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Journal of Organometallic Chemistry 575 (1999) 214–222

Journal of Organo metallic Chemistry

Transition metal complexes with sterically demanding ligands. I. Synthesis and X-ray crystal structure of 1,5-cyclooctadiene palladium methyl triflate, (COD)Pd(Me)(OTf) and its cationic penta-coordinate adducts with sterically demanding 2,9-diaryl-substituted 1,10-phenanthroline ligands

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Received 22 July 1998

Abstract

The synthesis, use and X-ray crystal structure of the novel cyclooctadiene Pd–triflate methyl complex **1** is described. Evidence for ionization of the triflate ligand in **1** in solution is presented through IR, ^{19}F-NMR and conductivity measurements. The high reactivity of this starting material is exemplified through the preparation of the novel cationic pentacoordinate Pd complexes **4** and **5**, from **1** and the sterically demanding 2,9-diarylsubstituted 1,10-phenanthroline ligands **2** and **3**. Complexes **4** and **5** have a pseudo-trigonal bipyramidal structure and display significant differences of the binding mode of the two olefin moieties of the cyclooctadiene ligand. This has been substantiated through ^{1}H- and ^{13}C-NMR spectroscopic data and for complex **4** by an X-ray crystallographic study. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Trigonal-bipyramidal Pd complexes; Palladium-triflate; Sterically demanding phenanthroline ligands; Triflate ionization; Conductivity measurements

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1. Introduction

Cationic Ni(II) and Pd(II) complexes with sterically demanding nitrogen ligands have recently attained considerable interest due to their catalytic applications in the Ziegler-Natta olefin polymerization process [1,2]. The readily available diimine ligands R–N=CR′–R′C=NR, where R = bulky aryl substituent, have been mostly utilized in these systems and allowed to tailor highly active catalysts and even to design living polymerization systems [3]. In order to explore the steric requirements in these catalysts further, we have turned to 2,9-diaryl substituted 1,10-phenanthroline ligands (phen′) for which we anticipated a more narrow coordination gap in the corresponding square planar complexes compared to the *N*-substituted diimine donors. This becomes immediately apparent from the inspection of the ligand framework in both systems presented in Fig. 1.

This can be rationalized based on the directionality of the 2,9-substituents in the 1,10-phenanthroline system which are pointing more towards the two remaining coordination sites in square planar geometry. As evidenced by Brookhart et al. in the diimine systems, the latter are occupied by the olefin and the growing polymer chain in the proposed resting state of the olefin polymerization process [2,4].

Prior to catalytic studies, however, novel reactive starting materials had to be identified for the synthesis of Pd catalysts with such sterically very demanding nitrogen donor ligands. Herein, we will report on the

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PII: S0022-328X(98)00997-8

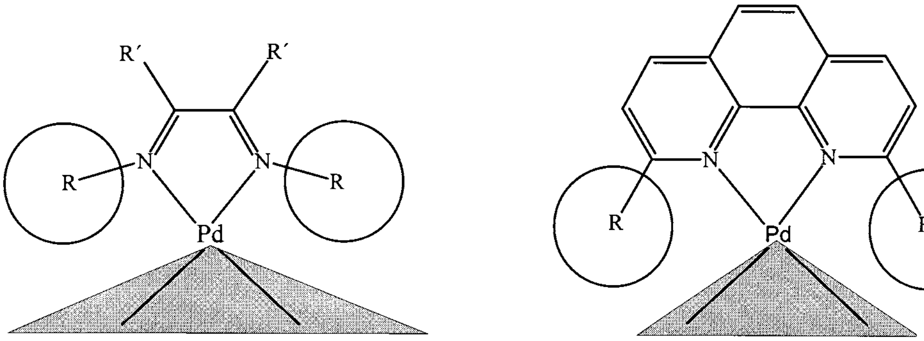
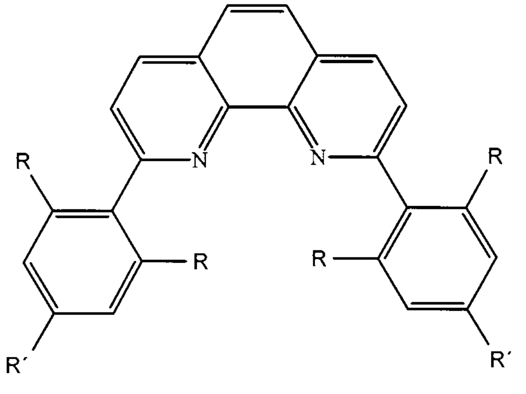


Fig. 1. Steric requirements of ligands in square planar Pd complexes. The triangles represent the size of reasoned coordination gaps.



2: R = H, R′ = tBu **3**: R = OMe, R′ = H

Fig. 2. Sterically demanding 2,9-diaryl substituted 1,10-phenanthroline ligands.

synthesis and X-ray crystal structure of such a compound, the novel palladium methyl triflate complex, (COD)Pd(Me)(OTf), **1**, and will exemplify its use in the synthesis of the novel penta-coordinated 2,9-diaryl-substituted phenanthroline Pd complexes, **5** and **6**.

2. Results and discussion

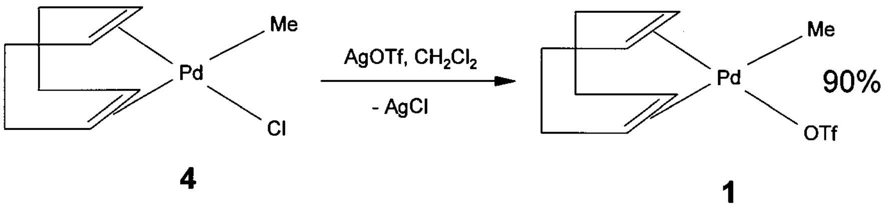
2.1. Ligand synthesis

The desired 2,9-diaryl-substituted ligands shown in Fig. 2 have been prepared in analogy to a route published by Sauvage et al. [5] for the novel ligand **2**, with R = 4-*t*-Bu-C_6H_4, and for the 2,6-dimethoxyphenyl substituted ligand, **3**, following a synthesis reported by Lüning and coworkers [6].

2.2. Complex synthesis

In a first attempt to prepare the desired organometallic Pd methyl phenanthroline complexes with the sterically demanding ligands **2** and **3**, the reaction of the frequently used starting material, (COD)Pd(Me)(Cl), **4**, with the phenanthroline derivatives **2** and **3** was studied. However, while compound **4** has been found to be quite versatile for the synthesis of a variety of Pd complexes, including those with sterically demanding ligands [2,7,8], only unchanged **4** was recovered in these reactions even under very forcing conditions, i.e. high reaction temperatures and long reaction times. A more reactive starting material was therefore sought and let us consider the corresponding triflate (OTf) complex, (COD)Pd(Me)(OTf), **1**, for which more facile substitution was anticipated due to the more labile OTf group. Since this propensity of the triflate ligand has now been widely recognized and used [9–18], we surprisingly had to note that this complex had not been reported in the literature. We had therefore to develop a synthesis for **1** and considered direct metathesis of the chloride ligand in complex **4** with silver triflate (Eq. (1)).

(1)



As presented in Eq. (1), the desired complex **1** can be prepared in excellent yield from this reaction and is obtained as a white, analytically pure solid after recrystallization from CH_2Cl_2/pentane. Complex **1** is thermally stable in the solid state and can be stored and handled at room temperature. Since decomposition in solution (with concomitant formation of Pd metal) is slow and only observed over an extended period of time, compound **1** was deemed as an excellent starting material for the synthesis of a variety of Pd methyl complexes (vide supra).

Table 1
Crystal and data collection parameters for compounds **1** and **5**

Compound	**1**	**5**
Formula	$C_{10}H_{15}F_3O_3PdS$	$C_{42}H_{44}F_3N_2O_3PdS \cdot CH_2Cl_2$
Formula weight	378.7	908.3
Habitus	Colorless cube	White rect., parallelepiped
Crystal size (mm)	0.2 × 0.2 × 0.2	0.6 × 0.4 × 0.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/c}$ (No. 14)	C_c (No. 9)
a (Å)	12.429(3)	12.259(2)
b (Å)	7.529(2)	24.889(5)
c (Å)	15.134(3)	14.625(2)
β (°)	108.95(1)	113.09(1)
V (Å^3)	1339.5(5)	4104.8(12)
Z	4	4
Density$_{\mathrm{calc}}$ (g cm^{-3})	1.878	1.470
Absorption coefficient (mm^{-1})	1.573	0.688
F(000)	1662	1872
Temperature (K)	298	193
λ (Å), Mo–K$_\alpha$	0.707173	0.707173
Scan type	ω	ω
2Θ range (°)	4–54	4–56
No. of reflections measured	2816, 2816	8927, 8296
Total, unique no. of parameters	163	522
R_1 ($F^2 > 2\sigma(F^2)$)	0.067	0.0555
wR_2 ($F^2 > 2\sigma(F^2)$)	0.158	0.211
Goodness-of-fit, S	1.272	1.055
Res. e^- density (e Å^{-3})	1.35, −1.21	0.91, −0.72

2.3. X-ray crystal structure of *1*

The details of the data collection in Table 1 are given in Table 1; selected bond lengths and angles are compiled in Table 2. The triflate ligand is coordinated to the Pd center in the solid state which is best illustrated through the molecular structure presented in Fig. 3.

This leads to tetra-coordination with a square planar ligand arrangement, taking the midpoints of the olefin moieties as representatives of the COD ligand. The most prominent feature in the crystal structure of **1** is the observed large *trans* influence which is indicated through the large differences of the palladium carbon bond distances of the olefin moieties in the *trans* positions to the methyl and the triflate ligands. The averaged carbon–Pd bond length of 239 pm (Pd(1)–C(2) 241.1(8) pm, Pd(1)–C(3) 237.7(7) pm) to the *trans*-methyl olefin ligand is apparently 26 pm, or 10%, longer than the corresponding distance of the olefin unit *trans* to the triflate group (Pd(1)–C(6) 214.4(7) pm, Pd(1)–C(7) 212.0(8) pm). The Pd(1)–O(1) (OTf) bond distance of 212.6(5) pm is in the range observed in other palladium triflate complexes [13,14,19]; it is however somewhat longer than the Pd–methyl bond length (Pd(1)–C(1)) of 201.7(8) pm. Considering the smaller covalent radius for carbon compared to oxygen, this

Table 2
Selected bond distances (Å) and angles (°) with estimated S.D.s for complex **1**

Pd(1)–C(1)	2.017(8)	Pd(1)–C(2)	2.411(8)
Pd(1)–C(3)	2.377(7)	Pd(1)–C(6)	2.144(7)
Pd(1)–C(7)	2.120(8)	Pd(1)–O(1)	2.126(5)
C(2)–C(3)	1.344(13)	C(6)–C(7)	1.368(12)
Pd(1)–Z1[a]	2.29	Pd(1)–Z2[a]	2.02
C(1)–Pd(1)–O(1)	88.7(3)	Z1–Pd(1)–Z2	86.0
Z2–Pd(1)–C(1)	91.0	Z1–Pd(1)–O(1)	94.6
Sum of angles at Pd(1)	360.3		

[a] Z1 and Z2 are the midpoints of carbon atoms C(2) and C(3) and C(6) and C(7), respectively.

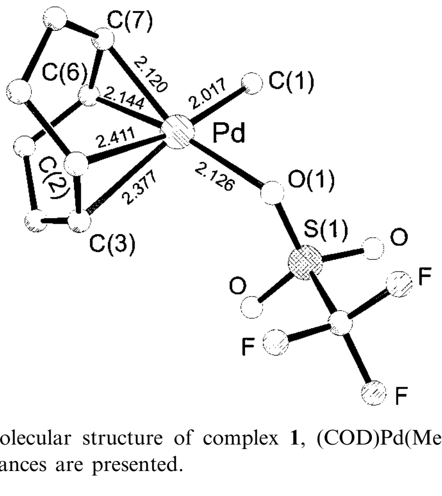


Fig. 3. Molecular structure of complex **1**, (COD)Pd(Me)(OTf); selected distances are presented.

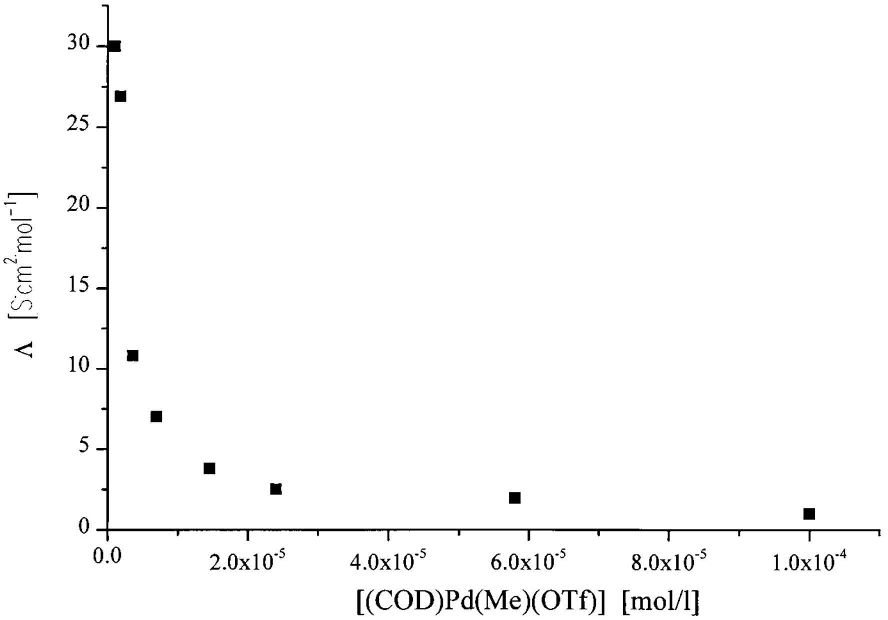


Fig. 4. Concentration dependent molar conductivity of complex **1**.

implied a weakened Pd–O bond. Hence, it was anticipated that ionization of the OTf ligand might still occur in solution and evidence for this will be presented in the next section.

2.4. Solution studies of complex 1

2.4.1. Molar conductivity

In order to study the binding mode of the triflate group in solution, we have turned to conductivity measurements of complex **1**, in both dichloromethane and in the more polar solvent, acetone.

Conductivity measurements in CH_2Cl_2 solvent: At 10^{-4} M concentration, the molar conductivity, Λ, of **1** in CH_2Cl_2 amounts to just $\Lambda = 1$ S cm^2 mol^{-1} suggesting only negligible dissociation of the triflate group. However, upon lowering of the concentrations of complex **1**, a steep increase of the molar conductivity is observed (Fig. 4).

The concentration dependence of the molar conductivity of **1** presented in Fig. 4 clearly demonstrates that complex **1** behaves as an ionophore, i.e. is only *partially* dissociated at higher concentrations and *fully* dissociated at very low concentrations.

Molar conductivity of **1** in acetone: In acetone solvent at 1.1×10^{-3} M concentration, a molar conductivity of $\Lambda = 103$ S cm^2 mol^{-1} was determined for complex **1**. This is in the typical range for 1:1 electrolytes in acetone solvent [20] and shows that the triflate group is fully dissociated, even at this quite high concentration.

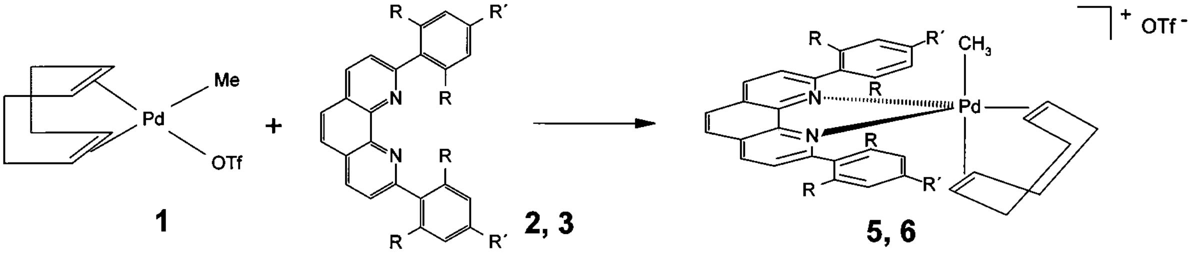
2.4.2. IR- and ^{19}F-NMR-spectroscopy

In the solution IR-spectrum of **1** in CD_2Cl_2 at ca. 10^{-3} M concentration, a strong band at 1321 cm^{-1}, indicative of a covalent bound OTf ligand, and a very weak band at 1269 cm^{-1} in the typical range for an ionic triflate group were observed [9,12]. The weak intensity of the low energy ν(S=O) band at 1269 cm^{-1} is consistent with the aforementioned conductivity measurements, since just very little dissociation would be expected at the 10^{-3} M concentration based on the conductivity data. Further evidence for the preference for covalent bonding of the triflate ligand in **1** at higher concentrations (in the 10^{-1}–10^{-2} M range), was obtained through ^{19}F-NMR spectroscopy in dichloromethane. At ca. 10^{-1} M concentration, the ^{19}F-NMR resonance of the OTf group appears at $\delta = -79.76$ and shifts to higher field ($\delta = -79.82$) at ca. 2×10^{-2} M concentration. This should be compared to the ^{19}F-NMR chemical shift of the OTf group of $\delta = -80.47$ in PPN^+OTf^- ($PPN^+ = Ph_3P{=}N{=}PPh_3^+$), a source of ionic triflate [21]. The significant difference of the chemical shifts of the OTf groups in **1** and PPN^+OTf^- suggests that the triflate group is only dissociated to a very a small extent in the NMR-samples of **1** which is consistent with the IR-spectroscopic and conductivity data. There is however a noticeable trend of the triflate resonance to shift upfield towards the chemical shift ($\Delta\delta = 0.06$) of the free triflate ion at lower concentrations. In acetone solvent, full dissociation of the triflate in **1** is indicated through the ^{19}F-NMR resonance at $\delta = -79.1$ ppm which is identical to the chemical shift of PPN^+OTf^- in this solvent.

The conductivity and IR- and NMR-spectroscopic data of complex **1** clearly demonstrate that facile and complete dissociation of the triflate group occurs in polar solvents such as acetone. In weaker coordinating and less polar solvents, e.g. dichloromethane, complex **1** behaves as an ionophore and displays concentration dependent ionization of the OTf ligand. As will be presented in the next section, triflate dissociation plays an important role for the ligand substitution reactions in complex **1**.

2.5. Formation of penta-coordinated complexes *5* and *6*

The facile and clean reactions of complex **1** with the sterically demanding phenanthroline ligands **2** and **3** presented in Eq. (2) indeed confirmed our expectations.



(2)

2, **5**: R = H, R′= tBu **3**, **6**: R = OMe, R′ = H

The ^{1}H-NMR spectra of complex **5** obtained from the reaction according to Eq. (2), displayed two multiplets (1:1 integration ratio) in the olefin range which immediately indicated that the 1,5-cyclooctadiene group was still incorporated into the reaction product, **5** (i.e. that it had not been substituted). Most noticeably, in CD_2Cl_2 solution the latter resonances were separated by ca. 1 ppm in **5** with the downfield triplet ($\delta = 4.93$) in proximity to the chemical shift of the olefinic protons in the free COD ligand ($\delta = 5.56$). In line with this observation, the ^{13}C-NMR resonances of the olefinic carbon atoms corresponding to the downfield triplet in the ^{1}H-NMR spectrum were only slightly shifted ($\Delta\delta = -1.0$ in **5** and -1.7 in **6**) to higher field from the observed chemical shift in free 1,5-cyclooctadiene ($\delta(\mathrm{CH_{olefin}}) = 128.9$). The remaining olefinic resonances in **5** and **6** on the other hand experienced a significant high-field shift of $\Delta\delta = -39.6$ and -42.1, respectively, when compared to the free COD ligand indicating strong Pd–olefin back donation. While it could be quite safely concluded that the latter resonances originated from a metal coordinated olefin moiety, the NMR-data did not allow to distinguish between (a) an η^4-binding mode with differentiated weak and a strong back donation of the Pd center or (b) an η^2-coordination of only *one* olefin moiety of the COD ligand. The NMR-spectroscopic data allowed to establish an (at least) overall *Cs*-symmetrical structure and also revealed an intact Pd methyl bond evidenced through singlets in the ^{1}H-NMR spectra for the Pd methyl groups in **5** and **6**. Conductivity measurements of complexes **5** and **6** in dichloromethane provided support for 1:1 electrolytes (**5**, $\Lambda = 43$ S cm^2 mol^{-1} at 10^{-3} M concentration) and suggested cationic phenanthroline Pd adducts with ionic (non-coordinated) triflate counterions. At this point, it was not completely clear whether the Pd centers in complexes **5** and **6** were four- or five-coordinate, i.e. with an η^4-bisolefin unit in the latter case.

Prior to an X-ray crystal structure analysis for complex **5**, we were therefore glad to note the extended and excellent work of Albano et al. on penta-coordination in Pd and Pt complexes bearing dinitrogen donor ligands [22,23]. These authors have put forward that penta-coordination with a trigonal-bipyramidal structure is preferred over a square-planar tetra-coordinate geometry in complexes with sterically demanding ligand frameworks. The aforementioned observations for the chemical shifts of the olefinic NMR-resonances in **5** and **6** were similar to their findings in related bisolefin complexes [23]. Since the latter had been shown to possess penta-coordinated metal centers, we also assumed a trigonal-bipyramidal structure for complexes **5** and **6**. This was later confirmed by the X-ray crystal structure analysis of complex **5** which is described in the next section.

2.6. X-ray crystal structure analysis of *5*

The X-ray diffraction study of **5** established the penta-coordinate trigonal-bipyramidal structure with an η^4-coordination mode of the bisolefin. The molecular structure of complex **5** is presented in Fig. 5, selected bond angles and distances are given in Table 3, details of the data collection, solution and refinement in Table 1.

The equatorial sites are occupied by the phenanthroline *N*,*N*-donor ligand and by one of the olefin moieties of the COD (C(40), C(41)) ligand. The other COD olefin unit (C(44),C(45)) and the Pd–methyl group are coordinated in the apical positions of the pseudo trigonal-bipyramid and an angle of 173.5° is observed between the olefin midpoint (Z2) and the methyl ligand ($\sphericalangle$(Z2–Pd(1)–C(50))). While the Pd–methyl and Pd–N ligand distances are in the expected range, a quite significant difference in the binding modes of the two

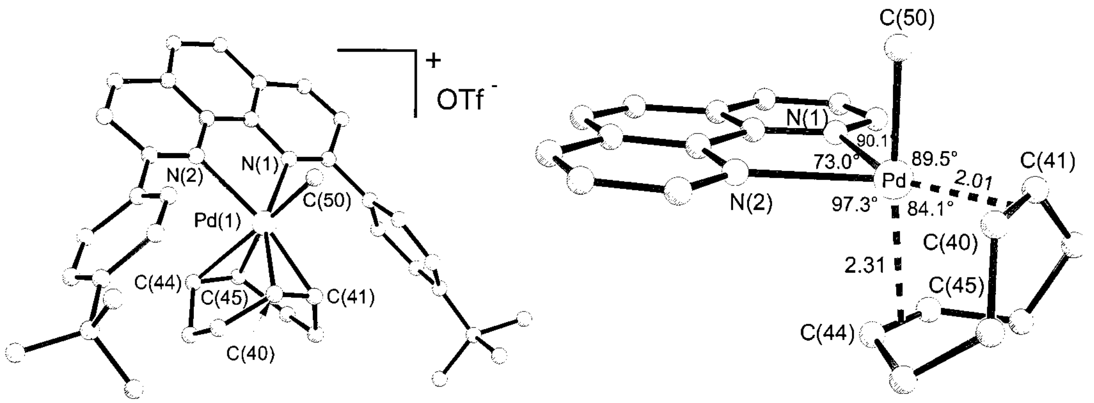


Fig. 5. Right hand: Molecular structure of cationic complex **5**. Left hand: The 2,9-(4-*t*-butyl-phenyl)-substituents have been omitted for clarity; selected distances and angles presented. The triflate ion is not shown.

olefin moieties was noticed for the bisolefin ligand. Rather short Pd carbon bond lengths of 212.2(5) and 213.1(5) pm (Pd(1)–C(40), Pd(1)–C(41)) were observed for the olefin oriented in the equatorial plane, while noticeably longer distances were found for the Pd carbon bond distances to the apical olefin (Pd(1)–C(44) 237.7(6) pm and Pd(1)–C(45) 244.4(6)). Such a difference had been recognized earlier by Albano et al. in a related penta-coordinated platinum COD complex and was used to explain the observed differences of the ^{1}H- and ^{13}C-NMR shifts of the olefin moieties (vide supra) [22,23]. The stronger bonding to the equatorial olefin ligand has been rationalized based on the stronger π-back donation from the higher lying (better donating) and more extended Pd d_{xy}-orbital, which is oriented in the equatorial plane [22,24].

3. Conclusion

The triflate complex **1** is an excellent and readily available starting material for the synthesis of complexes with sterically demanding donor ligands. Currently, we are studying the reaction chemistry of **5** and **6** and will report on olefin and CO insertion processes in these complexes in due course [25].

Table 3
Selected bond distances (Å) and angles (°) with estimated S.D.s for complex **5**

Pd(1)–C(50)	2.041(5)	Pd(1)–C(40)	2.122(5)
Pd(1)–C(41)	2.131(5)	Pd(1)–C(44)	2.377(6)
Pd(1)–C(45)	2.444(6)	Pd(1)–N(1)	2.311(4)
Pd(1)–N(2)	2.377(4)	C(40)–C(41)	1.401(8)
C(44)–C(45)	1.361(12)	Pd(1)–Z1[a]	2.01
Pd(1)–Z2[a]	2.31		
N(1)–Pd(1)–N(2)	73.0(2)	C(50)–Pd(1)–N(1)	90.1(2)
C(50)–Pd(1)–N(2)	87.1(2)	C(50)–Pd(1)–Z(1)	89.5
C(50)–Pd(1)–Z(2)	173.5	Z1–Pd(1)–Z(2)	84.1
N(1)–Pd(1)–Z(1)	143.7	N(2)–Pd(1)–Z(1)	143.2
N(1)–Pd(1)–Z2	95.7	N(2)–Pd(1)–Z(2)	97.3

[a] Z1 and Z2 are the midpoints of carbon atoms C(40) and C(41) and C(44) and C(45), respectively.

4. Experimental section

Reactions were carried out under a dinitrogen atmosphere with thoroughly dried solvents using glovebox and Schlenk techniques. (COD)Pd(Me)(Cl), **4** [8], and 2,9-di-(2,6-dimethoxyphenyl)-1,10-phenanthroline, **3** [6], were prepared according to published methods. ^{1}H-, ^{19}F- and ^{13}C-NMR spectra were recorded on a Varian Gemini 200 and 300 spectrometers. Chemical shifts are given in ppm and referenced to the residual H solvent shifts or ^{13}C-NMR solvent shifts and for the ^{19}F-NMR resonances to the ^{19}F-NMR chemical shift of trifluorotoluene. The assignment of ^{1}H-NMR and ^{13}C-NMR resonances is based on NOE, DEPT and selective ^{1}H–^{13}C decoupling experiments. IR-spectra were measured on a Biorad FTS-45 Fourier IR-spectrometer. X-ray crystal structure analyses have been performed on a Nicolet-Siemens P4 four-circle diffractometer with monochromated Mo–K_α (0.70713 Å) beam. CHN-analyses were carried out with a LECO CHNS-932 elemental analyzer in our institute. Conductivity measurements were performed with an Amel-160 conductometer using a glass cell with Pt electrodes ($K = 1.0$).

4.1. *2,9-Di-(4-tert-butylphenyl)-1,10-phenanthroline*, *3*

(a) Synthesis of 4-lithio-*t*-butyl benzene: 45 ml (75 mmol) of a 1.6 M solution of *n*-butyllithium was added to a stirred solution of 15 g 1-bromo-4-*t*-butylbenzene (70 mmol) in 100 ml pentane. After 2 days at room temperature (r.t.), a white suspension was obtained from which the desired lithium salt was collected by filtration. The solid was washed twice with pentane and finally dried in high vacuum to give 9.5 g (68 mmol, 91%) 4-lithio-*t*-butyl benzene. (b) Addition to 1,10-phenanthroline: The obtained lithium salt (9.5 g, 68 mmol) was dissolved in 50 ml diethyl ether, cooled to − 70°C and added to a cooled solution (− 70° C) of 3.06 g (17 mmol) anhydrous 1,10-phenanthroline in 100 ml toluene. Immediately, a red solution was obtained which was allowed to warm up to r.t. overnight under stirring. The solution was then cooled to 0°C and hydrolyzed slowly with 20 ml H_2O giving a yellow organic phase. The organic phase was separated and the aqueous phase was extracted twice with CH_2Cl_2. The organic phases were combined and dried over Na_2SO_4. Upon filtration, 100 g MnO_2 (Fluka No. 63548) was added to the solution and the reaction mixture was stirred for 30 min at r.t. After this time, the mixture was filtered through celite giving a pale yellow solution, which was evaporated to dryness with a rotary evaporator giving a white, slightly yellowish solid. This material was taken up in a mixture of CH_2Cl_2: pentane (9:1) and filtered through a short column of silica (40–63 μm) yielding **3** as an analytically pure white solid. Overall yield: 5.4 g (12.3 mmol; 74% based on 1,10-phenanthroline). ^{1}H-NMR (200 MHz, $CDCl_3$, 298 K): $\delta = 1.41$ (s, 18H, ^{t}Bu), 7.6 (d, $J = 8$ Hz, 4H, $H_{2,2'}$ (*tBu*-phenyl)), 7.72 (s, 2H, $H_{5,6}$), 8.09 (d, $J = 8$ Hz, 2H, $H_{3,8}$), 8.25 (d, $J = 8$ Hz, 2H, $H_{4,7}$), 8.38 (d, $J = 8$ Hz, 4H, phenyl−$H_{3,3'}$); $^{13}C\{^1H\}$-NMR (50.3 MHz, $CDCl_3$, 298 K): $\delta = 156.6$ (s, quart. $C_{arom.}$), 152.6 (s, quart. $C_{arom.}$), 145.7 (s, quart. $C_{arom.}$), 136.9 (s, $CH_{arom.}$), 136.5 (s, quart. $C_{arom.}$), 127.7 (s, quart. $C_{arom.}$), 127.4 (s, $CH_{arom.}$), 125.8 (s, $CH_{arom.}$), 125.7 (s, $CH_{arom.}$), 119.7 (s, $CH_{arom.}$); 34.7 ($C(CH_3)$), 31.3 ($C(CH_3)$). Elemental analysis: Calc.: C: 86.45, H: 7.25, N 6.30; Found: C: 86.40, H: 7.37, N: 6.23.

4.2. Synthesis of (COD)Pd(CH_3)(OTf), **1**

1.07 g (4.2 mmol) finely powdered AgOTf and 0.91g (3.4 mmol) (COD)Pd(Me)(Cl), **4**, in 10 ml dichloromethane were stirred for 2 h at r.t. After this time AgCl and excess AgOTf were removed by filtration through celite. The volume of the filtrate was reduced to one third and the remainder layered with 10 ml of pentane. From this mixture, the product was obtained as colorless crystals within several days upon cooling at − 36°C. The mother liquor was decanted off and the crystals were washed with a small volume of cold CH_2Cl_2, followed by pentane and finally dried in high vacuum. A second crop could be obtained by recrystallization from the mother liquor and the washing solutions. Combined Yield: 1.13 g (3.1 mmol, 90% based on (COD)Pd(Me)(Cl)). ^{1}H-NMR (200 MHz, CD_2Cl_2, 298 K): $\delta = 1.23$ (s, 3H, CH_3), 2.5 (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 5.14 (m, 4H, CH), 5.96 (m, 4H, CH); $^{13}C\{^1H\}$-NMR (50.3 MHz, CD_2Cl_2, 298 K): $\delta = 16.8$ (s, Pd−CH_3), 27.5, 31.2 (s, CH_2, COD), 98.1 (s, CH, COD, *trans* to Pd−OTf,), 125.1 (CH, COD, *trans* to Pd−methyl). The ^{13}C-NMR resonance of the triflate group could not be detected. ^{19}F-NMR(282.3 MHz, CD_2Cl_2, 298 K) $\delta = -79.8$ (s, CF_3SO_3) (cf. Text). ^{19}F-NMR (282.3 MHz, [D$_6$]acetone, 298 K) $\delta = -79.1$ (s, CF_3SO_3). IR(S=O range, CD_2Cl_2) 1321 (vs), 1269 (vw) cm^{-1}. Elemental analysis: Calc.: C: 31.72, H: 3.99; Found: C: 31.74, H: 4.19.

4.3. Synthesis of complex **5**

At r.t., 760 mg (2.1 mmol) (COD)Pd(Me)(OTf), **1**, and 2.2 mmol of the phenanthroline derivative **2** were stirred for 15 min in 4 ml acetone upon which precipitation of **5** was observed. Complex **5** was isolated from this mixture by centrifugation, washed twice with ca. 2 ml acetone and finally dried in high vacuum. Analytically pure material was obtained by recrystallization from CH_2Cl_2/pentane at − 36°C. Yield: 1.43 g (1.8 mmol, 85% based on (COD)Pd(Me)(OTf)). ^{1}H-NMR (200 MHz, CD_2Cl_2, 298 K): $\delta = 0.93$ (m, 2H, CH_2), 1.41 (s, 3H, CH_3); 1.43 (s, 18H, ^{t}Bu), 1.68 (m, 6H, CH_2), 3.92 (m, 2H, H_{olefin}), 4.93 (m, 2H, H_{olefin}), 7.69 (s, 8H, phenyl), 8.03 (d, $J = 8$ Hz, 2H, $H_{3,8}$), 8.17 (s, 2H, $H_{5,6}$), 8.70 (d, $J = 8$ Hz, 2H, $H_{4,7}$); $^{13}C\{^1H\}$-NMR (CD_2Cl_2, r.t., 50.3 MHz): $\delta = 162.8$ (s, quart. $C_{arom.}$), 154.0(s, quart. $C_{arom.}$), 143.5(s, quart. $C_{arom.}$), 139.7 (s, $CH_{arom.}$), 139.1 (s, quart. $C_{arom.}$), 129.7(s, $CH_{arom.}$), 130.1 (s, $CH_{arom.}$), 127.9 (s, CH_{COD}), 127.9 (s, $CH_{arom.}$), 125.9 (s, $CH_{arom.}$), 89.3 (s, CH_{COD}), 34.2(s, $C(CH_3)$), 31.4 (s, $C(CH_3)$) 26.3 (s, $CH_{2_{COD}}$), 16.3 (s, Pd−CH_3). The ^{13}C-NMR resonance of the OTf group could not be detected. ^{19}F-NMR(282.3 MHz, CD_2Cl_2, 298 K) $\delta = -80.47$ (s, CF_3SO_3). IR(S=O range, CD_2Cl_2) 1269 cm^{-1}. Elemental Analysis: Calc.: C: 61.27, H: 5.75, N: 3.40; Found: C: 61.00, H: 5.81, N: 3.47.

4.4. Synthesis of complex **6**

At r.t., 190 mg (0.55 mmol) (COD)Pd(Me)(OTf), **1**, and 0.55 mmol of the phenanthroline derivative **3** were dissolved in 5 ml dichloromethane, stirred for 30 min at r.t. and then concentrated to ca. 3 ml by evaporation in vacuo. From this solution, **7** crystallized at − 36°C. A further crop could be obtained from the mother liquor by crystallization after further concentration. Combined yield: 410 mg, 0.54 mmol (98%). ^{1}H-NMR (200 MHz, CD_2Cl_2, 298 K): $\delta = 8.59$ (d, $J = 8$ Hz, 2 H), 8.12 (s, 2H, H), 7.78 (d, $J = 8$Hz, 2H), 7.60 (t, $J = 8$ Hz, 2H), 6.80 (t, $J = 8$ Hz, 4H), 5.50 (m, 2 H_{olefin}), 3.77 (s, 6H, OCH_3) 3.64 (s, 6H, OCH_3) 1.90–1.65 (m, 8H, CH_2(COD)), 1.35-1.1 (m, 2 H_{olefin}), 0.96 (s, 3H, Pd−CH_3); $^{13}C\{^1H\}$-NMR (75.4 MHz, acetone-d$_6$, 298 K) $\delta = 159.0$ (s, quart. $C_{arom.}$), 159.0 (s, quart. $C_{arom.}$), 158.7 (s, quart. $C_{arom.}$), 144.2 (s, quart. $C_{arom.}$), 139.7 (s,

$C\mathrm{H}_{\mathrm{arom.}}$), 133.0(s, $C\mathrm{H}_{\mathrm{arom.}}$), 130.4 (s, quart. $C_{\mathrm{arom.}}$), 130.2 (s, $C\mathrm{H}_{\mathrm{arom.}}$), 128.4 (s, $C\mathrm{H}_{\mathrm{arom.}}$), 126.2 (s, $C\mathrm{H}_{\mathrm{COD}}$), 119.9 (s, quart. C_{arom}) 105.2(s, $C\mathrm{H}_{\mathrm{arom.}}$), 104.9 (s, $C\mathrm{H}_{\mathrm{arom.}}$) 86.8 (s, $C\mathrm{H}_{\mathrm{COD}}$), 56.3 (s, $\mathrm{O}C\mathrm{H}_3$), 55.8 (s, $\mathrm{O}C\mathrm{H}_3$), 32.1 (s, $C\mathrm{H}_{2_{\mathrm{COD}}}$) 26.3 (s, $C\mathrm{H}_{2_{\mathrm{COD}}}$), 17.1 (Pd–$C\mathrm{H}_3$). ^{19}F-NMR (282 MHz, acetone-d_6, 298 K) $\delta = -79.1$(s, $\mathrm{C}F_3\mathrm{SO}_3$). ^{19}F-NMR (282.1 MHz, $\mathrm{CD_2Cl_2}$, 298 K) $\delta = -80.47$ (s, $\mathrm{C}F_3\mathrm{SO}_3$). Elemental analysis: Calc.: C: 54.91, H: 4.73, N: 3.37; Found: C: 55.06, H: 4.99, N: 3.40.

4.5. X-ray crystal structure analyses

4.5.1. Complex **1**

Single crystals suitable for X-ray diffraction were obtained by slow crystallization from $\mathrm{CH_2Cl_2}$: pentane at −36°C. A colorless cube of approximate dimensions 0.2 × 0.2 × 0.2 mm was mounted on a glass fiber using 5 min epoxy resin. Forty-eight well-centered reflection in the range of $20° \leq 2\Theta \leq 32°$ were used for the cell determination and refinement and from this a monoclinic cell with $a = 12.429(2)$ Å, $b = 7.529(2)$ Å, $c = 15.134$ Å, $\beta = 108.95°(1)$, space group $P2_1/n$ (No. 14) was derived. The data were collected on a Nicolet-Siemens-P4 four circle diffractometer at room temperature using graphite-monochromated Mo–K_α radiation with $4° \leq 2\Theta \leq 54°$ ($-15 \leq h \leq 14$, $0 \leq k \leq 9$, $0 \leq l \leq 19$). Three check reflections were monitored periodically as a check for crystal decomposition or movement and showed no significant variation. Intensities were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method using the SHELXS-86 program package [26] from which the position of the Pd atom was localized. The position of the residual non-hydrogen atoms were obtained in subsequent difference Fourier maps during refinement. All non-hydrogen atoms were refined anisotropically; the positions of the hydrogen atoms were calculated in idealized positions (C–H bonds fixed at 0.96 Å) and refined as riding model with a fixed isotropic displacement factor of $U = 0.08$ Å^2. The refinement was carried out against F^2 with the SHELXL93 program [27] and converged at final R-values $R(F, I > 2\sigma(I))$ of $R_1 = 0.0667$ and $wR_2 = 0.1582$.

4.5.2. Complex **5**

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a solution of **5** in $\mathrm{CH_2Cl_2}$. The $\mathrm{CH_2Cl_2}$ solvent is also contained in the crystals of complex **5** (one molecule $\mathrm{CH_2Cl_2}$ per complex **5**). A colorless rectangular parallelepiped of approximate dimensions 0.6 × 0.4 × 0.2 mm was mounted on a glass fiber in Paratone-N and transferred on the goniometerhead to a Siemens-Nicolet-P4 four circle diffractometer. The crystal was then cooled to −80°C in a $\mathrm{N_2}$-cryostream and centered in the beam. Forty-eight well-centered reflection in the range of $18° \leq 2\Theta \leq 30°$ were used for the cell determination and refinement and from this a monoclinic cell with $a = 12.259(2)$ Å, $b = 24.889(5)$ Å, $c = 14.625$ (2) Å, $\beta = 113.09°(1)$, space group C_c (No. 9) was derived. The data were collected using graphite-monochromated Mo–K_α radiation with $4° \leq 2\Theta \leq 56°$ ($-15 \leq h \leq 14$, $0 \leq k \leq 9$, $0 \leq l \leq 19$ and Friedel pairs). Three check reflections were monitored periodically as a check for crystal decomposition or movement and showed no significant variation. Intensities were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method with the SHELXS-86 program package [26]. The refinement was carried with SHELXL-93 [27] against F^2. All non-hydrogen atoms were refined anisotropically; the positions of the hydrogen atoms were calculated in idealized positions (C–H bonds fixed at 0.96 Å) and refined as riding model with a fixed isotropic displacement factor of $U = 0.08$ Å^2. One of the t-butyl groups was found to be disordered and was refined in two split positions. The occupation factor of the disordered groups was given free and converged at 0.76 and 0.24. The refinement converged at final R-values R (F, $I > 2\sigma(I)$) of $R_1 = 0.0555$ and $wR_2 = 0.211$.

Crystallographic data for complexes **1** and **5** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data center as supplementary publication numbers CCDC-101672 and CCDC-101673, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We are indebted to Professor Heinz Berke for his generous support. A loan of $\mathrm{PdCl_2}$ from Johnson-Matthey is gratefully acknowledged.

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