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REACTION OF DI-SUBSTITUTED MANGANESE CARBONYL ANION, $[Mn(CO)_3L_2]^-$ (L = $P(OPh)_3$ AND PPh_3), WITH R_3MX (M = C, Si, Ge, AND Sn; R = CH_3, C_2H_5, C_6H_5, AND Cl; X = Cl OR Br) AND NMR STUDY OF THE MOLECULAR DYNAMICS IN A NEW TYPE OF CONFORMERS FOR $R_3Sn—Mn(CO)_3[P(OPh)_3]_2$

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Summary

The reactions of the title anion with R_3MX for various combinations of R have been studied. The hydride, $HMn(CO)_3L_2$, is obtained with Me_3CCl, Me_3SiCl, and Me_3GeBr and both the hydride and $Ph_3Sn—Mn(CO)_3L_2$ are obtained with Ph_3SnCl in the case of L = $P(OPh)_3$. $R_3Sn—Mn(CO)_3L_2$ type compounds are obtained with Me_3SnBr, Me_2SnCl_2, $Me_2PhSnBr$, $MePhSnCl_2$, Et_3SnCl, and Et_2SnCl_2. $Hg[Mn(CO)_3L_2]_2$ is also obtained as a by-product for all of these reactions. ^{13}C NMR spectroscopy for $Me_3Sn—Mn(CO)_3L_2$ indicates that the compound has a *mer-trans* configuration. From the reaction of $[Mn(CO)_3L'_2]^-$ ($L' = PPh_3$) with Me_3SnBr, a mixture of *fac-cis* and *mer-trans* isomers of $Me_3Sn—Mn(CO)_3L'_2$ is obtained at room temperature and the *trans* isomer is obtained at reflux temperature. ^1H NMR study has shown that a minor isomer is present for $(CH_3)_x(C_6H_5)_yX_zSn—Mn(CO)_3L_2$ and $Et_3Sn—Mn(CO)_3L_2$ at room temperature in toluene-d_8. Their dynamical properties have been studied by ^{13}C and ^1H NMR spectroscopy at various temperatures and the exchange has been proved to proceed by way of an intramolecular rearrangement process. By the comparison of ^1H NMR spectra of *mer-trans* $Me_3Sn—Mn(CO)_3L'_2$ at various temperatures, it has been concluded that the exchange proceeds via rearrangement of P—O—Ph orientations.

Introduction

Previous papers from this (S.O.'s) laboratory have shown that the ^{119}Sn-Mössbauer quadrupole splitting for $R_3Sn—Mn(CO)_{5-n}L_n$ (n = 0 or 1) systems is greatly influenced by the substituents attached to the manganese atom in the *trans* position to the tin atom [1,2]. As a logical extension of this finding, the synthesis of di-substituted compounds, $R_3Sn—Mn(CO)_3L_2$, was attempted in order to obtain further information regarding the influence of weaker π-accepting ligands on the ^{119}Sn-Mössbauer quadrupole splitting. During the course of this study, a new type of stereochemical nonrigidity for six coordinate compounds has been found; this phenomenon is one of the current topics of interest in the study of organometallic compounds [3]. In the present paper, characterization of the reaction products of $[Mn(CO)_3L_2]^-$ (L = $P(OPh)_3$ and PPh_3) with R_3MX and molecular dynamics study of $R_3Sn—Mn(CO)_3[P(OPh)_3]_2$ by NMR are presented.

Experimental

General procedures. All reactions were conducted under dry nitrogen. Solvents were dried over calcium hydride and freed from dissolved molecular oxygen by distillation under dry nitrogen.

Materials. cis- and *trans*-$BrMn(CO)_3[P(OPh)_3]_2$ and *trans*-$BrMn(CO)_3(PPh_3)_2$ were prepared following the literature method [4]. Ph_3SnCl, Me_3SnBr, Et_3SnCl, Me_2SnCl_2, and Me_3GeBr were prepared by the procedures described in the previous papers [1,2,5,6]. Me_3SiCl and Me_3CCl were purchased from Wako Chemical Company. $PhMeSnCl_2$ was prepared according to the literature method [7]. $Me_2PhSnBr$ was prepared as follows: 1.5 g (5 mmol) of Me_2Ph_2Sn was dissolved into 20 ml of ether. To this, 0.8 g (5 mmol) of Br_2 in 10 ml of ether was added with stirring. The mixture was stirred at room temperature for 1 h. The solvent was evaporated at reduced pressure to leave a pale-yellow oil. To this oil was added 10 ml of ether and the resulting white precipitate was removed by filtration. Ether was vacuum stripped and fractional distillation gave a colorless liquid (76—78°C/2 mmHg) (yield: 1.1 g, 72%). (Checked by ^{1}H NMR.)

Synthesis of $Me_3Sn—Mn(CO)_3[P(OPh)_3]_2$ (II). 1.2 g (1.4 mmol) of *trans*-$BrMn(CO)_3[P(OPh)_3]_2$ in 30 ml of THF was reduced to $[Mn(CO)_3\{P(OPh)_3\}_2]^-$ (I) with an excess amount of 1% Na amalgam at room temperature for 2 h and the supernatant solution was decanted into another flask. To this, 0.35 g (1.4 mmol) of Me_3SnBr in 30 ml of THF was added with stirring and the mixture was stirred overnight. The resulting pale-yellow solution was filtered and the solvent was evaporated at reduced pressure to leave a pale-brown oil. The oil was extracted with two 20 ml portions of hot n-hexane. The combined extracts were concentrated to about half the volume and stored in a refrigerator for a weak to give pale-yellow crystals of II. These were collected on a frit and vacuum-dried (yield: 0.7 g, 54%). The same product was also obtained from *cis*-$BrMn(CO)_3[P(OPh)_3]_2$, and it is highly probable that the anion I prepared from *cis*-$BrMn(CO)_3[P(OPh)_3]_2$ has the same structure as that prepared from the *trans* analog. Indeed, the anion prepared from *cis*-$BrMn(CO)_3[P(OPh)_3]_2$ exhibited the same IR spectrum in ν(CO) region in THF solution as that of the anion prepared from *trans* analog. For this reason, only *trans*-$BrMn(CO)_3$-$[P(OPh)_3]_2$ was employed in all other syntheses as the starting manganese carbonyl derivative. A second extraction of the brown residue of the n-hexane extraction was made with 15 ml of hot benzene, and 20 ml of hexane was added to the extract. The mixture was stored in a refrigerator for a week to afford yellow rhombic crystals (III, yield 0.15 g). The ^1H NMR spectrum of III did not display any methyl proton signal and only phenyl protons were detected. Atomic absorption spectroscopy revealed the presence of Hg in III and thus it was characterized as $Hg[Mn(CO)_3\{P(OPh)_3\}_2]_2$. A small portion of the mercury used for sodium amalgam formation undoubtedly is halogenated to $HgBr_2$, and this yields compound III on reaction with the anion. In order to minimize the mercury contamination, the THF solution containing the anion I was filtered using a frit of fine porosity in the later syntheses instead of decantation. Osmometry in benzene solution showed product II was monomeric.

$Et_3Sn—Mn(CO)_3[P(OPh)_3]_2$ (IV), $PhMe_2Sn—Mn(CO)_3[P(OPh)_3]_2$ (V), $ClMe_2Sn—Mn(CO)_3[P(OPh)_3]_2$ (VI), $Et_2ClSn—Mn(CO)_3[P(OPh)_3]_2$ (VII), and $ClMePhSn—Mn(CO)_3[P(OPh)_3]_2$ (VIII) were prepared in a similar fashion.

Reaction of I with Ph_3SnCl. A reaction mixture of the anion I prepared from 1.7 g (2 mmol) of $BrMn(CO)_3[P(OPh)_3]_2$ and 0.77 g (2 mmol) of Ph_3SnCl was similarly worked up. Careful recrystallization from n-hexane afforded white needle-like crystals of $Ph_3Sn—Mn(CO)_3[P(OPh)_3]_2$ (IX) (yield 0.2 g, 9%) and pale yellow crystals of $HMn(CO)_3[P(OPh)_3]_2$ (X) (yield 0.2 g)

Reaction of the anion I with Me_3MX (M = Ge, Si, and C; X = Cl or Br). Two mmol of Me_3MX in 20 ml of THF was added with stirring at room temperature to the THF solution of the anion I, which had been obtained from 2 mmol of $BrMn(CO)_3[P(OPh)_3]_2$. Similar treatment of the reaction mixture gave pale-yellow crystals. IR, NMR, and elemental analyses showed the crystals to be $HMn(CO)_3[P(OPh)_3]_2$ (X). The yield depends on M and ranges from 0.5 to 0.1 g.

Reaction of the $[Mn(CO)_3(PPh_3)_2]^-$ anion with Me_3SnBr. To a THF solution of $[Mn(CO)_3(PPh_3)_2]^-$ (I′), obtained from 2 mmol of *trans*-$BrMn(CO)_3(PPh_3)_2$, was added with stirring 2 mmol of Me_3SnBr in 20 ml of THF, and the mixture was stirred overnight at room temperature. The reaction mixture was similarly worked up and was recrystallized from benzene/petroleum ether to afford a pale-yellow precipitate of XI and XI′ (yield less than 0.1 g). The same reaction was carried out at reflux temperature. Similar work up gave a yellow precipitate (XI′, yield less than 0.1 g).

The results of elemental analyses for these compounds are given in Table 1.

Stability of the hydride X. A *trans*-decalin solution of hydride X in an evacuated pyrex tube was heated at 160°C for 85 h. The IR spectrum of this reaction mixture showed the presence of only starting material. A THF solution of X was allowed to react with a THF solution of Me_3SnBr at 50°C for 24 h. IR monitoring showed that a new peak at 1780 cm^{-1} appeared after 7 h, and its intensity increased with the reaction time. However, we failed to isolate the species which gave rise to the peak at 1780 cm^{-1} and only the starting hydride X was recovered. The hydride was dissolved into $CDCl_3$ and the proton NMR signal at τ 18.1 ppm due to hydrido proton was monitored at room temperature. Even after 96 h, no appreciable proton exchange was detected.

Physical measurements. Infrared spectra were obtained from Nujol mulls or from solution using a JASCO IR-G or JASCO IR-701G spectrometer. IR results are shown in Table 2.

TABLE 1

ANALYTICAL DATA, MELTING POINTS, AND COLORS

Compound	M.p. (°C)	Color	Analysis (Found (Calcd.) (%))		
			C	H	Hg
$(CH_3)_3Sn-Mn(CO)_3[P(OPh)_3]_2$ (II)	111.0—111.5	pale-yellow	54.66	3.90	
			(54.63)	(4.26)	
$Hg[Mn(CO)_3\{P(OPh)_3\}_2]_2$ (III)	135.0—140.0	yellow	54.79	3.56	12.7
			(54.48)	(3.52)	(11.7)
$(C_2H_5)_3Sn-Mn(CO)_3[P(OPh)_3]_2$ (IV)	82.5—83.5	pale-yellow	56.12	4.70	
			(55.98)	(4.70)	
$(C_6H_5)(CH_3)_2Sn-Mn(CO)_3[P(OPh)_3]_2$ (V)	86.5—88.5	white	57.59	4.21	
			(56.76)	(4.25)	
$Cl(CH_3)_2Sn-Mn(CO)_3[P(OPh)_3]_2$ (VI)	106.5—107.5	white	52.15	4.00	
			(52.18)	(3.85)	
$Cl(C_2H_5)_2Sn-Mn(CO)_3[P(OPh)_3]_2$ (VII)	95.5—96.0	white	53.42	4.08	
			(53.14)	(4.15)	
$Cl(CH_3)(C_6H_5)Sn-Mn(CO)_3[P(OPh)_3]_2$ (VIII)		white	54.77	3.73	
			(54.93)	(3.81)	
$(C_6H_5)_3Sn-Mn(CO)_3[P(OPh)_3]_2$ (IX)	112.0—116.0	white	61.68	4.21	
			(61.70)	(4.09)	
$HMn(CO)_3[P(OPh)_3]_2$ (X)	85.0—86.0	white	61.60	3.94	
			(61.66)	(4.08)	
$(CH_3)_3Sn-Mn(CO)_3(PPh_3)_2$ (XI), (XI′)	179—181 [a]	pale-yellow	60.67	4.87	
			(60.97)	(4.75)	

[a] Melting point measured of the *trans* isomer.

TABLE 2

IR DATA IN CO STRETCHING REGION

Compound	ν(CO) (cm^{-1})
II	2000w, 1925vs [a] 2000w, 1940vs, 1930s(sh) [b]
III	2000w, 1972m, 1920s, 1900vs [a] 2000w, 1972vs, 1921vs [c]
IV	1995w, 1920vs [a]; 2005m, 1938vs [c]
V	2006m, 1940vs, 1925vs [a]; 2010m, 1942vs [c]
VI	2011m, 2010(sh), 1955vs, 1942vs, 1925(sh), 1910(sh) [a]; 2028m, 1963vs, 1949s(sh)
VII	2010m, 1955vs, 1935vs, 1910(sh) [a]; 2023m, 1960vs, 1946s(sh) [c]
VIII	2013s, 2005(sh), 1960vs, 1940vs, 1920(sh), 1905(sh) [a]; 2030m, 1968vs, 1951s(sh) [c]
IX	2012s, 1940vs, 1905(sh) [a]; 2019m, 1952vs [c]
X	1997w, 1940vs [a]
XI′ *trans-*	1985w, 1920m, 1895vs [a]; 1990w, 1928m(sh), 1905vs [c]
XI *cis-*	1962w, 1930m, 1876vs [a]; 1970w, 1928m(sh), 1895vs [c]

[a] Nujol mull. [b] Cyclohexane solution. [c] $CHCl_3$ solution.

^1H NMR spectra were taken using a Hitachi—Perkin—Elmer R-20B (60 MHz) apparatus equipped with a variable temperature probe or a Hitachi—Perkin—Elmer R-24A apparatus. TMS was employed as the internal standard. Temperatures were calibrated by use of ethyleneglycol standard. ^{13}C NMR spectra were obtained by the pulse Fourier transform technique using a JEOL JNM-FX60 spectrometer operating at 15.04 MHz. The NMR results are stated in Table 3.

Kinetic analysis. Line shape analysis was performed with a simulation program, which was originally written by Nakagawa [8] and extensively modified by the present author (S.O.). The program utilizes the formalism of Gutowsky and Holm [9]. Chemical shifts and population ratio change with temperature and they were plotted against T^{-1} in the region just below and just above slow exchange [10]. The values obtained by extrapolation of these approximately linear curves to higher temperature regions were used for line-shape simulation. Kinetic data were treated with least-squares fitting [3,11] with the program

TABLE 3

NMR DATA AT ROOM TEMPERATURE

Compound	Chemical shift of alkyl protons, τ (ppm) [a]	$J(^{119,117}Sn—C—H)$ (Hz)
II	9.15(0.84), 9.36(0.16)	43 ± 1.2
IV	8.34(0.68), 8.54(0.32)	
V	8.98(0.84), 9.18(0.16)	44 ± 1.2
VI	8.87(0.90), 9.01(0.10)	41 ± 1.2
VIII	8.66(0.84), 8.83(0.16)	40 ± 1.2
X	18.11 [b] (hydride proton)	50.1 [c]
XI′ *trans-*	9.28 [b]	34 ± 1
XI *cis-*	9.76 [b]	38 ± 1

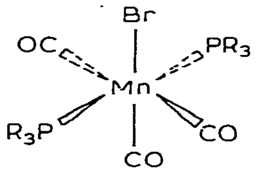
[a] Relative to TMS = 10.0. Solvent toluene-d_8 except where noted otherwise. Numerical values in parentheses are relative populations. [b] Solvent benzene-d_6. [c] J(P—Mn—H) (Hz), triplet.

constructed by the present author (S.O.). All the calculations were carried out by the use of FACOM 230-60 or 230-75 in the Computation Center of Nagoya University or by the use of HITAC 8450 of Nagoya Institute of Technology.

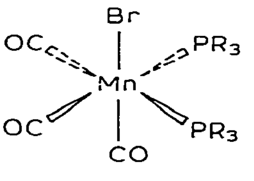
Results and discussion

The reaction of the anion I with Me_3GeBr or Me_3SiCl or Me_3CCl yielded the hydride, $HMn(CO)_3[P(OPh)_3]_2$ (X), instead of the expected $Me_3M{-}Mn(CO)_3[P(OPh)_3]_2$ (M = Ge, Si, and C). Also in the reaction of the anion I with Ph_3SnCl, both the hydride X and $Ph_3Sn{-}Mn(CO)_3[P(OPh)_3]_2$ (IX) were formed. In this reaction, the bulky phenyl groups attached to the tin atom have an unfavorable influence on the formation of IX. Therefore, one dominant factor of the hydride formation in the present type of reaction is the extent of steric repulsion between the R groups in R_3M and the phenyl groups in $P(OPh)_3$. To study the origin of the hydride-hydrogen atom, $(CD_3)_3GeBr$ was synthesized and was allowed to react with the anion I. The resulting compounds was $HMn(CO)_3[P(OPh)_3]_2$. As was already mentioned in the Experimental section, proton exchange seems to proceed quite slowly and it is unlikely that D is exchanged with H after $DMn(CO)_3[P(OPh)_3]_2$ is once formed. This excludes the possibility that the hydrogen comes from the methyl groups. Ugo et al. have shown that for $HMn(CO)_3(PPh_3)_2$ the hydrogen did not come from the ligand PPh_3 when the compound was synthesized by the reaction of dimanganese decacarbonyl with PPh_3 in xylene [12]. For the present hydride, therefore, the hydrogen must come from the solvent (THF) or from a trace amount of water contained in the solvent.

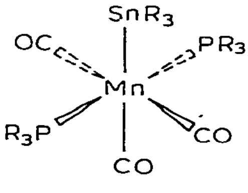
Two specimens of $Me_3Sn{-}Mn(CO)_3[P(OPh)_3]_2$, prepared from *trans*-$BrMn(CO)_3[P(OPh)_3]_2$ (a) and from *cis*-$BrMn(CO)_3[P(OPh)_3]_2$ (b), exhibited the same IR spectrum in the region from 4000 to 400 cm^{-1}, and displayed three peaks in the ν(CO) region. The ^{13}C NMR spectrum of this compound (II) in bromobenzene showed only one triplet signal of 1/2/1 intensities in the carbonyl carbon region and at least three distinct signals in the phenyl carbon region, one of which has a triplet-like structure (Fig. 1). This indicates that two $P(OPh)_3$ groups are located in *trans* position with respect to each other (c).



(a)



(b)



(c)

On the other hand, the IR spectra in the ν(CO) region of the yellow precipitates (XI and XI′) which were synthesized from Me_3SnBr and $[Mn(CO)_3(PPh_3)_2]^-$ at room temperature are quite complex, showing six peaks for the solid sample and five peaks for a chloroform solution, which are double the theoretically allowed number of peaks for *mer-trans* or *fac-cis* configuration. The ^1H NMR spectrum of this precipitate (Fig. 2) clearly exhibited two methyl proton signals which have different coupling constants with $^{119,117}Sn$-nuclei. The ^1H NMR

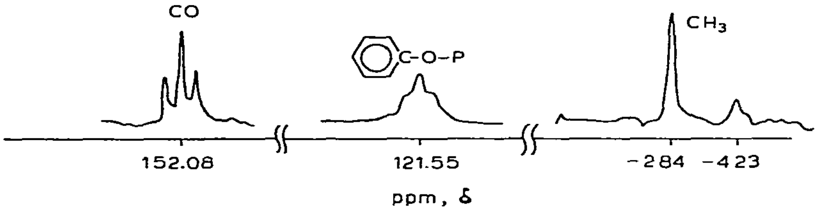


Fig. 1. ^{13}C NMR spectrum of $Me_3Sn{-}Mn(CO)_3[P(OPh)_3]_2$ in C_6H_5Br at room temperature (TMS standard).

spectrum of the yellow precipitate similarly synthesized at reflux temperature, however, showed only one methyl proton signal which corresponds to the lower field peak in Fig. 2 and the IR spectrum in the ν(CO) region for a chloroform solution displayed only three peaks at 1990, 1920, and 1905 cm^{-1} (Table 2). These observations clearly demonstrate that the yellow precipitate obtained from the reaction at room temperature is a mixture of *fac-cis* and *mer-trans* isomers and that the precipitate obtained from the reaction at reflux is a *mer-trans* isomer similar to that of $Me_3Sn{-}Mn(CO)_3[P(OPh)_3]_2$ (c).

Figure 3 shows 60 MHz ^{1}H NMR spectra of the compounds II and IV at room temperature. The methyl derivative II shows an extra weak feature besides the strong methyl proton signal and its satellites due to ^{119,117}Sn—C—H coupling, and the weak feature itself has satellites which are equal in size within the experimental error to the satellites of the strong peak. The ethyl derivative IV exhibits a strong extra peak besides the main peak (relative intensity 1/2) in the alkyl proton signal region. In a previous study [2], it has been found that the coupling between methyl and methylene protons in the ethyl groups of $Et_3Sn{-}Mn(CO)_{5-n}(PPh_3)_n$ (n = 0 or 1) is negligibly small and only one main

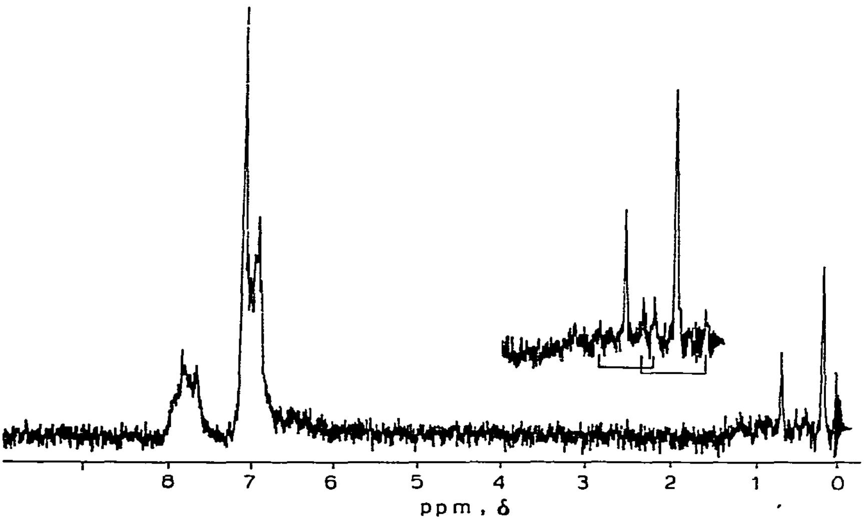


Fig. 2. ^{1}H NMR spectrum of *fac-cis* and *mer-trans* $Me_3Sn{-}Mn(CO)_3(PPh_3)_2$ in C_6D_6 at room temperature with TMS standard.

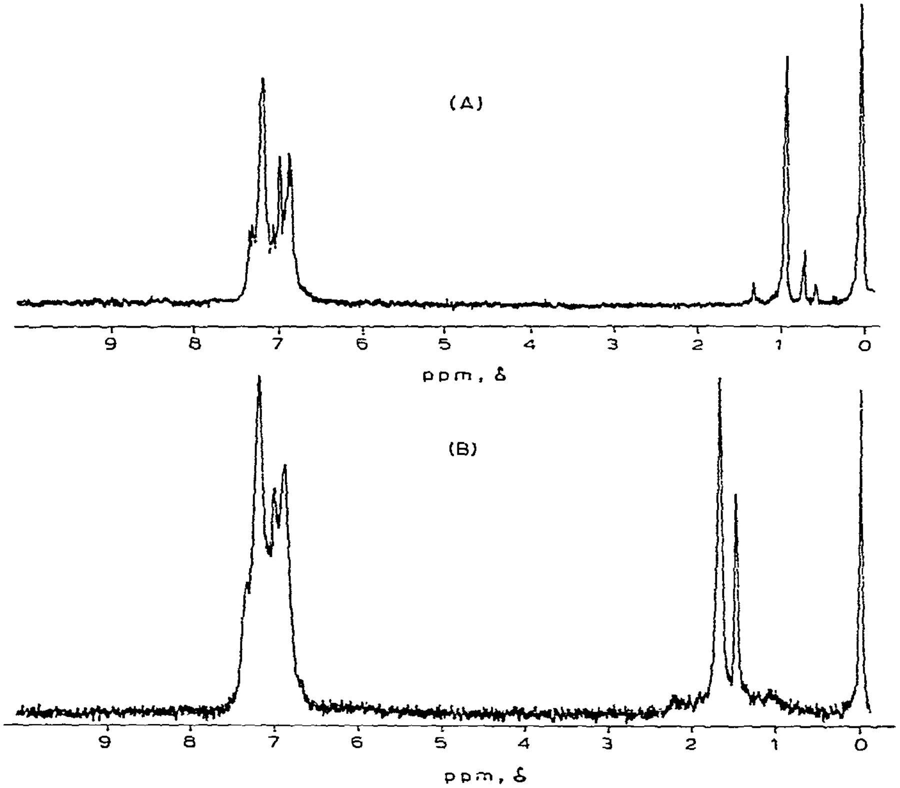


Fig. 3. ^1H NMR spectra of (A) $Me_3Sn—Mn(CO)_3[P(OPh)_3]_2$ and (B) $Et_3Sn—Mn(CO)_3[P(OPh)_3]_2$ in C_6D_6 at room temperature with TMS standard.

peak is observed in ^1H NMR spectra for ethyl groups. On this basis, it is unlikely that the two peaks with 2/1 intensity for the present ethyl compound are due to methyl and methylene protons in the C_2H_5 groups. To clarify the origin of these extra features, the following types of experiments were undertaken; (1) solvent and concentration dependences of the relative intensity, (2) variable-temperature ^1H and ^{13}C NMR studies, (3) synthesis of alkyl-substituted compounds such as $Me_2PhSn—Mn(CO)_3L_2$ (V), and (4) synthesis of the compound such as $Me_3Sn—Mn(CO)_3(PPh_3)_2$ where the phosphite is replaced by a phosphine. First, the concentration dependence of the population ratio was examined for $Me_3Sn—Mn(CO)_3L_2$ (II) in toluene-d_8. The concentration was increased by a factor of four from 8 to 32 wt%. However, no appreciable change in the relative intensity was detected and the line shape was also insensitive to the change of the concentration at room temperature. C_6D_6 and $CDCl_3$ were used as alternative solvents. Fair broadening was observed in $CDCl_3$. However, this broadening was turned out to be due to sample decomposition.

Variable temperature ^1H NMR results for II and IV are displayed in Fig. 4 along with simulated spectra. The two peaks in the alkyl proton region broadened and coalesced into one peak with increasing temperature for each of these two compounds. Variable temperature ^{13}C NMR studies for II in toluene-d_8 have

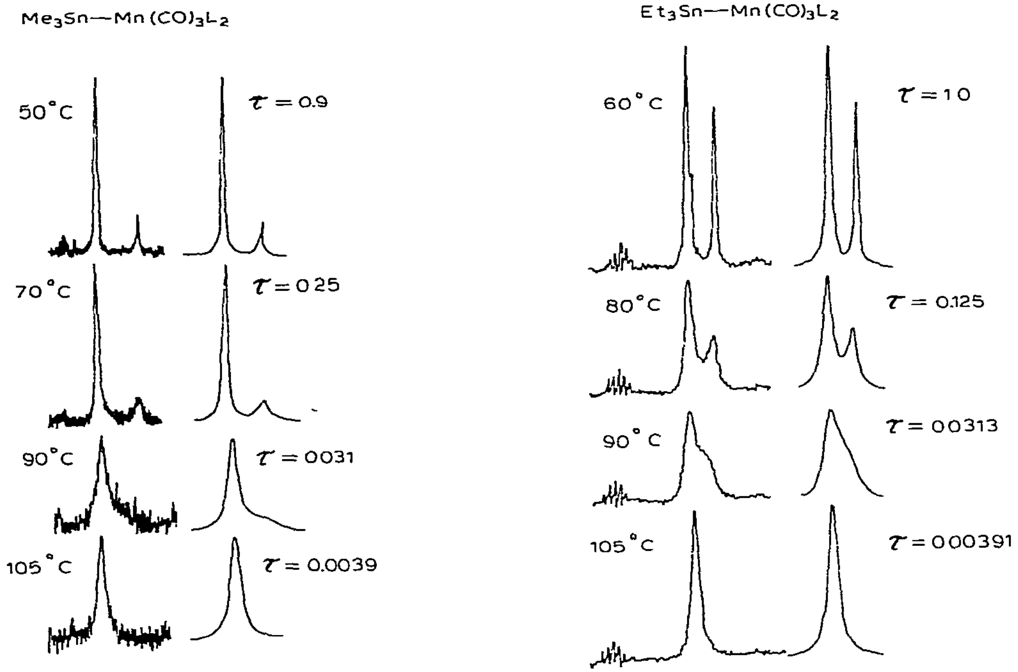


Fig. 4. ^{1}H NMR spectra of Me_3Sn—$Mn(CO)_3[P(OPh)_3]_2$ and Et_3Sn—$Mn(CO)_3[P(OPh)_3]_2$ in $C_6D_5CD_3$ at various temperatures in the methyl and ethyl proton regions (left) and computer simulated spectra (right).

shown that the two methyl carbon peaks observed at room temperature coalesced into one peak with increasing temperature, whereas only one carbonyl carbon peak with triplet structure ($J(^{31}P$—Mn—C) 5.2 Hz) was detected throughout the temperature changes. This finding indicates that the exchange proceeds via an intramolecular rearrangement process and excludes the possibility of the exchange between ligand dissociated species and ligand associated species. To provide more experimental data, similar types of compounds such as $PhMe_2Sn$—$Mn(CO)_3L_2$ (V), $ClMe_2Sn$—$Mn(CO)_3L_2$ (VI), and ClMePhSn—$Mn(CO)_3L_2$ (VIII) were synthesized and line-shape analyses were performed. A common feature of ^{1}H NMR data at room temperature for these methyl derivatives was that the relative population of the main isomer was more than 80% and this population was insensitive to change of solvent. The rate data obtained from line-shape analyses were subjected to least-squares fitting to obtain activation parameters. These indicated that the activation energy, ΔE_a (or $\Delta H^{\neq}$ or $\Delta G^{\neq}$) is increased by the introduction of bulky groups such as ethyl or phenyl groups on the tin atom (Table 4). This fact supports the idea that a kind of rotational mechanism is responsible for the exchange process. The calculated activation energies are in the range from 21.3 to 35.7 kcal/mol and these are significantly higher than those for *cis-trans* interconversion of $(Me_3M)_2M'(CO)_4$ [13] or for axial—equatorial interchange of R groups in $[\mu\text{-}PhMeSn]_2Fe_2(CO)_7$ [7]. The high enthalpies and entropies of activation for IV and V may suggest that the bulky and non-spherical substituents, ethyl and phenyl groups, are highly distorted in the activated state

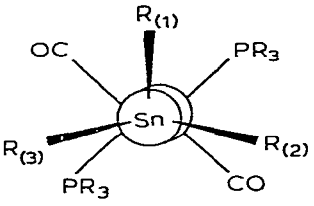
TABLE 4

ACTIVATION PARAMETERS [a]

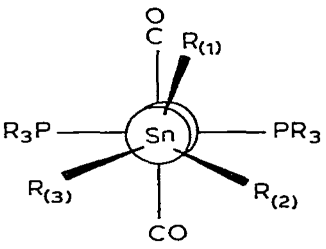
Compound	ΔE_a (kcal/mol)	log A	$\Delta G^{\neq}(298)$ (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (cal mol^{-1} deg^{-1})
II	27.1(1.6)	16.0(1.5)	22.8(3.3)	26.4(2.5)	12,2(7.1)
IV	31.9(1.6)	18.9(1.0)	23.5(2.1)	31.2(1.6)	25.8(4.5)
V	35.7(1.9)	20.9(1.1)	24.7(2.4)	35.0(1.9)	34.7(5.2)
VI	21.3(2.1)	11.5(1.2)	23.0(2.7)	20.6(2.1)	−8.3(5.5)
VIII	28.5(2.3)	15.3(1.3)	25.1(2.9)	27.8(2.3)	8.8(5.9)

[a] Values in parentheses are estimated standard deviations.

of the complexes. On the other hand, the negative entropy of activation for VI (and also the relatively low value for VIII) may indicate that the presence of a small and spherical substituent, Cl, will provide the complex with a narrow reaction path of a low activation enthalpy. It is unlikely, in our view, that the difference in the activation entropy would mean any essential difference in exchange mechanism. The following three rotational exchange mechanisms are possible; (i) interconversion between rotational isomers about the Sn—Mn bond, (ii) exchange among the conformational isomers about the P—Mn—P axis, and (iii) exchange between conformational isomers regarding the orientation of the P—O—Ph bonds. For rotational isomers about the Sn—Mn bond, two conformers, (d) and (e), are possible. In conformation (d), three alkyl groups should be inequivalent at low temperatures and become equivalent when the R_3Sn moiety starts to rotate around the Sn—Mn bond overcoming the rotational barrier at high temperatures. In conformation (e), one alkyl group, $R_{(1)}$, should not be equivalent with the other two alkyl groups, $R_{(2)}$ and $R_{(3)}$, at low temperature and becomes equivalent with increase of temperature in a similar fashion. Five compounds subjected to variable temperature ^{1}H NMR measurements cannot be explained by this interconversional mechanism of conformation (e) with a possible exception of $Et_3Sn—Mn(CO)_3L_2$ (IV) on the basis of intensity consideration. An alternative explanation using the rotational mechanism about the Sn—Mn bond is that interconversion occurs between the two conformers (d) and (e); this type of rotational isomers was already reported by Graham et al. for $Cl_2MeSi—Fe(CO)_2Cp$ [14]. However, we could not get any hint to infer the presence of this type of rotational isomers from our solution IR measurements



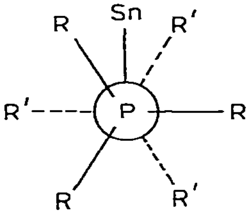
(d)



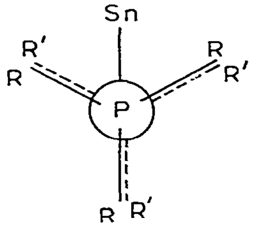
(e)

for the present type of compounds *. In addition to that, this explanation demands that three alkyl groups in each conformer should be equivalent and that the magnetic field which three alkyl groups feel in each conformer should be equivalent. Such a magnetic field equivalence is possible for adequate orientations of P—O—Ph bond and appropriate tilt of the phenyl rings. Therefore, this type of exchange mechanism can be regarded as the mechanism (ii) and (iii).

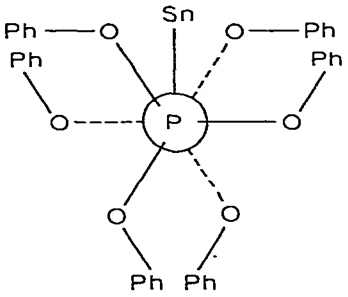
As for conformational isomers about the P—Mn—P bond, conformers such as (f) and (g) are expected (carbonyl and alkyl groups are omitted for clarity). Different orientations of the P—O—Ph bonds provide conformers such as (h) and (i). In the conformer (h), the manganese atom is placed at the center of chilarity, whereas the conformer (i) has an S_6 axis, if carbonyl and R_3Sn groups are disregarded. Aforementioned *mer-trans* $Me_3Sn—Mn(CO)_3(PPh_3)_2$ (XI′) did not display any extra feature in the methyl proton region in the ^1H NMR spectra taken at room temperature and down to −50°C. This suggests that the extra feature observed in the phosphite compounds should result from isomers characteristic of P—O—Ph orientations, i.e., conformers such as (h) and (i), and the exchange seems to proceed via intramolecular rearrangement of P—O—Ph orientations. Although stereochemical nonrigidity for six-coordinate metal—metal bonded compounds has recently been reported [13,15,16], this type of exchange



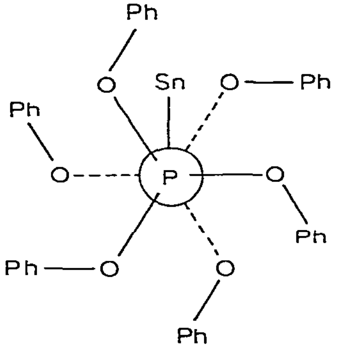
(f)



(g)



(h)



(i)

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* An observation of more than three ν(CO) peaks for solid samples of VI and VIII is due to solid state splitting [17].

process has not yet been established to our knowledge and our interpretation is open to further discussion.

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