



Dalton
Transactions

**Open Clamshell Dinuclear Palladium(II) Complexes
Possessing Out-of-Plane Anisotropy**

Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-COM-01-2020-000323.R1
Article Type:	Communication
Date Submitted by the Author:	14-Feb-2020
Complete List of Authors:	Yamamoto, Koji; Gunma University, Faculty of Science and Technology Higuchi, Kazuki; Tokyo Institute of Technology, Department of Chemical Science and Engineering Kuwata, Shigeki; Tokyo Institute of Technology, Department of Chemical Science and Engineering Hayashi, Yoshihiro; Tokyo Institute of Technology, Department of Chemical Science and Engineering, School of Materials and Chemical Technology Kawauchi, Susumu; Tokyo Institute of Technology, Department of Chemical Science and Engineering Takata, Toshikazu; Tokyo Institute of Technology, School of Materials and Chemical Technology, Tokyo Institute of Technology; JST, Core Research for Evolutional Science and Technology (CREST)

SCHOLARONE™
Manuscripts

Open Clamshell Dinuclear Palladium(II) Complexes Possessing Out-of-Plane Anisotropy

Received 00th January 20xx,
Accepted 00th January 20xx

Koji Yamamoto,^{†a} Kazuki Higuchi,^a Shigeki Kuwata,^b Yoshihiro Hayashi,^b Susumu Kawauchi^b and Toshikazu Takata^{*a}

DOI: 10.1039/x0xx00000x

www.rsc.org/

Double cyclometalation of planar, oligomeric phenylpyridines yielded dinuclear palladium(II) complexes with novel out-of-plane anisotropy. An X-ray crystal structure analysis revealed that the complexes exhibit concave–convex geometry, and ¹H NMR measurement evidenced the occurrence of stable out-of-plane anisotropy. The dipole moment and Pd–Pd interaction were investigated by theoretical calculations.

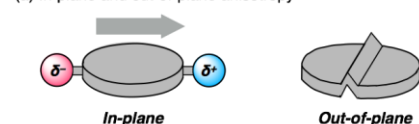
Anisotropic molecules exhibit intriguing physical properties such as nonlinear optics,¹ molecular recognition² and molecular alignment at interfaces.³ In-plane anisotropy (Figure 1a, left) in a flat molecule provides a dipole moment parallel to the molecular surface. In contrast, out-of-plane anisotropy (Figure 1a, right) shows a dipole moment perpendicular to the molecular surface, which has been used as a key building block for functional organic materials and devices.⁴ The introduction of out-of-plane anisotropy to a flat metal complex renders it with molecular recognition ability, which in turn induce unique catalytic activity and selectivity. Thus, a metal complex possessing out-of-plane anisotropy (Figure 1b) is an attractive research target. As out-of-plane anisotropic molecules, nonplanar, bowl-shaped aromatic compounds have attracted much attention in recent years.^{5,6} However, reports on bowl-shaped metal complexes are still quite limited due to the lack of synthetic routes to this type of metal complexes.^{7,8} Meanwhile, although transition metal complexes with facial arene ligands⁹ are also considered to possess out-of-plane anisotropy, to the best of our knowledge, their anisotropic properties have not been investigated.

In this study, we synthesised open clamshell dinuclear Pd(II) complexes featuring out-of-plane anisotropy (Figure 1c). Dinuclear Pd(II) complexes bearing a 2-phenylpyridine ligand are known as catalysts or intermediates of a variety of C–H

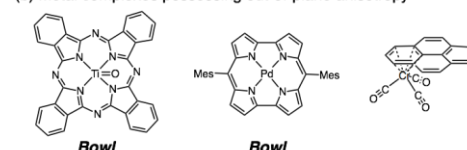
functionalisation reactions such as acetoxylation,¹⁰ hydroxylation,¹¹ arylation,¹² alkylation,¹³ nitration¹⁴ and other transformations.¹⁵ Thus, the development of a dinuclear Pd(II) complex with out-of-plane anisotropy seems to be an interesting target; however, the reported dinuclear Pd(II) complexes have been limited to planar geometry or clamshell geometry with small opening angles,¹⁶ which have no convex–concave surface. Here we found that the connection of two Pd(II) mononuclear centres with a rigid *m*-phenylene moiety affords dinuclear Pd(II) complexes possessing convex–concave surfaces, which provide them with out-of-plane anisotropy. Their geometry is stable even in solution. Theoretical calculations revealed the degree of dipole moments of the dinuclear Pd(II) complexes and the presence of a bonding interaction between the two Pd(II) atoms in each complex.

Previously, we reported cyclic and acyclic ligands **1** and **2**

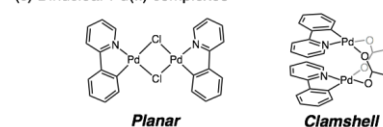
(a) In-plane and out-of-plane anisotropy



(b) Metal complexes possessing out-of-plane anisotropy



(c) Dinuclear Pd(II) complexes



This work
Dinuclear Pd(II) complexes possessing out-of-plane anisotropy

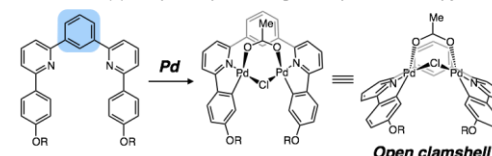


Figure 1 Illustration of in-plane and out-of-plane anisotropy (a). Structures of metal complexes possessing out-of-plane anisotropy (b) and dinuclear Pd(II) complexes (c).

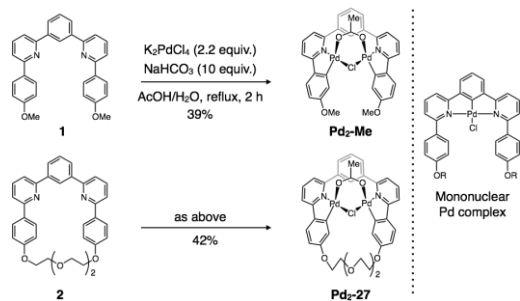
^a Department of Chemical Science and Engineering, Tokyo Institute of Technology 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503 (Japan)

^b Department of Chemical Science and Engineering, Tokyo Institute of Technology 2-12-1 (H-126), Ookayama, Meguro-ku, Tokyo 152-8552 (Japan)

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

possessing a bis(6-arylpyridin-2-yl)benzene (NCN) skeleton and their mononuclear palladium and platinum complexes.¹⁷ The mononuclear palladium complex bearing the planar, N^{^C}N pincer-type ligand **1** was synthesised in 42% yield by heating of **1**, 1.1 equivalents of potassium tetrachloropalladate(II) and 1.1 equivalent of sodium hydrogen carbonate in a mixture of acetic acid and water at reflux temperature for 2 h. During the optimisation of the synthetic conditions for the mononuclear palladium complex of **1**, we found that an increase of the loading of potassium tetrachloropalladate(II) (2.2 equivalent) and sodium hydrogen carbonate (10 equivalent) resulted in the selective formation of the doubly cyclopalladated dinuclear Pd(II) complex **Pd₂-Me** in 39% isolated yield (Scheme 1). Stereoisomers of **Pd₂-Me** were not observed in ¹H NMR of crude mixture. The isolated **Pd₂-Me** was present as a single stereoisomer even in solution, which was confirmed by ¹H NMR. To investigate the effect of the flexibility of the NCN skeleton on the generation of the dinuclear Pd(II) complex, a cyclic ligand **2** possessing a restricted conformation was reacted under the same conditions to give **Pd₂-27** as a single stereoisomer in 42% yield, which was similar to that of **1**. Both **Pd₂-Me** and **Pd₂-27** were stable to air and water, and were isolated by silica gel chromatography. ¹H and ¹³C NMR, IR, ESI-TOF-MS and elemental analysis clearly underlined the formation of a bridged system consisting of C^{^N} cyclometalated structures and a single bridging acetate ligand. The similar yields of **Pd₂-Me** and **Pd₂-27** implied that the double palladation reaction was unaffected by the flexibility of the ligand. It is worth noting that the addition of sodium

Pd centres in these complexes, summarised in Tables S1–S2, are almost the same as those in related dinuclear Pd(II) complexes, such as [Pd(C–N)(μ–Cl)]₂ (**Pd₂-(μ–Cl)**); C–N = 2-phenylpyridine-κC,N)^{16e} and [Pd(C–N)(μ–OAc)]₂ (**Pd₂-(μ–OAc)**)^{16e} (Tables S3–S4). The front views of the doubly cyclopalladated complexes (Figures 2c and S1c) show slight deviation from the typical square-planar coordination of the Pd(II) centre¹⁶ with the smaller C–Pd–OAc angles (157.7(3) and 163.0(2)° for **Pd₂-Me**; 159.3(2) and 165.1(2)° for **Pd₂-27**). This deformation can be ascribed to the distortion of the rigid polyaromatic ligand derived from the intramolecular bridge formed by the two C–N chelate moieties. The dihedral angles between the two (2-pyridyl)benzene units in **Pd₂-Me** and **Pd₂-27** are 114.8°–126.4° and 110.0°–114.2°, respectively (measured through the torsion of the A–B and D–E planes) (Figures 2b and 2d), which are smaller than that of **Pd₂-(μ–Cl)** (177.0°) but larger than that of **Pd₂-(μ–OAc)** (13.7°) (Figures S1c and S2d). The Pd–Pd distances of 2.934(2) and 2.955(2) Å for **Pd₂-Me** and 2.9420(9) and 2.9612(9) Å for **Pd₂-27** are below the sum of the van der Waals radii of two Pd atoms (3.16 Å), and marginally longer than that of **Pd₂-(μ–OAc)** (2.8621(1) Å)^{16e}. The theoretical calculations performed on **Pd₂-Me** and **Pd₂-27** indicated that the two Pd atoms of each complex interact as described below in detail.



Scheme 1 Synthesis of dinuclear complexes **Pd₂-Me** and **Pd₂-27**.

hydrogen carbonate was essential for the generation of the dinuclear Pd(II) complexes.

The molecular structures of **Pd₂-Me** and **Pd₂-27** were determined unambiguously by single-crystal X-ray diffraction analysis, which revealed that both complexes possess two separated Pd centres with an open clamshell geometry (Figure 2). Two crystallographically independent molecules were found in both **Pd₂-Me** and **Pd₂-27**. As also indicated by the NMR, IR, and ESI-TOF-MS data, the two C–N cyclometalated Pd centres are held in proximity by an intramolecular bridge consisting of one acetate and one chlorido ligands from the same side, which induces the concave–convex geometry exhibited by **Pd₂-Me** and **Pd₂-27**. In consistency with the ¹H NMR spectra, the structures of the two complexes are almost superimposable, except for the presence of a cavity in the cyclic complex **Pd₂-27**. The bond lengths and angles around the

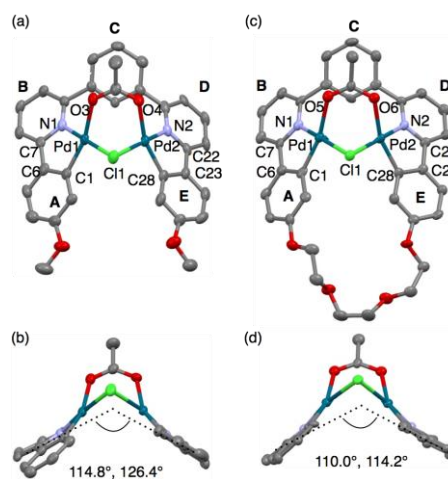


Figure 2 Crystal structures of **Pd₂-Me** (a and b) and **Pd₂-27** (c and d). A representative structure (one of two molecular structures) is shown. Hydrogen atoms and solvating molecules are omitted for clarity. The C ring and tether chains are also omitted for clarity (b and d).

The open clamshell structures of **Pd₂-Me** and **Pd₂-27** were expected to induce different electronic properties on the convex and concave surfaces. Density function theory (DFT) calculations (ω B97XD/6-311G(d,p) for C, H, N, O, Cl atoms and SDD+f for Pd atom) performed on a model compound **Pd₂**, in which the ether tethers were replaced by hydrogen atoms to estimate the degree of out-of-plane anisotropy induced by the open clamshell structure, suggested that the two curved surfaces exhibit the different electronic character, and confirmed the occurrence of out-of-plane anisotropy in **Pd₂-Me** and **Pd₂-27**. The molecular structure of **Pd₂-Me** obtained by the single-crystal X-ray analysis was used as the initial geometry for the structural optimisation of **Pd₂** (Figure S3). The calculated electrostatic potential surface (ESP) of **Pd₂**

showed negative and positive ESP values for the convex and concave surfaces, respectively (Figure 3). Thus, the molecular surface that contains the electron-rich acetate and chlorido anions (convex) exhibited a negative ESP value. Conversely, the molecular surface containing the NCN ligand (concave) exhibited a positive ESP value, in which the C–H terminals of the two pyridyl groups represented the most positive features. The observed electronic potentials resulted in a permanent out-of-plane dipole moment of 8.42 D for **Pd₂**, which is larger than that of **Pd₂-(μ-Cl)₂** (4.48 D) and **Pd₂-(μ-OAc)₂** (6.69 D) (Figures S4–S5). The dipole moments of complexes **Pd₂-Me** and **Pd₂-27** were calculated to be 8.19 D and 5.85 D, respectively (Figures S6–S7), which are smaller than that of the model compound **Pd₂** because of the direction of the electron-rich ether tethers. The model compound **Pd₂** was also compared with other molecules possessing out-of-plane anisotropy. To this aim, we calculated the dipole moments of titanium oxide phthalocyanine (TiOPc; 3.44 D), boron subphthalocyanine (SubPc; 5.01 D), subporphyrin (3.23 D), Pd-coordinated norcorrole (3.61 D) and sumanene (2.66 D) at the same level of theory (ωB97XD/6-311G(d,p) + SDD+f) (Figures S8–S12). These values agree well with the reported calculated dipole moments (B3LYP/6-31G(d)) of TiOPc, SubPc and sumanene, which are 3.73 D,⁵ⁱ 4.84 D⁵ⁱ and 1.96 D,⁵ⁱ respectively, and have revealed that the out-of-plane dipole moments of **Pd₂-Me** and **Pd₂-27** are much larger than those of the compared molecules.

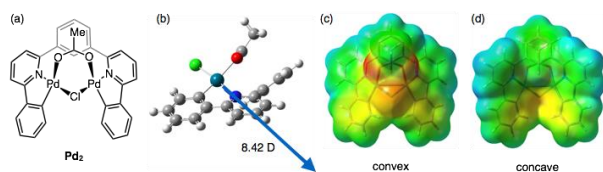


Figure 3 Molecular structure (a), dipole moment (b) and electrostatic potential surfaces (c and d) of **Pd₂** calculated at the ωB97XD/6-311G(d,p) (C, H, N, O, Cl atoms) and SDD+f (Pd atom) levels of theory (color code: red = -49.7 kcal/mol, blue = +49.7 kcal/mol).

The out-of-plane anisotropy in solution is important for molecular recognition properties. To evaluate the solution behaviour of the complexes, the ¹H NMR spectrum of **Pd₂-27** was measured in DMSO-*d*₆ (Figure 4). The two signals assigned to the nonequivalent α-protons of the triethylene glycol chain appear at 3.87–3.81 and 3.79–3.74 ppm. The difference in chemical shift reflects the different electronic environments of the convex and concave surfaces. Thus, this result clearly confirmed that the convex and concave surfaces of **Pd₂-27** are preserved in solution at ambient temperature, which suggests that the acetate and chlorido ligands that bridge tightly the Pd atoms stabilise the out-of-plane anisotropy of **Pd₂-27** even in solution.

Finally, to gain insight into the d⁸–d⁸ interaction between the two Pd atoms,^{16e,16f} we performed DFT calculations on **Pd₂-Me**, **Pd₂-27**, **Pd₂-(μ-OAc)₂** containing a d⁸–d⁸ bonding

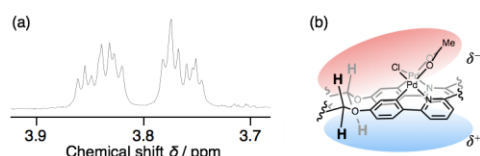


Figure 4 ¹H NMR signals for the nonequivalent α-protons of the triethylene glycol chain of **Pd₂-27** in DMSO-*d*₆ at ambient temperature.

This journal is © The Royal Society of Chemistry 20xx

interaction between the two Pd centres, and **Pd₂-(μ-Cl)₂** without any close Pd–Pd contact^{16e} (Figures S13–S16). The calculated structural parameters of **Pd₂-Me** and **Pd₂-27**, **Pd₂-(μ-Cl)₂** and **Pd₂-(μ-OAc)₂** were in good agreement with those observed for the crystal structures (Tables S1–S4 and S6–S9), suggesting the validity of our models. The calculations on **Pd₂-Me** and **Pd₂-27** showed that the HOMO consists of Pd–Pd antibonding orbitals, and spreads over the two Pd atoms and the A, B, D and E rings, while the LUMO and LUMO+1 are located on the B and D rings to a large extent and have mainly ligand character (Figures S17 and S18). The Pd–Pd σ-bonding character on **Pd₂-Me** was observed in three MOs (151, 153 and 154), which are mixed with the bridging acetate, B and D rings and A and E rings, respectively. Similarly, the Pd–Pd σ-bonding character on **Pd₂-27** was found in three MOs (174, 176 and 177). We estimated the bonding interaction between two Pd atoms by Wiberg bond index (WBI) analysis at the same level of theory. The WBI of Pd–Pd were found to be 0.12, 0.12, 0.03 and 0.13 for **Pd₂-Me**, **Pd₂-27**, **Pd₂-(μ-Cl)₂** and **Pd₂-(μ-OAc)₂**, respectively. This result indicates the presence of a weakly bonding d⁸–d⁸ interaction between the two Pd atoms in both **Pd₂-Me** and **Pd₂-27** comparable to that of **Pd₂-(μ-OAc)₂**.

Figure 5 shows the UV–vis absorption spectra of **1**, **2**, **Pd₂-Me** and **Pd₂-27** in DMSO, which exhibit intense absorption bands at 300–350 nm. In addition, complexes **Pd₂-Me** and **Pd₂-27** exhibit distinct and broad absorption bands at 360–420 nm, whereas absorptions in the visible region were not observed for **1** and **2**. The close similarity of the spectra of **Pd₂-Me** and **Pd₂-27** indicates that the cyclic topology does not affect their ground electronic state. The higher-energy bands are attributable to π–π* intraligand (IL) transitions, and the visible absorption bands of **Pd₂-Me** and **Pd₂-27** can be assigned to dσ*(Pd₂)–π*(2-phenylpyridine) metal–metal-to-ligand charge transfer (MMLCT). A similar dσ*(Pd₂)–π*(2-phenylpyridine) MMLCT transition for **Pd₂-(μ-OAc)₂** was reported to give rise to absorptions with maxima at 420 nm.^{16e} This observation supports the presence of a bonding d⁸–d⁸ interaction between the two Pd atoms in **Pd₂-Me** and **Pd₂-27**. Fluorescence was not detected from any of **Pd₂-Me** and **Pd₂-27** at ambient temperature in DMSO.^{16e, 16f}

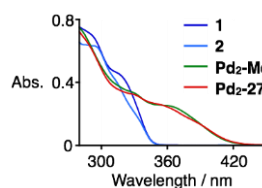


Figure 5 UV–vis spectra (0.02 mM, 1 cm, 25 °C) of **1**, **2**, **Pd₂-Me**, and **Pd₂-27** in DMSO solutions.

In conclusion, we synthesised open clamshell dinuclear Pd(II) complexes **Pd₂-Me** and **Pd₂-27** by double palladation of bis(6-arylpiperid-2-yl)benzene ligands, and elucidated their properties. Theoretical studies revealed the occurrence of considerable out-of-plane anisotropy and the presence of a bonding d⁸–d⁸ interaction between the two Pd atoms in both complexes. Further investigations regarding the unique selectivity generated by concave–convex surfaces are currently in progress in our laboratory.

Conflicts of interest

There are no conflicts to declare.

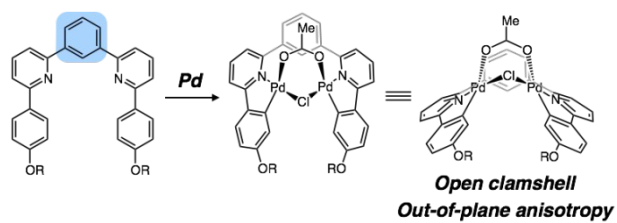
Acknowledgements

The numerical calculations were carried out on the TSUBAME 3.0 supercomputer at the Tokyo Institute of Technology, Tokyo, Japan and on the supercomputer at the Research Center for Computational Science, Okazaki, Japan. This work was supported by a Core Research for Evolutional Science and Technology (CREST) project from the Japan Science and Technology Agency (JST) grant number JPMJCR1522, a Grant-in-Aid for Specially Promoted Research (JSPS KAKENHI Grant Number JP17H06092 to S. Kawauchi) and a Grant-in-Aid for Young Scientists (B) (JSPS KAKENHI Grant Number 17K17720 to Y. H.). K. Y. acknowledges the Yoshida Foundation for Science and Technology.

Notes and references

†Present address: Division of Molecular Science, Faculty of Science and Technology, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515 (Japan)

- (a) S. R. Marder, B. Kippelen, A. K. Y. Jen and N. Peyghambarian, *Nature*, 1997, **388**, 845–851; (b) L. Beverina and G. A. Pagani, *Acc. Chem. Res.*, 2014, **47**, 319–329.
- (a) F. Biedermann and H.-J. Schneider, *Chem. Rev.*, 2016, **116**, 5216–5300; (b) F.-G. Klärner and B. Kahlert, *Acc. Chem. Res.*, 2003, **36**, 919–932; (c) C. R. Martinez and B. L. Iverson, *Chem. Sci.*, 2012, **3**, 2191–2201; (d) D. A. Dougherty, *Acc. Chem. Res.*, 2013, **46**, 885–893; (e) F. Würthner, T. E. Kaiser and C. R. Saha-Möller, *Angew. Chem. Int. Ed.*, 2011, **50**, 3376–3410.
- (a) J. V. Barth, G. Costantini and K. Kern, *Nature*, 2005, **437**, 671–679; (b) J. V. Birth, *Annu. Rev. Phys. Chem.*, 2007, **58**, 375–407.
- (a) A. Terentjev, M. P. Steele, M. L. Blumenfeld, N. Ilyas, L. L. Kelly, E. Fabiano, O. L. A. Monti and F. Della Sala, *J. Phys. Chem. C*, 2011, **115**, 21128–21138; (b) J. Gantz, D. Placencia, A. Giordano, S. R. Marder and N. R. Armstrong, *J. Phys. Chem. C*, 2013, **117**, 1205–1216; (c) S. Lacher, Y. Matsuo and E. Nakamura, *J. Am. Chem. Soc.*, 2011, **133**, 16997–17004.
- Reviews: (a) V. M. Tsefrikas and L. T. Scott, *Chem. Rev.*, 2006, **106**, 4868–4884; (b) Y.-T. Wu and J. S. Siegel, *Chem. Rev.*, 2006, **106**, 4843–4867; (c) A. Sygula, *Eur. J. Org. Chem.*, 2011, **2011**, 1611–1625; (d) S. Higashibayashi and H. Sakurai, *Chem. Lett.*, 2011, **40**, 122–128; (e) T. Amaya and T. Hirao, *Chem. Commun.*, 2011, **47**, 10524–10535; (f) M. Saito, S. Furukawa, J. Kobayashi and T. Kawashima, *Chem. Rec.*, 2016, **16**, 64–72; (g) M. Saito, H. Shinokubo and H. Sakurai, *Mater. Chem. Front.*, 2018, **2**, 635–661; selected examples: (h) T. Amaya, S. Seki, T. Moriuchi, K. Nakamoto, T. Nakata, H. Sakane, A. Saeki, S. Tagawa and T. Hirao, *J. Am. Chem. Soc.*, 2009, **131**, 408–409. (i) S. Furukawa, Y. Suda, J. Kobayashi, T. Kawashima, T. Tada; S. Fujii, M. Kiguchi and M. Saito, *J. Am. Chem. Soc.*, 2017, **139**, 5787–5792; (j) Y. Shoji, T. Kajitani, F. Ishiwari, Q. Ding, H. Sato, H. Anetai, T. Akutagawa, H. Sakurai and T. Fukushima, *Chem. Sci.*, 2017, **8**, 8405–8410.
- Review of bowl-shaped boron complexes: C. G. Claessens, D. González-Rodríguez, M. S. Rodríguez-Morgade, A. Medina and T. Torres, *Chem. Rev.*, 2014, **114**, 2192–2277.
- T. Yonezawa, S. A. Shafie, S. Hiroto and H. Shinokubo, *Angew. Chem. Int. Ed.*, 2017, **56**, 11822–11825.
- Recent examples of titanium oxide phthalocyanine: (a) S. Kera, Y. Yabuuchi, H. Yamane, H. Setoyama, K. K. Okudaira, A. Kahn and N. Ueno, *Phys. Rev. B*, 2004, **70**, 085304; (b) H. Fukagawa, H. Yamane, S. Kera, K. K. Okudaira and N. Ueno, *Phys. Rev. B*, 2006, **73**, 041302.
- For selected reviews of transition metal complexes with facial arene ligands: (a) M. Jiménez-Tenorio, M. C. Puerta and P. Valerga, *Eur. J. Inorg. Chem.*, 2004, **2004**, 17–32; (b) J. M. Gichumbi and H. B. Friedrich, *J. Organomet. Chem.*, 2018, **866**, 123–143; for selected recent examples: (c) A. Arrais, E. Diana, G. Gervasio, R. Gobetto, D. Marabello and P. L. Stanghellini, *Eur. J. Inorg. Chem.*, 2004, **2004**, 1505–1513; (d) A. Arrais, E. Diana, D. Marabello, G. Gervasio and P. L. Stanghellini, *J. Organomet. Chem.*, 2011, **696**, 2299–2305; (e) P. Hegele, G. Schnakenburg, J. Daniels and K. H. Dötz, *Eur. J. Inorg. Chem.*, 2014, **2014**, 1462–1469.
- (a) N. R. Deprez and M. S. Sanford, *J. Am. Chem. Soc.*, 2009, **131**, 11234–11241; (b) D. C. Powers, M. A. L. Geibel, J. E. M. N. Klein and T. Ritter, *J. Am. Chem. Soc.*, 2009, **131**, 17050–17051.
- (a) G. J. Chuang, W. Wang, E. Lee and T. Ritter, *J. Am. Chem. Soc.*, 2011, **133**, 1760–1762; (b) T. Yamaguchi, E. Yamaguchi, N. Tada and A. Itoh, *Adv. Synth. Catal.*, 2015, **357**, 2017–2021; (c) P. Das, D. Saha, D. Saha and J. Guin, *ACS Catal.*, 2016, **6**, 6050–6054; (d) S. S. Shah, A. Paul, M. Bera, Y. Venkatesh and N. D. P. Singh, *Org. Lett.*, 2018, **20**, 5533–5536.
- (a) J.-H. Chu, S.-L. Tsai and M.-J. Wu, *Synthesis*, 2009, **22**, 3757–3764; (b) N. R. Deprez and M. S. Sanford, *J. Am. Chem. Soc.*, 2009, **131**, 11234–11241; (c) T. W. Lyons, K. L. Hull and M. S. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 4455–4464; (d) A. J. Canty, A. Ariafard, M. S. Sanford and B. F. Yates, *Organometallics*, 2013, **32**, 544–555.
- (a) X. Chen, C. E. Goodhue and J.-Q. Yu, *J. Am. Chem. Soc.*, 2006, **128**, 12634–12635; (b) X. Wang, X. Ji, C. Shao, Y. Zhang and Y. Zhang, *Org. Biomol. Chem.*, 2017, **15**, 5616–5624.
- (a) Y.-K. Liu, S.-J. Lou, D.-Q. Xu and Z.-Y. Xu, *Chem. – Eur. J.*, 2010, **16**, 13590–13593; (b) W. Zhang, S. Lou, Y. Liu and Z. Xu, *J. Org. Chem.*, 2013, **78**, 5932–5948.
- (a) X. Jia, D. Yang, S. Zhang and J. Cheng, *Org. Lett.*, 2009, **11**, 4716–4719; (b) X. Peng, Y. Zhu, T. A. Ramirez, B. Zhao and Y. Shi, *Org. Lett.*, 2011, **13**, 5244–5247; (c) F. Zhou, D.-S. Wang, X. Guan and T. G. Driver, *Angew. Chem. Int. Ed.*, 2017, **56**, 4530–4534; (d) M. Chaitanya and P. Anbarasan, *Org. Lett.*, 2018, **20**, 3362–3366; (e) F. Li, Y. Zhou, H. Yang, Z. Wang, Q. Yu and F.-L. Zhang, *Org. Lett.*, 2019, **21**, 3692–3695.
- (a) M. A. Gutierrez, G. R. Newkome and J. Selbin, *J. Organomet. Chem.*, 1980, **202**, 341–350; (b) E. C. Constable and T. A. Leese, *J. Organomet. Chem.*, 1987, **335**, 293–299; (c) C. A. Craig and R. J. Watts, *Inorg. Chem.*, 1989, **28**, 309–313; (d) D. J. Cárdenas, A. M. Echavarren and M. C. R. de Arellano, *Organometallics*, 1999, **18**, 3337–3341; (e) J. E. Bercaw, A. C. Durrell, H. B. Gray, J. C. Green, N. Hazari, J. A. Labinger and J. R. Winkler, *Inorg. Chem.*, 2010, **49**, 1801–1810; (f) N. Marino, C. H. Fazen, J. D. Blakemore, C. D. Incarvito, N. Hazari and R. P. Doyle, *Inorg. Chem.*, 2011, **50**, 2507–2520; (g) Y. B. Dudkina, K. V. Kholin, T. V. Gryaznova, D. R. Islamov, O. N. Kataeva, I. K. Rizvanov, A. I. Levitskaya, O. D. Fominikh, M. Y. Balakina, O. G. Sinyashin and Y. H. Budnikova, *Dalton Trans.*, 2017, **46**, 165–177.
- K. Yamamoto, K. Higuchi, M. Ogawa, H. Sogawa, S. Kuwata, Y. Hayashi, S. Kawauchi and T. Takata, *Chem. Asian J. Accepted*, DOI: 10.1002/asia.201901561



Open clamshell dinuclear palladium(II) complexes possessing out-of-plane anisotropy were synthesised by double palladation of planar oligomeric phenylpyridines.