Direct regioselective exchange of H by Mn$^{II}$R on aromatic C–H frameworks is normally impossible owing to the low polarity (low basicity) of conventional organometallic manganese(II) compounds MnR$_2$. Indirect, two-step syntheses involving prior preparation of a polar organometallic compound (commonly an organolithium species) and subsequent metathesis with a Mn$^{III}$ salt have proved suitable for some aryl Mn$^{III}$ compounds$[^3]$ but this approach has significant limitations$[^2]$. However, we recently introduced the concept of alkali-metal-mediated manganation (AMMMn), a method for directly manganating aromatic molecules with Mn$^{II}$R units$[^2]$. Direct mono- and 1,4-dimanganation of benzene was accomplished using the sodium alkyl amidomanganate complex [(tmeda)Na(tmp)(R)Mn(tmp)] (tmeda = N,N$^\prime$,N$^\prime$-tetramethyl-1,2-diamine, tmp = 2,2,6,6-tetramethylpiperidide, R = CH$_2$SiMe$_3$) or (for dimanganation) an in situ mixture of BuNa, tmpH, and MnR$_2$ (in a 4:6:2 ratio) to afford [(tmeda)Na(tmp)(C$_6$H$_5$)Mn(tmp)] and the inverse crown complex [Na$_4$Mn$_2$(tmp)$_6$(C$_6$H$_4$)] (1), respectively.$[^3]$ If this bimetallic methodology were generally applicable to the chemistry of divalent transition metals, or at least extendable to several such metals (alkali-metal-mediated organotransitionmetalation (AMMO) could be an apt collective term for this type of reaction), then this type of reaction would add significantly to the synthetic chemist’s repertoire. Therefore, we have studied chromium and iron, the nearest neighbors of manganese, in the context of AMMO. Known homometallic chemistry suggests that metalating successfully with Cr or Fe represents a major challenge. Gambarotta and co-workers forewarn about “the remarkable chemical inertness of CrR$_2$ towards proton agents”, observing no reactivity even with carboxylic acids, phenols, and so forth, in a study of homoleptic Cr alkyl species.$[^4]$ An added reservation in the case of FeR$_2$ is the need for Lewis base stabilization (i.e., [LFeR$_2$]). Chirik and co-workers reported a crystallographically characterized example in which L is the chiral bidentate nitrogen donor (-)-sparteine.$[^5]$ Would such “prechelation” diminish the ability of FeR$_2$ to generate the desired mixed-metal products? As detailed herein, in practice, both Cr–H and Fe–H exchange reactions have been successfully accomplished.

Beginning with Cr, we first had to synthesize known homoleptic CrR$_2$, made previously by metathesis between LiR and [thf$_2$CrCl$_2$] in hexane solution (Scheme 1).$[^4,6]$ NMR spectroscopy confirmed the purity of the CrR$_2$ compound.$[^7]$ Next, we attempted to synthesize an alkyl amidochromate compound by directly combining CrR$_2$, Natmp, and tmeda (Scheme 1), reasoning that the diamine would accelerate cleavage of tetranuclear CrR$_2$, thus rendering it labile. The...
reaction did not proceed stoichiometrically to [(tmeda)Na-(tmp)(R)Cr(R)] but to the monoalkyl bisamidochromate complex [(tmeda)Na[tmp](R)Cr(tmp)] (2). This amide-rich product indicates that a dismutation has occurred; the likely coproduct is a trisalkyl chromate compound. Interestingly, previous attempts to prepare a CrII tmp species have led to oxidation to [Cr(tmp)3] [8].

Figure 1 shows the molecular structure of 2 as determined by an X-ray crystallographic study. [9] The CrII ion is surrounded by a distorted trigonal plane of one R (Cr–C 2.172(2) Å) and two tmp ligands, with the Cr–N2 bridge (2.0971(18) Å) being significantly longer than its terminal counterpart (Cr–N1 1.9782(18) Å). One N–C edge of the CrCN2 triangle is presented unsymmetrically to Na, being biased towards a short Na–N2(tmp) bond (2.372(2) Å) and a long Na–C19(alkyl) bond (2.734(3) Å). Chromate 2 represents a rare example of a heteroleptic alkyl amidochromium(II) species but is isomorphous with the aforementioned complex [(tmeda)Na[tmp](R)Mn(tmp)]. [3]

Formation of a chromium-based inverse crown complex akin to 1 requires twofold deprotonation of benzene, that is, two direct Cr–H exchanges on the same molecule. Without activating substituents, benzene is not easy to metalate (even BuLi requires tmeda activation to do so),[7] let alone dimetalate, so it provides an excellent benchmark to gauge metalating proficiency. As 1 was prepared in the absence of tmeda, an identical protocol was followed with Cr, using a reaction mixture with a 4:2:1 Na/Cr/benzene ratio (Scheme 1). This approach led to the crystallization of the first chromium inverse crown compound [Na4Cr2(tmp)6-(C6H4)] (3), thus confirming direct Cr–H exchange. To our knowledge, this represents the first intentional direct chromation with chromium(II) (and twofold chromation) of an arene. Gambarotta and co-workers reported[8] an unplanned intramolecular ortho chromation within [R′3CrC11Li1(thf)4] (R′ = Me3C(PH)C(CH3)3) on adding tmeda, during which an unexplained oxidation (CrII to CrIII) occurred. X-ray crystallography established the inverse crown nature of 3 (see below).[9]

Turning to Fe, we synthesized tmeda-stabilized [(tmeda)FeR2] (4) [5] from the corresponding chloride and MgR2 (Scheme 2). Me3Si (δ = 12.14 ppm) and tmeda resonances (CH3 δ = 86.8 ppm, CH2 δ = 72.6 ppm) in the 1H NMR spectrum of paramagnetic[13] 4 were easily assignable (the former appear in the same region as Me3Si resonances in [(trans-sparteine)FeR2][3] at δ = 10.14 and 15.71 ppm). The molecular structure of 4 (see the Supporting Information) [14] is a simple, distorted tetrahedral mononuclear arrangement with dimensions (mean Fe–C 2.078 Å, mean Fe–N 2.256 Å, C–Fe–C, 128.83(6)°) closely matching those of the chiral analogue (corresponding values: 2.090 Å, 2.256 Å, 129.46(6)°). Adding Na tmp to homometallic 4 facilitated its smooth conversion to the heteroleptic bisalkyl monoamido-ferrate [(tmeda)Na[tmp](R)Fe(R)] (5) in good yields of crystalline product (80.4%; Scheme 2).

No dismutation was evident in this reaction, in contrast to those producing the related monoalkyl bisamidochromium (2) and manganese complexes. [3] Furthermore, tmeda transfers from Fe to Na during the synthesis of 5; hence it does not interfere with the cocomplexation process forming the mixed-metal species. Resembling that of 2, the molecular structure of 5 (Figure 2) [15] exhibits a trigonal planar Fe center that presents a N–C edge unsymmetrically to a tmeda-chelated Na ion, leaving one terminal R ligand on Fe. There is little

Figure 1. Molecular structure of 2. Hydrogen atoms and minor disorder components are omitted for clarity.

Figure 2. Molecular structure of 5. Hydrogen atoms and minor disorder are omitted for clarity.

Scheme 2. Synthesis of the heteroleptic bisalkyl monoamidoferrate 5 (top) and the sodium ferrate inverse crown 6 (bottom).
distinction between Fe–C bond lengths for the bridging and terminal ligands (difference of 0.032 Å), with the mean (2.086 Å) close to that in 2 (2.078 Å). The Fe–N bond (the first recorded Fe–tmp bond)\[^6\] is shorter (2.010(2) Å). The tmp ligand also forms a strong bond to Na (Na–N1 2.403(2) Å; cf. the dative bonds to tmdea, mean length 2.445 Å), but the other bridge is extremely long (Na–C1 2.837(3) Å), indicative of a weak, electrostatic interaction.

Preparing 5 in situ in hexane and adding benzene did not afford a solid product. However, taking freshly sublimed 4, mixing it with BuNa and tmpH in a 2:4:8 molar ratio, and then affording a solid product. However, taking freshly sublimed iron brew deposited yellow needles of [Na\(_4\)Fe\(_2\)(tmp)\(_6\)(C\(_6\)H\(_4\))]\(^{2+}\), the first iron-host inverse crown complex.\[^{[17]}\] Isomorphous with 3 (and 1), the molecular structure of 6 (Figure 3)\[^{[19]}\] is centrosymmetric, comprising a 12-atom [(NaNaNaFeNa)]\(^{2+}\) “host” ring and a 1,4-dideprotonated benzene “guest”.

![Figure 3. Molecular structure of 6 (3 adopts the same motif). Hydrogen atoms are omitted for clarity. Symmetry operator A: -x+1, -y+2, -z+1 (for 3, A: -x, -y+1, -z+1).](image)

In a reversal of the normal bonding propclivities found in homometallic chemistry,\[^{[19]}\] the transition metals in heterometallic 6, 3, and 1 engage in σ bonding with the arene (Fe–C 2.115(4) Å, Cr–C 2.103(2) Å, Mn–C 2.201(2) Å), while sodium engages with its π system (mean Na–C: 2.698, 2.695, and 2.682 Å for 6, 3, and 1, respectively). Replacing the outgoing H atoms, the Fe, Cr, and Mn atoms occupy positions coplanar with the arene ring plane (deviations ±0.030, ±0.018, and ±0.005 Å, respectively), whereas the Na atoms lie almost orthogonal to it (mean values: 84.1, 85.5, and 82.4°, respectively). There is a uniform deformation of the benzene-dide ring across the series, with a narrowing at the transition-metalated carbon atoms (mean 112.57°) and a concomitant widening at the other carbon atoms (mean 125.53°). In 6, the mean Fe–N bond length (2.025 Å) compares well to that in 5 (2.101 Å) and to the Cr–N bonds in 2 and 3 (2.037 and 2.042 Å, respectively; cf. mean 1.916 Å in [Cr(tmp)]\(^{3+}\)).

The magnetic properties were explored by variable-temperature measurements in the range 2–300 K under an applied field of 1 T on powdered microcrystalline samples of complexes 1, 3, and 6 (Figure 4).\[^{[20]}\] For complex 1\[^{[3]}\] the \(\chi T\) product at room temperature is 8.72 cm\(^3\)K mol\(^{-1}\) and is very close to the expected value of 8.75 cm\(^3\)K mol\(^{-1}\) for two uncoupled Mn\(^{II}\) ions with a g value of 2.00. A significant decrease can only be observed below 70 K, indicating a weak antiferromagnetic exchange between the two manganese ions. The same behavior is observed for complex 6. The \(\chi T\) value at room temperature is 6.70 cm\(^3\)K mol\(^{-1}\) and therefore higher than the expected value of 6.00 cm\(^3\)K mol\(^{-1}\) for two uncoupled Fe\(^{III}\) ions with a g value of 2.00. In the range 300–100 K, the \(\chi T\) value is constant. Further cooling leads to a decrease of the \(\chi T\) product, thus indicating a weak antiferromagnetic coupling between the two iron ions. In contrast, complex 3 shows a different behavior. The \(\chi T\) value at room temperature at 4.52 cm\(^3\)K mol\(^{-1}\) is clearly below the expected value of 6.00 cm\(^3\)K mol\(^{-1}\) for two uncoupled Cr\(^{III}\) ions with a g value of 2.00. Decreasing temperature leads to a continuous decrease of the \(\chi T\) product, indicating a somewhat stronger antiferromagnetic exchange coupling between the two Cr ions.

All susceptibility data for complexes 1, 3, and 6 can be simulated satisfactorily using the spin Hamiltonian \(H = -\text{\(J\text{S}\text{S}^*\text{S}\)}\) for complexes 3 and 6. The best simulation for complex 1 can be obtained with an exchange coupling constant \(J = -0.70\ \text{cm}^{-1}\) and \(g = 2.05\). An additional small paramagnetic impurity of 4.4%, corresponding to an \(S = 5/2\) species, was taken into account. For complex 6 a slightly higher value for the exchange coupling constant \(J = -2.28\ \text{cm}^{-1}\) and \(g = 2.146\) were found. Compared to the first two complexes, a much larger exchange coupling constant with \(J = -12.09\ \text{cm}^{-1}\) and a \(g = 2.00\) is necessary for a satisfactorily simulation of the susceptibility data of 3. The larger exchange coupling constant is due to a greater overlap of the magnetic orbitals of the chromium ions with the orbitals of benzene. This situation can also be confirmed by DFT calculations at the B3LYP level using Alhrich’s TZVP basis set\[^{[21]}\] for all atoms. The exchange pathway involves the d orbitals of the benzene ring interacting with the d orbitals of the M\(^{III}\) centers, showing a larger overlap of the pair of magnetic orbitals in 3 (\(S = 0.034, J_{\text{dd}} = -13.6\ \text{cm}^{-1}\) than for two sets of overlapping magnetic orbitals in 1 (\(S = 0.034 \pm 0.015, J_{\text{dd}} = -1.0\ \text{cm}^{-1}\) and 6 (\(S = 0.037 \pm 0.027, J_{\text{dd}} = -1.4\ \text{cm}^{-1}\), in excellent agree-
ment with the experimental data. Moreover, these findings are supported by the considerably weaker spin delocalization to the adjacent nitrogen atoms of the tnp groups in 3 compared to 1 and 6, as shown in the calculations.

In conclusion, we have demonstrated with both Cr(II) and Fe(II) in reactions with the weak C acid benzene that AMMO is a powerful new technique for executing direct transition-metal/hydrogen exchange on aromatic compounds. The first Cr and Fe host inverse crown species are produced as a result. Given that CrR₂ (a tetranuclear structure), FeR₂ (an unstable molecule that requires Lewis base support), and MnR₂ (an infinite polymer) are all significantly different transition-metal alkyl compounds, it is extremely surprising that they all form isomorphous inverse crown complexes (along with the Mg precedent).

**Experimental Section**

All reactions were carried out under argon. Mg(CH₃SiMe₃)₂ was made from the corresponding Grignard reagent using dioxane and subsequently filtered and sublimed at 175°C at a pressure of 10⁻² Torr. For experimental details of 4, see the Supporting Information.

2: A 1:1 mixture of Natmp and tmpH was made by addition of tmpH (0.34 mL, 2.0 mmol) to a suspension of BuNa (0.08 g, 1.0 mmol) in n-hexane (20 mL). After stirring for ½ hour, Cr(CH₃SiMe₃)₂ (0.23 g, 1.0 mmol) was added. Subsequently, one molar equivalent tmpH (0.15 mL, 1.0 mmol) was added, and the dark brown solution was stirred for another 30 min. The solution was filtered and concentrated by removing some solvent under vacuum, then the solution was stored at 0°C. A crop of large, colorless crystals (2.46 g, 80.4%). M.p. 106.697(2), 10.890(4) °C, TMS: δ = -29.7 (s, Δν₁₂ = 5000 Hz, 12H), 3.94 (s, Δν₁₂ = 100 Hz, 12H), 5.81 (s, Δν₁₂ = 200 Hz, 18H), 6.42 (s, Δν₁₂ = 130 Hz, 4H), 28.6 ppm (s, Δν₁₂ = 400 Hz, 4H).

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