

[2 + 2] Cross Coupling of Benzene and Tropylium Ligands in Reductively Activated Piano Stool Complexes of Mn, Cr, and W

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Low hapticity coordination of an arene to a transition metal disrupts the aromaticity of the ligated arene and can induce reactivity patterns of potential interest in organic synthesis that are complementary to the electrophilic reactivity characteristic of π -coordinated arenes;¹ examples include the electron-rich diene chemistry of η^2 -arene complexes of Os(II)² and the [2 + 2] dimerization of η^4 -arene complexes of Mn(-I).³ We have shown that the latter reaction involves in situ addition of the initial η^4 -arene product of reduction of $[\text{Mn}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]\text{PF}_6$ (**1PF**₆) to the starting η^6 -arene complex to give dinuclear $[\{\text{Mn}(\text{CO})_3\}_2(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-C}_6\text{H}_6\text{-C}_6\text{H}_6)]$ (**2**) which undergoes further reduction to $[\{\text{Mn}(\text{CO})_3\}_2(\mu_2\text{-}\eta^4\text{:}\eta^4\text{-C}_6\text{H}_6\text{-C}_6\text{H}_6)]^{2-}$; the tetrahydrophenylene bridge between the Mn(-I) centers in this species is the [2 + 2] dimer of benzene.⁴

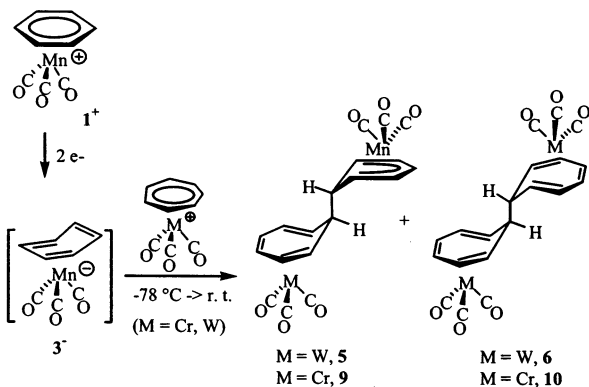
Research by ourselves and by Brown and co-workers has extended this two-electron reductive [2 + 2] dimerization of aromatic ligands to include tropylium complexes of chromium(I), molybdenum(I), and tungsten(I);^{5,6} annulations offer powerful strategies for the functionalization of arenes, and the question that arose is whether we can achieve cross dimerization of benzene and tropylium ligands. We now wish to report cation/anion coupling reactions of $[\text{M}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+$ (M = Cr, W) and $[\text{Mn}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^-$ (**3**⁻) (Scheme 1; for related reactions, see ref 7) that can be followed in the Cr, Mn case by further two-electron reduction of the neutral coupling product to give a dianionic [2 + 2] fusion product of the six- and seven-membered rings (Scheme 2).

Potassium naphthalenide (KNap) reduction of **1PF**₆ to **3**⁻ followed by reaction with $[\text{W}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]\text{PF}_6$ (**4PF**₆) offered a promising pathway to dimer **5** (Scheme 1), and the reaction was examined in a double Schlenk tube in which a yellow slurry of **1PF**₆ in THF was reacted first with 2.1 equiv of KNap in THF at -78 °C. An orange slurry of **4PF**₆ in THF in the other side of the tube was then stirred vigorously with the solution of **3**⁻ to form a red-brown slurry. After the mixture had been run through a flash silica gel column with toluene/hexanes (1:1.5) as the eluant, two red fractions were collected.

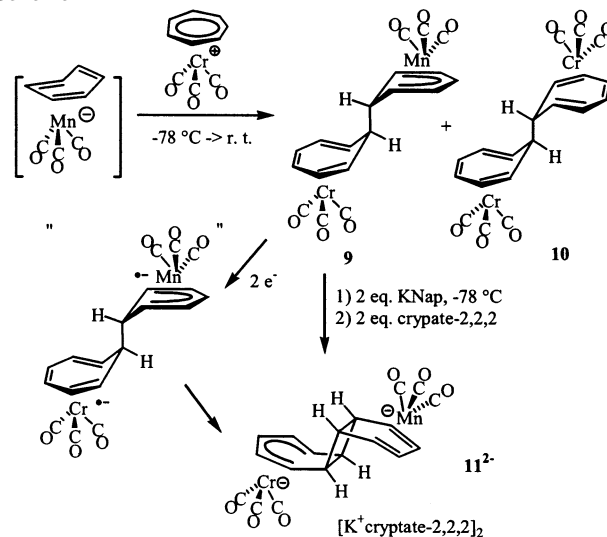
The first fraction was fully characterized as $[\text{W}(\text{CO})_3(\mu_2\text{-}\eta^6\text{:}\eta^5\text{-C}_7\text{H}_7\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3]$ (**5**) (see Supporting Information). Both ¹H and ¹³C{¹H} NMR spectra of **5** show bilateral symmetry for the $(\mu_2\text{-}\eta^6\text{:}\eta^5\text{-C}_7\text{H}_7\text{-C}_6\text{H}_6)$ organic ligand. The chemical shift and coupling of the two bridge endo-protons of **5** differ from data for the corresponding bridge protons of $[\{\text{W}(\text{CO})_3\}_2(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-C}_7\text{H}_7\text{-C}_7\text{H}_7)]$ (**6**) and of **2**. Crystals of **5** (Figure 1) were obtained by recrystallization from toluene, and a single-crystal diffraction structure analysis confirms the connectivity of the molecule as determined from NMR spectra and assigned on the basis of ¹H-¹H and ¹³C-¹H COSY NMR spectra.

The yield of dinuclear complex **5** is low after the column (11%), but the higher yield (19%) in two-electron reduction of $[\text{Cr}(\eta^7\text{-$

Scheme 1



Scheme 2



$\text{C}_7\text{H}_7)(\text{CO})_3]\text{PF}_6$ (**7PF**₆) to $[\{\text{Cr}(\text{CO})_3\}_2(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-C}_7\text{H}_7\text{-C}_7\text{H}_7)]^{2-}$ (**8**²⁻)⁸ suggested that the reaction might be cleaner if two 3d metals were involved. A slurry of **1PF**₆ was reduced to **3**⁻ with 2 equiv of KNap in THF and then mixed with 1 equiv of **7PF**₆ in THF to form a red solution. The red residue was extracted into toluene and then concentrated, and dinuclear complexes (Scheme 2) were isolated from two of the four fractions obtained when the solution was run through an Al₂O₃ (neutral, activity I) flash column with toluene/hexanes as the eluant. The first and second fractions contained traces of unidentified compounds, but the third orange fraction and the fourth red fraction crystallized from toluene and pentane and were identified as the desired $[\text{Cr}(\text{CO})_3(\mu_2\text{-}\eta^6\text{:}\eta^5\text{-C}_7\text{H}_7\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3]$ (**9**) (yield 24%) and $[\{\text{Cr}(\text{CO})_3\}_2(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-C}_7\text{H}_7\text{-C}_7\text{H}_7)]$ (**10**) (yield 2.8%) by ¹H, ¹³C NMR, mass spectroscopy and C, H analysis.

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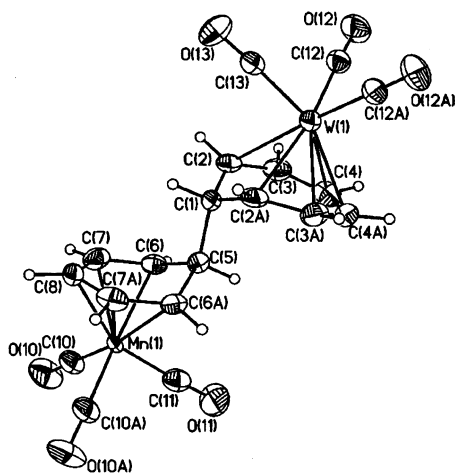


Figure 1. Molecular structure of **5**.

The 6,7 dinuclear Mn, Cr complex **9** is, as anticipated, more readily available than the corresponding 6,7 dinuclear Mn, W complex **5**, but definitive determination of the molecular structure of **9** depends on spectroscopic comparison with crystallographically characterized **5**, since crystalline samples of **9** are disordered and not amenable to X-ray diffraction studies.

We first attempted to prepare a product in which there had been [2 + 2] fusion of the six- and seven-membered rings through in situ reduction of **9** to $[\text{Cr}(\text{CO})_3(\mu_2\text{-}\eta^5\text{-}\eta^4\text{-C}_7\text{H}_7\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3]^{2-}$ (**11**²⁻). In this procedure, simple two-electron reduction of the neutral solution from mixing of **3**⁻ and **7**⁺ gave a solution of a 1.5:1 mixture of the desired product **11**²⁻ and the 7,7 dinuclear Cr,Cr complex **8**²⁻ (¹H NMR). This could reflect a scrambling process that involves cleavage of the inter-ring C–C bond in **9**, but none of the expected coproduct $\{[\text{Mn}(\text{CO})_3]_2(\mu_2\text{-}\eta^4\text{-}\eta^4\text{-C}_6\text{H}_6\text{-C}_6\text{H}_6)\}^{2-}$ (**12**²⁻) was observed.

To achieve clean reduction of **9** to **11**²⁻ we added 2.2 equiv of 0.2 M KNap/THF to a solution of purified **9** in THF at –78 °C to give a solution containing **11**²⁻ (IR, ν_{CO} only, THF: 1922(s), 1885(s), 1828(m, br), 1801(s, br), 1761(m, br) cm⁻¹). ¹H, ¹³C{¹H} and ¹³C–¹H coupling spectra confirm the presence in solutions of **11**²⁻ of $(\mu_2\text{-}\eta^5\text{-}\eta^4\text{-C}_7\text{H}_7\text{-C}_6\text{H}_6)$ ligands (with sp³ bridge carbons with distinctive NMR characteristics)⁹ in which the six- and seven-membered rings have been fused.

IR data for solutions of **11**²⁻ in THF were compared carefully with IR data for **8**²⁻ and **12**²⁻ to evaluate the possibility that we had prepared a mixture of the homodinuclear complexes rather than the desired heterodinuclear complex **11**²⁻; it was also conceivable that **11**²⁻ is in equilibrium with **8**²⁻ and **12**²⁻. IR peaks for **11**²⁻ overlap partially with peaks of **8**²⁻, but peaks for **11**²⁻ are distinct from those of **12**²⁻ in THF,¹⁰ and IR spectra of the reduced solution unambiguously indicate formation of the new product **11**²⁻ rather than a mixture of **8**²⁻ and **12**²⁻.

A crystalline salt of **11**²⁻ was obtained following addition of a cryptand (cryptate-2,2,2;¹¹ 2.0 equiv) to a solution of **11**²⁻ at –78 °C. The mixture was allowed to warm slowly to room temperature, and bright yellow crystals of $[\text{K}(\text{cryptate-2,2,2})]_2[\text{11}[\text{C}_{10}\text{H}_8]_{0.25}]$ (yield 63% from **9**) were obtained at –30 °C from MeCN/Et₂O (Scheme 2). Crystals of $[\text{K}(\text{cryptate-2,2,2})]_2[\text{11}[\text{C}_{10}\text{H}_8]_{0.25}]$ large enough for diffraction studies are readily prepared but are disordered. Elemental analysis is consistent with the proposed formulation.

The four-membered ring is the central feature of the $(\mu_2\text{-}\eta^5\text{-}\eta^4\text{-C}_7\text{H}_7\text{-C}_6\text{H}_6)$ ligand in **11**²⁻, and ¹H 1D decoupling, ¹H–¹H COSY and ¹³C–¹H HMQC 2D NMR spectra were used to assign ¹³C, ¹H NMR peaks in **11**²⁻ and to prove the connectivity of the carbon framework. Both 1D ¹H decoupling and ¹H–¹H COSY spectra show correlation between the bridge hydrogens on the two rings, and HMBC (heteronuclear multiple bond correlation) ¹³C–¹H 2D NMR spectra established unambiguously the structure of the $(\mu_2\text{-}\eta^5\text{-}\eta^4\text{-C}_7\text{H}_7\text{-C}_6\text{H}_6)$ ligand through observation of long-range C–H correlation between the six-membered ring bridge carbons and the seven-membered ring bridge hydrogens.

The formation of **11**²⁻ from **9** most reasonably involves a diradical intermediate (Scheme 2), especially since alternative mechanisms involving cleavage of the C–C bond in **9** are ruled out by the observation that **8**²⁻ and **12**²⁻ (both reported previously)^{3,8} are not formed during reduction of **9**. Intermediacy of 19-electron complexes would be consistent with the growing body of evidence for the role of such species in reductions of sandwich and half-sandwich molecules.^{1,12}

The results above establish for the first time that benzene and tropylium ligands can be selectively cross coupled, and the sequence involving reductive activation of the η^6 -arene ligand in $[\text{Mn}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]^+$, subsequent addition of the η^4 -arene complex **3**⁻ to **7**⁺, and reduction of intermediate **9** to form **11**²⁻ constitutes an intriguing new annulation of benzene that could have potential applications in transition metal-mediated organic synthesis.

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Supporting Information Available: Experimental details for synthesis and characterization of compounds (PDF), crystallographic data for **5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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