Journal of Organometallic Chemistry, 120 (1976) 347—353

^{1}H NMR OF THE α,α'-BIPYRIDINE AND *o*-PHENANTHROLINE ADDUCTS OF n-BUTYLTIN TRICHLORIDE

GEN-ETSU MATSUBAYASHI * and TOSHIO TANAKA
Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka 565 (Japan)
(Received April 13th, 1976)

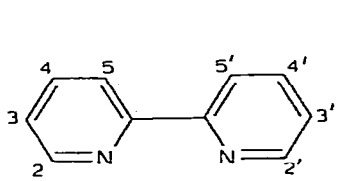
Summary

^{1}H NMR spectra of the α,α'-bipyridine adduct of n-$BuSnCl_3$ indicated the non-equivalence of the two pyridine rings. In particular the signals of the proton on the carbon atom adjacent to the two nitrogen atoms were widely separated. Similar spectral behavior was observed in the *o*-phenanthroline adduct. These adducts therefore are concluded to have the n-butyl group lying on the N—Sn—N plane of the hexacoordinated complexes. The configurational rearrangement of these adducts was markedly accelerated in the presence of excess n-$BuSnCl_3$.

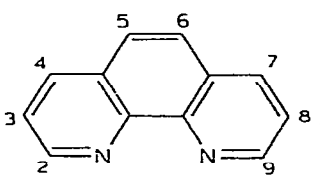
Introduction

Monoorganotin(IV) halides ($RSnX_3$) react with many organic donors to form stable adducts; $RSnX_3 \cdot 2L$ (L monodentate ligands). Several infrared and Mössbauer investigations on the adducts in the solid state have been reported [1—9]. There is, however, little information on their configuration in solution. This is partly due to the fact that the adducts are often too insoluble in organic solvents to perform physical and spectral measurements. In addition, even when dissolved in any organic solvent, they dissociate into $RSnX_3$ and L to some extent [9—12].

Recently, we have found that the α,α'-bipyridine (Bipy) and *o*-phenanthroline (Phen) adducts of n-butyltin trichloride are fairly soluble in acetonitrile or *N,N*-dimethylacetamide without dissociation. This paper reports the configuration and rearrangement of these adducts in solution which have been clarified on the basis of ^{1}H NMR spectra.



(Bipy)



(Phen)

Experimental

Preparation of Bipy and Phen adducts of n-BuSnCl$_3$

To a dichloromethane solution of Bipy or Phen was added an equimolar amount of n-BuSnCl$_3$. The white precipitate which appeared immediately was collected and recrystallized from acetonitrile, n-BuSnCl$_3$ · Bipy: m.p. 234—236°C (lit. [5] 226°C). Found: 38.35; H, 3.71; N, 6.53 $C_{14}H_{17}N_2Cl_3Sn$ calcd.: C, 38.36; H, 3.91; N, 6.39%. n-BuSnCl$_3$ · Phen: m.p. 240°C (decomp.) (lit. [5] 223—225°C, 237—239°C). Found: C, 41.50; H, 3.50; N, 6.25 $C_{16}H_{17}N_2Cl_3Sn$ calcd.: C, 41.56; H, 3.71; N, 6.06%.

Physical measurements

The molecular weight of the Bipy adduct was determined in acetonitrile at 37°C using a Mechrolab vapor pressure osmometer. Found: 426 (2.03×10^{-3} *M*) n-BuSnCl$_3$ · Bipy calcd.: 438. The Phen adduct was not soluble enough in the same solvent to permit the same measurement.

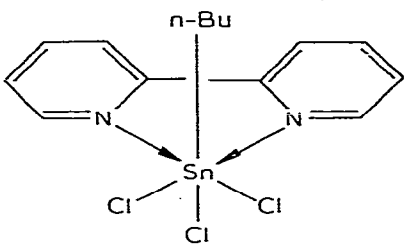
The molar conductance was determined in acetonitrile at 25°C using an Yokogawa universal bridge BVZ-13A as described previously [13]. n-BuSnCl$_3$ · Bipy: 0.43 ohm^{-1} cm^2 mol^{-1} (2.97×10^{-3} *M*). n-BuSnCl$_3$ · Phen: 0.50 ohm^{-1} cm^2 mol^{-1} (0.50×10^{-3} *M*). ^{1}H NMR spectra were measured as described previously [14].

Results and discussion

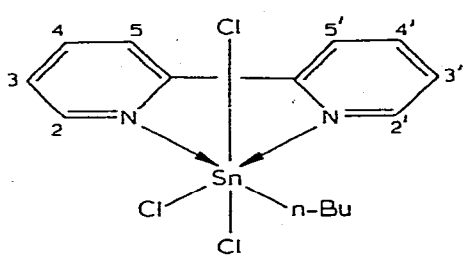
Configurations

Fig. 1 shows the ^{1}H NMR spectrum of n-BuSnCl$_3$ · Bipy in the ring proton region in acetonitrile at room temperature. Proton signals of the complexed Bipy are easily assigned by comparing them with those of uncomplexed Bipy [15]. All the signals of Bipy move downfield upon complex formation. This is due to inductive effect of the metal ion. It is to be noted that H(2) and H(2′) signals with identical intensity were widely separated, while the other pairs of signals (H(3)—H(3′), H(4)—H(4′), and H(5)—H(5′)) were closely spaced *.

The Bipy adduct is monomeric and a non-electrolyte in acetonitrile. Two possible configurations (A and B) are therefore suggested for the adduct in solution.



(A)



(B)

* Another weak doublet was observed at about δ 9.4 ppm. A similar doublet also occurred at about δ 9.7 ppm in the Phen adduct (see Fig. 2). The assignment of these signals is not obvious.

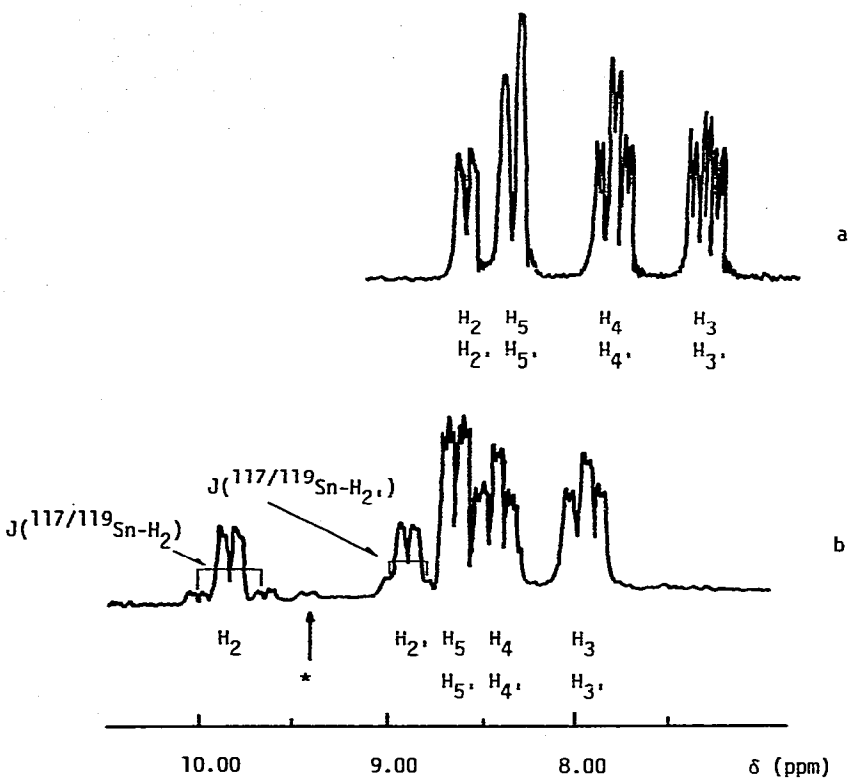
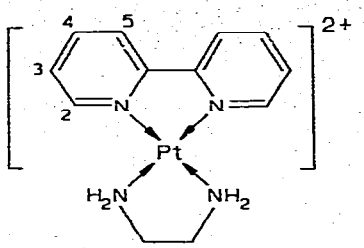


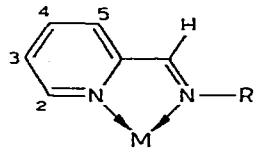
Fig. 1. ^{1}H NMR spectra of α,α'-bipyridine (a) and its adduct with n-butyltin trichloride (b) in acetonitrile at 24°C (* not assigned).

Configuration A predicts the occurrence of one signal due to each pair of H(2)—H(2′), H(3)—H(3′), H(4)—H(4′), and H(5)—H(5′), which is not compatible with the ^{1}H NMR spectrum. On the other hand, configuration B may well explain the large separation between the H(2) and H(2′)signals as well as small separations of the other signal pairs. The H(2) and H(2′) signals give satellites due to spin—spin coupling with the $^{117/119}$Sn nuclei. This is due to the strong Lewis acidity of n-$BuSnCl_3$. The Bipy adduct of $(n\text{-}Bu)_2SnCl_2$ was reported to dissociate considerably into neutral species in acetonitrile [16]. In accordance with this, the spin—spin interaction between the $^{117/119}$Sn and the ring protons is not observable in this solvent and each pair of the H(2)—H(2′), H(3)—H(3′), H(4)—H(4′), and H(5)—H(5′) protons appears as one signal, indicating that rapid exchange takes place between the complexed and free ligands. The present adduct may be one of the few examples [14,17] of organotin(IV) halide adducts in which the spin—spin coupling between the tin atom and ligand protons is observed. The coupling constants are larger in the downfield signal than in the upfield signal. If one can assume that the N(1′)—Sn bond is weaker than the N(1)—Sn because of the steric hindrance of the n-butyl group, the downfield signal would be assigned to the H(2) proton and the upfield one to H(2′). The values of coupling constants (^3J(M←NCH)) obtained here are comparable to

those in the following addition compounds;



$^3J(^{195}Pt-H_2)$; 32 Hz [18,19]



M = n-$BuSnCl_3$ $^3J(^{117/119}Sn-H_2)$; 29–33 Hz [17]

M = $PtCl_2$ $^3J(^{195}Pt-H_2)$; 38–40 Hz [20]

(R ; alkyl and aryl groups)

An acetonitrile solution of the Bipy adduct and excess Bipy exhibited two kinds of the Bipy proton signals due to the complexed and uncomplexed ligands at room temperature, indicating that the rate of exchange of Bipy between the coordination sphere and the bulk solution is slow on the NMR time scale. On the other hand, in the presence of excess n-$BuSnCl_3$ only one signal was observed for H(2)—H(2′), H(3)—H(3′), H(4)—H(4′), and H(5)—H(5′), respectively, and the H(2) (or H(2′)) signal appeared at the averaged position between those of the original H(2) and H(2′) signals. The $J(^{117/119}Sn-H(2)(H(2'))$ value (25 Hz) also agreed with the mean of the original two. These observations suggest that the presence of excess n-$BuSnCl_3$ could accelerate the rapid rearrangement between

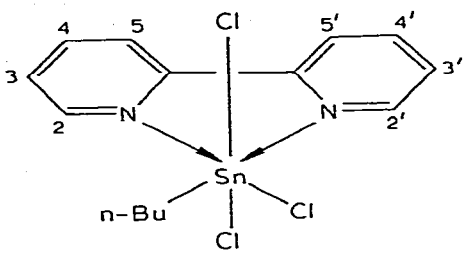
TABLE 1

RELEVANT ^1H NMR DATA [a] OF THE ADDUCTS n-$BuSnCl_3$(L—L)

L—L	Solvent	Chemical shift δ(ppm) [b]					
		H(2) (H(2))	H(2′) (H(9))	H(3), H(3′)	H(3), H(8)	H(4), H(4′)	(H(4), H(7))
Bipy	Acetonitrile	9.80 (—1.18)	8.83 (—0.23)	7.91 (—0.59)		8.37 (—0.54)	
	N,N-Dimethylacetamide	9.84 (—1.14)	9.24 (—0.54)	8.18 (—0.74)		8.63 (—0.69)	
	Dimethylsulfoxide	9.72 (—1.01)	8.97 (—0.26)	8.08 (—0.62)		8.55 (—0.60)	
Phen	*N,N*-Dimethylacetamide	10.16 (—1.01)	9.62 (—0.47)		8.55 8.47 (—0.76) (—0.68)		9.28 9.25 (—0.75) (—0.71)
	Dimethylsulfoxide	10.01 (—0.84)	9.45 (—0.26)		8.42 8.35 (—0.63) (—0.56)		9.17 (—0.65)

[a] Measured at 24°C. [b] The values in parentheses are (δ(free)—δ(complexed)). [c] Could not be obtained since the signal was obscured by the H(5),H(5′) signals.

the configurations B and B′, although the mechanism of this process is uncertain.



(B′)

The Bipy adduct in *N,N*-dimethylacetamide showed quite similar NMR spectral behavior to the observations in acetonitrile solution, both in the absence and in the presence of excess Bipy. However, the addition of excess n-$BuSnCl_3$ to the adduct in solution also showed separate H(2) and H(2′) signals. This observation, which is in contrast to that found in acetonitrile solution, indicates that the rapid rearrangement of the n-$BuSnCl_3$ moiety does not take place in this solvent. *N,N*-dimethylacetamide is known to have a stronger coordinating ability toward tin(IV) halides [21,22]. Thus, the excess n-$BuSnCl_3$ would be strongly solvated by the solvent molecules and so would be less active in the rearrangement. In dimethylsulfoxide, a more basic solvent, the adduct partly dissociates into n-$BuSnCl_3$ and Bipy, and signals of both the coordinated and free ligands were observed.

The spectrum of the Phen adduct in *N,N*-dimethylacetamide at room temperature is similar in its appearance to that of the Bipy adduct, as illustrated in Fig. 2; the H(2) and H(9) signals occurred separately with equal intensity as well as H(3)—H(8) and H(4)—H(7). This adduct was also a non-electrolyte in acetonitrile. In view of these results, the configuration around the tin atom of the Phen adduct in solution would be similar to that of the Bipy adduct. The ^{1}H NMR data of the Bipy and Phen adducts are summarized in Table 1.

		Coupling constant (Hz)	
H(5),H(5′)	(H(5),H(6))	$^3J\{^{117/119}Sn—H(2)(H(2))\}$	$^3J\{^{117/119}Sn—H(2′)(H(9))\}$
8.60 (—0.23)		39	11
9.13 (—0.65)		38	*c*
8.97 (—0.55)		40	*c*
	8.54 (—0.51)	40	11
	8.46 (—0.45)	41	12

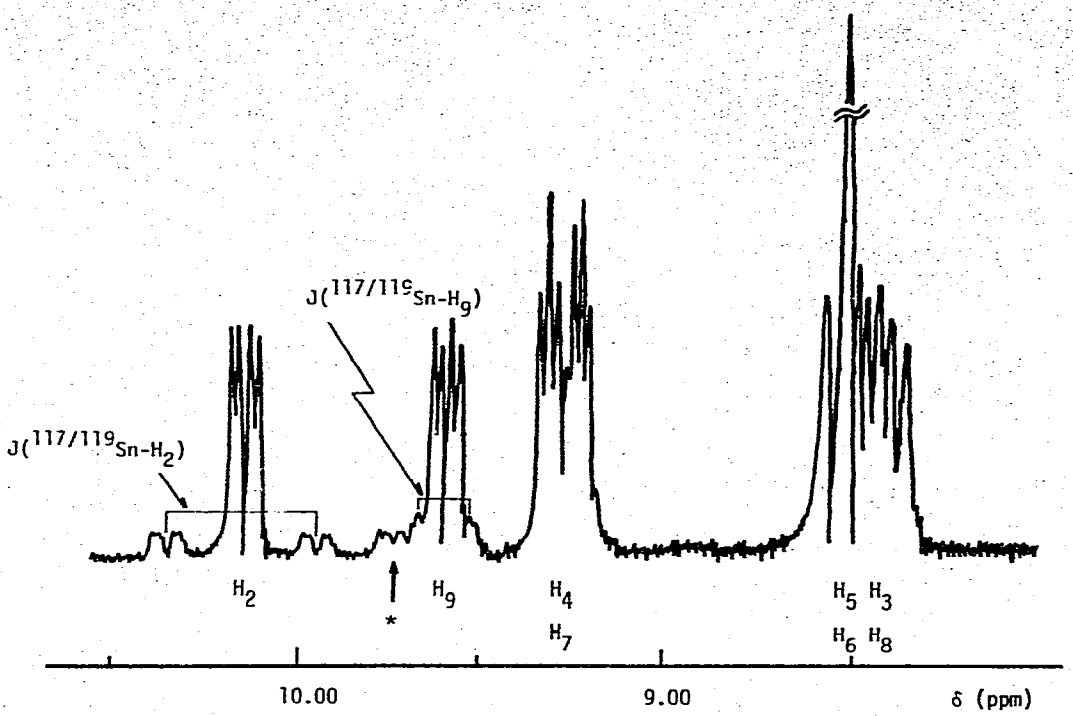


Fig. 2. ^{1}H NMR spectrum of the *o*-phenanthroline adduct of n-butyltin trichloride in *N,N*-dimethylacetamide at 24°C (* not assigned).

Variable temperature spectra

The H(2) and H(2′) signals of the Bipy adduct in acetonitrile broadened on raising the temperature and coalesced at 57°C. The signal became sharp again gradually at higher temperatures, and the satellites of the H(2) and H(2′) signals became undetectable up to about 95°C. On the other hand, the positions of the other proton signals were unchanged throughout the temperature range. These phenomena may be due to rapid exchange between the structures B and B′ without dissociation. The Gibbs energy of activation ($\Delta G^{\ddagger}_{Tc}$) of the rearrangement at the coalescence temperature was estimated to be 15.9 kcal/mol, using the approximate equation [23]. Similar spectra were observed in the Bipy and Phen adducts in *N,N*-dimethylacetamide; the H(2) and H(2′) signals of the Bipy adduct and of the H(2) and H(9) of the Phen adduct coalesced at 96°C and 108°C, respectively. The adducts in this solvent, however, partly dissociate into n-$BuSnCl_3$ and the ligands near these temperatures.

References

1 I.R. Beattie and G.P. McQuillan, J. Chem. Soc., (1963) 1519.
2 H.G. Langer and A.H. Blut, J. Organometal. Chem., 5 (1966) 288.
3 R.C. Poller and D.L.B. Toley, J. Chem. Soc., A (1967) 1578.
4 R.J.H. Clark, A.G. Davies and R.J. Puddephatt, J. Chem. Soc., A (1968) 1828.
5 A.G. Davies, L. Smith and P.J. Smith, J. Organometal. Chem., 23 (1970) 135.
6 R. Barbieri, R. Cefalu, S.C. Chandra and R.H. Herber, J. Organometal. Chem., 32 (1971) 97.

7 R. Cefalu, L. Pellerito and R. Barbieri, J. Organometal. Chem. 32 (1971) 107.
8 V.S. Petrosyan, N.S. Yashina, O.A. Reutov, E.V. Bryuchova and G.K. Semin, J. Organometal. Chem., 52 (1973) 321.
9 L. Pellerito, R. Cefalu, A. Gianguzza and R. Barbieri, J. Organometal. Chem., 70 (1974) 303.
10 J.L. Wardell, J. Organometal. Chem., 9 (1967) 89; 10 (1967) 53.
11 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, J. Inorg. Nucl. Chem., 28 (1966) 2937.
12 Y. Farhangi and D.G. Graddon, J. Organometal. Chem., 87 (1975) 67.
13 G. Matsubayashi, K. Wakatsuki and T. Tanaka, Org. Magn. Resonance, 3 (1971) 703.
14 G. Matsubayashi, M. Okunaka and T. Tanaka, J. Organometal. Chem., 56 (1973) 215.
15 T. McL. Spotswood and C.I. Tanzer, Aust. J. Chem., 20 (1967) 1227.
16 M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, J. Organometal. Chem., 4 (1965) 308.
17 G. Matsubayashi and T. Tanaka, to be published.
18 S.T. Chow and R.B. Martin, Inorg. Nucl. Chem. Lett., 10 (1974) 1131.
19 L.E. Erickson, J.E. Sarneski and C.N. Reilley, Inorg. Chem., 12 (1975) 3007.
20 K. Kawakami, T. Ohara, G. Matsubayashi and T. Tanaka, Bull. Chem. Soc. Japan, 48 (1975) 1440.
21 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, Bull. Chem. Soc. Japan, 40 (1967) 1566.
22 T.F. Bolles and R.S. Drago, J. Amer. Chem. Soc., 88 (1966) 3921; 5730.
23 J.A. Pople, W.G. Schneider and H.J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959, p. 233.