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# Alkali-Metal-Mediated Manganation: A Method for Directly Attaching Manganese(II) Centers to Aromatic Frameworks**

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A keystone methodology in synthetic chemistry, metalation (metal–hydrogen exchange) reactions of aromatic compounds are usually the domain of highly reactive polar organometallics such as alkyllithium compounds, LICKOR (alkyllithium compounds cocomplexed with potassium *tert*-butoxide) superbases, or lithium amides.[1] Strictly these reactions are lithiations (or potassiations) as the incoming lithium atom (or potassium atom) takes the place of the outgoing hydrogen atom. The lower-polarity metals magnesium, zinc, and aluminum generally form slow-reacting metalating agents which are ineffective towards aromatic compounds. Therefore, to attach these less reactive metals directly to an aromatic scaffold, the lithiated aromatic compound must be synthesized beforehand and then an additional metathetical reaction often involving a metal halide (for example, RMgX, $ZnX_2$, or $R_2AlX$) has to be carried out. The presence of the ionic halide often limits the range of solvents available for such reactions with hydrocarbons and arenes, which are generally ruled out in favor of polar substitutes (commonly ether or THF). Recently, however, it has been shown that pairing lithium (or another alkali metal) with one of these inferior multivalent metals in the same organometallic molecule (an "-ate" formulation), can generate "synergic", mixed-metal reagents capable of directly magnesiating,[2,3] zincating,[3] or aluminating[4] aromatic substrates, thus circumventing the need for a subsequent metathesis. In addition to this new inorganic (metal) perspective, these synergic reagents can open up new organic horizons by promoting unusual regioselective deprotonations (for example, *meta*-orientated in the cases of toluene[5] and *N*,*N*-dimethylaniline[6]) or special polydeprotonations (for example, 2,6-twofold in the case of naphthalene[7] and 1,1′,3,3′-fourfold in the cases of ferrocene and its Group 8 homologues[8]).

This Communication addresses the question, "could this developing idea of alkali-metal-mediated metalation, established with the main-group/pseudo-main-group s-electron metals Mg, Zn, and Al, be extended to other categories of metal?" Incorporating a transition metal as the divalent partner would be especially attractive, for it would potentially open up a treasure chest of new chemistry given the much greater breadth of properties (for example, redox, magnetic, catalytic) available to a bona fide d-block element. Herein, we report our success in this endeavor with the Group 7 metal manganese.

Our first task was to design a suitable mixed alkali-metal/manganese(II) reagent in the mould of, for example, [(tmeda)Na(tmp)(*t*Bu)Zn(*t*Bu)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, tmp = 2,2,6,6-tetramethylpiperidide),[9] which has proved extremely adept at accomplishing alkali-metal-mediated zincation (AMMZ) of aromatic substrates. Conscious of the general instability of organomanganese(II) compounds, we selected the known[10] thermally stable (no β-H decomposition pathway is possible) neutral dialkyl complex $[(MnR_2)_\infty]$ (**1**; $R = CH_2SiMe_3$) as the $Mn^{II}$ source. Another important aspect of the design strategy was to use a bulky amide coligand that would help suppress coordination of a fourth ligand at the Mn center (with R alone, the four-coordinate ate complex "$Li_2MnR_4$" is produced[10]). Power reported[11] a precedent in the tris(silylamide) $[(thf)LiMn(hmds)_3]$ (hmds = $N(SiMe_3)_2$) with a three-coordinate, trigonal-planar Mn center, but we opted for the enhanced basicity of the tmp ligand, a key component of many magnesiate and zincate bases.[3] The final design criterion was to include tmeda, primarily to prevent polymerization at the Li center. Experimentally (Scheme 1), this design was realized by mixing together $MnR_2$, LiTMP, and TMEDA to afford the heteroleptic alkyl/amido manganate reagent [(tmeda)Li(tmp)(R)Mn(R)] (**2**) in 67% yield as a crystalline product. Paramagnetic and thus not amenable to a useful NMR spectroscopic study, **2** was characterized by X-ray crystallography. Its molecular structure (Figure 1)[12] fits the connectivity template of certain magnesiate and zincate metalating reagents, thus auguring well for its potential to effect alkali-metal-mediated manganation (AMMMn). Thus, the Mn center has a distorted trigonal-planar $C_2N$ coordination (sum of bond angles: 358.09°) comprising one tmp and two R ligands. Slightly more pyramidal (sum of bond angles: 353.51°), the $N_3$ coordination of the Li center is made up of one tmp ligand and one bidentate tmeda ligand. The distinct metal centers are connected by a tmp bridge (through the N atom) with nearly equal span lengths (N−Li 2.066(5) Å, N−Mn 2.116(2) Å). The N1-Mn-C1 bond angle (128.62(11)°) is larger than the theoretical 120° for a trigonal-planar Mn center, and concomitantly the N1-Mn-C5 bond angle (108.85(10)°) is smaller.

Though this narrowing might be construed as signifying an interaction between C5 and Li, the long separation involved

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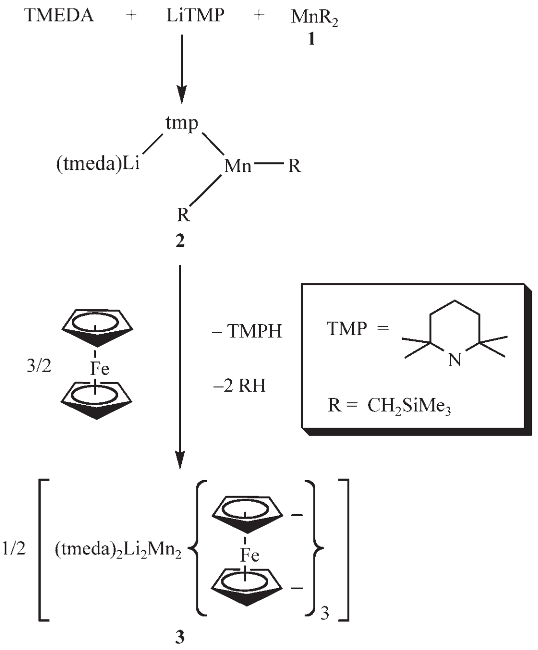

***Scheme 1.*** Synthesis of the reactive "open" mixed lithium/manganese reagent **2** and its manganation reaction with ferrocene.

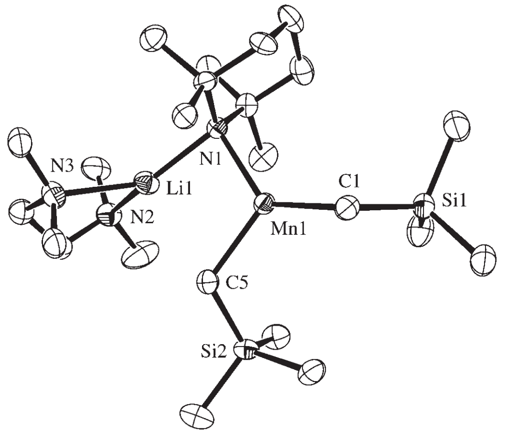

***Figure 1.*** Molecular structure of **2** with selective atom labeling; thermal ellipsoids are shown at 50% probability. Hydrogen atoms and minor disorder components are omitted for clarity.

(2.742(6) Å), coupled with the near equivalency of the Mn–C5 and Mn–C1 bond lengths (2.159(3), 2.140(3) Å), suggests that any interaction is minimal. The core of **2** is therefore best regarded as an open dinuclear LiNMnC arrangement. A similar open LiNZnC arrangement was noted in the related zincate [(tmta)Li(hmds)(R)Zn(R)][13] (tmta = 1,3,5-trimethyl-1,3,5-triazinane), with a corresponding Li···C separation of 2.736 Å. To the best of our knowledge, **2** represents the first alkali-metal mixed alkyl/amido complex of $Mn^{II}$ to be structurally characterized. Aside from aforementioned [(thf)LiMn(hmds)$_3$], the only other alkali-metal amide complex of $Mn^{II}$ to be crystallographically characterized is sodium-rich $[Na_2Mn(NPh_2)_4]\cdot 2\,C_7H_8$,[14] which has a three-dimensional lattice structure.

We chose ferrocene as the substrate for testing the manganating ability of **2** as it has hitherto never been metalated directly by $Mn^{II}$,[15,16] nor have any manganated ferrocene crystal structures been reported previously. Avoiding the use of an ethereal solvent (the standard solvent system employed in metathesis reactions), we treated a freshly prepared solution of **2** in hexane with ferrocene (several stoichiometries were explored, but a 2:3 base/ferrocene molar ratio proved optimal). The isolated product was $[(tmeda)_2Li_2Mn_2\{Fe(C_5H_4)_2\}_3]$ (**3**) in a best yield of 82.6% (Scheme 1). Ferrocene has been twofold deprotonated (in the 1,1′-positions) in **3** and is thus the first substrate to undergo AMMMn. The high yield of **3** reveals that **2** must function as a stoichiometrically efficient, tribasic dialkyl/monoamido reagent towards ferrocene. In the context of alkali-metal-mediated metalation, this reaction represents unprecedented reactivity for any metal–metal partnership. TMP–magnesiate reagents usually function only as monoalkyl bases, while only in the cases of anisole[17] and *N,N*-diisopropylbenzamide[18] have lithium TMP–zincates functioned at a dibasic level (as dialkyl and monoalkyl/monoamido reagents, respectively).

The molecular structure of **3** (Figure 2)[19] consists of three 1,1′-ferrocenediyl fragments connected by two $Mn^{II}$ and two tmeda-chelated $Li^+$ cations. Two of the ferrocenediyl fragments (with Fe1 and Fe1*) are symmetry-equivalent owing to a twofold rotation axis running through Fe2 and bisecting the Mn···Mn centerline. This pair of ferrocenediyl groups acts as a bidentate ligand to each Mn center through the deprotonated C11 and C21 atoms, while the unique ferrocenediyl (with Fe2) acts as a monodentate, bridging ligand to both Mn atoms through the deprotonated C31/C31* atoms. Collectively, this arrangement means that the Mn center has a distorted tetrahedral environment (range of bond angles: 95.21(14)–125.70(13)°) that is made up of four Mn–C bonds (range of

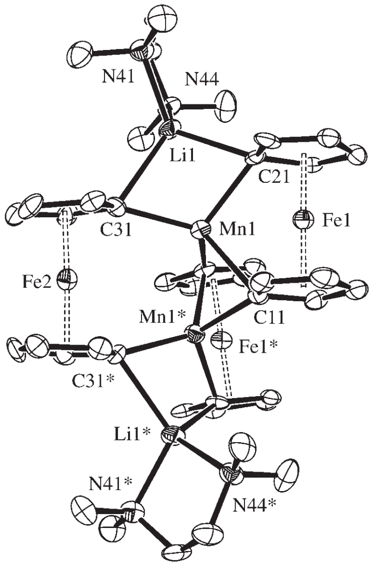

***Figure 2.*** Molecular structure of **3** with selective atom labeling; thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

bond lengths: 2.135(3)–2.320(3) Å) involving all three ferrocenediyl fragments. The Mn$\cdots$Mn separation is 2.5197(11) Å. The distorted tetrahedral Li center binds to one C atom of two distinct ferrocenediyl groups (Li−C21 2.243(7) Å, Li−C31 2.375(7) Å) and to two tmeda N atoms (Li−N44 2.120(6) Å, Li−N41 2.034(7) Å). This structure is unique for manganese, but beyond manganese, a few other compounds with three ferrocenediyl fragments are known. Among them is the magnesiate $[(\text{pyridine})_2\text{Li}_2(\text{tmp})_2\text{Mg}_3\{\text{Fe}(\text{C}_5\text{H}_4)_2\}_3]$,[20] which in comparison to **3** has an extra divalent metal atom (Mg) to balance the extra tmp anions. The lower nuclearity of **3** could reflect the use of bidentate tmeda versus monodentate pyridine, though it may be that the manganese base **2** that was used to form **3** is simply more effective than its magnesium counterpart (formed from *n*BuLi/$\text{Bu}_2\text{Mg}$/3TMPH). A closer analogy is the pentanuclear $\text{Fe}^{\text{II}}$ cluster $[(\text{tmeda})_2\text{Li}_2\text{Fe}_2\{\text{Fe}(\text{C}_5\text{H}_4)_2\}_3]$,[21] but significantly it was synthesized by the classical metathesis approach (Li precursor with $\text{FeCl}_2$) in a reaction requiring two days (compared with only two hours for **3**).

In summary, this paper introduces a new bimetallic lithium/manganese(II) reagent that is superior to related alkali-metal magnesiate and zincate reagents in utilizing all three of its ligand arms as bases. As illustrated with ferrocene, this reagent can directly attach $\text{Mn}^{\text{II}}$ centers to aromatic scaffolds, in contrast to $\text{MnR}_2$ alone (with or without TMEDA), which is inert towards ferrocene. Hence, this reactivity is best described as AMMMn. Clearly this promising development opens up a new gateway to aromatic organomanganese(II) compounds. Moreover, if the concept could be cultivated further with other divalent transition metals such as $\text{Cr}^{\text{II}}$, $\text{Fe}^{\text{II}}$, $\text{Co}^{\text{II}}$, $\text{Ni}^{\text{II}}$, and so on, then it would greatly enrich the landscape of metalation chemistry.

## Experimental Section

All reactions were carried out in a protective argon atmosphere.

**2**: $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (0.46 g, 2 mmol) was added to a solution of LiTMP in hexane, which had been prepared in situ by reaction of BuLi (1.25 mL, 1.6 M in hexane) with TMPH (0.34 mL, 2 mmol) in hexane (20 mL). The resulting suspension was allowed to stir for 30 min. Subsequently, a molar equivalent of TMEDA (2.0 mmol, 0.30 mL) was added and the pale yellow solution was stirred for another 30 min. The solution was concentrated by removing some solvent in a vacuum and placed in the freezer (−27 °C). A crop of pink crystals was deposited overnight (0.66 g, 67 %). M.p. 105 °C.

**3**: By the same procedure described above for **2**, $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (0.46 g, 2 mmol) was added to a solution of LiTMP (2 mmol) in hexane (20 mL), and a molar equivalent of TMEDA (2 mmol, 0.30 mL) was subsequently added. Ferrocene (0.56 g, 3 mmol) was introduced and the resulting yellow solution was heated at reflux for two hours. First a color change to red, then a precipitation could be observed. The cold solution was filtered and the solid was washed with hexane (20 mL; by $^1$H NMR spectroscopy the coproducts $\text{SiMe}_4$ ($\delta = 0.00$ ppm) and TMPH ($\delta = 1.06$ ppm) could be detected in the filtrate). After the product had been dried under vacuum, a red-brown crystalline powder could be isolated (0.75 g, 82.6 %). To obtain crystals suitable for X-ray crystallography, the reaction was carried out with half amounts of the reagents in 40 mL hexane. The resulting solution was placed in the refrigerator (0 °C) for two weeks. A crop of brown crystals was deposited (0.30 g, 65.2 %). The powder and the crystals showed identical IR spectra. Decomposition temperature > 190 °C.

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[12] Crystal data for **2**: $\text{C}_{23}\text{H}_{56}\text{LiMnN}_3\text{Si}_2$, $M_r = 492.77$, approximate crystal dimensions $0.45 \times 0.20 \times 0.10$ mm$^3$, orthorhombic, space group $P2_12_12_1$, $a = 10.2961(6)$, $b = 15.7003(10)$, $c = 19.1253(13)$ Å, $V = 3091.6(3)$ Å$^3$, $T = 123$ K, $Z = 4$, $\rho_{\text{calcd}} = 1.059$ Mg m$^{-3}$, $2\theta_{\text{max}} = 54.22°$, $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.71073$ Å). All structures were solved and refined to convergence on $F^2$ (SHELXS and SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany). $R1 = 0.0464$ (for 4819 reflections with $I > 2\sigma(I)$), $wR2 = 0.0787$ and $S = 1.021$ for 300 parameters and 6642 unique reflections. Minimum/maximum residual electron density $-0.246/0.267$ e Å$^{-3}$. CCDC-626422 and 626423 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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[19] Crystal data for **3**: $C_{42}H_{56}Fe_3Li_2Mn_2N_4$, $M_r = 908.22$, approximate dimensions of crystal fragment $0.35 \times 0.20 \times 0.20$ mm$^3$, monoclinic, space group *C*2/*c*, $a = 21.534(1)$, $b = 10.616(1)$, $c = 17.833(1)$ Å, $\beta = 97{,}928(2)°$, $V = 4037.7(5)$ Å$^3$, $T = 123$ K, $Z = 4$, $\rho_{calcd} = 1.494$ Mg m$^{-3}$, $2\theta_{max} = 52.02°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Intensities were corrected for twinning effects (180° rotation about *a* axis). $R1 = 0.0584$ (for 5239 reflections with $I > 2\sigma(I)$), $wR2 = 11.03$ and $S = 1.052$ for 245 parameters and 7666 unique reflections. Minimum/maximum residual electron density $-0.568/0.552$ e Å$^{-3}$.

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