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Ferrocenyl-Substituted (η^5-Hydroxyalkylcyclohexadienyl) tricarbonylmanganese Complexes: Synthesis, Structural Determinations, and Formation of Carbenium Ions

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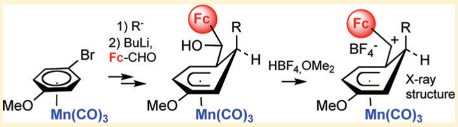
S *Supporting Information*

ABSTRACT: Ferrocenyl-substituted (η^5-hydroxyalkylcyclohexadienyl)-tricarbonylmanganese complexes have been synthesized as well as the corresponding carbenium dinuclear complexes after dehydroxylation. Studies in solution and in the solid state of these zwitterionic species show not only the electronic influence of the positive charge on the η^5-Mn complex but also the participation of the two metal atoms in the stabilization of this charge. Catalytic tests show a high activity of these cations as Lewis acids in a typical Diels–Alder reaction.



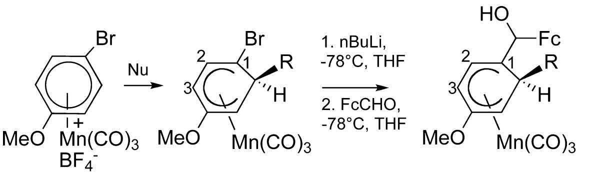
The reactivity of an arene ring is dramatically modified by coordination to a metal tricarbonyl tripod such as $Cr(CO)_3$ or $Mn(CO)_3$, allowing a variety of transformations which are impossible to achieve on a free arene.[1] The reactivity is altered of not only ring carbons but also that of groups in benzylic positions. In terms of the side-chain reactivity of π-complexed arenes, (η^6-arene)$Cr(CO)_3$ compounds have been extensively studied, showing interesting reactivities, stereoselectivities, and stereospecificities.[2] They have been described as "hermaphroditic",[3] and their reactivity toward anions, cations, and radicals gave rise to remarkable computational and experimental studies.[4] In contrast, very few studies have appeared on the isoelectronic cationic (η^6-arene)$Mn(CO)_3^+$ complexes.[5] For example, deprotonation at a benzylic position in the $[(\eta^6\text{-alkylarene})Mn(CO)_3]^+$ series using a large excess of strong base occurred with formation of (η^5-alkylbenzyl)Mn-$(CO)_3$ complexes presenting a highly activated exocyclic double bound.[6] As for the neutral (η^5-cyclohexadienyl)$Mn(CO)_3$ derivatives whose chemical properties have been shown to be very close to those of (η^6-arene)$Cr(CO)_3$,[7] the first functionalization at a "benzylic" position (i.e., α to the η^5 system) by a lithiation/electrophilic quench sequence was very recently described involving the formation of an intermediate "benzylic" carbanion.[8] In the course of the studies of (η^5-hydroxyalkylcyclohexadienyl)$Mn(CO)_3$ complexes, the formation of "benzylic" carbocations was postulated to explain the reactivity of such complexes but, in all the examples studied, the intermediate carbocation was too unstable to be isolated.[9,10] Indeed, only products due to the rearrangement of these elusive species were obtained. We wondered whether it would be possible to stabilize these cationic species by an electron-donor substituent such as a ferrocenyl group.[11,12] This paper is devoted to the synthesis and structural determination of ferrocenyl-substituted (η^5-hydroxyalkylcyclohexadienyl)Mn-$(CO)_3$ complexes and their transformation into the corresponding carbocations by elimination of the hydroxy group. Furthermore, the first catalytic tests are described using these bimetallic carbocations in a typical Diels–Alder reaction.

Hydroxyalkyl-substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes have been described in the literature and can be obtained using two methodologies: either by reduction of the corresponding keto or aldehyde derivative complexes[13a,b] or by lithiation of the corresponding (η^5-cyclohexadienyl)$Mn(CO)_3$ complex followed by quenching with an aldehyde or a ketone.[13c]

In the present study, we chose two synthetic strategies for the preparation of ferrocenyl-substituted (η^5-hydroxyalkylcyclohexadienyl)$Mn(CO)_3$ complexes at the three different positions of the π-system. Both are based on the lithiation–electrophilic quenching sequence of a η^5-Mn complex but differ in the lithiation first step: one occurs by deprotonation,[7b,13] whereas the other involves metal–halogen exchange starting from bromo η^5-Mn complexes.[14]

The C1 regioisomers were synthesized as depicted in Scheme 1. The starting bromo-substituted η^5-Mn complexes **2**,[14] **3**,[14]

Scheme 1. Synthesis of C1 Hydroxyalkyl Complexes



1

2 Nu = LiAlH4, R = H (65%)
3 Nu = PhMgCl, R = Ph (94%)
4 Nu = MeMgCl, R = Me (60%)

5 R = H (2 diast. 2.5/1, 68%)
6 R = Ph (1 diast, 90%)
7 R = Me (1 diast, 52%)

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and **4** were readily formed by addition of $LiAlH_4$, PhMgCl, and MeMgCl, respectively, to the (*p*-bromoanisole)$Mn(CO)_3$ complex **1**[14] regioselectively at the C6 carbon atom. After reaction with nBuLi at −78 °C in THF and then with ferrocenecarboxaldehyde at the same temperature, complexes **5**−**7** were isolated in 68, 90, and 52% yields, respectively.

It is worth noting the formation of a single diastereoisomer in the case of **6** and **7**, whereas two diastereoisomers in a 2.5/1 ratio were obtained in the case of **5**. This selectivity is likely due to the differences of steric hindrance at the C6 carbon atoms.

We were lucky enough to obtain single crystals of **6** suitable for X-ray diffraction analysis by slow evaporation of a dichloromethane/pentane solution of the purified diastereoisomer. The ORTEP view of the molecular structure is presented in Figure 1. The η^5-cyclohexadienyl moiety exhibits the classical five-coplanar geometry (C1C2C3C4C5), with the C6 carbon lying out of this plane with a dihedral angle of 39°. The 1.422(4) Å value for the C7−O8 bond length of the alcohol group is in agreement with a single C−O bond. The cyclohexadienyl plane and that of the substituted cyclopentadienyls are almost perpendicular, with the Fe atom far from the sterically demanding $Mn(CO)_3$ group. The main features of this structure are very close to those of two other structures of (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes substituted by an hydroxyalkyl group at the C1 position, with the thienyl group instead of the ferrocenyl group, and with the phenyl[13b] or the thienyl group[10] at the C6 carbon.

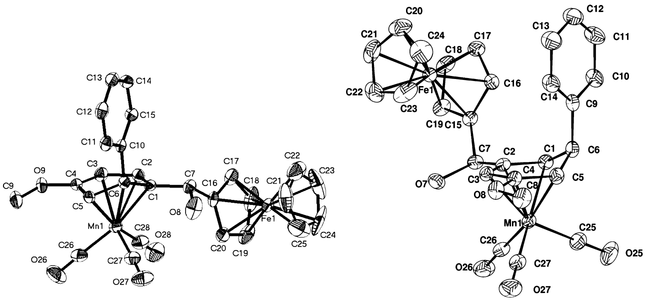
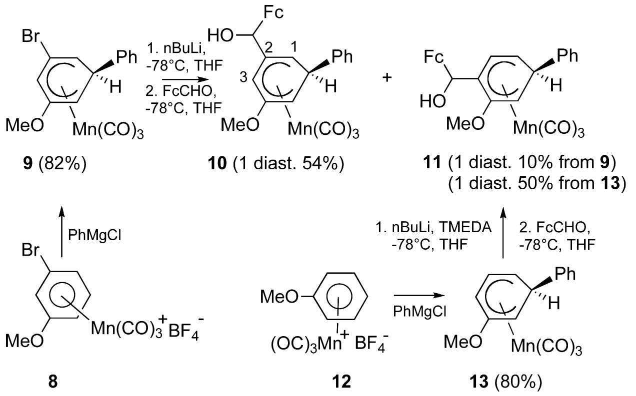


Figure 1. ORTEP views of complexes **6** (left) and **10** (right) with thermal ellipsoids at the 30% probability level.

Starting from the η^5-Mn complex **9**, easily obtained by regioselective addition of PhMgCl to the cationic (*m*-bromoanisole)$Mn(CO)_3$ complex **8**,[14] the same experimental conditions delivered not only the corresponding alcohol **10** as a single diastereoisomer in 54% yield but also the unexpected regioisomer **11** functionalized at the C3 carbon atom. Its formation is likely due to the reaction of the initial carbanion from **9** with *n*-BuBr that is generated from the *n*-BuLi, to afford small amounts of complex **13**, which is then deprotonated to form the rearranged anion, giving **11** after quenching with the ferrocenecarboxaldehyde (Scheme 2). The X-ray structure of **10** reported in Figure 1 shows clearly the position of the ferrocenyl moiety above the η^5 plane in order to avoid the sterically demanding $Mn(CO)_3$ group.

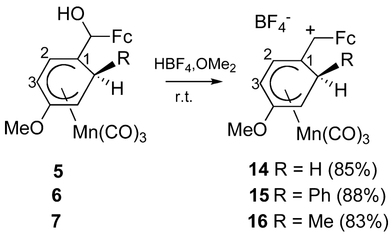
An alternative for the formation of the C3 regioisomer **11** was proposed starting from the η^5-Mn complex **13** readily obtained by regioselective nucleophilic addition of PhMgCl to the cationic (η^6-anisole)$Mn(CO)_3$ complex **12**[15] (Scheme 2). Regioselective deprotonation ortho to the methoxy group followed by electrophilic quenching with ferrocenecarboxaldehyde delivered complex **11** in a more satisfying 50% yield.

Scheme 2. Synthesis of C2 and C3 Hydroxyalkyl Complexes



After the preparation of these different regioisomers of ferrocenyl-substituted (η^5-hydroxyalkylcyclohexadienyl)Mn-$(CO)_3$ complexes, the next goal was to achieve the synthesis of the corresponding carbocations by a dehydroxylation reaction, achieved in the presence of an acid. In a typical example, treatment of the alcohol **5** with 3 equiv of the ether complex $HBF_4{\cdot}OMe_2$ in CH_2Cl_2 at room temperature furnished within 10 min a deep blue solution from which complex **14** could be isolated in 85% yield as the BF_4^- salt after precipitation by addition of diethyl ether. Under the same experimental conditions, the cationic complexes **15** and **16** were obtained as dark blue powders from **6** and **7** in >80% yields (Scheme 3).

Scheme 3. Synthesis of C1 Carbenium Ions



^1H and ^{13}C NMR spectra of complex **14** unfortunately could not be recorded, likely because of the presence of some paramagnetic impurities due probably to the oxidation of the ferrocenyl unit. As for **15** and **16**, the signals for the C^+−H protons in acetone-d_6 both lie downfield, as expected for protons on a positively charged center: 8.16 ppm for **15** and 7.92 ppm for **16**, in good agreement with data for various ferrocenyl carbenium ions previously reported.[16] An overall deshielding effect of the cyclohexadienyl protons and a spectacular deshielding effect of H2 protons (6.98 and 6.66 ppm for **15** and **16**, respectively) with respect to the H3 protons (6.66 and 6.61 ppm) have to be pointed out as being certainly due to the strong electronic effect of the C7 carbocations, whereas in the starting neutral alcohol complexes **6** and **7**, the H3 protons are, as expected for η^5-Mn complexes, the most deshielded.[17] These data reveal a significant electronic perturbation of the η^5-Mn moiety which participates in the distribution of the positive charge. The IR spectra show two absorption bands in the region of the carbonyl ligands which are compared to those of the parent alcohol complexes. As evidenced by results gathered in Table 1, in the salts the

Table 1. ν(CO) Stretching Bands (cm^{-1})

5	6	7	14	15	16
1898	1908	1910	1937	1949	1966
1996	2005	2009	2026	2027	2032

carbonyl absorptions are displaced to higher frequencies due to the strong electron-withdrawing effect of the cations.[18]

The molecular structure of **15** is displayed in Figure 2. In contrast to the case of alcohol **6**, the two metal atoms now lie on opposite faces of the η^5 system, with the ferrocenyl moiety axis almost perpendicular to the carbenium plane. First, this avoids the hindrance by sterically demanding Mn(CO)$_3$ tripod, and second, this permits a better overlap between iron and carbenium orbitals. Furthermore, C1−C7 and C7−C16 bond lengths move from 1.512(4) and 1.497(4) Å in **6** to 1.432(4) and 1.414(4) Å in **15**, thus exhibiting a partial double-bond character. The C7−Mn and C7−Fe distances vary from 3.399(3) and 3.144(3) Å in the alcohol **6** to 3.035(2) and 2.818(3) Å, respectively, in the carbenium **15**. The differences correspond to deviation angles of 17.4[19] and 16.8° (bending of the C7−C1 and C7−C16 bonds toward Mn and Fe, respectively).

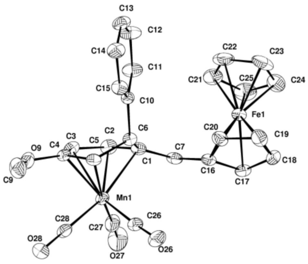
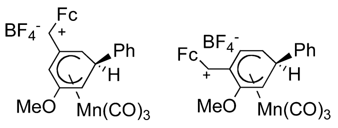


Figure 2. ORTEP view of complex **15** with thermal ellipsoids at the 30% probability level. The BF$_4^-$ anion is omitted for clarity.

These significant bendings of the exocylic carbenium atom, not only out of the Cp ring plane toward the iron atom but also out of the η^5-cyclohexadienyl ring plane toward the manganese atom, are in good agreement with a direct participation of both metals in the stabilization of the positive charge.

The same experimental conditions as for **14−16** were used to generalize the formation of carbenium to C2 and C3 regioisomers. Thus zwitterionic complexes **17** and **18** were isolated in 68 and 54% yields, respectively, starting from parent alcohols **10** and **11** (Figure 3).

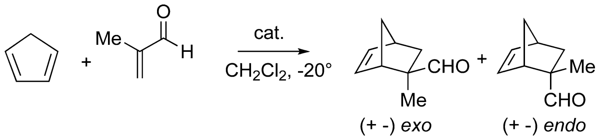


17 (68%) **18** (54%)

Figure 3. C2 and C3 carbenium complexes **17** and **18**.

The catalytic activity of the novel binuclear Lewis acids was then tested in a Diels−Alder reaction. The regioisomers **15**, **17**, and **18** were chosen as potential catalysts in the reaction of cyclopentadiene with methacrolein. Selected results are gathered in Table 2. First of all, under the conditions used, −20 °C in CH$_2$Cl$_2$ for 24 h, no reaction was observed in the presence of parent alcohols **6**, **10**, and **11** as catalysts. C1 and C3 carbenium regioisomers proved to be active, affording the same exo/endo ratio (85/15) but with a better conversion for **18** (71%) than for **15** (30%) (Table 2, entries 1 and 3). A noticeable progress was observed in the case of the C2 regioisomer, for which the reaction is very fast (2 h) and quantitative, with the best selectivity being a 90/10 exo/endo ratio (entry 2).[20] Furthermore, it is worth noting that the quantity of catalyst used is very low, 0.1 mol % in comparison with monometallic ferrocene carbenium complexes described in the literature,[16] and that the catalyst can be recovered by precipitation in ether and reused without loss of its efficiency.

Table 2. Catalytic Tests in a Diels−Alder Reaction: Results Followed by ^{1}H NMR Spectroscopy



entry no.	1	2	3
cat.	**15**	**17**	**18**
quantity[a]	3	0.1	3
time[b]	24	2	24
conversion[c]	30	100	71
exo/endo	85/15	90/10	85/15

[a] In percent mol equiv. [b] Reaction time in hours. [c] In percent.

In conclusion, we have reported the synthesis of ferrocenyl-substituted (η^5-hydroxyalkylcyclohexadienyl)-tricarbonylmanganese complexes which can be easily converted to unique stable carbenium dinuclear complexes by dehydroxylation. The preliminary results of the studies in solution (NMR, IR) and in the solid state (crystallography) of these ionic species show not only the electronic influence of the positive charge on the η^5-Mn complex but also the participation of the **two** metal atoms to the stabilization of the positive charge through significant deviation angles toward Fe and Mn in the structure of the corresponding cation. This is the first evidence of stabilization of "benzylic" cations in (η^5-cyclohexadienyl)tricarbonylmanganese series. Work is in progress to develop the reactivity of such species toward nucleophiles. As the stabilization of "benzylic" anions of η^5-Mn complexes has been recently described,[8] it seems that the term "hermaphroditic" could be applied to η^5-Mn complexes in analogy with what is well precedented in (η^6-arene)-tricarbonylchromium series.[3,4] Although the catalytic tests are in their infancy, the C2 dinuclear carbocation shows a high activity as a Lewis acid catalyzing a typical Diels−Alder reaction. These results shed new light on the applications of η^5-Mn complexes in organic and organometallic syntheses.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for complexes **6**, **10**, and **15** (CCDC 845687, 845149, and 845688, respectively), tables giving crystal data and refinement details, and text giving details of the syntheses. This material is available free of charge via the Internet at http://pubs.acs.org.

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