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Notes

Metal−Ligand Interactions in Bis(isodicyclopentadienyl)iron Complexes

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Introduction

The structure and bonding in isocyclopentadienide (isodicp) containing iron organometallics,[1] and in particular the evaluation of the spin density in these complexes, have been the subject of extensive investigation in the past several decades, and a number of detailed studies—especially those employing nuclear magnetic resonance techniques—have been reported in the recent literature.[2] In the present study, the Mössbauer spectra of bis(isodicyclopentadienyl)iron, **1**, and the corresponding ferrocenium hexafluorophosphate, **2**, have been determined over the temperature range 90 < *T* < 300 K and the resultant parameters compared to those of the parent ferrocene, **3**, (dicyclopentadienyl)(cyclopentadienyl)iron, **4**, bis(pentadienyl)iron, **5**, and bis(cyclooctadienyl)iron, **6**. The structures of these complexes are summarized in Chart 1.

Experimental Section

The synthesis of the compounds examined in this study has been reported earlier,[2−4] except for **6**,[5] as has the ^{57}Fe Mössbauer spectroscopic technique applied to ferrocene-related complexes.[6−8] All isomer shifts (IS) are reported with respect to the centroid of a room-temperature α-iron spectrum.

Results and Discussion

The Mössbauer spectra of all of the neutral complexes examined in this study consist of well-resolved doublets in the temperature range employed (90 < *T* < 300 K), and a typical spectrum of **1** at 90 K is shown in Figure 1. In contrast, the spectra of the cationic complex, **2**, shown in Figure 2, consist of a broad resonance which can best be fitted by a spin−lattice relaxation algorithm.[9] The parameters extracted from these spectra, and their temperature dependencies, are summarized in Table 1.

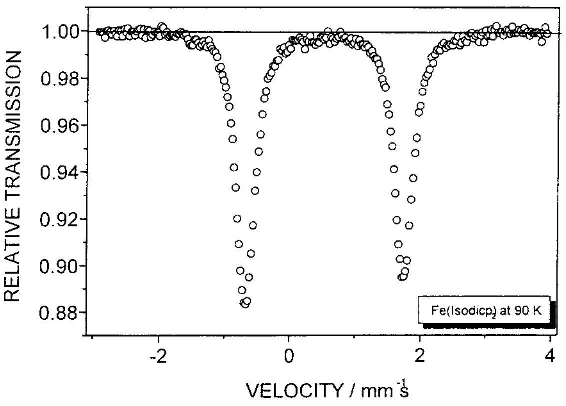


Figure 1. Mössbauer spectrum of **1** at 90 K.

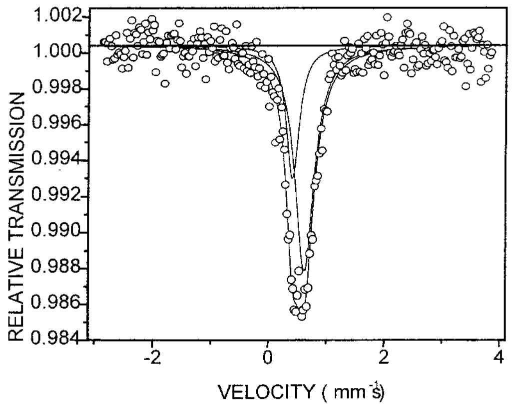
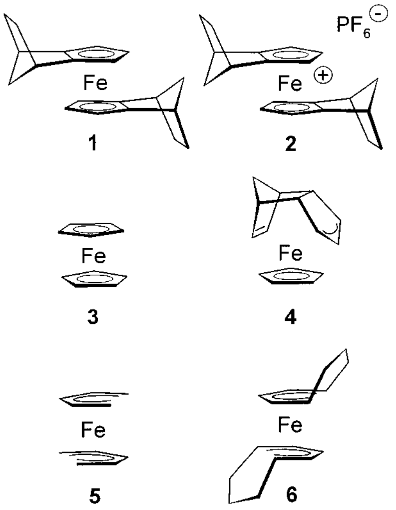


Figure 2. Mössbauer spectrum of **2** at 90 K.

Chart 1. Structures Discussed in the Text



The hyperfine interaction parameters of **1** are very similar to those reported for ferrocene,[6−8] except for the temperature

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(1) Paquette, L. A.; Schirch, P. F. T.; Hathaway, S. J.; Hsu, L.-H.; Galluci, J. C. *Organometallics* **1986**, *5*, 490−499.

(2) Gattinger, I.; Herker, M. A.; Hiller, W.; Köhler, F. H. *Inorg. Chem.* **1999**, *38*, 2359−2368.

(3) Blümel, J.; Hertkorn, N.; Kanellakopulos, B.; Köhler, F. H.; Lachmann, J.; Müller, G.; Wagner, F. E. *Organometallics* **1993**, *12*, 3896−3905.

(4) Ernst, R. D.; Wilson, D. R.; Herber, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 1646−1650.

(5) Ernst, R. D. To be published. The authors are grateful to Prof. Ernst for providing a sample of this compound for study.

(6) Herber, R. H.; Hanusa, T. *Hyperfine Interact.* **1997**, *108*, 563−575.

(7) Herber, R. H.; Temple, K.; Manners, I.; Buretea, M.; Tilley, T. D. *Inorg. Chim. Acta* **1999**, *287*, 152−158.

(8) Herber, R. H. *Inorg. Chim. Acta* **1999**, *291*, 74−81.

(9) Nowik, I.; Wickmann, H. H. *Phys. Rev. Lett.* **1966**, *17*, 949−951.

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Table 1. Summary of Mössbauer Parameters[a] of the Compounds Discussed in the Text

	$Fe(Dicp)_2$ (**1**)	$Fe(Dicp)_2PF_6$ (**2**)	$Fe(Cp)_2$ (**3**)	Fe(Dicp)(Cp) (**4**)	$Fe(pentad)_2$ (**5**)	$Fe(cyclooct)_2$ (**6**)	units
IS(90)	0.533(3)	0.546(25)	0.531(3)		0.447(10)	0.446(1)	mm s^{-1}
IS(300)	[0.498]		[0.501]	0.352	[0.401(10)]	0.360(1)	mm s^{-1}
QS(90)	2.415(1)	0.208(10)	2.419(1)			1.529(1)	mm s^{-1}
QS(300)	2.415(1)		2.408(1)	1.736(9)	1.40(2) at 78 K		mm s^{-1}
$-dIS/dT$	3.86		3.86		3.52	4.13	mm $s^{-1} \times 10^4$
$-d \ln A/dT$	3.505	5.66	3.505		5.13	7.20	$K^{-1} \times 10^3$
M_{eff}	108		108		118	100	Da
Θ_M	143		143		160	177	K

[a] The values in brackets are those extrapolated from the low-temperature data.

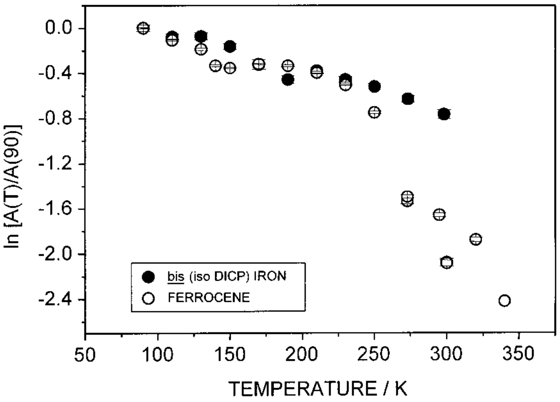

Figure 3. Temperature dependence of the logarithm of the area under the resonance curve for **1** (filled circles) and **3** (empty circles). The data for ferrocene are taken from ref 7.

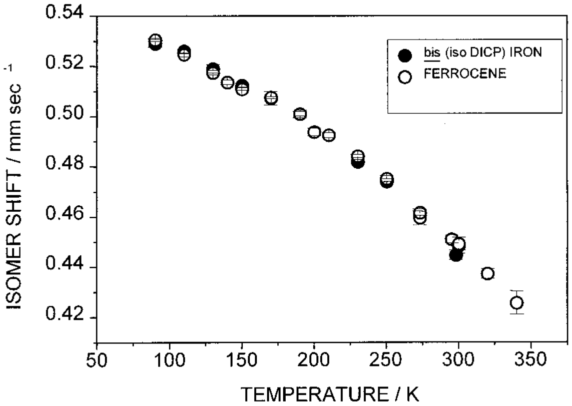

Figure 4. Temperature dependence of the isomer shift for **1** (filled circles) and **3** (empty circles). The isomer shift scale is referenced to α-iron at room temperature.

dependence of the recoil-free fraction ($-d \ln A/dT$) as summarized in Figure 3. These data suggests a somewhat "softer" lattice for **1** compared to **3**, as reflected in the iron atom motion. Of particular interest is the comparison of the quadrupole hyperfine interaction parameter (QS) for **1** and **3** compared to the mixed sandwich compound **4** (Table 1) for which the room-temperature Mössbauer data have been reported earlier,[4] as well as the corresponding values for **5** and **6**. It is clear that the field gradient at the metal center is much larger in the former than in the latter. The temperature dependence of QS ($-d\,QS/dT$) is slightly negative (-7.6×10^{-5} mm s^{-1} K^{-1}) over the range $90 \leq T \leq 300$ K, as it is in **3** above the 169 K phase transition.[10,11] According to the generally accepted molecular orbital scheme of ferrocene, the d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals are filled, whereas the d_{xz} and d_{yz} orbitals are largely empty, while in the Dicp(Cp) iron complex (**4**) the latter two are mixed in with the other d orbitals, thereby increasing the symmetry of the d-electron distribution and, hence, decreasing the QS interaction. Moreover, the d-orbital mixing in **4** is less than that in the pentadienyl homologue **5**. There is, in addition, the observation that in the mixed Dicp(Cp)iron complex (**4**) the Fe−C distances in the Fe−Cp interaction are essentially the same as in the Fe−Dicp bonding, wheras a considerable difference is encountered for the distances between Fe and the best bonding planes of Cp and Dicp (1.73 and 1.21 Å, respectively).[12] The Fe−ring distance clearly depends not only on the orientation of the ligands but also on the exo,endo position of the methylene groups. For a ferrocene that is very similar to **1**, Paquette et al.[1] have established an eclipsed arrangement of the ligands with both CH_2 groups pointing toward iron; the Fe−ring distance is 1.655 Å, very similar to the value of 1.651 Å found by Seiler and Dunitz[13] for the parent ferrocene, **3**.

The d-orbital involvement is also reflected in the IS parameter, which is larger (by ~0.5 mm s^{-1}) in **1** and **3** compared to **4**, indicating a smaller s-electron density in the former due to the shielding effects of the d orbitals. It is interesting to note that the IS parameter in the mixed complex, **4**, has been reported[3] to be similar to that in the two pentadienyl complexes, **5** and **6**.

The temperature dependence of the IS of **1** shown in Figure 4, together with the corresponding data for **3**, and reflects the similarity in the two data sets. Although there is some curvature in the IS versus T data, assuming a linear dependence leads to an effective mass (M_{eff})[14] of 108 Da for **1** as well as for **3**. The departure of this parameter from the "bare atom" value of 57 Da is, of course, a reflection of the covalency of the Fe−ligand bonding interaction. It is nearly identical in all of the compounds summarized in Table 1 (as it is in fact for most η^5-ligand-Fe complexes studied to date). It arises from the fact that the metal atom experiences only the π-electron density of the five-membered ring and is relatively insensitive to the presence of other σ-bonded alkyl or aryl substituents on the ligand. An independent proof for the predominance of π-bonding is provided by the ^{57}Fe, ^{13}C coupling constants. For ferrocene this amounts to only 4.7−4.9 Hz,[15] which is indicative of a very small σ content of the Cp−Fe bond. Similarly, ^{57}Fe, ^{13}C couplings of 2.6. 5.2, and 6.0 Hz have been found for **4**.[3]

As noted above, the Mössbauer spectrum of **2** (Figure 2) consists of a broad resonance which is characteristic of a fast

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(10) Edwards, J. W.; Kington, R. L.; Mason, R. *Trans. Faraday Soc.* **1960**, *56*, 660−667.

(11) Gibb, T. C. *J. Chem. Soc., Dalton Trans.* **1976**, 1237−1242.

(12) Blümel, J.; Köhler, F. H.; Wilkinson, D. H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 977−979.

(13) Seiler, P.; Dunitz, J. D. *Acta Crystallogr. B* **1979**, *35*, 2020−2032.

(14) Herber, R. H. In *Chemical Mossbauer Spectroscopy*; Herber, R. H., Ed.; Plenum Press: New York, 1984; Chapter VII, pp 199−216.

(15) Koridze, A. A.; Petrovskii, P. V.; Gubin, S. P.; Fedin, E. I. *Organomet. Chem.* **1975**, *93*, C26−30. Nielsen, P. S.; Hansen, R. S.; Jacobsen, H. J. *J. Organomet. Chem.* **1976**, *114*, 145−155.

($10^{-7}-10^{-9}$ s on the Mössbauer time scale) spin−lattice relaxation and is similar to a wide range of ferrocenium ion spectra reported earlier.[6,16,17] As a general observation, one-electron oxidation of ferrocene derivatives with only aromatic ring substituents leads to a (near) collapse of the QS parameter, wheras the presence of nonaromatic ring substituents gives rise to resonance spectra with an essentially undiminished QS interaction. Due to the fact that only ∼9.1 mg of **2** (20 μmol) was available for the present study, the experimental data could not be extended above ∼210 K due to the very small resonance effect magnitude at higher temperatures. However, in the range $90 < T < 210$ K, it is seen (Table 1) that the QS parameter is ∼0.208(10) mm s^{-1} and that the temperature dependence of the recoil-free fraction ($-d \ln A/dT$) is ∼$5.7(5) \times 10^{-3}$ K^{-1}, somewhat larger than that observed for the neutral complex, **1**. Presumably this is due to a larger mean-square amplitude of motion of the metal for which more space is available. The reason is that the metal atom radius becomes smaller since one d electron has been removed and that the Cp−Fe distance has increased to 1.72 Å in **2**[2] from 1.651 Å in ferrocene[13] and 1.655 Å in a related ferrocene very similar to **1**.[1] The d-electron removal is not, however, reflected in the IS of **2** compared to **1**, which are the same within experimental error.

Summary

Mössbauer spectra of a bis(isocyclopentadienyl)iron complex and its one-electron oxidation product have been determined at a number of different temperatures and compared to those of ferrocene and related complexes. The temperature dependencies of the hyperfine and lattice dynamical parameters are reported in detail and discussed in terms of the molecular architecture of these complexes.

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(16) Buchmeiser, M. R.; Schottenberger, H.; Herber, R. H. Submitted for publication in *Inorg. Chem*.

(17) Webb, R. J.; Lowery, M. D.; Shiomi, Y.; Sorai, M.; Wittebort, R. J.; Hendricksen, D. N. *Inorg. Chem.* **1992**, *31*, 5211−5219.