feature of platinum(II)-olefin complexes and takes place usually under very mild conditions in nonaqueous solvents such as dichloromethane and acetone. The resulting aminoalkyl complexes undergo cleavage of the platinum–carbon σ bond upon treatment with aqueous hydrochloric acid to give olefin-free complexes and the *N*-alkylated derivatives of the attacking amine. Incidentally, the reaction of Zeise's salt with alanine described in this paper might also have involved initial nucleophilic attack of the amino group on ethylene to give an aminoalkyl platinum complex. However, this is not actually the case since the reaction product is exclusively *N*-*trans*-[Pt(Ala)(C_2H_4)Cl],[1,3a] which is completely dissociated in 3 *N* HCl to give back the starting [Pt(C_2H_4)Cl_3]$^-$. Apparently, formation of an aminoalkyl complex in this case is unfavored (i) by the use of water as a solvent which effectively deactivates the amino group by solvation and (ii) by the negative charge on the substrate complex.

Registry No. K[Pt(C_2H_4)Cl_3], 12012-50-9; DL-alanine, 302-72-7; *trans*-[Pt(C_2H_4)(H_2O)Cl_2], 12275-01-3; *N-trans*-[Pt(Ala)(C_2H_4)Cl_2]$^-$, 42996-29-2; *N-trans*-[Pt(Ala)(C_2H_4)Cl], 42996-30-5.

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Nuclear Magnetic Resonance Study of a Platinum–Ethylene Complex in a Liquid Crystal Solvent

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The nmr spectrum of the olefin resonance of *trans*-(py)(C_2H_4)$PtCl_2$ dissolved in a nematic solution of poly-γ-benzyl-L-glutamate and methylene chloride has been observed. In C_{2v} symmetry only two ordering parameters are required. As a result the three interproton coupling constants will determine one structure parameter. For a rigid molecule the ratio of the H–H distance of geminal hydrogens to the H–H distance of hydrogens cis to each other on the C–C skeleton could be determined. This analysis of the spectrum reported here gave a ratio for the olefin moiety in solution which compares quite favorably to previously reported results in the solid state. It is expected that dynamic processes are present in the system studied. However, conditions under which this method of analysis is still valid are discussed. Severely overlapping resonances were found and the standard method of analysis could not be used. A method was developed in which the spectrum intensities, rather than transition frequencies, were fit.

Transition metal–olefin complexes have been widely studied,[1-3] and several workers have discussed the structure of the olefin moiety in these complexes.[2,4,5] Recent crystal structure studies have shown that in Zeise's salt[6] and in (C_5H_5)Rh(C_2H_4)(C_2H_4)[7] the C–H bonds are bent back away from the metal center. Figure 1 shows the ethylene in the conformation found in the solid-state studies. It was of interest to determine features of the geometry of a platinum–olefin complex in solution for several reasons. One is that the olefin rotates about the platinum–olefin bond in solution[2] and several authors have suggested[2,8] there is a variation in the binding of the olefin with rotation. The platinum orbitals are proposed to be best suited for bonding to the olefin when the olefin C–C axis is perpendicular to the plane of the two chlorines and L in Figure 1. The geometry within the ethylene moiety is expected to be sensitive to the particular conditions of overlap and bonding between the metal and the olefin. Thus, in solution, the ethylene might assume a number of geometries in time and, on the average, exhibit a structure different from that observed in the solid state. MO calculations[5] have predicted that the olefin spends most of its time with its C–C axis parallel to the *y* axis. Another reason these systems are interesting is that ligand exchange has been observed in solution,[3] though the olefin remains bound to platinum, at least on the nmr time scale. This dynamic process could possibly affect the average olefin geometry as well if the olefin geometry is a sensitive function of the metal environment in solution.

A technique suited to measuring structural parameters in solution is nuclear magnetic resonance spectroscopy in a nematic liquid crystal solvent,[9] but the method is subject to some limitations. Foremost are the experimental ones; the molecule must be soluble in the nematic solvent but must not decompose in it. With these considerations in mind, the complex *trans*-Pt(C_2H_4)(py)Cl_2 (hereafter referred to as I) was chosen and its spectrum examined in several commercially available liquid crystal solvents. None gave a usable spectrum. The complex was found to be soluble in the nematic phase of a mixture of poly-γ-benzyl-L-glutamate (PBLG) and CD_2Cl_2, and reproducible spectra were obtained. This particular solvent is very weakly orienting and, as a result, energy absorption occurs over a narrow range of frequencies, and hence extensive overlap of peaks is observed. For this reason, the usual frequency-fitting procedures are of no use in the spectral analysis. Instead, we developed a procedure in which the spectrum intensity at various frequencies was fit by a calculated intensity at that frequency which would result from the set of calculated peaks. Lorentzian line shapes of identical line width were assumed. A discussion of this assumption is presented in the Appendix.

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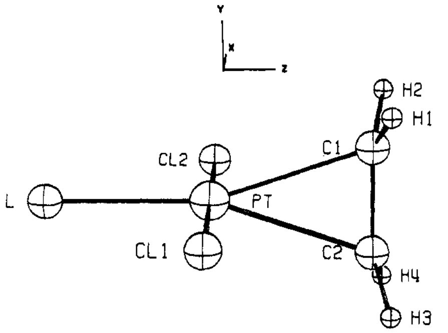

Figure 1. Perspective drawing of *trans*-$(C_2H_4)LPtCl_2$. The C-H bonds are shown bending away from the platinum. The ethylene C-C axis is perpendicular to the plane determined by the chlorines and L.

Experimental Section

The complex (I) was prepared by the method of Orchin.[3] Reagent grade pyridine-d_5 was used without further purification, as was methylene chloride-d_2. The PBLG was obtained from Pierce Chemical Co. and was dried under vacuum at 70° before use. The solutions used were approximately 10 mol % in acid residue, 20 mol % in I, and 70 mol % in CD_2Cl_2. The solutions were mixed by repeated centrifugation. It was a practical impossibility to determine exact proportions because the proportions required several adjustments before a satisfactory spectrum could be obtained. Spectra were taken with a Jeolco 60-MHz nmr instrument with external lock (probe temperature of 26°), a Varian 220-MHz instrument (probe temperature 28°), and a Varian HA100 instrument (probe temperature 28°). The 220-MHz instrument gave apparently improved resolution, but see below. The solutions were quite viscous and the line widths were probably broadened because of this effect. All protons have identical chemical shifts so that increased field strength had no effect on peak separation. An effort was made to decouple ^{195}Pt on the HA100, but apparently insufficient power was available and no effect was noted. The analysis of the spectra indicate, *vide infra*, that the ethylene remains coordinated to platinum. TMS was added to the sample and it gave a single broad line. Attempts were made to fit the TMS signal to a gaussian line shape and a lorenztian line shape. A considerably better fit was achieved, using a lorenztian shape, and it was then assumed to be true of all peaks in the spectrum. The spectra were digitized on an Oscar Model F electronic digitizer.

Results

A 60-MHz nmr spectrum is shown in Figure 2 along with a computer-simulated spectrum. Figure 3 shows the same sample run at 220 MHz. In Table I, the coupling constants and line widths used to generate the calculated spectra are reported.

In C_{2v} symmetry (*vide infra*), the ethylene moiety should give a 12-line spectrum[10] in a nematic solvent, and, including satellites from the 33% ^{195}Pt ($I = 1/2$), 36 lines are expected. It is apparent from Figures 2 and 3 that significantly fewer peaks are experimentally resolved because of extensive overlap. Thus, it was not feasible to employ the usual procedure of fitting the frequencies of experimental peaks with peaks calculated from a set of coupling constants. Instead the experimental intensities at several frequencies were fit to calculated intensities, based on a set of peaks calculated from a set of coupling constants and assuming lorenztian line shapes. Details of the fitting procedure are outlined in the Appendix.

The coordinate system is shown in Figure 1 and the platinum lies on the twofold axis. Two ordering parameters, S_{11} and S_{22}, are needed to describe the average orientation of any axis within the ethylene. Moreover, because platinum is on the twofold axis, even with free rotation of the ethylene, these two parameters suffice to describe the average ordering of any internuclear vector connecting platinum and ethylene.

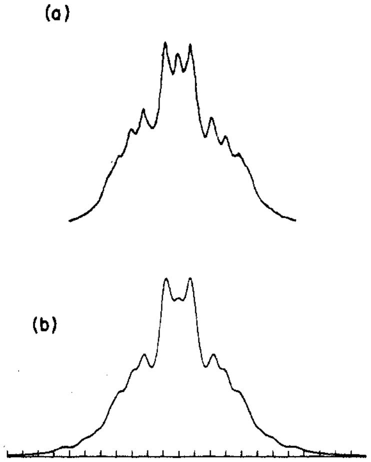

Figure 2. Proton nmr spectra of the ethylene moiety of I at 60 MHz: (a) experimental spectrum–frequency scale same as in calculated spectrum; (b) calculated spectrum–hash marks are at intervals of 10 Hz.

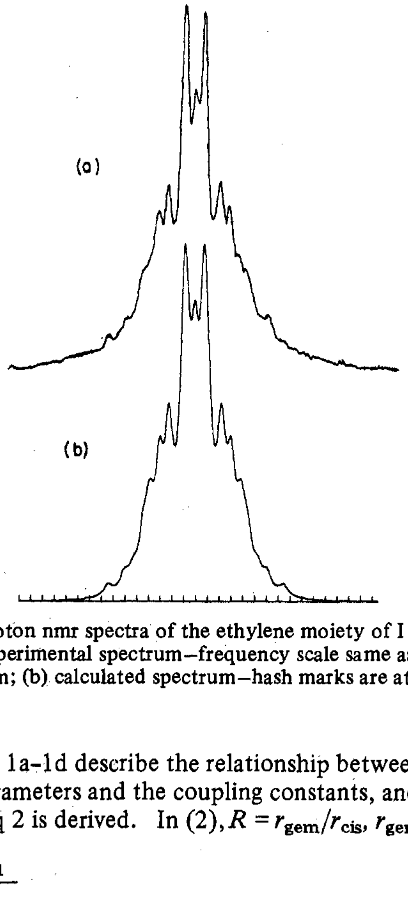

Figure 3. Proton nmr spectra of the ethylene moiety of I at 220 MHz: (a) experimental spectrum–frequency scale same as in calculated spectrum; (b) calculated spectrum–hash marks are at intervals of 10 Hz.

Equations 1a–1d describe the relationship between these ordering parameters and the coupling constants, and from eq 1a–1d, eq 2 is derived. In (2), $R = r_{gem}/r_{cis}$, r_{gem} is the

$$B_{gem} = k\frac{S_{11}}{r^3_{gem}} \tag{1a}$$

$$B_{cis} = k\frac{S_{22}}{r^3_{cis}} \tag{1b}$$

$$B_{trans} = k\frac{r^t_{trans} \cdot S \cdot r_{trans}}{r^3_{trans}} \tag{1c}$$

$$k = -\frac{h}{8\pi^2}\gamma^2 \tag{1d}$$

$$B_{cis} = (1 + R^2)^{5/2}B_{trans} - R^5 B_{gem} \tag{2}$$

distance between two hydrogen nuclei on the same carbon of the ethylene, r_{cis} is the distance between two hydrogen nuclei

Table I. Parameters for the Calculated Spectra

Parameter	60-MHz spectrum[a,b]	220-MHz spectrum[a,b]
J_{gem}, Hz	0.0	0.0
J_{cis}, Hz	9.0	9.0
J_{trans}, Hz	14.4	14.4
$J_{\text{Pt-H}}$, Hz	−60.6	−60.6
B_{gem}, Hz	−7.56 ± 0.36	−7.69 ± 0.40
B_{cis}, Hz	9.70 ± 0.14	9.96 ± 0.17
B_{trans}, Hz	2.60 ± 0.64	2.59 ± 0.76
$B_{\text{Pt-H}}$, Hz	−0.07 ± 0.56	0.00 ± 0.78
Δ,[c] Hz	10.24 ± 0.60	8.56 ± 0.75
RF[d]	0.038	0.079
GRF[e]	0.042	0.084

[a] Marginal standard deviations were estimated using the linearized treatment of a non-linear least squares problem as described in by W. C. Hamilton, "Statistics in Physical Science," Ronald Press Co., New York, N. Y., 1964. [b] The opposite choice of signs for the *B*'s gave a much poorer fit. [c] Δ is the full width at half-height. [d] The conventional *R* factor (see Hamilton reference in footnote *a*) given by $\Sigma(I_{\text{obsd}} - I_{\text{calcd}})/\Sigma I_{\text{obsd}}$. [e] The generalized *R* factor (see Hamilton reference in footnote *a*) given by $\Sigma(I_{\text{obsd}} - I_{\text{calcd}})^2/\Sigma(I_{\text{obsd}})^2$.

cis to each other on the ethylene, and r_{trans} is a vector connecting the trans protons and written in the molecular axis system. *S* is the order matrix. Equation 2 was arrived at[9] by combining (1a)–(1c) and eliminating ordering parameters and can be solved for *R* using the coupling constants from Table I. The *R* values obtained are reported in Table II, as well as ratios reported from solid-state studies. The effects of vibrations have been neglected as is usually the case.[9]

Discussion

C_{2v} symmetry was used to fit the spectrum and we shall now discuss how the various solution processes give rise to this effective symmetry. As Diehl has pointed out,[10] we must consider the relative time scales of internal motion, solute reorientation, and the nmr experiment. In this study, we have the complication of ligand exchange as well.

In order to discuss the dynamic nature of our species in solution, we must first get some feeling for how the net orientation is achieved. The solute molecule visits regions of locally isotropic solution and regions of locally anisotropic solution in the PBLG and CD_2Cl_2 solution.[11] The internuclear vectors of a solute species long-lived enough to tumble and diffuse through the solvent will assume a net average orientation with respect to the direction of the magnetic field. The time scale for chemical exchange and other dynamic processes must be compared to the time scale for ordering in the analysis of the nmr spectra.

The simplest case to consider is one in which ethylene rotation is fast compared to solute tumbling, but the ethylene rotates as a rigid unit. C_{2v} symmetry obtains and eq 2 can be used to calculate a value for *R*. If more than one spectrum had been found, similar considerations would apply for the analysis of each spectrum. More than one spectrum would be seen, for example, if two complexes with different ligands trans to the olefin were present and their interconversion were slow on the nmr time scale.

For the next case, we assume that L = pyridine is the only species with appreciable concentration. If ethylene rotation is slow compared to solute ordering and the only conformation of ethylene with significant probability is that with the C1–C2 axis perpendicular to the Cl–Cl axis, eq 2 can be used to give the value of *R*. It is likely that rotation about the platinum–nitrogen bond would be rapid on the nmr time scale, leading to C_{2v} symmetry for the ethylene moiety. However, C_{2v} still applies if the rotation is slow and the pyridine plane is either perpendicular to or contains the C1–C2 axis. Again, eq 2 will give *R*.

Table II. Reported *R* Ratios

Compd	Ratio	Source
$KPtCl_3(C_2H_4)\cdot H_2O$	0.742	Reference 6
$(C_5H_5)Rh(C_2F_4)(C_2H_4)$[a]	0.742	Reference 7
trans-$Pt(C_5H_5N)(C_2H_4)Cl_2$	0.755 ± 0.015[b]	This work at 220 MHz
trans-$Pt(C_5H_5N)(C_2H_4)Cl_2$	0.748 ± 0.015[b]	This work at 60 MHz
trans-$Pt(C_5H_5N)(C_2H_4)Cl_2$	0.733 ± 0.015[b]	This work at 60 MHz with $J_{\text{gem}} = 6.0$ Hz

[a] Reference 7 reports their results are essentially the same as those in ref 6. [b] Error is based on the standard deviations in the *B*'s, assuming them to be independently distributed and using an approximate form of eq 2. Vibrational effects and anisotropies in the indirect coupling have been neglected.

If a nonnegligible amount of a conformation with the C1–C2 axis parallel to the Cl–Cl axis (and with different ordering parameters) also exists along with the conformation described above, eq 2 applies only *if the geometry of the ethylene is the same in both conformations.* The interconversion between these two conformations will be fast on the nmr time scale and a mole fraction weighted average ordering matrix would be observed, and hence average coupling constants. Now, we consider ligand exchange. It should be slow compared to rotational diffusion of the molecules. The exchange of pyridine for I in CH_2Cl_2 solution has been found to be fast on the nmr time scale at room temperature.[3] The $PtCl_2(C_2H_4)$ moiety may bind to basic sites on the polypeptide chain in our solution as well. If the $PtCl_2(C_2H_4)$ exchange between the polypeptide sites and pyridine sites is slow on the nmr time scale, we would not expect to observe olefin resonance for the peptide complex because of the slow tumbling of the polypeptide chain and the resulting short transverse relaxation times. This exchange could be at a rate that would lead to lifetime broadening of the olefin resonances of I. To evaluate the possible contributions from this effect, one might consider comparing the line widths of the resonances of I and TMS in the same solution. In the case where both were present, the TMS line width was 40% smaller than that of the complex. No conclusions can safely be drawn from this observation, however, because the distributions of TMS and I between local solvent environments, hence local viscosities, etc., could differ significantly. If, on the other hand, the exchange is fast on the nmr time scale, effective C_{2v} symmetry obtains as well and eq 2 can be used to find *R*, provided the ethylene has a fixed internal geometry. If the latter conditions of exchange were operative and an appreciable amount of peptide complex were present, a larger average ordering might be expected.

The other species which we might expect to have some probability, though probably not much, is the dimer $[Pt(C_2H_4)Cl_2]_2$. This species may be involved in the pyridine-exchange process. Equation 2 does not apply for this molecule for slow olefin rotation (compared to molecular tumbling), and if it were present in appreciable amounts, eq 2 would not be valid and we would obtain an unreasonable value for *R* by employing it. If there is a very small fraction of ethylene molecules which have a geometry different from that of the predominant species, however, they would have negligible effects on our results. That eq 2 predicts an *R*

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Table III. Coupling Constants for Olefin Compounds[a]

Compd	J_{gem}	J_{cis}	J_{trans}	Ref
C_2H_4	2.3	11.5	19.1	*b*
C_3H_6	2.08	10.2	16.81	*b*
(acac)ClPt(C_3H_6)[c]	0.0	7.5	14.0	*b*
(acac)BrPt(C_3H_6)[c]	0.0	8.0	13.0	*b*
(acac)BrPt(C_2H_4)[c]	0.0	9.5	14.4	*b*
$C_5H_5Rh(C_2H_4)_2$	−0.06	8.8	12.2	*d*
$C_5H_5Rh(C_2H_4)SO_2$	−0.07	8.8	14.4	*d*
$C_5H_5Rh(C_2H_4)(C_2F_4)$		~8	~13	*d*
(py)Cl_2Pt(C_3H_6)[e]	6.0	7.6	14.2	*f*
$K^+[PtCl_3(C_3H_6)]^-$	−0.3	8.0	13.0	*g*

[a] *J* is given in hertz. [b] C. E. Holloway, *et al.*, *J. Chem. Soc. A*, 1653 (1970). [c] Acetylacetonato is abbreviated acac. [d] R. Cramer, *et al.*, *J. Amer. Chem. Soc.*, 91, 2519 (1969). [e] Pyridine is abbreviated py. [f] R. Lazzaroni and C. A. Veracini, *J. Organometal. Chem.*, 33, 131 (1971). [g] H. P. Fritz, *ibid.*, 6, 551 (1966).

value so similar to that observed in the solid suggests that the predominant ethylene geometry is the same in solution as in the solid. Thus, the dynamic processes which are known to be occurring in solution have no measurable effect on the geometry of the ethylene moiety that is detected by the method used in this study.

The *B*'s found in eq 2 come from a spin Hamiltonian which contains indirect coupling constants (*J*'s) as well. In general, the *J*'s are determined from studies in isotropic solvents on the molecule of interest or from studies in a related system. The latter method was necessary in this study, since the *J*'s do not influence the spectrum of I in isotropic solution. A list of coupling constants reported for other systems in given in Table III. Except for the results reported for $Pt(C_3H_6)(py)Cl_2$, J_{gem} equals 0.0. The spectra obtained in our study are very insensitive to the value of J_{gem} and do not answer the question whether $J_{gem} = 0.0$ or 6.0 Hz. In view of what most workers have found, we assumed $J_{gem} = 0.0$. Moreover, as can be seen from Table II, *R* is unchanged within experimental error if $J_{gem} = 6.0$ Hz or $J_{gem} = 0.0$. It should be noted that the 12 theoretical lines for the ethylene moiety appear as six doublets symmetric about the spectrum center and only two of the doublets are influenced by the indirect couplings. It is thus not surprising that our distance ratio is insensitive to the magnitude of the indirect couplings.

Conclusions

It has been shown that reasonably accurate geometrical information can be obtained from an organometallic complex dissolved in a liquid crystal solvent, even when the medium is very weakly orienting.

It has been shown that parameters related to geometry in solution can be obtained for an organometallic complex dissolved in a liquid crystal solvent and with reasonable precision. This is despite the fact that the medium was very weakly orienting. The analysis is complex, however, and is probably limited to rather simple systems. We find that the ratio of r_{gem}/r_{cis} in solution compares favorably with that found in solid-state studies and is consistent with a structure in which the C-H bonds are bent back away from the metal. It is quite interesting that the ratio we find and that of the solid compare so favorably in view of the dynamic processes which occur in solution. Thus, our results are consistent with the model of a predominant species with a fixed configuration of the ethylene moiety, even though it undergoes rapid rotation about the bond to platinum.

Acknowledgment. We are grateful to Drs. T. Needham and S. Sykora for helpful discussions. This work was supported by the National Science Foundation through Grant USNSF GP 31431X.

Appendix

The four-spin system has been studied several times.[9,12] Only slight changes are required from those reported in ref 12 where a different point group was used. Twelve transitions of significant intensity are predicted for the ethylene moiety. For those molecules where ^{195}Pt is found, these 12 lines are split into 24 with each of these down in intensity by a factor of 3.91—below that of the corresponding line in the 12 where platinum has zero spin.

A set of coupling constants predicts a set of transitions and their relative intensities. Lorenztian line shapes with full width at half-height Δ were then used for each calculated peak and, after multiplying by a scale factor, *S*, the calculated intensity at frequency ν_i, $I(\nu_i; S, \Delta, B, J)$, could be determined by summing the contribution to the intensity at that frequency from all peaks. This calculated intensity could then be compared to the experimental intensity, and an iterative nonlinear least-squares refinement[13] could be performed to find the best fit of *S*, Δ, and the coupling constants. In the analysis, the partial derivatives of intensities at frequencies ν_i with respect to the *j*th coupling constants, B_j, were needed, and eq 3 was used to compute these,

$$\frac{\partial I}{\partial B_j} = \sum_k \left(\frac{\partial I}{\partial w_k} \frac{\partial w_k}{\partial B_j} + \frac{\partial I}{\partial A_k} \frac{A_k}{\partial B_j} \right) \qquad (3)$$

where the sum is over the *k* calculated peaks, each with frequency w_k and with relative intensity A_k. The $\partial w_k/\partial B_j$ values were computed by the standard method,[14] and the $\partial A_k/\partial B_j$ were computed numerically. The basic program was a modified version of HERPIEN, written by Needham.[15]

It is appropriate to consider the assumption of lorenztian line shapes with identical widths. Previous studies[16] have found variable and increased line widths in the outer wings of the observed spectra. This effect has been ascribed to temperature in homogeneity in the sample.[16] In thermotropic liquid crystals, where high temperatures are required, this effect can be pronounced and can lead to nonlorenztian line shapes. The 60-MHz spectrum was run at room temperature, however, and this effect should be minimized. Instrumental effects and broadening because of the viscoscity are probably the major effects and would be expected to broaden all peaks of the same molecule equally. Sample spinning was used in the 220-MHz spectrum, but magnetic field inhomogeneity is a problem with this instrument, usually resulting in rather intense spinning side bands. No allowance for these side bands was made in our analysis, and our inability to correct for this effect may be the reason that the expected errors in the coupling constants are larger for the 220-MHz results than those at 60-MHz (Table I). The temperature was regulated at 28° when the 220-MHz instrument was used and temperature inhomogeneity may have added to the above problem.

Registry No. *trans*-$Pt(C_5H_5N)(C_2H_4)Cl_2$, 35861-72-4.

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