**Solid State Structure of (Pentamethylcyclopentadienyl)(2,4-Dimethylpentadienyl)iron,
Fe(C₅Me₅)(2,4-C₇H₁₁), and its incorporation into silica aerogels**

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Dedicated to Malcolm L. H. Green, an icon and everlasting inspiration for the fields of inorganic
and organometallic chemistry

The structure of Fe(C₅Me₅)(2,4-C₇H₁₁) has been determined (C₇H₁₁ =
dimethylpentadienyl), and found to be isomorphous with its ruthenium analogue. The Fe-C bond
distances for the open pentadienyl ligand have been found to be about 0.02 Å shorter than those
for the aromatic pentamethylcyclopentadienyl ligand, whereas for the simple cyclopentadienyl
analogue, the Fe-C bond distances for the two ligand types were nearly identical. While the
structural data support proposals that the pentadienyl ligand is more strongly bound, the complex
reacts readily with silica aerogel, during which it is the nonaromatic pentadienyl ligand which is
removed via protonation. Solid state ¹³C NMR spectra are consistent with incorporation of the
metal into one major environment, with lesser degrees of incorporation into alternative
environments.

Keywords: Cyclopentadienyl; Pentadienyl; Half-Open Metallocene; Half-Open Ferrocene

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Introduction

Pentadienyl ligands, though not nearly so well studied as their more familiar cyclic counterparts, have nonetheless been shown to display very interesting structural and reactivity behaviors [1]. Thus, for example, it has been demonstrated that pentadienyl may simultaneously be more strongly bound and more reactive than cyclopentadienyl, and that bis(pentadienyl)metal (“open metallocene”) complexes can serve as effective vapor phase sources for metal film depositions [2]. Ruthenium has been found to be quite useful and/or promising for commercial electronics applications, such as for random access memory storage, semiconductors, copper interconnects, capacitors, or transistors [2b-f], and its incorporations via the commercially available $\text{Ru}(2,4\text{-C}_7\text{H}_{11})_2$ (**1**; $2,4\text{-C}_7\text{H}_{11}$ = dimethylpentadienyl; $\text{M} = \text{Ru}$) have been shown to be ideal for many of these processes. $\text{Ru}(2,4\text{-C}_7\text{H}_{11})_2$ has also been found to yield other complexes of chemical interest, such as a highly active catalyst for phase transfer hydrogenation of ketones [3]. Half-open metallocenes, such as $\text{M}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$ and related complexes, have also been useful for a number of the above applications, and have been especially helpful in evaluating the relative bonding favorabilities of pentadienyl vs. cyclopentadienyl ligands with various metals [1b]. In general, the pentadienyl ligands are especially favored for early, low valent transition metals, often as a result of significant δ backbonding interactions [1b].

Additional potential for these compounds lies in their depositions on oxide supports. Given that allyl and pentadienyl ligands have been demonstrated to react readily with surface hydroxyl groups of silica and alumina [4,5], their complexes have become quite promising agents for the selective generation of single-site metal catalysts, which can lead to greatly increased (as well as decreased) activities and selectivities. Though single-site catalysts may be disadvantageous in Fischer-Tropsch synthesis, there is much promise in other cases for these or similarly highly dispersed, metal-derived catalysts, such as in the water gas shift reaction [5]. In

this aspect, early studies involving complexes with the related, highly reactive allyl (C_3H_5 , **2**) ligand, such as $\text{Rh}(\text{C}_3\text{H}_5)_3$, have provided excellent precedent for such expectations [4]. In fact, the incorporation of $\text{Pd}(\text{C}_5\text{H}_5)(\text{C}_3\text{H}_5)$ into aerogel supports, followed by reduction to the metal, has led to exceptionally high dispersions and water gas shift reactivities, which decrease with time due to agglomeration of the initially well-dispersed metal sites [5a]. It can then also be expected that the series of open metallocenes, having the general formula $\text{M}(\text{2,4-C}_7\text{H}_{11})_2$, **1**, would offer substantial promise, in that a variety of both early and late transition metal sources is available (e.g., $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Ru}, \text{Os}$) [6], as well as related species for at least zirconium, the lanthanides, and uranium [6, 7].

In addition to their structural and catalytic interests, the half-open species provide ideal opportunities to compare the relative reactivities of the open and closed dienyl systems. Herein we will structurally examine the known half-open metallocene compound, $\text{Fe}(\text{C}_5\text{Me}_5)(\text{2,4-C}_7\text{H}_{11})$ (**3**, C_5Me_5 = pentamethylcyclopentadienyl), to evaluate the relative bonding favorabilities for iron relative to the two ligand types, and also examine its potential utility for incorporation of iron into alumina and silica aerogels.

Material and Methods

$\text{Fe}(2,4\text{-C}_7\text{H}_{11})_2$, $\text{Ru}(2,4\text{-C}_7\text{H}_{11})_2$, and $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$ were prepared as described previously [8-10]. $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$ was prepared by a modification of a previously reported procedure [11], carried out under an inert atmosphere. A suspension of $\text{FeBr}_2(\text{dme})$ [12] ($\text{dme} = \text{C}_4\text{H}_{10}\text{O}_2$) (305 mg, 1.0 mmol) in *ca.* 10 mL THF was cooled to -78°C . A solution of $\text{NaC}_5(\text{CH}_3)_5$ [13] (150 mg, 0.95 mmol) in *ca.* 10 mL was added dropwise to the iron bromide suspension, yielding an olive-green solution, which was allowed to stir at -78°C for 30 min. A THF solution of $\text{K}(2,4\text{-C}_7\text{H}_{11})$ (125 mg, 0.93 mmol) was then added to the olive green solution. Once a dark red solution had formed, the flask was placed in a warm water bath and allowed to warm to room temperature. After a few minutes at room temperature, the solvent was removed *in vacuo*, and the residue was taken up in pentane and filtered through Celite. The solvent and volatiles were removed in *vacuo* again, yielding 205 mg of a red solid, found to be approximately 84% $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$, 16% *bis*(2,4-dimethylpentadienyl)iron, and 0% decamethylferrocene by $^1\text{H-NMR}$. The title compound can be isolated by recrystallizing the mixture from pentane (3 mL) cooled to -60°C , yielding 160 mg (58%) of reasonably pure

(~97% by ^1H -NMR) complex. Crystals suitable for X-ray crystallographic study were grown from a nearly saturated solution of pentane slowly cooled to $-30\text{ }^\circ\text{C}$. The proton NMR data were identical to those previously reported [11].

The aerogels were prepared according to published procedures [14]. For the incorporation of metal species into the aerogel monoliths, having diameters close to 10 mm, the metal complex was first placed in the bottom of a Schlenk tube, after which iron mesh was added in order to prevent direct contact with the monolith, which was placed on the mesh. The tube was then evacuated (ca. 10^{-3} mm Hg or lower). Generally the incorporation could be observed visibly within seconds for silica, though alumina incorporations were slower and could take a minute or more to be seen. For the C_5Me_5 complex, the incorporations were also slower, while for ferrocene much less incorporation was observed. For the incorporations into powdered aerogel samples, which were used for ^{13}C NMR studies, the aerogels were first crushed to powders with a mortar and pestle, and sieved to yield particle sizes between 60 – 110 mesh. These were then mixed with the metal complex in a Schlenk tube, which was evacuated under a dynamic vacuum (ca. 10^{-3} mm Hg) and rotated using a rotary evaporator. Incorporations of at least 1-2% could generally be obtained within 1-2 days, with progress being judged visibly by the lack of remaining metal complex. Solid state ^{13}C NMR spectra were obtained as previously described [8].

Crystallographic studies.

Single crystals were selected under Paratone oil, and transferred to an Enraf-Nonius Kappa CCD diffractometer for low temperature unit cell determination and data collection. A cold nitrogen stream was used to maintain nearly constant low temperatures, and to protect the compound from air. The structure was solved by SIR 97 [15], and improved from difference

Fourier maps and least-squares refinements using SHELXL97 [16], and published scattering factors [17]. All nonhydrogen atoms were refined anisotropically, while the hydrogen atoms could all be successfully refined isotropically. Pertinent crystallographic information is contained in Table 1, while selected bonding parameters are given in Table 2.

Results and Discussion

The synthetic approach described herein results in a yield in excess of 50%, as compared to an 18% yield reported from the previous method. The new procedure is similar to the original, with the exception that the ligand precursor anions are not mixed, but instead are added to the $\text{FeBr}_2(\text{dme})$ starting material separately. It is possible that in the previous method, the 1:1 ratio of anions leads to a statistical distribution of products (25% decamethylferrocene, 25% *bis*(2,4-dimethylpentadienyl)iron, and 50% of the intended product, $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$, but that the difficulty in separating the desired product from decamethylferrocene, as a result of their similar solubilities, adds a substantial complication towards obtaining a better yield. These distribution and solubility patterns were, in fact, also encountered for the synthesis of $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$ [10].

It appears that by adding slightly less than a stoichiometric amount of sodium pentamethylcyclopentadienide, the new variation leads to a (pentamethylcyclopentadienyl)iron bromide complex having an olive green color, which is expected to be stable at $-78\text{ }^\circ\text{C}$ for a reasonable amount of time. It is likely that a combination of the steric bulk of the pentamethylcyclopentadienyl and bromide ligands shields the complex from the incorporation of another pentamethylcyclopentadienyl ligand. Though the acyclic dienyl ligands are even more sterically demanding (once coordinated) than the C_5Me_5 ligand [18], they nonetheless may more readily approach a metal complex through just one (terminal) carbon atom of their π systems.

As well, there is the possibility that a (pentamethylcyclopentadienyl)iron bromide tetramer or other oligomer is responsible for its stability; (pentamethylcyclopentadienyl)ruthenium halide complexes are isolable and synthetically useful starting materials for preparing $\text{Ru}(\text{C}_5\text{Me}_5)(\text{pentadienyl})$ complexes [19-31]. In the second step the pentadienyl ligand is expected to be incorporated by a conventional anion metathesis with the remaining bromide ligand. The only impurity is *bis*(2,4-dimethylpentadienyl)iron, which is significantly more soluble than the intended product and retained in solution during recrystallization. This method can likely be further optimized and should be applicable to the preparations of other (pentamethylcyclopentadienyl)iron compounds.

The molecular constitution of $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$ has been confirmed by a single crystal X-ray diffraction study. The compound is isomorphous with its ruthenium [23], but not chromium [32], analogue. The structure of $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$ (Fig. 1) is similar to its ruthenium analogue in having a C_5Me_5 methyl group positioned between the two CH_2 termini of the 2,4- C_7H_{11} ligand. There is an angle of $10.9(2)^\circ$ between the two ligand planes, each defined by its five metal-bound atoms. The tilt is such that the pentadienyl ligand's C(1,5) atoms are closest to the cyclic ligand plane at ca. 2.98 Å, with the C3 atom being furthest at 3.40 Å. Although the two sets of metal-bound carbon atoms are each nearly planar, their substituents are not. On average the methyl groups of the C_5Me_5 ligand tilt 3.4° away from Fe. For the 2,4- C_7H_{11} ligand, one hydrogen substituent on each of the terminal CH_2 groups also points away from the metal, by an average of 47.4° , while the other CH_2 , CH , and $\text{C}(\text{CH}_3)$ substituents tilt toward the iron center by 19.0 , 7.8 , and 10.3° , respectively. The corresponding values for $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$ are similar, being 46.2 , 17.6 , 6.8 , and 12.3° [33]. The methyl substituents on the open dienyl ligand lead to the usual contraction of their $\text{C-C}(\text{Me})\text{-C}$ angles, averaging $121.3(2)^\circ$, vs. $125.5(3)^\circ$ for the $\text{C}(2)\text{-C}(3)\text{-C}(4)$ angle.

The Fe–C distances for the more reactive 2,4-C₇H₁₁ ligand average 2.062 Å, vs. 2.083 for the C₅Me₅ ligand. Thus there is some lengthening of the Fe–C bonds for the aromatic cyclopentadienyl ligand from what is observed in Fe(C₅H₅)(2,4-C₇H₁₁) [33], for which the Fe–C distances for the two ligands are essentially equal at 2.060 and 2.063 Å, respectively. This could be a result of the fact that the methyl groups of the cyclic ligand undergo their usual tilt away from the metal center, whereas hydrogen substituents would tilt toward the metal, in an attempt to point the ligand's carbon atoms toward the metals. Alternatively, this could be a result of the increased steric influence being more effectively relieved in the former complex by having the C₅Me₅ ligand back off as its resulting loss in overlap with the metal orbitals might not be so severe as what would take place for a pentadienyl ligand. For comparison, the average Fe–C distance in ferrocene, 2.064 Å, is significantly shorter than that of 2.089 Å in Fe(2,4-C₇H₁₁)₂, which has been clearly attributed to substantial steric repulsions between the open dieny ligands. An interesting, even more crowded half-open ferrocene, Fe[1,2,4-(*t*-C₄H₉)₃C₅H₂][2,4-(*t*-C₄H₉)₂C₅H₅], shows slightly longer average distances for both the open and closed ligands, at 2.092 and 2.116 Å, again favoring the open pentadienyl ligand [34].

A further useful comparison may also be made with Ru(C₅Me₅)(2,4-C₇H₁₁), for which the average Ru–C distances for the two ligands are 2.203 and 2.167 Å, respectively [23]. The additional shortening of the M–C (pentadienyl) distances vs. its iron counterpart nicely coincides with expectations of increased bonding favorability for these ligands as the metal size increases, as noted already above. A similar observation can be made for Cr(C₅Me₅)(2,4-C₇H₁₁), for which the respective average Cr–C bond distances are 2.195(3) and 2.127(3) Å [32]. Both values are shorter than for their ruthenium counterparts, but especially notable is the increase in favorability for the open ligand, despite the smaller metal size. These features have been observed in general for the earlier transition metals, but could be explained to a large extent by steric and overlap

influences. In this case, however, the data point as well to enhanced electronic interactions between earlier transition metals and the pentadienyl ligands, likely through the stronger delta backbonding interactions that can take place for metals with lower effective nuclear charges. In both early and late complexes, the shorter distance between the metal center and the pentadienyl, as opposed to cyclopentadienyl, ligand plane promotes the delta interaction, as does the lower energy of the pentadienyl anion's LUMO.

Although the open and half-open metallocenes of iron and ruthenium exhibit significant stability toward air and water, their vapors react with surface hydroxyl groups of silica and alumina aerogels. The reactions with the silica aerogels are particularly rapid, consistent with the greater Bronsted acidity of silica relative to alumina [35-37]. Thus, the evacuation of a glass vessel containing $\text{Fe}(\text{C}_5\text{H}_5)(2,4\text{-C}_7\text{H}_{11})$ or $\text{Fe}(2,4\text{-C}_7\text{H}_{11})_2$ and a silica aerogel monolith results within seconds in the adoption of an orange coloration by the aerogel (Fig. 2), under conditions for which sublimation of the complex would otherwise be only very slowly observable. The analogous ruthenium complexes behave similarly, leading to a dark brown or black coloration. In contrast, ferrocene incorporation is much slower, leads to a much lower loading, and the observation of unreacted ferrocene in the aerogel via NMR spectroscopy. Notably, the NMR signals for the ferrocene guest are sharp even in the absence of any spinning of the sample, revealing that the ferrocene must be undergoing a rapid tumbling motion in the aerogel.

Consistent with the above observations, one equivalent of 2,4-dimethyl-1,3-pentadiene is liberated (gc, nmr) as a result of the incorporations of the 2,4-dimethylpentadienyl complexes, as indicated by Scheme 1 ($\text{M} = \text{Fe}$ or Ru). The chemical nature of the incorporation process, and its very high facility, are also revealed via examination of cross sections of the aerogel monoliths,

Scheme 1

which evidence selective metal incorporation close to the aerogel surface (Fig. 2), except for ferrocene which is incorporated without actual chemical bonding. Thus, the pentadienyl-containing complexes react with surface hydroxyl groups quickly enough that they are not able to penetrate very far, at least not until the outermost hydroxyl groups have reacted.

To achieve relatively high metal loadings in these aerogels, one can make resort to pulverized samples, which naturally reduce the depth of penetration that is required for high loadings. These incorporations may be brought about simply by mechanical stirring of the powdered and sieved aerogels with the metal pentadienyl complex under an inert atmosphere. Quite surprisingly, on some occasions the metallated aerogels, particularly the powders, can be extremely sensitive to air, even being pyrophoric, thus requiring a very pure nitrogen glovebox atmosphere for manipulation. This dramatic air sensitivity appears quite unusual for species that may be considered to belong to the generally quite stable class of divalent $M(C_5H_5)(L)_n$ species. It may well be that this is a reflection of the open nature of the aerogel supports, which could

provide a relatively poor coordination environment for the metal, rendering it exposed to attack by oxygen. This open nature may also contribute to the high facilities of the initial incorporations, as protons in the surface hydroxyl groups may also not experience a significant degree of stabilization via hydrogen bonding, leading to enhanced acidities. Notably, it has been reported that the incorporation of $\text{Rh}(\text{C}_3\text{H}_5)_3$ into silica gel occurs preferentially at isolated, rather than hydrogen-bonded, silanol sites [4a]. Likewise, the solution phase incorporations of iron siloxides and ruthenium chloride complexes into silica and hydroxyapatite, respectively, have been reported [38,39].

However, both the rate of metal incorporation and the air sensitivity of the resulting metal species are significantly affected by the steric nature of the ligand remaining after metal incorporation. Thus, the $\text{L} = \text{C}_5\text{Me}_5$ (Scheme 1) complexes incorporate more slowly than their C_5H_5 analogues, especially for the less acidic alumina aerogels, and lead to significantly less air-sensitive surface-bound species. This has facilitated the examination of the aerogel-anchored $\text{Fe}(\text{C}_5\text{Me}_5)$ species via solid state ^{13}C NMR spectroscopy (Fig. 3). The large peaks near 10 and 90 ppm match the C_5Me_5 and C_5Me_5 resonances for the $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$ precursor (10.2 and 84.1 ppm) [11], as well as the known $\text{Ru}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$ complex (ca. 10.6 and 89.5 ppm) [21,22], suggesting that one major environment is being occupied. The small accompanying peaks may then indicate the presence of at least one additional, but minor, environment. This would be in accord with other studies which have established the presence of multiple accessible environments in these systems [40]. The observation of sharp NMR signals in the diamagnetic region, as well as the air-sensitivity of some samples, is in accord with the expectation that the metals would be incorporated in the divalent oxidation state.

Conclusions

The complex $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$ has been found to possess slightly shorter Fe-C bonds to the open pentadienyl ligand as compared to those for the aromatic C_5Me_5 ligand. This is in accord with the energetic differences of their π molecular orbitals, which should lead to pentadienyl ligands being both better donors and acceptors. Despite the apparent stronger binding of the open pentadienyl, rather than the pentamethylcyclopentadienyl, ligand to the metal, it is nonetheless the pentadienyl ligand that is more reactive, undergoing facile protonation with silica aerogel, leading to anchoring of the remaining $\text{Fe}(\text{C}_5\text{Me}_5)$ unit to the surface. The air-sensitivity of some samples is in line with the expectation that the metal centers are present in the divalent state.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Appendix A. Supplementary data

CCDC 1426951 contains the supplementary crystallographic data for $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Figure Captions

- Figure 1. Structure of $\text{Fe}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$. The 30% probability ellipsoids are shown.
- Figure 2. Cross section of an aerogel monolith after exposure to $\text{Fe}(2,4\text{-C}_7\text{H}_{11})_2$. The depth of penetration is ca. 2 mm.
- Figure 3. Solid state ^{13}C NMR spectrum of silica aerogel-anchored $\text{Fe}(\text{C}_5\text{Me}_5)$.

Figure 1

Figure 2

Figure 3

Table 1. Crystal and experimental data

Empirical formula	
Formula weight	286.23
Temperature (K)	150(1)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å)	
a	10.2049(1)
b	11.6500(3)
c	12.4546(3)
Volume (Å ³)	1480.69(5)
Z	4
D _{calcd} (g cm ⁻³)	1.284
$\mu(\text{MoK}\alpha)$ (mm ⁻¹)	1.000
F(000)	616
θ range (°)	3.71-27.46
Limiting indices	$-13 \leq h \leq 13$
	$-15 \leq k \leq 15$
	$-16 \leq \ell \leq 16$
Reflections unique/observed	3960/2961
Completeness (%)	99.4
Goodness of fit on F ²	1.051
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0337$, $wR_2 = 0.0777$
R indices (all data)	$R_1 = 0.0435$, $wR_2 = 0.0838$
$(\Delta\rho)_{\text{max, min}}$	0.570, -0.345

Table 2. Selected bond lengths (Å) and angles (°) for Fe(C₅Me₅)(2,4-C₇H₁₁).

<i>Bond distances</i>			
Fe–C1	2.072(2)	Fe–C8	2.081(3)
Fe–C2	2.053(2)	Fe–C9	2.111(3)
Fe–C3	2.067(3)	Fe–C10	2.100(3)
Fe–C4	2.049(3)	Fe–C11	2.074(2)
Fe–C5	2.067(3)	Fe–C12	2.047(2)
C1–C2	1.421(4)	C3–C4	1.418(4)
C2–C3	1.418(4)	C4–C5	1.422(5)
 <i>Bond angles</i>			
C1–C2–C3	121.3(3)	C2–C3–C4	125.5(3)
C3–C4–C5	121.3(3)		