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# Self-assembly of Schiff-base palladacycle-based discrete pseudo-macrocycles: Evidence for hemilability of oxalate ligand

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Bis-bidentate tetra-coordinated oxalato bridged binuclear Schiff-base palladacycles $[\mathrm{Pd}\{C,N\text{-}\kappa^2\text{-}(4\text{-R})\mathrm{C_6H_3CH{=}NC_6H_3}\text{-}2,6\text{-}i\text{-}\mathrm{Pr_2}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}\mathrm{C_2O_4})$ (R = H; OMe) were synthesized. Reactions of $\mu$-oxalato bridged Schiff-base palladacycles $[\mathrm{Pd}\{C,N\text{-}\kappa^2\text{-}(4\text{-R})\mathrm{C_6H_3CH{=}NC_6H_3}\text{-}2,6\text{-}i\text{-}\mathrm{Pr_2}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}\mathrm{C_2O_4})$ (R = H; OMe) with 1,4-bis(diphenylphosphino)butane (dppb) and 1,4-bis(diphenylphosphino)pentane (dppp) generated discrete pseudo-macrocycles with 1,1′-bicoordinated oxalato bridge. Unexpectedly, $\mu$-oxalato bridged Schiff-base palladacycle $[\mathrm{Pd}(C,N\text{-}\kappa^2\text{-}\mathrm{C_6H_4CH{=}NC_6H_3}\text{-}2,6\text{-}i\text{-}\mathrm{Pr_2})]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}\mathrm{C_2O_4})$ reacted with $\mathrm{PPh_3}$ to form unusual bidentate/monodentate tri-coordinated oxalato bridged binuclear cyclopalladated complex $[\mathrm{Pd}(C,N\text{-}\kappa^2\text{-}\mathrm{C_6H_4CH{=}NC_6H_3}\text{-}2,6\text{-}i\text{-}\mathrm{Pr_2})(\mathrm{PPh_3})](\mu\text{-}\eta^2\text{-}\eta^1\text{-}\mathrm{C_2O_4})[\mathrm{Pd}(C\text{-}\kappa^1\text{-}\mathrm{C_6H_4CH{=}NC_6H_3}\text{-}2,6\text{-}i\text{-}\mathrm{Pr_2})(\mathrm{PPh_3})]$.

## Introduction

The formation of discrete supramolecular structure via coordination-driven self-assembly has become an active area of research and an important component of supramolecular chemistry and nanoscience [1–6]. As a subset of discrete supramolecular complexes, the assemblies of organometallic supramolecule have attracted more and more interest because of their potential application as promising molecular materials [7–16]. Most of the discrete metallosupramolecular ensembles are built from metal palladium or platinum species with *cis*-coordinated diamines or diphosphines as supporting ligands that are linked by classical Werner-type polydentate ligands, such as pyrazine, 4,4′-bipyridine, or 2,4,6-tris(4-pyridyl)-1,3,5-triazine [17–26]. A few phosphorous and oxygen donor linkers are preferred in directed self-assembly of metallamacrocycles [18,27–29]. Cyclometallated Pd(II) or Pt(II) complexes with *C*,*N*-donor ligands as corner species have rarely been used for the construction of metallosupramolecular assemblies [30–33]. Moreover, Mirkin and co-workers reported the synthesis of 2D and 3D supramolecular assemblies using hemilabile ligands and transition metals [34,35]. Hence, if cyclometallated Pd(II) fragments with blocked *C*,*N*-donor ligands ($[\mathrm{Pd}\{C,N\text{-}\kappa^2\text{-}(4\text{-R})\mathrm{C_6H_3CH{=}NC_6H_3}\text{-}2,6\text{-}i\text{-}\mathrm{Pr_2}\}]^+$) were bridged by appropriate hemilabile linkers, it seems feasible for the assembly of metallamacrocycles via cleavage of the weaker metal-ligand bonds. Furthermore, it is well known that coordinated oxalato group shows various possible coordination modes (Chart 1) [36–42]. The oxalato group as bis-bidentate bridging ligands (Chart 1, b) are more frequently exhibited [43–48]. In Pd and Pt systems, bridging bis-bidentate, terminal bidentate and bridging bis-monodentate bonding modes have been observed for the oxalato group [49–58]. To our best knowledge, the Pd or Pt compounds structurally characterized in which the oxalato group acts as bidentate/monodentate bridging ligand (Chart 1, d) have not been reported. Herein, we describe the synthesis and structure of bis-bidentate tetra-coordinated oxalato bridged binuclear Schiff-base palladacycles $[\mathrm{Pd}\{C,N\text{-}\kappa^2\text{-}(4\text{-R})\mathrm{C_6H_3CH{=}NC_6H_3}\text{-}2,6\text{-}i\text{-}\mathrm{Pr_2}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}\mathrm{C_2O_4})$ and self-assembly of discrete pseudo-macrocycles with 1,1′-bicoordinated oxalato bridge based on tetra-coordinated oxalato bridged binuclear Schiff-base palladacycles. Also we report an unexpected binuclear Schiff-base palladacycle containing unusual bidentate/monodentate tri-coordinated oxalato bridge.

## Results and discussion

### *Synthesis of bis-bidentate tetra-coordinated oxalato bridged Schiff-base palladacycles*

Recently, we investigated the reactivity of $\mu$-chloro, $\mu$-azido and $\mu$-thiocyanato bridged Schiff-base palladacycles with aromatic *N*-

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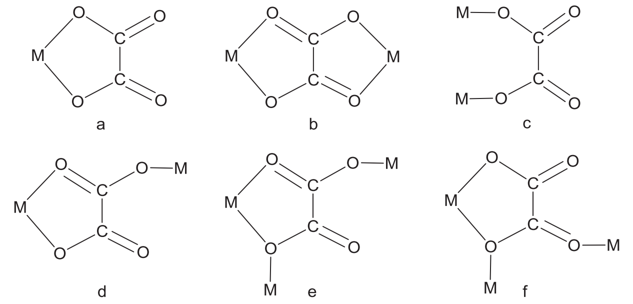
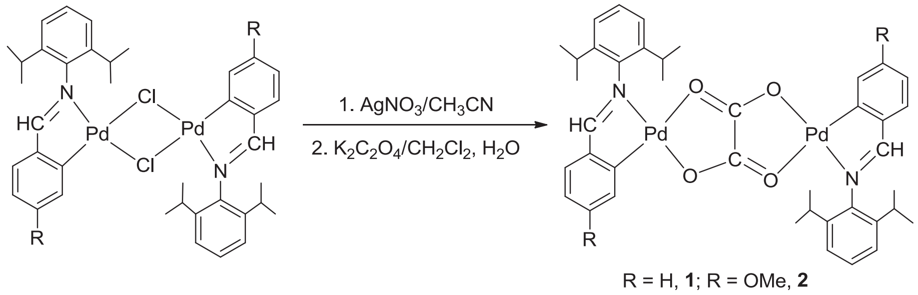


**Chart 1.** Several possible coordination modes of oxalato group.

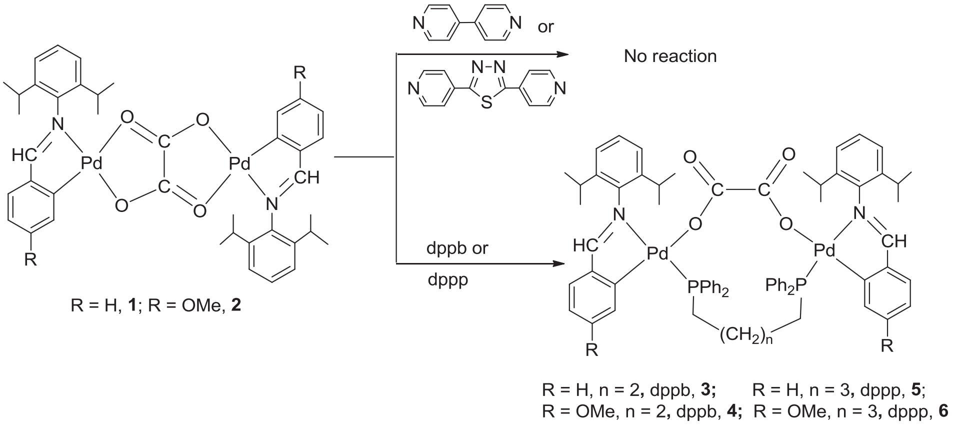
heterocycles or phosphines. A series of mono-, bi- and tri-nuclear Schiff-base palladacycles were obtained [59,60]. On the basis of these results, we considered to synthesize hemilabile chelate ligand bridged Schiff-base palladacycles. We expected that the formation of discrete macrocycles by selectively attacking the weaker metal-ligand bonds of hemilabile chelate ligand bridged Schiff-base palladacycles with molecules that have stronger affinity for metal center. Since oxalato group with various coordination modes perhaps can act as hemilabile chelate ligand. We decided to synthesize $\mu$-oxalato bridged Schiff-base palladacycles. Cyclopalladated chloro dimer [Pd{$C,N$-$\kappa^2$-(4-R) $C_6H_3CH{=}N{-}C_6H_3$-2,6-$i$-$Pr_2$}($\mu$-Cl)]$_2$ (R = H; OMe) were treated by $AgNO_3$ in $CH_3CN$, subsequently reacted with an aqueous solution of $K_2C_2O_4$ in $CH_2Cl_2$ at room temperature to produce pale yellow $\mu$-oxalato bridged Schiff-base palladacycles [Pd{$C,N$-$\kappa^2$-(4-R) $C_6H_3CH{=}N{-}C_6H_3$-2,6-$i$-$Pr_2$}]$_2$($\mu$-$\eta^2$-$\eta^2$-$C_2O_4$) (R = H, **1**; OMe, **2**) (Scheme 1). The identities of **1** and **2** were determined by FT-IR, $^1$H NMR spectroscopy, elemental analysis and single crystal X-ray diffraction. The FT-IR spectra of **1** and **2** showed a strong absorption at approximately 1622 $cm^{-1}$ and 1623 $cm^{-1}$, respectively, due to the C=O stretching of bis-bidentate oxalato bridge [56,57]. The $^1$H NMR spectra of **1** and **2** displayed the resonance for $CH{=}N$ protons at $\delta$ 7.75 and $\delta$ 7.61, respectively, which was not shifted in comparison to that of corresponding cyclopalladated chloro dimmer.

### *Self-assembly of discrete pseudo-macrocycles with 1,1′-bicoordinated oxalato bridge*

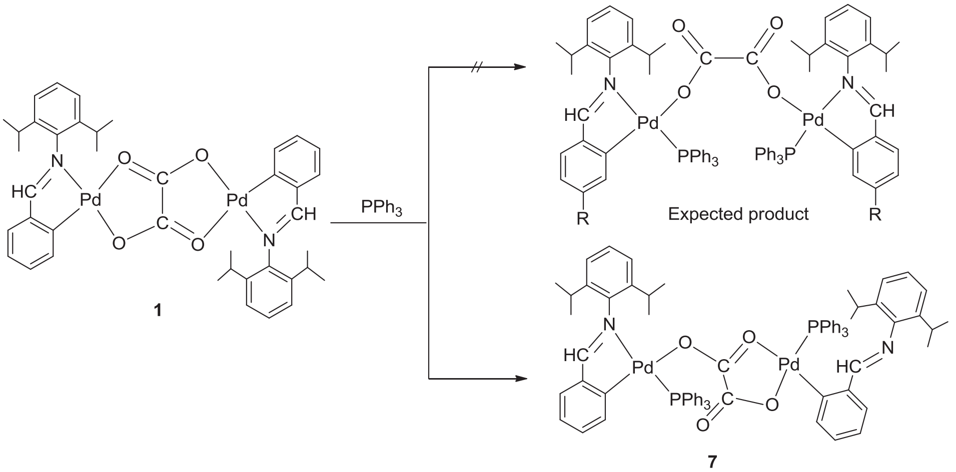
Based on the above results, we primarily attempted the reactions of $\mu$-oxalato bridged Schiff-base palladacycles with rigid bipyridyl ligands. Unexpectedly, when complex **1** and **2** was treated by 4,4′-bipyridyl (bpy) or 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (bpt), respectively, no any novel metallacycles were isolated. This result reveals that the chelation of oxalato group with Pd is enough strong not to be cleaved by bipyridyl ligand. Subsequently, we examined the reactions of complexes **1** and **2** with flexible bis-monodentate phosphines, such as 1,4-bis(diphenylphosphino)butane (dppb) and 1,4-bis(diphenylphosphino)pentane (dppp) (Scheme 2), expecting the formation of novel macrocycles based on cleavage of Pd–O in $\mu$-oxalato bridged Schiff-base palladacycles. Recently, we reported the cleavage reactions of $\mu$-azido and $\mu$-thiocyanato bridged Schiff-base palladacycles with tertiary and bis-monodentate phosphines [60]. In contrast, the cleavage reactions of $\mu$-oxalato bridged Schiff-base palladacycles are unknown. Treatment of complex **1** and **2** with stoichiometric amount of dppb or dppp in $CH_2Cl_2$ at room temperature, respectively, produced binuclear Schiff-base palladacycles concomitant with bridging bis-monodentate oxalato ligand and bridging bis-monodentate phosphine ligand [Pd{$C,N$-$\kappa^2$-(4-R)$C_6H_3CH{=}NC_6H_3$-2,6-$i$-$Pr_2$]$_2$($\mu$-$\eta^1$-$\eta^1$-$C_2O_4$)($\mu$-dppb) (R = H, **3**; OMe, **4**) and [Pd{$C,N$-$\kappa^2$-(4-MeO) $C_6H_3CH{=}NC_6H_3$-2,6-$i$-$Pr_2$]$_2$($\mu$-$\eta^1$-$\eta^1$-$C_2O_4$)($\mu$-dppp) (R = H, **5**; OMe, **6**). The results indicate that phosphines are a kind of better donors for soft acceptors Pd(II) due to their softer base compared with nitrogen and oxygen donors. And thus phosphine ligands have enough strong affinity for palladium to cleave one of the Pd–O bonds in chelate oxalate group. Complexes **3**–**6** were characterized



**Scheme 1.** Synthesis of $\mu$-oxalato bridged Schiff-base palladacycles **1** and **2**.



**Scheme 2.** Synthesis of macrocycles **3**–**6**.



**Scheme 3.** Synthesis of bidentate/monodentate oxalato bridged binuclear cyclopalladated complex **7**.

by spectroscopic and elemental analysis. Molecular structure of **3**, **5** and **6** was determined by X-ray diffraction, respectively. The FT-IR spectra of **3**–**6** showed characteristic strong bands of the oxalato ligand at 1612 $cm^{-1}$ ($\nu_{as}$COO) and 1263 $cm^{-1}$ ($\nu_{s}$COO), 1608 ($\nu_{as}$COO) and 1269 $cm^{-1}$ ($\nu_{s}$COO), 1613 ($\nu_{as}$COO) and 1260 $cm^{-1}$ ($\nu_{s}$COO), 1607 ($\nu_{as}$COO) and 1265 $cm^{-1}$ ($\nu_{s}$COO), respectively. The large difference of 349 $cm^{-1}$, 339 $cm^{-1}$, 353 $cm^{-1}$ and 342 $cm^{-1}$ between the two bands indicates that the carboxylate group of oxalato ligand is coordinated to the metal in monodentate fashion [58,62,63]. The $^{1}H$ NMR spectra of **3**–**6** displayed the resonance for *CH*=N protons at $\delta$ 7.94, $\delta$ 7.80–7.86, $\delta$ 8.00 and $\delta$ 7.88, respectively, which was shifted to downfield compared to that ($\delta$ 7.75 and $\delta$ 7.61) of corresponding bis-bidentate oxalato-bridged cyclopalladated complexes **1** and **2**. Other protons of complexes **3**–**6** have been identified by the chemical shift in the rest of their spectrum. Molecular structure of **3**, **5** and **6** unambiguously confirmed the formation of binuclear Pd pseudo-macrocycles.

### *Synthesis of bidentate/monodentate tri-coordinated oxalato bridged Schiff-base palladacycle*

For the sake of further confirming the hemilability of bis-bidentate bridging oxalate ligand, we examined the reaction of $\mu$-oxalato bridged Schiff-base palladacycle **1** with $PPh_3$, expecting the formation of bis-monodentate oxalato bridged binuclear cyclometallated Pd complex. Unexpectedly, one Pd–O bond and one Pd–N bond was cleaved respectively to give unusual bidentate/monodentate tri-coordinated oxalato bridged Schiff-base palladacycle $[Pd(C,N\text{-}\kappa^2\text{-}C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(PPh_3)](\mu\text{-}\eta^2\text{-}\eta^1\text{-}C_2O_4)[Pd(C\text{-}\kappa^1\text{-}C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(PPh_3)]$ (**7**) (Scheme 3). Complex **7**

**Table 1**
X-ray data collection and structure refinement for **1**, 2, **3**, **5**, **6**, **7**.

| | **1** | **2**·0.5$Et_2O$ | **3**·$CH_2Cl_2$ | **5** | **6**·$CH_2Cl_2$·$H_2O$ | **7**·2$CH_2Cl_2$·0.5$H_2O$ |
|---|---|---|---|---|---|---|
| Formula | $C_{40}H_{44}N_2O_4Pd_2$ | $C_{44}H_{53}N_2O_{6.50}Pd_2$ | $C_{69}H_{74}Cl_2N_2O_4P_2Pd_2$ | $C_{69}H_{74}N_2O_4P_2Pd_2$ | $C_{72}H_{80}Cl_2N_2O_7P_2Pd_2$ | $C_{156}H_{156}Cl_8N_4O_9P_4$ $Pd_4$ |
| Formula weight | 829.57 | 926.68 | 1340.94 | 1270.04 | 1431.02 | 3063.93 |
| Temperature (k) | 296(2) | 296(2) | 113(2) | 296(2) | 296(2) | 296(2) |
| Crystal size | 0.30 × 0.27 × 0.22 | 0.33 × 0.27 × 0.21 | 0.24 × 0.18 × 0.10 | 0.20 × 0.18 × 0.12 | 0.20 × 0.20 × 0.20 | 0.20 × 0.20 × 0.16 |
| Crystal system | Hexagonal | Monoclinic | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | *R*-3 | $P2_1/n$ | $P2_1/c$ | *P*1 | $P2_1/n$ | $P2_1/n$ |
| *a*, Å | 28.8606(14) | 15.5551(18) | 14.380(2) | 14.2167(5) | 13.7661(19) | 14.704(4) |
| *b*,Å | 28.8606(14) | 11.8754(14) | 23.024(4) | 22.9641(7) | 13.1768(18) | 21.254(6) |
| *c*,Å | 12.5204(12) | 26.403(3) | 20.817(3) | 21.6201(8) | 42.330(6) | 25.118(8) |
| $\alpha$, deg | 90.00 | 90 | 90 | 90 | 90 | 90 |
| $\beta$, deg | 90.00 | 101.860(2) | 105.036(2) | 103.391(2) | 101.205(8) | 105.432(7) |
| $\gamma$, deg | 120.00 | 90 | 90 | 90 | 90 | 90 |
| *V*, $Å^3$ | 9031.5(11) | 4773.2(10) | 6655.9(19) | 6866.5(4) | 7532.0(18) | 7567(4) |
| *Z* | 9 | 4 | 4 | 4 | 4 | 2 |
| $d_{cal}$, g $cm^{-3}$ | 1.373 | 1.290 | 1.338 | 1.229 | 1.262 | 1.345 |
| $\mu$, $mm^{-1}$ | 0.934 | 0.797 | 0.715 | 0.615 | 0.639 | 0.707 |
| *F*(000) | 3798 | 1900 | 2760 | 2624 | 2952 | 3144 |
| $T_{min}$ | 0.775 | 0.783 | 0.8470 | 0.8870 | 0.8828 | 0.8714 |
| $T_{max}$ | 0.827 | 0.858 | 0.9319 | 0.9299 | 0.8828 | 0.8952 |
| No. of reflns measured | 10,708 | 30,095 | 85,104 | 44,578 | 46,193 | 56,587 |
| No. of reflns unique | 3591 | 10,827 | 15,842 | 12,049 | 13,071 | 13,321 |
| No. of params refined | 221 | 569 | 798 | 720 | 795 | 856 |
| Max., in $\Delta\rho$ (e $Å^{-3}$) | 1.254 | 0.531 | 1.413 | 1.827 | 1.328 | 1.298 |
| Min., in $\Delta\rho$ (e $Å^{-3}$) | −0.480 | −0.344 | −2.142 | −2.017 | −2.116 | −1.009 |
| GOF on $F^2$ | 1.149 | 1.036 | 1.063 | 1.051 | 1.138 | 1.105 |
| *R* ($I > 2\sigma(I)$) | 0.0401 | 0.0460 | 0.0453 | 0.1292 | 0.1213 | 0.0607 |
| $wR_2$[a] ($I > 2\sigma(I)$) | 0.1344 | 0.0951 | 0.1212 | 0.3097 | 0.2850 | 0.1389 |
| *R* (all data) | 0.0564 | 0.0977 | 0.0494 | 0.1929 | 0.1351 | 0.0806 |
| $wR_2$[a] (all data) | 0.1664 | 0.1132 | 0.1243 | 0.3430 | 0.2915 | 0.1534 |

[a] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

was characterized by FT-IR, ${}^1$H NMR spectroscopy, elemental analysis and single crystal X-ray diffraction. To our best knowledge, complex **7** represents the first structurally characterized palladium complex containing bidentate/monodentate tri-coordinated oxalato bridge. The FT-IR spectra of **7** showed two strong absorptions at approximately 1649 cm$^{-1}$ and 1612 cm$^{-1}$, respectively, due to the C=O stretching of bidentate/monodentate oxalato bridge. The ${}^1$H NMR spectra of **7** displayed the resonance for C*H*=N protons at $\delta$ 8.36, which was distinctly shifted to downfield compared to that ($\delta$ 7.75) of corresponding cyclopalladated complex **1**. Molecular structure of **7** further confirmed the formation of unusual bidentate/monodentate oxalato bridged binuclear cyclopalladated complex **7**.

## *Structures of compounds*

The structures of **1**–**3** and **5**–**7** were unambiguously determined by X-ray diffraction. Single crystals of **1**–**3** and **5**–**7** suitable for X-ray diffraction analysis were obtained from a dichloromethane/hexane solution while single crystals of **2** from a slowly evaporated ether solution. Details on crystal data, intensity collection, and refinement details are given in Table 1. In all structures, the coordination of the Pd metal is essentially square-planar.

As shown in Fig. 1, the molecular of complex **1** has a dinuclear structure bridged by oxalato group. Oxalato ligand links two $[Pd\{C,N\text{-}\kappa^2\text{-}(4\text{-}R)C_6H_3CH{=}N{-}C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}]$ moieties in bis-bidentate mode to give a binuclear compound, and the distance of Pd1···Pd1A is 5.4046(7) Å. Two cyclometallated ligands are in a *trans* arrangement with respect to the Pd···Pd axis. Two five-membered chelate rings that contain the imine functionality are nearly coplanar with oxalato chelate ring as shown by the maximum deviation of 0.123 Å, to which the diisopropylphenyl ring is almost perpendicular with a dihedral angle 85.8(1)°. The Pd1–C15 bond [1.947(5) Å] and Pd1–N1 [2.015(4) Å] are marginally shorter than those ([1.971(4) Å] and [2.036(3) Å]) of corresponding cyclopalladated chloro dimmer [57]. Two Pd–O bonds are regarded to be non-equivalent. Pd1–O2A [2.146(4) Å] bond located on the *trans*-position of Pd1–C15 bond is significantly longer than Pd1–O1 bond [2.063(3) Å] located on the *trans*-position of Pd1–N1 bond. It can be ascribed to different *trans* influence of carbon and nitrogen. The data of these bond lengths indicate that oxalato group can be used as hemilabile linkers. It is feasible for assembling of metalla-macrocycles via cleavage of weaker Pd–O bonds. Fig. 2 reveals that the molecular structure of **2** is similar to **1**. Depending on the solvent, molecules of **2** adopt quite different stacking mode, as represented in Fig. 3.

Complexes **3** (Fig. 4), **5** (Fig. 5) and **6** (Fig. 6) have similar binuclear structure. In complex **3**, oxalato ligand in bis-monodentate mode and dppb respectively link two Pd centers to form anomalous 12-membered macrocycle. The distance of Pd1···Pd2 (6.8979(9) Å) is longer than that of complex **1** due to the cleavage of two weaker Pd–O bonds in **1**. Two five-membered chelate rings that contain the imine functionality are twisted with a dihedral angle 84.8° due to the formation of macrocycle. Likewise, in complexes **5** and **6**, oxalato ligand in bis-monodentate mode and dppp respectively link two Pd centers to form anomalous 13-membered macrocycle, in which the distance of Pd1···Pd2 is 7.0292(13) Å and 6.8826(15) Å, respectively. Fig. 7 shows clearly the 13-membered macrocycles of complexes **5** and **6**.

Fig. 8 reveals that one $PPh_3$ cleaves one Pd–O bond and another $PPh_3$ cleaves one Pd–N bond to produce novel binuclear cyclopalladated complex **7**. Oxalato ligand bridges two palladium metals through bidentate/monodentate tri-coordinated mode. It indicates that bis-bidentate bridging oxalato ligand possesses different hemilability depending on attacking ligands. The distance of Pd1···Pd2 is 5.826(1) Å, which is slightly longer than that of complex **1** due to the cleavage of one Pd–O bond. The five-membered chelate ring that contains the imine functionality is not coplanar with oxalato chelate ring, being twisted to a dihedral angle of 61.2° due to the intervention of $PPh_3$.

In summary, bis-bidentate tetra-coordinated oxalato bridged binuclear Schiff-base palladacycles were synthesized. Discrete pseudo-macrocycles with 1,1′-bicoordinated oxalato bridge were obtained by self-assembly of tetra-coordinated oxalato bridged binuclear Schiff-base palladacycles with bis-monodentate phosphines. When tetra-coordinated oxalato bridged binuclear Schiff-base palladacycle reacted with triphenylphosphine, unusual bidentate/monodentate tri-coordinated oxalato bridged Schiff-base palladacycle was isolated. All these results offered the evidence for hemilability of oxalato ligand.

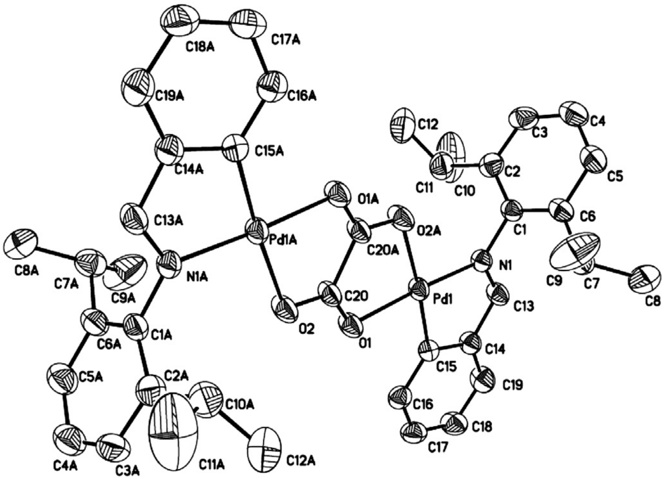


**Fig. 1.** Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Pd1–C15 1.947(5), Pd1–N1 2.015(4), Pd1–O1 2.063(3), Pd1–O2A 2.146(4); C20–O1–Pd1 113.2(3) C15–Pd1–N1 81.85(19), C15–Pd1–O1 94.90(18), N1–Pd1–O1 176.61(15), N1–Pd1–O2A 102.60(15).

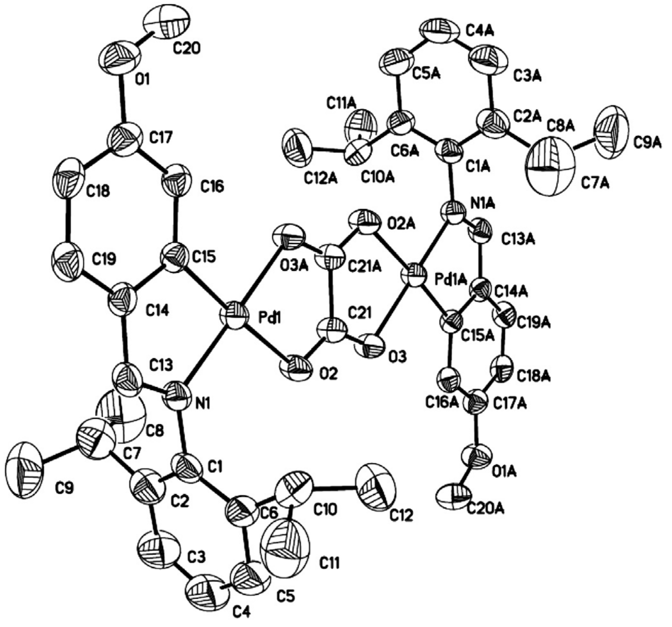


**Fig. 2.** Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Pd1–C15 1.951(4), Pd1–N1 2.000(3), Pd1–O2 2.146(3), Pd1–O3A 2.049(3); C15–Pd1–N1 80.93(15), C15–Pd1–O3A 96.70(13), N1–Pd1–O3A 176.93(12), N1–Pd1–O2 101.74(12).

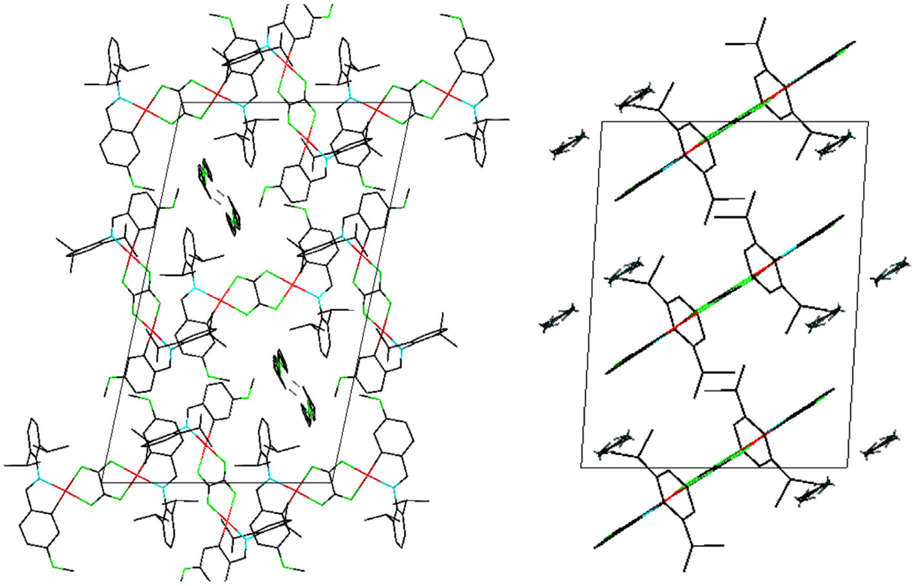

(a) (b)

**Fig. 3.** The stacking of the molecules in crystals **2** depending on different solvents. (a): $CH_3CH_2OCH_2CH_3$; (b): $CH_2Cl_2$.

## Experimental

### General, materials and measurements

All manipulations of air-sensitive compounds were performed under nitrogen by standard Schlenk techniques. All solvents were purified and degassed by standard procedures. Other regents were used as supplied. $^1H$ NMR spectra were obtained using a Mercury-300 spectrophotometer in $CDCl_3$, for all compounds using TMS as an internal standard. $^{31}P\{^1H\}$ NMR spectra were obtained using a Bruker-600 spectrophotometer in $CDCl_3$, for all compounds using 85% $H_3PO_4$ as an external standard. IR spectra were recorded on a Niclolet AVATAR 330FT-IR spectrometer. Elemental analyses were performed on a Thermo Flash EA1112 Analyzer.

$[Pd\{C,N\text{-}\kappa^2\text{-}(4\text{-}R)C_6H_3CH{=}N{-}C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}(\mu\text{-}Cl)]_2$ (R = H; OMe) were prepared according literature methods [61].

### Preparations

#### $[Pd(C,N\text{-}\kappa^2\text{-}C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C_2O_4)$ (*1*)

To a 20 mL $CH_3CN$ solution of complex $[Pd(C,N\text{-}\kappa^2\text{-}C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}Cl)]_2$ (0.196 g, 0.241 mmol) was added $AgNO_3$ (0.093 g, 0.548 mmol). After stirring for 15 h in dark at room temperature, insoluble materials were filtered off. The solvent of the

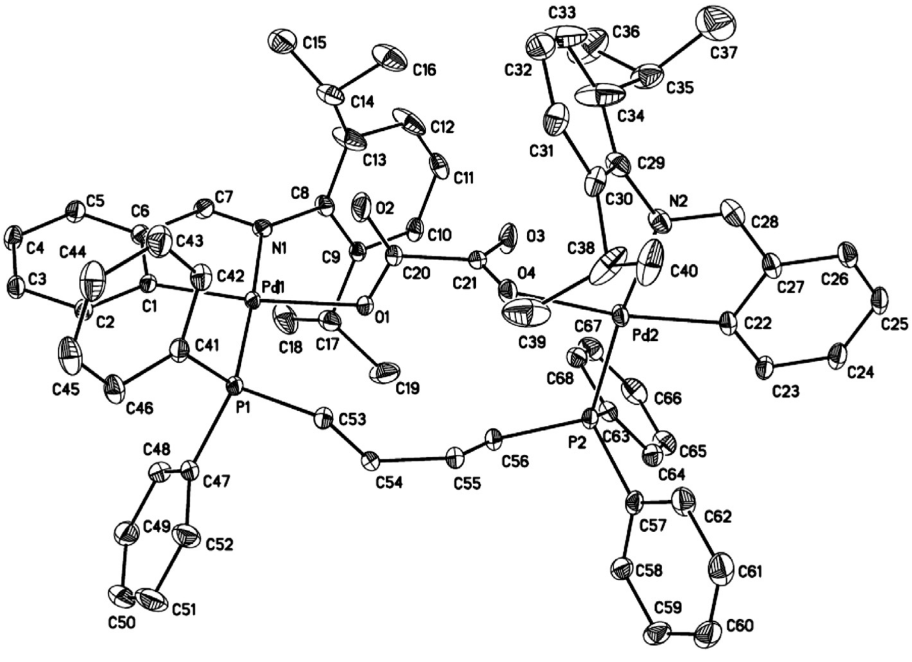


**Fig. 4.** Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Pd1–C1 2.009(3), Pd2–C22 2.006(3), Pd1–N1 2.099(2), Pd2–N2 2.117(2), Pd1–O1 2.0974(19), Pd2–O4 2.108(2), Pd1–P1 2.2459(7), Pd2–P2 2.2618(8); C1–Pd1–O1 171.92(9), C1–Pd1–N1 81.45(10), O1–Pd1–N1 90.58(9), C1–Pd1–P1 95.39(8), O1–Pd1–P1 92.62(6), N1–Pd1–P1 176.28(7), C22–Pd2–O4 172.13(10), C22–Pd2–N2 81.26(11), O4–Pd2–N2 92.08(9), C22–Pd2–P2 94.61(9), O4–Pd2–P2 92.38(6), N2–Pd2–P2 173.63(8).

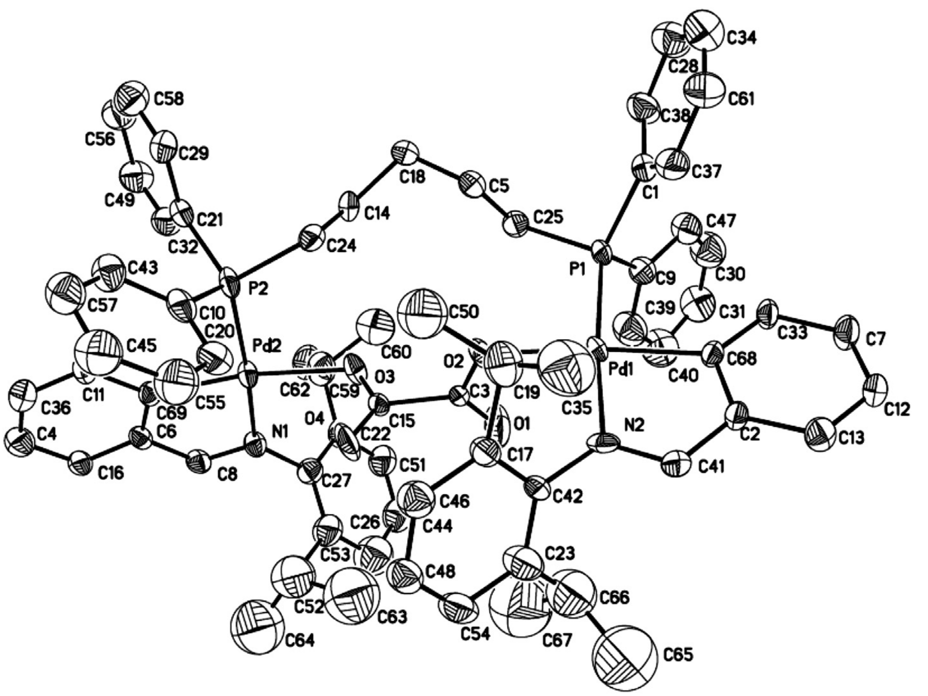


**Fig. 5.** Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Pd1–C68 2.033(12), Pd2–C69 1.989(12), Pd1–N1 2.121(11), Pd2–N4 2.102(9), Pd1–O2 2.118(9), Pd2–O3 2.134(9), Pd1–P1 2.233(3), Pd2–P2 2.249(4); C68–Pd1–O2 174.0(4), C68–Pd1–N2 81.9(5), O2–Pd1–N2 92.1(4), C68–Pd1–P1 93.1(3), O2–Pd1–P1 92.9(3), N2–Pd1–P1 172.8(3), C69–Pd2–O3 171.4(5), C69–Pd2–N1 80.3(5), O3–Pd2–N1 92.9(4), C69–Pd2–P2 95.3(4), O3–Pd2–P2 92.1(3), N1–Pd2–P2 171.7(3).

filtrate was fully removed by rotatory evaporator. The resulting pale yellow oil was dissolved in 10 mL $CH_2Cl_2$ and filtered to a Schlenk tube. Then $K_2C_2O_4 \cdot H_2O$ solution (0.052 g, 0.282 mmol) dissolved in 4 mL $H_2O$ was added to the $CH_2Cl_2$ solution. After stirring for 16 h at room temperature, the organic phase was separated and dried over anhydrous $MgSO_4$, and then the solvent was completely removed under vacuum to give crude solid. Recrystallization from $CH_2Cl_2$/hexane gave pale yellow crystals of [Pd(*C*,*N*-$\kappa^2$-$C_6H_4CH{=}NC_6H_3$-2,6-*i*-$Pr_2$)]$_2$($\mu$-$\eta^2$-$\eta^2$-$C_2O_4$) (**1**, 0.160 g, 80%). IR (KBr, $cm^{-1}$): 1597 (C=N), 1622 (C=O); m.p.: 275–276 °C; $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$): 7.75 (2H, s, –C*H*=N), 7.27–7.51 (6H, m, Ar), 7.02–7.19 (8H, m, Ar), 3.45 (hepta, 2H, –C*H*($CH_3$)$_2$), 1.24 (24H, ddd, *J* = 6.6, 6.3, 6.3 Hz, –CH(C*H*$_3$)$_2$); Anal. Calcd for $C_{40}H_{44}N_2O_4Pd_2$: C, 57.91; H, 5.37; N, 3.38. Found: C, 57.82; H, 5.37; N, 3.12.

### *[Pd{C,N-$\kappa^2$-(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-$Pr_2$}]$_2$($\mu$-$\eta^2$-$\eta^2$-$C_2O_4$) (**2**, 84%)*

Complex **2** was prepared in a similar manner as described for **1**. IR (KBr, $cm^{-1}$): 1596 (C=N), 1623 (C=O); m.p.: 287–289 °C; $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$): 7.61 (2H, d, *J* = 5.4 Hz, –C*H*=N), 7.24–7.33 (4H, m, Ar), 7.13 (4H, dd, *J* = 7.5 Hz, Ar), 6.87–6.96 (2H, m, Ar), 6.63–6.71 (2H, m, Ar), 3.90 (6H, d, *J* = 16.5 Hz, –OC*H*$_3$), 3.45 (4H, hepta, –C*H*($CH_3$)$_2$), 1.28 (12H, dd, *J* = 6.6, 6.6 Hz, –CH(C*H*$_3$)$_2$), 1.15 (12H, d, *J* = 6.9, 7.2 Hz, –CH(C*H*$_3$)$_2$); Anal. Calcd for

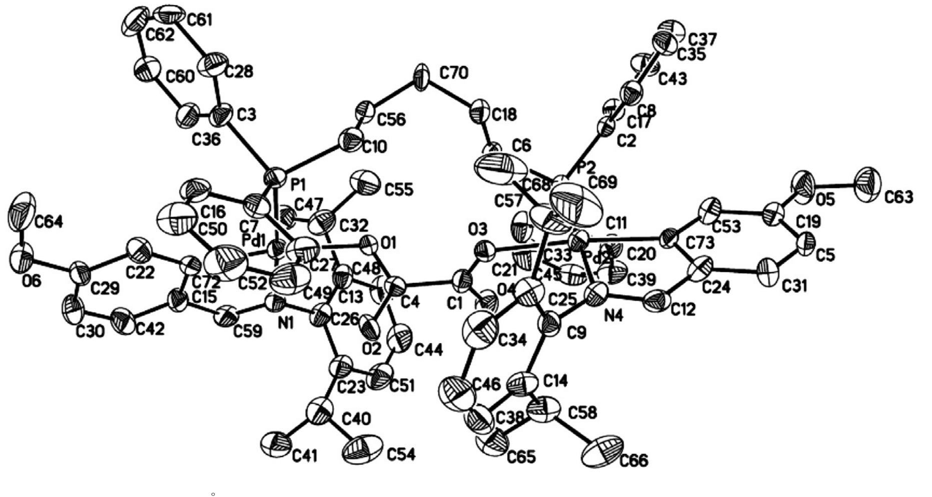
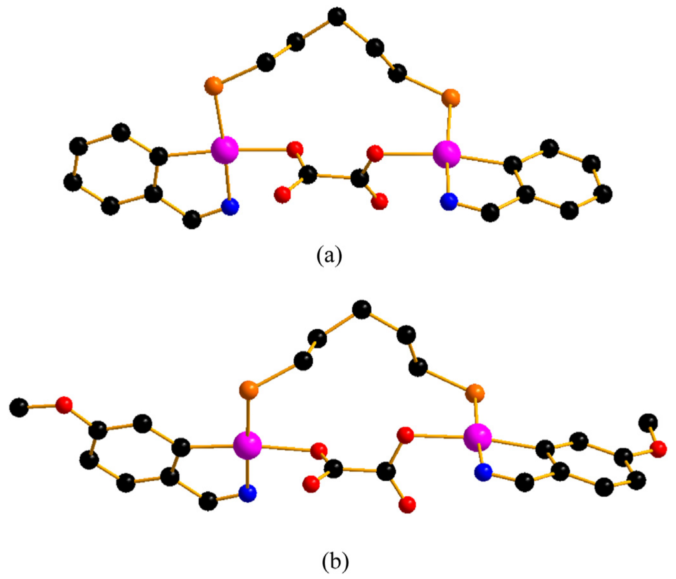


**Fig. 6.** Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Pd1–C72 1.988(12), Pd2–C73 1.973(11), Pd1–N1 2.114(9), Pd2–N4 2.102(9), Pd1–O1 2.102(7), Pd2–O3 2.083(8), Pd1–P1 2.253(3), Pd2–P2 2.265(3); C72–Pd1–O1 171.3(4), C72–Pd1–N1 81.2(5), O1–Pd1–N1 91.9(4), C72–Pd1–P1 97.2(4), O1–Pd1–P1 90.3(2), N1–Pd1–P1 173.3(3), C73–Pd2–O3 170.2(4), C73–Pd2–N4 80.4(5), O3–Pd2–N4 89.8(3), C73–Pd2–P2 100.2(4), O3–Pd2–P2 89.6(2), N4–Pd2–P2 176.3(3).



(a)

(b)

**Fig. 7.** Macrocycle views of **5** (a) and **6** (b). 2,6-Diisopropyl phenyl, phenyl of dppb and dppp, and hydrogen atoms were omitted for clarity. Palladium, nitrogen, oxygen, phosphorus and carbon are represented by purple, blue, red, orange and black spheres, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$C_{42}H_{48}N_2O_6Pd_2 \cdot 0.25CH_2Cl_2$: C, 55.71; H, 5.37; N, 3.08. Found: C, 55.40; H, 5.35; N, 2.72.

*[Pd(C,N-$\kappa^2$-$C_6H_4CH{=}NC_6H_3$-2,6-i-$Pr_2$)]$_2$($\mu$-$\eta^1$-$\eta^1$-$C_2O_4$)($\mu$-dppb) (**3**)*

To a 6 mL $CH_2Cl_2$ solution of complex **1** (0.094 g, 0.113 mmol) was added 1,4-(diphenylphosphino)butane (0.049 g, 0.115 mmol). After stirring for 14 h at room temperature, the solvent was completely evaporated and the resulting residue was isolated by ether to give pale yellow solids. Recrystallization from $CH_2Cl_2$/hexane generated pale yellow crystals of [Pd(*C*,*N*-$\kappa^2$-$C_6H_4CH{=}NC_6H_3$-2,6-*i*-$Pr_2$)]$_2$($\mu$-$\eta^1$-$\eta^1$-$C_2O_4$)($\mu$-dppb) (**3**, 0.106 g, 75%). IR (KBr, $cm^{-1}$): 1612 (C=N; C=O); m.p.: 228–230 °C; $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$): 7.94 (2H, d, *J* = 7.2 Hz, –C*H*=N), 7.78–7.84 (8H, m, –P*Ph*$_2$–), 7.27–7.43 (16H, m, –P*Ph*$_2$–, Ar), 7.15 (4H, d, *J* = 7.5 Hz, Ar), 6.88–6.93 (2H, m, Ar), 6.61–6.68 (4H, m, Ar), 3.55 (4H, hepta, –C*H*($CH_3$)$_2$), 2.14 (4H, br, P–C*H*$_2$–$CH_2$–$CH_2$–C*H*$_2$–P), 1.31 (12H, d, *J* = 6.3 Hz, –CH(C*H*$_3$)$_2$), 1.12 (12H, d, *J* = 6.6 Hz, –CH(C*H*$_3$)$_2$), 1.00 (4H, br, P–$CH_2$–C*H*$_2$–C*H*$_2$–$CH_2$–P); $\delta_P$ ($CDCl_3$): 33.4 (s); Anal. Calcd for $C_{68}H_{72}N_2O_4P_2Pd_2 \cdot 0.25CH_2Cl_2$: C, 64.18; H, 5.72; N, 2.19. Found: C, 64.29; H, 5.82; N, 1.88.

Complexes **4**–**7** were prepared in a similar manner as complex **3**.

*[Pd{C,N-$\kappa^2$-(4-MeO)$C_6H_3CH{=}NC_6H_3$-2,6-i-$Pr_2$]$_2$($\mu$-$\eta^1$-$\eta^1$-$C_2O_4$)($\mu$-dppb) (**4**, 43%)*

IR (KBr, $cm^{-1}$): 1608 (C=N; C=O); m.p.: 203–205 °C; $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$): 7.80–7.86 (10H, m, –C*H*=N, –P*Ph*$_2$–), 7.27–7.44 (14H, m, –P*Ph*$_2$–, Ar), 7.18 (2H, d, *J* = 8.4 Hz, Ar), 7.13 (4H, d, *J* = 7.5 Hz, Ar), 6.40 (2H, dd, *J* = 2.4, 2.4 Hz, Ar), 6.13 (2H, dd, *J* = 2.1, 2.1 Hz, Ar), 3.54 (4H, hepta, –C*H*($CH_3$)$_2$), 3.14 (6H, s, –OC*H*$_3$), 2.14 (4H, br, P–C*H*$_2$–$CH_2$–$CH_2$–C*H*$_2$–P), 1.27 (12H, d, *J* = 6.9 Hz, –CH(C*H*$_3$)$_2$), 1.09 (16H, d, *J* = 6.9 Hz, –CH(C*H*$_3$)$_2$, P–$CH_2$–C*H*$_2$–C*H*$_2$–$CH_2$–P); $\delta_P$ ($CDCl_3$): 33.3 (s); Anal. Calcd for $C_{70}H_{76}N_2O_6P_2Pd_2 \cdot 0.25CH_2Cl_2$: C, 63.09; H, 5.77; N, 2.09. Found: C, 62.89; H, 6.00; N, 2.46.

*[Pd(C,N-$\kappa^2$-$C_6H_4CH{=}NC_6H_3$-2,6-i-$Pr_2$)]$_2$($\mu$-$\eta^1$-$\eta^1$-$C_2O_4$)($\mu$-dppp) (**5**, 76%)*

IR (KBr, $cm^{-1}$): 1613 (C=N; C=O); m.p.: 206–208 °C; $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$): 8.00 (2H, d, *J* = 7.2 Hz, –C*H*=N), 7.69–7.75 (8H, m, –P*Ph*$_2$–), 7.35–7.47 (12H, m, –P*Ph*$_2$–), 7.27–7.32 (4H, m, Ar), 7.21 (4H, d, *J* = 7.5 Hz, Ar), 6.91–6.96 (2H, m, Ar), 6.70–6.78 (4H, m, Ar), 3.65 (4H, hepta, –C*H*($CH_3$)$_2$), 2.02 (4H, br, P–C*H*$_2$–$CH_2$–$CH_2$–$CH_2$–C*H*$_2$–P), 1.60 (4H, br, P–$CH_2$–$CH_2$–C*H*$_2$–$CH_2$–$CH_2$–P), 1.32 (12H, d, *J* = 6.9 Hz, –CH(C*H*$_3$)$_2$), 1.26 (4H, br, P–$CH_2$–C*H*$_2$–$CH_2$–C*H*$_2$–$CH_2$–P), 1.13 (12H, d, *J* = 6.9 Hz, –CH(C*H*$_3$)$_2$), 0.98 (4H, br,

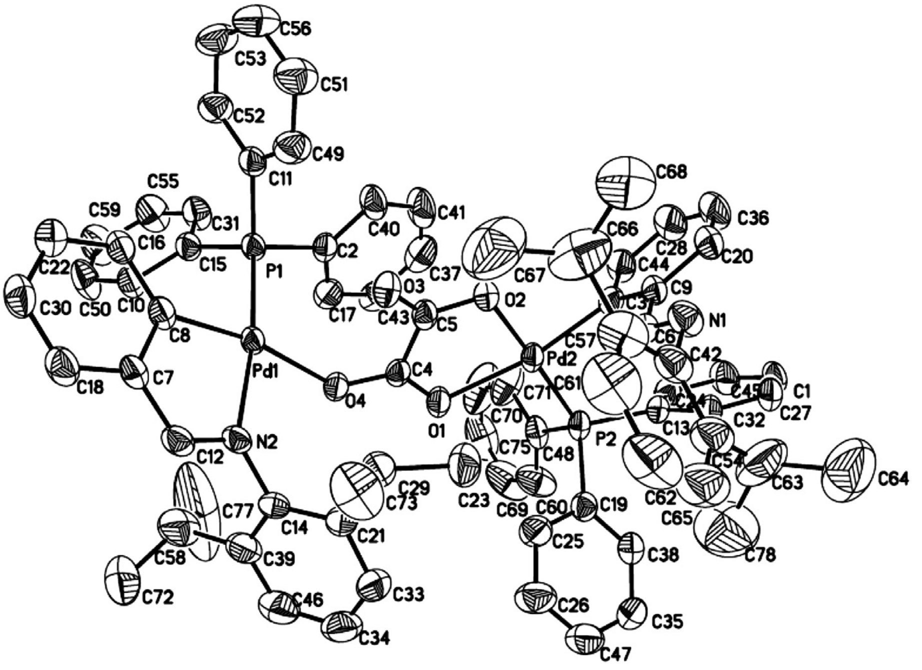


**Fig. 8.** . Molecular structure of **7**. Selected bond lengths (Å) and angles (°): Pd1–C8 1.995(6), Pd1–N2, 2.098(4), Pd1–O4, 2.135(4), Pd1–P1 2.2569(15), Pd2–C3 1.986(5), Pd2–O1 2.128(4), Pd2–O2 2.075(4), Pd2–P2 2.2244(17), C8–Pd1–N2 81.4(2), C8–Pd1–O4 168.73(19), C8–Pd1–P1 95.18(16), N2–Pd1–O4 87.63(16), C4–O4–Pd1 127.3(4), C3–Pd2–O2 91.15(19), C3–Pd2–O1 169.32(19), O1–Pd2–O2 79.49(15), O1–Pd2–P2 99.38(11), C4–O1–Pd2 111.9(3).

P—$CH_2$—$CH_2$—$CH_2$—$CH_2$—$CH_2$—P); $\delta_P$ ($CDCl_3$): 33.0 (s); Anal. Calcd for $C_{69}H_{74}N_2O_4P_2Pd_2\cdot0.25CH_2Cl_2$: C, 64.41; H, 5.81; N, 2.17. Found: C, 64.61; H, 6.18; N, 2.47.

### $[Pd\{C,N\text{-}\kappa^2\text{-}(4\text{-}MeO)C_6H_3CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2\}]_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-}C_2O_4)(\mu\text{-}dppp)$ (**6**, 45%)

IR (KBr, $cm^{-1}$): 1607 (C=N; C=O); m.p.: 229–230 °C; $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$): 7.88 (2H, d, $J = 7.2$ Hz, —$CH$=N), 7.69–7.75 (8H, m, —P$Ph_2$—), 7.37–7.48 (12H, m, —P$Ph_2$—), 7.29 (2H, d, $J = 8.1$ Hz, Ar), 7.21 (2H, d, $J = 8.4$ Hz, Ar), 7.18 (4H, d, $J = 7.2$ Hz, Ar),6.43 (2H, dd, $J = 2.4$, 2.4 Hz, Ar), 6.26 (2H, dd, $J = 2.4$, 2.4 Hz, Ar), 3.64 (4H, hepta, —$CH(CH_3)_2$), 3.27 (6H, s, —$OCH_3$), 2.03 (4H, br, P—$CH_2$—$CH_2$—$CH_2$—$CH_2$—$CH_2$—P), 1.31 (12H, d, $J = 6.6$ Hz, —$CH(CH_3)_2$), 1.27 (4H, br, P—$CH_2$—$CH_2$—$CH_2$—$CH_2$—$CH_2$—P), 1.13 (12H, d, $J = 6.9$ Hz, —$CH(CH_3)_2$), 1.02 (2H, br, P—$CH_2$—$CH_2$—$CH_2$—$CH_2$—$CH_2$—P); $\delta_P$ ($CDCl_3$): 32.9 (s); Anal. Calcd for $C_{71}H_{78}N_2O_6P_2Pd_2\cdot2CH_2Cl_2$: C, 58.45; H, 5.51; N, 1.87. Found: C, 58.63; H, 5.64; N, 2.20.

### $[Pd(C,N\text{-}\kappa^2\text{-}C_6H_4CH{=}NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(PPh_3)](\mu\text{-}\eta^2\text{-}\eta^1\text{-}C_2O_4)[Pd(C\text{-}\kappa^1\text{-}C_6H_4CH{=}N\text{—}C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(PPh_3)]$ (**7**, 78%)

IR (KBr, $cm^{-1}$): 1591 (C=N), 1612 (C=N; C=O), 1649 (C=O); m.p.: 157–159 °C; $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$): 8.36 (2H, br, —$CH$=N), 7.26–7.72 (32H, m, $PPh_3$, Ar), 6.91–7.03 (8H, m, Ar), 6.61–6.69 (4H, m, Ar), 3.05 (4H, br, —$CH(CH_3)_2$), 1.07 (24H, s, —$CH(CH_3)_2$). $\delta_P$ ($CDCl_3$): 39.8 (s), 40.3 (s); Anal. Calcd for $C_{76}H_{74}N_2O_4P_2Pd_2\cdot2CH_2Cl_2$: C, 61.47; H, 5.16; N, 1.84. Found: C, 61.35; H, 5.18; N, 2.28.

### *X-ray structure determination*

Suitable crystals for X-ray analysis of **1**–**3** and **5**–**7** were obtained by recrystallization from $CH_2Cl_2$/hexane except **2** from slowly evaporating ether solution of **2**. X-ray data of complexes **1**–**3** and **5**–**7** were collected on Bruker APEX-II area-detector diffractometer, or Rigaku Saturn 724 CCD. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All data were collected at room temperature using the ω-scan technique except **3** at −160 °C. Details of the data collection and refinement are summarized in Table 1. All calculations were carried out with the SHELX-97 programs [64]. All structures were solved by direct methods. In All non-hydrogen atoms were refined with anisotropic thermal parameters by using full-matrix least-squares methods.

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## Appendix A. Supplementary material

CCDC 957807–957812 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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