

Synthesis, crystal structures and properties of two Pd(II) and Pt(II) complexes involving 3,5-diphenylpyrazole and NO₂ donor ligands

Jishnunil Chakraborty^a, Manas K. Saha^b, Pradyot Banerjee^{a,*}

^a Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India

^b Department of Chemistry, University of Houston, Houston, TX 77054, USA

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Abstract

A pyrazolate bridged binuclear Pd(II) complex $[\text{Pd}_2(\mu\text{-dppz})_2(\text{Hida})_2] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**1**) (dppz = 3,5-diphenylpyrazolate) with monoprotonated iminodiacetate (Hida) and a mononuclear Pt(II) complex containing Hdppz and 2,6-pyridinedicarboxylate (2,6-dipic) $[\text{Pt}(\text{Hdppz})(2,6\text{-dipic})] \cdot \text{CH}_3\text{OH}$ (**2**) have been synthesized and characterized by elemental analysis, ¹H NMR, ESI-MS and single crystal X-ray diffraction studies. The molecular packing for **1** shows a 2D network while that for **2** constitutes a left-handed 1D helix. Moderate luminescence property and antimicrobial activity against *Bacillus subtilis* have been noted for both.

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The coordination chemistry of neutral pyrazole (HRpz) or anionic pyrazolate (Rpz) ligands has been enormously developed over many years [1] and thoroughly reviewed [2–5]. Recently, unprecedented compounds showing new bonding modes for the pyrazolate ligands have been reported [6–10]. In spite of this, the number of palladium and platinum complexes is rather small. Only a few examples of mononuclear complexes: $[\text{Pd}(\text{Hpz})_4]\text{Cl}_2$ [11], $[\text{Pd}(\text{dmpz})_2(\text{Hdmpz})_2]$ [12], $[\text{Pt}(\text{pz})_2(\text{Hpz})_2]$ [11,13], $[\text{Pt}(\text{Hpz})_4]\text{Cl}_2$ [13], binuclear complexes: $[\text{Pd}_2(\mu\text{-dmpz})_2(\text{dmpz})_2(\text{Hdmpz})_2]$ [14], $[\text{Pd}_2(\mu\text{-3-}t\text{Bupz})_2(3\text{-}t\text{Bupz})_2(\text{H}_3\text{-}t\text{Bupz})_2]$ [11], $[\text{Pd}_2(\mu\text{-pz})_2(\text{Hpz})_4](\text{BF}_4)_2$ [15] and trinuclear complexes: $([\text{Pd}(\mu\text{-pz})_2]_3)$ [11], $([\text{Pd}(\mu\text{-4-Mepz})_2]_3)$ [11], $([\text{Pt}(\mu\text{-pz})_2]_3)$ [11,16] containing only pyrazoles (HRpz) and/or pyrazolates (Rpz) as ligands have been reported till now. We have reported recently an unsymmetrical binuclear palladium(II) complex $[(\text{Hdmpz})_2\text{Pd}_2(\mu\text{-dmpz})_2(2,6\text{-dipicolinate})]$ [17], where the terminal Hdmpz ligands bonded to one Pd(II) center act as a hydrogen bond donor

and a free-carboxylate group of the 2,6-dipicolinate moiety acts as the hydrogen bond acceptor. The hydrogen bonds of the type N–H–O form a 1D zigzag network. With an aim to construct such hydrogen bonded low dimensional as well as higher dimensional networks, we have attempted to synthesize Pd(II) and Pt(II) complexes with another kind of substituted pyrazole, 3,5-diphenylpyrazole (Hdppz) and carboxylic acids such as iminodiacetic acid and 2,6-pyridinedicarboxylic acid. The syntheses, structural characterization, luminescence property and antimicrobial activity of a dppz bridged binuclear palladium(II) complex and a mononuclear Hdppz coordinated platinum(II) complex are reported herein.

The reaction of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with 3,5-dimethylpyrazole and monosodium salt of iminodiacetic acid in 1:1:1 molar ratio in DMF–MeOH–H₂O mixture at 50 °C afforded the formation of a binuclear pyrazolate bridged Pd(II)-iminodiacetate complex $[\text{Pd}_2(\mu\text{-dppz})_2(\text{Hida})_2] \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**1**), where the Hida binds the palladium center in a bidentate fashion leaving one free carboxylate group protonated. No external base was employed to deprotonate the Hdppz moiety. Complex **2** was obtained

* Corresponding author. Fax: +91 33 2473 2805.

E-mail address: icpb@mahendra.iacs.res.in (P. Banerjee).

by the reaction of $\text{PtCl}_2(\text{dmsO})_2$ with Hdppz and monosodium salt of 2,6-pyridinedicarboxylic acid in a 1:1:1 molar ratio in MeOH–H₂O medium at 50 °C. This compound can be formulated as $[\text{Pt}(\text{Hdppz})(2,6\text{-dipic})] \cdot \text{CH}_3\text{OH}$.

The ¹H NMR spectrum of **1** shows the signals of –CH₂ protons of the ida unit as well as the signals in the aromatic region confirming the presence of dppz moiety. Compound **2** shows signals in the aromatic region showing the presence of both 2,6-dipic and the Hdppz moieties. The patterns of the ¹H NMR spectra are consistent with the presence of the complex structure in solution [18a,18b].

Compounds **1** and **2** have been characterized by ESI-MS positive measurements in acetonitrile [18] (Figures S1 and S2 in supporting information).

The single-crystal X-ray structures for both complexes have been determined [19]. The molecular graphics and selected bond lengths and angles are depicted in Figs. 1 and 3 and more elaborately in the supporting information (Tables S1, S2 and S3).

The asymmetric unit (Fig. 1) shows that **1** is a binuclear Pd(II) complex containing two dppz and two Hida units. The coordination environments for both the palladium centers are same. The two 3,5-dmpz units bridge the metal centres in an exobidentate fashion. The Pd–Pd separation is 3.030 Å which is shorter than that observed in other pal-

ladium complexes Pd₂L₄ (L = 3-phenyl-5-(6-methyl-(2-pyridyl)) pyrazolate (3.097(2) Å) [20], [(Hdmpz)₂Pd₂(μ-dmpz)₂(2,6-dipic)] (3.397 Å) [17], [{Pd₂(μ-3,5-dmpz)(3,5-dmpz)(3,5-Hdmpz)}₂] (3.4020 Å) [14], [Pd(μ-3,5-dmpz)(η³-C₃H₄)₂] (3.343 Å) [21], [Pd₂Cl₂(μ-3,5-dmpz)₂(PMe₂Ph)₂] (3.115(1) Å) [22] and [{Pd₂(CH₂C₆H₄P(*o*-tolyl)₂-κC, P)₂(μ₃-3,5-dmpz-*N,N',C^4*)₂Ag(μ-ClO₄)₂] (3.2297(7) Å) [4] but is almost identical to 3.029(1) Å in {[(phen)Pd]₂L₂} (NO₃)₂ [23], where phen = 1,10-phenanthroline and L = dppz. Each palladium center is in an almost square-planar coordination environment. The central six-member [Pd(μ-dppz)₂Pd] core is non-planar with Pd–N_{dppz} distances between 2.009(2) and 2.036(2) Å comparable to other Pd(II) complexes with the same bridging ligand [23]. The almost similar bond lengths within the pyrazolate rings suggest substantial delocalization upon deprotonation. The N–Pd–N angles are 86.68(9°) and 86.17(9°) between the diphenylpyrazolate groups. The Pd₂N₄ six-member ring reveals a *boat* like conformation [14,15,20]; the dihedral angle formed by the best least-squares coordination planes of the metals is 63.14°. The metal atoms are situated at the vertices of the boat and the angle between the planes containing the Pd–N–N–Pd fragments is 82.49°. The mean deviation of the plane constructed by the four nitrogen atoms N1, N2, N4 and N3 is 0.025 Å. The displacement

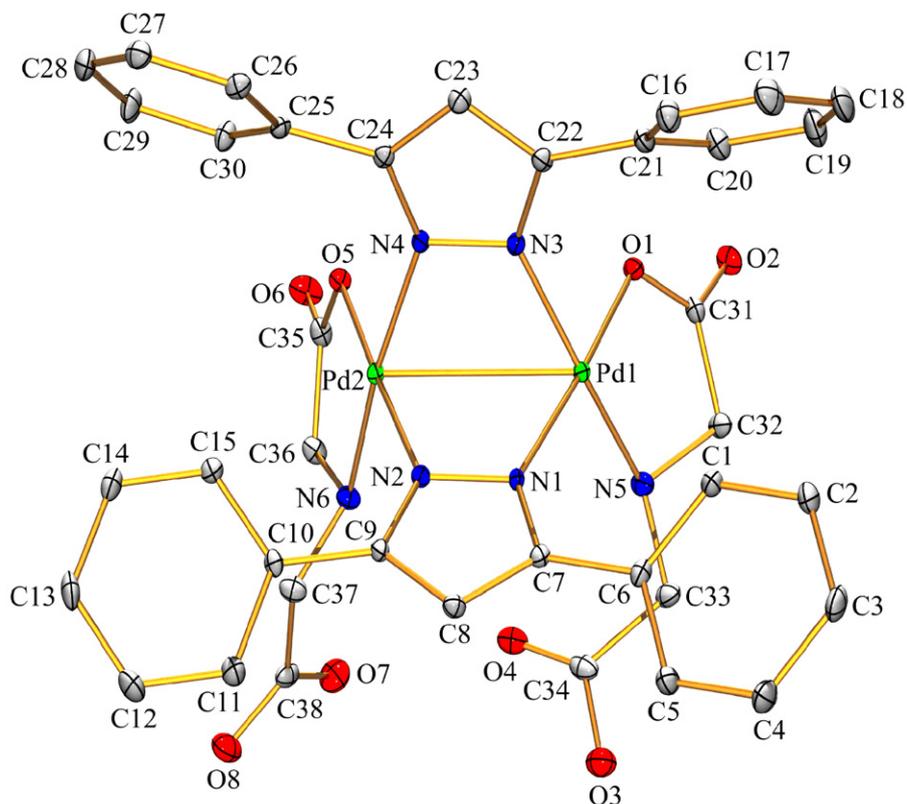


Fig. 1. ORTEP drawing of **1**. Thermal ellipsoids are at 30% probability level. All hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–Pd2, 3.030; Pd1–O1, 2.005(2); Pd2–O5, 2.006(2); Pd1–N1, 2.009(2); Pd1–N3, 2.013(2); Pd1–N5, 2.049(3); Pd2–N2, 2.013(2); Pd2–N4, 2.036(2); Pd2–N6, 2.050(3); O1–Pd1–N1, 175.66(10); O1–Pd1–N3, 91.86(9); O1–Pd1–N5, 81.59(11); N1–Pd1–N3, 86.68(9); O5–Pd2–N2, 176.77(10); O5–Pd2–N4, 94.27(9); O5–Pd2–N6, 84.35(10); N2–Pd2–N4, 86.17(9).

of Pd1 towards this plane is 1.192 Å while that for Pd2 towards the same plane is 1.230 Å. The dppz ligands are planar within experimental error. The bow angles between the planes N1–N2–N4–N3 and N1–Pd1–N3, N2–Pd2–N4 are 54.61° and 56.33°, respectively, creating an ‘open book’ disposition for the square-planar environment of the palladium centers. The dihedral angle between the dppz bridged ligands N1–C7–C8–C9–N2 and N3–C22–C23–C24–N4 is 88.21°, larger than the dihedral angle between the Pd1–N1–N2–Pd2 and Pd1–N3–N4–Pd2 planes (82.49°). The dihedral angle between the phenyl rings attached to the N1–N2–C9–C8–C7 dppz unit is 28.15° while that for the phenyl rings attached to the N3–N4–C24–C23–C22 dppz unit is 18.55°. On the other hand, the dihedral angle between the phenyl rings situated at the same side of two dppz moieties is larger and found to be 66.80° and 78.62°. These large magnitudes reflect that the restricted rotation of the phenyl rings attached to the N1–N2–C9–C8–C7 dppz unit is due to the presence of the Hida moieties. The ligand NaHida coordinates both the metal centers in a bidentate fashion (N,O) while the other carboxylate group remains free. The noncoordinated oxygen atoms O3 and O8 of the free carboxylate groups must be protonated for internal charge balance. The other carboxylate group remains nonchelating and protonated. The Pd–N bond lengths are 2.049(3) and 2.050(3) Å which are considerably smaller than that observed in *trans*-[Pd(Hida)₂] (2.061(4) Å) previously reported by us [24]. The Pd–O bond distances are 2.005(2) and 2.006(2) Å, which are close to the literature values [25]. The O1–Pd1–N5 and O5–Pd2–

N6 bond angles are 81.59(11)° and 84.35(10)°, respectively. It may be noted that in this complex the metal–nitrogen bond length is longer than that of the metal–oxygen reflecting the greater *trans* influence of N-atom compared to O-atom of the ligand.

The molecular packing of **1** (Fig. 2) shows an infinite 2D network formed by the intermolecular hydrogen bonding between the hydrogen atom of free carboxylic acid and the MeOH solvent molecule (O3–O9 = 2.590(4) Å), and between the imino group and a carboxylate moiety of the adjacent unit (N5–O2 = 3.049(4) Å). The carboxylate O2 and methanol O9 atoms provide the hydrogen bond acceptor sites for the hydrogen atoms H5A and H3A (from N5 and O3, respectively), respectively, from two neighboring formula units. A strong O1–O9 interaction is also present (2.684 Å). In addition there is an intramolecular hydrogen bonding between the imino group and the carboxylate moiety (N6–O4 = 3.058(4) Å). The shortest distance between two Pd(II) centers lying in two adjacent sheets is 7.208 Å.

The X-ray crystal structure of **2** (Fig. 3) shows that the 3,5-diphenylpyrazole moiety coordinates the platinum center in a monodentate fashion leaving the noncoordinated pyrazole nitrogen atom protonated. There is a solvent MeOH molecule outside the coordination sphere. The 2,6-dipic²⁻ unit coordinates the central platinum atom in a tridentate fashion via the ring nitrogen atom and two oxygen atoms, one from each of the two carboxylate groups producing a Pt(N₂O₂) coordination environment. The molecule is essentially planar with a mean deviation from planarity of 0.046 Å. The geometry around the Pt(II)

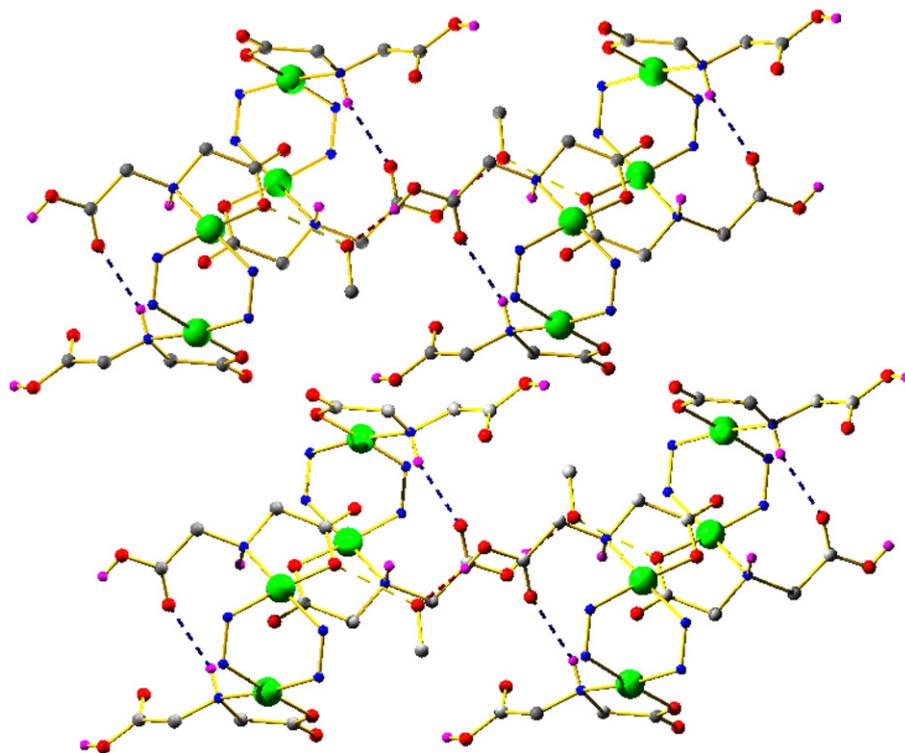


Fig. 2. A perspective view of the packing of complex **1**.

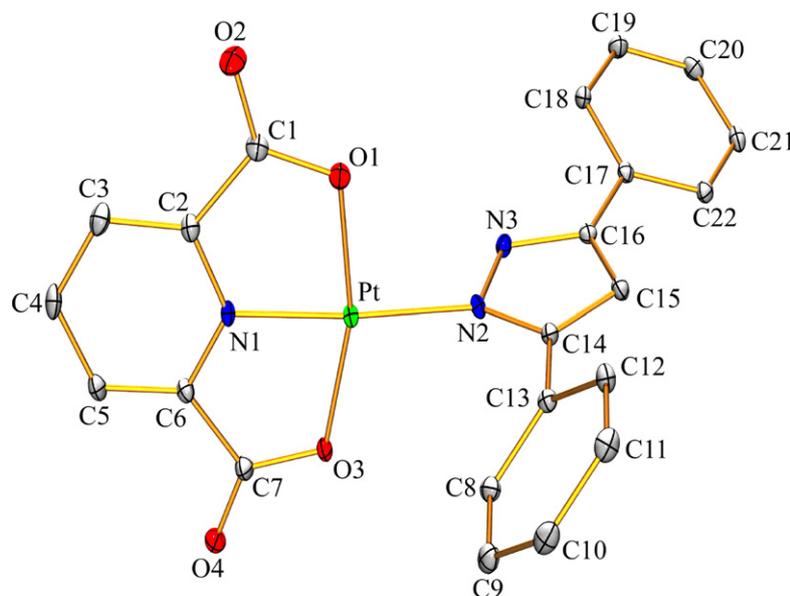


Fig. 3. ORTEP drawing of **2**. Thermal ellipsoids are at 30% probability level. All hydrogen atoms and solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pt–O1, 2.029(2); Pt–O3, 2.049(2); Pt–N1, 1.918(3); Pt–N2, 2.027(3); O1–Pt–O3, 163.33(10); O1–Pt–N1, 82.06(11); O1–Pt–N2, 95.63(11); O3–Pt–N1, 81.27(11); O3–Pt–N2, 101.01(11); N1–Pt–N2, 175.11(13).

center is very slightly distorted; the N1 and N2 atoms lie 0.046 and 0.036 Å, respectively, above the mean Pt(N₂O₂) plane, whilst O1 and O3 lie 0.025 and 0.023 Å, respectively, below it. The principal distortion in the Pt(N₂O₂) coordination geometry is non-linear in the 2,6-dipic O–Pt–O angle (O1–Pt–O3 = 163.33(10)°) which is consistent with another 2,6-dipic coordinated Pt(II) complex Pt(2,6-dipic)(H₂O) [26]; the N1–Pt–N2_{Hdppz} bond is nearly linear (175.11(13)°). The Pt–N_{2,6-dipic} bond distance is slightly shorter (1.918(3) Å) than the Pt–N_{Hdppz} distance (2.027(3) Å). The Hdppz moiety and the 2,6-dipic unit are not in the same plane. The dihedral angle between the planes containing individual units is 84.14°.

The packing feature of complex **2** shows that the individual molecules are packed together by noncovalent interactions that lead to the formation of a one-dimensional network (see Figure S3). The hydrogen atom of the Hdppz moiety is involved in hydrogen bonding interactions with the solvent MeOH molecule (N3–H3A–O5). In addition, there is an appreciable degree of interaction present between the same methanol oxygen atom and the carboxylate oxygen atom of another asymmetric unit (O5–O4 = 2.699 Å). Interestingly, complex **2** forms left-handed helical supramolecular chains involving the intermolecular hydrogen bonding (N3–O5 = 2.683(4) Å) as well as O–O interactions. The tilt angle between the planar Hdppz and a carboxylate ligand could be responsible for the formation of such helical structure. The ball and stick model extending along the crystallographic *b*-axis displays such helicates (Fig. 4) which may have resulted from metal–ligand interactions coupled with stereoelectronic characteristics of the ligands and conditions prevailing during the synthesis. An inspection of the structure of **2** leads to the belief that the metal coordi-

nated ligand molecules play key roles in the formation of the helices by acting as structure-directing agents to induce a helical array. The angles N2–N3–O5 and O5–O4–C1 in the helix are 116.72 and 107.85°, respectively. The unit cell packing shows the presence of two helices located at the center of the *b*- and *c*-axes.

The absorption spectrum of complex **1** in DMF solution is dominated by the intense band with the maximum at 254 nm in the ultraviolet region ($\epsilon = 1.32 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) which is assigned to a spin-allowed π – π^* transition. At longer wavelength in the range 350–425 nm, a shoulder is obtained which may be attributed to a metal-to-ligand charge transfer (MLCT) transition. Complex **2** in acetonitrile medium also exhibits a strong band centered at 285 nm with molar absorption coefficient of $6.17 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. In addition, the lower energy band in the range 325–400 nm is assigned to be the spin allowed MLCT transition. In the fluorescence emission spectrum of the solution of **1** in DMF ($5.0 \times 10^{-6} \text{ M}$) at room temperature on excitation at 274 nm, the emission peaks are observed at 333 and 640 nm in the visible region which are independent of the concentration of the solution. The luminescence spectrum of complex **2** in acetonitrile solution exhibits similar emission pattern with that of complex **1**. Excitation at 254 nm reveals two emission peaks centered at 338 and 644 nm. The same type of emission peaks observed in both the complexes may be assigned to the π – π^* and MLCT transitions for the shorter and longer wavelengths, respectively (see Figure S4).

The antimicrobial activities of compounds **1** and **2** were determined against *Bacillus subtilis* in a medium of nutrient. 0.1 mL of cell suspension ($5.0 \times 10^5 \text{ cfu/mL}$) from 18 h cell culture of bacteria grown on nutrient agar at 37 °C was added per 5 mL of the medium. The compounds

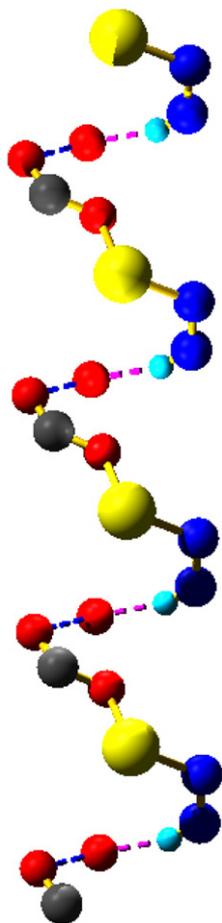


Fig. 4. A view of the 1D helical propagation in complex **2**.

were dissolved in a mixture of 1:1 DMSO and absolute ethanol. Control sets containing only $\text{PdCl}_2(\text{CH}_3\text{CN})_2$, $\text{PtCl}_2(\text{DMSO})_2$, NaHida, NaH2,6-dipic and Hdppz were also prepared. All the tubes were incubated at 37 °C for 24 h for the growth of the bacteria. The lowest concentrations of the compounds that resulted in complete inhibition of the visible growth after incubation were recorded as MIC (minimum inhibitory concentration). No activity of the constituents was detected. The MIC's of the compounds **1** and **2** against *B. subtilis* have been found to be 100 and 50 $\mu\text{g}/\text{mL}$, respectively. These are in accord with the value found for $[(\text{Hdmpz})_2\text{Pd}_2(\mu\text{-dmpz})_2(2,6\text{-dipicolinate})]$ previously reported by us [17]. Complexes **1** and **2** are coordinately saturated, and are believed to show antimicrobial activity through physical interactions in which the first step could be an adsorption reaction involving noncovalent interactions. It may be noted that both the complexes are neutral, hence no electrostatic interaction could be conceived.

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Appendix A. Supporting information

CCDC 632402 and 632403 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Full crystallographic details including pertinent bond distances and angles for compounds **1** and **2**. Tables of structural refinements and bond distances and angles are included in the supplementary information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.02.028.

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- [18] (a) Compound **1**: IR spectrum (KBr disk, v/cm^{-1}): 1722 (medium, v_{COOH}), 1612 (strong, v_{COO^-}); ^1H NMR (300 MHz, $[\text{d}_6]\text{dmso}$, 25 °C, TMS as the internal standard): δ = 8.29 (d, 4H; $\text{ph}_{\text{dppz}}\text{-H}_{1,5}$), 7.88 (d, 4H; $\text{ph}'_{\text{dppz}}\text{-H}_{1,5}$), 7.37 (t, 4H; $\text{ph}_{\text{dppz}}\text{-H}_{2,4}$), 7.21 (t, 4H; $\text{ph}'_{\text{dppz}}\text{-H}_{2,4}$), 7.67 (m, 4H; $\text{ph}_{\text{dppz}}\text{-H}_{3,3}$), $\text{ph}'_{\text{dppz}}\text{-H}_{3,3}$), 3.88, 3.89 (AB pattern, 4H; $-\text{CH}_2$ ring acetate), 2.89 (AB pattern, 4H; $-\text{CH}_2$ free acetate), 6.39 (s, 2H; Hida-NH), 12.83 (s, 2H; Hida- CO_2H); this spectral pattern reflects that same conformational rigidity exists in solution yielding unsymmetrical proton distribution of phenyl protons; elemental analysis: calc. for $\text{C}_{39}\text{H}_{42}\text{N}_6\text{O}_{11}\text{Pd}_2$, C, 47.62%; H, 4.27%; N, 8.55%; found: C, 47.90%; H, 3.44%; N, 8.56%; ESI-MS (m/z): $[\text{1} + \text{Na}]^+$ 938.3; X-ray quality crystals were grown from a DMF-MeOH- H_2O medium after 15 days;
- (b) Compound **2**: IR spectrum (KBr disk, v/cm^{-1}): 1684, 1653 (strong, v_{COO^-}); ^1H NMR (300 MHz, CD_3CN , 25 °C, TMS as the internal standard): δ = 7.77 (d, 2H; $\text{ph}_{\text{Hdppz}}\text{-H}_{1,5}$), 7.74 (d, 2H; $\text{ph}'_{\text{Hdppz}}\text{-H}_{1,5}$), 7.47 (m, 3H; $\text{ph}_{\text{Hdppz}}\text{-H}_{2,3,4}$), 7.46 (m, 3H; $\text{ph}'_{\text{Hdppz}}\text{-H}_{2,3,4}$), 7.80 (s, 1H; Hdppz- H_4), 7.07 (s, 1H; Hdppz-NH), 8.31 (dd, 3H; $\text{ph}_{2,6\text{-dipic}}\text{-H}_{1,2,3}$); elemental analysis: calc. for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_5\text{Pt}$, C,

45.09%; H, 3.10%; N, 6.86%; found: C, 45.06%; H, 2.89%; N, 6.78%; ESI-MS (m/Z): $[2 + Na]^+$ 603.4; X-ray quality crystals were grown from a MeOH–H₂O medium after six days.

- [19] *Crystal data: For complex 1:* C₃₉H₃₄N₆O₁₁Pd₂, $M_r = 975.40$, $T = 77$ K, $\lambda = 0.71073$ Å, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.3792(12)$ Å, $b = 11.8281(14)$ Å, $c = 16.637(2)$ Å, $\alpha = 96.964(6)^\circ$, $\beta = 93.036(7)^\circ$, $\gamma = 99.668(7)^\circ$, $V = 1993.0(4)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.625$ g/cm³, $F(000) = 948$, $R_1(I > 2\sigma(I)) = 0.0469$ and wR_2 (all data) = 0.098; the water molecule O11 is disordered; *for complex 2:* C₂₃H₁₅N₃O₅Pt, $M_r = 608.46$, $T = 77$ K, $\lambda = 0.71073$ Å, monoclinic, space group $P2_1/c$ (No. 14), $a = 5.9103(5)$ Å, $b = 32.029(4)$ Å, $c = 11.1916(13)$ Å, $\beta = 98.012(5)^\circ$, $V = 2097.9(4)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.926$ g/cm³, $F(000) = 1168$, $R_1(I > 2\sigma(I)) = 0.032$ and wR_2 (all data) = 0.0709.

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