Carbon-13 Chemical Shifts in Solid Metal Sandwich Compounds[‡]

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Abstract: Chemical shielding parameters are reported for the metallocenes of Fe, Ru, and Mg, bis(cyclopentadionyl) complexes Cp_2TiCl_2, $(CpMe_5)_2CoCl$, and $(CpMe_5)_2Fe$, and bis(benzene)chromium. The shielding tensor anisotropy seems to reflect the character of bonding. Motion is detected in many of these compounds and has been used in some cases to assign the shielding tensor principal directions.

1. Introduction

Since the development of the cross-polarization method[1] for obtaining high-resolution solid-state NMR spectra of dilute spins in solids, a variety of chemical shielding tensors for various nuclei have been reported.[2] A knowledge of the complete tensor provides more information (three shielding parameters and three orientational parameters) than the isotropic chemical shift and hence provides a much more rigorous connection for understanding of the effects of bonding on chemical shielding. The detailed information about the local electronic structure surrounding a spin has proved useful in studies of such diverse problems as hydrogen bonding,[3] conduction anisotropy in "one-dimensional" conductors,[4] and dynamics of phase transitions in antiferroelectrics.[5]

Although a wide variety of ^{13}C shielding tensors in aromatic molecules are known, there is only one previous study of aromatic organometalic complexes.[6] The metallocene type of compound is of considerable interest because of the unusual bonding and their practical uses as catalysts. Although isotropic shifts for protons and carbon are known for a variety of metallocenes,[7] there have been no reports of the anisotropic couplings. In cases where anisotropic motion is present at some temperatures but may also be frozen out, it is known that some information may be obtained from powder spectra about the orientation of the shielding tensor relative to the molecular frame. Such information is normally available only from the study of oriented single crystals. In addition, knowledge of the shielding tensor provides the basis for detailed studies of molecular dynamics, of particular interest for C_5 symmetry. In this paper we present results of shielding values and an example of orientation assignment from a motional study.

2. Anisotropic Chemical Shielding

A chemical shielding tensor σ may be characterized fully by specifying its principal values σ_{11}, σ_{22}, and σ_{33}, together with a set of angles relating the tensor's orientation to some external reference frame. The chemical shift observed for any particular spin is easily calculated from the principal values and Euler angles (ϕ, θ, Ψ) relating tensor and laboratory axis frames.

$$\sigma_{obsd} = \sigma_{11} \sin^2 \theta \cos^2 \phi + \sigma_{22} \sin^2 \theta \sin^2 \phi + \sigma_{33} \cos^2 \theta \quad (1)$$

where θ is the angle between σ_{33} and lab z directions and ϕ between σ_{11} and x. Of course while systematic variation of the angles in a single-crystal sample allows a determination of both principle valves and orientation of the tensor, it is not often convenient and possible to have oriented crystals. In favorable cases, however, anisotropic averaging of the tensor through molecular motion has been used to assign tensor element directions. Such an effect is easily calculated using an Euler rotation (α, β, γ) analogous to

that in (1) above, except that the angles define the relative orientation of the tensor and the rotation axis systems, and the tensor elements are averaged over the motion. For a uniform uniaxial rotation the averaged tensor is axially symmetric with

$$\sigma_\perp = 1/2(1 - \cos^2 \alpha \sin^2 \beta)\sigma_{11} + \\ 1/2(1 - \sin^2 \alpha \sin^2 \beta)\sigma_{22} + 1/2 \sin^2 \beta \sigma_{33}$$

$$\sigma_\parallel = \cos^2 \alpha \sin^2 \beta \sigma_{11} + \sin^2 \alpha \sin^2 \beta \sigma_{22} + \cos^2 \beta \sigma_{33} \quad (2)$$

where $\sigma_\parallel$ is the tensor element along the rotation axis and $\sigma_\perp$ is the element perpendicular to it. When both the unaveraged and averaged tensor elements are known, eq 2 may be solved (to within a sign) for the angles α and β. If the axis of rotation is known or assumed, then the tensor orientation in the molecular frame may be calculated.

The determination of tensor elements from powder spectra is quite straightforward for molecules which have a very small number of carbons with different shielding tensors. The powder patterns which may be observed have characteristic features at the values σ_{11}, σ_{22}, and σ_{33} in the general case and $\sigma_\parallel$ and $\sigma_\perp$ in the axially symmetric case. In more complex cases it is possible to use slow magic angle spinning together with a theoretical analysis to extract the principal values for several overlapping tensors. The simplicity of the compounds in this study precluded the necessity of use of such techniques.

3. Experimental Section

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Table I[e]

compd[a]	Tr(σ)	σ_i[b]	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$[c]
$(C_5H_5)_2Fe$	59	58.6	34	34	110	76
$(C_5H_5)_2Ru$	55		29	29	108	79
$(C_5H_5)_2Mg$	20	19.2	−24	−24	108	132
$(C_5H_5)_2TiCl_2$	13		−39	−39	116	155
$(C_5(CH_5)_5)_2Fe$	49		1	42	105	83.5
			27	27	94	(67)
$(C_5(CH_3)_5)_2CoCl$[d]	15		−51	5	90 ± 10	113 ± 15
	22		−43	18	90 ± 10	102 ± 15
$(C_6H_6)_2Cr$	52		14	14	128	114
C_6H_6	−1	0	−59	−59	115	174

[a] In cases for which $\sigma_{11} = \sigma_{22}$ we assume that fast rotation of the substituant ring is present, causing the tensor to be axially symmetric. Short proton relaxation times are additional evidence for such motions. [b] Isotropic solution value from the literature. [c] $\Delta\sigma = \sigma_{33} - (1/2)(\sigma_{11} + \sigma_{22})$. [d] Due to overlap of several shielding tensors these values are less precise and correspondence of σ_{11} and σ_{22} values, and hence Tr(σ), are tentative. The apparent intensities are two carbons for the first tensor and three carbons for the second. Rotation of C_5 rings in this compound does not occur below 100 °C. Errors in σ_{11} and σ_{22} values are estimated ±5 ppm. [e] Tensor elements were determined by comparison with appropriately broadened computer-generated powder line shapes.

4. Results and Discussion

The chemical shielding parameters measured for several simple metallocenes and several more complex organometallic compounds are shown in Table I. In most cases rapid rotation of the C_5 rings causes averaging of the tensor at room temperature for unsubstituted rings; the rotation generally does not freeze out until below liquid-nitrogen temperatures and hence the rigid-tensor values were not obtained in this study. Comparison of the trace values of the tensors determined in the solid state with the literature isotropic phase values shows little change occurs in chemical shielding upon condensation, consistent with other measurements in organic solids.

It is particularly interesting to note the small differences in σ_{33} values for the various metallocenes. The largest contribution to the difference in isotropic shifts comes from the σ_{11} and σ_{22} values. Similar effects have been observed for (arene)chromium complexes. One must be somewhat careful in interpretation of these shielding parameters since they are for the most part motionally averaged.

The case of permethylferrocene is particularly favorable in this sense since its spectra may be observed at temperatures where it is rigid as well as where it undergoes rapid rotation. In isolated molecules it is often possible to determine some of the principal directions from symmetry arguments alone. In an isolated planar five-carbon ring there must be a principal direction perpendicular to each of the two symmetry planes passing through a carbon. Since the three axes must be mutually orthogonal, this fixes all of the principal directions: one perpendicular to the ring plane, one along the ring center to carbon atom vector in the ring plane, and one tangential to the ring of carbons. In the presence of a metal atom the plane of symmetry containing the ring carbons is removed and two principal directions may be rotated from the directions described above. If we assume that motion occurs as a rotation about the ring C_5 axis (a detailed study of the dynamics of this motion, with justification of this assumption, will be published separately),[8] then we may almost completely determine the tensor orientation. We note that upon rotation all three of the tensor values change, indicating that the rotation axis is not a principal direction, as was observed for rotation in hexamethylbenzene. However, since the degenerate element for the averaged tensor lies between σ_{11} and σ_{22} for the rigid molecule, we know that σ_{33} lies nearest to the rotation axis. Using eq 2 and the symmetry arguments above, we conclude that the σ_{33} element is rotated 19° from the rotation axis. Although the NMR ex-
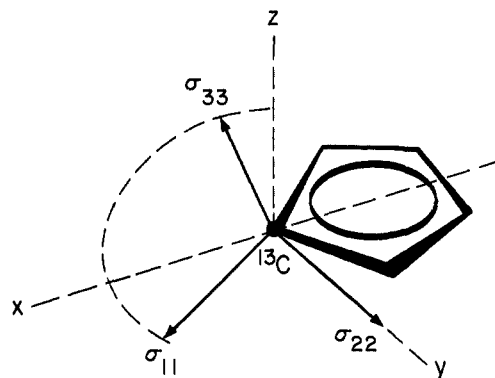
(8) D. E. Wemmer, D. J. Ruben, and A. Pines, submitted for publication in *J. Am. Chem. Soc.*

Figure 1. Orientation of principal axis of ^{13}C shielding tensor in permethylcyclopentadionyl ring in permethylferrocene.
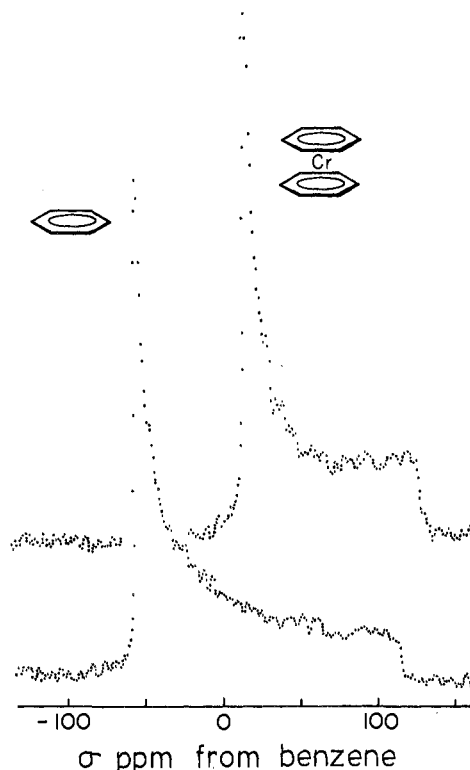

σ ppm from benzene

Figure 2. ^{13}C powder spectra of (benzene)- and bis(benzene)chromium on the same scale. Large shifts in the tensor elements are observed upon binding.

periment cannot determine the sign of this angle, this most shielded direction is probably rotated to pass close to the iron atom, giving the orientation depicted in Figure 1. This relatively small rotation of the tensor reinforces our conclusion that most of the change in shielding comes from changes in the σ_{11} and σ_{22} elements.

From the data of Table I it is clear that the shielding anisotropy is very sensitive to the nature of the ring–metal interactions. The very similar covalently bonded metallocene of iron and ruthenium from the same column of the periodic table have almost identical shielding. However, the structurally identical magnesium compound, with much more ionic bonding character, has much larger shielding anisotropy. Qualitatively it is reasonable that more electron density in the ring orbitals will lead to greater shielding. Since it is not possible to study an isolated anionic cyclopentadiene ring, we have also studied bis(benzene)chromium, where shielding parameters for the isolated benzene are well-known. As expected there is a significant decrease in the anisotropy, shown in Figure 2. Although motion is present, the upfield shift of the σ_{33} element (which cannot stem from averaging) indicates that rotation of the tensor analogous to that in permethylferrocene cannot account for the observed changes.

Although quantitative analysis of chemical shielding from a

purely theoretical standpoint is still at a very crude stage, measurement of anisotropic shielding can clearly provide a qualitative picture of the differences in bonding in organometalic compounds. Further investigation of such compounds from both experimental and theoretical views seems warranted and may prove fruitful in understanding their chemical properties.

Unimolecular Reactions of Ionized Methyl Acetate and Its Enol: Mechanism for the Enol to Keto Isomerization

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Abstract: Both the methyl acetate molecular ion and its enol fragment by loss of CH$_3$O· and show identical kinetic energy releases for decompositions occurring in the first drift region of a double-focusing mass spectrometer, consistent with fragmentation from the same structure. However, collisional activation mass spectra indicate that both keto and enol ions of lower energies retain their original structures. For fragmentation reactions occurring in the ion source, a study of methyl-d_3 acetate confirms that the methoxy group is lost directly in this fragmentation, while examination of the labeled enol ions CD$_2$C(OH)OCH$_3$$^+$· and CH$_2$C(OH)OCD$_3$$^+$· show that the methoxy neutral lost contains largely the enol hydrogen and two of the methoxy hydrogens. The results indicate that the enol structure does not fragment directly but isomerizes to the keto structure by two consecutive [1,4]-hydrogen shifts rather than by a direct [1,3]-hydrogen shift. With increasing lifetime methyl acetate molecular ions show extensive interchange of hydrogens between the two methyl groups; the extent of hydrogen interchange is less for the enol structure, presumably due to their different distribution of internal energy values. A detailed potential energy profile for the unimolecular reactions of the two structures is constructed.
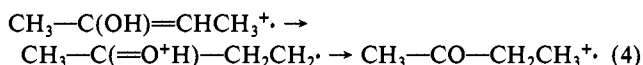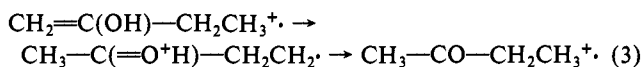
A ubiquitous rearrangement of carbonyl compounds, eq 1,

$$>C=C< \quad + \quad >C=C(OH)-Y^+· \quad (1)$$
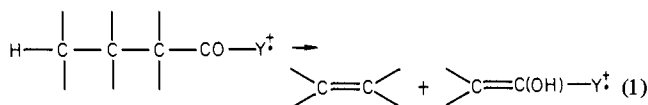
results in the formation of the ionized enol of $>$C(H)—CO—Y as the product ion. The evidence supporting the specificity of the γ-hydrogen transfer and the initial enolic structure of the product has been amply reviewed.[2]

The question of the ketonization of the enol structure, $>$C=C(OH)Y$^+$· → $>$C(H)—CO—Y$^+$·, also has received considerable attention, with mixed results. A number of studies[2,3] have presented evidence that, at least in the specific systems studies, ketonization does not occur prior to fast unimolecular reactions occurring in the ion source. The stable C$_3$H$_6$O$^+$· rearrangement product from 2-hexanone retains the enol structure,[4,5] and a wide variety of enolic ions are more stable thermodynamically than their corresponding keto ions.[6] On the other hand, Bursey et al.[7] have

shown that the enol ion obtained from dissociative ionization of 2-*n*-propylcyclopentanone isomerizes slowly to the keto structure as its lifetime in an ICR spectrometer is increased from 10^{-3} to 10^{-1} s. The enolic C$_3$H$_6$O$^+$· and C$_4$H$_8$O$^+$· ions formed from alkanones have been shown[5,8] to rearrange to the keto form prior to fragmentation in the drift regions of a mass spectrometer. Of particular interest in the present context is the observation[8] that low-energy, C$_4$H$_8$O$^+$· enolic ions do not rearrange to the ketonic structure to a significant extent by the direct [1,3]-hydrogen shift (eq 2) but rather rearrange either by two consecutive [1,4]-hy-

$$CH_2=C(OH)-CH_2CH_3^+· \rightarrow CH_3-CO-CH_2CH_3^+· \quad (2)$$

$$CH_2=C(OH)-CH_2CH_3^+· \rightarrow$$
$$CH_3-C(=O^+H)-CH_2CH_2· \rightarrow CH_3-CO-CH_2CH_3^+· \quad (3)$$

$$CH_3-C(OH)=CHCH_3^+· \rightarrow$$
$$CH_3-C(=O^+H)-CH_2CH_2· \rightarrow CH_3-CO-CH_2CH_3^+· \quad (4)$$

drogen shifts (eq 3) or by a [1,2]-H shift followed by a [1,4]-H shift (eq 4). This work also showed that the direct shift (eq 2) became more important at higher internal energies, suggesting a high activation energy, but a more favorable energy-independent term, for the direct [1,3]-H shift.

More recently Schwarz and Wesdemiotis[9] have reported that the structurally similar ion CH$_2$=C(OH)—OCH$_3$$^+$·, the enol form of ionized methyl acetate, isomerizes to the keto form by a sym-

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