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^{55}Mn Nuclear Magnetic Resonance Studies of the Compounds with Manganese-Tin Bonds

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The nature of Mn-Sn bonds has been studied by ^{55}Mn-NMR and IR spectroscopies of a series of compounds, $R_{3-x}X_xSn\text{-}Mn(CO)_5$, where R is C_6H_5 or CH_3 and where X is Cl or Br. Molecular orbital considerations have shown that the chemical shift of the ^{55}Mn-NMR spectra is a measure of the σ-polarity of the L-Mn bond in L-$Mn(CO)_5$-type complexes, and that the linewidth is mainly determined by the π-interaction between Mn and Sn. The π-interaction (back-donation from Mn to Sn) seems to be most pronounced in $Br_3Sn\text{-}Mn(CO)_5$ in the series of $(CH_3)_{3-x}Br_xSn\text{-}Mn(CO)_5$ compounds. The relationships among the chemical shift, the wave numbers of CO stretching modes, and the eqQ are also shown.

The aim of the present report is to ascertain, by the aid of the ^{55}Mn-NMR, the σ-character and the π-character of metal-metal bonds in the complexes, $R_{3-x}X_x$ $Sn\text{-}Mn(CO)_5$, which have been studied using Mössbauer spectroscopy,1) where X and R stand for Cl, Br and C_6H_5, CH_3 respectively.

The L-$M(CO)_5$-type compounds, where L and M represent a ligand and a metal atom respectively, have been extensively investigated, since the octahedral symmetry around the metal atom permits the independent treatment of the σ- and the π-characteristics of the chemical bonds in these complexes.2–9) The most successful method thus far employed to study these complexes is to measure the CO stretching frequencies in the infrared region and to interpret the data in terms of the σ- or the π-electron donation from L to M or the back donation from M to L, including cases of M-M′ bonds.10) According to Graham,10) these two donation powers can be quantitatively expressed by the two parameters, σ and π, which can be calculated from the CO stretching data. We have found that the NMR spectra of ^{55}Mn offer useful information concerning these two characteristics.

Some NMR data on organometallic compounds containing the Mn atom have been reported by Calderazzo, Lucken, and Williams11) and by Miles *et al.*,12) but no compound containing metal-metal bonds has thus far been subjected to similar study.

The NQR techniques were also introduced by Brown to the study of metal-metal bonds in cobalt complexes with a C_{3v} symmetry.13,14)

Experimental

Materials. All the compounds except $(CH_3)Cl_2Sn\text{-}Mn(CO)_5$, $(CH_3)_2BrSn\text{-}Mn(CO)_5$, and $(CH_3)Br_2Sn\text{-}Mn(CO)_5$ were prepared by the methods of Gorsich15) and Graham.16) All the reactions were carried out under a dried nitrogen atmosphere.

$(CH_3)_2BrSn\text{-}Mn(CO)_5$: A solution of $NaMn(CO)_5$ was prepared from 5.9 g (0.015 mol) of $Mn_2(CO)_{10}$ in 100 m*l* of anhydrous tetrahydrofuran (THF) by stirring the mixture over an excess of 1% sodium amalgam; it was then slowly dropped into a stirred solution of 9.24 g (0.03 mol) of $(CH_3)_2SnBr_2$ in 100 m*l* of THF. The THF solution was kept overnight in a refrigerator. The organic layer separated from fine precipitates by using a centrifugal separator was condensed under reduced pressure. The yellow residue thus obtained was recrystallized from hexane at 0°C; yellow crystals were then obtained by filtration (yield, 80%).

Found: C, 19.96; H, 1.25%. Calcd for $C_7H_6O_5BrMnSn$: C, 19.84; H, 1.43%.

$(CH_3)Cl_2Sn\text{-}Mn(CO)_5$: A mixture of 2.1 g (0.005 mol) of $Cl_3Sn\text{-}Mn(CO)_5$ and an equimolar amount of $(CH_3)_2ClSn\text{-}Mn(CO)_5$ was heated at 130°C for 10 min. The crude product was recrystallized from hexane to give 2.9 g of pale yellow crystals (yield, 50%).

Found: C, 18.18; H, 0.68%. Calcd for $C_6H_3O_5Cl_2MnSn$: C, 18.03; H, 0.76%.

$(CH_3)Br_2Sn\text{-}Mn(CO)_5$: A mixture of 1.95 g (0.0035 mol) of $Br_3Sn\text{-}Mn(CO)_5$ and 0.63 g (0.00175 mol) of $(CH_3)_3Sn\text{-}Mn(CO)_5$ was heated at 130°C for an hour. The crude product was then recrystallized from hexane to give 0.71 g of yellow crystals (yield, 28%).

Found: C, 14.77; H, 0.45%. Calcd for $C_6H_3O_5Br_2MnSn$: C, 14.75; H, 0.62%.

The purities were determined by carbon and hydrogen analyses and by melting-point or decomposition-point measurements.

NMR Spectra. The ^{55}Mn-NMR spectra were registered as derivative curves at 10 KOe and 10.55 MHz on a Varian

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Table 1. ^{55}Mn-NMR chemical shift, linewidth and CO stretching frequencies

	Compound	Chemical shift (ppm±10)	Linewidth (oersted±0.01)	CO-Stretching frequencies (cm^{-1})		
				A_1^2	E	A_1^1
1.	$Cl_3Sn\text{-}Mn(CO)_5$	2024	0.18	2126	2046	2040
2.	$Br_3Sn\text{-}Mn(CO)_5$	2044	0.17	2124	2045	2038
3.	$PhCl_2Sn\text{-}Mn(CO)_5$	2278	0.30	2116	2033	2025
4.	$(CH_3)Cl_2Sn\text{-}Mn(CO)_5$	2312	0.28	2114	2032	2020
5.	$PhBr_2Sn\text{-}Mn(CO)_5$	2252	0.24	2116	2034	2026
6.	$(CH_3)Br_2Sn\text{-}Mn(CO)_5$	2256	0.25	2116	2034	2021
7.	$Ph_2ClSn\text{-}Mn(CO)_5$	2460	1.45	2104	2017	2013
8.	$(CH_3)_2ClSn\text{-}Mn(CO)_5$	2520	1.10	2102	2008	2016
9.	$Ph_2BrSn\text{-}Mn(CO)_5$	2468	1.70	2106	2019	2010
10.	$(CH_3)_2BrSn\text{-}Mn(CO)_5$	2485	1.00	2104	2010	2018
11.	$Ph_3Sn\text{-}Mn(CO)_5$	2610	3.57	2095	2004	2004
12.	$(CH_3)_3Sn\text{-}Mn(CO)_5$	2660	1.58	2090	1994	2002
13.	$Mn_2(CO)_{10}$	2331	<0.1			
14.	$Cl\text{-}Mn(CO)_5$[a]	1005	0.182			
15.	$Br\text{-}Mn(CO)_5$[a]	1160	0.378			
16.	$I\text{-}Mn(CO)_5$[a]	1485	0.557			
17.	$CF_3\text{-}Mn(CO)_5$[a]	1850	1.76			
18.	$CF_3CO\text{-}Mn(CO)_5$[a]	1850	1.83			
19.	$CHF_2\text{-}Mn(CO)_5$[a]	1970	2.30			
20.	$CH_2F\text{-}Mn(CO)_5$[a]	2130	2.38			
21.	$CH_3\text{-}Mn(CO)_5$[a]	2265	1.69			
22.	$H\text{-}Mn(CO)_5$[a]	2630	2.39			
23.	$CH_3CO\text{-}Mn(CO)_5$[a]	1895	2.11			
24.	$NaMn(CO)_5$[a]	2780	5.82			

a) F. Calderazzo, E. A. C. Lucken, and D. F. Williams, *J. Chem. Soc.*, *A*, **1967**, 154.

Associates VF-16 NMR spectrometer at room temperature. The manganese samples were sealed, as 0.25 mol solutions in methylene chloride, into glass tubes 8 mm in diameter under a nitrogen atmosphere. An aqueous solution of potassium permanganate (10% concentration) was used as the external standard. The linewidth, ΔH, was represented by the interval between the points of the maximum slopes.

Infrared Spectra. The spectra in the CO-stretching region were recorded with a Hitachi EPI-G2 spectrometer in hexane solutions (2—3 mg/m*l* except $Cl_3Sn\text{-}Mn(CO)_5$) with a 0.1-mm KBr liquid cell. The spectra of $Cl_3Sn\text{-}Mn(CO)_5$ were measured with a KBr variable-path-length liquid cell in a hexane solution because of its low solubility in the solvent.

All the results of the NMR and IR measurements are listed in Table 1, together with some data cited from the report by Calderazzo *et al.*[11)]

Discussion

Infrared Spectra. Graphs presenting the linear relationship between the infrared wave numbers of A_1^2, A_1^1, and E modes and the chemical shift are shown in Fig. 1. The force constants, not found in the literature, of $R_{3-x}Br_xSn\text{-}Mn(CO)_5$ were obtained by the method of Cotton and Kraihanzel[4)]; the results are listed in Table 2, along with the values of k_2, k_1, k_i and σ- and π-parameters[10)] for the compounds $R_{3-x}Br_xSn\text{-}Mn(CO)_5$ (R is CH_3 and C_6H_5).

NMR Data. The NMR data in Table 1 show that the successive substitution of the halogen atoms on the tin atom by phenyl or methyl groups results in changes in the chemical shift of ^{55}Mn as large as 600 ppm. The chemical shift increases almost linearly with the number of the organic group on the tin atom, as

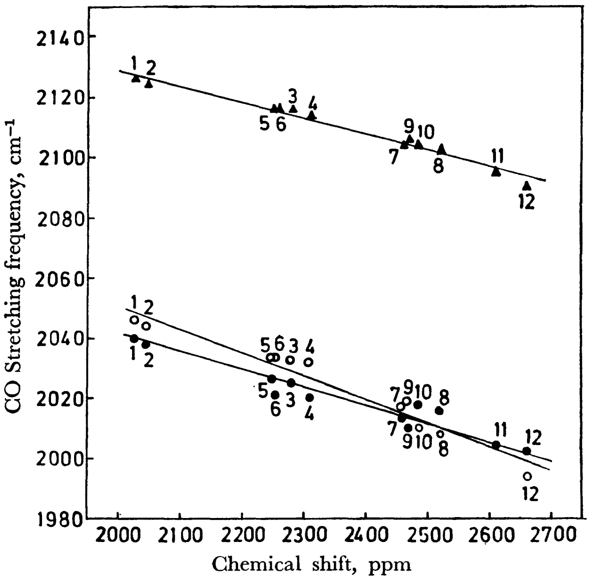
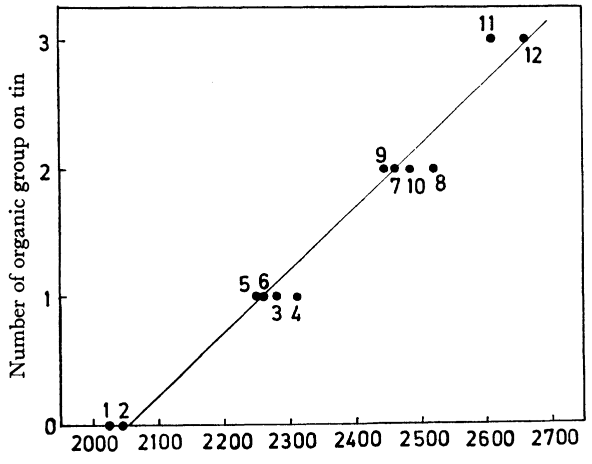


Fig. 1. Stretching frequency of A_1^2, A_1^1, and E bands *versus* ^{55}Mn-chemical shift. Upper series assigned as A_1^2 and lower series as E and A_1^1. Points labeled by ○ and ● correspond to E and A_1^1 bands respectively. The numbers in the graphs represent the compounds in Table 1.

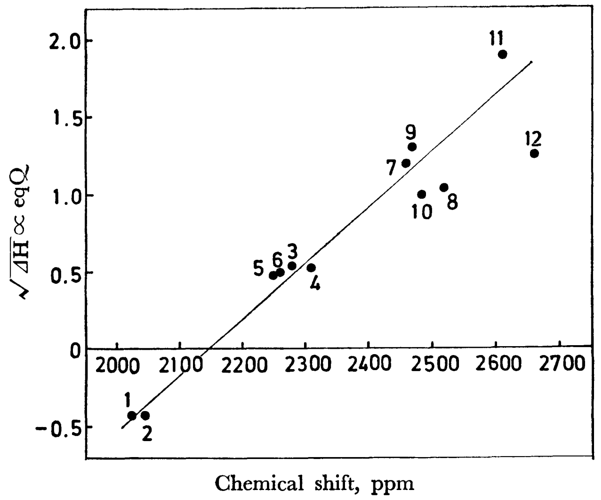
Table 2. CO stretching force constants and Graham's σ- and π-parameter

Compound	Force constant, mdyn/Å			Graham's σ- and π-parameter, mdyn/Å	
	k_1	k_2	k_i	σ	π
Br_2PhSn–$Mn(CO)_5$	16.67	17.14	0.21	0.08	0.24
$Br_2(CH_3)Sn$–$Mn(CO)_5$	16.59	17.13	0.21	0.14	0.17
$BrPh_2Sn$–$Mn(CO)_5$	16.62	16.85	0.19	−0.45	0.48
$Br(CH_3)_2Sn$–$Mn(CO)_5$	16.60	16.80	0.24	−0.53	0.51



Chemical shift, ppm

Fig. 2. Effect of organic groups on ^{55}Mn-chemical shift.



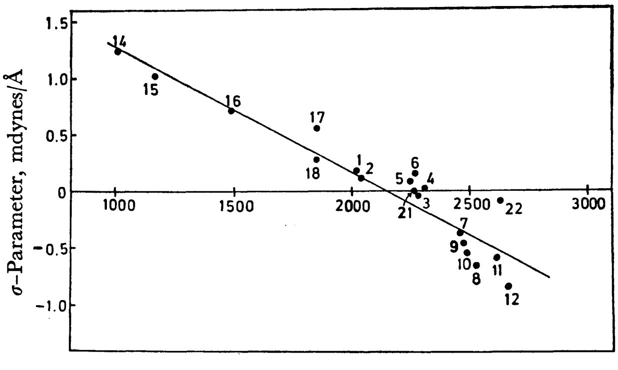
Chemical shift, ppm

Fig. 3. The relationship between chemical shift and quadrupolar coupling constant. The signs of $\sqrt{\Delta H} \propto$ eqQ for X_3Sn-$Mn(CO)_5$ are chosen as minus signs.

is shown in Fig. 2.[17] On the other hand, the change in halogen atoms in $X_xR_{3-x}Sn$–$Mn(CO)_5$ from Cl to Br causes only a slight shift, as is shown in Table 1. All the NMR data can be most conveniently presented on the $\sqrt{\Delta H}$ *versus* chemical-shift graph given in Fig. 3. A remarkable feature of the graph, which is a characteristic of the compounds containing Sn–Mn bonds, is that the linewidth narrows drastically from Ph_3Sn–$Mn(CO)_5$ to X_3Sn–$Mn(CO)_5$, along with the change in the ligands on the tin atom. In the CH_xF_{3-x}–$Mn(CO)_5$ series, no such abrupt narrowing has been reported.[11] The sign of $\sqrt{\Delta H}$ is not obtained from the experiments described in this paper, but a change in the sign of the field gradient between X_3Sn–$Mn(CO)_5$ and X_2RSn–$Mn(CO)_5$ in the present series of compounds is suggested by the data shown in Fig. 3.

As we have reported previously,[1] the plotting of the NMR chemical shift of ^{55}Mn against the isomer shift of the ^{119}Sn-Mössbauer spectra suggests that the ^{55}Mn-chemical shift can be interpreted in terms of the σ-electron transfer from Mn to Sn. This finding that the ^{55}Mn-chemical shift can be interpreted in terms of the σ-character of the L–Mn bond is substantiated by the following relationship. As is shown in Fig. 4, the ^{55}Mn-chemical shift is linear to the σ-parameters[18] which are concerned with the σ-character of the L–Mn bond.[19] For these reasons, the following molecular orbital considerations are acceptable.

According to Ramsey,[21] the so-called paramagnetic shift, which mainly determines the variations in the chemical shift of transition elements, is given by the



Chemical shift, ppm

Fig. 4. The relationship between ^{55}Mn-chemical shift and Graham's σ-parameter. Graham's σ-parameters are cited from the literature, (W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).), and from Table 2.

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[17] The linearity of the chemical shift with the sum of the electronegativity of the halogen atoms on tin is also observed. The analogous linearity of the CO stretching frequencies with the sum of the electronegativity of the halogen atoms on tin has been already reported by Patmore, Thompson, and Graham in cases of the complexes $R_{3-x}X_xGe$-$Co(CO)_4$ and $R_{3-x}X_xSn$-$Mn(CO)_5$: D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967), J. A. J. Thompson and W. A. G. Graham, *ibid.*, **6**, 1875 (1967).

[18] Graham's σ-and π-parameters are obtained by the use of these formulae: $k_1=\sigma+2\pi+c_1$, $k_2=\sigma+\pi+c_2$. He rather arbitrarily assumed that $\sigma=\pi=0$ for the CH_3-$Mn(CO)_5$ complex in order to fix the two constants c_1 and c_2.

[19] The correspondence of σ-bond polarity with the "σ-parameter" calculated from infrared data has been reported for many cases.[7,17,20]

[20] F. R. Dean and J. C. Green, *J. Chem. Soc.*, *A*, **1968**, 3047.

[21] N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

expression:

$$\sigma_p = -\frac{e^2}{2m^2c^2}\sum_{n\neq 0}(E_n-E_0)^{-1}[\langle\psi_0|\sum_i l_i|\psi_n\rangle\langle\psi_n|\sum_k l_k r_k{}^{-3}|\psi_0\rangle$$
$$+\langle\psi_n|\sum_i l_i|\psi_0\rangle\langle\psi_0|\sum_k l_k r_k{}^{-3}|\psi_n\rangle]$$

where ψ_0 and ψ_n denote wave functions of, respectively, the ground and excited states of the atom in question, and where l_i and r_i are angular operators and the distance from the metal nucleus to the i-th electron. Single-electron molecular energy schemes for L–Mn(CO)$_5$ have been reported by Gray and Billing[22] and by Anderson and Brown.[23] The one-electron *d-d* transitions from the ground state ($^1A_1$) are:

$$b_2\ (\pi,\ 3d_{xy}) \longrightarrow b_1\ (\sigma^*,\ 3d_{x^2-y^2}),\ (^1A_1-{}^1A_1),\ \Delta E_1$$
$$b_2\ (\pi,\ 3d_{xy}) \longrightarrow a_1\ (\sigma^*,\ 3d_{z^2}),\ (^1A_1-{}^1B_2),\ \Delta E_2$$
$$e\ (\pi,\ 3d_{xy,yz}) \longrightarrow b_1\ (\sigma^*,\ 3d_{x^2-y^2}),\ (^1A_1-{}^1E_u),\ \Delta E_3$$
$$e\ (\pi,\ 3d_{xz,yz}) \longrightarrow a_1\ (\sigma^*,\ 3d_{z^2}),\ (^1A_1-{}^1E_v),\ \Delta E_4$$

The second transition does not contribute to the shift in the case of the present molecular symmetry, and ligand-charge transfer transitions from e (π, L and CO) to the upper σ-antibonding levels are disregarded because of very low values of both r^{-3} and $\Delta E_n{}^{-1}$. The values of ΔE may be obtained by measuring the *d-d* transition spectra, but, in the present case, no data are available because of the intense charge-transfer bands in this region. When this approach is used, the following expression is obtained for the paramagnetic shift:

$$\sigma_p = -\frac{e^2\hbar^2}{2m^2c^2}\langle r^{-3}\rangle C_{a_1g}\left[\frac{8C_{a_2}}{\Delta E_1}+\frac{4C_{E_u}}{\Delta E_3}+\frac{12C_{E_v}}{\Delta E_4}\right]$$

where C_n denotes the coefficient of the metal *d*-orbital in the molecular orbitals.[20,24] However, it is characteristic of the octahedral L–Mn(CO)$_5$-type compounds that the b_2 (π, $3d_{xy}$) and e (π, $3d_{xz,yz}$) levels are virtually non-bonding, so the values of ΔE_1, ΔE_3, and ΔE_4 are mainly determined by the b_1 (σ^*, $3d_{x^2-y^2}$) and a_1 (σ^*, $3d_{z^2}$) levels, which are correlated only with the σ-bonding between manganese and tin atoms or carbon atoms of carbonyl groups. As the strength of the σ-bond between Sn and Mn increases, the value of ΔE_n increases. The molecular antibonding orbital constants, C_n, increase from $Mn(CO)_5^-$ to $Mn(CO)_5^+$ through $R_3Sn-Mn(CO)_5$, $X_3Sn-Mn(CO)_5$, and X–Mn(CO)$_5$. The increase in ΔE_n causes the paramagnetic shift to decrease, while an increase in C_n causes the paramagnetic shift to increase. Thus, changes in C_n rather than in ΔE_n or in $\langle r^{-3}\rangle$ must be mainly responsible for the observed trend in the chemical shift, as has been reported in the case of platinum complexes.[22] Therefore, the following order of the values of the chemical shift may be a good measure of the σ-bond polarity of the L–Mn bonds:[11]

$Cl<Br<I<CF_3=CF_3CO<CH_3CO<CHF_2<Cl_3Sn\leqq Br_3Sn<CH_2F<PhBr_2Sn\leqq(CH_3)Br_2Sn\leqq CH_3\leqq PhCl_2Sn\leqq(CH_3)Cl_2Sn\leqq Mn(CO)_5<Ph_2ClSn\leqq Ph_2BrSn\leqq(CH_3)_2BrSn<(CH_3)_2ClSn<Ph_3Sn\leqq H\leqq(CH_3)_3Sn$

The L–Mn bond may be most ionic in $Cl^{\delta-}$—$^{\delta+}Mn(CO)_5$ and in $(CH_3)_3Sn^{\delta+}$—$^{\delta-}Mn(CO)_5$ and "covalent" at $(CO)_5Mn-Mn(CO)_5$.

The linewidth of the ^{55}Mn-NMR absorption is expressed by this formula:[25]

$$\Delta H = \frac{9}{500\sqrt{2}}\cdot\left(1+\frac{\eta^2}{3}\right)\cdot\left(\frac{eQ}{\hbar}\cdot\frac{\partial^2V}{\partial z^2}\right)^2\cdot\tau_c$$

In the present type of complex, the asymmetry parameter, η, is of zero value because of the C_{4v} symmetry around the Mn nucleus. Accordingly, the linewidth of LMn(CO)$_5$ complexes is determined by two factors, the principal field gradient, $\partial^2V/\partial z^2$, and the correlation time, τ_c. However, the changes in the linewidth in a series of complexes of the $(CH_3)_{3-x}Br_xSn-Mn(CO)_5$ type, as is shown in Table 1, are attributable to the change in the field gradient, because these complexes, being similar in molecular size, will give almost the same τ_c value.[26,27] Following the molecular orbital treatment of LMn(CO)$_5$ by Gray and Billing,[22] it may be deduced that the energy difference, ΔE_0, between two π-orbitals, b_2 (π, $3d_{xy}$) and e (π, $3d_{xz,yz}$) localized on Mn determines the field gradient at the Mn nucleus, or that the field gradient at the Mn nucleus is sensitive to the π-interaction between Mn and Sn. The contributions from other orbitals may be of secondary importance because of their small r^{-3} values. From the above consideration, we obtain the following order of the π-interaction between manganese and tin atoms from the linewidths:

$Br_3Sn-Mn(CO)_5>(CH_3)Br_2Sn-Mn(CO)_5>(CH_3)_2BrSn-Mn(CO)_5>(CH_3)_3Sn-Mn(CO)_5$

The fact that the π-accepting tendency of the X$_3$Sn-group is stronger than that of the (CH$_3$)$_3$Sn-group[28] is well expressed by the larger differences in the linewidth, but Graham's π-parameters of $Br_3Sn-Mn(CO)_5$, $Br_2(CH_3)Sn-Mn(CO)_5$, $Br(CH_3)_2Sn-Mn(CO)_5$, and $(CH_3)_3Sn-Mn(CO)_5$ all have practically the same values within the limits of experimental error.[10] The linewidth of the ^{55}Mn-NMR spectra can, then, be thought to be a better measure of the π-interaction than the π-parameter proposed by Graham, at least in the present case.

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25) A. Abragam, "The principle of Nuclear Magnetism," Chapter VIII, Oxford (1962).

26) P. Debye, "Polar Molecules," Chapter V. Reinhold (1928).

27) According to the ^{55}Mn-NMR work on compounds of $Mn(CO)_{5-x}(PF_3)_xH$, the linewidth is mainly dependent on the eqQ value and not on τ_c.[12]

28) P. N. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc., A*, **1967**, 1889.