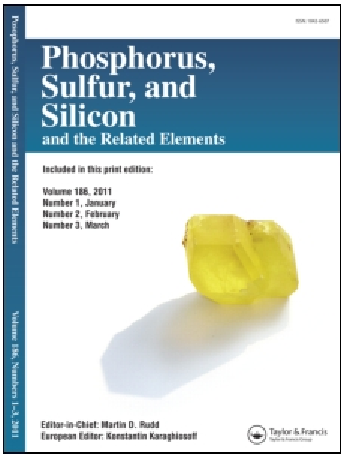

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Tin(IV) Tetrachloride Complexes with Bis-(Dialkylamino)phosphoryl Fluoride: A Multinuclear (^{119}Sn, ^{31}P, ^{19}F, and ^{1}H) NMR Characterization in Solution

M. A. M. Khouna[a]; M. T. Ben Dhia[a]; M. R. Khaddar[a]
[a] Laboratory of Coordination Chemistry, Department of Chemistry, University of Tunis El Manar, Tunis, Tunisia

To cite this Article Khouna, M. A. M. , Dhia, M. T. Ben and Khaddar, M. R.(2005) 'Tin(IV) Tetrachloride Complexes with Bis-(Dialkylamino)phosphoryl Fluoride: A Multinuclear (^{119}Sn, ^{31}P, ^{19}F, and ^{1}H) NMR Characterization in Solution', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 7, 1673 — 1682

To link to this Article: DOI: 10.1080/104265090885110

URL: http://dx.doi.org/10.1080/104265090885110

Phosphorus, Sulfur, and Silicon, 180:1673–1682, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090885110

Tin(IV) Tetrachloride Complexes with Bis-(Dialkylamino)-phosphoryl Fluoride: A Multinuclear (^{119}Sn, ^{31}P, ^{19}F, and ^{1}H) NMR Characterization in Solution

M. A. M. Khouna
M. T. Ben Dhia
M. R. Khaddar
Laboratory of Coordination Chemistry, Department of Chemistry,
University of Tunis El Manar, Tunis, Tunisia

The two octahedral complexes $SnCl_4{\cdot}2(O)PF(NR_2)_2$ (R = Me or Et) were prepared from reaction of $SnCl_4$ with the ligand $(R_2N)_2P(O)F$ in anhydrous $CHCl_3$. The new adducts have been characterized by elemental analysis, IR, and multinuclear (^{119}Sn, ^{31}P, ^{19}F, and ^{1}H) NMR spectroscopy. The NMR data show that the adducts exist in solution as a mixture of cis and trans isomers with markedly different proportions. When compared with previously described hexamethylphosphoramide (HMPA) and trimethylphosphate (TMPA) analogues, our results indicate that the cis isomer is the predominant species in solution. Low temperature ^{31}P and ^{119}Sn NMR spectra show that the compounds partially dissociate in dichloromethane.

Keywords ^{31}P NMR; ^{119}Sn NMR; ^{119}Sn-^{31}P coupling constants; phosphoryl ligands; tin tetrachloride

INTRODUCTION

Phosphine oxides of the type $R_1R_2R_3P{=}O$ are known to behave as donor ligands to Lewis acids by coordination through oxygen.[1–3] The substituent effects of various R groups (R = alkyl, aryl, halogen, dialkylamino, alkoxy, etc) on the particular donor character and the interplay between p_π-d_π bonding of (P=O) and (P–R) components are perhaps the main features in terms of coordination patterns.[4] Tin(IV) tetrachloride forms with such phosphoryl ligands octahedral complexes having the general formula $SnCl_4 \cdot 2L$ (L is the phosphoryl ligand).[5,6]

Received June 23, 2004; accepted August 12, 2004.

The authors wish to thank Professor A. Baklouti of the Department of Chemistry, Faculty of Sciences of Tunis, University of Tunis El Manar for his valuable help and discussions of this work.

Address correspondence to M. R. Khaddar, Laboratory of Coordination Chemistry, Department of Chemistry, Faculty of Sciences of Tunis, University of Tunis El Manar, 1060 Tunis, Tunisia. E-mail: senhourry@yahoo.com

In these compounds, two isomers, with the ligand L in cis or trans mutual orientations, are possible. The complex of $SnCl_4$ with HMPA, $SnCl_4 \cdot 2HMPA$, has been shown to exist as a trans-adduct in the solid by X-ray diffraction[7] and in solution as a mixture of both cis and trans isomers by IR and NMR spectroscopies,[8,9] whereas the complex with TMPA is mainly a cis-adduct.[8] Steric factors and the base strength (i.e., the donor character of the P=O group of the ligand) as well as other factors (solvent polarity, temperature, etc.) may be held responsible for the differences observed.

In order to explore effects of substitution of a dimethylamino group by a fluorine atom on the donor character of the P=O group in HMPA, we have previously studied beryllium complexes containing the ligand $(Me_2N)_2P(O)F$ by multinuclear NMR in solution.[10]

Here we report the synthesis of two new complexes of tin(IV) tetrachloride with the ligands $(R_2N)_2P(O)F$ (R = Me or Et). The compounds were characterized by elemental analysis, IR, and multinuclear (^{119}Sn, ^{31}P, ^{19}F, and ^{1}H) NMR spectroscopy. On the basis of NMR data, we postulate the predominance in solution of the cis isomer.

RESULTS AND DISCUSSION

Treatment of $SnCl_4$ in a chloroform solution with the $(R_2N)_2P(O)F$ (R = Me or Et) gives white solids with the composition $SnCl_4 \cdot 2L$ ($L = (R_2N)_2P(O)F$). These complexes are soluble in nitromethane and acetonitrile and sparingly soluble in dichloromethane and chloroform. The characterization of the complexes prepared was based particularly on their NMR data and comparison with the corresponding data for the free ligands.

The infrared spectra show strong bands within the range 1220–1230 cm^{-1} attributed to $\nu_{P=O}$. The P=O stretching vibration is shifted towards lower wave numbers on coordination to the tin atom compared with its value for the free ligands. The coordination shift is about 100 cm^{-1} and is consistent with relatively strong phosphoryl coordination to the tin atom. This shift is 103 cm^{-1} for $(Me_2N)_2P(O)F$ against 138 cm^{-1} for HMPA,[5] explaining the difference in the basicity strength between these two ligands which is most likely due to the substitution of a dimethylamino group by a fluorine atom. The absorption band at 514 cm^{-1} corresponds to Sn—O group.

The NMR spectra of the two complexes prepared are quite similar and the data obtained from these spectra are summarized in Table I.

The ^{31}P NMR resonances of bound ligands are shifted to a higher field compared with those of the free ligand, whereas the ^{19}F and ^{1}H NMR resonances show a down field shift on complexation. The difference in

TABLE I NMR Data (NMR Data (δ/ppm and J/Hz) for the Complexes $SnCl_4 \cdot 2L$ and the Ligands $(R_2N)_2P(O)F$ in CD_2Cl_2 at −5°C

Compound	δ_{31P}	δ_{19F}	δ_{119Sn}	$^1J_{P-F}$	$^2J_{31P-119Sn}$	$(^3J_{P-H})^*$
L = $(Me_2N)_2P(O)F$	19.13	81.0	—	943	—	10.68
cis-$SnCl_4 \cdot 2(O)PF(NMe_2)_2$	13.80	81.5	−546	957	126	11.40
trans-$SnCl_4 \cdot 2(O)PF(NMe_2)_2$	14.73	82.0	−567	955	192	11.40
L = $(Et_2N)_2P(O)F$	16.3	85.0	—	950	—	—
cis-$SnCl_4 \cdot 2(O)PF(NEt_2)_2$	10.80	85.0	−550	973	145	—
trans-$SnCl_4 \cdot 2(O)PF(NEt_2)_2$	12.74	85.6	−567	975	196	—

*Proton–phosphorus coupling ($^3J_{P-H}$) was measured at −25°C.

the ^{31}P chemical shift between free and bound ligands is more important than that observed in ^{19}F and ^1H NMR spectra, confirming coordination of the fluorophosphoramide ligand through the oxygen atom. The coupling constants $^1J_{P-F}$ and $^3J_{P-H}$ are larger for the complexed ligand than for the free one (Table I).

The ^{31}P NMR spectra of each of the complexes prepared showed the expected doublet pattern (the doublet being due to phosphorus–fluorine coupling) with splitting due to ^{31}P-^{119}Sn coupling. The latter splitting can be clearly seen only at a low temperature.

In addition, the spectra also contain a doublet of low intensity indicating the existence of small amount of another species. This minor doublet showed also ^{31}P-^{119}Sn splitting even at room temperature (Figure 1).

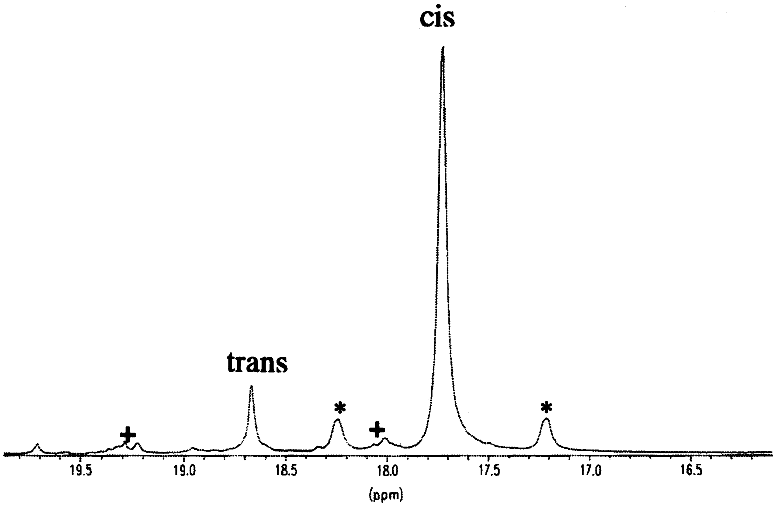

FIGURE 1 The low-field half of the ^{31}P-$\{^1H\}$ NMR spectrum of $SnCl_4 \cdot 2(O)PF(NMe_2)_2$ in CD_2Cl_2 at −5°C (* and + designate satellites of cis and trans complexes, respectively).

The ^{119}Sn NMR spectrum of each complex displayed at room temperature two broad signals in the region of hexacoordinated species.[11] These broad signals were converted at low temperature into the expected triplets. At −5°C, the spectrum showed therefore tow triplets, a major triplet and a very small intensity triplet with different $^{2}J_{31P-119Sn}$-coupling constants. Clearly two species with markedly different proportions were present and in the two species each tin atom is coupled to two phosphorus atoms, showing a stoichiometry of $SnCl_4{\cdot}2L$. This is in agreement with the ^{31}P NMR spectra where two doublets displaying ^{119}Sn satellites with corresponding coupling constants were present (Figure 1).

In the presence of excess ligand, the ^{119}Sn NMR spectrum of the complex $SnCl_4{\cdot}2(O)PF(NEt_2)_2$ showed, in addition to the two broad signals observed above, a very broad peak at −473 ppm and a resoled quartet at −570 ppm (Figure 2(a)). This quartet is due to coupling with three ligand molecules.

We attribute the quartet ($^{2}J_{31P-119Sn} = 147$ Hz) observed in the hexacoordinate region to the ion $SnCl_3[(Et_2N)_2P(O)F]_3^+$ similar to the quartet observed for the ion $Ph_2SnBr(TBPO)_3^+$.[12] Following the reasoning of Colton and Dakternieks,[12] we believe that the ion is formed by displacement of chloride by a ligand molecule. At low temperature, the ^{119}Sn spectrum (Figure 2(b)) showed, instead of the broad peak, two doublets in the region of pentacoordinated tin,[11] whereas two triplets and the quartet were observed in the hexacoordinate region. This indicates that these different tin species are presumably in rapid equilibrium with each other and with the free ligand, consistent with ^{1}H and ^{19}F NMR spectra (Figures 3 and 4(a)) where ligand exchange reactions are fast at room temperature. The rate of these reactions were decreased by lowering the temperature and separate doublets corresponding to the free ligand and to the major species present in solution (Figures 3 and 4(b)).

Cooling to −30°C revealed the presence in the ^{31}P NMR spectrum a new signal at 11.42 ppm (10% of relative intensity) with $^{119/117}$Sn satellites with corresponding $^{2}J(Sn\text{-}P)$ couplings of 147 and 141Hz, in addition to $SnCl_4{\cdot}2L$ and to the free ligand which we assign to $SnCl_4{\cdot}L$. This assignment is supported by the presence of a doublet pattern in the ^{119}Sn NMR spectrum. Further cooling of the sample increased the ^{31}P NMR signal at 11.42 ppm to 30% relative intensity and at 10.90 ppm another less intense peak began to appear, in agreement with the presence of two doublets in the ^{119}Sn NMR spectrum at −35°C (Figure 2(b)). This result suggests that the 1:1 complex is in equilibrium with 1:2 complex and is detectable at −35°C in significant concentration. Such an

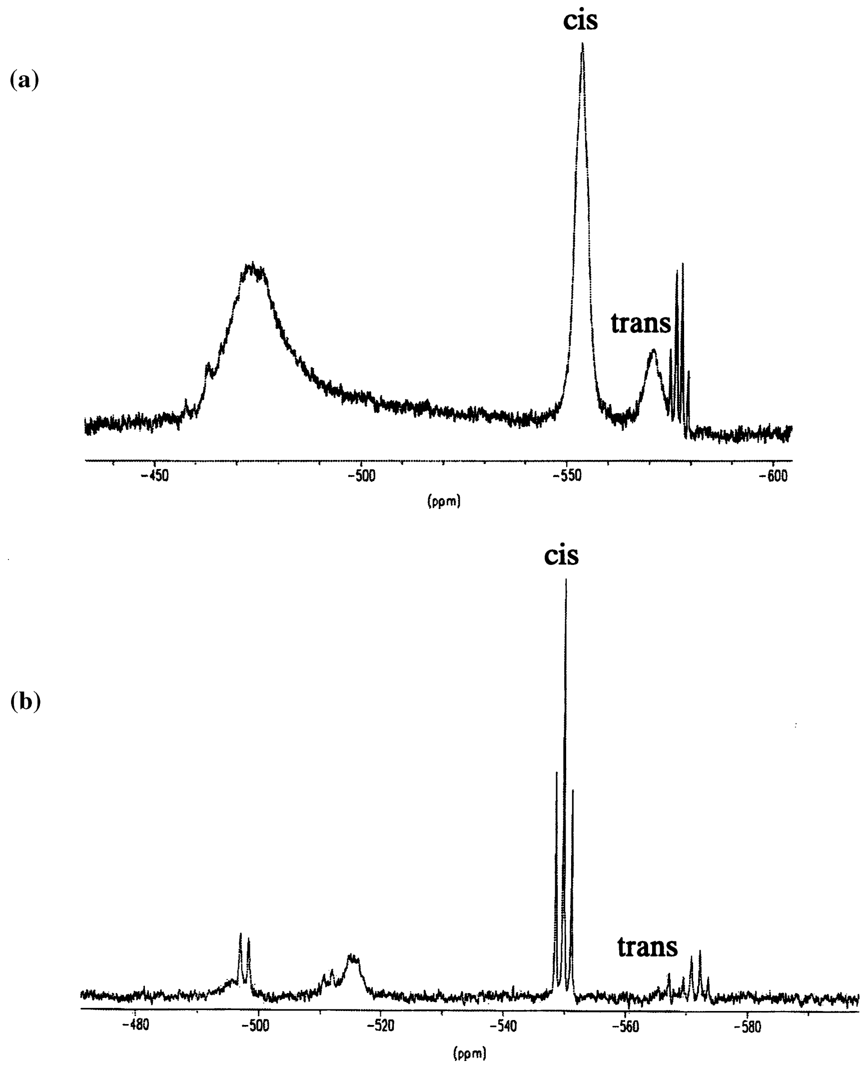

FIGURE 2 ^{119}Sn NMR spectra of a mixture of the complex $SnCl_4{\cdot}2(O)PF(NEt_2)_2$ and the ligand in CD_2Cl_2 (a) at 25°C, and (b) at −35°C.

equilibrium was observed by Denmark et al.,[13] sometimes referred to as partial dissociation of the type:

$$SnCI_4 \cdot 2L \rightleftharpoons SnCI_4 + L.$$

In solution, complexes of the general formula $SnCl_4{\cdot}2L$ exist as a mixture of both cis and trans isomers.[14] By correlating the IR and

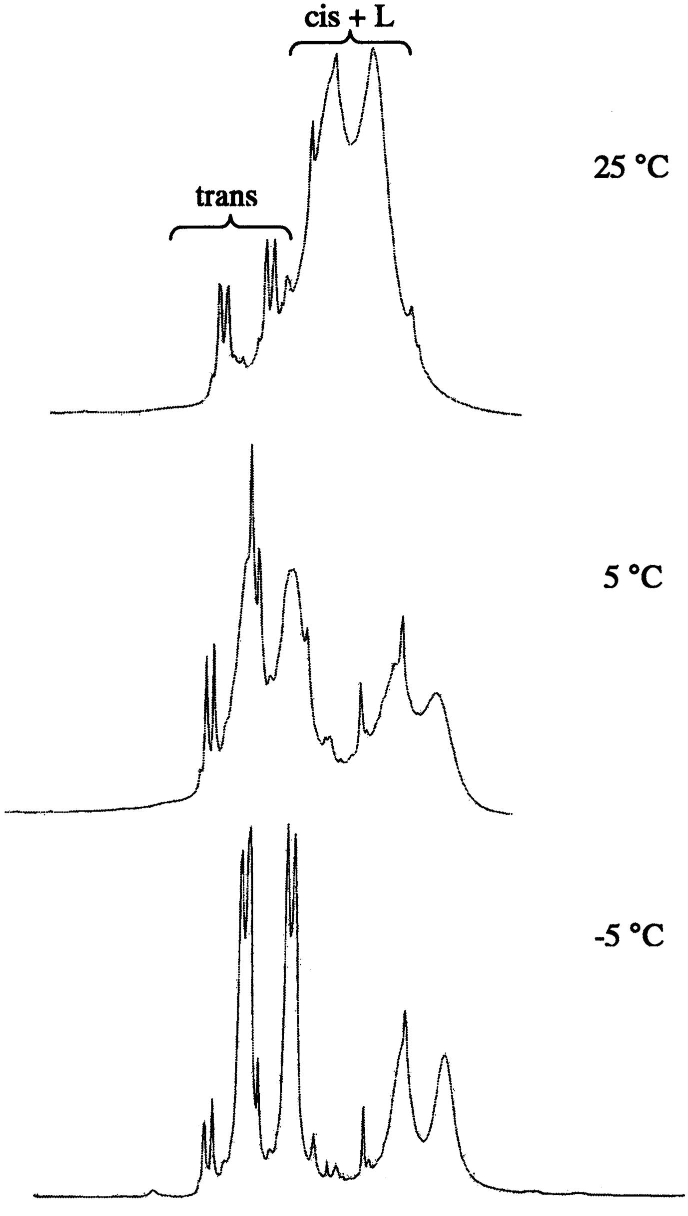

FIGURE 3 ^{1}H NMR spectra of a mixture of the complex $SnCl_4 \cdot 2(O)PF(NMe_2)_2$ and the ligand in CD_2Cl_2 at different temperatures. *(Continued)*

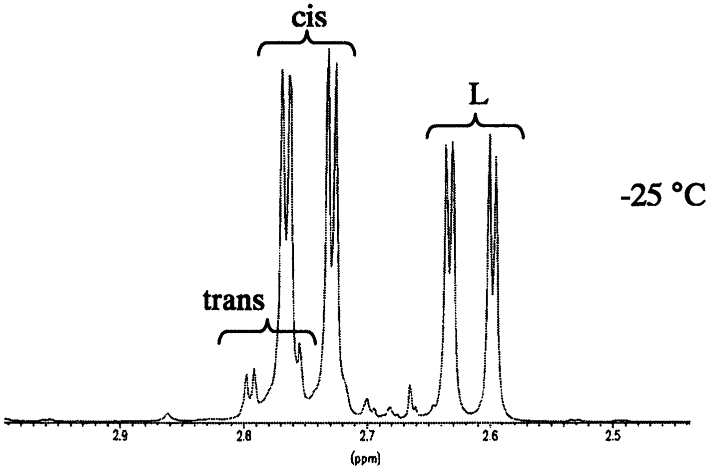

FIGURE 3 (Continued)

Raman data of the complex $SnCl_4 \cdot 2(HMPA)$ with ^1H and ^{31}P NMR studies, Ruzicka and Merbach[8] showed that increasing the temperature to 300 K led to coalescence of ^1H NMR signals of free and cis ligands, leaving the trans signal unaffected. This result is in agreement with our observation of ^1H and ^{19}F NMR spectra where trans signals appeared at a lower field than the cis ones (Figures 3 and 4). Furthermore, the authors have shown that the coupling constants $^2J_{31P-119Sn}$ were different for cis and trans isomers in the complexes of $SnCl_4$ with $(Me_2O)_3PO$ (TMPA) and $Me_2N(Me_2O)_2PO$. At 203 K, the cis isomers of the two complexes had $^2J(^{31}P\text{-}^{119}Sn)$ of 146 and 141 Hz, respectively, and that the trans isomers were 195 and 194 Hz respectively, whereas coupling constants of 102 and 168 Hz at 183 K were observed for the cis and trans complexes of $SnCl_4 \cdot 2HMPA$,[9] respectively. These results are in agreement with the coupling constants of 126 and 192 Hz observed for $SnCl_4 \cdot 2(O)PF(NMe_2)_2$ at 268 K in our case. It is therefore possible to assign the major species observed in the NMR spectra of the complex $SnCl_4 \cdot 2(O)PF(NMe_2)_2$ at 268 K to the cis isomer ($^2J(^{31}P\text{-}^{119}Sn) =$ 126 Hz). By comparing the coupling constants, the major species of the complex $SnCl_4 \cdot 2(O)PF(NEt_2)_2$ could also be assigned to the cis isomer and the minor species to the trans one. This assignment is also confirmed by ^{119}Sn and ^{31}P chemical shifts, which showed that the cis signals (the major triplet) appeared at a higher field than the trans ones in the ^{119}Sn NMR spectra, whereas those of the trans isomer were shifted to a lower field in the ^{31}P NMR spectra compared with the signals (the major doublet) of the cis isomer, in agreement with literature results.[9,15]

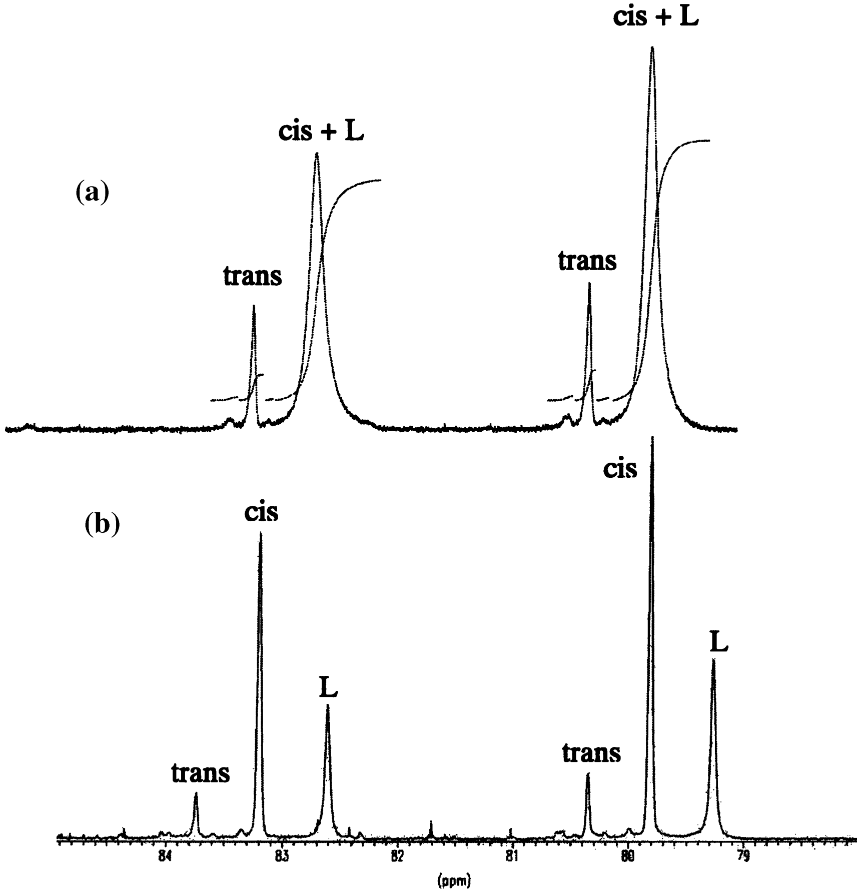

FIGURE 4 ^{19}F NMR spectra of a mixture of the complex $SnCl_4{\cdot}2(O)PF(NMe_2)_2$ and the ligand in CD_2Cl_2 (a) at 25°C, and (b) at −5°C.

On the basis of the above results, the NMR data suggest the predominance of the cis geometry for the complexes $SnCl_4{\cdot}2(O)PF(NR_2)_2$ in dichloromethane solution within the temperature range studied. This could be explained in terms of a decrease both in the base character of the P=O group of the ligand $(O)PF(NR_2)_2$ and in its bulkiness compared with HMPA as a result of the substitution of a dialkylamino group in the ligand $(R_2N)_3P(O)$ by a fluorine atom.

The quartet observed in the ^{119}Sn NMR spectrum (Figure 2) at −571 ppm is presumed to be a result of the equivalency of ligand molecules produced by exchange between two or more octahedral isomers also suggested by Yoder et al. for the ion $BuSnCl_2(TBPO)_3^+$.[16] The two doublets observed in the five-coordinate adduct region of the ^{119}Sn NMR spectrum at −35°C (Figure 2b) presumably correspond to the two possible trigonal bipyramidal isomers. The chemical shifts and the magnitude of the couplings suggest that the downfield doublet at −497 ppm ($^{2}J(^{31}P\text{-}^{119}Sn) = 147$ Hz) is due to the equatorial isomer while the upfield doublet at −511 ppm ($^{2}J(^{31}P\text{-}^{119}Sn) = 130$ Hz) is due to an axial phosphorus.[17,18]

EXPERIMENTAL

All preparations were carried out under a nitrogen atmosphere in solvents dried by standard techniques[19] and stored over molecular sieves. NMR spectra were recorded on a Bruker Ac-300 instrument in CD_2Cl_2 as solvent, ^{31}P at 121 MHz (85% H_3PO_4), ^{19}F at 282 MHz ($CFCl_3$), ^{1}H at 300 MHz (TMS), and ^{119}Sn at 111 MHz ($SnCl_4$). IR spectra: Perkin Elmer Paragon 1000 PC.

Tin tetrachloride was distilled under vacuum before use. The ligands $(R_2N)_2P(O)F$ were prepared according to methods described in literature (R = Me[20], R = Et[21]).

In a typical reaction $(Me_2N)_2P(O)F$ (1.26 g, 8.2 mmol) in dry $CHCl_3$ (10 cm^3) was slowly added to $SnCl_4$ (0.5 cm^3, 4.1 mmol) in $CHCl_3$ (20 cm^3) over a 30-minute period. The resulting solution, on continual stirring, began to precipitate the white solid complex $SnCl_4{\cdot}2(O)PF(NMe_2)_2$. The precipitation was complete when the product was left 24 h at −15°C. This was collected, washed with n-hexane/CCl_4, and recrystallized from nitromethane as a white powder (Yield: 2.3 g, 65%). Analysis: Calc. for $C_8H_{24}N_4O_2P_2F_2SnCl_4$: C, 16.89; H, 4.25; N, 9.85%. Found: C, 17.75; H, 3.87; N, 9.83%.

IR: $\nu_{P=O}$(1221 cm^{-1}); ν_{Sn-O} (514 cm^{-1}).

REFERENCES

[1] N. M. Karayannis, C. M. Mikulski, and L. L. Pytlewski, *Inorg. Chim. Acta Rev.*, **5,** 69 (1971).

[2] J. P. Rose, R. A. Lalancette, J. A. Potenza, and H. L. Schugar, *Acta Crystallogr. Sect. B*, **36,** 2409 (1980).

[3] C. A. Kosky, J.-P. Gayda, J. F. Gibson, S. F. Jones, and D. J. Williams, *Inorg. Chem.*, **21,** 3173 (1982).

[4] H. R. Hays and D. J. Peterson, *Organic Phosphorus Compounds*, G. M. Kosolopoff, and L. Mair (Eds), Vol. 3. Wiley, New York (1972).

[5] E. Le Coz and J. E. Guerchais, *Bull. Soc. Chim. Fr.*, 80 (1971).

[6] S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta*, **20,** 223 (1976).

[7] L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin, and V. S. Petrosyan, *Zhur. Strukt. Khim.*, **18,** 1103 (1977).

[8] S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta*, **22,** 191 (1977).

[9] S. E. Denmark and X. Su, *Tetrahedron*, **55,** 8727 (1999).

[10] M. A. M. Khouna, M. T. Ben Dhia, and M. R. Khaddar, *Phosphorus, Sulfur, and Silicon*, **178,** 2309 (2003).

[11] M. S. Holt, W. L. Wilson, and J. H. Nelson, *Chem. Rev.*, **89,** 11 (1989).

[12] R. Colton and D. Dakternieks, *Inorg. Chim. Acta*, **148,** 31 (1988).

[13] S. E. Denmark, B. R. Henke, and E. Weber, *J. Am. Chem. Soc.*, **109,** 2512 (1987).

[14] (a) R. Selvaraju and K. Panchanatheswaran, *Polyhedron*, **16,** 2621 (1997); (b) J. Rupp-Bensadon and E. A. C. Lucken, *J. Chem. Soc. Dalton Trans.*, 495 (1983).

[15] S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8,** 1716 (1969).

[16] C. H. Yoder, L. A. Margolis, and J. M. Horne, *J. Organomet. Chem.*, **633,** 33 (2001).

[17] J. Holecek, M. Nadvornik, K. Handlir, and A. Lycka, *J. Organomet. Chem.*, **241,** 177 (1983).

[18] C. J. Jameson, In J. Mason (Ed.), *Multinuclear NMR*, Plenum Press, New York, p. 89 (1987).

[19] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford (1966).

[20] E. A. Robinson and D. S. Lavery, *Spectrochim. Acta*, **28A,** 1099 (1972) and references therein.

[21] G. Schrader, *Monographie N°. 62 zu "Angewandte Chemie" und "Chemie—Ingenieur—Technik,"* Verlag Chemie, Weinheim/Bergstrasse (1951).