Electron Density and Charge Distribution around the Metal Atom in [Cp*Fe(η^5-As$_5$)]

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Keywords: Sandwich complexes / Iron / Arsenic / Moessbauer spectroscopy / Calorimetry

^{57}Fe Mössbauer effect spectroscopy has been used to study the charge density, charge distribution, and lattice dynamics in the ferrocene-related compound [Cp*Fe(η^5-As$_5$)]. The isomer shift (at 90 K) is significantly more positive than that observed for the related η^5-P$_5$ homologue reported earlier, while the quadrupole hyperfine interaction is essentially the same in both compounds, but only about a quarter of that observed in related ferrocenes with only carbon atoms in the ring structure. The temperature dependence of the recoil-free fraction evidences a discontinuity centered at about 213 K, which is also observed in the DSC data. These data are compared to related results acquired for homologous ferrocenes with variable ring substitution.

Introduction

Due to its centrality in the development of organometallic chemistry over the past several decades, ferrocene [(η^5)(Cp)$_2$Fe] has been the subject of a multitude of physical and chemical characterizations, and is, undoubtedly, among the best characterized organometallic compounds in the chemical literature.[1] Among these characterizations have been temperature-dependent ^{57}Fe Mössbauer effect studies[2,3] designed to explore the charge density and symmetry of the charge distribution around the metal atom, and to relate these to a satisfactory description of the bonding and dynamics in this compound. In a recent study,[4] these investigations have been extended to [Cp*FeP$_5$] (**1**) and [Cp^{R}FeP$_5$] (**2**) [Cp* = C$_5$(CH$_3$)$_5$, Cp^R = C$_5$(CH$_3$)$_4$(C$_2$H$_5$)] and it was noted that the replacement of five C(CH$_3$) ring components by the isoelectronic P atom resulted in a marked change in both the isomer shift (IS) and quadrupole splitting (QS) parameters over the temperature range $90 \leq T \leq 340$ K, compared to the parent ferrocene homologues. The recently reported synthesis[5a] and manifold chemistry[5b] of the corresponding [Cp*Fe (η^5-As$_5$)] (**3**) has made it possible to extend these studies to the arsenic congener, and the details of this study are the subject of the present communication. The structure of the related homologue of **3,** with Cp^R instead of Cp*[5a] is shown in Figure 1.

To overcome the pronounced nonresonant scattering by arsenic of the 14.4 keV gamma radiation accompanying the Mössbauer transition, the recent availability of strong (≈ 100 mCi) sources of ^{57}Co radiation, and the use of fast detector electronics, has made possible studies of arsenic containing iron organometallics which to date have been very limited.[6] The experimental details governing these measurements are briefly described below.

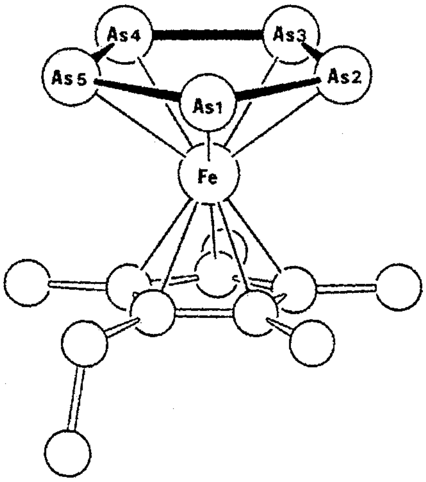

Figure 1. Structure of Cp^{R}Fe(η^5-As$_5$) at 298 K; the X-ray structure of **3** with Cp* instead of Cp^R has not yet been reported

Results and Discussion

The ^{57}Fe Mössbauer spectra of all the compounds reported here consist of well-resolved doublets, and a typical spectrum is shown in Figure 2.

The IS, QS, and related parameters at 90 K are summarized in Table 1. A number of features of these data are worthy of comment. Compared to the corresponding data[4] for **1** and **2**, the IS of **3** is significantly more positive, and has nearly the same value as that of the parent ferrocene without ring substituents **6**, but is significantly smaller than that reported for [Cp*FeCp][7,8] and [Cp*$_2$Fe], indicating a reduction of the s-electron density at the metal center. It is well-known that changes in the Cp ring substituents which are bonded to the carbon atoms by σ bonds have relatively little effect on the electron density at the iron atom since

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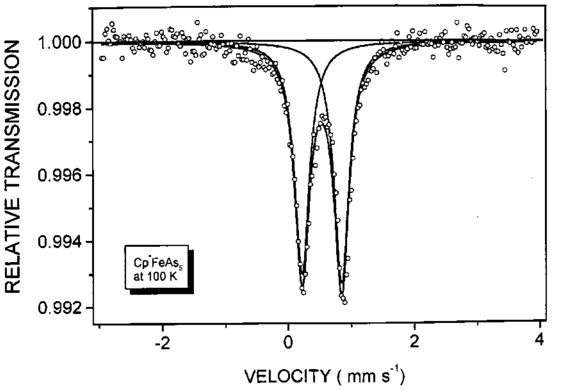

Figure 2. ^{57}Fe Mössbauer spectrum of **3** at 90 K; the velocity scale is with respect to the centroid of an α-Fe spectrum at 300 K; the small effect magnitude (even at 100 K) is a reflection of the presence of large amounts of arsenic in the sample, as discussed in the text

the latter is bonded primarily by overlap between the metal atom d-orbitals and the π density associated with the carbon atoms of the ring structure. Clearly, the effect of the presence of the electron-donating methyl groups is offset by the larger size of the As atoms constituting the ring, and presumably arises from the increase in shielding by the presence of 10 d-electrons in As compared to P and CH. This shielding reduces the s-electron density at the Fe nucleus and thus leads to the observed increase in the IS parameter. The temperature dependence of the IS is well represented by a linear regression over the range $90 \leq T \leq 273.2$ K: IS = $0.592 - (3.66 \pm 0.13) \times 10^{-4}$ T mm s^{-1}, with a correlation coefficient of 0.986 for 25 data points. This temperature dependence corresponds to an M_{eff} [9] of 113 daltons, reflecting the covalency of the metal-ligand bonding interaction.

Turning next to the QS interaction, it is seen (Table 1) that the numerical value of this parameter is essentially identical to that observed in **1** and **2**; that is, about a quarter of the size of that observed in complexes with Cp_2, Cp^*_2 and CpCp*[7] ligands. The likely explanation of this observation in the case of **1** and **2** has been discussed earlier.[4] It is to be noted, however, that going from the 3s,3p orbitals of P to the 4s,4p (and 3d) orbitals of As does not result in a further diminution of the QS. Again, it can be inferred that the electron density in the metal−ring atom overlap in latter case is − due to greater delocalization and the effect of the intervening 3d orbitals − essentially equivalent to that in the case of the P atoms, keeping in mind that the covalent atomic radii in the two cases are nearly identical (2.19 and 2.18 Å). The temperature dependence of the QS is essentially zero within the error limits of the present measurements, in contrast to the small positive value of d (QS)/d T observed[4] for **1** and **2**. Due to the unavailability of well-formed single crystals of **3**, it is not possible to infer the sign of the QS from the presently available data (compare the intensity asymmetry shown in Figure 2 to that reported earlier for **1** at 90 K), and such an inference — in the absence of single crystal samples — would have to be based on measurements in high magnetic fields[10] to remove the (magnetic) degeneracy of the ±3/2 and ±1/2 spin levels observed in the present study.

Turning next to the dynamics of the metal atom motion in **3**, this characteristic is most clearly revealed in the temperature dependence of the area (A) under the resonance curve, which (for a thin absorber) scales directly with the recoil-free fraction, and hence with the mean-square amplitude of the metal atom relative to the center of symmetry of the molecule as a whole. It is amply clear from the temperature insensitivity of the intensity ratio R [= A(+)/A(−)] that there is no resolvable Gol'danskii−Karyagin asymmetry[11] of the metal atom motion in this compound despite the presence of the five heavy As atoms. The temperature dependence of A over the range $90 \leq T \leq 273.2$ K is summarized graphically in Figure 3, in which the open and closed points refer to data accumulated in the warming and cooling modes, respectively, and illustrate the reversibility of these data. It is clear that there are two distinct regimes in this plot separated by a transition region centered at about 213 K. The slopes in the two regions are nearly identical [$-(7.79 \pm 0.36) \times 10^{-3}$ and $-(8.58 \pm 0.78) \times 10^{-3}$ K^{-1} in the ranges $90 \leq T \leq 205$ and $220 \leq T \leq 273.2$ K, respectively] and are very similar to the behavior reported[4] for **1** in which the mid-point of the discontinuity was observed at 195 K. As in the earlier study, the identification of this discontinuity is supported by the DSC data summarized in Figure 4.

The relatively broad endotherm at 217 K, observed at a warming rate of five degrees per minute, is in reasonable agreement (midpoint about 213 K) with the data summarized in Figure 3, which show Mössbauer data accumulated over a period of several hours at each temperature. It is tempting to identify this transition with the lambda point

Table 1. Summary of Mössbauer data for the compounds discussed in the text [Cp = η^5-C_5H_5, Cp* = η^5-$C_5(CH_3)_5$, Cp^R = η^5-$C_5(CH_3)_4(C_2H_5)$ P_5 = η^5-P_5, As_5 = η^5-As_5]

Compd.	1	2	3	4	5	6	Units
	Cp*FeP$_5$	Cp^{R}FeP$_5$	Cp*FeAs$_5$	Cp*FeCp	Cp*FeCp*	CpFeCp	
IS(90)	0.468(4)	0.456(20)	0.559(1)	0.499(5)	0.492(3)	0.525(5)	mm s^{-1}
QS(90)	0.624(1)	0.652(1)	0.626(21)	2.436(1)	2.473(2)	2.388(1)	mm s^{-1}
−d lnA/dT	8.09(26)[a] 11.20(29)[e]		7.79(36)[b] 8.58(78)[f]	7.55(10)	7.97(40)[c]	6.23(23)[d] 7.20(23)[g]	$K^{-1}\cdot 10^3$

[a] $90 \leq T \leq 170$ K. − [b] $90 \leq T \leq 205$ K. − [c] Below 273 K. − [d] Below λ-point. − [e] $195 \leq T \leq 340$ K. − [f] $220 \leq T \leq 273.2$ K. − [g] Above λ-point.

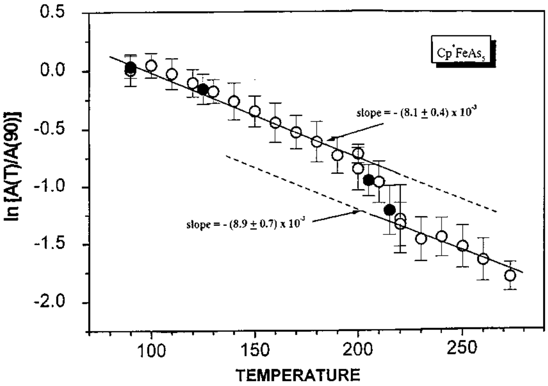

Figure 3. Temperature dependence of the area under the resonance curve for **3**; the open and closed points refer to data acquired during warming and cooling regimes, respectively

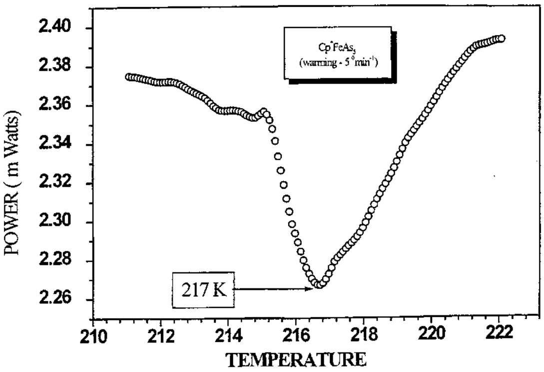

Figure 4. Portion of the differential scanning calorimetry data for **3**, showing the endotherm at about 217 K

(at 169 K) reported for ferrocene, which is related[12] to a change from the triclinic (low *T*, nearly eclipsed rings) to the orthorhombic/monoclinic (high *T*, staggered rings) form, but additional support for this identification cannot be extracted from the presently available data. The gas phase (473 K) structure of [Cp*FeP_5] has been reported by Blom et al.,[13] and consists of a staggered conformation of the two five-membered rings. No comparable data for **3** have been reported to date, although the X-ray diffraction data for [$Cp^R FeAs_5$] have been summarized by Scherer et al.[5a]

Experimental Section

A sample of **3** was synthesized as described earlier,[5a] and, because of its (slight) light and air sensitivity, quickly mixed in subdued light with an equal weight of BN to optimize random crystallite orientation. This sample was then mounted in a standard plastic sample holder and immediately cooled to 78 K before transferring to the Mössbauer spectrometer. The other compounds cited in this study were obtained as described previously.[4]

For the gamma ray resonance measurements, a strong (≈100 mCi) ^{57}Co/Rh source was used at room temperature in connection with a fast proportional counter able to handle input rates in excess of 10^5 Hz. The problem of the efficient detection of the resonantly scattered 14.4 keV gamma radiation in the presence of As is, of course, exacerbated by the reduction in the recoil-free fraction with increasing temperature. To obtain reasonably reliable data, in excess of 5×10^7 counts per channel were scaled at the higher temperatures indicated above. Temperature control was maintained by use of a regulated proportional feedback circuit, and temperatures maintained at better than ±0.2 degrees over the data collection interval. Spectrometer calibration was effected before and after the data collection period, using a standard α-Fe foil at room temperature, and all IS values are quoted with reference to the centroids of these spectra. Data reduction was effected as detailed earlier.[3,4]

The DSC data were acquired using a Mettler Toledo Model DSC30 differential scanning calorimeter at heating and cooling rates of 2 and 5 degrees per minute over the temperature interval $173 \leq T \leq 308$ K.

Acknowledgments

The authors are indebted to Ms. Sigalit Gura of Bar Ilan University for the DSC measurements, and to Prof. I. Nowik for helpful discussions concerning data reduction. This research was supported in part by the Israel National Academy of Science.

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Received June 5, 2000
[I00226]