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Nonrigid Molecules. Enthalpy and Entropy Differences between Rotational Isomers of (π-Cyclopentadienyl)(methyldichlorosilyl)dicarbonyliron[1,2]

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The solution infrared spectrum of the title compound (I) has been thought[3] to indicate rotational isomerization about the Fe–Si bond. This view was supported by the assignment of the CO stretching region of the spectrum to the individual rotational isomers.[1] In this paper are reported measurements of the enthalpy and entropy differences between these isomers.

Experimental Section

Samples of I were prepared by the method of Jetz and Graham.[3] Spectroscopic samples were purified by slow sublimation onto a water-cooled probe at ~0.2 Torr. Infrared spectra were taken on a Perkin-Elmer 257 spectrophotometer using a Research and Industrial Instruments Model VLT-2 variable-temperature infrared cell. The path length was 1.0 mm, the solvent was *n*-hexane, and a variable-path-length cell containing *n*-hexane was placed in the reference beam and adjusted to provide a flat base line at machine ambient temperature. Since a weak *n*-hexane absorption at ~2025 cm^{-1} proved to be temperature sensitive, only the two lower energy CO stretching absorptions were used to calculate relative intensities. Replicate measurements were made at +25, +3, −25, and −75°. The results were analyzed by the method of Noack,[4] using the band assignments proposed earlier.[1] The least-squares fit to Noack's equation was a line with gradient 0.81, intercept 1.36, and correlation coefficient 1.00. The gradient is probably an underestimate of the enthalpy change due to incomplete band separation.

Results and Discussion

The measured entropy difference between symmetric and unsymmetric isomers[5] was 1.4 ± 0.5 eu. Its sign was such as to favor the unsymmetrical isomers. Since the symmetry number of each isomer is 5 and the other components of their partition functions should be similar in size, the calculated value is ~0 eu. However the infrared experiment is blind to the difference between the two unsymmetrical enantiomers, resulting in a statistical contribution of $R \ln 2$ (~1.4 eu) in their favor (compare ref 6, p 315). The agreement confirms the assignments[1] and the interpretation[3] of the spectrum upon which they are based.

The measured enthalpy difference, of course, provides only a lower limit for the average potential barrier to rotation about the Fe–Si bond. Its value was found to be 0.8 (−0.1, +0.7) kcal mol^{-1} in favor of the symmetrical isomer, which was the isomer with the lower average CO stretching frequency. Thus the observed enthalpy difference cannot be due to differential Fe→Si π bonding between the isomers.

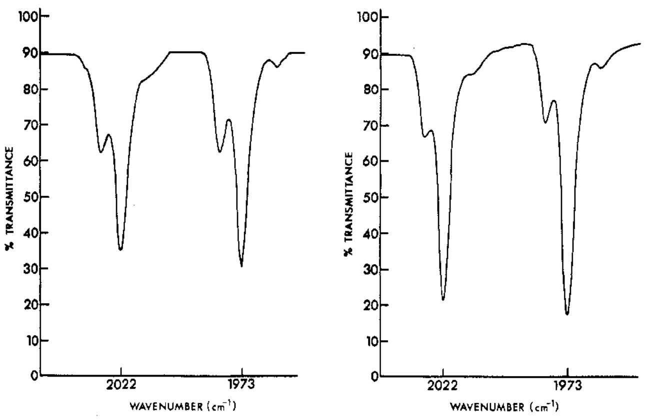

Figure 1.—Infrared transmittance of a *n*-hexane solution of $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_2CH_3$ at +25° (left) and −78° (right).

It is commonly accepted that the π^* orbitals of CO become partially occupied upon coordination to a metal. This electron density, being antibonding in character, must swell the van der Waals envelope of the ligand. Steric compression should therefore destabilize these orbitals, causing a decrease in their electron density and raising the vibrational frequency of the CO bond. Therefore the relative CO stretching frequencies of the isomers are consistent with the view that steric compression is responsible for most of the enthalpy difference between them. It follows that both the average CO stretching frequency difference and the enthalpy difference between isomers should decrease with increasing size of the group IV ligand atom in a related series of complexes. This result is consistent with the observation[7] by Bryan, *et al.*, that intramolecular forces exercise very little constraint upon the conformation around the Fe–Sn bonds in the complexes $(\pi\text{-}C_5H_5)Fe(CO)_2SnX_3$ where X = phenyl, Cl, or Br.

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[1] Part II; for part I see J. Dalton, *Inorg. Chem.*, **10**, 1822 (1971).

[2] Experimental work from the laboratories of Professor F. G. A. Stone, Bristol, U. K., whom I thank for facilities and encouragement.

[3] W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967).

[4] K. Noack, *Helv. Chim. Acta*, **47**, 1064 (1964).

[5] Newman projections of the isomers, along the Fe–Si bond axis, are reproduced in ref 3. There is one symmetric conformation, with a reflection plane bisecting the cyclopentadienyl and methyl groups, and two enantiomeric conformations with no nontrivial symmetry elements.

[6] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Hangen, H. E. O'Neal, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

[7] R. F. Bryan, P. T. Greene, G. A. Melson, P. R. Stokely, and A. R. Manning, *Chem. Commun.*, 722 (1969).

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Transition Metal π Complexes. I. Reactions of π-Cycloheptatrienyldicarbonyl Iodides of Molybdenum and Tungsten with Tertiary Phosphines and Phosphites

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Considerable interest has developed in recent years in the detection and interconversion of isomeric forms of transition metal organometallic carbonyls of the general types $(\pi\text{-ring})M(CO)_nL_{2-n}X$ or $(\pi\text{-ring})MCOLX$. The existence of at least three general types of isomerism has been observed. Examples include cis–trans isomerism in $\pi\text{-}C_5H_5Mo(CO)_2P(OC_6H_5)_3R$ (R = CH_3