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Synthesis and crystal structure of twisted dinuclear η^3-allylpalladium complexes containing tetradentate nitrogen ligands

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Abstract

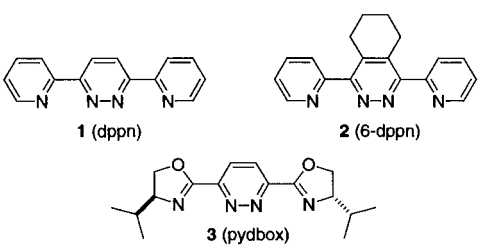
The dinuclear palladium allyl complexes **7** and **12**, which contain tetradentate nitrogen ligands **2** or **3** as bridging ligands, respectively, were synthesized and characterized. Crystal X-ray analysis of these complexes reveal that the two coordination planes of the palladium are twisted, although each of the coordination spheres presents roughly the same structural features as the related (bipyridine)allylpalladium complex.

Keywords: Palladium; π-Allylpalladium; Dinuclear complex

1. Introduction

Catalysis by dinuclear transition metal complexes has attracted considerable interest in recent years [1]. In particular the synthesis of model complexes that mimic enzymes containing dinuclear copper, iron or manganese metals has received great attention [2]. Since these studies indicate that complexes having two metal centers [3] in close proximity have the potential of catalyzing a reaction more efficiently, or regio- and stereoselectively than mononuclear metal complexes, several examples have been reported for synthetic dinuclear metal catalysts showing unusual selectivities or distinct advantages over mononuclear ones [4–8]. For example, dinuclear metal complexes can stimulate two different reactants by independent coordination to both metallic sites [4] or activate a substrate by simultaneous coordination at two metal centers [5]. Multi-electron transfers can also be mediated by dinuclear metal complexes [6]. An excellent example of a dinuclear catalyst which exhibits higher regioselectivity and reactivity than those of the related mononuclear system by bimetallic co-operation is the rhodium system reported by Stanley and co-workers for the hydroformylation of α-olefins [7].

For synthesis of new complexes that have two metal centers in close proximity, use of a tetradentate ligand including a pyridazine ring as a backbone is one of the appropriate approaches [9]. Since a pyridazine skeleton is rigid and each of its two proximal nitrogen atoms interacts with two different metals, the ligand can fix two metals in an adjacent position without metal–metal bonds. Ghedini and co-workers reported the syntheses of homo- and hetero-binuclear complexes using 3,6-bis(2′-pyridyl)pyridazine (dppn, **1**) as a binucleating ligand [9b–f]. In the complexes, two metals are not only bridged with **1**, but also with chlorine or a nitrosyl group. We now report the syntheses of dinuclear palladium complexes containing only binucleating ligands **2** and **3** without additional bridging ligands.



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2. Results and discussion

Treatment of the solution of **1** and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2:1) in acetonitrile with silver hexafluorophosphate afforded the mononuclear palladium allyl complex **4** in 74% yield (Eq. (1)). However, synthesis of the corresponding dinuclear complex **5** failed; either the reaction of **4** with $1/2[(\eta^3\text{-}C_3H_5)PdCl]_2$–$AgPF_6$ or the reaction of **1** with two equivalents of $1/2[(\eta^3\text{-}C_3H_5)PdCl]_2$–$AgPF_6$ gave only the mononuclear complex **4**. Considering the possibility that the coordination of acetonitrile to palladium inhibits the formation of **5**, the reaction in dichloromethane was investigated. However, the characterization of the product failed in order to its low solubility. The result that complex **5** was not obtained in acetonitrile may be due to the planarity of **1** to which two palladiums coordinate. Since three aromatic rings of **1** become coplanar by the coordination of two palladiums, the coordination planes of each palladium are also forced to lie on the same plane. Therefore, a steric interaction is generated between two allyl ligands of each palladium, and makes the coordination of the second palladium difficult (Chart 1, **A**). According to the inference, the ligand 2 (6-dppn) [10] was thought to be appropriate for making dinuclear complexes, because the steric repulsion between the pyridine proton and the methylene protons at the benzylic position does not permit the aromatic rings to be coplanar (Chart 1, **B**). The consequent twist of two coordination planes makes it possible for the simultaneous coodination of the two metals. Actually, the reaction of **2** and one or two equivalents of $1/2[(\eta^3\text{-}C_3H_5)PdCl]_2$–$AgPF_6$ afforded the mononuclear complex **6** or the dinuclear complex **7**, respectively (Eq. (2)).

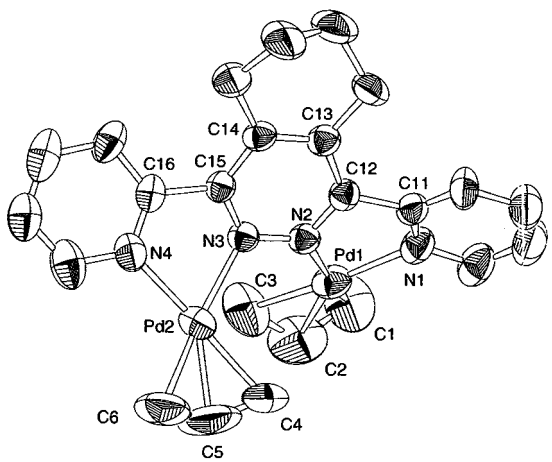
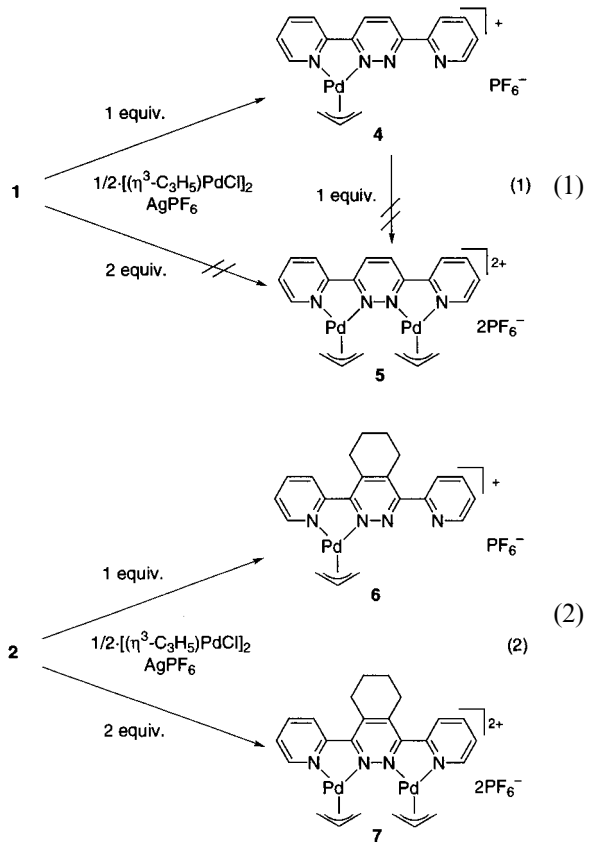


Fig. 1. ORTEP drawing of the cation of **7** with H atoms omitted for clarity.

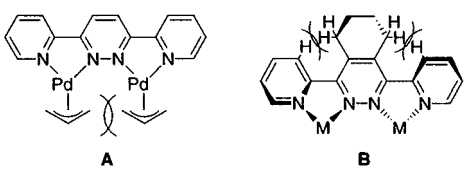
Table 1
Selected bond lengths (Å) and bond angles (°) for **7**

Bond lengths			
Pd(1)–N(1)	2.086(8)	Pd(1)–N(2)	2.127(7)
Pd(2)–N(3)	2.098(7)	Pd(2)–N(4)	2.088(8)
Pd(1)–C(1)	2.14(1)	Pd(1)–C(2)	2.12(1)
Pd(1)–C(3)	2.12(1)	Pd(2)–C(4)	2.12(1)
Pd(2)–C(5)	2.06(1)	Pd(2)–C(6)	2.12(1)
Bond angles			
N(1)–Pd(1)–N(2)	77.5(3)	N(1)–Pd(1)–C(1)	105.3(5)
N(2)–Pd(1)–C(3)	107.0(4)	C(1)–Pd(1)–C(3)	68.4(5)
N(3)–Pd(2)–N(4)	77.1(3)	N(3)–Pd(2)–C(4)	107.5(4)
N(4)–Pd(2)–C(6)	106.2(5)	C(4)–Pd(2)–C(6)	68.3(6)



(1) (1)

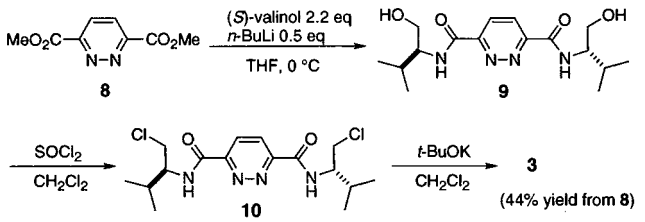
(2) (2)



A B

Chart 1

Crystallization of **7** by vapor diffusion of diethyl ether into a solution of acetone afforded a slightly yellow crystal suitable for X-ray analysis. Complex **7** exists in two forms in the unit cell which slightly differ from one another, together with two molecules of acetone. One of the two independent molecules in the crystals of **7** is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. The molecule is



Scheme 1.

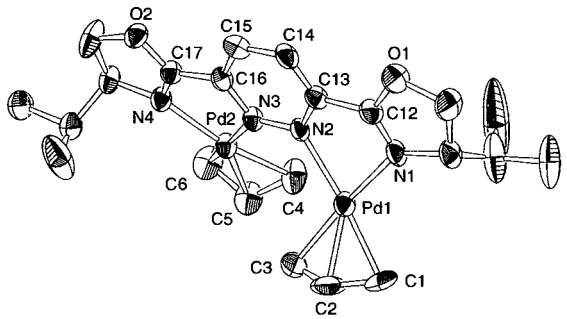


Fig. 2. ORTEP drawing of the cation of **12** with H atoms omitted for clarity.

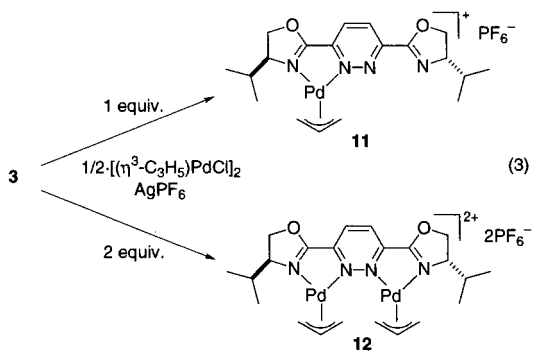
Table 2
Selected bond lengths (Å) and bond angles (°) for **12**

Bond lengths			
Pd(1)–N(1)	2.095(5)	Pd(1)–N(2)	2.166(6)
Pd(2)–N(3)	2.167(5)	Pd(2)–N(4)	2.083(6)
Pd(1)–C(1)	2.106(9)	Pd(1)–C(2)	2.06(1)
Pd(1)–C(3)	2.122(8)	Pd(2)–C(4)	2.125(8)
Pd(2)–C(5)	2.132(8)	Pd(2)–C(6)	2.095(8)
Bond angles			
N(1)–Pd(1)–N(2)	77.6(2)	N(1)–Pd(1)–C(1)	104.5(4)
N(2)–Pd(1)–C(3)	107.8(3)	C(1)–Pd(1)–C(3)	69.3(4)
N(3)–Pd(2)–N(4)	78.1(2)	N(3)–Pd(2)–C(4)	108.3(3)
N(4)–Pd(2)–C(6)	103.5(3)	C(4)–Pd(2)–C(6)	68.0(4)

nearly C_2 symmetrical, in which two pyridine rings twist from the plane of pyridazine to similar degree. One palladium atom is 1.13 Å above the pyridazine plane and another palladium atom is 1.08 Å under the plane. Twists of the pyridine rings are 26(1)° for N(1)–C(11)–C(12)–N(2) and 24(1)° for N(3)–C(15)–C(16)–N(4). The torsion angle for Pd(1)–N(2)–N(3)–Pd(2) is 68.5(7)°. The coordination sphere of each palladium exhibits a distorted-square-planar geometry and presents roughly the same structural features as the related (bipyridine)allylpalladium complex [11]. The distances for Pd–N (2.086–2.127 Å) and Pd–C (2.06–2.14 Å), as well as the angles for N–Pd–N (77.1–77.5°) and C–Pd–C (68.3–68.4°), are all within the expected range.

In the ^{1}H-NMR spectra of **4**, **6** and **7**, three signals of the allyl ligands are displayed, although five protons of the allyl ligands are originally nonequivalent. This would be a result of 'ligand rotation' [12]. The two *syn* protons and the two anti protons are equivalent by ligand rotation, respectively. The ^{1}H-NMR spectra of **4** and **6** show differences in the signals of the nitrogen ligands. While two pyridine rings of **4** afford eight peaks, only four broad peaks are displayed for those of **6** at 27°C. In an experiment in acetone-d_6 at a lower temperature (− 30°C) the spectrum shows eight sharp peaks for the pyridines (Section 4.4). This equivalence of two pyridines of **6** at 27°C would be due to an inter- or intramolecular fast ligand exchange. The forced twist of the pyridazine between the pyridine in **6** unstabilizes the coordination of the palladium to **2**, and makes the ligand exchange of **6** faster than that of **4**.

The complex **7** has C_2 symmetry including two palladium atoms. If an optically active C_2 symmetrical ligand is used, a novel reaction site consisting of two metal centers for asymmetric catalysis would be created. For this purpose, we choose 3,6-bis[(4*R*)-4-isopropyl-4,5-dihydrooxazol-2-yl]pyridazine (pydbox, **3**), which has two chiral oxazoline rings at three- and six-positions of the pyridazine ring. Although a synthesis of a ligand similar to **3** was reported by Fahrni and Pfaltz [13], we synthesized **3** from pyridazine diester by another route shown in Scheme 1. The reaction of **3** with one or two equivalents of 1/2[(η^3-C_3H_5)PdCl]$_2$–$AgPF_6$ in dichloromethane gave the mononuclear complex **11** and dinuclear complex **12**, respectively. Crystallization of **12** by vapor diffusion of diethyl ether into a solution of CH_2Cl_2 afforded a yellow crystal suitable for X-ray analysis. The ORTEP of **12** is shown in Fig. 2, and selected bond lengths and angles are given in Table 2. While compound **7** was nearly C_2 symmetrical, compound **12** was not. One center carbon of allyl moieties pointed to the inside, and another pointed to the outside of the molecule. The distances from the palladium to the plane including pyridazine were also different (0.56 and − 0.70 Å). Both of these distances were shorter than those of **7**, and the torsion angle 38.0(8)° for Pd(1)–N(2)–N(3)–Pd(2) was also smaller than that of **7**. In connection with the short distances, twists of the oxazolines between the pyridazine are quite small; 5(1)° for N(1)–C(12)–C(13)–N(2) and 6(1)° for N(3)–C(16)–C(17)–N(4). The different angle of the lone pair of oxazoline nitrogen from that of pyridine may make it possible for the simultaneous coordination of two palladiums to **3** without the forced twists of the rings.



3. Conclusion

The reactions of tetradentate nitrogen ligands **2** and **3** with $[(\eta^3\text{-}C_3H_5)PdCl]_2$–$AgPF_6$ gave dinuclear complexes **7** and **12**, respectively, which have two metal centers in close proximity without additional bridging ligands, while the reaction of **1** afforded only mononuclear complex **4**. This combined analysis of the π-allylpalladium complexes containing several pyridazine-based tetradentate ligands reveals that the degree of twists between the rings and the size of the heterocycles influence the ability to hold two metals proximally.

4. Experimental

4.1. General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk techniques under nitrogen. Tetradentate ligands dppn (**1**) [14] and 6-dppn (**2**) [15] were prepared according to the literature procedures. NMR spectra were recorded with either a Bruker DPX-400 spectrometer operating at 100 (^{13}C) MHz, 400 (^{1}H) MHz, or Bruker DRX-500 spectrometer operating at 125 (^{13}C) MHz, 500 (^{1}H) MHz, at 27°C unless otherwise indicated.

4.2. Synthesis of 3,6-bis[(4S)-4,5-dihydro-4-isopropyloxazol-2-yl]pyridazine (3)

Fahrni and Pfaltz synthesized 3,6-bis[(4*S*)-4,5-dihydro-4-benzyloxazol-2-yl]pyridazine from pyridazine-3,6-dicarboxylic acid [13]. Since we could not prepare the acid even if according to the literature [16], we synthesized **3** from **8** [16].

To a stirred suspension of **8** (2.82 g, 14.4 mmol) and L-valinol (3.26 g, 31.6 mmol) in THF (20 ml) at −50°C was added *n*-butyllithium (4.5 ml of 1.6 M, 7.2 mmol). The mixture was allowed to warm to 0°C and maintained at this temperature for 6 h. The reaction mixture was hydrolyzed with a saturated, aqueous ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product (**9**) was used in the following reaction without purification. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.03 (d, $J = 6.8$ Hz, 6H), 1.06 (d, $J = 6.8$ Hz), 2.09 (m, 2H), 2.59 (br s, 2H), 3.84–3.88 (m, 4H), 4.05 (m, 2H), 8.32 (br s, 2H), 8.48 (s, 2H). ^{13}C-NMR (100 MHz, CD_3CN) δ 18.7, 19.6, 29.2, 57.7, 63.6, 127.4, 153.6, 162.3.

To a stirred solution of the above product **9** in CH_2Cl_2 (30 ml) at 0°C was added thionyl chloride (4.0 ml, 56 mmol). The mixture was allowed to warm to room temperature (r.t.) and maintained at this temperature for 19 h. The reaction mixture was hydrolyzed with a saturated, aqueous $NaHCO_3$ solution. Extraction with CH_2Cl_2, drying over anhydrous $MgSO_4$, and condensation under reduced pressure gave the crude product (**10**), which was used in the following reaction without purification.

To a stirred solution of the product **10** in CH_2Cl_2 (30 ml) was added *t*-BuOK (4.85 g, 43.2 mmol). After 0.5 h, brine was added, and the reaction mixture was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography and recrystallization from ethyl acetate to afford **3** (1.93 g, 6.38 mmol, 44% from **8**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.97 (d, $J = 6.7$ Hz, 6H), 1.06 (d, $J = 6.7$ Hz, 6H), 1.91 (m, 2H), 4.20 (m, 2H), 4.31 (t, $J = 8.6$ Hz, 2H), 4.61 (dd, $J = 8.6$, 9.7 Hz, 2H), 8.28 (s, 2H). ^{13}C-NMR (100 MHz, CD_3CN) δ 18.3, 18.9, 32.8, 71.4, 73.0, 127.0, 151.0, 161.0. IR (KBr) 1650, 1469, 1107 cm^{-1}. Anal. Calc. for $C_{16}H_{22}N_4O_2$: C, 63.55; H, 7.33; N, 18.52. Found: C, 63.58; H, 7.36; N, 18.33%.

4.3. Preparation of 4

To a solution of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (55 mg, 0.15 mmol) and **1** (70 mg, 0.30 mmol) in CH_3CN (5 ml) was added dropwise under nitrogen a solution of $AgPF_6$ (76 mg, 0.30 mmol) in CH_3CN (10 ml). The resulting suspension was stirred at r.t. for 24 h and then filtered. Addition of ether to the filtrate led to the precipitation of a colorless powder, which was separated by filtration, washed with ether, and dried in vacuo to give **4** (117 mg, 74% yield). ^{1}H-NMR (500 MHz, CD_3CN) δ 3.63 (d, $J = 13$ Hz, 2H), 4.42 (d, $J = 6.7$ Hz, 2H), 6.10 (m, 1H), 7.55 (m, 1H), 7.78 (m, 1H), 7.98 (m, 1H), 8.31 (m, 1H), 8.41 (d, $J = 8.0$ Hz, 1H), 8.51 (d, $J = 7.9$ Hz, 1H), 8.66 (d, $J = 9.1$ Hz, 1H), 8.76 (d, $J = 3.8$ Hz, 1H), 8.88 (d, $J = 4.9$ Hz, 1H), 8.97 (d, $J = 9.1$ Hz, 1H). ^{13}C-NMR (125 MHz, CD_3CN) δ 122.0, 123.0, 125.5, 127.4, 129.1, 129.9, 130.0, 138.9, 142.3, 151.2, 151.9, 153.1, 155.8, 159.5, 161.4. IR (KBr) 3102, 1604, 1455, 1435, 1419, 968, 836, 780, 560 cm^{-1}. Anal. Calc. for $C_{17}H_{15}N_4F_6PPd$: C, 38.77; H, 2.87; N, 10.64. Found: C, 39.37; H, 3.29; N, 10.40%.

4.4. Preparation of 6

Complex **6** was synthesized by a method similar to that for **4** in 88% yield, using CH_3CN as solvent. ^{1}H-NMR (400 MHz, CD_3CN) δ 1.86 (m, 4H), 3.14 (br s, 4H), 3.56 (d, $J = 13$ Hz, 2H), 4.24 (d, $J = 7$ Hz, 2H), 6.01 (m, 1H), 7.65 (br s, 2H), 8.14 (br s, 4H), 8.85 (br s, 2H). IR (KBr) 3090, 2954, 1601, 1473, 1385, 1169, 1013, 834, 752, 558 cm^{-1}. Anal. Calc. for

$C_{21}H_{21}N_4F_6PPd$: C, 43.43; H, 3.64; N, 9.65. Found: C, 43.68; H, 3.79; N, 9.88%.

^{1}H-NMR in acetone-d_6 at 27 and −30°C, at 400 MHz. 27°C; δ 1.93 (m, 4H), 3.29 (br s, 4H), 3.68 (d, $J = 13$ Hz, 2H), 4.38 (d, $J = 7$ Hz, 2H), 6.14 (tt, $J = 13$, 7 Hz, 1H), 7.5–9.5 (broad peaks, 8 H). −30°C; δ 1.91 (br s, 2H), 3.20 (br s, 2H), 3.40 (br s, 2H), 3.68 (br s, 2H), 4.39 (br s, 2H), 6.19 (m, 1H), 7.68 (m, 1H), 8.00 (m, 1H), 8.04 (m, 1H), 8.16 (m, 1H), 8.54 (m, 1H), 8.73 (m, 1H), 8.84 (m, 1H), 9.25 (m, 1H).

4.5. Preparation of **7**

Complex **7** was synthesized by a method similar to that for **4** in 90% yield, using CH_3CN as solvent. ^{1}H-NMR (400 MHz, CD_3CN) δ 2.85 (s, 4H), 3.43 (br s, 4H), 3.64 (d, $J = 12$ Hz, 4H), 4.57 (d, $J = 6.6$ Hz, 4H), 6.18 (m, 2H), 7.94 (br s, 2H), 8.48 (m, 2H), 8.64 (br s, 2H), 9.12 (br s, 2H). ^{13}C-NMR (125 MHz, CD_3CN) δ 21.3, 28.8, 64.4, 120.3, 127.8, 128.4, 140.7, 143.5, 153.9, 154.1, 159.9. IR (KBr) 3059, 2938, 1598, 1585, 1571, 1474, 1383, 1230, 1058, 839, 794, 557 cm^{-1}. Anal. Calc. for $C_{24}H_{26}F_{12}N_4P_2Pd_2$: C, 33.01; H, 3.00; N, 6.42. Found: C, 32.96; H, 3.09; N, 6.25%.

Table 3
Crystal and refinement data for **7** and **12**

	7	**12**
Formula	$2(C_{24}H_{26}N_4Pd_2P_2F_{12})\cdot 2(CH_3)_2CO$	$C_{22}H_{34}N_4O_2P_2F_{12}Pd_2\cdot CH_2Cl_2$
Formula weight	1862.61	972.18
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)
a (Å)	18.767(3)	9.780(5)
b (Å)	16.062(3)	42.159(4)
c (Å)	22.940(2)	8.425(6)
β (°)	93.382(9)	
Z	4	4
V (Å^3)	6902(1)	3473(2)
D_{calc} (g cm^{-3})	1.792	1.863
Radiation	Mo–K_α	Mo–K_α
Crystal size (mm^3)	$0.30\times0.10\times0.30$	$0.20\times0.20\times0.20$
Absorption coefficient (cm^{-1})	12.29	13.76
Scan mode	ω–2θ	ω
Temperature (°C)	22	–150
2θ max (°)	50.0	65.0
Data collected	13031	6510
Number of observations	7075	4347
Number of variables	865	493
R [$I>3\sigma(I)$]	0.049	0.044
R_w [$I>3\sigma(I)$]	0.049	0.044
Goodness-of-fit on F^2	1.76	1.85

4.6. Preparation of **11**

Complex **11** was synthesized by a method similar to that for **4**, using CH_2Cl_2 as solvent (quantitive yield). ^{1}H-NMR (500 MHz, CD_3CN) δ 0.95 (d $J = 6.8$ Hz, 6H), 1.03 (d, $J = 6.9$ Hz, 6H), 2.08 (m, 2H), 3.3–3.5 (m, 2H), 4.3–4.5 (m, 4H), 4.62 (br s, 2H), 4.80 (br s, 2H), 5.86 (m, 1H), 8.49 (br s, 2H). IR (KBr) 3090, 2964, 1648, 1584, 1482, 1374, 1297, 1261, 1159, 1119, 950, 839, 558 cm^{-1}. Anal. Calc. for $C_{19}H_{27}F_6N_4O_2PPd$: C, 38.37; H, 4.58; N, 9.42. Found: C, 39.27; H, 4.28; N, 9.52%.

4.7. Preparation of **12**

Complex **12** was synthesized by a method similar to that for **4**, using CH_2Cl_2 as solvent (quantitive yield). ^{1}H-NMR (500 MHz, CD_3CN) δ 0.95 (d, $J = 6.8$ Hz, 6H), 1.05 (d, $J = 6.9$ Hz, 6H), 2.23 (m, 2H), 3.30 (m, 4H), 4.37 (d, $J = 6.7$ Hz, 4H), 4.47 (m, 2H), 4.70 (t, $J = 8.4$ Hz, 2H), 4.85 (t, $J = 9.7$ Hz, 2H), 5.81 (m, 2H), 8.50 (s, 2H). ^{13}C-NMR (500 MHz, CD_3CN) δ 16.1, 18.6, 31.9, 55.1, 63.6, 72.3, 73.3, 118.8, 131.9, 152.2. IR (KBr) 3090, 2967, 1647, 1586, 1483, 1376, 1297, 1177, 1105, 837, 557 cm^{-1}. Anal. Calc. for $C_{22}H_{32}F_{12}N_4O_2P_2Pd_2$: C, 29.78; H, 3.64; N, 6.31. Found: C, 29.74; H, 3.73; N, 6.16%.

4.8. Crystal structure determination of **7**

Recrystallization of **7** by vapor diffusion of diethyl ether into a solution of acetone afforded a slightly yellow crystal. A Rigaku AFC-7R diffractometer with graphite monochromated Mo–K_α radiation ($\lambda =$ 0.71069 Å) was used for data collection. The collected data were solved by direct methods (SIR-88), and refined by a full-matrix least-square procedure using TEXSAN programs. The reflections with $|F_o| > 3\sigma|F_o|$ were used in the refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and were not refined. Relevant and data statistics are summarized in Table 3.

4.9. Crystal structure determination of **12**

Recrystallization of **12** by vapor diffusion of diethyl ether into a solution of dichloromethane afforded a yellow crystal. A Rigaku AFC-5R diffractometer with graphite monochromated Mo–K_α radiation ($\lambda =$ 0.71069 Å) was used for data collection. The collected data were solved by direct methods (SIR-92), and refined by a full-matrix least-square procedure using TEXSAN programs. The reflections with $|F_o| > 3\sigma|F_o|$ were used in the refinements. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Hydrogen atoms were placed in calculated positions and were not refined. Relevant and data statistics are summarized in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 154109 for **7** and 154110 for **12**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) E. K. van den Beuken, B. L. Feringa, Tetrahedron 54 (1998) 12985. (b) H. Steinhagen, G. Helmchen, Angew. Chem. Int. Ed. Engl. 35 (1996) 2339. (c) R.M. Bullock, C.P. Casey, Acc. Chem. Res. 20 (1987) 167.

[2] (a) J. Reedijk, E. Bouwman (Eds.), Bioinorganic Catalysis, Marcel Dekker, New York, 1999. (b) B. Meunier (Ed.), Biomimetic Oxidations Catalyzed by Transition Metal Complexes, Imperial College Press, London, 2000.

[3] Examples for the synthesis of dinuclear complexes designed for catalysis. (a) D.A. Wrobleski, T.B. Rauchfuss, J. Am. Chem. Soc. 104 (1982) 2314. (b) B.A. Boyce, A. Carroy, J.-M. Lehn, D. Parker, J. Chem. Soc. (1984) 1546. (c) T.G. Schenck, J.M. Downes, C.R.C. Milne, P.B. Mackenzie, H. Boucher, J. Whelan, B. Bosnich, Inorg. Chem. 24 (1985) 2334. (d) G.M. Gray, N. Takada, M. Jan, H. Zhang, J.L. Atwood, J. Organomet. Chem. 381 (1990) 53. (e) A. Kless, R. Kadyrov, A. Börner, J. Holz, H.B. Kagan, Tetrahedron Lett. 36 (1995) 4601. (f) A.L. Airey, G.F. Swiegers, A.C. Willis, S.B. Wild, J. Chem. Soc. Chem. Commun. (1995) 693. (g) D.G. McCollum, G.P.A. Yap, A.L. Rheingold, B. Bosnich, J. Am. Chem. Soc. 118 (1996) 1365. (h) A.G.J. Ligtenbarg, E.K. van den Beuken, A. Meetsma, N. Veldman, W.J.J. Smeets, A.L. Spek, B.L. Feringa, J. Chem. Soc. Dalton Trans. (1998) 263. (i) M. Gómez, S. Jansat, G. Muller, D. Panyella, P.W.N.M. van Leeuwen, P.C.J. Kamer, K. Goubitz, J. Fraanje, Organometallics 18 (1999) 4970.

[4] (a) C.J. McKenzie, R. Robson, J. Chem. Soc. Chem. Commun. (1988) 112. (b) P. Kalck, D.C. Park, F. Serein, A. Thorez, J. Mol. Cat. 36 (1986) 349. (c) J. Jenck, P. Kalck, E. Pinelli, M. Siani, A. Thorez, J. Chem. Soc. Chem. Commun. (1988) 1428. (d) P. Kalck, Polyhedron 7 (1988) 2441. (e) H. Matsuzaka, Y. Takagi, Y. Ishii, M. Nishio, M. Hidai, Organometallics 14 (1995) 2153. (f) J.-P. Qu, D. Masui, Y. Ishii, M. Hidai, Chem. Lett. (1998) 1003. (g) M. Shibasaki, H. Sasai, Adv. Asymmetric Synth. 3 (1998) 191. (h) M. Shibasaki, H, Sasai, Transition Met. Org. Synth. 1 (1998) 313. (i) K. Yamakoshi, S.J. Harwood, M. Kanai, M. Shibasaki, Tetrahedron Lett. 40 (1999) 2565. (j) E.M. Vogl, S. Matsunaga, M. Kanai, T. Iida, M. Shibasaki, Tetrahedron Lett. 39 (1998) 7917. (k) R. Konsler, J. Karl, E.N. Jacobsen, J. Am. Chem. Soc. 120 (1998) 10780. (l) R. Breinbauer, E.N. Jacobsen, Angew. Chem. Int. Ed. Engl. 39 (2000) 3604.

[5] F. Arena, C. Floriani, A. Chiesi-Villa, C. Guastini, Inorg. Chem. 25 (1986) 4589.

[6] R. Guilard, S. Brandés, C. Tardieux, A. Tabard, M. L'Her, C. Miry, P. Gouerec, Y. Knop, J.P. Collman, J. Am. Chem. Soc. 117 (1995) 11721.

[7] (a) M.E. Broussard, B. Juma, S.G. Train, W.-J. Peng, S.A. Laneman, G.G. Stanley, Science 260 (1993) 1784. (b) G.G. Stanley, in: R.D. Adams, F.A. Cotton (Eds.), Catalysis by Di- and Polynuclear Metal Cluster Complexes, Wiley–VCH, New York, 1998, p. 345. (c) G.G. Stanley, in: M.G. Scaros, M.L. Prunier (Eds.), Catalysis of Organic Reactions, Marcel Dekker, New York, 1995, p. 363. (d) S.A. Laneman, F.R. Fronczek, G.G. Stanley, J. Am. Chem. Soc. 110 (1988) 5585.

[8] (a) M. Quirmbach, A. Kless, J. Holz, V. Tararov, A. Börner, Tetrahedron: Asymmetry 10 (1999) 1803. (b) C.J. Fahrni, Tetrahedron 54 (1998) 5465. (c) A.M. Joshi, K.S. MacFarlane, B.R. James, J. Organomet. Chem. 488 (1995) 161. (d) P. Braunstein, X. Morise, Organometallics 17 (1998) 540. (e) R. Choukroun, A. Iraqi, C. Rifai, D. Gervais, J. Organomet. Chem. 353 (1988) 45. (f) A.M. Trzeciak, J.J. Ziólkowski, R. Choukroun, J. Mol. Cat. A 110 (1996) 135.

[9] (a) P. W. Ball, A. B. Blake, J. Chem. Soc. A (1969) 1415. (b) M. Ghedini, G. De Munno, G. Denti, A. M. Manotti-Lanfredi, A. Tiripicchio, Inorg. Chim. Acta. 57 (1982) 87. (c) A. Tiripicchio, A. M. Manotti Lanfredi, M. Ghedini, F. Neve, J. Chem. Soc. Chem. Commun. (1983) 97. (d) M. Ghedini, F. Neve, J. Chem. Soc. Dalton Trans. (1984) 1417. (e) M. Ghedini, F. Neve, F. Morazzoni, C. Oliva, Polyhedron 4 (1985) 497. (f) A. M. Manotti Lanfredi, A. Tiripicchio, F. Ugozzoli, M. Ghedini, F. Neve, J. Chem. Soc. Dalton Trans. (1988) 651. (g) P. Dapporto, G. De Munno, A. Sega, C. Mealli, Inorg. Chim. Acta. 83 (1984) 171. (h) N. Rahmouni, A. A. Bahsoun, M.-T. Youinou, J. A. Osborn, J. Fischer, A. Ezzamarty, Polyhedron 17 (1998) 3083.

[10] (a) M.A. Atfah, J. Heterocyclic Chem. 26 (1989) 717. (b) M.A. Atfah, A.H. Tuhl, T.S. Akasheh, Polyhedron 10 (1991) 1485.

[11] (a) A. Albinati, R.W. Kunz, C.J. Ammann, P.S. Pregosin, Organometallics 10 (1991) 1800 and refs. therein. (b) S. Ramdeehul, L. Barloy, J.A. Osborn, A. De Cian, J. Fischer, Organometallics 15 (1996) 5442.

[12] (a) A. Gogoll, J. Örnebro, H. Grennberg, J.-E. Bäckvall, J. Am. Chem. Soc. 116 (1994) 3631. (b) A. Albinati, H. Rüegger, Organometallics 9 (1990) 1826. (c) S. Hansson, P.-O. Norrby, M.P.T. Sjögren, B. Åkermark, M.E. Cucciolito, F. Giordano, A. Vitagliano, Organometallics 12 (1993) 4940. (d) J.W. Faller, M.J. Incorvia, M.E. Thomsen, J. Am. Chem. Soc. 91 (1969) 518. (e) D.L. Tibbetts, T.L. Brown, J. Am. Chem. Soc. 92 (1970) 3034.

[13] (a) C.J. Fahrni, A. Pfaltz, Helv. Chim. Acta 81 (1998) 491. (b) C.J. Fahrni, A. Pfaltz, M. Neuburger, M. Zehnder, Helv. Chim. Acta 81 (1998) 507.

[14] W.A. Butte, F.H. Case, J. Org. Chem. 26 (1961) 4690.

[15] M.A. Atfah, J. Heterocycl. Chem. 26 (1989) 717.

[16] S. Sueur, M. Lagrenee, F. Abraham, C. Bremard, J. Heterocycl. Chem. 24 (1987) 1285.