Journal of Organometallic Chemistry, 202 (1980) C93—C94
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

^{119}Sn CHEMICAL SHIFTS IN SEVEN-COORDINATE ORGANOTIN COMPOUNDS

JUNZO OTERA*, TOMOYA HINOISHI, and ROKURO OKAWARA
Okayama University of Science, Ridai-cho, Okayama 700 (Japan)

(Received September 30th, 1980)

Summary

The FT NMR studies revealed that ^{119}Sn chemical shifts in seven-coordinate organotin compounds are more than 100 ppm upfield from those in six-coordinate analogues.

One of the most notable features of ^{119}Sn NMR spectroscopy is the dependence of ^{119}Sn chemical shifts ($\delta(^{119}\text{Sn})$) on the coordination number of tin; that is, $\delta(^{119}\text{Sn})$ moves upfield with increasing coordination number from four to five and six [1]. Although seven coordination in organotin compounds has been the subject of considerable interest in recent years [2], few studies have been made on ^{119}Sn NMR spectra of these compounds. As a part of our studies of ^{119}Sn NMR spectra, we investigated the $\delta(^{119}\text{Sn})$ values in some seven-coordinate organotin compounds in the hope of obtaining further insight into the relation between $\delta(^{119}\text{Sn})$ and the coordination number.

The ^{119}Sn FT NMR spectra with complete proton noise decoupling were measured using a Jeol FX-100 spectrometer operating at 37.08 MHz at 22°C. Field-frequency control was made with an external D_2O lock. The chemical shifts were determined relative to external tetramethyltin ($\delta = 0$) and were found to be accurate to ± 1 ppm by repeated measurements. The results are summarized in Table 1, in which the $\delta(^{119}\text{Sn})$ values in six-coordinate analogues are also given in order to show the effect of seven coordination.

Compounds I [3], III [4] and IV [5] have already been reported to maintain the seven coordination in solution. Compound II [6] is not soluble in common organic solvents except for DMF, in which this compound was confirmed to have virtually seven-coordinate tin, since the value of $^2J(\text{CH}_3\text{—}^{119}\text{Sn})$ (114.0 Hz) is close to that of I (115.8 Hz)[3].

Apparently the $\delta(^{119}\text{Sn})$ values in seven-coordinate compounds except II are more than 100 ppm upfield from those in six-coordinate analogues. The low $\delta(^{119}\text{Sn})$ value for II might be due to a slight dissociation of ligands in a polar medium such as DMF. A slight ionic dissociation of II in this solvent was also

TABLE 1

^{119}Sn CHEMICAL SHIFTS IN SEVEN-COORDINATE AND CORRESPONDING SIX-COORDINATE ORGANOTIN COMPOUNDS[a]

Seven-coordinate			Six-coordinate		
Compound	Solvent	$\delta(^{119}Sn)$ (ppm)	Compound	Solvent	$\delta(^{119}Sn)$ (ppm)
$(CH_3)_2Sn(pan)(acac)$ (I)	30% $CHCl_3$	—463	$(CH_3)_2Sn(acac)_2$	10% $CHCl_3$	—365(—366 [1])
$(CH_3)_2Sn(NCS)_2(TPy)$ (II)	20% DMF	—409	$(CH_3)_2Sn(NCS)_2(DPy)$	20% DMF	—363
$BuSn(Ox)_3$ (III)	10% $CHCl_3$	—561	$BuSn(OEt)_3$ $BuSn(Ox)_2Cl$	48% C_6H_6 sat. $CHCl_3$	(—432 [7]) (—395 [7])
$PhSn(dtc)_3$ (IV)	5% $CHCl_3$	—695	$PhSn(dtc)_2Cl$	5% $CHCl_3$	—361

[a] Abbreviations for ligands; pan = 1-(2-pyridylazo)-2-naphtholate, acac = acetylacetonate, TPy = 2,2',2''-terpyridyl, DPy = 2,2'-dipyridyl, Ox = oxinate, and dtc = *N,N'*-dimethyldithiocarbamate.

suggested by its molar conductivity (0.211 Ω^{-1} cm^2 mol^{-1} at 10^{-4} mol l^{-1}). While six-coordinate organotin compounds usually have octahedral configuration, the most probable ligand arrangement for seven-coordinate compounds is that of a pentagonal bipyramid with axial Sn—C bonds [2], which have increased *s*-character as is evident from the large $^2J(CH_3—^{119}Sn)$ values. It has been reported that the increase in *s*-character in Sn—C bonds induces an upfield shift of $\delta(^{119}Sn)$ values [8].

References

1 P.J. Smith and A.P. Tupciauskas, Ann. Rep. NMR Spectroscopy, 8 (1978) 291.
2 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24 (1978) 251.
3 Y. Kawasaki and T. Sasaki, Chem. Lett., (1979) 279.
4 K. Kawakami, Y. Kawasaki, and R. Okawara, Bull. Chem. Soc. Japan, 40 (1967) 2693.
5 J.C. May, D. Petridis, and C. Curran, Inorg. Chim. Acta, 5 (1971) 511.
6 J.C. May and C. Curran, J. Organometal. Chem., 39 (1972) 289.
7 J.D. Kennedy, W. McFarlane, P.J. Smith, and R.F.M. White, J. Chem. Soc. Perkin II, (1973) 1785.
8 P.J. Smith and L. Smith, Inorg. Chim. Acta Rev., 7 (1973) 11.