

Palladium(II) complexes with *o*-aryl substituted 1,1'-bis(phosphino)ferrocenes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PR}_2)_2\text{Pd}(\text{NCMe})_n](\text{OTf})_2$ ($\text{R} = o\text{-MeOC}_6\text{H}_4, o\text{-MeC}_6\text{H}_4, o\text{-Pr}^i\text{C}_6\text{H}_4, \text{C}_6\text{F}_5$): Synthesis, structure and catalytic properties in methoxycarbonylation of ethylene

Alexander M. Kalsin, Nikolai V. Vologdin, Tat'yana A. Peganova, Pavel V. Petrovskii, Konstantin A. Lyssenko, Fedor M. Dolgushin, Oleg V. Gusev *

A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilov St. 28, 119991 Moscow, Russian Federation

Received 29 September 2005; received in revised form 24 October 2005; accepted 25 October 2005

Available online 19 December 2005

Abstract

The cationic palladium(II) complexes with 1,1'-bis(phosphino)ferrocenes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PR}_2)_2\text{Pd}(\text{NCMe})_n](\text{OTf})_2$ ($n = 0\text{--}2$) ($\text{OTf} = \text{CF}_3\text{SO}_3$; **5**, $\text{R} = o\text{-MeOC}_6\text{H}_4$, $n = 0$; **6**, $\text{R} = o\text{-MeC}_6\text{H}_4$, $n = 1$; **7**, $\text{R} = o\text{-Pr}^i\text{C}_6\text{H}_4$, $n = 1$; **8**, $\text{R} = \text{C}_6\text{F}_5$, $n = 1$) have been prepared by treatment of the corresponding dichlorides $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PR}_2)_2\text{PdCl}_2]$ (**1–4**) with silver triflate in the presence of acetonitrile. The structures of **5** and **7** have been determined crystallographically. The oxygen of one of the methoxy groups in **5** has been found to coordinate the palladium resulting in decrease of the bite angle P–Pd–P to $94.74(5)^\circ$. In contrast, the bulky *ortho*-isopropylphenyl groups at the phosphorus atoms in **7** increase the P–Pd–P angle to $99.98(6)^\circ$ and cause also a significant distortion of the square-planar coordination around the palladium atom. A preliminary study on methoxycarbonylation of ethylene catalyzed by **5–8** has been carried out and revealed great effect of the *ortho*-aryl substituent on both catalyst's activity and selectivity. The anisyl complex **5** was moderately active for production of alternating polyketone, while the *o*-tolyl derivative **6** gave selectively methyl propanoate. The cationic palladium(II) complexes with highly sterically congested isopropylphenyl ligand and strongly electron withdrawing pentafluorophenyl substituted phosphine, **7** and **8**, respectively, under the reaction conditions undergo facile reduction to Pd^0/Pd^I species and are therefore inactive in the process. © 2005 Elsevier B.V. All rights reserved.

Keywords: Palladium complexes with 1,1'-bis(phosphino)ferrocenes; Methoxycarbonylation of ethylene; Alternating copolymerization of ethylene and CO

1. Introduction

Cationic palladium(II) complexes with chelating diphosphines have been found to be efficient catalysts for methoxycarbonylation of α -olefins with the catalytic properties strongly dependent on the nature of the diphosphine ligand [1]. The steric and electronic properties of the diphosphine's backbone has been partially studied earlier and found to influence the direction of the process either towards the

alternating $\text{C}_2\text{H}_4/\text{CO}$ copolymerization or to formation of methyl propanoate [2]. In particular, the complexes with 1,1'-bis(diphenylphosphino)metallocene ligands, which are able to form M–Pd bonded species during catalysis, have been found to catalyze selective production of methyl propanoate [3]. Recently, palladium complexes with 1,1'-bis(dimethylphosphino)ferrocene and 1,1'-bis(diethylphosphino)ferrocene have been shown to be effective catalysts for alternating copolymerization of ethylene and CO, while palladium complexes with 1,1'-bis(diisopropylphosphino)ferrocene catalyzes formation of diethylketone and of methyl propanoate [3]. However the

* Corresponding author. Tel.: +7 095 1359337; fax: +7 095 1355085.
E-mail address: gusev@ineos.ac.ru (O.V. Gusev).

influence of the substituents at the phosphorus, other than the backbone bridge, has been poorly investigated, with the only indication that the *ortho*-substitution in the phenyl rings in bis(diphenylphosphino)methane ligand affects dramatically on the activity of palladium complexes in the alternating C₂H₄/CO copolymerization, coming from the recent paper [4].

Here we report on the synthesis of new palladium(II) complexes with 1,1'-bis(phosphino)ferrocenes, bearing various substituents at the phosphorus, as well as preliminary study on their catalytic activity in the methoxycarbonylation of α -olefins, which confirms the relevant effect of the phosphorus substituents on both catalyst activity and selectivity.

2. Results and discussion

The cationic palladium complexes **5–8** were prepared by treatment of the dichloride complexes **1–4** [5], with silver triflate in the presence of acetonitrile (Scheme 1).

The complexes obtained were characterized by elemental analysis and by multinuclear NMR spectroscopy. According to these data the complexes **5–8** have a square-planar coordination around palladium and a *cis*-chelating diphosphine. In complexes with bulky substituents **6–8** only one molecule of acetonitrile is coordinated to palladium, the second coordination site at palladium in the solid state can be occupied by triflate counter-ion. The anisyl complex **5** does not contain any solvent molecule that is likely due to coordination of the oxygen of the methoxy group to palladium.

The phosphorus atoms are equivalent in [Fe(η^5 -C₅H₄-P{*o*-C₆H₄OMe}₂)₂)₂Pd(OTf)](OTf) (**5**) and [Fe(η^5 -C₅H₄-P{C₆F₅}₂)₂)₂Pd(NCMe)(OTf)](OTf) (**8**) and exhibit singlets at δ 51.1, 17.2, respectively, in the ³¹P{¹H} NMR spectra, which is consistent with complex cations being in fast exchange with solvent and triflate. The α - and β -cyclopentadienyl protons in the complexes with relatively small *ortho*-anisyl (**5**) and pentafluorophenyl (**8**) aryl substituents appear as non-resolved multiplets at δ 4.74, 5.04 for **5** and at δ 4.81, 5.35 for **8**. The aryl protons in **5** arise as multiplets in the region δ 6.96–7.56, and the methoxyl groups – as a singlet at δ 3.98. The pentafluorophenyl rings in **8**

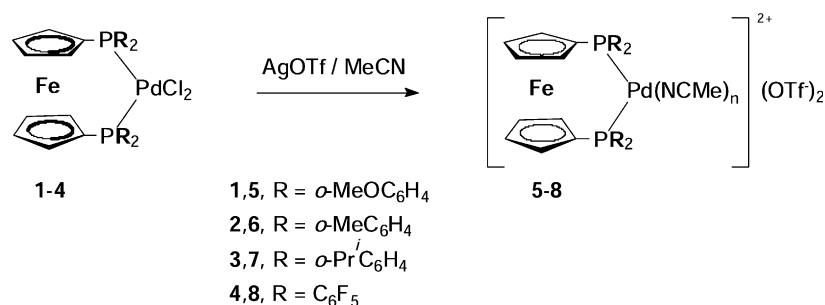
are equivalent according to the ¹⁹F{¹H} NMR spectrum. In the ¹³C{¹H} NMR spectrum of **5** one singlet at δ 58.21 arises from the methoxy group, the Cp-carbons appear at δ 72.01, 75.28 and 79.30, and the six aryl carbons are in the region δ 110–160. These spectral data for **5** and **8** imply facile rotation of the aryl rings around the P–C bonds.

Increasing the size of the substituents in the *ortho* positions of [Fe(η^5 -C₅H₄P{*o*-C₆H₄Pr^{*i*}}₂)₂)₂Pd(NCMe)(OTf)](OTf) (**7**) reduces the symmetry of the cation, most likely due to hindered rotation of the aryl groups, resulting in nonequivalence of the two phosphorus atoms, which are observed in the ³¹P{¹H} NMR spectrum as two doublets at δ 48.9 and 61.1. The asymmetry of the cation of **7** is furthermore confirmed by the presence of eight signals of the Cp protons, and four fully nonequivalent *i*-Pr groups with eight different methyls and four different CH groups.

Interestingly, the NMR spectra of the *o*-tolyl derivative [Fe(η^5 -C₅H₄P{*o*-C₆H₄Me}₂)₂)₂Pd(NCMe)(OTf)](OTf) (**6**) exhibit an intermediate situation. Both the ¹H and ³¹P{¹H} NMR spectra of this compound are featured by very broad signals at room temperature (Fig. 1(a)). Upon lowering the temperature to –80 °C (Fig. 1(b)), the ³¹P{¹H} NMR singlet splits into two doublets at δ 52.1 and 49.0, which correspond to the unsymmetrical complex B (Fig. 1(b), inset). Besides these doublets the singlet at δ 51.2 appears, which probably corresponds to the symmetrical form A (Fig. 1(b), inset)). The ¹H NMR signals remain unresolved even at –80 °C, hence their unambiguous assignment cannot be accomplished. Analogous temperature behavior has been observed for the corresponding dichloride complex [Fe(η^5 -C₅H₄P{*o*-C₆H₄Me}₂)₂)₂PdCl₂] (**2**) [5].

The crystal structure of the anisyl substituted compound [Fe(η^5 -C₅H₄P{*o*-C₆H₄OMe}₂)₂)₂Pd(OTf)](OTf) (**5**) shows the palladium atom coordinated to two *cis* phosphorus atoms from the 1,1'-bis(di-*o*-methoxyphenylphosphino)ferrocene and to two oxygen atoms, one from a triflate ion, the other from a methoxy substituent at phosphorus (Fig. 2).

The intramolecular coordination of the methoxy group generates a five-membered ring, which decreases the P–Pd–P bite angle to 94.74(5)° as compared to the corresponding dichloride complex **1** (100.14°) [5]. Also the palladium atom in **5** deviates from the plane defined by the



Scheme 1.

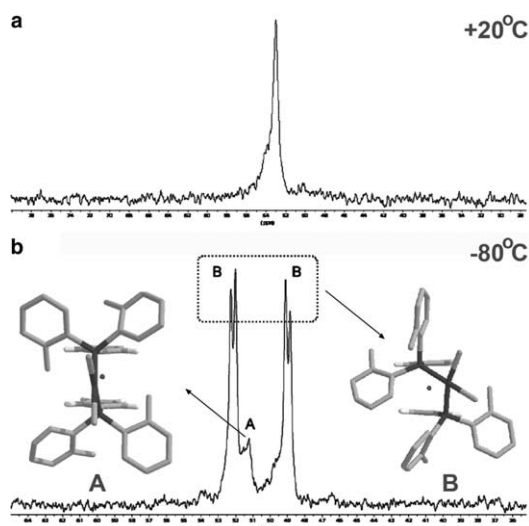


Fig. 1. The VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complex **6** in CD_2Cl_2 : (a) at $+20^\circ\text{C}$; (b) at -80°C , two isomers, symmetrical A and unsymmetrical B, are shown.

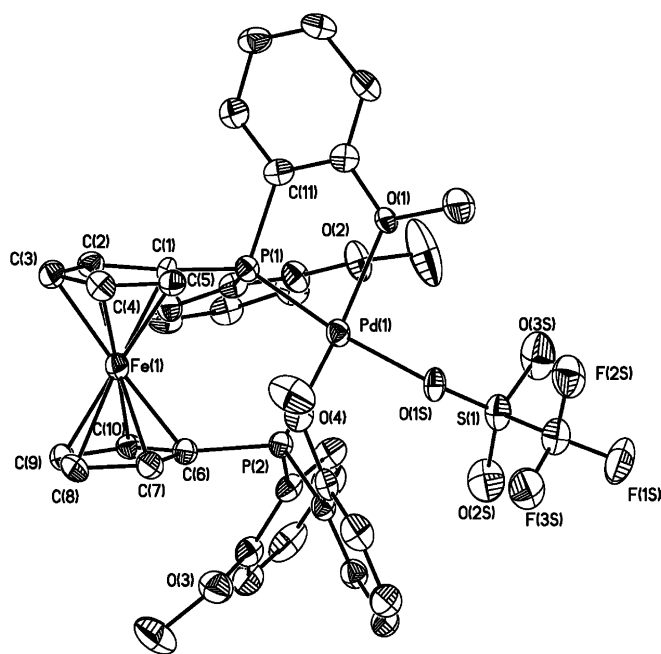


Fig. 2. The general view of cation **5** with the representation of atoms by the thermal ellipsoids at 50% probability level. Selected bond lengths (Å): Pd(1)–P(1) 2.211(1), Pd(1)–P(2) 2.261(1), Pd(1)–O(1) 2.211(3), Pd(1)–O(1S) 2.140(3), Fe(1)–C(Cp) 2.010(5)–2.073(5), Fe(1)–C_{Pcent} 1.645 Å, P–C(Cp) 1.766(5)–1.808(5), P–C(Ph) 1.805(5)–1.826(5); selected bond angles (°): O(1S)–Pd(1)–O(1) 91.0(1), P(1)–Pd(1)–P(2) 94.74(5).

atoms P(1)–Fe(1)–P(2), the dihedral angle between the planes P(1)–Pd(1)–P(2) and P(1)–Fe(1)–P(2) is 42.5° , while it is only 0.5° for **1**. The conformation of the Cp-rings is staggered, with the torsion angle C(1)–Cp(1)–Cp(2)–C(6) of 30.9° . The two Pd–P (2.211(1) and 2.261(1) Å) distances are significantly different, showing different trans influence of the oxygen atoms as well as the fact that P(1) takes part in a five-membered cycle.

The crystal structure of the complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-P}\{o\text{-C}_6\text{H}_4\text{Pr}^i\}_2)_2\text{Pd}(\text{NCMe})(\text{OTf})](\text{OTf})$ (**7**) shows the palladium centre to be four coordinated by a *cis* 1,1'-bis(di-*o*-isopropylphenylphosphino)ferrocene one acetonitrile molecule and one triflate anion (Fig. 3), however the square-planar configuration at palladium is significantly distorted (the dihedral angle between the planes P(1)–Pd(1)–P(2) and N(1N)–Pd(1)–O(1) is 13.2°). The complex **7** is highly sterically congested most likely due to steric repulsions between the PAr_2 groups so that both aryls at the same phosphorus cannot be located at one side of the Cp-plane, resulting in increase of the bite angle P–Pd–P to $99.98(6)^\circ$ and of the dihedral angle P(1)–Pd(1)–P(2)/P(1)–Pd(1)–P(2) to 41.4° . The conformation of the Cp-rings is staggered, the torsion angle C(1)–Cp(1)–Cp(2)–C(6) is 36.0° . The Pd–P distances are slightly different, Pd(1)–P(1): 2.308(2) Å and Pd(1)–P(2): 2.292(2) Å. The isopropyl groups apparently block the molecule in a fixed conformation that persists even in solution ($^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy).

The complexes **5–8** have been tested as catalyst precursors for the carbonylation of ethylene in MeOH under standard experimental conditions [3] and the results

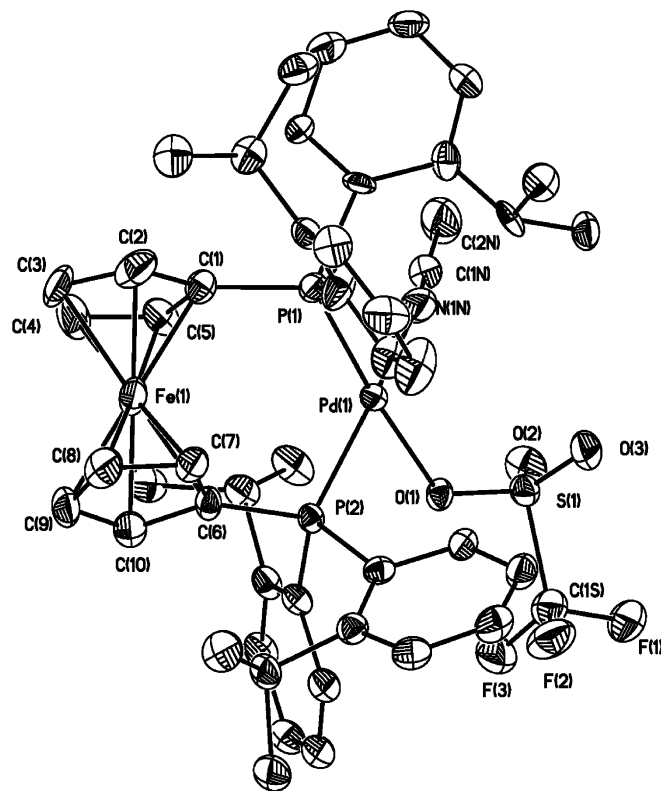


Fig. 3. The general view of cation **7** with the representation of atoms by the thermal ellipsoids at 50% probability level. The disorder is omitted for clarity. Selected bond lengths (Å): Pd(1)–P(1) 2.308(2), Pd(1)–P(2) 2.292(2), Pd(1)–O(1) 2.145(4), Pd(1)–N(1N) 2.045(5), Fe(1)–C(Cp) 2.012(8)–2.084(8), Fe(1)–C_{Pcent} 1.655 Å, P–C(Cp) 1.801(7)–1.807(6); selected bond angles (°): O(1S)–Pd(1)–O(1) 87.5(2), P(1)–Pd(1)–P(2) 99.98(6).

Table 1
Methoxycarbonylation of ethylene catalyzed by Pd(II) complexes stabilized with $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PR}_2)_2^{\text{a}}$

Entry	R	Polyketone (TON)	A (TON)	B (TON)	C (TON)	D (TON)
1	9 , Ph	1070	1380	1780	30	1890
2	5 , <i>o</i> -MeOC ₆ H ₄	340	0	0	0	0
3	6 , <i>o</i> -MeC ₆ H ₄	0	550	0	0	0
4	7 , <i>o</i> -Pr ⁱ C ₆ H ₄	0	10	0	0	0
5	8 , C ₆ F ₅	0	0	0	20	0

^a Catalyst (0.01 mmol); 1:1 CO/C₂H₄ (600 psi); *p*-BQ (80 equiv.); *p*-TsOH (20 equiv.); MeOH (100 mL); 85 °C; 1 h; 1400 rpm. TON as mol ethene incorporated (mol cat)⁻¹.

obtained have been compared to those reported for the prototypical dppf complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Pd}(\text{H}_2\text{O})_2](\text{OTf})_2$ (**9**) [6]. Selected data are given in Table 1.

The dppf complex has been found to produce a variety of compounds, spanning from high molecular weight copolymer to short chain oxygenates (Scheme 2) [6].

The presence of methoxy group in the *ortho*-position of the aryl ring, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{P}\{o\text{-C}_6\text{H}_4\text{OMe}\}_2)_2\text{Pd}(\text{OTf})_2](\text{OTf})$ (**5**), results in decrease of the activity as compared to the dppf catalyst **9** and gives the polyketone as the only product (Table 1, entry 2). Possibly the coordination of the labile methoxy groups to the palladium centre can compete with the coordination of ethylene thus slowing down the catalytic reaction.

Further increase of steric bulk of the *ortho*-aryl substituents changed the catalytic behavior dramatically. The complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{P}\{o\text{-C}_6\text{H}_4\text{Me}\}_2)_2\text{Pd}(\text{NCMe})(\text{OTf})_2](\text{OTf})$ (**6**) catalyzes selective production of methyl propanoate (Table 1, entry 3). A similar behavior has been previously observed for palladium(II) complexes with 1,1'-bis(diphenylphosphino)osmocene and 1,1'-bis(diphenylphosphino)octamethylferrocene and was rationalized in terms of the formation of acyl or ester transient species with a tridentate $\kappa^3\text{-P,P,M}$ 1,1'-bis(diphenylphosphino)metallocene ligand [3]. Since it has been demonstrated that the formation of dative M–Pd bonds (M = Fe, Os) is favored also by bulky substituents on the phosphorus atoms [7], it may be suggested that the *o*-tolyl groups in **6** similarly promote the formation of Fe–Pd interactions during the catalysis.

Palladium complexes with the *ortho*-isopropylphenyl $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{P}\{o\text{-C}_6\text{H}_4\text{Pr}^i\}_2)_2\text{Pd}(\text{NCMe})(\text{OTf})_2](\text{OTf})$ (**7**) and the pentafluorophenyl $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{P}\{\text{C}_6\text{F}_5\}_2)_2\text{Pd}(\text{NCMe})(\text{OTf})_2](\text{OTf})$ (**8**) substituted ligands, have been found to be almost inactive (Table 1, entries 4 and 5). Prob-

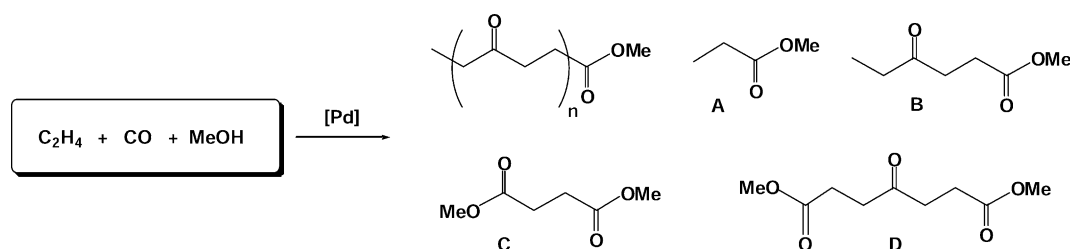
ably the sterically hindered *ortho*-isopropylphenyl and the electron-withdrawing pentafluorophenyl substituents at the phosphorus destabilize the cationic palladium(II) complexes and facilitates the reduction of catalytically active Pd²⁺ to inactive Pd¹⁺/Pd⁰ species. Indeed, the cyclic voltammetry study showed that **7** and **8** exhibit lower reduction potentials of –0.24 and –0.31 V, respectively, in comparison with the dppf $[(\text{dppf})\text{Pd}(\text{H}_2\text{O})_2](\text{OTf})_2$ (–0.77 V) and the anisyl **7** (–0.78 V) analogs [8].

In conclusion, new palladium(II) complexes with 1,1'-bis(phosphino)ferrocenes bearing various substituents at the phosphorus atoms have been synthesized. The *ortho*-anisyl and the *ortho*-tolyl substituted complexes have been found to be selective catalysts of moderate activity for methoxycarbonylation of ethylene.

3. Experimental

3.1. General procedures

All experiments were performed under argon in solvents purified by standard methods. ¹H, ³¹P{¹H}, ¹⁹F{¹H} and ¹³C{¹H} NMR spectra were recorded on Bruker AMX 400, Bruker WP 200SY and Varian VXR 400 spectrometers. Chemical shifts are reported in ppm (δ) with reference to TMS as an internal standard (¹H and ¹³C{¹H} NMR spectra), and CF₃COOH for ¹⁹F{¹H} NMR or 85% H₃PO₄ for ³¹P{¹H} NMR spectra as an external standard. GC analyses were performed on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and a 30-m (0.25 mm i.d., 0.25-μm film thickness) SPB-1 Supelco fused silica capillary column. The product composition was determined by using dimethoxyethane as external standard. The GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column



Scheme 2.

identical with that used for GC analysis. Carbonylation reactions were performed at constant pressure with a 250-mL stainless steel autoclave, constructed at the ICCOM-CNR (Firenze, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. Microanalyses were performed at the A.N. Nesmeyanov Institute of Organoelement Compounds. The compounds **1–4** were synthesized according to published procedures [5].

3.2. Synthesis of $[Fe(\eta^5-C_5H_4P\{o-C_6H_4OMe\}_2)_2-Pd(OTf)](OTf)$ (**5**)

Silver triflate (0.57 g, 2.22 mmol) was added with stirring to a solution of **1** (0.91 g, 1.07 mmol) in CH_2Cl_2 (40 mL)/MeCN (0.2 mL) at $-78^\circ C$. This mixture was allowed to warm to room temperature and stirred overnight. The solvent was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (30 mL). The solution was filtered through celite, the filtrate was concentrated to 10 mL and then 5–10 mL of Et_2O were added to induce slow precipitation of dark-green crystals. They were filtered off, washed with Et_2O and dried in vacuum. Yield of **5** $\times CH_2Cl_2$: 0.80 g (64%). Anal. Calc. for $C_{41}H_{38}Cl_2F_6FeO_{10}P_2PdS_2$: C, 42.31; H, 3.29. Found: C, 42.54; H, 3.34%. 1H NMR ($CDCl_3$): δ 3.98 (s, 12H, OMe), 4.74 (s, 4H, C_5H_4), 5.04 (s, 4H, C_5H_4), 6.96 (br. m, 4H, $o-C_6H_4OMe$), 7.09 (br. m, 4H, $o-C_6H_4OMe$), 7.56 (br. m, 8H, $o-C_6H_4OMe$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.1 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 58.21 (s, OMe); 72.0 (d, $^1J_{PC} = 77.1$ Hz, *ipso*-Cp); 75.28 (t, $^3J_{PC} = 4.6$ Hz, β -Cp); 79.30 (t, $^2J_{PC} = 6.6$ Hz, α -Cp); 112.91 (t, $^2J_{PC} = 2.6$ Hz, Ar); 115.96 (d, $^1J_{PC} = 63.4$ Hz, *ipso*-C(Ar)); 120.23 (q, $^1J_{CF} = 320.0$ Hz, CF_3SO_3); 122.27 (t, $^3J_{PC} = 5.6$ Hz, Ar); 134.17 (t, $^3J_{PC} = 4.0$ Hz, Ar); 135.90 (s, *p*-Ar); 160.23 (t, $^2J_{PC} = 2.0$ Hz, *ipso*-C(OMe)).

3.3. Synthesis of $[Fe(\eta^5-C_5H_4P\{o-C_6H_4Me\}_2)_2-Pd(NCMe)(OTf)](OTf)$ (**6**)

Silver triflate (0.26 g, 1.02 mmol) was added with stirring to a solution of **2** (0.40 g, 0.51 mmol) in CH_2Cl_2 (40 mL)/MeCN (0.2 mL) at $-78^\circ C$. This mixture was allowed to warm to room temperature and stirred overnight. The precipitate was filtered off and the filtrate was concentrated to 5 mL and then treated with Et_2O (40 mL). The light green crystals were filtered off, washed with Et_2O and dried in vacuum. Yield of **6**: 0.46 g (91%). Anal. Calc. for $C_{42}H_{39}F_6FeNO_6P_2PdS_2$: C, 47.77; H, 3.72; N, 1.33. Found: C, 47.74; H, 3.92; N, 1.75%.

1H NMR ($CDCl_3$): δ 1.63 (br. s, 6H, Me), 3.39 (br. s, 6H, Me), 4.32 (br. s, 2H, C_5H_4), 4.34 (br. s, 2H, C_5H_4), 4.51 (br. s, 2H, C_5H_4), 4.89 (br. s, 2H, C_5H_4), 7.2–7.6 (br. m, 16H, $o-C_6H_4Me$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.1 (br. s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at $-80^\circ C$): δ 49.0 (d, $^2J_{PP} = 41.5$ Hz); 52.1 (d, $^2J_{PP} = 41.5$ Hz); 51.2 (s).

3.4. Synthesis of $[Fe(\eta^5-C_5H_4P\{o-C_6H_4Pr^i\}_2)_2Pd(NCMe)(OTf)](OTf)$ (**7**)

Silver triflate (0.21 g, 0.82 mmol) was added with stirring to a solution of **3** (0.36 g, 0.40 mmol) in CH_2Cl_2 (20 mL)/MeCN (1 mL) at $-78^\circ C$. The mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed in vacuum and the residue was dissolved in CH_2Cl_2 (30 mL). The solution was filtered through celite, the filtrate was concentrated to 3–5 mL followed by the addition of Et_2O (30 mL). The solution was kept in a fridge overnight to give green crystalline product. It was filtered off, washed with Et_2O and dried in vacuum. Yield of **7**: 0.27 g (58%). Anal. Calc. for $C_{50}H_{55}F_6FeNO_6P_2PdS_2$: C, 51.40; H, 4.75, N, 1.20. Found: C, 51.19; H, 4.87; N, 1.23%. 1H NMR ($CDCl_3$): δ 0.01 (s, 3H, Me); 0.24 (s, 3H, Me); 0.71 (s, 3H, Me); 0.95 (s, 3H, Me); 1.29 (s, 3H, Me); 1.45 (s, 3H, Me); 1.81 (s, 3H, MeCN); 1.82 (s, 3H, Me); 2.02 (s, 3H, Me); 2.00 (s, 1H, $CHMe_2$); 2.71 (s, 1H, $CHMe_2$); 3.64 (s, 1H, $CHMe_2$); 4.35 (s, 1H, C_5H_4); 4.42 (s, 1H, C_5H_4); 4.51 (s, 1H, C_5H_4); 4.58 (s, 1H, C_5H_4); 4.72 (s, 1H, C_5H_4); 4.79 (s, 1H, C_5H_4); 5.53 (s, 1H, C_5H_4); 5.67 (s, 2H, 1H C_5H_4 + 1H $CHMe_2$); 6.6–8.0 (br. m, 14H, C_6H_4); 8.62 (br. m, 1H, $o-H(Ar)$); 9.17 (br. m, 1H, $o-H(Ar)$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.9 (br. d, 1P, $^2J_{PP} = 42$ Hz); 61.1 (br. d, 1P, $^2J_{PP} = 42$ Hz).

3.5. Synthesis of $[Fe(\eta^5-C_5H_4P\{C_6F_5\}_2)_2Pd(NCMe)(OTf)](OTf)$ (**8**)

Silver triflate (0.25 g, 0.97 mmol) was added with stirring to a solution of **4** (0.50 g, 0.46 mmol) in CH_2Cl_2 (30 mL) MeCN (0.2 mL) at $-78^\circ C$. The mixture was slowly warmed to room temperature and stirred for 3 h. The precipitate of AgCl was filtered off and the solvent was removed in vacuum. The residue was then washed with CH_2Cl_2 (2×10 mL) to afford green crystalline poorly soluble in CH_2Cl_2 . It was washed with Et_2O and dried in vacuum. Yield of **8**: 0.27 g (42%). Anal. Calc. for $C_{38}H_{11}F_{26}FeNO_6P_2PdS_2$: C, 33.57; H, 0.82; N, 1.03. Found: C, 34.17; H, 1.03; N, 1.22%. 1H NMR (CD_3CN): δ 4.81 (s, 4H, C_5H_4), 5.35 (s, 4H, C_5H_4). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 17.2 (br. s). $^{19}F\{^1H\}$ NMR (CD_3CN): δ -82.1 (t, $^3J_{FF} = 19.3$ Hz, 8F, *m*-F(C_6F_5)); -66.5 (t, $^3J_{PP} = 19.3$ Hz, 4F, *p*-F(C_6F_5)); -50.1 (br. t, 8F, *o*-F(C_6F_5)); -1.3 (s, $CF_3SO_3^-$).

3.6. Catalytic carbonylation of ethene in methanol

Typically, MeOH (100 mL) was introduced by suction into a 250-mL autoclave, previously evacuated by a vacuum pump, containing 0.01 mmol of precatalyst along with 0.8 mmol of 1,4-benzoquinone (BQ) and 0.2 mmol of *p*-toluenesulfonic acid (TsOH). The autoclave was then pressurized with 1:1 CO/C_2H_4 (600 psi) at room temperature and

heated to 85 °C. As soon as the reaction mixture reached the desired temperature, stirring (1400 rpm) was applied for 1 h. A constant pressure was maintained all over the experiment time, by a constant feeding of the same mixture of CO/C₂H₄ from a gas reservoir. The reaction was stopped by cooling the autoclave to room temperature by means of an ice-acetone bath. After the unreacted gases were released, the insoluble copolymer, if any, was filtered off and washed with cold methanol and dried overnight under reduced pressure at 70 °C. In any case the filtrate was analysed by GC using dimethoxyethane as the external standard.

3.7. X-ray structure determination

Crystals of **5** and **7** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into solutions of the complexes in dichloromethane. X-Ray diffraction experiments for **5** and **7** were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å, ω -scans with a 0.3° step in ω and 10 s per frame exposure) at 110 K [9]. Reflection intensities were integrated using SAINT software [10] and absorption correction was applied semi-empirically. The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for no-hydrogen

atoms. Hydrogen atoms in **5** and **7** were placed in geometrically calculated positions and included in final the refinement using the “riding” model with the $U_{\text{iso}}(\text{H})$ parameters equal to 1.2 $U_{\text{eq}}(\text{C}_i)$ or 1.5 $U_{\text{eq}}(\text{C}_{ii})$, where $U(\text{C}_i)$ and $U(\text{C}_{ii})$ are, respectively, the equivalent thermal parameters of the aromatic and methylene carbon atoms to which corresponding H atoms are bonded. The analysis of the Fourier density synthesis have revealed that Et₂O solvate in **5** and **7** as well as SO₃CF₃ anion and one of the *o*-Pr^{*i*}C₆H₄ substituents in **7** are disordered by two positions with equal occupancies. Crystal data and structure refinement parameters for **5** and **7** are given in Table 2. All calculations were performed using the SHELXTL software [10].

4. Supplementary material

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 251344 for **5** and No. 251345 for **7**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgments

Authors gratefully acknowledge Dr. Claudio Bianchini and Dr. Werner Oberhauser for the catalytic testing of the cationic palladium complexes. Thanks are due to a CNR-RAS bilateral agreement, to the Russian Foundation for Basic Research (Grant 03-03-32471) and to the Science Support Foundation of Russian Federation for financial support.

References

- [1] (a) E. Drent, H.M. Budzelaar, Chem. Rev. 96 (1996) 663; (b) R.A. Robertson, D. Cole-Hamilton, J. Coord. Chem. Rev. (225) (2002) 67; (c) C. Bianchini, A. Meli, Coord. Chem. Rev. 225 (2005) 35.
- [2] (a) E. Drent, J.A.M. van Broekhoven, M.J. Doyle, J. Organomet. Chem. 417 (1991) 235; (b) W. Clegg, G.R. Eastham, M.R.J. Elsegood, R.P. Tooze, X.L. Wang, K. Whiston, J. Chem. Soc., Chem. Commun (1999) 1877.
- [3] (a) C. Bianchini, A. Meli, W. Oberhauser, P.W.N.M. van Leeuwen, M.A. Zuideveld, Z. Freixa, P.C.J. Kamer, A.L. Spek, O.V. Gusev, A.M. Kalsin, Organometallics 22 (2003) 2409; (b) O.V. Gusev, A.M. Kalsin, P.V. Petrovskii, K.A. Lyssenko, Yu.F. Oprunenko, C. Bianchini, A. Meli, W. Oberhauser, Organometallics 22 (2003) 913.
- [4] S.J. Dossett, A. Gillon, A.G. Orpen, J.S. Fleming, P.G. Pringle, D.F. Wass, M.D. Jones, J. Chem. Soc., Chem. Commun (2001) 699.
- [5] O.V. Gusev, A.M. Kalsin, N.V. Vologdin, K.A. Lyssenko, P.V. Petrovskii, A.L. Tsvetkov, I.P. Beletskaya, Organometallics, submitted for publication.
- [6] O.V. Gusev, A.M. Kalsin, M.G. Peterleitner, P.V. Petrovskii, K.A. Lyssenko, N.G. Akhmedov, C. Bianchini, A. Meli, W. Oberhauser, Organometallics 21 (2002) 3637.
- [7] (a) M.A. Zuideveld, B.H.G. Swennenhuis, P.C.J. Kamer, P.W.N.M. van Leeuwen, J. Organomet. Chem. 637 (2001) 805;

Table 2
Crystallographic data for complexes **5** and **7**

	5	7
Formula	C ₄₀ H ₃₆ F ₆ FeO ₁₀ P ₂ PdS ₂ · 1/2(C ₄ H ₁₀ O)	C ₅₂ H ₅₄ F ₆ FeNO ₆ P ₂ PdS ₂ · 1/2(C ₄ H ₁₀ O) · (CH ₃ CN)
<i>T</i> (K)	120	120
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, <i>Pbca</i>
<i>a</i> (Å)	11.1598(9)	21.288(2)
<i>b</i> (Å)	11.6408(9)	16.084(1)
<i>c</i> (Å)	17.422(1)	33.584(6)
α (°)	100.319(2)	
β (°)	99.789(2)	
γ (°)	91.668(2)	
<i>V</i> (Å ³)	2190.2(3)	11,499(2)
<i>Z</i> (<i>Z'</i>)	2(1)	8(1)
<i>M</i>	1116.06	1245.37
μ (cm ⁻¹)	9.95	7.62
<i>F</i> (000)	1130	5120
ρ_{calcd} (g cm ⁻³)	1.692	1.439
$2\theta_{\text{max}}$ (°)	58.00	52.00
No. of reflections measured (<i>R</i> _{int})	19,503 (0.0630)	62,970 (0.0815)
No. of independent reflections	11,023	11,349
No. of reflections with <i>I</i> > 2 σ (<i>I</i>)	6573	7256
No. of parameters	579	872
<i>R</i> ₁	0.0630	0.0757
<i>wR</i> ₂	0.1422	0.1877
GOF	1.059	1.069
Maximum/minimum peak (e Å ⁻³)	1.082/−0.631	0.748/−0.568

- (b) M.A. Zuideveld, B.H.G. Swennenhuis, M.D.K. Boele, Y. Guari, G.P.F. van Strijdonck, J.N.H. Reek, P.C.J. Kamer, K. Goubitz, J. Fraanje, M.L. Lutz, A.L. Spek, P.W.N.M. van Leeuwen, *J. Chem. Soc., Dalton Trans.* (2002) 2308.
- [8] (a) O.V. Gusev, M.G. Peterleitner, N.V. Vologdin, A.M. Kalsin, *Elektrokhimiya* 39 (2003) 1444;
- (b) O.V. Gusev, M.G. Peterleitner, A.M. Kalsin, N.V. Vologdin, *Russ. J. Electrochem.* 39 (2003) 1293.
- [9] SMART V5.051 and SAINT V5.00, Area Detector Control and Integration Software, 1998, Bruker AXS Inc., Madison, WI-53719, USA.
- [10] G.M. Sheldrick, *SHELXTL-97*, Version 5.10, Bruker AXS Inc., Madison, WI-53719, USA.