

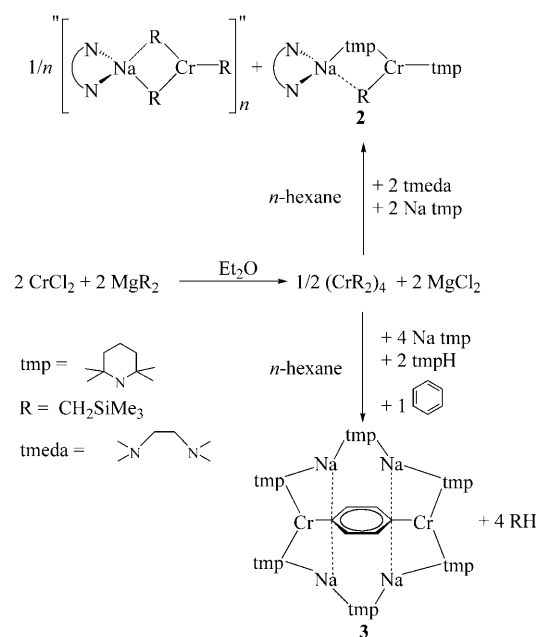
Direct C–H Metalation with Chromium(II) and Iron(II): Transition-Metal Host/Benzenediide Guest Magnetic Inverse-Crown Complexes**

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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 MnR₂. Indirect, two-step syntheses involving prior preparation of a polar organometallic compound (commonly an organolithium species) and subsequent metathesis with a Mn^{II} salt have proved suitable for some aryl Mn^{II} compounds,^[1] 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,N',N'-tetramethyl-1,2-diamine, tmp = 2,2,6,6-tetramethylpiperidide, R = CH₂SiMe₃) or (for dimanganation) an in situ mixture of BuNa, tmpH, and MnR₂ (in a 4:6:2 ratio) to afford [(tmeda)Na(tmp)(C₆H₅)Mn(tmp)] and the inverse crown complex [Na₄Mn₂(tmp)₆(C₆H₄)] (**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 CrR₂ 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 FeR₂ is the need for Lewis base stabilization (i.e., [LFeR₂]). 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 FeR₂ 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 CrR₂, made previously by metathesis between LiR and [(thf)₂CrCl₂] in hexane solution (Scheme 1).^[4,6] NMR



Scheme 1. Synthesis of the heteroleptic monoalkyl bisamidochromate **2** (top) and the sodium chromate inverse crown **3** (bottom).

spectroscopy confirmed the purity of the CrR₂ compound.^[7] Next, we attempted to synthesize an alkyl amidochromate compound by directly combining CrR₂, Na tmp, and tmeda (Scheme 1), reasoning that the diamine would accelerate cleavage of tetranuclear CrR₂,^[4] thus rendering it labile. The

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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 disproportionation has occurred; the likely coproduct is a trialkyl chromate compound. Interestingly, previous attempts to prepare a Cr^{II} 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 Cr^{II} 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

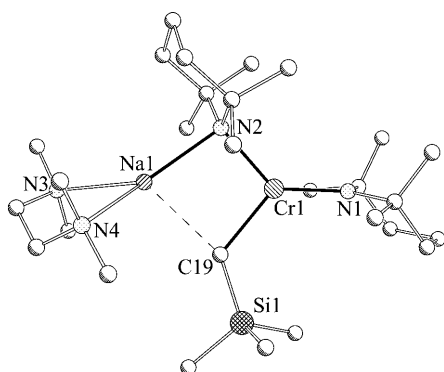


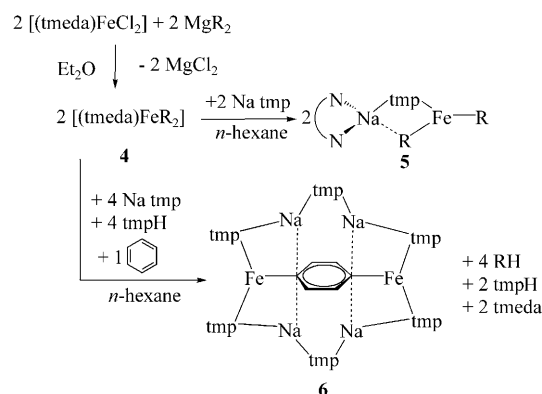
Figure 1. Molecular structure of **2**. Hydrogen atoms and minor disorder components are omitted for clarity.

(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),^[10] 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^[6] an unplanned intramolecular *ortho* chromation within [R''₈Cr₂Li₄(thf)₄] (R'' = Me₂C(Ph)CH₂)^[11] on adding tmeda, during which an unexplained oxidation (Cr^{II} to Cr^{III}) occurred. X-ray crystallography established the inverse crown nature of **3** (see below).^[12]

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



Scheme 2. Synthesis of the heteroleptic bisalkyl monoamidoferrate **5** (top) and the sodium ferrate inverse crown **6** (bottom).

former appear in the same region as Me₃Si resonances in [(-)-sparteine]FeR₂^[5] 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 2.243 Å, C–Fe–C, 128.83(14)°) 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 monoamidoferrate [(tmeda)Na(tmp)(R)Fe(R)] (**5**) in good yields of crystalline product (80.4%; Scheme 2).

No disproportionation was evident in this reaction, in contrast to those producing the related monoalkyl bisamido chromium (**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

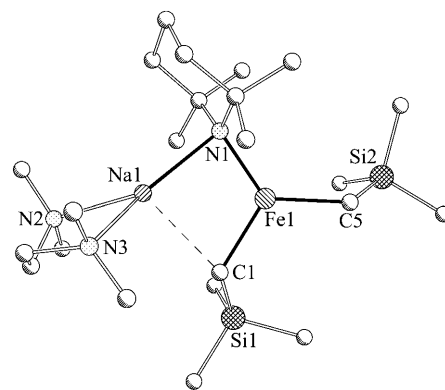


Figure 2. Molecular structure of **5**. Hydrogen atoms and minor disorder are omitted for clarity.

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)^[16] 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 tmeda, 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 adding one equivalent of benzene was more successful. This iron brew deposited yellow needles of [Na₄Fe₂(tmp)₆(C₆H₄)] (**6**), the first iron-host inverse crown complex.^[17] Isomorphous with **3** (and **1**), the molecular structure of **6** (Figure 3)^[18] is centrosymmetric, comprising a 12-atom [(NaNNaFeN)₂]²⁺ “host” ring and a 1,4-dideprotonated benzene “guest”.

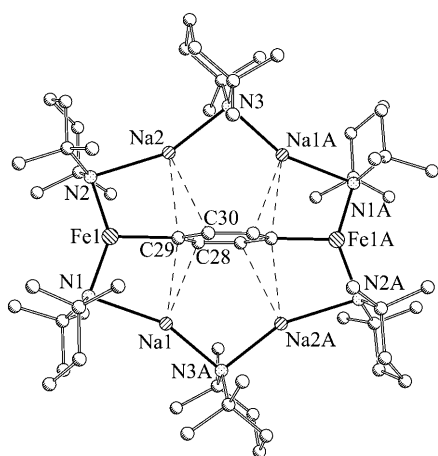


Figure 3. Molecular structure of **6** (**3** adopts the same motif). Hydrogen atoms are omitted for clarity. Symmetry operator A: $-x+1, -y+2, -z+1$ (for **3**, A: $-x, -y+1, -z+1$).

In a reversal of the normal bonding proclivities 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 ± 0.085 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 benzenediide 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 χT product at room temperature is 8.72 cm³K mol⁻¹ and is very close to the expected value of 8.75 cm³K mol⁻¹ for two uncoupled Mn^{II} ions with a g value of 2.00. A significant

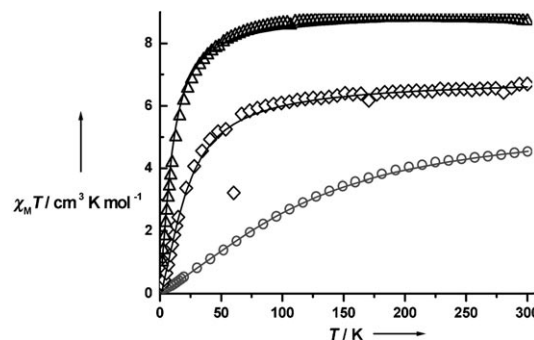


Figure 4. $\chi_M T$ vs. T for complexes **1** (Δ), **3** (\circ), and **6** (\diamond) and best simulations (lines).

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 χT value at room temperature is 6.70 cm³K mol⁻¹ and therefore higher than the expected value of 6.00 cm³K mol⁻¹ for two uncoupled Fe^{II} ions with a g value of 2.00. In the range 300–100 K, the χT value is constant. Further cooling leads to a decrease of the χT product, thus indicating a weak antiferromagnetic coupling between the two iron ions. In contrast, complex **3** shows a different behavior. The χT value at room temperature at 4.52 cm³K mol⁻¹ is clearly below the expected value of 6.00 cm³K mol⁻¹ for two uncoupled Cr^{II} ions with a g value of 2.00. Decreasing temperature leads to a continuous decrease of the χT 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 $\hat{H} = -J\hat{S}_1\hat{S}_2$, with $\hat{S}_1 = \hat{S}_2 = 5/2$ for complex **1** and $\hat{S}_1 = \hat{S}_2 = 2$ for complexes **3** and **6**. The best simulation for complex **1** can be obtained with an exchange coupling constant $J = -0.70$ 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 $J = -2.28$ cm⁻¹ and $g = 2.146$ were found. Compared to the first two complexes, a much larger exchange coupling constant with $J = -12.09$ cm⁻¹ and a $g = 2.00$ is necessary for a satisfactory 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 σ orbitals of the benzene ring interacting with the d orbitals of the M^{II} centers, showing a larger overlap of the pair of magnetic orbitals in **3** ($S = 0.100$, $J_{\text{calcd}} = -13.6$ cm⁻¹) than for two sets of overlapping magnetic orbitals in **1** ($S = 0.034$ and 0.015, $J_{\text{calcd}} = -1.0$ cm⁻¹) and **6** ($S = 0.037$ and 0.027, $J_{\text{calcd}} = -1.4$ 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 tmp 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(CH₂SiMe₃)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 1/2 hour, Cr(CH₂SiMe₃)₂ (0.23 g, 1.0 mmol) was added. Subsequently, one molar equivalent tmeda (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 turquoise crystals was deposited overnight (0.17 g, 30.4%). The compound decomposed slowly at room temperature under the influence of light. Elemental analysis calcd (%) for C₂₈H₆₃CrN₄NaSi (558.91): C 60.17, H 11.36, N 10.02; found: C 60.17, H 11.13, N 9.94.

3 (and **6**): A 2:1 mixture of Natmp and tmpH was made by addition of tmpH (0.51 mL, 3.0 mmol) to a suspension of BuNa (0.16 g, 2.0 mmol) in *n*-hexane (20 mL). After stirring for 1/2 hour Cr(CH₂SiMe₃)₂ (0.23 g, 1.0 mmol for **3**; [(tmeda)FeR₂] (**4**), 0.23 g, 1.0 mmol for **6**) was added (in an alternative route to **6**, a 1:1 mixture of Natmp and tmpH can be mixed with one equivalent of **5**). Subsequently, benzene (0.9 mL, 0.5 mmol) was added and heated for 5 min (10 min for **6**). After cooling, the dark brown solution was filtered and stored in a dark place for 7 days (2 days for **6**). A crop of pale yellowish-green needles was deposited (0.03 g, ca. 5% **3**; yellow needles, 0.22 g, 39.2% **6**). Decomposition above 150 °C; elemental analysis calcd (%) for C₆₀H₁₁₂Cr₂N₆Na₄ (1113.54): C 64.72, H 10.14, N 7.55; found: C 64.72, H 10.18, N 7.56. For **6**: decomposition above 140 °C; elemental analysis calcd (%) for C₆₀H₁₁₂Fe₂N₆Na₄ (1121.24): C 64.27, H 10.07, N 7.50; found: C 64.27, H 9.86, N 7.91.

5: [(tmeda)FeR₂] (2.1 g, 6.0 mmol) was added to a suspension of Natmp, which had been prepared by reaction of BuNa (0.48 g, 6.0 mmol) with tmpH (1.02 mL, 6.0 mmol) in *n*-hexane (50 mL). After stirring for 1 h and filtering, most solvent was removed under vacuum. The colorless solution was allowed to stand for two days to furnish **5** as a crop of large, colorless crystals (2.46 g, 80.4%). M.p. 94 °C; elemental analysis calcd (%) for C₂₃H₅₆FeN₃NaSi₂ (509.73): C 54.20, H 11.07, N 8.24; found: C 54.20, H 11.39, N 8.34; ¹H NMR (400 MHz, C₆D₆, 20 °C, TMS): δ = -29.7 (s, Δν_{1/2} = 5000 Hz, 12H), 3.94 (s, Δν_{1/2} = 100 Hz, 12H), 5.81 (s, Δν_{1/2} = 200 Hz, 18H), 6.42 (s, Δν_{1/2} = 130 Hz, 4H), 28.6 ppm (s, Δν_{1/2} = 400 Hz, 4H).

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- a) S. U. Koschmieder, G. Wilkinson, *Polyhedron* **1991**, *10*, 135; b) R. A. Bartlett, M. M. Olmstead, P. P. Power, S. C. Shoner, *Organometallics* **1988**, *7*, 1801; c) R. J. Wehmschulte, P. P. Power, *Organometallics* **1995**, *14*, 3264.
- J. Garcia-Álvarez, A. R. Kennedy, J. Klett, R. E. Mulvey, *Angew. Chem.* **2007**, *119*, 1123; *Angew. Chem. Int. Ed.* **2007**, *46*, 1105.
- L. M. Carrella, W. Clegg, D. V. Graham, L. M. Hogg, A. R. Kennedy, J. Klett, R. E. Mulvey, E. Rentschler, L. Russo, *Angew. Chem.* **2007**, *119*, 4746; *Angew. Chem. Int. Ed.* **2007**, *46*, 4662.
- C. Schulzke, D. Enright, H. Sugiyama, G. LeBlanc, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 3810.
- S. C. Bart, E. J. Hawrelak, A. K. Schmisser, E. Lobkovsky, P. J. Chirik, *Organometallics* **2004**, *23*, 237.
- For related chromium(II) organochromates, see: S. Hao, J. I. Song, P. Berno, S. Gambarotta, *Organometallics* **1994**, *13*, 1326.
- We found that one of the signals in the ¹H NMR spectrum, reported to be the CH₂ group of Me₃SiCH₂,^[4] disappeared on subliming CrR₂. We therefore believe this signal is due to residual THF. See the Experimental Section for full details.
- K. B. P. Ruppá, K. Feghali, I. Kovacs, K. Aparna, S. Gambarotta, G. P. A. Yap, C. Bensimon, *J. Chem. Soc. Dalton Trans.* **1998**, 1595.
- Crystal data for **2**: C₂₈H₆₃CrN₄NaSi, *M*_r = 558.9, monoclinic, space group *P2₁/n*, *a* = 11.654(4), *b* = 14.817(5), *c* = 19.868(6) Å, β = 90.832(6)°, *V* = 3430.4(19) Å³, *Z* = 4, ρ_{calcd} = 1.082 g cm⁻³, μ = 0.402 mm⁻¹, *T* = 150 K, *R* (*F*; *F*² > 2σ) = 0.0373, *R*_w (*F*², all data) = 0.1056, *S* = 1.050 for 5908 unique data (θ < 25.5°; Nonius KappaCCD diffractometer, MoKα radiation, λ = 0.71073 Å) and 331 refined parameters; final difference synthesis within ± 0.35 e Å⁻³. CCDC 670763 (**2**), 670764 (**3**), 670765 (**4**), 670766 (**5**), and 670767 (**6**) 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.
- A. J. Chalk, T. J. Hoogeboom, *J. Organomet. Chem.* **1968**, *11*, 615.
- The neophyl ligand appears susceptible to intramolecular ortho metalation, see, for example: R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1976**, 2204.
- Crystal data for **3**: C₆₀H₁₁₂Cr₂N₆Na₄, *M*_r = 1113.5, monoclinic, space group *P2₁/n*, *a* = 15.161(5), *b* = 8.194(3), *c* = 25.301(8) Å, β = 92.630(4)°, *V* = 3139.9(17) Å³, *Z* = 2, ρ_{calcd} = 1.178 g cm⁻³, μ = 0.41 mm⁻¹, *T* = 150 K, *R* (*F*; *F*² > 2σ) = 0.034, *R*_w (*F*², all data) = 0.085, *S* = 1.01 for 5468 unique data (θ < 25°; Bruker SMART 1 K diffractometer, MoKα radiation, λ = 0.71073 Å) and 337 refined parameters; final difference synthesis within ± 0.35 e Å⁻³.
- For a review on paramagnetic NMR spectroscopy see: I. Bertini, C. Luchinat, *Coord. Chem. Rev.* **1996**, *150*, 1.
- Crystal data for **4**: C₁₄H₃₈FeN₃Si₂, *M*_r = 346.49, triclinic, space group *P1̄*, *a* = 9.8900(4), *b* = 9.9171(4), *c* = 13.1225(6) Å, α = 106.697(2), β = 90.705(2), γ = 118.005(2)°, *V* = 1071.82(8) Å³, *Z* = 2, ρ_{calcd} = 1.074 g cm⁻³, μ = 0.809 mm⁻¹, *T* = 123 K, *R* (*F*; *F*² > 2σ) = 0.0474, *R*_w (*F*², all data) = 0.1248, *S* = 1.087 for 4197 unique data (θ < 26°; Nonius Kappa CCD diffractometer, MoKα radiation, λ = 0.71073 Å) and 198 refined parameters; final difference synthesis within ± 0.837 e Å⁻³.
- Crystal data for **5**: C₂₃H₅₆FeN₃NaSi₂, *M*_r = 509.73, orthorhombic, space group *P2₁2₁2₁*, *a* = 10.5430(3), *b* = 15.9871(2), *c* = 18.9219(4) Å, *V* = 3189.32(12) Å³, *Z* = 4, ρ_{calcd} = 1.062 g cm⁻³, μ = 0.575 mm⁻¹, *T* = 123 K, *R* (*F*; *F*² > 2σ) = 0.0436, *R*_w (*F*², all data) = 0.0841, *S* = 1.047 for 7305 unique data (θ < 27.5°; Nonius

- Kappa CCD diffractometer, Mo_{Kα} radiation, $\lambda = 0.71073 \text{ \AA}$) and 340 refined parameters; final difference synthesis within $\pm 0.710 \text{ e \AA}^{-3}$.
- [16] A search of the Cambridge Crystallographic Database revealed no hits for tmp bound to iron(II) atoms or indeed to iron atoms of any oxidation state. Nevertheless, there are several comparable structures containing bis(trimethylsilyl)amido ligands: a) M. M. Olmstead, P. P. Power, S. C. Shoner, *Inorg. Chem.* **1991**, *30*, 2547; b) M. A. Putzer, B. Neumüller, K. Dehnicke, J. Magull, *Chem. Ber.* **1996**, *129*, 715; c) U. Siemeling, U. Vorfeld, B. Neumann, H. G. Stammer, *Inorg. Chem.* **2000**, *39*, 5159.
- [17] For recent reviews on inverse crowns and related species, see: a) R. E. Mulvey, *Organometallics* **2006**, *25*, 1060; b) M. West-erhausen, *Dalton Trans.* **2006**, 4755.
- [18] Crystal data for **6**: C₆₀H₁₁₂Fe₂N₆Na₄, $M_r = 1121.22$, monoclinic, space group $P2_1/n$, $a = 15.1087(6)$, $b = 8.2255(2)$, $c = 25.3560(11) \text{ \AA}$, $\beta = 93.294(2)^\circ$, $V = 3146.0(2) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.184 \text{ g cm}^{-3}$, $\mu = 0.529 \text{ mm}^{-1}$, $T = 123 \text{ K}$, $R(F; F^2 > 2\sigma) = 0.0649$, $R_w(F^2, \text{all data}) = 0.1323$, $S = 1.024$ for 5555 unique data ($\theta < 25.1^\circ$; Nonius KappaCCD diffractometer, Mo_{Kα} radiation, $\lambda = 0.71073 \text{ \AA}$) and 348 refined parameters; final difference synthesis within $\pm 0.593 \text{ e \AA}^{-3}$.
- [19] R. Poli, *Chem. Rev.* **1996**, *96*, 2135.
- [20] Magnetic susceptibility data for polycrystalline samples of **3** and **6** were collected in the temperature range 2–300 K in an applied magnetic field of 1 T with a SQUID magnetometer (MPMS-7, Quantum Design). Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants. The temperature-dependent magnetic contribution of the glassholder was experimentally determined and subtracted from the measured susceptibility data. The routine JULIUS was used for spin Hamiltonian simulations of the data (C. Krebs, E. Bill, F. Birkelbach, V. Staemmler, unpublished results).
- [21] M. J. Frisch et al., *Gaussian 03, Revision D.01*, Gaussian, Inc., Pittsburgh PA, **2003**, see the Supporting Information.