

## Alkali-Metal-Mediated Manganation(II) of Naphthalenes: Constructing Metalla-Anthracene and Metalla-Phenanthrene Structures

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Alkali-metal-mediated manganation (AMMMn) reactions of the synergic base sodium monoalkyl-bisamidomanganate [(tmeda)Na(tmp)(CH<sub>2</sub>SiMe<sub>3</sub>)Mn(tmp)] (**1**) with naphthalene, 1-methoxynaphthalene, or 2-methoxynaphthalene are reported. These novel direct manganation [Mn(II)] reactions produced the crystalline ortho-manganated naphthyl products [(tmeda)Na(tmp)(2-C<sub>10</sub>H<sub>7</sub>)Mn(tmp)] (**3**), [(tmeda)Na(tmp){2-(1-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(CH<sub>2</sub>SiMe<sub>3</sub>)] (**4**), and [(tmeda)Na(tmp){3-(2-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(tmp)] (**5**) in reasonable to good isolated yields of 88, 65, and 85%, respectively. All three new complexes have been crystallographically characterized, showing discrete molecular structures with trigonal planar Mn centers forming  $\sigma$  bonds to the deprotonated C atoms of the naphthyl ligands, whereas Na interacts with the aromatic  $\pi$  system in **3** or with the MeO substituent in **4** and **5**. These latter interactions lead to interesting 5,6,7,8-tetrahydrophenanthrene-like and 1,2,3,4-tetrahydroanthracene-like metallacyclic motifs in **4** and **5**, respectively. The sensitivity of these AMMMn reactions to impurities has been illustrated in the serendipitous preparation of the benzenediide complex [(tmeda)<sub>2</sub>Na<sub>2</sub>(tmp)<sub>2</sub>(1,4-C<sub>6</sub>H<sub>4</sub>)Mn<sub>2</sub>(tmp)<sub>2</sub>] (**6**) from one attempted repeat synthesis of **5**. An “open inverse crown” arrangement with a 1,4-dimanganated benzene molecule is revealed in the crystal structure of **6**.

### Introduction

Synthetic chemists searching for new chemical reagents are being increasingly seduced by the charms of organomanganese(II) compounds. Part of the appeal lies in their superior stability to rival transition metal organometallics and their ability to function both stoichiometrically and catalytically. Other attractions especially important in the context of modern industrial chemistry are the relative cheapness, toxicological benignity, and high relative natural abundance of manganese metal, which is in plentiful supply globally in the form of high-grade ores.<sup>1</sup> Giants in the development of organomanganese(II) compounds in organic synthesis during the past 30 years, Cahiez and his co-workers Duplais and Buendia have recently penned an authoritative review<sup>2,3</sup> of this chemistry which provides an excellent introduction to newcomers to the area. Complementary to this organic research, more inorganic-focused structural work has recently been covered in another review by Layfield.<sup>4</sup>

Recently, we have contributed a new synthetic aspect to organomanganese(II) chemistry under the description alkali-metal-mediated manganation (AMMMn). Here accompanied by an alkali metal in structurally defined mixed-ligand (alkyl-amido) molecules, Mn(II) can perform direct metalations (manganations!) of aromatic compounds including benzene,<sup>5</sup> toluene,<sup>6</sup> anisole,<sup>7</sup> *N,N*-diisopropylbenzamide,<sup>7</sup> and ferrocene.<sup>8,9</sup> When separated from the alkali metal in conventional organomanganese(II) compounds, Mn(II) is inert to these weakly acidic C–H aromatic compounds.

In this paper, we extend AMMMn into the territory of naphthalene chemistry. Direct C–H metalation of this polycyclic aromatic hydrocarbon is challenging even with powerful polar organometallic reagents. Subjecting the parent

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unsubstituted hydrocarbon to *n*BuLi<sup>10,11</sup> or superbasic LICKOR<sup>12</sup> leads to nonselective mixtures of 1- and 2-monosubstituted naphthalenes as well as all 10 possible disubstituted isomers in the LICKOR case. This poor uncontrolled chemoselectivity has resulted in additional-step metal–halogen exchange reactions being the preferred method of choice for directly attaching a metal to a naphthalene framework.<sup>13,14</sup> Recently, however, we have shown that alkali-metal-mediated zincation (AMMZn) executed by the structurally authenticated sodium dialkyl-monoamido-zincate [(tmeda)Na(tmp)(*t*Bu)Zn(*t*Bu)]<sup>15</sup> (tmeda = *N,N,N',N'*-tetramethylethylenediamine, tmp = 2,2,6,6-tetramethylpiperidide) leads to the successful mono- and dizincation of naphthalene<sup>16</sup> with high chemoselectivity and stoichiometric control, allowing pure crystalline compounds retaining C–Zn bonds to be isolated in yields in excess of 50%.

Utilizing the sodium monoalkyl-bisamidomanganate [(tmeda)Na(tmp)(R)Mn(tmp)]<sup>5</sup> (1; R = CH<sub>2</sub>SiMe<sub>3</sub>), we report here the first direct manganation of naphthalene and its 1-methoxy or 2-methoxy substituted derivatives. Structural authentication of these novel (naphthalenide)C–Mn(II) bonded systems has been established via X-ray crystallographic studies of the resulting sodium naphthylmanganate products. Also reported is the unexpected fortuitous synthesis of a compound containing a 1,4-dimanganated benzene fragment in an “open inverse crown” structural arrangement.

## Experimental Section

All reactions were carried out under a protective argon atmosphere by using standard Schlenk techniques. The starting metal alkyl reagents Mn(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub><sup>17,18</sup> and BuNa<sup>19</sup> were made according to literature procedures. *n*-Hexane was dried by heating to reflux over solutions of sodium/benzophenone. Data for X-ray crystal structure determination were obtained at 150 K with a Bruker SMART 1K diffractometer and Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Selected crystallographic data for compounds 3–6 are given in Table 1. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyzer, and melting/decomposition points were measured with a Buchi Melting Point B-545 apparatus.

[(tmeda)Na(tmp)(2-C<sub>10</sub>H<sub>7</sub>)Mn(tmp)] (3). Na(tmp) was prepared in situ by the reaction of *n*BuNa (0.16 g, 2 mmol) with tmpH (0.34 mL, 2 mmol) in 20 mL of dry hexane. Mn(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (0.46 g, 2 mmol), tmpH (0.34 mL, 2 mmol), and tmeda (0.30 mL, 2 mmol) were then introduced, and the mixture was stirred for 15 min to afford a light yellow/orange solution. Naphthalene (0.256 g, 2 mmol) was

subsequently added, affording an orange solution that was stirred at room temperature for 12 h. A color change to red was observed, and the solution was concentrated by the removal of some solvent under a vacuum. Storage of the solution at room temperature afforded a crop of red plate crystals of 3 (0.76 g, 88%). Mp: 156.1 °C. Elem anal. calcd (%) for MnNaNa<sub>4</sub>C<sub>34</sub>H<sub>59</sub> (601.78): C, 67.85; H, 9.88; N, 9.31. Found: C, 67.12; H, 10.09; N, 8.98.

[(tmeda)Na(tmp){2-(1-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(CH<sub>2</sub>SiMe<sub>3</sub>)] (4). Na(tmp) was prepared in situ by the reaction of *n*BuNa (0.16 g, 2 mmol) with tmpH (0.34 mL, 2 mmol) in 20 mL of dry hexane. Mn(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (0.46 g, 2 mmol), tmpH (0.34 mL, 2 mmol), and tmeda (0.30 mL, 2 mmol) were then introduced, and the mixture was stirred for 15 min to afford a light yellow/orange solution. 1-Methoxynaphthalene (0.29 mL, 2 mmol) was added, and a color change to red was seen immediately. The reaction mixture was stirred at room temperature for 12 h. The resultant deep red solution was filtered and the filtrate concentrated by the removal of some solvent under a vacuum. A crop of red block crystals of 4 (0.75 g, 65%) was deposited upon storage of the solution in the refrigerator (5 °C). Mp: 122.2 °C. Elem anal. calcd (%) for MnNaOSi<sub>3</sub>C<sub>30</sub>H<sub>54</sub> (578.78): C, 62.26; H, 9.40; N, 7.26. Found: C, 62.33; H, 9.87; N, 6.94.

[(tmeda)Na(tmp){3-(2-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(tmp)] (5). Na(tmp) was prepared in situ by the reaction of *n*BuNa (0.16 g, 2 mmol) with tmpH (0.34 mL, 2 mmol) in 20 mL of dry hexane. Mn(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (0.46 g, 2 mmol), tmpH (0.34 mL, 2 mmol), and tmeda (0.30 mL, 2 mmol) were then introduced, and the mixture was stirred for 15 min to afford a light yellow/orange solution. Next, 2-methoxynaphthalene (0.32 g, 2 mmol) was added, and a color change to red was seen. The reaction mixture was stirred at room temperature for 12 h, filtered, and the filtrate concentrated by the removal of some solvent under a vacuum. A crop of red block crystals of 5 (1.07 g, 85%) was deposited upon storage of the solution at room temperature. Mp: 147.4 °C. Elem anal. calcd (%) for MnNaON<sub>4</sub>C<sub>35</sub>H<sub>61</sub> (631.81): C, 66.54; H, 9.73; N, 8.87. Found: C, 66.13; H, 10.12; N, 8.56.

[(tmeda)<sub>2</sub>Na<sub>2</sub>(tmp)<sub>2</sub>(1,4-C<sub>6</sub>H<sub>4</sub>)Mn<sub>2</sub>(tmp)<sub>2</sub>] (6). Following the same synthetic procedure as described for the synthesis of 5, compound 6 was fortuitously obtained from one repeat synthesis. Two types of crystals were observed during the crystallization process, namely, red block crystals identified by X-ray crystallography to be the previously synthesized 5 as the bulk material and a minor crop of yellow needle crystals identified as compound 6. Unfortunately, attempts to prepare 6 rationally have so far been unsuccessful.

**Reaction of Crude Solutions of 3, 4, and 5 with Iodine: General procedure.** I<sub>2</sub> (3 mL of 1 M THF solution, 3 mmol) was added to a crude hexane solution of 3, 4, or 5 (1 mmol). After stirring for 18 h at room temperature, the mixture was quenched with saturated Na<sub>2</sub>SO<sub>4</sub> (10 mL). The crude bilayer was filtered through Celite into a separating funnel and the aqueous layer subsequently discarded. The organic layer was washed with brine (10 mL) and distilled water (3 × 10 mL) and dried under anhydrous MgSO<sub>4</sub> for 1 h and filtered through Celite to produce a transparent light yellow solution. The solvent was removed in vacuo to give a yellow oil which was purified by SiO<sub>2</sub> column chromatography with hexane/ethylacetate (23:2) as the eluent to give the respective iodonaphthalene.

2-Iodonaphthalene as a white solid (3) (23.1 mg, 45%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  8.03 (br, s, 1H), 7.72 (m, 4H), 7.31 (m, 2H).

2-Iodo-1-methoxynaphthalene as an oily solid (4) (20.3 mg, 38%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  8.36 (d, 1H), 7.98 (d, 1H), 7.61 (d, 1H), 7.47–7.22 (m, 2H), 6.94 (d, 1H), 3.59 (s, 3H).

3-Iodo-2-methoxynaphthalene as an off-white solid (5) (27.3 mg, 51%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C)  $\delta$  = 7.73 (s, br, 1H), 7.70–7.65 (m, 2H), 7.37 (m, 1H), 7.24 (m, 1H), 7.03 (s, br, 1H) 3.52 (s, 3H).

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Table 1. Selected Crystallographic Data for Compounds 3, 4, 5, and 6

	3	4	5	6
formula	C <sub>34</sub> H <sub>59</sub> MnN <sub>4</sub> Na	C <sub>30</sub> H <sub>54</sub> MnN <sub>3</sub> NaOSi	C <sub>35</sub> H <sub>61</sub> MnN <sub>4</sub> NaO	C <sub>54</sub> H <sub>108</sub> Mn <sub>2</sub> N <sub>8</sub> Na <sub>2</sub>
<i>M<sub>r</sub></i> (g mol <sup>-1</sup> )	601.8	578.8	631.8	1025.3
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	11.432(4)	9.736(3)	32.418(7)	8.333(3)
<i>b</i> (Å)	19.935(7)	11.466(3)	11.587(3)	22.027(7)
<i>c</i> (Å)	30.932(10)	15.810(4)	19.770(4)	16.320(5)
$\alpha$ (deg)		78.302(4)		
$\beta$ (deg)		79.619(4)	99.003(4)	91.466(5)
$\gamma$ (deg)		84.163(4)		
<i>V</i> (Å <sup>3</sup> )	7049(4)	1696.0(7)	7335(3)	2994.3(17)
<i>Z</i>	8	2	8	2
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.134	1.133	1.144	1.137
$\mu$ (mm <sup>-1</sup> )	0.413	0.462	0.402	0.475
measured reflns	48024	12089	12721	20471
ind. reflns	6130	5866	6355	5207
<i>R</i> <sub>int</sub>	0.055	0.016	0.021	0.029
obsd reflns <sup>a</sup>	4007	5059	5245	4966
refined params	452	346	392	310
<i>R</i> <sup>b</sup> (observed data)	0.079	0.042	0.040	0.077
<i>R</i> <sub>w</sub> <sup>c</sup> (all data)	0.238	0.118	0.105	0.158
goodness of fit <sup>d</sup>	1.03	1.03	1.04	1.52
max/min el dens (e Å <sup>-3</sup> )	+0.86/−0.77	+0.70/−0.49	+0.59/−0.36	+0.46/−0.76

<sup>a</sup>Observation criterion:  $F^2 > 2\sigma(F^2)$ . <sup>b</sup> $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>c</sup> $R_w = \{\sum [w(F^2_o - F^2_c)^2] / \sum [w(F^2_o)^2]\}^{1/2}$ . <sup>d</sup>Goodness of fit =  $\{\sum [w(F^2_o - F^2_c)^2] / (\text{no. of data} - \text{no. of params})\}^{1/2}$ .

## Results and Discussion

The amido-rich manganate **1** was used as the AMMMn reagent in all of the reactions reported here due to its previous success in manganating a range of monocyclic aromatic substrates.<sup>5,7</sup> A solution of **1** prepared in situ in hexane solvent was reacted with one molar equivalent of either naphthalene (**2a**), 1-methoxynaphthalene (**2b**), or 2-methoxynaphthalene (**2c**) (Scheme 1) at room temperature, resulting in a bright red solution in all three cases. Storage of these solutions at room temperature or in a refrigerator (5 °C) afforded isolable red crystalline products that were analyzed by X-ray crystallography. These studies revealed the respective products to be [(tmeda)Na(tmp)(2-C<sub>10</sub>H<sub>7</sub>)Mn(tmp)] (**3**), [(tmeda)Na(tmp){2-(1-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(CH<sub>2</sub>SiMe<sub>3</sub>)] (**4**), and [(tmeda)Na(tmp){3-(2-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(tmp)] (**5**). The isolated crystalline yields obtained were 88%, 65%, and 85%, respectively. During one attempt to repeat the synthesis of **5**, the unexpected product [(tmeda)<sub>2</sub>Na<sub>2</sub>(tmp)<sub>2</sub>(1,4-C<sub>6</sub>H<sub>4</sub>)Mn<sub>2</sub>(tmp)<sub>2</sub>] (**6**) containing a 1,4-dimetalated benzene ring was fortuitously prepared and subsequently isolated and structurally characterized.

In the first three planned cases, the polycyclic aromatic substrates have been successfully regioselectively deprotonated, with each having a Mn(II) atom now occupying the vacated hydrogen site in either the 2 position for complexes **3** and **4** or the 3 position for complex **5**. To the best of our knowledge, these three structures represent products of the first examples of direct manganation reactions using Mn(II) sources of substituted and unsubstituted naphthalenes, or indeed of any polycyclic aromatic hydrocarbons. There is seemingly a significant distinction in the reactivity of base **1** toward the different naphthalenes. To explain, **1** possesses a heteroleptic formulation which in theory means it could behave in an amido (tmp) or alkyl (Me<sub>3</sub>SiCH<sub>2</sub>) deprotonative fashion, or indeed both. This choice in basicity is observed in practice in the reactions of **1** with substrates **2a**, **2b**, and **2c** or at least in the nature of the crystalline products isolated from

solution. When **1** is reacted with substrates **2a** and **2c**, it behaves ultimately as an alkyl base, generating a tetramethylsilane coproduct as well as manganate **3** or **5**, respectively, both of which possess a bisamido-monoaryl composition. In contrast, the reaction with substrate **2b** shows the alternative basicity with **1** acting as an amido base to give the novel heterotriamionic monoalkyl–monoamido–monoaryl complex **4** with a concomitant loss of tmpH. These results establish that **1** is a versatile manganating reagent with a ligand transfer switch (potentially tunable to alkyl or amido) dependent on conditions and possibly on the nature of the polycyclic aromatic substrate. Interestingly, we have observed this switch in basicity before when **1** was reacted with the functionalized arenes anisole<sup>7</sup> and *N,N*-diisopropylbenzamide.<sup>7</sup> Clearly distinct mechanisms must therefore be available to **1** in its reactions with aromatic substrates. Due to the paramagnetic nature of high-spin d<sup>5</sup> manganese(II), conventional NMR spectroscopy cannot be used for the characterization of **1** or any of its Mn(II)-containing products, making monitoring possible reaction pathways more challenging. Thermodynamically, the loss of volatile Me<sub>4</sub>Si from such manganations is likely to be greatly preferred. Recently, investigations by Uchiyama et al.<sup>20–24</sup> have shown that similarly composed lithium or sodium dialkyl-tmp-zincates investigated via DFT calculations will preferentially deprotonate organic substrates in two steps: in step 1, the tmp abstracts a proton from the substrate to form tmpH; in step 2, tmpH is deprotonated to revert back to the tmp anion and rejoins (or never leaves) the heterometallic structure

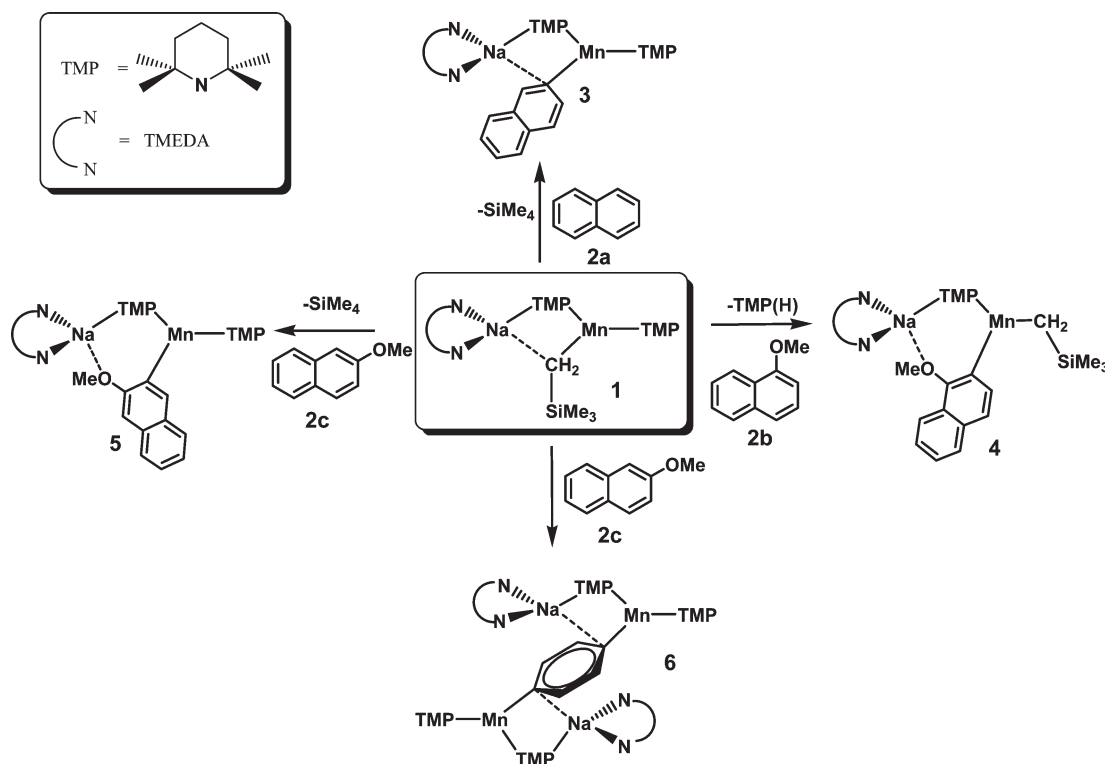
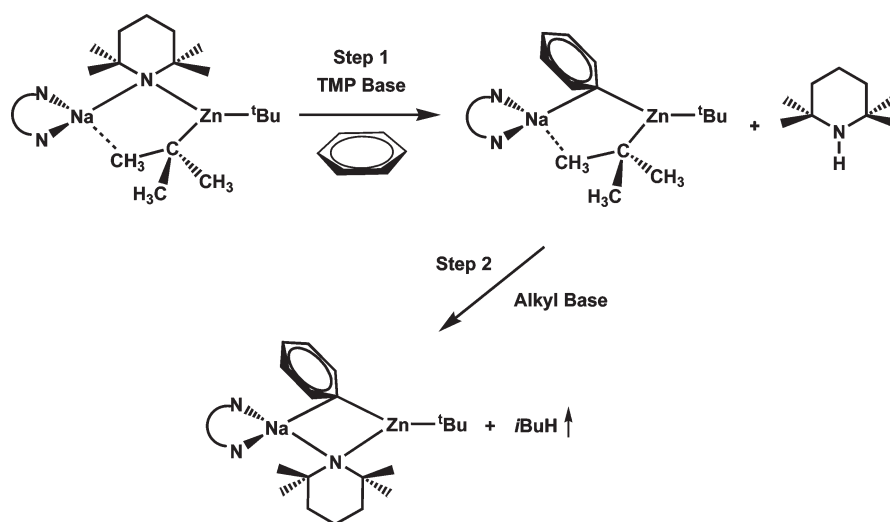
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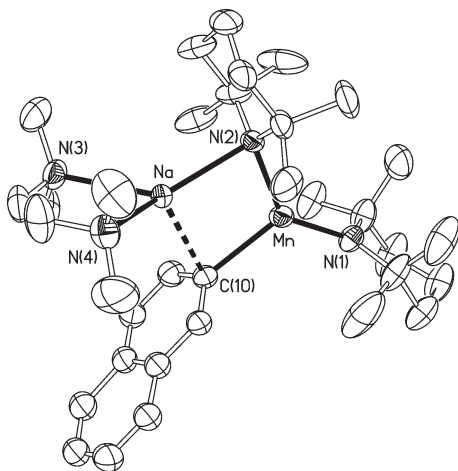
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Scheme 1. Reactivity of Manganate Base **1** Towards Polycyclic Aromatic Compounds **2a**, **2b**, and **2c**Scheme 2. Proposed Two-Step Reaction Pathway for the AMM $Zn$  of Benzene

with an irreversible elimination of alkane, showing an overall alkyl basicity (Scheme 2). Admittedly, this zincate work cannot be directly compared to the manganate work discussed here as the heterobimetallic base used by Uchiyama et al. [ $\text{LiZn}(\text{tmp})\text{tBu}_2$ ]<sup>22</sup> possesses a 2:1 alkyl/amido stoichiometry in contrast to reagent **1**, where the stoichiometry is reversed. Clearly, the factors governing whether an alkali-metal-mediated metalation follows a kinetic (amido-basicity) or thermodynamic (alkyl basicity) path are subtle, and changing the substrate to be deprotonated can lead to a modification in the transition structure that can apparently tip the balance in favor of one path or the other. Several more substituted naphthalenes would have to be subjected to AMM $Mn$  before any definitive conclusions related to the nature of the substrate could be drawn.

**Solid State Structures.** The successful growth of crystalline material from all four reactions allowed useful structural information of products **3–6** to be obtained. Unfortunately, due to 2-fold positional disorder of the naphthalene ligand of **3**, which required constraints and restraints for its successful resolution, bond lengths and angles in this structure are less precise. However, the connectivity of **3** is definite and therefore can be discussed, and the observed bond lengths and angles around the metal atoms are consistent with those of the other, more precise, structures discussed later. Categorized as a contact ion pair, **3** (Figure 1) displays a trigonal planar  $\text{Mn(II)}$  coordination (involving N, N, and C atoms) comprising two tmp ligands, one terminal and one

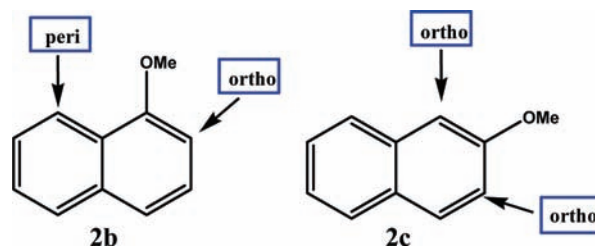


**Figure 1.** Molecular structure of **3** with selective atom labeling and 30% probability displacement ellipsoids. Hydrogen atoms and one disorder component of the naphthyl ligand have been omitted for clarity.

bridging, and a C(10) (2 position) deprotonated naphthyl ring system. Defining this metalation reaction as a manganation, the deprotonated naphthyl atom C(10) makes a  $\sigma$  bond with the Mn(II) atom. The Na atom also engages with this deprotonated atom but in more of a perpendicular fashion (with respect to the naphthyl ring plane) to the  $\pi$  system. Counting this long-range interaction (shown as a dashed line in Figure 1), Na features in a four-element central ring (NaCMnN) including the bridging tmp ligand. A tmeda ligand completes the distorted tetrahedral coordination around sodium. To the best of our knowledge, **3** represents the first structurally characterized example of a Mn(II) metalated naphthalene molecule. On searching the Cambridge Structural Database,<sup>25</sup> only two other structures containing Mn and naphthalene have been structurally characterized, namely, PPN[Mn( $\eta^4$ -C<sub>10</sub>H<sub>8</sub>)(CO)<sub>3</sub>]<sup>26</sup> [(PPN = (Ph<sub>3</sub>PNPh<sub>3</sub>)] and the mixed Fe/Mn zwitterionic complex ( $\eta^4, \eta^6$ -naphthalene)Mn(CO)<sub>3</sub>FeCp.<sup>27</sup> However, these two Mn(I) complexes are not products of direct (or indirect) metalation; instead, the Mn(I) is  $\pi$ -coordinated by the reductively activated naphthalene ligand, which retains all of its hydrogen atoms. Moreover, there are only three previous mixed-metal structures containing Na and naphthalene ligands. These are the closely related mono- and dinuclear complexes [(tmeda)Na(tmp)(2-C<sub>10</sub>H<sub>7</sub>)Zn(*t*Bu)] and [(tmeda)<sub>2</sub>Na<sub>2</sub>(tmp)<sub>2</sub>( $\mu$ -2,6-C<sub>10</sub>H<sub>6</sub>)Zn<sub>2</sub>(*t*Bu)<sub>2</sub>],<sup>16</sup> respectively, which show the same regioselective metalation of naphthalene in the 2 position and the remotely related lutetium complex [{(C<sub>5</sub>Me<sub>5</sub>Lu)<sub>3</sub>(C<sub>10</sub>H<sub>8</sub>)(C<sub>10</sub>H<sub>7</sub>)(H)}][Na(thf)<sub>3</sub>]<sub>2</sub>C<sub>10</sub>H<sub>8</sub>.<sup>28</sup> Therefore, complex **3** represents the first structure containing the specific combination of Na, Mn, and a naphthalide ligand.

Following the success of directly manganating the parent naphthalene, it was decided to test the metalating ability of the synergic base toward the functionalized

**Scheme 3.** Possible Metalation Sites for 1-Methoxynaphthalene (**2b**) and 2-Methoxynaphthalene (**2c**)



methoxy-naphthalene isomers **2b** and **2c**. In conventional metalation chemistry, the electron-donating methoxy functional group, here in the 1 or 2 position of the naphthalene ring, can (weakly) direct the metalation in two main positions, namely, (i) ortho to the functional group, as the proton is sufficiently acidified by the inductive effect of the oxygen as well as close enough to the lone-pair-containing functional group to allow dative coordination of the metalating reagent, or (ii) peri to the functional group, which is possible only in the case of **2b**. Note that there are two possible ortho positions (1 and 3 on the ring) available in **2c** (Scheme 3).

When the same synthetic protocol as successfully practiced before with naphthalene was repeated, the synergic base **1** was reacted with one molar equivalent of **2b** or **2c** in a hexane solution. After 4 h of stirring at room temperature, dark red solutions were afforded. Crystallization proved problematic, as often a microcrystalline dark red solid formed that was unsuitable for X-ray crystallography. However, increasing the solvent volume and allowing the reaction mixture to stand at room temperature or in a refrigerator for one week allowed the growth of red block crystals that were subsequently identified by X-ray crystallography to be the new ortho-manganated compounds [(tmeda)Na(tmp){2-(1-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(CH<sub>2</sub>SiMe<sub>3</sub>)] (**4**) and [(tmeda)Na(tmp){3-(2-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(tmp)] (**5**).

The molecular structures of **4** and **5** (Figures 2 and 3, respectively) share a common structural motif of a six-membered central ring. The Mn adopts a trigonal planar coordination (made up of C, N, and C atoms in **4** and N, N, and C atoms in **5**) comprising one terminal (CH<sub>2</sub>SiMe<sub>3</sub> in **4**, tmp in **5**) and two bridging ligands (tmp and an ortho-deprotonated methoxynaphthalene in both). A  $\sigma$  bond is formed between the deprotonated C atom [C(14) in **4**; C(19) in **5**] on the naphthalene ring system and Mn, defining the metalation reactions that produced these complexes as manganations (that is, Mn–H exchange). Na, in contrast, interacts with the deprotonated naphthalene ligand through the O heteroatom of its substituent to form a six-membered, five-element (NaNMnCCO) ring in both **4** and **5**. The core of each structure is therefore made up of three fused rings, with **4** resembling a 5,6,7,8-tetrahydrophenanthrene metallacycle and **5** a 1,2,3,4-tetrahydroanthracene metallacycle (Scheme 4). Counting the tmp bridge and tmeda chelation of Na, **4** and **5** both contain five fused rings overall. Table 2 lists the key structural dimensions of **4** and **5**, along with those of **6**.

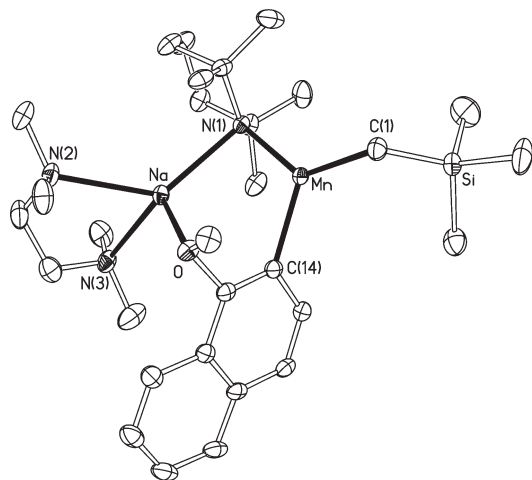
To the best of our knowledge, **4** and **5** represent the first structurally characterized examples of Mn(II) methoxy-naphthalenes and in fact appear to be the first structurally

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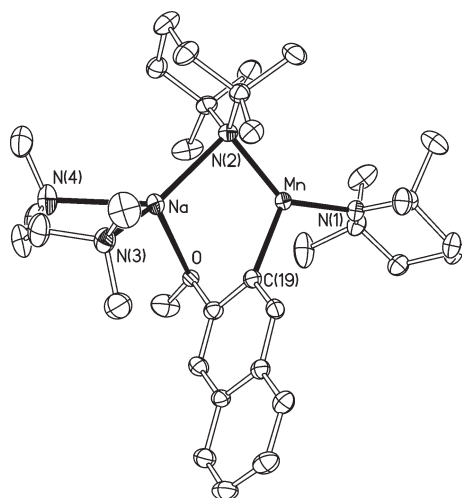
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**Figure 2.** Molecular structure of **4** with selective atom labeling and 30% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

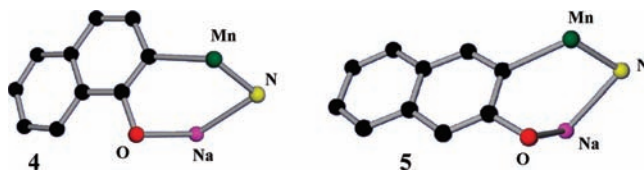


**Figure 3.** Molecular structure of **5** with selective atom labeling and 30% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

characterized 2- or 3-metallated methoxynaphthalenes of any metal in the periodic table. There has been some literature by Mannschreck and Kiefl<sup>29</sup> on the direct metalation of 1-methoxynaphthalene followed by Li–Mn(II) exchange and further reactions with electrophiles, where they propose an ortho-manganated 1-methoxynaphthalene as an intermediate; however, they stress that the structures of these Mn(II) compounds are not yet known.

On further searching the Cambridge Structural Database,<sup>25</sup> it can be seen that the best comparisons for **4** and **5** are provided by the monocyclic ortho-manganated anisole complex [(tmeda)Na(tmp)(*o*-C<sub>6</sub>H<sub>4</sub>OMe)Mn(tmp)]<sup>7</sup> (**7**) and the remotely related peri-lithiated dimer (1-methoxy-8-naphthylithium·THF)<sub>2</sub>(THF)<sub>2</sub> (**8**).<sup>30</sup> There are also some NMR spectroscopic and DFT-calculational studies<sup>31</sup> on the regioselective lithiation of 1-methoxynaphthalene, but as of yet no structurally characterized

**Scheme 4.** Ring Frameworks of Phenanthrene-Like **4** and Anthracene-Like **5**



**Table 2.** Selected Bond Lengths [Å] and Bond Angles [deg] for **4**, **5**, and **6**

	<b>4</b>	<b>5</b>	<b>6</b>
Mn–N (tmp)	2.0789(19)	2.1059(17) <sup>a</sup> 2.0220(17) <sup>b</sup>	2.125(3) <sup>a</sup> 2.029(3) <sup>b</sup>
Mn–C (R)	2.141(2)		
Mn–C (aryl)	2.177(2)	2.201(2)	2.185(4)
Na–N (tmp)	2.497(2)	2.4981(19)	2.454(14)
Na–O	2.4174(18)	2.6843(19)	
N–Mn–N		134.96(7)	135.13(14)
N–Mn–C (R)	129.29(9)		
N–Mn–C (aryl)	111.60(8)	110.84(7) <sup>a</sup> 114.12(8) <sup>b</sup>	104.75(13) <sup>a</sup> 120.12(12) <sup>b</sup>
C–Mn–C	118.31(9)		
O–Na–N (tmp)	104.99(6)	93.49(6) <sup>a</sup>	
O–Na–N (tmeda)	98.87(7) <sup>c</sup>	120.00(6) <sup>d</sup>	
O–Na–N (tmeda)	106.98(7) <sup>d</sup>	104.47(7) <sup>e</sup>	
(tmeda)N–Na–N (tmeda)	74.01(8)	73.37(7)	73.87(13)
(tmp)N–Na–N (tmeda)	129.47(8) <sup>c</sup>	136.11(7) <sup>a,d</sup>	135.03(13) <sup>a,d</sup>
(tmp)N–Na–N (tmeda)	135.79(8) <sup>d</sup>	128.01(8) <sup>a,e</sup>	130.86(13) <sup>a,e</sup>

<sup>a</sup> Bridging. <sup>b</sup> Terminal. <sup>c</sup> N(2) of tmeda. <sup>d</sup> N(3) of tmeda. <sup>e</sup> N(4) of tmeda.

ortho-metallated complexes are available for comparison. The Mn–C(aryl) distance in **7** [2.189(2) Å] lies between those found in **4** [2.177(2) Å] and **5** [2.201(2) Å]. The Mn(II) atom lies almost coplanar with the aryl ring system in complexes **4** and **5** (deviation: 0.106 Å, **4**; 0.426 Å, **5**), comparing favorably to that found in compound **7** (deviation 0.558 Å), which has the same six-membered, five-element central ring (NaNMnCCO) as that in **4** and **5**. These metallocyclic rings which make up the pseudophenanthrene and pseudoanthracene arrangements are highly puckered; Na and N(1) lie out of the naphthyl plane by 2.373 and 1.976 Å, respectively, in **4**, and Na and N(2) lie out of the naphthyl plane by 2.404 and 1.335 Å in **5**. In **8**, the 1-methoxynaphthalene molecule is lithiated, not ortho to the methoxy group but peri with a Li–C(aryl) distance of 2.162(5) Å. This difference in metalation position (peri- in **8** compared to ortho- in **4** and **5**) causes a smaller five-membered central (OCCCLi) ring to form, which lies coplanar with the naphthyl system.

Interestingly, the selective metalation of 1-methoxynaphthalene in either the 2 or 8 position (ortho and peri respectively) has been extensively studied. According to Shirley and Cheng,<sup>32</sup> the metalation can be regioselectively controlled by changing the metalation reagent. Employing an equimolar *n*BuLi/tmeda mixture and quenching with solid CO<sub>2</sub> results selectively in greater than 99% carbonylation in position 2 (59% overall yield), whereas reaction with *t*BuLi and subsequent quenching leads to greater than 98% carbonylation in the 8 position (but in a poorer 20–35% overall yield). When the selectivity of our synergic base **1** is compared to these precedent literature methods, good regioselectivity can

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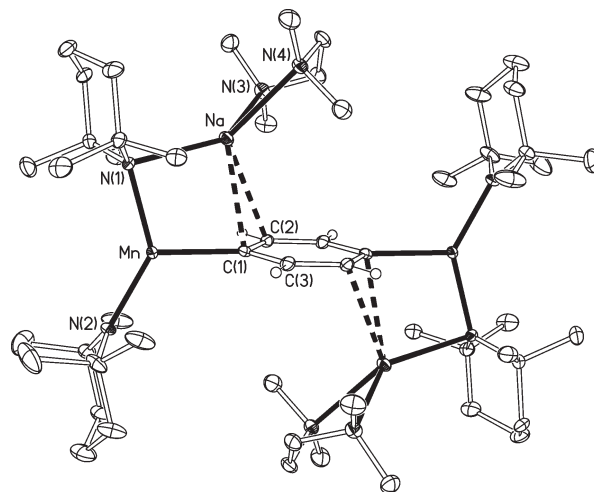
(32) Shirley, D. A.; Cheng, C. F. *J. Organomet. Chem.* **1969**, 20, 251.

also be achieved in the 2 position with 1-methoxynaphthalene and in the 3 position with 2-methoxynaphthalene, with both being isolated in respectable crystalline yields of up to 85% and 65%, respectively. From these results, our base (**1**) compares favorably with the aforementioned *n*BuLi and *t*BuLi methodologies, offering an alternative method of metalation. Next, we subjected compounds **3**, **4**, and **5** to electrophilic quenching reactions with iodine where their metal substitution patterns were confirmed by the formation of 2-iodonaphthalene, 2-iodo-1-methoxynaphthalene, and 3-iodo-2-methoxynaphthalene after aqueous workup in isolated yields of 45%, 38%, and 51%, respectively.

When synthesizing these air- and moisture-sensitive naphthalenide complexes, the purity of the starting reagents and solvents as well as a rigorous exclusion of oxygen in the system is important. This came to mind during one repeat synthesis of **5**, when two types of crystalline product were observed, namely, a crop of red block crystals and a few yellow needles (note that complex **5** is red). X-ray crystallography confirmed the red block crystals to be the known complex **5**; however, surprisingly the yellow needles were determined to be the 1,4-dimetalated benzene species  $[(\text{tmeda})_2\text{Na}_2(\text{tmp})_2(1,4\text{-C}_6\text{H}_4)\text{-Mn}_2(\text{tmp})_2]$  (**6**). The unexpected presence of a benzene-derived molecule could be explained by trace amounts of benzene contaminating the starting material 2-methoxynaphthalene. More often than not, commercial aromatic compounds contain trace amounts of benzene, and due to **6** being the minor product of the reaction, this would seem the most plausible explanation for its presence. Unfortunately, all attempts to date to synthesize **6** rationally have led to the exclusive formation of the previously reported monomanganated phenyl compound  $[(\text{tmeda})\text{Na}(\text{tmp})(\text{C}_6\text{H}_5)\text{Mn}(\text{tmp})]$ ,<sup>5</sup> even when a 2- or 4-fold excess of the synergic base was used.

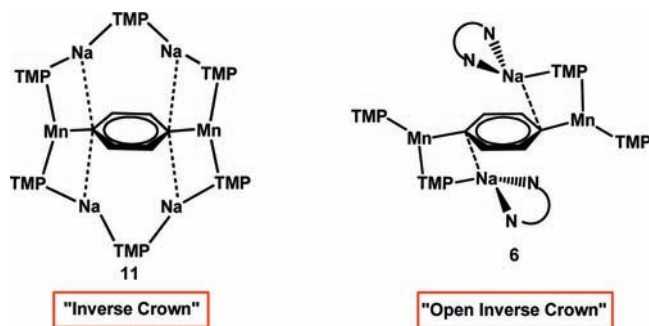
The centrosymmetric molecular structure of **6** (Figure 4 and Table 2) contains a trigonal planar Mn(II) atom with a terminal tmp, a bridging tmp, and a bridging dideprotonated benzene ligand. The last named ligand has lost its two hydrogen atoms from the sterically optimal 1 and 4 positions, which are now occupied by Mn(II) atoms. In the coordination sphere of Na, a bridging tmp is seen along with the chelating bidentate ligand tmeda. More ionic than manganese, the alkali-metal satisfies its coordination demands by also interacting electrostatically with the  $\pi$  system of the benzene ring in an  $\eta^2$  manner through the C1 and C2 positions [lengths, Na–C(1) = 2.688(4) Å, Na–C(2) = 2.859(4) Å], with the former bond inclined at an angle of 71.1° to the aromatic ring plane.

Complex **6** is isostructural to the magnesium and zinc complexes  $[(\text{tmeda})_2\text{Na}_2(\text{tmp})_2(1,4\text{-C}_6\text{H}_4)\text{Mg}_2(\text{tmp})_2]$  (**9**) and  $[(\text{tmeda})_2\text{Na}_2(\mu\text{-tmp})_2(1,4\text{-C}_6\text{H}_4)\text{Zn}_2(\text{tBu})_2]$  (**10**) previously made within our laboratory.<sup>33</sup> Consistent with the relative metal sizes, the Mn–C(aryl) distance in **6** [2.185(4) Å] compares favorably to the Mg–C(aryl) (2.179(4) Å) distance in **9** but is somewhat longer than its zinc counterpart in **10** (2.0657(18) Å). In all three



**Figure 4.** Molecular structure of **6** with selective atom labeling and 30% probability displacement ellipsoids. Na interactions with the  $\pi$  system are denoted as dashed lines. Hydrogen atoms (except benzenediide ones) have been omitted for clarity.

**Scheme 5.** Comparison of Benzene-Based “Inverse Crown” and “Open Inverse Crown” Structural Arrangements



compounds, the Na atom prefers to interact with the benzene ring in an  $\eta^2$  fashion to give relatively short but weaker contacts to the C1 and C2 atoms in the benzene ring (Na–C average lengths: 2.774 Å (**6**), 2.772 Å (**9**), and 2.767 Å (**10**)). The common motif in **6**, **9**, and **10** can be viewed as an “open inverse crown” arrangement with the benzenediide ring encapsulated in the center and dideprotonated selectively in the 1 and 4 positions. This structural arrangement differs from the conventional “inverse crown” structure<sup>6,34</sup> where an additional two units of Na(tmp) allow the formation of a closed 12-membered (NaNNaNMN) ring (M = Mn or Mg) containing the dideprotonated anionic guest (benzene in Scheme 5). The dimanganation of benzene in the 1 and 4 positions has been previously reported by our group in the form of the inverse crown complex  $[\text{Na}_4\text{Mn}_2(\text{tmp})_6(\text{C}_6\text{H}_4)]$  (**11**).<sup>5</sup> In both the “open” and the “closed” inverse crown structural arrangements, the Mn–C(aryl) distances compare favorably [2.185(4) Å in **6** and 2.201(2) Å in **11**]; however, one noteworthy difference is in the tmp–Mn–tmp angle. In the closed inverse crown (**11**), both the tmp ligands are bridging to give an angle of 145.74(17)°. In **6**, there is one bridging tmp and one

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terminal tmp ligand, which results in a significantly smaller angle of 135.13(14)°.

### Conclusions

AMMMn has been extended to polycyclic aromatic hydrocarbon substrates, with three new selectively ortho-manganated naphthyl complexes [(tmeda)Na(tmp)(2-C<sub>10</sub>H<sub>7</sub>)Mn(tmp)] (**3**), [(tmeda)Na(tmp){2-(1-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(CH<sub>2</sub>SiMe<sub>3</sub>)] (**4**), and [(tmeda)Na(tmp){3-(2-MeOC<sub>10</sub>H<sub>6</sub>)}Mn(tmp)] (**5**) being crystallographically characterized. These results highlight the efficiency of the synergic base system at achieving metalations that would otherwise not be possible with conventional organomanganese(II) reagents, allowing the generation of metallacyclic products that resemble pseudophenanthrene (**4**) and pseudoanthracene (**5**) arrangements. In fact, the base's potency is best displayed in that unsubstituted (and therefore unactivated) naphthalene can successfully undergo regioselective metalation at room temperature and in an almost quantitative yield. Investigating the structural changes that accompany the Mn(II)–H exchange reactions shows that the synergic reagent can ultimately function as an

alkyl or amido-base depending on the specific substrate. The sensitivity of these organometallic mixed-metal-based reactions to impurities has been displayed in the serendipitous synthesis of the benzenediide complex [(tmeda)<sub>2</sub>Na<sub>2</sub>(tmp)<sub>2</sub>(1,4-C<sub>6</sub>H<sub>4</sub>)Mn<sub>2</sub>(tmp)<sub>2</sub>] (**6**) in which a molecule of benzene has been selectively dimanganated in the 1 and 4 positions. Collectively, these results help to broaden the new and emerging scope of AMMMn in synthesizing new compounds with novel structures in organomanganese(II) chemistry.

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**Supporting Information Available:** Full crystallographic data in CIF format for compounds **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.