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

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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-dipyridylbenzene 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

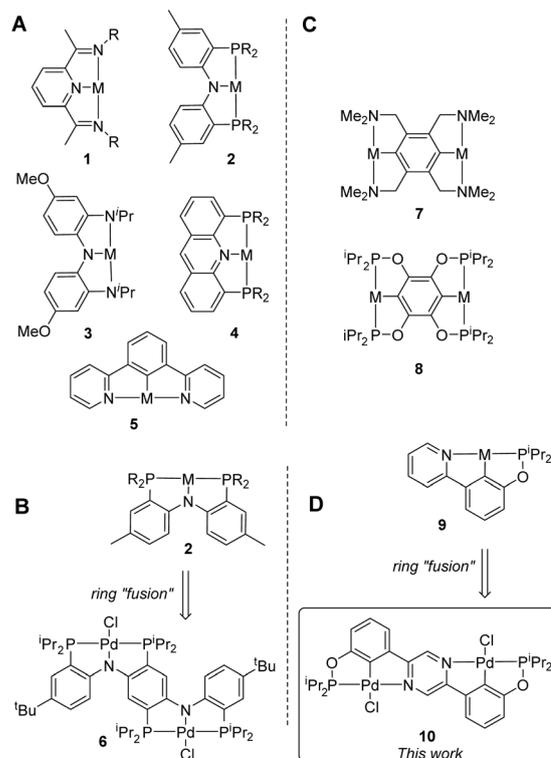


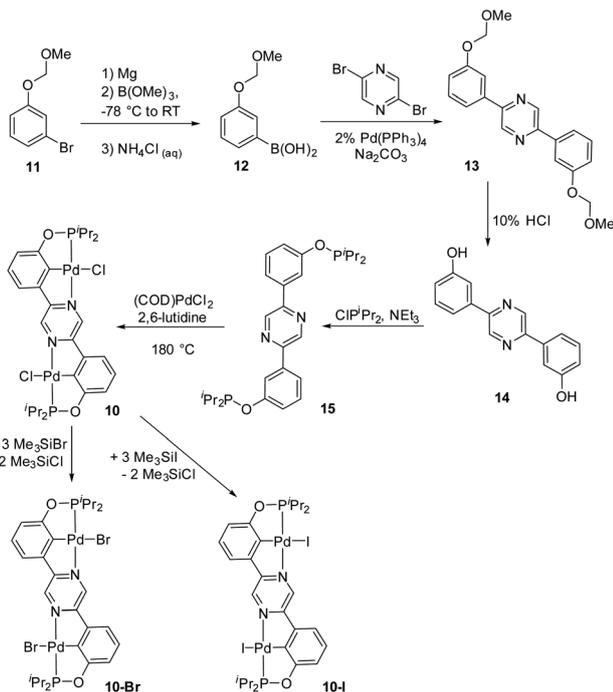
Fig. 1 (A) Redox active pincer ligands that contain a central pyridine or amido donor. (B) A bis-pincer complex that shows synergistic redox activity. (C) Non-redox active bis-pincer ligands that contain a central aryl carbon donor. (D) This work.

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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

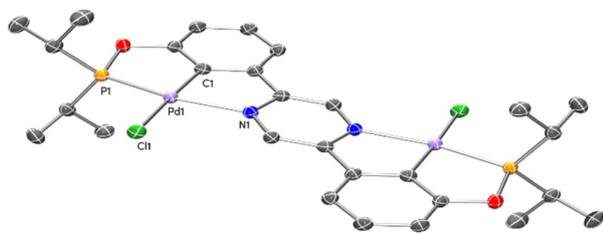


Fig. 2 POV-ray renditions of ORTEP drawings (50% thermal ellipsoids) of compound **10**. Selected bond distances (Å) and angles (°): Pd₁–Cl₁: 2.3710(4); Pd₁–P₁: 2.2068(4); Pd₁–N₁: 2.1360(15); Pd₁–Cl₁: 1.9545(18); Cl₁–Pd₁–Cl₁: 174.38(5); P₁–Pd₁–N₁: 159.12(4).

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 –PⁱPr₂ 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 $\lambda_{\text{ex}} = 250\text{--}480$ 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 [ⁿBu₄N]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

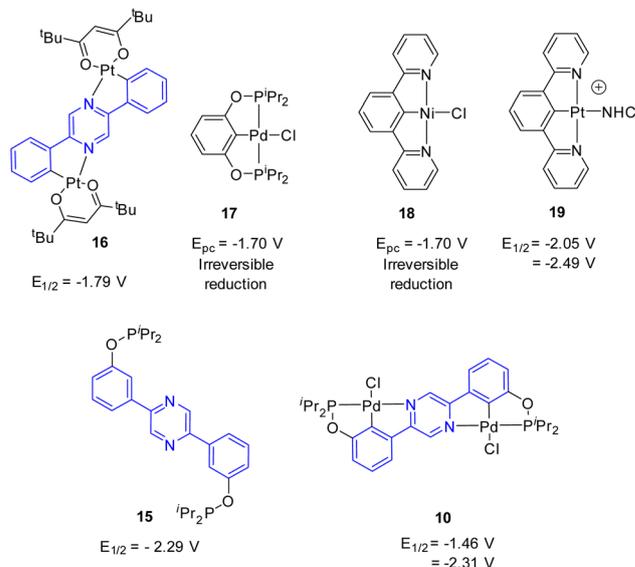


Fig. 3 Top: Examples of relevant literature complexes and their associated electrochemical data. Bottom: Compounds **15** and **10**, and their redox potentials determined by cyclic voltammetry.



(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 $[^n\text{Bu}_4\text{N}]\text{Cl}$.³² Taking a cue from that, we redid the cyclic voltammetry (CV) study of **10** in the presence of 20 equiv. of $[^n\text{Bu}_4\text{N}]\text{Cl}$. 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

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