ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 12, pp. 1765–1772. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © L.I. Goryunov, N.M. Romanova, G.S. Zhilovskii, V.D. Shteingarts, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 12, pp. 1765–1771.

Arene Complexes of Transition Metals in Reactions with Nucleophilic Reagents: XXX.* Reaction of π-Halomesitylene [Tetramethyl(ethyl)cyclopentadienyl]rhodium(II) Complexes with Anions Derived from CH Acids

L. I. Goryunov[a], N. M. Romanova[a,b], G. S. Zhilovskii[c], and V. D. Shteingarts[a,c]

[a] *Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia*
e-mail: shtein@nioch.nsc.ru

[b] *Novosibirsk State Pedagogical University, Novosibirsk, Russia*

[c] *Novosibirsk State University, Novosibirsk, Russia*

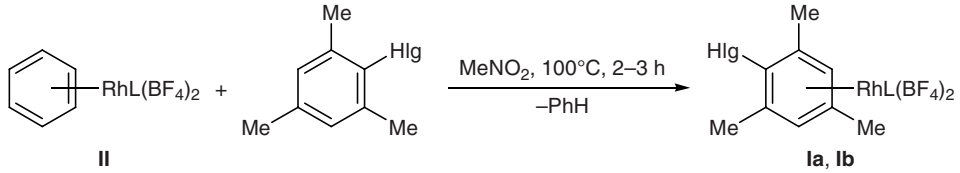
Received November 22, 2006; revised July 12, 2007

Abstract—Reactions of fluoro- and chloromesitylene π-complexes $[(\eta^6\text{-1-Hlg-2,4,6-Me}_3C_6H_2)(\eta^5\text{-}C_5EtMe_4)Rh](BF_4)_2$ (Hlg = F, Cl) with diethyl malonate anion in THF or acetone-d_6 at 20°C initially (within the first 5–30 min) involve nucleophile addition at unsubstituted carbon atom in the arene ligand with formation of π-cyclohexadienyl complexes $\{[\eta^5\text{-1-(EtOCO)}_2\text{CH-1-H-3-Hlg-2,4,6-Me}_3C_6H_2](\eta^5\text{-}C_5EtMe_4)Rh\}(BF_4)$. The subsequent replacement of the halogen atom yields $\{[\eta^6\text{-1-(EtOCO)}_2\text{CH-2,4,6-Me}_3C_6H_2](\eta^5\text{-}C_5EtMe_4)Rh\}(BF_4)_2$, where the arene ligand is readily withdrawn from π-coordination by the action of chloride ion or the solvent. Dimethyl mesitylmalonate was isolated in 76% yield. Likewise, the reactions with anions derived from malononitrile and ethyl cyanoacetate gave 25–38% of the corresponding derivatives 1-R-2,4,6-$Me_3C_6H_2$ where R = $(NC)_2CH$ or EtOCO(NC)CH.

DOI: 10.1134/S1070428007120056

Activation of haloarenes via π-coordination to tricarbonylchromium, cyclopentadienyliron, and cyclopentadienylruthenium complexes is widely used in reactions leading to formation of new C_{arom}–C bonds as a result of nucleophilic replacement of the halogen atom (fluorine or chlorine) by anions derived from CH acids [2–4]. Arenes modified in such a way are withdrawn from the π-complexes containing $Cr(CO)_3$ or FeC_5H_5 fragments by oxidation or pyrolysis which leads to decomposition of the complexes. Moriarty et al. [3] succeeded in replacing the RuC_5H_5 fragment by the action of acetonitrile under irradiation and obtained the complex $(MeCN)_3RuC_5H_5(PF_6)$ which can be used repeatedly [3]. Dicationic cyclopentadienylrhodium fragments exert a powerful activating effect, which is comparable with the overall effect of three nitro groups in the *ortho* and *para* positions with respect to halogen; in addition, these fragments are capable of readily exchanging π-coordinated arene ligands. As a result, catalytic aromatic nucleophilic substitution of halogen atoms by alkoxy groups has become possible [5]. Therefore, synthesis of π-halo-

Scheme 1.



II **Ia**, **Ib**

L = C_5EtMe_4, Hlg = F (**a**, 90%), Cl (**b**, 93%).

* For communication XXIX, see [1].

arene rhodium(III) complexes and their reactions with CH acid anions attract interest.

In the present work we examined reactions of 1-fluoro- and 1-chloro-2,4,6-trimethylbenzene complexes $[(\eta^6\text{-1-Hlg-2,4,6-Me}_3\text{C}_6\text{H}_2)(\eta^5\text{-C}_5\text{EtMe}_4)\text{Rh}](\text{BF}_4)_2$ as model substrates with anions derived from diethyl malonate, malononitrile, and ethyl cyanoacetate. These complexes were synthesized previously from the benzene-containing analog $[(\eta^6\text{-C}_6\text{H}_6)(\eta^5\text{-C}_5\text{EtMe}_4)\text{Rh}](\text{BF}_4)_2$ (**II**) via ligand exchange, and complex **Ia** was generated only *in situ* [5, 6]. We have isolated complex **Ia** in 90% yield according to Scheme 1 under the conditions analogous to those reported for the synthesis of individual complex **Ib** [6].

Several procedures have been proposed for the preparation of benzene complex **II**. These procedures are based on generation of $[(\eta^5\text{-C}_5\text{EtMe}_4)\text{Rh}]^{2+}$ dication via elimination of chloride ions from the complex $[(\eta^5\text{-C}_5\text{EtMe}_4)\text{RhCl}_2]_2$ by the action of strong acids (such as CF_3COOH [7] or H_2SO_4 [8]) or anhydrous silver salts ($AgBF_4$ [9] or $AgBF_4\cdot C_6H_6$ [10]). In the present work we used $AgBF_4$ complex with 1,4-dioxane; this complex is nonhygroscopic, and it can be stored for several months in the dark at room temperature [11]. Complex **II** was thus obtained in a fairly high yield (74%). Taking into account simplicity of the preparation of the reagent and complex **II**, our modification may be regarded as convenient and efficient.

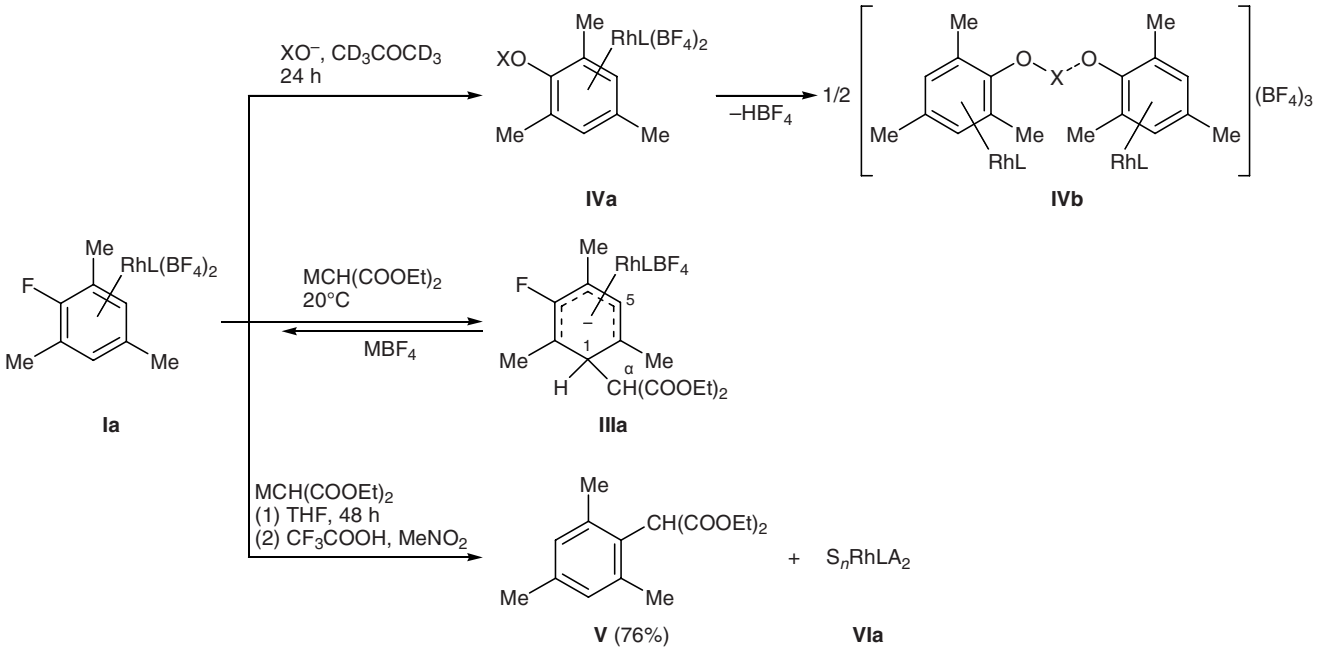
π-Haloarene rhodium complexes **Ia** and **Ib** were examined by ^{13}C NMR spectroscopy (see table). The given data are very consistent with those reported previously for benzene rhodium(III) complexes [12] and the data obtained in the present work for the mesitylene π-complex $[(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)(\eta^5\text{-C}_5\text{EtMe}_4)\text{Rh}](\text{BF}_4)_2$ (**Ic**). Signals from carbon atoms in the methyl and ethyl groups of the pentaalkylcyclopentadienyl fragment are observed at δ_C 8.5–10.8, 10.8–12.8 (CH_3) and 17.4–18.9 ppm (CH_2). Carbon nuclei in the cyclopentadienyl ring resonate at δ_C 109.5–114.8 (C^2, C^5), 108.4–113.8 (C^3, C^4), and 111.8–117.0 ppm (C^1); the downfield signal belongs to the carbon atom bearing ethyl group. The C^1–C^5 signals are split into doublets due to coupling with rhodium, $J(^{103}\text{Rh}–^{13}\text{C}) = 7–9$ Hz. Aromatic carbon atoms give rise to signals in the regions δ_C 105.7–107.6 (CH, cf. δ_C 106.6 ppm for benzene complex **II**) and 113.0–123.2 ppm (**C**Me). All aromatic carbon signals are split into doublets with a coupling constant $J(^{103}\text{Rh}–^{13}\text{C})$ of 3–5 Hz, indicating η^6-coordination to the rhodium atom [13]. Methyl carbon atoms in coordinated mesitylene and chloromesitylene and the methyl carbon atom in the *para* position with respect to fluorine in fluoromesitylene are characterized by similar chemical shifts (δ_C 17.4–17.9 ppm), while signals from the *o*-methyl groups in the latter appear in a stronger field (δ_C 12.1 ppm) and are split into doublets due to coupling with fluorine, $J_{CF} = 2$ Hz. The effect of the chlorine atom in the benzene ring of **Ib** on the chemical shift of the adjacent carbon atom (δ_C 122.4 ppm) is comparable with that of methyl group, but no appreciable effect of chlorine on the position of the other aromatic carbon signals is observed. The presence of fluorine atom in complex **Ia** leads to a considerable downfield shift of the C–F carbon signal (δ_C 141.2 ppm) and an appreciable upfield shift of signals from the neighboring carbon atoms (δ_C 113.0 ppm). All aromatic carbon nuclei in complex **Ia** (except for C^4) show coupling with fluorine: $J_{CF} = 285$ (C^1), 17 (C^2, C^6), 6 Hz (C^3, C^5).

^{13}C NMR spectra of complexes $[(\eta^6\text{-(1-X-2,4,6-Me}_3\text{C}_6\text{H}_2)(\eta^5\text{-C}_5\text{EtMe}_4)\text{Rh}](\text{BF}_4)_2$ [**Ia**–**Ic**; X = F (**a**), Cl (**b**), H (**c**)]

Complex no.	^{13}C NMR spectrum, δ_C, ppm ($J_{Rh,C}$, Hz)			
	1-X-2,4,6-$Me_3C_6H_2$	1-Et-C_5Me_4	Et	Me
Ia[a]	141.2 d.d (4) (C^1, J_{CF} = 285), 113.0 d.d (3) (C^2, C^6, J_{CF} = 17), 107.6 t (C^3, C^5, $J_{CF} \approx J_{Rh,C} \approx 6$), 120.7 (4) ($C^4$), 12.1 d (2-$CH_3$, 6-$CH_3$, J_{CF} = 2 Hz), 17.4 (4-CH_3)	112.1 (8) (C^3, C^4), 113.2 (7) (C^2, C^5), 114.7 (8) (C^1)	11.7 (CH_3), 17.6 (CH_2)	8.8, 9.1
Ib[a]	122.4 (4) (C^1), 122.3 (4) (C^2, C^6), 107.1 (5) (C^3, C^5), 120.8 (4) (C^4), 17.7 (2-CH_3, 6-CH_3), 17.5 (4-CH_3)	111.8 (8) (C^3, C^4), 112.9 (8) (C^2, C^5), 114.3 (8) (C^1)	11.5 (CH_3), 17.4 (CH_2)	8.5, 8.8
Ic[b]	123.2 (4) (C^1, C^3, C^5), 105.7 (3) (C^2, C^4, C^6), 17.9 (CH_3)	111.1 (9) (C^3, C^4), 112.2 (7) (C^2, C^5), 113.8 (8) (C^1)	11.9 (CH_3), 17.8 (CH_2)	9.1, 9.4

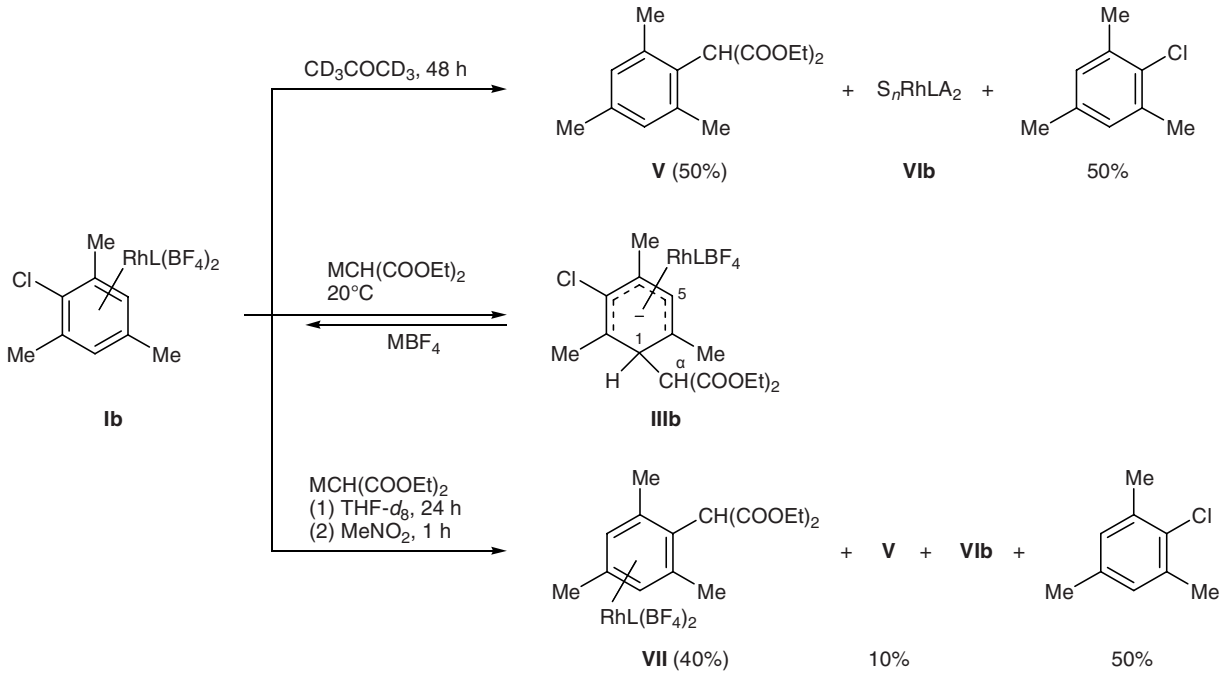
[a] In $MeNO_2$–acetone-d_6.
[b] In $MeNO_2$.

Scheme 2.



L = C_5EtMe_4; M = Li, Na; X = H, D; S is solvent; A = BF_4, $CH(COOEt)_2$.

Scheme 3.

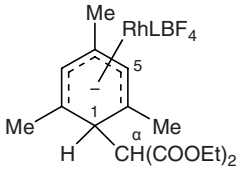


L = C_5EtMe_4; M = Li, Na; S is solvent; A = Cl, BF_4, $CH(COOEt)_2$.

According to the ^1H and ^{19}F NMR data, reactions of complexes **Ia** and **Ib** with $[CH(COOEt)_2]^-$ ion generated from diethyl malonate and MeONa, EtONa, NaH, or LiH initially (within 5–30 min) give {2–6-η-1-*exo*-[bis(ethoxycarbonyl)methyl]-3-fluoro-2,4,6-trimethylcyclohexadienyl}(η^5-tetramethylethylcyclopentadienyl)rhodium(III) (**IIIa**) (Scheme 2) and {2–6-η-1-*exo*-[bis(ethoxycarbonyl)methyl]-3-chloro-2,4,6-trimethyl-

cyclohexadienyl}(η^5-tetramethylethylcyclopentadienyl)rhodium(III) (**IIIb**) (Scheme 3), respectively. Complex **IIIa** displayed the following signals in the ^{1}H NMR spectrum, δ, ppm: 5.41 d (1H, 5-H, J_{HF} = 4 Hz), 3.83 m (1H, 1-H, J_{HH} = 4 Hz), 3.11 d (1H, α-H, J_{HH} = 4 Hz). Likewise, signals at δ 5.47 (s, 1H, 5-H), 3.87 (d, 1H, 1-H, J_{HH} = 4 Hz), and 3.08 ppm (d, 1H, α-H, J_{HH} = 4 Hz) were assigned to complex **IIIb**.

Analogous reaction of mesitylene complex **Ic** with diethyl malonate in the presence of a base gave a mixture of {2,6-η-1-*exo*-[bis(ethoxycarbonyl)methyl]-2,4,6-trimethylcyclohexadienyl}(η^5-tetramethylethylcyclopentadienyl)rhodium(III) tetrafluoroborate (**IIIc**) (70%) and solvate complex **VIa** (30%).



IIIc

The following signals in the ^{1}H NMR spectrum of the product mixture were assigned to complex **IIIc**, δ, ppm: 5.26 s (2H, 3-H, 5-H), 4.08 q (4H, OCH_2, J = 7.0 Hz), 3.63 d (1H, 1-H, J = 5.0 Hz), 2.97 d (1H, α-H, J = 5.0 Hz), 2.35 q (2H, C**H**$_2$CH$_3$, J = 7.5 Hz), 2.26 s (3H, CH_3), 1.94 s (6H, CH_3), 1.92 s (6H, CH_3), 1.18 t (6H, CH_3, J = 7.0 Hz), 1.06 t (3H, CH$_2$C**H**$_3$, J = 7.5 Hz). The ^{1}H NMR parameters of complexes **IIIa**–**IIIc** are very consistent with each other and those reported previously for cyclohexadienyl complexes obtained from acetylacetone or methyl ketone anion and benzene [9] or *p*-xylene [14] pentaalkylcyclopentadienyl rhodium complexes. The ^{19}F NMR spectrum of the product mixture obtained from complex **Ia** contained a signal at δ_F 18.4 ppm (cf. δ_F 36.2 ppm for **Ia**).

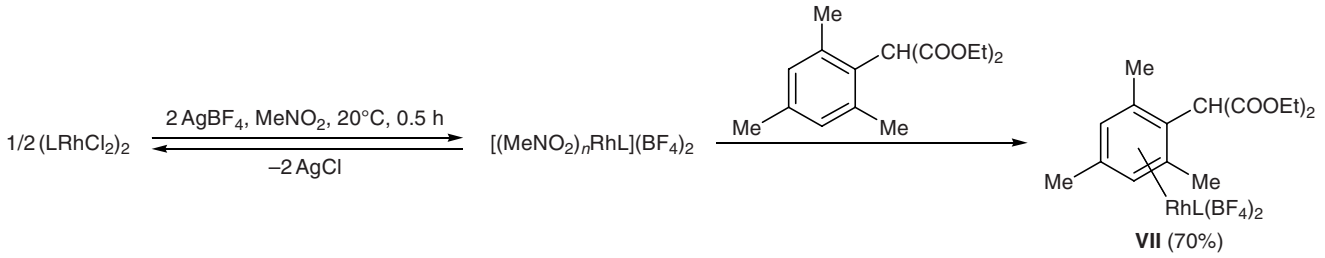
The fraction of **IIIa** in the reaction mixtures in acetone-d_6 or THF was 50 and 80%, respectively. When the reaction mixture in acetone-d_6 was kept for 24 h, dimeric complex **IVb** was obtained (see Experimental), presumably as a result of replacement of the fluorine atom by H(D)O$^-$ anion generated from water present in the solvent. Using tetrahydrofuran as solvent, we isolated diethyl mesitylmalonate (**V**) in 76% yield. Compound **V** was synthesized previously in 65% yield by reaction of ethyl mesitylacetate with diethyl oxalate [15].

According to the ^{1}H NMR spectra of the reaction mixtures, the fraction of complex **IIIb** among the products formed from complex **Ib** and diethyl malonate anion in acetone-d_6 was 50% (Scheme 3). After keeping the mixture for 12–24 h at 20°C, signals of complex **IIIb** disappeared from the spectrum, and the final products were compounds **V** and **VIb** and uncoordinated chloromesitylene. Unlike the reaction with fluoromesitylene complex **Ia**, no 2,4,6-trimethylphenol complex **IV** was detected. A probable reason is higher affinity of the chloromesitylene complex, which is a softer electrophile than its fluorine-containing analog, for relatively soft [CH(COOEt)$_2$]$^-$ nucleophile rather than for hard D(H)O$^-$ species.

Another specificity of the transformation of chloromesitylene complex **Ib** is that the reaction mixture contains chloride ions. The latter are capable of effectively interacting with the metal-containing fragment [(C$_5$EtMe$_4$)Rh]$^{2+}$ with liberation of the arene and formation of solvate complex like **VIb**. The ^{1}H NMR spectrum of the reaction mixture in THF-d_8, recorded in 30 min after mixing the reactants, contained signals of cyclohexadienyl complex **IIIb** whose fraction attained 82%. In addition, initial complex **Ib**, uncoordinated chloromesitylene, and solvate complex **VIb** were present. After 3 h, a large amount of a solid material separated from the reaction mixture. Presumably, this material was [η^6-1-bis(ethoxycarbonyl)methyl-2,4,6-dimethylbenzene](η^5-tetramethylethylcyclopentadienyl)rhodium(III) tetrafluoroborate (**VII**) which (as might be expected) is poorly soluble in THF. When the mixture was kept for 24 h more and nitromethane was added, the precipitate dissolved. In the ^{1}H NMR spectrum of the solution thus formed we observed a singlet at δ 7.36 ppm, which is likely to belong to protons in the aromatic ring of complex **VII**. Its fraction among the products was ~40%, but we failed to isolate it as individual substance because of its transformation into compounds **V** and **VIb**. Treatment of a solution of [(η^5-C$_5$EtMe$_4$)RhCl$_2$]$_2$ in nitromethane with AgBF$_4$ in the presence of excess diethyl mesitylmalonate gave a mixture which contained (according to the ^{1}H NMR data) up to 70% of complex **VII**. Obviously, it was formed according to Scheme 4. Apart from the aromatic proton signal at δ 7.36 ppm, the ^{1}H NMR spectrum of the mixture contained signals at δ 2.4–2.6 and 2.0–2.1 ppm, which are typical of methyl protons in the arene and cyclopentadienyl ligands in rhodium(III) π-complexes [5, 6, 9, 12].

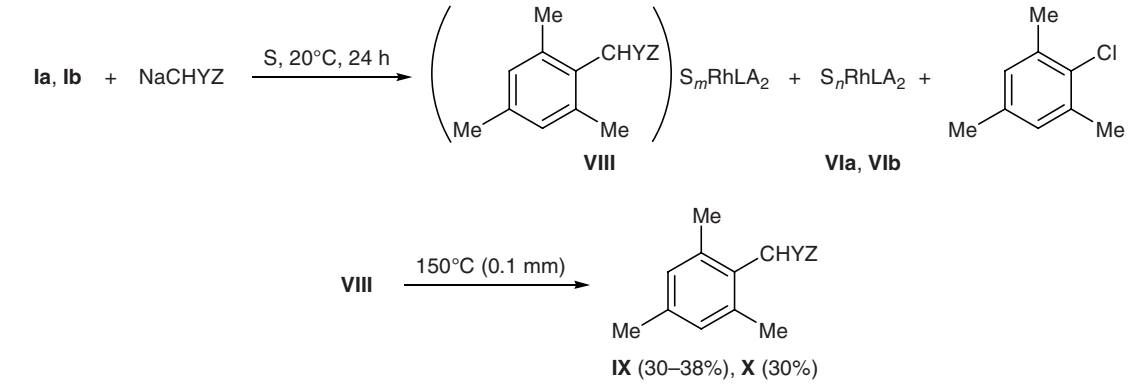
With a view to extend the series of CH acids capable of reacting with complexes **Ia** and **Ib** we examined their reactions with malononitrile in the

Scheme 4.



L = C_5EtMe_4.

Scheme 5.



L = C_5EtMe_4; Hlg = F, Cl; S = CD_3COCD_3, THF; A = BF_4, Cl; **IX**, Y = Z = CN; **X**, Y = CN, Z = COOEt.

presence of sodium carbonate in acetone-d_6 and with ethyl cyanoacetate sodium salt (generated by the action of sodium hydride) in THF. According to the ^{1}H NMR data, these reactions resulted in the formation of uncoordinated halomesitylenes and complexes like **VIII** and **VI** (Scheme 5). The latter displayed signals in the region δ 1.5–1.8 ppm, which are typical of methyl groups in the cyclopentadienyl ligand in rhodium(III) solvate complexes [5, 6, 16]. In this case, no appreciable amounts of cyclohexadienyl complexes analogous to **IIIa** or **IIIb** were formed. Presumably, the reason is that malononitrile and ethyl cyanoacetate (pK_a 11–12 and 9, respectively [17]) are considerably stronger CH acids than diethyl malonate (pK_a 13); therefore, the equilibrium in the formation of complexes like **IIIa** or **IIIb** is displaced almost completely toward initial compounds **Ia** and **Ib**, as it was reported for arene (tricarbonyl)chromium complexes [2].

The isolation of mesitylmalononitrile (**IX**) and ethyl mesityl(cyano)acetate (**X**) was more difficult as compared to diethyl mesitylmalonate, and it required pyrolytic vacuum distillation (see Experimental); their yields were 38 and 25%, respectively. Compound **IX** was prepared previously in 54% yield from iodomesitylene and malononitrile in basic medium in the presence of CuI [18]. Analogous transformations of bromoarenes are characterized by poor yields, while chloroarenes fail to react at all. Compound **X** was synthesized previously from 2,4,6-trimethylbenzonitrile and diethyl carbonate (yield 41%) [19], as well as from bromomesitylene and ethyl cyanoacetate in the presence of Pd complex as catalyst (yield 88%) [20].

Taking into account that the coordination entity [(η^5-C_5EtMe_4)Rh]$^{2+}$ is very stable, it seemed to be possible to recycle it via transformation into the initial complexes. In fact, treatment of solvate complexes **VIb**, formed in the reaction of **Ib** with diethyl malonate anion in THF, with benzene or chloromesitylene with addition of $AgBF_4$ gave complexes **II** (80%) and **Ib** (86%), respectively. Thus we have demonstrated the possibility for repeated use of the activating cyclopentadienylrhodium fragment in the above transformations which can be regarded as occurring in a pseudocatalytic way.

On the whole, our results show prospects in using π-coordination with rhodium(III)-based complexes as a method for activation of haloarenes to reactions with anions derived from CH acids.

EXPERIMENTAL

The NMR spectra were recorded on Bruker WP-200SY (200.13 MHz for ^1H and 188.28 MHz for ^{19}F) and Bruker AM-400 spectrometers (100.61 MHz for ^{13}C). The chemical shifts were measured relative to acetone-d_6 (^1H, δ 2.04 ppm), $MeNO_2$ (^1H, δ 4.29 ppm), $CDCl_3$ (^{13}C, δ_C 76.09 ppm), and C_6F_6 (^{19}F, δ_F 0.0 ppm).

Nitromethane was kept for 24 h over P_2O_5 and distilled twice, a fraction with bp 101°C being collected. Benzene of chemically pure grade was purified by distillation, bp 80°C. Diethyl ether was distilled and dried first over $CaCl_2$ and then over sodium. Diethyl malonate of pure grade was distilled (bp 165°C) and stored over 3-Å molecular sieves. Acetone-d_6 was kept for 48 h over anhydrous potassium carbonate and was distilled under reduced pressure into a receiver containing 3-Å molecular sieves. Tetrahydrofuran and THF-d_8 were purified by treatment with potassium diphenylketyl. Malononitrile of pure grade was purified by chromatography on aluminum oxide using diethyl ether as eluent and was dried by evacuation at a residual pressure of 0.06 mm. Ethyl cyanoacetate was distilled under reduced pressure (0.06 mm). Tris-(1,4-dioxane)silver tetrafluoroborate was prepared according to the procedure reported in [11]. The complexes $[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)(\eta^5\text{-}C_5EtMe_4)Rh](BF_4)_2$ [3] and $[(\eta^6\text{-}1\text{-}Cl\text{-}2,4,6\text{-}Me_3C_6H_2)(\eta^5\text{-}C_5EtMe_4)Rh](BF_4)_2$ [4] were synthesized by known methods.

Complex (Ia). A mixture of 0.915 g (1.82 mmol) of complex **II**, 0.456 g (3.30 mmol) of fluoromesitylene, and 4 ml of nitromethane was heated for 2 h at the boiling point with simultaneous removal of the liberated benzene by distillation. The mixture was diluted with ~5 ml of diethyl ether, and the crystalline product was separated by centrifugation, washed with diethyl ether (3×5 ml), and dried for 2 h at 20°C in a vacuum (0.1 mm). Yield 0.92 g (90%). The ^1H and ^{19}F NMR spectra were consistent with those given in [3]. The ^{13}C NMR spectrum of **Ia** is given in table. Found, %: C 42.67; H 5.14; F 30.20. $C_{20}H_{28}B_2F_9Rh$. Calculated, %: C 42.59; H 5.01; F 30.32.

Complex (II). A mixture of 1.10 g (1.7 mmol) of $[(C_5EtMe_4)RhCl_2]_2$, 3.16 g (6.8 mmol) of $AgBF_4 \cdot 3C_4H_8O_2$, 0.5 ml of benzene, and 2.5 ml of nitromethane was stirred for 10 min under argon. The precipitate of AgCl was separated by centrifugation, the liquid phase was diluted with ~60 ml of diethyl ether, and the colorless crystals were separated by centrifugation, washed with diethyl ether (2×10 ml), and dried for 1 h at 20°C under reduced pressure (0.1 mm). Yield 1.26 g (74%). The ^1H NMR spectrum of **II** was consistent with that reported in [7].

Reaction of complex Ia with diethyl malonate. *a*. A solution of 0.02 g (0.355 mmol) of sodium methoxide in 0.24 ml of methanol and 0.113 g (0.71 mmol) of diethyl malonate were placed into a reactor connected to a high-vacuum setup. The mixture was stirred for 30 min at 20°C under argon, the solvent was distilled off under reduced pressure (0.06 mm), 0.2 g (0.36 mmol) of complex **Ia** and 0.5 ml of acetone-d_6 were added, and the mixture was stirred at 0–15°C. The reaction course was monitored by ^1H and ^{19}F NMR spectroscopy in 5-min intervals and after 24 h. 2,4,6-Trimethylphenol complex **IV** was isolated and identified as described in [6].

b. A reactor was charged under argon with 0.016 g (0.67 mmol) of sodium hydride and 0.137 g (0.85 mmol) of diethyl malonate, the reactor was evacuated, ~2 ml of THF was condensed thereto, and the mixture was stirred until hydrogen no longer evolved. Complex **Ia**, 0.235 g (0.42 mmol), was then added, the mixture was stirred for 48 h, 4 drops of CF_3COOH and ~1 ml of $MeNO_2$ were added, the mixture was filtered, and the filtrate was evaporated at 20°C under reduced pressure (0.06 mm). The residue was treated with hexane (3×2 ml), the extract was evaporated, and the residue was purified by thin-layer chromatography (Silufol, hexane–CH_2Cl_2, 1:1). Yield of diethyl mesitylmalonate (**V**) 0.089 g (76%). ^1H NMR spectrum, δ, ppm: 6.85 s (2H), 2.30 s (6H), 2.24 s (3H), 1.25 t (6H, J = 7.5 Hz), 4.20 q (4H, J = 7.5 Hz), 4.97 s (1H).

Reaction of complex Ib with diethyl malonate. *a*. A reactor was charged under argon with 0.002 g (0.24 mmol) of LiH and 0.035 g (0.22 mmol) of diethyl malonate. The mixture was evacuated and stirred for 30 min, excess diethyl malonate was distilled off under reduced pressure (0.05 mm), 0.116 g (0.20 mmol) of complex **Ib** and 0.5 ml of acetone-d_6 were added, and the mixture was stirred for 15 min and analyzed by ^1H NMR spectroscopy. The mixture was then stirred for 48 h, 2 drops of hydrochloric acid were added, and the solvent was distilled off under reduced pressure (water-jet pump). The residue was extracted with diethyl ether (4×5 ml), the solvent was distilled off, and the residue was purified by TLC (Silufol, hexane–CH_2Cl_2, 1:1). Yield of **V** 0.031 g (56%).

b. A reactor was charged with 0.015 g (0.66 mmol) of metallic sodium, 0.2 ml of ethanol was condensed thereto under reduced pressure (0.06 mm), and the mixture was stirred until the sodium dissolved completely. Diethyl malonate, 0.147 g (0.92 mmol), was then added under argon, the mixture was stirred for 30 min, the solvent was distilled off under reduced pressure (0.06 mm), 0.367 g (0.63 mmol) of complex **Ib** was added, and ~1 ml of THF-d_8 was condensed thereto. The mixture was stirred for 10 min and analyzed by ^{1}H NMR spectroscopy. After 24 h, THF-d_8 was distilled off under reduced pressure, and the residue was dissolved in nitromethane and analyzed by ^{1}H NMR spectroscopy.

Reaction of complex Ic with diethyl malonate. Diethyl malonate, 0.073 g (0.416 mmol), was added to a solution of 0.04 g (0.364 mmol) of potassium *tert*-butoxide in 0.45 ml of *t*-butyl alcohol, the mixture was stirred for 5 min under argon, 0.19 g (0.35 mmol) of complex **Ic** and 0.5 ml of acetone were added, and the mixture was stirred for 10 min and diluted with ~5 ml of diethyl ether. The precipitate was separated by centrifugation, washed with ~5 ml of diethyl ether, and dried for 1 h under reduced pressure (water-jet pump) at 20°C. The product was 0.150 g (~70%) of a mixture of complexes **IIIc** and **VIa** at a molar ratio of 7:3.

Reaction of complex Ia with malononitrile. A mixture of 0.113 g (0.20 mmol) of complex **Ia**, 0.02 g (0.37 mmol) of sodium carbonate, 0.015 g (0.22 mmol) of malononitrile, and 0.5 ml of acetone-d_6 was stirred for 5 h. The mixture was filtered, the filtrate was evaporated, and the residue was heated at 110–220°C under reduced pressure (0.065 mm). The distillate collected in a cooled receiver was subjected to thin-layer chromatography (Silufol, hexane–CH_2Cl_2, 1:1) to isolate 0.014 g (38%) of mesitylmalononitrile (**IX**). ^{1}H NMR spectrum, δ, ppm: 6.94 s (2H), 2.47 s (6H), 2.27 s (3H), 5.27 s (1H).

Reaction of complex Ib with malononitrile. A mixture of 0.116 g (0.20 mmol) of complex **Ib**, 0.053 g (0.5 mmol) of sodium carbonate, 0.0146 g (0.22 mmol) of malononitrile, and 0.5 ml of acetone-d_6 was stirred for 48 h using a magnetic stirrer. The mixture was filtered, the filtrate was evaporated, and the residue was heated at 110–220°C under reduced pressure (0.06 mm). The distillate collected in a cooled receiver was subjected to thin-layer chromatography (Silufol, hexane–CH_2Cl_2, 1:1) to isolate 0.011 g (30%) of mesitylmalononitrile (**IX**).

Reaction of complex Ib with ethyl cyanoacetate. A reactor was charged under argon with 0.054 g (0.19 mmol) of sodium hydride, 0.039 g (0.35 mmol) of ethyl cyanoacetate, and ~1 ml of THF. The mixture was stirred for 30 min, 0.100 g (0.17 mmol) of complex **Ib** was added, the mixture was stirred for 24 h, one drop of hydrochloric acid was added, and the solvent was distilled off under reduced pressure (0.04 mm). The residue was heated at 150–200°C under reduced pressure (0.04 mm), and the distillate collected in a cooled receiver was subjected to thin-layer chromatography (Silufol, hexane–CH_2Cl_2, 1:1) to isolate 0.01 g (25%) of ethyl cyano(mesityl)acetate (**X**). The ^{1}H NMR spectrum of the product was identical to that given in [19].

This study was performed under financial support by the Ministry of Education of the Russian Federation (project no. 2000.5.90).

REFERENCES

1. Goryunov, L.I. and Shteingarts, V.D., *Russ. J. Org. Chem*., 1999, vol. 35, p. 246.
2. Semmelhack, M.F., *Comprehensive Organometallic Chemistry II*, Abel, E.W., Stone, F.G.A., and Wilkinson, G., Eds., Oxford: Pergamon, 1995, vol. 12, p. 979.
3. Moriarty, R.M., Ku, Y.-Y., and Gill, U.S., *J. Chem. Soc., Chem. Commun*., 1987, p. 1493.
4. Moriarty, R.M., Ku, Y.-Y., and Gill, U.S., *Organometallics*, 1988, vol. 7, p. 660.
5. Goryunov, L.I., Terent'eva, Yu.A., Litvak, V.V., and Shteingarts, V.D., *Zh. Org. Khim*., 1990, vol. 26, p. 1058.
6. Goryunov, L.I. and Shteingarts, V.D., *Zh. Org. Khim*., 1991, vol. 27, p. 1144.
7. Rybinskaya, M.I., Kudinov, A.R., and Kaganovich, V.S., *J. Organomet. Chem*., 1983, vol. 246, p. 279.
8. Kaganovich, V.S., Kudinov, A.R., and Rybinskaya, M.I., *Metalloorg. Khim*., 1988, vol. 1, p. 294.
9. Bailey, N.A., Blunt, E.H., Fairhurst, G., and White, C., *J. Chem. Soc., Dalton Trans*., 1980, p. 829.
10. Goryunov, L.I. and Nikitin, Yu.M., *Russ. J. Gen. Chem*., 1994, vol. 64, p. 648.
11. Lapitskaya, M.A., Mel'nikova, V.I., Vorob'eva, L.G., Kerzina, Z.A., and Pivnitskii, K.K., *Zh. Obshch. Khim*., 1990, vol. 60, p. 1496.
12. Goryunov, L.I., Nikitin, Yu.M., and Shteingarts, V.D., *Russ. J. Org. Chem*., 1998, vol. 34, p. 1645.
13. Espinet, P., Bailey, P.M., Downey, R.F., and Maitlis, P.M., *J. Chem. Soc., Dalton Trans*., 1980, p. 1048.

14. Fish, R.H., Kim, H.S., Fong, R.H., and Adams, R.D., *Organometallics*, 1990, vol. 9, p. 1327.
15. Van Zanter, B. and Nauta, W., *Recl. Trav. Chim. Pays–Bas*, 1960, vol. 79, p. 1211.
16. Houghton, R.P., Voyle, M., and Price, R., *J. Chem. Soc., Perkin Trans. 1*, 1984, p. 925.
17. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.
18. Suzuki, H., Kobayashi, T., and Osuka, A., *Chem. Lett*., 1983, vol. 12, p. 589.
19. De Jongh, H.A.P., De Jongh, C.R.H.I., Sinnige, J.M., De Klein, W.J., Huysmans, W.G.B., Mijs, M.J., Van den Hoek, W.J., and Smidt, J., *J. Org. Chem*., 1972, vol. 37, p. 1960.
20. You, J. and Verkade, J.G., *J. Org. Chem*., 2003, vol. 68, p. 8003.