Contribution from Unilever Research, Vlaardingen, The Neteherlands

Ethylene Reorientation in Solid Chlorotetrakis (Ethylene)Iridium(I)

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Received November 16, 1972

The proton spin-lattice relaxation behaviour of solid chloro-tetrakis(ethylene)iridium(I) has been investigated between liquid nitrogen and room temperature.

The results can be explained by 180°-flip reorientations about the metal ligand axes. The activation energy determining the reorientation of the axial ethylene ligand is 1.6 kcal/mol and the one of the equatorial ethylene ligands is 5.3 kcal/mol.

Introduction

The temperature dependence of PMR spectra of rhodium(I)[1,2] and platinum(II)[3,4] alkene complexes is consistent with an intramolecular reorientation process involving rotation of the alkene ligand around the metal-alkene bond. On the basis of the Dewar, Chatt, Duncanson model[5,6] of the transition metal-alkene bond one might expect that especially the breaking of the π component of this bond during rotation is responsible for the value of the barrier to rotation. The reported values from 10-15 kcal/mol, however, would seem to indicate that this barrier is rather insensitive towards electronic and steric effects. Recently Cramer and Mrowca[7] reported the impossibility to freeze out on the NMR time scale the rotation of coordinated ethylene in $(\pi\text{-}C_5H_5)Rh(C_2H_4)_2 \cdot HgCl_2$ at −70°C. They interpreted this in terms of a rotation barrier lower than 10 kcal/mol.

We found the same behaviour of coordinated ethylene in $IrCl(C_2H_4)_4$ and Ir(acetylacetonato)$(C_2F_4)(C_2H_4)$.[9] The PMR spectrum of $IrCl(C_2H_4)_4$ in chloroform shows at −20°C and −50°C sharp resonances in the ratio 1:3. The spectrum is consistent with the trigonal bipyramidal molecular structure to be reported with the ethylene ligands fast rotating around the metal-alkene bond.

We now report the value of the barriers to reorientation of axial and equatorial ethylene in solid $IrCl(C_2H_4)_4$ by nuclear magnetic relaxation measurements.

Experimental Section

The spin-lattice relaxation measurements were performed on a Bruker pulse spectrometer, type BKr 304s, using the null method.[11] The measuring frequencies were 60 and 15 MHz and the lengths of the 90° and 180° pulses were 2 and 4 μs respectively. The measurements below −50°C were carried out under vacuum, above this temperature under d_0- or d_4-ethylene.

$IrCl(C_2H_4)_4$ was prepared as described previously.[8] The partly deuterated sample was prepared on the vacuum line.

After the relaxation measurements the sample was allowed to decompose to the chlorobis(ethylene)iridium(I) dimer, which in its turn was treated with excess triphenylphosphine. The d_4-ethylene contents in the obtained gas samples were determined by mass-spectrometry to be 44 and 46%.

Results and Discussion

The spin-lattice relaxation behaviour is caused by time-dependent magnetic dipole-dipole interactions. It can be investigated by the measurement of the magnetization recovery curve, which shows the falling off with time of the magnetization after a ratio frequency pulse. Due to fast spin diffusion caused by strong spin-spin interactions the spin-lattice relaxation behaves exponentially. The characteristic spin-lattice relaxation time T_1 is given by:[12]

$$\frac{1}{T_1} = \sum_i \alpha_i C_i \left\{ \frac{\tau_{ci}}{1+\omega_o^2\tau_{ci}^2} + \frac{4\tau_{ci}}{1+4\omega_o^2\tau_{ci}^2} \right\} \qquad (1)$$

where ω_o the Larmor precession frequency and τ_{ci} the correlation time of motion i of the protons relative towards each other. τ_{ci} is related to the activation energy (E_i^{act}) by $\tau_{ci} = \tau_{coi}e^{-E_i^{act}/RT}$[2] The value of the relaxation efficiency parameter c_i depends on the change in dipole-dipole interaction during motion i, α_i is the portion of protons involved in this motion. If the several τ_{ci} differ considerably from each other, each motion i correlates, according to eq. (1), with a T_1-minimum proportional to ω_o at $\omega_o\tau_{ci} = 0.616$.

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The experimental ln T_1 versus $1/T$ curve (Figure 1) shows two minima, indicating two motions with different correlation times by which relaxation takes place. At 60 MHz, the minimum T_1 values are 270 ms at 84°K and 93 ms at 263°K. This latter minimum becomes 24.5 ms at 232°K for 15 MHz as measuring frequency. This demonstrates, in accordance with eq. (1), the proportionality of T_1 with ω_o. These results can be explained if we assume the axial ethylene ligand to function in the low-temperature region as a spin-lattice relaxation sink for all protons whereas the three equatorial ethylene ligands function as relaxation sinks for all protons in the high-temperature region. The T_1-minima ratio found (i.e. 3) reflects the ratio of relaxing protons per relaxation sink in the low- and high-temperature region. The slope of the spin-lattice relaxation curve yields the activation energy E^{act} for the reorientation process of the axial ethylene ligand is 1.6 ± 0.1 kcal/mol and the one of the equatorial ethylene ligands as calculated from the slope in the high-temperature range of the T_1 curve at 15 MHz is 4.9 ± 0.2 kcal/mol. E^{act} can also be calculated from the difference in temperature at which the T_1 minimum occurs at different measuring frequencies. E^{act} thus calculated, yields 5.3 ± 0.2 kcal/mol for the equatorial ethylene ligands, which agrees with the one found from the slope of the T_1 curve. Replacement of 45% of the ethylene ligands by deuterated ethylene resulted in an increase of both T_1 minima at 60 MHz by a factor ≈ 1.8. This indicates that the spin-lattice relaxation efficiency parameters c_i are largely determined by interactions between protons on different ethylene ligands. Linear extrapolation of this dilution experiment to complete deuteration yields at 60 MHz for an isolated reorienting equatorial ethylene ligand a T_1 minimum of 0.6 ± 0.1 s and for an isolated axial ligand a T_1 minimum much larger than 0.6 s.

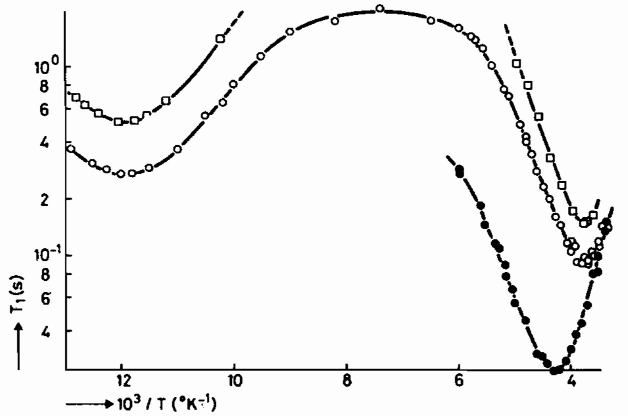

Figure 1. T_1 as a function of inverse temperature for $IrCl(C_2H_4)_4$ (O) at 60 MHz: (●) at 15 MHz; (□) 45% deuterated at 60 MHz.

The large difference between the inter and intra contribution to the relaxation rules out the explanation that oscillations around the metal-alkene axes over small angles (<20°) are responsible for the relaxation process. In this case contributions of comparable magnitude are to be expected.

In case of a pure 180° flip process around the metal-alkene axis no intra ethylene spin-lattice relaxation takes place.[13] The relaxation of the axial ligand, the T_{1intra} minimum being $\gg 0.6$ s, may well be explained by such a process. Since the symmetry of the equatorial coordination plane is 3-fold it must be concluded that this process is determined by the interactions of the axial ethylene ligand with its square intermolecular environment formed by four chlorine atoms.[11] So the intramolecular barrier to rotation of this ligand will even be less than the measured value of 1.6 kcal/mol. The relaxation of the equatorial ethylene ligands can be caused either by a 180°-flip process around the metal-alkene axis with a finite lifetime in a transition state or by a reorientation of the whole equatorial plane around the molecular axis with jumps over large angles. In the latter case jumps over 60° would cause dynamic disorder in the crystal structure. The occurrence of distorder, whether static or dynamic was demonstrated by X-ray investigations.[10] However, such a process would not result in the earlier mentioned averaging of the equatorial protons in the high resolution spectrum. We therefore prefer the interpretation of 180°-flip rotations around the metal-alkene axis to explain the relaxation behaviour of equatorial ethylene ligands.

During rotation the σ part of the metal-alkene bond remains more or less unperturbed. The π part, in contrast, is ruptured during rotation and is only replaced by another bond of π symmetry if suitable metal orbitals are available in the transition state. This is the case in four-coordinated square planar and five-coordinated trigonal bipyramidal complexes. Apart from steric effects the barrier is therefore mainly determined by the difference in π backbonding in the equilibrium and transition states. The low barriers to rotation in $IrCl(C_2H_4)_4$ are well below the region of 10-15 kcal/mol found in rhodium(I) and platinum(II) alkene complexes. The main reasoin may well be the absence of ligands with sufficient π-bonding capacity from the latter. In $IrCl(C_2H_4)_4$ the four ethylene ligands are competing for the metal electron density. During the rotation flip of one of the ethylene ligands the other ones may act as electron sinks to and from which the metal electron density shifts.

Acknowledgments. Thanks are due to Messrs. J. van den Enden and A.L. Onderdelinden for their assistance and to Mr. J. de Bruyn for the mass-spectrometer analysis of the ethylene samples.

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