# Substituent effects in radical cations of linear oligosilanes

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The dependence was analyzed of the first ionization potential $I$(Si—Si) corresponding to detachment of an electron from the σ(Si—Si) highest occupied molecular orbital on the parameters of organic (X = Me, Et, Bu$^t$, Ph, CH=CH$_2$), inorganic (X = F, Cl, Br), and organosilicon (X = SiR$_3$; R is organic radical) substituents in di-, tri-, and tetrasilanes $X_3SiSiX_3$. It was found by correlation analysis that out of the three possible effects of substituents X (the inductive, polarizability, and resonance effects), only the first two of them affect the $I$(Si—Si) values. This means that no conjugation between the substituent X and the radical cation center occurs in $X_3Si\overset{\cdot+}{-}SiX_3$.

**Key words:** linear oligosilanes, ionization potential, radical cations, substituent effects.

The electronic structure of linear polysilanes R—(SiR$_2$)$_n$—R ($n \geq 2$) that currently find a wide field of application has been studied in detail.[1—6] Theoretical studies of these compounds are of great importance for revealing the peculiarities of the Si—Si chemical bond and for solving actual problems of the chemistry of organoelement compounds (in particular, for development of the modern concept of conjugation in the compounds of the silicon subgroup elements). According to the current concept,[7] organoelement substituents MR$_3$ (M = Si, Ge, Sn, Pb; R is organic radical) in R$_\pi$MR$_3$ molecules exhibit simultaneously resonance donor and resonance acceptor properties toward the π-electron centers R$_\pi$ (C$_6$H$_5$, H$_2$C=CH, HC≡C, *etc.*). The resonance acceptor effect (d,π-conjugation) is due to the interaction of the vacant $n$d-orbitals of the M atom and antibonding σ*-orbitals of the M—R bonds with the orbitals of the R$_\pi$ fragment. This effect decreases as the atomic number of the M atom increases, *i.e.*, in the series Si > Ge > Sn > Pb. The resonance donor effect (σ,π-conjugation), which is due to the interaction of the σ-orbitals of the M—R bonds with the orbitals of the R$_\pi$ fragment, increases as the number of the M atom increases (Si < Ge < Sn < Pb). In the R$_\pi$CH$_2$MR$_3$ molecules, d,π-conjugation is absent, while σ,π-conjugation with R$_\pi$ involves the σ-orbitals of the C—M bond of the CH$_2$M fragment. Both resonance effects are present in R$_\pi$SiR$_2$SiR$_3$ compounds, namely, d,π-conjugation with the π-electron system of R$_\pi$ involves the orbitals of the SiR$_2$ fragment, while σ,π-conjugation occurs involving the σ-orbitals of the Si—Si bond.

These regularities are characteristic of the above-mentioned neutral systems in the ground electron state. At small perturbations, *e.g.*, in the case of the formation of a H-complex of the π-donor center R$_\pi$ with an acceptor molecule (phenol, pyrrole, *etc.*), the effective negative charge of the R$_\pi$ fragment is somewhat decreased (by $n$ = 0.01e), which increases σ,π-conjugation. Appreciable decrease ($n$ = 0.1e) in the negative charge on the R$_\pi$ substituent (*e.g.*, in the excited state of π,π-type charge-transfer complexes of R$_\pi$MR$_3$ and R$_\pi$CH$_2$MR$_3$ molecules with tetracyanoethylene) leads to a sharp increase in σ,π-conjugation.[7—10]

We have developed a new procedure for assessing the resonance effects of the substituents by using the first ionization potentials ($I$) of unsaturated, aromatic, and heteroaromatic R$_\pi$MR$_3$ and R$_\pi$CH$_2$MR$_3$ molecules in which the highest occupied molecular orbital (HOMO) is mainly localized on the R$_\pi$ fragment.[11—14] The generation of the radical cation center on the R$_\pi$ fragment after detachment of an electron from the HOMO strengthens the donor properties of MR$_3$ and CH$_2$MR$_3$ substituents by the mechanism of σ,π-conjugation. The opposite effect is likely observed in R$_\pi$SiR$_2$SiR$_3$ (R$_\pi$ = C$_6$H$_5$, H$_2$C=CH) molecules in which the HOMO is mainly localized on the Si—Si σ-bond. It cannot be ruled out that the generation of a radical cation center on the SiR$_2$SiR$_3$ fragment after detachment of an electron from the HOMO can make this fragment a weaker donor toward R$_\pi$, *i.e.*, can weaken its σ,π-conjugation. No analysis of the $I$ values from this point of view has been reported to date.

The aim of this work was to study the effects of organic, inorganic, and organosilicon substituents on the ionization potentials of the Si—Si bond in oligosilanes

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**Table 1.** The first vertical ionization potentials *I*(Si—Si) and the sums of σ-parameters of substituents X in $X_3SiSiX_3$ molecules

| Compound | *I*(Si—Si) /eV | Reference | $\Sigma\sigma_I$ | $\Sigma\sigma_R^+$ | $\Sigma\sigma_p^+$ | $\Sigma\sigma_\alpha$ |
|---|---|---|---|---|---|---|
| $H_3Si-SiH_3$ (**1**) | 10.53 | 3 | 0 | 0 | 0 | 0 |
| $H_3Si-SiH_2SiH_3$ (**2**) | 9.87 | 3 | −0.04 | 0.03 | −0.01 | −0.59 |
| $H_3SiH_2Si-SiH_2SiH_3$ (**3**) | 9.62 | 3 | −0.08 | 0.06 | −0.02 | −1.18 |
| $Me_3Si-SiMe_3$ (**4**) | 8.69 | 3 | −0.30 | −1.56 | −1.86 | −2.10 |
| $Me_3Si-SiMe_2SiMe_3$ (**5**) | 8.19 | 3 | −0.40 | −1.28 | −1.68 | −2.47 |
| $Me_3SiMe_2Si-SiMe_2SiMe_3$ (**6**) | 7.98 | 3 | −0.50 | −1.00 | −1.50 | −2.84 |
| $Et_3Si-SiEt_3$ (**7**) | 8.39 | 15 | −0.30 | −1.50 | −1.80 | −2.94 |
| $Bu^tMe_2Si-SiMe_2Bu^t$ (**8**) | 8.52 | 3 | −0.34 | −1.42 | −1.76 | −2.90 |
| $Me_3Si-SiHMeSiMe_3$ (**9**) | 8.35 | 2 | −0.35 | −1.02 | −1.37 | −2.12 |
| $HMe_2Si-SiMe_2SiHMe_2$ (**10**) | 8.50 | 2 | −0.22 | −1.17 | −1.39 | −2.08* |
| $F_3Si-SiF_3$ (**11**) | 13.20 | 3 | 2.70 | −3.12 | −0.42 | 0.78 |
| $Cl_3Si-SiCl_3$ (**12**) | 10.91 | 3 | 2.52 | −1.86 | 0.66 | −2.58 |
| $Br_3Si-SiBr_3$ (**13**) | 10.10 | 4 | 2.70 | −1.80 | 0.90 | −3.54 |
| $Me_3Si-SiMeClSiMe_3$ (**14**) | 8.42 | 2 | 0.07 | −1.33 | −1.26 | −2.55 |
| $Me_2ClSi-SiMe_2SiMe_2Cl$ (**15**) | 8.73 | 2 | 0.33 | −1.41 | −1.08 | −2.60* |
| $Me_3Si-SiMe_2Ph$ (**16**) | 8.35 | 3 | −0.13 | −1.60 | −1.73 | −2.56 |
| $PhMe_2Si-SiMe_2Ph$ (**17**) | 8.23 | 15 | 0.04 | −1.64 | −1.60 | −3.02 |
| $Me_3Si-Si(CH=CH_2)Me_2$ (**18**) | 8.56 | 3 | −0.12 | −1.59 | −1.71 | −2.25 |
| $Me_2(H_2C=CH)Si-Si(CH=CH_2)Me_2$ (**19**) | 8.63 | 3 | 0.06 | −1.62 | −1.56 | −2.40 |
| $PhMe_2Si-SiMe_2SiMe_3$ (**20**) | 8.15 | 16 | −0.23 | −1.32 | −1.55 | −2.93 |

*Note*. The $\sigma_I$, $\sigma_R^+$, and $\sigma_p^+ = \sigma_I + \sigma_R^+$ values were taken from Refs. 8 and 11; the $\sigma_\alpha$ constants were taken from Refs. 11 and 17. * The $\sigma_\alpha$ values for $SiHMe_2$ (−0.68) and $SiMe_2Cl$ (−0.77) were assessed by the additivity scheme based on the $\sigma_\alpha$ values for the substituents of similar structure

and to reveal dominating electronic effects in their radical cations.

## Calculation procedure

The first vertical ionization potentials *I*(Si—Si) of linear oligosilanes, corresponding to detachment of an electron from the HOMO localized mainly on the Si—Si σ-bond,[1—6] are listed in Table 1. The *I* values were determined by photoelectron spectroscopy (PES) with an accuracy of 0.01 eV.

Based on Koopmans theorem (see, *e.g.*, Ref. 18), one could expect that the following simple dependence is valid:

$$I(\mathrm{Si{-}Si}) = -E_{\mathrm{HOMO}}, \tag{1}$$

where $E_{\mathrm{HOMO}}$ is the HOMO energy. However, for all series of $R_\pi MR_3$ and $R_\pi CH_2MR_3$ ($R_\pi$ = aryl, heteryl, $H_2C=CH$, $HC\equiv C$) compounds we studied previously, as well as for hydrogen sulfide derivatives, this approximation is invalid.[11—14] This means that the MO of the neutral molecule A substantially differs from that of the radical cation $A^{\cdot+}$ formed from A on photoionization

$$A + h\nu \rightarrow A^{\cdot+} + e^- \tag{2}$$

(see, *e.g.*, Refs. 12—14).

Let us consider the differences in intramolecular electronic interactions in the A and $A^{\cdot+}$ systems from the viewpoint of physical organic chemistry. Two intramolecular electronic effects, namely, the inductive and resonance (conjugation) effects, are characteristic of neutral $R_\pi X$ ($R_\pi = C_6H_5$, $H_2C=CH$, $HC\equiv C$; X is organic substituent) molecules.[19] The resonance constant $\sigma_R^0$ of substituent X is the quantitative characteristic of conjugation between $R_\pi$ and X. When studied by PES, the $R_\pi^{\cdot+}X$, $H-S^{\cdot\pm}X$, and $X_2S^{\cdot\pm}$ (X = R, $MR_3$, $CH_2MR_3$) radical cations of unsaturated, aromatic, and heteroaromatic compounds, as well as those of hydrogen sulfide derivatives, are in the gas phase. Analysis of the *I* values showed that three electronic effects, namely, the inductive, resonance (conjugation), and polarizability effects, occur in these radical cations.[11—14] Quantitatively, conjugation between $R_\pi^{\cdot+}$ (or $-S^{\cdot+}$) and X is characterized by the resonance parameter $\sigma_R^+$ of substituent X. Unlike $\sigma_R^0$, the $\sigma_R^+$ values take into account the increase in donor properties of resonance electron donors X ($NR_2$, OR, $CH_2MR_3$, *etc.*) due to the positive charge on the radical cation center.

The polarizability component appreciably contributes to electronic interactions in the radical cations. The Hammett—Taft correlation equations can be used for analyzing the *I* values only after taking into account this contribution.[11—14] The positive charge *q* of the radical cation center polarizes the substituent X by inducing a dipole moment, thus stabilizing the system due to the electrostatic attraction between the charge and the induced dipole. The stabilization energy is defined by the following formula[20]:

$$E_{\mathrm{st}} = -\alpha q^2/2\varepsilon r^4, \tag{3}$$

where α is the polarizability of the substituents, ε is the dielectric constant, and *r* is the distance between the charge and the induced dipole. Considerable difficulties in calculating $E_{\mathrm{st}}$ arise when the charge and induced dipole are parts of the same ion (as in this case), so formula (3) can be used for qualitative assessment only.[20]

It is convenient to use the $\sigma_\alpha$ constant of substituent X as a quantitative characteristic of stabilization of the positive charge of the radical cation center due to polarizability of X. The $\sigma_\alpha$ values for most organic substituents (X = R) were obtained with a high accuracy from *ab initio* quantum-chemical calculations of electrostatic polarizability potentials.[21] They are tabulated and are used in studies of ionic processes in the gas phase.[17,21] The $\sigma_\alpha$ constants of several substituents of the $MR_3$ and $CH_2MR_3$ types are also known.[11–14]

Three contributions to the overall electronic effect in the $R_\pi^{\cdot+}X$ radical cations appear in the equation for the *I* values of $R_\pi X$ derivatives[11–14]

$$I = I_0 + a\sigma_I + b\sigma_R^{+} + c\sigma_\alpha, \qquad (4)$$

where $I_0$ is the *I* value for an unsubstituted $R_\pi H$ molecule; $\sigma_I$ is the universal inductive constant of substituent X, which is independent of the type of $R_\pi$; and *a*, *b*, and *c* are coefficients dependent on the type of $R_\pi$.

Let us consider the applicability of the correlation equation (4) to the compounds listed in Table 1. Calculations were carried out using the Statgraphics 3.0 program package on an AT/286 personal computer. The data were processed by the least squares method at a 95% confidence level.

## Results and Discussion

Equation (4), as applied to compounds **1—8** (Table 1), has the form:

$$I(\text{Si—Si}) = 10.35 + 2.69\Sigma\sigma_I - 0.03\Sigma\sigma_R^{+} + 0.40\Sigma\sigma_\alpha; \quad (5)$$
$$S_a = 0.13,\ S_b = 0.91,\ S_c = 0.19,\ S_d = 0.18,\ S_y = 0.17,$$
$$r = 0.982,\ n = 8.$$

The coefficient at the third term in Eq. (5) is close to zero (0.19) and is much smaller than the standard deviation. Therefore, the resonance effect of the substituents at the Si—Si bond does not affect the *I*(Si—Si) of compounds **1—8** despite the fact that for most of them the absolute values of $\Sigma\sigma_R^{+}$ are larger than the corresponding values of $\Sigma\sigma_I$.

At first glance, the absence of conjugation between substituents X (Me, Et, Bu$^t$, $SiMe_3$) and the radical cation center in the $X_3Si^{\cdot\pm}SiX_3$ systems is unexpected for at least two reasons. First, as was mentioned above, analysis of the *I* values for all the series of $R_\pi X$ ($R_\pi$ — const) compounds studied revealed conjugation between organic, organometallic, or inorganic substituents X and $R_\pi^{\cdot+}$ in the $R_\pi^{\cdot+}X$ radical cations.[11–14] Second, quantum-chemical calculations of neutral polysilane molecules unambiguously confirm that the HOMO is mainly localized on the Si—Si σ-bond[1–6,22] and that the AOs of substituents contribute to the HOMO. For instance, according to MS—$X_\alpha$ calculations, this contribution to the HOMO of the $Me_3SiSiMe_3$ molecule exceeds 20%.[22] The semiempirical AM1 calculations showed that the contributions of the AOs of H and C atoms to the HOMOs of $Si_nR_{2n+2}$ (R = H, Me; *n* = 3 — 5) derivatives vary from 5 to 20%.[5]

The composition of the lowest unoccupied molecular orbital (LUMO) σ*(Si—Si) of polysilanes[6] appreciably differs from the HOMO composition established previously.[5,22] According to electron transmission spectroscopy data, the σ*(Si—Si) MOs of $Me(SiMe_2)_nMe$ molecules (*n* = 2—4) are slightly mixed with the σ*(Si—C) MOs (hence, they are to an even lesser extent mixed with the σ(Si—C) MOs with stronger energies) and are delocalized over the polysilane chain rather than over the substituents.[6]

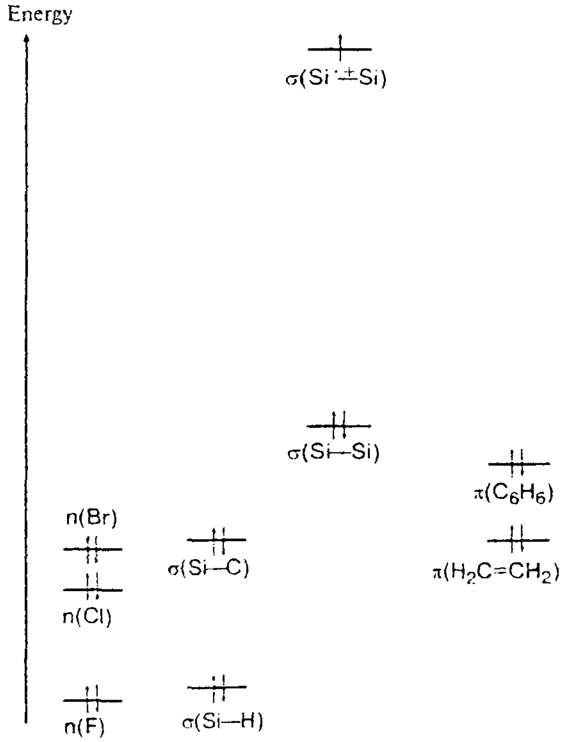

**Fig. 1.** Qualitative scheme of the orbital energy levels.

We believe that, from the viewpoint of conjugation with substituents X, the properties of the σ(Si$^{\cdot\pm}$Si) MO occupied by the unpaired electron in $X_3Si^{\cdot\pm}SiX_3$ radical cations resemble the properties of the σ*(Si—Si) MO rather than those of the σ(Si—Si) MO. In fact, the decrease in the number of electrons on the σ(Si—Si) bonding MO on going from neutral $X_3Si—SiX_3$ molecules (compounds **1—8**) to $X_3Si^{\cdot\pm}SiX_3$ radical cations is accompanied by destabilization of this MO, *i.e.*, by increase in the *E*(Si$^{\cdot\pm}$Si) energy compared to the *E*(Si—Si) energy. This is schematically depicted in Fig. 1.

According to MO perturbation theory (see, *e.g.*, Ref. 7), the mixing energy δ*E* of two MOs with energies $E_1$ and $E_2$ is defined by the following relationship:

$$\delta E \sim S^2/\Delta E, \qquad (6)$$

where *S* is the overlap integral and $\Delta E = E_1 - E_2$. From analysis of the qualitative scheme of the orbital energy levels shown in Fig. 1 it follows that the difference between *E*(Si$^{\cdot\pm}$Si) and *E*(Si—C) is appreciably larger than that between *E*(Si—Si) and *E*(Si—C). Assuming the *S* value to be constant, we find that the δ*E* value for the radical cation is smaller than for a neutral molecule, *i.e.*, that conjugation of substituents X (Alk, H) with the radical cation center in $X_3Si^{\cdot}\overset{+}{-}SiX_3$ is weaker than with the Si—Si bond in $X_3Si—SiX_3$ systems.

The increase in the size of the sample (compounds **1**—**15**) leads to the following equation:

$$I(Si—Si) = 10.39 + 0.85\Sigma\sigma_I + 0.01\Sigma\sigma_R^+ + 0.69\Sigma\sigma_\alpha; \quad (7)$$
$$S_a = 0.15,\ S_b = 0.07,\ S_c = 0.10,\ S_d = 0.05,\ S_y = 0.23,$$
$$r = 0.986,\ n = 15,$$

whose third term can also be ignored. From Eq. (7) it follows that no conjugation between substituents X and the radical cation center occurs in the $X_3Si^{\cdot}\overset{+}{-}SiX_3$ radical cations of compounds **1**—**15** despite the presence of the lone electron pairs in some of them (compounds **11**—**15**). It is well known that d,n-conjugation between Si and X atoms (the interaction of both the 3d-AO of the Si atom and the σ*-MOs of its bonds with the orbitals of the lone electron pairs of substituent X) occurs in the neutral molecules containing Si—X (X = F, Cl, Br) bonds.[7] The absence of conjugation in $X_3Si^{\cdot}\overset{+}{-}SiX_3$ radical cations (X = F, Cl, Br) is likely explained analogously to the previously considered case (X = H, Alk), *i.e.*, by large $\Delta E = E(Si^{\cdot}\overset{+}{-}Si) - E(n)$ values, where $E(n)$ is the energy of the orbital of the lone electron pair of the X atom, and, hence, by a small $\delta E$ value (see formula (6)).

The following equation is valid for all compounds listed in Table 1:

$$I(Si—Si) = 10.40 + 0.87\Sigma\sigma_I + 0.04\Sigma\sigma_R^+ + 0.69\Sigma\sigma_\alpha; \quad (8)$$
$$S_a = 0.12,\ S_b = 0.06,\ S_c = 0.08,\ S_d = 0.05,\ S_y = 0.20,$$
$$r = 0.988,\ n = 20.$$

It has better statistical characteristics (the lower $S$ value and higher correlation coefficient $r$) compared to those of Eq. (7), despite the presence of phenyl or vinyl substituents in molecules **16**—**20**. As in the case of Eqs. (5) and (7), the coefficient at the third term of Eq. (8) is smaller than the standard deviation (0.04 *vs.* 0.08, respectively). Therefore, the resonance effect of the substituent on the $I$(Si—Si) values can be neglected since it is insignificant compared to the inductive and polarizability effects. At the same time, the presence of conjugation in neutral molecules containing the $R_\pi$—Si—Si fragment, the more so in the case of excess positive charge on the π-system of $R_\pi$, is undoubted (see, *e.g.*, Ref. 23). The virtual absence of conjugation between the substituents and the radical cation center in the $Ph—Si^{\cdot}\overset{+}{-}Si$ and $H_2C{=}CH—Si^{\cdot}\overset{+}{-}Si$ fragments can be explained, as for other substituents considered above, by unfavorable energy factors. From the data shown in Fig. 1 it follows that for neutral molecules the energy difference $\Delta E = E(Si—Si) - E(\pi)$ between the interacting MOs is small (here, $E(\pi)$ is the energy of the π-MO either in $C_6H_5$ or $H_2C{=}CH$), whereas the mixing energy $\delta E$ (a characteristic of conjugation, see Eq. (6)) is rather high. For radical cations, the corresponding differences $\Delta E = E(Si^{\cdot}\overset{+}{-}Si) - E(\pi)$ are much larger, whereas the $\delta E$ values are smaller, so the conditions for conjugation are less favorable.

Neglecting the resonance effect, we get instead of Eq. (8)

$$I(Si—Si) = 10.37 + 0.86\Sigma\sigma_I + 0.70\Sigma\sigma_\alpha; \quad (9)$$
$$S_a = 0.10,\ S_b = 0.04,\ S_c = 0.04,\ S_y = 0.20,$$
$$r = 0.988,\ n = 20.$$

The standard deviations $S_a$, $S_b$, and $S_c$ become somewhat smaller compared to those of Eq. (8), which again confirms the absence of conjugation between substituents X and the radical cation center in $X_3Si^{\cdot}\overset{+}{-}SiX_3$ systems.

Equation (9) can be used to assess the $I$(Si—Si) values for the $X_3Si—SiX_3$ compounds with known values of $\sigma_I$ and $\sigma_\alpha$ constants of substituents X. We used dependence (9) in the form

$$I(Si—Si) = I_0 + In + P \quad (10)$$

for calculating the inductive and polarizability contributions ($In = 0.86\Sigma\sigma_I$ and $P = 0.70\Sigma\sigma_\alpha$, respectively) to the changes in the $I$(Si—Si) values of molecules **1**—**20**. The $In$ and $P$ contributions are, respectively, equal to 48% and 52%, *i.e.*, the inductive and polarizability effects of substituents commensurably affect the $I$ values of compounds **1**—**20**. Hence, Koopmans approximation (1), which ignores the polarizability contribution to the $I$ value, is not valid for the compounds under study.

Using relationship (3), one can explain the large $P$ contribution (52%) to the $I$ value. This contribution decreases inversely proportionally to the fourth degree of the distance between the charge and the induced dipole moment. If (i) the unpaired electron (and, hence, the positive charge) in the radical cation particle is delocalized and (ii) the positive charge is partly compensated due to conjugation with the substituent, the $P$ contribution is relatively small. For instance, $P = 12\%$ for the series of $^{\cdot+}PhX$ radical cations.[12] In $X_3Si^{\cdot}\overset{+}{-}SiX_3$ systems, the radical cation center is localized on the $Si^{\cdot}\overset{+}{-}Si$ fragment that is not conjugated with substituents X. For this reason, the $P$ contribution increases to 52%.

## References

1. R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359.
2. C. G. Pitt, in *Homoatomic Rings, Chains and Macromolecules of Main-Group Elements*, Ed. A. L. Rheingold, Elsevier, Amsterdam, 1977, 203.
3. H. Bock and B. Solouki, in *The Chemistry of Organic Silicon Compounds*, Eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1989, Pt. 1, 555.
4. H. Bock and B. Solouki, *Chem. Rev.*, 1995, **95**, 1161.
5. Y. Apeloig and D. Danovich, *Organometallics*, 1996, **15**, 350.
6. A. Modelli, D. Jones, L. Favaretto, and G. Distefano, *Organometallics*, 1996, **15**, 380.
7. A. N. Egorochkin, *Usp. Khim.*, 1992, **61**, 1092 [*Russ. Chem. Rev.*, 1992, **61**, 600 (Engl. Transl.)].
8. A. N. Egorochkin and G. A. Razuvaev, *Usp. Khim.*, 1987, **56**, 1480 [*Russ. Chem. Rev.*, 1987, **56**, 846 (Engl. Transl.)].

9. A. N. Egorochkin, G. A. Razuvaev, and M. A. Lopatin, *J. Organomet. Chem.*, 1988, **344**, 49.
10. A. N. Egorochkin, S. E. Skobeleva, E. T. Bogoradovsky, and T. P. Zubova, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1041 [*Russ. Chem. Bull.*, 1994, **43**, 976 (Engl. Transl.)].
11. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1626 [*Russ. Chem. Bull.*, 1997, **46**, 1549 (Engl. Transl.)].
12. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1481 [*Russ. Chem. Bull.*, 1998, **47**, 1436 (Engl. Transl.)].
13. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2434 [*Russ. Chem. Bull.*, 1998, **47**, 2352 (Engl. Transl.)].
14. A. N. Egorochkin, M. G. Voronkov, S. E. Skobeleva, T. G. Mushtina and O. V. Zderenova, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 25 [*Russ. Chem. Bull.*, 2000, **49**, 26 (Engl. Transl.)].
15. V. I. Nefedov and V. I. Vovna, *Elektronnaya struktura organicheskikh i elementoorganicheskikh soedinenii* [*The Electronic Structure of Organic and Organoelement Compounds*], Nauka, Moscow, 1989 (in Russian).
16. V. F. Traven', R. West, V. F. Donyagina, and B. I. Stepanov, *Zh. Obshch. Khim.*, 1975, **45**, 824 [*J. Gen. Chem. USSR*, 1975, **45** (Engl. Transl.)].
17. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
18. V. I. Nefedov and V. I. Vovna, *Elektronnaya struktura khimicheskikh soedinenii* [*The Electronic Structure of Chemical Compounds*], Nauka, Moscow, 1987 (in Russian).
19. S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1984, **106**, 277.
20. P. D. Pacey and Q.-T. N. Tan, *J. Phys. Chem.*, 1995, **99**, 17729.
21. R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1987, **16**, 1.
22. D. G. J. Sautherland, J. Z. Xiong, Z. Liu, T. K. Sham, G. M. Bancroft, and K. M. Baines, *Organometallics*, 1994, **13**, 3671.
23. A. N. Egorochkin, *Usp. Khim.*, 1984, **53**, 772 [*Russ. Chem. Rev.*, 1984, **53**, 445 (Engl. Transl.)].

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