Journal of Organometallic Chemistry, 295 (1985) 149–158
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND SPECTROSCOPIC STUDIES OF SOME CYCLIC UREA ADDUCTS OF TRIPHENYL-TIN AND -LEAD HALIDES *

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(Received March 13th, 1985)

Summary

1,3-Dimethyl-2-imidazolidinone (dimethylethylene urea, DMEU) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (dimethylpropylene urea, DMPU) adducts of the type $Ph_3SnX \cdot L$ (X = Cl, Br and I), $Ph_3PbX \cdot L$ (X = Br, I), $3Ph_3PbCl \cdot 2DMEU$ and $2Ph_3PbCl \cdot DMPU$ have been prepared and characterized. Assignments are made for $\nu(CO)$ and $\nu(CN)$ frequencies in the IR, and for skeletal frequencies observed in both the IR and Raman spectra in the range 400 to 100 cm^{-1}. Infrared measurements show that the adducts are bound through the carbonyl oxygen, and are highly dissociated in dichloromethane solution. ^1H and ^{119}Sn or ^{207}Pb NMR measurements reveal that ligand exchange, fast on the NMR time scale, occurs in solution. Coordination of the ligand causes a large upfield shift in the ^{119}Sn or ^{207}Pb resonances, but $Ph_3MI \cdot L$ have shifts similar to those for the parent iodides, indicating almost complete dissociation. Thermodynamic parameters are reported for the dissociation of $Ph_3SnX \cdot DMPU$ (X = Cl, Br) in CH_2Cl_2 solution.

Introduction

Recently, it has been proposed that the carcinogenic hexamethylphosphoramide (HMPA) be replaced by the cyclic urea DMPU for reactions requiring a dipolar aprotic solvent [1]. HMPA is a powerful ligand [2–4] and a number of adducts of the type $Ph_3MX \cdot HMPA$, where M = Sn or Pb, and X = Cl, Br and I, have been prepared and studied spectroscopically [5,6]. It was of particular interest, therefore, to attempt the preparation of a series of analogous adducts using DMPU and the

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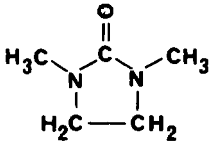
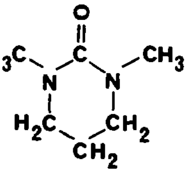
* Presented by C.T.A. at the Fourth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead, Montreal, Canada, 1983, paper H-6.

similar DMEU as ligands, illustrated below, and to study them by vibrational and NMR spectroscopy.



DMEU



DMPU

Little has been reported in the literature on organometallic compounds of Group IV elements with either acyclic or cyclic ureas, despite the fact that these molecules offer both nitrogen and oxygen atoms for coordination. To date, no cyclic urea complexes of phenyltin or lead halides have been reported, perhaps due to the cyclic ureas not being commercially available until recently. Studies of 2-imidozolidinone (ethylene urea) and 2(1*H*)-tetrahydropyrimidinone (propylene urea) as ligands in a variety of non-Group IV complexes, show that these ligands coordinate via the oxygen atom [7,8]. Shifts in the ν(CO) frequency of the ligands tetramethylurea and urea upon coordination to methyl- and phenyl-tin halides also indicate that it is the oxygen atom which coordinates to the metal [9].

Experimental

Deuterated solvents were used as received from Merck, Sharp and Dohme. Non-deuterated solvents were purified by standard methods. The compounds Ph_3SnCl and Ph_3PbCl were used as received from Alfa; Ph_3PbBr and Ph_3PbI were supplied by R. Cuenca of our laboratory, and were used as obtained. Ph_3SnBr was prepared by the reaction of Ph_3SnCl with excess NaBr in methanol. Ph_3SnI was prepared by the reaction of Ph_3SnCl with excess NaI in acetone.

The adducts were prepared in the same way for L = DMEU and DMPU. The parent compound, Ph_3MX (2 g) was suspended in toluene (5 ml) together with the appropriate liquid ligand (3 ml, excess). Upon addition of the ligand, the parent compound dissolved. The adducts tended to crystallize upon cooling at 0°C for 1 h. In some cases a few drops of pentane were added to initiate crystallization. All the complexes were recrystallized from hot toluene and dried in air. The DMEU adducts appeared to be 'wet' and so were pumped in a vacuum overnight at room temperature. Elemental analyses for C, H and N were determined in duplicate by Guelph Chemical Laboratories, Guelph, Ontario. Melting points were measured on a Thomas Hoover melting point apparatus and are uncorrected.

Raman spectra of powders in capillary tubes and both mid- and far-IR spectra of samples as Nujol mulls were measured as described elsewhere [10]. Solution IR were recorded on a Perkin–Elmer 297 instrument using NaCl cells. All frequencies are accurate to ± 1 cm^{-1} for sharp peaks.

Nuclear magnetic resonance spectra were recorded on a 200 MHz Varian XL-200 FT spectrometer. ^1H NMR spectra were measured at 200 MHz as 5% w/v solutions in CD_2Cl_2 with TMS as internal standard. The chemical shifts were measured with digital resolution of 0.25 Hz. The FIDs were collected into 16K data points using a spectral width of 2000 Hz. Chemical shifts were accurate to within ± 0.005 ppm.

^{119}Sn and ^{207}Pb NMR spectra were obtained at natural abundance for 0.25 *M* solutions in dry CH_2Cl_2 or as saturated solutions, and were measured at 74.6 MHz (digital resolution 3.1 Hz) and 41.8 MHz (digital resolution 3.3 Hz), respectively, using as external references Me_4Sn or Et_4Pb in C_6D_6 (50%), the latter providing the external lock signal. Negative chemical shift values indicate upfield shifts from the references. The FIDs were collected into 32K data points with a spectral width of 50,000 Hz. In the ^{207}Pb spectra, complete proton noise decoupling was employed. The decoupler was 'gated' in the case of the ^{119}Sn spectra with a delay of 5 s. This led to much longer spectral collection times for this nucleus. All spectra were measured at room temperature (20 ± 3°C).

Results and discussion

Analytical data

The analytical data for all the adducts prepared are summarized in Table 1. These adducts are air-stable, crystalline solids which are soluble in dichloromethane, but insoluble in pentane. Ten of the twelve complexes made, namely **1** to **3**, **5** to **9**, and **11** to **12**, have analyses corresponding to 1 : 1 molecular adducts, $R_3MX \cdot L$, but complexes **4** analyzed as a 3 : 2 adduct, while complex **10** is a 2 : 1 adduct. Nine of the twelve adducts melted sharply. The complexes **4**, **6**, and **10** decomposed when heated in the range 96 to 123°C.

Vibrational spectra

Infrared ν(CO) and ν(CN) group frequencies for adducts **1** to **12** in the solid state (Table 1) indicate a decrease in ν(CO) and, in most cases, a small increase in ν(CN) upon coordination, consistent with coordination being through the carbonyl oxygen rather than through ring nitrogen atoms. Moreover, solution spectra gave $\nu(CO)_{free}$ peaks more intense than $\nu(CO)_{bound}$ (Table 1), showing that, at least qualitatively, adducts **1** to **12** are highly dissociated in CH_2Cl_2 solution.

Skeletal frequencies (400–100 cm^{-1}) in both the IR and the Raman are given in Tables 2 and 3, with assignments based on those for the parent phenyllead halides reported by Clark et al. [12], and by Wharf et al. [5,6] for the analogous HMPA adducts. The presence of distinct peaks for $\nu_{as}(SnPh_3)$ and $\nu_s(SnPh_3)$ modes in IR and Raman spectra, respectively, suggests a symmetry lower than C_{3v}, probably due to asymmetry of the ligand. Lead–oxygen stretching bands have been assigned in the region 195–206 cm^{-1}, slightly lower than in the corresponding tin complexes whose tin–oxygen stretching bands ranged from 225 to 238 cm^{-1}. These ranges are similar to those obtained for the analogous HMPA complexes [4,5]. Values of ν(M–X) are lower than those found in the parent, monomeric and four-coordinate Ph_3MX [5,12]; they are consistent with a five-coordinate structure, like that in HMPA adducts [6], Ph_nSnX_{3-n} ($n = 2, 3$) [10], and $Ph_3PbX_2^-$ (X = I, Br) [13], probably with M–X bonds axial.

The formulation of complexes **4** and **10** as 3 : 2 and 2 : 1 adducts, respectively, as determined by elemental analysis, implies the presence of bridging chlorines in molecular, ionic, or polymeric structures. Vibrational data do not allow us to distinguish among the possible structures; single crystal X-ray data are necessary. Bands in the infrared due to bridging chlorines are lower in frequency than terminal ones, but the presence of internal ligand vibrations below 200 cm^{-1} prevented the

(*Continued on p. 155*)

TABLE 1

ANALYTICAL AND INFRARED DATA

Compound	Colour	Yield [a] (%)	M.p. (°C)	Analysis (Found (calcd.) (%))			$\Delta\nu$(CO) [c]	$\Delta\nu$(CN) [d]	ν(CO) [e]		ν(CN) [f]
				C	H	N			free	bound	
$Ph_3SnCl \cdot DMEU$	white	71	113	55.42	5.18	5.80	−63	+3	1694	1656	[g]
(1)				(55.20)	(5.04)	(5.60)					
$Ph_3SnBr \cdot DMEU$	cream	47	95–97	50.74	4.58	5.07	−62	+1	1694	1656	[g]
(2)				(50.70)	(4.63)	(5.15)					
$Ph_3SnI \cdot DMEU$	yellow	59	106–108	46.80	4.27	4.76	−60	+1	1685	1658	[g]
(3)				(46.70)	(4.26)	(4.74)					
$3Ph_3PbCl \cdot 2DMEU$	white	80	121–123 [b]	46.87	4.33	3.71	−50	+5	1696	1666	[g]
(4)				(46.61)	(3.97)	(3.40)					
$Ph_3PbBr \cdot DMEU$	white	54	108–110	43.63	4.15	4.44	−41	+3	1691	1661	[g]
(5)				(43.67)	(3.99)	(4.43)					
$Ph_3PbI \cdot DMEU$	pale	63	96 [b]	40.60	3.78	4.03	−44	+5	1691	1658	[g]
(6)	yellow			(40.68)	(3.71)	(4.12)					
$Ph_3SnCl \cdot DMPU$	white	45	121–122	56.03	5.41	5.62	−63	+8	1629	1581	1316
(7)				(56.12)	(5.30)	(5.45)					
$Ph_3SnBr \cdot DMPU$	pale	76	137–139	51.63	4.90	5.09	−65	+5	1631	1580	1318
(8)	yellow			(51.65)	(4.88)	(5.02)					
$Ph_3SnI \cdot DMPU$	bright	82	146–148	47.55	4.46	4.61	−62	+5	1628	1579	1310
(9)	yellow			(47.64)	(4.50)	(4.63)					
$2Ph_3PbCl \cdot DMPU$	white	67	123 [b]	46.70	3.52	2.77	−54	+6	1630	1594	1310
(10)				(46.89)	(3.94)	(2.60)					
$Ph_3PbBr \cdot DMPU$	white	56	126	44.39	4.25	4.39	−58	+1	1631	1596	1310
(11)				(44.62)	(4.21)	(4.34)					
$Ph_3PbI \cdot DMPU$	cream	45	136–137	41.57	3.96	4.07	−48	+3	1636	1598	1310
(12)				(41.56)	(3.92)	(4.04)					

[a] After recrystallization from toluene. [b] Decomposition temperatures. [c] For complexes as Nujol mulls, $\Delta\nu(CO) = \nu(CO)_{bound} - \nu(CO)_{free}$. [d] $\Delta\nu(CN) = \nu(CN)_{bound} - \nu(CN)_{free}$, where C is the carbonyl for complexes as Nujol mulls. [e] For complexes in CH_2Cl_2 solution; for DMEU and DMPU in CH_2Cl_2 ν(CO) are 1696 and 1631 cm^{-1}, respectively. [f] For complexes in CH_2Cl_2 solution; ν(CN) are 1287 and 1318 cm^{-1} for DMEU and DMPU, respectively. [g] Peak present as a diffuse, broad band.

TABLE 2

SKELETAL VIBRATIONS (cm^{-1}) FOR $Ph_3SnX \cdot L$ ADDUCTS [a]

Assignment	$Ph_3SnCl \cdot DMEU$		$Ph_3SnBr \cdot DMEU$		$Ph_3SnI \cdot MDEU$		$Ph_3SnCl \cdot DMPU$		$Ph_3SnBr \cdot DMPU$		$Ph_3SnI \cdot DMPU$	
	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R
$\nu_{as}(Sn-Pb)$ $(t)^b$	274s		274s	274w	276s		274s [c]		278s	275w	276s	274w
$\nu(Sn-Cl)$	267sh	264m					274s [c]	267m				
$\nu(Sn-O)$	238m 230sh	237w	233sh 228m	232w	232s	228w	236m	233w	235s	229w	230s	225sh
u^b	210m	218vs	214w	215vs	213sh	212m [c]	212m	217vs	206w	211vs	199s	213m
$\nu_s(Sn-Ph)$ $(t_1)^b$	203w	205s	204w	205s	208w	212m [c]	202m	202s	190sh	[d]	193sh	[d]
$\nu(Sn-Br)$			172s	171m					172s	167vs		
$\nu(Sn-I)$					134s	132vs					131s	127vs
x^b	195sh		80w 155w			152m		193sh		158sh		155w
$\delta(Sn-Cl)$	153m							146m				
Deformations										105sh		101sh
$\delta(Sn-Br)$										71sh		

[a] As Nujol mulls between polyethylene plates; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. [b] Whiffen's notation [11]. [c] Superimposed. [d] Hidden under u.

TABLE 3

SKELETAL VIBRATIONS (cm^{-1}) FOR $Ph_3PbX \cdot L$ ADDUCTS [a]

Assignment	$3Ph_3PbCl \cdot 2DMEU$		$Ph_3PbBr \cdot DMEU$		$Ph_3PbI \cdot DMEU$		$2Ph_3PbCl \cdot DMPU$		$Ph_3PbBr \cdot DMPU$		$Ph_3PbI \cdot DMPU$	
	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R
ν_{as}(Pb–Ph) (*t*) [b]	235sh 229s	234w	228s	229w	227s		230s	234w	229s	229w		230sh 220s
ν(Pb–Cl)	222sh	218w					212m	220w				
ν(Pb–O)	203m		203m		201m		205m		206m		195w	
u [b]	182m	186w 173w		179sh			184m				172w	170sh
ν_s(Pb–Ph) (t_1) [b]	206sh	198vs		194vs	206w	197m		200vs	199m	201vs	207m	202vs
ν(Pb–Br)			152s	151w					149s	151m		
ν(Pb–I)					122s	121vs					119s	117vs
x [b]		151w						155w				155w
		101sh		94sh								
Deformations		69sh		62sh		150w		108sh				96sh
		55sh		42sh		60sh						58sh

[a] As Nujol mulls between polyethylene plates. [b] Whiffen's notation [11].

assignment of any bridging Pb–Cl stretching frequencies. The IR spectra of both $3Ph_3PbCl \cdot 2DMEU$ and $2Ph_3PbCl \cdot DMPU$ did, however, show a lower baseline relative to that observed in the bromide and iodide complexes, below approximately 200 cm^{-1}. This suggests the presence of a superimposed peak (or peaks) in the bridging chlorine region.

^1H NMR spectra

Only single ^1H NMR peaks were observed for ligand protons in CD_2Cl_2 solution spectra of the complexes (Table 4), suggesting that rapid exchange occurs between free and complexed species on an NMR time scale. In fact, proton chemical shifts $\delta(CH_3)$ and $\delta(CH_2)$ were either unchanged or only slightly shifted from those of the free cyclic ureas in CD_2Cl_2 solution. These observations strongly support the conclusion, previously made on the basis of infrared data, that complexes are highly dissociated in CD_2Cl_2 solution.

Aromatic proton resonances appeared as two, well separated sets of multiplets; the one at low field arising from *ortho* protons, and other at high field from the *meta* and *para* protons. This pattern has been shown by Sau et al. [14,15] to be characteristic of phenyl-substituted pentacoordinated compounds of Main Group elements, when the separation between the two multiplets is greater than in those of related tetracovalent compounds. The multiplet separation for Ph_3SnCl in CD_2Cl_2

TABLE 4

^1H NMR DATA FOR COMPLEXES $Ph_3MX \cdot L$[a] WHERE M = Sn AND Pb, X = Cl, Br AND I, AND L = DMEU AND DMPU

Complex		$\delta(CH_3)$	$\delta(CH_2)$	^3J(H–H)	δ(*ortho*)[b]	δ(*meta/para*)[c]	Δ[d]	$^3J(^{207}Pb–H)$
$Ph_3SnCl \cdot DMEU$	**(1)**	2.67	3.20		7.69	7.49	0.20	
$Ph_3SnBr \cdot DMEU$	**(2)**	2.71	3.22		7.66	7.47	0.19	
$Ph_3SnI \cdot DMEU$	**(3)**	2.72	3.22		7.66	7.46	0.20	
$3Ph_3PbCl \cdot 2DMEU$	**(4)**	2.53	3.14		7.75	7.44	0.31	128
$Ph_3PbBr \cdot DMEU$	**(5)**	2.63	3.18		7.75	7.47	0.28	112
$Ph_3PbI \cdot DMEU$	**(6)**	2.69	3.21		7.73	7.46	0.27	104
$Ph_3SnCl \cdot DMPU$	**(7)**	2.77	1.89 [e] 3.16 [f]	6	7.71	7.45	0.26	
$Ph_3SnBr \cdot DMPU$	**(8)**	2.81	1.91 [e] 3.19 [f]	6	7.68	7.47	0.21	
$Ph_3SnI \cdot DMPU$	**(9)**	2.82	1.92 [e] 3.19 [f]	6	7.64	7.45	0.19	
$2Ph_3PbCl \cdot DMPU$	**(10)**	2.67	1.82 [e] 3.11 [f]	6	7.76	7.51	0.25	111
$Ph_3PhBr \cdot DMPU$	**(11)**	2.73	1.88 [e] 3.14 [f]	6	7.78	7.53	0.25	111
$Ph_3PbI \cdot DMPU$	**(12)**	2.81	1.92 [d] 3.18 [f]	6	7.72	7.47	0.25	104

[a] Measured in CD_2Cl_2. Chemical shifts measured in ppm relative to internal TMS accurate to ±0.005 ppm. Coupling constants measured in Hz. Digital resolution 0.25 Hz. [b] *Ortho* protons of phenyl rings. [c] *Meta/para* protons of phenyl rings. [d] $\Delta = \delta$(*ortho* multiplet)$-\delta$(*meta/para* multiplet) in ppm. [e] Middle CH_2-quintet. [f] CH_2's bonded to N.

was 0.20 ppm, almost the same as that observed in five of the six cyclic-urea complexes of Ph$_3$SnX in Table 1. However, for Ph$_3$SnCl · DMPU the multiplet separation increased from 0.26 to 0.34 and 0.44 ppm as 0.01 and 0.03 ml of DMPU was added to the solution in the NMR tube, indicating that the concentration of the 5-coordinate species in the equilibrium $\mathrm{Ph_3SnCl + DMPU \rightleftharpoons Ph_3SnCl \cdot DMPU}$ had increased. The neutral triphenyltin halide complexes examined by Sau et al. [14,15] were assumed to remain pentacoordinate in solution with no obvious dissociation in solution. This assumption is not true in at least two of the complexes they studied, for Ph$_3$SnCl · HMPA [5] and Ph$_3$PbCl · HMPA [6] have been shown to dissociate in benzene solution. In the more polar solvents used by Sau et al. [14,15] dissociation should be even greater.

^{119}Sn and ^{207}Pb NMR spectra

In their report of the ^{119}Sn NMR spectra of a number of organotin compounds, Holeček et al. [16] found that the ^{119}Sn chemical shifts of 5-coordinate complexes are upfield from those of tetracovalent complexes. Similarly, Cox [18] has shown that ^{207}Pb chemical shifts of tetracovalent compounds, such as Me$_3$PbCl in CHCl$_3$, increase dramatically when placed in highly coordinating solvents such as HMPA. Thus, there appears to be a correlation between chemical shifts and coordination number in these systems. Both ^{119}Sn and ^{207}Pb chemical shifts obtained in this work (Table 5) were to high field of the reference compound. In spite of the fast exchange occurring between free and complexed species in solution, the large ^{119}Sn and ^{207}Pb chemical shifts confirm the presence of complexes in solution. In both tin and lead series trends in Δ values are in the orders: DMPU > DMEU and Cl > Br > I, suggesting that these might be the orders of adduct stability. Interestingly, two sets of adducts, Ph$_3$SnX · DMEU (X = Cl, Br) and Ph$_3$SnX · DMPU (X = Cl, Br), have

TABLE 5

^{119}Sn AND ^{207}Pb CHEMICAL SHIFTS [a]

Compound	$\delta(^{119}\mathrm{Sn})$	$\Delta\delta(^{119}\mathrm{Sn})$ [b]	$\delta(^{207}\mathrm{Pb})$	$\Delta\delta(^{207}\mathrm{Pb})$ [b]
Ph$_3$MCl	−48 (−44.7 [c])		−42 [d] (−38 [e])	
Ph$_3$MBr	−62 (−59.8 [c])		−74 [d] (−68 [e])	
Ph$_3$MI	−113 (−112.8 [c])		−195 [d] (−202 [e])	
3Ph$_3$PbCl·2DMEU			−144 [d]	102
Ph$_3$SnCl·DMEU	−85	37		
Ph$_3$MBr·DMEU	−84	22	−123	49
Ph$_3$MI·DMEU	−118	5 [g]	−196	1
2Ph$_3$PbCl·DMPU			−124 [d]	82
Ph$_3$SnCl·DMPU	−108 (−103 [f])	60		
Ph$_3$MBr·DMPU	−105	43	−141	67
Ph$_3$MI·DMPU	−128 (−123 [f])	15 [g]	−201	6

[a] Measured in ppm for 0.25 *M* solutions in CH$_2$Cl$_2$, unless otherwise indicated, at 20°C relative to Me$_4$Sn and Et$_4$Pb, respectively. [b] Differences in ppm between free and complexed species. [c] Ref. 16; measured in CDCl$_3$. [d] Measured for saturated solutions (< 0.25 *M*). [e] Ref. 17; measured for saturated solutions in CDCl$_3$ relative to MePb$_4$, but corrected to Et$_4$Pb. [f] Values for saturated solution in C$_6$H$_6$. [g] Coupling constants $^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ were 574.8 and 578.3 Hz for Ph$_3$SnI·DMEU and Ph$_3$SnI·DMPU, respectively, compared with 567.6 Hz for Ph$_3$SnI [16].

TABLE 6

THERMODYNAMIC DATA FOR DISSOCIATION OF TRIPHENYLTIN HALIDE COMPLEXES

Complex	K (mol l^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})
$Ph_3SnCl \cdot DMPU$ [a]	0.32 ± 0.01	36.5 ± 0.5	2.8 ± 0.1	115 ± 2
$Ph_3SnBr \cdot DMPU$ [a]	0.53 ± 0.02	40 ± 1	1.5 ± 0.05	130 ± 3
$Ph_3SnCl \cdot py$ [b]	1.1	41	0.3	134

[a] Measurements in CH_2Cl_2 solution. [b] Measurements in benzene solution [20].

similar ^{119}Sn chemical shifts, whereas the corresponding iodide compounds have different values. This might be due to an ionization: $Ph_3SnX \cdot L \rightleftharpoons Ph_3SnL^+ + X^-$, which is less likely for X = Cl and Br than for X = I because of the weaker Sn–I bond. Alternatively, the dissociation: $Ph_3SnX \cdot L \rightleftharpoons Ph_3SnX + L$ is more favourable with the least electronegative iodine atom which would make Ph_3SnI the weakest acceptor. That dissociation that is almost complete in Ph_3SnI and Ph_3PbI systems is supported by the fact that $\delta(^{119}Sn)$ of $Ph_3SnI \cdot DMEU$ in solution is almost the same as that of Ph_3SnI in solution and values of $\delta(^{207}Pb)$ are little different in Ph_3PbI and its DMEU and DMPU adducts in solution.

The degrees of dissociation of $Ph_3SnCl \cdot DMPU$ and $Ph_3SnBr \cdot DMPU$ were estimated from $\delta(^{119}Sn)$ values of Ph_3SnCl (−225 ppm) and Ph_3SnBr (−230 ppm) in pure DMPU and the corresponding values for $Ph_3SnCl \cdot DMPU$ and $Ph_3SnBr \cdot DMPU$ in CH_2Cl_2 solution, assuming that the species in pure DMPU were only the 1 : 1 adducts. Although this is the usual assumption [16,18], the possibility that dissociation occurs in pure DMPU and fast exchange results cannot be excluded. The observed chemical shift (δ_{obs}) of $Ph_3SnX \cdot DMPU$ as a 0.25 M solution in CH_2Cl_2 is given by [19]: $\delta_{obs} = \nu_A P_A + \nu_B P_B$, where ν_A = chemical shift of Ph_3SnX in CH_2Cl_2; ν_B = chemical shift of $Ph_3SnX \cdot DMPU$ as Ph_3SnX in neat DMPU; P_A = mole fraction of Ph_3SnX, and P_B = mole fraction of $Ph_3SnX \cdot DMPU$. Dissociations were calculated to be 66% for a 0.25 M solution of $Ph_3SnCl \cdot DMPU$ at 293 K, and 74% for $Ph_3SnBr \cdot DMPU$. The corresponding dissociation constants are $K = 0.32 \pm 0.01$ mol l^{-1} at 293 K, for $Ph_3SnCl \cdot DMPU$ and 0.53 ± 0.02 mol l^{-1} for $Ph_3SnBr \cdot DMPU$. Thermodynamic parameters for these dissociations were obtained by recording $\delta(^{119}Sn)$ in the temperature range of 20 to −50°C and doing regression analysis of $\ln K$ against $1/T$ plots. The results (regression coefficient = 0.999) are shown in Table 6, together with corresponding data for $Ph_3SnCl \cdot py$ obtained by Farhangi and Graddon [20] using a calorimetric method. Despite pyridine being a *N*-donor ligand, the values are similar in the three complexes.

Acknowledgement

We are grateful for the financial support of the Natural Sciences and Engineering Research Council of Canada and of le Gouvernement du Québec, Ministère de l'Education. We thank Drs. F. Sauriol and I. Wharf for helpful discussions.

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