

Effects of *ortho*-substituents in S_E1 protonolysis of phenylmercuric chloride

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ABSTRACT: The kinetics of the reactions of *o*-substituted phenylmercuric chlorides, *o*-RC₆H₄HgCl (R = CH₃, H, C₂H₅O, CH₃O, C₆H₅, F, COOC₂H₅, Cl, Br, CF₃, NO₂), with hydrochloric acid in 80% aqueous dioxane in the presence of NaI were studied. The reactions are of the first order. The rate constant at 40°C decreases in the order of R: CH₃ > H > C₂H₅O > CH₃O > C₆H₅ > F > COOC₂H₅ > Cl > Br > CF₃ > NO₂. The analysis of effects of those *o*-substituents is carried out through multiple regression of log k/k_H with the corresponding inductive substituent constants σ_I and the various resonance substituent constants σ_R^0 , $\sigma_R(BA)$, σ_R^+ , σ_R^- and σ_x , and the corresponding Swain–Lupton field effect constant \mathfrak{F} and resonance effect constant \mathfrak{R} . The results showed that *o*-substituent intramolecular coordination with the neighbor mercury (field effect) is the main effect in effects of *o*-substituents on rate of the S_E1 protonolysis. Copyright © 2007 John Wiley & Sons, Ltd.

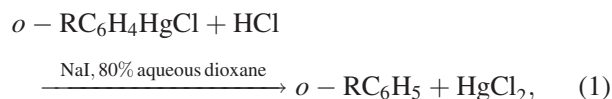
KEYWORDS: kinetics; *o*-substituted phenylmercuric chlorides; neighbor mercury; S_E1 protonolysis

INTRODUCTION

Among the electrophilic substitution reactions investigated with organomercury compounds a larger number follow the S_E2 mechanism.¹ Few examples of kinetic evidence for S_E1 reactions exist at present. In general, the effects of *o*-substituents on reaction rate, including electronic inductive, resonance, steric, and field effects, are more complex than that of *p*- or *m*-substituents, hence the investigations on effects of *o*-substituents are rather few. In recent years, however, the multiple regression on appropriate parameters becomes possible in isolation of a blend of *o*-substituent effects. This approach has been successful in our earlier research on the effects of *o*-substituents in S_E2 protonolysis.² In order to get revealing information about the effects of *o*-substituents in S_E1 protonolysis, we have studied the kinetics of the reactions of *o*-substituted phenylmercuric chlorides, *o*-RC₆H₄HgCl (R = H, CH₃, CH₃O, C₂H₅O, CF₃, COOC₂H₅, C₆H₅, Cl, Br, F, NO₂), with hydrochloric acid in the presence of sodium iodide in 80% aqueous dioxane.

RESULTS

The observed reactions of *o*-substituted phenylmercuric chlorides with HCl in 80% aqueous dioxane catalyzed by NaI are described by Eqn (1):



where R = H, CH₃, CH₃O, C₂H₅O, CF₃, COOC₂H₅, C₆H₅, Cl, Br, F, and NO₂.

The overall order of reactions equal to one was found by linear regression of $\ln C_0/(C_0 - X)$ versus time t . The results for the reactions at 40°C and the reactions of *o*-fluorophenylmercuric chloride at various temperatures are depicted in Figures 1 and 2, respectively.

The rate constants, k_1 , were determined graphically from Eqn (2):

$$k_1 = \frac{1}{t} \ln \frac{C_0}{C_0 - X} \quad (2)$$

where C_0 and X represent the initial and disappeared concentration of the reactant at the reaction time t , respectively. The experiments were repeated several times so that the relative precision, σ_{rel} , falls in all cases below 4.5%.

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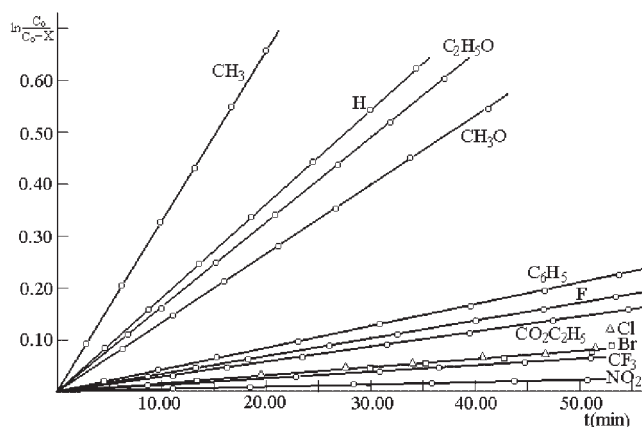


Figure 1. The reactions of *o*-XC₆H₄HgCl with HCl catalyzed by NaI in 80% aqueous dioxane at 40°C

According to the Arrhenius equation (Eqn 3):

$$k = A \cdot e^{-E/RT} \quad (3)$$

The energies of activation, E , for the protonolysis were obtained from the linear regression of $\log k_1$ versus $1/T$. The frequency factor, $\ln A$, was also calculated. The entropy of activation, ΔS^\ddagger , was obtained from Eqn (4):

$$\ln k = \ln \left(\frac{RT}{Nh} \right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (4)$$

where $\Delta H^\ddagger = E - RT$, and other symbols have their usual significance. The values of k_1 , E , $\ln A$ and ΔS^\ddagger for the reactions of *o*-RC₆H₄HgCl (R = F, CF₃) with HCl at various temperatures in 80% aqueous dioxane are given in Table 1, and the values of k_1 and their relative precision, σ_{rel} , for the reactions of *o*-RC₆H₄HgCl (R = H, CH₃, CH₃O, C₂H₅O, CF₃, COOC₂H₅, C₆H₅, Cl, Br, F, NO₂) at 40°C in 80% aqueous dioxane are summarized in Table 2.

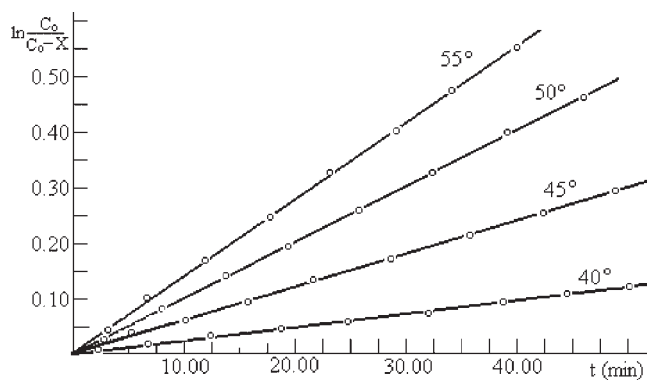


Figure 2. The reactions of *o*-FC₆H₄HgCl with HCl catalyzed by NaI in 80% aqueous dioxane at various temperatures

Table 1. Rate constants k_1 and thermodynamic parameters for the NaI-catalyzed reaction of *o*-R-C₆H₄HgCl (R = F, CF₃) with HCl in 80% aqueous dioxane (molar ratio [ArHgCl]/[NaI] = 1:7; [ArHgCl] = [HCl] = 3.875 · 10⁻³ mol L⁻¹)

R	T/°C	$k_1 \cdot 10^5 \text{ s}^{-1}$	σ_{rel} (%)	E kJ mol ⁻¹	ln A	ΔS_{40}^\ddagger J mol ⁻¹ K
F	40.0	5.78	3.8	92.06	25.60	-40.83
	45.0	10.00	3.3			
	50.0	17.00	3.9			
	55.0	23.67	4.3			
CF ₃	40.0	2.08	4.1	70.30	16.22	-118.80
	45.0	3.18	3.1			
	50.0	4.67	3.8			
	55.0	7.17	4.2			

DISCUSSION

Inductive and resonance effects of *o*-substituents on the rate of reactions

In general, the main approaches to understanding the effects of substituents include attempts to specify quantitatively the polar effect and then to draw inferences about the contribution of other factors. In recent years, a more complete analysis through multiple regression on appropriate parameters has become possible in some cases. In Table 3, we have summarized the values of $\log k/k_{\text{H}}$ at 40°C in 80% aqueous dioxane together with the corresponding inductive substituent constants, σ_{I} , the various resonance substituent constants σ_{R}^0 , σ_{R} (BA), σ_{R}^+ , σ_{R}^- , σ_{x} , the corresponding Swain–Lupton field effect constant, \mathfrak{F} , and resonance effect constant, \mathfrak{R} (Ref. 3, pp. 157–158), to facilitate ready comparison. The regression of $\log k/k_{\text{H}}$ with σ_{I} and σ_{R} shows the dual-parameter equation (Eqn 5)

$$\log \frac{k}{k_{\text{H}}} = \rho_{\text{I}} \sigma_{\text{I}} + \rho_{\text{R}} \sigma_{\text{R}} \quad (5)$$

fits the reaction series.

Table 2. Rate constants of the reactions of *o*-RC₆H₄HgCl with HCl(NaI) at 40°C in 80% aqueous dioxane (molar ratio [ArHgCl]/[NaI] = 1:7; [ArHgCl] = [HCl] = 3.875 · 10⁻³ mol L⁻¹)

R	$k_1 \cdot 10^5 \text{ s}^{-1}$	σ_{rel} (%)	R	$k_1 \cdot 10^5 \text{ s}^{-1}$	σ_{rel} (%)
C ₂ H ₅ O	27.30	2.1	F	5.78	3.8
CH ₃ O	22.20	3.0	Cl	2.74	2.2
CH ₃	54.78	1.9	Br	2.43	2.5
H	30.05	1.6	CF ₃	2.08	4.1
C ₆ H ₅	7.07	4.1	NO ₂	0.70	1.9
CO ₂ C ₂ H ₅	4.85	2.3			

Table 3. Rate constants of the reactions of *o*-RC₆H₄HgCl with HCl(NaI) at 40 °C in 80% aqueous dioxane and the corresponding substituent constants³

R	log <i>k</i> / <i>k</i> _H	σ _I	σ _R ⁰	σ _R (BA)	σ _R ⁺	σ _R ⁻	σ _x	ℑ	ℜ
C ₂ H ₅ O	-0.046							0.61	-1.72
CH ₃ O	-0.131	0.26	-0.41	-0.61	-1.02	-0.45	0.44	0.54	-1.68
CH ₃	0.262	-0.05	-0.10	-0.11	-1.25	-0.11	0.17	-0.01	-0.41
H	0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C ₆ H ₅	-0.628	0.10	-0.11	-0.11	-0.30	-0.04		0.25	-0.37
CO ₂ C ₂ H ₅	-0.793	0.31	0.15	0.14	0.14	0.34	0.19	0.47	0.67
F	-0.715	0.15	-0.34	-0.45	-0.57	-0.45	0.52	0.74	-0.60
Cl	-1.043	0.47	-0.21	-0.23	-0.23	-0.35	0.28	0.72	-0.24
Br	-1.093	0.45	-0.16	-0.19	-0.19	-0.30		0.72	-0.18
CF ₃	-1.159	0.41	0.13	0.08	0.08	0.17	0.17	0.64	0.76
NO ₂	-1.62	0.64	0.19	0.15	0.15	0.46	0.40	1.00	1.00

In the case of $\sigma_R = \sigma_R^0$, the fitted equation is expressed as Eqn (6)

$$\log \frac{k}{k_H} = -2.491\sigma_I - 0.277\sigma_R^0 \quad (6)$$

The equation is significant at $\alpha = 0.01$ ($F = 16.1687 > F_c \langle 5, 4; 0.01 \rangle = 15.52$). The coefficient of determination R^2 and the adjusted coefficient of determination R_{adj}^2 are 0.8821 and 0.7966, respectively.

In the case of $\sigma_R = \sigma_R(\text{BA})$, the fitted equation is expressed as Eqn (7)

$$\log \frac{k}{k_H} = -2.5205\sigma_I - 0.2648\sigma_R(\text{BA}) \quad (7)$$

The equation is significant at $\alpha = 0.01$ ($F = 16.6851 > F_c \langle 5, 4; 0.01 \rangle = 15.52$). The coefficient of determination R^2 and the adjusted coefficient of determination R_{adj}^2 are 0.8266 and 0.8018, respectively.

In the case of $\sigma_R = \sigma_R^+$, the fitted equation is expressed as Eqn (8)

$$\log \frac{k}{k_H} = -2.5048\sigma_I - 0.1419\sigma_R^+ \quad (8)$$

The equation is significant at $\alpha = 0.01$ ($F = 17.2173 > F_c \langle 5, 4; 0.01 \rangle = 15.52$). The coefficient of determination R^2 and the adjusted coefficient of determination R_{adj}^2 are 0.8310 and 0.8069, respectively.

In the case of $\sigma_R = \sigma_R^-$, the fitted equation is expressed as Eqn (9)

$$\log \frac{k}{k_H} = -2.4666\sigma_I - 0.1762\sigma_R^- \quad (9)$$

The equation is significant at $\alpha = 0.01$ ($F = 16.0548 > F_c \langle 5, 4; 0.01 \rangle = 15.52$). The coefficient of determination R^2 and the adjusted coefficient of determination R_{adj}^2 are 0.8210 and 0.7954, respectively.

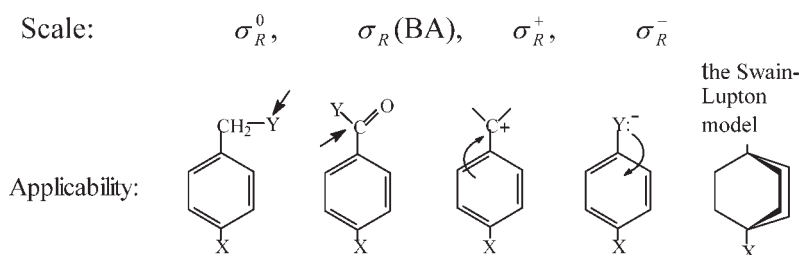
For the above four equations (Eqns 6–9) the ratios (ρ_R/ρ_I) of their two regression coefficients are 0.1113, 0.1051, 0.0567, and 0.0714, respectively. This indicates that for the studied reaction series the inductive effects of the *o*-substituents are much more significant than their resonance effects.

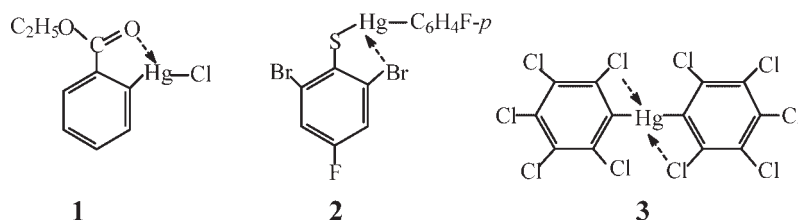
For the dual-parameter equation (Eqn 5), the applicability of four resonance substituent constants, σ_R^0 , $\sigma_R(\text{BA})$, σ_R^+ , σ_R^- , and the model of the Swain–Lupton equation (Eqn 10), is obvious from Scheme 1.

In Swain–Lupton model, resonance effect is discounted. If rate data for the studied reaction series fitted Swain–Lupton equation (Eqn 10), the inductive effects of the *o*-substituents being dominant would be confirmed.

$$\log \frac{k}{k_H} = f\mathfrak{S} + r\mathfrak{R} \quad (10)$$

The regression of $\log k/k_H$ with \mathfrak{S} and \mathfrak{R} shows the Swain–Lupton Eqn (10) fits the reaction series. The fitted

**Scheme 1.**



Scheme 2.

equation is expressed as Eqn (11)

$$\log \frac{k}{k_H} = -1.3746\sigma - 0.3612\sigma_x \quad (11)$$

The equation is significant at $\alpha = 0.01$ ($F = 43.4473 > F_c(5, 5; 0.01) = 10.97$). The coefficient of determination, R^2 and the adjusted coefficient of determination, R_{adj}^2 are 0.9157 and 0.9052, respectively. The ratios (*r/f*) of their two regression coefficients are 0.2628.

Among those five dual-parameter equations (Eqns 6–9 and 11), Eqn (11) has the largest coefficient of determination R^2 and adjusted coefficient of determination R_{adj}^2 . The best fit of rate data for the studied reaction series to the Swain–Lupton parameters further indicates that the inductive effects of the *o*-substituents are dominant.

Field effects of *o*-substituents on the rate of reaction

It is known that the inductive parameter, σ_I , is an operational measure of the non-resonance effect and is almost certainly a blend of ‘through-bond’ (true inductive or electronegative) and ‘through-space’ (field) effects, the later predominating (Ref. 3, p. 163) The σ_x scale (Table 3) differs significantly from the σ_I scale, the differences being related to the field effect. To confirm that the field effects are predominant, it is necessary to fit the $\log k/k_H$ data for the reaction series to the dual-parameter equation

(Eqn 12).

$$\log \frac{k}{k_H} = \rho_I \sigma_I + \rho_x \sigma_x \quad (12)$$

The regression of $\log k/k_H$ with σ_I and σ_x shows the dual-parameter Eqn (12) fits the reaction series. The fitted equation is expressed as Eqn (13)

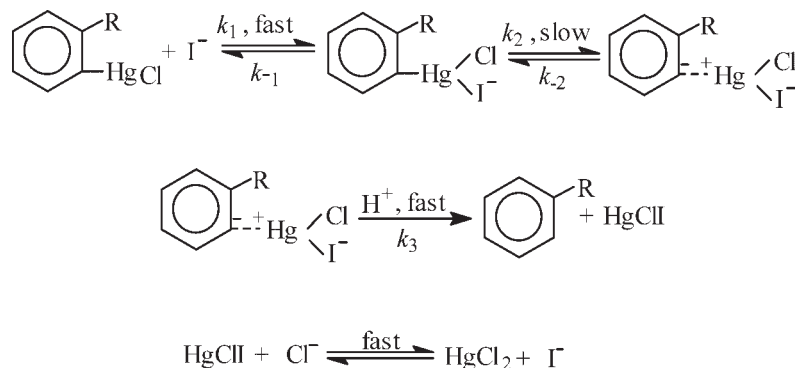
$$\log \frac{k}{k_H} = -2.5065\sigma_I - 0.1032\sigma_x^0 \quad (13)$$

The equation is significant at $\alpha = 0.05$ ($F = 14.2882 > F_c(4, 3, 0.05) = 9.12$). The coefficient of determination R^2 and the adjusted coefficient of determination R_{adj}^2 are 0.8511 and 0.8213, respectively. This significant fit indicates that the field effects of the *o*-substituents are indeed predominant.

For the reaction series, the field effects are resulted from the intramolecular coordination of *p*- or π -electron pairs of *o*-substituents with vacant orbital of neighboring mercury atoms. This coordination was confirmed by our early research on the crystal structure, UV and MS spectra of *o*-ethoxycarbonyl-phenylmercuric chloride⁴ (**1** in Scheme 2), and was also reported in literature (**2**, **3** in Scheme 2).⁵

Effects of *o*-substituents on the rate of S_E1 protonolysis

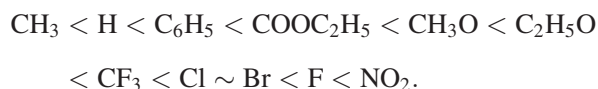
A mechanism (Scheme 3) was proposed for this monomolecular protonolysis in our earlier report.²



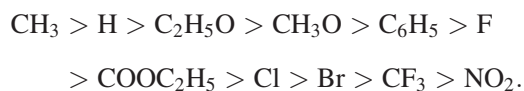
Scheme 3.

Effects of solvent, kinetic isotope effect, effects of HCl, and results of the first order kinetics entirely accord with the proposed mechanism.⁶ In accordance with the proposed mechanism, the slow ionization of the C—Hg bond of the complex $[o\text{-RC}_6\text{H}_4\text{HgClI}]^-$ determines the reaction rate. In this case, there might be many effects of *o*-substituents on the ionization of the C—Hg bond, such as electronic inductive, resonance, steric, and field effects. However, among them there would exist main one. The different main effect would cause obviously quite different results in reaction rate. If electronic inductive effects (true inductive or electronegative), for example, were the main effects, the rate of ionization of the C—Hg bond would be increased by electron-withdrawing substitutes; however, if field effects (the *o*-substituent intramolecular coordination with the neighbor mercury) were the main effects, the rate of ionization of the C—Hg bond would be decreased by the substitutes with strong coordination ability because of the following two obvious reasons. One reason is that this intramolecular coordination would form a five- or four-ring containing the C—Hg bond, this formed ring would make the ionization of the C—Hg bond more difficult than the open link chain. In the case of *o*-ethoxycarbonylphenylmercuric chloride (**1** in Scheme 2), for example, the five-ring formed by intramolecular coordination make the C—Hg bond length (2.06 Å) shorter than that (2.16 Å of its covalent bond).⁴ The other reason is that this intramolecular coordination would obstruct the coordination of mercury with I^- , decreasing the nucleophilic catalytic action of I^- on increasing the reactivity of the C—Hg bond. This nucleophilic catalytic action of I^- on increasing the reactivity of the C—Hg bond has been reported and confirmed in previous papers.²

It is conformed by above analysis through multiple regression on appropriate parameters that *o*-substituent intramolecular coordination with neighbor mercury is the main effect. From Table 3 it is also obvious that the values of Swain–Lupton field parameters increase for the substituents in the order



The values (Table 2) of the reaction rate constants for the studied reaction series decreased in the order



The later series roughly correlates with the former series on the whole. The other little difference in the two series could be explained by the proposed mechanism (Scheme 1). The values of Swain–Lupton field parameters ρ of F, Cl, and Br, for example, are very close to each

other; they are 0.72, 0.72, and 0.74, respectively (see Table 3). In this case, their inductive effects would play a role in their reaction rate, hence the values of their reaction rate constants decreased in the order: $\text{F} > \text{Cl} > \text{Br}$. The steric effects of C_6H_5 on obstructing the coordination of neighboring position mercury with I^- would be responsible for its little slower rate. In the cases of COOC_2H_5 and CF_3 , the intramolecular coordination would form a five-ring containing the C—Hg bond. This formed five-ring is more stable than other four-rings, and would make the ionization of the C—Hg bond more difficult. As for the order of $\text{C}_2\text{H}_5\text{O}$ and CH_3O , the larger ethyl in $\text{C}_2\text{H}_5\text{O}$ would obstruct the intramolecular coordination of oxygen with mercury, and as a result, the rate of *o*- $\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{HgCl}$ is faster than that of *o*- $\text{CH}_3\text{OC}_6\text{H}_4\text{HgCl}$.

EXPERIMENTAL SECTION

o-Trifluoromethylphenylmercuric chloride, mp 132.5–132.7 °C, was prepared from *o*-trifluoro- methylnitrobenzene, and *o*-fluorophenylmercuric chloride, mp 151.5–152 °C, was prepared from *o*-chloronitrobenzene.⁷ *o*-Ethoxycarbonylphenylmercuric chloride, mp 150–151 °C, *o*-methylphenylmercuric chloride, mp 142–143 °C, phenylmercuric chloride, mp 258.5 °C, *o*-methylphenylmercuric chloride, mp 143 °C, *o*-chlorophenylmercuric chloride, mp 149 °C, *o*-bromo-phenylmercuric chloride, mp 158 °C, *o*-nitrophenylmercuric chloride, mp 186–187 °C, *o*-methoxyphenylmercuric chloride, mp 178 °C, *o*-ethoxyphenylmercuric chloride, mp 114–114.5 °C, and *o*-biphenylmercuric chloride, mp 167–168 °C were prepared and purified using the literature procedure.⁸ Sodium iodide was purchased and purified by being recrystallized from distilled water and dewatered at 160 °C for 24 h. Hydrochloric acid, special pure grade, was used directly as obtained. Dioxane, analytically pure, was purchased and purified by hydrochloric acid, potassium hydrate, then distilled from sodium, bp. 100–100.8 °C, n_D^{25} 1.4200. Methods of kinetic measurements are the same as that shown in our earlier paper.²

Acknowledgements

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REFERENCES

1. Reutov A. *Tetrahedron* 1978; **34**: 2827–2855.
2. Wang Y, Wu Y. *Collect. Czech. Chem. Commun.* 2000; **65**: 35–46.

3. Isaacs NS. In *Physical Organic Chemistry*. New York: John Wiley & Sons, Inc., New York. 1987; pp. 157–163.
4. (a) Pan Z, Wei X, Shao M, Wu Y, Chen Y, Wang Y, Hu H. *Huaxue Xuebao* 1985; **83**: 801; (b) Wu Y, Chen Z, Zhang X, Zhang Z, Liu Y, Ni J. *Chem. J. Chin Univ* 1983; **4**: 335; (c) Chen Z, Wu Y, Zhang X, Chen R, Hu H. *Acta Chimica Sinica* 1983; **41**: 57–66.
5. (a) Kravtsov DN, Kvasov BA, Golovchenko LS, Rokhlina EM, Fedin EI. *J. Organomet. Chem.* 1972; **39**: 107; (b) Bregadge VI, Babushkina TA, Okhibystin O, Yu, Syomin GK. *Teor. Eksp. Khim.* 1967; **3**: 547–555
6. beletskaya IP, Meicki LE, Reutov OA. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1965; **2**: 240–249.
7. Wang Y, Wu Y. *Syn. React. Inorg. Metal-org. Chem.* 1998; **28**(9): 1535–1540.
8. Hu H, Ni J, Gao J. *Acta Chimica Sinica* 1979; **37**: 9–14.