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SOME OBSERVATIONS ON PENTACARBONYLMANGANESE-SUBSTITUTED TIN HYDRIDES

STEPHEN P. FOSTER and KENNETH M. MACKAY *

Department of Chemistry, University of Waikato, Private Bag, Hamilton (New Zealand)

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Summary

The substituted tin hydrides, $(CO)_5MnSnH_3$, $(CO)_5MnSnMeH_2$, and $(CO)_5MnSnMe_2H$, have been synthesised and characterised with reasonable certainty by IR, MS and ^1H NMR spectroscopy, despite some difficulties with decomposition. $(CO)_5MnSnH_3$ is the least stable, steadily eliminating $HMn(CO)_5$ at room temperature.

Introduction

Simple tin hydrides are thermally unstable and relatively little explored. SnH_4 decomposes slowly at room temperature, while Sn_2H_6 does not survive above −112°C [1]. Stability increases markedly with alkyl substitution: thus Me_2SnH_2 survives for a few weeks while R_3SnH species are stable indefinitely at room temperature. In contrast, electronegative substituents greatly decrease the lifetimes, with $SnClH_3$ decomposing at −70°C [2].

Only a few transition metal derivatives of the stannanes have been reported. Monohydrides of the types M_3SnH and MPh_2SnH ($M = Mn(CO)_5$, $Re(CO)_5$ [3], also $[R_3P(CO)_3Co]_3SnH$ [4]) parallel the trialkyls R_3SnH, but even the dihydrides M_2SnH_2 survive to over 100°C [3]. Perhaps most striking of all is the distannane $[\{(CO)_5Mn\}_2SnHSnH\{Mn(CO)_5\}_2]$, which only starts to decompose about 150°C [5].

The stability of the monohydrides and the distannane probably results, in part, from the lack of the intramolecular H_2-elimination route, but there is an implication of additional stabilisation by the $Mn(CO)_5$ and similar groups. This was also suggested by the properties of metal carbonyl substituted polygermanes [6], and can be rationalised on steric or electronic grounds.

In this work we report efforts to make $(CO)_5MnSnR_3$ species, especially the polyhydrides, where $R_3Sn = H_3Sn$, H_2SnMe or $HSnMe_2$. It was also of interest to see if the halostannanes were sufficiently stable to be used in the convenient

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synthesis involving alkali halide elimination (eq. 1).

$$R_nSnH_{4-n} \rightarrow [R_nSnClH_{3-n}] \xrightarrow{NaMn(CO)_5} (CO)_5MnSnR_nH_{3-n} + NaCl \qquad (1)$$

Results

The spectroscopic data (Tables 1, 2, 3) provide clear evidence that the substituted stannanes $(CO)_5MnSnH_3$, $(CO)_5MnSnMeH_2$ and $(CO)_5MnSnMe_2H$ were formed according to eq. 1. There were, however, difficulties in each case. $(CO)_5MnSnH_3$ evolved $HMn(CO)_5$ and deposited a red solid steadily on handling. The infrared spectrum was determined by difference from that of $HMn(CO)_5$, and no conclusion could be drawn from the intensities of $(H)Mn(CO)_n{}^+$ ions in the mass spectrum.

$(CO)_5MnSnMeH_2$ was obtained as a clear liquid whose colour and vapour pressure of 1–2 mm did not change over periods of an hour or so. Its ^1H NMR spectrum was clean, with no sign of $HMn(CO)_5$, but the mass spectrum did suggest enhanced formation of the manganese hydride in contact with the metals of the ion source. Ions containing both Sn and Mn carried only 36% of the total ion current, in contrast with the observation of 75% for $(CO)_5MnGeMeH_2$ [7].

The mass spectrum of $(CO)_5MnSnMe_2H$ showed no such indication of $HMn(CO)_5$ elimination or enhanced Mn–Sn cleavage as ions containing both metals carried 56% of the total ion current, comparable with the 52% found [8] for $(CO)_5MnGeMe_2H$ and suggesting the same pattern as found for the trimethyls, $(CO)_5MnMMe_3$ (52% for M = Ge, 59% for M = Sn [9]). However, the ^1H NMR spectrum showed pronounced contamination by $(CO)_5MnSnMe_3$. This probably arose from a minor contamination of Me_3SnH in the starting material which was enhanced in the preparation (especially as Me_3SnCl is more stable than Me_2SnClH). Since $(CO)_5MnSnMe_3$ is less volatile than $(CO)_5MnSnMe_2H$, its ions appeared only weakly in the mass spectrum and it did not complicate the infrared spectrum measured in the gas phase.

With these problems in mind, the spectroscopic properties may be reviewed. The ^1H NMR spectra are shown in Table 1, along with data for various analogues

TABLE 1

CHEMICAL SHIFTS (τ) OF GROUP IV PENTACARBONYLMANGANESE SPECIES

		M*H*	MC*H*$_3$	Solvent
$(CO)_5MnMH_3$	M = Si [10]	6.41		neat
	M = Ge [a]	6.72		C_6H_6
	M = Sn	6.53		C_6H_6
$(CO)_5MnMMeH_2$	M = Ge [7]	6.30	9.33	$SiCl_4$
	M = Sn	5.75	9.36	neat
$(CO)_5MnMMe_2H$	M = Ge [b]	5.60	8.94	neat
	M = Sn	5.40	9.07	neat
$(CO)_5MnMMe_3$	M = Si [12]		9.51	C_6H_{12}
	M = Ge [13]		9.38	$CDCl_3$
	M = Sn [14]		9.53	neat

[a] Also 6.37 τ in $SiCl_4$ [8,11]. [b] Also 5.8 and 9.3 τ in $SiCl_4$ [8].

[10–14]. Although obscured somewhat by solvent shifts, the Sn*H* chemical shifts lie consistently below Ge*H*, while SnC*H*$_3$ lies a little to high field of GeC*H*$_3$. The expected low field shifts of M*H* on successive methyl substitution form a consistent pattern for M = Sn and Ge and help to support the assignment of the singlet of $(CO)_5MnSnH_3$. For the methyl and dimethyl species, the identification is further confirmed by the multiplicities, relative intensities, and *J* values.

The gas phase vibrational spectra are recorded in Table 2. There is a close resemblance in position, relative intensity, and band envelope shape, with the spectra of the corresponding germanes. The number of bands is in accord with

TABLE 2

INFRARED GAS PHASE SPECTRA OF $(CO)_5MnMR_3$ SPECIES (cm^{-1})

(s, strong; m, medium; w, weak; sh, shoulder; v, very; br, broad)

R_3M					
SnH_3 [a]	GeH_3 [11]	$SnMeH_2$ [b]	$GeMeH_2$ [7]	$SnMe_2H$ [b]	Assignment
		2994vw	2963w	2997vw	$\nu_{as}(CH_3)$
		2920vw	2926w	2916vw	$\nu_s(CH_3)$
			2877w		
2109R 2106Q ms 2103P	2117 2114 m 2111	2104 2101 vs 2098	2107m	2094vs	$\nu(CO)_{ax}$ (a_1 or a')
2021R 2018Q vvs 2015P	2022 2019 vvs 2016	2029 2026 s 2023	2029vs	2024vs	$\nu(CO)_{eq}$ (a_1 or a')
		2012vvs	2018vs	2006vvs	$\nu(CO)_{eq}$ (e)
1983w	1981m	1976mw	1985w	1970m	$\nu(^{13}CO)$
1973 ?vw	1975				
1865br,w		1845vw			$\nu_{as}(SnH_x)$
1846R 1833Q m 1840P		1828 1825 s 1822		1810 1808 ms 1805	$\nu_s(SnH_x)$
		1346vw	1460w		
			1080w		$\delta(CH_3)$
			1030w		
		768 766 m	877w	867w 766ms	$\rho(CH_3)$
696R 694Q mw 692P	821 818 s 815	718 715 m 712	838s	728w	$\delta_s(MH_x)$
667sh 657vs	685w 663vs	666 658 vs	670sh 660s	669 657 vs	$\delta(MnCO)$
638?w			609w,br		
		575ms	695sh		$\rho(MH_x)$
		517m	583m	557 507 ms	$\nu(MC)$
474w	474m	476m	482m	477m	$\nu(MnC)$

[a] Contaminated with $(CO)_5MnH$, see Experimental. [b] Low vapour pressure-weaker methyl modes not seen.

TABLE 3

FRAGMENT IONS CONTAINING (Sn+Mn) OR Sn FOUND IN THE MASS SPECTRA OF $(CO)_5MnSnR_3$ SPECIES (m/e)

Compound	Ions containing	Relative intensities for n					
		5	4	3	2	1	0
$(CO)_5MnSnH_3$	$(CO)_nMnSnH_x{}^+$ [a]	w	m	w	vw	[b]	s
$(CO)_5MnSnMeH_2$	$(CO)_nMnSnMeH_x{}^+$ [c]	13	17	66	36	14	34
	$(CO)_nMnSnH_x{}^+$	30	33	29	21	21	26
$(CO)_5MnSnMe_2H$	$(CO)_nMnSnMe_2H_x{}^+$ [d]	50	42	34	32	12	24
	$(CO)_nMnSnMeH_x{}^+$	1	1	2	5	36	36

[a] Most abundant ion has $x = 3$ for $n = 5$, 4 and $x = 1$ for others. [b] Weak spectrum obscured by background in this region. [c] Base peak $Me_2SnH_x{}^+$: $MeSnH_x{}^+ = 93$, $Me_3SnH_x{}^+ = 66$, $SnH_x{}^+ = 83$. [d] Base peak $Me_3SnH_x{}^+$: $MnSnH_x{}^+ = 30$, $Me_2SnH_x{}^+ = 15$, $MeSnH_x{}^+ = 70$, $SnH_x{}^+ = 14$.

expectations based on local symmetry (e.g., three CO stretches for the $2a_1 + e$ infrared-active species expected for the C_{4v} unit). For all these molecules, the symmetric modes show an unsymmetric type A contour with pronounced Q branch and relatively weak P branch.

The assignments require few comments. Unlike GeH stretches, the SnH modes are well clear of the carbonyl region and decrease in frequency with increasing methyl substitution. The strong a_1 and e carbonyl stretches overlap in both $(CO)_5MnMH_3$ species, but are separated for the methyl and dimethyl derivatives. For the $MMeH_2$ species, it is likely that the MH_2 bend and wag overlap at 715 (M = Sn) or 838 cm^{-1} (M = Ge) with the rock much lower at 575 (Sn) or 695 cm^{-1} (Ge): the two upper modes are close together at 726 (bend) and 712 cm^{-1} (wag) for Me_2SnH_2 [15].

The tin-containing ions found in the mass spectra are summarised in Table 3. Although Sn–Mn cleavage undoubtedly occurs, no weight can be placed on the data for $(H)Mn(CO)_x{}^+$ species except possibly in the case of $(CO)_5MnSnMe_2H$. Here the observed species were limited to $HMn(CO)_4{}^+$ (30) and $Mn(CO)_x{}^+$ for $x = 4$ (10), 3 (5), 2 (4) and 1 (5) where the intensities are in brackets. This pattern is similar to that seen for the germanes. For all three molecules, all members of the $SnMn(CO)_x{}^+$ series are found and loss of substituents on the Sn is most prominent after loss of one or two CO units. Methyl transfer between Sn atoms is consistent with observations on other systems [9].

The reaction with excess CCl_4 followed the same path (eq. 2) as observed [7] for

$$(CO)_5MnSnMeH_2 + CCl_4 \rightarrow (CO)_5MnSnMeCl_2 \qquad (2)$$

the germanium analogue with $CHCl_3$ as the probable fate of the CCl_4.

Discussion

Although complete certainty is precluded by the facile rearrangements, there seems adequate evidence for the existence of $(CO)_5MnSnH_3$, $(CO)_5MnSnMeH_2$ and $(CO)_5MnSnMe_2H$. This adds two more members to the short list of tin polyhydrides. Since decomposition to tin was not observed, these species are more stable than stannanes, but the presence of the $Mn(CO)_5$ unit facilitates an alternative reaction involving $HMn(CO)_5$ elimination, especially for $(CO)_5MnSnH_3$. The red solid decomposition product requires further study and is reminiscent of the species formed, at a high temperature, in the course of the pyrolysis of $(CO)_5MnSiH_3$ [10].

Thus, while the pentacarbonylmanganese unit may stabilise the SnH_x unit towards H_2 elimination, paralleling the observations on substituted di- and tri-germanes, these pentacarbonylmanganese substituted stannyls show alternative reactions which would appear to reduce their general utility for studying Sn–H species.

While the synthesis via the chlorostannanes worked, their extreme instability does outweigh the other advantages of this synthesis and further progress will require an alternative route, perhaps via Sn–N species.

Experimental

General. IR spectra were measured on gas samples with a Perkin–Elmer 180 spectrometer, ^1H NMR spectra on a JEOL C-60HL machine, and mass spectra on a Varian CH5 instrument.

The stannanes were prepared by $LiAlH_4$ reduction of the chlorides and characterised spectroscopically. All compounds were manipulated under vacuum.

Preparation. In a typical run, $MeSnH_3$ (163 mg, 1.19 mmol) was allowed to react with dry HCl (35 mg, 0.96 mmol) at $-70°C$ until H_2 evolution ceased after 11/2 h. Unreacted stannane was removed. $Mn_2(CO)_{10}$ (388 mg, 0.995 mmol) was reduced with excess 1% sodium amalgam in dry ether. The green solution was isolated from the amalgam, the chlorostannane condensed in, and the mixture allowed to warm to ambient temperature. The colour became pale orange and NaCl deposited. The volatile products were fractionated and a very pale yellow liquid was held at $-45°C$. This showed an envelope in the mass spectrum at $m/e = 326–336$ corresponding to $C_6H_5O_5MnSn$ with the appropriate intensity pattern for the tin isotopes. The ^1H NMR spectrum of the liquid with 10% TMS showed a quartet at 5.75 ± 0.03 τ and a triplet at 9.36 ± 0.03 τ with J 3.8 ± 0.2 Hz and intensity ratio 2/3. The fragment ions in the mass spectrum (Table 3) and the infrared spectrum (Table 2) confirm the species as pentacarbonyl(methylstannyl)manganese, $(CO)_5MnSnMeH_2$, yield 17 mg (0.05 mmol, 5.3% based on HCl). Further runs also yielded ca. 6%.

Similar preparations using Me_2SnH_2 gave $(CO)_5MnSnMe_2H$ as a white solid freed, with some difficulty, from $(CO)_5MnH$ at $-63°C$. The ^1H NMR spectrum showed signals at 5.40 τ (septet intensity 0.9) and 9.07 τ (doublet intensity 6.0) with J 3.2 Hz, contaminated by a species with a singlet at 9.53 τ attributed to $(CO)_5MnSnMe_3$. The mass spectrum of the head fraction showed an ion family at $m/e = 341–50$ of appropriate intensity pattern for $C_7H_7O_5MnSn$ accompanied by the much weaker (14% relative intensity) parent ion of $(CO)_5MnSnMe_3$. These properties, with the details shown in Tables 1 to 3, support the attribution as pentacarbonyl(dimethylstannyl)manganese, $(CO)_5MnSnMe_2H$.

When SnH_4 was used, the $-45°C$ fraction was briefly clear, but readily deposited a red solid while the proportion of $(CO)_5MnH$ increased. In addition to intense ions of the $HMn(CO)_x^+$ and $Mn(CO)_x^+$ families, a weak family was seen at $m/e =$ 311–322 corresponding to $C_5H_3O_5MnSn$ (strongest $m/e = 318$ matching $(CO)_5Mn^{120}SnH_3^+$) together with the fragments listed in Table 3. It was only possible to procure a dilute solution in C_6H_6 for ^{1}H NMR observation. This showed a singlet at 6.53 ± 0.02 τ, but Sn satellites could not be confirmed. This signal had disappeared after 10 h, when the clear solution had turned dark red. Table 2 lists the infrared absorptions which remained after subtraction of bands at (cm^{-1}) 2124w, 2095sh, 2048sh, 2032, 2028, 2023vvs, [2015s], 1993ms, 1936w, 1784m, 731s, 718w, 670w, 663s, [657vs], 612s and 462m attributed to $(CO)_5MnH$. Thus, the product is suggested to be pentacarbonyl(stannyl)manganese, $(CO)_5MnSnH_3$.

Reaction with CCl_4. $(CO)_5MnSnMeH_2$(40 mg, 0.12 mmol) was condensed into excess CCl_4 (ca 1 mmol). As the mixture warmed slowly to room temperature, the clear solution turned pale yellow. Volatiles were pumped away to leave $(CO)_5MnSnMeCl_2$(51 mg, 0.13 mmol, ≃ 100%) identified spectroscopically [16].

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