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Notes

^{13}C NMR Studies on Zr(ansa-Fluorenyl) Complexes. Molecules with Flexible Bonding Modes

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*Summary: ^{13}C NMR spectra for the zirconium−fluorenyl complexes $ZrCl_2(\eta^5\text{-}C_5H_4CR_2\text{-}\ \eta^5\text{-}C_{13}H_8)$, R = Ph, Me, **3** and **4**, respectively, have been recorded. Analyses of the chemical shift data suggest that the hapticity is strongly distorted from that indicated above and that η^3 and η^1, respectively, would be better, but still not exact descriptions. Long-range (multiple bond) ^{13}C,^{1}H correlations are shown to be important, in that without a complete ^{13}C assignment one can easily be mislead.*

Introduction

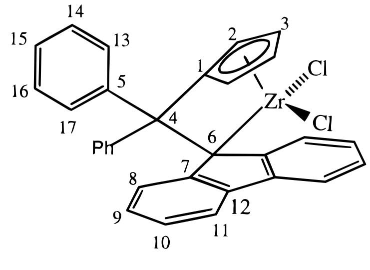
The synthesis of chiral ansa-metallocene complexes of the early transition metals and their applications in homogeneous catalysis continues to attract attention.[1] Apart from their inherent interest, Ti, Zr, and Hf Cp-derived compounds have found extensive use in stereoselective polymerization reactions.[2,3]

In addition to basic Cp-complexes, indenyl and fluorenyl ligand systems have been studied extensively,[3−5] with increasing emphasis on the use of bridges connecting the two Cp-type ligands. This area of chemistry has been recently reviewed.[1] A considerable crystallographic effort[1−5] has led to an increased understanding of how the various Cp-ligands dictate the molecular structure of the products arising from the catalysis. Nevertheless, the subtle interplay between, for example, Zr(IV) and the bulky indenyl or fluorenyl ligands is not always readily quantified by X-ray diffraction. In some ways NMR spectroscopy is more sensitive to minor changes in such bonding. A seminal study by Lappert and coworkers[6] and later contributions by Jordan[7] and Alt[8] have confirmed that NMR can provide additional insight.

We report here on ^{13}C data for two Zr(IV)−fluorenyl complexes containing the dianionic ligands diphenyl methylidene-μ-(cyclopentadienylfluorenyl)methane, **1**, and 2-(cyclopentadienyl)-2-(fluorenyl)propane, **2**. Our results suggest that the bonding is somewhat more subtle than originally thought.

Results

The Zr complexes **3** and **4**, derived from **1** and **2**, respectively, have been characterized by ^{1}H and ^{13}C one- and two-dimensional NMR spectra. The long-range (multiple-bond) ^{13}C,^{1}H correlations are critical in that these lead to a *complete* assignment and are especially useful for recognizing fully substituted aromatic carbon signals, e.g., the use of ^3J(C,H) via H-9 and H-11 to find C-7, or H-8 and H-10 to find C-12; see Figure 1 (or H-14 and H-16 to find C-5, etc).



3

ZrCl$_2$(1), 3. The ^{1}H NMR spectrum of **3** reveals a series of aromatic protons plus two virtual triplets, from an AA′XX′ spin system, centered at 5.84 and 6.40 ppm, whose chemical shifts are consistent with protons H-2 and H-3 in the monosubstituted Cp moiety. Interestingly, although the two phenyl groups are equivalent, a ^{1}H,^{1}H COSY measurement reveals that there are five nonequivalent protons; that is, there is restricted rotation around the C(quaternary)−C(ipso) bond. The spin

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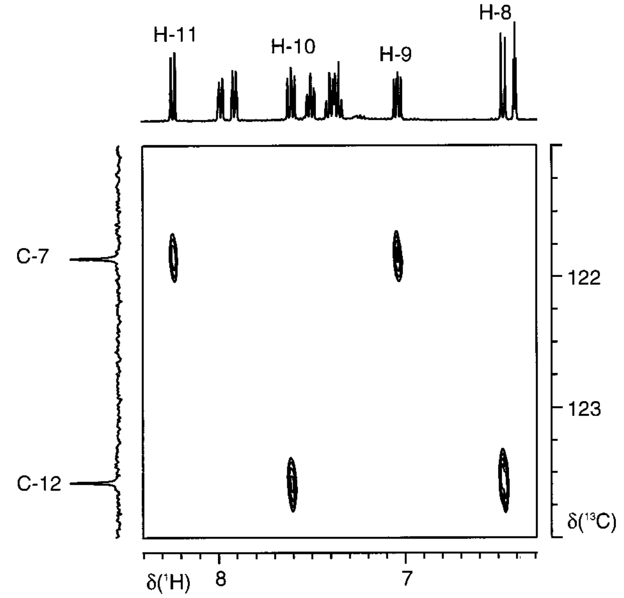


Figure 1. Section of the ^{13}C,^{1}H long-range correlation for **3** showing the assignment of the fluorenyl carbons C-7 and C-12. Each of these carbons shows two correlations stemming from the values $^{3}J(^{13}C,^{1}H)$. These assignments are important in that they reveal that the fluorenyl has some η^5-character; see text. $^{3}J(^{13}C,^{1}H)$ is usually, but not always, larger than $^{2}J(^{13}C,^{1}H)$ (400 MHz, CD_2Cl_2).

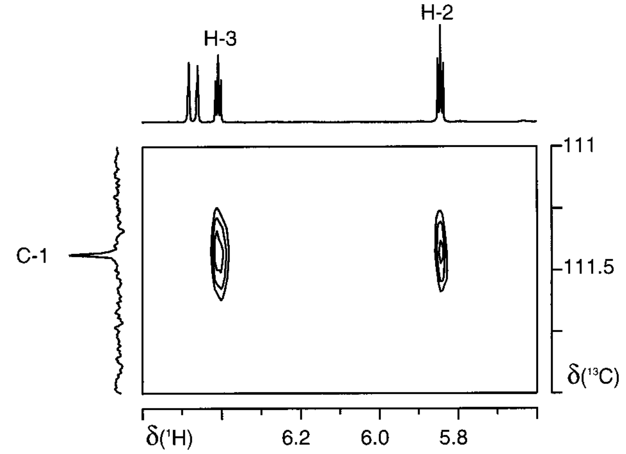


Figure 2. Section of the ^{13}C,^{1}H long-range correlation for **3** showing the assignment of C-1 of the monosubstituted Cp, via correlations to H-2 and H-3. $^{3}J(^{13}C,^{1}H)$ is usually, but not always, larger than $^{2}J(^{13}C,^{1}H)$; however, in this case one observes both interactions (400 MHz, CD_2Cl_2).

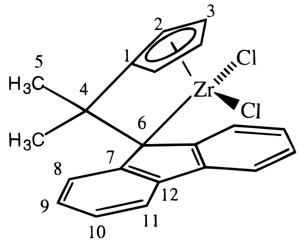
set from the four fluorenyl protons, each of integral 2, is also readily recognized via the same COSY spectrum.

The ^{13}C NMR spectrum of **3** shows 17 resonances, 11 of which can be shown to arise from =CH type carbons. Both one-bond and long-range carbon−proton correlations were used to make the ^{13}C assignments. Of the 17 absorptions, five resonate lower than 120 ppm (119.1, 111.4 and 104.3, 79.4, and 58.9 ppm). Three of these five, 119.1, 104.3, and 111.4 ppm, can be assigned to the monosubstituted Cp ring carbons C3, C2, and C1, respectively. Figure 2 shows a section of the long-range correlation in which both H-2 and H-3 are used to identify the fully substituted carbon C-1.

The aliphatic carbon C-4 can be pinpointed via the long-range correlations from H-2, H-13, and H-17, so that the remaining low-frequency signal at 79.4 ppm can be assigned as C-6. In agreement with this assignment, the same long-range correlation shows cross-peaks from the proton H-8 in the fluorenyl moiety to the resonance at 79.4, C-6.

Given the correlation of H-8 with C-6, the remaining three ^{1}H-fluorenyl spins can be definitively assigned via the COSY spectrum. Except for the phenyl ipso carbons, C-5 with a chemical shift of 145.2 ppm, all of the remaining signals in the ^{13}C spectra fall in the range between 120 and 130 ppm.

$ZrCl_2(2)$, 4. The ^{1}H spectrum of **4** is simpler and reveals a six-proton methyl singlet, the two virtual triplets from the AA′XX′ spin system of the monosubstituted Cp moiety (5.82 ppm (H-2) and 6.33 ppm (H-3), plus the four well-dispersed fluorenyl protons.



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The ^{13}C spectrum of **4** shows 12 resonances, seven of which can be shown to arise from carbons bearing protons. Of the remaining five signals, the quaternary carbon, C-4 at 41.1 ppm, is assigned by its two-bond correlation to the methyl groups. The three signals of the monosubstituted Cp could be recognized as described above and are found at 115.6, 102.8, and 119.6 ppm, for C1−C3, respectively. The ^{13}C,^{1}H long-range correlation of C-1 to the methyl protons, plus an NOE from the methyls to H-2, adds an extra degree of certainty. Again, the C-6 carbon, at 80.4 ppm, falls at relatively low frequency. The same ^{13}C,^{1}H long-range correlation connects C-6 to H-8, thus allowing the full assignment of the fluorenyl protons with the help of a routine COSY spectrum. The substituted fluorene carbons, C-7 (123.1 ppm) and C-12 (123.8) are (i) not very different and (ii) found close to their corresponding positions in **3**.

Apart from selected proton resonances, which are subject to local anisotropic effects, e.g., the low-frequency position of H-8, in **3**, due to the anisotropy of a proximate phenyl ring, **3** and **4** show similar proton NMR characteristics.

Discussion

With the assignment completed it remains to comment on the hapticity of the monosubstituted-Cp and fluorenyl five-membered rings, and this follows from their ^{13}C chemical shifts (Table 1).

A preliminary analysis of the ^{13}C data for **3** and **4** suggests a coordination mode for the fluorenyl group with η^1 hapticity. The two C-6 values, 79.4 and 80.4 ppm, respectively, strongly suggest aliphatic character for this carbon. Jordan and co-workers[7] report a value of 61.1 ppm for the σ-bound benzylic carbon of $Zr(MeCp)_2(CH_2Ph)_2$. Carbon substitution at the CH_2 would be

Table 1. ^{13}C Chemical Shifts[a] for 3 and 4

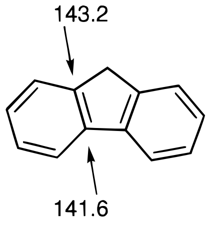
carbon	**3**	**4**
1	111.4	115.6
2	104.3	102.8
3	119.1	119.6
4	58.9	41.1
5	145.2	28.9
6	79.4	80.4
7	121.8	123.1
8	124.4	124.0
9	128.6	129.4
10	125.8	125.4
11	125.0	125.1
12	123.6	123.8
13	127.0	
14	*b*	
15	*b*	
16	127.7	
17	*b*	

[a] Relative to TMS. [b] The three resonances in **3**, C-14, C-15, and C-17, appear at 129.49, 129.52, and 129.57 and were not assigned further, as these shifts are, for all practical purposes, identical.

expected to shift this primary carbon resonance to an even higher frequency, making ca. 80 ppm a reasonable, if not precise, estimate of where such a carbon might appear. This hapticity would allow the two benzene rings to retain their aromaticity and perhaps relieve some steric strain.

The chemical shifts of the remaining carbons of the fluorenyl five-membered ring in **3** and **4**, C-7 (121.8 and 123.1 ppm) and C-12 (123.6 and 123.8 ppm, respectively), are superficially consistent with pronounced sp^2 character. Further, X-ray data for **3** show[2,5d] that the Zr−C(fluorenyl five-membered ring) separations are very different: 2.417(8) Å, to C-6, 2.513(6) Å, to C-7, and 2.680(6) Å, to C(12). Lappert et al.[6] note that the mean Zr−C(η^5- C_5H_4-R) distance can be ca. 2.48−2.56 Å, suggesting a fairly short, perhaps η^1-Zr−C, bond to C-6.

Although we believe the above analysis to be basically correct, it is slightly flawed. The ^{13}C chemical shifts for the fully substituted carbons in fluorene, **5** are as shown:



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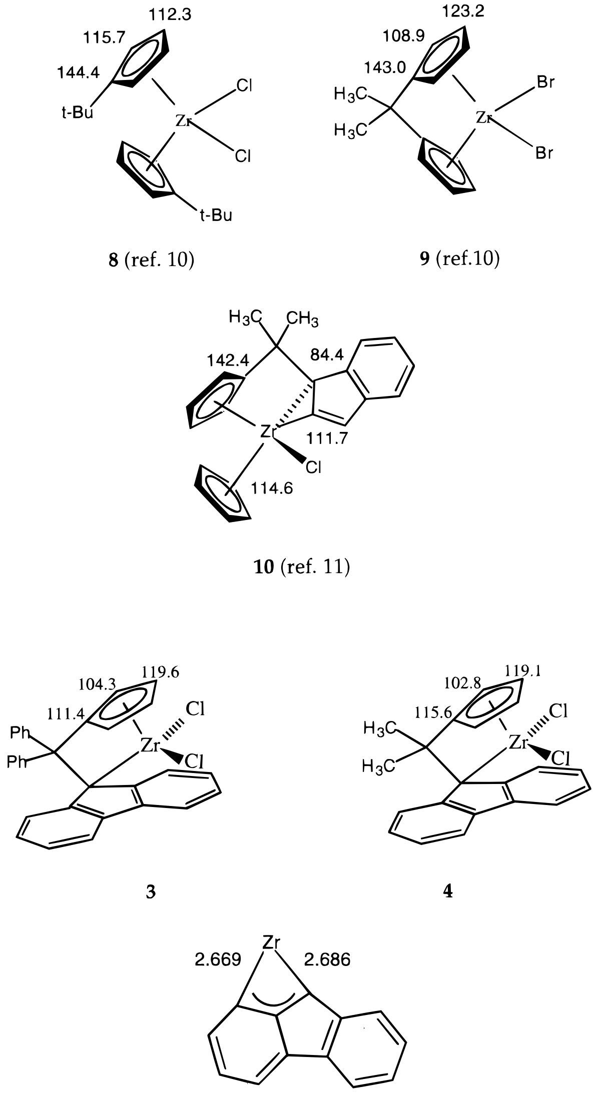
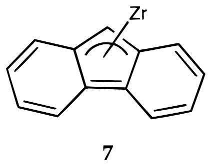
Since our observed chemical shifts for these two carbons, C-7 and C-12, are on the order of ca. 122−124 ppm, these data (plus additional work by Alt and co-workers[8]) indicate that the coordination chemical shift, Δδ, for C-7 and C-12 in **3** and **4** is likely to be on the order of 20 ppm. Consequently, the Zr interacts somewhat with these carbons, and a "pure" η^1-Zr−C bond is not indicated. Without an unambiguous assignment of both C-7 and C-12, the interpretation of the bonding is questionable. Further, Bochmann et al.[9] have shown that relatively long Zr−C distances, e.g., ca. 2.67−2.69 Å, in the bridging hydride **6**, do not preclude a bonding situation.

Scheme 1. Selected ^{13}C Chemical Shifts



fragment of the structure of $[Me_2C(C_5H_4)(Flu)Zr(\mu\text{-}H)Cl]_2$ **6**[9] indicating the relatively long Zr-C separations.

It should be remembered that although the Zr may be relatively far from the fluorenyl carbons, C-7 and C-12, the metal is not so far from the π-electrons. The ^{13}C signals of the fluorenyl ligand in **6** were not assigned by the authors, but a resonance at 95.4 ppm is given, and it would not be unreasonable to think that this might be the carbon with the 2.686 Å separation. In any case, based on the C-6, C-7, and C-12 ^{13}C resonances in **3** and **4**, plus the distances in **6**, we can exclude a symmetrical allyl structure such as **7** as a major contributor since it ignores the significant coordination chemical shift for C-12.



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The chemical shifts of the monosubstituted Zr−Cp carbons in **3** and **4** are also of considerable interest. The

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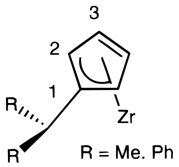
[9] Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Mazid, M. *Organometallics* **1993**, *12*, 4718−4720.

model complexes, **8**−**10**,[10,11] indicated in Scheme 1, suggest that this resonance should appear at ca. 142−144 ppm, a much higher frequency. This high-frequency position in **8**−**10** is "normal" and is a consequence of well-known deshielding β-alkyl substituent effects on ^{13}C chemical shifts.[12] However, the two ipso carbons in **3** and **4** at 111.4 and 115.6 ppm, respectively, are shifted ca. 25 ppm to *low* frequency. Equally unexpected are the observed low-frequency positions of C-2 in **3** and **4**: 104.3 and 102.8 ppm, respectively. Obviously, *both* C-1 and C-2 in **3** and **4** reflect interesting bonding modes. We believe that these data are best understood in terms of a polarized allyl structure, i.e., **11**, and this bonding mode has been suggested previously.[8] The known ^{13}C shift for $ZrCl_2(Cp)_2$ is 115.7 ppm,[6] so that the values of ca. 119 ppm for C-3 suggest that the Zr interacts somewhat with these carbons. The existing X-ray data[2,5] for **3** and **4** support this view in that the Zr−C distances to C-1 and C-2 are ca. 2.44−2.45 Å, whereas the Zr−C-3 separation is ca. 2.51 Å.



	3	4
C-1	111.4	115.6
C-2	104.3	102.8
C-3	119.1	119.6

11, fragment of the structures of **3** and **4**

It is worth noting that, **10**, described as an η^2 C_9H_6-ligand, shows the indenyl benzyl carbon at 84.4 ppm (see Scheme 1), another indication that our values of ca. 79−80 ppm for C-6 reflect a strong tendency toward η^1.

Comment. All of the ^{13}C data for **3** and **4** point toward distorted bonding modes for the fluorenyl *and* monosubstituted Cp ligands. Naturally, one would like to put forward some extreme situation, e.g., purely η^1 for the fluorenyl and purely η^3 for the monosubstituted Cp, in the hopes of connecting such a ground-state distortion to catalytic activity; however, careful inspection of the ^{13}C data suggest that the Zr is involved with the remaining double bonds. Nevertheless, the bonding in both the η^5-C_5H_4 and η^5-$C_{13}H_8$ moieties is tending toward a reduced hapticity.

Experimental Section

The NMR spectra were obtained from CD_2Cl_2 solutions using a Bruker DPX 400 MHz spectrometer. Standard pulse sequences were used for the ^{13}C,^{1}H one-bond and long-range HMBC spectra. Complexes **3** and **4** were available and have been described earlier.[2,5]

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