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Mechanism of hindered rotation of the trifluorosilyl group in trifluorosilyl 3,6-di-tert-butylorthosemiquinolate

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17.75 MHz (^{29}Si) for sealed, evacuated 10% solutions of (I) in $\text{CDCl}_3-\text{CCl}_4-\text{CD}_2\text{Cl}_2$ relative to TMS. The ^{29}Si NMR measurements were carried out using the INEPT method.

2-[Dimethyl(pentafluorophenyl)siloxy]-2-penten-4-one (I). A solution of 10.0 g dimethyl-(pentafluorophenyl)chlorosilane in 15 ml petroleum ether (bp 30-60°C) was added slowly to a mixture of 3.1 g pyridine and 3.8 g acetylacetone, and the mixture was stirred for 15 h at 60°C. The precipitate was filtered off. Solvent removal in vacuum gave 2.1 g (17%) (I), bp 86-89°C (1 mm), n_D^{20} 1.4630. Found: C 48.39; H 3.89; F 29.53; Si 8.51%. Calculated for $\text{C}_{13}\text{H}_{13}\text{F}_5\text{O}_2\text{Si}$: C 48.14; H 4.04; F 29.23; Si 8.66%.

CONCLUSIONS

^1H , ^{13}C , and ^{29}Si NMR spectroscopy was used to study the structure and silylotropy of 2-[dimethyl(pentafluorophenyl)siloxy]-2-penten-4-one. The temperature dependence of the ^{29}Si NMR chemical shifts indicated the existence of an intermediate with pentacoordinated silicon.

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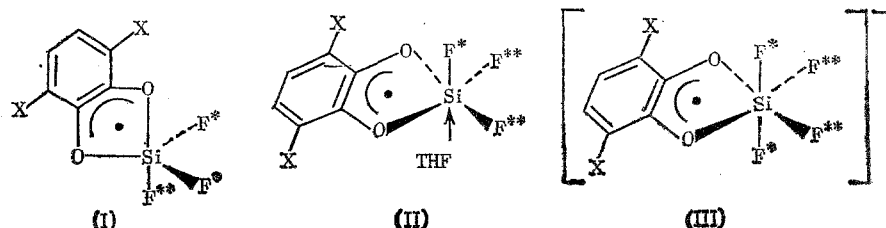
OPENING OF THE CHELATE RING IN PARAMAGNETIC

3,6-DI-TERT-BUTYLPYROCATECHATE TRIFLUOROSILICATE

BY THE ACTION OF ELECTRON-DONOR MOLECULES

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 N. N. Bubnov, S. P. Solodovnikov,
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In our previous work [1, 2], we studied orthosemiquinolate complexes containing SiF_3 and SiF_4 groups. The electron-withdrawing capacity of the silicon atom in such groups results in the coordination of both oxygen atoms of the pyrocatechate ligand with the central silicon atom and the formation of chelate structures (I)-(III):



A decrease in the electronegativity of the substituents at the silicon atom leads to a reduction in its electron-withdrawing activity and opening of the chelate ring. Thus, the trimethylsilyl derivative has phenoxyl structure [3]:

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 6, pp. 1426-1429, June, 1986. Original article submitted October 8, 1985.

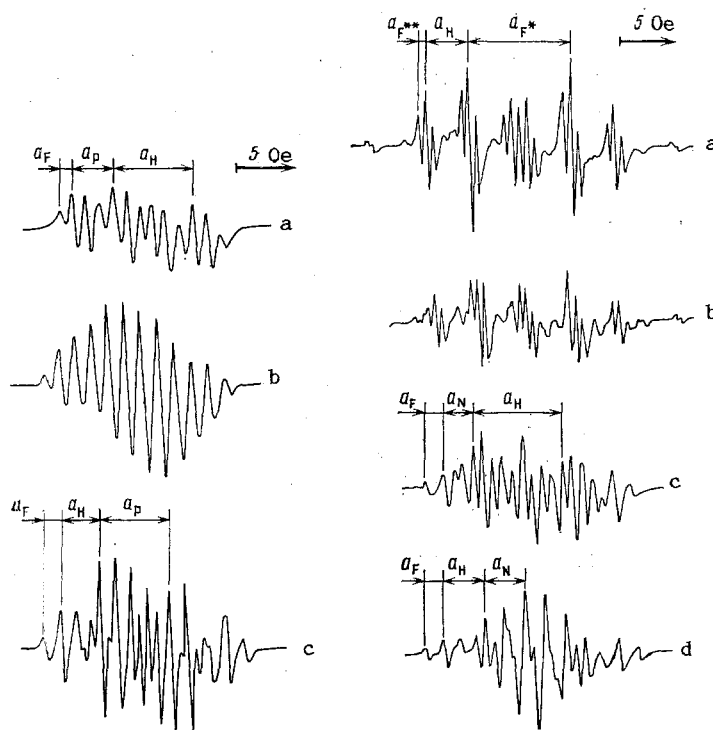
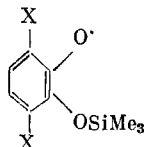


Fig. 1

Fig. 2

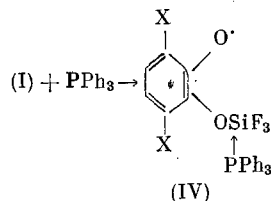
Fig. 1. Temperature dependence of the ESR spectra of radical (IV) in toluene: a) -50; b) 10; c) 40°C.

Fig. 2. Temperature dependence of the ESR spectra of radical (II) in benzonitrile: a) -15; b) 10; c) 100°C.



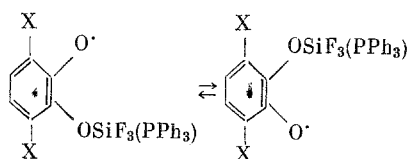
Here and subsequently, X = t-Bu.

The coordination of sufficiently strong electron-donor ligands with the silicon atom in (I) should also lead to a decrease in its electron-withdrawing properties and opening of the chelate ring. Indeed, the addition of PPh₃ to a toluene solution of (I) leads to an ESR spectrum corresponding to phenoxyl radical (IV):



The hyperfine structure of the ESR structure of (IV) at -50°C (Fig. 1a) has significant inequivalence of the coupling constants with the protons of the pyrocatechate ligand ($a_H^4 = 7.2$ Oe, $a_H^5 \sim 0$), which is typical for phenoxyl radicals of this type [4]. Coupling is also found with three equivalent ¹⁹F nuclei ($a_F = 1.3$ Oe) and a ³¹P nucleus ($a_P = 3.9$ Oe). The ¹⁹F nuclei in chelate complex (I) are inequivalent and coupling is found with two equivalent ¹⁹F nuclei lying out of the plane of the pyrocatechate ligand ($a_{F^*} = 10.1$ Oe) and with one ¹⁹F nucleus lying in this plane ($a_{F^{**}} = 0.3$ Oe).

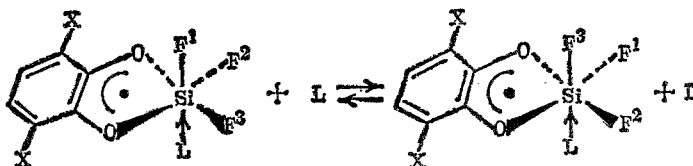
Migration of the heteroorganic group between the oxygen atoms of the pyrocatechate ligand occurs with increasing temperature,



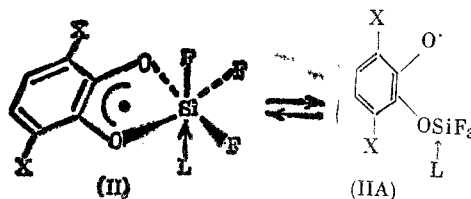
leading to equalization of the coupling with the pyrocatechate ligand protons, which become spectrally equivalent above 0°C : $a_{\text{H}^4} = a_{\text{H}^5} = 3.9 \text{ Oe}$ (see Fig. 1b, c).

An increase in temperature leads also to a change in the coupling constants with the ^{19}F ($a_{\text{F}} = 1.3 \text{ Oe}$ at -50°C and $a_{\text{F}} = 1.6 \text{ Oe}$ at 40°C) and ^{31}P nuclei ($a_{\text{P}} = 3.9 \text{ Oe}$ at -50°C and $a_{\text{P}} = 6.1 \text{ Oe}$ at 40°C). The increase in the coupling constants occurs along with an increase in the rate of migration of the heteroorganic group. An increase in the coupling constants with increasing temperature in radicals of this type is a result of delocalization of the spin density onto nuclei of the lateral ligands (F and P atoms) by a hyperconjugation mechanism and the generation of positive spin density in these ligands [5].

Similar effects are also observed upon the coordination of MeCN or PhCN molecules with the central silicon atom. Such complexes were obtained by the reaction of 3,6-di-tert-butyl-orthobenzoquinone with SiF_4 in MeCN or PhCN. Figure 2 gives the temperature dependence of the ESR spectra of the paramagnetic formed with PhCN. At -15°C , the ESR spectrum (see Fig. 2a) corresponds to an octahedral complex of type (II) which we obtained previously in THF [1]. The spectral parameters of this complex were found independent of the solvent (THF, glyme, MeCN, PhCN) and coupling is found with the ^{19}F nucleus lying out of the plane of the pyrocatechate ligand ($a_{\text{F}^*} = 9.2 \text{ Oe}$), the two equivalent ^{19}F nuclei lying in this plane ($a_{\text{F}^{**}} = 0.7 \text{ Oe}$) and the two equivalent protons of the pyrocatechate ligand ($a_{\text{H}^4} = a_{\text{H}^5} = 4.0 \text{ Oe}$). The observed spectral evolution from -15 to $+10^{\circ}\text{C}$, as in the case of the solution in THF [2], corresponds to ligand permutation in a type-(II) complex due to solvent molecule exchange between the complex and solvent bulk.



The rate of the permutation processes in THF increases with a further increase in temperature, and the complete spectral equivalence of the three ^{19}F nuclei is observed at 40°C ($a_{\text{F}} = 2.6 \text{ Oe}$). Such exchange rates are not achieved in benzonitrile. The ESR spectrum recorded at 40°C (see Fig. 2c) corresponds to phenoxyl radical (IIa), formed upon the opening of the chelate ring in the type-(II) complex:



where $\text{L} = \text{MeCN}$ and PhCN .

In this case, as in the case of Ph_3P , the pyrocatechate ligand protons become inequivalent ($a_{\text{H}^4} = 8.0 \text{ Oe}$, $a_{\text{H}^5} \sim 0$) and coupling is found with three equivalent ^{19}F nuclei ($a_{\text{F}} = 1.65 \text{ Oe}$) and ^{14}N nucleus ($a_{\text{N}} = 3.0 \text{ Oe}$).

Complex spectral behavior is found at from 10 to 40°C due to overlap of the ESR spectra of the type-(II) complex with hindered rotation of the SiF_3 group and phenoxyl radical (IIA). Migration of the heteroorganic group occurs above 40°C , leading to equalization of the coupling constants with the pyrocatechate ligand protons, which become completely equivalent at 100°C ($a_{\text{H}^4} = a_{\text{H}^5} = 4.0 \text{ Oe}$, see Fig. 2d). Upon increasing the temperature from 40 to 100°C , the coupling constant with the ^{14}N nucleus (a_{N}) increases from 3.0 to 3.5 Oe ,

which may be explained, as in the case of complex (IV), by the generation of positive spin density at the nitrogen nucleus.

The temperature dependences of the ESR spectra in these cases, are entirely reversible.

CONCLUSIONS

The changes in the ESR spectra of 3,6-di-*tert*-butylpyrocatechate trifluorosilicate in the presence of electron-donor Ph_3P , MeCN, and PhCN molecules indicate coordination of these molecules with the central silicon atom and subsequent opening of the chelate pyrocatechate ring with formation of phenoxyl complexes. Migration of the heteroorganic group occurs between the oxygen atoms of the pyrocatechate ligand at elevated temperatures.

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DECOMPOSITION OF METHYL DERIVATIVES OF TRANSITION METALS

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UDC 541.124:542.92:547.1'13

Gilman et al. [1] were the first to study the products of the decomposition of methyl derivatives of various transition metals including Ni, Co, Cr, Zr, Fe, Mn, Ag, and Cu formed upon the reaction of CH_3Li with the halides of these metals. The major products are methane (in the case of TiCl_4 , TaCl_5 , ZrCl_4 , MnBr_2 , and CeCl_3), ethane (in the case of AgBr, CuCl, and CuCl_2), of a mixture of methane and ethane (in the case of AuCl_3 , FeCl_2 , and NiCl_2). They assumed that the formation of these products is related to generation of methyl radicals in the decomposition. De Vries [2] and D'yachkovskii [3] showed that the major product of the decomposition of $(\text{CD}_3)_4\text{Ti}$ is CD_4 , whose formation cannot be related to a radical mechanism. The reaction products contained only about 5% CD_3N , which may be formed as a result of the homolytic decomposition of the organometallic compound and the reaction of the CD_3 radical with the solvent [3]. Similar results were obtained for the decomposition of $(\text{CH}_3)_5\text{Nb}$ and $(\text{CH}_3)_5\text{Ta}$ [4]. In our previous work [5], we studied the decomposition of perdeuteromethyl derivatives of Mo and W formed in situ upon the reaction of WCl_6 and MoCl_5 with CD_3Li and found that the gaseous reaction products, viz., methane, ethane, and ethylene, are fully deuterated, i.e., their formation is not related to radical reactions.

In the present work, we studied the mechanism for the decomposition of the perdeuteromethyl derivatives of a series of transition metals upon their formation. For this purpose, we investigated the composition of the gaseous products of the reaction of CD_3Li and CD_3MgI with the chlorides of Cr, Co, Ni, Ru, Rh, Pd, Re, Os, Pt, and W. The reactions were carried out at about 20°C by the addition of a solution of CD_3Li or CD_3MgI in dibutyl ether to the solid metal salts. In the case of WCl_6 , we used its solution in benzene. The gaseous reaction products were analyzed chromatographically, and the isotopic composition was determined by chromatography/mass spectrometry.

The composition of the gaseous products of reaction of CD_3Li with these transition metal chlorides is given in Table 1, which shows that the major reaction products are methane,

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