL, 1 mmol) was then added and the solution was heated to reflux for 30 min. The bright orange solution was allowed to cool to room temperature, depositing a crop of yellow crystalline needles (0.51 g). Removal of the mother liquor with a canula and reduction of the solvent volume under vacuum allowed a second batch of product to be isolated as a yellow microcrystalline solid (0.26 g); total yield 68.0%. Elemental analysis calcd (%) for $\text{C}_{61}\text{H}_{114}\text{Mn}_2\text{N}_6\text{Na}_4$ (1133.45): C 64.64, N 7.41, H 10.14; found: C 64.73, N 7.32, H 10.15. M.p. 185 °C (decomp).

4: Following the procedure for **3**, $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ (0.6 g, 3 mmol) was added to a mixture of BuNa (0.48 g, 6 mmol) and Htmp (1.6 mL, 9.0 mmol) in *n*-hexane (20 mL). Toluene (0.16 mL, 1.5 mmol) was then added and the mixture was heated for 10 min to give a clear yellow solution. After cooling and filtering, the solution was allowed to stand for 2 d. A crop of yellow needles (0.64 g, 39.8%) was obtained. ¹H NMR (400 MHz, C_6D_6 , 20 °C, TMS): δ = 8.06 (s, 1H), 7.57 (s, 2H), 2.14 (s, 3H), 1.92 (m, 2H), 1.68 (m, 4H), 1.53 (s, 12H), 1.52 (s, 12H), 1.42 (s, 12H), 1.37 (s, 12H), 1.31 (s, 12H), 0.87 ppm (s, 12H). Elemental analysis calcd (%) for $\text{C}_{61}\text{H}_{114}\text{Mg}_2\text{N}_6\text{Na}_4$ (1072.19): C 68.33, N 7.82, H 10.72; found: C 68.33, N 7.74, H 11.00. M.p. 185 °C (decomp).

Reaction of **3** [or crystalline **3**] with I_2 : Iodine in THF (2.8 mL, 2.8 mmol) [3.5 mL, 3.5 mmol] was added to a suspension of **3** (0.7 mmol) [0.5 g, 0.44 mmol] in hexane (20 mL) [10 mL]. After stirring for 18 h, the mixture was quenched with saturated Na_2SO_4 solution (5 mL), saturated NH_4Cl solution (5 mL), distilled water (15 mL) and hexane (15 mL). The crude bilayer was filtered through celite into a separating funnel, with the aqueous layer subsequently discarded. The organic layer was then washed with distilled water (15 mL $\times$ 3), dried under anhydrous MgSO_4 for 1 h and then filtered through celite to produce a clear yellow solution. The solvent was then removed in vacuo and then dissolved in the minimum volume of hexane. The solution was purified by SiO_2 column chromatography using pure hexane as the eluant to give, after removal of solvent, 3,5-diiodotoluene as colorless oil (62.5 mg, 26%) [81.2 mg, 54.5%].

Reaction of a crude solution of **4** [or crystalline **4**] with I_2 : A solution of iodine in THF (4 mL, 4 mmol) [4.8 mL, 4.8 mmol] was added to a suspension of **4** (0.5 mmol) [0.64 g, 0.6 mmol] in hexane (20 mL) [10 mL]. The workup, following the procedure used for the reaction of **3** with I_2 , afforded 3,5-diiodotoluene as colorless oil (94.4 mg, 55%) [62.5 mg, 30%].

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- [12] Crystal data for **3**: $C_{61}H_{114}Mn_2N_6Na_4$, $M = 1133.4$, monoclinic, space group $P2_1/c$, $a = 29.375(6)$, $b = 8.4546(17)$, $c = 29.742(6)$ Å, $\beta = 117.14(3)^\circ$, $V = 6573(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.145$ g cm⁻³, $T = 150$ K, $\mu(\text{Mo}_{K\alpha}) = 0.45$ mm⁻¹ ($\lambda = 0.71073$ Å); 56250 reflections measured, 10225 unique, $R_{\text{int}} = 0.091$; $R(F, F^2 > 2\sigma) = 0.089$, $wR(F^2, \text{all data}) = 0.204$, $S(F^2) = 1.138$, 687 refined parameters, constrained H atoms, difference map extremes +0.36 and -0.59 e Å⁻³. Crystal data for **4**: $C_{61}H_{114}Mg_2N_6Na_4$, $M = 1072.2$, monoclinic, space group $C2/c$, $a = 30.194(6)$, $b = 8.4843(17)$, $c = 29.403(6)$ Å, $\beta = 118.85(3)^\circ$, $V = 6597(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.079$ g cm⁻³, $T = 150$ K, $\mu(\text{Mo}_{K\alpha}) = 0.10$ mm⁻¹; 15250 reflections measured, 5665 unique, $R_{\text{int}} = 0.059$; $R(F, F^2 > 2\sigma) = 0.068$, $wR(F^2, \text{all data}) = 0.126$, $S(F^2) = 1.071$, 344 refined parameters, constrained H atoms, difference map extremes +0.20 and -0.20 e Å⁻³. CCDC-675288 (**3**) and CCDC-675289 (**4**) contain the supplementary crystallographic data for this paper. These data 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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