An unusual example of *endo*-stereoselectivity in the ligand exchange reactions of rhodium(I)diethylene derivatives with *para*-semiquinoid ligands

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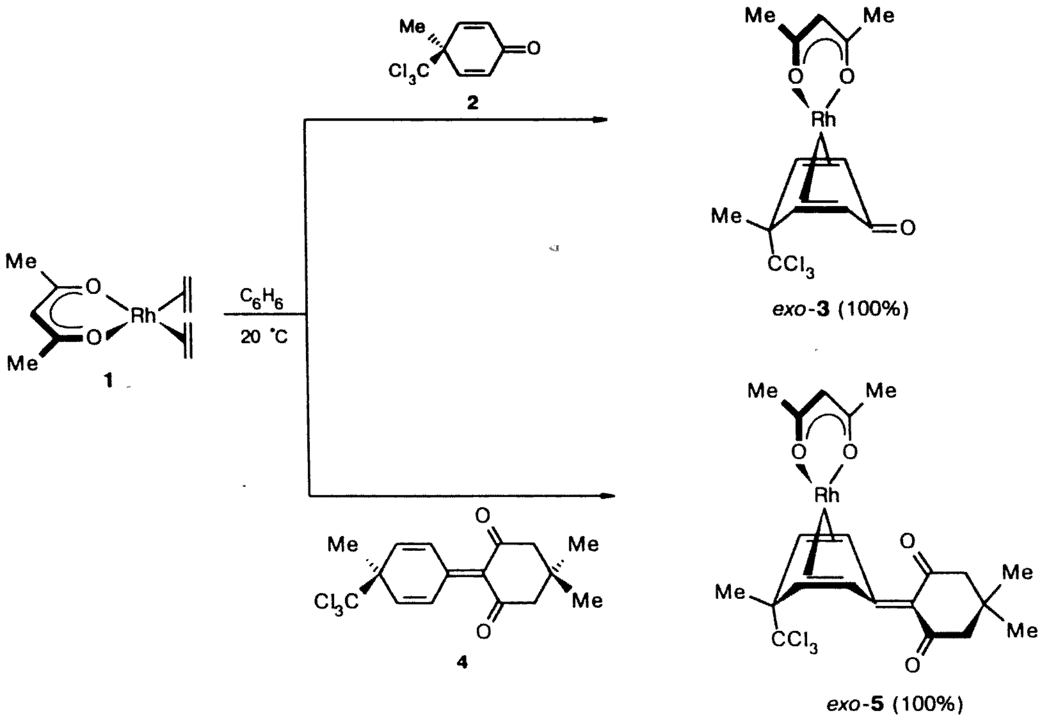
The ligand exchange reactions of $[(C_2H_4)_2Rh(acac)]$ in benzene and $[(C_2H_4)_2RhCl]_2$ in CH_2Cl_2 with 4-methyl-4-trichloromethyl-2,5-cyclohexadiene-1-one occur with 100% *exo*-stereoselectivity. The similar process with 4-methyl-4-trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadiene (trienedione) is strictly *exo*-stereospecific only if $[(C_2H_4)_2Rh(acac)]$ in benzene is used, while in the case of $[(C_2H_4)_2RhCl]_2$ in CH_2Cl_2, it proceeds with an *endo*-stereoselectivity of 43%. An explanation for these facts has been suggested that assumes that the metal atom initially attacks the central double bond in the trienedione, which is removed from the area of main steric hindrance. The subsequent metallotropic rearrangement of the resulting ethylene-triene intermediate gives rise to the final η^4-coordinated π-diene structures.

Key words: cyclohexadienones, alkylidenecyclohexadienes; coordination; stereocontrol, *exo*-stereoselectivity, *endo*-stereoselectivity.

Exo/endo-selectivity in the reactions of ligand exchange of transition metal complexes with asymmetrically shielded olefins and cyclopolyolefins (cyclopentadienes, cyclohexadienes, cyclooctadienes, cycloheptatrienes) is a key problem in organometallic stereochemistry.[1] The current views on the nature of this kind of stereoselectivity is that in the absence of specific electronic factors, coordination preferentially occurs on the less shielded *exo*-side of the ligand. However, if there is a possibility for the metal atom to be preliminarily

Scheme 1



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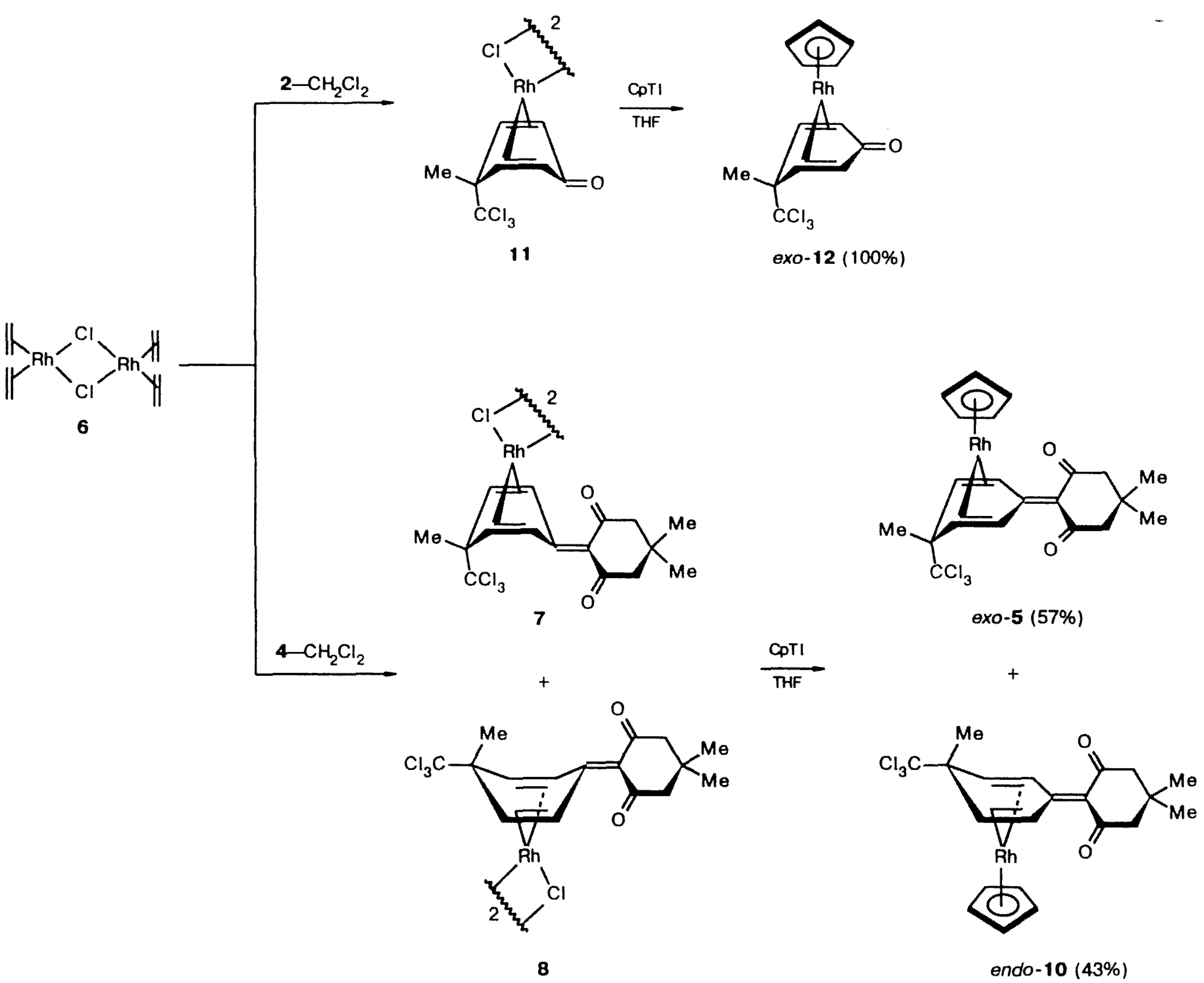
Scheme 2



coordinated to the *endo*-substituent (even if it is relatively bulky), the *endo*-attack also may contribute substantially to the process.[2]

We have shown previously[3] (Scheme 1) that ligand exchange between the Kramer complex $[(C_2H_4)_2Rh(acac)]$ (**1**) and 4-methyl-4-trichloromethyl-2,5-cyclohexadien-1-one (**2**) in benzene occurs 100% *exo*-stereoselectively to give complex **3**; later the same was also found[4] for a similar reaction of 4-methyl-4-trichloromethyl-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadiene (**4**) in benzene yielding compound **5**. In the present work, we showed that in this reaction involving the dimeric complex $[(C_2H_4)_2RhCl]_2$ (**6**) and trienedione **4** in dichloromethane, the process unexpectedly occurs with clear-cut *exo*/*endo*-stereoselectivity and gives a mixture of *exo*- and *endo*-isomers **7** and **8**, which was subsequently converted into the corresponding CpRh derivatives **9** and **10** (**9** : **10** = 57 : 43),[*] *i.e.*, the reaction involves a substantial contribution of the metal coordination to the strongly sterically shielded side of ligand **4** (Scheme 2).

It could have been suggested that the phenomenon observed is explained by some specific features of the metallating system **6** under consideration, for example, by the fact that a CH_2Cl_2 molecule preliminarily occupies a coordination site in the dimeric molecule of the

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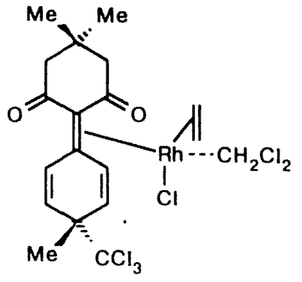
[*] The coordination of the organometallic moiety [RhL] to the *exo*-side of the π-diene system of dienone **2** and trienedione **4** results in a downfield shift of the signal corresponding to the geminal methyl group in the ^1H NMR spectrum (in $CDCl_3$), $\Delta\delta$ = 1.0 (L = acac), 0.4 (L = Cp).[3,4] The upfield shift ($\Delta\delta$ = 0.45) of the ^1H NMR signal of the geminal methyl group in complex **10** found in this study is evidence for its *endo*-configuration.

reactant. However, a special experiment has shown that in the case of dienone **2**, the *exo*-stereospecificity peculiar to it is completely retained under similar conditions, and the reaction yields complex **11** (which was then converted into complex **12**). Therefore, the result obtained in the case of trienedione **4** cannot be explained by the possibility of this preliminary coordination. This experiment also makes it possible to exclude from consideration processes in which the CCl_3 group of trienedione acts as a metal-coordinating fragment affecting the stereochemistry of the reaction under consideration. In order to explain the facts observed, one may assume that the inter-ring double bond of the trienedione ligand, which is relatively free from steric hindrances, rather than its cyclohexadiene fragment acts as the primary reaction center of molecule **4** in the **6**—CH_2Cl_2 system. The formation of the final product is due to the subsequent metallotropic rearrangement of the intermediate complex **13** to the final η^4-coordinated structure **8**. This hypothesis is supported by the fact that this double bond exhibits obvious electron-withdrawing properties (since it is conjugated with the two adjacent carbonyl groups) when it is attacked by the electron-donating Rh^I atom. This hypothesis is supported by the data from Ref. 5 on coordination binding involving the exocyclic cumulene fragment of similar unsaturated groups in Rh^I carbonyl complexes derived from quinoid systems **14**, and by the synthesis[6] of stable mixed ethylene-triene Rh^I complexes **15**.



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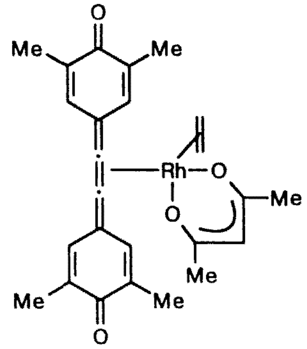

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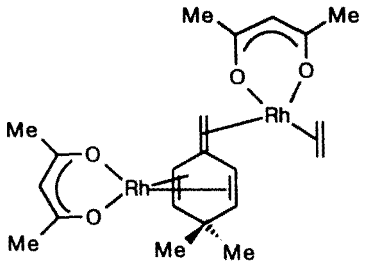

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The structures of the new metallocomplexes **7**, **8**, **10**, and **12** obtained in the present study were determined from the data of elemental analysis, IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and mass spectrometry (for compounds **10** and **12**).

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker WP-200 SY spectrometer (200.13 and 50.1 MHz, respectively); chemical shifts were related to $SiMe_4$ (^1H) or to the signals of the deuterated solvents used (^{13}C). IR spectra were obtained on a UR-20 spectrophotometer (Karl Zeiss) for pellets with KBr. Mass spectra (EI) were obtained on a Kratos-MS30 spectrometer with an ionization energy of electrons of 70 eV.

The initial complex **6**,[7] CpTl,[8] ketone **2**,[9] and trienedione **4** [10] were synthesized by previously described procedures.

Di-μ-chlorobis[(2,3,5,6-η)-4-methyl-4-trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadiene]dirhodium (mixture of isomers 7 and 8). A solution of trienedione **4** (2.2 g, 6.35 mmol) in 20 mL of CH_2Cl_2 was added with stirring to a mixture of compound **6** (1.16 g, 5.98 mmol) and CH_2Cl_2 (5 mL). The reaction mixture was stirred for 4 h at 20 °C, allowed to stand overnight, and evaporated on a rotary evaporator. The residue was treated with Et_2O (20 mL) and filtered, and the precipitate was washed successively with benzene (2×15 mL) and Et_2O (3×15 mL) and dried *in vacuo* to give 2.7 g (93%) of a mixture of isomers **7** and **8** as a finely dispersed crystalline red powder, almost insoluble in organic solvents. Found (%): C, 39.06; H, 4.10; Cl, 29.08. $C_{32}H_{34}Cl_8O_4Rh$. Calculated (%): C, 39.54; H, 3.53; Cl, 28.18. IR, ν/cm^{-1}: 790, 805, 1228, 1285, 1355, 1385, 1445, 1535, 1570, 1630 (C=C—C=O); 2890, 2970 (C—H).

Reaction of the mixture of isomers 7 and 8 with CpTl. CpTl (0.59 g, 2.2 mmol) was added to the mixture of isomers **7** and **8** (1.0 g, 1.0 mmol) in 30 mL of THF. The reaction mixture was stirred for 1.5 h at 50 °C, then the solvent was evaporated on a rotary evaporator, the solid residue was extracted with $CHCl_3$ (2×25 mL), the combined extracts were filtered, and the filtrate was concentrated. According to ^1H NMR spectroscopy data, the residue (0.99 g, 96%) was a mixture of isomers **9** and **10** in 57 : 43 ratio. The products were separated by chromatography on a column with SiO_2 (the Silpearl UV-254 silica gel); the elution was carried out successively with $Pr^iOH—CHCl_3$, 1 : 3 and 2 : 3 mixtures.

The combination and concentration of the fractions that contained the compound with R_f 0.49 (Silufol UV-254, $Pr^iOH-CHCl_3$, 2 : 3) followed by crystallization of the solid residue from a $CHCl_3$—*n*-heptane mixture gave 0.49 g of **[(1,2,3,5,6-η)-4-methyl-4-*exo*-trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadien-1-yl]-(η^5-cyclopentadienyl)rhodium (9)**, whose ^1H NMR spectrum and decomposition point corresponded to the data published previously.[11] IR, ν/cm^{-1}: 785, 810, 830, 840, 1140, 1275, 1345, 1390, 1425, 1510, 1550 (C=C—C=O); 2960 (C—H). MS, *m/z* (I_{rel} (%)): 514 $[M]^+$ (2.3), 444 $[M-2Cl]^+$ (5.0), 397 $[M-CCl_3]^+$ (31.5), 276 $[M-CpRh-2HCl]^+$ (5.2), 225 (100).

The combination and concentration of the fractions that contained the compound with R_f 0.69 followed by crystallization of the solid residue from a CH_2Cl_2—hexane mixture gave **[(1,2,3,5,6-η)-4-methyl-4-*endo*-trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadien-1-yl]-(η^5-cyclopentadienyl)rhodium (10)** as yellow crystals, decomp.p. 205—210 °C. Found (%): C, 48.68; H, 4.13; Cl, 20.68. $C_{21}H_{22}Cl_3O_2Rh$. Calculated (%): C, 48.91; H, 4.30; Cl, 20.63. IR, ν/cm^{-1}: 630, 785, 820, 1145, 1265, 1350, 1385, 1425, 1500, 1545 (C=C—C=O); 2940, 2965 (C—H). MS, *m/z* (I_{rel} (%)): 514 $[M]^+$ (0.6), 444 $[M-2HCl]^+$ (2.3), 397 $[M-CCl_3]^+$ (5.9), 276 $[M-CpRh-2HCl]^+$ (33.1), 225 (100). ^1H NMR ($CDCl_3$), δ: 1.06 (s, 6 H, 2 Me); 1,12 (s, 3 H, Me); 2.37 (s, 4 H, 2 CH_2); 4.29 (dd, 2 H, 2 CH, $^3J_{H-H}$ = 6.8 Hz, $^2J_{H-Rh}$ = 1.35 Hz); 5.54 (d, 5 H, Cp, $^2J_{H-Rh}$ = 1.1 Hz); 6.92 (dd, 2 H, 2 CH_2, $^3J_{H-H}$ = 6.8 Hz, $^2J_{H-Rh}$ = 1.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 28.40 (s, 2 Me); 30.58 (s, $\underline{C}Me_2$); 31.53 (d, Me, $^4J_{C-Rh}$ = 2.8 Hz); 50.94 (d, 2 CH, $^1J_{C-Rh}$ = 9.5 Hz); 52.34 (s, 2 CH_2); 54.68 (s, $\underline{C}(CCl_3)Me$); 82.86 (br.s, 2 CH); 88.87 (d, Cp, $^1J_{C-Rh}$ = 5.7 Hz); 101.85 (s, CCl_3); 105.64 (s, $\underline{C}=C$); 119.11 (br.s, $C=\underline{C}$); 194.35 (s, 2 C=O).

Di-μ-chlorobis[(2,3,5,6-η)-4-methyl-4-*exo*-trichloromethyl-2,5-cyclohexadien-1-one]dirhodium (11). A solution of ketone **2** (0.096 g, 0.425 mmol) in 1 mL of CH_2Cl_2 was added with stirring to a mixture of complex **6** and 1 mL of CH_2Cl_2. The mixture was stirred for an additional 3 h at 20 °C, allowed to stand overnight, and evaporated to dryness on a rotary evaporator. The residue was washed with Et_2O (4×5 mL) and dried *in vacuo* to give 0.112 g (80%) of complex **11** as a yellow microcrystalline powder, poorly soluble in organic solvents. Found (%): C, 26.16; H, 2.15; Cl, 38.85. $C_{16}H_{14}Cl_2O_2Rh_2$. Calculated (%): C, 26.41; H, 1.94; Cl, 38.97. IR, ν/cm^{-1}: 500, 520, 605, 680 1360, 1400, 1450, 1470, 1580 (C=C—C=O); 1650 (C=O).

Reaction of complex 11 with CpTl. CpTl (0.074 g, 0.273 mmol) was added to a mixture of complex **11** (0.1 g, 0.137 mmol) and 5 mL of THF. The reaction mixture was stirred for 2 h at 20 °C, the solvent was evaporated on a rotary evaporator, the solid residue was extracted with $CHCl_3$ (2×5 mL), the combined extracts were filtered, and the filtrate was concentrated. The residue was reprecipitated from a solution in CH_2Cl_2 with hexane, and the resulting yellow precipitate was washed with Et_2O and dried *in vacuo* to give 0.065 g (60%) of **[(1,2,3,5,6-η)-4-methyl-4-*exo*-trichloromethyl-2,5-cyclohexadien-1-one]-(η^5-cyclopentadienyl)rhodium (12)**, decomp.p. 140—145 °C. Found (%): C, 39.31; H, 3.02; Cl, 27.45. $C_{13}H_{12}Cl_3ORh$. Calculated (%): C, 39.68; H, 3.07; Cl, 27.03. IR, ν/cm^{-1}: 1230, 1355, 1390, 1420, 1445, 1470, 1618 (C=C—C=O). MS, *m/z* (I_{rel} (%)): 357 $[M-Cl]^+$ (1.0), 322 $[M-2Cl]^+$ (19.4), 294 $[M-2Cl-CO]^+$ (15.9), 275 $[M-CCl_3]^+$ (75.7), 247 $[M-CCl_3-CO]^+$ (17.9), 203 [CpRhCl] (51.3), 168 $[CpRh]^+$ (100). ^1H NMR ($CDCl_3$), δ: 2.06 (s, 3 H, Me); 3.78 (dd, 2 H, 2 CH, $^3J_{H-H}$ = 6.7 Hz, $^2J_{H-Rh}$ = 1.2 Hz); 4.88 (dd, 2 H, 2 CH, $^3J_{H-H}$ = 6.7 Hz, $^2J_{H-Rh}$ = 1.2 Hz); 5.53 (d, 5 H, Cp, $^2J_{H-Rh}$ = 1.0 Hz). $^{13}C\{^1H\}$ NMR (CD_3OD), δ: 31.05 (s, Me); 54.85 (d, 2 CH, $^1J_{C-Rh}$ = 10.5 Hz); 56.73 (d, $\underline{C}(CCl_3)Me$, $^3J_{C-Rh}$ = 3.3 Hz); 76.54 (d, Cp, $^1J_{C-Rh}$ = 7.4 Hz); 88.89 (d, 2 CH, $^1J_{C-Rh}$ = 5.5 Hz); 109.45 (s, CCl_3); 163.60 (s, C=O).

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