Spectral Studies of the Isomerization of Dihydridotetrakis(diethyl phenylphosphonite)metal(II) Complexes in Solution

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Abstract: Methylcyclohexane solution infrared spectra of H_2FeL_4 ($L = C_6H_5P(OC_2H_5)_2$) as a function of temperature show that two isomers are in equilibrium. The equilibrium constant for the isomerization reaction has a temperature dependence such that only one isomer is observed in significant amounts above about 0°, whereas both isomers are detectable in varying concentrations from 0 to $-100°$. Infrared and Raman spectral data establish that the predominant isomer above 0° has a distorted cis octahedral configuration. The other isomeric form, which accumulates at low temperature, is proposed to have a structure based on a very slightly distorted FeP_4 tetrahedron, with the hydrogens in either a face–face or face–edge arrangement. Analysis of temperature-dependent nmr spectra gives $\Delta H = 3.12 \pm 0.15$ kcal mol^{-1} and $\Delta S = 15.6 \pm 1.0$ eu for the isomerization reaction tetrahedral $FeP_4(-H_2) \rightleftharpoons$ cis. The enthalpic preference for the tetrahedral $FeP_4(-H_2)$ form of H_2FeL_4 is believed to be due to steric factors. Infrared and Raman spectra show that the complex H_2RuL_4, which has a trans octahedral structure in the solid, rearranges significantly in methylcyclohexane solution.

Extensive ^1H and ^{31}P nmr spectroscopic studies have established that the complexes H_2FeL_4 and H_2RuL_4, where $L = C_6H_5P(OC_2H_5)_2$, are stereochemically nonrigid in solution.[1,2] At low temperature the ^1H nmr spectrum of H_2FeL_4 shows that two isomeric forms are present, one giving rise to six lines and the other to five; the isomers have been assigned cis and trans structures, respectively, of distorted octahedral stereochemistry. At higher temperatures nmr spectra are obtained which are attributable to rapid intramolecular rearrangement, and a ligand exchange mechanism termed "tetrahedral tunneling" has been proposed[1-3] for H_2FeL_4 and related dihydride complexes.

We have investigated the isomerization of H_2FeL_4 and H_2RuL_4 in solution by nmr, infrared, and Raman spectral methods. Our results on H_2FeL_4, while confirming that the six-line isomer is a cis dihydride, show conclusively that the five-line isomer does not contain a trans FeH_2 subunit. A proposed structure for the five-line isomer and its probable role as a stable intermediate in the "tetrahedral tunneling" exchange mechanism for *cis*-H_2FeL_4 are presented in this paper.

Experimental Section

The synthesis of H_2FeL_4 was accomplished as described in the literature.[4] D_2FeL_4 was synthesized by substituting $NaBD_4$ for $NaBH_4$ and C_2H_5OD for ethanol in the procedure. The H_2RuL_4 complex was obtained in low yield by the same method, using commercial "$RuCl_3 \cdot 3H_2O$." Better yields, but still only about 25%, were obtained by first treating the commercial ruthenium chloride solution with hydrogen[5] and then evaporating to dryness under an inert atmosphere and redissolving in ethanol.

Infrared spectra were measured on a Perkin-Elmer Model 225 spectrometer. Spectra of solid samples were obtained using Nujol mulls on KBr plates. Methylcyclohexane solution spectra at various temperatures were measured utilizing a cell with AgCl windows mounted in a Research and Industrial Instruments Co. VLT-2 dewar. Sample temperatures were measured with a copper–constantan thermocouple and are accurate to ±3°. Raman spectra of solid samples were measured on a Cary Model 81 spectrometer equipped with a 65-mW He–Ne laser.

Proton nmr spectra were measured in methylcyclohexane solution from +60 to $-50°$ on a Varian HR-220 spectrometer. The nmr spectrum of H_2FeL_4 at approximately $-100°$ was obtained on a Varian HA-100 modified as described by Cooper, Weber, and Manatt.[6] Temperatures for the nmr spectra were determined from ethylene glycol and methanol chemical shift separations.

Results and Discussion

The infrared and Raman spectra of solid H_2FeL_4 are shown in Figure 1 along with the thin-film ir spectrum of the neat ligand. The infrared spectrum of the solid complex was also measured at $-170°$, but no significant changes were observed. The medium intensity band at 1973 cm^{-1} in the infrared spectrum (1978 cm^{-1} in the Raman spectrum) is assigned to ν(Fe–H). This assignment is supported by the absence of the band in the spectrum of a solid sample of D_2FeL_4. The ir and Raman spectra are as expected for a dihydride known[7] to have a distorted cis octahedral geometry in crystalline samples. Although there are not many examples of cis octahedral dihydrides of first- or second-row transition metals, those whose ir spectra have been reported all show[8] ν(M–H) bands in the range 1800–2200 cm^{-1}.

Figure 2 shows the infrared spectra of methylcyclohexane solutions of H_2FeL_4 at three temperatures. We have also measured the spectra of solutions of D_2FeL_4 at approximately the same temperatures. In the region 1500–2000 cm^{-1} the spectrum of D_2FeL_4 is identical with that of the ligand and changes only slightly with temperature. We can then identify a

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[1] F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties' *J. Amer. Chem. Soc.*, **92**, 1068 (1970).

[2] (a) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, **92**, 3482 (1970); (b) P. Meakin, E. L. Muetterties, and J. P. Jesson, *ibid.*, **95**, 75 (1973).

[3] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971).

[4] D. Titus, A. A. Orio, and H. B. Gray, *Inorg. Syn.*, **13**, 117 (1972).

[5] J. F. Harrod, S. Ciccone, and J. Halpern, *Can. J. Chem.*, **39**, 1372 (1961).

[6] A. Cooper, H. Weber, and S. Manatt, *J. Amer. Chem. Soc.*, **93**, 2369 (1971).

[7] L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *ibid.*, **94**, 1135 (1972).

[8] D. N. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, Chapter 1.

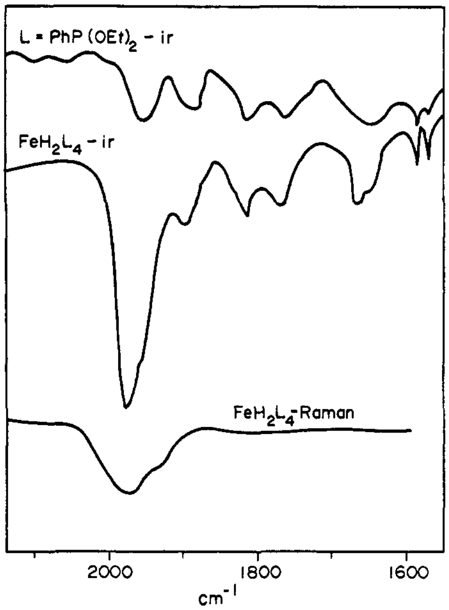

Figure 1. Infrared and Raman spectra of solid H_2FeL_4 and the thin-film ir spectrum of uncomplexed L, ambient conditions.

weak, broad band at 1929 cm^{-1} as ν(Fe–H). At $-50°$ the solution spectrum shows two weak bands, one centered at 1919 cm^{-1} and one at 1818 cm^{-1}. The 1919-cm^{-1} band splits at $-100°$ into bands at 1920 and 1965 cm^{-1}, but the splitting appears to be a result of changes in the ligand spectrum.

Consideration of both the ir and nmr[1,2] solution spectra leads us to conclude that there is only one isomer present in any significant concentration above about 0°, with a cis configuration of distorted octahedral stereochemistry. The cis solution structure is probably very similar to the structure found[7] in the solid. As the temperature is lowered, an additional solution species is observed, characterized by a five-line ^{1}H nmr spectrum[1,2] and a broad ir absorption centered at 1818 cm^{-1}. We have studied the ^{1}H nmr spectra of H_2FeL_4 in methylcyclohexane solution in the temperature range $+60$ to $-100°$ and find that at $-100°$ the five-line isomer greatly predominates. From a plot of ln K *vs.* $10^3/T$, we obtain $\Delta H = 3.12 \pm 0.15$ kcal mol^{-1} and $\Delta S = 15.6 \pm 1.0$ eu for the reaction five-line $\rightleftharpoons$ cis. Our values of ΔH and ΔS are close to those obtained by Meakin, *et al.*,[2b] for the analogous isomerization of $H_2Fe[C_6H_5P(OCH_3)_2]_4$ in toluene-d_8 solution.

The ir results show that the five-line isomer does not contain a trans FeH_2 subunit. Trans dihydride metal complexes, both in solids and solutions, always exhibit[8] sharp, very intense ir absorption bands in the region 1600–1750 cm^{-1}, or about 200–400 cm^{-1} lower than the characteristically broader bands of cis dihydrides. Even at $-100°$, where the relative concentration of the five-line isomer is extremely high, there is no hint of an ir band which could be assigned to *trans*-H_2FeL_4.

The above conclusion is reinforced upon examination of the ir and Raman spectra of a solid sample of *trans*-H_2RuL_4.[9] In the ir spectrum ν_{as}(Ru–H) is observed as a sharp and very intense band centered at 1643 cm^{-1}

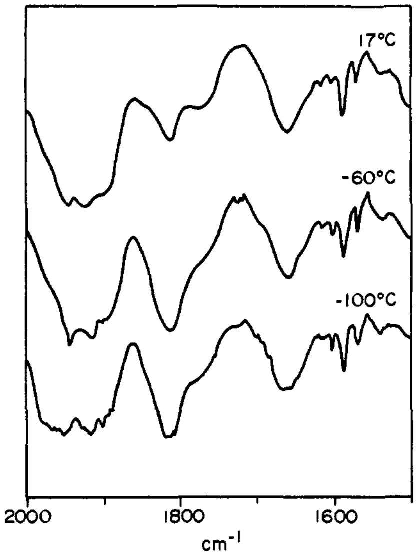

Figure 2. Infrared spectra of H_2FeL_4 in metyhlcyclohexane solutions at 17, -60, and $-100°$.

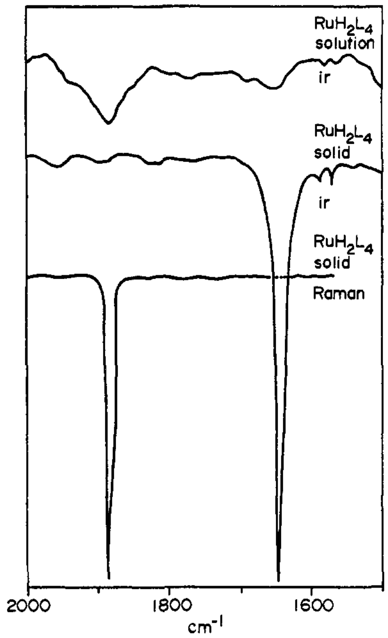

Figure 3. Infrared and Raman spectra of solid H_2RuL_4, and the ir spectrum in a methylcyclohexane solution, ambient conditions.

and the Raman spectrum shows ν_{sym}(Ru–H) as a similarly intense, sharp peak at 1886 cm^{-1} (Figure 3).[10] As in the case of H_2FeL_4, however, a methylcyclohexane solution of H_2RuL_4 does not contain any significant concentration of a trans octahedral isomer. The solution ir spectrum of H_2RuL_4 in the ν(Ru–H) region exhibits only a broad absorption centered at 1894 cm^{-1} (Figure 3), which could possibly represent a cis dihydride species. Although assignment of the solution ir spectrum cannot be made with certainty, there is no question that substantial geometrical rearrangement of H_2RuL_4 has occurred. It is also of interest to note that

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(9) L. J. Guggenberger has communicated to us that he has determined the structure of crystalline H_2RuL_4 by X-ray techniques and found the stereochemistry to be trans octahedral.

(10) The appearance of the symmetric mode at higher energy than the asymmetric mode is consistent with the strong trans influence of the hydride ligand. The asymmetric stretch involves lengthening one Ru–H bond while shortening the other one, which should be energetically favorable relative to symmetrical stretching for a strong trans directing group such as H^-.

the ir spectrum of H_2RuL_4 in solution does not change on lowering the temperature, in contrast to the situation for H_2FeL_4.

The structure of the five-line isomer of H_2FeL_4 is not easily established. In order to be compatible with the ir results, the H–Fe–H angle must be drastically smaller than the 180° value for a trans FeH_2 subunit. We suggest therefore, that the stereochemistry of the five-line isomer is based on a very slightly distorted FeP_4 tetrahedron, with the hydrogens placed in a face–face ($\angle$H–Fe–H = 109°) or possibly in a face–non-adjacent edge ($\angle$H–Fe–H = 135°) arrangement. The exchange of hydrogen ligands in an isomer of the tetrahedral $FeP_4(-H_2)$ type would require minimal phosphorus motion and therefore could continue to very low temperatures.

The existence of a tetrahedral $FeP_4(-H_2)$ species as a stable entity in the H_2FeL_4 system fits nicely into the "tetrahedral tunneling" intramolecular ligand exchange mechanistic scheme for distorted cis dihydrides proposed by Meakin, *et al.*,[3] on the basis of their detailed analysis of the temperature-dependent ^1H nmr spectra of $H_2Fe[P(OC_2H_5)_3]_4$. Using a "jump" model calculation it was concluded[3] that the most probable mechanism of intramolecular rearrangement of $H_2Fe[P(OC_2H_5)_3]_4$ involves passage of a hydrogen from one face to another, through an edge position, of a tetrahedral $FeP_4(-H_2)$ structure. Apparently the complex H_2FeL_4 represents the interesting special case of "tetrahedral tunneling" in which it is possible to distinguish between tetrahedral $FeP_4(-H_2)$ and distorted *cis*-H_2FeL_4 isomers, a remarkable situation in view of the fact[7] that the four phosphorus donor atoms in the cis structure are already fairly close to idealized tetrahedral positions. Thus, at +50° the tetrahedral $FeP_4(-H_2)$ isomer is cast in the role of a stable intermediate in the rapid intramolecular ligand exchange of *cis*-H_2FeL_4. Lowering the temperature slows the exchange reaction of the cis isomer, as evidenced by broadening of all ^1H nmr spectral lines,[11] and at −50° a slow exchange limiting spectrum is obtained. The barrier to the exchange reaction of the tetrahedral $FeP_4(-H_2)$ isomer itself, on the other hand, would be expected to be extremely small.

Finally, we turn to the question of the special stability of the tetrahedral $FeP_4(-H_2)$ isomer of H_2FeL_4 for L = $C_6H_5P(OC_2H_5)_2$ or $C_6H_5P(OCH_3)_2$.[2b] The entropy term is obviously unfavorable for the tetrahedral $FeP_4(-H_2)$ isomer, and we assume that this will always be the case, irrespective of the nature of L. However, we find from model building that, of all the H_2FeL_4 complexes studied to date,[1-3] only for the above two L's is the tetrahedral $FeP_4(-H_2)$ form relatively uncrowded, as compared with the cis dihydride. In these two cases, then, steric factors make an important contribution to the observed enthalpic preference for the unusual isomeric form.

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(11) In a "tetrahedral tunneling" mechanism not involving a stable intermediate, the outer two lines in the ^1H nmr spectra should remain sharp in going from the fast to the slow exchange limit, as indeed is observed[3] for $H_2Fe[P(OC_2H_5)_3]_4$, because the energy of certain transitions are unaffected by permutations of the phosphorus and hydrogen nuclei when the spin–spin interaction manifold for the structures on both sides of the "jump" are identical. The fact that *all* the lines broaden in proceeding toward the slow exchange limiting ^1H nmr spectrum of *cis*-H_4FeL_4 is consistent with the proposal that the tetrahedral $FeP_4(-H_2)$ isomer is involved as a stable intermediate in this particular exchange process, because permutations of the phosphorus and hydrogen nuclei would affect the energy of all transitions in a "jump" model which included a third structure with a different set of energy levels for spin–spin interaction.