SYNTHESIS, STRUCTURE, AND PROPERTIES OF 2-(TRI-PHENYLSTANNYLOXY)-3,6-DI-*tert* BUTYL-1,4-BENZO-QUINONE

N. Yu. Kabarova, V. K. Cherkasov, L. N. Zakharov, G. A. Abakumov, Yu. T. Struchkov, and L. G. Abakumova

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2-(Triphenylstannyloxy)-3,6-di-tert-butyl-1,4-benzoquinone (1) was obtained from the potassium salt of 3,6-ditert-butyl-2-hydroxy-1,4-benzoquinone and triphenyltin bromide in methanol and characterized by x-ray diffraction analysis, electronic, IR, and NMR spectroscopy. According to x-ray diffraction data, the single crystal of 1 has the structure of a chain metal polymer with bridging hydroxy-para-quinone ligands; the coordination number of tin is six. Complex 1 is reduced by cobaltocene to the corresponding radical anion. In solutions, 1 reacts with metal-centered radicals $SnPh_3$, $PbPh_3$, and $Mn(CO)_5$ with formation of paramagnetic binuclear ortho-semiquinone complexes.

Keywords: 2-triphenylstannyloxy-3,6-di-text-butyl-1,4-benzoquinone, synthesis, x-ray diffraction analysis, electronic absorption spectra, IR spectroscopy, NMR spectroscopy, reaction with radicals.

Ortho-benzosemiquinones (SQ) are some of the most widely distributed and universal types of free-radical ligands presently known in organometallic and coordination chemistry [1-3]. Complexes containing them have been obtained for practically all the metallic elements of D. I. Mendeleev's periodic table. The presence of a radical ligand bonded to a metallic center within the molecule determines the novel and unusual properties of this class of compounds, due to the possible metal-ligand interaction. In SQ complexes with diamagnetic ions of variable-valency metals, under certain conditions such an interaction is realized as the phenomenon of redox-isomerism [4]. SQ complexes with paramagnetic ions of transition metals display interesting magnetic properties due to metal-ligand exchange magnetic interactions [5].

Continuing and extending our investigations in the chemistry of metal complexes with free-radical ligands, in this work we have synthesized 2-(triphenylstannyloxy)-3,6-di-*tert*-butyl-1,4-benzoquinone (1) as the starting ligand to obtain binuclear complexes with free-radical ligands. We have also determined its structure and investigated some interactions of 1 by EPR, including reactions leading to binuclear paramagnetic complexes with an unpaired electron on the ligand.

RESULTS AND DISCUSSION

Complex 1 was synthesized from the potassium salt of 2-hydroxy-3,6-di-*tert*-butyl-1,4-benzoquinone and triphenyltin bromide in a mixture of methanol and water. Single crystals of 1 were obtained by recrystallization from methanol. Considering the possibility of isomerism of 2-hydroxy-3,6-di-*tert*-butyl-1,4-benzoquinone and its metal complexes [6], we carried out an x-ray diffraction study of 1 to objectively establish its structure.

As we see from Fig. 1, in which we depict a fragment of the crystal structure of 1, the triphenylstannyl moiety is bonded to the O^1 atom of the quinone ligand by an ordinary covalent bond and by an additional coordination bond to the O^2 atom of

Institute of Organometallic Chemistry, Russian Academy of Sciences, 603600 Nizhnii Novgorod. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences, 117813 Moscow. Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 12, pp. 2798-2804, December, 1992. Original article submitted August 16, 1991.



Fig. 1. Fragment of the crystal structure of 1.

the carbonyl group adjacent to the triphenylstannyl group. The length of the $Sn-O^1$ bond, 2.095(5) Å, is close to the sum of the covalent radii of these atoms according to Pauling [7]. The $Sn-O^2$ distance, 2.654(5) Å, is significantly shorter than the sum of the van der Waals radii of the Sn and O atoms (3.60 Å [8]), clearly suggesting the existence of a $Sn...O^2$ interaction. Furthermore, the tin atom is bonded to the $O^{3'}$ atom of the neighboring molecule in the crystal by a $Sn-O^{3'}$ coordination bond, whose length 2.821(5) Å is also significantly shorter than the sum of the van der Waals radii of Sn and O. As a result of these bonds, the molecules form one-dimensional chains in the crystal with bridging η^3 -oxyquinone ligands. The lengths of the bonds $Sn-C^{15}$ 2.153, $Sn-C^{21}$ 2.149, and $Sn-C^{27}$ 2.135 Å, connecting the tin atom with the phenyl substituents, are also close to the sum of the sum of the covalent radii of the Sn and C atoms [7].

Thus, the Sn atom in the single crystal of 1 has coordination number six, and the coordination polyhedron is distorted from tetrahedral toward trigonal-pyramidal with the three C¹⁵, C²¹, and C²⁷ atoms in equatorial positions and the O^{3'} atom and the chelate group O¹...O² in apical positions. The average plane of the chelate group SnO¹C¹C²O² is oriented in such a way that the angle C¹⁵SnC²⁷ is approximately bisected; in this case, the O¹SnO^{3'} is 171.3(1)°. The Sn atom deviates from the plane of the C¹⁵C²¹C²⁷ atoms by 0.3 Å. The O¹SnC^{Ph} angles lie in the range 93.4(2)-100.7(2)°, the O^{3'}SnC^{Ph} angles lie in the range 78.4(2)-86.8(2)°. The bond angles in the coordination polyhedron of the Sn atom are presented in Table 1.

The six-membered $C^1 - C^6$ ring is nonplanar. It is bent along the line $C^2 \dots C^5$ so that the dihedral angle between the average $C^2C^3C^4C^5$ and $C^2C^1C^6C^5$ planes is equal to 13.9°.

The values obtained for the lengths of the $C^1 - O^1 1.3214^8$, $C^2 - O^2 1.220^8$, $C^5 - O^3 1.245^8$, $C^1 - C^6 1.38^1$, $C^3 - C^4 1.33^1$ Å (Table 2), and the rest of the C-C bonds in the benzoquinone ligand, lying in the range 1.46(1)-1.52(1) Å, are close to the average values of the double bonds $C(sp^2) = O(1.222 \text{ Å})$, $C(sp^2) = C(sp^2)(1.349 \text{ Å})$ and the single bonds $C(sp^2) - C(sp^2)(1.478 \text{ Å})$ in *para*-benzoquinones [9].

Thus 1, according to x-ray diffraction data, is a derivative of 3,6-di-tert-butyl-2-hydroxy-1,4-benzoquinone.

In solutions, 1 is probably monomeric. Evidence for this comes from the differences in the IR spectra of its polycrystalline samples (obtained by grinding the single crystals) and the samples in solutions. The changes occurring in the IR spectra of 1 involve only the frequency region from 1500 to 1700 cm⁻¹. In the rest of the regions, the IR spectra are practically identical. The IR spectrum of the polycrystalline sample contains four intense bands in the indicated region: $v_1 = 1660$, $v_2 = 1646$, $v_3 = 1595$, $v_4 = 1530$ cm⁻¹. The two highest frequency bands clearly belong to stretching vibrations of uncoordinated or very weakly coordinated carbonyl groups [10]. (Very close frequencies are observed in the IR spectra of the original hydroxy-ortho-quinone.) The other two bands (v_3 and v_4), judging from the reduced frequency, can be assigned to vibrations connected with carbonyl groups coordinated to the tin atom.

The IR spectra of 1 in solutions (CCl₄, THF) in the indicated region contain two very intense bands instead of four: $v_1 = 1630$ and $v_2 = 1555$ cm⁻¹, assigned to vibrations of carbonyl groups respectively uncoordinated and coordinated to the tin atom.

The electronic absorption spectrum of 1 in solution contains an intense (log $\varepsilon = 3.25$) absorption band in the visible region of the spectrum whose frequency weakly depends on the nature of the solvent ($\nu_{max} = 21,750$ in toluene; $\nu_{max} = 22,000$ cm⁻¹ in THF). This band, connected with the $\pi \rightarrow \pi^*$ transition [10], is also present in the electronic absorption spectra of the

Angle	۵, deg	Angle	ω, deg
$\begin{array}{c} 0^{4}-\mathrm{Sn}-\mathrm{C}^{15}\\ \mathrm{C}^{15}-\mathrm{Sn}-\mathrm{C}^{21}\\ \mathrm{C}^{15}-\mathrm{Sn}-\mathrm{C}^{27}\\ 0^{4}-\mathrm{Sn}-\mathrm{C}^{27}\\ 0^{4}-\mathrm{Sn}-\mathrm{C}^{12}\\ 0^{4}-\mathrm{Sn}-\mathrm{C}^{12}\\ 0^{4}-\mathrm{Sn}-\mathrm{C}^{27}\\ 0^{2}-\mathrm{Sn}-\mathrm{C}^{27}\\ 0^{3}-\mathrm{Sn}-\mathrm{C}^{21}\\ \mathrm{Sn}-\mathrm{O}^{4}-\mathrm{C}^{1}\\ 0^{4}-\mathrm{C}^{4}-\mathrm{C}^{6}\\ 0^{2}-\mathrm{C}^{2}-\mathrm{C}^{1}\\ \mathrm{C}^{1}-\mathrm{C}^{2}-\mathrm{C}^{3}\\ \mathrm{C}^{2}-\mathrm{C}^{2}-\mathrm{C}^{1}\\ \mathrm{C}^{1}-\mathrm{C}^{2}-\mathrm{C}^{3}\\ \mathrm{C}^{2}-\mathrm{C}^{3}-\mathrm{C}^{6}\\ \mathrm{O}^{3}-\mathrm{C}^{5}-\mathrm{C}^{6}\\ \mathrm{O}^{3}-\mathrm{C}^{5}-\mathrm{C}^{6}\\ \mathrm{O}^{3}-\mathrm{C}^{5}-\mathrm{C}^{6}\\ \mathrm{C}^{3}-\mathrm{C}^{4}-\mathrm{C}^{5}\\ \mathrm{C}^{5}-\mathrm{C}^{6}-\mathrm{C}^{7}-\mathrm{C}^{9}\\ \mathrm{C}^{6}-\mathrm{C}^{7}-\mathrm{C}^{19}\\ \mathrm{C}^{6}-\mathrm{C}^{7}-\mathrm{C}^{10}\\ \mathrm{C}^{9}-\mathrm{C}^{7}-\mathrm{C}^{10}\\ \mathrm{C}^{3}-\mathrm{C}^{14}-\mathrm{C}^{13}\\ \mathrm{C}^{13}-\mathrm{C}^{14}-\mathrm{C}^{14}\\ \mathrm{C}^{13}-\mathrm{C}^{14}-\mathrm{C}^{14}\\ \mathrm{C}^{13}-\mathrm{C}^{14}-\mathrm{C}^{14}\\ \mathrm{C}^{15}-\mathrm{C}^{20}-\mathrm{C}^{19}\\ \mathrm{Sn}-\mathrm{C}^{21}-\mathrm{C}^{26}\\ \mathrm{C}^{21}-\mathrm{C}^{22}-\mathrm{C}^{23}\\ \mathrm{C}^{23}-\mathrm{C}^{24}-\mathrm{C}^{25}\\ \mathrm{C}^{24}-\mathrm{C}^{25}\\ \mathrm{C}^{24}-\mathrm{C}^{25}\\ \mathrm{C}^{24}-\mathrm{C}^{25}\\ \mathrm{C}^{25} \end{array}$	$\begin{array}{c} 98.8(2)\\ 109.1(2)\\ 129.4(2)\\ 66.0(1)\\ 98.8(2)\\ 100.7(2)\\ 122.4(2)\\ 74.8(2)\\ 74.8(2)\\ 78.5(2)\\ 130.0(5)\\ 124.4(7)\\ 117.8(6)\\ 119.7(6)\\ 120.7(6)\\ 124.4(7)\\ 124.4(8)\\ 114.9(7)\\ 123.7(6)\\ 114.4(7)\\ 123.7(6)\\ 114.4(7)\\ 108.1(8)\\ 107.4(9)\\ 110.9(6)\\ 108.2(6)\\ 108.4(8)\\ 123.6(4)\\ 121.3(5)\\ 120.0(6)\\ 120.4(5)\\ 122.0(4)\\ 121.8(5)\\ 120.2(6)\\ 109.4(5)\\ 120.2(6)\\ 109.4(5)\\ 120.2(6)\\ 120.2(6)\\ 120.2$	$\begin{array}{c} O^{i}-Sn-C^{2i}\\ O^{i}-Sn-C^{2i}\\ O^{i}-Sn-C^{2i}\\ O^{j}-Sn-C^{2i}\\ O^{j}-Sn-C^{2i}\\ O^{j}-Sn-C^{2i}\\ O^{j}-Sn-C^{2i}\\ O^{j}-Sn-C^{2i}\\ O^{j}-Sn-C^{2i}\\ O^{j}-Sn-C^{2i}\\ O^{j}-C^{i}-C^{i}\\ O^{j}-C^{j}-C^{i}\\ C^{j}-C^{i}-C^{i}\\ C^{j}-C^{i}-C^{i}\\ C^{j}-C^{i}-C^{i}\\ C^{i}-C^{j}-C^{i}\\ C^{i}-C^{j}-C^{i}\\ C^{i}-C^{i}-C^{i}\\ C^{i}-C$	$\begin{array}{c} 93.4(2)\\ 100.7(2)\\ 115.8(2)\\ 171.3(1)\\ 93.4(2)\\ 122.4(1)\\ 158.8(2)\\ 80.4(2)\\ 112.4(1)\\ 158.8(2)\\ 80.4(2)\\ 1122.6(7)\\ 122.6(7)\\ 122.6(7)\\ 122.6(7)\\ 122.6(7)\\ 122.6(7)\\ 122.6(7)\\ 122.6(7)\\ 122.6(6)\\ 122.6(6)\\ 122.6(6)\\ 120.5(6)\\ 120.5(6)\\ 120.5(6)\\ 120.4(4)\\ 110.1(6)\\ 117.9(4)\\ 119.4(5)\\ 120.3(5)\\ 120.4(4)\\ 117.0(4)\\ 120.0(6)\\ 119.0(5)\\ 149.8(6)\\ 149.8($
$\begin{array}{c} C^{21} - C^{26} - C^{25} \\ Sn - C^{27} - C^{32} \\ C^{27} - C^{28} - C^{29} \\ C^{29} - C^{30} - C^{31} \\ C^{27} - C^{32} - C^{31} \end{array}$	122.1 (5) 124.8 (4) 119.8 (5) 119.3 (6) 120.2 (5)	$\begin{array}{c} \operatorname{Sn-C^{22}-C^{24}}\\ \operatorname{C^{28}-C^{27}-C^{32}}\\ \operatorname{C^{28}-C^{29}-C^{30}}\\ \operatorname{C^{30}-C^{3i}-C^{32}} \end{array}$	115.8(4) 119.0(5) 120.9(6) 120.8(5)

TABLE 1. Bond Angles in Structure 1 (ω , deg)

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original hydroxy-para-quinone ($\nu_{max} = 24,700 \text{ cm}^{-1}$; log $\varepsilon = 3.06$; toluene) and its potassium salt ($\nu_{max} = 18,850 \text{ cm}^{-1}$; $\varepsilon = 3.42$; *i*-PrOH). Reduction of the frequency of this tranistion in the series H⁺ > Ph₃Sn⁺ > K⁺ reflects the decrease in the degree of covalency of the bond between the organic ligand and the cation, accompanied by an increase in the negative charge on the ligand.

Complex 1 is easily reduced to the radical anion (2) upon action of cobaltocene. The EPR spectrum of 2 is a doublet, due to hyperfine coupling of the unpaired electron with the ring proton, $A_i(H) = 0.566$ mT. Hyperfine coupling with the magnetic isotopes ¹¹⁷Sn and ¹¹⁹Sn appears in the EPR spectrum as satellite lines $A_i(Sn) = 0.386$ mT.

Complex 1 can react with metal-centered radicals $SnPh_3$, $PbPh_3$, $Mn(CO)_5$, forming paramagnetic binuclear metal complexes with an unpaired electron on the inorganic ligand.

$$R^{+} + \int_{0}^{+} \int_{0}^{+} \int_{0}^{+} \int_{0}^{+} \int_{0}^{+} \int_{0}^{+} \int_{0}^{0} \int_{0}^{+} Sn^{ph_{3}}$$
(1)

The parameters of the isotropic EPR spectrum of these complexes are presented in Table 3. Their preliminary analysis shows that the paramagnetic complexes formed have an *ortho*-semiquinone character. The values of g_i and $A_i(M)$ in the EPR spectra are close to the corresponding values for analogous *ortho*-semiquinone complexes, such as 3,6-di-*tert*-butyl-4-methoxy-1,2-semibenzoquinone. The EPR spectroscopy data also show that in at least one case, upon reaction of 1 with $\dot{Mn}(CO)_5$, migration of the Ph₃Sn group occurs from the O¹ atom to the O³ atom with formation of complex 3 as the end product.

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TABLE	2.	Bond	Lengths	in	Structure	1	(d, 1	\)
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Bond	d, A	Bond	đ, A
$\begin{array}{c} Sn-O^{4}\\ Sn-C^{21}\\ O^{4}-C^{1}\\ O^{3}-C^{5}\\ C^{1}-C^{6}\\ C^{3}-C^{4}\\ C^{4}-C^{5}\\ C^{6}-C^{7}\\ C^{7}-C^{9}\\ C^{11}-C^{14}\\ C^{15}-C^{20}\\ C^{17}-C^{18}\\ C^{19}-C^{20}\\ C^{23}-C^{24}\\ C^{25}-C^{26}\\ C^{27}-C^{32}\\ C^{29}-C^{30}\\ C^{31}-C^{32} \end{array}$	$\begin{array}{c} 2.095 (5) \\ 2.149 (5) \\ 1.314 (8) \\ 1.245 (8) \\ 1.38 (1) \\ 1.33 (1) \\ 1.49 (1) \\ 1.52 (1) \\ 1.52 (1) \\ 1.55 (1) \\ 1.55 (1) \\ 1.387 (7) \\ 1.385 (8) \\ 1.388 (9) \\ 1.388 (8) \\ 1.388 (7) \\ 1.375 (8) \\ 1.382 (8) \end{array}$	$\begin{array}{c} {\rm Sn-C^{15}}\\ {\rm Sn-C^{27}}\\ {\rm O^2-C^2}\\ {\rm C^1-C^2}\\ {\rm C^2-C^3}\\ {\rm C^3-C^{11}}\\ {\rm C^5-C^6}\\ {\rm C^7-C^6}\\ {\rm C^7-C^6}\\ {\rm C^{1-C^{13}}}\\ {\rm C^{15}-C^{16}}\\ {\rm C^{16}-C^{17}}\\ {\rm C^{18}-C^{19}}\\ {\rm C^{21}-C^{22}}\\ {\rm C^{22}-C^{23}}\\ {\rm C^{24}-C^{25}}\\ {\rm C^{24}-C^{25}}\\ {\rm C^{24}-C^{25}}\\ {\rm C^{25}-C^{26}}\\ {\rm C^{25}-C^{26}}\\ {\rm C^{26}-C^{29}}\\ {\rm C^{30}-C^{31}} \end{array}$	$\begin{array}{c} 2.153(6)\\ 2.135(5)\\ 1.220(8)\\ 1.52(1)\\ 1.48(1)\\ 1.53(1)\\ 1.53(1)\\ 1.53(1)\\ 1.54(2)\\ 1.52(1)\\ 1.52(1)\\ 1.383(7)\\ 1.383(7)\\ 1.384(8)\\ 1.384(8)\\ 1.379(9)\\ 1.384(8)\\ 1.379(9)\\ 1.384(9)\\ \end{array}$

TABLE 3. Parameters of Isotropic EPR Spectra of Binuclear Metal Complexes: Adducts of 1 with Metal-Centered Radicals (toluene, 285 K, A_i (mT))

R	\$ _i	A_i (H _{SQ})	A _i (Sn)	A ₁ (M)
Mn (CO) 4 SnPh3 PbPh3	2.0070 2.0076 2.0063	0.396 0.356 0.378	1.092(¹¹⁷ Sn) 1.147(¹¹⁹ Sn) 1.129(¹¹⁷ Sn) 1.177(¹¹⁹ Sn) 0.791(Sn)	0.546 (⁵⁵ Mn) 0.877 (Sn) 2.141 (²⁰⁷ Pb)

A special paper will be devoted to investigation of reactions of 1 with metal-centered radicals.

EXPERIMENTAL

The solvents used in this work were purified by the familiar technique in [11]. The EPR spectra were recorded on the Bruker ER 200D-SRC instrument. The IR spectra were recorded on the Specord M-80 spectrometer. The electronic absorption spectra were recorded on the SF-14 spectrophotometer. The x-ray experiment was conducted on the Siemens P3/PC diffractometer at $\approx 20^{\circ}$ C (λ MoK_{α}, graphite monochromator, $\theta/2\theta$ scanning, 2.0 < 2 θ < 56.0°). Crystals of 1 are monoclinic, a = 15.896(2), b = 11.923(3), c = 17.611(4) Å, $\beta = 116.42(2)^{\circ}$; V = 2738.5(2,2) Å³, Z = 4, $d_{calc} = 1.420$ g · cm⁻³, space group $P2_1/n$.

The intensities of 4725 reflections were measured, of which 3643 reflections with $|F| > 4.0 \sigma(F)$ were used to decipher and refine the structure. No correction was made for absorption; $\mu(MoK_{\alpha}) = 7.24 \text{ cm}^{-1}$. The structure was determined by combining direct methods and difference electron density syntheses. The structure was refined by full-matrix least-squares treatment with anisotropic thermal vibration parameters for nonhydrogen atoms, and isotropic parameters for hydrogen atoms. For the refinement we used the following weighting scheme: $W^{-1} = \sigma^2(F)$. The final value of the *R*-factor was R = 0.036. The coordinates of the basis atoms are presented in Table 4; the bond lengths and bond angles are presented in Tables 1 and 2, respectively. The values of the thermal vibration parameters of the atoms in structure 1 can be obtained from the authors.

In this work, we used commercial triphenyltin bromide, dimanganese decacarbonyl, hexaphenyldistannane, and hexaphenyldiplumbane. Cobaltocene was obtained using the technique in [12]; 3,6-di-tert-butyl-4-methoxy-1,2-benzoquinone was obtained using a technique analogous to that in [13], from 3,6-di-tert-butyl-1,2-benzoquinone.

Atom	x	Ŷ	Z	U
Sn	6485(1)	2175(1)	8993(1)	19(1)
01	5657 (4)	3217 (5)	7919(3)	24(2)
O^2	4826(4)	1186(5)	8017 (3)	24(2)
O ³	2827 (4)	4004(5)	5456(3)	25(2)
Ci	4767 (5)	3098(7)	7377 (4)	20(3)
C^2	4313(5)	1947 (7)	7519(4)	19(3)
C ³	3285 (5)	1794(7)	7064(5)	21(3)
C4	2843(5)	2564(7)	6423(4)	21 (3)
C ⁵	3319(5)	3539(7)	6161 (5)	20(3)
C ⁶	4283(5)	3898(7)	6721(5)	21(3)
C ⁷	4775(6)	5014(8)	6559(5)	29(3)
C ⁸	5293(8)	5748(9)	7379(7)	49(5)
C ⁹	4117(7)	5882(9)	5874(7)	51(5)
C ¹⁰	5500(7)	4542(10)	6272(7)	48(5)
Č11	2788(6)	812(7)	7339(5)	25 (3)
Č ¹²	3107 (7)	-466(8)	7217(6)	35(4)
Č13	1727 (6)	908(9)	6827(6)	37 (4)
Č14	3042(6)	1023 (8)	8287 (5)	30(3)
Č15	5618(3)	2297 (4)	9644(3)	18(2)
Č16	5044(4)	3311(5)	9489(3)	24(2)
Č ¹⁷	4448(4)	3443(5)	9872(3)	30(2)
C18	4430(4)	25/5(5)	10422 (3)	29/2)
C19	5004 (4)	1527 (5)	10581(3)	28/2)
C20	5580(3)	4306(4)	10194(3)	23(2)
C21	7570(3)	35/0/5)	9494 (3)	23(2)
C22	7959(4)	/738(5)	0500(3)	20(2)
C23	9044(4)	5502(5)	10031(4)	30(3)
C24	0044(4)	5989(7)	40379(4)	48(3)
C25	0909(0)	5202(7) (080(6)	10372(4)	44(9)
C26	9219(4)	3930/5)	0826(3)	31(2)
C27	6797(2)	0209(0) 695(E)	9620(3)	94(9)
C28	0/0/(0)	020(0) 708(5)	7589(2)	30(2)
C ²⁹	0000(4) 67/6(4)	190(3)	7498(2)	37(2)
C30	0/40(4)		140(3)	35(2)
01	0948(4)	-1000(0)	(401(3)	26(2)
G**	70/2(4)	-1000(5)	0000(4)	04(2)
U**	6990(4)	-532(5)	8768(3)	28(2)

TABLE 4. Atomic Coordinates (×10⁴) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$)

2-Hydroxy-3,6-di-*tert*-butyl-1,4-benzoquinone. A sample of 1.45 ml 40% HBr was added dropwise to a solution of 0.250 g (1 mmole), 3,6-di-*tert*-butyl-4-methoxy-1,2-benzoquinone in 3 ml methanol and allowed to stand for 3 h. The solution took on an orange color. Upon addition of water, yellow crystals of 3,6-di-*tert*-butyl-2-hydroxy-1,4-benzoquinone precipitated. EPR spectrum: $\nu = 24,690 \text{ cm}^{-1}$; log $\varepsilon = 3.05$. PMR spectrum (CDCl₃, δ , ppm): 1.26 (6C(CH₃)₃), 1.36 (3C(CH₃)₃), 6.38 (5H), 7.62 (OH).

2-(Triphenylstannyloxy)-3,6-di-*tert*-**butyl-1,4-benzoquinone**. A solution of 0.430 g (1 mmole) triphenyltin bromide in 2 ml methanol was added dropwise to a solution of the potassium salt of 2-hydroxy-3,6-di-*tert*-butyl-1,4-benzoquinone obtained from 0.236 g (1 mmole) of 2-hydroxy-3,6-di-*tert*-butyl-1,4-benzoquinone with stirring. The reaction mixture was held in a refrigerator for one day. The solution was decanted with precipitated red crystals, which were washed and dried. Found, %: C 65.59; H 6.18; Sn 19.57. C₃₂H₃₄O₃Sn. Calculated, %: C 65.75; H 5.82; Sn 20.20. IR spectrum (ν , cm⁻¹): 1292, 1530, 1595, 1630, 1646, 1660; (vaseline); 905, 1075, 1170, 1220, 1295, 1310, 1555, 1630 (solution in CCl₄). EPR spectrum: $\nu =$ 21,740 cm⁻¹; log $\varepsilon = 3.25$. PMR spectrum (CDCl₃, δ , ppm): 1.15 br. (6C(CH₃)₃), 1.37 (3C(CH₃)₃), 6.29 (5H), 7.4-7.8 (C₆H₅).

Metal-centered radicals nPh_3 , $PbPh_3$, $Mn(CO)_5$ were generated directly in the resonant cavity of the rf spectrometer in the presence of 1 by photolysis of the corresponding organometallic compound.

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