

Communication

New paramagnetic *N*-heterocyclic stannylenes: An EPR study

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Abstract

The reactions of *N,N'*-bis[(2,6-di-*iso*-propylphenyl)-1,2,3-diazastannole-2-ylidene] with some radicals, mercury(II) or silver(I) halides have been investigated. The formation of new paramagnetic stannylene complexes has been shown by EPR spectroscopy.
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1. Introduction

Diazabutadiene derivatives of divalent silicon [1] and germanium [2] are well-known class of compounds which shows great potential both as reagents in synthesis of different heterocyclic derivatives and as ligands in coordination chemistry. Recently, analogous stannylene [3] complexes have been described. The new direction of investigations in this area is a search of synthetic routes to divalent species of group 14 elements containing paramagnetic ligands. The use of EPR spectroscopy for this type of compounds would give us essential information about their structure and behaviour.

The first stable paramagnetic germylene containing radical-anion 1,2-bis(arylimino)-acenaphthene ligand was obtained by Fedushkin et al. [4]. In previous work [5] *N*-heterocyclic paramagnetic stannylene derivatives were obtained in solution for the first time by the exchange reaction of tin(II) chloride with lithium radical-anion salts of diazabutadienes in THF. Recently [6], the radical addition to the substituted *N*-heterocyclic silylenes (germylenes) or single-electron oxidation of the later was found to be the most convenient method to prepare appropriate complexes

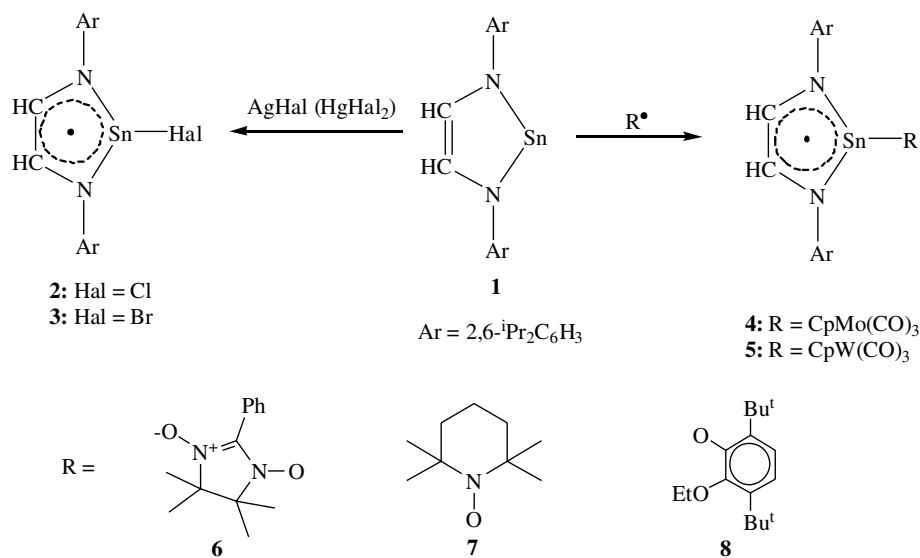
containing unpaired electron. Here we report preliminary results of EPR studies of paramagnetic stannylene species which were obtained by the reaction between stable stannylene **1** and mercury(II) (silver(I)) halides or by the interaction of **1** with free radicals from different sources (Scheme 1).

2. Results and discussion

It was found that the oxidation of *N,N'*-di-*tert*-butyl-1,2,3-diazagermole-2-ylidene with mercury(II) halides is a useful technique to obtain paramagnetic germylene derivatives for EPR investigation [6b]. In the course of the interaction of toluene solution of compound **1** with mercury(II) chloride or bromide, or with silver chloride solids, the reaction mixture turns to orange and simultaneously gives rise to EPR spectrum (Fig. 1). These spectra are well resolved at room temperature. The linewidth is about 1.5 G at 290 K. The hyperfine structure arises from hyperfine coupling (HFC) of unpaired electron to magnetic nuclei ¹H (99.98%, *I* = 1/2, $\mu_N = 2.7928$), ¹⁴N (99.63%, *I* = 1, $\mu_N = 0.4037$), ¹¹⁷Sn (7.68%, *I* = 1/2, $\mu_N = 1.000$), ¹¹⁹Sn (8.58%, *I* = 1/2, $\mu_N = 1.046$), ³⁵Cl (75.77%, *I* = 3/2, $\mu_N = 0.8218$), and ³⁷Cl (24.23%, *I* = 3/2, $\mu_N = 0.6841$) for the chloro derivative, as well as ⁷⁹Br (50.69%, *I* = 3/2, $\mu_N = 2.1064$) and ⁸¹Br (49.31%, *I* = 3/2, $\mu_N = 2.2706$) [7] for the bromo derivative. The EPR parameters are summarized in Table 1. These spectra evidence the formation of

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Scheme 1.

paramagnetic halogen-containing stannylene complexes **2** and **3** (Scheme 1). It should be noted, that spectrum of **2** is identical to that of the product obtained by the exchange reaction between tin(II) chloride and lithium radical-anionic derivative of corresponding diazabutadiene [5].

As it was found for silicon and germanium derivatives [6], tin(II) complex **1** can add some different radical species. Thus, products of the reaction of **1** with metal-centered radicals Cp(CO)₃Mo• or Cp(CO)₃W•, obtained by irradiation of corresponding dimers in the reaction mixture in tol-

uene at about 220 K, exhibit EPR spectra (Fig. 2). These spectra are due to HFC of unpaired electron to magnetic nuclei ¹H, ¹⁴N, ¹¹⁷Sn and ¹¹⁹Sn (Table 1), indicating the formation of **4** and **5** adducts (Scheme 1). In the case of **4**, HFC to ⁹⁵Mo (15.92%, *I* = 5/2, $\mu_N = 0.9133$) and ⁹⁷Mo (9.55%, *I* = 5/2, $\mu_N = 0.9335$) [7] is also observed. EPR spectra of compounds **4** and **5** in toluene solution remain for several hours after discontinuance of irradiation at 220 K. At ambient temperature these complexes decompose faster.

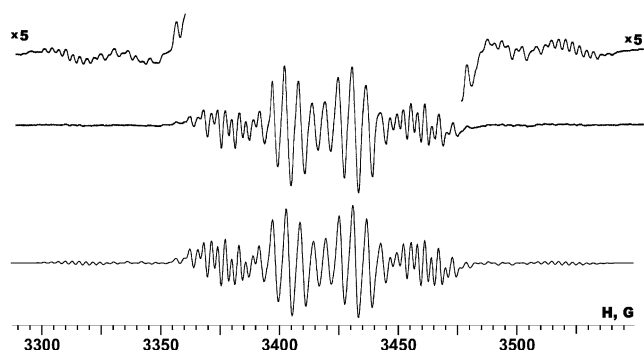
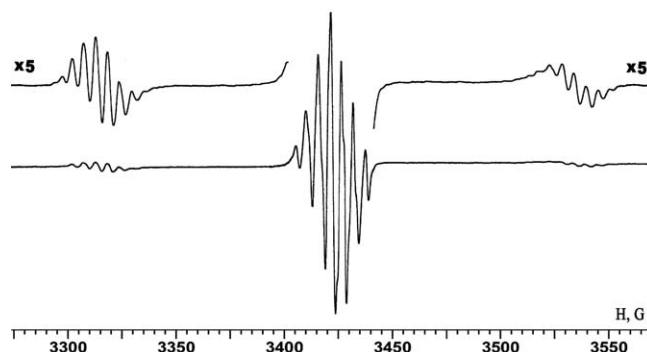
Fig. 1. Experimental X-band EPR spectrum of **3** in toluene at 290 K (top) and its simulation (bottom).Fig. 2. Experimental X-band EPR spectrum of **4** in toluene at 220 K.

Table 1
EPR parameters (*A_i* in G) for complexes **2–8**

	<i>g_i</i>	<i>A_i</i> (² H)	<i>A_i</i> (¹⁴ N)	<i>A_i</i> (¹¹⁷ Sn), <i>A_i</i> (¹¹⁹ Sn)	<i>A_i</i> (³⁵ Cl), <i>A_i</i> (³⁷ Cl)	<i>A_i</i> (⁷⁹ Br), <i>A_i</i> (⁸¹ Br)	<i>A_i</i> (^{95,97} Mo)
2	1.9997	5.8	5.8	145.3, 152.0	5.5, 4.6	–	–
3	2.0011	5.8	5.8	115.2, 120.5	–	26.9, 29.1	–
4	1.9983	4.8	5.7	215.0, 225.0	–	–	0.8
5	1.9964	5.2	5.4	206.5, 216.0	–	–	–
6	1.9999	6.0	6.0	133.8, 140.0	–	–	–
7	1.9997	6.0	6.0	146.2, 153.0	–	–	–
8	1.9990	5.7	5.7	124.3, 130.0	–	–	–

Irradiation of toluene solution containing **1** and $\text{Co}_2(\text{CO})_8$ at 220 K results in a weak broad singlet in EPR spectrum, which disappears under further irradiation or increase temperature. When $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ were used as radical sources, we were unable to detect any EPR signals both under ambient temperature and when cooled.

2-Phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxy-3-oxide and TEMPO radicals add to stannylene **1** giving rise to EPR spectra, indicating the formation of derivatives **6** and **7** (Scheme 1), respectively. In these spectra, HFC of unpaired electron to magnetic nuclei ^1H , ^{14}N , ^{117}Sn and ^{119}Sn (Table 1) can be observed.

We have found no sign of interaction between the tin complex and carbon-centered trityl radical. Thus, the toluene solution containing **1** and trityl radical does not change for several days, showing neither initial EPR spectrum decrease, nor new spectra appearance.

As we have reported recently, addition of 3,6-di-*tert*-butyl-2-ethoxyphenoxy radical to *N,N'*-substituted 1,2,3-diazagermole-2-ylidenes yields the radical germylene adducts. The enhanced stability of the latter was explained by the following: a weak ancillary coordination bond between germanium and ethoxy group causes considerable steric hindrances in the coordination sphere of germanium, and thus prevents addition of the second radical [6b]. Taking into account the fact, that the tetracoordinate state is more usual for tin(II) than for germanium(II) derivatives [8], we proposed, that the product of above mentioned phenoxyl addition to stannylene **1** would show even higher stability.

Actually, interaction between **1** and 3,6-di-*tert*-butyl-2-ethoxyphenoxy radical in toluene leads to paramagnetic products and EPR spectrum appearance. The latter is caused by the HFC of unpaired electron to magnetic nuclei ^1H , ^{14}N , ^{117}Sn and ^{119}Sn (Table 1). The spectrum can be explained by the formation of product **8** (Scheme 1).

Paramagnetic stannylene **8** is stable in toluene solution at ambient temperature for about two months. Compounds **2**, **3**, **6**, **7** are significantly less stable: their solutions keep EPR-activity for no more than two weeks at 290 K.

The HFC constants on two equivalent protons and two equivalent nitrogen nuclei (A_{H} (^1H) and A_{N} (^{14}N)) for derivatives **2–8** are analogous to the values obtained for paramagnetic stannylene [5], germylene and silylene [6] complexes. The HFC constants due to magnetic isotopes of tin A_{Sn} (^{117}Sn) and A_{Sn} (^{119}Sn) are in the same range as those for the short-living ($\tau_{1/2} \sim 2$ min) radical-anion stannylene $\text{Ar}_2\text{Sn}^{\cdot-}$ (A_{Sn} (Sn) = 151 G; Ar = 2,6-diethylphenyl) [9] and substantially exceed the HFC constants for paramagnetic tin(IV) complexes (5–20 G) [10]. On the other hand, A_{H} (^{17}H) and A_{N} (^{15}N) constants for **2–8** are approximately tenfold lower than the corresponding values for the known tin-centered radicals (1700–3300 G) [11]. This fact indicates that spin density in **2–8** is delocalized over the entire chelate ring as in germanium and silicon [6] derivatives.

Available data on the structures of the β -diketoiminate three-coordinate tin(II) complexes [12] and the EPR parameters for compounds **2** and **3** allow us to assume a similar geometry of a distorted trigonal pyramid with nitrogen, tin, and halide atoms at apical sites. This is also supported by large HFC constants on magnetic isotopes of chlorine and bromine. The position of the Sn–Hal bond being close to perpendicular to the chelate ring plane will be favorable for a larger contribution of the $\sigma(\sigma^*)$ orbital of M–Hal to the π -MO occupied by unpaired electron.

3. Experimental

EPR spectra were recorded on Bruker ER 200 D-SRC (working frequency ~ 9.5 GHz) spectrometer with ER041 MR microwave bridge, ER 4105 DR double resonator and ER 4111 VT variable temperature unite. The irradiation of samples was made with focused light of incandescent lamp (250 W) in resonator of EPR spectrometer. The g_i values were determined using diphenylpicrylhydrazyl as the reference ($g_i = 2.0037$). HFC constants were obtained by simulation with the WinEPR SimFonia Software (Bruker).

Treatment of **1** with mercury or silver halides and free radicals was made by addition of stannylene (15 mg, 0.03 mmol) solution in toluene (2 ml) to solid reagents under EPR conditions. Tin complex was taken in approximately tenfold excess to radical sources or metal halides. When transition metals carbonyls were used, the reaction mixture was cooled to about 220 K and irradiated in EPR resonator to produce corresponding metal-centered radicals.

All reagents were grade. Solvents were purified following standard methods [13]. 3,6-Di-*tert*-butyl-2-ethoxyphenoxy radical [14] and 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-1-oxy-3-oxide [15] were prepared according to known procedures.

3.1. Synthesis of *N,N'*-bis[(2,6-di-*iso*-propylphenyl)-1,2,3-diazastannole-2-ylidene

Stannylene **1** was synthesized as follows: the THF solution of dilithium derivative [16] of corresponding diazabutadiene (1.88 g, 5 mmol), was added dropwise to cooled at -20 °C THF solution, containing SnCl_2 -diox [17] complex (1.39 g, 5 mmol). After mixing, THF was evaporated and the residue was dissolved in hexane. The solution was separated from lithium chloride deposit by filtration. After partial evaporation, **1** precipitated from hexane solution as needle orange crystals (Yield: 0.68 g, 1.38 mmol, 27.5%. m.p. 206 °C (decomp.) ^1H NMR (toluene- d_6): δ 1.22 (d, 6 H, 6.8 Hz, CH_3 , ^iPr), 1.24 (d, 6 H, 6.8 Hz, CH_3 , ^iPr), 3.31 (septet, 4 H, 7.0 Hz, CH, ^iPr), 7.03 (s, 2 H, NCH, $^3\text{J}(^{119}\text{Sn}-\text{H}) = 9.0$ Hz), 7.15–7.22 (br, 6 H, CH, Ar). Anal. Calc. for $\text{C}_{26}\text{H}_{36}\text{N}_2\text{Sn}$ (495.29): C, 63.05; H, 7.33; Sn, 23.97. Found: C, 63.39; H, 7.37; Sn, 23.76%). All manipulations on complexes were carried out under conditions excluding air oxygen and moisture.

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References

- [1] (a) N.J. Hill, R. West, *J. Organomet. Chem.* 689 (2004) 4165;
(b) B. Gehrhus, M.F. Lappert, *J. Organomet. Chem.* 617 (2001) 209;
(c) T.A. Schmedake, M. Haaf, R. West, *Acc. Chem. Res.* 33 (2000) 704.
- [2] (a) O. Kuhl, P. Lonnecke, J. Heinicke, *Polyhedron* 20 (2001) 2215;
(b) O. Kuhl, *Coord. Chem. Rev.* 248 (2004) 411.
- [3] T. Gans-Eichler, D. Gudat, M. Nieger, *Angew. Chem.* 114 (2002) 1966.
- [4] I.L. Fedushkin, N.M. Khvoinova, A.Yu. Baurin, G.K. Fukin, V.K. Cherkasov, M.P. Bubnov, *Inorg. Chem.* 43 (2004) 7807.
- [5] G.A. Abakumov, V.K. Cherkasov, A.V. Piskunov, N.O. Druzhkov, *Dokl. Chem. (Engl. Ed.)* 399 (2004) 223.
- [6] (a) B. Tumanskii, P. Pine, Y. Apeloig, N.J. Hill, R. West, *J. Am. Chem. Soc.* 126 (2004) 7786;
(b) G.A. Abakumov, V.K. Cherkasov, A.V. Piskunov, I.A. Aivaz'yan, N.O. Druzhkov, *Dokl. Chem. (Engl. Ed.)* 404 (2005) 189;
(c) B. Tumanskii, P. Pine, Y. Apeloig, N.J. Hill, R. West, *J. Am. Chem. Soc.* 127 (2005) 8248.
- [7] J. Emsley, *The Elements*, Clarendon Press, Oxford, 1991, p. 256.
- [8] N.N. Zemlyanskii, I.V. Borisova, M.S. Nechaev, V.N. Khrustalev, V.V. Lunin, M.Yu. Antipin, Yu.A. Ustynyuk, *Russ. Chem. Bull. Int. Ed.* 53 (2004) 980.
- [9] I.S. Orlov, A.A. Moiseeva, K.P. Butin, L.R. Sita, M.P. Egorov, O.M. Nefedov, *Mend. Commun.* (2002) 125.
- [10] A.G. Davies, J.A.-A. Hawari, *J. Organomet. Chem.* 251 (1983) 53.
- [11] M.A.D. Bona, M.C. Cassani, J.M. Keates, G.A. Lawless, M.F. Lappert, M. Sturmman, M. Weidenbruch, *J. Chem. Soc., Dalton Trans.* (1998) 1187.
- [12] (a) A. Akkari, J.J. Byrne, I. Sour, G. Rima, H. Gornitzka, J. Barrau, *J. Organomet. Chem.* 622 (2001) 190;
(b) A.E. Ayers, H.V.R. Dias, *Inorg. Chem.* 41 (2002) 3259.
- [13] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1980.
- [14] G.A. Abakumov, V.K. Cherkasov, V.I. Nevodchikov, N.O. Druzhkov, G.K. Fukin, Y.A. Kursky, A.V. Piskunov, *Tetrahedron Lett.* 46 (2005) 4095.
- [15] J.H. Osiecki, E.F. Ullman, *J. Am. Chem. Soc.* 90 (1968) 1078.
- [16] E.S. Schmidt, A. Jockisch, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* (2000) 1039.
- [17] E. Hough, D.G. Nicholson, *J. Chem. Soc., Dalton Trans.* (1976) 1782.