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Redox troponization of (η^5-cyclopentadienyl)(η^4-4-methyl-4-*exo*-trichloromethylcyclohexa-2,5-dien-1-one)rhodium as a novel approach to the synthesis of metal-coordinated nonbenzenoid aromatics of the tropone series

V. A. Nikanorov, T. V. Storozhev, S. G. Novikov, S. V. Sergeev, and D. V. Zverev*

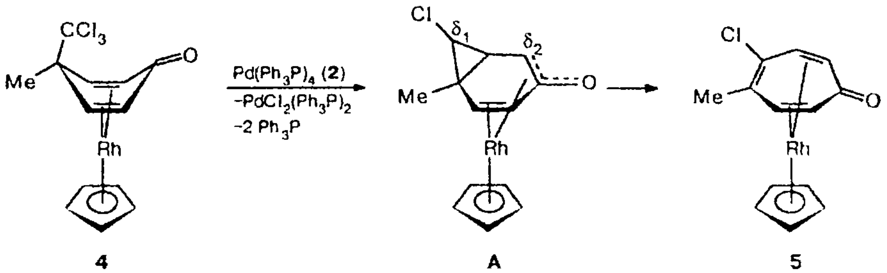
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: vanik@ineos.ac.ru

The possibility of redox troponization of a gem-polyhalomethylated semiquinoid system, π-coordinated to a metal atom, was shown in relation to the reaction of (η^5-cyclopentadienyl)(η^4-4-methyl-4-*exo*-trichloromethylcyclohexa-2,5-dien-1-one)rhodium with $Pd(PPh_3)_4$. The reaction occurs with retention of the metal coordination affording a seven-membered organometallic derivative of the nonbenzoid aromatic series, namely, (η^5-cyclopentadienyl)(η^4-4-chloro-5-methylcyclohepta-2,4,6-trien-1-one)rhodium, whose structure was established by means of elemental analysis, NMR, and mass-spectral data.

Key words: cyclohexadienones, tropones; redox troponization; rhodium(I) π-complexes; Pd(0) complexes, use in the fine organic sysnthesis.

Our earlier studies dealing with the development of the heteroorganic chemistry of semiquinoid systems (cyclohexadienones, alkylidenecyclohexadienes, and their analogs and derivatives)[1] resulted in the discovery of the redox troponization of 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-one (**1**) induced by tetrakistriphenylphosphine complex of palladium(0) (**2**); this reaction provides an original method for the synthesis of polysubstituted cyclohepta-2,4,6-trien-1-ones (**3**) (see a review[2]). In this work (Scheme 1), we found that dienone **1** coordinated to a transition metal atom, (η^5-cyclopentadienyl)(η^4-4-methyl-4-*exo*-trichloromethylcyclohexa-2,5-dien-1-one)rhodium (**4**), can also be involved in this reaction giving (η^5-cyclopentadienyl)(η^4-4-chloro-5-methylcyclohepta-2,4,6-trien-1-one)rhodium (**5**), whose structure was established by ^{1}H and ^{13}C NMR and mass spectra. The (2,3,6,7-η)-type of coordination of the RhCp fragment in complex **5** is confirmed, first, by a substantial upfield shift of the ^{1}H NMR signals for all the four olefinic protons in the seven-membered ring in relation to the signals of the corresponding protons in the spectrum of non-coordinated 4-chloro-5-methylcyclohepta-2,4,6-trien-1-one[1] ($\Delta\delta \cong 2-2.5$, $CDCl_3$) and, second, by the presence of clearly defined $^{13}C-^{103}Rh$ spin-spin coupling constants for C(2), C(3), C(6), and C(7) in their ^{13}C NMR spectra ($^1J \cong 6-15$ Hz). The discovered reaction, which apparently proceeds *via* a Rh-coordinated norcaradiene intermediate (A; δ_1, δ_2 = +, −, ·) is a new approach to the synthesis of metal-coordinated nonbenzoid aromatic systems, which extends radically the synthetic potential of the redox troponization processes in organometallic chemistry.

Scheme 1



4 **A** **5**

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Experimental

All the reactions were carried out under argon and monitored by TLC on Silufol UV-254 plates; preparative column chromatography was performed using SiO_2 Silpearl UV-254. NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-400 instrument operating at 400.13 MHz (^1H) and 100.61 MHz (^{13}C). The chemical shifts were referenced to the signal of the residual $CHCl_3$. EI mass spectra (70 eV) were run on an MS-890 spectrometer.

All solvents were thoroughly purified by known procedures. Complexes **2** [3] and **4** [4] were prepared by previously reported procedures.

(η^5-Cyclopentadienyl)(η^4-4-chloro-5-methylcyclohepta-2,4,6-trien-1-one)rhodium (5). A solution of a mixture of complex **4** (0.05 g, 0.127 mmol) and **2** (0.16 g, 0.140 mmol) in 8 mL of C_6H_6 was stirred for 72 h at 20 °C and concentrated on a rotary evaporator. The dry residue was chromatographed on SiO_2 (using a 3 : 1 C_6H_6—EtOH mixture as the eluent); the fraction with $R_f = 0.5$ was isolated. Evaporation of the solvent and crystallization of the residue from a C_6H_6—hexane (1 : 1) mixture gave 0.014 g of **5** (34%). Found (%): C, 48.44; H, 3.82. $C_{13}H_{12}ClORh$. Calculated (%): C, 48.40; H, 3.75. ^1H NMR, δ: 1.53 (s, 3 H, Me); 4.06 (d, 1 H, CH, $^2J_{H-H}$ = 7.8 Hz); 4.20 (d, 1 H, $^3J_{H-H}$ = 7.8 Hz); 4.92 (m, 2 H, 2 CH); 5.47 (d, 5 H, Cp, $^2J_{H-Rh}$ = 0.7 Hz). ^{13}C NMR, δ: 18.4 (s, Me); 64.9 (d, CH, $^1J_{C-Rh}$ = 15.1 Hz); 66.8 (d, CH, $^1J_{C-Rh}$ = 15.1 Hz); 72.9 (d, CH, $^1J_{C-Rh}$ = 7.0 Hz); 73.46 (d, CH, $^1J_{C-Rh}$ = 6.0 Hz); 87.3 (d, Cp, $^1J_{C-Rh}$ = 5.0 Hz). MS *m/z* (I_{rel}, (%)): 322 $[M]^+$ (18), 294 $[M-C=O]^+$ (16), 168 $[RhCp]^+$ (93), 154 $[M-RhCp]^+$ (6), 91 (100).

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Tetramethylsilane as reagent gas: mass spectra of nitrocarboxylic acid esters and nitroalcohols

V. I. Kadentsev, N. G. Kolotyrkina, A. A. Stomakhin, O. S. Chizhov, S. L. Ioffe,*
I. M. Lyapkalo, A. D. Dil'man, and A. A. Tishkov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

Nitrocarboxylic acid esters and nitroalcohols react with trimethylsilyl cation in the gas phase under conditions of chemical ionization to form stable $[M+SiMe_3]^+$ ions. The pathways of their fragmentation were established and characteristic distinctions in the mass spectra caused by mutual arrangement of functional groups were found.

Key words: mass-spectrometry, chemical ionization, trimethylsilyl cation, nitrocarboxylic acid esters, nitroalcohols.

In a continuation of our studies of reactions between the trimethylsilyl cation and nitroalkanes and halonitroalkanes in the gas phase,[1] in this work the chemical ionization (CI) mass spectra of nitroalcohols and carboxylic acid esters were studied using tetramethylsilane as the reagent gas.

Experimental

NMR spectra were recorded on a Bruker AM 300 spectrometer at 300.13 MHz (^1H), 75.47 MHz (^{13}C), 59.63 MHz (^{29}Si, INEPT) (with tetramethylsilane as internal standard), and 21.69 MHz (^{14}N) (with $MeNO_2$ as external standard).

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