Carbon-13 Shielding Tensors of Zeise's Salt and Zeise's Dimer

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The ^{13}C cross-polarization magic angle spinning NMR spectra of crystalline Zeise's salt, $K[PtCl_3(\eta^2-C_2H_4)]$, and Zeise's dimer, *trans*-$[\{PtCl_2(\eta^2-C_2H_4)\}_2]$, have been recorded at room temperature. The ^{13}C chemical shift tensors have been determined. The values of the tensor elements are compared to those of the free ethylene ligand and are discussed in terms of the bonding.

Zeise's salt $K[PtCl_3(\eta^2-C_2H_4)]\cdot H_2O$, was the first organometallic compound to be described [1] and still serves as the simplest example of transition-metal olefin chemistry. The bonding interaction between the metal and ethylene has been the subject of numerous investigations and, since the chemical shift tensor can provide information on the chemical bonding interaction, we report here the solid-state ^{13}C NMR spectrum of Zeise's salt, together with that of the closely related dimer, *trans*-$[\{PtCl_2(\eta^2-C_2H_4)\}_2]$.

Experimental

Zeise's salt and Zeise's dimer purchased from Aldrich Chemical and Strem Chemical, respectively, were used as received. The ^{13}C chemical shift tensors were obtained by graphical analysis [2] of the sideband intensities of the magic angle spinning (MAS) spectra. The measurements were made at room temperature on a Chemagnetics CMX-300 solid-state NMR spectrometer operating at 75.36 MHz with cross-polarization (CP) and high-power proton decoupling.

Results and Discussion

Figs. 1 and 2 show typical ^{13}C CP MAS NMR spectra of crystalline Zeise's salt and Zeise's dimer, respectively. The carbon resonance of Zeise's salt is split into two components of about equal intensity. The observed splitting apparently results from solid-state effects since the molecules are located at general positions in the $P2_1/c$ unit cell and, therefore, either the two-fold axis passing through the Pt atom and midpoint of the C=C double bond or the mirror perpendicular to the C=C bond is removed by the packing forces, resulting in the two carbon sites in Zeise's salt becoming magnetically non-equivalent. This suggestion is consistent with the results of X-ray and neutron diffraction studies,[3,4] which have shown that the $PtCl_3$ moiety is not exactly planar with the Pt atom being 0.03 Å from the best plane through the $PtCl_3$ group and the C–C bond of the ethylene ligand making an angle of 5.9° with the normal to this plane. The precise symmetry of the Zeise's salt anion may be best described as C_s. The absence of any similar solid-state splitting in the high-resolution spectrum of Zeise's dimer indicates that the plane of symmetry and the two-fold axis of the isolated molecule appear to be retained in this crystal.

The experimentally determined principal components of the ^{13}C chemical shift tensors of Zeise's salt and Zeise's dimer, together with the isotropic shifts, are listed in Table 1. The calculated unbroadened powder patterns of Zeise's salt and Zeise's dimer, and free ethylene, are shown in Fig. 3 for the purposes of comparison. The 63 ppm isotropic shift for Zeise's salt in the solid is very close to the 67 ppm for the solution spectrum.[7] Zeise's salt shows higher carbon shielding than Zeise's dimer, by 15 ppm.

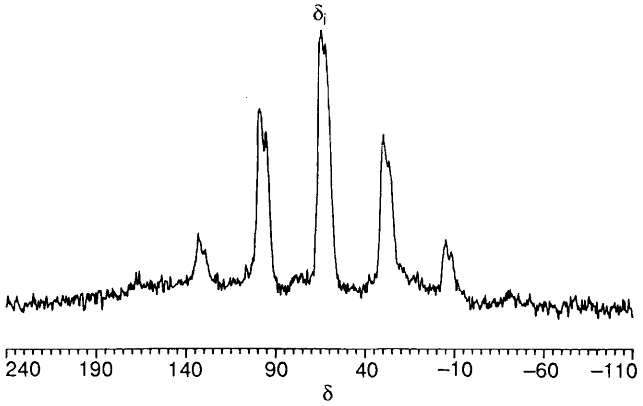

Fig. 1 Carbon-13 CP MAS NMR spectrum of Zeise's salt; sample spinning at 2.6 kHz; 8104 transients accumulated; 10 s pulse delay

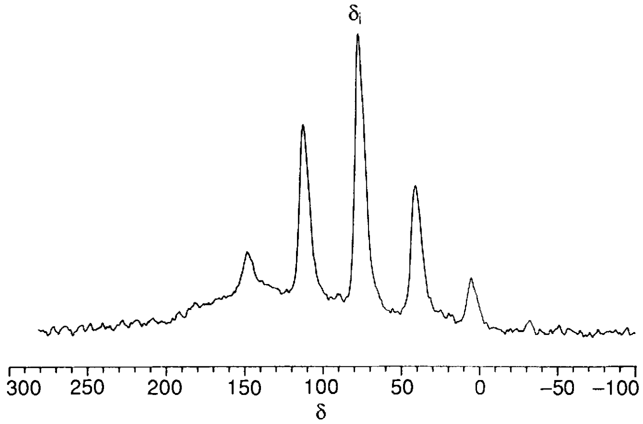

Fig. 2 Carbon-13 CP MAS NMR spectrum of Zeise's dimer: spinning at 2.7 kHz; 15 000 transients accumulated; 15 s pulse delay employed

Individual gauge for different localized orbitals (IGLO) calculations on olefins have shown that the orientation of the principal axis system for the olefinic carbons is fairly insensitive to the presence of substituents and to the bonding situation of the carbon.[8] The principal axes of a molecule having D_{2h}, C_{2v}, or higher symmetry are restricted to the same directions as in ethylene and, even for lower-symmetry molecules, the orientation of the principal axis system deviates only by small angles from the principal axes of the shielding tensor in ethylene

Table 1 Principal components and isotropic values of the ^{13}C shielding tensors and chemical shift anisotropies for Zeise's salt and Zeise's dimer[a]

Compound	δ_{11}	δ_{22}	δ_{33}	δ_i	$\Delta\delta$
Zeise's salt[b]	135	67	−10	63	111
	133	64	−12	61	111
Zeise's dimer	157	84	−14	77	134
Ethylene[c]	234	120	24	123	153
Cyclopropene[c]					
olefinic carbons	239	79	5	108.7	154
Methylene carbon	40	29	−59	2.3	94
Cyclopropane[d]	22	2	−36	2.3	48

[a] Values of principal elements and isotropic shifts are in ppm, relative to external $SiMe_4$; uncertainties are ±10 ppm. [b] Note two sets of values for Zeise's salt (see text). [c] From ref. 5. [d] From ref. 6.

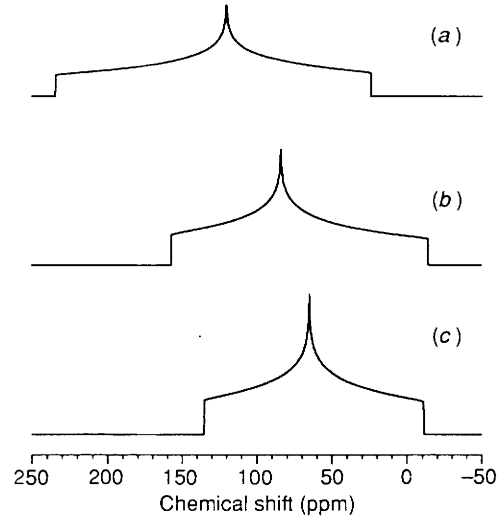

Fig. 3 Calculated ^{13}C powder pattern lineshapes of (*a*) free ethylene, (*b*) Zeise's dimer and (*c*) Zeise's salt

itself.[5,8] Since the symmetry of $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$ in the crystal is still close to C_{2v} (splitting is only 2 ppm at 7.05 T), while that of the Zeise's dimer is C_{2h}, we can determine the effects of olefin complexation by comparing each individual shielding component with the corresponding tensor element for the free ethylene molecule.

For the isolated ethylene molecule the direction of δ_{22} lies along the C=C bond axis, the low-frequency component, δ_{33}, lies along the normal to the molecule plane, and δ_{11} lies in the molecular plane but perpendicular to the C=C bond.[9,10] Both δ_{11} and δ_{22} can be affected directly by changes in π-electron charge densities since the axes of these components lie in the plane containing the C=C bond.[11] Upon co-ordination, the shieldings of the δ_{11} and δ_{22} components in both compounds increase, by more than 99 and 53 ppm for Zeise's salt and by 77 and 36 ppm for Zeise's dimer, respectively, from the values for ethylene (Fig. 3). The neutron diffraction study showed that the hybridization of the carbon atoms, although nearly sp^2, tends slightly towards sp^3.[12] This slight loss of π-bonding character for the carbon atoms may partially account for the relatively large shift in the values of δ_{11} and δ_{22} towards lower frequencies.

The fundamental factor which affects the shieldings is the change in excitation energy. It has been pointed out by Jameson and Mason[13] that the magnetically allowed excitations between the local orbitals are the only ones that determine NMR shifts. For the ethylene molecule, the $\pi \longrightarrow \sigma^*$ and $\sigma \longrightarrow \pi^*$ excitations are important to the δ_{11} and δ_{22} components. Although the $\pi \longrightarrow \pi^*$ excitation in free ethylene is not magnetically active, it can also affect the δ_{11} and δ_{22} components since an increase in the $\pi \longrightarrow \pi^*$ excitation energy also increases the $\pi \longrightarrow \sigma^*$ and $\sigma \longrightarrow \pi^*$ excitation energies. The $\sigma \longrightarrow \sigma^*$ excitations are the only magnetically active ones for δ_{33}, which samples the in-plane paramagnetic circulations. Complexation of the ethylene ligand to the metal will alter these energy gaps to different extents and, therefore, will affect the shielding. The δ_{11} component of both complexes, associated with the in-plane perpendicular axis, depends primarily on the carbon–carbon π and σ electrons and experiences the major changes since this axis mainly mixes σ(CC) electrons and orbitals with π(CC) which are affected greatly by co-ordination. The δ_{22} component along the C=C bond involves the magnetic field mixing of the π electrons with carbon σ electrons external to the C=C bond.[5] Therefore, this component is more affected by the steric features related to these external σ bonds. Accordingly, the formation of the C–Pt–C triangle and the bending of the hydrogens away from the central platinum may contribute to the observed δ_{22} values. The δ_{11} and δ_{22} components for Zeise's salt show greater shielding than those of the dimer, by about 25 and 18 ppm, respectively, possibly reflecting the slight difference in the strengths of the π-back bonding between the platinum and the ethylene ligand in the two complexes. The negative charge on $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$ may cause the metal to transfer more electron density to the π* orbital of the ethylene ligand and, consequently, higher shielding along the δ_{11} and δ_{22} directions. The different values of the δ_{11} and δ_{22} components in the two complexes may also reflect the difference in the overall electron distribution within the molecules since there are two bridging chlorides in the dimer.

Upon complexation to the metal the δ_{33} component of ethylene shifts to lower frequency by about 37 ppm for both complexes. Since the magnitude of this component depends upon the σ electrons, which are not greatly affected by complexation,[5,14] the value of this component for both complexes is expected to be about the same and to fall in the range found for cyclic alkenes. As expected, the δ_{33} components for Zeise's salt and Zeise's dimer do have almost identical values; however, they show much higher shielding than those of normal olefinic carbons. These observations can readily be explained by the formation of a three-membered C–Pt–C ring. It has been noticed that three-membered rings are very unusual in that the δ_{33} component shows high shielding (Table 1).[15] For instance, the values of δ_{33} for the methylene carbon in cyclopropene and cyclopropane are −59 and −36 ppm, respectively,[5,6] and the relatively low frequencies of this component for both compounds have been attributed to the small C–C–C angle in the three-membered rings.[6] The δ_{33} value for the olefinic carbon of cyclopropene is 5 ppm, which displays much more shielding than for other alkenes and cycloalkenes.[5] Therefore, the −12 and −14 ppm values of δ_{33} for Zeise's salt and Zeise's dimer are possibly the result of the formation of a three-membered C–Pt–C ring and these values are in between the corresponding components of the methylene and olefinic carbons in cyclopropane and cyclopropene, suggesting that the carbon–carbon bond order in both compounds is in between that of a single and a double bond. It should be kept in mind that the direction of δ_{33} in cyclopropene is along the out-of-plane axis, but, for the three-membered C–Pt–C ring in both platinum complexes the direction is located in the C–Pt–C plane because the π bond in cyclopropene is perpendicular to the plane while in the complexes the π bond lies in the plane. Since the δ_{33} values for both complexes are almost identical, the 15 ppm difference in isotropic shift between Zeise's salt and the dimer is due to the fact that the carbon nuclei in the dimer are more deshielded along δ_{11} and δ_{22} directions than those in Zeise's salt.

The ^{13}C chemical shielding anisotropies, $\Delta\delta = \frac{1}{2}(\delta_{11} + \delta_{22}) - \delta_{33}$, for Zeise's salt and Zeise's dimer, as well as for the free ethylene ligand, are also listed in Table 1. The anisotropy decreases from 153 ppm in free ethylene to 134 ppm in the dimer and to 111 ppm in Zeise's salt, implying an increase in the overall ($\sigma + \pi$) bonding to Pt.

The barriers to rotation of the ethylene group in Zeise's salt and its derivatives in solution have been reported.[16] However, this reorientation does not apparently occur in the solid state for either complex at room temperature, since rotation about an axis perpendicular to the C=C bond would result in averaging δ_{22} and δ_{11} to give an axial symmetric powder pattern.

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