

PENTACOORDINATE [8-(DIMETHYLAMINO)NAPHTHYL]DIORGANOTIN HALIDES CONTAINING A RIGID, FLAT $\overline{\text{NCCCSn}}$ CHELATE RING. AN UNEXPECTED REDISTRIBUTION REACTION BETWEEN [8-(DIMETHYLAMINO)NAPHTHYL]TRIMETHYLTIN AND TRIMETHYLTIN HALIDE

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Summary

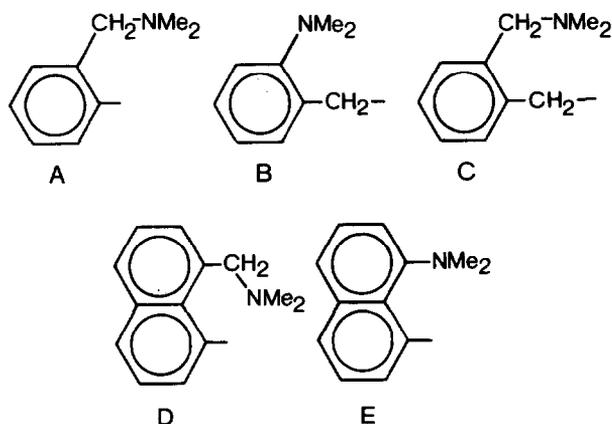
The tetraorgano- and triorgano-halotin compounds $\text{Me}_3(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{Sn}$ and $\text{RR}'(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{SnX}$ ($\text{R} = \text{R}' = \text{Me}$ or Ph , $\text{X} = \text{Cl}$ or Br and $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$, $\text{X} = \text{Br}$) have been obtained from the 1/1 reaction of 8-dimethylamino-1-naphthyl-lithium ($8\text{-Me}_2\text{NC}_{10}\text{H}_6\text{Li}$) with the relevant organotin halide (Me_3SnCl or $\text{RR}'\text{SnX}_2$). On the basis of the ^1H NMR data a trigonal bipyramidal structure with intramolecular Sn–N coordination is proposed for the $\text{RR}'(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{SnX}$ compounds, in which the organo ligands occupy the equatorial and the N and X atoms the axial positions. The Sn center in chiral $\text{MePh}(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{SnBr}$ has considerable configurational stability (at least on the NMR timescale, 60 MHz): the Me groups of the coordinated NMe_2 group remain diastereotopic up to at least 120°C . This relatively high stability is ascribed to the fixed position of the Sn and N atoms respectively connected to the 1- and 8-positions of the flat naphthyl ring. Reaction of Me_3SnX with $\text{Me}_3(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{Sn}$ results in quantitative formation of Me_4Sn and $\text{Me}_2(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{SnX}$ ($\text{X} = \text{Cl}, \text{Br}$). Overcrowding in the $8\text{-Me}_2\text{N-1-Me}_3\text{SnC}_{10}\text{H}_6$ compound as well as the formation of the Sn–N bond are suggested as driving forces for this Me/Cl exchange reaction. This methylating property of $8\text{-Me}_2\text{N-1-Me}_3\text{SnC}_{10}\text{H}_6$ also leads to quantitative formation of $\text{MePtCl}(\text{COD})$ from $\text{PtCl}_2(\text{COD})$ at room temperature.

Introduction

The potentially bidentate organo ligands A–E have been extensively used to synthesize organometallic compounds showing improved stability [1–5] or special

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reactivity [6].



This increase in stability compared to organometallic compounds in which the heteroatom and organo group are not interconnected can be considerable. Clear examples can be found in IB metal [2,7] and early transition metal [4,5] chemistry. However, in spite of the numerous examples it is still unclear for a particular bidentate group which factors contribute most to the stabilization. In some cases the chelate effect seems to be important [1], whereas in others, in particular when the metal–nitrogen interaction is weak because of softness of the metal (e.g. Cu^{I} or Ag^{I}), the increased stability seems to be brought about by steric effects of the built-in, hard nitrogen ligand [2,7]. These steric effects may involve, for example, shielding of the M–C bonds from further reaction. Another possibility is stabilization of specific M–C rotamers, in which additional overlap between metal and carbon orbitals is possible, thereby increasing the overall stability of this M–C bond.

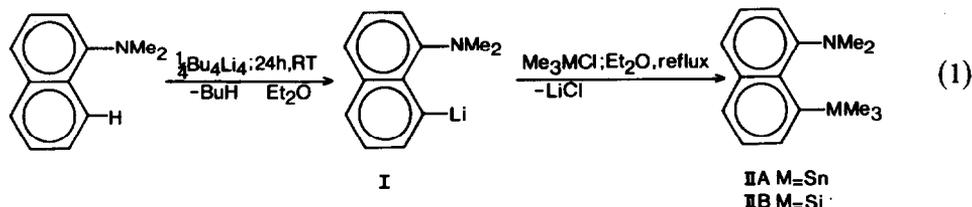
Recently, we proposed that the stability of the tetranuclear structure $[\text{2-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Li}]_4$, containing the first example of 4 centre-2 electron bonding of an aryl group (A) to a Li_4 tetrahedron, arises from the Li–N interaction and the favourable stereochemistry of the puckered, five-membered chelate ring [3]. The completely different structure obtained [9] when instead of (A) the flat bidentate naphthyl ligand (E) [1,8] is incorporated emphasizes the importance of the chelate stereochemistry in determining the nuclearity of the Li clusters.

Much information about the importance of the metal–nitrogen bond strength and the chelate ring stereochemistry of Li_n clusters can be obtained by studying the corresponding air stable mononuclear organotin compounds [10]. These are easily accessible from the organolithium compounds. In this paper we report a series of tetraorgano- and triorgano-halotin compounds containing the potentially bidentate 8-(dimethylamino)-1-naphthyl ligand (E). It will be shown that as a result of the favourable stereochemistry of the 8- $\text{Me}_2\text{NCCCSn-1}$ arrangement the triorganohalotin compounds $\text{RR}'(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{SnX}$ have a five-coordinate Sn centre which has a relatively high configurational stability. The tetraorganotin compounds $\text{R}_3(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{Sn}$ bear an interesting structural relationship to the 1,8-di(R_3M)naphthalene compounds (M = C, Si, Ge or Sn) in which an MR_3 group has replaced an NMe_2 unit and its lone pair. Apart from the theoretical interest in these compounds [11] it can be expected that the intramolecular strain caused by overcrowding in such

1,8-disubstituted naphthalenes will induce special reactivity. This is demonstrated by the unexpected Me/Cl exchange products Me_4Sn and $\text{Me}_2(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{SnCl}$ from the 1/1 reaction of $\text{Me}_3(8\text{-Me}_2\text{NC}_{10}\text{H}_6)\text{Sn}$ with Me_3SnCl .

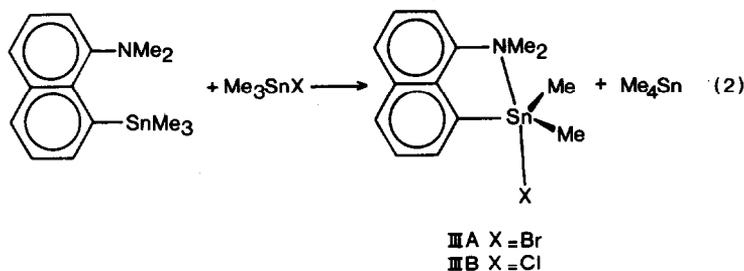
Results

The 1/1 molar reaction of 1-(dimethylamino)naphthalene with *n*-butyllithium in diethyl ether affords 8-(dimethylamino)-1-naphthyllithium etherate (I) quantitatively by the H/Li exchange reaction shown in eq. 1. Its characterisation by ^1H , ^{13}C and ^7Li NMR spectroscopy and X-ray structure determination has been reported [9].



Reaction of a suspension of I in diethyl ether with Me_3SnCl or Me_3SiCl in a 1/1 molar ratio gives the corresponding derivatives IIA and IIB respectively, as in eq. 1. Both IIA and IIB were obtained as colourless oils, which could be purified by distillation at reduced pressure.

It is important that excess of Me_3MX is avoided in these reactions. ^1H NMR spectroscopy showed that during 10 h a 1/1 molar mixture of the trimethyltin derivative IIA and trimethyltin bromide was completely converted into the dimethyl-naphthyltin bromide IIIA and tetramethyltin. This unexpected redistribution reaction is shown in eq. 2. In the same way it was possible to prepare the chloride analogue of IIIA, IIIB, by using Me_3SnCl instead of Me_3SnBr .



Direct synthesis of IIIA was possible by treating the naphthyllithium derivative I with dimethyltin dibromide. Furthermore, reaction of I with diphenyltin- or methylphenyltin dibromide afforded (see experimental) the diorganonaphthyltin compounds IIIC and IIID, after work-up, as white crystalline solids, see eq. 3.

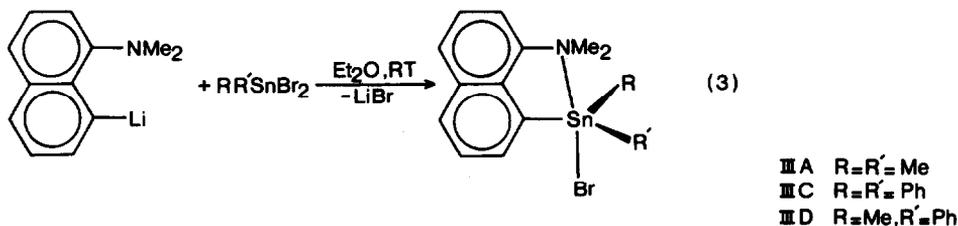


TABLE 1
RELEVANT ^1H NMR DATA FOR THE COMPOUNDS IIA, B, IIIA, B, C AND D^a

Compound	$\delta(\text{NMe}_2)$	$\delta(\text{H}(2)(\text{naphthalene}))$	$\delta(\text{MeSn})$	$^2J(^{117,119}\text{Sn}-\text{H})^b$	$\delta(\text{Aromatic-H})$
Ia	2.31(s)	^d	0.31(s)	50, 52.5	6.8–8.0(m)
IIB	2.36(s)	^d	^c	–	7.0–8.1(m)
IIIA	1.89(s)	8.80(d of d) ^e	0.61(s)	63.66	6.6–7.6(m)
IIIB	1.77(s)	9.28(d of d) ^e	–	–	6.6–7.8(m)
IIIC	1.64(s) and 1.93(s)	8.95(d of d) ^e	0.89(s)	64.67	6.6–7.7(m)
IIID	2.00(s)	8.99(d of d) ^e	0.67(s)	64.67	6.7–7.7(m)

^a At 60 MHz; all values are in ppm relative to TMS internal, in C_6D_6 , at ambient temperature. ^b In Hz. ^c Me_3Si resonance at 0.41 ppm (s). ^d Signals masked by other aromatic resonances. ^e $^3J(\text{H}-\text{H})$ 6.25 and $^4J(\text{H}-\text{H})$ 1.5 Hz. ^f No coalescence was observed up to 125°C.

According to molecular weight determinations (cryoscopy in C_6H_6) these diorganonaphthyltin bromides are monomeric in solution. Elemental analytic data (see experimental) and ^1H NMR spectroscopic data (see Table 1) are in agreement with the stoichiometry of the diorganonaphthyltin compounds indicated in eq. 3.

Discussion

The ^1H NMR spectra of the diorganonaphthyltin halides IIIA–IIID point to a structure in which there is a trigonal-bipyramidal Sn geometry (see Fig. 1) instead of the tetrahedral one present in II. The carbon ligands in III are in the equatorial plane of the TBP array which is perpendicular to the plane of the naphthalene ring. The NMe_2 and halide ligands occupy the axial sites. The methyl-Sn protons in the ^1H NMR spectra have a $^2J(^{117,119}\text{Sn}-\text{CH}_3)$ of about 65 Hz, which is the value expected for five-coordinate triorganotin halides [12]. Furthermore, the large downfield shift of H(2) in III and IV* to about 9.0 ppm is in agreement with the proposed structure which places this proton in the proximity of the Sn–Br bond. For the trimethylnaphthyltin derivative IIA a $^2J(^{117,119}\text{Sn}-\text{CH}_3)$ of 50 Hz was observed, a value which is in the range reported for four-coordinate tetra-organotin compounds.

The trigonal bipyramidal geometry of the Sn centre in III is interesting in view of earlier observations in the X-ray structures of a series of related triorganotin halides

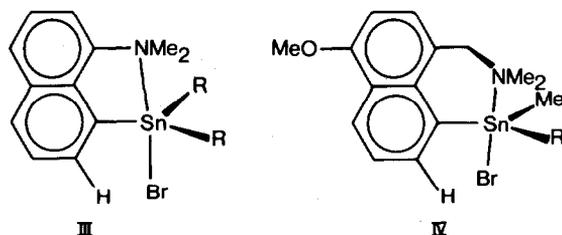


Fig. 1

* ^1H NMR of IV; R = Me, $\delta\text{H}(2)$ 8.99 and R = Ph, $\delta\text{H}(2)$ 9.12 [12].

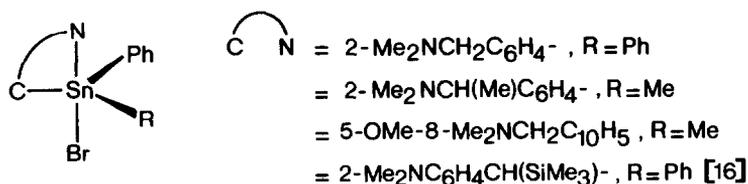


Fig. 2

(Fig. 2) [c.f. 12]. There it appears that the sum of apical Sn–N and Sn–Br bonds is remarkably constant (5.15 Å) notwithstanding appreciable variations in the individual bond lengths. Consequently this comparison shows that as the Sn–N bond becomes shorter the Sn–Br bond lengthens, reflecting the characteristic changes in bond lengths (and angles) known for S_N2 reaction pathways [12]. A similar conclusion was reached by Britton and Dunitz in their comparison of the structural correlation of trigonal bipyramidal SnC_3XY ensembles with trans X, Y and monodentate C, X and Y ligands [13]. However, in our compounds the “incoming” NMe_2 ligand is part of a skeletal system connected to Sn via C(1) in the equatorial position. The intrinsic strain in this system determines the smallest possible values for the Sn–N bond. This is a fixed value in the absence of skeletal distortions in III, and amounts to about 2.40 Å based on the calculated C(1)...C(8) distance. Although the C(1)–Sn and C(8)–N bond lengths are different (2.14 and 1.46 Å [12], respectively) it can be concluded that the five-membered chelate ring in III will be close to planar. In contrast an X-ray structure IV shows that the six-membered chelate ring containing a tetrahedral sp^3 C atom leads to considerable ring puckering. Furthermore, this puckering leads to the existence of IV ($\text{R} = \text{Ph}$) in two diastereoisomeric forms, which can be detected by NMR at low temperature.

A dynamic ^1H NMR spectroscopic study of the diorganonaphthyltin bromide IIIc reveals that the molecule exists in two enantiomeric forms. Two Me resonances are observed for the NMe_2 grouping, which establishes that this group has become diastereotopic as a result of Sn–N coordination. These methyl groups remain diastereotopic up to 120°C (^1H 1.64 and 1.93 ppm) the highest temperature studied. This indicates that the inversion of configuration at the Sn center, as well as the Sn–N bond dissociation followed by rotation around C(8)–N (in order to remove the N lone pair away from the Sn center), with concomitant pyramidal inversion, are both slow on the NMR time scale or are blocked. Even in the absence of inversion of configuration at Sn, the latter process, which has been found for IV and other intramolecularly chelated triorganotin halides [12], would have rendered the Me groups enantiotopic. Because of the fixed positions of the N and Sn atoms in III, rotation around the C(8)–N bond is a particularly unlikely process because it would require extensive distortion of the naphthalene skeleton*.

Finally, release of repulsion between the NMe_2 and the SnMe_3 group on going from II to III can be called upon to explain the redistribution reaction between IIA and Me_3Sn halides. In the product III, not only is there formation of a Sn–N bond

* Whether this chiral Sn compound is configurationally stable on the laboratory time scale, which would allow separation of the enantiomers, cannot be deduced from these results.

(and thus a chelate ring) but there is also a favourable arrangement of the Sn and N substituents relative to the naphthyl skeleton, and either or both of these factors may provide driving force for the observed reaction. It is surprising that this reaction occurs at room temperature and is so selective. Other workers have shown that a 1/1 mixture of Me_3SnBr and Et_4Sn gives rise to a mixture of all possible redistribution products, $\text{Me}_{4-n}\text{Et}_n\text{Sn}$ $n = 0, 1, 2, 3, 4$ and $\text{Me}_{3-n}\text{Et}_n\text{SnBr}$ $n = 0, 1, 2, 3$, though this reaction only occurs under forcing conditions [14].

The potential methylating properties of IIA towards transition metal halides has been shown by a preliminary reaction of IIA with $\text{PtCl}_2(\text{COD})$, which led to the quantitative formation of IIB and $\text{MePtCl}(\text{COD})$. (Normally reaction of mixed aryl(alkyl)tin compounds with platinum halides give rise to the transfer of an aryl group from tin to the platinum atom [15]). However methyl transfer has been observed in the 1/1 reaction of Me_4Sn with $\text{PtCl}_2(\text{COD})$ but this reaction requires forcing conditions and provides $\text{MePtCl}(\text{COD})$ in 60% yield [15].

This very interesting property of IIA is now under investigation.

Experimental

All reactions were carried out under dry oxygen-free nitrogen. ^1H NMR spectra were recorded on Varian T60 and A60 spectrometers.

8-(Dimethylamino)-1-naphthyllithium etherate (I)

To a solution of 15 mmol of 1-dimethylaminonaphthalene in diethyl ether (15 ml) was added a solution of n-butyllithium (15 mmol) in hexane (14 ml). This mixture was stirred for 24 h, during which a yellow precipitate was slowly formed. The solid was filtered off, washed with n-pentane (2×20 ml), and dried in vacuo. Pure yellow I was obtained in 60% yield.

1-(Trimethyltin)- and 1-(trimethylsilyl)-8-dimethylaminonaphthalene IIA and IIB

To a suspension of 10 mmol of 8-dimethylamino-1-naphthyllithium etherate in 40 ml of diethyl ether was added either 10 mmol of trimethyltin chloride or 10 mmol of trimethylsilyl chloride. The mixture was refluxed for 4 h. Evaporation of the solvent at reduced pressure yielded a white oily residue, which was extracted with n-pentane (3×20 ml), leaving a white solid (LiCl). The combined pentane extracts were evaporated under reduced pressure, yielding pure IIA or IIB as a colourless oil in 90% yield.

1-(Diorganobromotin)-8-(dimethylamino)naphthalene IIIA, IIIC, IIID

The lithium compound I (10 mmol) was added in small portions to a stirred solution of 10 mmol of the corresponding diorganotin dibromide (Me_2SnBr_2 , MePhSnBr_2 or Ph_2SnBr_2) in 25 ml of diethyl ether. The resulting colourless solution was stirred for 1 h, after which the solvent was removed in vacuo to leave a white solid. This was extracted with two 20 ml portions of hot benzene and the extract was filtered to remove LiBr. The combined benzene extracts were evaporated at reduced pressure and the resulting white solids were washed with n-pentane and dried in vacuo, yielding the diorganonaphthyltin bromides IIIA, IIIC and IIID in 90% yield as white solids. For analytical purposes the compounds were recrystallised from benzene/hexane mixtures.

IIIA: M.p. 123–124°C (found; C, 42.01; H, 4.49; N, 3.28; Br, 20.12. $C_{14}H_{18}BrNSn$ calcd.: C, 42.15; H, 4.55; N, 3.51; Br, 20.03%).

IIIC: M.p. 200–201°C, (found: C, 55.32; H, 4.31; N, 2.74; Br, 14.85. $C_{24}H_{22}BrNSn$ calcd.: C, 55.11; H, 4.24; N, 2.68; Br, 15.28%).

IIID: M.p. 159–160°C (found: C, 49.50; H, 4.33; N, 2.72; Br, 17.57, $C_{19}H_{20}BrNSn$ calcd.: C, 49.51; H, 4.37; N, 3.04; Br, 17.32%).

1-Dimethylchlorotin-8-(dimethylamino)naphthalene IIIB

1-Trimethyltin-8-(dimethylamino)naphthalene IIA (5 mmol) and trimethyltin chloride (5 mmol) were dissolved in 10 ml of benzene. 1H NMR spectra recorded at various time intervals showed the slow disappearance of IIA and the formation of IIIB and Me_4Sn . After 10 h all IIA was converted into IIIB. The solvent and Me_4Sn were evaporated at reduced pressure and the resulting white solid was washed with n-pentane to give white crystalline IIIB (95%). For analytical purposes IIIB was recrystallized from a benzene/hexane mixture. M.p. 120–122°C (found: C, 47.42; H, 5.08; N, 3.68; Cl, 9.78. $C_{14}H_{18}ClNSn$ calcd: C, 47.44; H, 5.12; N, 3.95; Cl, 10.00%).

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