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Ethylene Ligand Structures of $Os(CO)_4(C_2H_4)$ and $Os_2(CO)_8(C_2H_4)$ Determined by ^1H NMR in Liquid Crystal Solvents

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The ethylene complexes $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)$ (**1**) and $Os(CO)_4(\eta\text{-}C_2H_4)$ (**2**) have been studied by ^1H NMR in liquid crystal (nematic phase) solvents. For **1** or **2**, three dipolar couplings were observed and assigned to intramolecular geminal, cis, and trans $^1H{-}^1H$ dipolar couplings. The ^1H NMR spectrum of $Os(CO)_4(^{13}CH_2\text{-}CH_2)$(**2**-^{13}C) has also been analyzed and two additional $^{13}C{-}^1H$ dipolar couplings have allowed determination of the absolute bond angles and relative bond lengths of the ethylene portion of **2**-^{13}C. The observed dipolar couplings for **2**-^{13}C have been corrected for harmonic vibrations. A comparison of the ethylene geometry of **2** with that of other transition metal ethylene complexes and with free ethylene shows that the $(C_2H_4)Os$ unit of **2** is best described as a metallacyclopropane. Deuterium substitution is used to demonstrate liquid crystal NMR as a stereochemical probe. The ^1H NMR spectrum of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}^{13}CH_2CH_2)$ (**1**-^{13}C) has also been analyzed in a nematic phase solvent. The dimetallacyclobutane ring of **1**-^{13}C is best described as two rapidly interconverting ring-puckered conformers of C_2-symmetry. The liquid crystal NMR derived structural parameters for **1**-^{13}C are compared with those previously determined by neutron diffraction. The solution and solid-state structures are very similar. The ethylene complexes **1** and **2** are proposed as structural and spectroscopic models for ethylene chemisorbed on metal surfaces.

Our need to distinguish deuterium-labeled isotopomers of $Os_2(CO)_8(C_2H_4)$ (**1**) (Figure 1) first led us to examine that diosmacyclobutane by ^1H NMR spectroscopy in liquid crystal solvents.[1a] More common spectroscopic signatures such as IR bands and vicinal ($^3J_{HH}$) NMR coupling constants were unsuited for distinguishing *cis*- and *trans*-**1**-d_2 (which we needed to determine the stereochemistry of ethylene elimination from **1**),[1] so we sought another assay of those deuterium-labeled diosmacyclobutanes. Distance- and isotope-sensitive intramolecular dipolar couplings observed by ^1H NMR in liquid crystal solvents were uniquely suited to that challenge.

Diosmacyclobutane **1** and the related osmacyclopropane $Os(CO)_4(\eta\text{-}C_2H_4)$ (**2**) are, together with Zeise's salt, $K[PtCl_3(\eta\text{-}C_2H_4)]$ (**3**), vibrational models for three ways that ethylene is bound to single-crystal metal surfaces (Figure 2).[2] Ethylene bridging two metal surface atoms in a "di-σ-bonded" fashion shows vibrational spectra classified as type I.[3] Ethylene that sits atop a single metal atom on a metal surface displays distinct vibrational spectra classified as type I′ or type II, corresponding to the metallacyclopropane and π-complex bonding extremes familiar from organotransition metal chemistry.[4]

cis-**1**-d_2 *trans*-**1**-d_2

Figure 1. *cis*- and *trans*-**1**-d_2.

Because the osmium complexes **1** and **2** were excellent vibrational models for type I and type I′ chemisorbed ethylene, we wanted a detailed knowledge of their ethylene ligand structures. While the basic dimetallacyclobutane structure of **1** had been clearly established by X-ray diffraction[5] (and with much greater precision by neutron diffraction),[6] the structure of **2** was much less defined: our X-ray diffraction study[7] of **2** had shown its C−C bond length to be relatively long (r_{CC} =

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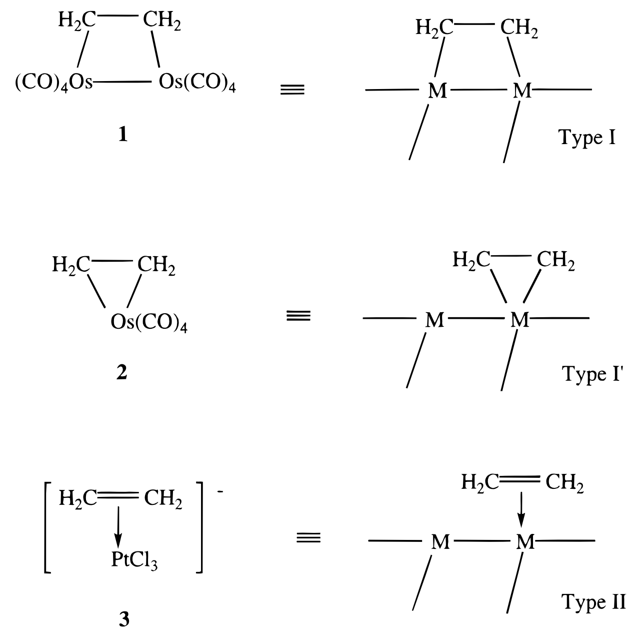

Figure 2. Ethylene complexes **1**, **2**, and **3** and their surface analogues.

1.49 (2) Å) but did not locate the hydrogen atoms of its coordinated ethylene. And while the $^1J_{CC}$ NMR coupling constant and ab initio calculations[7] as well as vibrational assignments[4] had supported the metallacyclopropane nature of **2**, we sought a *direct* measure of the bond angles and bond lengths around the ethylene carbons in **2** *in solution.* We therefore turned to NMR spectroscopy in liquid crystal solvents.[8]

The NMR spectra of molecules dissolved in liquid crystal solvents display direct dipolar couplings that depend on the internuclear distances between pairs of magnetically active nuclei. Intramolecular dipolar coupling may be observed for molecules dissolved in anisotropic solvents (liquid crystals) because the magnetic field oriented solvent molecules prevent the isotropic tumbling of *solute* molecules; the solute thus becomes partially oriented with respect to the applied magnetic field direction. Because rates of solute translation and rotation are similar to those in isotropic solvents, inter- (but not intra-) molecular solute dipolar couplings are averaged to 0 and narrow lines (like those in Figure 3) result. Because hydrogen atoms (often difficult to locate by X-ray or electron diffraction, especially in molecules containing third-row transition metals such as osmium) can be located relative to other atoms, liquid crystal NMR is a powerful physical method for probing the structure of organometallic complexes in solution.[9] Two previous studies of ethylene complexes using liquid crystal NMR have been reported.[9j,l]

Here we report our analyses of the ^{1}H NMR spectra of **1** and **2** and their ^{13}C-labeled isotopologues observed in liquid crystal (nematic phase) solvents. We have determined the absolute C_2H_4 bond angles, relative C_2H_4 bond distances, and molecular orientation parameters for **1**-^{13}C and **2**-^{13}C from observed $^1H-^1H$ and $^{13}C-^1H$ dipolar couplings. Our structural results for **2**-^{13}C have been corrected for harmonic vibrations and thus may be compared with the structures of ethylene complexes determined by other physical methods. Our structural results for

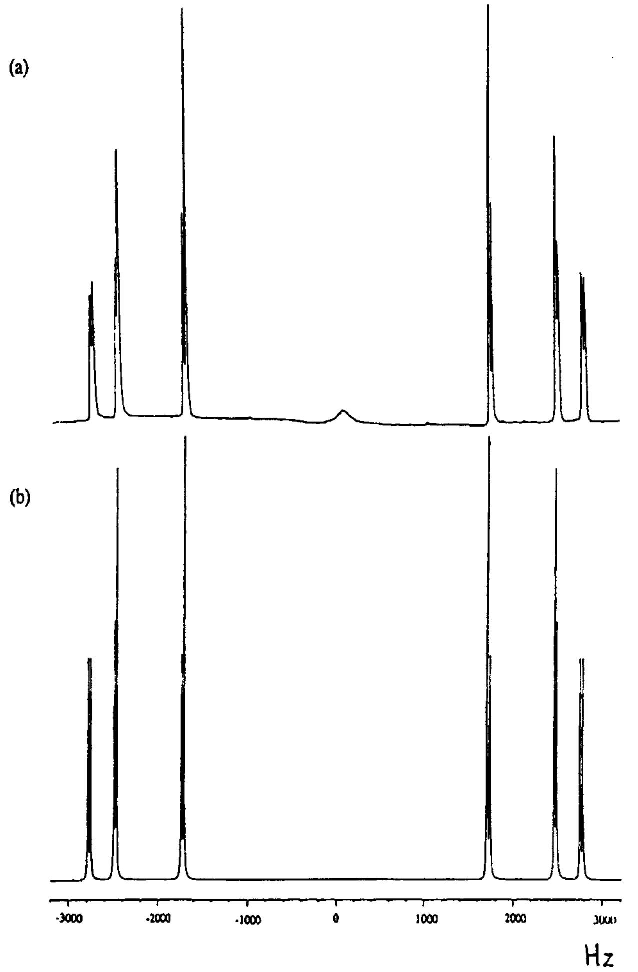

Figure 3. ^{1}H NMR spectrum of (η-C_2H_4)$Os(CO)_4$, **2**, oriented in nematic phase ZLI-1565 (E. Merck): (a) experimental and (b) calculated.

1-^{13}C, though not corrected for harmonic vibrations, may be judiciously compared with our earlier neutron diffraction structural results for **1**.[6]

Experimental and Calculational Details

$Os_2(CO)_8(\mu$-η^1,η^1-$C_2H_4)$ (**1**), $Os_2(CO)_8(\mu$-η^1,η^1-$^{13}CH_2CH_2)$ (**1**-^{13}C), $Os(CO)_4(\eta$-$C_2H_4)$ (**2**), and $Os(CO)_4(\eta$-$^{13}CH_2CH_2)$ (**2**-^{13}C) were prepared

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Table 1. Isotropic *J*-Coupling Constants (Hz)[a] for **1**-^{13}C and **2**-^{13}C

pair	**2**-^{13}C	**1**-^{13}C
$^2J_{\text{gem}}$	−9.8(2)	−9.9(2)
$^3J_{\text{cis}}$	+9.0(2)	+7.4(2)
$^3J_{\text{trans}}$	+11.1(2)	+8.4(2)
$^1J_{\text{CH}}$	+158.1(2)	+135.3(2)
$^2J_{\text{CH}}$	+0.3(2)	−2.5(2)
$^1J_{\text{CC}}$[b]	+39.0(2)	+34.0(2)

[a] The relative signs of all coupling constants have been determined by spectrum simulation; the absolute signs given are based on the assumption that $^1J_{\text{CH}}$ is positive. [b] J_{CC} was determined from doubly ^{13}C labeled **1** and **2**.

and isolated as previously reported.[10] Liquid crystal solvents ZLI-1565 and ZLI-1132 (both E. Merck) and E-38 (BDH Industries) were used as received. (ZLI-1565 is a eutectic mixture of two *p*-(4′-alkylcyclohexyl)benzonitrile components, two cyclohexylphenyl ether components, and two cyclohexylbiphenyl components and thus contains no functional groups likely to react with **1** or **2**; its nematic range is from −40 to +85 °C.) Solutions of **2** and **2**-^{13}C in liquid crystal solvents were prepared by vacuum transfer of the ethylene complex into 5-mm NMR tubes containing enough degassed liquid crystal solvent (0.5 mL) to give approximately 0.085 mM solutions. The sample tubes were then sealed under vacuum. Solutions of **1** and of **1**-^{13}C were prepared by transferring solutions (approximately 10.8 mg, 0.017 mmol, of the compound dissolved in ca. 1 mL of CH_2Cl_2) by syringe into 5-mm NMR tubes attached to a vacuum line. After solvent (CH_2Cl_2) removal under high vacuum, liquid crystal solvent (ca. 0.5 mL) was added to the NMR tube under a flow of dry N_2 to give about 0.04 mM solutions of **1** and **1**-^{13}C. Samples were then freeze−pump−thaw degassed and flame-sealed under vacuum.

All ^{1}H NMR spectra were measured on an IBM WP 200 SY (200 MHz) spectrometer. ^{1}H NMR spectra were measured at 300 K using the Bruker temperature control unit supplied with the spectrometer. All ^{1}H NMR spectra were recorded unlocked with a spectral width (SW) of 5 kHz. Acquisition time and data block size were adjusted to ensure adequate digital resolution (<0.1 Hz). Subtraction of background liquid crystal signal was found to enhance the appearance of spectra of relatively dilute samples of **1** and **1**-^{13}C. All ^{1}H NMR spectra were simulated with the iterative program PANIC[11] supplied with the spectrometer software. The *J*-coupling constants used in spectrum simulations were fixed at their isotropic values previously reported[7] for **2**-^{13}C and reported here for **1**-^{13}C (Table 1).[12]

Analysis of Structural Parameters from Dipolar Couplings. When two magnetically active nuclei exhibit dipolar coupling in a liquid crystal solvent, the magnitude of that coupling depends on the two gyromagnetic ratios (γ_i and γ_j), on the angle, Θ_{ij}, subtended between the internuclear (*ij*) vector and the applied magnetic field direction, and on the inverse-cubed internuclear separation (r_{ij}^{-3}), according to eq 1.[8a] The angular brackets in eq 1 indicate averaging over molecular vibrational and reorientational motions.

$$D_{ij}\,(\text{Hz}) = -\frac{\mu_0\hbar}{8\pi^2}\gamma_i\gamma_j\left(\frac{1}{2}\right)\left\langle\frac{3\cos^2\Theta_{ij}-1}{r_{ij}^{\;3}}\right\rangle \qquad (1)$$

The average orientational dependence of internuclear vector(s) $\langle 3\cos^2\Theta_{ij} - 1\rangle$ is conventionally expressed in a molecule-fixed *x, y, z* coordinate frame by a second-rank Cartesian tensor, $\mathbf{S}_{\alpha\beta}$ ($\alpha, \beta = x, y, z$), introduced by Saupe.[13] The Saupe tensor is diagonal ($\mathbf{S}_{\alpha\beta} = \mathbf{S}_{\beta\alpha}$, $\alpha \neq \beta$) and traceless ($\mathbf{S}_{xx} + \mathbf{S}_{yy} + \mathbf{S}_{zz} = 0$), and thus the 3 × 3 array has at most five independent elements.

For "rigid" molecules that exist in only one configuration, and for which correlation between intramolecular motions and orientation can be neglected, dipolar coupling may be expressed as shown in eq 2.[8] For brevity, the constant $k_{ij} = (\mu_0\hbar/8\pi^2)\gamma_i\gamma_j$ has been introduced.[14]

$$D_{ij}\,(\text{Hz}) = -k_{ij}\sum_{\alpha\beta}\mathbf{S}_{\alpha\beta}\langle\Delta\alpha_{ij}\,\Delta\beta_{ij}/r_{ij}^{\;5}\rangle \qquad (2)$$

The orientational tensor elements, $\mathbf{S}_{\alpha\beta}$, in eq 2 define the average orientational order of a suitably chosen *molecular* coordinate system relative to the magnetic field direction; the elements in the angular brackets, $\Delta\alpha_{ij}$ and $\Delta\beta_{ij}$, are Cartesian components of internuclear (*ij*) vectors relative to that molecular coordinate system (the angular brackets indicate averaging over molecular vibrational motions). A more common version of eq 2 makes use of trigonometric identities (eq 3).[15]

$$\begin{aligned} D_{ij}\,(\text{Hz}) = -(k_{ij}/2)\langle 1/r_{ij}^{\;3}\rangle[\mathbf{S}_{zz}(3\cos^2\theta_{ijz} - 1) + {} \\ (\mathbf{S}_{xx} - \mathbf{S}_{yy})(\cos^2\theta_{ijx} - \cos^2\theta_{ijy}) + 4\mathbf{S}_{xy}\cos\theta_{ijx}\cos\theta_{ijy} + {} \\ 4\mathbf{S}_{xz}\cos\theta_{ijx}\cos\theta_{ijz} + 4\mathbf{S}_{yz}\cos\theta_{ijy}\cos\theta_{ijz}] \end{aligned} \qquad (3)$$

In eq 3, θ_{ijx}, θ_{ijy}, and θ_{ijz} are the angles subtended between internuclear (*ij*) vectors and the principal axes of the *molecular* coordinate system.

The $\mathbf{S}_{\alpha\beta}$ tensor elements (often called molecular orientation parameters) are also experimental unknowns, and for this reason, fewer structural details may be extracted from liquid crystal NMR experiments than one might hope. Indeed, the sum of unknown structural and unknown orientational parameters *must* be equal to or less than the number of observable experimental quantities (unique dipolar couplings) if one wishes to confirm a structure by experiment.

Fortunately, molecular symmetry often reduces the number of required orientation parameters and leads to considerable simplification of eq 3. For a molecule with C_2 symmetry, two molecular orientational parameters ($\mathbf{S}_{xz}$ and $\mathbf{S}_{yz}$) become 0-valued; for a molecule with C_{2v} symmetry, a third molecular orientational parameter ($\mathbf{S}_{xy}$) also becomes 0-valued. A table of molecular point group symmetries and the number of required orientational parameters may be found in refs 8b and 8c.

Equation 3 is the basis for our analysis of the liquid crystal NMR spectra of **1** and **2**. A program was written in Microsoft Basic to compute Cartesian coordinates from variable bond lengths and angles and was used to fit structural and orientational parameters to observed dipolar couplings. Structural fitting for the binuclear complex **1**-^{13}C was performed with the program SHAPE[16] using the minimization routine NL2SNO.[17] A normal coordinate analysis of **2** and its d_4- and ^{13}C-labeled isotopologues provided the mass-weighted Cartesian displacement coordinates used to correct the observed dipolar couplings of **2**-^{13}C for harmonic vibrations. The normal coordinate analysis of **2** and its isotopologues will be published elsewhere.[18]

Results

The Rectangular Proton Geometry of 2. The experimental and calculated ^{1}H NMR spectra of **2** partially oriented in Merck ZLI-1565 (TN) are shown together in Figure 3. The ^{1}H NMR signal for the four protons of **2** is a singlet in normal (isotropic) solvents but is split into a 12-line pattern in liquid crystal solvents.

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(10) For the preparation of **1** and **1**-^{13}C see ref 6; for **2** and **2**-^{13}C see ref 7; for **1**-d_2 and **2**-d_2 see ref 1b.

(11) A computer program known as Parameter Adjustment in NMR by Iteration Calculation (PANIC) was used for simulation of spectra and refinement of parameters on an Aspect 2000 computer.

(12) The *J*-coupling constants for **1** were determined from ^{1}H NMR spectra of **1**-^{13}C and **1**-$^{13}C_2$ in CD_2Cl_2 using the method previously reported for **2**-^{13}C and **2**-$^{13}C_2$ (ref 7).

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(14) For D_{HH}, $k_{ij} = 120.101\,06$ kHz Å^3; for D_{CH}, $k_{ij} = 30.204\,09$ kHz Å^3, ref 8a, p 59.

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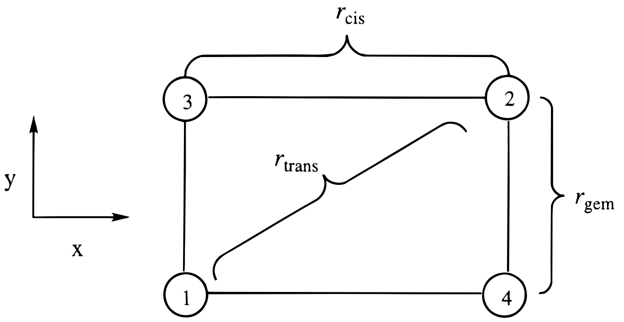

Figure 4. The rectangular arrangement of the four protons in **1** and **2** and the three unique geometric distances.

Table 2. Dipolar Couplings for $(C_2H_4)Os(CO)_4$ in Different Nematic Phase Solvents

	dipolar couplings (Hz)		
pair	Merck ZLI-1565	Merck ZLI-1132	BDH E38
$D_{\mathrm{gem}} = D_{(H_1H_3)} = D_{(H_2H_4)}$	−1497.6(5)	−1265.8(5)	−1714.9(5)
$D_{\mathrm{cis}} = D_{(H_2H_3)} = D_{(H_1H_4)}$	+349.1(5)	+248.5(5)	+387.9(5)
$D_{\mathrm{trans}} = D_{(H_3H_4)} = D_{(H_1H_2)}$	+10.3(5)	−7.8(5)	+7.6(5)
$r_{\mathrm{cis}}/r_{\mathrm{gem}} = X$	1.363(2)	1.361(3)	1.362(3)

Three unique dipolar couplings may be extracted from trial and error simulation of the experimental spectrum shown in Figure 3; these couplings are related to the three unique interproton distances, r_{gem}, r_{cis}, and r_{trans} depicted in Figure 4. However, because two orientational parameters ($\mathbf{S}_{zz}$ and $\mathbf{S}_{xx} - \mathbf{S}_{yy}$) are required to define the orientation of the rectangular proton geometry of **2**, only a single geometric ratio may be determined from the three observed dipolar couplings. Equation 4, which results when the three expressions for D_{gem}, D_{cis}, and

$$D_{\mathrm{trans}} = (X^2 + 1)^{-5/2}\,[D_{\mathrm{cis}}X^5 + D_{\mathrm{gem}}] \qquad (4)$$

D_{trans} are combined,[8] permits only one solution with a meaningful value of X, the unitless $r_{\mathrm{HH_{cis}}}/r_{\mathrm{HH_{gem}}}$ distance ratio.[1a]

Dipolar couplings for **2** were measured in three different nematic phase solvents, and the results have been placed in Table 2 for comparison. Some variation in the degree of average solute orientation (and thus the magnitudes of dipolar couplings) was evident. However, the results showed that all three liquid crystal solvents oriented molecules of **2** in a similar way; the invariance of the calculated distance ratio X showed that solvent effects on solute structure were minimal. The value of X (1.363) determined for **2** in three nematic phase solvents is similar to the X value measured for thiirane.

Analysis of *cis*- and *trans*-2-d_2. By correcting the three dipolar couplings for **2** for the smaller gyromagnetic ratio of deuterium, ^{1}H NMR spectra were calculated for *cis*- and *trans*-**2**-d_2 (Figure 5b,c). The ^{1}H NMR spectrum of *trans*-**2**-d_2 in ZLI-1565 agrees well with the predicted one (Figure 5a). This analysis illustrates the ability of liquid crystal NMR to distinguish and assay the stereochemical purity of deuterium-labeled isotopomers of **2**, as was previously described for *cis*- and *trans*-**1**-d_2.[1a]

Ethylene Structure of 2-^{13}C. The acute angles inherent in three-membered rings preclude idealized sp^3 hybridization, that is, with tetrahedral HCH and HCC bond angles.[19] The best measure of ethylene carbon "rehybridization" for metal olefin complexes is the nonplanarity of the bound olefin, as defined by the α parameter proposed by Stalick and Ibers.[20] In Figure 6, α is the angle between the normals of the HCH "methylene" planes. The angle α is related to the "bending back" of the ethylene hydrogens: α/2 corresponds to the angle between the methylene (CH_2) plane and the CC bond.

Table 3. Observed and Vibrationally Corrected Dipolar Couplings and Structural and Orientational Parameters for **2**-^{13}C in Nematic Phase ZLI-1565 (E. Merck)

	D-couplings (Hz)	
	uncorrected	corrected
$D_{\mathrm{gem}} = D_{(H_1H_3)} = D_{(H_2H_4)}$	−1516.7(5)	−1567.2
$D_{\mathrm{cis}} = D_{(H_2H_3)} = D_{(H_1H_4)}$	+355.1(5)	+352.0
$D_{\mathrm{trans}} = D_{(H_3H_4)} = D_{(H_1H_2)}$	+11.4(5)	+14.3
$D_{\mathrm{CH}} = D_{(C_{10}H_1)} = D_{(C_{10}H_3)}$	−927.9(5)	−987.9
$D_{\mathrm{CH'}} = D_{(C_{10}H_2)} = D_{(C_{10}H_4)}$	+68.6(5)	+69.7

Structural and Orientational Parameters

	uncorrected	corrected
r_{CC} (Å)	1.488(24)^a	1.488^a
r_{CH} (Å)	1.113(3)	1.083(2)
θ (∠HCH) (deg)	112.69(5)	113.48(5)
∠α (deg)	65.18(4)	62.54(4)
$\mathbf{S}_{zz}$	−0.032 675(3)	−0.031 622(3)
$\mathbf{S}_{xx} - \mathbf{S}_{yy}$	−0.128 190(3)	−0.123 657(3)

^{a} X-ray-determined value.

The ethylene ligand geometry of **2** may be described as a trapezoidal solid (Figure 7) with the four hydrogen atoms defining the base and the two carbon atoms defining the apical edge. Just three structural parameters define the relative *shape* of that geometry: the $r_{\mathrm{CH}}/r_{\mathrm{CC}}$ distance ratio, the HCH bond angle θ, and the aforementioned α parameter. The C_{2v} molecular symmetry of **2** requires two orientational parameters ($\mathbf{S}_{zz}$ and $\mathbf{S}_{xx} - \mathbf{S}_{yy}$) to describe its average orientation in a magnetic field.[8] Thus *five* unknowns must now be determined from the observed dipolar couplings.

We obtained two additional dipolar couplings for **2** from ^{13}C−^{1}H dipolar couplings. Figure 8 shows the ^{1}H NMR spectrum of **2**-^{13}C measured in the liquid crystal solvent ZLI-1565 along with the corresponding calculated spectrum. The five dipolar couplings derived by trial and error simulation of the spectrum of **2**-^{13}C have been placed in Table 3. The spectrum of **2**-^{13}C now reflects five independent dipolar couplings, namely, the three HH dipolar couplings (D_{cis}, D_{gem}, and D_{trans}), plus two distinct D_{CH} couplings. The equations containing five unknown structural and orientational parameters are thus exactly determined by the five observed dipolar couplings.

Structural parameters (the CH bond length and the two unique bond angles) of **2**-^{13}C were varied independently, and values of $\mathbf{S}_{zz}$ and $\mathbf{S}_{xx} - \mathbf{S}_{yy}$ were computed. The mean square deviation between experimental and calculated dipolar couplings was minimized to obtain the best-fit structure. The structural and orientation parameters for the best-fit structure of **2**-^{13}C have been placed in Table 3. Because liquid crystal NMR cannot determine absolute bond lengths,[8] we have used the X-ray-determined CC bond length[7] to scale the molecular shape of **2**-^{13}C (Figure 7). The best-fit structure of **2**-^{13}C has the following values: $r_{\mathrm{CH}} = 1.113$ Å; ∠HCH, $\theta = 112.69°$; $\angle\alpha = 65.2°$. The errors accompanying the molecular parameters for **2**-^{13}C shown in Table 3 were estimated by comparing the bond lengths and angles for structures that had the same (within two esd's of these order parameters) values of $\mathbf{S}_{zz}$ and $\mathbf{S}_{xx} - \mathbf{S}_{yy}$.

Vibrationally Corrected Structure of 2-^{13}C. The structural and orientational parameters for **2**-^{13}C shown in Table 3 were

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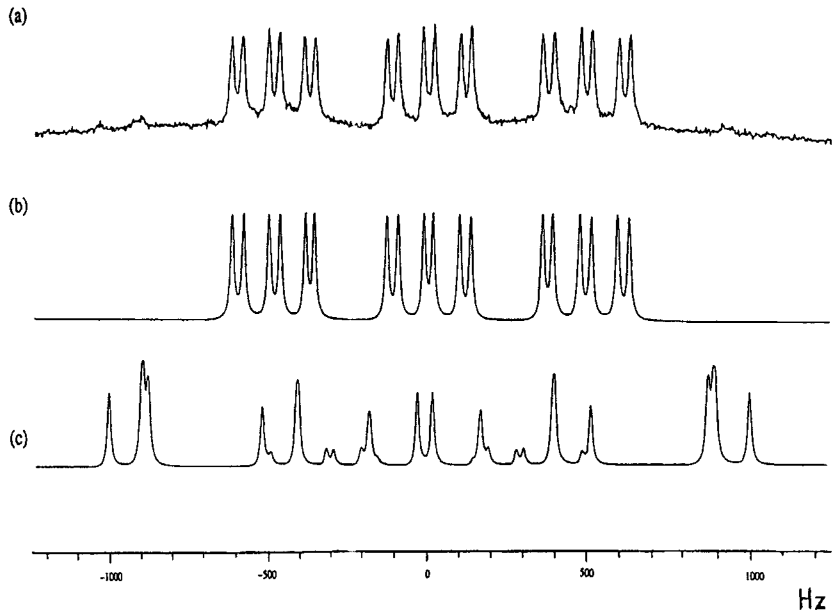

Figure 5. ^1H NMR spectrum of *trans*-(CHDCHD)Os(CO)$_4$, *trans*-**2**-d_2 oriented in nematic phase ZLI-1565 (E. Merck): (a) experimental, (b) calculated for *trans*-**2**-d_2 and (c) calculated for *cis*-**2**-d_2.

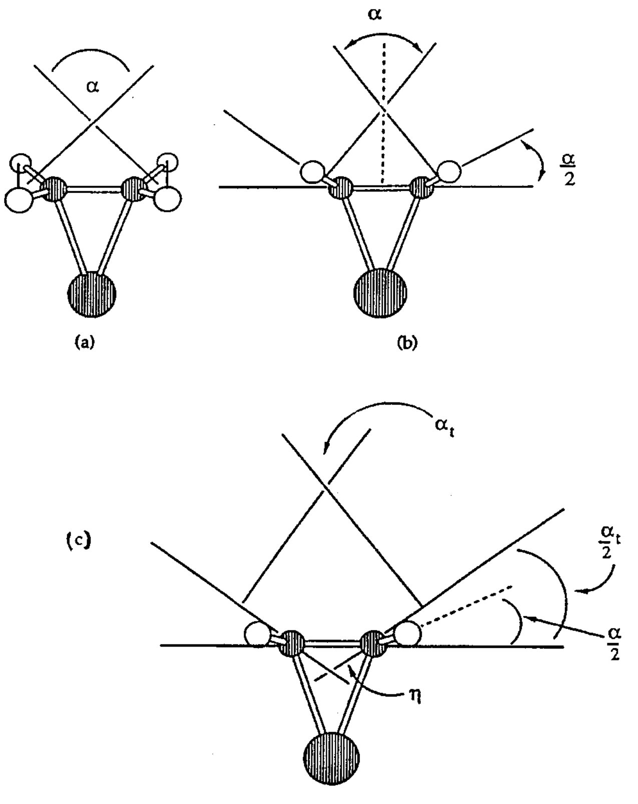

Figure 6. Two views of Ibers's α angle (a and b). The definition of the angles α_t and $\alpha_t/2$ (c). The angle η is the CCM bisector.

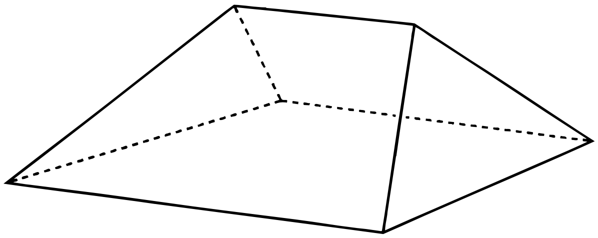

Figure 7. Molecular shape of the ethylene ligand in **2**.

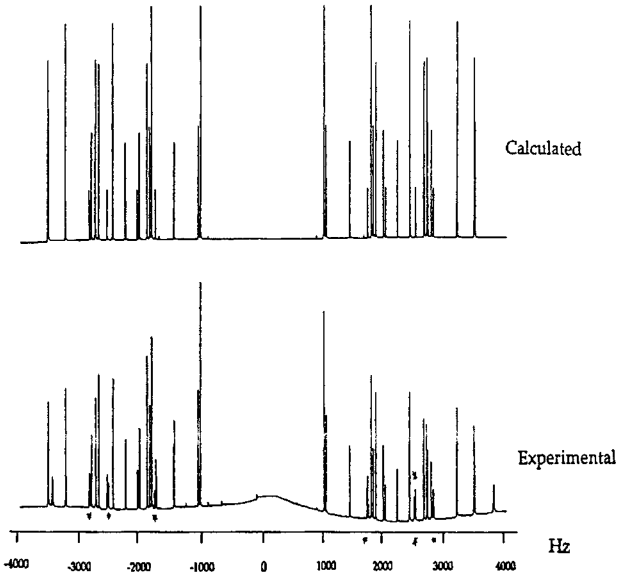

Figure 8. ^1H NMR spectrum of ($^{13}CH_2CH_2$)Os(CO)$_4$, **2**-^{13}C oriented in nematic phase ZLI-1565 (E. Merck): (a) experimental and (b) calculated. Peaks marked with an asterisk are from approximately 10% unlabeled material.

derived from dipolar couplings determined from the NMR spectrum. These couplings are averages over molecular vibrations. Therefore, the observed NMR dipolar couplings do not reflect the equilibrium structure, but rather a vibrationally averaged one. A meaningful comparison of structural data derived from different physical methods should take into account the effects of molecular vibrations. Since the anharmonic vibrations affect the bond distances determined from experimental measurements in essentially the same way, it is common to use a molecular structure corrected for harmonic vibrations only, which is called an r_α structure.[21] (Molecular structures determined by liquid crystal NMR are usually *not* corrected for anisotropic and higher-order vibrational correction terms.) In

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(21) Sykora, S.; Vogt, J.; Boesiger, H.; Diehl, P. *J. Magn. Reson.* **1979**, *36*, 53.

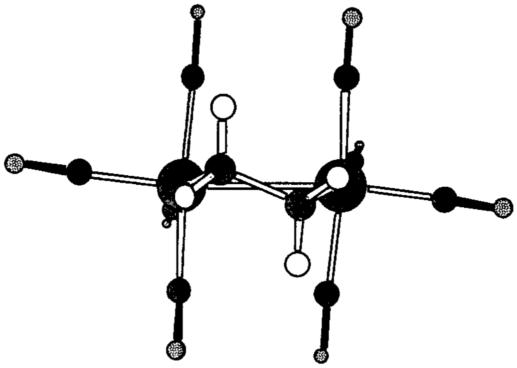

Figure 9. Neutron diffraction determined structure of **1**.

general, harmonic vibrational corrections for dipolar couplings between nonbonded nuclei are small, but such corrections for directly bonded nuclei are often greater than the experimental error.[22]

We have used the established procedure to calculate contributions to the observed dipolar couplings from harmonic vibrations.[21] The contributions to the observed dipolar couplings from harmonic vibrations were then eliminated, and vibrationally corrected dipolar couplings (D_{ij}^{α}) then yielded the r_α structure and the vibrationally corrected orientational parameters; these have been placed together with the uncorrected parameters for comparison in Table 3. Vibrational corrections significantly decrease both the CH bond length (ca. 3%) and the angle α (ca. 4%), whereas the corrected HCH bond angle, θ, is only slightly greater (0.7%).

Ethylene Structure of the Diosmacyclobutane 1-^{13}C. Our X-ray diffraction study of **1** implied[5] (and our more precise neutron diffraction study showed[6]) that the puckered diosmacyclobutane ring of **1** had "axial" and "equatorial" hydrogen atoms in the solid state that were not equivalent (Figure 9). However, the ^{1}H NMR spectrum of unlabeled **1** in solution was a single, sharp line down to −90 °C, establishing that ring inversion was rapid on the NMR time scale and that all protons were equivalent in chemical shift[1a,5,23] (indeed, ab initio calculations have predicted the ring inversion barrier for **1** to be around 1 kcal/mol[24]).

The ^{1}H NMR spectrum of **1** in anisotropic solution was a 12-line pattern (like that of **2**[1a]), and three dipolar couplings, D_{gem}, D_{cis}, and D_{trans}, were obtained by trial and error spectrum simulation. Analysis of the three unique ^{1}H−^{1}H dipolar couplings and their predicted changes on deuteration uniquely distinguished *cis*- and *trans*-**1**-*d*$_2$. But, just as in the case of **2**,[1a] three ^{1}H−^{1}H dipolar couplings were not sufficient to define the ethylene structure of **1** and the additional ^{13}C−^{1}H dipolar couplings were required.

The experimental and calculated ^{1}H NMR spectra of **1**-^{13}C oriented in the liquid crystal solvent ZL1-1565 (TN) are compared in Figure 10. As for the case of **2**-^{13}C, five unique dipolar couplings were obtained by trial and error simulation using PANIC and they have been placed in Table 4. Because only five dipolar couplings are observed for **1**-^{13}C, the dipolar couplings must represent averaged values (a "frozen" C_2 symmetric structure like that in Figure 9 would predict more than five dipolar couplings).

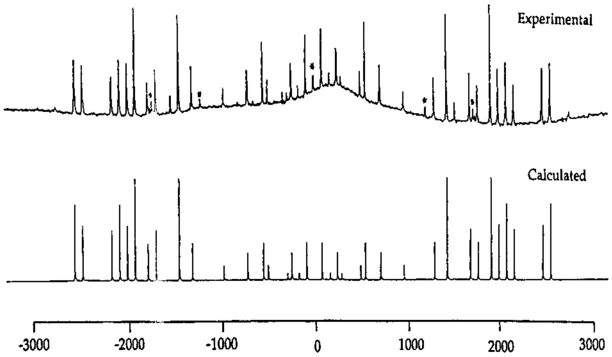

Figure 10. ^{1}H NMR spectrum of (^{13}CH$_2$CH$_2$)Os$_2$(CO)$_8$, **1**-^{13}C oriented in nematic phase ZLI-1565 (TN): (a) experimental and (b) calculated. Peaks marked with an asterisk arise from approximately 10% unlabeled material.

Table 4. Observed Dipolar Couplings[a] for **1**-^{13}C Oriented in Merck ZLI-1565 (TN)

pair	D_{ij} (exptl) (Hz)
$D_{\mathrm{gem}} = D_{(\mathrm{H_1H_3})} = D_{(\mathrm{H_2H_4})}$	+429.0(4)
$D_{\mathrm{cis}} = D_{(\mathrm{H_2H_3})} = D_{(\mathrm{H_1H_4})}$	−964.2(4)
$D_{\mathrm{trans}} = D_{(\mathrm{H_3H_4})} = D_{(\mathrm{H_1H_2})}$	−540.4(4)
$D_{\mathrm{CH}} = D_{(\mathrm{C_{10}H_1})} = D_{(\mathrm{C_{10}H_3})}$	+697.2(4)
$D_{\mathrm{CH'}} = D_{(\mathrm{C_{10}H_2})} = D_{(\mathrm{C_{10}H_4})}$	−268.3(4)

[a] The relative signs of all coupling constants have been determined by spectrum simulation; the absolute signs given are based on the assumption that $^1J_{\mathrm{CH}}$ is positive.

Rapid intramolecular motion (like ring puckering for **1**) complicates the analysis of liquid crystal NMR data, and the problem has received considerable attention in the literature.[25] For conformationally "rigid" molecules, a single **S** tensor is taken to describe the average orientation of solute molecules. However, if a conformational change (rapid on the NMR time scale) interconverts one or more conformers, an averaged dipolar coupling constant will be observed (eq 5); P$_\mathrm{n}$ is the probability of finding conformer n, and $D_{ij}^{(\mathrm{n})}$ is given by eq 3 for each conformer.

$$D_{ij} = \sum_{\mathrm{n}} \mathrm{P}_{\mathrm{n}} D_{ij}^{(\mathrm{n})} \qquad (5)$$

Because the molecular orientation may differ for each conformer, these averaged dipolar couplings may involve not only a different structure but also a different averaged **S** tensor for each conformer. As a consequence of these complications, structural solutions will usually be underdetermined and useful geometric information can only be obtained by making structural assumptions.

We began our structural analysis of **1**-^{13}C where we left off our investigation of complex **2**-^{13}C. Because the available data (five observables) would allow an exact determination of a C_{2v} symmetry structure for **2**-^{13}C, we first tested the same structure (a flattened ring) for **1**-^{13}C. We then systematically began to "relax" the C_{2v} symmetry structure toward that in the solid state (Figure 9), borrowing more and more structural parameters from the neutron structure. Our end result shows that the solution structure of **1**-^{13}C indeed closely resembles that found in the solid state.

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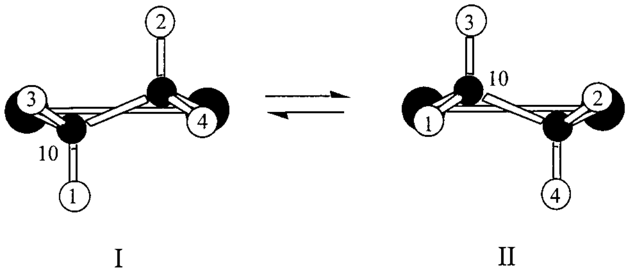

Figure 11. Equivalent conformers I and II of **1**.

Table 5. Dipolar Coupling Fit for **1** with C_{2v} structure

D_{ij}	calcd (Hz)	exptl (Hz)
D_{gem}	+429.0	+429.0(4)
D_{cis}	−964.2	−964.2(4)
D_{trans}	−540.4	−540.4(4)
D_{CH}	+697.2	+697.2(4)
$D_{\text{CH}'}$	−268.3	−268.3(4)

parameter	value
θ (deg)	83.9
α (deg)	105.6
r_{CC} (Å)	1.523
r_{CH} (Å)	0.869
$\mathbf{S}_{zz}$	−0.09286
$\mathbf{S}_{xx} - \mathbf{S}_{yy}$	0.10403
X	1.9868

***C*$_{2v}$ Symmetry Model of 1-^{13}C.** As was the case for **2**-^{13}C above, a C_{2v} model for the ethylene structure of **1**-^{13}C requires two orientation parameters and three structural parameters. The CC bond length was fixed at the neutron diffraction determined value of 1.523 Å,[6] while the HCH angle θ, the r_{CH} bond length, and the angle α were varied independently. An exact mathematical fit was obtained, and the resulting structural and orientational parameters are shown in Table 5 along with the calculated and experimental dipolar coupling constants. As Table 5 shows, the C_{2v} fit required an unreasonable HCH angle (83.9°) with an equally unreasonable $r_{\text{cis}}/r_{\text{gem}}$ distance ratio (X value) of 1.99. We concluded that the time averaged structure of **1**-^{13}C is not C_{2v} symmetric.

Idealized *C*$_2$-Symmetry Models of 1-^{13}C. We next considered **1**-^{13}C as two rapidly interconverting conformers of C_2 symmetry (like conformers I and II in Figure 11). Each of these conformers more closely resembles the ring-puckered diosmacyclobutane structure found in our neutron diffraction study of **1**.[6] One such "idealized" C_2 symmetry conformer may be generated from the previous C_{2v} symmetry model by introducing a dihedral twist angle, τ. The CH$_2$ units on each carbon are rotated about the CC bond by $\tau/2$ in equal but opposite directions from their initial eclipsed position (Figure 11). The other conformer may be obtained by a simple reflection through the xz or yz plane; the two conformers I and II are enantiomers.

Because both conformers I and II of **1** are equally probable in solution, intramolecular dipolar couplings are averaged equally over both conformers (eq 5). For example, the trans HH-dipolar coupling is averaged over equally probable axial−axial and equatorial−equatorial HH vectors in conformers I and II. The r_{CH} vector for D_{CH} also changes orientation with respect to the molecular coordinate system in accord with equally probable "axial" and "equatorial" CH bonds; the nonbonded CH vector related to $D_{\text{CH}'}$ is likewise averaged over conformers I and II.

Molecular C_2 symmetry now requires a *third* orientation parameter, $\mathbf{S}_{xy}$, in addition to $\mathbf{S}_{zz}$ and $\mathbf{S}_{xx} - \mathbf{S}_{yy}$.[8] The tensor elements $\mathbf{S}_{zz}$ and $\mathbf{S}_{xx} - \mathbf{S}_{yy}$ are identical for conformers I and II, while the off-diagonal orientational parameter, $\mathbf{S}_{xy}$, changes sign (as does the term $\cos \theta_{ijx} \cos \theta_{ijy}$) for conformers I and II in eq 3. Because one additional orientational parameter *and* one additional angle, τ, are now required, the problem is underdetermined by two unknowns and structural assumptions *must* be made to obtain a meaningful solution; the question is which *two* independent structural parameters are least likely to change between the solid state and the liquid phase.

Table 6. Dipolar Coupling Fits for Idealized C_2 Structures of **1**

$r_{\text{CC}}{}^{a}$ (Å)	1.523	1.523
$r_{\text{CH}}{}^{a}$ (Å)	1.097	1.113
$\angle\theta^{a}$ (deg)	107.6	107.6
$\angle\alpha$ (deg)	128.72	116.62
$\angle\tau$ (deg)	51.28	42.99
$\mathbf{S}_{zz}$	−0.12230	−0.13243
$\mathbf{S}_{xx}$	0.11852	0.13581
$\mathbf{S}_{xy}$	0.02259	−0.02063

[a] Not varied in the fit. x direction is along CC bond; z direction is along C_2 axis.

We began by fixing r_{CH} and the HCH angle θ to their average neutron diffraction determined values. We further assumed equal CCH angles at each carbon. With these assumptions, the structure for **1**-^{13}C may be defined with just two independent geometric parameters: a new angle τ (the dihedral angle between CH bonds on opposite carbons) and α (the same angle defined as before for a C_{2v} symmetry structure before imposing the twist τ). The results for C_2 treatment are shown in column 1 of Table 6. The structural and orientational parameters derived from the best-fit parameters using the neutron value of $r_{\text{CH}} = 1.097$ Å gave an rms error of 0.24 Hz. However, the values of α, and also τ, are unreasonable and also do not reflect those found in the neutron structure (the value of α in the neutron structure is approximately 101°, and the value of τ is approximately 33°).

Recognizing that we did not have corrections for harmonic vibrations (and noting that the uncorrected r_{CH} for **2**-^{13}C was 1.113 Å), we next set $r_{\text{CH}} = 1.113$ Å. As before, we fixed the CC bond length $r_{\text{CC}} = 1.523$ Å, and $\angle$HCH, θ, = 107.6°. For these fixed parameters we obtained the results in column 2 of Table 6. An exact fit to the experimental dipolar couplings is now obtained. Such an exact fit is not possible with r_{CH} values <1.104 Å. While the values of α and τ are closer than in the previous fit to the neutron values, they are still unacceptable.

We realized that better fits to the observed dipolar couplings could be obtained by letting the idealized C_2 symmetry model relax to a more realistic solid-state-like structure. This involved allowing the two CCH angles on each carbon to differ (while maintaining overall C_2 symmetry). Our neutron diffraction study had shown that the average "equatorial" CCH and "axial" CCH angles on each carbon were different: 113.00(27)° and 110.88(25)°, respectively.[6] The average of the H(1)−C(10)−C(9)−H(4) and H(2)−C(9)−C(10)−H(3) dihedral angles was 33.1°.

Thus for our final approach to fitting the observed dipolar couplings for **1**-^{13}C to a solution structure, we chose a new set of structural fitting parameters: instead of varying α and τ, we used two different τ values, one for each type of hydrogen, axial or equatorial (the previous τ is the sum of those two values). We varied the axial and equatorial CCH values independently; we fixed r_{CC} and $r_{\text{CH}_1} - r_{\text{CH}_2}$ to the neutron diffraction determined values; and of course we varied the three independent order parameters. Obviously, we now had too many independent parameters.

Table 7. Solution-State Parameters for **1** Fitted Using Neutron Diffraction Determined Parameters as "Predicate Observations"

parameters		comments
r_{CC} (Å)	1.523	neutron
r_{CH_1} (Å)	1.104550	neutron = 1.1025
r_{CH_3} (Å)	1.093550	set = $r_{CH_1} - 0.011$
$\angle CCH_1$ (deg)	112.86	neutron av =113.0
$\angle CCH_3$ (deg)	111.8	neutron av =110.875
$\angle HCH$ (deg)	107.78	neutron = 107.65
τ_1 (deg)	72.85	
τ_2 (deg)	−48.86	$\tau = 23.99°$; neutron = 33.1°
$\mathbf{S}_{xx}$	0.156 83	
$\mathbf{S}_{zz}$	−0.138 40	
$\mathbf{S}_{xy}$	−0.210 54	

Calculated and Observed Dipolar Couplings (Hz)

D_{ij}	calcd	exptl
$D(1,3) = D_{gem}$	+429.0	+429.0(4)
$D(1,2) = D_{trans}$	−540.4	−540.4(4)
$D(1,4) = D_{cis}$	−964.2	−964.2(4)
$D(1,10) = D_{CH}$	+697.2	+697.2(4)
$D(2,10) = D_{CH'}$	−268.3	−268.3(4)

Structural data from other sources may be successfully combined with complementary liquid crystal data to obtain a more meaningful solution-state structure for underdetermined cases. To do this we add extra equations containing "constraints" to the least-squares fitting routine for the dipolar couplings. In our case, we added structural constraints from the neutron diffraction structure (we call these "predicate observations" [26]). We give each of these equations a weight of $(2\ \mathrm{Hz})^{-2}$ for the least-squares fitting. Thus, if the fitted value gets too far from the value in the equation above, the rms goes up, much like the fitting procedure to the experimental dipolar couplings. The results are gathered in Table 7.

The inclusion of structural constraints from the neutron diffraction data gives an excellent fit to the dipolar couplings. The ethylene structure derived from the liquid crystal data resembles the ethylene structure of **1** determined by neutron diffraction (except τ is 9° smaller in solution). The excellent fit to the observed dipolar couplings and the neutron diffraction determined coordinates (Table 7) implies that the solution-state structure of **1** closely resembles that in the solid state, that is, there is no evidence for any isomeric forms of **1**-^{13}C other than two equivalent C_2 symmetric conformers.

Discussion

Two studies[9j,l] prior to ours had established that ^{1}H NMR in liquid crystal solvents was an excellent physical method for determining the structures of metal−ethylene complexes *in solution*. McMillin and Drago had studied the ethylene ligand structure of *trans*-$PtCl_2(C_2H_4)$(pyridine) (**4**) using ^{1}H NMR in a liquid crystal solvent.[9j] They observed three dipolar couplings, D_{gem}, D_{cis}, and D_{trans}, related to three unique interproton distances, r_{gem}, r_{cis}, and r_{trans}. However, just three dipolar couplings did not suffice to define *both* the ligand structure and the molecular orientation of **4** in the liquid crystal solvent, and thus, only one geometric ratio ($r_{HH_{cis}}/r_{HH_{gem}}$) could be deduced from the liquid crystal NMR experiment: that ratio, $r_{HH_{cis}}/r_{HH_{gem}}$, for **4** was essentially the same as the corresponding ratio for Zeise's salt, **3**, determined by neutron diffraction.[27]

Emsley and Evans reexamined **4**-(pyr-d_5) but used a different liquid crystal solvent mixture which gave both better line resolution and greater solute orientation.[9l] With the inclusion of an observed ^{195}Pt−^{1}H dipolar coupling and one assumed absolute bond distance ($r_{HH_{cis}}$), Pt−H and H−H distances were obtained and were corrected for harmonic vibrations by using a normal coordinate vibrational analysis of Zeise's salt. The liquid crystal NMR derived parameters for **4**-(pyr-d_5) and those of **3** determined by neutron diffraction were the same within experimental error. No structural information was obtained concerning relative carbon−hydrogen positions.

Complexes **3** and **4**, and other related Pt(II) alkene π-complexes, are held together largely by electron donation from the olefin, with little metal 5*d* to alkene π^* back-bonding and consequently little distortion of their ethylene ligands.[19] Although the structures of other ethylene complexes described as metallacyclopropanes have been determined (chiefly by X-ray diffraction,[28] but also in one case by neutron diffraction[29]), only complex **2** had been characterized vibrationally in sufficient detail to permit comparison with surface ethylene vibrational data.[4]

The Range of Structural Parameters For η^2-Ethylene−Metal Complexes. Table 8 compares the structural parameters of several well-characterized η^2-ethylene−metal complexes. The corresponding structural parameters for free ethylene, thiirane, and cyclopropane are included for comparison. The entries in Table 8 are arranged with increasing CC bond length. The longest CC bond length reported for a mononuclear ethylene complex (not shown in Table 8) appears to be 1.486(8) Å for the complex $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}C_2H_4)(PMe_3)$.[30] However, an X-ray crystal structure of the same molecule was determined independently by a different group, and the CC bond distance was found to be significantly shorter, 1.449(6) Å.[31] Indeed, about 1.50 Å appears to be the upper limit for the CC bond length in mononuclear (η^2-C_2H_4) transition-metal complexes. Of course longer CC bond distances have been reported for coordinated alkenes bearing electron-withdrawing substituents.[19]

The entries in Table 8 show that r_{CC} and the Ibers α parameter are the most sensitive parameters of ethylene rehybridization. For η^2-ethylene complexes, α increases with metal $\rightarrow \pi^*$ back-bonding until it reaches the value α_t characteristic of a metallacyclopropane.[19] The angle α_t is the angle between the normals of the planes that bisect the M−C−C angle, η (see Figure 6c). The data in Table 8 also show that the HCH angle, θ, and r_{CH} are *not* sensitive parameters of ethylene rehybridization for η^2-ethylene complexes. This was first rationalized by Tolman and co-workers who pointed out that the s-character in the CH bonds of cyclopropane is about equal to that in ethylene.[32] Indeed, the measured $^1J_{CH}$ coupling constant for **2**-^{13}C (158 Hz)[7] lies in the narrow range between that for ethylene (156 Hz) and that for cyclopropane (160 Hz).

Our liquid crystal NMR measured value of α for **2** (62.5°) is nearly twice the value of α for Zeise's salt **3** ($\alpha = 32.5°$) and is similar to that of other compounds described in the literature as metallacyclopropanes (we also note that our experimentally measured angle α is significantly larger than the value (48°)

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Table 8. The Range of Structural Parameters for Ethylene Complexes

complex	r_{CC} (Å)	r_{CH} (Å)	θ (deg)	α (deg)	α_t (deg)	ref
ethylene	1.335(3)	1.090(3)	116.6(8)	0	0	34
$Pt(C_2H_4)_2(C_2F_4)$	1.365(8)	1.080	114.9	32	74	35
	1.378(8)	1.078	118.6	32	74	
$K[PtCl_3(C_2H_4)]$	1.375(4)	1.087(8)	114.9(6)	32.5	71.2	27
$[PtCl(TMEDA)(C_2H_4)]ClO_4$	1.376(3)	1.083(3)	115(1)	32.0	71.6	36
$Pt(C_2H_4)_3$	1.402(7)	1.102(5)	111.5(4)	31	74	35
$[WH(C_2H_4)O_2CCH{=}CH_2(PMe_3)_2]_2$	1.443(3)	1.091(5)	113.1(4)	60.7	71.0	37
$Cp^*Ta(C_2H_4)(CHCMe_3)(PMe_3)$	1.474(3)	1.090(7)	114.1(5)	68.5	70.9	29
$Os(CO)_4(C_2H_4)$	1.488(24)	1.083(2)	113.5(1)	62.4	70.5	this work
thiirane	1.484(3)	1.083(2)	115.8	58.4	65.9	38
cyclopropane	1.504(4)	1.083(5)	114.5(9)	60	60	39

calculated by DFT techniques[33]). The structural parameters of **2**, that is, r_{CH}, θ, and α, closely resemble those of thiirane, consistent with the close vibrational analogy between **2** and thiirane.[4]

Summary and Conclusions

We have used ^{1}H NMR and liquid crystal solvents to locate the hydrogen atoms of the coordinated ethylene in $Os(CO)_4(\eta$-$C_2H_4)$, **2**, *in the solution phase*. We have also confirmed that the solution phase and solid-state structures of $(\mu,\eta^1,\eta^1$-$C_2H_4)$-$Os_2(CO)_8$, **1**, closely resemble one another. We conclude by suggesting that NMR in liquid crystal solvents should find more widespread use in locating hydrogen atoms in organometallic complexes (especially those containing heavy atoms), or in solving structural problems for which suitable single crystals cannot be obtained.

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