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Synthesis of mono- and di-aryltin(IV) complexes containing the ligand 2-(phenylazo)phenyl by use of organomercury compounds

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Abstract

Reaction of $[Hg(2\text{-}C_6H_4N{=}NPh)Cl]$ with $SnCl_2$ (1/1) in refluxing xylene gives the monoaryl complex $[Sn(2\text{-}C_6H_4N{=}NPh)Cl_3]$ (I) and Hg. Complex I reacts with excess of NaBr to give $[Sn(2\text{-}C_6H_4N{=}NPh)Br_3]$ (II) and with $HgPh_2$ (1/1) to give $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2]$ (III), which reacts with 1,10-phenanthroline (phen) to give $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2(phen)]$ (IV); this in turn, reacts with $Na[BPh_4]$, to give the cationic complex $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl(phen)][BPh_4]$ (V). The complex $[Sn(2\text{-}C_6H_4N{=}NPh)_2Cl_2]$ reacts with excess of NaBr or KSCN to give the corresponding $[Sn(2\text{-}C_6H_4N{=}NPh)_2X_2]$ ($X = Br$ (VI), NCS (VII)) complexes, and with $AgClO_4$ to give AgCl and a solution from which, by addition of pyridine (py), the complex $[Sn(2\text{-}C_6H_4N{=}NPh)_2(py)_2](ClO_4)_2$ (VIII) can be isolated.

Introduction

We have synthesized 2-(phenylazo)phenyl complexes of gold(III) [1], tin(IV) [2] and thalium(III) [3] by using the corresponding mercury derivatives $[Hg(2\text{-}C_6H_4N{=}NPh)_2]$ and $[Hg(2\text{-}C_6H_4N{=}NPh)Cl]$. The reactions were of two different types, the gold complexes were obtained by transmetallation reactions (e.g. $[Hg(R)Cl] + [AuCl_3(tht)] + Cl^- \rightarrow [Au(R)Cl_2] + [HgCl_3]^-$), while the tin complex $[Sn(2\text{-}C_6H_4N{=}NPh)_2Cl_2]$ was prepared by a redox transmetallation reaction involving $[Hg(2\text{-}C_5H_4N{=}NPh)Cl]$ and metallic Sn [2a]. We describe here the synthesis of derivatives of this diaryltin complex.

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We recently obtained a mixed diaryltin(IV) complex, $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2]$, by reaction of $[Sn(Ph)Cl_3]$ with $[Hg(2\text{-}C_6H_4N{=}NPh)_2]$ [2b]. We show below that this complex can also be obtained by treating $[HgPh_2]$ with $[Sn(2\text{-}C_6H_4N{=}NPh)Cl_3]$. The latter complex has been obtained by use of a new method of making mono-organotin trihalide compounds, i.e. by treating $[Hg(2\text{-}C_6H_4N{=}NPh)Cl]$ with $SnCl_2$. The reactions between $[Hg(Ph)Cl]$ or $[Hg(CH_2Ph)Cl]$ with $SnCl_2$ were found to lead to $[SnR_2Cl_2]$ derivatives, rather the expected $[Sn(R)Cl_3]$ compounds, which were detected just in trace amounts [4].

Results and discussion

Synthesis. Refluxing a mixture of equimolar amounts of $[Hg(2\text{-}C_6H_4N{=}NPh)Cl]$ and $SnCl_2$ in xylene gave metallic mercury and a solution containing the complex $[Sn(2\text{-}C_6H_4N{=}NPh)Cl_3]$ (I) (72% yield). Complex I reacted with an excess of KBr in acetone to give $[Sn(2\text{-}C_6H_4N{=}NPh)Br_3]$ (II) (62% yield).

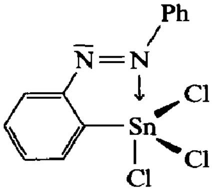
We recently prepared the mixed diaryltin(IV) complex, $[Sn(2\text{-}C_6H_4\text{-}N{=}NPh)(Ph)Cl_2]$ (III) by reaction of $[Sn(Ph)Cl_3]$ with $[Hg(2\text{-}C_6H_4N{=}NPh)_2]$ [2b]. We find that this complex can be prepared in better yield (83%) by reaction of complex I with $[HgPh_2]$ (1/1) in refluxing acetone. This provides a further illustration of the versatility of arylmercury compounds in synthesis of aryl complexes of other metals. We have also used them to prepare the mixed diarylgold(III) complex $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4N{=}NPh)Cl]$, which was also made following two ways, which differ in the order in which the aryl ligands were transferred from the mercury to the gold centre [1c]. We have also succeeded in preparing mixed diarylthallium complexes by use of transmetallation reactions with organomercury compounds [3b].

We reported [2b] that complex III did not react with pyridine or 2,2′-bipyridine. However, we find that when an ethereal solution of III is treated with an equimolar amount of 1,10-phenanthroline · H_2O at room temperature for 24 h, an orange precipitate of $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2(phen)]$ (IV) is obtained, and this in turn can be converted into the cationic species $[Sn(2\text{-}C_6H_4\text{-}N{=}NPh)(Ph)Cl(phen)][BPh_4]$ (V) by treatment with an excess of $NaBPh_4$ in acetone. Complex V can also be obtained directly by reaction of III with 1,10-phenanthroline · H_2O and $Na[BPh_4]$ in the molar ratio 1/1/3.

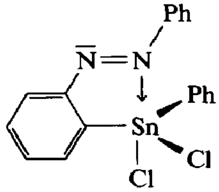
Complex $[Sn(2\text{-}C_6H_4N{=}NPh)_2Cl_2]$ (A) was previously obtained through a redox transmetallation reaction between $[Hg(2\text{-}C_6H_4N{=}NPh)Cl]$ and metallic tin [2a]. It reacts with an excess of NaBr or KSCN to give the corresponding $[Sn(2\text{-}C_6H_4\text{-}N{=}NPh)_2X_2]$ (X = Br (VI), NCS (VII)) complexes. Complex A does not react with pyridine in the presence of $NaClO_4$, but it does react with $AgClO_4$ (1/2) in acetone to give AgCl and a solution from which, by addition of pyridine (py), the complex $[Sn(2\text{-}C_6H_4N{=}NPh)_2(py)_2](ClO_4)_2$ (VIII) can be isolated.

Several attempts to grow single crystal of complexes I, II, IV–VIII were unsuccessful. However, some of their structural features can be rationalized in the light of earlier information. Complexes related to $[Sn(2\text{-}C_6H_4N{=}NPh)Cl_3]$, such as $[Sn\{2\text{-}C_6H_4C(Ph){=}NMe\}Cl_3]$ [5] or $[Sn\{CH_2CH_2C(O)OPr^i\}Cl_3]$ [6], have trigonal bipyramidal structures with two chlorines and carbon equatorial and the remaining chlorine and the nitrogen or oxygen axial. Because of the small bite size of 2-(phenylazo)phenyl ligand (for example, the average is 70° in $[Sn(2\text{-}C_6\text{-}$

$H_4N{=}NPh)_2Cl_2]$ [2a] and in $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2]$ [2b]), complex I should also adopt this type of structure, with the more electronegative atom of the organic ligand, i.e. N, in an axial position and the carbon atom in equatorial position. If this is the case, the structure of $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2]$ [2b] can be regarded as resulting from replacing an equatorial chlorine by a phenyl ligand.



Proposed structure of I



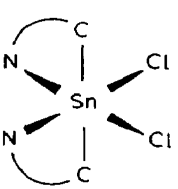
Structure of III

Complex I shows two strong IR bands at 330 and 370 cm^{-1}, which, in view of the expected weaker strength of the axial than of the equatorial Cl–Sn bonds, can be respectively assigned to $\nu(Cl\text{–}Sn)_{ax}$ and to the two IR active $\nu(Cl\text{–}Sn)_{eq}$ modes. A similar difference between the ν(Cl–Sn) IR bands from $[Sn(2\text{-}C_6H_4\text{-}N{=}NPh)(Ph)Cl_2]$ has been observed, but in this case the bands are at lower wavenumbers (290 and 340 cm^{-1}) [2b].

The IR spectrum of I and $[Sn(2\text{-}C_6H_4N{=}NPh)Br_3]$ are almost identical in the 4000–400 cm^{-1} region, suggesting that they are isostructural. The only differences involve the replacement of the ν(Cl–Sn) bands by two new ones at 215 and 255 cm^{-1}, which must be assigned to ν(Br–Sn) modes.

The two bands (290 and 340 cm^{-1}) assigned in complex $[Sn(2\text{-}C_6H_4\text{-}N{=}NPh)(Ph)Cl_2]$ to ν(Cl–Sn) are replaced by a single band, at 270(m) cm^{-1} in $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2(phen)]$ and at 255(w) cm^{-1} in $[Sn(2\text{-}C_6H_4\text{-}N{=}NPh)(Ph)Cl(phen)][BPh_4]$ (another band at 310(w) cm^{-1} may be due to the presence of the anion BPh_4). It has recently been shown [7] that in complexes of the type $[Sn(Ar)_2Cl_2(L\text{–}L)]$ (Ar = aryl, L–L = bidentate ligand) *cis* or *trans* dispositions of the two aryl groups in the octahedron are equally probable. Both have been obtained for Ar = $4\text{-}ClC_6H_4$ and L–L = 4,4′-Me_2bipy. It is thus impossible with the restricted data available to decide on the structures of complexes $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2(phen)]$ and $[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl(phen)][BPh_4]$. The first complex could be heptacoordinate.

The IR spectra of complexes VI and VII are very similar to that of the starting complex $[Sn(2\text{-}C_6H_4N{=}NPh)_2Cl_2]$ (A), except for the absence in the bromo complex, VI, of the bands at 320(w) and 290(s) present for complex A, and for the presence of a new band at 200(s) cm^{-1}, and so we can assign these bands to ν(Cl–Sn) and ν(Br–Sn), respectively. In the IR spectrum of the NCS complex VII there are several bands in the 400–200 cm^{-1} region that must be assigned to δ(NCS) and some Sn-ligand modes. The only other main change from the IR



Structure of complex A, C ~ N = $2\text{-}C_6H_4N{=}NPh$

spectrum of A is the presence of a very strong and broad band at 2010–2020 cm^{-1} in VII corresponding to ν(CN). It is thus reasonable to assume that the structures of complexes VI and VII are the same as that reported for complex A [2a].

We conclude that in complex VII the NCS ligand is bonded through the nitrogen atom. This conclusion is based on the following facts: (a) this is the expected situation for a class A or hard acid, which Sn^{IV} is; (b) the ν(CN) band appears below 2050 cm^{-1} [8]; and (c) the internal standard method [9] involving use of salicylic acid gives, for the bands corresponding to ν(CN) of the complex and ν(CO) of the standard, a ratio of molar areas of 8, which is far above the minimum expected value of 1.5 for the ligand bonded through the nitrogen atom. Although none of these criteria is in itself sufficient to assume the coordination mode of the ligand the combination of the three gives us confidence in our suggestion.

All complexes have molar conductivities (Λ_M) in acetone corresponding with their formulations [10]. Thus, while all the neutral complexes give values of Λ_M in the range 0–4 Ω^{-1} cm^2 M^{-1}, the cationic complexes V and VIII behave as 1/1 and 2/1 electrolytes, respectively, giving values of Λ_M of 91 and 150 Ω^{-1} cm^2 M^{-1}, respectively.

In the mass spectra of most of the complexes the molecular ion is observed (see Experimental).

Experimental

Infrared spectra were recorded in the range 4000–200cm^{-1} on a Perkin–Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured for ca. 10^{-4} mol dm^{-3} solutions with a Philips 9501 conductimeter, and Λ_M is given in Ω^{-1} cm^2 mol^{-1}. Melting points were determined on a Reichert apparatus and are uncorrected. C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyzer. Mass spectra were determined with a Hewlett–Packard GC/MS System 5993 at 70 eV. Reactions were carried out at room temperature with magnetic stirring and without special precautions against light or atmospheric moisture unless otherwise stated.

[$\overline{Sn(2\text{-}C_6H_4N}$=NPh)$Cl_3$] (I). A suspension of [Hg(2-C_6H_4N=NPh)Cl] [11] (500 mg, 1.2 mmol) and anhydrous $SnCl_2$ (227.2 mg, 1.2 mmol) in xylene (20 cm^3) was refluxed for 5 h. The suspension was then filtered hot, and the filtrate concentrated (to 1 cm^3) and n-hexane (10 cm^3) added. The yellow precipitate was recrystallized from dichloromethane/n-hexane to give I. Yield: 72%, m.p.: 160–162°C, Λ_M: 0 Ω^{-1} cm^2 mol^{-1} (5×10^{-4} M acetone). Mass spectrum: m/z 409, 407–403, 401 (M^+, 17%); 374, 372–368, 366, ($M^+ -$ Cl, 15%); 302, 300, 298 ($M^+ -$ 3Cl 3.5%); 161, 159, 157–150 ($SnCl^+$, 92%); 120–116 (Sn^+, 10%); 105 ($PhN_2{}^+$, 69%); 77 (Ph^+, 100%). Anal: Found: C, 35.49; H, 2.28; N, 7.31. $C_{12}H_9N_2Cl_3Sn$ calcd.: C, 35.44; H, 2.23; N, 6.89%.

[$\overline{Sn(2\text{-}C_6H_4N}$=NPh)$Br_3$] (II). To a solution of I (80 mg, 0.19 mmol) in acetone (15 cm^3) was added a suspension of NaBr (121.6 mg, 1.18 mmol) in acetone (5 cm^3). After 24 h the solvent was evaporated, the residue shaken with dichloromethane (10 cm^3), and the suspension filtered. The filtrate was concentrated (to 1 cm^3) and n-hexane (5 cm^3) added to precipitate a yellow-orange solid, which was recrystallized from dichloromethane/n-hexane to give II. Yield: 62%, m.p.: 165°C, Λ_M: 0 Ω^{-1} cm^2 mol^{-1} (4.9×10^{-4} M acetone). Mass spectrum: m/z 540 (M^+, 1.6%); 467,

465–455, 453 ($M^+ -$ Br, 269%); 301, 299 ($M^+ -$ 3Br, 3.4%); 205, 203, 201–195, 193 ($SnBr^+$, 167%); 120–116 (Sn^+, 16%); 105 (PhN_2^+, 31.5%); 77 (Ph^+, 100%). Anal: Found: C, 27.10; H, 1.82; N, 4.95. $C_{12}H_9N_2Br_3Sn$ calcd.: C, 26.70; H, 1.68; N, 5.19%.

$[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2]$ (III). To a solution of I (180 mg, 0.44 mmol) in acetone (10 cm^3) was added solid $[HgPh_2]$ (157.2 mg, 0.44 mmol). The suspension was refluxed for 5 h, the solvent evaporated, the residue shaken with diethyl ether (10 cm^3), and the suspension filtered. The filtrate was concentrated (to 0.5 cm^3) and n-hexane (2 cm^3) added to precipitate a yellow-orange solid, which was washed with n-hexane (2 cm^3) to give III [2b] (83% yield). Mass spectrum: m/z 450, 448, 446 (M^+, 1.1%); 413, 411 ($M^+ -$ Cl, 0.7%); 375, 373–367 ($M^+ -$ Ph, 8%); 336, 334 ($M^+ -$ Ph $-$ Cl, 0.5%); 120–116 (Sn^+, 8%); 105 (PhN_2^+, 22%); 77 (Ph^+, 100%).

$[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl_2(phen)]$ (IV). To a solution of III (100 mg, 0.22 mmol) in diethyl ether (3 cm^3) was added solid 1,10-phenanthroline $\cdot$ H_2O (44.3 mg, 0.22 mmol). After 24 h stirring the suspended orange solid, IV, was filtered off. Yield: 75%, m.p.: 104°C, Λ_M: 4 Ω^{-1} cm^2 mol^{-1} (4.46×10^{-4} M acetone). Mass spectrum: m/z 454, 452–444 ($M^+ -$ phen, 6%); 420–408, 406, 405 ($M^+ -$ phen $-$ Cl, 6%); 377–365, 363 ($M^+ -$ phen $-$ Ph, 26%); 341–332 ($M^+ -$ phen $-$ Ph $-$ Cl, 3.2%); 179–181 ($phen^+$ 151%); 105 (PhN_2^+, 28%); 77 (Ph^+, 76%). Anal: Found: C, 56.53; H, 3.79; N, 9.15. $C_{30}H_{22}N_4Cl_2Sn$ calcd.: C, 57.37; H, 3.53; N, 8.92%.

$[Sn(2\text{-}C_6H_4N{=}NPh)(Ph)Cl(phen)][BPh_4]$ (V). To an acetone suspension (10 cm^3) of IV (100 mg 0.16 mmol) was added solid $Na[BPh_4]$ (163 mg, 0.48 mmol). The mixture was stirred at room temperature for 24 h and the resulting solution then concentrated to dryness, the residue treated with dichloromethane (10 cm^3), and the suspension filtered. The filtrate was concentrated (to 1 cm^3) and diethyl ether (10 cm^3) added to precipitate V, which was recrystallized from dichloromethane/diethyl ether (1/15). V can also be obtained by a one-pot synthesis involving 24 h reaction in acetone of III, 1,10-phenanthroline $\cdot$ H_2O, and $Na[BPh_4]$ in molar ratio 1/1/3. Yield: 75%, m.p.: 119°C, Λ_M: 91 Ω^{-1} cm^2 mol^{-1} (4.46×10^{-4} M acetone). Anal: Found: C, 71.50; H, 5.18; N, 6.82. $C_{54}H_{42}N_4BClSn$ calcd.: C, 71.12; H, 4.64; N, 6.14%.

$[Sn(2\text{-}C_6H_4N{=}NPh)_2Br_2]$ (VI). To a suspension of $[Sn(2\text{-}C_6H_4N{=}NPh)_2Cl_2]$ (60 mg, 0.11 mmol) in acetone (15 cm^3) was added a suspension of NaBr (67.2 mg, 0.65 mmol) in acetone (5 cm^3). After 17 h the solvent was evaporated and the residue shaken with dichloromethane (10 cm^3). The suspension was filtered and the filtrate was concentrated (to 1 cm^3); n-hexane (20 cm^3) was added to precipitate a yellow-orange solid, which was recrystallized from dichloromethane/n-hexane to give VI. Yield: 67%, m.p.: 205–208°C, Λ_M: 0 Ω^{-1} cm^2 mol^{-1} (5×10^{-4} M, acetone). Mass spectrum: m/z 565–557 ($M^+ -$ Br, 71%); 203–195 ($SnBr^+$, 68%); 77 (Ph^+, 100%). Anal: Found: C, 45.20; H, 3.11; N, 9.05. $C_{24}H_{18}N_4SnBr_2$ calcd.: C, 45.12; H, 2.52; N, 8.77%.

$[Sn(2\text{-}C_6H_4N{=}NPh)_2(NCS)_2]$ (VII). To a suspension of $[Sn(2\text{-}C_6H_4N{=}NPh)_2Cl_2]$ (76 mg, 0.14 mmol) in acetone (15 cm^3) was added a solution of KSCN (80.26 mg, 0.82 mmol) in acetone (5 cm^3). The resulting suspension was stirred for 1 h, the solvent was evaporated, the residue shaken with dichloromethane (10 cm^3), and the suspension filtered.The filtrate was concentrated (to 1 cm^3) and n-hexane (20 cm^3) added to precipitate a yellow solid, which was recrystallized from dichloromethane/n-hexane to give VII. Yield: 66%, m.p.: 230°C, Λ_M:0 Ω^{-1} cm^2 mol^{-1} (4.2×10^{-4}

M acetone). Mass spectrum: m/z 542–536 M^+ – NCS, 90%); 77 (Ph^+, 100%). Anal: Found: C, 52.30; H, 2.81; N, 13.50. $C_{26}H_{18}N_6S_2Sn$ calcd.: C, 52.59; H, 3.02; N, 14.07%.

$[Sn(2\text{-}C_6H_4N{=}NPh)_2(py)_2](ClO_4)_2$ (VIII). To a suspension of $[Sn(2\text{-}C_6H_4\text{-}N{=}NPh)_2Cl_2]$ (80 mg, 0.14 mmol) in acetone (15 cm^3) was added an acetone (5 cm^3) solution of $AgClO_4$ (60 mg, 0.29 mmol). The resulting suspension was stirred for 10 min then filtered and pyridine (0.15 cm^3) was added to the filtrate. (All the preceding steps were carried out under N_2). After 15 min the solvent was evaporated (to 1 cm^3) and n-hexane (5 cm^3) added to precipitate a yellow-orange solid, which was washed repeatedly with n-hexane and recrystallized from dichloromethane/diethyl ether to give VIII. Yield: 92%, m.p.: 236 °C, Λ_M: 150 Ω^{-1} cm^2 mol^{-1} (5×10^{-4} *M* acetone). Anal: Found: C, 49.63; H, 3.88; N, 10.11. $C_{34}H_{28}N_6Cl_2O_8Sn$ calcd.: C, 48.79; H, 3.35; N, 10.04%.

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