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Phosphine, Arsine, and Stibine Derivatives of $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$. The Nature of the Iron–Tin Bond[1]

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Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ (R = CH_3, C_6H_5, Cl) with L (L = phosphine, arsine, stibine) gives $(\pi\text{-}C_5H_5)Fe(CO)(L)SnR_3$ and, in some cases, also $(\pi\text{-}C_5H_5)FeL_2SnR_3$. The ^{119m}Sn and ^{57}Fe Mössbauer spectra of the complexes are reported. Values for the isomer shift (δ) for both nuclei become more positive upon introduction of L thus suggesting that metal–metal π bonding is of little importance. Infrared spectra of the monocarbonyl derivatives in the carbonyl stretching region exhibit doublets in some cases, suggesting that rotational isomers are present in solution. Proton and ^{19}F nmr spectra of the complexes are discussed. For disubstituted complexes containing the phosphine ligands $(C_6H_5)_{3-n}P(CH_3)_n$ (n = 1, 2) 1:2:1 triplets are obtained for the methyl resonances. These give additional evidence that virtual coupling can occur when ligands are mutually cis.

Introduction

Although the covalency of heteronuclear metal–metal bonds has been established for some time, there is still some controversy over their exact nature and, in particular, over the existence of multiple bonding between metals such as silicon, germanium, and tin and the transition metals iron, cobalt, or manganese.

The concept of a multiple bond has been used to explain some features of the chemistry of this type of compound.[2] Thus, the carbonyl infrared data of $Co(CO)_4$[3], $Mn(CO)_5$,[2b,d] and $(\pi\text{-}C_5H_5)Fe(CO)_2$[4] derivatives have been interpreted in terms of π bonding and in the case of $R_3MMn(CO)_5$ compounds a "quasi-theoretical" treatment[5] of force constant data separated σ and π effects.[6] Similar ir results along with dipole moment measurements were used by Ugo and coworkers to show that π effects were unimportant,[7] thus reversing their conclusions of an earlier paper.[2d] They concluded that observed trends in carbonyl stretching frequencies could be ascribed to a purely inductive mechanism through a very polarizable σ bond. However, values of ν(Sn–Fe), ν(Sn–Mn), etc. have been interpreted[8] in terms of a π-bonding model.

Fluorine-19 nmr studies on pentafluorophenyltin derivatives of manganese pentacarbonyl by Graham and his associates[9] indicated that the acceptor strength of the tin atom decreased going from SnC_6H_5 to $SnMn(CO)_5$. This was considered to be consistent with the view that the Sn–Mn bond is multiple in character involving donation of electrons from filled 3d manganese orbitals to vacant 5d orbitals of tin. A similar view is held by Brown and coworkers[10] as a result of ^{59}Co and ^{35}Cl nuclear quadrupole resonance studies.

Of all the instrumental methods available, the one supplying the least ambiguous information on bonding is X-ray crystallography. A number of structure determinations have been carried out, primarily on Sn–Mn, Sn–Fe, and Si–Co systems.[11] In most cases to date, a metal–metal bond length shorter than that of the sum of covalent radii has been found and from this information multiple-bond character has been inferred. Depending upon covalent radii chosen, metal–metal bond lengths have been shortened as much as 0.22 Å. However, *not* all distances which should be indicators of π bonding are shortened.[12] Bryan[13] has also shown that trans substitution by $(C_6H_5)_3P$ (a weaker π acceptor) for carbon monoxide in $(C_6H_5)_3SnMn(CO)_5$ brings about a shortening of the Mn–Sn bond by 0.04 Å, an observation which would be expected on the basis of a simple π-bond model.[2c] Recently, Bryan and coworkers[14] have shown that the Sn–Fe bond in $(\pi\text{-}C_5H_5)Fe(CO)_2SnX_3$ (X = Cl, Br) is shortened relative to the same bond in the triphenyltin derivative (X = C_6H_5), to what appears to be a limiting value.

Calculations on the extent of d-orbital participation in the Co–Si bond show that this is very slight.[11]

Although the application of Mössbauer spectroscopy to metal–metal bond studies is not new,[15,16] there is still much to be done in development of the technique for this purpose. For this present study we have chosen the system $(\pi\text{-}C_5H_5)Fe(CO)(L)SnR_3$ (R = CH_3, C_6H_5,

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[1] Presented in part at the Joint National Meeting of the American Chemical Society and the Chemical Institute of Canada, Toronto, May 1970.

[2] For example: (a) R. D. Gorsich, *J. Amer. Chem. Soc.*, **84**, 2486 (1962); (b) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966); (c) R. B. King and K. H. Pannell, *ibid.*, **7**, 1510 (1968); (d) R. Ugo, F. Cariati, F. Bonati, S. Cenini, and D. Morelli, *Ric. Sci.*, **36**, 253 (1966); (e) R. D. Cramer, R. V. Lindsay, Sr., C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, **87**, 658 (1965); (f) G. W. Parshall, *ibid.*, **88**, 704 (1966).

[3] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

[4] J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc. A*, 2744 (1969).

[5] W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

[6] See L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, **12**, 53 (1969), for a critical evaluation of these procedures.

[7] R. Ugo, S. Cenini, and F. Bonati, *Inorg. Chim. Acta*, **1**, 451 (1967).

[8] N. A. D. Carey and H. C. Clark, *Inorg. Chem.*, **7**, 94 (1968).

[9] M. G. Hogben, R. S. Gay, A. S. Oliver, J. A. J. Thompson, and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 291 (1969).

[10] T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *Inorg. Chem.*, **8**, 763 (1969); see also D. D. Spencer, J. L. Kirsch, and T. L. Brown, *ibid.*, **9**, 235 (1970).

[11] For aré sumé of Sn–Mn and Si–Co bonded structures, see A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

[12] K. Emerson, P. R. Ireland, and W. T. Robinson, *Inorg. Chem.*, **9**, 436 (1970).

[13] R. F. Bryan, *J. Chem. Soc. A*, 172 (1967).

[14] (a) R. F. Bryan, P. T. Greene, G. A. Melson, and P. F. Stokely, *Chem. Commun.*, 722 (1969); (b) R. F. Bryan, *J. Chem. Soc. A*, 192 (1967).

[15] D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **90**, 6226 (1968).

[16] R. H. Herber and Y. Goscinny, *Inorg. Chem.*, **7**, 1293 (1968).

TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES

	R	L	Color	Mp,[a] °C	% calcd		% found		Yield, %	Crystallization solvent
					C	H	C	H		
				Compounds of the Type $(\pi\text{-}C_5H_5)Fe(CO)(L)SnR_3$						
1	C_6H_5	$(C_6H_5)_3P$[b]	Orange	192–194	66.3	4.6	66.1	4.7	46	Benzene–ethanol
2		$(C_6H_5)_3As$[c]	Red	154–158 dec	62.7	4.4	63.2	4.6	28	Benzene–ethanol
3		$(C_6H_5)_3Sb$	Red	127–129	59.2	4.1	59.2	4.1	65	Benzene–ethanol
4		f_6fos[d]	Red	170–175 dec	60.4	4.8	60.4	4.2	21	CH_2Cl_2–hexane or CH_2Cl_2–ethanol
5	CH_3	$(C_6H_5)_2CF_3P$[e]	Orange	142–144	59.0	4.0	58.9	4.1	39	
6		$(C_6H_5)_2CH_3P$	Orange	180–182	63.6	4.8	63.4	4.7	. . .	CH_2Cl_2–methanol
7		$(C_6H_5)(CH_3)_2P$	Yellow	~30	60.3	4.9	60.6	4.9	~20	Hexane at −78°
8		$(C_6H_5)_3P$	Orange[f]	95–103 (125–127)	58.7	5.3	58.7	5.4	61	Benzene–ethanol
9		$(C_6H_5)_3As$	Red-brown	120–122	52.4	4.7	51.7	5.1	50	Acetone–methanol
10		$(C_6H_5)_3Sb$	Orange-red	92–94	48.7	4.4	48.7	4.4	33	Ether–ethanol
11		f_6fos[g]	Brown-red	144–145 dec	53.3	4.0	53.5	4.2	35	Benzene–ethanol or ether–methanol
12		$(C_6H_5)_2CF_3P$[h]	Orange	108–110	46.6	4.3	46.6	4.3	. . .	Methanol[j]
13		$(C_6H_5)_2CF_3As$[i]	Orange	85–87	43.3	4.0	43.6	4.0	18	Methanol[k]
14	Cl	$(C_6H_5)_3P$	Red	175–185 dec	41.6	3.1	41.6	2.9	21	Benzene–petroleum ether or CH_2Cl_2–petroleum ether at −78°
				Compounds of the Type $(\pi\text{-}C_5H_5)FeL_2SnR_3$						
15	C_6H_5	$(C_6H_5)_2CH_3P$	Red-brown	110–140 dec	67.5	5.3	67.6	5.4	. . .	CH_2Cl_2–methanol
16		$(C_6H_5)(CH_3)_2P$	Red-brown	170–180 dec	62.7	5.7	62.3	5.5	30	CH_2Cl_2–methanol
17	CH_3	$(C_6H_5)_3Sb$	Dark red	130–148 dec	53.3	4.5	53.8	4.6	23	Benzene–petroleum ether

[a] All melting points uncorrected. [b] Fe analysis: calcd, 7.3; found, 7.1. P analysis: calcd, 4.1; found, 4.3. Molecular weight (osmometric in acetone solution): calcd, 761; found, 731. [c] As analysis: calcd, 9.3; found, 8.9. O analysis: calcd, 2.0; found, 2.1. Molecular weight (osmometric in acetone): calcd, 805; found, 801. [d] P analysis: calcd, 5.9; found, 5.9. [e] F analysis: calcd, 7.6; found, 7.4. [f] Analysis results are for molecule containing 0.5 mol of benzene. O analysis: calcd, 2.6; found, 3.1. P analysis: calcd, 5.0; found, 5.1. Melting point in parentheses is for nonsolvated material (lit.[2c] mp 127–128°). [g] F analysis: calcd, 13.3; found, 12.9. [h] F analysis: calcd, 9.9; found, 9.8. [i] F analysis: calcd, 9.3; found, 9.1. [j] Purified by chromatography on Florisil using 80:20 petroleum ether–benzene. [k] Purified by chromatography on Florisil using 95:5 petroleum ether–benzene.

Cl) because of the number of spectroscopic handles (two Mössbauer nuclei, proton nmr, and ir) that it possesses. Hopefully by combining the two sets of Mössbauer parameters with nmr (and possibly ir) data, we would be able to obtain useful information about the metal–metal bond.

Experimental Section

New compounds of the type $(\pi\text{-}C_5H_5)Fe(CO)(L)SnR_3$ (R = C_6H_5, CH_3, Cl) were prepared in a manner similar to that of King and Pannell.[2e] Benzene or acetone solutions of the complexes $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ (usually 1 mmol) together with excess (50–100%) ligand were exposed to ultraviolet radiation from a 450-W Hanovia lamp for not less than 5 hr. The uv source was contained in a water-cooled quartz jacket. All reactions were carried out under nitrogen in Pyrex flasks approximately 6 in. from the source. The reactions were monitored by following the disappearance of the CO absorptions due to the starting carbonyl complexes. General procedure for work-up involved the removal of the reaction solvent and addition of hexane or petroleum ether to the red oil thus obtained in order to precipitate decomposition products.[17] After filtration, the solvent was again removed and the red oil recrystallized from the appropriate solvent as given in Table I. Where both the mono- and disubstituted complexes were obtained from one reaction (see text), separation was accomplished by fractional crystallization.

The complexes $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ were prepared using published procedures,[2a] as were the ligands $(C_6H_5)_2PCF_3$[18] and $(C_6H_5)_2AsCF_3$.[19] The ditertiary phosphine f_6fos was prepared as reported previously[20] and all other ligands were obtained commercially. Reagent grade solvents were used in all cases and petroleum ether used had the boiling range 30–60°.

Infrared spectra were obtained on a Perkin-Elmer Model 457 grating instrument and calibrated against polystyrene. Nmr measurements were made on Varian Associates Models A-60, T-60, and HA-100 spectrometers. The ^{57}Fe and ^{119m}Sn Mössbauer data were collected and analyzed as described previously.[20,21] In computer fitting the Mössbauer data using a nonlinear least-squares method, Lorentzian line shapes were assumed, but no other constraints were imposed. Several of the ^{119}Sn spectra exhibited what appeared to be a single broad absorption which was clearly non-Lorentzian. In these cases statistically significant improvements in fit resulted from the use of two Lorentzians rather than one.

Microanalyses were carried out by Mr. P. Borda of this department. Melting points were obtained using a Gallenkamp apparatus and are uncorrected.

Results and Discussion

Preparation.—The physical properties and analytical data for the new complexes reported here are given in Table I.

There have been numerous descriptions[22] in the

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(17) In some instances decomposition was severe and yields (Table I) were accordingly low.

(18) M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, **40**, 283 (1962).

(19) W. R. Cullen, *ibid.*, **30**, 445 (1960).

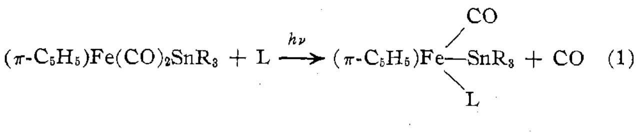
(20) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 95 (1969).

(21) P. A. Yeats, J. R. Sams, and F. Aubke, *ibid.*, **9**, 740 (1970).

(22) For examples see P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *ibid.*, **5**, 1177 (1966); R. B. King, *ibid.*, **2**, 531 (1963); R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 38 (1964); R. B. King, K. H. Pannell, C. R. Bennett, and M. Ishaq, *ibid.*, **19**, 327 (1969).

literature of various derivatives containing the π-cyclopentadienyliron dicarbonyl group, $\pi\text{-}C_5H_5Fe(CO)_2X$. Derivatives with $X = R_3Sn$ ($R = C_6H_5$, CH_3, Cl) were first reported by Gorsich.[2a] Trihalogenotin derivatives have also been reported by Mays and Pearson[23] and Edmondson and Newlands.[24] Although these complexes containing iron–tin bonds have been known for some time, there has been but one cursory investigation[2c] of their ability to undergo carbonyl substitution by tertiary phosphines and other group V ligands. Consequently, because of the necessity to investigate a number of compounds for our Mössbauer studies we undertook to prepare derivatives containing a wide range of ligands.

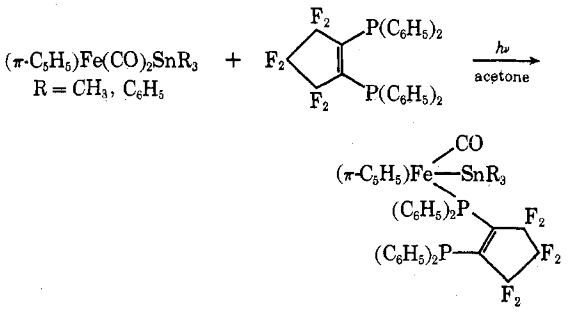
Ultraviolet irradiation of benzene or acetone solutions of $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ ($R = C_6H_5$, CH_3, Cl) and excess ligand was found to be the only method resulting in displacement of carbon monoxide by the ligand. No reaction occurred when the starting materials were refluxed in high-boiling solvents such as toluene or heated in sealed Carius tubes. In the majority of reactions, only the monocarbonyl product was formed



$$(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3 + L \xrightarrow{h\nu} (\pi\text{-}C_5H_5)\underset{L}{\overset{CO}{Fe}}—SnR_3 + CO \quad (1)$$

Three reactions, however, did yield the disubstituted complexes. One, involving $(C_6H_5)_3Sb$ as ligand, produced the complexes **10** and **17** (Table I) in about equal yield. This result was unexpected since $(C_6H_5)_3P$ or $(C_6H_5)_3As$ gave only the monosubstituted derivatives even when a large excess of the ligand was used and reactions were run for an extended time. That the bis-stibine compound was obtained is unusual in view of its much weaker nucleophilicity and large size. Furthermore the weaker π-acceptor properties of triphenylstibine should result in a stronger Fe–CO bond once one carbonyl group has been replaced. Also, in the $(C_6H_5)_3Sn$ series, the phosphines $(C_6H_5)_2PCH_3$ and $(C_6H_5)P(CH_3)_2$ provided the disubstituted complexes **15** and **16** and the monosubstituted complexes **6** and **7** were also obtained. (The last of these (**7**) was extremely difficult to isolate and purify.) Here the facile formation of the disubstituted compound may be due to steric effects and to the greater nucleophilic ability of the phosphine as the number of methyl groups is increased.

King and Pannell[2c] have described the preparation of a chelate complex formed by treating the ditertiary phosphine 1,2-bis(diphenylphosphino)ethane, diphos, with $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(CH_3)_3$. This result was confirmed in the present investigation. However, from a reaction involving the fluorocarbon-bridged ditertiary phosphine $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2(CF_2)_2CF_2}$, f6fos,[20] only the monocarbonyl derivative was obtained (eq 2). This is one of the few instances where a ligand of this kind is monodentate.[25–27] In this case the rigid structure of the ligand does not allow steric interaction to be minimized enough to allow displacement of the second carbonyl group.


(2)

King and coworkers[28] reported that diphos reacts with compounds of the type $(\pi\text{-}C_5H_5)Fe(CO)_2R_f$ (R_f = fluorocarbon group) to give both monosubstituted and disubstituted derivatives, yet the unsaturated ligand *cis*-$(C_6H_5)_2P(H)C{=}(CH)P(C_6H_5)_2$ gives only the disubstituted derivatives. It is claimed[28] that the unsaturated ditertiary phosphine is a better chelating ligand than the saturated one.

All the new complexes are crystalline solids ranging in color from orange to dark red-brown. All are indefinitely stable to air or light in the solid state and decompose slowly in solution. The $(CH_3)_3Sn$ derivatives are less stable in solution and in some cases decomposed while nmr measurements were being made. The $(C_6H_5)_3As$ derivative decomposed partially during recrystallization making good elemental analyses difficult to obtain. Ligands containing the trifluoromethyl group enhanced stability in solution but the methylphosphines decreased stability to the point where the products in the reaction mixture could be identified only by their infrared spectra. Both the $(C_6H_5)_3Sn$ and $(CH_3)_3Sn$ series of derivatives were most stable in acetone or carbon disulfide.

Infrared Spectra.—The infrared data for the carbonyl regions of the monocarbonyl species are given in Table II. All compounds give either two stretching frequencies or one rather broad and unresolved absorption. Two examples are given in Figure 1.

As would be expected, there is a noticeable drop in frequency upon substitution of a group V ligand for a carbon monoxide group. When the ligand contains a fluorocarbon group or is a phosphite, there is less change. This is the usual effect of substituting an electronegative group for a phenyl on the ligand and is often attributed to an enhanced π-acceptor ability.

The observation of either resolved doublets or broad singlets can be attributed to the presence of more than one isomer in solution, the most likely cause being restricted rotation. Jetz and Graham[29] found extra CO

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[23] M. J. Mays and and S. M. Pearson, *J. Chem. Soc. A*, 136 (1969).

[24] R. C. Edmondson and M. J. Newlands, *Chem. Ind. (London)*, 1888 (1966).

[25] The related ditertiary arsine ffars which shows a reluctance to form chelate complexes with iron carbonyls is bismonodentate in the complex $ffarsFe_2(CO)_8$.[27]

[26] W. R. Cullen and D. A. Harbourne, *Inorg. Chem.*, **9**, 1839 (1970).

[27] W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *ibid.*, **8**, 1464 (1969).

[28] R. B. King, R. N. Kapoor, and K. H. Pannell, *J. Organometal. Chem.*, **20**, 187 (1969).

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

TABLE II

IR AND NMR DATA

R	L	ν(CO),[a] cm^{-1}	$\tau_{C_6H_5}$[b]	$\tau_{C_5H_5}$[b]	τ_{CH_3}[b]	J(H–C–^{119}Sn),[b] Hz
		$(\pi\text{-}C_5H_5)Fe(CO)(L)SnR_3$				
C_6H_5	$(C_6H_5)_3P$	1923 sh (5.1), 1911 (10)	2.95	5.78 d[c]	. . .	. . .
	$(C_6H_5)_3As$	1923 (8.3), 1914 (10)	2.91 m[d]	5.72 s	. . .	. . .
	$(C_6H_5)_3Sb$	1919 b	2.90 m	5.60 s	. . .	. . .
	f$_6$fos	1931 b	2.81 m	5.50 d	. . .	. . .
	$(C_6H_5)_2CF_3P$[e]	1935 b	2.93 m	5.47 d	. . .	. . .
	$(C_6H_5)_2CH_3P$	1917 b	2.67 m	5.57 d	8.43 d	. . .
	$(C_6H_5)(CH_3)_2P$	1917 b	2.77 m	5.67 d	8.34, 8.60[f]	. . .
CH_3	$(C_6H_5)_3P$	1921 (4.0), 1911 (10)[g]	2.60 m	5.77 d	10.07 s	40.4[h]
	$(C_6H_5)_3As$	1920 (3.2), 1909 (10)	2.60 m	5.69 s	10.00 s	40.2
	$(C_6H_5)_3Sb$	1921 (sh, 3.7), 1911 (10)	2.62 m	5.58 s	9.97 s	41.4
	f$_6$fos	1923	2.67 m	5.72 d	10.08 s	41.2
	$(C_6H_5)_2CF_3P$[i]	1933 (10), 1923 sh (9)	2.55 m	5.43 d	10.12 s	41.2
	$(C_6H_5)_2CF_3As$[j]	1927 (10), 1921 sh (7.8)	2.51 d	5.47 s	10.03 s	42.2
	$(C_6H_5O)_3P$[k]	1939	2.70 m	5.43	9.60	44.0
Cl	$(C_6H_5)_3P$	1969	2.60 m	5.33 d	. . .	. . .
		$(\pi\text{-}C_5H_5)FeL_2SnR_3$				
C_6H_5	$(C_6H_5)_2PCH_3$	. . .	2.68 m	5.78 t	8.28 t[l]	. . .
CH_3	$(C_6H_5)P(CH_3)_2$	. . .	2.90 m	6.12 t	8.78, 8.62[m]	. . .

[a] Cyclohexane solution. Numbers in parentheses indicate relative intensities of peaks normalized to 10. [b] Ppm relative to $(CH_3)_4Si$. Measured in CS_2 solution unless otherwise indicated. τ values are ±0.03 ppm; J values, ±0.5 Hz. [c] All J(Cp–P) ≃ 1.2 Hz. [d] Most intense peak. [e] The ^{19}F spectrum: δ_F 57.1 ppm (doublet) upfield from $CFCl_3$. J(P–C–F) = 56 Hz. [f] Doublet of doublets. Separation between centers 17.6 Hz. [g] Literature values:[2c] ν(CO) 1918 cm^{-1} (cyclohexane); τ 2.7 (C_6H_5), 5.80 (C_5H_5), 10.11 (CH_3); J(Sn–CH_3) = 39 Hz. [h] $CDCl_3$ solution. [i] The ^{19}F spectrum: δ_F 58.3 ppm (doublet) upfield from $CFCl_3$. J(P–C–F) = 58 Hz. [j] The ^{19}F spectrum: δ_F(acetone solution) 55.6 ppm upfield from $CFCl_3$. [k] Literature values:[2c] ν(CO) 1949 cm^{-1} (cyclohexane); τ 2.78 (C_6H_5), 5.95 (C_5H_5), 9.69 (CH_3); J(Sn–CH_3) = 44 Hz ($CDCl_3$ solution). [l] Apparent J(P–C–H) ≃ 4 Hz. [m] Apparent J(P–C–H) = 4.5 Hz; separation of triplets 16.8 Hz.

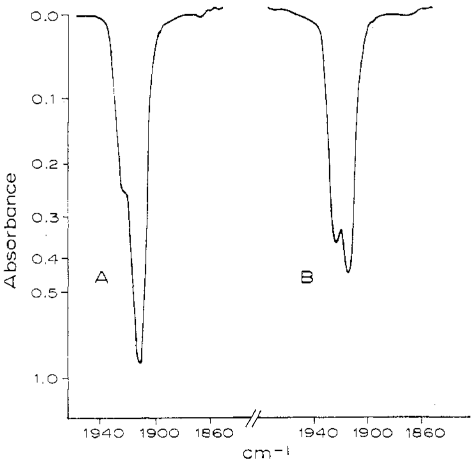

Figure 1.—Infrared spectra in cyclohexane solution of $(\pi\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]Sn(C_6H_5)_3$ (A) and $(\pi\text{-}C_5H_5)Fe(CO)[As(C_6H_5)_3]Sn(C_6H_5)_3$ (B).

stretching bands in the solution spectrum of the compound $CH_3SiCl_2Fe(\pi\text{-}C_5H_5)(CO)_2$ which they attribute to different rotational isomers. A similar phenomenon has been observed[28] for the compound $(CF_3)_2CFFe(CO)(diphos)(\pi\text{-}C_5H_5)$. We feel that the present results indicate that a more subtle manifestation of rotational isomerism is observable in compounds which do *not* have different groups on the atom attached to the iron. The X-ray-determined structure[14a] of the compound $(C_6H_5)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ shows the existence in the solid state of two different molecules per asymmetric unit which differ by rotation about the Sn–Fe bond. The solid compounds $(\pi\text{-}C_5H_5)Fe(CO)_2SnX_3$ (X = Cl, Br) also have different conformations about the Sn–Fe bond[14a] which are different from the two conformations adopted by the solid compound where R = C_6H_5. Figures 2a and 2b show two idealized structures of the compound $(\pi\text{-}C_5H_5)Fe(CO)LSnR_3$ which are different because the R group bisects a different angle at the approximately octahedrally coordinated iron atom[14] (the $\pi\text{-}C_5H_5$ group can be thought of as occupying three coordination positions). Three

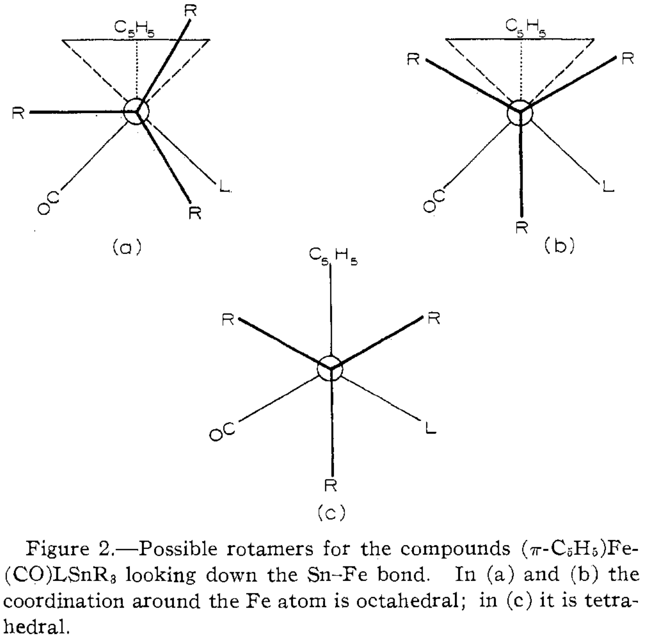

Figure 2.—Possible rotamers for the compounds $(\pi\text{-}C_5H_5)Fe(CO)LSnR_3$ looking down the Sn–Fe bond. In (a) and (b) the coordination around the Fe atom is octahedral; in (c) it is tetrahedral.

TABLE III

MÖSSBAUER DATA AT 78°K[a]

$(\pi\text{-}C_5H_5)Fe(CO)(L)SnR_3$		δ,[b] mm/sec		Δ,[c] mm/sec		Γ,[d] mm/sec	
R	L	Sn	Fe	Sn	Fe	Sn	Fe
C_6H_5	CO[e]	1.41	0.35	...	1.82	0.96	0.28, 0.28
	$(C_6H_5)_3P$	1.48	0.46	0.69	1.84	0.83, 0.83	0.25, 0.26
	$(C_6H_5)_3As$	1.46	0.53	0.67	1.90	0.77, 0.79	0.24, 0.25
	$(C_6H_5)_3Sb$	1.42	0.55	0.56	1.90	1.02, 0.98	0.25, 0.23
	$(C_6H_5)_2PCF_3$	1.50	0.46	0.44	1.83	0.82, 0.65	0.21, 0.22
	$(C_6H_5)_2PCH_3$	1.42	0.47	0.55	1.76	0.80, 0.97	0.23, 0.22
	$(C_6H_5)P(CH_3)_2$	1.47	0.43	0.78	1.71	0.65, 0.91	0.25, 0.25
	$f_6$fos	1.44	0.48	...	1.78	1.03	0.23, 0.24
CH_3	CO	1.41	0.36	0.46	1.75	0.87, 0.73	0.27, 0.29
	$(C_6H_5)_3P$	1.41	0.48	0.42	1.87	0.60, 0.77	0.25, 0.25
	$(C_6H_5)_3As$	1.43	0.53	...	1.94	1.13	0.22, 0.25
	$(C_6H_5)_3Sb$	1.44	0.55	...	1.93	1.03	0.28, 0.29
	$(C_6H_5)_2PCF_3$	1.40	0.44	...	1.91	0.87	0.23, 0.23
	$(C_6H_5)_2AsCF_3$	1.41	0.53	...	1.98	1.07	0.26, 0.25
	$f_6$fos	1.46	0.46	...	1.86	1.01	0.23, 0.22
	$(C_6H_5O)_3P$[f]	1.39	0.39	...	1.86	0.87	0.23, 0.23
Cl	CO[g]	1.77	0.39	1.80	1.84	0.99, 0.99	0.25, 0.25
	$(C_6H_5)_3P$	1.88	0.47	1.88	1.85	0.82. 0.80	0.24, 0.24
Other compds							
$(\pi\text{-}C_5H_5)Fe[Sb(C_6H_5)_3]_2Sn(CH_3)_3$		1.47	0.80	0.73	2.09	0.83, 0.87	0.23, 0.21
$(\pi\text{-}C_5H_5)Fe(diphos)Sn(CH_3)_3$		1.50	0.59	0.70	1.63	1.02, 0.92	0.23, 0.21
$(\pi\text{-}C_5H_5)Fe[(C_6H_5)_2PCH_3]_2Sn(C_6H_5)_3$		1.58	0.67	1.14	1.70	0.95, 0.88	0.21, 0.21
$(\pi\text{-}C_5H_5)Fe[C_6H_5P(CH_3)_2]_2Sn(C_6H_5)_3$		1.71	0.63	1.25	1.70	0.98, 0.74	0.28, 0.26

[a] All measurements made on the neat solids, with the source (^{57}Co (Pd) or Ba^{119m}SnO$_3$) at room temperature. Estimated errors: Fe, ±0.01 mm/sec; Sn, ±0.03 mm/sec. [b] Isomer shift relative to sodium nitroprusside (Fe) or SnO_2 (Sn). [c] Quadrupole splitting. [d] Full width at half-maximum. In the case of doublets, the value listed first corresponds to the lower energy absorption. [e] Literature values:[16] δ_{Sn} 1.50, δ_{Fe} 0.37, Δ_{Sn} 0, Δ_{Fe} 1.83 mm/sec. [f] Reference 2c. [g] Literature values:[16] δ_{Sn} 1.74, δ_{Fe} 0.40, Δ_{Sn} 1.77, Δ_{Fe} 1.86 mm/sec.

such rotamers are possible each having a fully staggered R group. If both the iron and the tin atom were tetrahedrally coordinated (Figure 2c), then only one completely staggered conformation would be possible. We suggest that rotamers of the type shown in Figure 2a exist in solution and have a sufficiently long lifetime to be detected by infrared spectroscopy. The intensities of the bands are not equal, showing that there is a greater population of one of the rotamers. It is also noteworthy that while the more intense band moves to higher or lower energies depending on the electronegativity of the ligand, the less intense shoulder is seen at 1920–1923 cm^{-1}. It should be noted that this type of rotational isomerization could be present *in addition to* that suggested by Jetz and Graham[29] when the groups on the atom attached to iron are not identical. However the derivatives of $(C_6H_5)_2MCF_3$ (M = P or As) or $f_6$fos which should have rotamers of one sort or the other failed to show even doublets in their spectra.

The Iron–Tin Bond —In choosing systems containing two Mössbauer nuclei for study, it was presupposed that changing the chemical environment about the iron would have some effect upon the tin as well as the iron parameters. We began by considering what possible changes in the isomer shift, δ, would be expected depending upon whether or not there was significant π bonding between the metal atoms. If the π bonding was between the filled 3d orbitals on iron and the vacant tin 5d orbitals, replacement of one or both carbonyl groups of the compounds $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ would be expected to have the net effect of decreasing the π interaction between the ligand and the iron atom, thus allowing greater d-electron density for donation from the iron atom to the tin. This would probably result in a decrease in s-electron density (increased shielding) at the iron nucleus. At the tin nucleus, the greater shielding by acquired d electrons would reduce the s-electron density here as well. Accordingly, on replacing CO by a worse π acceptor, we would expect a positive shift in δ for iron and a negative shift in δ for tin.

As can be seen from the data presented in Table III, the reverse is what actually occurs for tin. Isomer shift values, upon the substitution of L for CO, *increase* for both tin and iron, indicating a *decrease* of s-electron density at the latter and an *increase* at tin. Values of δ_{Sn} are essentially independent of L whereas those for iron are not—a point we shall return to below.

The values for the tin–methyl proton coupling constants (Table II) for the methyl series all fall when L replaces CO[30] and, like δ_{Sn}, are substantially independent of L. Assuming the main contribution to $J(^{119}Sn\text{–}C\text{–}H)$ is from the Fermi contact term, then we can relate the coupling constants to the fraction of "s" character in the tin–carbon bond.[31,32] If it is also assumed that there is a constant amount of tin "s" orbital used in the tin sp^3 hybrids in this series (this does not seem unreasonable since the atoms bonded to Sn do not change), the increase in s-electron density at tin (as reflected by δ_{Sn}) is accompanied by a *decrease* in s character in the Sn–C bonds (as reflected by

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(30) $J(^{119}Sn\text{–}C\text{–}H)$ for the dicarbonyl is 47.2 Hz.

(31) J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

(32) T. F. Boles and R. S. Drago, *ibid.*, **88**, 5730 (1966).

$J(^{119}Sn\text{-}C\text{-}H)$. This suggests that there is an increased s-electron transfer from iron to tin on substituting CO by L and a concentration of s character in the Fe–Sn bond.[33] A similar conclusion has been reached by Fenton and Zuckerman[15] with respect to the M–Sn bond in the compounds $(CH_3)_{4-n}SnM_n$ where M_n is a metal carbonyl group. If we define the Fe–Sn bond direction as the z axis, we can say that the s and p_z orbitals on tin will be mainly involved in the bond to Fe, while p_x and p_y are mainly used for bonding the methyl groups. This will result in an imbalance in p-orbital charge densities (and concomitant distortion from tetrahedral symmetry) which can account for any quadrupole splitting that might be observed in the Sn resonance (*vide infra*).

As mentioned above, data for the tin and iron isomer shifts show also that δ_{Fe} is dependent upon L whereas that for tin is not. Unlike δ_{Sn} which is affected by what transpires in the metal–metal bond, δ_{Fe} is affected both by this *and* by the nature of L. From the results for the methyl compounds we find the following ordering of s-electron density at iron: CO > $(C_6H_5O)_3P$ > $(C_6H_5)_2PCF_3$ > f$_6$fos > $(C_6H_5)_3P$ > $(C_6H_5)_3As$ > $(C_6H_5)_2AsCF_3$ > $(C_6H_5)_3Sb$. We suggest that this ordering is a measure of the relative ability of these ligands to act as π acceptors; *i.e.*, the metal to ligand back-π-donation is greatest for CO and least for $(C_6H_5)_3Sb$. (This is supported by the remarkably high δ_{Fe} for the disubstituted $(C_6H_5)_3Sb$ complex, **17**.) For the phenyl derivatives there are some differences in the ordering and values for the phosphines show less numerical differences. The overall trend, however, is much the same.

Table III shows that quadrupole splitting values, Δ, for the trimethyltin monocarbonyl compounds are zero except for the case where L = $(C_6H_5)_3P$. For analogous $(C_6H_5)_3Sn$ derivatives, however, most exhibit Δ values ranging from 0.44 to 0.69 mm/sec.[34,35] The fact that $\Delta_{Sn} \neq 0$ (Figure 3b) for the phenyltin series can be readily explained by the model defining the z axis as the Sn–Fe bond direction. There will be a smaller imbalance in p-orbital charge densities in the methyl series and hence a smaller electric field gradient (EFG).

The splitting of 0.42 mm/sec for the $(C_6H_5)_3P$ complex, **8**, is the smallest ever observed and very near the limit of resolution. The fact that a half-width of 0.596 mm/sec is less than the minimum observable width of 0.62 mm/sec suggests the resolution here may be fortuitous.

The Δ values for iron in the methyl series show a trend similar to that of the isomer shifts although the value is approximately constant for the arsenic and antimony derivatives. This could arise from Fe–L π interactions although steric effects might also play an important role.

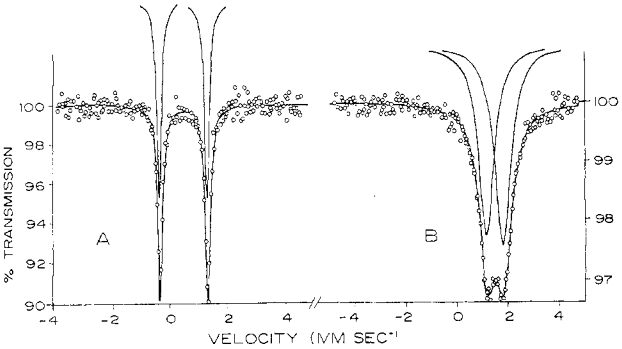

Figure 3.—The ^{57}Fe (A) and ^{119}Sn (B) Mössbauer spectra of $(\pi\text{-}C_5H_5)Fe(CO)[As(C_6H_5)_3]Sn(C_6H_5)_3$. The Lorentzian components are given by the solid lines.

Steric effects probably are more dominant in the disubstituted complexes. All exhibited nonzero Δ values for tin which, as in the monosubstituted compounds, were higher for the phenyl series. Although the spectra were poorly resolved, these higher values of Δ_{Sn} suggest that there must be a greater displacement of the groups around tin away from tetrahedral symmetry so that the second ligand can be accommodated. This effect may also be aided by additional concentration of s character in the Sn–Fe bond.

Table III shows that Δ_{Fe} for the disubstituted complexes have no apparent trend. It can be noted however that, where phosphines are involved, values decrease from those of either the dicarbonyls or the monocarbonyls. The bis-stibine complex, **17**, was the only one which brought about a substantial increase to over 2 mm/sec. This, again, could be a result of the bulkiness of the $(C_6H_5)_3Sb$ ligand.

Herber and Goscinny[16] have pointed out that the iron parameters are essentially independent of R in the compounds $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ (R = CH_3, C_6H_5, Cl). The lower δ_{Sn} value for R = C_6H_5 as compared to R = Cl was ascribed[16] to a closer approach to tetrahedral bond angles about tin in the former and the tin splitting in the chloro compound was ascribed to (d–p)-π effects. However, an alternative explanation now seems more likely.

If in the methyl compound the bonds from tin to iron on the one hand and tin to the methyl groups on the other have similar charge densities, no splitting would be observed. The situation would be nearly the same in the phenyl compound, although there is apparently a small increase in p-electron withdrawal toward the phenyl groups, resulting in a slightly higher δ_{Sn}. In the chloro compound a marked increase in p character in the bonds to the more electronegative substituents would be predicted. Thus there will be a significant difference in charge densities in the p_z orbital (directed toward iron), on the one hand, and the p_x and p_y orbitals (directed toward the chlorine), on the other. This will both distort the bond angles from tetrahedral (Cl–Sn–Cl decreasing, Fe–Sn–Cl increasing) and withdraw p-electron density from tin. Hence we have the increase in δ_{Sn} and the EFG needed to produce a splitting. On this model the increase in δ, the nonzero Δ, and the distor-

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[33] This would indicate also that the $(\pi\text{-}C_5H_5)Fe(CO)L$ moiety has become more electropositive according to the ideas of H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[34] It is interesting to note that this is the opposite of observations made for a series of organotin complexes, *i.e.*, $\Delta(C_6H_5\text{-}Sn) < \Delta(CH_3\text{-}Sn)$.[33]

[35] R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 2145 (1969).

tion from tetrahedral symmetry are all explained by the imbalance in p-electron density, without resorting to π bonding.

The Mössbauer data given above by themselves argue against appreciable π-bonding effects between the two metals and indeed this is also the conclusion reached as a result of X-ray structural studies. However, two factors which must be considered give us reason to inject a small note of caution into the conclusions based on our Mössbauer data. First, it is difficult to know just how big an effect produced by the introduction of L is required to give a noticeable change in the isomer shifts. Ideally a small effect producing a sizable change would be desirable. We have shown that introduction of a group V ligand has the effect of giving initial positive shifts to both iron and tin parameters. However, only iron appears to be sensitive to the nature of the ligand. We have suggested that this observation, together with the result that a change of the R group on tin has little effect on the iron atom, is good evidence against (d–d)π interactions. However, it may be argued that changing L has not been a great enough effect to produce a noticeable trend in δ_{Sn}. We feel that the fact alone that δ_{Sn} is more positive is sufficient to counter this argument.

Second, other work[13] has suggested that substitution of phosphine for a CO group in $(C_6H_5)_3SnMn(CO)_5$ and a concomitant shortening of the Sn–Mn bond is evidence for an increase in Sn–Mn π bonding over that which existed in the parent compound.

In an octahedral complex a ligand trans to another will share two potentially π-bonding d orbitals whereas cis ligands will share only one. Since the iron complexes are approximately octahedral if the π-C_5H_5 ring is regarded as occupying three coordination sites and all ligands are mutually cis, it might be supposed that π-bonding effects would not be as pronounced and hence may not be reflected in the ^{119m}Sn Mössbauer parameters.

The X-ray crystal structure[36] of $(\pi\text{-}C_5H_5)Fe(CO)(f_6fos)Sn(CH_3)_3$, **11**, has been determined and one striking feature of the structure is that there appears to be no shortening of the Sn–Fe bond. The length of 2.56 Å, although shorter than the sum (2.67 Å) of covalent radii, is actually slightly longer (0.02 Å) than that of $(\pi\text{-}C_5H_5)Fe(CO)_2Sn(C_6H_5)_3$.[14b] Here, since there is, as yet, no structure of the $(CH_3)_3Sn$ parent compound, we are assuming similar Sn–Fe distances. This, we feel, is a valid assumption judging from the identical values obtained for $(CH_3)_3SnMn(CO)_5$[37] and $(C_6H_5)_3SnMn(CO)_5$.[38] Although there might be a slight tendency for the electronegative fluorocarbon group to strengthen the P–Fe bond (which would weaken any existing Fe–Sn π linkage), the effect is probably not overly great[39] and the ligand would have roughly the same effect as $(C_6H_5)_3P$. Thus, substitution of a phosphine for a CO group need not lead to bond shortening as previously suggested.[13]

The position of substitution clearly needs to be taken into consideration when discussing the effects on π bonding in the molecule. In this connection it is worth noting that there are three independent Ru–Sn bond lengths in the compound $[(CH_3)_3Sn(CO)_3RuSn(CH_3)_2]_2$.[40] Two of these are approximately equal to the sum of the covalent radii for tin and ruthenium (~2.70 Å) and the other which is trans to a carbonyl group is shortened. This shortening is ascribed to (d–d)π bonding even though it is trans to what is presumably the best π acceptor in the molecule. One other feature of the molecule is that it contains a second-row transition metal which ought to facilitate[41] π bonding to the tin but apparently does not.

^{1}H and ^{19}F Nmr Studies.—The nmr data for the new complexes prepared in this study are shown in Table II. Phenyl proton resonances as usual were observed in the τ 2.5–3.0 region. Cyclopentadienyl resonances occurred from τ 5.3 to 6.1 depending upon the electronegativity of the ligand and the degree of substitution. As expected, the chemical shifts for C_5H_5 decreased owing to greater electron density on the iron. Coupling of the ring protons to phosphorus produced either 1:1 doublets (monosubstituted) or 1:2:1 triplets (disubstituted) and all such compounds exhibited J(H–P) values of approximately 1.2 Hz. That the splittings were indeed due to P–H coupling was confirmed *via* heteronuclear decoupling. This technique was applied to the disubstituted $(C_6H_5)P(CH_3)_2$ compound, **16**. Irradiation of the triplet due to the C_5H_5 group caused collapse to a singlet (Figure 4). Similar treatment of the methyl resonances (a doublet of triplets) at the same frequency brought about collapse (Figure 5) to a doublet (with a separation of 16.8 Hz) which would be due to the magnetic nonequivalence of the methyl groups.[42] A

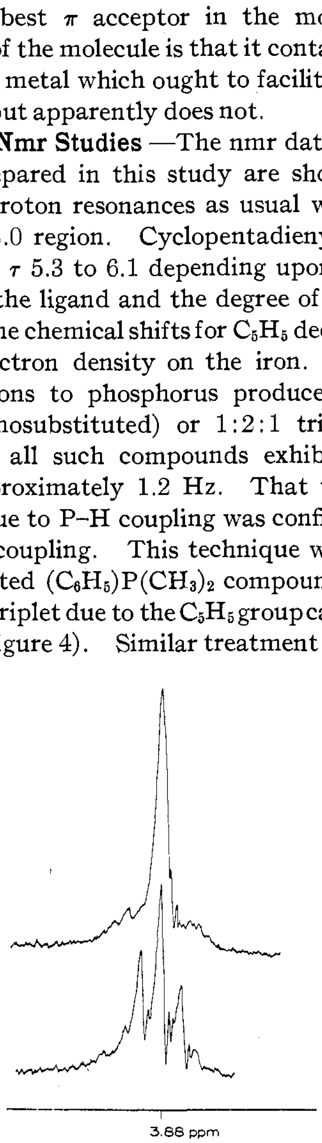

Figure 4.—Proton nmr spectra of the cyclopentadienyl region for $(\pi\text{-}C_5H_5)Fe[(C_6H_5)P(CH_3)_2]_2Sn(C_6H_5)_5$. The upper spectrum shows the result of ^{31}P–C–H spin decoupling.

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(36) F. W. B. Einstein and R. Restivo, to be submitted for publication.

(37) R. F. Bryan, *J. Chem. Soc. A*, 696 (1968).

(38) H. P. Weber and R. F. Bryan, *Acta Crystallogr.*, **22**, 822 (1967).

(39) There is a rise of 12 cm^{-1} (Table II) in the carbonyl stretching frequency of the $f_6$fos compound over that for the $(C_6H_5)_3P$ derivative, indicating a *slight* decrease in the Fe–C bond strength.

(40) S. F. Watkins, *J. Chem. Soc. A*, 1552 (1969).

(41) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **9**, 440 (1970).

(42) Similar to that seen in $\sigma\text{-}C_6H_5CH_2(\pi\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3]$, due to inequality of the benzylic methylene protons: J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **91**, 1550 (1969).

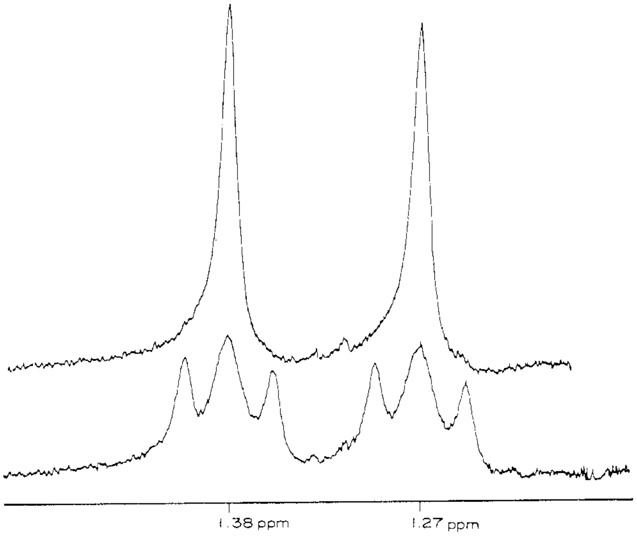

Figure 5.—Methyl proton nmr spectra of (π-C_5H_5)Fe[(C_6H_5)P$(CH_3)_2$]$_2$Sn$(C_6H_5)_3$ before and after (upper spectrum) ^{31}P–C–H spin decoupling.

single triplet was obtained for the $((C_6H_5)_2PCH_3)_2$ complex, **15**. In both cases where triplets were obtained the methyl groups are strongly coupled to both phosphorus atoms. This "virtual coupling" phenomenon has been used previously to establish a trans disposition of ligands in square-planar Pt and Pd complexes[43] and to distinguish between isomers of octahedral Rh[44] and Ir[45] complexes. However, in the light of recent ^{31}P–^{31}P coupling studies[46] it now appears as if this phenomenon must be interpreted with a degree of caution. The appearance of an apparent triplet cannot be interpreted strictly in terms of trans ligands. It seems apparent that several factors govern the magnitude of the coupling of the phosphorus atoms. The systems in the present investigation serve to emphasize caution that must be applied since, although ligands are arranged cis about iron, triplets are still obtained and coupling between methyl protons is apparently just as strong. The apparent J(P–C–H) values are 4.5 Hz for the $(C_6H_5)P(CH_3)_2$ compound, **16**, and 4 Hz for the $(C_6H_5)_2PCH_3$ derivative, **15**. These values are similar to those found by Shaw and coworkers[43–45] for the Pt, Ir, and Rh complexes. It is worth mentioning that the central line in the triplet from **15** is much broader than the other two. This is in contrast with the methyl spectrum of **16** in which the central lines of both triplets are quite sharp. The former case is probably similar to the intermediate coupling pattern observed by Shaw and coworkers.[47]

The tin–methyl coupling constants have been discussed above. The chemical shifts are in all cases higher ($\tau \geq 10$) than the parent dicarbonyl. King[2c] has reported similar values which are among the highest known for methyltin–metal carbonyl derivatives. This reflects the increased σ-electron density produced by the presence of the donor ligands.

The ^{19}F spectra were obtained for the trifluoromethylphosphine and -arsine derivatives **5**, **12**, and **13**. The phosphine spectra appeared as the expected doublets with J(F–C–P) values varying little from those of the free ligands.

One purpose in preparing complexes of $(C_6H_5)_2PCF_3$[13] and $(C_6H_5)_2AsCF_3$[19] was to look for the presence of rotamers by studying their ^{19}F nmr spectra. It was hoped that, upon cooling, the singlet of the arsine or the doublet of the phosphine would split. However, cooling to the point of crystallization ($\sim -100°$ in both cases) brought about only a slow normal line broadening due to decreased resolution. Apparently either the isomers that are evident in the infrared spectra have too short a lifetime to be observed on the nmr time scale or the cooling reduces the equilibrium amount of one rotamer so that it is unobservable.[48]

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(43) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 770 (1966).

(44) P. R. Brookes and B. L. Shaw, *ibid.*, 1079 (1967).

(45) B. L. Shaw and A. C. Smithies, *ibid.*, 2784 (1968).

(46) R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1908 (1970); F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *ibid.*, 1916 (1970).

(47) J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc. A*, 2796 (1969).

(48) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and F. S. Denisov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1348 (1968).