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Note

Synthesis of manganese tricarbonyl cationic complexes of ferrocenyl substituted arenes via a manganese tricarbonyl cation transfer reaction

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Abstract

Manganese tricarbonyl cations of ferrocenyl substituted arenes were synthesized by the reaction of [(naphthalene)$Mn(CO)_3$]BF_4 with the corresponding arenes in dichloromethane. When the arenes are phenylferrocene, 4-methylphenyl-ferrocene, 2,6-dimethylphenyl-ferrocene, 2,4,6-trimethylphenyl-ferrocene, *trans*-(4-methylstyryl)-ferrocene, or *trans*-(2,4,6-trimethylstyryl)-ferrocene, the diiron compounds [(Fc-arene)FeCp]$^+$ and [(Fc-arene)Fe(C_5H_4-arene)]$^+$ are obtained as side-products. One of the diiron compounds was characterized by X-ray crystallography.

Keywords: Crystal structures; Ferrocene complexes; Arene complexes; Manganese complexes; Heterobimetallic complexes

1. Introduction

Heterobimetallic compounds containing a metallocenyl group have received considerable attention with regard to their role in redox switching [1]. Recently we reported the synthesis of $Cr(CO)_3$ compounds of ferrocenyl substituted arenes to be used as redox switches [2]. Although a wide variety of heterobimetallic compounds containing a metallocenyl group have been prepared, it is difficult to devise systematically a strategy for the synthesis of desired products, e.g. manganese tricarbonyl cations coordinated to a ferrocenyl substituted arene. Cationic manganese arene complexes are attracting special interest because of their high reactivity toward nucleophiles [3].

The coordination of $Mn(CO)_3^+$ to ferrocenyl substituted arenes usually requires severe reaction conditions. As a result, there are only rare examples of manganese tricarbonyl complexes of ferrocenyl-substituted arenes. Recently, we published a report of the mild $Mn(CO)_3^+$ transfer reaction using (naphthalene)$Mn(CO)_3^+$, and its use in synthesizing chromium–manganese diarene heterobimetallic complexes [4,5]. In this paper, we report the synthesis of new ferrocenyl-substituted arene manganese tricarbonyl cations (**A**) and the concomitant formation of [(Fc-arene)FeCp]$^+$ (**B**) and [(Fc-arene)Fe(C_5H_4-arene)]$^+$ (**C**) complexes as by-products (Fc = $CpFeC_5H_4$, Fc-arene = phenylferrocene, 4-methylphenyl-ferrocene, 2,6-dimethylphenyl-ferrocene, 2,4,6-trimethylphenyl-ferrocene, 2-thienyl-ferrocene, *trans*-(4-methylstyryl)-ferrocene, *trans*-(2,4,6-trimethylstyryl)-ferrocene, and *trans*-1-ferrocenyl-2-(2-thienyl)ethylene).

2. Experimental

All reactions were conducted under nitrogen using a standard Schlenk type flask. Work-up procedures were done in air.

Elemental analyses were done at the Chemical Analytical Center, College of Engineering, Seoul National University. ^1H NMR spectra were obtained with a Bruker BPX-300 or AMX-500 spectrometer. IR spectra were recorded on a Shimadzu IR-470 spectrometer (spectra measured as film on NaCl by evaporation of solvent). FAB mass spectra were recorded with a Jeol JMS AX 505 WA double-focusing mass spectrometer. All ligands, except for *trans*-(2,4,6-trimethylstyryl)-ferrocene, were known compounds [6] and were synthesized by modified known procedures. Compounds **1B** and **1C** were reported previously [7]. (Ferrocenylmethyl)triphenylphosphonium iodide salt was prepared by the method in the literature [8], starting from (ferrocenylmethyl)dimethyl amine.

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2.1. Preparation of trans-(2,4,6-trimethylstyryl)-ferrocene

Compound [Fc-CH_2PPh_3]I (1.41 g, 2.4 mmol) was dissolved in 40 ml of CH_2Cl_2. To the solution was added 18-crown-6 (0.01 equiv.) and KOt-Bu (0.27 g, 2.4 mmol). The color of the solution turned to deep red. After stirring the solution for 1 h at room temperature, 2,4,6-trimethylbenzaldehyde (0.30 g, 2 mmol) was added slowly to the solution. After stirring the resulting solution for 5 h at room temperature, the solution was poured into 50 ml of a saturated aqueous NH_4Cl solution. The methylene dichloride layer was separated, dried over anhydrous $MgSO_4$, and evaporated to dryness. Chromatography on the silica gel column eluting with hexane gave *cis* and *trans* isomers in yields of 19 and 51%, respectively. The *trans* isomer was used for the synthesis of **7A**. ^{1}H NMR of *trans*-isomer ($CDCl_3$): δ 6.89 (s, 2H, Ph), 6.68 (d, 16.6 Hz, 1H, vinyl), 6.30 (d, 16.4 Hz, 1H, vinyl), 4.44 (t, 1.7 Hz, 2H, Cp), 4.26 (t, 1.8 Hz, 2H, Cp), 4.15 (s, 5H, Cp), 2.34 (s, 6H, 2 Me), 2.27 (s, 3H, Me) ppm. *Anal.* Calc. for $C_{21}H_{22}Fe$: C, 76.34; H, 6.73. Found: C, 76.17; H, 6.26%.

2.2. Preparation of compounds A

A typical reaction procedure. A mixture of 2.0 equiv. Fc-arene and 1.0 equiv. [(naphthalene)$Mn(CO)_3$]BF_4 was dissolved in CH_2Cl_2. The solution was heated at reflux for 2–3 h. After the solution was cooled at room temperature, the solution was filtered of any solids. The filtrate was concentrated and recrystallized by addition of excess Et_2O. To obtain pure products, recrystallization by CH_2Cl_2–Et_2O was performed. When a mixture of **A** and **C** was obtained as product, **A** and **C** were usually separated by careful crystallization. The mixture of **A** and **C** was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was contacted with a mixture of Et_2O and hexane. Slow crystal growth afforded **A** and **C** in different crystalline forms. When a mixture of **A**, **B**, and **C** was obtained as reaction product, it was not possible to separate them from each other. In this case, the relative ratios of **A**, **B**, and **C** were determined by integration of the characteristic peaks in the ^{1}H NMR spectrum.

Compound **1A**. Yield 20%. IR (NaCl): ν(CO) 2070, 2016 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 7.08–6.89 (m, 5H), 5.18 (t, 1.8 Hz, 2H), 4.80 (t, 1.9 Hz, 2H), 4.26 (s, 5H) ppm. FAB-MS (*m/z*): 401 (M^+), 317 (M^+–3CO), 262 (M^+–$Mn(CO)_3$).

^{1}H NMR of **1B** (d_6-acetone): δ 6.62–6.55 (m, Ph), 5.09, 4.99, 4.46, 4.11 ppm.

^{1}H NMR of **1C** (d_6-acetone): δ 7.60–7.37 (m, free Ph), 6.46–6.30 (m, coordinated Ph), 5.60, 5.06, 4.77, 4.49, 4.02 ppm.

Compound **2A**. Yield 9%. IR (NaCl): ν(CO) 2064, 2008 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 6.99 (d, 7.3 Hz, 2H), 6.68 (d, 7.3 Hz, 2H), 5.16 (t, 1.7 Hz, 2H), 4.74 (t, 1.6 Hz, 2H), 4.24 (s, 5H), 2.56 (s, 3H, CH_3) ppm. FAB-MS (*m/z*): 415 (M^+), 331 (M^+–3CO), 276 (M^+–$Mn(CO)_3$).

Compound **2B**. ^{1}H NMR (d_6-acetone): δ 6.65 (m, Ph), 6.40 (m, Ph), 5.08, 4.58, 4.10, 2.54 (s, 3H, Me) ppm. FAB-MS (*m/z*): 397.

Compound **2C**. ^{1}H NMR (d_6-acetone): δ 7.49 (m, Ph), 7.18 (m, Ph), 6.37 (m, Ph), 6.20 (m, Ph), 5.56, 5.02, 4.80, 4.48, 2.34 (s, 3H, Me), 2.26 (s, 3H, Me) ppm. FAB-MS (*m/z*): 487.

Compound **3A**. Yield 60%. IR (NaCl): ν(CO) 2056, 2004 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 6.83 (d, 6.6 Hz, 1H), 6.72 (d, 6.6 Hz, 2H), 4.82 (t, 1.9 Hz, 2H), 4.77 (t, 1.9 Hz, 2H), 4.41 (s, 5H), 2.92 (s, 6H, $2CH_3$) ppm. *Anal.* Calc. for $C_{21}H_{18}BF_4FeMnO_3$: C, 48.89; H, 3.52. Found: C, 48.65; H, 3.32%.

^{1}H NMR of **3C** (d_6-acetone): δ 7.27 (m, Ph), 7.19 (m, Ph), 6.40, 6.31, 5.36, 5.15, 4.81, 4.67, 2.74 (s, 3H, Me), 2.64 (s, 3H, Me) ppm. FAB-MS (*m/z*): 515.

Compound **4A**. Yield 59%. IR (NaCl): ν(CO) 2052, 2000 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 6.59 (s, 2H), 4.75 (t, 2.0 Hz, 2H), 4.73 (t, 2.0 Hz, 2H), 4.40 (s, 5H), 2.90 (s, 6H, $2CH_3$), 2.54 (s, 3H, CH_3) ppm. *Anal.* Calc. for $C_{22}H_{20}BF_4FeMnO_3$: C, 49.81; H, 3.80. Found: C, 49.60; H, 3.95%.

^{1}H NMR of **4C** (d_6-acetone): δ 7.06 (m, Ph), 6.29 (m, Ph), 5.34, 5.12, 4.67, 4.65, 2.71 (s), 2.61 (s), 2.29 (s), 2.22 (s) ppm. FAB-MS (*m/z*): 543.

Compound **5A**. Yield 29%. IR (NaCl): ν(CO) 2064, 2016 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 7.74 (d, 16.5 Hz, 1H, vinyl), 7.00 (d, 6.7 Hz, 2H), 6.89 (d, 6.8 Hz, 2H), 6.72 (d, 16.1 Hz, 1H, vinyl), 4.68 (br s, 2H), 4.53 (br s, 2H), 4.23 (s, 5H), 2.57 (s, 3H, CH_3) ppm. FAB-MS (*m/z*): 441 (M^+), 357 (M^+–3CO), 302 (M^+–$Mn(CO)_3$).

Compound **6A**. Yield 36%. IR (NaCl): ν(CO) 2060, 2008 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 7.06 (d, 16.4 Hz, 1H, vinyl), 6.73 (d, 16.4 Hz, 1H, vinyl), 6.56 (s, 2H), 4.71 (br s, 2H), 4.44 (br s, 2H), 4.23 (s, 5H), 2.63 (s, 6H, 2 CH_3), 2.50 (s, 3H, CH_3) ppm. FAB-MS (*m/z*): 469 (M^+), 385 (M^+–3CO), 330 (M^+–$Mn(CO)_3$).

Compound **7A**. Yield 90%. IR (NaCl): ν(CO) 2052, 2004 cm^{-1}. ^{1}H NMR (d_6-acetone): δ 7.15 (dd, 1.1, 3.2 Hz, 1H), 7.10–7.08 (m, 2H), 5.16 (br s, 1H), 4.95 (br. s, 1H), 4.80 (br s, 1H), 4.76 (br s, 1H), 4.35 (s, 5H) ppm. *Anal.* Calc. for $C_{17}H_{12}BF_4FeMnO_3S$: C, 41.30; H, 2.45; S, 6.47. Found: C, 41.49; H, 2.60; S, 6.31%.

Compound **8A**. Yield 94%. IR (NaCl): ν(CO) 2064, 2008 cm^{-1}. ^{1}H NMR (CD_3NO_2): δ 7.34 (d, 15.9 Hz, 1H, vinyl), 6.71 (br s, 1H), 6.63 (br s, 1H), 6.54 (br s, 1H), 4.60 (br s, 2H), 4.33 (br s, 2H), 4.27 (s, 5H) ppm. *Anal.* Calc. for $C_{19}H_{14}BF_4FeMnO_3S$: C, 43.89; H, 2.71; S, 6.34. Found: C, 43.78; H, 2.71; S, 6.34%.

2.3. Nucleophilic addition to 3A and 4A

A typical reaction procedure. 1.0 equiv. **A** was dissolved in THF or CH_2Cl_2. To the solution, 1.2 equiv. $NaBH_3CN$ or PhMgBr was added. After stirring the solution for 1 h, the solution was quenched by excess brine solution and extracted

by excess Et_2O. The etheral solution was dried over anhydrous $MgSO_4$, concentrated, and chromatographed on a silica gel column eluting with hexane and diethyl ether. Purification was done by recrystallization from hexane and diethyl ether.

3A(H). Yield 56%. IR (NaCl): ν(CO) 2000, 1904 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.39 (t, 1.9 Hz, 2H, Cp), 4.30 (t, 1.9 Hz, 2H, Cp), 4.20 (s, 5H, Cp), 2.86 (dd, 0.6, 6.0 Hz, 2H), 2.49 (dt, 6.0, 12.8 Hz, 1H), 2.03 (d, 12.9 Hz, 1H), 2.01 (s, 6H, CH_3) ppm. *Anal.* Calc. for $C_{21}H_{19}FeMnO_3$: C, 58.60; H, 4.45. Found: C, 58.40; H, 4.58%.

3A(Ph). Yield 48%. IR (NaCl): ν(CO) 1997, 1906 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.28 (t, 7.3 Hz, 2H), 7.17 (t, 7.2 Hz, Ph), 7.00 (d, 7.0 Hz, 2H), 4.50 (t, 1.8 Hz, 2H, Cp), 4.37 (t, 1.8 Hz, 2H, Cp), 4.20 (s, 5H, Cp), 3.67 (t, 6.0 Hz, 1H), 3.47 (d, 6.0 Hz, 2H), 2.16 (s, 6H, CH_3) ppm. *Anal.* Calc. for $C_{27}H_{23}FeMnO_3$: C, 64.03; H, 4.98. Found: C, 64.27; H, 4.85%.

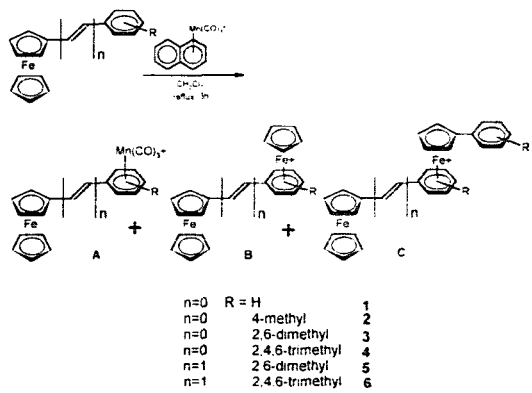
4A(Ph). Yield 13%. IR (NaCl): ν(CO) 1995, 1904 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.29 (t, 7.4 Hz, 2H), 7.23 (t, 7.2 Hz, 1H), 7.09 (d, 7.2 Hz, 2H), 4.62 (s, 1H), 4.48 (br s, 1H, Cp), 4.36 (br s, 1H, Cp), 4.32 (br s, 1H, Cp), 4.28 (br s, 1H, Cp), 4.18 (s, 5H, Cp), 3.72 (s, 1H), 2.88 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.72 (s, 3H, CH_3) ppm. *Anal.* Calc. for $C_{28}H_{25}FeMnO_3$: C, 64.61; H, 4.84. Found: C, 64.15; H, 4.79%.

2.4. X-ray structure determination of 4C

Crystals of **4C** were grown by slow evaporation of a solution of **4C** in CH_2Cl_2–Et_2O. Diffraction was measured by an Enraf-Nonius CAD4 automated diffractometer with a $\omega/2\theta$ scan method. Unit cells were determined by centering 25 reflections in the appropriate 2θ range. Other relevant experimental details are listed in Table 1. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically using a riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

Table 1
Crystal data and structure refinement for **4C**

Empirical formula	$C_{21}H_{19}BF_4Fe_2$
Formula weight	630.12
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	14.174(3)
b (Å)	17.397(3)
c (Å)	23.163(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	5711(2)
Z	8
Density (calc.) (Mg m^{-3})	1.466
Absorption coefficient (mm^{-1})	1.064
θ Range for data collection (°)	1.76 to 24.93
Index ranges	$0 \le h \le 16$, $0 \le k \le 20$, $0 \le l \le 27$
Reflections collected	1865
Independent reflections	1865 ($R_{int} = 0.0000$)
Refinement method	Full-matrix least-squares on F^2
Data, restraints, parameters	1843, 0, 361
Goodness-of-fit on F^2	1.169
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0785$, $wR2 = 0.1553$
R indices (all data)	$R1 = 0.0983$, $wR2 = 0.1943$
Largest difference peak, hole (e Å^{-3})	0.351, −0.332



(1)

3. Results and discussion

The ligands used to synthesize compounds **1–8** were prepared according to the published procedures [6]. To synthesize ferrocenyl substituted arene manganese tricarbonyl cations under the mild reaction condition, we used (naphthalene)$Mn(CO)_3^+$ as the $Mn(CO)_3^+$ transfer reagent, Eq. (1) [2].

The yields of **A** were 9–94% depending upon the aryl-substituted ferrocenes. Most of the reactions proceeded within 2 h. However, depending upon the ferrocenyl-substituted arene ligand and the reaction temperature, dinuclear cationic complexes **B** and **C** appeared as side products in different ratios. When we used $Mn(CO)_5BF_4$ as an $Mn(CO)_3^+$ transfer reagent [9], a mixture of **A**, **B**, and **C** was obtained in poor yield (total yields 10–20%).

When the ligand was phenylferrocene, 4-methylphenylferrocene, *trans*-(4-methylstyryl)-ferrocene, or *trans*-(2,4,6-trimethylstyryl)-ferrocene, **B** and **C** were obtained as side products. Treatment of (2,4,6-trimethylphenyl)-ferro-

cene with (naphthalene)$Mn(CO)_3^+$ at 40°C gave **4A** as sole product. At the high reaction temperature, we could observe the formation of **C**. When the reaction was carried out at 83°C, the product distribution of **4A** and **4C** was 5.9:1. Similar results were observed for the reaction of 2,6-dimethylphenyl-ferrocene with (naphthalene)$Mn(CO)_3^+$. By careful experimentation, we could confirm the formation of $CpMn(CO)_3$ and $ArCpMn(CO)_3$, in addition to **A**, **B**, and **C**, in the solution. The formation of $CpMn(CO)_3$ and $ArCpMn(CO)_3$ was related closely to the formation of **B** and **C**. Astruc and Dabard [7] reported the preparation of type **B** compounds through auto-condensation of arylferrocenes via ligand exchange. They added $AlCl_3$ as a catalyst. We do not have any direct evidence for the mechanism of formation of **B** and **C**. However, from the observation of $CpMn(CO)_3$ and $ArCpMn(CO)_3$ and Astruc's study, we propose a plausible reaction mechanism in Scheme 1.

We expect that (naphthalene)$Mn(CO)_3^+$ may act as a Lewis acid and accept an electron from the ferrocene with the concomitant liberation of $Mn(CO)_3$. The liberated $Mn(CO)_3$ can bind to any cyclopentadienyl ring in the solution. Thus, $CpMn(CO)_3$ and $ArCpMn(CO)_3$ can be formed and the $ArCpFe^+$ and $CpFe^+$ generated in situ would react with another ArCpFeCp to give **B** and **C**. In the cases of **3A**/**C** and **4A**/**C**, compounds **A** and **C** are easily separated by recrystallization. The formation of **4C** was confirmed by X-ray structure determination (Fig. 1). The bond lengths and most bond angles in **4C** are ordinary and require no comment. The Cp (C10–C14) ligand is nearly planar; the dihedral angle between the η^6-arene ring plane and the Cp (C10–C14) plane is 6.2°. Because of the methyl groups on the free arene ring, the free phenyl ring is prevented from being coplanar and in conjugation with the Cp (C10–C14) ring. The angle between these two planes is 30.2° in the solid state. For the same reason, the Cp (C24–C28) ring is not coplanar with the complexed arene ring (C1–C6). The angle between these two planes is 52.0°. The distance between the iron atom and the center of gravity of the arene ring is 1.54(5) Å, while the distance to the Cp ring is 1.68(5) Å.

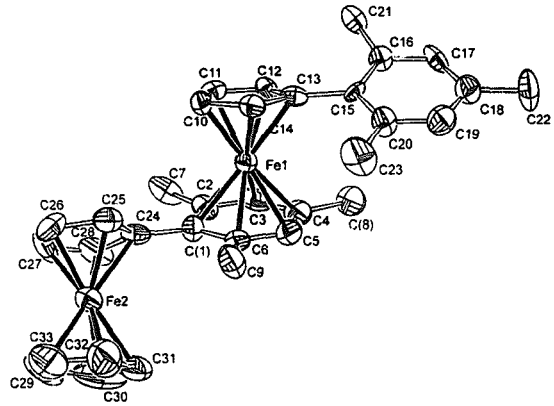
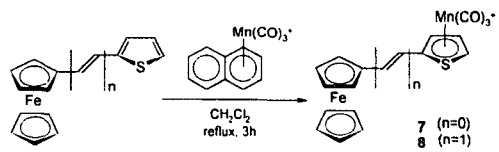


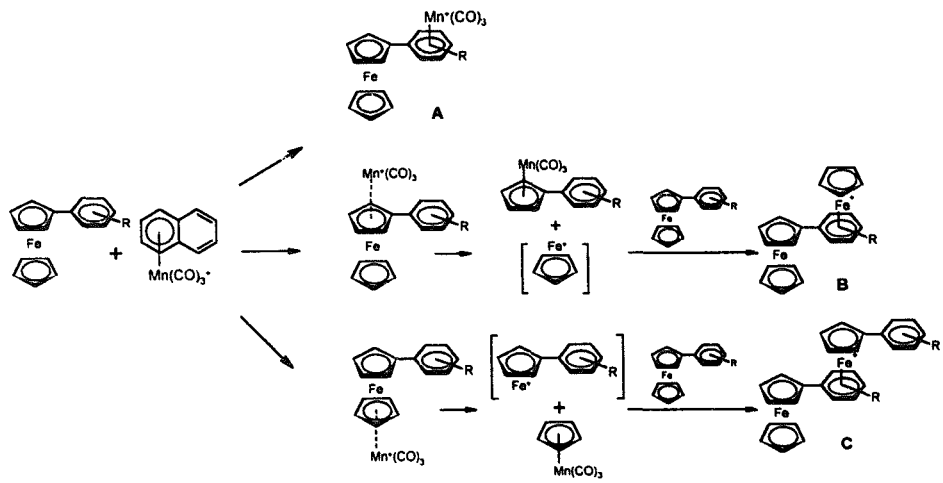
Fig. 1. An ORTEP drawing of **4C**. Selected bond lengths (Å) and angles (°): Fe(1)–C(1) 2.13(2), C(1)–C(2) 1.46(2), C(1)–C(24) 147(2), C(13)–C(15) 1.51(2), C(15)–C(16) 1.40(2); C(1)–C(2)–C(3) 118.4(14), C(1)–C(24)–C(25) 127(2), C(13)–C(15)–C(16) 118.5(12).

For the formation of **7A** and **8A**, there was no side product, presumably owing to the high coordination ability of $Mn(CO)_3^+$ to bind to the thiophene ring, Eq. (2).



(2)

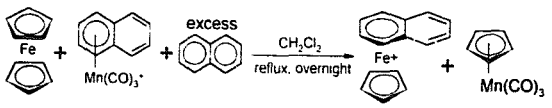
Thus, **3A**, **4A**, **7A**, and **8A** were characterized by elemental analyses. However, **1A**, **2A**, **5A**, and **6A** were characterized



Scheme 1.

by FAB mass spectra instead of elemental analyses. The yields of **1A**, **2A**, **5A**, and **6A** and the relative ratio **A**:**B**:**C** were determined by the integration of ^{1}H NMR peaks. When phenylferrocene was treated with (naphthalene)$Mn(CO)_3^+$ in CH_2Cl_2 at 40°C for 3 h, the relative ratio **1A**:**1B**:**1C** was 4:1:2.8. Treatment of 4-methylphenyl-ferrocene, *trans*-(4-methylstyryl)-ferrocene, and *trans*-(2,4,6-trimethylstyryl)-ferrocene with (naphthalene)$Mn(CO)_3^+$ in CH_2Cl_2 at 40°C for 3 h gave **2A**:**2B**:**2C**, **5A**:**5B**:**5C**, and **6A**:**6B**:**6C** in the relative ratios 1.2:1:2.2, 5.4:1:1.7, and 7.2:1:1.5, respectively.

The formation of **B** and **C** suggests that we can make $CpFe(arene)^+$ by using ferrocene as a starting material. Thus, when ferrocene was treated with [(naphthalene)-$Mn(CO)_3$]BF_4 in the presence of excess naphthalene, we could isolate [(naphthalene)$FeCp$]BF_4 [10] in 53% yield. Eq. (3).

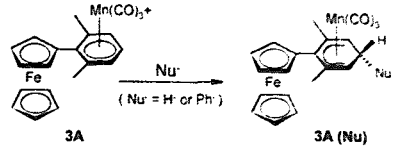


(3)

Treatment of ferrocene with [(naphthalene)-$Mn(CO)_3$]BF_4 in the presence of excess phenanthrene afforded [(phenanthrene)$FeCp$]BF_4 and [(phenanthrene)$Mn(CO)_3$]BF_4 in 28 and 24% yields, respectively [2,10]. One of the most versatile methods of preparing η^6-arene-η^5-cyclopentadienyliron cations is the ligand exchange reaction between an arene and ferrocene in the presence of $AlCl_3$ [11]. However, treatment of ferrocene with $AlCl_3$ in the presence of excess naphthalene afforded (1,2,3,4-tetrahydronaphthalene)$FeCp^+$ [12]. The advantage of our method over the $AlCl_3$ method is that there is no hydrogenation of the reaction product during the reaction.

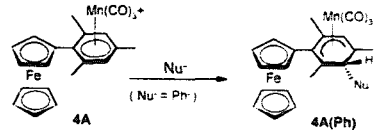
Complex **7** is rather unstable in polar organic solvents such as acetone. Thus, **7** was decomposed in acetone within 10 min. It is known that most (thiophene)$Mn(CO)_3^+$ cations are unstable in polar organic solvents [13]. Thus, the instability of **7** is intrinsic and not due to the ferrocenyl moiety. Compounds **5**, **6**, and **8** have a very similar structure to *p*-nitrostyryl ferrocene, which has been studied with respect to its non-linear optical properties [14]. Instead of the *p*-nitro-group, **5**, **6**, and **8** have $Mn(CO)_3^+$, which may be a stronger electron-withdrawing group than the *p*-nitro-group. As we expected, **7** shows some solvatochromism. Since subtle alterations in molecular structure offer a means of optimizing material properties in a controlled fashion, the introduction of an $Mn(CO)_3^+$ moiety provides the possibility of the creation of new chemical and physical properties [15].

Nucleophilic addition ($NaBH_3CN$ and/or PhMgBr) to compounds **3A** and **4A** was studied. When **3A** was treated with $NaBH_3CN$ in THF, we could observe the formation of a hydride-adduct, Eq. (4).



(4)

Treatment of **3A** with PhMgBr in THF yielded only one isomer as expected. When **4A** was treated with PhMgBr in THF, only one isomer was isolated. Eq. (5).



(5)

For the reaction of **4A** with PhMgBr, the yield was poor (13%), probably owing to steric congestion. For other compounds **A**, it was difficult to study the nucleophilic addition reaction because of difficulty in separating the pure compounds (for **1A**, **2A**, **5A**, and **6A**) and the instability of the reaction products (for **7A** and **8A**). We have only a few results to draw any conclusions about the nucleophilic addition.

4. Conclusions

In conclusion, we have demonstrated the synthesis of manganesetricarbonyl cations of ferrocene-substituted arenes via the $Mn(CO)_3^+$ transfer reaction. Depending upon the arenes, **B** and **C** were obtained as side-products. One of the **C** compounds was characterized by X-ray crystallography and the $Mn(CO)_3^+$ transfer reaction can be used to make [(naphthalene)$FeCp^+$]BF_4.

5. Supplementary material

Tables of atomic coordinates and equivalent isotropic parameters, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **4C** may be obtained directly from the authors on request.

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