

COMMUNICATION

View Article Online
View Journal | View Issue


Cite this: *Dalton Trans.*, 2024, **53**, 6520

Received 18th December 2023,
Accepted 25th March 2024

DOI: 10.1039/d3dt04248k

rsc.li/dalton

A bis(PCN) palladium pincer complex with a remarkably planar 2,5-diarylpyrazine core†

Derek W. Leong,† Yanwu Shao,‡ Zhen Ni, Nattamai Bhuvanesh and
Oleg V. Ozerov *

A bimetallic Pd complex of a bis(pincer) with a diarylpyrazine core has been prepared. The complex demonstrates near-perfect coplanarity of the aromatic core, is fluorescent under UV irradiation, and displays two quasi-reversible reduction events.

Transition metal complexes of redox non-innocent pincer^{1,2} ligands have attracted considerable attention owing to the potential of metal–ligand cooperation to open up reactivity avenues not available to the particular metal alone.^{3–8} Many of the redox-active pincer designs contain either a central diarylamido donor, which renders the ligand oxidizable, or a central pyridine/azine donor with additional conjugation, which renders the ligand reducible (Fig. 1(A)). For example, complexes 1–4 display well behaved and controlled redox behavior.^{9,10} On the other hand, pincers with the very common^{1,2,11} phenyl-type central donor are rarely considered in the context of redox non-innocence because of the relative difficulty of the reversible oxidation or reduction of a benzene ring. However, introduction of other π -systems conjugated with the central benzene ring may make reversible redox events more accessible. Pincer complexes derived from 2,6-dipyridyl-benzene framework (5) represent a rare example of this strategy.¹²

Recently, we explored¹³ the redox properties of binucleating diarylamido-centered pincer complexes,¹⁴ in which the fusion of the two (PNP)M sites permitted two reversible oxidations per molecule, instead of a single event¹⁵ for an isolated (PNP)M core, Fig. 1(B). We surmised that a fused bis(pincer) construction may open up the possibility of well-behaved reductions of the C-aryl centered pincer system. Some aryl-centered Janus bis(pincer) complexes have been previously studied, but were not intrinsically redox-active in a well-

behaved reversible fashion, Fig. 1(C).^{16–21} We instead focused on the structure 10, which can be viewed as derived from the known PCN pincer ligand in complexes of the type 9^{22–24} by fusion of the two pyridine rings into a pyrazine ring in 10.

The synthesis of the bis-PCN pincer complex 10 is detailed in Scheme 1. The boronic acid 12 was made through the *in situ* generation of an aryl magnesium bromide from 11 and its reaction with trimethyl borate, followed by acidic aqueous

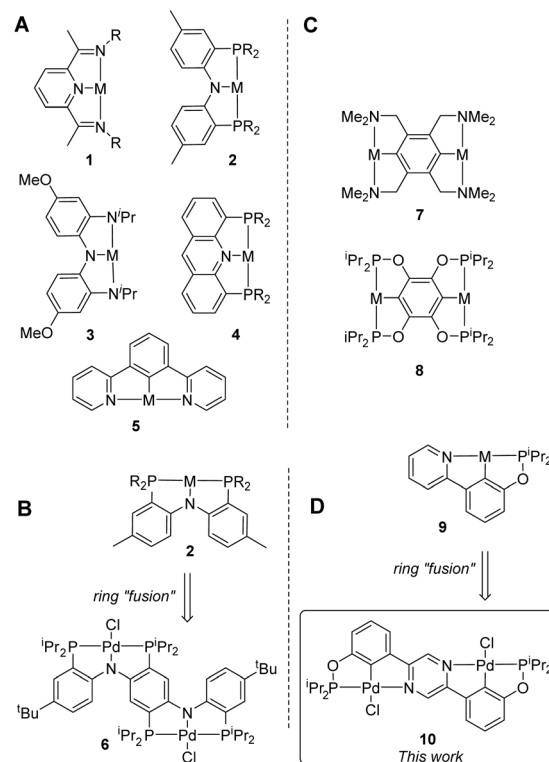


Fig. 1 (A) Redox active pincer ligands that contain a central pyridine or amido donor. (B) A bis-pincer complex that shows synergistic redox activity. (C) Non-redox active bis-pincer ligands that contain a central aryl carbon donor. (D) This work.

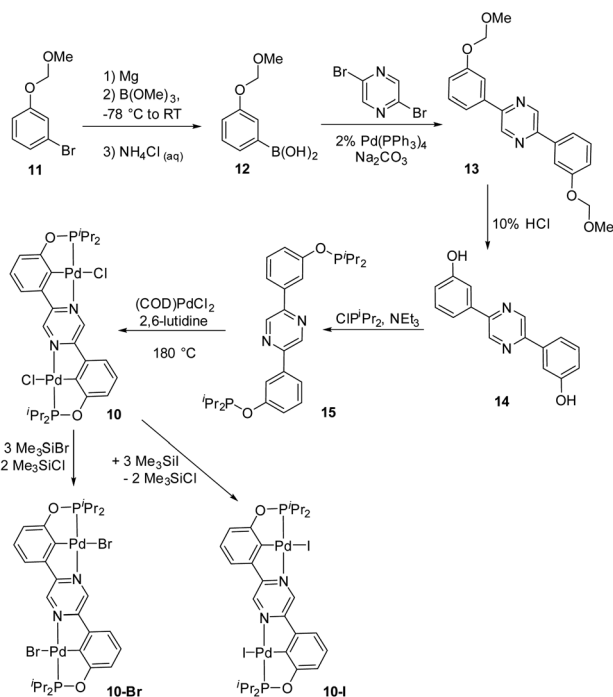
Department of Chemistry, Texas A&M University, College Station, TX 77842, USA.

E-mail: ozerov@chem.tamu.edu

†Electronic supplementary information (ESI) available: NMR spectra, X-ray crystallographic data. CCDC 2110893. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3dt04248k>

‡These authors contributed equally.





Scheme 1 Synthesis of a planar bis-pincer palladium complex.

workup. Suzuki–Miyaura coupling of **12** with 2,5-dibromopyrazine produced **13** in good yield. Deprotection of **13** led to the dihydroxy precursor **14**, whose phosphination led to the isolation of **15** in 62% yield and 95% purity. Metalation of the ligand with (COD)PdCl₂ and 2,6-lutidine required forcing conditions, but nonetheless proceeded well to give **10** in 74% isolated yield upon workup. Treatment of **10** with three equiv. of either Me₃SiBr or Me₃SiI led to near-quantitative halide meta-thesis (as evidence by NMR spectroscopy) and conversion to compounds **10-Br** and **10-I**, respectively.

The solid-state structure of **10** was determined by single-crystal X-ray diffractometry (Fig. 2). The molecule lies on an inversion center. The three aromatic rings are nearly perfectly coplanar, with the Pd and the O atoms located in that same plane, as well. The phosphorus and chlorine atoms deviate from this plane only slightly. The environment about the Pd center is approximately square-planar, with the main deviation

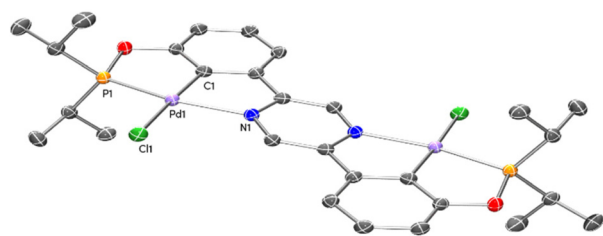


Fig. 2 POV-ray renditions of ORTEP drawings (50% thermal ellipsoids) of compound **10**. Selected bond distances (Å) and angles (°): Pd₁–Cl₁: 2.3710(4); Pd₁–P₁: 2.2068(4); Pd₁–N₁: 2.1360(15); Pd₁–Cl₁: 1.9545(18); Cl₁–Pd₁–Cl₁: 174.38(5); P₁–Pd₁–N₁: 159.12(4).

being the P1–Pd1–N1 angle of *ca.* 159°, as is typical for a number of [5,5]-pincers.²⁵ The Pd–element bond distances are likewise unremarkable. In spite of possessing extended planar sections, molecules of **10** in the crystal avoid π -stacking. Ostensibly, the voluminous –P^{*i*}Pr₂ groups extending above and below the main plane prevent close approach of the π -systems of molecules of **10** in the crystal.

The UV-Vis spectra of compound **10** in both tetrahydrofuran and dichloromethane were recorded at room temperature at 0.13 and 0.06 mM (Fig. S17†). The spectra exhibit absorption bands at *ca.* 298 nm and 365 nm both solvents. Fluorescence was initially tested with a handheld UV lamp at 254 nm using 0.6 mM solutions and fluorescence was seen for both tetrahydrofuran and dichloromethane. Unlike other previously reported pincer-Pd(II) complexes, **10** displays luminescence properties at room temperature.^{26–28} The fluorescent properties of **10** were then studied in both solvents at room temperature (Fig. S18 and S19†). Upon excitation at λ_{ex} = 250–480 nm, **10** shows one strong emission peak at *ca.* 600 nm and a weaker emission peak at *ca.* 650 nm. The emission patterns and λ_{max} seen for **10** are similar to those seen for **16**, which are in part due to the ligand backbone and its planarity.²⁹ The similarities in the ligand backbone between **10** and **16** (Fig. 3) might explain why **10** demonstrates room temperature fluorescence.

Cyclic voltammetry studies of the proto-ligand **15** in a tetrahydrofuran solution with a [^{*n*}Bu₄N]PF₆ electrolyte showed a single, quasi-reversible reduction event at $E_{1/2}$ = –2.29 V (Fig. S12†). In contrast, cyclic voltammetry of **10** under the same conditions showed a quasi-reversible reduction at $E_{1/2}$ = –1.49 V and an irreversible reduction at –2.44 V, in addition to at least two minor, but prominent irreversible reductions

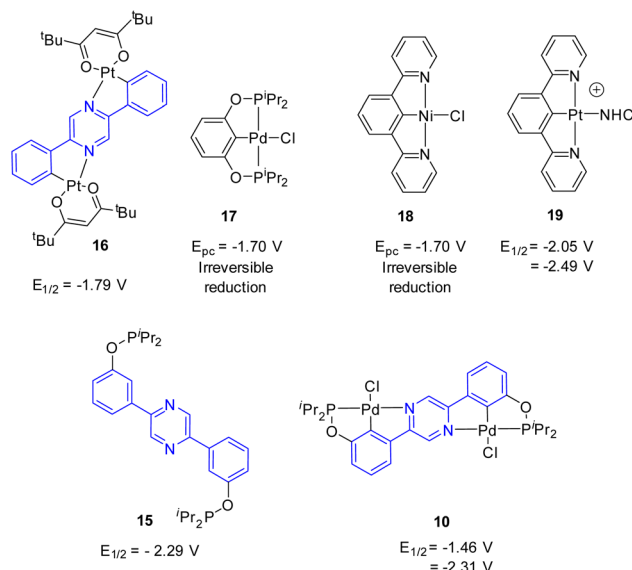


Fig. 3 Top: Examples of relevant literature complexes and their associated electrochemical data. Bottom: Compounds **15** and **10**, and their redox potentials determined by cyclic voltammetry.



(Fig. S8†). We surmised that the irreversibility and potentially the extra waves were caused by the partial loss of chloride from the complex upon reduction. It is relevant to note that irreversible reduction was reported for (POCOP)PdCl (**17**) at -1.70 V.³⁰ Chemical reduction of the related (PCP)PdCl complex was reported to lead to loss of chloride and loss of the pincer structure.³¹ Likewise, the reduction of **18** was reported³² to be irreversible, whereas the cationic Pt complex **19** displayed two quasi-reversible reductions.³³ The reversibility of the reductions in **19** is probably owed to the absence of an easily lost anionic ligand. Kletsch *et al.* also noted that the reversibility of the reduction of **18** was improved upon addition of 10 equiv. of $[\text{Bu}_4\text{N}]\text{Cl}$.³² Taking a cue from that, we redid the cyclic voltammetry (CV) study of **10** in the presence of 20 equiv. of $[\text{Bu}_4\text{N}]\text{Cl}$. This resulted in the ostensible quasi-reversibility of the both main waves ($E_{1/2} = -1.46$ and -2.31 V) and a diminished presence of the minor, irreversible waves (Fig. S11†). Electrochemical studies of **10-Br** and **10-I** did not offer additional insight. Compound **10-Br** showed qualitatively similar behavior under the analogous CV conditions (Fig. S13 and S14†), while **10-I** did not show any reversible reduction events (Fig. S15 and S16†).

Metalation works to planarize the core of the molecule and thus allow better orbital overlap within the extended π -system, making the reduction events more accessible. The more accessible reduction of the planarized diarylpyrazine system is also evident in the previously reported Pt complex **16**.²⁹ **10** is more easily reduced (by *ca.* 0.3 V) than **16**, but this may be a consequence of the presence of the electron-withdrawing oxygens in **10**. Electrochemistry of Ru complexes derived from bis(2-hydroxyphenyl)pyrazine has also been also studied in the literature.^{34,35}

In summary, we have demonstrated the synthesis of a planar bis(pincer) ligand containing a central C-aryl donor that displays well-behaved redox activity. The redox activity is achieved for a central C-aryl donor in part due to the increased conjugation from the planarity of the ligand as well as the presence of the electron deficient pyrazine ring.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are thankful to the US National Science Foundation (grant CHE-2102324 to O. V. O.) for support of this research. We are also thankful to the Welch Foundation (grant A-1717 to O. V. O.) for partial support of Y.S.

References

- 1 *Organometallic Pincer Chemistry*, ed. G. Van Koten and D. Milstein, Springer, Heidelberg, 2013.

- 2 E. Peris and R. H. Crabtree, *Chem. Soc. Rev.*, 2018, **47**, 1959–1968.
- 3 V. Lyaskovskyy and B. de Bruin, Redox non-innocent ligands: versatile new tools to control catalytic reactions, *ACS Catal.*, 2012, **2**, 270–279.
- 4 P. J. Chirik, Preface: Forum on redox-active ligands, *Inorg. Chem.*, 2011, **50**, 9737–9740.
- 5 B. de Bruin, P. Gualco and N. D. Paul, in *Ligand Design in Metal Chemistry*, John Wiley & Sons, Ltd, 2016, pp. 176–204.
- 6 A. I. Nguyen, R. A. Zarkesh, D. C. Lacy, M. K. Thorson and A. F. Heyduk, Catalytic nitrene transfer by a zirconium(IV) redox-active ligand complex, *Chem. Sci.*, 2011, **2**, 166–169.
- 7 J. J. Davidson, J. C. DeMott, C. Douvris, C. M. Fafard, N. Bhuvanesh, C.-H. Chen, D. E. Herbert, C.-I. Lee, B. J. McCulloch, B. M. Foxman and O. V. Ozerov, Comparison of the electronic properties of diarylamido-based PNZ pincer ligands: redox activity at the ligand and donor ability toward the metal, *Inorg. Chem.*, 2015, **54**, 2916–2935.
- 8 D. M. Beagan, N. A. Maciulis, M. Pink, V. Carta, I. J. Huerfano, C.-H. Chen and K. G. Caulton, A Redox-Active Tetrazine-Based Pincer Ligand for the Reduction of N-Oxanions Using a Redox-Inert Metal, *Chem. – Eur. J.*, 2021, **27**, 11676–11681.
- 9 P. J. Chirik and K. Wieghardt, Radical ligands confer nobility on base-metal catalysts, *Science*, 2010, **327**, 794.
- 10 P. Daw, A. Kumar, D. Oren, N. A. Espinosa-Jalapa, D. Srimani, Y. Diskin-Posner, G. Leituss, L. J. W. Shimon, R. Carmieli, Y. Ben-David and D. Milstein, Redox Noninnocent Nature of Acridine-Based Pincer Complexes of 3d Metals and C–C Bond Formation, *Organometallics*, 2020, **39**, 279–285.
- 11 A. Kumar, T. M. Bhatti and A. S. Goldman, Dehydrogenation of Alkanes and Aliphatic Groups by Pincer-Ligated Metal Complexes, *Chem. Rev.*, 2017, **117**, 12357–12384.
- 12 J. A. G. Williams, *Chem. Soc. Rev.*, 2009, **38**, 1783–1801.
- 13 C.-H. Yu, C. Zhu, X. Ji, W. Hu, H. Xie, N. Bhuvanesh, L. Fang and O. V. Ozerov, Palladium Bis-Pincer Complexes with Controlled Rigidity and Inter-Metal Distance, *Inorg. Chem. Front.*, 2020, **7**, 4357–4366.
- 14 For another closely related example, see: J. R. Gardinier, J. S. Hewage, B. Bennett, D. Wang and S. V. Lindeman, Tricarbonylrhenium(I) complexes of dinucleating redox-active pincer ligands, *Organometallics*, 2018, **37**, 989–1000.
- 15 D. Adhikari, S. Mossin, F. Basuli, J. C. Huffman, R. K. Szilagyi, K. Meyer and D. J. Mindiola, Structural, spectroscopic, and theoretical elucidation of a redox-active pincer-type ancillary applied in catalysis, *J. Am. Chem. Soc.*, 2008, **130**, 3676–3682.
- 16 P. Steenwinkel, H. Kooijman, W. J. J. Smeets, A. L. Spek, D. M. Grove and G. van Koten, Intramolecularly stabilized 1,4-phenylene-bridged homo- and heterodinuclear palladium and platinum organometallic complexes containing n,c,n-coordination motifs; $\eta^1\text{-SO}_2$ coordination and for-



- mation of an organometallic arenium ion complex with two Pt–C σ -bonds, *Organometallics*, 1998, **17**, 5411–5426.
- 17 S. L. Jeon, D. M. Loveless, W. C. Yount and S. L. Craig, Thermodynamics of pyridine coordination in 1,4-phenylene bridged bimetallic (Pd, Pt) complexes containing two N,C,N' motifs, 1,4-M₂–[C₆(CH₂NR₂)₄–2,3,5,6], *Inorg. Chem.*, 2006, **45**, 11060–11068.
 - 18 S. J. Loeb and G. K. H. Shimizu, Dimetallated thioether complexes as building blocks for organometallic coordination polymers and aggregates, *J. Chem. Soc., Chem. Commun.*, 1993, 1395–1397.
 - 19 S. J. Loeb, G. K. H. Shimizu and J. A. Wisner, Mono- versus dipalladation of the durene-based tetrathioether ligand 1,2,4,5-(tBuSCH₂)₄C₆H₂. Structures of [PdCl((^tBuSCH₂)₄C₆H)] and [Pd₂((^tBuSCH₂)₄C₆)(MeCN)₂][BF₄]₂, *Organometallics*, 1998, **17**, 2324–2327.
 - 20 D. Das, P. Singh, M. Singh and A. K. Singh, Tetradentate selenium ligand as a building block for homodinuclear complexes of Pd(II) and Ru(II) having seven membered rings or bis-pincer coordination mode: high catalytic activity of Pd-complexes for Heck reaction, *Dalton Trans.*, 2010, **39**, 10876–10882.
 - 21 N. P. N. Wellala, H. T. Dong, J. A. Krause and H. Guan, Janus POCOP Pincer Complexes of Nickel, *Organometallics*, 2018, **37**, 4031–4039.
 - 22 X. Jia, L. Zhang, C. Qin, X. Leng and Z. Huang, Iridium complexes of new NCP pincer ligands: catalytic alkane dehydrogenation and alkene isomerization, *Chem. Commun.*, 2014, **50**, 11056–11059.
 - 23 Y. Wang, Z. Huang, X. Leng, H. Zhu, G. Liu and Z. Huang, Transfer Hydrogenation of Alkenes Using Ethanol Catalyzed by a NCP Pincer Iridium Complex: Scope and Mechanism, *J. Am. Chem. Soc.*, 2018, **140**, 4417–4429.
 - 24 G. W. Roffe, G. J. Tizzard, S. J. Coles, H. Cox and J. Spencer, Synthesis of unsymmetrical NCN' and PCN pincer palladacycles and their catalytic evaluation compared with a related SCN pincer palladacycle, *Org. Chem. Front.*, 2016, **3**, 957–965.
 - 25 For the Fryzuk notation of pincer ring systems, see: M. D. Fryzuk and P. A. MacNeil, *J. Am. Chem. Soc.*, 1981, **103**, 3592.
 - 26 T. Kanbara and T. Yamamoto, *J. Organomet. Chem.*, 2003, **688**, 15–19.
 - 27 M. Akaiwa, T. Kanbara, H. Fukumoto and T. Yamamoto, *J. Organomet. Chem.*, 2005, **690**, 4192–4196.
 - 28 V. A. Kozlov, D. V. Aleksanyan, Y. V. Nelyubina, K. A. Lyssenko, E. I. Gutsul, L. N. Puntus, A. A. Vasil'ev, P. V. Petrovskii and I. L. Odinets, *Organometallics*, 2008, **27**, 4062–4070.
 - 29 S. Culham, P.-H. Lanoë, V. L. Whittle, M. C. Durrant, J. A. G. Williams and V. N. Kozhevnikov, *Inorg. Chem.*, 2013, 10992–11003.
 - 30 N. A. Espinosa-Jalapa, S. Hernández-Ortega, D. Morales-Morales and R. Le Lagadec, *J. Organomet. Chem.*, 2012, 103–109.
 - 31 For chemical reduction of (PCP)PdCl with the loss of chloride and loss of the pincer structure, see: C. M. Frech, L. J. W. Shimon and D. Milstein, Redox-Induced Collapse and Regeneration of a Pincer-Type Complex Framework: A Nonplanar Coordination Mode of Palladium(II), *Angew. Chem., Int. Ed.*, 2005, **44**, 1709–1711.
 - 32 L. Kletsch, G. Hörner and A. Klein, Cyclometalated Ni(II) Complexes [Ni(N[^]C[^]N)X] of the Tridentate 2,6-di(2-pyridyl)phen-ide Ligand, *Organometallics*, 2020, **39**, 2820–2829.
 - 33 K. Li, T. Zou, Y. Chen, X. Guan and C.-M. Che, Pincer-Type Platinum(II) Complexes Containing N-Heterocyclic Carbene (NHC) Ligand: Structures, Photophysical and Anion-Binding Properties, and Anticancer Activities, *Chem. – Eur. J.*, 2015, **21**, 7441–7453.
 - 34 S. Maji, B. Sarker, S. M. Mobin, J. Fiedler, W. Kaim and G. K. Lahiri, *Dalton Trans.*, 2007, 2411–2418.
 - 35 I. Brady, D. Leane, H. P. Hughes, R. J. Forster and T. E. Keyes, *Dalton Trans.*, 2004, 334–341.

