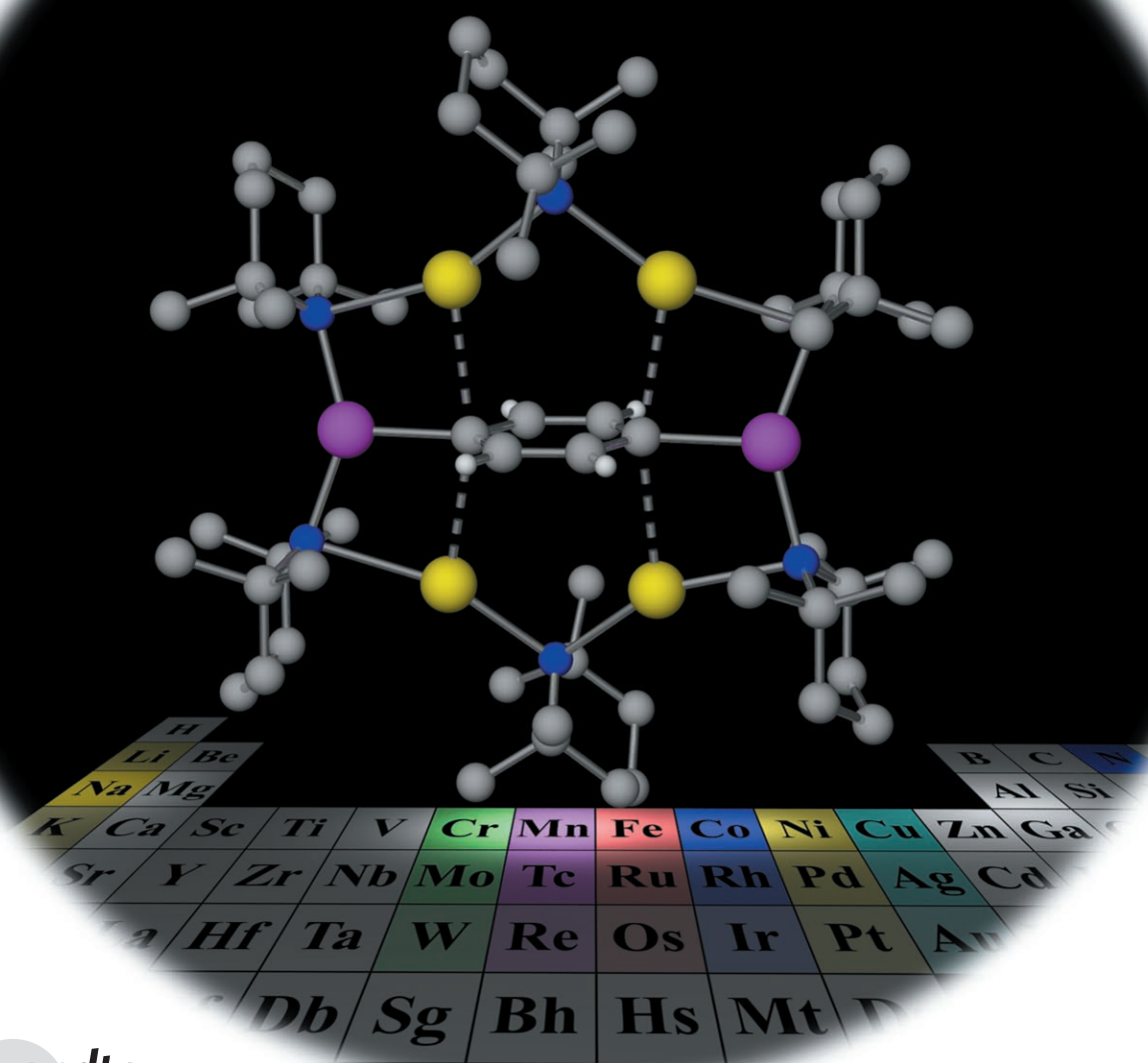


Sodium-Mediated Manganoxylation: Direct Mono- and Dimanganoxylation of Benzene and Synthesis of a Transition-Metal Inverse-Crown Complex**

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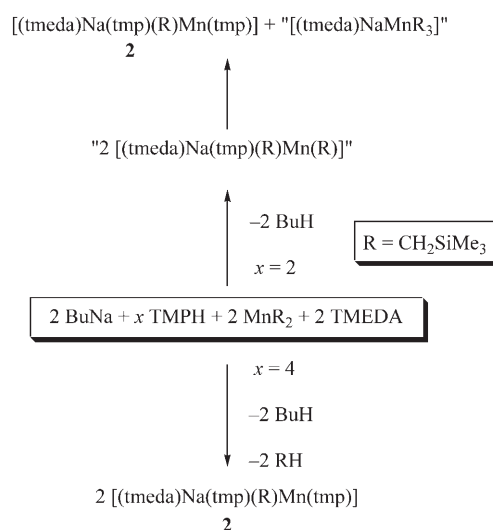
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Recently, we introduced the concept of alkali-metal-mediated manganation (AMMMn).^[1] The first transition-metal example of a developing new metalation strategy that started with magnesiation and zincation,^[2] AMMMn establishes a method for *directly* attaching Mn^{II} atoms to aromatic frameworks, as illustrated through ferrocene. The reagent designed to effect AMMMn was the lithium bisalkyl-monoamido manganate [(tmeda)Li(tmp)(R)Mn(R)] (**1**, tmeda = *N,N,N',N'*-tetramethyl-1,2-diamine, tmp = 2,2,6,6-tetramethylpiperidide, R = CH₂SiMe₃), so the reaction was a lithium-mediated manganation. As alkali-metal effects are a common feature of this chemistry, with sodium-magnesium and sodium-zinc cooperativity often more effective than the corresponding lithium-based cooperativity,^[2] it was desirable to develop a complementary sodium-mediated manganation. This desire became all the more urgent since our follow-up work^[3] has revealed that **1** cannot manganate toluene under the conditions studied (a 1:1 stoichiometric mixture in hexane heated for two hours). Devising a method for directly manganating (with Mn^{II} atoms) arenes would be a valuable addition to the synthetic chemists' repertoire, thereby opening the way to new organomanganese(II) compounds and potentially many novel structures. Hitherto there has been no systematic way of accomplishing this, although in an early report^[4] Wilkinson and co-workers proposed that the neophyl dimer [Mn₂(CH₂CMe₂Ph)₄] thermally decomposed through an intramolecular *ortho* manganation to generate [{MnCH₂CMe₂(C₆H₄)₂]₂] with elimination of *tert*-butylbenzene. To date, manganate(II) arenes have generally been made indirectly by transmetalation of lithiated or magnesiated arenes with Mn^{II} halides,^[5] but this method has limited scope, mainly because of the poor solubility of halide salts in common organic solvents. In contrast, (direct) cyclomanganation of substituted, donor-activated arenes by Mn^I reagents such as R'Mn(CO)₅ (R' = Me, CH₂Ph, etc) is a well-documented methodology.^[6]

With this background, the present study initially had two principal aims: 1) to design a sodium-manganese alkylamido

reagent akin to lithium reagent **1**, and 2) to utilize this new reagent and derivatives thereof in reactions with arenes to establish the concept of sodium-mediated manganation. If successful in these aims, the burning question to be answered next was: could we exploit this new modification of AMMMn to build the first inverse crown^[7] ring system in which the transition-metal atoms form part of the host?

A marked effect of changing from lithium to sodium in the attempted preparation of the target reagent was immediately apparent. Following the procedure for the preparation of **1**, but substituting NaTMP for LiTMP, led to the isolation of the monoalkyl-bisamido product [(tmeda)Na(tmp)(R)Mn(tmp)] (**2**, Scheme 1), and not the anticipated bis(alkyl)monoamide.



Scheme 1. Synthesis of the sodium-manganese monoalkyl bisamido reagent **2** by dismutation (top) and directly (bottom).

This finding suggests that the anticipated product [(tmeda)Na(tmp)(R)Mn(R)] is unstable with respect to dismutation, thereby generating **2** and the putative all-alkyl co-product [(tmeda)NaMnR₃] which remains in solution. Introduction of an extra equivalent of TMPH to the reaction mixture resulted in dismutation being avoided and **2** being accessible in a higher yield. As determined by X-ray crystallographic analysis,^[8] structurally **2** (Figure 1) fits the design template (established with **1**) that appears to prime the molecule for executing synergic manganation. Most importantly, the coordinatively unsaturated three-coordinate Mn atom is enriched with three (potentially) strong basic limbs (1 terminal tmp, 1 bridging tmp, and 1 bridging R ligand) connected through mixed N,C bridges to the Na center, the debilitating intermolecular bonding tendencies of which are overcome by N,N chelation of the tmeda ligand. Although this molecular connectivity is definite, disorder in two of the ligands makes it inappropriate to discuss the dimensions involved (see the Supporting Information for bond lengths/bond angles).

We elected to test the second aim with benzene. This choice may have appeared unrealistically ambitious given the

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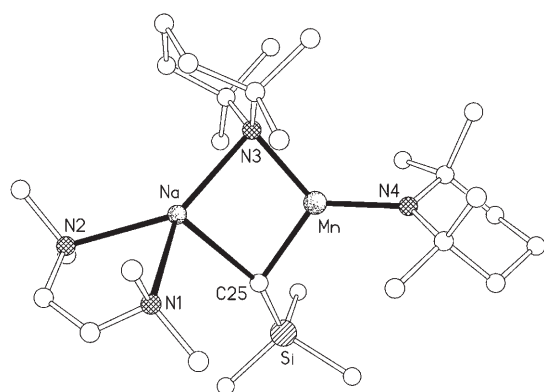


Figure 1. Molecular structure of **2** with selective atom labeling. Hydrogen atoms and minor disorder components are omitted for clarity.

low acidity and lack of substitution/donor activation of benzene, but previous work had established that it succumbs to synergic sodium-mediated magnesiation and zincation.^[9] Thus, **2** was prepared in situ in hexane, a stoichiometric amount of benzene was added, and the solution was heated for eight hours. The reaction (Scheme 2) progressed with a pale pink to yellow color change to produce the new aryl manganate [(tmeda)Na(tmp)(Ph)Mn(tmp)] (**3**), which was isolated as yellow needle crystals in a good yield of 61 %. Having successfully deprotonated the benzene ring stoichiometrically to a C_6H_5^- ion, sodium-mediated manganation was

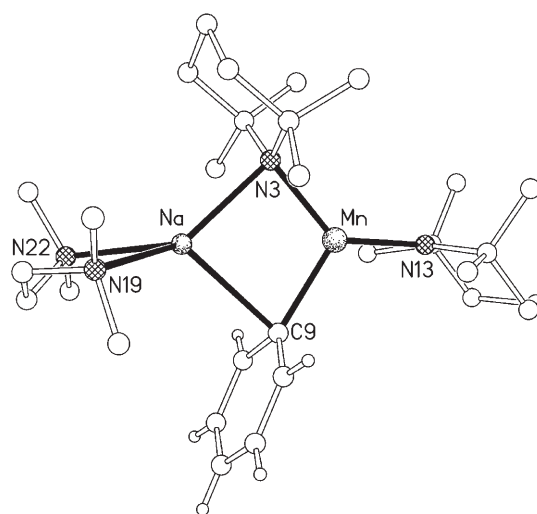
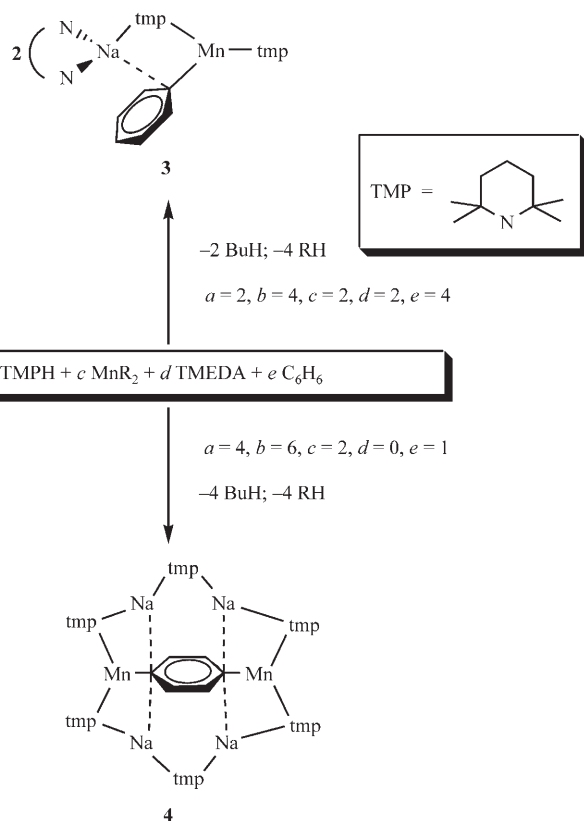


Figure 2. Molecular structure of **3** with selective atom labeling. Hydrogen atoms (except arene ones) are omitted for clarity.

allows the deprotonation reaction to be defined in lucid structural terms. Essentially, the stronger base R bridging the Na and Mn atoms has been selectively expelled in favor of the incoming weaker base Ph which occupies the same bridging position, while there is retention of the molecular connectivity of the [(tmeda)Na(μ -tmp)Mn(tmp)] unit. The most interesting geometrical feature of **3** is how the incoming Ph group engages differently with the Mn and Na atoms. The Mn center lies almost coplanar with the aryl ring plane (deviation 0.339 Å) and interacts strongly with the *ipso*-C9 atom (bond length: 2.207(4) Å), whereas the Na–C9 bond inclined at an angle of 72.7° to this plane is much weaker (bond length: 2.731(4) Å). This finding implies a σ (covalent)/cation– π (electrostatic) distinction to the Mn–/Na–arene bonding, thus echoing that found in the alkali-metal–Mg–, or Zn–arene complexes.^[2]

Logically, if benzene yields to AMMMn then substituted, donor-activated aromatic compounds should be even more submissive to this new manganation methodology. That idea clearly represents a promising line of research for future development, but to conclude the present study we pondered, given the close structural/bonding similarities between **3** and the sodium-magnesium areneide [(tmeda)Na(tmp)(Ph)Mg(tmp)],^[11] whether a manganese inverse crown complex could be synthesized. Arene-based inverse crown compounds are known for alkali-metal/Mg partnerships,^[2] but conspicuously not as yet for alkali-metal/Zn partnerships.

As tmeda chelation could compete with aggregation, the diamine was omitted from our exploratory reaction mixture to make the inverse crown complex, which consisted of BuNa, TMPH, MnR_2 , and benzene in a 4:6:2:1 stoichiometry



Scheme 2. Mono- (top) and dimanganation (bottom) of benzene using sodium-mediated manganation to generate **3** and **4**, respectively.

(Scheme 2). This reaction produced yellow needle crystals of $[\text{Na}_4\text{Mn}_2(\text{tmp})_6(\text{C}_6\text{H}_4)]$ (**4**), which were characterized by X-ray crystallography^[12] as the first inverse crown complex in which the host is comprised of transition metal atoms (Figure 3). This example demonstrates the first direct diman-

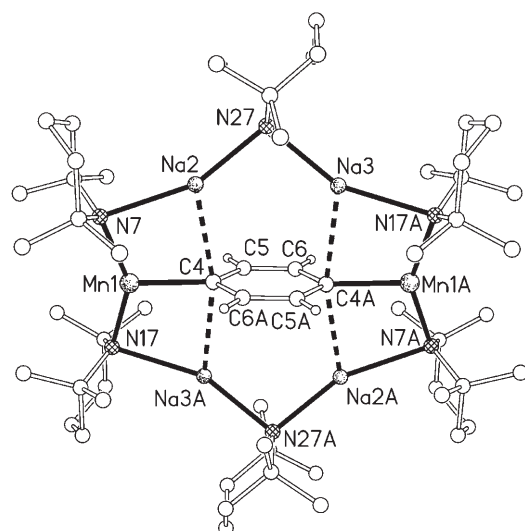


Figure 3. Molecular structure of **4** with selective atom labeling. Hydrogen atoms (except arene ones) are omitted for clarity. Symmetry operator A: $2-x$, $1-y$, $-z$.

ganation of an arene:^[13] in this case the benzene ring has been regioselectively doubly deprotonated at the sterically minimizing 1,4-positions. Synthetically this represents an advance on the preparation of the related Mg inverse crown complex $[\text{Na}_4\text{Mg}_2(\text{tmp})_6(\text{C}_6\text{H}_4)]$ (**5**), as it cannot be prepared in the same rational stoichiometric manner, but requires a vast excess of benzene and a 1:1 Na/Mg ratio of reactants. Isostructural to **5**, the centrosymmetric molecule of **4** comprises a 12-atom $\{(\text{NaNNaNMnN})_2\}$ “host” ring, which is severely puckered, and an encapsulated benzenediide “guest”. The Mn atoms are coplanar with the arene ring plane (deviations ± 0.085 Å) and replace the outgoing H atoms in bonding to the C4/C4A atoms (2.201(2) Å), whereas the Na atoms, which are situated almost orthogonal to the arene ring plane (at 79.6 and 85.2°) form longer, weaker contacts to the same C atoms (Na2-C4: 2.710(2) Å, Na3-C4A: 2.715(2) Å). This pattern which fits the σ/π distinction in the bonding noted for **3**, mimics that in **5** (corresponding bond lengths: Mg-C: 2.192(5) Å, Na-C: 2.689(5) Å, 2.676(5) Å). Of course, what this structural similarity between **4** and **5** masks is the far greater breadth of new chemical opportunities open to the transition metal Mn than to its s-block rival Mg. Clear possibilities exist within redox chemistry, catalysis (there is current interest in Mn^{II} complexes for olefin polymerization),^[15] and magnetochemistry. As regards the last point, unlike **5**, **4** is paramagnetic as evident from our failure to collect useful NMR spectra.

The magnetic properties of the inverse crown complex was explored by variable-temperature magnetization measurements on a powdered sample of **4** (Figure 4).^[20] Using the

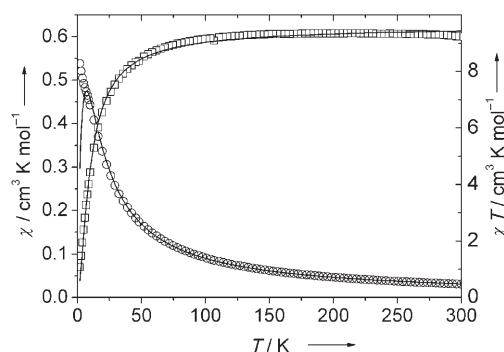


Figure 4. Molar susceptibility ($\square$) and $\chi_M T$ ($\circ$) versus T for **4**.

spin Hamiltonian $\mathcal{H} = -2JS_1S_2$ the susceptibility data were simulated satisfactorily with $S_1 = S_2 = 5/2$, $J = -0.70$ cm⁻¹ and $g = 2.05$. An additional small paramagnetic impurity of 4.4% corresponding to an $S = 5/2$ species had to be taken into account.

As, to our knowledge, no previous magnetic investigations on benzene-bridged dimanganese compounds are reported in the literature, the observed magnetic exchange has to be rationalized using the spin polarization mechanism. The model developed by Longuet-Higgins^[16] predicts that an alternant hydrocarbon contains $x = (N - 2T)$ nonbonding molecular orbitals (NBMOs) in which N is the number of carbon atoms and T is the maximum number of double bonds, thus the *para* isomer of the metalated benzene ring can be drawn with a maximum number of four double bonds and as a consequence there are zero NBMOs, and therefore a singlet spin state arises. In the model of spin polarization developed by Ovchinnikov^[17] on the basis of full MO calculations, including configuration interaction, the sign of the spin densities on neighboring carbon atoms alternates. Spin polarization can be rationalized by inspection of a molecular bond between atoms of a conjugated molecule. Electrons in the π orbital and σ orbital on one atom will have similar spin orientations as a consequence of more favorable exchange. Since the σ orbital also contains an electron of the neighboring atom it must have an antiparallel alignment (Pauli's principle) that results in a π electron with the opposite spin at the other atom.

Thus, the exchange interaction in **4** is expected to be antiferromagnetic in nature, as observed experimentally. The magnitude of the spin exchange interaction between the two manganese(II) atoms by way of the benzene ligand can be best compared to pyrazine-bridged Mn^{II} ions, which show smaller magnetic exchange interactions of -0.47 cm⁻¹ and -0.34 cm⁻¹, for $[\text{Mn}_2(\text{hfac})_4(\text{pyz})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ ^[18] (Hhfac = hexafluoroacetylacetone) and $[\text{L}[\text{Mn}(\text{hfac})_2]_2]$ with $\text{L} = 2,3$ -di(2-pyridyl)pyrazine,^[19] respectively, as expected considering the coordination of the lone pair of electrons on the nitrogen atom to the metal ions.

In conclusion, the first inverse crown complex in which transition-metal atoms form part of the host, coincidentally the first magnetic inverse crown complex, has been synthesized and structurally characterized.

Experimental Section

All reactions were carried out under a protective argon atmosphere.

2: A 1:1 mixture of NaTMP and HTMP was made by addition of HTMP (0.68 mL, 4.0 mmol) to a suspension of BuNa (0.16 g, 2.0 mmol) in *n*-hexane (20 mL). After stirring the mixture for 30 min, Mn(CH₂SiMe₃)₂ (0.46 g, 2.0 mmol) was added. Subsequently, a molar equivalent of TMEDA (0.30 mL, 2.0 mmol) was added and the pale yellow solution was stirred for another 30 min. The solution was concentrated by removing some solvent under vacuum, and the crystallized product redissolved by warming the solution. After cooling down the solution, a crop of pink plates was deposited (0.60 g, 53 %), m.p. 134 °C.

3: Following the same procedure described above for **2**, Mn(CH₂SiMe₃)₂ (0.46 g, 2 mmol) was added to a mixture of NaTMP (2.0 mmol) and TMPH (2.0 mmol) in hexane (20 mL) followed by the addition of a molar equivalent of TMEDA (0.30 mL, 2.0 mmol). Next, benzene (0.18 mL, 2.0 mmol) was introduced and the resulting solution was heated under reflux for 8 h. First a color change to a deep yellow, then a fine precipitation could be observed. By using two equivalents of benzene (0.36 mL, 2.0 mmol), the crystallization could be improved to get yellow needles after storing the solution at –27 °C overnight (0.67 g, 61 %). m.p. > 155 °C (decomp).

4: BuNa (0.16 g, 2.0 mmol) was suspended in *n*-hexane (10 mL) and sonicated for 10 minutes to form a fine dispersion. TMPH (0.51 mL, 2.0 mmol) was added and the creamy, white suspension formed was allowed to stir for 1 h. Mn(CH₂SiMe₃)₂ (0.23 g, 2.0 mmol) was added to give a pink/brown solution which was stirred for around 45 min before benzene (0.5 mL, 0.5 mmol) was added. A small amount of precipitation occurred, but this dissolved after gentle heating for about 5 min. The translucent, brown solution which formed was left in a Dewar flask of hot water overnight and a large crop of yellow, needlelike crystals formed (0.32 g, 57.2 %), m.p. 160 °C.

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