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Alcohol–alkoxide exchange between $Sn(OBu^t)_4$ and $HOBu^t$ in co-ordinating and non-co-ordinating solvents†

James Caruso,[a] Todd M. Alam,[a] Mark J. Hampden-Smith,*[,a] Arnold L. Rheingold[b] and Glenn A. P. Yap[b]

[a] *Department of Chemistry and Center for Micro-Engineered Ceramics, University of New Mexico, Albuquerque, NM 87131, USA*
[b] *Department of Chemistry, University of Delaware, Newark, DE 19716, USA*

Proton NMR magnetization-transfer experiments have been utilized to measure the kinetic parameters of alcohol interchange between the homoleptic tin(IV) alkoxide $Sn(OBu^t)_4$ and Bu^tOH in various solvents. The reaction was studied in pyridine with rate constants measured over the temperature range 24–112 °C (k_1 = 0.22 s^{-1} at 24 °C to 12 s^{-1} at 112 °C) from which activation parameters were derived ($\Delta G^{\ddagger}_{298}$ = 18.8 kcal mol^{-1}, $\Delta H^{\ddagger}$ = 9.5 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −30 cal K^{-1} mol^{-1}). These data along with variable-temperature $^{119}Sn-\{^1H\}$ NMR data are consistent with a five-co-ordinate intermediate such as $[Sn(OBu^t)_4 \cdot HOBu^t]$ and suggest that the metal, even in sterically encumbered metal alkoxide compounds such as $Sn(OBu^t)_4$, is sufficiently co-ordinatively and electronically unsaturated to react with bulky alcohols. In non-co-ordinating solvents such as benzene the exchange rate is faster (k = 1.93 s^{-1} at 24 °C). Room-temperature solution $^{119}Sn-\{^1H\}$ NMR spectroscopy of $Sn(OBu^t)_4$ dissolved in pyridine (py) shows evidence for formation of $Sn(OBu^t)_4 \cdot py$, consistent with an exchange mechanism in which py competes with Bu^tOH for co-ordination sites at tin(IV). Unambiguous evidence for the co-ordination of donor molecules to tin(IV) in homoleptic tin(IV) alkoxide compounds was obtained from the isolation and structural characterization of $Sn(OSiPh_3)_4(NC_5H_5)_2 \cdot 0.5NC_5H_5$, the first example of a donor adduct of a homoleptic tin(IV) alkoxide. Single-crystal X-ray diffraction showed that this compound is monomeric and approximately octahedral with *trans* pyridine groups.

There is currently a great deal of interest in the chemistry of metal alkoxide compounds especially with respect to their use as precursors for the formation of metal oxides. Compared to silicon alkoxide compounds,[1] the quantitative understanding of the fundamental steps of sol–gel type hydrolysis and condensation of non-silicon metal alkoxide compounds is relatively poor because they are more reactive which can lead to rapid and often uncontrolled hydrolysis.[2–6] One strategy to avoid this problem is to conduct the hydrolysis of the metal alkoxide compounds in the presence of less labile so-called 'modifying' compounds such as multidentate alcohols, β-diketonates or carboxylic acids.[3,6–9] These reagents replace some of the alkoxide ligands and reduce the reactivity of the metal centre by increasing its co-ordination number and removing sites of potential reactivity. An alternative strategy to render metal alkoxide compounds less reactive is to use sterically demanding alkoxide ligands to limit the steric accessibility of reagents to the metal centre. Both strategies are complicated by the fact that in most cases hydrolysis reactions are carried out in alcohol solution, where the alcohol can also participate in exchange reactions with the metal centre. Indeed, the reaction between an alcohol and a metal alkoxide compound is a well known method of metal alkoxide preparation.[10] As a result, it would be valuable to understand better the nature of alcohol–alkoxide exchange in these non-silicate systems.

There has been interest in the chemistry of tin(IV) alkoxide compounds as a model non-silicate sol–gel system because they exhibit all the attributes of typical non-silicon metal alkoxides and tin has two NMR-active nuclei facilitating structural characterization in solution.[11–16] Tin tetra-*tert*-butoxide, $Sn(OBu^t)_4$, is monomeric in the solid state and in benzene solution[11] and has been used in the formation of sol–gel derived tin oxides.[15,17,18] Here we report the kinetic parameters of the alcohol exchange reaction (1) between this monomeric

$$Sn[OC(CH_3)_3]_4 + (CH_3{}^*)_3COH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Sn[OC(CH_3)_3]_3[OC(CH_3{}^*)_3] + (CH_3)_3COH \quad (1)$$

compound, and its parent alcohol, Bu^tOH, where the asterisk indicates labelled alcohol and alkoxide groups that are otherwise chemically equivalent. This alcohol–alkoxide exchange reaction is slow relative to the NMR lineshape time-scale and did not produce spectra that were significantly exchange broadened. Inspection of the ^1H NMR spectrum leads to the conclusion that no exchange occurs, consistent with the large steric demands of the OBu^t ligands. Only a ^{17}O-labelling experiment revealed this exchange.[12] Owing to the degeneracy of the exchange, kinetic data could not be obtained by monitoring the ^1H NMR signal intensity. However, by use of magnetization-transfer experiments,[19] exchange rates were evaluated. This technique is a powerful method to determine quantitative activation parameters in these systems, but has rarely been used to study two-site exchange processes which result in static spectra.[20]

To investigate the exchange mechanism further a series of variable-temperature $^{119}Sn-\{^1H\}$ NMR control experiments were undertaken and are consistent with the formation of a five-co-ordinate intermediate, $Sn(OBu^t)_4 \cdot HOBu^t$. The influence of donor ligands on this exchange process was probed and evidence for co-ordination of donor ligands to the tin(IV) centre is provided through $^{119}Sn-\{^1H\}$ NMR data and structural characterization of $Sn(OSiPh_3)_4(NC_5H_5)_2 \cdot 0.5NC_5H_5$.

† *Non-SI unit employed:* cal = 4.184 J.

Experimental

General procedures

All syntheses and manipulations were carried out under a dry nitrogen atmosphere using standard inert-atmosphere techniques.[21] Tetrahydrofuran (thf) was freshly distilled over sodium–benzophenone and pyridine over sodium metal. Both solvents were stored over pre-dried 4 Å molecular sieves. The reagent $Sn(OBu^t)_4$ was prepared by the literature method.[11] The ^{17}O-enriched (≈25%) Bu^tOH was prepared by a modification of the procedure of Read and Prisley.[22] All NMR samples were prepared from sublimed $Sn(OBu^t)_4$, freshly distilled Bu^tOH (CaH), dry 99.9% [$^2H_5$]pyridine (Cambridge Isotopes), 99.6% [$^2H_8$]toluene (Isotec) and 99.6% [$^2H_6$]-benzene (Isotec). The reagent $Sn(OBu^t)_4$ (0.05 g, 0.12 mmol) was added to a 5 mm NMR tube with Bu^tOH (0.045 cm^3, 0.48 mmol) and C_5D_5N (0.5 cm^3) for the variable-temperature experiments, $Sn(OBu^t)_4$ (0.025 g, 0.061 mmol), C_5D_5N (0.5 cm^3) and $Sn(OBu^t)_4$ (0.05 g, 0.12 mmol), Bu^tOH (0.11 cm^3, 1.17 mmol) and C_6D_6 (0.5 cm^3) were added for the benzene experiments and $Sn(OBu^t)_4$ (0.05 g, 0.12 mmol) and Bu^tOH (0.06 cm^3, 0.64 mmol) and [$^2H_5$]toluene (0.5 cm^3) for the variable-temperature $^{119}Sn-\{^1H\}$ NMR experiments. All NMR spectra were obtained on a Bruker AC-250 spectrometer operating at a ^1H frequency of 250.1 MHz. The $^{119}Sn-\{^1H\}$ NMR spectra were recorded at 93 MHz utilizing a composite pulse sequence. Temperature control was ± 1 °C using heated nitrogen and a thermocouple previously calibrated using external standards.

Synthesis of $Sn(OSiPh_3)_4(NC_5H_5)_2$

To a Schlenk flask (200 cm^3) was added $Sn(OBu^t)_4$ (1.06 g, 2.6 mmol) dissolved in dry thf (30 cm^3) and a solution consisting of $SiPh_3OH$ (2.85 g, 10.3 mmol) (Aldrich) dissolved in dry thf (30 cm^3) was slowly added. After the addition was complete a white precipitate formed. The volatile components were removed under vacuum and the solid washed with benzene to give 2.94 g of product [94% yield based on formation of $Sn(OSiPh_3)_4$]. Recrystallization from a concentrated pyridine solution at room temperature overnight afforded X-ray diffraction-quality crystals as colourless, transparent blocks. NMR (C_5D_5N): $^{119}Sn-\{^1H\}$, δ −725 (s); ^1H, δ 7.1 (m) and 7.3 (m); $^{29}Si-\{^1H\}$, δ 29 (s); $^{13}C-\{^1H\}$, δ 127 (s), 129 (s) and 140 (s) (Found: C, 71.30; H, 5.05; N, 3.05. Calc. for $Sn(OSiPh_3)_4(NC_5H_5)_2 \cdot 0.5NC_5H_5$, $C_{84.5}H_{72.5}N_{2.5}O_4Si_4Sn$: C, 71.50; H, 5.10; N, 2.45%). The crystalline material was shown to be a pyridine solvate by single-crystal X-ray diffraction.

Crystallography

Crystal, data collection and refinement parameters are given in Table 2. A suitable crystal for single-crystal X-ray diffraction was selected and mounted within a thin glass capillary. The unit-cell parameters were obtained by least-squares refinement of the angular settings of 24 reflections (20 ⩽ 2θ ⩽ 25°).

No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data. The E-statistics suggested a centrosymmetric space group and $P\bar{1}$ was chosen. This was subsequently verified by the chemically reasonable results of the refinement. The structure was solved by direct methods, completed by subsequent Fourier-difference syntheses and refined (on F^2) by full-matrix least-squares procedures. Absorption corrections were ignored because of the < 5% variation in the integrated intensities of the ψ-scan data. Two independent, but chemically equivalent molecules and one disordered pyridine solvent molecule were located in the asymmetric unit. Phenyl rings and the disordered pyridine solvent molecule were refined as hexagonal bodies. Remaining peaks in the difference map (maximum = 1.68 e $Å^{-3}$) occurred at chemically unreasonable positions and were considered as noise. All non-hydrogen atoms except those associated with the disordered atoms of the pyridine solvate molecule, were refined anisotropically. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.02) program library.[23] Selected bond lengths and angles are presented in Table 3.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/86.

Magnetization-transfer experiments

The rate constants for the alcohol–alkoxide exchange were determined using selective inversion-transfer experiments. In these studies the resonance of one species is selectively inverted, for example B in equation (2) while the transfer of the inverted

$$A^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B^* \quad (2)$$

magnetization to the other chemical species in equilibrium with B is monitored. In this paper B denotes Bu^tOH while A denotes $Sn(OBu^t)_4$. For these simple two-resonance spectra the magnetization experiments were performed using the pulse sequence $\frac{\pi}{2}-\tau_1-\frac{\pi}{2}-\tau_2-\frac{\pi}{2}-$ acquisition and an eight-pulse-phase cycle. The interpulse delay, τ_1, was set to the reciprocal of twice the difference in chemical shift, $(2\Delta\nu_{cs})^{-1}$, where $\Delta\nu_{cs} = |\Delta\nu^A{}_{cs} - \Delta\nu^B{}_{cs}|$. All magnetization-transfer experiments utilized eight scans, 30 variable delays (τ_2), pulsewidth = 3.5 μs with a recycle delay of 40–60 s and all samples internally referenced to the protio impurity in the deuteriated solvents. To invert the alcohol resonance the carrier frequency was placed on the alkoxide resonance. The pseudo-first-order rate constants (k_1, k_{-1}) as defined in equation (2) for exchange can be determined by plotting the evolution of magnetization for resonances A and B as a function of the variable time delay τ_2. The time evolution of magnetization during the inversion-transfer experiment is given by equations (3) and (4) where $R_{1z}{}^A$ and

$$dM_z{}^A/dt = -(M_z{}^A - M_e{}^A)R_{1z}{}^A - k_1M_z{}^A + k_{-1}M_z{}^B \quad (3)$$

$$dM_z{}^B/dt = -(M_z{}^B - M_e{}^B)R_{1z}{}^B + k_1M_z{}^A - k_{-1}M_z{}^B \quad (4)$$

$R_{1z}{}^B$ are the spin–lattice relaxation rates ($R_{1z} = 1/T_{1z}$), $M_z{}^A(t)$ and $M_z{}^B(t)$ are the nuclear magnetizations at time t for species A and B, and $M_e{}^A$ and $M_e{}^B$ are the unperturbed magnetizations of A and B at equilibrium. Solution of these Bloch equations by the Laplace–Carson operator method[24] leads to equations (5)

$$M_z{}^A(t) = [M_e{}^A - M_0{}^A\varphi_1 \exp(-\lambda_1 t) - M_0{}^A\varphi_2 \exp(-\lambda_2 t)] \quad (5)$$

and (6) where $M_0{}^A$ and $M_0{}^B$ are the initial magnetizations and φ_1, φ_2, φ_3, φ_4, λ_1 and λ_2 are constants previously defined.[24]

$$M_z{}^B(t) = [M_e{}^B - M_0{}^B\varphi_3 \exp(-\lambda_1 t) - M_0{}^B\varphi_4 \exp(-\lambda_2 t)] \quad (6)$$

The pseudo-first-order rate constants k_{-1} and k_1 (or reciprocal lifetimes, $1/\tau_{-1}$ and $1/\tau_1$ respectively) were obtained using equations (7) and (8). The relationship between them and

$$k_{-1} = \frac{\lambda_1 + \lambda_2 - R_{1z}{}^A - R_{1z}{}^B}{1 + K_e} \quad (7)$$

$$K_e = M_e^B / M_e^A \quad (8)$$

the exchange rate defined in equation (1) depends on the mechanism of exchange and is discussed in the Results and Discussion section.[25]

Spin–lattice relaxation rates ($R_{1z} = 1/T_{1z}$) were obtained using the standard T_1 software on the Bruker instrument while the exchange rate constants were obtained by a non-linear fit of equations (3) and (4) using the Marquardt–Levenberg algorithm (Sigma Plot on a 486 personal computer). Kinetic parameters were obtained from the resulting Eyring plots giving the enthalpy ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$).[26]

Results and Discussion

Exchange reactions between free and co-ordinated alcohol are often diagnostic of free co-ordination sites at the metal centre in metal alkoxide compounds. These reactions frequently occur on the NMR time-scale and can be characterized by variable-temperature studies.[27] In the case of the exchange reaction between Bu^{t}OH and $Sn(OBu^t)_4$ variable-temperature ^1H NMR data do not reveal any evidence of exchange-broadened lineshapes. This observation is consistent with the interpretation that the tin centre is sterically protected by the four bulky *tert*-butoxide ligands. However, the addition of ^{17}O-enriched Bu^{t}OH to a pyridine solution of $Sn(OBu^t)_4$ results in incorporation of the oxygen-17 label into the alkoxide sites as determined by ^{17}O NMR spectroscopy. This exchange occurred so rapidly that it could not be monitored by ^{17}O NMR spectroscopy. Since the exchange between an alkoxide and its parent alcohol gives rise to a static spectrum, ^1H NMR spectroscopy did not allow monitoring of the exchange process by changes in signal intensity. In addition, changes in the linewidth due to this exchange process were estimated to be similar to variations in field homogeneity, so lineshape analysis was not a viable possibility. As a result, the kinetics of this exchange process was investigated using ^1H NMR magnetization-transfer techniques. This technique does not require physical labelling of any site, but rather relies on magnetic labelling of the exchanging sites.

Magnetization-transfer experiments were conducted in pyridine as a function of temperature. Fig. 1 displays typical NMR spectra of the two exchanging ^1H resonances at 297 K, where the low-frequency peak at δ 1.38 derived from Bu^{t}OH was selectively inverted. The peak at δ 1.48 [$Sn(OBu^t)_4$] changes in peak area with time and clearly shows the incorporation or transference of inverted magnetization from the alcohol resonance. Fig. 2 shows a plot of peak area *versus* delay time at four different temperatures for (*a*) the non-inverted high-frequency $Sn(OBu^t)_4$ resonance and (*b*) the selectively inverted Bu^{t}OH resonance. The smooth curve is obtained from the non-linear regression of the data using equations (5) and (6) as described in the Experimental section. It is evident from Fig. 2 that the reaction rate increases with temperature. The data allow determination of the forward and reverse pseudo-first-order rate constants k_1 and k_{-1} ($1/\tau_1$ and $1/t_{-1}$) which are reported in Table 1 along with the activation parameters derived from an Eyring plot.[26] No assumption about the reaction order is inherent in the measurement of the rate constants for exchange of magnetization. The values $\Delta G^{\ddagger}_{298} = 18.8$ kcal mol^{-1}, $\Delta H^{\ddagger} = 10.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27$ cal K^{-1} mol^{-1} are consistent with an associative reaction mechanism and a highly ordered transition state.

To investigate this exchange process further, a series of variable-temperature ^{119}Sn-{^1H} NMR experiments were undertaken. The ^{119}Sn chemical shift is highly dependent on the co-ordination number around the tin, and typical changes of ± 110–150 ppm accompany a change in co-ordination number by one unit with the same ligand set, an increase in co-ordination number resulting in a low-frequency shift.[28] Fig. 3 shows the

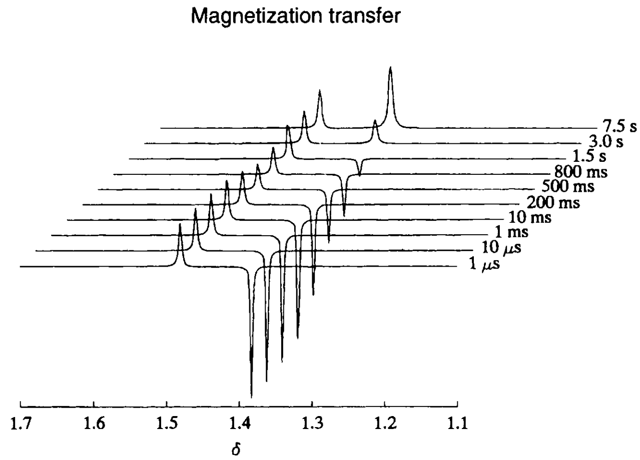

Fig. 1 Proton NMR magnetization-transfer spectra of exchanging resonances $Sn(OBu^t)_4$ (δ 1.48) and Bu^{t}OH (δ 1.38) at 297 K following selective inversion of the Bu^{t}OH resonance

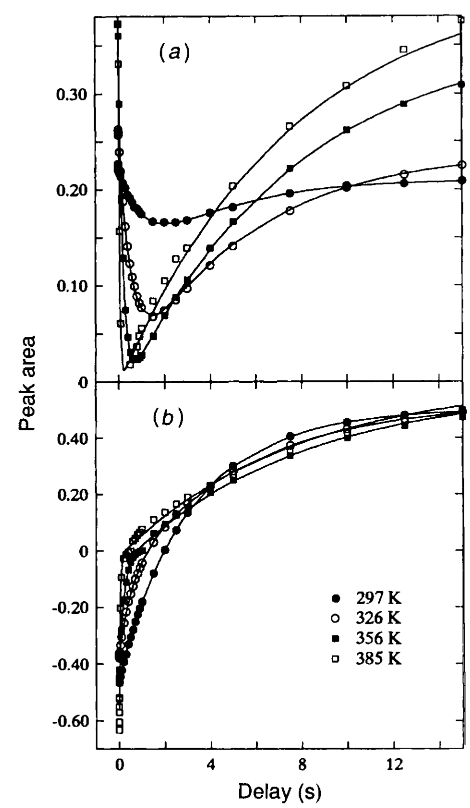

Fig. 2 Plot of peak area of the $Sn(OBu^t)_4$ (*a*) and inverted Bu^{t}OH resonances (*b*) *versus* variable delay time as a function of temperature obtained as described in the text. Solid lines represent theoretical fits

Table 1 Alcohol-exchange rate constants and activation parameters

T/K	k_1/s^{-1}	k_{-1}/s^{-1}
297	0.22 ± 0.09	0.09 ± 0.03
326	1.1 ± 0.2	0.50 ± 0.04
356	3.2 ± 0.3	2.1 ± 0.2
385	12.4 ± 1	8.7 ± 0.8
	$\Delta H^{\ddagger}$ = 9.5 ± 0.4	10.9 ± 0.4 kcal mol^{-1}
	$\Delta S^{\ddagger}$ = −30 ± 1	−27 ± 1 cal K^{-1} mol^{-1}
	$\Delta G^{\ddagger}_{298}$ = 18.8 ± 0.7 kcal mol^{-1}	

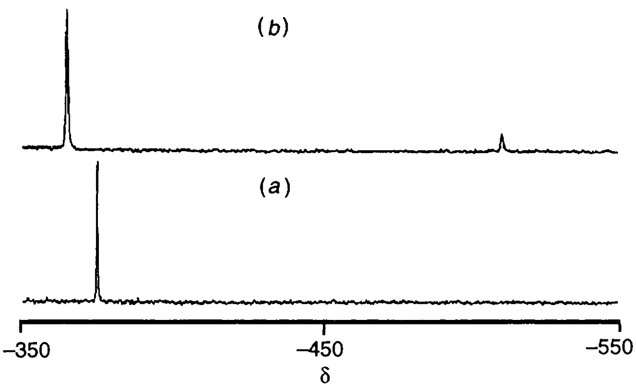

Fig. 3 The $^{119}Sn-\{^{1}H\}$ NMR spectra of $Sn(OBu^t)_4$ with 4 equivalents of Bu^tOH in $[^2H_8]$toluene at (*a*) 25 and (*b*) −30 °C

$^{119}Sn-\{^{1}H\}$ NMR spectra of $Sn(OBu^t)_4$ in toluene with 4 equivalents of added Bu^tOH at +25 (*a*) and −30 °C (*b*). At room temperature a single, time-averaged resonance is observed at δ −374, a chemical shift identical to that of pure $Sn(OBu^t)_4$ in toluene at this temperature. At lower temperature, −30 °C, a second resonance is clearly visible at δ −510 which is consistent with formation of a small amount of a five-co-ordinate tin centre such as $Sn(OBu^t)_4{\cdot}HOBu^t$ in equilibrium with the reagents. Unfortunately, there are no examples of unambiguously characterized neutral five-co-ordinate homoleptic tin(IV) alkoxide compounds with which to compare this ^{119}Sn chemical shift. In a control experiment, low-temperature $^{119}Sn-\{^{1}H\}$ NMR spectra of $Sn(OBu^t)_4$ in toluene in the absence of any added Bu^tOH did not reveal the formation of any new ^{119}Sn resonances. Variable-temperature ^1H NMR spectroscopy showed only broad peaks which did not aid further structural elucidation. Although $Sn(OBu^t)_4$ is monomeric in solution and possesses sterically demanding Bu^tO^- ligands, there is literature precedent for higher co-ordination numbers. The compound $K[Sn(OBu^t)_5]$ has been isolated and structurally characterized in the solid state where it was shown to contain five-co-ordinate $[Sn(OBu^t)_5]^-$ moieties.[29] Furthermore, we have found that this compound has a ^{119}Sn chemical shift in benzene of δ −589, consistent with a five-co-ordinate tin centre in solution.

The activation parameters along with the $^{119}Sn-\{^{1}H\}$ NMR data are consistent with the existence of an associated five-co-ordinate transition state in the exchange process such as $[Sn(OBu^t)_4{\cdot}HOBu^t]$. However, while these data reveal an increased co-ordination number at tin, they do not give any information on hydrogen bonding. This interpretation is consistent with studies in which the initial hydrolysis rate of tetraethyl orthosilicate $Si(OEt)_4$ was measured by $^{29}Si-\{^{1}H\}$ NMR spectroscopy and indicated that the rate-determining step was nucleophilic attack of the oxygen lone pair of a water molecule at the Si.[30,31]

When the exchange process is monitored in C_6D_6 as solvent the rate of exchange, $k_1 = 1.93\ s^{-1}$, is approximately 10 times faster than in pyridine solution under otherwise analogous conditions. It is clear from this result that there is a strong solvent dependency of the exchange rate, which is faster in a non-co-ordinating solvent. An increase in the co-ordination number of $Sn(OBu^t)_4$ in pyridine solvent is evident from its ^{119}Sn NMR chemical shift of δ −420 at room temperature, which is substantially different from that in toluene of δ −374. Clearly, pyridine can interact with the tin centre which increases its co-ordination number and results in a low-frequency shift. Based on the $^{119}Sn-\{^{1}H\}$ NMR chemical shift we believe the species formed is a monosubstituted pyridine adduct such as $Sn(OBu^t)_4{\cdot}(py)$. This is consistent with the decreased rate of the associative reaction (1) in the presence of pyridine. Attempts to isolate this pyridine adduct have been unfruitful. Again, variable-temperature ^1H NMR spectra are unrevealing due to the broadness of the peaks.

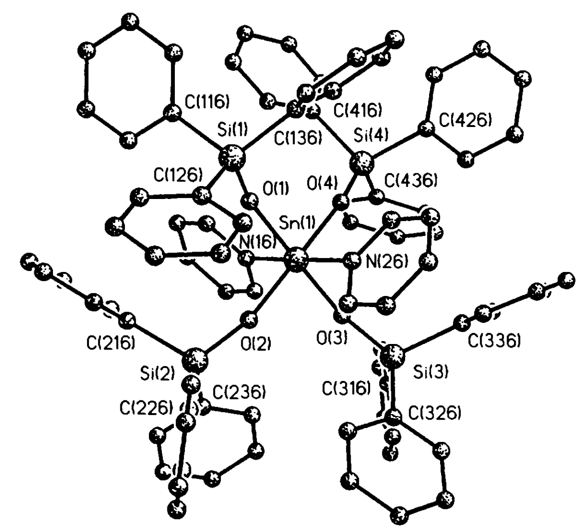

Fig. 4 Ball-and-stick drawing of the molecular structure of $Sn(OSiPh_3)_4(NC_5H_5)_2$

In previous work we have isolated and characterized a number of alcohol adducts of tin(IV) alkoxide compounds, including $[Sn(OR)_4{\cdot}HOR]_2$ where R = Pr^i or Bu^i.[11,27] For these compounds with less sterically demanding alkoxide ligands the alcohol adducts can be obtained from pyridine solutions which suggests that in these systems the alcohol adducts are thermodynamically more stable than the pyridine adducts even when pyridine is present in large excess. We attribute this preference to the stability of the intramolecular hydrogen bonding in these compounds which has also been observed by others.[32]

During the course of the present study we prepared $Sn(OSiPh_3)_4$ to study its reactivity towards metal carboxylate compounds *via* ester elimination.[16] However, as a result of its insolubility in toluene or benzene, $Sn(OSiPh_3)_4$ was recrystallized from pyridine resulting in the formation of $Sn(OSiPh_3)_4(NC_5H_5)_2$, the first example of a donor adduct of a homoleptic tin(IV) alkoxide compound. Owing to its relevance to this work, the compound was structurally characterized by single-crystal X-ray diffraction in the solid state. The compound $Sn(OSiPh_3)_4(NC_5H_5)_2{\cdot}0.5NC_5H_5$ crystallizes in the space group $P\bar{1}$ with two crystallographically independent, but structurally similar molecules. A ball-and-stick drawing of one of these molecules is shown in Fig. 4 and relevant bond lengths and angles are presented in Table 3. The tin(IV) is six-co-ordinate and approximately octahedral with four *cis*-$OSiPh_3$ groups in the same plane and *trans* pyridine groups. The bond lengths are in the ranges expected and the Sn–O–Si angles lie in the range 150–160° which is significantly more linear than terminal alkoxide ligands.

These data provide unambiguous evidence for the co-ordination of pyridine to the tin(IV) and this is the first example of a structurally characterized homoleptic tin(IV) alkoxide compound with co-ordinated pyridine. We believe the tin(IV) in this species satisfies its co-ordination requirements by bonding to pyridine rather than oligomerizing because the alkoxide oxygens are too sterically encumbered by the $SiPh_3$ groups. The pyridine molecules do not dissociate in a non-co-ordinating solvent as evidenced from the ^{119}Sn resonance of δ −725 in both pyridine and toluene solution. We believe that the solid-state structure is retained in solution based on the observations of a single type of Ph and py groups by ^1H NMR spectroscopy, a single $^{29}Si-\{^{1}H\}$ chemical shift and the absence of ^{119}Sn-to-^{117}Sn coupling in the $^{119}Sn-\{^{1}H\}$ NMR spectrum. The $^{119}Sn-\{^{1}H\}$ chemical shift is consistent with the retention of a six-co-ordinate tin centre.

Table 2 Crystallographic data for $Sn(OSiPh_3)_4(NC_5H_5)_2 \cdot 0.5NC_5H_5$

(a) Crystal parameters			
Formula	$C_{84.5}H_{72.5}N_{2.5}O_4Si_4Sn$	$\gamma/^\circ$	90.20(2)
M	1418	$U/Å^3$	7573(3)
Crystal system	Triclinic	Z	4
Space group	$P\bar{1}$	Crystal dimensions/mm	0.12 × 0.13 × 0.16
$a/Å$	17.809(3)	Crystal colour	Colourless
$b/Å$	18.015(4)	$D_c/g\ cm^{-3}$	1.244
$c/Å$	24.460(6)	$\mu(Mo\text{-}K\alpha)/cm^{-1}$	4.51
$\alpha/^\circ$	103.10(2)	T/K	296
$\beta/^\circ$	97.51(2)		
(b) Data collection			
Diffractometer	Siemens P4	Reflections collected	16 819
Monochromator	Graphite	Independent reflections	16 332
Radiation	Mo-Kα (λ = 0.710 73 Å)	Independent observed reflections $[F_o \geq 4\sigma(F_o)]$	8857
2θ Scan range/°	4.0–42.0	Standard reflections	3 every 197
Data collected (h,k,l)	±17, ±17, +24	Variation in standards (%)	1
(c) Refinement *			
R	0.0601	$\Delta\rho/e\ Å^{-3}$	1.677
R'	0.1703	N_o/N_v	11.7
$\Delta\sigma_{max}$	0.00	Goodness of fit	1.0

* $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $R = \Sigma\Delta/\Sigma(F_o)$ where $\Delta = |F_o - F_c|$.

Table 3 Selected bond lengths (Å) and angles (°) for $Sn(OSiPh_3)_4(NC_5H_5)_2$

Sn(1)–O(3)	1.976(7)	Sn(1)–O(2)	1.983(6)
Sn(1)–O(4)	1.987(6)	Sn(1)–O(1)	2.004(6)
Sn(1)–N(26)	2.243(7)	Sn(1)–N(16)	2.241(8)
Si(1)–O(1)	1.599(7)	Si(1)–C(116)	1.881(6)
Si(1)–C(126)	1.909(6)	Si(1)–C(136)	1.916(6)
Si(2)–O(2)	1.621(7)	Si(2)–C(236)	1.889(6)
Si(2)–C(216)	1.907(6)	Si(2)–C(226)	1.908(6)
Si(3)–O(3)	1.620(7)	Si(3)–C(326)	1.887(6)
Si(3)–C(316)	1.893(6)	Si(3)–C(336)	1.909(5)
Si(4)–O(4)	1.603(7)	Si(4)–C(436)	1.886(6)
Si(4)–C(416)	1.897(6)	Si(4)–C(426)	1.908(5)
O(3)–Sn(1)–O(2)	89.0(3)	O(3)–Sn(1)–O(4)	90.7(3)
O(2)–Sn(1)–O(4)	178.4(3)	O(3)–Sn(1)–O(1)	177.8(3)
O(2)–Sn(1)–O(1)	90.8(3)	O(4)–Sn(1)–O(1)	89.6(3)
O(3)–Sn(1)–N(26)	89.1(3)	O(2)–Sn(1)–N(26)	90.6(3)
O(4)–Sn(1)–N(26)	91.0(3)	O(1)–Sn(1)–N(26)	88.6(3)
O(3)–Sn(1)–N(16)	90.6(3)	O(2)–Sn(1)–N(16)	90.0(3)
O(4)–Sn(1)–N(16)	88.4(3)	O(1)–Sn(1)–N(16)	91.7(3)
N(26)–Sn(1)–N(16)	179.4(3)	O(1)–Si(1)–C(116)	105.8(4)
O(1)–Si(1)–C(126)	113.8(4)	C(116)–Si(1)–C(126)	107.9(4)
O(1)–Si(1)–C(136)	112.5(4)	C(116)–Si(1)–C(136)	110.5(4)
C(126)–Si(1)–C(136)	106.2(3)	O(2)–Si(2)–C(236)	113.0(4)
O(2)–Si(2)–C(216)	112.8(4)	C(236)–Si(2)–C(216)	106.9(3)
O(2)–Si(2)–C(226)	107.2(4)	C(236)–Si(2)–C(226)	107.8(4)
C(216)–Si(2)–C(226)	109.0(4)	O(3)–Si(3)–C(326)	113.5(4)
O(3)–Si(3)–C(316)	107.7(4)	C(326)–Si(3)–C(316)	108.6(3)
O(3)–Si(3)–C(336)	113.5(4)	C(326)–Si(3)–C(336)	104.7(3)
C(316)–Si(3)–C(336)	108.5(3)	O(4)–Si(4)–C(436)	114.6(4)
O(4)–Si(4)–C(416)	112.5(4)	C(436)–Si(4)–C(416)	105.6(3)
O(4)–Si(4)–C(426)	107.8(3)	C(436)–Si(4)–C(426)	107.7(3)
C(416)–Si(4)–C(426)	108.5(3)	Si(1)–O(1)–Sn(1)	152.8(4)
Si(2)–O(2)–Sn(1)	150.6(4)	Si(3)–O(3)–Sn(1)	156.6(4)
Si(4)–O(4)–Sn(1)	159.2(4)		

In summary, the kinetics of alcohol–alkoxide exchange between $Sn(OBu^t)_4$ and Bu^tOH has been reported. The activation parameters and the solvent dependence of the rate constant are consistent with an associative mechanism in which the electropositive tin can bind a free alcohol leading to a five-co-ordinate intermediate. Variable-temperature $^{119}Sn\text{-}\{^1H\}$ NMR spectroscopy in the presence of added L, where L = Bu^tOH or py, is consistent with the formation of $Sn(OR)_4 \cdot L$. These observations show that, even in systems which contain sterically demanding substituents, facile chemical exchange occurs between the alkoxide ligands and parent alcohol. Direct evidence for co-ordination of pyridine to the tin(IV) centre was obtained in the solid state through structural characterization of $Sn(OSiPh_3)_4(NC_5H_5)_2$ by single-crystal X-ray diffraction.

The alcohol–alkoxide exchange and the influence of donor solvents observed here is likely to influence the course of sol–gel type reactions employing $Sn(OBu^t)_4$ significantly and other metal alkoxides, especially under conditions of high alcohol or pyridine concentration (*e.g.* where the alcohol or pyridine is the solvent).[4] Indeed it has been shown that pyridine interacts with the tin centre even with bulky alkoxides such as $Sn(OBu^t)_4$, hindering ester-elimination reactions with $Sn(O_2CMe)_4$ and leading to ligand exchange with formation of species such as $Sn(OBu^t)_3(O_2CMe)(py)$.[12]

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