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Bonding, Hyperfine Interactions, and Lattice Dynamics of Bis(pentadienyl)iron Compounds

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Abstract: The ^{57}Fe Mössbauer effect parameters have been determined for five bis(pentadienyl)iron compounds and compared to the corresponding data for ferrocene and azaferrocene. The decrease in the isomer shift parameter in going from the cyclic to the open ligand structures can be accounted for by a change in the oribtal population around the metal atom resulting in an increase in the electron density at the iron nucleus. The quadrupole splitting parameter for the pentadienyl compounds at liquid nitrogen temperature is about 50% of the value observed for the corresponding cyclopentadienyl homologues. An effective Mössbauer lattice temperature for these covalent solids has been determined from the temperature dependence of the recoil-free fraction of the ^{57}Fe resonances. The ^{57}Fe Mössbauer parameters for bis(2,4-dimethylpentadienyl)iron dissolved in an inert glass forming solvent are identical with those of the neat solid, suggesting that there are no significant structural changes between the molecule present in solution and that which makes up the solid, thus permitting a direct comparison between the X-ray diffraction data and the solution spectroscopic data for these "open ferrocene" compounds.

A major factor in the growth of interest in organometallic chemistry during the last three decades derives from the unusual properties of ferrocene and related "sandwich" compounds. A great deal of effort has been expended in theoretical studies to arrive at an appropriate description of the bonding in such molecules and to account for the wealth of experimental data available for these compounds. It is interesting to note, in reference to the spectroscopic studies that have been published in the literature, that ferrocene was the first organometallic compound for which information was obtained by using ^{57}Fe Mössbauer effect methods,[1-6] and the results of such studies are now considered to be reasonably well understood in terms of a complete MO description of $(\eta^5\text{-}C_5H_5)_2Fe$.

More recently, a series of "open ferrocenes" has been reported by Ernst et al.,[7] and the electronic structures, photoelectron spectra, and semiempirical calculations for these new compounds have been discussed.[7a] In the present paper we report detailed ^{57}Fe Mössbauer effect studies of five bis(pentadienyl)iron compounds, together with corresponding data for ferrocene and azaferrocene, and relate the results of this investigation to the MO descriptions of the bonding in these organometallics.

Experimental Section

Synthesis. Samples of bis(pentadienyl)iron (**1**), bis(2-methylpentadienyl)iron (**2**), bis(3-methylpentadienyl)iron (**3**), bis(2,4-dimethylpentadienyl)iron (**4**), and bis(2,3-dimethylpentadienyl)iron (**5**) were obtained as reported previously.[7a,c] Azaferrocene was prepared by literature methods[8] and generously made available to us by Prof. A. Efraty. Ferrocene was obtained commercially[9] and recrystallized repeatedly from anhydrous ethanol.[10] All compounds were stored under vacuum or in an inert atmosphere until just prior to spectroscopic examination.

^{57}Fe Mössbauer Spectroscopy. Mössbauer measurements were carried out by using the constant acceleration spectrometer described earlier.[11] Spectrometer calibration was effected by using 0.82-mil National Bureau of Standards SRM iron foil at 295 K, and all isomer shifts reported in this paper are with reference to the centroid of such a spectrum.[12] Data analysis was done by using the SPECTRA[13] program described earlier, in which line position, line width, and effect magnitude are allowed to vary as independent parameters in a matrix inversion least-squares fitting routine.

The experimental samples (solids) were mounted as thin layers of powder between two 6.25 mg/cm^3 foils of 99.999% aluminum, rigidly clamped to a copper sample holder. The latter, in turn, was attached to a copper sample mount that is thermally clamped to the cold head of a Heli-tran cryostat[14] and fitted with two Chromel/Au-0.07% Fe thermocouples. Temperature control to better than ±0.5 °C was achieved by the use of a proportional temperature controller. Thermocouple calibration is based on NBS data.

Results and Discussion

The results of the ^{57}Fe Mössbauer experiments are summarized in Table I and a representative spectrum is shown in Figure 1. All of the spectra consist of two well-resolved resonance lines, each of which has a full width at half-maximum (0.25 to 0.30 mm s^{-1}) corresponding to a single iron site (i.e., there is no evidence for an unresolved hyperfine interaction in any of the resonance spectra). In addition to the isomer shift (IS) and quadrupole splitting (QS) data that can be obtained from a spectrum at a single temperature, two other parameters of interest can be extracted from spectra obtained over a temperature range. These parameters elucidate the motional properties of the Mössbauer atom and provide information about the lattice temperature (θ_M) and the motional anisotropy (R) of the metal atom in the compounds under study.

The temperature dependence of the recoil-free fraction for a thin absorber, for which saturation effects can be neglected, is given by the temperature dependence of the area under the resonance curve and obeys a relationship of the form

$$\frac{d[\ln f]}{dT} = \frac{d[\ln(\text{area})]}{dT} = -\frac{3E_\gamma^2}{M_{\text{eff}}c^2k\theta^2{}_M} \qquad (1)$$

A typical data set for ferrocene and **4** is shown in Figure 2. In (1), M_{eff} is the effective vibrating mass that participates in the

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Table I. Summary of ^{57}Fe Mössbauer Data

compound	ferrocene	azaferrocene	1	2	3	4	5
IS (78 K), mm s^{-1} [a]	0.542 ± 0.009	0.592 ± 0.005	0.479 ± 0.010	0.462 ± 0.005	0.482 ± 0.005	0.498 ± 0.007	0.461 ± 0.005
QS (78 K), mm s^{-1}	2.453 ± 0.017	2.494 ± 0.010	1.402 ± 0.015	1.206 ± 0.008	1.255 ± 0.041	1.516 ± 0.010	1.261 ± 0.006
-dIS/dT, 10^4 mm s^{-1} K^{-1}	3.74	3.11	3.52	3.84	4.06	3.60	2.30
M_{eff}, amu [b]	111 ± 8	134 ± 10	118 ± 9	108 ± 9	103 ± 8	116 ± 9	182 ± 15
-dln$A$/dT, 10^3 K^{-1}	8.09 ± 0.22	7.44 ± 0.65	5.13 ± 0.22	7.29 ± 0.35	5.49 ± 0.41	5.48 ± 0.25	7.94 ± 0.46
θ_M, K [c]	130 ± 6	135 ± 6	160 ± 7	137 ± 7	157 ± 11	157 ± 7	131 ± 8

[a] With respect to the center of a metallic iron spectrum at 295 ± 2 K. [b] Calculated from eq 2. [c] Calculated from eq 3.

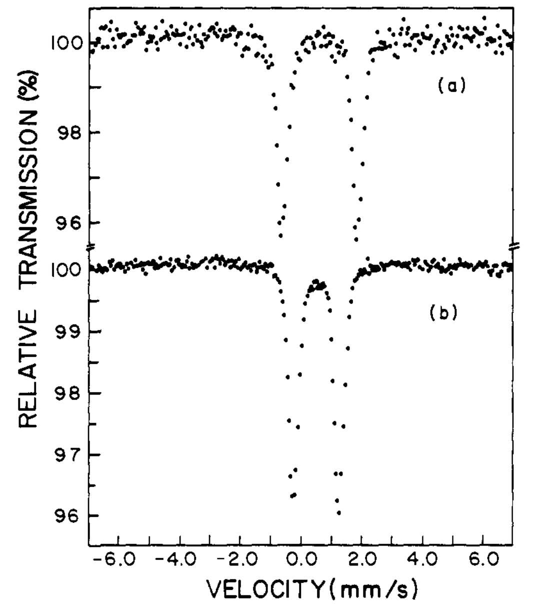

Figure 1. ^{57}Fe Mössbauer spectra of ferrocene (a) and bis(2,4-dimethylpentadienyl)iron (**4**) (b) at liquid nitrogen temperature. The isomer shift (horizontal) scale is with reference to metallic iron at room temperature.

lattice dynamical processes in the solid, and θ_M is a lattice temperature as probed by the Mössbauer-active atom. For many covalent solids, M_{eff} can be replaced by the molecular weight, provided that specific intermolecular interactions are negligible, and the solid can be approximated by point masses having the expected molecular weight. In cases where this assumption is not valid, the effective vibrating mass can be related to the temperature dependence of the isomer shift through the second-order Doppler shift, and this relationship is of the form

$$\frac{d(IS)}{dT} = -\frac{3}{2}\frac{k}{M_{eff}c} \qquad (2)$$

A typical data set reflecting the temperature dependence of the isomer shift for **3** is shown in Figure 3.

Using the atomic mass of ^{57}Fe in (1) leads to a lattice temperature given by

$$\theta_M = 11.659[-d(\ln A)/dT]^{-1/2} \qquad (3)$$

whereas substitution of M_{eff} from (2) leads to a lattice temperature given by

$$\theta'_M = (4.320 \times 10^2)\left[\frac{d(IS)/dT}{d(\ln A)/dT}\right]^{1/2} \qquad (4)$$

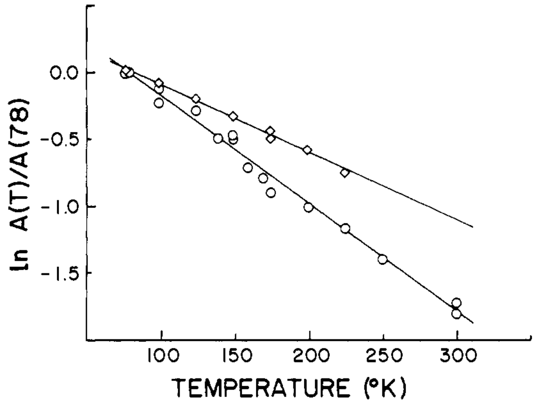

Figure 2. Temperature dependence of the recoil-free fraction (normalized to the 78 K value) for ferrocene (circles) and bis(2,4-dimethylpentadienyl)iron (**4**) (diamonds).

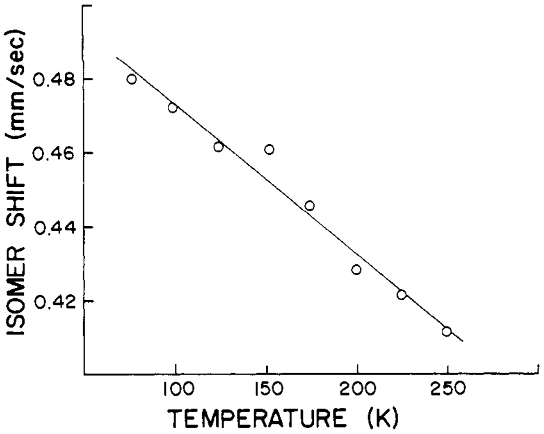

Figure 3. Temperature dependence of the isomer shift for bis(3-methylpentadienyl)iron (**3**).

The vibrational anisotropy of the metal atom in a molecule possessing an axis of molecular symmetry can be deduced from the temperature dependence of the intensity asymmetry in a Mössbauer spectrum of the type under discussion. In the absence of crystal orientation effects and of an angular dependence of the recoil-free fraction, the intensity (area) of the two components of a quadrupole split spectrum will be identical. When there is a directional dependence of the recoil-free fraction with respect to the molecular symmetry axis, the intensity ratio will become temperature dependent (the Gol'danskii–Karyagin effect).[15] This temperature-dependent intensity ratio, $R(T)$, can be related to the anisotropy of the mean-square amplitude of vibration parallel and perpendicular to the molecular symmetry axis, using the numerical solutions of the Gol'danskii–Karyagin equation of Flinn, Ruby, and Kehl.[16]

Ferrocene. The ^{57}Fe Mössbauer parameters for ferrocence are summarized in Table I, and a typical spectrum is shown in Figure 1.

The IS and QS parameters at liquid nitrogen temperature are in good agreement with published data[1–6,17,18] and provide a basis for comparison with the other compounds discussed in the present study. The temperature dependence of the area under the reso-

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nance curve, d(ln A)/dT, is well fitted by a linear regression with a correlation coefficient of 0.996 for the 16 data points (Figure 2). There is no evidence for a change in the slope of this curve above or below the λ point observed in the heat capacity data of Edwards et al.[19] at 163.9 K, in consonance with the absence of any discontinuity in the unit cell parameters above and below this point. The value of M_{eff} calculated from (2) is approximately twice the atomic mass of the metal atom and reflects the bonding interaction between the metal atom and the cyclopentadienyl ligands. The calculated lattice temperatures, making the assumption discussed above, are also summarized in Table I. The intensity ratio of the two components of the quadrupole doublet is temperature independent over the range $78 \leq T \leq 300$ K, indicating that the vibrational motion of the metal atom is effectively isotropic in this molecule. The small (~5%) departure from unity of the R parameter is temperature independent and arises from preferential crystal orientation in the sample holder.

Appropriate molecular orbital descriptions of the bonding in ferrocene have been worked out by Dahl and Ballhausen,[20] Shustorovich and Dyatkina,[21] and others[22] and account for three related observations arising from the ^{57}Fe Mössbauer effect studies of ferrocene and related molecules. The first of these concerns the fact that the isomer shifts for ferrocenes are essentially insensitive to skeletal ring substitution and replacement of the protons of the cyclopentadienyl ring by either electron-donating or electron-withdrawing groups.[17,18] The second observation relates to the fact that oxidation of the ferrocene molecule to a ferricinium cation results in only a minor change in the isomer shift parameter. Typically, on oxidation the isomer shift becomes less positive by ~0.1 to 0.2 mm s^{-1}, indicating a small increase in the electron density at the metal atom nucleus. Thirdly, this oxidation causes an almost complete collapse of the large quadrupole splitting that is observed in ferrocene itself (2.46 ± 0.01 mm s^{-1} at 78 K). Thus, the ^{57}Fe Mössbauer spectra of a number of ferricinium salts show only a very small quadrupole splitting at 78 K (typically on the order of 0.1–0.6 mm s^{-1}).[23] These three observations can be understood in terms of the MO description of the bonding in ferrocene in which the three highest occupied MO's (d_{z^2}, $d_{x^2-y^2}$, and d_{xy}) are mainly located on the metal atom. On oxidation, however, significant electron reorganization occurs so that the metal atom charge actually does not change substantially.[24] On this basis, then, one might easily expect only very small changes in the value of the isomer shift parameter to result on oxidation of ferrocene, and indeed only small differences have been reported.[18] However, while the net metal charge is not drastically altered, a substantial change does occur in the relative populations of the iron d orbitals. In particular, the d_{xy} and $d_{x^2-y^2}$ orbitals seem to be partially depopulated on oxidation, while the d_{xz} and d_{yz} orbitals are in turn somewhat more populated. The net result is to make the relative d-orbital populations more nearly equal, leading to a smaller value of the electric field gradient, q_{zz}, and hence a smaller QS. This agrees well with the near collapse of the quadrupole splitting that takes place on oxidation of ferrocene.

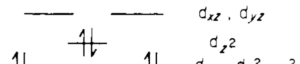
Azaferrocene. The results for azaferrocene, summarized in Table I, are consistent with the MO description presented above. The introduction of a heteroatom into the cyclic ligand causes only minor changes in the electron density and the electric field gradient at the metal atom, and hence the IS and QS parameters at liquid nitrogen temperature are indistinguishable (within experimental error) from the corresponding values in ferrocene. The similarity of the ^{1}H and ^{13}C NMR data and the ionization potential observed in the mass spectral data for ferrocene and azaferrocene has in fact been discussed by Efraty et al.[25] in light of the very distinct chemistry of the two compounds.

The effective vibrating mass of the Mössbauer active atom in azaferrocene is somewhat larger than it is in ferrocene itself and is related to the smaller temperature coefficient of the recoil-free fraction. The lattice temperatures, θ_M, calculated from these data are little different from the values obtained for the parent organometallic.

Finally, in terms of the discussion of the ^{57}Fe Mössbauer parameters of the cyclic sandwich compounds, it is interesting to note that bis(η^5-pentamethylcyclopentadienyl)iron shows an isomer shift at liquid nitrogen temperature which is essentially unchanged from that of the parent ferrocene,[26] although the quadrupole splitting parameter increases by 0.11 ± 0.04 mm s^{-1} for the ring-substituted compound.

Bis(pentadienyl)iron Compounds. Rather than consider the five pentadienyl compounds examined in the present study separately, the following discussion will focus on the significant experimental data that distinguish this group as a distinct class of organometallics. It is clear from the data summarized in Table I that the most dramatic difference between ferrocene and the "open ferrocenes" lies in the fact that the latter compounds show QS parameters (1.2–1.5 mm s^{-1}), which are on the order of $^1/_2$ as large as those observed for ferrocene and azaferrocene (~2.47 mm s^{-1}). The principal and (in terms of an MO description) significant conclusion to be drawn from this difference is the fact that the relative d-orbital populations in the "open ferrocenes" are much more nearly equal to one another than in the case of ferrocene itself, since an equally populated set of d orbitals in cubic symmetry would give rise to QS = 0. It is particularly notable that this conclusion regarding the more equal d-orbital populations agrees well with recent theoretical results on the "open ferrocene" systems.[7b]

In order to better understand the correlation between the experimental observations and the description of the bonding in these compounds, it is useful to make reference to the d-orbital splitting pattern appropriate for the metal atom in ferrocene and to consider the effects that are brought about on replacing the cyclopentadienyl ligands with pentadienyl ligands according to the MO study. In the ferrocene molecule, the metal d orbitals adopt the following approximate configuration prior to metal–ligand orbital interactions (with the molecular z axis being oriented parallel to the high-symmetry axis through the metal atom).



Quite clearly, prior to the onset of any metal–ligand bonding interactions, there exists very different relative d-orbital population on the iron atom. Moreover, MO studies suggest that since very little metal–ligand orbital mixing occurs, the ultimate populations are only slightly affected,[7b] accounting for the large QS parameters in ferrocene and related compounds, as noted above. To a first approximation,[27] the results for the pentadienyl compounds may be considered in the same manner. Here, however, the MO results indicate a much higher degree of metal–ligand orbital mixing compared to ferrocene itself, in large part due to the lower molecular symmetry in the pentadienyl compounds, although energetic arguments may also contribute. Thus, three molecular

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(27) Because of the lower molecular symmetry in the "open ferrocenes", one would not expect degeneracies to occur between the various d orbitals, and in fact substantial mixing also takes place between these orbitals. However, one would still expect the d_{xz} and d_{yz} orbitals to lie significantly higher in energy than the other three metal d orbitals.

orbitals were found to possess comparable metal and ligand character, compared to zero for ferrocene itself.[7b] In fact, besides substantial metal–ligand orbital mixing, significant mixing of the d orbitals themselves was observed. The net effect of these enhanced interactions in the "open ferrocenes" is to depopulate the d_{xy} and $d_{x^2-y^2}$ orbitals while increasing the d_{xz} and/or d_{yz} orbital populations, leading to more nearly equal d-orbital populations in the pentadienyl compounds. The d_{z^2} orbitals in both the open and closed systems are essentially totally filled, and thus do not enter into this discussion. The observed decrease in the QS parameter is going from ferrocene to the pentadienyl compounds is thus seen to provide important experimental verification of the general conclusions reached for the MO calculations on the "open ferrocene" systems.

In addition, the above MO differences can also be used to explain the observation of smaller isomer shifts for these compounds (0.46–0.50 mm s^{-1} at 78 K), compared to ferrocene itself (0.54 mm s^{-1} at 78 K), with the lower value for the open ligand system resulting from an increased s-electron density at the metal nucleus. Two possible mechanisms could bring about this increase. The first is that, compared to the cyclopentadienyl ligand, the various pentadienyl ligands could serve as better σ donors to the Fe 4s orbital. In fact, the appropriate σ-donor orbital for the pentadienyl ligand is substantially higher in energy than that for the cyclopentadienyl ligand, and this should increase the σ-donor capability of the former. However, the larger size of the pentadienyl ligands could decrease the orbital overlap for the ligand–metal interaction, and therefore it is not clear from the presently available data whether the relative direct σ-donor influences are dominant.

However, it is also possible that the change in d-orbital populations between the two systems could affect the net charge (or perhaps simply the screening) on the metal centers. If the iron atom were somewhat more positively charged in the "open ferrocenes", the core s orbitals would be contracted somewhat, thereby increasing the s-electron density at the iron nucleus. In fact, some experimental evidence exists to support this possibility. In both (pentadienyl)manganese tricarbonyl[28] and bis(2,4-dimethylpentadienyl)vanadium monocarbonyl,[29] the C–O stretching vibrational modes occur at considerably higher frequencies than those for the corresponding cyclopentadienyl analogues, $(C_5H_5)Mn(CO)_3$[30] and $(C_5H_5)_2V(CO)$.[31] Thus, it would appear that the pentadienyl ligands withdraw greater electron density from the metal than do their cyclic analogues, although this trend may not be entirely general.

Should the IS differences actually be due the just described d-orbital population changes, it might be expected that a rough correlation between IS and QS values might exist, since the QS differences between the open and closed systems also appear to be primarily dependent on d-orbital population differences.[32] A graphic representation of these data is shown in Figure 4 in which the straight line reflects a linear regression through the data (correlation coefficient 0.84). The relatively low value of the correlation coefficient for the five data pairs could reflect, in part, the relatively large standard errors associated with the isomer shifts in comparison to the observed isomer shift differences. Despite this limited correlation, it appears from the available data that a low value of one parameter correlates with a low value of the other, as suggested above. In fact, ferrocene itself is characterized both by higher IS and higher QS values. Moreover, differences in the σ-donor capabilities of the ligands are expected to be significant, as are second-order effects. Thus, it is not too surprising that the IS–QS correlation summarized in Figure 4 is not without limitations.

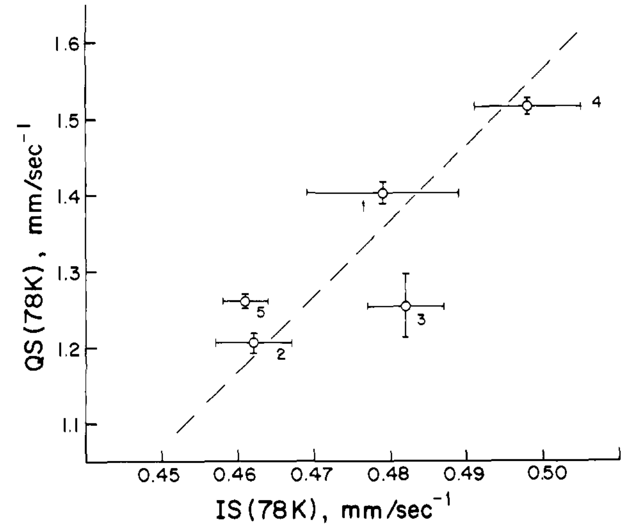

Figure 4. Correlation diagram for the isomer shift (IS) and quadrupole splitting (QS) at 78 K for the compounds discussed in the text. The error bars shown are those associated with the individual measurements of the ^{57}Fe Mössbauer parameters.

It is tempting to interpret the effect that methylation at different ligand positions has on the observed Mössbauer parameters in a quantitative manner. However, in view of the limited data available, such an interpretation of the data does not seem warranted at the present time. For example, on going from **1** to **2**, both the IS and QS parameters are decreased, but the addition of a second methyl group in the 4-position, as in **4**, leads to an increase in both IS and QS. Similarly, the isomer shift data for **1** and the analogous compound with the ligand methyl group in the 3 position, **3**, show that this change causes no change in the IS but a marked increase in the QS parameter. Clearly, these trends involve subtle electronic effects that will require a more sophisticated and detailed examination than is justified by the presently available data. Such efforts are, in fact, under way. As noted above, the Mössbauer data for ferrocene and decamethylferrocene reported by Sano et al.[26] showed that there is no appreciable isomer shift difference (78 K) between the two compounds and that the quadrupole splitting difference is well within the limits of twice the experimental errors quoted by these authors. Thus it seems clear from the present results that the Mössbauer parameters for the "open ferrocenes" may be more sensitive to methylation than has been observed for the ferrocene analogues under similar conditions.

Lattice Temperatures. As noted above, a lattice temperature, θ_M, can be extracted from the temperature dependence of the area under the resonance curve, subject to the uncertainty concerning the appropriate value for M_{eff} in eq 1. In view of the relatively large errors associated with the evaluation of M_{eff} from eq 2, the following discussion will concern itself only with θ_M calculated from eq 3, rather than with θ'_M calculated from eq 4. From the data summarized in Table I it is seen that for **1**, **3**, and **4** the lattice temperature is nearly constant and approximately 22 K higher than for **2** and **5**. In this context it is interesting to note that both **2** and **5** exist as a mixture of two stereoisomers,[7c] whereas the symmetrical ligand compounds exist in a single stereochemical configuration. It appears from these data that the nonstereoisomeric "open ferrocenes" have a lattice temperature approximately 25 °C higher than ferrocene and azaferrocene, and this observation—which reflects a lower mean-square amplitude of the iron atom at a given temperature—implies a tighter binding of the iron atom to the pentadienyl ligands than to the cyclic moieties. Moreover, symmetrical methyl group substitution does not seem to have a perceptible effect on the vibrational motion of the iron atom in these complexes.

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(32) Of course, one could bring about a more symmetric d-orbital population (thereby decreasing the QS) without effecting the iron atom charge (and IS), so correlation is not required. However, the fact that one seems to exist suggest that similar changes are responsible.

Molecular Structure in Solution. A sample of **4** was dissolved in *n*-butylbenzene, and the resulting solution was injected into a sample cell that consisted of a copper sample holder fitted with two Mylar windows as described in an earlier study.[33] The cell containing the solution was rapidly frozen with liquid nitrogen and mounted on the precooled cold finger of a Heli-tran cryostat. The ^{57}Fe Mössbauer parameters of this frozen (glassy) solution sample of **4** were identical with the values observed for the neat solid sample (Table I), and hence it can be concluded that there are no structural changes of the molecule between the neat crystalline solid and isolated molecules in solution that can be detected at the metal atom site. Thus probably it is valid to ascribe the structural and bonding parameters that are derived from solution spectroscopic techniques (^{1}H and ^{13}C NMR, infrared, etc.) in solvents as innocuous as *n*-butylbenzene to the structures that are derived from single-crystal X-ray diffraction experiments. The ^{57}Fe Mössbauer data thus provide a significant bridge between the structural inferences drawn from the two types of experiments that have been used to elucidate this new class of bis(pentadienyl)iron compounds.

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Registry No. 1, 74910-62-6; **2**, 88293-56-5; **3**, 74910-63-7; **4**, 74920-98-2; **5**, 74910-64-8; ferrocene, 102-54-5; azaferrocene, 11077-12-6.

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The Mechanism and Thermodynamics of Alkane and Arene Carbon–Hydrogen Bond Activation in $(C_5Me_5)Rh(PMe_3)(R)H$

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Abstract: The complexes $(C_5Me_5)Rh(PMe_3)(R)X$ (R = Me, Ph, *p*-tolyl, 3,4-$C_6H_3Me_2$, 3,5-$C_6H_3Me_2$, 2,5-$C_6H_3Me_2$, and $\overline{C{=}CH{-}CH_2{-}CH_2{-}CH_2}$; X = Br) react with the hydride donors $Li^+[HB(sec\text{-}Bu)_3]^-$ or $Na^+[H_2Al(OCH_2CH_2OCH_3)_2]^-$ to produce $(C_5Me_5)Rh(PMe_3)(R)H$. The complexes with R = alkyl or R = vinyl are unstable, undergoing rapid reductive elimination at 25 °C, but can be observed by ^{1}H NMR below −20 °C. $(C_5Me_5)Rh(PMe_3)(CH_3)H$ undergoes first-order reductive elimination with $k = (6.38 \pm 0.10) \times 10^{-5}\ s^{-1}$ at −17 °C. In contrast, $(C_5Me_5)Rh(PMe_3)(C_6H_5)H$ undergoes a more complicated first-order process in C_6D_6, producing C_6H_6 and $(C_5Me_5)Rh(PMe_3)(C_6D_5)D$ with the overall activation parameters $\Delta H^* = 30.5 \pm 0.8$ kcal/mol and $\Delta S^* = 14.9 \pm 2.5$ eu. The alkyl and aryl hydride complexes can also be generated by photochemical extrusion of H_2 from $(C_5Me_5)Rh(PMe_3)H_2$ in the presence of alkane or arene solvent. In a competition experiment, a 5.4:1 selectivity for benzene over cyclopentane was exhibited at −35 °C. Irradiation in toluene solvent at −45 °C produced products in which activation of all possible C–H bonds of toluene was observed: 57% meta, 36% para, 7% ortho, and <1% benzyl. Thermodynamically controlled competition between activation of benzene and toluene, *m*-xylene, *o*-xylene, or *p*-xylene showed preferences for benzene of 2.7, 12.1, 7.6, and 58.6. The aryl complexes $(C_5Me_5)Rh(PMe_3)(aryl)H$ were found to be in rapid equilibrium with their η^2-arene derivatives at temperatures above −15 °C. Mechanistic studies revealed a [1,2]-shift pathway around the ring with $\Delta H^* = 16.3 \pm 0.2$ kcal/mol and $\Delta S^* = -6.3 \pm 0.8$ eu for the derivative with R = 2,5-$C_6H_3Me_2$. Generation of the coordinatively unsaturated species $(C_5Me_5)Rh(PMe_3)$ in the presence of *p*-$[C_6H_4(t\text{-}Bu)_2]$ permitted the direct observation of an η^2-arene complex at −15 °C. The kinetics of C–H bond activation in this system are interpreted in terms of two distinct rate-determining reactions, arene coordination vs. alkane oxidative addition. The rhodium–phenyl bond is found to be about 13 kcal/mol stronger than the rhodium–methyl bond.

One of the most beneficial features of transition-metal complexes is their ability to promote chemical reactions in organic molecules. Oxidative addition is a fundamental process that produces a species capable of reacting in numerous ways characteristic of the molecule that has been activated.[1] For example, aldehydes and acid chlorides can be decarbonylated following oxidative addition of the C–H or C–Cl bonds.[2] The oxidative addition of alkyl and aryl halides produces organometallic complexes in which the metal–carbon bond can undergo a variety of insertion and elimination reactions, leading to substantial changes in the structure of the organic ligand.[3] Until recently, however,

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