

REACTIVITY OF MAIN GROUP—TRANSITION METAL BONDS

III*. REACTIONS OF HALOGENS WITH $\text{Ph}_3\text{SiMn}(\text{CO})_5$ AND $\text{Ph}_3\text{SnMn}(\text{CO})_5$

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(Received July 8th, 1975)

Summary

The products of the reaction of $\text{Ph}_3\text{MMn}(\text{CO})_5$ ($\text{M} = \text{Si}$ or Sn) with chlorine, bromine and iodine in tetrachloromethane, have been determined.

$\text{Ph}_3\text{SiMn}(\text{CO})_5$ does not react with iodine, and the Si—Mn bond is cleaved by chlorine and by bromine.

$\text{Ph}_3\text{SnMn}(\text{CO})_5$ reacts in a much more complex manner, Ph—Sn bond cleavage occurring with all three halogens to give mono-, di-, and, with the exception of iodine, tri-halogenated derivatives. Bromine, in high concentration, and iodine also cleave the Sn—Mn bond.

Introduction

The reactions of $\text{Ph}_3\text{MMn}(\text{CO})_5$ ($\text{M} = \text{Si}$ or Sn) with halogens have not, so far, been the subject of a systematic study. Gorsich [2] found that in tetrachloromethane at 25°C $\text{Ph}_3\text{SnMn}(\text{CO})_5$ reacts with an excess of chlorine or bromine to give $\text{Cl}_3\text{SnMn}(\text{CO})_5$ and $\text{Br}_3\text{SnMn}(\text{CO})_5$ respectively; cleavage of the metal—metal bond did not occur. With lower $\text{Br}_2/\text{Ph}_3\text{SnMn}(\text{CO})_5$ molar ratios (1/1 or 2/1) $\text{Br}_2\text{PhSnMn}(\text{CO})_5$ was found. Other work on reactions of $\text{Ph}_3\text{GeMn}(\text{CO})_5$ [3], $\text{Ph}_2\text{BrGeMn}(\text{CO})_5$ [4], $\text{Ph}_3\text{GeRe}(\text{CO})_5$ [5] and $\text{Ph}_3\text{SnRe}(\text{CO})_5$ [6] with chlorine and bromine presents a confused picture as many different reaction conditions (solvents and temperatures) have been used. The main conclusion is that the trichloro-germanium or -tin compounds $\text{X}_3\text{MM}'(\text{CO})_5$ ($\text{M} = \text{Ge}$ or Sn ; $\text{M}' = \text{Mn}$ or Re ; $\text{X} = \text{Cl}$ or Br) are fairly resistant to metal—metal bond cleavage by excess chlorine or bromine.

We have studied the reactions of $\text{Ph}_3\text{MMn}(\text{CO})_5$ ($\text{M} = \text{Si}$ or Sn) with halogens under controlled conditions (20°C, tetrachloromethane solvent) and ob-

* For Part II see ref. 1.

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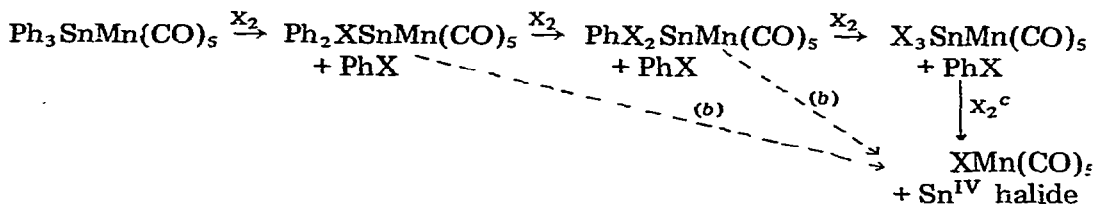
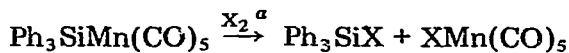
TABLE 1

REACTIONS OF $\text{Ph}_3\text{MMn}(\text{CO})_5$ WITH HALOGENS (X_2) IN TETRACHLOROMETHANE AT 20°C

M	X_2	[X_2]/[$\text{Ph}_3\text{-MMn}(\text{CO})_5$]	Products ^b				M—Mn bond broken $\text{XMn}(\text{CO})_5$ formed
			$\text{Ph}_{(3-n)}\text{X}_n\text{MMn}(\text{CO})_5 + \text{PhX}$				
			$n = 0$ ^a	$n = 1$	$n = 2$	$n = 3$	
Si	Cl_2	1	(X)				• X
Si	Cl_2	4	(X)				X
Si	Br_2	0.5	X				X X X X ↓ increase in yield of $\text{XMn}(\text{CO})_5$ no reaction
Si	Br_2	1	X				
Si	Br_2	2	X				
Si	Br_2	4	(X)				
Si	I_2	1	X				
Sn	Cl_2	0.5	X	X	X		
Sn	Cl_2	1	X	X	X		
Sn	Cl_2	2			X	(X)	
Sn	Cl_2	3				X	
Sn	Cl_2	4				X	
Sn	Br_2	0.5	X	X	X		
Sn	Br_2	1	X	X	X		
Sn	Br_2	1.5	X	X	X		
Sn	Br_2	2	(X)		X		
Sn	Br_2	3				X	
Sn	Br_2	4				X	X
Sn	Br_2	8				X	X
Sn	I_2	1	X	X	X		(X)
Sn	I_2	2		(X)	X		X
Sn	I_2	3			X		X
Sn	I_2	8					X

^a Starting material. ^b Parentheses denote minor constituent.

served the products formed with different molar ratios of halogen/ $\text{Ph}_3\text{MMn}(\text{CO})_5$. The results are shown in Table 1, and are consistent with the equations ($\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2$).

[^a $\text{X} = \text{Cl}, \text{Br}$; ^b with I_2 only; ^c $\text{X} = \text{Br}, \text{I}$]

Discussion

Table 1 shows that phenyl—silicon bonds are not cleaved by any of the halogens and are thus less reactive than phenyl—tin bonds. This is in line with

the rates of protodemetalation of Me_3MPh ($\text{M} = \text{Si}$ or Sn) where the silane is 3.5×10^5 less reactive than the stannane analogue [7]. Covalent bonds formed by silicon are usually stronger than those formed by tin.

Replacement by a halogen of a phenyl group attached to tin has little effect on the strength of the bonds to remaining phenyl groups. At low molar ratios of iodine/organometallic the products are mono- and di-halogenated derivatives, mixed with unreacted starting material. If replacement of a phenyl group by a halogen greatly strengthened the remaining tin-phenyl bonds only monohalogenated product would be found, whereas if the tin-phenyl bonds were weakened when some had been replaced then only starting material and polyhalogenated tin compounds would be found.

However, the results indicate that dihalogenated tin compounds are somewhat stabilised as no trichloro- or tribromo-tin compounds are formed until all starting material has been converted to the dihalogenated tin compound. Furthermore, $\text{I}_3\text{SnMn}(\text{CO})_5$ was never detected.

The reactivity of tin-manganese bonds appears to be changed by the nature of groups attached to the tin atom.

With chlorine the tin-phenyl bond is more reactive than the tin-manganese bond; tin-manganese bonds in neither $\text{Ph}_3\text{SnMn}(\text{CO})_5$ nor $\text{Cl}_3\text{SnMn}(\text{CO})_5$ are cleaved.

Bromine reacts at the phenyl-tin bond in preference to the tin-manganese bond, but we found that, contrary to Gorsich's observation, $\text{Br}_3\text{SnMn}(\text{CO})_5$ reacts further with bromine, cleavage of the tin-manganese bond occurring. This tin-manganese bond cleavage does not occur until all the $\text{Ph}_3\text{SnMn}(\text{CO})_5$ has been converted into its tribromotin derivative.

In contrast to the reactions with chlorine and bromine, products of tin-manganese bond cleavage are found even at low iodine/organometallic ratios. The tin-manganese bonds in $\text{Ph}_3\text{SnMn}(\text{CO})_5$, $\text{IPh}_2\text{SnMn}(\text{CO})_5$ and $\text{I}_2\text{PhSnMn}(\text{CO})_5$ must be of a similar strength to that of tin-phenyl bonds so that subsequent reaction with iodine can result in cleavage of either bond (dotted line in equation). It would seem that replacement of phenyl groups by iodine weakens the tin-manganese bond so much that $\text{I}_3\text{SnMn}(\text{CO})_5$ is not formed under our conditions. In this context it is interesting that the force constant for tin-manganese bond stretching in $\text{I}_3\text{SnMn}(\text{CO})_5$ is only a half that found in $\text{Br}_3\text{SnMn}(\text{CO})_5$ [8].

Replacing phenyl groups by electronegative chlorine atoms will make the $5d$ -orbitals more compact [9]. In trichlorotin derivatives of transition metals there is overlap of filled d orbitals of the transition metal with empty $5d$ orbitals of the tin. Thus Cl_3Sn has a large *trans* effect arising from its strong π acceptor properties [10], and this overlap will strengthen tin-transition metal bonds compared with those in Ph_3Sn derivatives. Onaka [8,11] has calculated that the force constants for tin-manganese bond stretching in $\text{X}_3\text{SnMn}(\text{CO})_5$ increases in the order ($\text{X} =$) $\text{Me}/\text{Br}/\text{Cl} = 0.70/0.82/1.0$. Also the Sn-Mn bond length in $\text{Cl}_3\text{SnMn}(\text{CO})_5$ is 0.08 Å shorter than that found in both $\text{Ph}_3\text{SnMn}(\text{CO})_5$ and $\text{Me}_3\text{SnMn}(\text{CO})_5$ [12].

The strong tin-manganese bond in $\text{Cl}_3\text{SnMn}(\text{CO})_5$ satisfactorily explains its stability to chlorine.

The relative strengths of silicon-manganese and tin-manganese bonds in the methyl analogues of the silicon and tin compounds used here ($\text{Me}_3\text{MMn}(\text{CO})_5$)

have been discussed by Burnham and Stobart [13] who conclude that $D(\text{Me}_3\text{Si}-\text{Mn}(\text{CO})_5)$ is substantially greater than $D(\text{Me}_3\text{Sn}-\text{Mn}(\text{CO})_5)$ (1.04 eV and 0.69 eV respectively). Our results support these figures, and further suggest that the tin-manganese bond in $\text{Cl}_3\text{SnMn}(\text{CO})_5$ (which is not cleaved by Cl_2) is stronger than the silicon-manganese bond in $\text{Ph}_3\text{SiMn}(\text{CO})_5$ (broken by chlorine) with respect to electrophilic attack.

We conclude that spectroscopic estimates of metal-metal bond strengths are in line with the observed halogenations of compounds containing silicon-manganese or tin-manganese bonds.

Experimental

Reactions were carried out in a Schlenk tube at room temperature under an atmosphere of nitrogen. About 1 mmol of organometallic compound was dissolved in 10 cm³ tetrachloromethane (B.D.H. Spectroscopic grade) and the appropriate quantity of halogen in tetrachloromethane was added. After reaction appeared complete (no further colour change) an IR spectrum of the solution was recorded as previously described [14], and after evaporation of tetrachloromethane a mass spectrum of the residue was recorded. Manganese-containing products were identified by assignment of the peaks in the carbonyl region of the IR spectrum, using published data for the IR spectra of the products [15-18], and also from the mass spectra. Phenyl halides were identified by GLC analysis.

$\text{Ph}_3\text{SnMn}(\text{CO})_5$ was prepared in tetrahydrofuran by the reaction of $\text{Ph}_3\text{-SnCl}$ with $\text{NaMn}(\text{CO})_5$ as previously described [14], and was recrystallised from n-hexane before use. $\text{Ph}_3\text{SiMn}(\text{CO})_5$ was prepared by heating Ph_3SiH and $\text{Mn}_2(\text{CO})_{10}$ together in a Carius tube at 165°C for 60 h [15] and was recrystallized from n-hexane before use.

Acknowledgement

We thank J. Dale for help with the experimental work.

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