Aromatizational rhodiation of 1-cyclopentadienylidene-4-methyl-4-trichloromethylcyclohexa-2,5-diene under the action of $(Ph_3P)_3Rh(CO)H$ and $(C_2H_4)_2Rh(acac)$ as a novel route to *p*-tolylcyclopentadienyl complexes of transition metals

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Condensation of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone with cyclopentadiene gave the first representative of cross-conjugated pentafulvenes of the *para*-semiquinoid series: 1-cyclopentadienylidene-4-methyl-4-trichloromethylcyclohexa-2,5-diene. This fulvene undergoes a novel redox aromatizational skeletal rearrangement under the action of $(Ph_3P)_3Rh(CO)H$ and $(C_2H_4)_2Rh(acac)$ to give triphenylphosphine[η^5 -(*p*-tolylcyclopentadienyl)]dichlororhodium and bis[$(\eta^5$ -*p*-tolylcyclopentadienyl)(μ -chloro)chlororhodium], respectively.

Key words: cyclopentadiene; cyclohexa-2,5-dienone; condensation; pentafulvenes; crossconjugation; metallation; redox transformations; aromation; skeletal molecular rearrangements; cyclopentadienyl complexes of rhodium(1) and rhodium(11).

In a continuation of our studies on the "cascade" principle for the construction of polyconjugated metal complexes¹ (1, 2), in this work, we synthesized the first representative of pentafulvenes of the *para*-semiquinoid series 3, which contains two cross-conjugated π -diene rings capable of coordinating transition metals.



Polyunsaturated fulvenes of related classes (see the relevant reviews^{2,3}) have long attracted the attention of researchers.^{4,5} The reactivity of "dendralene" cross-conjugated systems is also of substantial interest (see the relevant review⁶). Type 3 fulvenes can be regarded as cyclovinylogs of alkylidenecyclohexadienes 4, which we have studied previously. Based on their treatment with derivatives of a number of nontransition metals, Hg, Sn, Au, Ge, we developed an ingenious method for the synthesis of the corresponding σ -benzylic organometallic systems, the so-called aromatizational metallation (for a review, see Ref. 7). From this viewpoint, the introduction of two additional double bonds into the exocyclic fragment of trienes 4 should ensure the most efficient aromatization under the conditions of metallation, especially through the action of transition metals. The latter are known to exhibit special affinity for fiveand six-electron fragments, which are present in pentaenes 3. Attempts to carry out cyclopentadienylation of dienone 5 by the classical method,⁸ viz., through the action of C₅H₅MgI, gave only polymeric products with decomposition temperature above 230 °C. The first parasemiquinoid representative of fulvenes 6 was obtained by condensation of dienone 5 with cyclopentadiene using a known procedure⁹ in MeOH in the presence of pyrrolidine as a catalyst. The dark-red crystalline product 6 is readily soluble in Et₂O, C₆H₆, and CHCl₃, less soluble in MeOH, and poorly soluble in hexane; it is stable

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during storage in a refrigerator over a period of 1 month.* The structure of compound 6 was confirmed by the data of elemental analysis, NMR spectroscopy, and mass spectrometry. When we studied metallation of fulvene 6 with $(Ph_3P)_3Rh(CO)H$ and $(C_2H_4)_2Rh(acac)$, we found a novel complex multistage redox transformation involving the abstraction of the CCl₃ group, transfer of two Cl atoms to the low-valence metal atom,** and the formation of mixed *p*-tolylcyclopentadienyl chloride derivatives of trivalent rhodium 7 and 8 (Scheme 1). The structures of products were confirmed by analytical and spectroscopic data as well as by the transformation of the binuclear complex 8 into mononuclear complex 7 through the action of Ph_3P .

Thus, two metallating reagents of different natures react with fulvene 6 to give products of actually the same type via thermodynamically favorable aromatization of both unsaturated rings.

The *para*-semiquinoid fulvene system $\mathbf{6}$ is a novel promising ligand in the organometallic chemistry.

Experimental

NMR spectra were recorded on a Bruker WP 200 SY spectrometer (1 H, 200.12 and 13 C, 50.1 MHz) using tetra-

** The mechanism of this reaction requires special investigation. It can be suggested that the activation and transfer of CCl₃ are intermolecular processes, since in related systems, this bulky substituent directs an attack by a metal atom from the opposite side of the ring (see Refs. 10 and 11). methylsilane as the internal standard. The IR spectrum was measured on a UR-20 spectrophotometer (Karl Zeiss). EI mass spectra were obtained on an MS-890 instrument (70 eV). The course of the reactions was monitored by TLC on Silufol-254 plates, the compounds being visualized by UV irradiation or by treatment with a 10 % solution of phosphomolybdic acid in EtOH.

Ketcne 5 was obtained by a known procedure.¹² Solvents were dried by standard procedures.¹³ Cyclopentadiene was distilled just before use. The complexes $(Ph_3P)_3Rh(CO)H$ ¹⁴ and $(C_2H_4)_2Rh(acac)$ ¹⁵ were prepared as described previously.

1-Cyclopentadienylidene-4-methyl-4-trichloromethylcyclohexa-2,5-diene (6). Pyrrolidine (6.25 mL, 75 mmol) was added to a solution of ketone 5 (11.3 g, 50 mmol) and cyclopentadiene (8.25 g, 125 mmol) in 70 mL of MeOH, and the mixture was stirred for 1.5 h at 20 °C. A dark-red solution gradually formed. When the reaction was over, the mixture was diluted with 35 mL of water. The precipitated dark-red crystals were separated by filtration, washed successively with a 50 % aqueous solution of MeOH (20 mL) and with water (20 mL), and dried *in vacuo* to give 10.7 g of compound 6, yield 78 %, m.p. 88-89 °C (MeOH). R_f 0.5 (hexane). Found (%): C, 56.94; H, 3.78; Cl, 38.78. C₁₃H₁₁Cl₃. Calculated (%): C, 57.07; H, 4.05; Cl, 38.87.

¹H NMR (CDCl₃), δ : 1.36 (s, 3 H, Me); 6.18 (d, 2 H, H(2) and H(6), ${}^{3}J_{H(2)-H(3)} = 10.3$ Hz); 6.61 (m, 4 H, C₅H₄); 6.85 (d, 2 H, H(3) and H(5), ${}^{3}J_{H(3)-H(2)} = 10.3$ Hz). ¹³C NMR (CDCl₃), δ : 24.9 (q, ${}^{1}J_{C-H} = 139$ Hz); 120.0 (d, ${}^{1}J_{C-H} = 167$ Hz); 127.1 (d, ${}^{1}J_{C-H} = 156$ Hz); 131.8 (s); 132.2 (s); 132.5 (d, ${}^{1}J_{C-H} = 162$ Hz); 135.7 (d, ${}^{1}J_{C-H} = 156$ Hz). MS, m/z (${}^{1}f_{el}$ (%)): 272 [M]⁺ (6.7), 236 [M-HCI]⁺ (90), 201 [M-HCI-CI]⁺ (95), 166 [M-HCI-2 CI]⁺ (100).

Triphenylphosphine[η^5 -(*p*-tolylcyclopentadienyl)]dichlororhodium (7). A solution of $(Ph_3P)_3Rh(CO)H$ (150 mg, 0.182 mmol) in 5 mL of dioxane was added to a solution of fulvene 6 (50 mg, 182 mmol) in 5 mL of dioxane. The mixture was boiled for 2 h, concentrated to 5 mL, and 5 mL of C_6H_6 was added with stirring. The precipitated dark-red crystals of an adduct of compound 7 with dioxane (4 : 1) were



^{*} Upon more prolonged storage, fulvene 6 partly decomposes with evolution of HCl to give oligomeric products; the shelf life of this compound substantially increases in the presence of traces of MeOH.

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filtered off, washed with C₆H₆ (2×0.5 mL), and dried *in vacuo* to give 63 mg of compound 7, yield 59 %. $R_{\rm f}$ 0.75 (CHCl₃— EtOH, 25 : 1). Found (%): C, 60.68; H, 4.60; CI, 11.57. [C₃₀H₂₆Cl₂PRh]₄ · C₄H₈O₂. Calculated (%): C, 60.71; H, 4.60; CI, 11.56. ¹H NMR (CDCl₃), &: 2.37 (s, 3 H, Me); 3.73 (s, dioxane); 5.11 (br.s, 2 H, Cp); 5.63 (t, 2 H, Cp); 7.22 (d, 2 H, *p*-MeC₆H₄, ³J_{H-H} = 8 Hz); 7.36 (m, 9 H, Ph₃P); 7.48 (d, 2 H, *p*-MeC₆H₄, ³J_{H-H} = 8 Hz); 7.62 (m, 6 H, Ph₃P). The adduct of 7 with dioxane was recrystallized from a C₆H₆— EtOH mixture (1 : 1) to give the dihydrate of 7 as fibrous crystals with pearly luster, m.p. 221–223 °C. Found (%): C, 57.19; H, 4.61; CI, 11.62. [C₃₀H₂₆Cl₂PRh] · 2H₂O. Calculated (%): C, 57.43; H, 4.82; CI, 11.30. ¹H NMR (CDCl₃), &: 2.37 (s, 3 H, Me); 5.10 (br.s, 2 H, Cp); 5.64 (dd, 2 H, Cp); 7.20 (d, 2 H, *p*-MeC₆H₄, ³J_{H-H} = 8 Hz); 7.36 (m, 9 H, Ph₃P); 7.47 (d, 2 H, *p*-MeC₆H₄, ³J_{H-H} = 8 Hz); 7.63 (m, 6 H, Ph₃P).

Bis[$(\eta^5$ -*p*-tolylcyclopentadienyl)(μ -chloro)chlororhodium] (8). A solution of $(C_2H_4)_2$ Rh(acac) (268 mg, 1.03 mmol) in 20 mL of THF was added dropwise at -50 °C to a solution of fulvene 6 (284 mg, 1.03 mmol) in 20 mL of THF. The resulting dark-red solution was warmed up to 20 °C and filtered. A red finely crystalline solid precipitated from the filtrate over a period of 12 h; this gave 58 mg of product 8, yield 8.5 %. R_f 0.76 (CHCl₃-MeOH, 7 : 0.1). Found (%): C, 43.09; H, 3.58; Cl, 21.97; Rh, 31.62. $C_{24}H_{22}Rh_2Cl_4$. Calculated (%): C, 43.77; H, 3.34; Cl, 21.58; Rh, 31.31. IR (KBr), v/cm⁻¹: 830, 1205, 1470, 1618, 1660, 3070.

Reaction of complex 8 with Ph_3P. A solution of Ph_3P (4.8 mg, 0.018 mmol) in 0.2 mL of CDCl₃ was added to a suspension of complex 8 (6 mg, 0.009 mmol) in 0.4 mL of CDCl₃. A transparent bright-red solution formed immediately. The ¹H NMR spectrum of a sample taken from this solution is identical to that described above for complex 7.

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