$(C_6H_5)_3$ could not be obtained by similar hydrogenation reactions on $Ru(CO)_5$ and $Ru(CO)_4P(C_6H_5)_3$. The strong metal–hydrogen bond in the case of osmium makes it possible to synthesize the whole series of compounds, $OsH_2(CO)_4$,[1] $OsH_2(CO)_3P(C_6H_5)_3$,[1] and $OsH_2(CO)_2(P(C_6H_5)_3)_2$.

By the same principle, the still unknown dihydride compound of iron, $FeH_2(CO)_2(P(C_6H_5)_3)_2$, may be isolated by making use of a reaction similar to (1). Here, however, a lower thermal stability for the metal–hydrogen bond is to be expected. Attempts in this direction are now being made.

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, NEW JERSEY 08903

Mössbauer Spectroscopy of Organometallic Compounds. Isomerism in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ and Related Molecules

BY ROLFE H. HERBER AND YVES GOSCINNY[1]

Received February 5, 1968

The Mössbauer spectra of a number of organotin compounds derived from $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ have been examined at liquid nitrogen temperature, using both the 14.4-keV resonance γ radiation of ^{57}Fe and the 23.8-keV resonance γ radiation of ^{119}Sn. These measurements show that for $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ and $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ there are no observable conformational changes on dissolution of the crystalline solids in solvents which set to a glassy matrix at low temperatures. The ^{57}Fe Mössbauer parameters in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2GeCl_2$ are found to be invariant with respect to dissolution, and from these data it is concluded that the anomalous bond distances and bond angles, derived from the X-ray diffraction data for these compounds, arise from the specific bonding interactions within the molecule, and not from stacking forces between molecules in the crystalline state. The ^{119}Sn Mössbauer spectra and infrared data for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$, moreover, show the existence of two structural forms in solution, and these are identified with the two possible rotational isomers obtained by rotation of the metal–metal bond. On the basis of isomer shift systematics, an assignment of the parameters to the two forms can be made.

I. Introduction

Early in the development of the technique of recoilless emission and absorption of γ radiation (Mössbauer effect) it was recognized that this spectroscopic tool could be used to elucidate the structure and bonding of organometallic compounds, especially those containing iron and/or tin.[2] It was not recognized until recently however, that Mössbauer spectroscopy could be exploited in a unique manner to resolve some of the discrepancies which have been reported regarding the structural information obtained from X-ray diffraction methods, on the one hand, and that inferred from nuclear magnetic resonance and infrared investigations, on the other. This uniqueness derives from the fact that it is possible to extract a number of Mössbauer parameters not only from samples of the neat solid in question, but also from frozen solutions of the same material in structureless (glassy) matrices. A recent application of this technique—in conjunction with low-temperature nmr and infrared studies—has been in the elucidation of the conformation of $\pi\text{-}C_8H_8Fe(CO)_3$ and related molecules in solution at low temperatures.[3] In the present study, the Mössbauer spectra of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$, $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$, and a number of related molecules have been studied both in the neat solid and in frozen solutions in order to clarify some of the conformational features of these organometallic compounds. Of particular interest in this group of compounds is the fact that the Mössbauer parameters of both the ^{57}Fe and ^{119}Sn resonances can be obtained from the same sample prepared from natural abundance precursors, and the information derived from the two "probe" atoms can be used to derive structural information pertaining to only a portion of the whole molecule. Such structural information is particularly pertinent with respect to the existence of rotational isomers[4] in these compounds.

II. Experimental Section

A number of the absorbers used in this study were prepared from commercially available samples of the requisite starting materials. $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ (I), $\pi\text{-}C_5H_5Fe(CO)_2SnCl_3$ (II), and $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ (III) were synthesized using the method of Bonati and Wilkinson.[5] A sample of $[(\pi\text{-}C_5H_5)Fe(CO)_2]GeCl_2$ (IV) was generously made available to us by Dr. P. Woodward. The dimer, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (V), was obtained from Alfa Inorganics, Inc.

---

[1] On leave from Universite Libre de Bruxelles, Brussels, Belgium.

[2] See for example: Proceedings of the Panel on the Application of the Mössbauer Effect in Chemistry and Solid State Physics, International Atomic Energy Agency, Vienna, 1966; V. I. Gol'danskii, *At. Energy Rev.*, **1**, 3 (1962); V. I. Gol'danskii, "The Mössbauer Effect and Its Applications in Chemistry," Consultants Bureau, New York, N. Y., 1964; R. H. Herber, *Ann. Rev. Phys. Chem.*, **17**, 261 (1966).

[3] R. Grubbs, R. Breslow, R. H. Herber, and S. J. Lippard, Jr., *J. Am. Chem. Soc.*, **89**, 6864 (1967).

[4] The term "conformers" has been suggested for configurationally distinguishable species in equilibrium with each other by A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967), in conjunction with their nmr studies of $\pi\text{-}C_5H_5Mo(CO)_2$ allyl complexes. The term "isomers" has been retained in the present discussion for the sake of clarity, although the same type of rotational change is involved here as that discussed by these authors.

[5] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 179 (1964). The authors are indebted to A. Hoffman of this laboratory for carrying out these syntheses.

The Mössbauer spectrometer and the general aspects of the spectrometric method have been described previously.[6] The 14.4-keV resonance of ^{57}Fe was observed using a source of ^{57}Co diffused into palladium, and the pertinent isomer shifts are reported with respect to the centroid of a standard sodium nitroprusside (SNP) absorber[7] spectrum at room temperature. The 23.8-keV resonance of ^{119}Sn was observed using a barium stannate source,[8] and the pertinent isomer shifts are reported with respect to the centroid of a stannic oxide spectrum at room temperature. The neat solids and frozen solutions of the samples in methyltetrahydrofuran (MTHF) were mounted as reported previously.[3] Dilute solutions in poly(methyl methacrylate) were prepared by mixing benzene solutions of the polymer and of the sample in question, transferring this to shallow cups made of aluminum foil, and allowing the excess solvent to evaporate at room temperature. The resultant disks were stripped off, trimmed if necessary to remove excess material, and then mounted in stacks in the usual sample position of the liquid nitrogen dewar system.

Infrared spectra in the 2000-cm^{-1} region were obtained on Nujol mulls and MTHF and poly(methyl methacrylate) solutions of the organometallic samples using a Perkin-Elmer Model 521 spectrometer fitted with NaCl optics.

III. Results and Discussion

Typical Mössbauer spectra of I and II are shown in Figures 1–4, and the numerical values for the Mössbauer parameters (IS is the isomer shift from the appropriate reference absorber, QS is the quadrupole splitting, both in mm/sec) at liquid nitrogen temperature are summarized in Table I.

The ^{57}Fe spectra obtained for the neat solids (I, Figure 1a; II, Figure 3a) and the analogous ^{119}Sn spectra (I, Figure 2a; II, Figure 4a) typically show (uncorrected) resonance effects of 5–10%. The IS and QS parameters extracted from these data are in good agreement with those published earlier from this laboratory,[9] as well as with that reported for the ^{119}Sn data for $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$ by Gol'danskii, *et al.*[10] The QS parameter for II is somewhat larger than that given in ref 10, although the isomer shift values are in moderately good agreement after correction for the difference in reference points has been made.

The resonance spectra for the glassy matrix absorbers, Figures 1b, 2b, 3b, and 4b, typically show much smaller resonance effects, which are generally on the order of 1–2%. This situation is in part due to the small resonance thickness t $(=n\sigma_0 f')$ of the Mössbauer atom in the dilute matrices and in part to the participation of low-lying optical modes to the vibrational spectrum of the Mössbauer atom,[11] which in turn reduces the recoil-free fraction under the conditions of the present measurements. To offset the smaller signal-to-noise ratio in these spectra, data accumulation was continued until $\gtrsim 10^6$ counts/channel had been accumulated, so that the statistical counting error was reduced to $\lesssim 0.1\%$ for a signal-to-noise ratio of $\gtrsim 10$.

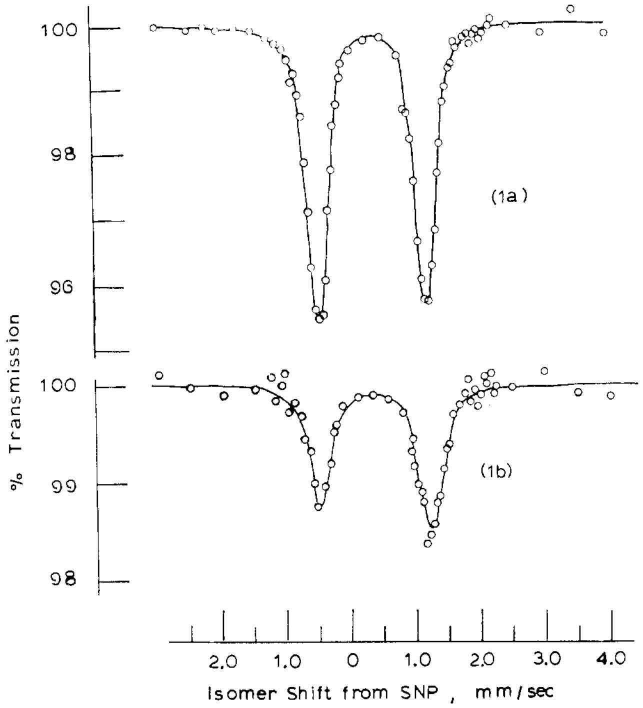

Figure 1.—The ^{57}Fe Mössbauer spectrum of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ at liquid nitrogen temperature: (a) neat solid and (b) poly(methyl methacrylate) solution.

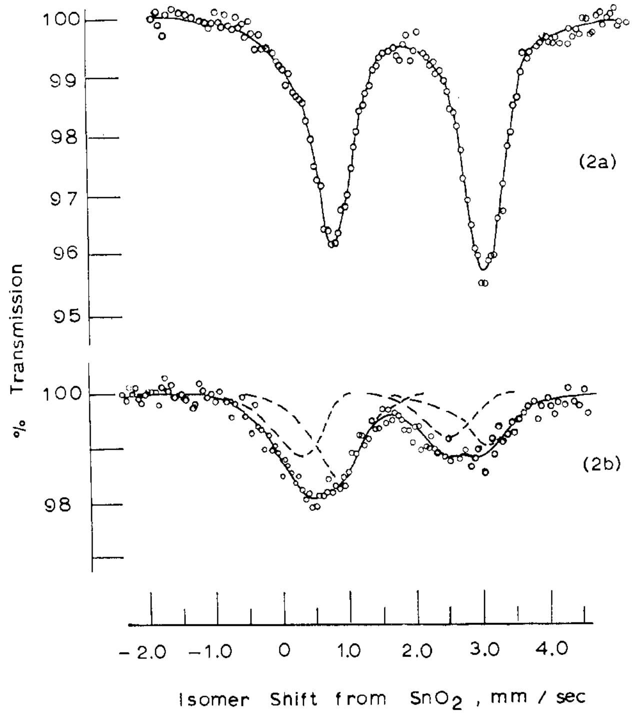

Figure 2.—The ^{119}Sn Mössbauer spectrum of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ at liquid nitrogen temperature: (a) neat solid and (b) poly(methyl methacrylate) solution.

It is clear from the data summarized in Table I that the ^{57}Fe resonance parameters for I and IV and the ^{57}Fe and ^{119}Sn resonance parameters for II and III are

---

(6) G. K. Wertheim, "Mössbauer Effect—Principles and Applications," Academic Press Inc., New York, N. Y., 1964; R. L. Cohen, P. G. MacMullin, and G. K. Wertheim, *Rev. Sci. Instr.*, **34**, 671 (1963); R. H. Herber in "The Mössbauer Effect and Its Application in Chemistry," Advances in Chemistry Series, No. 68, American Chemical Society, Washington, D. C., 1967, Chapter 1.

(7) National Bureau of Standards Reference Material 725, N.B.S. Miscellaneous Publication 260-13, U. S. Government Printing Office, Washington, D. C., 1965. The most reliable value for QS for this material at room temperature is 1.705 ± 0.003 mm/sec: U. Gonser private communication.

(8) H. Sano and R. H. Herber, *J. Inorg. Nucl. Chem.*, **30**, 409 (1968).

(9) R. H. Herber, *Progr. Inorg. Chem.*, **8**, 1 (1967).

(10) V. I. Gol'danskii, B. V. Borshagovskii, E. F. Makarov, R. A. Stukan, K. I. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Teor. i Eksperim. Khim., Akad. Nauk Ukr. SSR*, **3**, 478 (1967).

(11) R. H. Herber, Proceedings of the Symposium on the Mössbauer Effect, London, Dec 1967; Symposium of the Faraday Society, No. 1 in press.

TABLE I

SUMMARY OF MÖSSBAUER DATA AT LIQUID NITROGEN TEMPERATURE

Absorber	No.	Matrix[a]	Resonance	IS, mm/sec	QS, mm/sec
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$	V	Neat	Fe	+0.47 ± 0.01	1.91 ± 0.01
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$	I	Neat	Fe	+0.36 ± 0.01	1.68 ± 0.01
		MTHF	Fe	+0.36 ± 0.01	1.68 ± 0.01
		p	Fe	+0.35 ± 0.01	1.74 ± 0.05
		Neat	Sn	+1.95 ± 0.02	2.38 ± 0.02
		p	Sn	+1.96 ± 0.02	2.25 ± 0.02
				+1.31 ± 0.02	2.29 ± 0.02
$(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$	II	Neat	Fe	+0.40 ± 0.01	1.86 ± 0.01
		MTHF	Fe	+0.39 ± 0.01	1.76 ± 0.01
		p	Fe	+0.38 ± 0.01	1.78 ± 0.01
		Neat	Sn	+1.74 ± 0.02	1.77 ± 0.02
		MTHF	Sn	+1.54 ± 0.05	1.64 ± 0.05
		p	Sn	+1.66 ± 0.02	1.78 ± 0.02
$(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$	III	Neat	Fe	+0.37 ± 0.01	1.83 ± 0.01
		p	Fe	+0.35 ± 0.01	1.79 ± 0.01
		Neat	Sn	+1.50 ± 0.02	0
		p	Sn	+1.50 ± 0.02	0
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2GeCl_2$	IV	Neat	Fe	+0.36 ± 0.01	1.66 ± 0.01

[a] MTHF, 2-methylfuran; p, poly(methyl methacrylate).

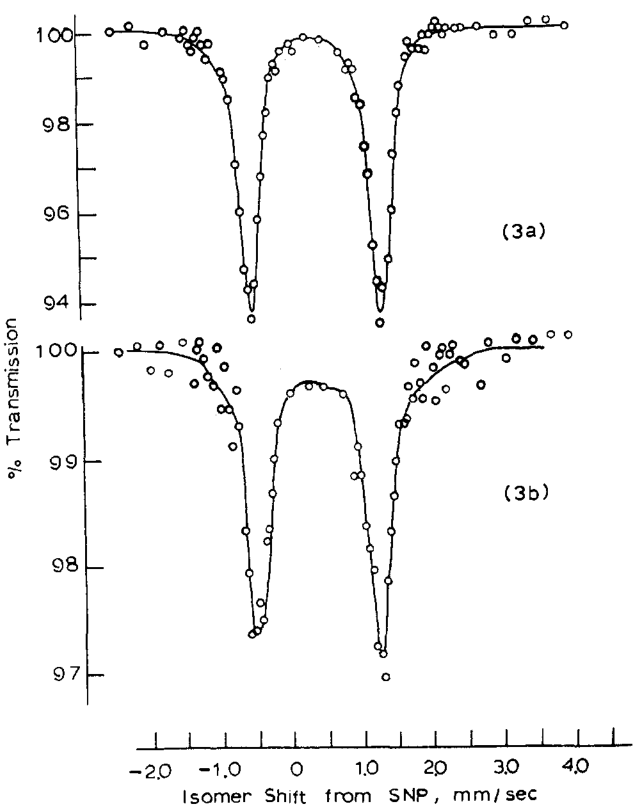

Figure 3.—The ^{57}Fe Mössbauer spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ at liquid nitrogen temperature: (a) neat solid and (b) poly(methyl methacrylate) solution.

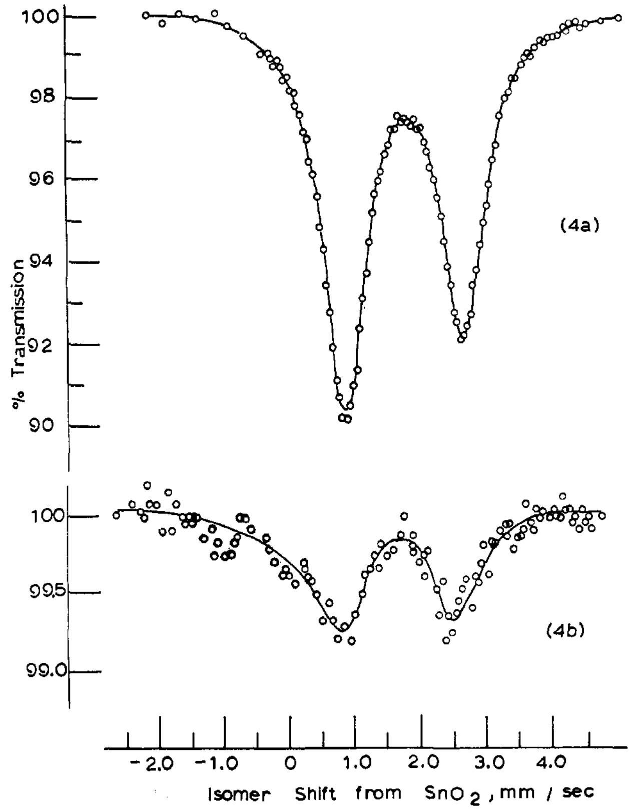

Figure 4.—The ^{119}Sn Mössbauer spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$ at liquid nitrogen temperature: (a) neat solid and (b) poly(methyl methacrylate) solution.

essentially invariant with respect to replacing the neat solid matrix by that provided by a structureless (glassy) solvent. This point is of particular interest with respect to the X-ray diffraction data reported for these materials and the chemical inferences based thereon. The X-ray data for I have been reported by O'Connor and Corey,[12] who point out that the Sn–Fe bond length of 2.492 Å is *shorter* than any previously reported tin to transition metal bond length and that the Sn–Cl bond length of 2.43 Å is *longer* than the metal–halogen bond lengths reported for $SnCl_4$, CH_3SnCl_3, etc. Moreover, the departure from tetrahedral values of the Cl–Sn–Cl bond angle (94.1 ± 0.6°) and of the Fe–Sn–Fe bond angle (128.6 ± 0.3°) is the largest yet observed for a four-coordinate tin atom. An essentially identical structure has been reported for the analogous germanium compound (IV) by Bush and Woodward.[13]

Such observations, which are derived from X-ray

---

[12] J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, **6**, 968 (1967).

[13] M. A. Bush and P. Woodward, *J. Chem. Soc.*, *A*, 1833 (1967).

diffraction data on single-crystal samples of the neat solids, naturally raise the question whether these unusual structural parameters are the consequences of intermolecular attractions and repulsions inherent in the "stacking" process by which the crystal is grown from solution or whether they arise from the specific nature of the chemical bonding between the two metal-atom-containing moieties. If the former is the case, a considerable conformational change would result on dissolving the solid in an appropriate structureless solvent, and such a conformational change should be reflected in the Mössbauer parameters (IS and QS) of the metal atoms.

That changes in the bond distance between the Mössbauer atom and its nearest neighbors give rise to measurably large changes in the Mössbauer parameters is readily apparent from the recent studies[14] of the effect of pressure on a number of compounds of iron. These authors have shown for example that the isotropic compression of ferrous fluoride causes a decrease in the isomer shift of ~ 0.12 mm sec^{-1} and an increase in the quadrupole splitting of ~ 0.53 mm sec^{-1} in the pressure range 1–200 kbars. Moreover the pressure dependence of the isomer shift is largest for covalent compounds such as ferrocene and $K_4Fe(CN)_6$. Using an average order of magnitude value for the compressibility of iron compounds[15] ($\beta \sim 7 \times 10^{-7}$), it is estimated that a bond length change of ~ 0.02 Å could be readily detected from changes in the isomer shift parameter.

On the other hand, if the bond angles and bond distances observed in the solid are consequences of the bonding interaction, dissolution of the crystal would be expected to leave the structure—and hence the Mössbauer parameters—essentially unchanged. That this latter situation obtains can be readily inferred from the ^{57}Fe data for I–IV and the ^{119}Sn data for II and III, for which both the IS and QS of the neat solid and the glassy matrix absorbers are within the quoted experimental error of each other. Any significant *lengthening* of the Sn–Fe bond or *shortening* of the Sn–Cl bond would have been reflected in a change in the isomer shifts of the two resonant atoms in question. Similarly, any significant change in the Fe–Sn–Fe or Cl–Sn–Cl bond angles would be expected to be reflected in systematic changes in the quadrupole splitting parameters (*vide infra*). From the data of Table I it is seen that such changes have *not* occurred in going from the neat solid to the glassy matrix, and hence it is reasonable to conclude that *the anomalous bond distances and bond angles which are observed in the X-ray diffraction data for the solids are a reflection of the bonding interactions within the molecule* and are not ascribable to the intermolecular forces in the solid.

A strikingly different phenomenon is observed in the ^{119}Sn resonance of the bis(π-cyclopentadienyliron dicarbonyl)tin dichloride (I). The resonance spectrum of the glassy solution matrix absorber, Figure 2b, shows the presence of two doublets, and these are associated with the existence of a pair of rotational isomers in the frozen solution. The existence of such isomers has been suggested for $(\pi\text{-}C_5H_5)Fe(CO)_2Si(CH_3)_2Cl$ on the basis of infrared data in the carbonyl region (cyclohexane solutions[16]) and comparison with the analogous spectra of $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_3$. The trichloride shows two strong bands at 2040 and 1995 cm^{-1}, while the dichloride spectrum consists of two strong bands at 2025 and 1975 cm^{-1} and two medium strong bands at 2033 and 1983 cm^{-1}. The two isomers postulated[16] for the dichloride differ from each other by 120° rotation of the Fe–Si bond. A similar conformational change on solution has also been suggested for the germanium dichloride compound[13,17] and for the tin dichloride compound.[12,17] It is interesting to note that the solid in each case shows only a structure with C_2 symmetry.

The Mössbauer spectra for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ in the glassy matrix, Figures 1b and 2b, clearly indicate the existence of two distinguishable environments around the tin atom (corresponding to the two rotational isomers) while the local environment about the iron atom has remained nearly invariant on dissolution of the neat crystalline solid.[18] There are, obviously, two ways in which the ^{119}Sn spectrum of I can be resolved into two pairs of peaks corresponding to two quadrupole-split doublets. One of these leaves the IS parameter constant and gives quadrupole splittings of 1.62 and 2.92 mm/sec (compared to 2.25 mm/sec for the neat solid). The other assignment leaves the QS parameter constant and gives two doublets with isomer shifts of +1.31 and +1.96 mm/sec with respect to SnO_2 (compared to a value of 1.96 mm/sec for the neat solid). In view of the data obtained for the tin trichloride compound (II), in which the IS and QS parameters do not change significantly between the neat solid and the poly(methyl methacrylate) solution, the more tenable hypothesis is the second of the above two assignments, and this conclusion is also in agreement with the infrared data (reported below) on Nujol mulls and solution samples in the carbonyl region.

From a variety of Mössbauer data on organotin compounds, it has become clear that the origin of the electrostatic field gradient at the metal atom nucleus in tetracoordinated organotin compounds lies in the imbalance in the 5p orbital occupancy and the presence of a high p_π–d_π bond order between the ligands and

---

[14] A. R. Champion, R. W. Vaughan, and H. G. Drickamer, *J. Chem. Phys.*, **47**, 2583 (1967); A. R. Champion and H. G. Drickamer, *ibid.*, **47**, 2591 (1967); R. W. Vaughan and H. G. Drickamer, *ibid.*, **47**, 468 (1967).

[15] "International Critical Tables," McGraw-Hill Book Co., Inc., Vol. III, New York, N. Y., 1928, p 44.

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

[17] N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc., A*, 1130 (1966).

[18] In order to ensure that this difference in the solution spectra was due to a conformational change on solution, rather than to a (reversible) reaction with the solvent, Mössbauer spectra were run on samples recovered from MTHF solutions after evaporation of the solvent. The IS and QS parameters (in mm/sec, conditions analogous to those summarized in Table I) were: for I(Fe), +0.391, 1.66; for I(Sn), +1.91, 2.30; for II(Fe), +0.391, 1.85; for II(Sn), +1.77, 1.78. Clearly the original conformers are recovered from the solutions, at least as far as the MTHF samples are concerned.

the central atom.[19,20] These effects arise primarily from the Sn–Cl interaction which is invariant with respect to the rotational isomerism. The isomer shift parameter, on the other hand, reflects a change in the occupancy of the four sp^3 hybridized orbitals. Since this occupation is expected to be directly related to the approach of the bond angles to tetrahedral values, the rotation with respect to the conformation found in the solid postulated for the isomeric form present only in solution can account for the observed assignment. The shift to more negative values in the IS parameter for the second doublet in the ^{119}Sn spectrum (Figure 2b) implies a decrease in the s-electron density at the tin nucleus. The more extensive delocalization of 5s electrons into the sp^3 hybridized orbitals expected for the rotational isomer possessing more nearly tetrahedral bond angles around the tin atom is in consonance with this interpretation of the data. It has been noted by several groups,[12,13] following the original suggestion by Bent,[21] that a metal which uses sp^3 hybrid orbitals in the bonding to two different ligands concentrates s character in the bonds to the less electronegative ligand (with a concomitant increase in the bond angle compared to tetrahedral values) and p character in the bonds to the more electronegative ligand (with a concomitant decrease in the bond angle). The assignment of the ^{119}Sn resonance doublet which has the more negative isomer shift (with respect to the standard) to the form which permits a closer approach to tetrahedral bond angles then follows directly from the above assignment of bond character and the known relationship between ^{119}Sn isomer shifts and s-electron densities in related compounds.[22] Any speculation relating the observation that only one of the two isomeric forms is found in the crystalline form to the relative magnitude of the energy barrier to rotation and the difference in the stacking energy of the two forms in the solid is not warranted on the basis of the presently available data.

In this context it is also worth noting that the ^{119}Sn isomer shift for the triphenyltin compound (III) is significantly smaller than that for the corresponding resonance either in I (neat solid) or in II (neat solid and glassy matrix). The X-ray data for III have been reported by Bryan[23] and show that the symmetry around the tin atom is nearly tetrahedral with C–Sn–C bond angles of 105.2° and an Fe–Sn–C bond angle of 113.4°. The Sn–Fe distances are 2.533 and 2.540 Å (there are two nonequivalent molecules per unit cell). Since it is known from previously reported data[2,9] on related organotin compounds that substitution of an sp^2 hybridized carbon atom for a halogen in nominally tetrahedral compounds has only a very small effect on the isomer shift parameter for the ^{119}Sn resonance (but very large effects on QS!), most of the shift to more negative values for III (+1.50 mm/sec) compared to I and II (1.96 and 1.72 mm/sec, respectively) must be ascribed to the closer approach to tetrahedral bond angles around the tin atom in the former. The absence of quadrupole splitting in the tin resonance spectra of III is completely consistent with earlier data on such molecules and in agreement with Greenwood's rule[19,20] for four-coordinate tin.

The foregoing analysis of the Mössbauer spectra is also consistent with the infrared data obtained on the experimental samples in the carbonyl stretching region. The Nujol-mull spectrum of I shows two strong absorptions at 2027 and 1972 cm^{-1}. In methyltetrahydrofuran solution, however, two additional absorptions are observed at 2005 and 1960 cm^{-1}. In the poly(methyl methacrylate) matrix, there is an additional absorption observed at about 2043 cm^{-1} (the spectrum below about 1980 cm^{-1} is inaccessible owing to high absorption by the matrix). Similar effects are observed in the infrared spectrum of IV, which shows two strong bands at 2030 and 1978 cm^{-1} in Nujol mulls (with very weak bands at 2015 and 1942 cm^{-1}) whereas the poly(methyl methacrylate) matrix samples showed strong bands at 2036, 2010, and 1982 cm^{-1} and a medium strong absorption at 2053 cm^{-1}. In contrast, the infrared spectra of II and III were essentially identical for Nujol-mull and poly(methyl methacrylate) absorbers, and showed no significant bands in the region between the two carbonyl bands observed for the solid. These results are in good agreement with those obtained for $(\pi\text{-}C_5H_5)Fe(CO)_2Si(CH_3)Cl_2$ and $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_3$ by Jetz and Graham,[16] for $(CH_3)_2ClSnMn(CO)_5$ by Jetz, *et al.*,[24] and qualitatively for those obtained for $(CH_3)_3SnW(CO)_3C_5H_5$ and $(CH_3)_2Sn[Mo(CO)_3C_5H_5]_2$ by Patil and Graham.[25] Since the poly(methyl methacrylate) disks used for the infrared measurements were those also used in the Mössbauer studies, it can be concluded that these matrices represent homogeneous solutions rather than small crystalline domains imbedded in the structureless matrix. In the case of the MTHF solutions, it has been noted that owing to the high-temperature dependence of the viscosity of this solvent, no evidence for nucleation and subsequent crystal growth has been observed when rapidly freezing solutions from room temperature to 78°K. In cases where preferential crystal orientation gives rise to large intensity asymmetries in the two quadrupole doublets (*e.g.*, $C_8H_8Fe(CO)_3$ and related compounds[3]), essentially equal intensities are observed in the MTHF frozen solution Mössbauer spectra, suggesting a random orientation of the solute molecules with respect to the optical axis.

Finally it should be noted that the data for the ^{57}Fe resonance in I and IV support and extend the conclu-

---

[19] (a) N. N. Greenwood, P. G. Perkins, and D. H. Wall, Proceedings of the Symposium on the Mössbauer Effect, London, Dec 1967; Symposium of the Faraday Society, No. 1, in press; (b) T. C. Gibb and N. N. Greenwood "Application of the Mössbauer Effect in Chemistry and Solid State Physics," Technical Reports, Series 50, IAEA, Vienna, 1966, p 163.

[20] R. H. Herber and G. I. Parisi, *Inorg. Chem.*, **5**, 769 (1966).

[21] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[22] J. P. Bocquet, Y. Y. Chu, O. C. Kistner, and M. L. Perlman, *Phys. Rev. Letters*, **17**, 809 (1966); V. I. Gol'danskii and E. F. Makarov, *Discussions Faraday Soc.*, in press; S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, *Phys. Rev.*, **159**, 239 (1967).

[23] R. F. Bryan, *J. Chem. Soc., A*, 192 (1967).

[24] W. Jetz, P. Simons, J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

[25] H. R. H. Patil and W. A. G. Graham, *ibid.*, **5**, 1401 (1966).

sions drawn by Jetz and Graham[16] concerning the nonuniqueness of group IVb trichlorides as ligands. Clearly the effect on the electronic environment around the iron atom in the (π-C_5H_5)Fe(CO)$_2$ moiety is the same for the $GeCl_2$ and $SnCl_2$ bridging groups in the neat solids. This observation can be exploited in the interpretation of data on analogous compounds in which the nature of the organic group bonded to the tin atom is systematically varied [*i.e.*, [(π-C_5H_5)Fe(CO)$_2$]$_2$SnR$_2$ and (π-C_5H_5)Fe(CO)$_2$SnR$_3$ in which R = CH_3, C_2H_5, C_6H_5, etc.]. Such experiments are currently under way in these laboratories.

IV. Summary and Conclusions

The preceding spectroscopic study suggests that the anomalous metal–metal and metal–halogen bond distances observed in [(π-C_5H_5)Fe(CO)$_2$]$_2$SnCl$_2$ and [(π-C_5H_5)Fe(CO)$_2$]$_2$GeCl$_2$ arise from the bonding interactions within the molecules rather than from intermolecular stacking forces between molecules in the solid. The ^{119}Sn resonance spectra of the –SnCl$_2$ compound—interpreted in conjunction with the ^{57}Fe resonance parameters and the infrared absorption data in the carbonyl region—show the existence of two different conformational entities in solution. These two forms are associated with the two rotational isomers which can be obtained by a rotation of the metal–metal bond and are analogous to those which have been suggested for related molecules in which the (π-C_5H_5)Fe(CO)$_2$ moiety is bonded to a fragment which lacks threefold or higher symmetry. It is obvious that Mössbauer spectroscopy can be used as a powerful spectroscopic tool in the study of organometallic compounds both as neat solids and in glassy matrices of appropriate solvents and thus provide a bridge between the structural information derived from X-ray diffraction data, on the one hand, and infrared and nuclear magnetic resonance data, on the other. In this way, the apparent discrepancy which has on a number of occasions been found to exist between the two sets of results may be resolved.

Acknowledgments.—This research was supported in part by the U. S. Atomic Energy Commission and constitutes Document NYO-2472-50. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Finally, the authors are indebted to Professor F. G. A. Stone and Drs. I. Paul and P. Woodward for a number of helpful discussions and for the samples generously provided.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA 27514

Metalocyclopentadiene Complexes of Iridium and Rhodium and Their Role in the Catalytic Cyclotrimerization of Disubstituted Acetylenes[1]

BY JAMES P. COLLMAN,[2] JUNG W. KANG, WILLIAM F. LITTLE, AND MICHAEL F. SULLIVAN[3]

Received January 29, 1968

Metalocyclopentadiene complexes of iridium(III) and rhodium(III) have been prepared from acetylenes. Provisional structures have been assigned to these metalocycles on the basis of infrared and nmr spectra of five- and six-coordinate complexes. Cyclotrimerization of disubstituted acetylenes is catalyzed by the coordinatively unsaturated metalocycles. Using an isotopically labeled substrate, the sequential cyclotrimerization of acetylenes has been elucidated. A tentative mechanism is proposed for acetylene cyclization.

A wide variety of transition metal complexes, especially carbon monoxide derivatives, act as catalysts for the cyclotrimerization of acetylenes to benzene derivatives.[4–6] These reactions usually require heating, and induction periods are often observed.

An early suggestion[7] that cyclobutene complexes are intermediates in cyclotrimerization was later discarded when cyclobutene complexes[8] were found to be stable under the usual conditions for acetylene cyclization. Three other mechanisms have been advanced to account for the catalytic trimerization of acetylenes. Schrauzer[5] proposed coupling of three acetylenes which are coordinated to the metal at mutually *cis* positions. This mechanism has the advantage of explaining the cyclotetramerization of acetylene when a fourth coordination site is available. Meriwether[9] proposed a scheme based on the oxidative addition of

---

(1) A preliminary account of this work was presented at the International Conference on Organometallic Chemistry, Munich, Aug 1967.

(2) Correspondence should be addressed to this author at the Department of Chemistry, Stanford University, Stanford, Calif.

(3) Abstracted from the Ph.D. Thesis of M. F. Sullivan, University of North Carolina, 1967.

(4) W. Hübel and C. Hoogzand, *Chem. Ber.*, **93**, 103 (1960).

(5) G. N. Schrauzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964).

(6) J. P. Collman in "Transition Metal Chemistry," Vol. II, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, pp 89–100.

(7) T. L. Cairns, V. A. Engelhardt, H. L. Jackson, G. H. Kalb, and J. C. Sauer, *J. Amer. Chem. Soc.*, **74**, 5636 (1952).

(8) P. M. Maitlis in "Advances in Organometallic Chemistry," Vol. IV, F. G. A. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1966, pp. 95–141.

(9) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962).