Brief Communications

Asymmetric cyclopalladation of 6-ferrocenyl-2,2´-bipyridine and 2-ferrocenyl-1,10-phenanthroline

L. A. Bulygina,[a] V. I. Sokolov,[a]★ I. A. Utepova,[b] V. L. Rusinov,[b] and O. N. Chupakhin[c]

[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (495) 135 5085. E-mail: sokol@ineos.ac.ru
[b]Ural State Technical University, 19 ul. Mira, 620002 Ekaterinburg, Russian Federation. Fax: +7 (343) 374 1189. E-mail: chupakhin@ios.uran.ru
[c]I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 22 ul. S. Kovalevskoi, 620219 Ekaterinburg, Russian Federation. Fax: +7 (343) 374 0458. E-mail: rusinov@htf.ustu.ru

Cyclopalladation of 6-ferrocenyl-2,2´-bipyridine and 2-ferrocenyl-1,10-phenanthroline in the presence of the *N*-acylamino acid salt as the asymmetric catalyst was performed. Some reactions of the resulting bicyclic palladium derivatives with tridentate (N,N,C) ligands were studied.

Key words: ferrocenes, 2,2´-bipyridines, 1,10-phenanthrolines, tridentate ligands, asymmetric cyclopalladation, palladacycles.

Asymmetric cyclopalladation of prochiral amines and imines using external optically active catalysts allows the synthesis of planar chiral palladacycles based on metallocenes, particularly, on ferrocene, in high enantiomeric yields.[1—4] In this connection, it is of interest to perform this reaction with such substrates as 6-ferrocenyl-2,2´-bipyridine (**1**) and 2-ferrocenyl-1,10-phenanthroline (**2**).[5,6] This may provide a route to optically active derivatives of these systems, which have found use in photophysics.[7,8] Earlier,[9,10] cyclopalladation of analogous 2-aryl-substituted systems, which are not prochiral and, consequently, cannot give optically active derivatives, has been documented. For these systems, the chelate unit with the tridentate (N,N,C)PdCl ligand was demonstrated to be very stable. In the case of ferrocenyl-substituted systems,[5,6] (1,5-cyclooctadiene)palladium dichloride, which cannot be, in principle, involved in the asymmetric reaction with external chiral catalysts, was used as the metalating agent.

We performed asymmetric cyclopalladation of compounds **1** and **2** in methanol under pH control catalyzed by an *N*-acetyl-D-leucine salt[1] and obtained palladium

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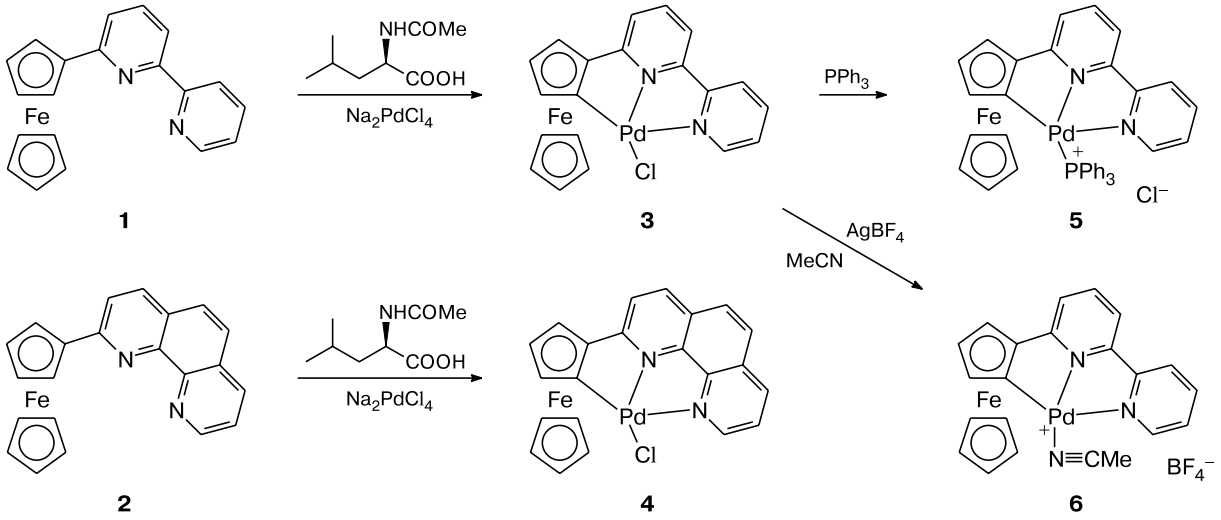
Scheme 1



bicyclic compounds **3** and **4**, respectively, in high yields (Scheme 1). In the case of phenanthroline derivative **2**, two equivalents of the salt were required to prevent the formation of the L_2PdCl_2-type complex. We failed to measure the optical rotation of the cyclopalladated products at 589 nm (the standard D line of a sodium lamp) because of high absorption by the intensively violet solution. Attempts to determine the enantiomeric compositions of **3** and **4** by HPLC on chiral columns failed. Hence, we performed a chiroptical study by circular dichroism, which confirmed optical activity of both compounds.

The reactivity of metallabicycles with tridentate (N,N,C) ligands has received little study. The reaction of aryl isocyanide with metallabicycles is the only recently described reaction[11] accompanied by cleavage of the metal—carbon bond. A detailed study of the behavior of compound **3** in a number of reactions typical of palladacycles with bidentate (N,C) ligands also demonstrated that this compound is very stable. The latter remained unconsumed after an attempt to perform its carbonylation in methanol, after refluxing with tolan in toluene, and after heating with alkyl acrylates in the presence of triethylamine.[12] The reaction with tin metal is the only reaction accompanied by the Pd—C bond cleavage, which was successfully performed; however, unlike the original studies with cyclopalladated tertiary amines,[13,14] the starting compound **1** rather than the tin chelate was obtained as the reaction product. On the contrary, the reactions at the Pd—Cl bond proceed in a standard fashion to give quaternary phosphonium salt **5** and moderately unstable borofluoride **6**, for which we failed to obtain satisfactory elemental analysis data.

Experimental

The starting compounds **1** and **2** were synthesized in 80% yield according to our procedure.[15] The ^{1}H NMR spectra were recorded on a Bruker instrument (400 MHz).

[2-(2,2′-Bipyridin-6-yl)ferrocen-1-yl]palladium chloride (3). A solution of compound **1** (0.25 g, 0.735 mmol) in MeOH (15 mL; since compound **1** is difficultly soluble, the solution was slightly warmed to dissolve the precipitate) was added to a solution of Na_2PdCl_4 (0.216 g, 0.735 mmol) and *N*-acetyl-D-leucine (0.1273 g, 0.735 mmol) in MeOH (10 mL) brought to pH 7.42 with a solution of NaOH (0.0294 g, 0.735 mmol) in H_2O (5 mL). The reaction mixture was stirred for 6 h (until the spot of the starting compound **1** in the TLC chromatogram disappeared; MeOH : $CHCl_3$, 1 : 10, as the eluent). Then the solvent was evaporated, the residue was dissolved in chloroform and washed with water, the organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo*. Product **3** was obtained in a yield of 0.34 g (96%).

Found (%): C, 49.87; H, 3.11; N, 5.61; Cl, 7.29. $C_{20}H_{15}ClFeN_2Pd$. Calculated (%): C, 49.93; H, 3.14; N, 5.82; Cl, 7.37. ^{1}H NMR ($CDCl_3$), δ: 4.20 (s, 5 H, C_5H_5); 4.54 (t, 1 H, C_5H_3, J = 2.3); 4.64 (d, 1 H, C_5H_3, J = 2.8 Hz); 4.92 (d, 1 H, C_5H_3, J = 2.6 Hz); 7.24 (d, 1 H, H_{pyr}, J = 8.0 Hz); 7.54—7.60 (m, 2 H, H_{pyr}); 7.78 (t, 1 H, H_{pyr}, J = 8.0 Hz); 7.94—8.04 (m, 2 H); 8.96 (d, 1 H, H_{pyr}, J = 4.3 Hz).

[2-(1,10-Phenanthrolin-2-yl)ferrocen-1-yl]palladium chloride (4). A solution of compound **2** (0.268 g, 0.735 mmol) in MeOH (15 mL) was added to a solution of Na_2PdCl_4 (0.216 g, 0.735 mmol) and *N*-acetyl-D-leucine (0.1273 g, 0.735 mmol) in MeOH (10 mL) brought to pH 7.36 with a solution of NaOH (0.0294 g, 0.735 mmol) in H_2O (5 mL). The reaction mixture was stirred for 6 h, *N*-acetyl-D-leucine (0.1273 g, 0.735 mmol) was again added, and the mixture was stirred for 6 h. Then the solvent was evaporated, the residue was dissolved in chloroform and washed with water, the organic layer was dried (Na_2SO_4),

and the solvent was removed *in vacuo*. The residue was dissolved in a 9 : 1 chloroform—methanol mixture and passed through a thin layer of SiO_2, the solvent was evaporated, and the compound was crystallized from CH_2Cl_2. Product **3** was obtained in a yield of 0.353 g (95%). Found (%): C, 46.09; H, 2.64; N, 4.62. $C_{22}H_{15}ClFeN_2Pd \cdot CH_2Cl_2$. Calculated (%): C, 46.82; H, 2.90; N, 4.75. ^{1}H NMR ($CDCl_3$), δ: 4.20 (s, 5 H, C_5H_5); 4.65 (t, 1 H, C_5H_3, J = 2.5 Hz); 4.73 (d, 1 H, C_5H_3, J = 2.3 Hz); 5.07 (d, 1 H, C_5H_3, J = 2.3 Hz); 7.52 (d, 1 H, H_{phen}, J = 8.5 Hz); 7.76—7.81 (m, 3 H, H_{phen}); 8.20 (d, 1 H, H_{phen}, J = 8.7 Hz); 8.39 (dd, 1 H, H_{phen}, J = 1.6 Hz); 9.05 (dd, 1 H, H_{phen}, J = 1.6 Hz).

(Triphenylphosphine)[2-(2,2′-bipyridin-6-yl)ferrocen-1-yl]palladium chloride (5). Triphenylphosphine (0.0545 g, 0.208 mmol) was added to a solution of compound **3** (0.1 g, 0.208 mmol) in benzene (30 mL). The reaction mixture was refluxed for 4 h. Then benzene was evaporated, and the residue was washed with diethyl ether and dried. Compound **5** was obtained in a yield of 0.09 g (58%) and was crystallized from $CHCl_3$. Found (%): C, 54.69; H, 3.34; N, 3.61. $C_{38}H_{30}ClFeN_2PPd \cdot \cdot CHCl_3$. Calculated (%): C, 54.23; H, 3.59; N, 3.24. ^{1}H NMR ($CDCl_3$), δ: 3.83 (s, 5 H, C_5H_5); 3.27 (br.s, 1 H, C_5H_3); 4.29 (br.s, 1 H, C_5H_3); 4.76 (br.s, 1 H, C_5H_3); 6.76—6.78 (m, 1 H); 7.06 (br.s, 1 H); 7.37 (d, 1 H, J = 8.6 Hz); 7.53—7.62 (m, 9 H, PPh_3); 7.78—7.84 (m, 6 H, PPh_3); 8.15 (br.s, 1 H, H_{pyr}); 8.27 (br.s, 1 H, H_{pyr}); 8.78 (br.s, 1 H, H_{pyr}); 9.27 (br.s, 1 H, H_{pyr}).

Reaction of complex 3 with tin metal. Activated tin (0.105 g) was added to a solution of complex **3** (0.021 g, 0.044 mmol) in toluene (50 mL) and refluxed for 2.5 h. (The tin powder was preliminarily shaken with a 10% NaOH solution for approximately 10 min, and then the precipitate was filtered off, washed several times with water and methanol, and dried.) The color of the solution changed from violet to yellow. The precipitate was filtered off, the filtrate was concentrated, and the residue was dissolved in a 1 : 1 methanol—chloroform mixture and passed through a thin layer of SiO_2. After evaporation of the solvent, compound **1** was obtained in a yield of 0.010 g (68%). ^{1}H NMR ($CDCl_3$), δ: 4.06 (s, 5 H, C_5H_5); 4.42 (t, 2 H, C_5H_4, J = 2.1 Hz); 5.04 (t, 2 H, C_5H_4, J = 2.1 Hz); 7.30—7.35 (m, 1 H, H_{pyr}); 7.44 (dd, 1 H, H_{pyr}, J = 1 Hz); 7.73 (t, 1 H, H_{pyr}, J = 7.67 Hz); 7.83—7.89 (m, 1 H); 8.22 (dd, 1 H, H_{pyr}, J = 1 Hz); 8.59 (d, 1 H, H_{pyr}, J = 8.3 Hz); 8.68—8.70 (m, 1 H).

(Acetonitrile)[2-(2,2′-bipyridin-6-yl)ferrocen-1-yl]-palladium tetrafluoroborate (6). Silver tetrafluoroborate (0.0145 g, 0.074 mmol) was added to a solution of complex **3** (0.0358 g, 0.074 mmol) in acetonitrile (30 mL), and the reaction mixture was stirred for 4 h (until the starting compound **3** was consumed, TLC monitoring, MeOH : $CHCl_3$, 1 : 10, as the eluent). The precipitate that formed was filtered off, the filtrate was concentrated, the residue was washed with diethyl ether and dried, and compound **6** was obtained in a yield of 0.035 g (92%). ^{1}H NMR (DMSO-d_6), δ: 4.30 (s, 5 H, C_5H_5); 4.70 (br.s, 1 H, C_5H_3); 4.76 (br.s, 1 H, C_5H_3); 5.02 (br.s, 1 H, C_5H_3); 7.78 (d, 1 H, H_{pyr}, J = 8.0 Hz); 7.93—7.97 (m, 1 H, H_{pyr}); 8.20—8.31 (m, 2 H); 8.38—8.43 (m, 1 H, H_{pyr}); 8.6 (d, 1 H, H_{pyr}, J = 8.0 Hz); 9.2 (d, 1 H, H_{pyr}, J = 6.2 Hz).

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References

1. V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, *J. Organomet. Chem.*, 1979, **182**, 537.
2. V. I. Sokolov, *Pure Appl. Chem.*, 1983, **55**, 1837.
3. V. I. Sokolov, *J. Organomet. Chem.*, 1995, 500, 299.
4. V. I. Sokolov, I. A. Mamedyarova, and M. N. Nefedova, *J. Organomet. Chem.*, 1996, 524, 181.
5. I. R. Butler and J. L. Roustan, *Canad. J. Chem.*, 1990, **68**, 2212.
6. I. R. Butler, *Organometallics*, 1992, **11**, 74.
7. S. W. Lai and C. M. Che, *Top. Curr. Chem.*, 2004, **241**, 27.
8. V. Balzani, in *Handbook of Photochemistry*, Ed. M. Montalti, Taylor and Francis, New York, 2006, p. 49.
9. E. C. Constable, R. P. G. Henney, P. R. Raithby, and L. R. Sousa, *J. Chem. Soc., Dalton*, 1992, 2251.
10. J. Dupont, C. S. Consorti, and J. Spencer, *Chem. Rev.*, 2005, **105**, 2527.
11. Y. J. Kim, X. Chang, J. T. Han, M. S. Lim, and S. W. Lee, *J. Chem. Soc., Dalton Trans.*, 2004, 3699.
12. G. Zhao, Q. G. Wang, and T. C. W. Mak, *J. Organomet. Chem.*, 1999, **574**, 311.
13. Y. J. Wu, L. Ding, Z. X. Zhou, C. X. Du, and W. L. Wang, *J. Organomet. Chem.*, 1998, **564**, 233.
14. V. I. Sokolov, S. T. Ovseenko, Z. A. Starikova, L. L. Troitskaya, and Wu Yangjie, *Zh. Org. Khim.*, 2003, **39**, 389 [*J. Org. Chem.*, 2003, **39** (Engl. Transl.)].
15. O. N. Chupakhin, I. A. Utepova, I. S. Kovalev, V. L. Rusinov, and Z. A. Starikova, *Eur. J. Org. Chem.*, 2007, **5**, 857.

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