The synthesis of bimetallic manganese tricarbonyl-capped metallocenes

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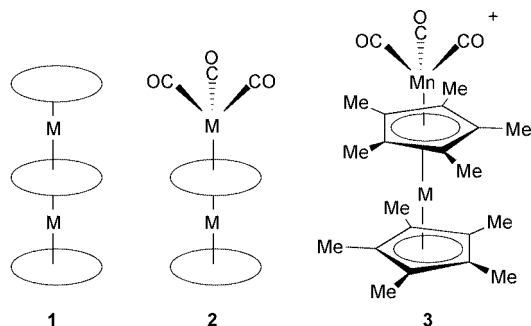*E-mail: Dwight_Sweigart@Brown.edu*
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Stable bimetallic 'capped' metallocenes are formed by the reaction of Cp*$_2$M (M = Fe, Ru, Os) with the manganese tricarbonyl transfer reagent [(η^6-naphthalene)Mn(CO)$_3$]$^+$.

Multimetallic complexes have generated great interest for many years due to their potentially useful electronic, redox and catalytic properties in comparison to monometallic analogues. Bimetallic 'triple-decker' complexes **1** containing cyclopenta-

dienyl, arene, and/or related heterocyclic π-ligands have been widely studied.[1] Bimetallics having the general structure **2**, in which a coordinated π-ring system is 'capped' with a M(CO)$_n$ carbonyl moiety, are much less common. Furthermore, in each complex of type **2** reported, the ring bridging the two metals is heterocyclic, most commonly being a borole based system.[2] Here we report the synthesis and characterization of bimetallic [Mn(CO)$_3$]$^+$ capped metallocenes **3**-Fe,Ru,Os, in which the bridging ligand is strictly carbocyclic.

It was recently shown by Chung and coworkers,[3] that ferrocene undergoes ring exchange with [(η^6-naphthalene)Mn(CO)$_3$]$^+$ according to eqn. (1). Since it is known[4] that

$$[(\eta^6\text{-}C_{10}H_8)Mn(CO)_3]^+ + [Cp_2Fe] \rightarrow$$
$$[(\eta^6\text{-}C_{10}H_8)FeCp]^+ + [CpMn(CO)_3] \quad (1)$$
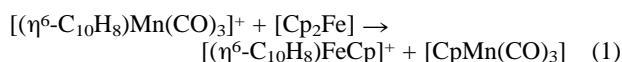
[(η^6-polyarene)Mn(CO)$_3$]$^+$ complexes readily transfer the [Mn(CO)$_3$]$^+$ moiety to suitable donor sites, it seemed possible that the bimetallic species [Cp–Fe–Cp–Mn(CO)$_3$]$^+$, in which one of the Cp rings is coordinated to both metals, occurs as an intermediate in this reaction. No such intermediate was actually observed with ferrocene, but we now report that changing the potential 'donor' from Cp$_2$Fe to the more electron-rich Cp*$_2$M (M = Fe, Ru, Os) results in the formation of stable isolable bimetallic capped metallocenes **3**-Fe, **3**-Ru and **3**-Os.

Refluxing equimolar amounts of Cp*$_2$M and the manganese tricarbonyl transfer reagent[4] [(η^6-polyarene)Mn(CO)$_3$]BF$_4$ (polyarene = 1-methylnaphthalene or acenaphthene) in CH$_2$Cl$_2$, followed by standard work-up procedures, led to moderate yields of the air-stable capped metallocenes [**3**]BF$_4$ (M = Fe, Ru, Os).[5] The iron complex is green while the ruthenium and osmium complexes are orange. The capped structure indicated for **3** is supported by IR, elemental analysis, MS, ^{1}H NMR, and ^{13}C NMR data (Table 1). Attempts to grow crystals of [**3**]BF$_4$ suitable for X-ray diffraction were not successful. However, acceptable crystals of [**3**-Ru]PF$_6$ were

Table 1 Characterization data for the capped metallocenes [Cp*MCp*Mn(CO)$_3$]BF$_4$

	Fe	Ru	Os
v_{CO}/cm^{-1} (CH$_2$Cl$_2$)	2050, 1975	2048, 1974	2051, 1976
EA (%):			
C(calc., found)	50.04, 49.85	46.25, 46.15	40.24, 40.34
H(calc., found)	5.48, 5.43	5.06, 5.00	4.40, 4.14
δ_H(CD$_2$Cl$_2$)	2.61(s), 1.66(s)	2.44(s), 1.59(s)	2.57(s), 1.62(s)
δ_C(CD$_2$Cl$_2$)	81.86, 81.33, 12.60, 8.31	87.56, 82.07, 12.96, 9.13	85.66, 72.66, 13.15, 9.63
$E_{1/2}$/V (CH$_2$Cl$_2$)^a	−1.44	−1.46	−1.42

^{a} At 25 °C, 0.10 M NBu$_4$PF$_6$, 500 mV s^{-1}, relative to Fc$^+$/Fc = 0.00 V.

obtained by diethyl ether vapor diffusion into a CH$_2$Cl$_2$ solution of [**3**-Ru]BF$_4$ containing a large excess of NH$_4$PF$_6$.

The X-ray structure of the cation in [**3**-Ru]PF$_6$ is shown in Fig. 1.[6] Both Cp* rings are highly planar (rms deviations 0.030, 0.019 Å) and adopt a staggered conformation. In contrast, the rings in Cp*$_2$Ru are eclipsed in the solid state.[7] The singly coordinated Cp* ring in [**3**-Ru]PF$_6$ has an average Ru–C bond length of 2.16 Å and an average ring C–C bond length of 1.42 Å. The corresponding distances in Cp*$_2$Ru are 2.18 and 1.42 Å.[7]
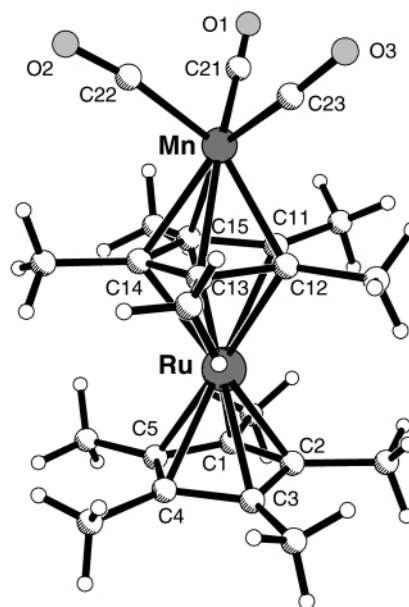
Fig. 1 Crystal structure of the cation in [**3**-Ru]PF$_6$. Selected bond lengths (Å) and angles (°): Mn–C(11) 2.180(7), Mn–C(12) 2.136(9), Mn–C(13) 2.186(5), Mn–C(14) 2.222(10), Mn–C(15) 2.163(13), Ru–C(11) 2.181(7), Ru–C(12) 2.225(7), Ru–C(13) 2.223(5), Ru–C(14) 2.215(11), Ru–C(15) 2.238(12), Ru–C(1) 2.144(5), Ru–C(2) 2.114(13), Ru–C(3) 2.203(12), Ru–C(4) 2.160(9), Ru–C(5) 2.182(9); Mn–C(21)–O(1) 176.1(10), Mn–C(22)–O(2) 169.6(9), Mn–C(23)–O(3) 167.6(10).

The reduced electron density in the doubly coordinated Cp* ring is reflected in longer average Ru–C and C–C bonds, 2.22 and 1.46 Å, respectively. The average Mn–C bond distance to the Cp* ring is 2.18 Å, which is *ca.* 0.04 Å longer than that typically found in neutral [(cyclopentadienyl)Mn(CO)$_3$] complexes.[8]

The ^{1}H NMR data in Table 1 for the Cp* methyls show a resonance at δ *ca.* 1.6, which is near that found for free Cp*$_2$M. The Cp* ring in **3**-Fe,Ru,Os that is bonded to both metals, however, has methyls shifted *ca.* 1 ppm downfield. This demonstrates the deshielding effect of the cationic [Mn(CO)$_3$]$^+$ fragment. Table 1 shows that the ν_{CO} bands for **3**-Fe,Ru,Os are at *ca.* 2050 and 1975 cm^{-1}. By comparison, the ν_{CO} bands occur at 2005 and 1914 cm^{-1} for [Cp*Mn(CO)$_3$] and at 2062 and 2002 cm^{-1} for [(η^6-C$_6$Me$_6$)Mn(CO)$_3$]$^+$. From this one concludes that electron donation to the [Mn(CO)$_3$]$^+$ moiety is in the order C$_5$Me$_5^-$ >> Cp*MCp* > C$_6$Me$_6$ and that much of the positive charge (LUMO) in **3** resides on the [Mn(CO)$_3$] fragment. This assertion is supported by electrochemical data, which show that the 30-electron bimetallic **3** is reduced in a one-electron chemically *reversible* manner at *ca.* −1.4 V relative to ferrocene. This is about the potential at which [(η^6-mono-arene)Mn(CO)$_3$]$^+$ complexes undergo reduction, although these species do so in a chemically *irreversible* manner.[9] In any case, the 31-electron neutral radical produced from **3** must have substantial stability for all three metals, and this aspect of the chemistry will be explored in future work.

Complexes **3**-Fe,Ru,Os are remarkably stable in CH$_2$Cl$_2$ and did not undergo a detectable reaction with P(OEt)$_3$ over 30 min. Similarly, a CH$_2$Cl$_2$ solution of **3**-Ru in the presence of naphthalene was unchanged after refluxing overnight. In MeCN solvent at room temperature, **3**-Ru was found to react with a half-life of *ca.* 1 h to afford predominantly the ring transfer product, [Cp*Mn(CO)$_3$], along with [Cp*Ru(MeCN)$_3$]$^+$. In contrast, the major products obtained from **3**-Fe in MeCN were [(MeCN)$_3$Mn(CO)$_3$]$^+$ and Cp*$_2$Fe, with a half-life of *ca.* 5 h. This difference in reaction pathway may be due to easier nucleophilic attack by MeCN at the larger ruthenium center, with concomitant Cp* ring displacement. The isolation and stability of **3**-Fe,Ru,Os strongly suggests a capped bimetallic as an intermediate in eqn. (1). An attempt was made to detect this species in the reaction of [(naphthalene)Mn(CO)$_3$]$^+$ with the bridged metallocene [3]ferrocenophane, the idea being that the –(CH$_2$)$_3$– strap would slow or prevent the Fe–Cp cleavage for entropy reasons. Unfortunately, the reaction was found to proceed analogously to eqn. (1).

In conclusion, we have shown that stable metal carbonyl capped metallocenes can be prepared from Cp*$_2$M.

Notes and references

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5 Syntheses: [**3**-Fe]BF$_4$: [(1-methylnaphthalene)Mn(CO)$_3$]BF$_4$ (100 mg, 0.275 mmol) and Cp*$_2$Fe (99 mg, 0.302 mmol) were added to CH$_2$Cl$_2$ (15 mL) under N$_2$ at room temperature. The solution was refluxed for 40 min, during which the color quickly changed from orange to green. The solution was cooled, the volume reduced to a few mL, and diethyl ether added to precipitate the product as a green powder. The product was redissolved in a minimal amount of CH$_2$Cl$_2$ and placed on a silica gel column wetted with CH$_2$Cl$_2$. Neutral species were eluted with CH$_2$Cl$_2$ and the green product was eluted with 1:10 (v/v) acetone–CH$_2$Cl$_2$, while unreacted [(1-methylnaphthalene)Mn(CO)$_3$]BF$_4$ remained on the column. The solvent was stripped and the product taken up in CH$_2$Cl$_2$ and reprecipitated with Et$_2$O. Yield 61% (93 mg); HRMS. calc. for C$_{23}$H$_{30}$FeMnO$_3$: *m/z* 465.0947; obs.: 465.0925. See Table 1 for other characterization data. [**3**-Ru]BF$_4$: A procedure essentially identical to that described for [**3**-Fe]BF$_4$ was followed, with Cp*$_2$Ru (112 mg, 0.30 mmol) replacing the Cp*$_2$Fe. Yield 32% (53 mg); HRMS: calc. for C$_{23}$H$_{30}$RuMnO$_3$: *m/z* 511.0626; obs.: 511.0619. See Table 1 for other characterization data. [**3**-Ru]BF$_4$ was also synthesized in a similar yield by reacting Mn(CO)$_5$Br with AgBF$_4$ in CH$_2$Cl$_2$ solution, followed by the addition of Cp*$_2$Ru. [**3**-Os]BF$_4$: A procedure essentially identical to that described for [**3**-Fe]BF$_4$ was followed, with Cp*$_2$Os (92 mg, 0.20 mmol) replacing the Cp*$_2$Fe and [(acenaphthene)Mn(CO)$_3$]BF$_4$ (83 mg, 0.22 mmol) replacing the [(1-methylnaphthalene)Mn(CO)$_3$]BF$_4$. Yield 30% (41 mg); HRMS. calc. for C$_{23}$H$_{30}$OsMnO$_3$: *m/z* 601.1190; obs.: 601.1186. See Table 1 for other characterization data. The yield in this reaction was artificially low because a significant amount of reactant [(acenaphthene)Mn(CO)$_3$]BF$_4$ was found to remain when the reaction was stopped.

6 The crystal structure of [**3**]PF$_6$ was determined by standard procedures. The crystal showed (chiral) $P2_1$ symmetry, but proved to be a racemic twin. The structure was readily solved. Each hydrogen was introduced in an ideal position, riding on the atom to which it is bonded; each was refined with an isotropic temperature factor 20% greater than that of the ridden atom. Both Cp* groups showed some librational disorder, and the atomic parameters were gently restrained to physically possible values. The three carbonyl groups and the PF$_6^-$ anion also showed evidence of disorder. In spite of the somewhat poorly defined parameters of the lighter atoms, the connectivity is clear. *Crystal data* for [**3**]PF$_6$: C$_{23}$H$_{30}$F$_6$MnO$_3$PRu, $M = 655.45$, data collected at 25 °C, monoclinic, space group $P2_1$, $a = 8.8909(11)$, $b = 8.9536(12)$, $c = 16.406(2)$ Å, $\beta = 94.905(2)°$, $V = 1301.2(3)$ Å^3, $Z = 2$, $\mu = 1.193$ mm^{-1}, 327 variables refined with 5673 independent reflections ($R_{int} = 0.0341$) to $R = 0.0530$, $wR2 = 0.1113$, GOF = 1.319. CCDC 148380. See http://www.rsc.org/suppdata/cc/b0/b009054i/ for crystallographic data in .cif or other electronic format.

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