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Synthesis and characterization of a stable bis-naphthyltin(II) compound. Bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(II) * and its $W(CO)_5$ adduct

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Abstract

Reaction of [8-(dimethylamino)-1-naphthyl-*C*,*N*]lithium with $SnCl_2$ affords the new monomeric stannylene bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(II) (**3**). The reaction between $W(CO)_5(NMe_3)$ and **3** yields {bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(II)}tungsten pentacarbonyl (**4**). The crystal structures of **3** and **4** have been determined by X-ray diffraction methods. **3**: $C_{24}H_{24}N_2Sn$, orthorhombic, space group *Pbca* with *a* 22.383(4), *b* 30.865(5), *c* 12.127(2) Å and $Z = 16$, final $R = 0.067$ for 4983 observed reflections. **4**: $C_{29}H_{24}N_2O_5SnW$, *a* 12.509(3), *b* 15.191(1), *c* 9.780(1) Å, α 98.42(1), β 104.33(1), γ 107.27(1)°, space group $P\bar{1}$, $Z = 2$, triclinic; $R = 0.046$ for 7116 observed reflections. The geometry about tin in **3** is distorted ψ-trigonal bipyramidal, and that in **4** is distorted trigonal bipyramidal. In both **3** and **4** the 8-(dimethylamino)-1-naphthyl groups are C,N-chelate bonded, with the C(1) atoms at equatorial sites and the nitrogen atoms at axial sites. The Sn lone pair in **3** and the $W(CO)_5$ moiety in **4** occupy the remaining equatorial sites. ^1H, ^{13}C, and ^{119}Sn solution NMR spectroscopic studies of **3** and **4** show that at low temperature (≤ -15 °C) they retain the structures found in the solid state. At higher temperatures fluxional processes become operative.

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* In this manuscript we use the more commonly encountered radical name naphthyl instead of naphthalenyl. Formally this compound should be named: bis[8-(dimethylamino)-1-naphthalenyl-*C*,*N*]tin(II).

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Introduction

Normally, organotin(II) compounds R_2Sn (stannylenes) having Sn–C covalent bonds are unstable and polymerize rapidly. Although the synthesis of diphenylstannylene (Ph_2Sn) has been reported several times, the material obtained is invariably the result of rapid oligomerization or polymerization of the diphenylstannylene intermediate [1–8]. However, under certain conditions it is possible to stabilize organotin(II) compounds having covalent Sn–C bonds. These conditions, each of which may be sufficient on its own, are: i, the use of bulky organic groups: ii, the coordination of the lone pair at the tin atom to a suitable transition metal acceptor, and: iii, the completion of the tin coordination sphere by substituents on the organic groups that are capable of intramolecular coordination. The first organotin(II) compound to be isolated with covalent Sn–C bonds, i.e. $Sn[CH(SiMe_3)_2]_2$ (**1**) [9], is an example of the use of the first approach. In this compound, the Sn centre is sufficiently shielded by the bulky trimethylsilyl groups to prevent polymerization. However, an X-ray crystallographic study of **1** revealed a dimeric structure with Sn–Sn bonding that can be described as a double dative bond [10,11]. In the gas-phase and in dilute solution **1** is a monomer [12]. ^{117}Sn and ^{13}C NMR studies have shown that in more concentrated solutions **1** is in equilibrium with its dimer [13].

Several diaryltin compounds in which the aryl group bears bulky or heteroatom-containing substituents on both *ortho* positions are thought to be monomeric stannylenes on the basis of Mössbauer data [14]. Unfortunately, no solution NMR data or solid state X-ray structures are available for any of these compounds. Recently, bis(2,4,6-triisopropylphenyl)tin(II) was found in solution to be a cyclotristannane in temperature dependent equilibrium with the distannene ($R_2Sn{=}SnR_2$) [15].

The complexes $(t\text{-}Bu)_2SnCr(CO)_5 \cdot C_5H_5N$ [16,17] and $(C_6H_4CH_2NMe_2\text{-}2)_2$-$SnW(CO)_5$ [18] are species illustrating the second approach, i.e. the stabilization by coordination of the Sn lone pair to a suitable transition metal.

Very recently, the first examples of diorganotin compounds stabilized by intramolecular coordination have been reported, i.e. $Sn\{[C(SiMe_3)_2C_5H_4N\text{-}2]\}_2$ (**2a**) [19] and $Sn(C_6H_4CH_2NMe_2\text{-}2)_2$ (**2b**) [20]. X-ray structure determinations of both compounds show them to have monomeric structures in which intramolecular coordination gives rise to four-coordinate tin(II) centres.

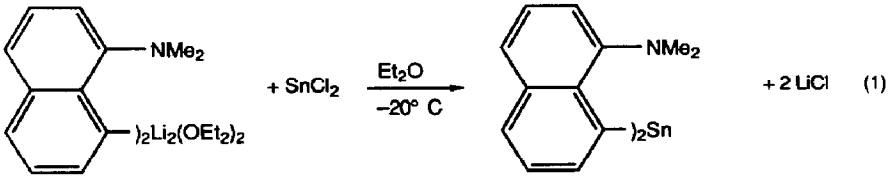
In recent studies we have found that as a consequence of the rigid planar C(1)–C–C(8)–NMe_2 skeleton of the 8-(dimethylamino)-1-naphthyl group, organometallic species derived from this ligand, such as tetrameric [8-(dimethylamino)-1-naphthyl-*C*,*N*]copper [21] and [8-(dimethylamino)-1-naphthyl-*C*,*N*]platinum compounds [22,23], have enforced geometries and special reactivities.

In this paper we report the synthesis and full characterisation in the solid state by X-ray crystallography and in solution by NMR spectroscopy of bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(II) (**3**). The formation and characterization of the $W(CO)_5$ adduct of **3**, and some oxidative addition reactions of **3**, are also described.

Results and discussion

Synthesis of bis[8-(dimethylamino)-1-naphthyl-C,N]tin(II) (3) and its $W(CO)_5$ adduct 4

The reaction of [8-(dimethylamino)-1-naphthyl-*C*,*N*]lithium with $SnCl_2$ (eq. 1) gives a high yield of bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(II) (**3**) *, obtained as a yellow crystalline solid after recrystallization from hot benzene. This novel dinaphthylstannylene is thermally stable up to 180 °C. It is readily soluble in common organic solvents, although it reacts with chlorinated solvents such as $CHCl_3$ to give oxidative-addition products (vide infra).

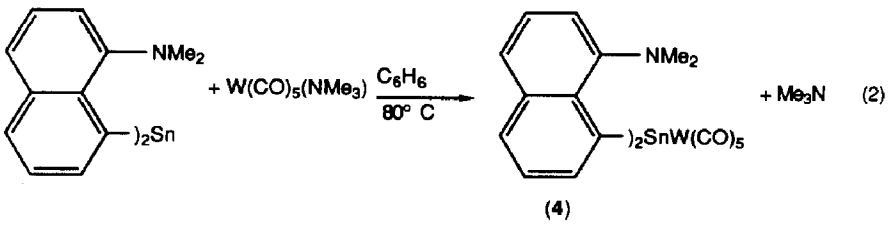


(3)

Both in solution and in the solid state, **3** is extremely sensitive towards oxygen. This reactivity was reflected in the quantitative formation of a precipitate of bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(IV) oxide (**5**) when a benzene solution of **3** was stirred in contact with dry air. The complete insolubility of **5** in organic solvents indicates that it probably has a polymeric structure, a common feature of diorganotin oxides [6]. Preliminary studies of the reaction of solutions of **3** with several other electrophiles confirmed that it readily undergoes oxidative addition reactions. For example, reaction of **3** in benzene with MeI affords pentacoordinate bis[8-(dimethylamino)-1-naphthyl-*C*,*N*](methyl)tin(IV) iodide, and its reaction with one equivalent of Br_2 affords hexacoordinate bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(IV) dibromide. These oxidative addition reactions and the structures of the products will be described elsewhere [24].

To obtain further insight into the factors stabilizing divalent organotin compounds, we thought it would be useful to compare the structural and spectroscopic features of **3** with those of its $W(CO)_5$ adduct. Attempts to prepare this $W(CO)_5$ adduct by heating equimolar amounts of **3** and $W(CO)_6$ at 80 °C for three days were unsuccessful, and starting materials were recovered. However, when a solution of **3** and one equivalent of $W(CO)_5(NMe_3)$ in benzene was heated for 2 h, {bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(II)tungsten pentacarbonyl (**4**) was formed in almost quantitative yield (eq. 2). After recrystallization from benzene/pentane, **4** was obtained as a white crystalline solid. It is readily soluble in most organic solvents and is thermally stable up to 170 °C, at which it melts with decomposition.

* So far, attempts to prepare the 8-methoxy analogue of **3** from the reaction of [8-(methoxy)-1-naphthyl-*C*,*O*]lithium with $SnCl_2$ have failed, and only dark coloured polymeric products have been obtained.



(4)

Solid state structures of bis[8-(dimethylamino)-1-naphthyl-C,N]tin(II) (3) and its $W(CO)_5$ adduct 4

The crystal structure of **3** involves the packing of 16 discrete mononuclear molecules in the unit cell. The asymmetric unit contains two independent molecules (**A** and **B**) which are chemically identical, but which differ slightly though not significantly in structure. Each tin is directly bonded to C(1) of two naphthyl ligands and as a result of intramolecular Sn–N coordination the tin centre is four coordinate. The N–Sn–N array is almost linear and the C–Sn–C angle is 93.8°. The best description of the geometry is a distorted ψ-trigonal bipyramid with axial positions occupied by N atoms and the equatorial positions taken up by two C atoms and a stereochemically active lone pair. Figure 1A presents a PLUTO view of representative molecule **A** together with the numbering scheme used.

The crystal structure of the $W(CO)_5$ adduct **4** involves a unit cell containing two mononuclear molecules, together with two solvated benzene molecules. In **4** the tin atom is pentacoordinate as a result of the C,N chelate bonding of two 8-(dimethylamino)-1-naphthyl groups and a bond to a $W(CO)_5$ unit in which the tungsten center is octahedrally coordinated. Figure 1B shows a PLUTO view of **4** together

Table 1

Selected geometrical data for **3** and **4**

	3 (molecule A)	**4**
Bond lengths (Å)		
Sn1–C1	2.229(9)	2.194(5)
Sn1–C13	2.233(10)	2.173(5)
Sn1–W1		2.822(2)
Sn1–N1	2.555(8)	2.588(5)
Sn1–N2	2.578(8)	2.586(5)
Bond angles (deg.)		
C1–Sn1–C13	93.8(5)	102.6(3)
C1–Sn1–W1		129.9(1)
C13–Sn1–W1		127.6(2)
C1–Sn1–N1	73.1(4)	71.6(2)
C1–Sn1–N2	96.0(4)	90.0(3)
C13–Sn1–N1	98.3(5)	90.2(3)
C13–Sn1–N2	71.9(5)	71.3(3)
W1–Sn1–N1		103.8(1)
W1–Sn1–N2		105.5(2)
N1–Sn1–N2	165.2(3)	150.7(2)

with the adopted numbering scheme. The solvated benzene molecule is omitted for clarity. Relevant bond distances and angles for **3** and **4** are given in Table 1.

Coordination geometry of the tin(II) centres in 3 and 4

Divalent tin compounds in which, besides the two covalent bonds, two additional donor atoms coordinate to the tin centre, have a ψ-trigonal bipyramidal geometry with the lone pair at an equatorial site; they may thus be regarded as containing sp^3d hybridized tin [25]. However, depending on the exact nature of the groups bound to the tin atom, considerable geometrical distortions from an ideal trigonal bipyramidal form have been found, including the extreme case of square pyramidal. Structures of four-coordinate tin(II) compounds covering the whole range between these two extremes have been reported [26]. The distorted ψ-trigonal bipyramidal arrangement in **3** is fully consistent with predictions using the VSEPR model [27–29] for discrete AX_2Y_2E species (A = central atom; E = lone pair; X, Y = ligands). In diorganotin N-donor complexes, repulsive forces between the Sn–C bonding electrons and the tin lone pair may be relieved either by a decrease in the C–Sn–C angle from 120° or by lengthening of the Sn–N bonds [29]. In **3** a reduction in C–Sn–C angle is observed (93.8(5) and 88.3(5)° for molecules **A** and **B**, respectively).

The overall structural geometry (bond distances and angles) of **3** is close to that reported for $Sn(C_6H_4CH_2NMe_2\text{-}2)_2$ [20]. The coordination geometry of the tin center in **3** is also related to that reported for dichloro(1,4-dioxane)tin(II) [30] and bis(1-phenylbutane-1,3-dionato)tin(II) [31]. In dichloro(1,4-dioxane)tin(II), in which the $SnCl_2$ units are linked by dioxane molecules into linear polymeric arrays, the coordination geometry of the tin is ψ-trigonal bipyramidal with the chlorine atoms and the lone pair at the equatorial sites (angle Cl–Sn–Cl 90.52(7)°) and the oxygen atoms at the axial sites. In the latter compounds the 1-phenylbutane-1,3-dionato units are chelate-bonded to an equatorial and an axial site of a ψ-trigonal bipyramidally coordinated tin atom, the lone pair occupying the remaining equatorial site. The difference between the equatorial and axial oxygen atoms is reflected in the different Sn–O distances of 2.135(1) and 2.290(6) Å, respectively.

The structure found for {bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(II)}tungsten pentacarbonyl (**4**) can be derived from that of **3** by using the lone pair at the tin atom for a coordinative bond to a $W(CO)_5$ moiety. This results in a trigonal bipyramidal coordination geometry around the tin atom with the W and C atoms at the equatorial sites and the two N atoms at the axial sites. As a consequence of the presence of the Sn–W bond the repulsive forces between the tin lone pair and the Sn–C bonding electrons are less than in **3**, as reflected in the C–Sn–C angle which in **4** is now 102.6°. The overall geometry of **4** (bond distances and angles) is close to that of $(C_6H_4CH_2NMe_2\text{-}2)_2SnW(CO)_5$ [18].

In **4**, although the interbond angles around the tin atom (see Table 1) deviate significantly from those of an ideal trigonal bipyramid, the best structural description is one based on this geometry. For example, the dihedral angle between the plane defined by C1, C13, and N1 and the plane defined by C1, C13, and N2 is 43°; this value is much closer to that of an ideal trigonal bipyramid (53.1°) than to that of an ideal square pyramid (0°) [32,33]. In both **3** and **4** the N–Sn–C angles in the five-membered chelate rings are about 72°. This value deviates considerably from the ideal value for a trigonal bipyramid (90°), but that is not unexpected,

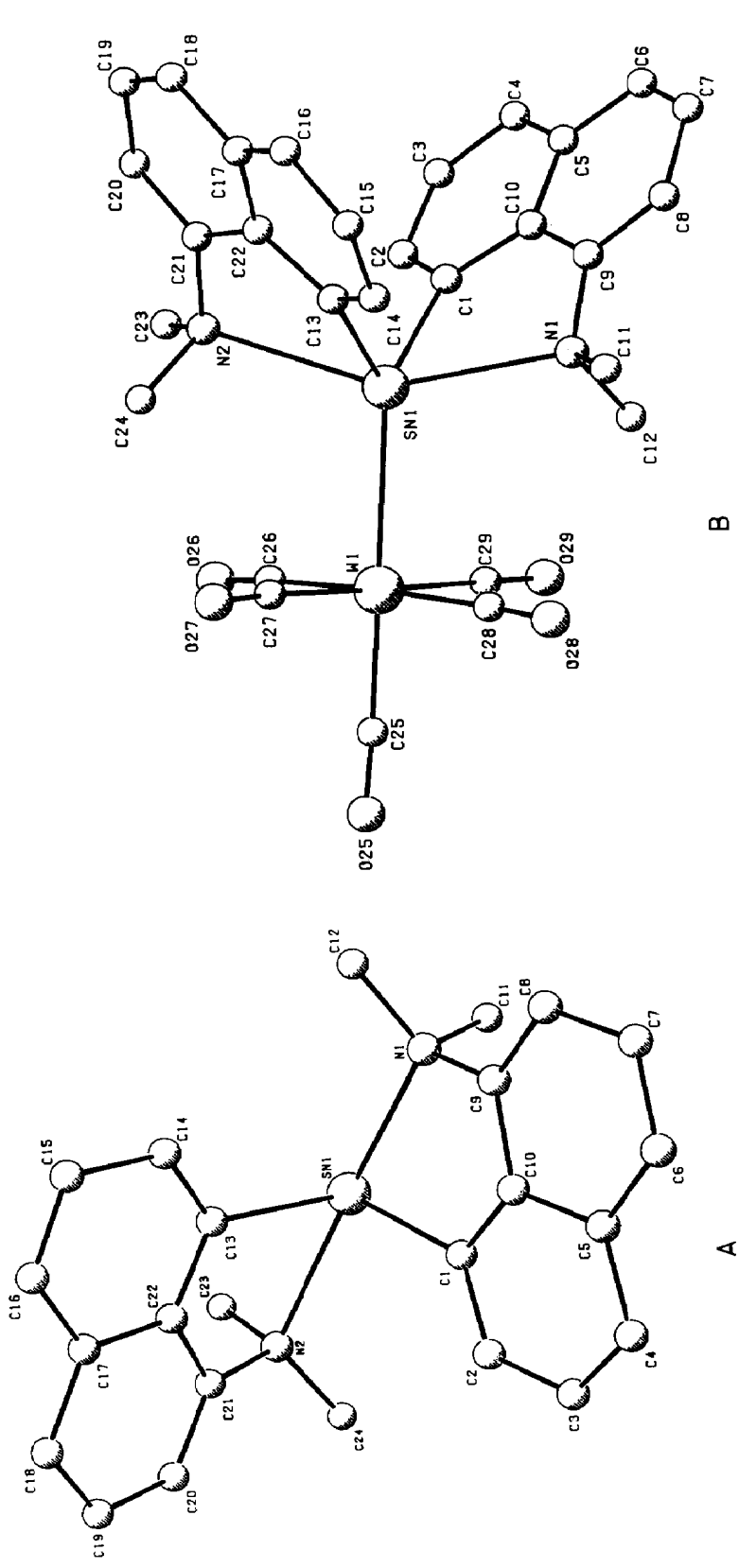


Fig. 1. PLUTO drawings of **A**: bis[8-(dimethylamino)-1-naphthyl-*C*,*N*]tin(II) (**3**), and **B**: {bis[8-dimethylamino)-1-naphthyl-*C*,*N*]tin(II) tungsten pentacarbonyl (**4**).

Table 2

Relevant ^{13}C, ^{1}H and ^{119}Sn NMR data for **3** and **4**

	^{13}C [a]				^{1}H [a]		^{119}Sn [b]
	C(1)	C(8)	NMe_2	others	H(2)	$N(Me)_2$	
3 [c]	169.1 [409,428] [f]	153.6	47.5		7.68	2.72 [d]	178.3 [e]
4 [c]	151.5 [120.125] [f]	152.3	50.5	201.5 [g], 200.5 [h] [122] [j]	8.21 [41] [k]	3.05 [i]	248.7 [e] [976] [l]

[a] δ in ppm relative to Me_4Si. [b] δ in ppm relative to Me_4Sn. [c] In toluene-d_8 at 25 °C. [d] At −20 °C two resonances at 2.58 and 2.78 ppm with $T_{coal.} \sim -5$ °C. [e] δ-value is strongly temperature dependent, see text. [f] $^{1}J(^{117,119}Sn-^{13}C)$. [g] CO_{trans}. [h] CO_{cis}. [i] At −20 °C two resonances at 2.81 and 3.11 ppm with $T_{coal.} \sim -15$ °C. [j] $^{1}J(^{183}W-^{13}C)$. [k] $^{3}J(^{117,119}Sn-^{1}H)$. [l] $^{1}J(^{119}Sn-^{183}W)$.

since in these complexes this angle is determined by the fairly inflexible values of the Sn–C and Sn–N bonding distances. This phenomenon is common for trigonal bipyramidal arrays in which a bidentate ligand forms a five-membered chelate ring bridging an equatorial and an axial site. (see ref. 34, 35, and 36 and references cited therein).

For 1,8-disubstituted naphthalenes it has been found that as a result of steric repulsion between the substituents the naphthalene skeleton is distorted and the substituents are bent out of the plane of the naphthalene skeleton [37]. However in the structure of **3** both naphthalene skeletons are flat, (as was also observed for triorganotin bromides containing the 1,8-(dimethylamino)naphthyl group [36]) and coplanar with their corresponding flat five-membered chelate rings. In **4** the naphthalene skeleton is not planar and the five-membered chelate rings are slightly puckered; the sum of the bond angles in these rings is about 10° less than is expected for a flat five-membered ring.

Solution behaviour of 3 and 4

Molecular weight determinations (cryoscopy in benzene) of **3** and **4** show that both compounds are monomeric in solution. Their ^{1}H and ^{13}C NMR spectra (see Table 2) indicate that the solid-state structures are retained in solution at low temperature (below −5 °C for **3** and below −15 °C for **4**). In these low-temperature spectra the NMe_2 groups are diastereotopic since these molecules lack a molecular symmetry plane containing the N atoms. This diastereotopicity in **3** is evidence that the tin lone pair is stereochemically active [19]. At higher temperatures (see Table 2) the NMe_2 resonance patterns for both **3** and **4** coalesce. There are a number of processes that could account for this. The coalescence could, for example, be the result of Sn–N dissociation followed by pyramidal inversion of the nitrogen atom, rotation around the naphthyl C–N bond and recoordination of the nitrogen atom to tin. This process seems very unlikely, since the rigid geometry of the naphthalene skeleton always keeps the nitrogen atom in close proximity to the Sn atom *. A more likely possibility is an intramolecular rearrangement involving simultaneous

* The NMe_2 resonances of chiral pentacoordinate [8-(dimethylamino)-1-naphthyl]methylphenyltin bromide remain diastereotopic up to 120 °C, the highest temperature studied [36].

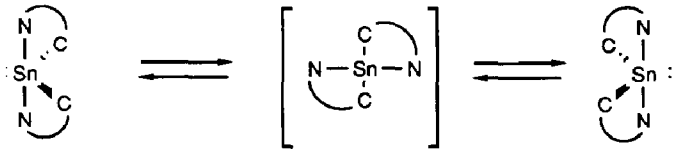
rotation of both naphthyl groups around the Sn–$C_{naphthyl}$ bonds with retention of Sn–N coordination (eq. 3).

(3)

(3) X = lone pair
(4) X = $W(CO)_5$

In view of the rigid stereochemistry of the 8-(dimethylamino)-1-naphthyl chelate system, the number of possible intermediate geometries is very restricted. For both **3** and **4** a rearrangement via a square pyramid with X at the axial position seems likely.

Alternatively, for **3** the rearrangement could occur via a square planar geometry of the type proposed for the inversion of configuration of the chiral sulfur atoms in spirosulfanes (eq. 4) [38].



(4)

For **4** such an intermediate geometry is impossible since its formation would require concurrent Sn–W bond dissociation and association.

It should be noted that the coalescence of the diastereotopic NMe_2 resonances in the ^{13}C NMR spectrum of the related compound $Sn(C_6H_4CH_2NMe_2\text{-}2)_2$ above $-80\,^{\circ}C$ was explained in terms of a rapid "polytopal" rearrangement [20]. In this case the $C_6H_4CH_2NMe_2$-2 chelate ligand lacks the rigid orientation of the C and N donor atoms found in the 8-(dimethylamino)-1-naphthyl ligand and Sn–N dissociation/association has also to be considered. Consequently, processes involving intermediates having a monodentate C-bonded $C_6H_4CH_2NMe_2$-2 ligand cannot a priori be excluded *. For example the NMR spectra of closely related chiral $Sn[(S)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]_2$ ** show coalescence of the diastereotopic NMe_2 at $\sim -40\,^{\circ}C$, and in this case, owing to the presence of the chiral label, the spectra provide unequivocal evidence for Sn–N dissociation/association [34].

It is known that ^{119}Sn NMR chemical shifts are strongly influenced by minor changes in geometry around the tin [39]. The ^{119}Sn shifts of **3** and **4** show strong temperature dependence (the value increases linearly for **3** from 150.9 at $-80\,^{\circ}C$ to 209.2 ppm at $80\,^{\circ}C$ and for **4** from 220.0 ppm at $-60\,^{\circ}C$ to 267.0 ppm at $50\,^{\circ}C$), and this may be associated with the fluxional processes reflected in the temperature dependent ^1H and ^{13}C NMR spectra (vide supra). Further interpretation of these

* An example is $Rh[C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}C,N](COD)$, in which only one of the two *ortho*-CH_2NMe_2 groups coordinates to rhodium(I) [44].

** $Sn[(S)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]_2$ is a yellow solid, prepared from chiral $Li[(S)\text{-}C_6H_4CH(Me)NMe_2\text{-}2]$ and $SnCl_2$ according to the procedures given by Angermund et al. [20].

data is difficult since there are very few reference data available for divalent organotin compounds: the values for **3** and **4** are close to those reported for $Sn(C_6H_4CH_2NMe_2\text{-}2)_2$ (169 ppm) [20] and $(C_6H_4CH_2NMe_2\text{-}2)_2SnW(CO)_5$ (195.4 ppm), respectively [18].

There is a marked decrease in $^1J(^{13}C-^{117,119}Sn)$ on going from **3** (409.6 and 428.7 Hz for ^{117}Sn and ^{119}Sn, respectively) to **4** (119.8 and 125.3), and this can be ascribed to a shift of σ-electron density from tin into the Sn–W bond [18]. The directly measured value of $^1J(^{119}Sn-^{183}W)$ of 976 Hz for **4** is fairly similar to that reported for $(C_6H_4CH_2NMe_2\text{-}2)_2SnW(CO)_5$ (892 Hz) [18]. Surprisingly, no or only a very small (< 2 Hz) coupling, is present between $^{117,119}Sn$ and the H(2) naphthyl proton in **3**, whereas in **4** the value of this coupling constant is 41 Hz.

Concluding remarks

By making use of a special feature, i.e. the rigid geometry of the 8-(dimethylamino)-1-naphthyl ligand with a fixed spatial orientation of the C,N donor atoms, it has proved possible to prepare a stable bis(naphthyl)tin(II) compound and its $W(CO)_5$ adduct. Since attempts to prepare the corresponding methoxynaphthalene analogue of **3** were unsuccessful, it can be inferred that the nature of the heteroatom-containing substituent plays an important role in the stabilization bis(naphthyl)tin(II) compounds. This topic is currently under investigation.

Experimental

Synthesis were carried out by standard Schlenk techniques under purified nitrogen. The solvents were dried and distilled from sodium prior to use. $[Li(C_{10}H_6NMe_2\text{-}8)(OEt_2)]_2$ [40] and $W(CO)_5(NMe_3)$ [41]) were prepared by published methods. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AC 200 spectrometer.

Synthesis of bis[8-(dimethylamino)-1-naphthyl-C,N)]tin(II) (3)

A suspension of $SnCl_2$ (3.07 g, 16.19 mmol) in diethyl ether (50 ml) was added during 30 min to a solution of [8-(dimethylamino)-1-naphthyl-*C*,*N*]lithium (5.7 g, 32.2 mmol) in diethyl ether (50 ml) at −20 °C. The brown-yellow suspension was stirred for 30 min. at −20 °C and then for 2 h at 25 °C. The solvent was removed in vacuo, and the residual solid was extracted with three 50 ml portions of warm (50 °C) benzene. The combined benzene extracts were evaporated under reduced pressure and the yellow solid residue was washed with two 50 ml portions of pentane and dried in vacuo. Recrystallization from boiling benzene afforded 5.16 g of yellow crystalline **3** (Yield 70%). Anal. Found: C, 62.65; H, 5.79; N, 5.99; MW 430 (cryoscopy in C_6H_6). $C_{24}H_{24}N_2Sn$ calcd.: C, 62.78; H, 5.27; N, 6.10%; MW 458. Melting point (sealed capillary under nitrogen) 180–182 °C.

Air oxidation of bis [8-(dimethylamino)-1-naphthyl-C,N]tin(II)

Dry air was bubbled through a solution of **3** (1.0 g, 2.2 mmol) in benzene (5 ml) for 2 h. The solid material thus formed was filtered off and dried in vacuo to yield 1.0 g of a white powder which, based on its elemental analysis, was judged to be

$C_{24}H_{24}N_2OSn$ (**5**) (yield 95%). Anal. Found: C, 60.31; H, 5.21; N, 5.68; O, 3.51. $C_{24}H_{24}N_2SnO$ calcd.: C, 60.67; H, 5.09; N, 5.90; O, 3.37%.

Synthesis of {bis[8-(dimethylamino)-1-naphthyl-C,N]tin(II)}tungsten pentacarbonyl (4)

To a solution **3** (1.4 g, 3.1 mmol) in benzene (25 ml) was added $W(CO)_5(NMe_3)$ (1.2 g, 3.1 mmol). The mixture was refluxed for 4 h, after which all volatile material was removed in vacuo. The residue was washed with two 10 ml portions of pentane and dried in vacuo, giving 1.31 g of pure **4** as a pale yellow solid (yield 53%). Elemental analysis, ^1H NMR spectroscopy and X-ray crystallography showed the presence of half an equivalent of benzene. Anal. Found: C, 47.71; H, 3.44; N, 3.37; O, 9.26. $C_{29}H_{24}N_2O_5SnW \cdot 0.5C_6H_6$ calcd.: C, 46.75; H, 3.31; N, 3.41; O, 9.73%.

Crystal structure determination of 3 *

The transparent yellow crystals of **3**, $C_{24}H_{24}N_2Sn$, obtained from recrystallization from boiling benzene, are of orthorhombic, space group *Pbca* with sixteen molecules in a unit cell of dimensions *a* 22.383(4), *b* 30.865(5) and *c* 12.127(2) Å. 12090 independent intensities ($2\theta < 60°$) were measured on a Nonius CAD4 diffractometer, at 25 °C, using graphite monochromated Mo-K_α radiation (λ Mo-K_α 0.71069 Å); 7107 of these were below the 2.5 $\sigma(I)$ level and were treated as unobserved.

The Sn positions were located by means of the symbolic addition program set SIMPEL 83 [42]. The positions of the C and N atoms were obtained by standard difference Fourier techniques. After isotropic block-diagonal least-squares refinement an empirical absorption correction (DIFABS [43]) was applied (crystal dimensions $1.25 \times 0.43 \times 0.15$ mm; μ(Mo-K_α) 12.3 cm^{-1}). Hydrogen atoms were introduced at their calculated positions. Continued refinement, anisotropic for Sn, C and N (the H atoms were kept at their idealized positions) converged to $R = 0.067$ ($R_w = 0.132$). A weighting scheme $\omega = 1/(6.46 + F_0 + 0.018\ F_0^2)$ was applied and the anomalous dispersion of Sn was taken into account. Coordinates of the non-hydrogen atoms are given in Table 3.

Crystal structure determination of 4

Transparent pale yellow crystals of **4**, $C_{29}H_{24}N_2O_5SnW \cdot 0.5C_6H_6$, obtained by vapour diffusion of pentane into a benzene solution of **4**, are triclinic, of space group $P\bar{1}$, with two molecules in a unit cell of dimensions *a* 12.509(3), *b* 15.191(1), *c* 9.780(1) Å, α 98.42(1), β 104.33(1) and γ 107.27(1)°. 9676 independent intensities ($2\theta < 60°$) were measured on a Nonius CAD4 diffractometer, at 25 °C, using graphite monochromated Mo-K_α radiation (λ(Mo-K_α) 0.71069 Å). Of these, 2560 were below the 2.5 $\sigma(I)$ level and were treated as unobserved. The Sn and W positions were located by means of the symbolic addition program set SIMPEL 83 [42]. The positions of the non-hydrogen atoms were obtained by standard difference Fourier techniques. It was found that the unit cell contains two molecules of benzene (solvent of crystallization) with each having a site population of 50%. After isotropic block-diagonal least-squares refinement an empirical absorption correction

* Complete Tables of bond distances and angles, and lists of thermal parameters and structure factors for complexes **3** and **4**, can be obtained from the authors.

Table 3

Atomic fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for **3**. $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$

Atom	x	y	z	U_{eq}
Sn1	0.37882(4)	0.16506(3)	0.33948(7)	0.0407(4)
Sn2	0.43053(4)	0.47332(3)	0.30307(8)	0.0436(4)
C1	0.4567(5)	0.1645(4)	0.454(1)	0.040(6)
C2	0.4642(7)	0.1361(5)	0.542(1)	0.051(8)
C3	0.5161(7)	0.1371(5)	0.609(1)	0.055(9)
C4	0.5598(7)	0.1665(6)	0.595(1)	0.061(9)
C5	0.5543(6)	0.1969(5)	0.508(1)	0.049(8)
C6	0.5963(9)	0.2305(6)	0.491(2)	0.08(1)
C7	0.5941(9)	0.2601(6)	0.409(2)	0.07(1)
C8	0.5431(8)	0.2592(5)	0.337(1)	0.065(10)
C9	0.5001(7)	0.2265(4)	0.347(1)	0.046(7)
C10	0.5010(6)	0.1956(4)	0.438(1)	0.042(7)
C11	0.4748(4)	0.1981(6)	0.171(1)	0.060(9)
C12	0.4274(8)	0.2647(6)	0.230(2)	0.08(1)
C13	0.3237(6)	0.2073(4)	0.449(1)	0.047(7)
C14	0.3206(7)	0.2507(5)	0.439(1)	0.069(10)
C15	0.2871(9)	0.2774(4)	0.515(2)	0.08(1)
C16	0.2636(8)	0.2578(5)	0.607(2)	0.07(1)
C17	0.2657(6)	0.2137(5)	0.622(1)	0.049(7)
C18	0.2391(8)	0.1928(6)	0.715(1)	0.064(10)
C19	0.2410(9)	0.1483(6)	0.726(1)	0.07(1)
C20	0.2644(7)	0.1235(5)	0.644(1)	0.055(8)
C21	0.2903(6)	0.1411(4)	0.550(1)	0.040(7)
C22	0.2939(5)	0.1873(4)	0.5398(9)	0.035(6)
C23	0.2618(6)	0.1109(6)	0.375(1)	0.060(9)
C24	0.3332(7)	0.0711(4)	0.490(1)	0.057(9)
C25	0.3316(7)	0.4739(4)	0.290(1)	0.053(8)
C26	0.2998(7)	0.5000(5)	0.219(1)	0.060(9)
C27	0.2354(8)	0.5004(6)	0.217(1)	0.07(1)
C28	0.2042(7)	0.4766(6)	0.294(2)	0.08(1)
C29	0.2352(7)	0.4493(5)	0.370(2)	0.069(10)
C30	0.2041(8)	0.4258(7)	0.453(2)	0.08(1)
C31	0.234(1)	0.4022(6)	0.526(2)	0.09(1)
C32	0.2960(8)	0.3996(5)	0.524(1)	0.060(9)
C33	0.3279(7)	0.4200(4)	0.447(1)	0.049(8)
C34	0.2979(6)	0.4504(4)	0.370(1)	0.046(7)
C35	0.4243(9)	0.4149(6)	0.540(2)	0.08(1)
C36	0.4032(8)	0.3772(5)	0.368(2)	0.08(1)
C37	0.4240(6)	0.5335(4)	0.409(1)	0.046(7)
C38	0.4214(7)	0.5321(6)	0.527(1)	0.061(9)
C39	0.406(1)	0.5709(6)	0.585(2)	0.08(1)
C40	0.3943(8)	0.6087(7)	0.531(1)	0.07(1)
C41	0.3996(7)	0.6100(5)	0.413(1)	0.053(8)
C42	0.3822(8)	0.6479(4)	0.353(1)	0.062(9)
C43	0.3876(7)	0.6495(5)	0.242(2)	0.061(9)
C44	0.4061(7)	0.6128(5)	0.183(1)	0.053(8)
C45	0.4224(6)	0.5760(4)	0.237(1)	0.041(6)
C46	0.4158(6)	0.5716(4)	0.354(1)	0.041(6)
C47	0.4337(7)	0.5327(5)	0.067(1)	0.056(8)
C48	0.5165(7)	0.5416(6)	0.191(1)	0.062(9)
N1	0.4519(5)	0.2225(3)	0.2701(10)	0.045(6)
N2	0.3115(5)	0.1159(3)	0.4582(9)	0.047(6)
N3	0.3920(6)	0.4163(4)	0.435(1)	0.053(7)
N4	0.4494(5)	0.5390(4)	0.1834(8)	0.043(6)

Table 4

Atomic fractional coordinates and equivalent isotropic thermal parameters (Å^2) for **4**. $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

Atom	x	y	z	U_{eq}
Sn1	0.30202(4)	0.64843(3)	0.30412(4)	0.0391(2)
W1	0.18106(2)	0.45708(2)	0.29284(3)	0.0445(1)
C1	0.2680(5)	0.7340(4)	0.1473(7)	0.042(3)
C2	0.1735(6)	0.7658(5)	0.1193(9)	0.054(4)
C3	0.1705(8)	0.8324(7)	0.0345(10)	0.069(5)
C4	0.2589(9)	0.8692(6)	−0.0211(9)	0.067(5)
C5	0.3545(7)	0.8369(5)	−0.0003(7)	0.052(3)
C6	0.4499(8)	0.8728(5)	−0.0545(9)	0.063(5)
C7	0.5383(9)	0.8398(7)	−0.036(1)	0.071(6)
C8	0.5373(8)	0.7631(6)	0.0319(9)	0.062(5)
C9	0.4450(6)	0.7256(4)	0.0851(7)	0.046(3)
C10	0.3565(6)	0.7654(4)	0.0797(6)	0.041(3)
C11	0.5338(8)	0.6165(6)	0.1804(10)	0.064(5)
C12	0.3444(8)	0.5602(5)	0.0044(8)	0.056(4)
C13	0.4575(6)	0.7474(5)	0.4733(7)	0.046(3)
C14	0.5687(7)	0.7410(7)	0.5074(9)	0.063(5)
C15	0.6685(8)	0.8179(8)	0.600(1)	0.074(5)
C16	0.6596(7)	0.9031(7)	0.6523(9)	0.070(5)
C17	0.5480(7)	0.9125(5)	0.6255(7)	0.057(4)
C18	0.5338(9)	0.9983(5)	0.6788(8)	0.065(4)
C19	0.423(1)	1.0032(5)	0.6549(8)	0.069(5)
C20	0.3222(9)	0.9214(5)	0.5879(8)	0.064(5)
C21	0.3327(7)	0.8376(5)	0.5367(7)	0.048(3)
C22	0.4451(7)	0.8312(4)	0.5423(7)	0.047(3)
C23	0.1182(8)	0.7580(8)	0.436(1)	0.078(6)
C24	0.2384(8)	0.6966(5)	0.6027(9)	0.065(5)
C25	0.0966(8)	0.3231(6)	0.287(1)	0.069(5)
C26	0.0389(7)	0.4899(5)	0.3238(8)	0.054(4)
C27	0.2578(8)	0.4817(6)	0.5123(9)	0.065(5)
C28	0.3152(9)	0.4168(6)	0.256(1)	0.068(5)
C29	0.1049(7)	0.4364(5)	0.0749(9)	0.056(4)
C100	0.138(2)	0.190(2)	0.922(3)	0.12(2)
C101	0.144(2)	0.226(2)	0.813(4)	0.12(2)
C102	0.137(2)	0.179(2)	0.688(3)	0.11(2)
C103	0.123(2)	0.090(2)	0.670(2)	0.11(2)
C104	0.112(2)	0.048(2)	0.776(4)	0.12(2)
C105	0.117(2)	0.098(3)	0.907(3)	0.12(2)
N1	0.4268(5)	0.6377(4)	0.1313(6)	0.047(3)
N2	0.2363(5)	0.7474(4)	0.4835(6)	0.049(3)
O25	0.0525(8)	0.2471(4)	0.2921(9)	0.098(5)
O26	−0.0443(6)	0.5020(6)	0.3314(8)	0.082(5)
O27	0.3016(9)	0.4898(7)	0.6316(7)	0.110(6)
O28	0.3865(8)	0.3914(6)	0.234(1)	0.104(7)
O29	0.0617(7)	0.4243(5)	−0.0464(6)	0.080(4)

(DIFABS [43]) was applied (crystal dimensions 0.13 × 0.40 × 0.55 mm; μ(Mo-K_α) 39.2 cm^{-1}). A difference Fourier map showed all hydrogen atoms, which were introduced in the refinement. Continued refinement, anisotropic for Sn, W, C, N and O, and isotropic for H (except for the H atoms of the solvent molecule, which

were kept fixed; U 0.045 Å^2) converged to $R = 0.046$; $R_w = 0.070$. An extinction correction and a weighting scheme $\omega = 1/(6.12 + F_0 + 0.0144\ F_0^2)$ was applied. The anomalous dispersion of Sn and W were taken into account. Coordinates of the non-hydrogen atoms are given in Table 4.

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