

Complexes *cis*-[PdCl₂(OSMeR)₂] (R = Me, Ph, and C₆H₄Me-4) in attempted asymmetric cyclometalation of dimethylaminomethylferrocene

Alexander D. Ryabov^{a,b,*}, Irina M. Panyashkina^a, Gregory M. Kazankov^a, Vladimir A. Polyakov^c, Lyudmila G. Kuz'mina^d

^a Department of Chemistry, M.V. Lomonosov Moscow State University, 119899, Moscow, Russia

^b Division of Chemistry, G.V. Plekhanov Russian Economic Academy, Stremyanny per. 28, 113054, Moscow, Russia

^c D.I. Mendeleev Moscow Academy of Chemical Technology, Miusskaya square 9, 125820, Moscow, Russia

^d N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Leninsky prosp. 31, 117907, Moscow, Russia

Received 23 October 1999; accepted 12 January 2000

Abstract

Cyclometalation of dimethylaminomethylferrocene by the sulfoxide complexes *cis*-[PdCl₂(OSMeR)₂] (R = Me, Ph, and C₆H₄Me-4) occurs in methanol or methylene chloride as solvent, the highest yields being 35, 25 and 15% in the series, respectively. The reaction affords complexes *trans*(*N,S*)-[Pd{(2-Me₂NCH₂C₅H₃)Fe(C₅H₅)Cl(OSMeR)] and the structure of the palladacycle with R = Me was established in the X-ray crystal study. Bound via sulfur, the sulfoxides dissociate in solution demonstrating, in contrast to the analogous Pt(II) complexes, extremely low affinity to palladium(II) centers. The latter effect is considered to be crucial to account for the failure to carry out attempted asymmetric cyclopalladation of dimethylaminomethylferrocene by the complex with the enantiomerically pure ligand *R*(+)-methyl *p*-tolyl sulfoxide. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Cyclometalation; Ferrocene; Sulfoxide; Asymmetric reaction

1. Introduction

Asymmetric reactions of metalacycles are investigated intensively nowadays due to the high potential of chiral cyclometalated compounds in various areas of chemistry, including asymmetric catalysis [1–3], resolution of donor molecules such as amines [4], phosphines and arsines [5,6], creation of planar-chiral structures via asymmetric cyclometalation [7–9], and synthesis of chiral organic molecules from chiral metalacyclic precursors [10–13]. Of particular interest is asymmetric cyclopalladation of prochiral metallocene molecules that do *not* contain extra orienting chiral fragments. Such a strategy was first introduced into synthetic practice by the Sokolov group [7,9,14]. The sodium salt of *N*-acetyl-*S*-valine has been used to promote asymmetric cyclopalladation of dimethylaminomethylfer-

rocene (**1**). These results are consistent with a mechanism wherein the base (acylated amino acid anion) is coordinated to palladium(II) during electrophilic metalation [15,16]. In the light of the Sokolov work, it was challenging to find chiral ligands other than acylated amino acids, which, on coordination with the metal center, provided a system capable of asymmetric cyclometalation. We have demonstrated recently [17] that chiral sulfoxides coordinated to Pt(II) show some promise. In fact, a reaction between **1** and *cis*-[PtCl₂(*S*-OSMeC₆H₄Me-4)₂] affords the two easily separable cycloplatinated *S_cR_p* and *S_cS_p* diastereomers, the structure of which was similar to **2**. However, the impact of the cycloplatination procedure is much lower compared with the cyclopalladation, since cycloplatinated ferrocenes are difficult to functionalize further. It seemed logical to transfer the knowledge obtained in the platinum chemistry to the corresponding cyclopalladated ferrocene complexes because of their recognized potential as starting materials in organic synthesis

* Corresponding author. Fax: +7-95-9395417.

E-mail address: ryabov@enz.chem.msu.ru (A.D. Ryabov)

[18–20]. Therefore, in this work we report on the cyclopalladation of **1** by the complexes *cis*-[PdCl₂(OSRMe)₂] (R = Me, Ph, and *p*-tolyl) which does lead to the goal palladacycles (**2**) (Scheme 1), but without evident asymmetric induction in the case of (*R*)-methyl *p*-tolyl sulfoxide.

2. Experimental

2.1. General

DMSO (Reakhim) was distilled in vacuum before use. Aryl methyl sulfoxides OSRMe {R = (*R,S*)-Ph and (*R*)-*p*-tolyl} were purchased from Aldrich and used as received. Complexes *cis*-[PdCl₂(OSRMe)₂] (R = Me, Ph) were prepared as described elsewhere [21]. ¹H-NMR spectra were recorded on a CXP-200 Bruker instrument with a residual solvent signal as an internal standard. All *J* values are in Hz. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer.

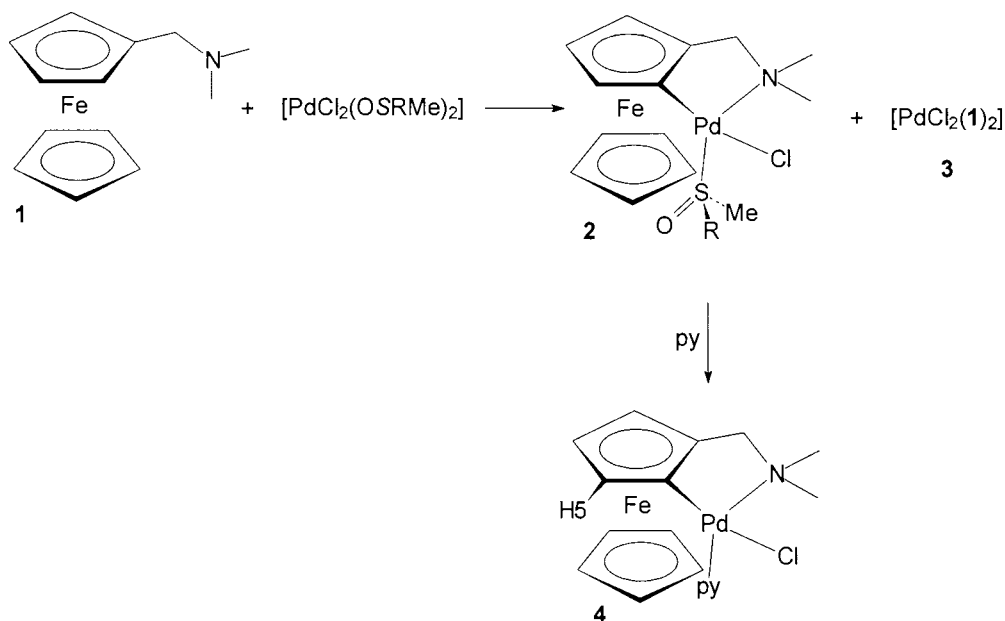
2.2. Reaction of [PdCl₂(DMSO)₂] with **1** in methanol

Dimethylaminomethylferrocene (0.073 g, 0.3 mmol) and [PdCl₂(DMSO)₂] (0.060 g, 0.18 mmol) were added to 15 ml of dry MeOH to yield a crimson solution which was stirred for 6 h at ambient temperature. Yellow crystals started to precipitate after 5 min. After 5 days, the crystals were filtered off, washed with

hexane, and air-dried to afford 0.070 g of **3** (58.8%). ¹H-NMR (δ, CDCl₃) 2.41(s, CH₃), 3.75 (s, CH₂), 4.16 (s, C₅H₅), 4.25 and 4.61 (t, *J* 2, H₂, 5 and H₃, 4). The crimson mother liquor was concentrated three-fold and allowed to stand at 5°C for 5 days. Analytically pure orange crystals of **2a** formed were filtered off, washed with hexane and dried (0.013 g). An additional portion of **2a** was isolated from the mother liquor by preparative TLC on Silufol plates (TLC: Silufol plates, benzene–*n*-hexane (4:1 v/v, *R*_f 0.6). Total yield of **2a**, 19%. IR (KBr disk) 1117s (S=O). Anal. Found: C, 39.7; H, 4.8; Cl, 7.8; S, 6.9. Anal. Calc. For C₁₅H₂₂ClFeNOPdS: C, 39.0; H, 4.8; Cl, 7.7; S, 6.9%.

2.3. Reaction of [PdCl₂(DMSO)₂] with **1** in methylene chloride

Compound **1** (0.166 g, 0.68 mmol) and [PdCl₂(DMSO)₂] (0.113 g, 0.34 mmol) were dissolved in 15 ml of dry methylene chloride and the mixture was refluxed for 5 h. The reaction course was monitored by TLC using Silufol plates and ethyl acetate–*n*-hexane (3:7 v/v) as an eluent (*R*_f (**2a**) = 0.5). The solution was evaporated to dryness and the residue recrystallized from benzene–*n*-hexane (4:1 v/v). Yellow microcrystals of **3** (0.055 g (24.5%), *R*_f = 0.0) were filtered off and dried. The filtrate was evaporated to dryness and the residue was recrystallized from benzene–*n*-hexane (1:1 v/v) to afford orange crystals of **2a**. The crystals were collected, washed with hexane and air-dried (0.0553 g, 35.3%).



R = Me (**a**), Ph (**b**), C₆H₄-4-Me (**c**)

Scheme 1.

2.4. Reaction of complex **2** with pyridine

Complex **2a** (32.1 mg, 0.07 mmol) was treated with pyridine (12 mg, 0.15 mmol) in 5 ml of dry benzene for 2 h at ambient temperature. *n*-Hexane (5 ml) was then added to form an orange precipitate (R_f (**4**) = 0.5, Silufol, benzene–acetone (7:3 v/v)). The precipitate was filtered off, washed with *n*-hexane and air-dried to yield 23 mg of complex **4** (71%), which was prepared by us previously from the corresponding chloro-bridged dimer [22]. ¹H-NMR (δ , CDCl₃) 2.95 and 3.20 (s, CH₃), 3.23 (d, *J* 2, H5), 3.33 and 3.66 (d, *J* 14, AB quartet, CH₂), 3.91 (t, *J* 2, H4), 4.07 (d, *J* 2, H3), 4.17 (s, C₅H₅), 7.41 (dd, *J* 6.5, 4.8; H3', 5'), 7.85 (t, *J* 6.5, H4'), 9.05 (d, *J* 4.8, H2', 6').

2.5. Reaction of [PdCl₂(OSMePh)₂] with **1**

Compound **1** (0.587 g, 2.4 mmol) and [PdCl₂(OSMePh)₂] (0.548 g, 1.2 mmol) were dissolved in 30 ml of dry CH₂Cl₂ by stirring the mixture for 30 min and the resulting crimson solution was refluxed for 5 h. The solvent was removed in vacuum and dry methanol (20 ml) was added to the residue. The undissolved crimson material (300 mg), which was a mixture of **2b** and **3**, was separated by filtration, dried, and 45 mg of bright-orange complex **2b** was obtained by using preparative TLC (silica gel, hexane–ethyl acetate (7:3 v/v), orange band R_f (**2b**) = 0.5). No attempt was made to isolate compound **3** (R_f = 0). The filtrate was evaporated to dryness and 20 ml of dry methanol was again added. Orange crystals of practically pure complex **2b** precipitated on cooling were filtered off and dried (49.7 mg). The solvent of the mother liquor which still contained **2b** was evaporated and additional amount of the complex was isolated (63.1 mg) by preparative TLC (silica gel, hexane–ethyl acetate (7:3 v/v), orange band R_f (**2b**) = 0.5). Total yield of **2b** was 25.1% (157.8 mg). The spectrally pure material (104.6 mg, 17%) was obtained by recrystallization from benzene–hexane (1:1 v/v). Reaction with pyridine to afford **4** was carried as described above for complex **2a**. Yield 46%.

2.6. Reaction of [PdCl₂(OSMeC₆H₄Me-4)₂] with **1**

R(+)-Methyl *p*-tolyl sulfoxide (249 mg, 1.62 mmol) and PdCl₂ (143 mg, 0.81 mmol) were added to 10 ml of dry methylene chloride. The mixture was stirred for 2 days at room temperature (r.t.) and then refluxed for 4 h. The reaction course was monitored by TLC using chloroform–methanol (5:1 v/v) as eluent. To thus prepared in situ orange–red solution of the complex [PdCl₂(OSMeC₆H₄Me-4)₂], a solution of **1** (194.5 mg, 0.8 mmol) in 10 ml of CH₂Cl₂ was added. Refluxing the resulting mixture for 1 h was followed by stirring at r.t. for 3 days. The course of this reaction was monitored

by TLC using hexane–ethyl acetate (7:3 v/v) as eluent (R_f (**2c**) = 0.5). The solution was evaporated to yield a brownish–red oil to which 15 ml of methanol was added. A dark-brown undissolved material, which was a mixture of **2c** and **3**, was filtered off, dried (137 mg), and small amount of **2c** (8.4 mg) was isolated from the latter by TLC. No attempt was made to isolate compound **3** (R_f = 0). The methanol filtrate was kept at 5°C for 4 days. Brownish–red precipitate of pure complex **2c** was filtered off and dried (35.3 mg). The mother liquor was evaporated to dryness and the residue was subjected to preparative TLC (silica gel, hexane–ethyl acetate (7:3 v/v)). The orange band with R_f (**2c**) = 0.5 was separated, the product washed off with CH₂Cl₂ to yield 20 mg of pure complex **2c**. Total yield 14.8% (63.7 mg). The reaction with pyridine to afford **4** was carried as described above for complex **2a**. Yield 30%.

3. Results and discussion

3.1. Complex [PdCl₂(DMSO)₂] as metalating agent

Cyclopalladation of **1** via the C–H bond cleavage by the Na₂PdCl₄–NaOAc system is characterized by a modest yield of the target compound [23] and therefore it was necessary first to test the complex [PdCl₂(DMSO)₂] in this reaction under various conditions. The principal results are summarized in Table 1 (runs 1–10). Two solvents, viz. methanol and methylene chloride, were used. The cyclopalladation does not occur in MeOH when the ligand-to-complex ratio equals 1:1 (runs 1–2). Complex **2a** is formed in a low yield at the 2:1 ratio, indicative of the necessity of an extra molecule of **1**, which acts as a base to abstract the leaving proton. In the methylene chloride solvent, which is less acidic than MeOH, complex **2a** is formed even at a 1:1 ligand-to-complex ratio at ambient temperature. The highest yield (35%) was nevertheless obtained at the 2:1 ratio at reflux (run 9). It should be mentioned that increasing the reaction time did not increase the yield, suggesting that target compound **2a** might be rather labile at reflux. The reaction with [PdCl₂(DMSO)₂] proceeds always with the formation of [PdCl₂(**1**)₂] as a by-product (Table 1). This should, of course, be anticipated, since the starting complex [PdCl₂(DMSO)₂] is substitutionally labile, accounting for the facile substitution of DMSO by a such N-donor ligand as **1**. The absence of the Pd–C bond and the existence of the Pd–N one is suggested by the ¹H-NMR spectra of [PdCl₂(**1**)₂] and free **1**. In fact, there are two triplets arising from the mono-substituted cyclopentadienyl ring in [PdCl₂(**1**)₂] and the singlets from the CH₂ and CH₃ protons are shifted downfield by 0.48 and 0.25 ppm, respectively, as a result of coordination of **1** to palladium(II) via tertiary amine nitrogen only. The

Table 1
Yields of palladacycles **2** on the reaction of **1** with complexes [PdCl₂(OSMeR)₂] under different conditions

Run	R	Ratio [1]/[PdCl ₂ (OSMeR) ₂]	Solvent	Conditions	Yield of 2 (%)	Yield of 3 (%)
1	Me	1:1	MeOH	2 h, 22 ± 2°C	0	0
2	Me	1:1	MeOH	2 h, reflux	0	0
3	Me	2:1	MeOH	10 h, 22 ± 2°C	15	67
4	Me	2:1	MeOH	120 h, 22 ± 2°C	19	59
5	Me	1:1	CH ₂ Cl ₂	120 h, 22 ± 2°C	18	^a
6	Me	1:1	CH ₂ Cl ₂	5 h, reflux	5	^a
7	Me	2:1	CH ₂ Cl ₂	6 h, 22 ± 2°C	12	^a
8	Me	2:1	CH ₂ Cl ₂	24 h, 22 ± 2°C	33	^a
9	Me	2:1	CH ₂ Cl ₂	5 h, reflux	35	25
10	Me	2:1	CH ₂ Cl ₂	10 h, reflux	18	^a
11	Ph	1:1	CH ₂ Cl ₂	5 h, 22 ± 2°C	6	^a
12	Ph	2:1	CH ₂ Cl ₂	5 h, reflux	25	32 ^b
13	C ₆ H ₄ Me-4	1:1	CH ₂ Cl ₂	1 h reflux, 18 h 22 ± 2°C	15	24 ^b
14	C ₆ H ₄ Me-4	2:1	CH ₂ Cl ₂	3 h reflux, 18 h 22 ± 2°C	5.3	^a

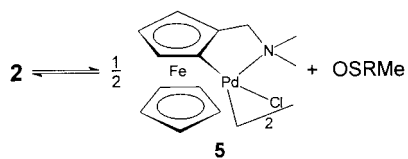
^a Was not determined.

^b Calculated as $(\mathbf{2} + \mathbf{3})_{\text{mixture}} - \mathbf{2}_{\text{pure}}$.

complex [PdCl₂(**1**)₂] reacts cleanly with the stoichiometric amount of pyridine to afford [PdCl₂(py)₂]. The ¹H-NMR spectrum of the latter contained resonances from the coordinated py only.

3.2. Assignment of the structure of **2a**

Determination of the structure of complex **2a** by investigation of its solutions turned out to be laborious, since the coordinated DMSO dissociates even in chloroform as solvent and equilibrium (1) should be taken into account.



(1)

As a result, the ¹H-NMR spectrum of the solution of **2a** in CDCl₃ is complicated in contrast to the analogous Pt(II) complex [24]. In particular, there is a strong singlet at δ 2.61 from free DMSO, whereas diastereotopic methyls from the coordinated DMSO are seen at δ 3.43 and 3.48. The relative integral intensity of the signals from free and coordinated DMSO is practically equal. There are two singlets at δ 2.85 and 3.11 from the *N*-methyls. These should be ascribed to complex **2a**, since their intensity is comparable to those at δ 3.43 and 3.48 from coordinated DMSO. The spectrum is also rich with a variety of signals of lower intensity presumably from **5**, because the dimer can provide a number of isomers. Among the latter are the geometrical *ab*-*hg* and *ab*-*gh* species (*syn* and *anti* isomers), and each generates two isomers with a different orientation of the (η⁵-C₅H₅)Fe-antenna with respect to the approximately planar {Pd(μ-Cl)₂Pd} unit [25,26]. To avoid the complications in interpreting the ¹H-NMR

spectra, complex **2a** was converted into pyridine derivative **4**, the ¹H-NMR spectrum of which is less complicated and fully consistent with the proposed structure. The py ligand is *cis* to the phenyl carbon suggested by a strong upfield shift of the H5 doublet due to the anisotropic effect of the py ring current [22]. In addition, the spectrum contains two singlets from the diastereotopic *N*-methyls, as well the AB quartet from the N-CH₂ protons. The conversion of other palladacycles **2** into diagnostic complex **4** has been further used for their structural characterization using the ¹H-NMR technique.

The lability of coordinated DMSO was also revealed in the course of the FAB⁺ mass-spectral study of **2a**. The most intensive peak with *m/z* 768 corresponded to the dimer **5**, the spectral pattern in the *m/z* range 760–777 being in a perfect agreement with the spectrum calculated for **5**. Remarkably, there was no peak with *m/z* 462, which corresponded to **2a**. Thus, equilibrium 1, as in solution, occurs in the gas phase where it is strongly shifted to the right.

A single-crystal structural study of complex **2a**, the details of which will be reported elsewhere [27], confirmed the assignment made on the basis of the analytical and spectral data. The structure of the compound is shown in Fig. 1 and, as seen, it is very similar to that of the platinum(II) analog [24] and platina(II) cycle based on acetyl ferrocene oxime [28]. Palladium(II) has a practically square-planar environment and DMSO is coordinated through sulfur which is *trans* to the amine nitrogen. The Pd-S bond is a feature that makes complex **2a** unique as compared with the DMSO coordination in related fully structurally characterized pallada(II) cycles [29–31] in which Pd(II) is bound with DMSO via oxygen.

3.3. Cyclopalladation of **1** by $[PdCl_2(SOMeR)_2]$ ($R = Ph$ and p -tolyl)

These transformations were carried by using initially an isolated complex $[PdCl_2(SOMePh)_2]$ with the racemic sulfoxide, whereas the enantiomerically pure complex of $R(+)$ -methyl p -tolyl sulfoxide was prepared in situ. Since higher yields for $[PdCl_2(DMSO)_2]$ were achieved in methylene chloride, the cyclopalladation by $[PdCl_2(SOMeR)_2]$ was carried out in the same solvent. As seen in Table 1, the reaction occurs for both $R = Ph$ and p -tolyl, the highest yields being 25 and 15%, respectively. These are lower than what was observed in the corresponding cycloplatination [17]. The reaction is also accompanied by the formation of complexes $[PdCl_2(1)_2]$.

As before, the 1H -NMR spectra of complexes **2b,c** are very complicated due to equilibrium (1). Thus, aryl sulfoxides, likewise DMSO, are also characterized by a low affinity toward Pd(II) centers. The fact of cyclopalladation was established by the conversion of **2b,c** into pyridine complex **4**. The spectra of complex **4** derived from either **2a**, on one hand, or **2b** and **2c**, on the other, were in fact identical. Naturally, our expectations were associated with the enantiomerically pure metalating agent in order to have an easy access to planar chiral palladacycles. However, the palladium(II) system appeared to be much less promising compared to the previously studied Pt(II) one [17]. Whereas in the latter case, one of the diastereomers crystallized from the reaction mixture as a diastereomerically pure material, and the second could be isolated by preparative TLC, no resolving of the diastereomers was achieved in the

palladium case. Analysis of crude **2b** or **2c** by TLC did not show resolution of the diastereomers as it was observed in the platinum system. As before, this behavior can be accounted for in terms of Eq. (1) taking place on a solvated silica gel surface. As a result, the diastereomers do not trivially exist under such conditions. Finally, the optical activity of complex **4** derived from **2c** was measured in a hope that the cyclopalladation in Scheme 1 could be asymmetric in character. The values of $[\alpha]^{25}$ measured were +5.5, +7.7, and +8.8 at 589, 578, and 546 nm, respectively (c 1.8, $CHCl_3$, $l = 5$ cm) and these are by two orders of magnitude lower compared to the numbers reported by Sokolov for **5** and its monomeric acetylacetonate derivative [7]. This comparison shows clearly the minor asymmetric induction in cyclopalladation of dimethylaminomethylferrocene by enantiomerically pure Pd(II) sulfoxide complexes.

4. Conclusions

The results presented here reveal that although the sulfoxide complexes cis - $[PdCl_2(SOMeR)_2]$ are capable of cyclometalation of ferrocene derivatives, their potential in asymmetric cyclopalladation is minor. In the latter respect, the behavior of Pd(II) complexes is much less advantageous compared with the analogous platinum(II) derivatives [17]. There is a clear mechanistic reason why the behavior of Pd(II) and Pt(II) is different. Sulfoxide palladium(II) complexes are too much labile either to assemble a proper transition state for asymmetric cyclopalladation or to form stable complexes of type **2** to generate a pair of diastereomers which could then be resolved successfully. Instability of cyclopalladated sulfoxide complexes of Pd(II) even in aprotic solvents, which has been demonstrated in this work, is rather unexpected in view of the absence of the dissociative processes in the case of analogous platinum species. The formation of substantial amount of complex **3** as a by-product is also in line with this hypothesis. The intermediates of the type **3** or $[PdCl_2(1)$ -(solvent)] generated rapidly from the starting sulfoxide species in solution are likely on the reaction coordinate of cyclopalladation. Hence, there is no principle source of chirality in these pathways.

Acknowledgements

The research described in this publication was made possible in part by financial support from the Russian Foundation for Fundamental Research (98-03-33023a) and INTAS (97-0166).

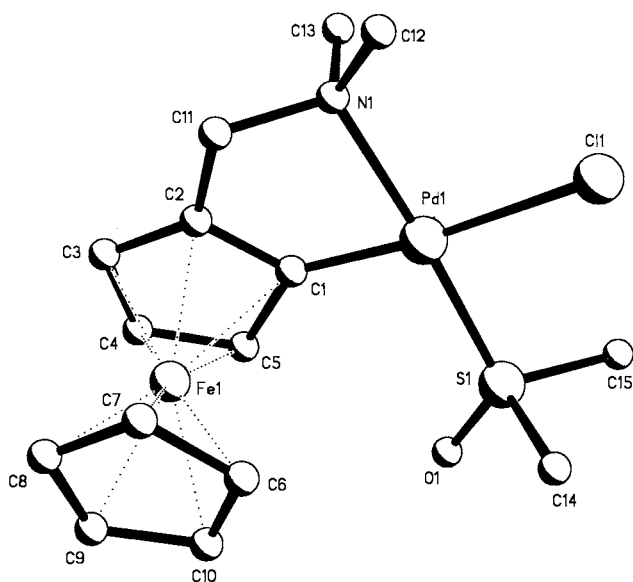


Fig. 1. Crystal structure of **2a**.

References

- [1] T.K. Hollis, L.E. Overman, *Tetrahedron Lett.* 38 (1997) 8837.
- [2] F. Cohen, L.E. Overman, *Tetrahedron: Asymmetry* 9 (1998) 3213.
- [3] A.D. Ryabov, G.M. Kazankov, S.A. Kurzeev, P.V. Samuleev, V.A. Polyakov, *Inorg. Chim. Acta* 280 (1998) 57.
- [4] V.V. Dunina, L.G. Kuzmina, A.G. Parfyonov, Y.K. Grishin, *Tetrahedron: Asymmetry* 9 (1998) 1917.
- [5] S. Otsuka, A. Nakamura, T. Kano, K. Tani, *J. Am. Chem. Soc.* 93 (1971) 431.
- [6] S.B. Wild, *Coord. Chem. Rev.* 166 (1997) 291.
- [7] V.I. Sokolov, L.L. Troitskaya, O.A. Reutov, *J. Organomet. Chem.* 182 (1979) 537.
- [8] G. Zhao, Q.-G. Wang, T.C.W. Mak, *Organometallics* 17 (1998) 3437.
- [9] V.I. Sokolov, *J. Organomet. Chem.* 500 (1995) 299.
- [10] V.I. Sokolov, *Pure Appl. Chem.* 55 (1983) 1837.
- [11] J. Spencer, M. Pfeffer, *Tetrahedron: Asymmetry* 6 (1995) 419.
- [12] G. Zhao, Q.-G. Wang, T.C.W. Mak, *Tetrahedron: Asymmetry* 9 (1998) 2253.
- [13] C. Richards, A.J. Locke, *Tetrahedron: Asymmetry* 9 (1998) 2377.
- [14] V.I. Sokolov, L.L. Troitskaya, O.A. Reutov, *Dokl. Acad. Nauk SSSR* 246 (1979) 124.
- [15] A.D. Ryabov, I.K. Sakodinskaya, A.K. Yatsimirsky, *J. Chem. Soc. Dalton Trans.* (1985) 2629.
- [16] A.D. Ryabov, *Chem. Rev.* 90 (1990) 403.
- [17] A.D. Ryabov, I.M. Panyashkina, V.A. Polyakov, J.A.K. Howard, L.G. Kuz'mina, M.S. Datt, C. Sacht, *Organometallics* 17 (1998) 3615.
- [18] A.D. Ryabov, *Synthesis* (1985) 233.
- [19] M. Pfeffer, *Recl. Trav. Chim. Pays-Bas* 109 (1990) 567.
- [20] J. Spencer, M. Pfeffer, in: L.S. Liebeskind (Ed.), *Advances in Metal-Organic Chemistry*, vol. 6, Jai Press, Stamford, 1998, p. 103.
- [21] J.H. Price, A.N. Williamson, R.F. Schramm, B.B. Wayland, *Inorg. Chem.* 11 (1972) 1280.
- [22] A.D. Ryabov, G.M. Kazankov, A.K. Yatsimirsky, L.G. Kuz'mina, O.Y. Burtseva, N.V. Dvortsova, V.A. Polyakov, *Inorg. Chem.* 31 (1992) 3083.
- [23] J.C. Gaunt, B.L. Shaw, *J. Organomet. Chem.* 102 (1975) 511.
- [24] P.R.R. Ranatunge-Bandarage, B.H. Robinson, J. Simpson, *Organometallics* 13 (1994) 500.
- [25] G. Zhao, Q.C. Wang, T.C.W. Mak, *Polyhedron* 18 (1998) 577.
- [26] G. Zhao, Q.-G. Wang, T.C.W. Mak, *Tetrahedron: Asymmetry* 9 (1998) 1557.
- [27] L.G. Kuz'mina, I.M. Panyashkina, A.D. Ryabov, to be published.
- [28] A.D. Ryabov, G.M. Kazankov, I.M. Panyashkina, O.V. Grozovsky, O.G. Dyachenko, V.A. Polyakov, L.G. Kuz'mina, *J. Chem. Soc. Dalton Trans.* (1997) 4385.
- [29] C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J.H. Rodríguez-Ramos, J.R. Masaguer, J.L. García-Ruano, X. Solans, *Organometallics* 12 (1993) 4104.
- [30] J.L. García-Ruano, I. López-Solera, J.R. Masaguer, M.A. Monge, C. Navarro-Ranninger, J.H. Rodríguez, *J. Organomet. Chem.* 476 (1994) 111.
- [31] M. Nonoyama, K. Nakajima, *Polyhedron* 18 (1998) 533.