ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2022, Vol. 48, No. 7, pp. 412–421. © Pleiades Publishing, Ltd., 2022.
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The authors congratulate Academician V.I. Ovcharenko on the occasion of his 70th jubilee

Tin Amides Based on Ligands of the Acenaphthene Imine Series

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Received December 27, 2021; revised January 25, 2022; accepted January 31, 2022

Abstract—The reaction of Dpp-Bian (Dpp-Bian is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with one equivalent of iodine and an excess of metallic tin affords paramagnetic complex [(Dpp-Bian)$^{1-}$SnI] (**I**). The reaction of this complex with one equivalent of *n*-butyllithium or lithium *tert*-butylate affords [(Dpp-Bian)$^{1-}$SnBu] (**II**) or [(Dpp-Bian)$^{1-}$SnO*t*Bu] (**III**), respectively, that rapidly decompose to form stannylene [(Dpp-Bian)$^{2-}$Sn] (**IV**). Stannylene **IV** exhibits reduction properties toward Dpp-Mian (Dpp-Mian is 2-mono[(2,6-diisopropylphenyl)imino]acenaphthen-1-one) with the formation of tin(IV) complex [{bis(Dpp-Mian)}$_2$Sn] (**V**). The reduction of the diimine ligand with more acceptor substituents CF$_3$-Bian (CF$_3$-Bian is 1,2-bis[(3,5-trifluoromethylphenyl)imino]acenaphthene), unlike Dpp-Bian, can occur directly with metallic tin resulting in [(CF$_3$-Bian)$_2^{2-}$(CF$_3$-Bian)$^{2-}$Sn] (**VII**). New compounds are characterized by IR, NMR, and EPR spectroscopy and elemental analysis. The molecular structures of complexes **I** and **VII** are determined by X-ray diffraction (CIF files CCDC nos. 2130839 (**I**) and 2130840 (**VII**)).

Keywords: tin, stannylenes, redox-active ligands, acenaphthene-1,2-diimines, molecular structure
DOI: 10.1134/S107032842207003X

INTRODUCTION

Considerable progress occurred in the chemistry of nontransition elements in the recent decade [1–3]. The progress is mainly related to achievements of the chemistry of nontransition elements in low-valent states [4, 5]. The ability of the low-valent derivatives of the main subgroups to the activation of small molecules [6–8], oxidative addition/reductive elimination [9, 10], and reversible addition [11] was discovered, although up to recently the latter was considered impossible for the main subgroup elements. These features of the reactivity of complexes of low-valent elements of the main subgroups are similar to those of transition metal complexes, which provides routes for the replacement of the precious metal derivatives used in industry by more available derivatives of the main subgroup elements.

One of the low-valent states, viz., divalent, is relatively stable for the group 14 elements. The low-valent derivatives of group 14 exhibit an unusual reactivity, which is not characteristic of the main group elements and resembles that of transition metals. Distannyne ArSn≡SnAr [12], digermyne ArGe≡GeAr [13, 14], diplumbyne ArPb≡PbAr [15], (Ar is terphenyl), stable diazadisilicacyclobutane biradicaloid [16], and low-valent hydrides of the group 14 elements are unusual derivatives assigned to the group of low-valent derivatives of group 14. All these compounds can activate H_2 [17–20], NH_3 [21, 22], PH_3, AsH_3 [23, 24], S_8 [25], olefins [26], alkynes [27], and P_4 [28] under mild conditions. The low-valent group 14 hydrides are capable of activating heteroallenes (CO_2, CS_2, RNCO) [29, 30] and catalyzing [31].

One of the approaches of controlling the reactivity of low-valent atoms of the main subgroup elements is the use of redox-active bulky ligands, for example, 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (Dpp-Bian). The metallacycloadditions of iso(thio)cyanates to the gallium [32, 33] and aluminum derivatives [34] of Dpp-Bian were discovered. Numerous activation reactions of CO_2 [35], SO_2 [36], carbodiimides [37], and other organic substrates [38–41] were carried out. It is important that the substrates in the activated state can be involved in further transformations [35]. Another feature of the Dpp-Bian ligand is its ability to store electrons and transfer them back to the metal when necessary [42, 43]. The first solvate-induced electron transfer [44] and ligand-maintained two-electron oxidative addition on the nontransition metal

[45] were thus performed. These peculiarities made it possible to produce the efficient catalysts for the hydroamination of alkenes [46, 47] and polymerization of cyclic esters [48, 49] with characteristics exceeding those of analogous transition metal complexes.

The purpose of this work is to synthesize low-valent tin derivatives based on Dpp-Bian and CF_3-Bian.

EXPERIMENTAL

The synthesized compounds are sensitive to air oxygen and moisture and, hence, all manipulations on the synthesis, isolation, and identification were carried out in vacuo using the Schlenk technique. Solvents were dehydrated using known procedures and sampled by condensation in vacuo prior to use [50].

IR spectra were recorded on an FSM-1201 spectrometer for suspensions of the compounds in Nujol. EPR spectra were detected on a Bruker ER 200 D-SRC spectrometer equipped with an ER 4105 DR double resonator (working frequency 9.5 GHz) and an ER 4111 VT thermal controller. Diphenylpicrylhydrazyl (DPPH, $g = 2.0037$) served as the standard for the determination of the g factor. Compounds Dpp-Bian [51], CF_3-Bian [52], and [(Dpp-Bian)SnCl] [53] were synthesized using published procedures. Other compounds were purchased from commercial sources and used as received. NMR spectra were recorded on Bruker DPX-200 (200 MHz), AvanceNEO300 (300 MHz), or Advance III (400 MHz) spectrometers. Elemental analyses to C, H, and N were carried out on an Elementar Vario Micro Cube instrument. The computer simulation of EPR spectra and calculation of hyperfine coupling constants were performed using the WinEPR Simfonia and EasySpin software [54].

Synthesis of [(Dpp-Bian)SnI] (I). A suspension of Dpp-Bian (0.5 g, 1.0 mmol) in ether (25 mL) was poured into an ampule with I_2 (0.13 g, 0.5 mmol) and metallic tin excess (5 g). The mixture was stirred at room temperature until Dpp-Bian was dissolved to form a red-brown solution. The formed solution of complex **I** was filtered, and the solvent was removed. The yield of the dry product was 0.634 g (85%).

IR (ν, cm^{-1}): 3065 w, 1671 w, 1591 w, 1531 vs, 1479 w, 1447 s, 1426 w, 1362 m, 1319 s, 1255 m, 1187 m, 1144 w, 1113 w, 1084 w, 1055 w, 1042 w, 934 w, 926 w, 861 m, 835 w, 821 s, 804 s, 787 m, 771 s, 762 s, 752 m, 697 w, 670 w, 544 w. EPR (toluene, 293 K): $g = 1.99898$; $A(^{119}Sn) = 13.508$, $A(^{117}Sn) = 12.911$, $A(^{127}I) = 3.144$, $A(2 \times {}^{14}N) = 0.573$, $A(2 \times {}^{1}H) = 0.422$, $A(2 \times {}^{1}H) = 0.222$ mT.

For $C_{36}H_{40}N_2ISn$

Anal. calcd., %	C, 57.93	H, 5.40	N, 3.75
Found, %	C, 57.55	H, 5.32	N, 3.72

Synthesis of [(Dpp-Bian)Sn] (IV). A solution of complex [(Dpp-Bian)SnCl] in diethyl ether (prepared from 0.5 g of Dpp-Bian) was separated from metallic tin and cooled to –78°C. A solution of *n*BuLi (1.6 mL, 1.05 mmol) in hexane (0.66 mol/L) was added with stirring, after which the mixture was heated to room temperature. The color of the solution changed from red-brown to violet, and a colorless precipitate was formed. The resulting suspension was centrifuged to separate LiCl and by-products, such as Dpp-Bian and metallic tin. The solution was concentrated to form fine dark crystals. The yield of product **IV** was 0.36 g (58%).

IR (ν, cm^{-1}): 3061 m, 3034 w, 1917 w, 1858 w, 1797 w, 1669 m, 1611 s, 1597 s, 1439 m, 1420 m, 1391 s, 1364 m, 1323 s, 1252 s, 1212 m, 1186 m, 1177 w, 1108 m, 1076 m, 1057 m, 1036 m, 934 s, 878 w, 833 w, 816 s, 804 s, 795 m, 780 w, 764 vs, 670 m, 642 w, 619 m, 594 w, 547 m. ^1H NMR (400 MHz; C_6D_6; 297 K; δ, ppm): 7.31 (s, 6H, arom.) 7.13 (d, 2H, CH naphth., $J = 8.3$ Hz), 6.85 (dd, 2H, CH naphth., $J = 8.3$ Hz, $J = 7.0$ Hz), 6.38 (d, 2H, CH naphth., $J = 7.0$ Hz), 3.50 (pseudosept, 4H, $4 \times C\underline{H}(CH_3)_2$, $J = 6.8$ Hz, $J = 7.0$ Hz), 1.27 (d, 12H, $4 \times CH(C\underline{H}_3)(CH_3)$, $J = 6.8$ Hz), 1.05 (d, 12H, $4 \times CH(CH_3)(C\underline{H}_3)$, $J = 7.0$ Hz). ^{119}Sn NMR (74.63 MHz; C_6D_6; 297 K; δ, ppm): 360.0.

For $C_{36}H_{40}IN_2Sn$

Anal. calcd., %	C, 57.93	H, 5.40	N, 3.75
Found, %	C, 57.55	H, 5.32	N, 3.72

Reaction of complex [(Dpp-Bian)SnCl] with *n*BuLi. Compound [(Dpp-Bian)SnCl] (60 mg, 0.092 mmol) was placed in an EPR tube. The sample was cooled to the temperature of liquid nitrogen (195°C), and Et_2O (1 mL) and then a 0.22 M solution of *n*BuLi (0.42 mL) in *n*-hexane were added. Thawing out of the tube was carried out in the resonator of the EPR spectrometer. As a result, the signal of complex **II** was detected at room temperature 5–10 min after thawing out and gradually (within a day) transformed into the signal of the starting [(Dpp-Bian)SnCl].

EPR (293 K, Et_2O): $g = 1.99893$; $A(^{119}Sn) = 8.160$, $A(^{117}Sn) = 7.800$, $A(2 \times {}^{14}N) = 0.547$, $A(2 \times {}^{1}H) = 0.151$, $A(2 \times {}^{1}H) = 0.096$, $A(2 \times {}^{1}H) = 0.028$ mT.

Reaction of complex [(Dpp-Bian)SnCl] with *t*BuOLi. Compound [(Dpp-Bian)SnCl] (50 mg, 0.076 mmol) and *t*BuOLi (6 mg) were placed in an EPR tube. Then the sample was cooled to the temperature of liquid nitrogen (195°C), and toluene (1 mL) was added. Thawing out of the tube was carried out in the resonator of the EPR spectrometer. As a result, the signal of complex **III** was detected at room temperature in 15–20 min after thawing out and gradually disappeared within a day.

EPR (293 K, toluene): $g = 1.99941$; $A(^{119}\mathrm{Sn}) = 10.500$, $A(^{117}\mathrm{Sn}) = 10.036$, $A(2 \times {}^{14}\mathrm{N}) = 0.503$, $A(2 \times {}^{1}\mathrm{H}) = 0.118$, $A(2 \times {}^{1}\mathrm{H}) = 0.083$, $A(2 \times {}^{1}\mathrm{H}) = 0.017$ mT.

Synthesis of [(bis(Dpp-Mian))$_2$Sn] (V). A solution of Dpp-Mian (0.08 g, 0.23 mmol) in toluene (2 mL) was added to a solution of [(Dpp-Bian)Sn] (0.148 g, 0.23 mmol) in toluene (2 mL). A yellow crystalline precipitate was formed and filtered off in 2 h. The NMR spectrum of the precipitate coincides with the NMR spectrum of Dpp-Bian [55]. Volatiles were removed in vacuo. The residue was dissolved in diethyl ether (10 mL). A yellow crystalline precipitate was formed from the obtained solution in a day at room temperature. The yield of compound **V** was 0.051 g (60%). According to the NMR data, compound [(bis(Dpp-Mian))$_2$Sn] [56] contains a Dpp-Bian impurity. According to the X-ray diffraction (XRD) data, the unit cell parameters coincide with the data for complex [(bis(Dpp-Mian))$_2$Sn] [56].

Synthesis of [(CF$_3$-Bian)$_2$Sn] (VI). A solution of CF$_3$-Bian (0.6 g, 1.0 mmol) in tetrahydrofuran (THF) (25 mL) was poured into an ampule with metallic tin excess (5 g). The formed mixture was stirred at room temperature for 5 days. The color of the solution changed from red-orange to bright blue. The formed solution of the complex was decanted from metallic tin excess, and the solvent was removed. The yield of the dry product was 0.65 g (98%).

IR (ν, cm^{-1}): 3056 w, 1912 w, 1758 vs, 1655 s, 1613 m, 1588 s, 1507 vs, 1429 m, 1341 s, 1259 s, 1210 w, 1190 w, 1175 m, 1150 m, 1092 s, 1057 s, 999 m, 962 w, 924 s, 873 s, 833 m, 804 s, 760 s, 744 m, 723 m, 699 m, 658 w, 619 s.

^{1}H NMR (200 MHz; THF-d$_8$; 297 K; δ, ppm): 7.69 (s, 4H, 2 × *o*-C$_6$H$_3$) 7.41 (d, 2H, CH naphth., J = 8.1 Hz), 7.33 (s, 2H, 2 × *m*-C$_6$H$_3$) 7.17 (dd, 2H, CH naphth., J = 8.1 Hz, J = 6.9 Hz), 7.01 (d, 2H, CH naphth., J = 6.9 Hz). ^{119}Sn NMR (74.63 MHz; THF-d$_8$; 24°C; δ, ppm): –103.59. ^{19}F NMR (376.54 MHz; THF-d$_8$; 297 K; δ, ppm): –63.97.

For $C_{56}H_{24}F_{24}N_4Sn$

Anal. calcd., %	C, 50.67	H, 1.82	N, 4.22
Found, %	C, 50.90	H, 1.99	N, 4.12

Synthesis of [(CF$_3$-Bian)$_3$Sn] (VII). Half an equivalent of CF$_3$-Bian (0.3 g, 0.5 mmol) was added to a solution of complex **VI** prepared from CF$_3$-Bian (0.6 g, 1.0 mmol) in THF. Then THF was replaced by toluene. As a result, a violet solution of complex [(CF$_3$-Bian)$_3$Sn] was formed and reversibly turned blue on cooling. After concentrating the toluene solution, the complex crystallized as orange crystals. The yield of the crystalline product was 0.73 g (69%) based on the amount of the ligand involved in the reaction.

IR (ν, cm^{-1}): 3066 w, 3044 w, 2726 w, 1815 w, 1676 w, 1651 w, 1605 m, 1593 m, 1530 s, 1438 m, 1425 m, 1408, 1373 s, 1300 w, 1276 vs, 1248 w, 1175 s, 1148 s, 1138 vs, 1105 m, 1077 w, 1042 w, 1013 m, 984 m, 957 w, 932 m, 911 m, 901 m, 893 m, 884 w, 858 m, 847 m, 832 w, 822 m, 766 s, 727 s, 706 m, 683 s.

For $C_{98}H_{52}N_6F_{36}Sn$

Anal. calcd., %	C, 55.62	H, 2.48	N, 3.97
Found, %	C, 55.21	H, 2.50	N, 4.01

XRD of compounds **I** and **VII** was carried out on a Bruker AXS SMART APEX automated diffractometer (graphite monochromator, MoK_α radiation, φ and ω scan modes, λ = 0.71073 Å). Experimental sets of intensities were integrated using the SAINT program [57]. Absorption corrections were applied using the SADABS program [58]. Both structures were solved by the "dual-space" method using the SHELXT program [59]. All non-hydrogen atoms in compounds **I** and **VII** were refined by full-matrix least squares for F^2_{hkl} in the anisotropic approximation using the SHELXTL software [60]. Hydrogen atoms were placed in geometrically calculated positions and refined by the riding model ($U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{equiv}}(\mathrm{C})$ for CH$_3$ groups and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{equiv}}(\mathrm{C})$ for other groups). Two toluene molecules disordered over two positions fall onto each molecule of the complex in the crystal of compound **VII**. The fluorine atoms of two CF$_3$ groups in complex **VII** are disordered over three positions, and those of two other CF$_3$ groups are disordered over two positions. The DFIX and ISOR instructions were applied when refining disordered fragments to obtain adequate geometric and thermal characteristics. Selected crystallographic characteristics and XRD experimental parameters for compounds **I** and **VII** are given in Table 1.

The additional structural results were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2130839 (**I**) and 2130840 (**VII**); deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

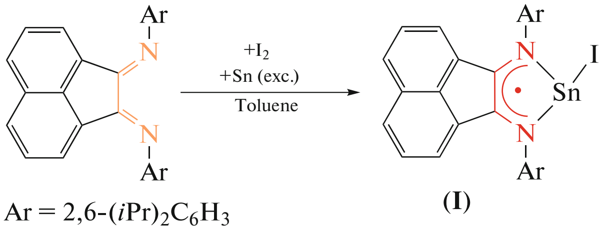
RESULTS AND DISCUSSION

In 2006 we found that Dpp-Bian can be reduced by metallic aluminum to the radical anion (in toluene) or dianion (in Et$_2$O) in the presence of aluminum halides [61]. In this work, we attempted to reduce Dpp-Bian with metallic tin. It is found that tin does not reduce Dpp-Bian in aromatic and aliphatic solvents, THF, 1,2-dimethoxyethane, or Et$_2$O. However, the addition of half an equivalent of iodine to a suspension of Dpp-Bian in a medium of toluene, benzene, or Et$_2$O gives a mixture of products. The treatment of the mixture with tin excess affords complex **I** in a high yield (Scheme 1).

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I** and **VII**

Parameter	Value	
	I	**VII**
Empirical formula*	$C_{36}H_{40}N_2ISn$	$C_{98}H_{52}N_6F_{36}Sn$
FW	746.29	2116.14
Temperature, K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Cell parameters:		
a, Å	10.5124(5)	28.901(3)
b, Å	15.7287(7)	13.4159(13)
c, Å	20.0481(9)	22.687(2)
α, deg	90	90
β, deg	97.1150(10)	101.881(4)
γ, deg	90	90
V, Å^3	3289.4(3)	8607.8(15)
Z	4	4
ρ_{calc}, mg/cm^3	1.507	1.633
μ, mm^{-1}	1.741	0.429
Crystal size, mm	0.96 × 0.67 × 0.40	0.52 × 0.35 × 0.17
$F(000)$	1492	4224
θ, deg	1.952–28.999	1.680–29.999
Number of reflections collected/independent	34329/8725	46099/12302
R_{int}	0.0179	0.0416
R_1, wR_2 ($I > 2\sigma(I)$)	0.0220, 0.0582	0.0440, 0.1013
R_1, wR_2 (for all data)	0.0242, 0.0591	0.0605, 0.1075
S	1.042	1.070
Residual electron density (max/min), e/Å^3	1.117/–0.776	1.165/–0.405

* The empirical formula for compound **VII** was calculated taking into account solvate molecules of the solvent.



Scheme 1.

Compound **I** is paramagnetic, and its EPR spectrum and computer model are shown in Fig. 1. Paramagnetism is caused by the localization of an unpaired electron on the conjugated Dpp-Bian system of complex **I**. Therefore, the main contribution to the hyperfine structure is made by interactions of the unpaired electron with the tin atom, iodine atom, two nitrogen atoms of the diimine moiety, and two pairs of protons of the naphthalene system of the Dpp-Bian ligand.

According to the XRD data, the tin atom in complex **I** is bound to the Bian ligand coordinated via the bidentate mode and iodide anion (Fig. 2). The bond lengths in the NCCN fragment (Table 2) indicate the radical-anion form of the Bian ligand. The Sn–N bonds in complex **I** (2.192(2) and 2.205(2) Å) are somewhat longer than those in the related iodine derivative of tin(II) with a less sterically hindered NCCN ligand (2.145(6)–2.154(5) Å) [62]. The five-membered metallocycle SnNCCN insignificantly deviates from the plane. The dihedral angle between the Sn(1)N(1)N(2) and N(1)C(1)C(2)N(2) planes is 5.24°. The Sn(1)–I(1) bond in complex **I** with the

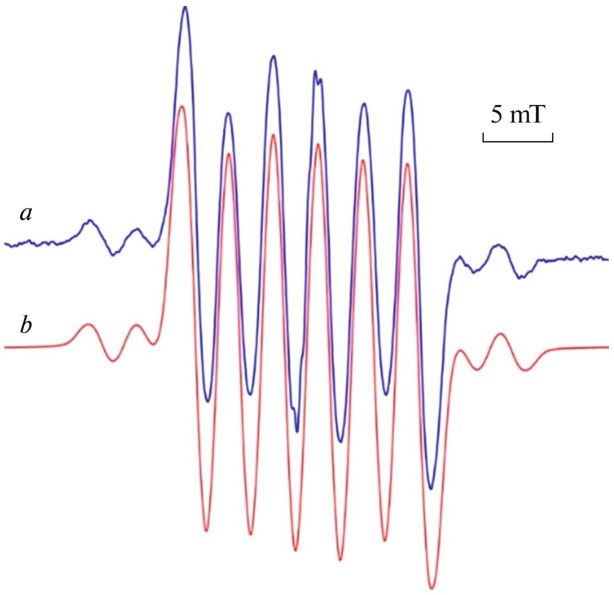


Fig. 1. (*a*) Experimental and (*b*) simulated EPR spectra of complex **I** in toluene at 293 K ($g = 1.99898$; $A(^{119}Sn) = 13.508$, $A(^{117}Sn) = 12.911$, $A(^{127}I) = 3.144$, $A(2 \times {}^{14}N) = 0.573$, $A(2 \times {}^{1}H) = 0.422$, $A(2 \times {}^{1}H) = 0.222$ mT).

plane of the acenaphthene diimine ligand forms an angle of 103.98°. This geometry is characteristic of the related complexes of the group 14 metals [62–64].

In 2005 we showed that the magnesium complex [(Dpp-Bian)Mg-*i*Pr(Et_2O)] was able to reductively eliminate isopropyl radical [65]. When diethyl ether (solvent) is replaced by THF, the isopropyl radical is eliminated from magnesium, and the magnesium atom remains bound to the Dpp-Bian ligand. The latter, in turn, undergoes transition from the radical anion to dianion.

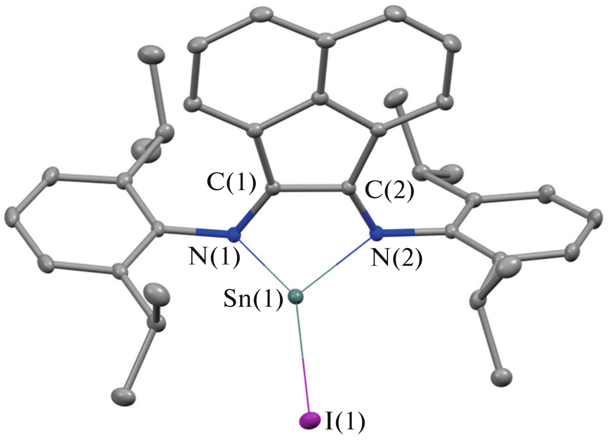
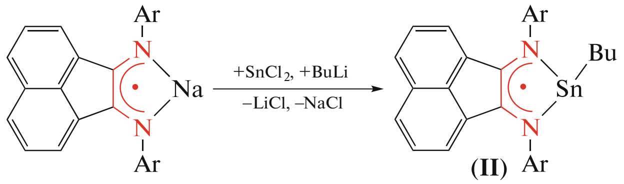


Fig. 2. Molecular structure of complex **I**. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted for clarity.

We proposed a resembling mechanism for the formation of complex **IV** under the treatment of complexes [(Dpp-Bian)SnCl] [53] and **I** with nucleophiles. To confirm this assumption, it was necessary to detect spectrally the formation of intermediates with the radical-anion ligand Dpp-Bian. For this purpose, the reaction of complex [(Dpp-Bian)SnCl] with *n*BuLi and LiO*t*Bu was carried out in the resonator of the EPR spectrometer. As a result, we detected the corresponding signals of paramagnetic compounds **II** and **III** (Figs. 3 and 4).

We failed to detect a signal from complex **II** formed by the reaction of monosodium salt [(Dpp-Bian)Na] [66] with the reaction mixture consisting of $SnCl_2$(dioxane) (1 equiv) and *n*BuLi (1 equiv) (Scheme 2).



Ar = 2,6-(iPr)$_2C_6H_3$

Scheme 2.

The NMR studies of these reactions show that stannylene **IV** is formed immediately after mixing of

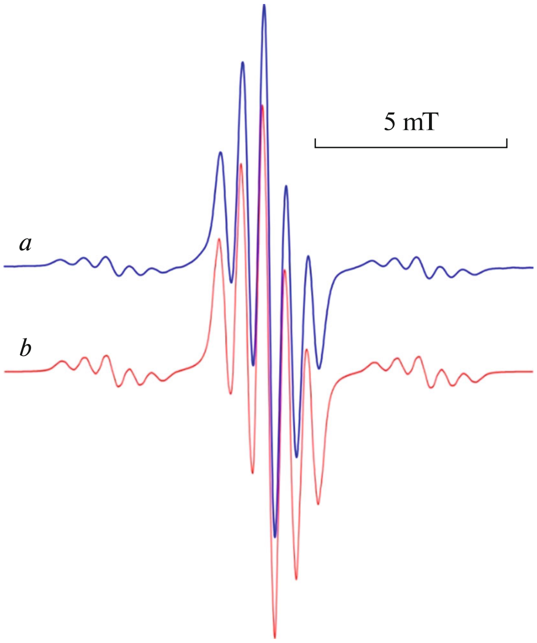


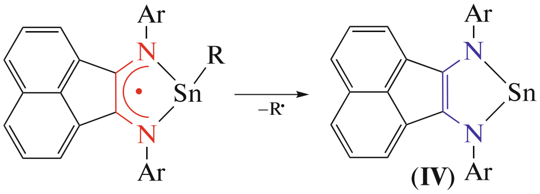
Fig. 3. (*a*) Experimental and (*b*) simulated EPR spectra of complex **II** in Et_2O at 293 K ($g = 1.99893$; $A(^{119}Sn) = 8.160$, $A(^{117}Sn) = 7.800$, $A(2 \times {}^{14}N) = 0.547$, $A(2 \times {}^{1}H) = 0.151$, $A(2 \times {}^{1}H) = 0.096$, $A(2 \times {}^{1}H) = 0.028$ mT).

Table 2. Selected bond lengths (Å) and angles (deg) in compounds **I** and **VII**

Bond	**I**	**VII**
	d, Å	
Sn(1)–N(1)	2.192(2)	2.175(2)
Sn(1)–N(2)	2.205(2)	2.197(2)
Sn(1)–N(3)		2.105(2)
Sn(1)–I(1)	2.823(1)	
N(1)–C(1)	1.331(2)	1.333(2)
N(2)–C(2)	1.329(2)	1.341(2)
N(3)–C(29)		1.396(2)
C(1)–C(2)	1.439(2)	1.445(2)
C(29)–C(29A)*		1.379(3)
Angle	ω, deg	
N(1)Sn(1)N(2)	76.65(5)	76.95(6)
N(1)Sn(1)I(1)	97.57(3)	
N(2)Sn(1)I(1)	97.01(3)	
N(1)Sn(1)N(3)		92.47(6)
N(1)Sn(1)N(1A)		163.58(8)
N(1)Sn(1)N(2A)		91.02(6)
N(1)Sn(1)N(3A)		99.98(6)
N(2)Sn(1)N(3)		96.08(6)
N(1)Sn(1)N(1A)		91.02(6)
N(1)Sn(1)N(2A)		86.54(8)
N(1)Sn(1)N(3A)		176.03(6)
N(3)Sn(1)N(3A)		81.46(8)

* Symmetry procedure used for the generation of equivalent atoms in complex **VII** (A): $-x, y, -z + 3/2$.

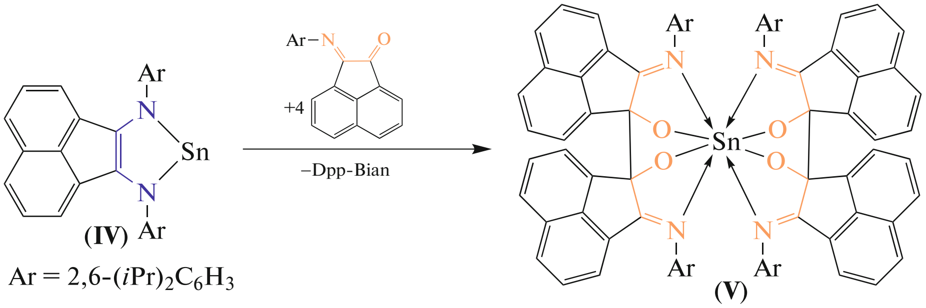
the reagents and gives a broadened signal of the formed compound, which becomes more resolved with time. A mixture of products of the reaction of the compound with *n*BuLi contains butane and octane as shown by gas chromatography coupled with mass spectrometry. Therefore, we believe that the formation of stannylene **IV** due to the reactions of complex [(Dpp-Bian)SnCl] with nucleophiles proceeds via the formation of the product of halogen exchange with the corresponding acid residue followed by elimination, which results in the reduction of the Dpp-Bian radical anion to dianion (Scheme 3).



R = Bu (**II**), O*t*Bu (**III**)
Ar = 2,6-$(i\text{Pr})_2C_6H_3$

Scheme 3.

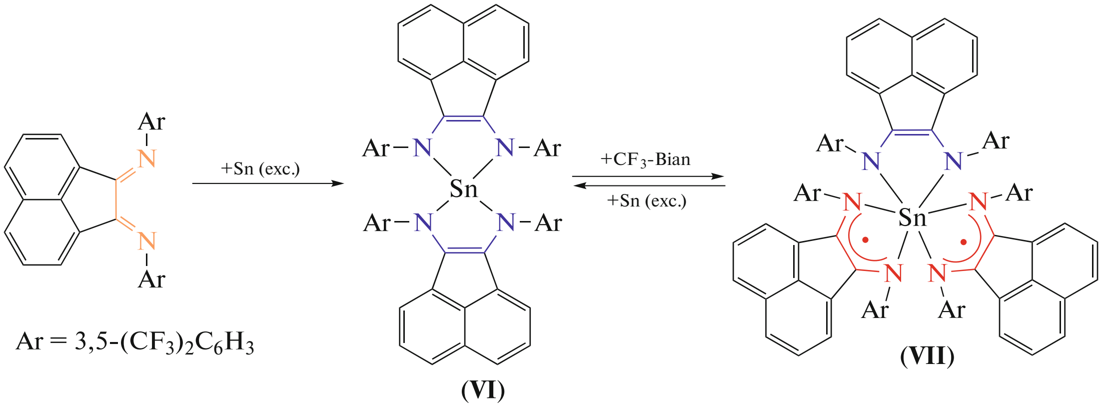
Stannylene **IV** exhibits the reduction properties toward another iminoacenaphthene: Dpp-Mian (Dpp-Mian is 2-mono[(2,6-diisopropylphenyl)imino]acenaphthen-1-one). We showed that the reaction of complex **IV** with Dpp-Mian in toluene afforded a compound, whose spectral and diffraction characteristics coincide with the data for complex **V** [56], where the tin atom is bound to two bis(Dpp-Mian) ligands formed by doubling two Dpp-Mian at the carbonyl carbon atom. The oxidation state of tin becomes equal to +4. The second reaction product is free Dpp-Bian (Scheme 4).



Scheme 4.

According to the data of cyclic voltammetry, the first reduction of CF_3-Bian occurs at a potential of −1.35 V and the second reduction takes place at −1.90 V, which are higher by 0.72 and 0.8 V, respectively, than those for Dpp-Bian (–2.07 and –2.73 V) under similar conditions (solvent THF; working electrode glassy carbon (GC); reference electrode $Ag/AgNO_3$, 0.01 M (CH_3CN); auxiliary electrode Pt; supporting salt NBu_4BF_4, 0.2 M; sweep rate 100 mV/s). Therefore, CF_3-Bian is reduced more easily than Dpp-Bian and, hence, it can be expected that ligand CF_3-Bian would be reduced by metals that do not directly reduce Dpp-Bian.

In fact, unlike Dpp-Bian, the CF_3-Bian ligand is reduced by metallic tin in a medium of coordinating solvents, such as dimethoxyethane or THF. The reaction occurs at room temperature and subsequently affords two products: tris(ligand) complex **VII** is formed at the first stage, and then bis(ligand) **VI** is formed (Scheme 5). Tris(ligand) complex **VII** can be prepared due to the reaction of bis(ligand) complex **VI** with one equivalent of CF_3-Bian. According to the data of IR spectroscopy, the spectrum of complex **VII** exhibits intense bands at 1605 and 1593 cm^{-1} assigned to stretching vibrations of the sesquialteral and ordinary CN bonds, respectively.



Scheme 5.

Unlike complex **I**, the tin atom in complex **VII** is surrounded by three Bian ligands (Fig. 5). The independent part of the unit cell contains only half a molecule (twofold symmetry axis passes through the Sn(1) atom and the middle of the C(29)–C(29A) bond). Thus, the coordination number of the tin atom in complex **VII** is six, and the coordination polyhedron is a distorted octahedron. The bond length distribution in two ligands (N(1)C(1)C(2)N(2) and N(1A)C(1A)C(2A)N(2A)) corresponds to the radical-anion form of the Bian ligand, and the bond lengths are well consistent with those in complex **I** (Table 2). In turn, the C–N bond elongation with the simultaneous C–C bond shortening is observed in the N(3)C(29)C(29A)N(3A) fragment, indicating the dianionic form of this ligand [67]. The oxidation state of tin(IV) is well consistent with the Sn(1)–N(1) and Sn(1)–N(2) bond length shortening in compound **VII** compared to complex **I**. The five-membered metallocycles in complex **VII** are nearly planar. The maximum deviation of the atoms from the corresponding planes does not exceed 0.019 Å for all the three ligands.

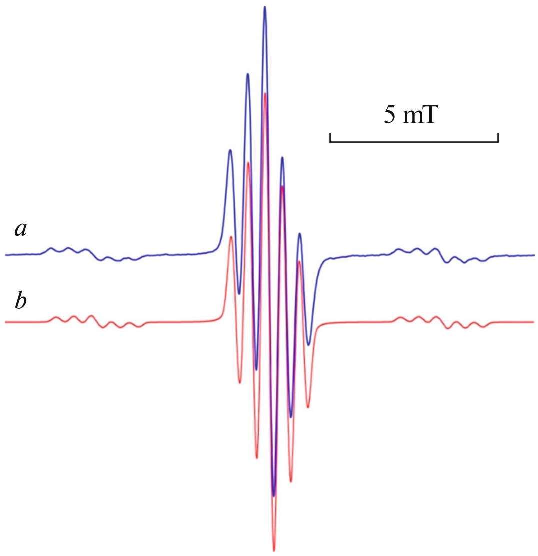


Fig. 4. (*a*) Experimental and (*b*) simulated EPR spectra of complex **III** in toluene at 293 K ($g = 1.99941$; $A(^{119}\mathrm{Sn}) = 10.500$, $A(^{117}\mathrm{Sn}) = 10.036$, $A(2 \times {}^{14}\mathrm{N}) = 0.503$, $A(2 \times {}^{1}\mathrm{H}) = 0.118$, $A(2 \times {}^{1}\mathrm{H}) = 0.083$, $A(2 \times {}^{1}\mathrm{H}) = 0.017$ mT).

The dihedral angles between the Sn(1)N(1)N(2) and N(1)C(1)C(2)N(2) and Sn(1)N(3)N(3A) and N(3)C(29)C(29A)N(3A) planes are 0.37° and 1.10°, respectively. The planes of the acenaphthene diimine fragments are arranged relative to each other at an angle of 81.42° (ligands N(1)N(2) and N(1A)N(2A)) and 86.53° (ligands N(1)N(2) and N(3)N(3A)).

FUNDING

This work was supported by the Russian Science Foundation (project no. 21-73-20153, the synthesis of the complexes based on Dpp-Bian) and Russian Foundation for Basic Research (project no. 20-03-00659, the synthesis of the complexes based on CF_3-Bian and the reaction of complex **IV** with Dpp-Mian) using the equipment of the Center for Collective Use "Analytical Center of the Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences" supported by the grant "Provision of Development of Material Technical Infrastructure of Centers for Collective Use of Scientific Equipment" (unique identifier RF-2296.61321X0017).

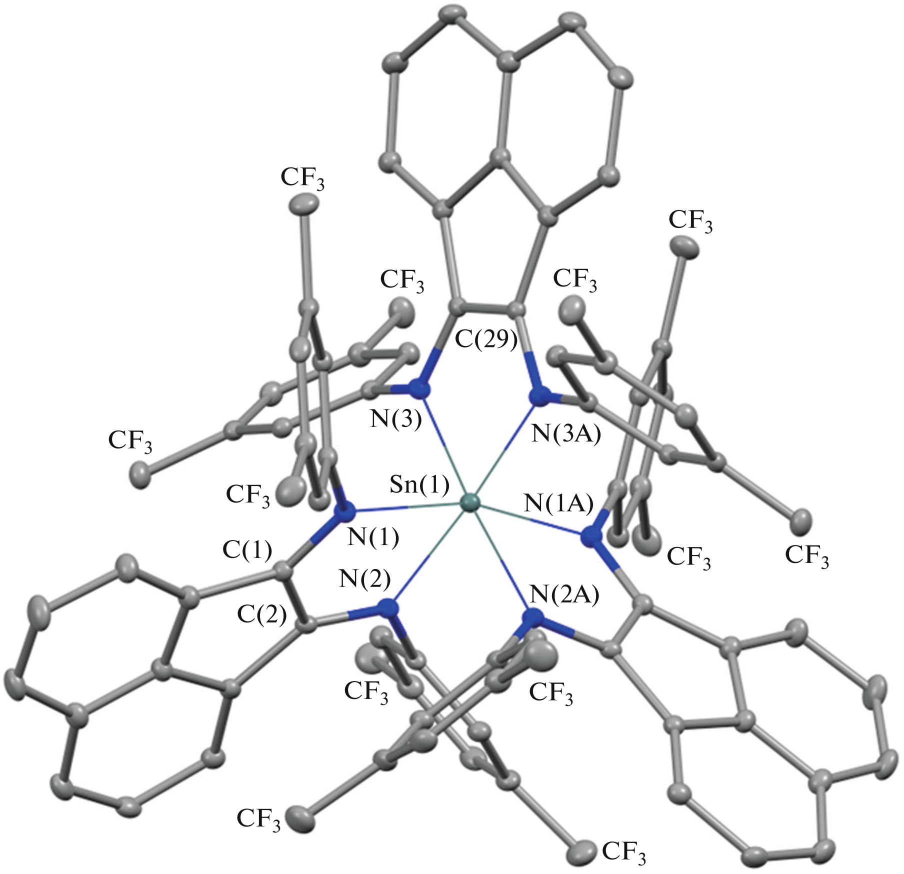


Fig. 5. Molecular structure of complex **VII**. Thermal ellipsoids are given with 30% probability. Hydrogen atoms are omitted, and CF_3 groups are presented by one carbon atom for clarity.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Yablonskaya