Organometallic Chemistry

Cyclopalladation of Schiff's bases in the ruthenocene series. The possibility of application of the asymmetric version of the reaction to metalloceneimines

L. L. Troitskaya,[a] S. T. Ovseenko,[a] V. I. Sokolov,[a] and M. Gruselle[b]*

[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085
[b]National Center for Scientific Research, URA 419, 4 pl. Jussieu, Bat. F, 75252 Paris, France. Fax: 33 (1) 4427 3841*

p-Tolyliminoalkylruthenocenes — Schiff's bases of the ruthenocene series — react with sodium tetrachloropalladate in the presence of carboxylate anion similarly to their ferrocenyl analogs to give cyclopalladation products. The optical rotation values of the products resulting from carbonylation of palladated ferrocene and ruthenocene aldimines, prepared under conditions of asymmetric catalysis, followed by liberation of the aldehyde group were used to determine the stereochemistry and enantiomeric purity of the cyclopalladation products.

Key words: ferrocene, ruthenocene, Schiff's bases, cyclopalladation.

Approaches to the synthesis of new ruthenocene derivatives, including optically active ones, are normally developed based on the similarity of the ruthenocene and ferrocene chemistry. Thus the known asymmetric cyclopalladation of dimethylaminomethylferrocene[1] has been recently extended to dimethylaminomethylruthenocene,[2] and the subsequent replacement of the Pd atom has resulted in the regio- and enantioselective introduction of several functional groups into the initial amine. In view of the recent publications dealing with cyclopalladation of ferrocene Schiff's bases,[3,4] which is also catalyzed by the carboxylate anion, in the present work we studied cyclopalladation of Schiff's bases of the ruthenocene series **1a—c**, subsequent transformations of the reaction products, and also the possibility of conducting the asymmetric versions of this reaction and of the corresponding reaction of ferrocene derivatives.

Results and Discussion

In a previous study[3] devoted to cyclopalladation of Schiff's bases of the ferrocene series, it has been noted

* Centre Nationale de Recherches Scientifiques, URA 419 4, pl. Jussieu, Bat. F, 75252 Paris, France.

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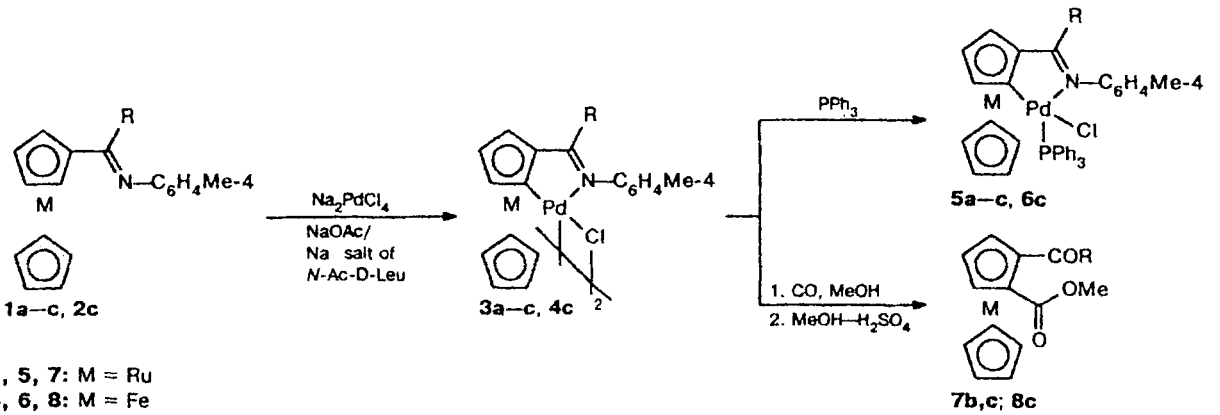
Scheme 1



1, 3, 5, 7: M = Ru
2, 4, 6, 8: M = Fe
R = Me (**a**), Ph (**b**), H (**c**)

that ketimines react much faster than aldimines. We found that ketimines **1a,b** derived from acetyl- and benzoylruthenocene, respectively, also readily react with sodium tetrachloropalladate in the presence of NaOAc. The σ-palladium derivatives **3a,b** thus obtained were characterized as the corresponding monomeric complexes **5a,b** prepared by treating **3a,b** with triphenylphosphine.

When aldimine **1c** derived from ruthenocenecarbaldehyde was introduced in the cyclopalladation reaction under the conditions described for its ferrocene analog,[3] only coordination complex of the L_2PdCl_2 type was obtained, but no desired product **3c**. Moreover, we were also unable to reproduce the procedure described in the study cited.[3] We carried out cyclopalladation of ferrocenylaldimine **2c** in a suspension, rather than in a solution as is done usually. After dissolution of the resulting compound in benzene, concentration of the benzene filtrate, and treatment of the residue with hexane, the product was converted into a triphenylphosphine complex by refluxing with triphenylphosphine in acetone. The aldimine, which is sparingly soluble in methanol, was used as a suspension in order to suppress the formation of the coordination complex L_2PdCl_2, since in the case of complete solubility of the palladating reagent, its excess with respect to the aldimine was created. However, under these drastic conditions, the subsequent cleavage of the dimer bridges in the cyclopalladation product follows an unusual pathway. (Normally, it occurs instantaneously at room temperature in benzene.)

Since the attempts to convert aldimines **1c** and **2c** into their cyclopalladated derivatives **3c** and **4c** by the above-mentioned procedure failed, the reaction was carried out in solution at an equimolar ratio of the reactants or with a 100% excess of the palladating agent for 10 days instead of 24 h. The precipitates that formed during the reaction were readily soluble in benzene solutions of triphenylphosphine at ~20 °C. The addition of hexane to these solutions resulted in the precipitation of complexes **5c** and **6c** with the metallocene—palladium σ-bonds, together with a small amount of the complex $(PPh_3)_2PdCl_2$, indicating that the reaction product contained the coordination complex L_2PdCl_2. In the presence of excess palladating agent, only **5c** and **6c** were formed, although their yield was lower than with an equimolar ratio of the reactants. The structures of compounds **5c** and **6c** are unambiguously proved by their ^1H NMR spectra; the spectrum of **6c** completely coincides with that reported previously.[3] It is beyond doubt that the authors of the study cited did synthesize complex **6c**, but cyclopalladation apparently occurred at the stage of refluxing of the palladium complex of aldimine L_2PdCl_2 with triphenylphosphine in acetone. Reactions of this type with elimination of one ligand and elements H and Hal have been reported previously.[5] Although the detailed mechanism of these reactions is unknown, they might be induced by triphenylphosphine.

Since cyclopalladation of ferrocene and ruthenocene Schiff's bases occurs in the presence of carboxylate anions (in the case of the ferrocenyl analog of **1a**, the cyclopalladation product is also produced without these anions but in a substantially lower yield[4]), the replacement of sodium acetate by a salt of an optically active amino acid could result in asymmetric induction, as had been observed for dimethylaminomethyl derivatives of ferrocene and ruthenocene.[1,2] In addition, in the case of dimethylaminomethylferrocene, a high enantiomeric yield of the product could be attained only if the effective pH of the medium was maintained in the 7.6—7.8 range. Cyclopalladation of dimethylaminomethylruthenocene also requires a weakly alkaline medium, but the particular pH value is not important. In both cases, the reaction was carried out in aqueous methanol. These conditions could not be exactly reproduced in the cyclopalladation of metallocene Schiff's bases, because the latter are poorly soluble and are hydrolyzed in aqueous solutions. Therefore, the reaction was carried out in neat methanol, and alkali was added to a mixture of sodium tetrachloropalladate and the sodium salt of

N-acetyl-D-leucine until an effective pH value of 7.3—7.8 was attained, and after that, the Schiff's base was added. Under these conditions, cyclopalladation products are obtained in all cases; however, their optical rotations cannot be measured, because solutions of palladium complexes are intensely colored. This requires the use of dilute solutions for which reliable readings of the polarimeter cannot be obtained. These results imply a relatively low degree of asymmetric induction. In fact, the usual $[\alpha]_D$ values for optically pure plane-chiral chelates are hundreds of degrees, and, hence, the optical rotations observed are rather large even for highly dilute solutions. The absence of asymmetric induction in the case of ketimines can be explained by the fact that the process largely occurs without participation of the carboxylate anion, as has been found earlier.[4]

Although, as noted above, a number of cyclopalladated Schiff's bases of ferrocene derivatives have been synthesized, no transformations of these compounds have been reported. Of the reactions known for this type of palladium derivatives, carbonylation appeared to be one proceeding most smoothly. In fact, when CO was passed through methanolic solutions of the cyclopalladation product **3b** derived from ketimine or products **3c** and **4c** derived from aldimines, the Pd atom was replaced by an ester group, and the subsequent acid hydrolysis of the compounds thus formed yielded the corresponding keto or aldehydo esters **7b,c** or **8c**. The recovery of the carbonyl function is accompanied by partial hydrolysis of the ester group; in the case of **7b**, the hydrolysis was brought to completion and gave the keto acid.

Carbonylation of the palladium derivatives of aldimines was carried out using the products obtained under the conditions of asymmetric catalysis. Since the resulting aldehydo esters are characterized by a lower absorption than the palladacycles, we were able to determine the optical activity more accurately: for **7c**, $[\alpha]_D = +57.3°$ and for **8c**, $[\alpha]_D = +69.5°$. Derivative **7c** is previously known as the racemic ethyl ester.[6] Aldehydo ester **8c** has been described in the optically active form, and the maximum value of its optical rotation amounts to −759° for the (*Rp*)-enaniomer.[7] Thus, (+)-**8c** is characterized by the (*Sp*)-absolute configuration of the chiral plane and by an enantiomeric purity of about 9%. Therefore, the initial cyclopalladium derivative **4c** and, evidently, **3c**, have the same configuration. This means that in the cyclopalladation of ferrocene and ruthenocene Schiff's bases, as in the case of dimethylaminomethyl derivatives, the *N*-acetyl-D-leucine anion induces the predominant formation of the (*S*)-configuration of the chiral plane, but the efficiency of the induction is substantially lower.

The results obtained in this study indicate that asymmetric catalysis in the cyclopalladation of metallocene Schiff's bases is, in principle, possible. However, under these conditions, the reaction cannot be regarded as a preparative route to optically active metallocenes due to low enantiomeric yields.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-200SY spectrometer in $CDCl_3$ solutions; IR spectra were measured on a UR-20 spectrometer, and mass spectra were obtained on a Kratos MS890 mass spectrometer. Optical rotations were measured on an A1-EPO polarimeter. In all syntheses, anhydrous solvents, purified by known methods, were used.

Aldimines were obtained by the solid-phase condensation of metallocenecarbaldehyde with *p*-toluidine.[8] Ketimines were synthesized by known procedures described for ferrocene.[9]

[1-(*p*-Tolylimino)ethyl]ruthenocene (1a). ^{1}H NMR, δ: 1.96 (s, 3 H, MeC=N); 2.31 (s, 3 H, Me, Tol); 4.60 (s, 5 H, unsubstit. Cp); 4.72 and 5.14 (both t, each 2 H, substit. Cp); 6.60 and 7.10 (AB system, 4 H, C_6H_4).

[α-(*p*-Tolylimino)benzyl]ruthenocene (1b). ^{1}H NMR, δ: 2.18 (s, 3 H, Me); 4.66 (s, 5 H, unsubstit. Cp); 4.73 and 4.95 (both t, each 2 H, substit. Cp); 6.50 and 6.87 (AB system, 4 H, C_6H_4); 7.21 (s, 5 H, Ph).

[(*p*-Tolylimino)methyl]ruthenocene (1c). ^{1}H NMR, δ: 2.29 (s, 3 H, Me); 4.60 (s, 5 H, unsubstit. Cp); 4.72 and 5.08 (both t, each 2 H, substit. Cp); 6.94 and 7.10 (AB system, 4 H, C_6H_4); 8.11 (s, 1 H, HC=N).

Cyclopalladation of ruthenocenealdimines and ruthenoceneketimines (general procedure). A suspension (for ketimines) or a solution (for aldimine) of a Schiff's base (0.2 mmol) and stoichiometric amounts of Na_2PdCl_4 and NaOAc in 5 mL of MeOH were stirred for 3.5 h (**1a**), 19 h (**1b**), or 10 days (**1c**). The precipitate was separated, washed with water and methanol, dried, and converted into the triphenylphosphine complex or subjected to carbonylation without further purification.

Cyclopalladation of Schiff's bases under conditions of asymmetric catalysis (general procedure). Concentrated NaOH was added to a solution of stoichiometric amounts of Na_2PdCl_4 and the sodium salt of *N*-acetyl-D-leucine in methanol until an effective pH value in the 7.3—7.8 range was attained. After that, a solution of equimolar amounts of aldimines **1c** and **2c** in methanol was added. Solid ketimines **1a**, **1b**, **2a**, and **2b** were stirred with a methanolic solution of stoichiometric amounts of Na_2PdCl_4 and the sodium salt of *N*-acetyl-D-leucine. The reaction time and subsequent workup were the same as described above for the corresponding ruthenocene derivatives.

Transformation of the cyclopalladation products into triphenylphosphine complexes (general procedure). Solid products of cyclopalladation of Schiff's bases were treated at room temperature with a benzene solution of triphenylphosphine (1.5 mol.-equiv.). The mixture was immediately filtered. In the case of complexes **5c** and **6c**, the filtrate was concentrated to dryness, and the residue was crystallized from a CH_2Cl_2—hexane mixture, while in other cases, the complex $(PPh_3)_2PdCl_2$ and the required triphenylphosphine complex were successively precipitated by gradual addition of hexane to the filtrate.

Carbonylation of cyclopalladation products of aldimines and hydrolysis of the resulting esters (general procedure). A flow of CO was passed for 3 h at −20 °C through a stirred suspension of the cyclopalladation products in MeOH. Then the mixture was filtered, and the methanol was evaporated. A mixture of equal volumes of methanol and 10% H_2SO_4 was added to the residue. The resulting mixture was allowed to stand for 24 h, diluted with water, and extracted with ether. The ethereal solution was washed with water and dried with $MgSO_4$, the ether was evaporated, and the residue was chromatographed on Silufol UV 254 plates (using a 5 : 1 benzene—ether mixture as the eluent).

Complex Pd[(η^5-C_5H_5)Ru(η^5-C_5H_3CMe=NC_6H_4Me-4](PPh$_3$)Cl (5a). Yield 34% (based on the Schiff's base). Found (%): C, 58.46; H, 4.62; P, 4.09. $C_{37}H_{33}ClNPPdRu$. Calculated (%): C, 58.05; H, 4.34; P, 4.34. ^{1}H NMR, δ: 1.97 (s, 3 H, MeC=N); 2.29 (s, 3 H, MeC$_6$H$_4$); 3.51, 4.34, 4.78 (all m, 3 H, substit. Cp); 4.42 (s, 5 H, unsubstit. Cp); 6.81 and 7.11 (AB system, 4 H, C_6H_4); 7.37—7.78 (m, 15 H, PPh$_3$).

Complex Pd[(η^5-C_5H_5)Ru(η^5-C_5H_3CPh=NC_6H_4Me-4](PPh$_3$)Cl (5b). Yield 57% (based on the Schiff's base). Found (%): C, 61.02; H, 4.37; P, 3.75. $C_{42}H_{35}CClNPPdRu$. Calculated (%): C, 60.95; H, 4.26; P, 3.74. ^{1}H NMR, δ: 2.18 (s, 3 H, MeC$_6$H$_4$); 4.11, 4.35, 4.42 (all m, 3 H, substit. Cp); 4.45 (s, 5 H, unsubstit. Cp); 6.77 and 6.90 (AB system, 4 H, C_6H_4); 7.23—7.27; 7.38—7.42 and 7.75—7.86 (m, 20 H, 4Ph).

Complex Pd[(η^5-C_5H_5)Ru(η^5-C_5H_3CH=NC_6H_4Me-4](PPh$_3$)Cl (5c). Yield 43% (based on the Schiff's base). Found (%): C, 58.85; H, 4.32. $C_{36}H_{31}ClNPPdRu \cdot 0.5\ C_6H_6$. Calculated (%): C, 59.25; H, 4.33. ^{1}H NMR, δ: 2.31 (s, 3 H, MeC$_6$H$_4$); 3.52, 4.37, 4.83 (all m, 3 H, substit. Cp); 4.42 (s, 5 H, unsubstit. Cp); 7.13 (br.s, 4 H, C_6H_4); 7.39—7.45 and 7.70—7.81 (all m, 15 H, PPh$_3$). When the reaction was carried out in the presence of *N*-acetyl-D-leucine (effective pH value 7.4), the yield was 30.5% (based on the Schiff's base). Found (%): C, 61.12; H, 4.24. $C_{36}H_{31}ClNPPdRu \cdot C_6H_6$. Calculated (%): C, 60.80; H, 4.49.

Complex Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3CH=NC_6H_4Me-4](PPh$_3$)Cl (6c). The ratio **4** : Na_2PdCl_4 : Na salt of *N*-acetyl-D-leucine was 1 : 2 : 2, the effective pH value was 7.3. Yield 40%. Found (%): C, 60.09; H, 4.64; N, 1.69. $C_{36}H_{31}ClFeNPPd$. Calculated (%): C, 61.22; H, 4.42; N, 1.98. ^{1}H NMR, δ: 2.33 (s, 3 H, MeC$_6$H$_4$); 3.46, 4.16, 4.51 (all m, 3 H, substit. Cp); 3.96 (s, 5 H, unsubstit. Cp); 7.14 and 7.20 (AB system, 4 H, C_6H_4); 7.27—7.47 and 7.68—7.77 (all m, 15 H, PPh$_3$); 8.26 (d, 1 H, CH=N).

Methyl 2-benzoylruthenocenecarboxylate (7b) was obtained from **4b** (86 mg, 0.15 mmol). Carbonylation followed by isolation of the product by chromatography on Alufol plates (using benzene as the eluent) gave 18.2 mg of **7b** (yield 31%) containing a small amount of nonhydrolyzed imino ester (the ^{1}H NMR spectrum exhibits residual signals due to the toluidine fragment). ^{1}H NMR, δ: 3.43 (s, 3 H, COOMe); 4.70 (s, 5 H, unsubst. Cp); 4.80, 5.03 and 5.21 (all m, 3 H, subst. Cp); 7.30—7.87 (m, 5 H, Ph). The product was left in a methanol—10% H_2SO_4 mixture for 3 days at ~20 °C. The methanol was evaporated, water was added, and the precipitate was filtered off and dissolved in ether. The solution was washed with water and dried with $MgSO_4$ to give 15 mg (88%) of 2-benzoylruthenocenecarboxylic acid. ^{1}H NMR, δ: 4.70 (s, 5 H, unsubst. Cp); 5.07 and 5.79 (m, 2 H and 1 H, respectively, substit. Cp); 7.39—7.84 (m, 5 H, Ph).

(+)-Methyl 2-formylruthenocenecarboxylate (7c) was prepared from **1c** (300 mg, 0.9 mmol). Cyclopalladation, carbonylation, and partial hydrolysis gave 24 mg of (+)-**7c** (yield 8.6%, based on the initial Schiff's base). ^{1}H NMR, δ: 3.76 (s, 3 H, COOMe); 4.68 (s, 5 H, unsubstit. Cp); 4.96 and 5.36 (both m, 1 H and 2 H, respectively, substit. Cp); 9.95 (s, 1 H, CHO). MS, *m/z*: 318 [M$^+$], 290 [M—CO], 259 [M—CO—MeO], 231 [M—CO—COOMe]. IR, ν/cm^{-1}: 1720 (COOMe), 1680 (CHO). $[\alpha]_D$ +57.3° (*c* 0.48; EtOH).

(+)-Methyl 2-formylferrocenecarboxylate (8c) was prepared from **4c** (95 mg, 0.21 mmol). The yield of (+)-**8c** was 9 mg (15.4%). ^{1}H NMR, δ: 3.76 (s, 3 H, COOMe); 4.21 (s, 5 H, unsubstit. Cp); 4.70 and 5.03 (both m, 1 H and 2 H, respectively, substit. Cp); 10.41 (s, 1 H, CHO). $[\alpha]_D$ +69.5° (*c* 0.18; EtOH).

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References

1. V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, *J. Organomet. Chem.*, 1979, **182**, 537.
2. I. A. Mamedyarova, M. N. Nefedova, and V. I. Sokolov, *J. Organomet. Chem.*, 1996, **524**, 181.
3. R. Bosque, C. Lopez, J. Sales, X. Solans, and M. Font-Bardia, *J. Chem. Soc., Dalton Trans.*, 1994, 735.
4. S. Huo, Y. Wu, C. Du, H. Yuan, and X. Mao, *J. Organomet. Chem.*, 1994, **483**, 139.
5. A. Albinati, S. Affolter, and P. S. Pregosin, *Organometallics*, 1990, **9**, 379.
6. P. Bickert, B. Hildebrandt, and K. Hafner, *Organometallics*, 1984, **3**, 653
7. V. Rapis, K. Schlogl, and B. Steinitz, *Monatsh. Chem.*, 1977, **108**, 767
8. N. S. Khrushcheva, N. M. Loim, and V. I. Sokolov, *Izv. Akad. Nauk., Ser. Khim.*, 1997, 2056 [*Russ. Chem. Bull.*, 1997, **46**, 1952 (Engl. Transl.)].
9. S. Huo, Y. Wu, and X. Mao, *Tetrahedron*, 1994, **50**, 10467.

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