Metal atom dynamics in organometallics: Vibrational amplitude determination for bis phosphino ferrocenes including a waxy system

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ABSTRACT

Three structurally related bis phosphino ferrocene complexes have been examined by ^{57}Fe Mössbauer effect (ME) spectroscopy in order to evaluate the hyperfine interaction parameters (IS and QS), their temperature dependencies, as well as the dynamics of the metal atom over a temperature range. For two of the compounds (**1** and **2**), for which single crystal X-ray diffraction data have been reported, a direct comparison can be effected between the $U_{i,j}$ values derived from the X-ray study and that extracted from the ME data, and are found to be in good agreement. For complex **3**, which is a waxy material at room temperature, no X-ray data can be obtained, but the ME data permit an evaluation of the metal atom vibrational amplitudes even in the high (>180 K) temperature regime. In addition, data are presented relating to the anisotropy of the metal atom motion in these ferrocene complexes.

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1. Introduction

Ferrocenyl-bis(phosphines) have been found to play a significant role in a variety of catalytic processes and their structure–reactivity relationships have been discussed in the literature [1–3]. In the past decade it has also become evident that temperature-dependent Mössbauer effect (ME) spectroscopy can serve to elucidate the bonding and dynamical behavior of the iron atom in such complexes and thus lead to a better understanding of the role of the metal center in the chemistry of these precursors to catalytically active solids [4]. In addition, it has been shown that such spectroscopy can be used to evaluate the vibrational behavior of the iron center and such data can be compared to the thermal factors ($U_{i,j}$) extracted from single crystal X-ray diffraction studies [5]. One of the advantages of the ME technique is that it can lead to an evaluation of the root-mean-square-amplitude-of-vibration (rmsav) over a wide temperature range even in non-crystalline materials. In the present study, this technique has been applied to three structurally related ferrocenyl bis phosphino compounds which, in one case is comprised of a waxy material which is not amenable to X-ray diffraction characterization. In addition the question of the anisotropy of the metal atom motion as a function of temperature has been derived from the ME data.

Three compounds examined in this study are 1,1′-bis(dichlorophosphino)ferrocene, $C_{10}H_8Cl_4FeP_2$, [1], 1,1′-bis diphenylphosphino ferrocene, $C_{34}H_{28}FeP_2$, [2], and 1,1′-bis[bis(diethylamino)-phosphino]ferrocene, $C_{26}H_{48}FeN_4P_2$, [3]

2. Experimental

(a) *Compounds*: Compound **2** was generously made available by Dr. T.J. Colacot of the Johnson Mathey corporation, while compounds **1** and **3** were provided by Professor M.S. Balakrishna. All compounds were examined as received.

(b) *Mössbauer spectroscopy (ME)*: These compounds were examined by transmission spectroscopy as previously described [4,5]. Spectrometer calibration was effected by the use of a 20 mg m cm^{-2} α Fe absorber at room temperature, and all isomer shifts are referenced to the centroid of such calibration spectra. Compounds **1** and **2**, which are modestly air-stable orange solids at room temperature, were ground with Pyrex powder, mixed with BN (to assure random crystallite orientation) and rapidly transferred to screw-cap Perspex sample holders and sealed with Teflon tape before introduction into the variable temperature cryostat. Compound **3**, which is a waxy material at room temperature, was transferred to the sample holder as received. Temperature monitoring and control, as well as data reduction, have been described previously [4,5].

As will be discussed below, the recoil-free fraction and its temperature dependence depend critically on the area under the resonance curve. To ensure that no sample loss occurred during spectral examination under vacuum, especially at higher temperatures, the transmission rate of the ME gamma rays through the sample was monitored both before and after each temperature point data acquisition, which generally required 5–36 h of counting time. No sample loss due to sublimation was detected in these experiments [6].

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3. Results and discussion

3.1. Hyperfine and related parameters

As has been noted previously [7] for all diamagnetic ferrocene complexes so far examined, the ME spectra of all three compounds examined in the present study consist of single well resolved doublet spectra, which can be characterized in terms of the hyperfine parameters, the isomer shift, IS, the quadrupole splitting, QS, and the area under the resonance curve, A, as well as the temperature dependencies of these parameters and these are summarized in Table 1. In addition, the area ratio of the two components of the quadrupole split spectrum, $R = A(+)/A(-)$, where $A(+)$ and $A(-)$ are the two areas of the components at velocities greater and less than the spectrum centroid, respectively, have been determined as a function of temperature.

(a) *Compound* **1**: The melting point of this compound has been reported [8] to be 165.5 °C and an improved synthesis of **1** has recently been described by Balakrishna et al. [3] who were able to isolate the final orange colored compound in 92% yield. The hyperfine parameters at 90 K, and the derived properties are included in Table 1. The temperature-dependence of the IS shows some curvature at temperatures below about 165 K, but the seven data points in the interval 176 < T < 303 K are well fitted by a linear regression to yield M_{eff} = 94 ± 1 Da. The QS parameter is essentially temperature independent with a value of 2.205 ± 0.010 mm s^{-1} over the whole T range. The temperature-dependence of the recoil-free fraction data also shows some curvature at low temperatures but the data in the high temperature limit are well accounted for by a linear correlation (cc: 0.997 for 7 data points). The area ratios of the two components of the spectra are temperature independent with a mean value of 1.03 ± 0.01, indicating no significant metal atom vibrational anisotropy over the total temperature range. The single crystal X-ray data for **1** have been reported by Pietschnig et al. [8] at 123 ± 2 K. The Mössbauer $\mathbb{F}$ value, which is defined as equal to $k^2\langle x_{ave}^2\rangle$, where k is the wave vector of the 14.4 keV gamma ray of ^{57}Fe, and $\langle x_{ave}^2\rangle$ is the expectation value of the mean square amplitude of vibration of the ME active atom, at this temperature has been evaluated by a linear extrapolation of the above high temperature data, and its significance with respect to the rmsav data for the iron atom will, again, be discussed below. The $\mathbb{F}$ data comparison between the ME and X-ray data is summarized graphically in Fig. 1. In contrast to the observations related to R for **2**, noted below the area ratio for **1** is temperature independent in the range 98 < T < 303 K. These data indicate that the metal atom motion in **1** is essentially isotropic over the above T range.

Fig. 1. Temperature dependence of the $\mathbb{F}$ values for **1**. The X-ray derived data reported by Pietshnig et al. [8] is indicated by the filled data point.

(b) *Compound* **2**: This compound has a reported [9] melting point of 183–4 °C. The IS at 90 K is somewhat smaller than that reported for the parent ferrocene, but reflects the relative insensitivity of this parameter to ring substitution. The temperature dependence of the IS is well accounted for by a linear regression over the whole temperature range, 97 < T < 311 K, with a correlation coefficient r = 0.996 for 12 data points. This linear correlation permits the calculation of an effective vibrating mass, M_{eff}, of 113 ± 2 Da. The difference between this value and the "bare" iron atom mass of 57 Da reflects the covalency of the metal ligand bonding interaction, and is similar to those reported [10] for related ferrocene complexes. The QS parameter has a temperature dependence of $-(1.49 ± 0.26) \times 10^{-4}$ mm s^{-1} K^{-1} over the above range, reflecting the usual effects of thermal expansion. The temperature dependence of the logarithm of the area under the resonance curve $(\ln A(T))$ is again well accounted for by a linear regression with r = 0.998 for 12 data points. The logarithm of the recoil-free fraction, f, is equal to $-k^2\langle x_{ave}^2\rangle$ where k is the wave vector of the ME gamma ray, and $\langle x_{ave}^2\rangle$ is the expectation value of the average mean square amplitude of vibration, msav, of the metal atom under study at a given temperature. As has been discussed in detail in earlier studies[4,7a], making the assumption that the high temperature lnA data extrapolate to zero in the low temperature limit permits a direct comparison between $k^2\langle x_{ave}^2\rangle$ ($\mathbb{F}_{MorX,T}$)) at temperature T extracted from the ME data and that calculated from the $U_{i,j}$ values derived from single crystal X-ray diffraction study. The single crystal X-ray structure of **2** at ambient temperature has been reported by Casellato et al. [11] at 293 K. For **2** these values are $\mathbb{F}_{M,293}$ = 3.0 ± 0.1 and $\mathbb{F}_{X,293}$ = 2.74 ± 0.11. A graphic representation of the Mössbauer values (open data points) and the X-ray value at 293 K (closed data point) of $\mathbb{F}$ is shown in Fig. 2. The relationship between these values and the rmsav of the iron atom will be discussed more fully below. Finally it is worth noting that the area ratio R is temperature dependent and increases from ~ unity at 90 K to 1.2 at 310 K. These data indicate an inequivalence in the iron atom motional amplitude parallel and perpendicular to the symmetry axis passing through the metal atom and orthogonal to the two Cp rings. It has been shown in a number of magnetic field experiments [12] that QS is positive in diamagnetic ferrocene compounds. Thus, since the area ratio, R, is greater than unity at the higher temperatures, it is clear that the iron atom vibrational amplitude perpendicular to the above symmetry axis is larger than the vibrational amplitude parallel; that is $k^2\langle x_{perp}^2\rangle$ is larger than $k^2\langle x_{para}^2\rangle$. This effect has been reported earlier for other ferrocenoids [13] itself, but may or may

Table 1
Summary of ^{57}Fe Mössbauer data for the compounds discussed in the text

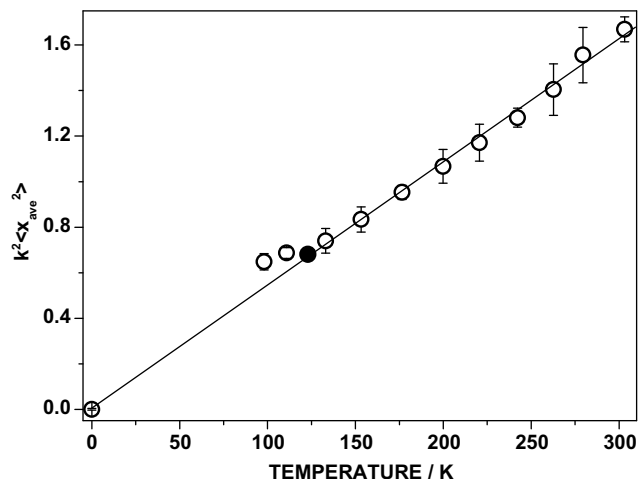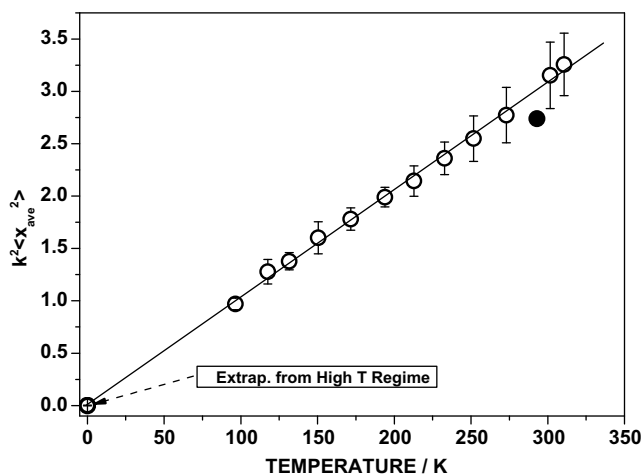| Compound	1	2	3	Units	Multiplier
IS(90)	0.512(3)	0.503(3)	0.501(3)	mm s^{-1}	
QS(90)	2.220(3)	2.342(3)	2.290(3)	mm s^{-1}	
−dIS/dT	4.87(8)[a]	4.08(9)[b]	3.50(10)[e]	mm s^{-1} K^{-1}	×10^{-4}
−QS/dT			1.40(42)[e]	mm s^{-1} K^{-1}	×10^{-4}
−dln A/dT	5.55(11)[a]	10.29(15)[b]	9.98(18)[f]	K^{-1}	×10^{-3}
Θ_M	94 ± 1	86 ± 3	81 ± 2	K	
M_{eff}	128 ± 2	113 ± 2	118 ± 3	Daltons	
$k^2\langle x_{ave}^2\rangle_M$	0.680[c]	3.01(11)[d]	n.a.		
$k^2\langle x_{ave}^2\rangle_X$	0.711[c]	2.74(11)[d]	n.a.		

Temperature ranges:
[a] 176–303 K.
[b] 96–310 K.
[c] 123 K.
[d] 293 K.
[e] 94–204 K.
[f] 94–178 K.

Fig. 2. Temperature dependence of the $\mathbb{F}$ values for **2** showing the extrapolation of the high temperature ME data to 0 K as discussed in the text. The value at 293 K reported in the single crystal X-ray study by Casselato et al. is indicated by the filled data point.
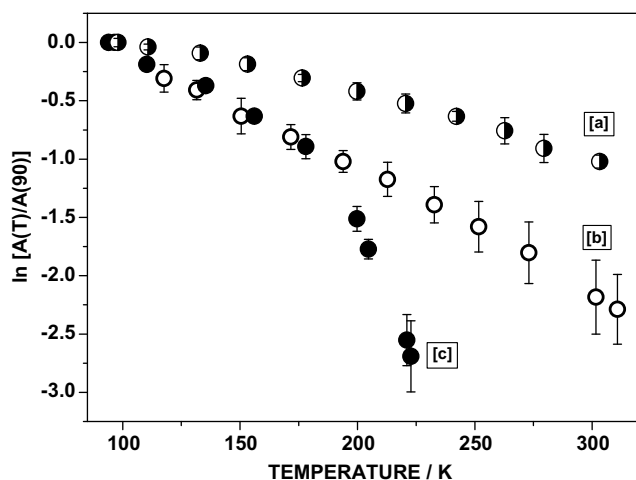
Fig. 3. Temperature dependencies of the ME recoil-free fraction data (normalized to the 90 K value) for **1, 2**, and **3**. The transition from a "normal" solid to the "waxy" state at ∼185 K is reflected in the data for **3**.

not be absent in other ferrocene related materials, depending on the steric requirements of the ring substituents.

(c) *Compound* **3**: An improved synthesis of this waxy compound, which is isolated [14] as a waxy dark orange phase in 98% yield, has also been described by Balakrishna et al. [3] and the hyperfine and derived parameters, included in Table reflect the unusual dynamics of the iron atom in this compound. The IS and QS values at 90 K are similar to those reported for **1** and **2**, but their temperature dependencies show a sharp change above 180 K. Most dramatic is the temperature dependence of ln$A$ shown graphically in Fig. 3. In the range $94 < T < 178$ K this temperature dependence for **3** is given by $(9.98 \pm 0.10) \times 10^{-3}$ K^{-1} with a correlation coefficient of 0.995 for five data points, and is very similar to that observed for **2**. Above 180 K there is a dramatic decrease in dln$A$/dT, reflecting strong phonon softening in the system. Although this break at ∼180 K is not evidenced in the temperature dependence of the IS, it is evident in the temperature dependence of QS and the area ratio parameter, R. The latter is nearly temperature independent below 180 K, but decreases significantly at higher temperatures. Due to the small value of the recoil-free fraction, f, above 180 K it

was not possible to extract detailed information relating to the anisotropy of the metal atom motion in the "waxy" temperature regime. The low temperature IS and ln$A$ data lead to values of M_{eff} = 118 ± 3 Da and Θ_M = 81 ± 2 K, similar to those observed for **1** and **2**.

3.2. Metal atom dynamical inferences

As has been noted earlier [4,7a,15], the evaluation of the rmsav of the metal atom in organometallics can be based on the $U_{i,j}$ values extracted from single crystal X-ray diffraction data on the one hand, and the recoil-free fraction data based on temperature dependent ME data, on the other, and in general the agreement is reasonably satisfactory except in cases where significant bond flexibility ligating the metal atom to the rest of the structure has been demonstrated as in the case of some organo-tin compounds [16,17]. In the present case, the good agreement between the X-ray and ME data for **1** and **2** noted above (Figs. 1 and 2), provides confidence that the rmsav data $[(\langle x_{ave}^2 \rangle)^{1/2}]$ so calculated permits a meaningful comparison of such data between structurally related compounds. The rmsav data appropriate for the three compounds examined in detail in the present study are summarized in Table 2. It should be noted that the extrapolation of $k^2 \langle x^2 \rangle$ for **3** are based on the low temperature ME data only, since no crystal X-ray data for a waxy phase (at T > 180 K) are obtainable. However, the good agreement in the low temperature data for **2**, for which X-ray data at 293 K have been reported, and the low temperature ME data for **3**, show that in the temperature region up to ∼180 K the rmsav data for the two compounds are essentially the same. The data for **3** in the low temperature region are in good agreement for those determined for **2** but deviate significantly in the region above 180 K. The non-linearity of $\mathbb{F}$ above the inflection temperature is clearly indicated in Fig. 4. These results demonstrate the utility of temperature dependent ME data to yield estimates of the metal atom rmsav in phases for which no X-ray diffraction data are obtainable such as waxy or glassy materials.

It is also worth noting that the Table 2 data for **1** are significantly smaller than those for **2** and **3**, indicating a smaller vibrational amplitude for the metal atom when the ring substituent is the (relatively) smaller halogen atom, compared to the phenyl and diethyl amino groups involved in the latter, as is also evident from the lattice temperature data (Θ_M) given in Table 1. It is plausible to assume that the smaller halogen atom structure results in stronger inter-molecular interactions leading to the observed relative values. An additional factor which contributes to the motional amplitude of the iron atom arises from the π-back bonding and negative hyperconjugation in such systems, as pointed out by Pietschnig et al. [8] in their discussion of ferrocenyl bis dihalophosphanes.

A reasonable inference at this point is that the *inter* molecular stacking forces in **2** are significantly governed by the presence of the aromatic phenyl rings, and that this interaction is absent when

Table 2
Root mean square amplitudes of vibration (rmsav) in Å of the metal atom in **1, 2** and **3** at selected temperatures

Compd.	1	2	3
100	0.107	0.139	0.130
125			0.150
150	0.1125	0.170	0.170
175			0.191
200	0.142	0.196	0.218
225			0.260
250	0.160	0.219	
300	0.177	0.240	
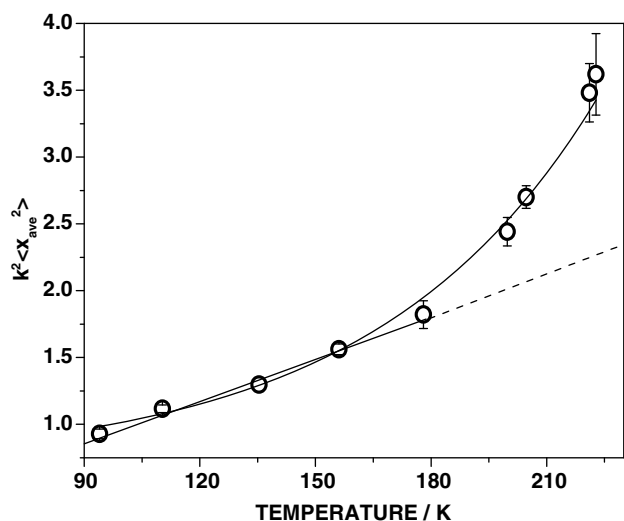
Fig. 4. Temperature dependence of **F** for **3** reflecting the non-linearity of this parameter in the high temperature regime due to the "waxy" nature of the solid above ~180 K. The solid line is provided only as a guide to the eye.

the phosphorus ligands are diethylamine groups, as in **3**. However, this is clearly a conjecture at this point and needs to be clarified by further examples of the two kinds of P ligands attached to the ferrocene moieties.

4. Summary and conclusions

The hyperfine parameters of three phosphino ferrocenes have been studied as a function of temperature by ^{57}Fe Mössbauer spectroscopy in order to elucidate the relationship between the nature of the Cp ligands and the dynamical behavior of the metal atom. In the case of compounds **1** and **2**, for which single crystal X-ray diffraction data exist, a direct comparison between these $U_{i,j}$ values and those extracted from ME data are in satisfactory agreement. The ME data at various temperatures has been used to estimate the mean-square-amplitude-of-vibration (rmsav) of the metal atom over a wide temperature range. For compound **3**, which is a

waxy material at room temperature the rmsav data are based solely on the ME data. The recoil-free fraction data, as reflected in the ln$A$ parameter, clearly indicate the onset of increased vibrational amplitudes of the metal atom above ~180 K.

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