Journal of Organometallic Chemistry, 136 (1977) 169—171
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

BEHAVIOUR OF 2,2'-BIPYRIDYL TOWARDS METHYLETHYL- AND n-PROPYL-(n-BUTYL)-TIN DICHLORIDES IN NITROBENZENE

K.L. JAURA and K. LAL
Department of Chemistry, Panjab University, Chandigarh-160014 (India)

(Received March 11th, 1977)

Summary

The conductivities of mixtures of 2,2'-bipyridyl with $MeEtSnCl_2$ or $BuPrSnCl_2$ in nitromethane are interpreted in terms of formation of (i) $RR'SnCl_2 \cdot bipy$, (ii) $[RR'SnClbipy]^+ Cl^-$, and (iii) $(RR'SnCl_3)^-$.

There is much interest in the adducts of 2,2'-bipyridyl (bipy) with organotin halides and pseudo-halides [1—10]. Mufti et al. [1] showed that in addition to complexes in which it acts as a bidentate chelating ligand, bipy also forms a 1/2 complex with $Ph_2Sn(NCO)_2$ in which it bridges the two tin atoms through nitrogens. Later Hollway et al. [8] prepared a 1/2 complex of bipy with $Me_3Sn(NCS)$ involving bipy as a bridging ligand, but attempts to prepare similar complexes with Me_3SnCl were unsuccessful.

To throw light on the nature of the reaction of bipy with organotin halides we have carried out conductometric studies of mixtures of bipy with $RR'SnCl_2$ (R, R' = methyl, ethyl and n-propyl, n-butyl) in nitrobenzene. Plots of relative conductance values vs. molar ratios of bipy to $RR'SnCl_2$ are shown in Fig. 1.

The conductance curves are similar to those obtained in the analogous reactions of pyrrolidine except that in the latter case an increase in the relative conductance beyond a 1/1 base to acid molar ratio was observed [11]. Increase in relative conductance until the concentration of bipy is almost half of that of $RR'SnCl_2$ may be explained on the basis of eq. 1—3.

$$RR'SnCl_2 + bipy \rightleftharpoons RR'SnCl_2 \cdot bipy \quad (1)$$

$$RR'SnCl_2 \cdot bipy \rightleftharpoons [RR'SnCl\ bipy]^+ + [Cl]^- \quad (2)$$

$$RR'SnCl_2 + [Cl]^- \rightleftharpoons [RR'SnCl_3]^- \quad (3)$$

Compounds containing 5-coordinate tin are now well known, and Joshi et al. also produced evidence for the formation of $[RR'SnCl_3]^-$ anions [12].

The above interpretation shows that even when $RR'SnCl_2$ is present in excess bipy does not form 1/2 adducts with $RR'SnCl_2$ in which it might act as a bridg-

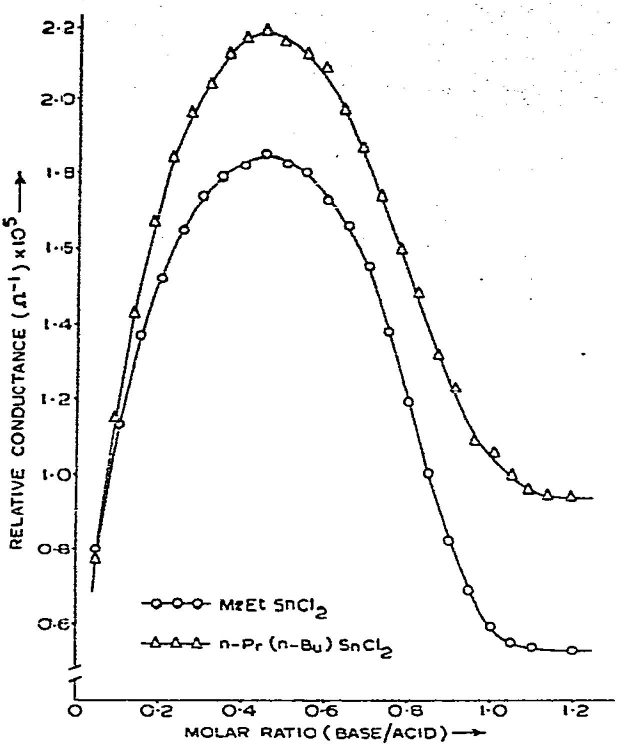

Fig. 1. Variation in the relative conductance of the solutions of RR'SnCl$_2$ in nitrobenzene on the addition of 2,2'-bipyridyl.

ing ligand. If 1/2 adducts were formed reaction 3 would have to stop well before the concentration of bipy reached half of that of RR'SnCl, since free Lewis acid is needed to take up the chloride ion liberated in reaction 2 and maxima would occur when the base to acid ratio reaches approximately 1/4.

Figure 1 shows that further addition of bipy after its concentration has reached almost half of that of RR'SnCl$_2$ causes a decrease in the relative conductance. This suggests that the added bipy reacts with the ions present to form a stable octahedral complex, which dissociates only to a small extent in the absence of free Lewis acid. The overall reaction may be as shown in eq. 4.

$$[\mathrm{RR'SnCl}\cdot\mathrm{bipy}]^+ + [\mathrm{RR'SnCl_3}]^- + \mathrm{bipy} \rightleftharpoons 2\ \mathrm{RR'SnCl_2}\cdot\mathrm{bipy} \qquad (4)$$

Lack of dissociation of the octahedral complex would be consistent with the observations by Fergusson et al. [3] on the bipy complex of Me$_2$SnCl$_2$. Further, since no increase in the conductance takes place on the addition of bipy after its concentration becomes almost equal to that of RR'SnCl$_2$, the equilibria analogous to those proposed by Tanaka et al. [9] for the bipy complex of Me$_2$SnI$_2$ do not seem to react in our case.

Experimental

Nitrobenzene (G.R. Grade) purified as before [13] was used. RR'SnCl$_2$(R, R' = Me, Et, n-Pr, n-Bu) were prepared by redistribution [14,15]. 2,2'-bipyridyl

(BDH, A.R. Grade) was used as supplied. Conductance measurements were made on the Phillips Conductivity Bridge Type PR 9500 and dip-type cells were used.

References

1 A.S. Mufti and R.C. Poller, J. Organometal. Chem., 3 (1965) 99.
2 R.J.H. Clark and C.S. Williams, Spectrochim. Acta, 21 (1965) 1861.
3 J.E. Ferguson, W.R. Roper and C.J. Wilkins, J. Chem. Soc., (1965) 3716.
4 J.P. Clark and C.J. Wilkins, J. Chem. Soc. A, (1966) 871.
5 R.J. Clark, A.G. Davies and R.J. Puddephatt, J. Chem. Soc. A, (1968) 1828.
6 B.W. Fitzmmons, N.J. Seeley and A.W. Smith, J. Chem. Soc. A, (1969) 143.
7 R.C. Poller, J.N.R. Ruddick, M. Thevarsa and W.R. McWhinnie, J. Chem. Soc. A, (1969) 2327.
8 J.H. Hollway, G.P. McQuillan and D.S. Ross, J. Chem. Soc. A, (1969) 2505.
9 T. Tanaka, G. Matsubayashi, A. Shimizu and S. Matsuo, Inorg. Chim. Acta, 3 (1969) 187.
10 F.P. Mullins, Can. J. Chem., 48 (1970) 1677.
11 K.L. Jaura and K. Lal, Inorg. Nucl. Chem. Lett., in press.
12 K.K. Joshi and P.A.H. Wyatt, J. Chem. Soc., (1959) 3825.
13 K.L. Jaura, K. Lal and S.N. Singla, J. Inorg. Nucl. Chem., 38 (1976) 2009.
14 K.L. Jaura and K. Lal, J. Less-Common Met., in press.
15 K.L. Jaura and K. Lal, Inorg. Nucl. Chem. Lett., submitted.