

Univalent transition metal complexes of arenes stabilized by a bulky terphenyl ligand: differences in the stability of Cr(I), Mn(I) or Fe(I) complexes†

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Two univalent transition metal complexes, $(\mu\text{-}\eta^6\text{-C}_7\text{H}_8)\{\text{MnAr}^*-3,5\text{-Pr}^i_2\}_2$ (**1**) and $(\eta^6\text{-C}_6\text{H}_6)\text{FeAr}^*-3,5\text{-Pr}^i_2$ (**2**) ($\text{Ar}^*-3,5\text{-Pr}^i_2 = \text{C}_6\text{H}_2\text{-}2,6\text{-}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Pr}^i_3)_2\text{-}3,5\text{-Pr}^i_2$), that have η^6 arene coordination were synthesized by reduction of the corresponding metal halides. The complexes are thermally stable in contrast to the corresponding Cr(I) complexes of benzene or toluene which decompose at room temperature.

Transition metal complexes in which a six π -electron aromatic ring, for example benzene or toluene, bridges two metal centers in an η^6 fashion are rare.¹ The first such compound, $(\mu\text{-}\eta^6\text{-C}_6\text{H}_6)\{\text{V}(\eta^5\text{-C}_5\text{H}_5)_2\}_2$,² was prepared in 1983 by reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{C}_3\text{H}_5)_2$ with an excess of 1,3-cyclohexadiene in refluxing *n*-heptane. More recent examples include the chromium(I) species $(\mu\text{-}\eta^6\text{-C}_7\text{H}_8)\{\text{Cr}[(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)\text{NCMe}]_2\text{CH}\}_2$ ³ and the p and f block metal derivatives $(\mu\text{-}\eta^6\text{-}\eta^6\text{-C}_7\text{H}_8)\{\text{Bi}[\text{N}(\text{CH}_2\text{C}_6\text{H}_2\text{-}1\text{-O-Bu}^i_2)_3]\}_2$ ⁴ and $(\mu\text{-}\eta^6\text{-}\eta^6\text{-C}_7\text{H}_8)\{\text{U}[\text{N}(\text{R})\text{Ar}]_2\}_2$ ⁵ (R = C(CH₃)₃, Ar = C₆H₃-3,5-Me₂). These so-called inverted sandwich complexes are closely related to half-sandwich compounds that incorporate a neutral η^6 -arene and a σ -bonded ligand. Although the latter are relatively common for organometallic complexes which conform to the 18-electron rule, they are relatively scarce for open-shell species with valence electron counts lower than 18. These electronically unsaturated complexes have attracted considerable interest because of their high reactivity and potential catalytic applications in small molecule activation.^{3,5–10} We have shown recently that the very large terphenyl ligand C₆H-2,6-(C₆H₂-2,4,6-Prⁱ₃)₂-3,5-Prⁱ₂ (abbreviated Ar^{*}-3,5-Prⁱ₂) could stabilize the unusual d⁵, Cr(I), two-coordinate complexes $[\text{3,5-Pr}^i_2\text{-Ar}^*\text{Cr}(\text{L})]$ (L = THF or PMe₃).¹¹ However, attempts to prepare $3,5\text{-Pr}^i_2\text{-Ar}^*\text{Cr}(\eta^6\text{-arene})$ complexes were unsuccessful. Reduction of $3,5\text{-Pr}^i_2\text{-Ar}^*\text{CrCl}$ in toluene with KC₈ or the reaction of $3,5\text{-Pr}^i_2\text{-Ar}^*\text{Cr}(\text{thf})$ with benzene or toluene initially afforded a red color, but decomposition occurs over several hours to afford intractable brown mixtures. Understanding the apparent lack of stability of this Cr(I) arene complex is of importance because of the presence

of weak secondary Cr(I)–arene interactions in the structure in the related quintuple bonded Ar'CrCrAr' (Ar' = C₆H₃-2,6-(C₆H₃-2,6-Prⁱ₂)₂).¹² Currently, it is not known if the instability of the interaction of a one-coordinate Cr(I) moiety with an arene¹³ is peculiar to chromium (*cf.* the stability of the Cr(I) complex $(\mu\text{-}\eta^6\text{-}\eta^6\text{-C}_7\text{H}_8)\{\text{Cr}[(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)\text{NCMe}]_2\text{CH}\}_2$)³ or if it is a more general property of one coordinate transition metal(I) moieties. We hypothesized that the attempted synthesis of the Cr(I) arene complex led in the first instance to the unstable toluene complex $3,5\text{-Pr}^i_2\text{-Ar}^*\text{Cr}(\eta^6\text{-C}_7\text{H}_8)$, which decomposed to unidentified products partly as a result of the presence of only 13 valence electrons. This led to the proposal that an increase in the number of valence electrons might lead to analogous complexes of the more electron rich later metals which would have sufficient stability for isolation. We now report that this approach has led to the synthesis and characterization of the stable inverted sandwich complex $(\mu\text{-}\eta^6\text{-}\eta^6\text{-C}_7\text{H}_8)\{\text{MnAr}^*-3,5\text{-Pr}^i_2\}_2$ (**1**) and the related iron(I) half sandwich complex $(\eta^6\text{-C}_6\text{H}_6)\text{FeAr}^*-3,5\text{-Pr}^i_2$ (**2**), which are the first open shell one coordinate metal moieties to be stabilized by coordination to a neutral arene.

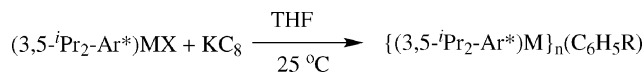
Compounds **1** and **2** were prepared (Scheme 1) by reduction of *in situ* generated $3,5\text{-Pr}^i_2\text{-Ar}^*\text{MnI}$ or $3,5\text{-Pr}^i_2\text{-Ar}^*\text{FeCl}$ with KC₈ in THF and were isolated in modest yields as air-sensitive brown (**1**) or orange (**2**) crystals after extraction with toluene and benzene, respectively.†

The structures of **1** and **2** were determined by X-ray crystallography.‡ Complex **1**, which crystallizes in a *Pna*2₁ space group, has two molecules with very similar structures in the asymmetric unit. One of these is illustrated in Fig. 1. The two manganese atoms are separated by a bridging toluene molecule, which is disordered axially over six positions (only one is shown in Fig. 1). The C–C bond lengths within the bridging toluene were constrained to be 1.3900 Å, which is essentially the same as it is in the uncomplexed molecule.¹⁴ The Mn(1)–centroid and Mn(2)–centroid distances, 1.7815(12) Å and 1.7798(12) Å, differ only slightly and the Mn–C(toluene) distances are in the range 2.237(3) Å to 2.279(3) Å. The Mn–centroid distances are longer than the usual range found

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Scheme 1 Reduction of the ligand halide precursors. **1** M = Mn, R = Me, X = I, *n* = 2; **2** M = Fe, R = H, X = Cl, *n* = 1.

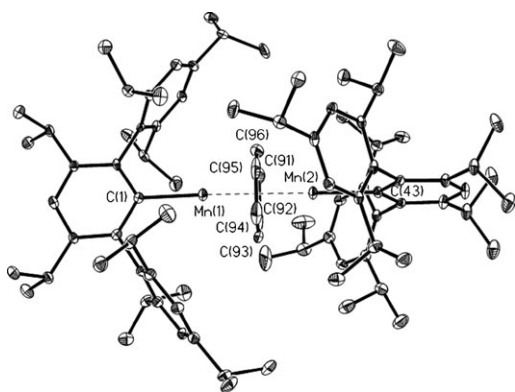


Fig. 1 Molecular structure of **1** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms, the disordered isopropyl groups and toluene methyl groups are not shown. Selected bond lengths (Å): Mn(1)–Mn(2) 3.5608(8), Mn(1)–C(1) 2.088(3), Mn(2)–C(43) 2.089(3), Mn(1)–C(toluene) 2.277(3), 2.275(3), 2.258(3), 2.245(3), 2.243(3), 2.262(3), Mn(2)–C(toluene) 2.279(3), 2.270(3), 2.249(3), 2.237(3), 2.246(3), 2.267(3), Mn(1)–centroid 1.7815(12), Mn(2)–centroid 1.7798(12).

in complexes having η -coordination to arene rings,¹⁵ due probably to the bridging nature of the interacting toluene in **1**. The Mn–C(*ipso*) distances to the η^1 terphenyl ligand are very similar at 2.088(3) Å and 2.089(3) Å and are close to those found in η^1 -aryl complexes, such as $\{[(C_6H_3-2,6-Pr^i_2)NCMe]_2CH\}Mn(C_6H_5)^{16}$ at 2.076(5) Å and $Mn(C_6H_2-2,4,6-Bu^i_3)_2^{17}$ at 2.108(2) Å, but somewhat shorter than the 2.181(4) Å distance in $(C_6H_2-2,4,6-Me_3)Mn\{MeC(O)CHC(Me)N-CH_2\}_2Li(1,2-dimethoxyethane)^{18}$ because of its anionic charge. The core C(1)–Mn(1)–centroid–Mn(2)–C(43) deviates slightly from linearity with C(1)–Mn(1)–centroid and C(43)–Mn(2)–centroid angles of 178.15(10)° and 176.76(10)°, respectively.

The complex **2** crystallizes in the *Pben* space group, with half of the molecule in the asymmetric unit. The structure of **2** is illustrated in Fig. 2. The iron is coordinated to the *ipso* carbon of the terphenyl ligand, with Fe(1)–C(1) distance of 2.029(4) Å, and to a benzene in an η^6 fashion, with Fe(1)–centroid distance of 1.6427(13) Å, which is in the expected range of 1.455 Å to 1.704 Å,¹⁹ and which is slightly longer than the Fe–centroid distance of 1.6245(8) Å in the related β -diketiminate Fe(i) complex $\{[(C_6H_3-2,6-Pr^i_2)NC(Me)]_2CH\}Fe(\eta^6-C_6H_6)^9$ and considerably longer than that of 1.5445(12) Å in $\{[RN=C(Me)]_2\}Fe(\eta^6-C_6H_5Me)$ (R = $C_6H_3-2,6-Pr^i_2$),¹⁰ which is short owing to the contribution of the ene-diamide canonical form to these structures. The average C–C bond length within the benzene ring is 1.408(5) Å, which is very similar to that in $\{[(C_6H_3-2,6-Pr^i_2)NC(Me)]_2CH\}Fe(\eta^6-C_6H_6)$.

Studies of the magnetic properties of **1** and **2** were undertaken to throw further light on their bonding. In **1**, each manganese atom is present in a highly distorted environment as Mn(i) with a nominal $3d^6 t_2^4 e^2$ electronic ground state, and $S = 2$. A plot of the inverse molar magnetic susceptibility *versus* temperature (Fig. 3) is linear in the range of 150–320 K and the corresponding μ_{eff} is 5.17 μ_B per manganese(i) ion, which is in agreement with 5.2 μ_B expected for two d^6 Mn(i) centers with no Mn–Mn bonding or any magnetic exchange.

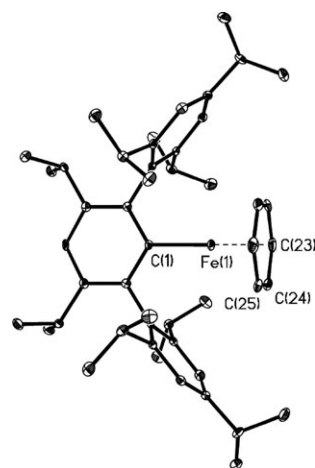


Fig. 2 Molecular structure of **2** with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms and disordered isopropyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1–C1 2.029(4), Fe1–C(benzene) 2.163(3), 2.166(3), 2.163(3), Fe(1)–centroid 1.6427(13), C(23)–C(24)–C(25) 119.9(3), C(24)–C(23)–C(25A) 120.1(3), C(23A)–C(25)–C(24) 120.0(3).

The μ_{eff} of **1** increases virtually linearly from 4.78 to 5.05 μ_B between 2 and 320 K whilst $\chi_M' \times T$ increases almost linearly from 2.87 to 3.19 emu K mol^{−1} per Mn between 2 and 320 K. In **2**, Fe(i) has a nominal $3d^7 t_2^5 e^2$ electronic ground state and $S = 3/2$. A plot of the inverse molar magnetic susceptibility *versus* temperature is linear in the range of 200–320 K and the corresponding μ_{eff} is 4.68 μ_B . However, a plot of $\chi_M' \times T$ *versus* temperature indicates that $\chi_M' \times T$ increases virtually linearly between 20 and 320 K; below 20 K $\chi_M' \times T$ decreases sharply as a result of the extensive zero-field splitting arising from the very low-symmetry of the iron(i) coordination environment.

In conclusion, the toluene bridged inverted sandwich Mn(i) complex (**1**) and the half sandwich Fe(i) complex (**2**) have been

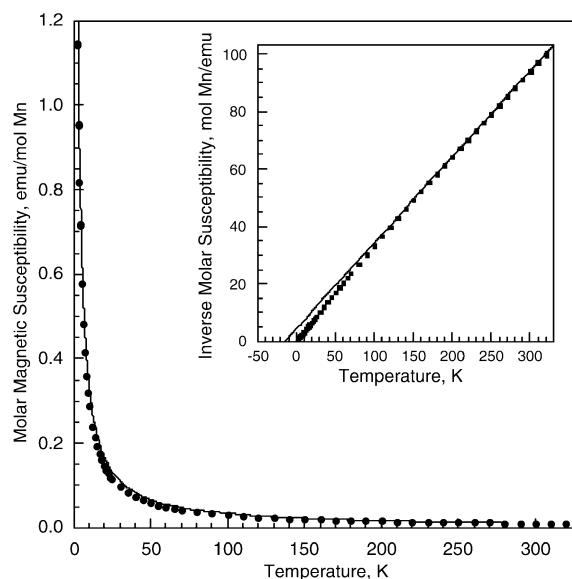


Fig. 3 A plot of the molar magnetic susceptibility of **1** *versus* temperature.

isolated and characterized. Unlike the chromium 3,5-Prⁱ₂-Ar*Cr moiety, whose complexes with PhMe or benzene decompose at room temperature,¹³ the corresponding manganese(i) and iron(i) moieties readily afford stable arene complexes.²⁰ The reasons for the apparent instability¹³ of the putative 3,5-Prⁱ₂-Ar*Cr(η⁶-C₇H₈) intermediate species are not well understood currently, but may be connected with the greater electron deficiency and the favorable exchange energy of the d⁵ electron configuration. Although an extremely bulky ligand such as 3,5-Prⁱ₂-Ar* creates sufficient protection at the metal centers for stability in **1** and **2**, the unsaturated geometry and low number of valence electrons (for Mn, 14 electrons; Fe, 15 electrons) make the compounds attractive substrates for small molecule activation. The investigation of their chemistry is now underway.

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Notes and references

† All manipulations were carried out under strictly anhydrous and anaerobic conditions.

Preparation of (μ-η⁶-C₇H₈)₂{MnAr^{3,5}-Prⁱ₂}₂ (**1**):* a pink solution of (3,5-Prⁱ₂-Ar*)MnI (2.24 g, 1.50 mmol), which was prepared *in situ* from (3,5-Prⁱ₂-Ar*)Li(Et₂O) and MnI₂ in diethyl ether, in *ca.* 30 mL of THF was added dropwise to a freshly prepared suspension of KC₈ (0.405 g, 3.00 mmol) in *ca.* 20 mL THF at 0 °C. The solution turned to yellowish brown immediately. The mixture was stirred for 2 days. The solvent was removed under reduced pressure and the resulting dark solid was extracted with toluene (*ca.* 40 mL). The solution was filtered and the reddish brown filtrate was concentrated to *ca.* 15 mL, which afforded X-ray quality reddish brown crystals of **1** after storage for 1 day at -18 °C. Yield 0.510 g (28.5%). The solid turned brown around 200 °C and melted at 216~218 °C. UV-vis (hexane, nm [ε, cm⁻¹ M⁻¹]): 312 (3050), 408 (shoulder).

Preparation of (η⁶-C₆H₆)FeAr^{3,5}-Prⁱ₂ (**2**):* a pale yellow solution of (3,5-Prⁱ₂-Ar*)FeCl (0.99 g, 0.75 mmol), which was prepared *in situ* from (3,5-Prⁱ₂-Ar*)Li(Et₂O) and FeCl₂ in diethyl ether, in *ca.* 25 mL THF was added dropwise to a freshly prepared suspension of KC₈ (0.202 g, 1.5 mmol) in *ca.* 15 mL THF at 0 °C. The solution turned orange brown immediately. The mixture was stirred for *ca.* 24 h. The solvent was removed and the black solid was extracted with benzene (*ca.* 30 mL). The orange filtrate was concentrated to *ca.* 10 mL, which afforded X-ray quality orange crystals of **2** after cooling for 1 day at -18 °C. Yield 0.160 g (15.2%). The compound decomposes at 162 °C and melts at 208 °C. UV-vis (hexane, nm [ε, cm⁻¹ M⁻¹]): 436 (4800).

1-4toluene: C₁₁₈H₁₅₉Mn₂, *T* = 90(2) K with MoKα (λ = 0.71073 Å), *F*_w = 1687.40, orthorhombic, space group *Pna*2₁, orange block, *a* = 23.2481(11), *b* = 18.7415(9), *c* = 46.380(2) Å, *V* = 20208.1(17) Å³, *Z* = 8, μ = 0.297 mm⁻¹, 169346 total reflections, 44483 independent, *R*_{int} = 0.0866, goodness-of-fit on *F*² = 1.046, final *R* indices [*I* > 2σ(*I*)] *R*1 = 0.0595 and *wR*2 = 0.1501 (all data). CCDC 662780. An extensive series of difference-Fourier maps were now implemented to locate the 8 toluene solvent molecules and to refine the bridging toluene molecules that were randomly disordered in both complexes.

After an exhaustive series of attempts, it was determined that no sensible solution was forthcoming, as a result of which the structure was refined to convergence with the bridging groups as benzene rings, the carbon atoms at full occupancy and the peripheral hydrogen atoms input at 5/6th occupancy since the terminal methyl group's multiple locations could not be ascertained reliably. The missing terminal -CH₃ group has been included in the overall formula.

2: C₄₈H₆₇Fe, *T* = 90(2) K with MoKα (λ = 0.71073 Å), *F*_w = 699.87, orthorhombic, space group *Pbcn*, orange block, *a* = 22.0866(14), *b* = 10.9907(7), *c* = 17.4459(11) Å, *V* = 4234.9(5) Å³, *Z* = 4, μ = 0.386 mm⁻¹, 43524 total reflections, 3842 independent, *R*_{int} = 0.1351, goodness-of-fit on *F*² = 0.998, final *R* indices [*I* > 2σ(*I*)] *R*1 = 0.0428 and *wR*2 = 0.1227 (all data). CCDC 662781. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b715027j

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