2212 *Russian Chemical Bulletin, International Edition, Vol. 50, No. 11, pp. 2212—2214, November, 2001*

Diastereoselectivity of the formation of planar chiral ruthenocenol in reactions of chiral tertiary phosphines with the (η^4-cyclopentadienone)(η^5-cyclopentadienyl)ruthenium cation

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The reactions of chiral benzyl- and ethyl(phenyl)ferrocenylphosphines with (acetonitrile)(η^4-cyclopentadienone)(η^5-cyclopentadienyl)ruthenium trifluoromethylsulfonate proceed diastereoselectively through the attack on the cyclopentadienone ring to form planar chiral 2-phosphonioruthenocenols as mixtures of two diastereomers in ratios of 1.7 : 1 and 2 : 1, respectively.

Key words: (cyclopentadienone)(cyclopentadienyl)ruthenium cation, chiral phosphines, benzyl(phenyl)ferrocenylphosphine, phosphonioruthenocenols, diastereoselectivity.

Organometallic analogs of phenols, *viz.*, hydroxymetallocenes, remain poorly studied because of their instability, although the first representative, *viz.*, ferrocenol, was prepared as early as 1959.[1] Hydroxymetallocenes attracted our attention in view of the fact that cyclopalladation of mixed phosphite esters of phenols (hydroxyarenes) discovered by us[2] was extended to ferrocenol.* Hence, we are interested in hydroxyruthenocene and its substituted chiral derivatives, which are readily accessible due to the special features of the chemistry of ruthenocene. Thus, Kirchner[3—5] has developed an ingenious approach to these compounds involving the reactions of nucleophiles with the cations of the salts $[Ru(L)(Cp)(C_5H_4O)]^+X^-$ (**1**), where L is a nitrogen-containing ligand, for example, acetonitrile, pyridine, or thiourea. In these cations, either of the two rings as well as the metal atom can be subjected to the nucleophilic attack, the direction of the attack being determined by the nature and properties of the nucleophile and the ligand coordinated to the metal atom. The evidence for the possibility of the addition of the cyanide and thiolate anions has been reported.[4] The addition of tertiary phosphines has been studied in detail.[3,5] The latter reactions afford either 1,2-homo- or 1,1′-heteroannular phosphonioruthenocenols depending on the basicity and steric characteristics of phosphines and the capability of the ligand bound to the ruthenium atom to be involved in complex formation. Based on the intermediates detected in a number of reactions, several reaction mechanisms were proposed. The reactions of more basic dialkylaryl- or trialkylphosphines with cations **1** yield heteroannular 1,1′-phosphonioruthenocenols, whereas homoannular 1,2-derivatives of ruthenocenol are generated in the reactions of **1** with low-basicity aromatic amines. Although these reactions give rise to planar chirality, the stereochemical aspect of the reactions remained unknown. However, the use of chiral phosphines in these reactions enables one to determine the diastereoselectivity and offers a route to new optically active ruthenocene derivatives, which are currently few in number.[6]

In the present study, we examined the reactions of (acetonitrile)(η^4-cyclopentadienone)(η^5-cyclopentadienyl)ruthenium salts (**1**) (X = CF_3SO_3 or PF_6) with P-chiral tertiary phosphines **2** or **3** yielding mixtures of diastereomeric salts of benzyl- (**4**) or ethyl(ferrocenyl)(2-hydroxyruthenocenyl)phenylphosphonium (**5**), respectively. Phosphines **2** and **3** are of particular interest because products **4** and **5** contain simultaneously two groups, which can be oxidized, *viz.*, ferrocenyl and ruthenocenyl, and in the limiting case they can reversibly donate three additional electrons.

The course of the reactions in acetone was monitored by ^{1}H NMR spectroscopy. After 2.5 h, approximately 50% of the initial cation **1** remained unconsumed, whereas phosphines **2** and **3**, which were taken in amounts from one equivalent to a 50% excess,* disappeared, and the NMR spectra show three groups of new signals both in the metallocenyl and aromatic regions. Two groups of signals, which are similar in shape and differ only in the intensities, were assigned (taking into account that each group has a pair of singlets of the

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* The results will be published in *J. Organomet. Chem.*

* The preliminary study demonstrated that compound **1** can be completely consumed in the reaction; however, it is necessary to use a substantial excess of phosphines, which are not easily accessible and which are difficult to recuperate because they are readily oxidized in solutions.

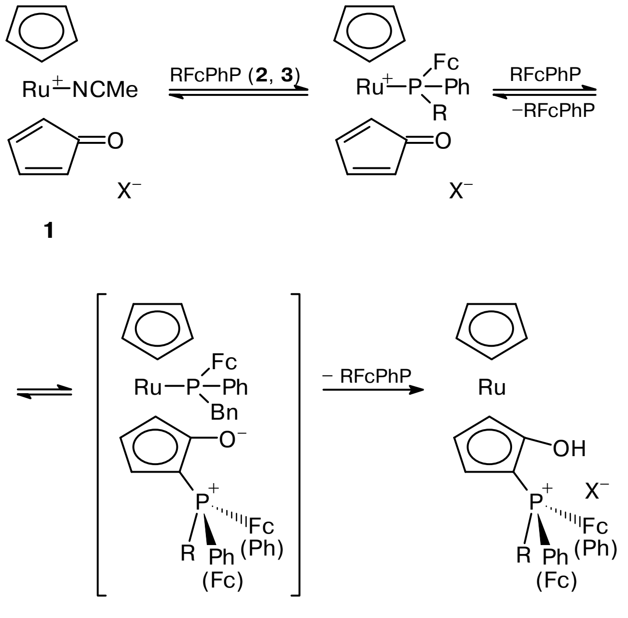
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2112—2114, November, 2001.

unsubstituted cyclopentadienyl rings both of the ruthenocenyl and ferrocenyl fragments) to homoannular compounds **4** and **5** with the diastereomeric ratios of 1.7 : 1 and 2 : 1, respectively. This is in agreement with the ^{31}P NMR spectra, which have signals at δ 25.4 and 27.6 for **4** and at δ 28.97 and 30.38 for **5** in virtually the same ratios.

The formation of phosphonium adducts **4** and **5** from cation **1** and neutral fragments **2** and **3** is accompanied by the distribution of the positive charge over two metallocenyl systems, which is in accordance with the downfield shifts of the signals for the protons of the ferrocenyl group and the upfield shifts of the signals for the protons of the ruthenocenyl fragment observed in the ^{1}H NMR spectra. At low field behind the aromatic region, broadened singlets were found at δ 8.60 and 8.97 with the intensity ratio of 1.7 : 1 for **4** and at δ 8.68 and 8.91 with the intensity ratio of 1.94 : 1 for **5**. These signals were assigned to the hydroxyl protons of the diastereomers of **4** and **5** and their broadening indicates that these protons are involved in slow exchange processes. The only difference in the behavior of **2** and **3** in the reaction under study is that the reaction of **3** gave rise to a small amount (about 10%) of heteroannular ethyl(ferrocenyl)(1′-hydroxyruthenocenyl)(phenyl)phosphonium trifluoromethanesulfonate (**6**). This result demonstrates that the replacement of the benzyl group by the ethyl group leads to an increase in the nucleophilicity of phosphine due to which it can attack the nonsubstituted cyclopentadienyl ring. The use of the pyridine complex of type **1** instead of the acetonitrile complex in the reaction with phosphine **2** resulted in a substantial decrease in its rate (after one day, the conversion was at most 25%) and the complete loss of diastereoselectivity. Hence, alkyldiarylphosphines **2** and **3** behave analogously to triarylphosphine rather than to dialkylphenylphosphines as one might expect taking into account the presence of the ferrocenyl group in **2** and **3**. The third product did not contain ruthenocene and was presumably the protonated form of the starting phosphine existing in equilibrium with the neutral form. Protonation may occur due to the labile proton of the hydroxy group in compounds **4** and **5** and hence, the betaine structure of their diastereomers is not inconceivable. Salt **4** was synthesized in a preparative amount and was isolated as a mixture of diastereomers in a ratio of approximately 1.2 : 1. The specimen was characterized by the reliable data from elemental analysis, and its ^{1}H and ^{31}P NMR spectral characteristics were identical with those obtained in analysis of the reaction mixture.

Of several reactions with cation **1**, which were examined for various tertiary phosphines, the reaction of the pyridine complex of **1** with PMe_3, like the reactions with phosphines **2** and **3**, was not brought to completion.[5] We modified the scheme proposed in the cited study[5] (see Scheme 1) taking into account the ability of phosphines **2** and **3** to attack the cyclopentadienone ring. In the first stage, phosphines **2** and **3** replace the MeCN ligand at the ruthenium atom followed by the attack of the second phosphine molecule on the cyclopentadienone ring to form the expected phosphonioruthenocenols due to dissociation of the intermediate complex. In our opinion, steric interactions of the second phosphine molecule with the phosphine molecule coordinated to the ruthenium atom may account for the observed diastereoselectivity of the reaction.

Scheme 1



4, **5**

2, **4**: R = Bn; **3**, **5**: R = Et, X = PF_6^-, $CF_3SO_3^-$

Experimental

All reactions were carried out under an atmosphere of argon. Anhydrous solvents were prepared according to standard procedures. Acetone used as a solvent was distilled off from the complex with NaI immediately before use. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 instrument. The chemical shifts of the phosphorus atom were measured relative to H_3PO_4.

Reaction of cation 1 with phosphine 2. NMR study. A mixture of **1** and **2** taken in a ratio of 1 : 1.5 was dissolved in acetone-d_6 in an NMR tube. After 2—2.5 h, the ^{1}H and ^{31}P NMR spectra were recorded.

^{1}H NMR, δ, for **1:** 4.66 (m, 2 H, C_5H_4ORu); 5.83 (s, 5 H, CpRu); 6.52 (m, 2 H, C_5H_4ORu); for **major diastereomer of 4:** 4.10 (br.s, 1 H, C_5H_3Ru); 4.32 (s, 5 H, CpFe); 4.46 and 4.50 (AB system, 2 H); 4.66 (s, 5 H, CpRu); 4.73 (br.s, 1 H, C_5H_3Ru); 4.80 (m, 2 H); 4.87 (m, 2 H, C_5H_3Fe); 5.16 (br.s, 1 H, C_5H_3Ru); 7.14 (m, 2 H, Bn); 7.29 (m, 3 H, Bn); 7.60 (m, 3 H, Ph); 8.16 (m, 2 H, Ph), 8.60 (br.s, 1 H, OH); for **minor diastereomer of 4:** 4.32 (br.s, 1 H, C_5H_3Ru); 4.40 (br.s, 5 H, CpFe); 4.56 and 4.60 (AB system, 2 H); 4.73 (br.s, 1 H, C_5H_3Ru); 4.76 (s, 5 H, CpRu); 4.83 (m, 2 H, C_5H_3, Fe); 4.9

(m, 2 H, C_5H_3Fe); 5.26 (br.s, 1 H, C_5H_3Ru); 7.06 (m, 2 H, Bn); 7.86 (m, 3 H, Ph); 8.30 (m, 2 H, Ph); 8.97 (br.s, 1 H, OH).

^{31}P NMR, δ for **4**: 25.4 (major diastereomer of **4**), 27.6 (minor diastereomer of **4**).

Synthesis of (benzyl)(ferrocenyl)(2-hydroxyruthenocenyl)(phenyl)phosphonium hexafluorophosphate (4). Phosphine **2** (46 mg, 0.12 mmol) was added to a solution of salt **1** (X = PF_6) (50 mg, 0.12 mmol) in acetone (2 mL). The reaction mixture was stirred for 2 h and kept for 12 h. Then the solvent was evaporated and the residue was dried. The crude product was obtained in a yield of 85 mg (94%). After washing with ether, compound **4** was obtained as a yellow-brown solid. Found (%): C, 52.16; H, 4.12; P, 7.96. $C_{33}H_{30}F_6FeOP_2Ru$. Calculated (%): C, 51.11; H, 3.90; P, 7.96. The ^1H and ^{31}P NMR spectra correspond to a mixture of diastereomers of **4** in a ratio of 1.3 : 1.

Reaction of cation 1 with phosphine 3. NMR study. The experiment was carried out as described above.

^1H NMR, δ for **major diastereomer of 5:** 1.39—1.48 (m, 3 H, Me); 3.15—3.38 (m, CH_2); 4.13 (m, 1 H, C_5H_3Ru); 4.37 (s, 5 H, CpFe); 4.54 (m, 1 H, C_5H_3Ru); 4.72 (s, 5 H, CpRu); 4.82 (m, 1 H, C_5H_3Ru); 4.87 (m, 2 H, C_5H_3Fe); 4.90 (m, 2 H, C_5H_3Fe); 5.13 (m, 1 H, C_5H_3Ru); 7.80 (m, 3 H, Ph); 8.20—8.25 (m, 2 H, Ph); 8.68 (br.s, 1 H, OH); for **minor diastereomer of 5:** 1.28—1.37 (m, 3 H, Me); 3.15—3.38 (m, CH_2); 4.47 (m, 1 H, C_5H_3Ru); 4.44 (s, 5 H, CpFe); 4.47 (m, 1 H, C_5H_3Ru); 4.73 (s, 5 H, CpRu); 4.85 (m, 1 H, C_5H_3Ru); 4.87 (m, 2 H, C_5H_3Fe); 4.90 (m, 2 H, C_5H_3Fe); 5.21 (m, 1 H, C_5H_3Ru); 7.84 (m, 3 H, Ph); 8.68 (m, 2 H, Ph); 8.91 (br.s, 1 H, OH). ^1H NMR of **product 6** (some signals): 2.19—2.26 (m, 2 H, CH_2); 4.42 (s, 5 H, CpFe); 5.03 (m, 1 H, C_5H_3Ru); 5.05 (m, 1 H, C_5H_3Ru); 5.07 (m, 1 H, C_5H_3Ru); 8.00 (br.s, 1 H, OH); 8.06—8.11 (m, 2 H, Ph).

^{31}P NMR, δ: 29.0 (major diastereomer of **5**); 29.8 (**6**); 30.4 (minor diastereomer of **5**).

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Received February 2, 2001;
in revised form April 10, 2001