2,6-Di-*tert*-butylphenols and phenoxyl radicals with metal—metal bonds

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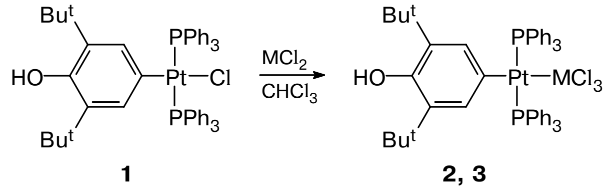
σ-Aryl *trans*-bistriphenylphosphine complexes based on 2,6-di-*tert*-butylphenol containing Pt—$SnCl_3$, Pt—$GeCl_3$ groups were synthesized. Oxidation of these compounds gives the corresponding phenoxyl radicals, which were studied by ESR spectroscopy. The transformation of the diamagnetic complexes to the paramagnetic state is accompanied by cleavage of the Pt—Sn, Pt—Ge bonds and by elimination of $SnCl_2$, $GeCl_2$.

Key words: sterically hindered phenols, phenoxyl radicals, σ-aryl metal complexes, ESR spectroscopy.

The change in the magnetic state of metal complexes can influence appreciably their reactivity and be responsible for directed activation of compounds.[1] Previously we showed, in relation to various organometallic and coordination compounds,[2] that diamagnetic complexes pass into the paramagnetic state if sterically hindered 2,6-di-*tert*-butylphenols, which are oxidized to give stable phenoxyl radicals, are used as specific ligands. An activating effect of the unpaired electron in the ligand on the metal atom (and the whole metal complex) by an intramolecular mechanism was established for compounds containing metal—carbon, metal—nitrogen, and metal—oxygen bonds.[3—6]

This paper is devoted to the synthesis and study of the properties of organometallic derivatives of 2,6-di-*tert*-butylphenols and the corresponding phenoxyl radicals containing groups with the carbon—metal—metal (C—Pt—Sn, C—Pt—Ge) bonds in the *para*-position. Diamagnetic compounds were prepared by insertion into the Pt—Cl bond[7] on treatment of *trans*-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-bis(triphenylphosphine)platinum chloride (**1**)[8] with dichlorostannylene and dichlorogermylene (taken as the $GeCl_2 \cdot$dioxane complex) ($CHCl_3$, 20 °C); the yields of complexes **2** and **3** were 58 and 69%, respectively (Scheme 1).

Scheme 1



1 **2, 3**

M = Sn (**2**), Ge (**3**)

Compounds **2** and **3** are crystalline solids stable in air both neat and in solutions. Their structure was proved by IR and ^{1}H, ^{31}P, and ^{119}Sn spectroscopy, mass spectrometry, electronic absorption spectroscopy, and elemental analysis. The IR spectra of complexes **2** and **3** exhibit characteristic bands in the region of 3600—3650 cm^{-1} due to the stretching vibrations of the O—H bonds in the phenolic groups and in the region of 520 cm^{-1} for the stretching vibrations of the C—Pt bonds. Data of electronic absorption spectroscopy show the presence of π—π* transitions in the aromatic systems of **2** and **3** in the region of 220 nm and the absence of intramolecular charge transfer bands in the ligand—metal system.

The ^{31}P NMR spectra confirm the *trans*-configuration of the compounds synthesized (Table 1). The values of direct spin-spin coupling constants $^1J_{^{195}Pt-^{31}P}$, which lie in the range of 2880—3120 Hz, correspond to those for the square-planar complexes *trans*-$RPt(PPh_3)_2X$.[9] The upfield shift of the proton signals of the equivalent phenolic *tert*-butyl groups (by ~1 ppm) for compounds **2** and **3** relative to those in the initial σ-aryl platinum complex **1** (0.98 ppm in MeCN) implies a more pronounced π-acceptor character of the trichlorostannyl and trichlorogermyl ligands compared to that of the Cl

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Table 1. Data of the ^{31}P NMR spectra of compounds **1—3** in different solvents

Compound	Solvent	δ	$^1J_{\text{Pt—P}}$ (Hz)	$J_{\text{Sn—P}}$ (Hz)	ε [12]	D_N [12]
1	$CDCl_3$	21.0	3196	—	—	—
2	C_6D_6	18.6	2880	236	2.27	—
	$CDCl_3$	17.4	2882	232	4.81	—
	MeCOMe	17.4	2903	—	20.56	17
	MeCN	17.1	3086	—	35.94	14.1
	C_5H_5N	18.0	3116	—	12.91	33.1
3	C_6D_6	20.9	2921	—	—	—
	$CDCl_3$	19.6	2927	—	—	—
	MeCN	19.1	3037	—	—	—

atom;[10] this was also observed for analogous σ-phenyl platinum complexes[11].

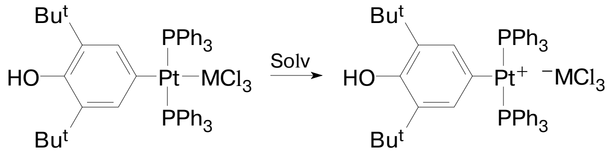
The Pt—Sn and Pt—Ge bonds in compounds **2** and **3** show a high degree of polarity in solutions. It was found by ^{31}P NMR spectroscopy that an increase in the polarity and coordination capacity of the solvent entails an increase in the direct spin-spin coupling constants $^1J_{^{195}\text{Pt}—^{31}\text{P}}$ (see Table 1). The data in Table 1 show that the $^1J_{\text{Pt—P}}$ values are correlated with the dielectric constant of the solvent ε. An exception is pyridine, which is, however, characterized by a rather high donor number D_N compared, for example, with those for acetone and acetonintrile. This fact allows one to take into account a substantial contribution of the coordination capacity of the solvent to its overall effect on the character of the Pt—Sn and Pt—Ge bonds in compounds **2** and **3**. The spectra of solutions of compound **2** in nonpolar solvents (benzene, chloroform) display signals corresponding to the splitting of the ^{31}P signals at the ^{117}Sn and ^{119}Sn nuclei; however, these signals are missing from the spectra in polar and coordinating solvents (*viz.*, acetone, acetonitrile, and pyridine). In addition, the ^{119}Sn NMR spectra of compound **2** in chloroform show spin-spin coupling with the nuclei of the two equivalent ^{31}P atoms ($J_{\text{P—Sn}}$ = 471 Hz); in acetonitrile, only a broadened singlet with ΔH = 200—250 Hz is observed.

Based on these results, it can be concluded that in polar solvents, the Pt—Sn and Pt—Ge bonds in complexes **2** and **3** are polarized to such a degree that the compounds exist in solutions as contact ion pairs (Scheme 2) (the solvolytic cleavage of the M=GeCl$_2$ bonds in the Cl$_5$M=GeCl$_2$ complexes, where M = Cr, Mo, W, is described in Ref. 13).

Solvents with a sufficient coordination capacity (high donor number D_N) appear to stabilize the organometallic fragment with predominant localization of the positive charge on the Pt atom due to the additional axial coordination.[14]

It was shown by ^{1}H NMR spectroscopy that diamagnetic complexes **2** and **3** are stable in solutions in the 20—80 °C temperature range. A different in kind situation is found when compounds **2** and **3** pass from the diamagnetic into the paramagnetic state.

Scheme 2



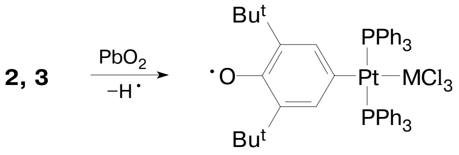
2, 3

Solv is a polar coordinating solvent

The oxidation of 2,6-di-*tert*-butylphenols is known[15] to start with single-electron oxidation giving rise to the corresponding radical cations. Experiments on the electrochemical oxidation of compounds **2** and **3** using a rotating disk-ring Pt electrode showed that the oxidation in a MeCN—CH$_2$Cl$_2$ (1 : 3) solution is irreversible, and the $E_{1/2}$ values of complexes **2** and **3** decrease with respect to that of the starting compound **1** [16] and are equal to 0.88, 0.92, and 1.14 V, respectively. The shift of the potential to the less anodic region ($\Delta E_{1/2}$ = 0.26 (**2**) and 0.22 V (**3**)) reflects apparently the decrease in the energy of the electrochemically active MO of the complexes upon the introduction of the SnCl$_3$ and GeCl$_3$ groups, possessing electron-acceptor properties.

The oxidation of organometallic phenol derivatives **2** and **3** on treatment with (Bu^{t}O)$_2$ with irradiation or on treatment with lead dioxide in benzene, toluene and THF, as in the case of compound **1**, gives rise to radical products **2a** and **3a** (Scheme 3).

Scheme 3



2a, 3a

Parameters of the ESR spectra of radicals **2a** and **3a** (Fig. 1, Table 2) point to spin density distribution over the whole molecular systems of complexes including both the organic moiety and the metals. The spectra exhibit the HFC of the unpaired electron with the two

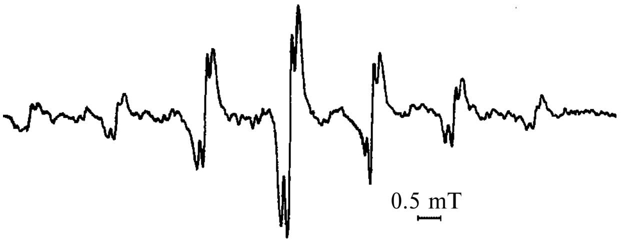


Fig. 1. ESR spectra of radical **2a** (benzene, 290 K).

Table 2. Parameters of the ESR spectra of radicals **1a**—**3a** (benzene, 293 K)

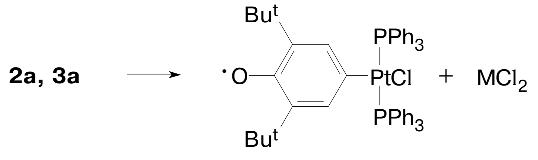
Radical	*g*-Factor	a_H	$a_{^{195}Pt}$	$a_{^{31}P}$	$a_{^{117/119}Sn}$
		mT			
1a[8]	2.0079	0.12	9.4	1.6	—
2a	2.01	0.13	7.75	1.9	1.6
3a	2.01	0.15	7.33	1.75	—

equivalent *meta*-protons of the phenoxyl ring (^{1}H), the ^{195}Pt nucleus, the ^{31}P nuclei, which are equivalent (due to the *trans*-structure), and the $^{117/119}$Sn nuclei in the case of radical **2a** (see Fig. 1).

The HFC constants a_{Pt} markedly decrease and the a_P values for radicals **2a** and **3a** increase with respect to the corresponding values for **1a**. The HFC constants depend not only on the electronic structure of the paramagnetic complex but on its geometric parameters. However, in this case, there are no grounds for suggesting that the geometry of radical species **2a** and **3a** deviates from the planar-square geometry because the spectral data confirm the equivalence of the P atoms. Therefore, the pronounced decrease in the HFC constants of the unpaired electron with the ^{195}Pt nucleus ($\Delta a_{Pt} \approx 2$ mT) and the presence of HFC with the $^{117/119}$Sn nucleus (**2a**) attests to spin density transfer from the Pt atom to the Sn and Ge atoms by the spin-polarization mechanism, which is due to both the π-acceptor properties of the MCl_3 groups and the ability of the Pt atom to transfer electron density (transmission effect).

These electronic effects influence the kinetic and thermodynamic stability of radicals **2a** and **3a**. According to ESR data, the stability of these species differs appreciably from that of diamagnetic precursors **2**, **3** and radical **1a**. The half-life ($\tau_{1/2}$) in solutions amounts to several minutes and decreases with an increase in temperature. Decomposition of radicals **2a** and **3a** is accompanied by elimination of MCl_2 giving rise to radical **1a** (Scheme 4).

Scheme 4



The signals of radicals **2a**, **3a** disappear from the ESR spectra, and a signal for radical **1a** appears (Fig. 2). The rate constants (*k*) for the unimolecular decomposition of **3a** at 323, 343, and 353 K are 2.27, 6.24, and $8.4 \cdot 10^3$ s^{-1}, respectively. In the case of radical **2a**, the reaction rate is higher, which hampers the kinetic studies due to signal overlap. The enthalpy for the elimination of $GeCl_2$ from radical **3a** is 10.2 kcal mol^{-1}.

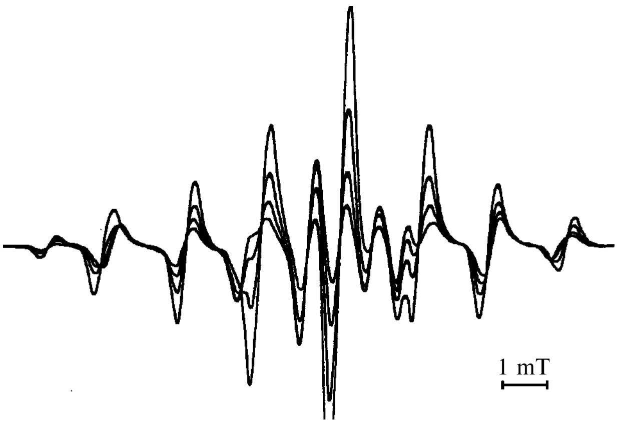


Fig. 2. Variation of the ESR spectrum corresponding to radical **3a** decomposition (benzene, 350 K, Scheme 4).

The results obtained provide the conclusion that the transfer of diamagnetic σ-aryl complexes **2** and **3** to the paramagnetic state upon oxidation of the organic ligand has an activating effect on the organometallic group by an intramolecular mechanism and results in a pronounced weakening of the Pt—M bond.

Experimental

IR spectra were recorded on an IKAR FT spectrophotometer in KBr pellets; electronic absorption spectra were measured on a Cari 219 Varian spectrophotometer. The NMR spectra were run on a Bruker AM-300 instrument operating at 300 MHz (^{1}H) and on a Varian VXR-400 instrument operating at 400 MHz (^{1}H), 161.9 MHz (^{31}P), and 149.1 MHz (^{119}Sn). Mass spectra were obtained on a LCQ (Finnigan) mass spectrometer. ESR spectra were recorded on a Varian E 12A and Bruker EMX-6 radiospectrometers. The measurements were carried out after pre-evacuation of tubes with solutions of samples (concentration $1 \cdot 10^{-4}$ mol L^{-1}). The oxidants were taken in a tenfold excess. Electrochemical measurements were carried out using an automated system consisting of a PI 50 potentiostat, a PR-8 programmer, and a Pentium MMX PC. A rotating disk-ring Pt electrode with a ring of diameter 2 mm, whose efficiency was 0.1, was used. The working rotation velocity of the electrode was 298.3 rad s^{-1}; Bu_4NClO_4 was used as the supporting electrolyte.

The solvents $CDCl_3$, C_6D_6 (Merck) were used without further purification; C_6H_6, C_6H_5Me, Me_2CO, MeCN, and THF were purified by standard procedures.[17] The $SnCl_2$ samples (Aldrich) were used without further purification, $GeCl_2$ was used as a complex with dioxane.[18] The kinetic measurements were performed in a temperature-controlled cell in a ESR spectrometer.

***trans*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-bis(triphenylphosphine)platinumtintrichloride (2).** Tin dichloride (0.15 mmol) was added under Ar to a solution of compound **1** (0.1 mmol)[8] in 3 mL of $CHCl_3$. The reaction mixture was stirred for 1 h and filtered and the filtrate was concentrated to dryness. The residue was dissolved in benzene, the insoluble impurities were filtered off, and the reaction product was precipitated by petroleum ether. Recrystallization from benzene gave **2** (yield 58%), m.p. 186 °C. ^{1}H NMR ($CDCl_3$), δ: 0.91 (s, 18 H, $C(C\underline{H}_3)_3$); 4.39 (s, 1 H, $O\underline{H}$); 6.31 (s, 2 H, $C_6\underline{H}_2$); 7.30—7.50 (m, 30 H, $C_6\underline{H}_5$). UV (MeCN), λ_{max}/nm (log ε): 219 (4.38). IR, ν/cm^{-1}:

3635 (O—H); 2920—3010 (C—H, C(C$\underline{H}_3$)$_3$). MS (electrospray), *m/z*: 924.7. [$C_{50}H_{51}OP_2Pt$]$^+$. Found (%): C, 52.95; H, 5.13. $C_{50}H_{51}Cl_3OP_2PtSn$. Calculated (%): C, 52.22; H, 4.43.

***trans*-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-bis(triphenylphosphine)platinumgermaniumtrichloride (3)** was prepared in a similar way from complex **1** (0.1 mmol) and $GeCl_2 \cdot$dioxane (0.14 mmol). The yield of compound **3** was 69%, m.p. 192—193 °C. ^{1}H NMR (CDCl$_3$), δ: 0.88 (s, 18 H, C(C$\underline{H}_3$)$_3$); 4.23 (s, 1 H, O$\underline{H}$); 6.49 (s, 2 H, C$_6\underline{H}_2$); 7.20—7.70 (m, 30 H, C$_6\underline{H}_5$). UV (MeCN), λ_{max}/nm (log ε): 220 (4.41). IR, ν/cm^{-1}: 3617 (O—H); 2900—3010 (C—H, C(C$\underline{H}_3$)$_3$). MS (electrospray), *m/z*: 924.7. [$C_{50}H_{51}OP_2Pt$]$^+$. Found (%): C, 54.52; H, 4.89. $C_{50}H_{51}Cl_3GeOP_2Pt$. Calculated (%): C, 54.40; H, 4.62.

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