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Synthesis and structure of palladium(II) complexes supported by *bis*-NHC pincer ligands for the electrochemical activation of CO₂

Gabriel A. Andrade, John L. DiMeglio, Eric T. Guardino, Glenn P.A. Yap, and Joel Rosenthal*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States

Abstract

A series of *bis*-NHC pincer complexes of palladium(II) have been prepared and characterized. These pyridyl-spaced dicarbene complexes ($[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$) were synthesized with substituents of varying steric bulk at the wingtip positions, which include R = methyl, ethyl, isopropyl, cyclohexyl, mesityl and 2,6-diisopropylphenyl. The synthesis of this library of complexes was accomplished either by direct metallation of the prerequisite pyridyl-spaced *bis*-imidazolium proligands with Pd(OAc)₂ or via treatment with Ag₂O to afford the corresponding silver carbenes, which were then transmetallated onto palladium. Solid-state structures for each of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ derivatives were obtained via X-ray crystallography and allowed for the steric properties of each PDC^R ligand to be evaluated by two methods. These analyses, which included calculation of the percent buried volume (%V_{Bur}) and solid angles of the PDC^R ligands, served to characterize the steric environment around the palladium center in each of the complexes that was prepared. Finally, voltammetry and controlled potential electrolysis studies were performed to characterize the redox chemistry of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ derivatives and assess if they could electrocatalyze the reduction of CO₂. The influence of the steric properties of the PDC^R ligand on the electrochemistry of the resulting complexes $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ is also discussed.

Keywords

N-heterocyclic carbene; Sterics; Percent buried volume; Solid angles; Carbon dioxide activation

1. Introduction

Palladium pincer complexes supported by pyridine spaced *bis*-N-heterocyclic carbene (NHC) ligands, have been successfully employed for many catalytic applications including Mizoroki-Heck coupling [1], Suzuki [2], and Sonagashira [2] coupling reactions. Palladium complexes supported by pincer ligands have also been recently reviewed for their broad use in catalytic applications [3]. Ligands incorporating NHCs are of interest due to their being

*Corresponding author. joelr@udel.edu (J. Rosenthal).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2017.06.018>.

strong σ -donors and their ability to form kinetically inert bonds with many transition metals [4].

Pincer complexes of palladium have also been studied for the reduction of carbon dioxide. Such efforts have been inspired by prior work by Dubois and coworkers, which demonstrated that complexes of palladium that are supported by tridentate phosphine ligands (triphos) display fast kinetics for CO₂ reduction with good selectivity for production of CO [5]. Despite the excellent kinetics and selectivity observed for Dubois' catalysts, the instability of the Pd(triphos) platform under electrocatalytic conditions limits the maximum turnover numbers (TONs) observed for these catalysts which range from ~10 to 150 [6], [7]. The labile nature of the flexible phosphine ligand, coupled with the general lability of low valent palladium centers, introduces the possibility for side reactions, which are believed to be responsible for the rapid loss in activity that is observed for Pd(triphos) electrocatalysts [5].

It has been speculated that palladium complexes supported by inert carbene ligands might be more robust platforms for the electrocatalytic reduction of CO₂ [8]. Along these lines, Wolf and coworkers have recently shown that palladium complexes incorporating pyridine and lutidine spaced *bis*-NHC pincer ligands can promote the electrocatalytic reduction of CO₂ to CO [9]. In related studies it was also shown that elaborating the substitution on the backbone of these *bis*-NHC pincer complexes impacts the ability of these systems to activate CO₂ [10]. It has also been shown that varying the substituent at the *para*-position of the pyridine ring impacts the ability of these types of complexes to promote CO₂ reduction [11], however, the substitution pattern on the imidazole, also known as the wingtip position of the *bis*-NHC ligand, has not been synthetically explored for CO₂ electrocatalyst development. Indeed, each of the palladium *bis*-NHC pincer complexes employed for CO₂ electrolysis that have been described to date have incorporated *n*-butyl substituents at the wingtip positions. Our lab has also investigated metal complexes supported by NHC ligands for small molecule activation [12,13], and recently undertook an effort to understand how the wingtip substituent of *bis*-NHC pincer complexes might influence the ability of such systems to activate CO₂. As such, herein we report the preparation and characterization of a set of pyridyl spaced dicarbene (PDC^R) ligand scaffolds with wingtips of varying steric bulk, since steric shielding of the metal has been reported to be important for palladium cross-coupling catalysis supported by NHC ligands [14], as well as for zinc complexes for CO₂ activation [15]. To understand the effect of different wingtip steric profiles, a series of pyridyl spaced dicarbene complexes (Fig. 1) or [(PDC^R)Pd(X)](Y) were prepared, where R, X, and Y denote the substitution on wingtip of the ligand, the ancillary ligand coordinated to palladium, and the outer sphere counter anion, respectively. Through analysis of the solid-state structures of these architectures, we were able to determine how steric shielding of the palladium center by the wingtip substituent of the PDC^R ligand correlates with the ability of such platforms to activate CO₂.

2. Experimental

2.1. General materials and methods

Reactions were performed in oven-dried round-bottomed flasks unless otherwise noted. Reagents and solvents were purchased from Sigma Aldrich, Acros, Fisher, Strem, Pressure Chemical or Cambridge Isotopes Laboratories. $[\text{Pd}(\text{Br})_2(\text{MeCN})_2]$ was synthesized using a published procedure [16]. Solvents for synthesis were of reagent grade or better and were dried by passage through activated alumina and then stored over 4 Å molecular sieves prior to use. Column chromatography was performed with 40–63 µm silica gel with the eluent reported in parentheses. Analytical thin-layer chromatography (TLC) was performed on precoated glass plates and visualized using UV light. The following compounds were previously reported and were prepared according to published methods: 1-(2,4,6-trimethylphenyl)-1H-imidazole [17], 1-(2,6-diisopropylphenyl)-1H-imidazole [17], 1-(isopropyl)-1H-imidazole [18], 2,6-di(1H-imidazol-1-yl)pyridine [19], 2,6-bis[3-(mesityl)imidazolium]pyridine dibromide (**5**) [20], 2,6-bis[3-(2,6-diisopropylphenyl)imidazolium]pyridine dibromide (**6**) [20], and $[\text{PDC}^{\text{Me}}\text{Pd}(\text{Br})]\text{Br}$ [21].

2.2. Compound characterization

^1H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Proton spectra are referenced to the residual proton resonance of the deuterated solvent ($\text{CDCl}_3 = \delta 7.26$; $\text{CD}_3\text{CN} = \delta 1.94$; $(\text{CD}_3)_2\text{SO} = \delta 2.50$) and carbon spectra are referenced to the carbon resonances of the solvent ($\text{CDCl}_3 = \delta 77.16$; $\text{CD}_3\text{CN} = \delta 1.32, 118.26$; $(\text{CD}_3)_2\text{SO} = \delta 39.52$). All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. LR-GCMS data were obtained using an Agilent gas chromatograph consisting of a 6850 Series GC System equipped with a 5973 Network Mass Selective Detector. Low resolution MS data was obtained using either a LCQ Advantage from ThermoFinnigan or a Shimadzu LC/MS-2020 single quadrupole MS coupled with an HPLC system, with dual ESI/APCI source. High-resolution mass spectrometry analyses were either performed by the Mass Spectrometry Laboratory in the Department of Chemistry and Biochemistry at the University of Delaware or at the University of Illinois at Urbana-Champaign.

2.3. X-ray crystallography and structural analyses

Crystals were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II DUO CCD diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å) and were focused by Goebbel mirrors for $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})]\text{Br}$. All other data were collected with Mo K α radiation ($\lambda = 0.71073$ Å) monochromated with graphite. Unit cell parameters were obtained from 36 data frames, $0.5^\circ \omega$, from three different sections of the Ewald sphere. The unit-cell parameters and systematic absences were uniquely consistent to the reported space groups for $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$, $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})_3]$, $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$, and proligand **4**; and for $Pna2_1$ and $Pnam$ [$Pnma$] for $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$. No symmetry higher than triclinic was observed in $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{Br})]\text{Br}$, $[(\text{PDC}^{\text{Cy}})\text{AgBr}]_2\text{-AgBr}$, $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})]\text{Br}$, $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{Br})]\text{Br}$, $[(\text{PDC}^{\text{iPr}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$, $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$, and $[(\text{PDC}^{\text{Me}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$. In all cases wherein

pairs of space groups are possible, excepting $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$, the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. In the case of $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$, only the noncentrosymmetric space group yielded chemically reasonable and computationally stable results of refinement. The data were treated with multi-scan absorption corrections. The structures were solved using direct methods or intrinsic phasing and refined with full-matrix, least-squares procedures on F^2 . The compound molecule resides on a mirror plane in $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$. Two compound molecules ($Z' = 2$) were located in the asymmetric units of $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{Br})]\text{Br}$ and $[(\text{PDC}^{\text{Cy}})\text{AgBr}_2\text{Ag}]\text{Br}$.

In the case of $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$, the slight but significant disorder in the PF_6^- leads to a level B alert in the checkCIF report with a second alert caused by AFIX 33 methyl H-atoms that require a large DAMP value because of their proximity to a mirror plane. The co-crystallized chloroform solvent molecule in $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})]\text{Br}$ was modeled isotropically with refined site occupancy of 54/46. An ethyl group was found disordered in $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ and was modeled with rigid-bond restraints with refined site occupancy of 56/44. An acetonitrile molecule of solvation was located in the asymmetric unit of $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$, and one of two counterions was found disordered in two positions with a refined site occupancy of 70/30. The disorder in the counterions in proligand **4**, and, the solvent molecules in $[(\text{PDC}^{\text{Cy}})\text{AgBr}_2\text{Ag}]\text{Br}$, precluded satisfactory modeling and were treated as diffused contributions [21].

All non-hydrogen atoms, excluding the disordered solvent in $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{Br})]\text{Br}$, were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2, or 1.5 for methyl, U_{eq} of the attached atom. Atomic scattering factors are contained in various versions of the SHELXTL program library. The CIFs have been deposited at the Cambridge Crystallographic Data Centre: CCDC 1539130, $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})]\text{Br}$; CCDC 1539131, $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$; CCDC 1539132, $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{Br})]\text{Br}$; CCDC 1539133, $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$; CCDC 1539134, $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$; CCDC 1539135, $[(\text{PDC}^{\text{iPr}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$; CCDC 1539136, $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})_3]$; CCDC 1539137, $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$; CCDC 1539138, $[(\text{PDC}^{\text{Me}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$; CCDC 1539139, proligand **4**; CCDC 1539140, $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{Br})]\text{Br}$; CCDC 1539141, $[(\text{PDC}^{\text{Cy}})\text{AgBr}_2\text{Ag}]\text{Br}$.

2.4. Electrochemical measurements

All electrochemistry was performed using either a CHI-620D potentiostat/galvanostat or a CHI-760D bipotentiostat. Cyclic voltammetry was performed using a standard three-electrode configuration. CV scans were recorded for quiescent solutions using a glassy carbon working disk electrode (3.0 mm diameter CH Instruments) and a platinum wire auxiliary electrode. All potentials were measured against a Ag/AgCl (1.0 M KCl) reference electrode. CV experiments were performed in DMF using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Concentrations of analytes were 1.0 mM. Controlled Potential Electrolysis (CPE) experiments were carried out using a platinum mesh counter electrode and the same working and reference electrodes as above.

CPE experiments were performed at 1.0 atm in an air tight single compartment cell saturated with CO₂. The electrolysis cell was sparged with DMF saturated CO₂ for approximately 30 min, following which time the system was sealed and electrolysis initiated. To determine Faradaic efficiencies for CO production, the headspace of the electrolysis cell was sampled periodically by manually removing 1.0 mL aliquots using a gas-tight syringe. These aliquots were analyzed by manual injection into a gas-sampling loop of a Shimadzu GC-2014 gas chromatograph (GC). This GC was equipped with two 10 port injection valves in line with 2 m HaySepT 80/100 columns. Quantification of CO was accomplished using a flame ionization detector (FID) with methanizer after passage through a 3 m HaySepD 80/100 column using helium (99.999%) as the carrier gas. Quantification of H₂ was accomplished using a thermal conductivity detector (TCD) after passage through a packed MolSieve 5A 60/80 column, using argon as the carrier gas (99.999%).

3. Synthesis and characterization

3.1. 1-Cyclohexyl-1H-imidazole

This compound was prepared by amending a previously published method [22]. Ammonium chloride (10.7 g, 0.200 mol), glyoxal (40%, 15.3 mL, 0.134 mol), formaldehyde (30 %, 16.0 mL, 0.134 mol), and deionized water (250 mL) were combined in a 1 L round bottom flask. In a separate flask, a solution of cyclohexylamine (11.5 mL, 0.100 mol) in deionized water (100 mL) was acidified with phosphoric acid (85%, 15 mL). The acidified amine was added to the ammonium chloride solution. After heating the resulting colorless solution at reflux for 12 h, the clear orange solution was cooled to room temperature and subsequently poured into a 1 L beaker that was half-filled with ice. The resulting mixture was made basic with sodium hydroxide (40%) until the pH was in the range of 10–12. The product was then extracted into ethyl acetate and the organic layer was washed with water and dried over sodium sulfate. Following removal of the solvent under reduced pressure, the desired product was purified via vacuum distillation (105 °C) to give 7.5 g of the title compound as a colorless oil. Yield = 50%. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ /ppm: 7.53 (s, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 3.90 (tt, J = 11.8, 3.8 Hz, 1H), 2.12–2.09 (m, 2H), 1.92–1.87 (m, 2H), 1.79–1.70 (m, 1H), 1.67–1.57 (m, 2H), 1.45–1.35 (m, 2H), 1.29–1.18 (m, 1H). ¹³C NMR (101 MHz, CDCl₃, 25 °C) δ /ppm: 135.43, 129.03, 117.10, 56.90, 34.54, 25.54, 25.34. HR-EI-MS [M]⁺ m/z : calculated for C₉H₁₄N₂ 150.1157; found, 150.1162.

4. Synthesis of the pyridyl-spaced *bis*-imidazolium based proligands

4.1. 2,6-Bis[3-(ethyl)imidazolium]pyridine dibromide (2)

The preparation of this compound was based on previously published methods [19,23]. 2,6-Bis(1-imidazolyl)pyridine (0.201 g, 0.095 mmol), bromoethane (0.70 mL, 0.94 mmol), and 3.0 mL of xylenes were added to a thick-walled glass tube. The tube was sealed with a screw top cap equipped with a rubber o-ring and the vessel was heated at 150 °C for 4 days. After cooling the reaction mixture to room temperature, the resulting material was triturated several times with ether and the solid was collected to yield 0.386 g of an off white solid. Yield = 94%. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) δ /ppm: 10.74 (s, 2H), 8.88 (s, 2H), 8.61 (t, J = 8.1 Hz, 1H), 8.29 (d, J = 8.1 Hz, 2H), 8.21 (s, 2H), 4.40 (q, J = 7.3 Hz, 4H), 1.55

(t, $J = 7.3$ Hz, 6H). ^{13}C NMR (101 MHz, DMSO, 25 °C) δ/ppm : 145.31, 144.84, 135.66, 123.52, 119.39, 114.12, 45.15, 15.03. HR-LIFDI-MS $[\text{M}-\text{Br}]^+$ m/z : calculated for $\text{C}_{15}\text{H}_{19}\text{N}_5\text{Br}$ 348.0824; found, 348.0830.

4.2. 2,6-Bis[3-(isopropyl)imidazolium]pyridine dibromide (3)

This compound was prepared by amending a previously published method [24]. Isopropyl imidazole (1.40 g, 12.7 mmol) was added to 2,6-dibromopyridine (1.50 g, 6.33 mmol) in a thick-walled glass tube. The neat mixture was stirred and heated at 150 °C for 4 days. After cooling the reaction to room temperature, the resulting brown solid was suspended in dichloromethane leaving the title compound as an insoluble white solid (2.24 g), which was isolated by vacuum filtration. Yield = 77%. All analytical data matched that previously reported for this compound [25]. ^1H NMR (400 MHz, d_6 -DMSO, 25 °C) δ/ppm : 10.60 (s, 2H), 8.90 and 8.31 (2 $\times$ t, $J = 1.94$ Hz, 2H), 8.62 (t, $J = 8.16$ Hz), 8.32 (d, $J = 8.16$ Hz, 2H), 4.87 (septet, $J = 6.66$ Hz, 2H), 1.63 (d, $J = 6.66$ Hz, 12H).

4.3. 2,6-Bis[3-(cyclohexyl)imidazolium]pyridine dibromide (4)

This compound was prepared by amending a previously published method [25]. 2,6-Dibromopyridine (8.36 g, 0.035 mol) and 1-Cyclohexyl-1H-imidazole (10.59 g, 0.706 mol) were mixed in a 50 mL thick-walled glass tube. The vessel was sealed and heated at 150 °C for 4 days. After cooling the reaction to room temperature, the desired product was purified from the resulting black residue by dissolving it in a minimal amount of CH_2Cl_2 and then cooling the solution to 0 °C to deliver 9.6 g of the title compound as a white solid. Yield = 51%. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ/ppm : 10.60 (s, 2H), 8.91 (s, 2H), 8.62 (t, $J = 8.1$, 1H), 8.13–8.31 (m, 4H), 4.54–4.43 (m, 2H), 2.17 (d, $J = 9.0$, 4H), 1.95–1.89 (m, 8H), 1.70 (d, $J = 12.5$, 2H), 1.48–1.38 (m, 4H), 1.32–1.22 (m, 2H). ^{13}C NMR (101 MHz, DMSO, 25 °C) δ/ppm : 145.35, 144.71, 134.65, 122.16, 119.52, 114.33, 59.80, 32.28, 24.56, 24.37. X-ray quality crystals of this compound were obtained by exchanging the Br^- counter anions to PF_6^- , followed by vapor diffusion of ether into a saturated acetonitrile solution. A labeled thermal ellipsoid plot for 2,6-Bis[3-(cyclohexyl)imidazolium]pyridine dihexafluorophosphate can be found in the Supporting Information (Figure S1).

4.4. General procedure (A): synthesis of $[(\text{PDC}^{\text{R}})\text{PdBr}]\text{Br}$ complexes via direct metalation using $\text{Pd}(\text{OAc})_2$

This procedure was adapted from a previously published method [1]. $\text{Pd}(\text{OAc})_2$ (1 equiv) and the pyridyl-spaced *bis*-imidazolium proligand (1 equiv) were added to a round bottom flask, which was then evacuated. DMSO (10 mL), which had been saturated with N_2 for 30 min, was added to the reaction flask via syringe, and the headspace was evacuated. The septum sealing the flask was then reinforced with copper wire and the reaction was heated at 150 °C for 3 h. After cooling the reaction to room temperature, the resulting mixture was filtered through celite and the solvent was removed under reduced pressure. The crude material was then purified via column chromatography on silica with the eluent mixture indicated for each compound detailed below.

4.5. General procedure (B): synthesis of [(PDC^R)PdBr]Br complexes via transmetalation

This procedure was adapted from previously published methods [19,25] The pyridyl-spaced *bis*-imidazolium proligand (1 equiv) and Ag₂O (1 equiv) were added to a round bottom flask along with 15 mL of DMSO. The resulting solution was shielded from light with aluminum foil and stirred for 12 h at room temperature. [Pd(Br)₂(MeCN)₂] (1.05 equiv) was then added to the reaction, which was stirred for an additional 3 h. The reaction was then filtered through celite and the solvent was removed under reduced pressure. The crude material was then purified via column chromatography on silica using the eluent mixture indicated for each compound detailed below.

4.6. [(PDC^{Et})Pd(Br)]Br

This compound was prepared via General Procedure A from proligand **2** (0.259 g, 0.060 mmol) and Pd(OAc)₂ (0.135 g, 0.060 mmol). The title compound was purified on silica using MeOH and CH₂Cl₂ (1:4) as the eluent to deliver 180 mg of an off white solid. Yield = 56%. X-ray quality crystals of this complex were grown via vapor diffusion of ether into a concentrated CH₂-Cl₂:MeOH solution. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) δ/ppm: 8.58 (t, *J* = 8.2 Hz, 1H), 8.47 (d, *J* = 2.2 Hz, 2H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 2.2 Hz, 2H), 4.56 (q, *J* = 7.2 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, DMSO, 25 °C) δ/ppm: 165.48, 150.26, 146.54, 123.91, 118.43, 108.83, 45.34, 16.49. HR-LIFDI-MS [M-Br]⁺ *m/z*: calculated for C₁₅H₁₇N₅PdBr 453.9697; found, 453.9684. X-ray quality crystals of this compound were obtained by vapor diffusion of pentane into a saturated chloroform solution. A labeled thermal ellipsoid plot for [(PDC^{Et})Pd(Br)]Br can be found in the Supporting Information (Figure S2).

4.7. [(PDC^{lpr})Pd(Br)]Br

This compound was prepared via General Procedure A from proligand **3** (0.400 g, 0.875 mmol) and Pd(OAc)₂ (0.196 g, 0.875 mmol). The title compound was purified on silica using increasing concentrations of MeOH in CH₂Cl₂ (from 0% to 20% MeOH in CH₂Cl₂) as the eluent to deliver 320 mg of an off white solid. Yield = 65%. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) δ/ppm: 8.58 (t, *J* = 8.23 Hz, 1H), 8.55 and 7.98 (2 × d, *J* = 1.95 Hz, 2H), 8.04 (d, *J* = 8.23 Hz, 2H), 5.78 (septet, *J* = 6.83 Hz, 2H), 1.47 (d, *J* = 6.83 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃, 25 °C) δ/ppm: 164.76, 150.29, 146.52, 120.39, 118.88, 108.75, 52.05, 39.52, 22.38. HR-ESI-MS [M-Br]⁺ *m/z*: calculated for C₁₇H₂₁N₅BrPd 480.0015; found, 480.0016.

4.8. [(PDC^{Cy})Pd(Br)]Br

This compound was prepared via General Procedure A from proligand **4** (0.802 g, 1.50 mmol) and Pd(OAc)₂ (0.335 g, 1.50 mmol). The title compound was purified on silica using MeOH and CH₂Cl₂ (1:5) as the eluent to deliver 408 mg of a yellow solid. Yield = 43%. This complex was also prepared via General Procedure B from proligand **4** (0.336 g, 0.630 mmol), Ag₂O (0.145 g, 0.630 mmol) and [Pd(Br)₂(MeCN)₂] (0.229 g, 0.660 mmol). The title compound was then purified on silica using MeOH and CH₂Cl₂ (1:10) as the eluent to deliver 0.193 g of an off-white solid. Yield = 55%. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) δ/ppm: 8.58 (t, *J* = 8.2 Hz, 1H), 8.51 (d, *J* = 2.2 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J*

= 2.2 Hz, 2H), 5.44 (t, J = 12.1 Hz, 2H), 2.12 – 1.61 (m, 14H), 1.53–1.11 (m, 7H). ^{13}C NMR (101 MHz, DMSO, 25 °C) δ /ppm: 165.20, 150.32, 146.51, 120.73, 118.66, 108.83, 58.64, 32.65, 25.01, 24.51. HR-ESI-MS $[\text{M}-\text{Br}]^+$ m/z : calculated for $\text{C}_{23}\text{H}_{29}\text{N}_5\text{PdBr}$ 562.0638; found, 562.0651. X-ray quality crystals of this compound were obtained by vapor diffusion of pentane into a saturated chloroform solution. A labeled thermal ellipsoid plot for $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})]\text{Br}$ can be found in the Supporting Information (Figure S3).

4.9. $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{Br})]\text{Br}$

This compound was prepared via General Procedure A from proligand **5** (1.01 g, 1.66 mmol) and $\text{Pd}(\text{OAc})_2$ (0.372 g, 1.66 mmol). The title compound was then purified on silica using a solvent gradient from pure CH_2Cl_2 to $\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1:4) to deliver 0.390 g of an off-white solid. Yield = 40%. This complex was also prepared via General Procedure B from proligand **5** (0.505 g, 0.829 mmol), Ag_2O (0.192 g, 0.829 mmol) and $[\text{Pd}(\text{Br})_2(\text{MeCN})_2]$ (0.303 g, 0.870 mmol). The title compound was then purified on silica using MeOH and CH_2Cl_2 (1:4) to deliver 0.396 g of an off-white solid. Yield = 67% yield. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ /ppm: 8.73 and 7.70 (2 $\times$ d, J = 2.22 Hz, 2H), 8.68 (t, J = 8.17 Hz, 1H), 8.20 (d, J = 8.17 Hz, 2H), 6.94 (s, 4H), 2.25 (s, 6H), 1.96 (s, 12H). ^{13}C NMR (101 MHz, CD_3CN , 25 °C) δ /ppm: 171.16, 151.90, 147.01, 140.47, 135.38, 135.27, 129.51, 125.76, 119.55, 118.26, 110.21, 21.00, 17.91. HR-ESI-MS $[\text{M}-\text{Br}]^+$ m/z : calculated for $\text{C}_{29}\text{H}_{29}\text{N}_5\text{PdBr}$ 632.0641; found, 632.0640.

4.10. $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{Br})]\text{Br}$

This compound was prepared via General Procedure B from proligand **6** (0.129 g, 0.186 mmol), Ag_2O (0.043 g, 0.19 mmol) and $[\text{Pd}(\text{Br})_2(\text{MeCN})_2]$ (0.068 g, 0.19 mmol). The title compound was then purified on silica using MeOH and CH_2Cl_2 (1:6.5) to deliver 0.093 g of an off white solid. Yield = 63%. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ /ppm: 8.73 (d, J = 2.2 Hz, 2H), 8.68 (t, J = 8.2 Hz, 1H), 8.18 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 2.1 Hz, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 4H), 2.39 (p, J = 6.8 Hz, 4H), 1.10 (d, J = 6.8 Hz, 12H), 1.05 (d, J = 6.8 Hz, 12H). ^{13}C NMR (101 MHz, DMSO, 25 °C) δ /ppm: 169.38, 150.45, 146.30, 144.23, 133.78, 130.05, 126.49, 123.54, 118.77, 109.76, 28.03, 24.36, 22.93. HR-ESI-MS $[\text{M}-2\text{Br}]^{2+}$ m/z : calculated for $\text{C}_{37}\text{H}_{44}\text{N}_6\text{Pd}$ 339.1326; found, 339.1330. X-ray quality crystals of this compound were obtained by vapor diffusion of pentane into a saturated chloroform solution. A labeled thermal ellipsoid plot for $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})]\text{Br}$ can be found in the Supporting Information (Figure S4).

4.11. General procedure for synthesis of $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes

A combination of 1 equivalent of $[(\text{PDC}^{\text{R}})\text{Pd}(\text{Br})]\text{Br}$ and 2 equivalents of AgPF_6 were dissolved in dry MeCN within a round bottom flask in a N_2 filled glovebox. The reaction vessel was then sealed with a rubber septum, reinforced with copper wire and shielded from light with aluminum foil. The reaction vessel was then taken out of the glovebox and heated in an oil bath at 70 °C for 3 h. After cooling the reaction to room temperature, the mixture was filtered through celite to remove the AgBr precipitate and the filtrate was concentrated in vacuo. The resulting crude material was then recrystallized from acetonitrile/ether to yield

a white solid, which was collected via vacuum filtration. X-ray quality crystals of each complex were grown by vapor diffusion of ether into concentrated acetonitrile solutions.

4.12. $[(\text{PDC}^{\text{Me}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$

This complex was prepared via the general method described above from $[(\text{PDC}^{\text{Me}})\text{Pd}(\text{Br})]\text{Br}$ (0.125 g, 0.0240 mmol) and AgPF_6 (0.125 g, 0.0490 mmol) to deliver 0.139 g of the title compound as a white solid. Yield = 83%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ /ppm: 8.62 (t, J = 8.2 Hz, 1H), 8.47 (d, J = 2.2 Hz, 2H), 8.03 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 2.1 Hz, 2H), 3.93 (s, 6H). ^{13}C NMR (101 MHz, DMSO , 25 °C) δ /ppm: 165.68, 150.99, 147.52, 125.39, 118.45, 109.18, 99.56, 36.92, 1.25. HR-ESI-MS $[\text{M}-\text{MeCN}-2\text{PF}_6]^{2+}$ m/z : calculated for $\text{C}_{13}\text{H}_{11}\text{N}_5\text{Pd}$ 172.5105; found, 172.5093.

4.13. $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$

This complex was prepared via the general method described above from $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{Br})]\text{Br}$ (0.235 g, 0.0440 mmol) and AgPF_6 (0.223 g, 0.0880 mmol) to deliver 0.269 g of the title compound as a white solid. Yield = 87%. ^1H NMR (400 MHz, CD_3CN , 25 °C) δ /ppm: 8.44 (t, J = 8.3 Hz, 1H), 7.90 (d, J = 2.2 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 2.3 Hz, 2H), 4.24 (q, J = 7.3 Hz, 4H), 1.52 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, CD_3CN , 25 °C) δ /ppm: 166.54, 152.45, 149.23, 124.54, 119.45, 110.44, 47.14, 16.64, 1.32. Elemental Analysis ($\text{C}_{17}\text{H}_{20}\text{N}_6\text{PdP}_2\text{F}_{12} + \text{CH}_3\text{OH}$): C 29.34; H, 3.28; N, 11.41, Found C, 29.48; H, 2.86, N, 11.67) HR-ESI-MS $[\text{M}-2\text{PF}_6]^{2+}$ m/z : calculated for $\text{C}_{17}\text{H}_{20}\text{N}_6\text{Pd}$ 207.0388; found, 207.0387.

4.14. $[(\text{PDC}^{\text{Ipr}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$

This complex was prepared via the general method described above from $[(\text{PDC}^{\text{Ipr}})\text{Pd}(\text{Br})]\text{Br}$ (0.80 g, 1.4 mmol) and AgPF_6 (0.72 g, 2.9 mmol) to deliver 0.660 g of the title compound as a white solid. Yield = 63%. ^1H NMR (400 MHz, CD_3CN , 25 °C) δ /ppm: 8.45 (t, J = 8.28 Hz, 1H), 7.94 and 7.51 ($2 \times$ d, J = 2.16 Hz, 2H), 7.69 (d, J = 8.28 Hz, 2H), 4.71 (septet, J = 6.73 Hz, 2H), 1.59 (d, J = 6.73 Hz, 12H). ^{13}C NMR (101 MHz, DMSO , 25 °C) δ /ppm: 163.91, 150.95, 147.56, 120.45, 119.37, 109.13, 51.86, 39.52, 22.57, 1.24. ESI-MS $[\text{M}-2\text{PF}_6]^{2+}$ m/z : calculated for $\text{C}_{19}\text{H}_{24}\text{N}_6\text{Pd}$ 221.0549; found, 221.0552.

4.15. $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$

This complex was prepared via the general method described above from $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})]\text{Br}$ (0.333 g, 0.500 mmol) and AgPF_6 (0.262 g, 1.00 mmol) to deliver 0.422 g of the title compound as a white solid. Yield = 92%. ^1H NMR (400 MHz, CD_3CN , 25 °C) δ /ppm: 8.45 (t, J = 8.2 Hz, 1H), 7.93 (d, J = 1.9 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 2.0 Hz, 2H), 4.30 (tt, J = 12.2, 3.8 Hz, 2H), 2.14–1.96 (m, 12H), 1.81 (ddd, J = 24.5, 12.1, 2.9 Hz, 7H), 1.51–1.25 (m, 7H). ^{13}C NMR (101 MHz, CD_3CN , 25 °C) δ /ppm: 165.61, 152.33, 149.20, 121.34, 119.63, 110.34, 61.42, 33.92, 26.15, 25.30. HR-ESI-MS $[\text{M}-2\text{PF}_6]^{2+}$ m/z : calculated for $\text{C}_{25}\text{H}_{32}\text{N}_6\text{Pd}$ 261.0856; found, 261.0857.

4.16. [(PDC^{Mes})Pd(MeCN)](PF₆)₂

This complex was prepared via the general method described above from [(PDC^{Mes})Pd(Br)]Br (0.34 g, 0.48 mmol) and AgPF₆ (0.24 g, 0.96 mmol) to deliver 0.302 g of the title compound as a white solid. Yield = 70%. ¹H NMR (400 MHz, CD₃CN, 25 °C) δ/ppm: 8.55 (t, *J* = 8.24 Hz, 1H), 8.13 and 7.39 (2 × d, *J* = 2.10 Hz, 2H), 7.83 (d, *J* = 8.24 Hz, 2H), 7.07 (s, 4H), 2.29 (s, 6H), 2.07 (s, 12H). ¹³C NMR (101 MHz, CD₃CN, 25 °C) δ/ppm: 169.02, 152.74, 149.41, 141.54, 135.86, 133.84, 130.09, 125.68, 120.29, 111.08, 20.90, 17.64. ESI-MS [M–PF₆]⁺ *m/z*: calculated for C₃₁H₃₂N₆PF₆Pd 739.1371; found, 739.1377.

4.17. [(PDC^{Dipp})Pd(MeCN)](PF₆)₂

This complex was prepared via the general method described above from [(PDC^{Dipp})Pd(Br)]Br (0.350 g, 0.439 mmol) and AgPF₆ (0.222 g, 0.877 mmol) to deliver 0.421 g of the title compound as a white solid. Yield = 99%. ¹H NMR (400 MHz, CD₃CN, 25 °C) δ/ppm: 8.61 (t, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 2.2 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.57–7.50 (m, 4H), 7.39 (d, *J* = 7.8 Hz, 4H), 2.52 (hept, *J* = 6.8 Hz, 4H), 1.99 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 12H), 1.15 (d, *J* = 6.8 Hz, 12H). ¹³C NMR (101 MHz, CD₃CN, 25 °C) δ/ppm: 168.81, 152.79, 149.61, 146.43, 133.23, 132.69, 126.60, 125.35, 120.24, 111.24, 29.18, 24.17, 23.94. HR-ESI-MS [M–PF₆]⁺ *m/z*: calculated for C₃₇H₄₄N₆PF₆Pd 823.2299, found 823.2303.

4.18. [((PDC^{Cy})Ag(Br))₂Ag]Br

This silver NHC complex was synthesized using a modified literature procedure [26]. 2,6-Bis[3-(cyclohexyl)imidazolium]pyridine dibromide (0.107 g, 0.200 mmol) and Ag₂O (0.046 g, 0.20 mmol) were combined in a round bottom flask to which 25 mL of CH₂Cl₂ was added. The reaction flask was shielded from light using aluminum foil and stirred at room temperature for 12 h. The resulting mixture was then filtered through celite and the solvent was removed under reduced pressure to yield the title compound (0.067 g, 60% yield) as an off-white powder. Single crystals of the title compound were obtained by diffusion of pentane into a saturated CH₂Cl₂ solution in an aluminum foil covered vial. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) δ/ppm: δ 8.50 (t, *J* = 8.0 Hz, 1H), 8.42 (s, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.79 (s, 2H), 3.88 (s, 2H), 1.69–1.28 (m, 13H), 1.05 (dd, *J* = 23.5, 16.4 Hz, 5H), 0.94–0.54 (m, 4H). HR-LIFDI-MS [M + H]⁺ *m/z*: calculated for C₂₃H₃₀N₅AgBr 564.0724; found, 564.0734.

5. Results and discussion

The synthetic pathway employed to prepare the pyridyl-spaced dicarbene palladium complexes utilized in this study is shown in Scheme 1. The synthesis began with preparation of the substituted imidazoles via condensation reactions with the properly substituted primary amines, glyoxal, and ammonium chloride under acidic conditions. The *N*-alkyl substituted imidazoles were purified via distillation while the *N*-aryl substituted derivatives were purified through sublimation. The substituted imidazoles were then reacted with 2,6-dibromopyridine under neat conditions at elevated temperatures for several days to afford the required bis-imidazolium proligands containing ancillary methyl (**1**), isopropyl (**3**), cyclohexyl (**4**), mesityl (**5**), or 2,6-diisopropylphenyl groups (**6**). The pyridyl spaced *bis*-

imidazolium with ethyl substituents (**2**) was prepared via alkylation of 2,6-di(1H-imidazol-1-yl)pyridine with ethylbromide. Each of the *bis*-imidazolium proligands were initially metallated by treatment with Pd(OAc)₂ in DMSO at 150 °C. The resultant [(PDC^R)Pd(Br)]Br complexes could be purified by column chromatography on silica, however, the yields for these metallation reactions were modest, ranging from approximately 40–60%.

A side product isolated upon reaction of the *bis*-imidazolium proligand bearing cyclohexyl groups with Pd(OAc)₂ shed light on a limitation of this metallation procedure. Crystallization of this byproduct, revealed a complex in which a Pd^{II}(Br)₃ core was bound to a single NHC on the PDC^{Cy} scaffold. Fig. 2 shows the thermal ellipsoid plot for this complex, in which a single NHC and three bromides bind the square planar Pd^{II} center. The second imidazolium unit on the ligand backbone remains protonated and serves as the counter cation to the anionic [(NHC)Pd(Br)₃][–] unit. Analysis of the solid-state structure shown in Fig. 2a showed that the interaction between the imidazolium proton on C11 and the nearest bromide ligand (Br1) is negligible [26,27], as the closest interaction between Br1 and H11 was measured to 2.864 Å, with a Pd–Br1–H11 angle of 71.35°. The presence of protonated ligand in the isolated side product suggests that a limitation of this metallation procedure may be the mismatched p*K*_a(DMSO) values of acetate (~13) [28] and imidazolium (~20) [29], which precludes complete deprotonation of the *bis*-imidazolium proligands.

In order to circumvent the formation of the unwanted side product shown in Fig. 2a, we also prepared the desired [(PDC^R)Pd(Br)] Br complexes via transmetalation from the corresponding silver carbene intermediates. This protocol involved treatment of the starting pyridyl-spaced *bis*-imidazolium derivatives with Ag₂O to produce the corresponding silver-carbene intermediates, which were then transmetalated onto [Pd(Br)₂(MeCN)₂] in a one pot, two-step reaction. Each of the [(PDC^R)Pd(Br)]Br complexes of Scheme 1 were easily prepared using this method, utilizing much milder conditions than the Pd(OAc)₂ route described above.

Although the silver transmetalation strategy was generally carried out without isolation of the silver–PDC^R intermediate, this species was prepared, isolated and characterized for the cyclohexyl-appended PDC^{Cy} ligand by reacting the proligand and Ag₂O in CH₂Cl₂ in a reaction vessel that was protected from light. After filtration the silver-carbene containing product was isolated and crystallized. The solid-state structure of this complex ([(PDC^{Cy}) AgBr)₂Ag]Br) is shown in Fig. 2b. The solid-state structure shows a central unit containing two PDC^{Cy} ligands bridging three Ag^I atoms and an outersphere bromide anion. The central Ag center (Ag2) is coordinated in *trans*-fashion by two separate PDC^{Cy} carbenes through C11 and C24. The central Ag2 center is in proximity to Ag1 and Ag3 and displays a Ag...Ag interaction (~3 Å) with both of these terminal silver atoms (Ag1 and Ag2). The distal separation of Ag1–Ag2 (2.998 Å) and Ag2–Ag3 (3.068 Å) is slightly more than two times the covalent radius of Ag (2.90 Å) [30]. Each of the PDC^{Cy} ligands that is bound to Ag2 bridges to the terminal Ag centers (Ag2 and Ag3). In addition to being coordinated to a PDC^{Cy} carbene, both Ag2 and Ag3 contain a bromide ligand. The NHC–Ag–Br bond angles are nearly linear. We note that bonding metrics similar to those observed for

$[(\text{PDC}^{\text{Cy}}\text{AgBr})_2\text{Ag}]\text{Br}$ have been reported for an analogous pyridine spaced *bis*-NHC complex of Ag [31] as well as other Ag NHC complexes [32,33,34].

Using the silver-transmetallation route we successfully prepared each of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{Br})]\text{Br}$ complexes of Scheme 1. Solid-state structures for the $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{Br})]\text{Br}$, $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})]\text{Br}$, and $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{Br})]\text{Br}$ complexes, which are reproduced in the Supporting Information (Figures S2–S4) were also obtained and are similar to that of $[(\text{PDC}^{\text{Me}})\text{Pd}(\text{Br})]\text{Br}$, which has been reported previously [1]. Each of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{Br})]\text{Br}$ complexes was converted to the corresponding solvato complex by treating with two equivalents of AgPF_6 in acetonitrile and removal of the precipitated AgBr . Single crystals of each of the resulting $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ were obtained and analyzed by X-ray crystallography and the resulting solid-state structures are shown in Fig. 3; selected bond metrics are reported in Table 1. All six $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ structures display a pseudo square planar geometry at palladium with a C1–Pd–C11 bond angle approaching 160° . As can be seen in Table 1, the bond lengths between the palladium center, PDC^{R} ligand and acetonitrile solvato ligand are similar for the entire $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ series. When taken as a whole, these results suggest that variation of the wingtip substituent on the PDC^{R} ligand does not induce significant electronic differences for the ligand backbone. Although each of the PDC^{R} ligands adopt similar structures when bound to palladium(II) the varying wingtip substituents induce distinct levels of steric demand about the pyridyl-spaced dicarbene ligand periphery. Two methods that have been developed to quantitate the steric properties of ligands are calculation of percent buried volume ($\%V_{\text{Bur}}$) [35] and the use of solid angles [36]. Both analyses can be completed with applications, which are freely available, [37] and utilize xyz coordinate files, which we readily obtained from the crystal data for the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ series. The $\%V_{\text{Bur}}$ is a measure of the percentage of space occupied by a ligand within a sphere, of radius of $3.5 \text{ \AA}$, centered at the metal. In assessing the steric properties of the PDC^{R} ligands, $\%V_{\text{Bur}}$ analyses were performed for each $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complex of Fig. 3, following removal of the acetonitrile ligand. As such, each of the $\%V_{\text{Bur}}(\text{PDC}^{\text{R}})$ values listed in Table 2 involved direct analysis of the $[(\text{PDC}^{\text{R}})\text{Pd}]^{2+}$ cores for each of the six complexes of Fig. 3. Inspection of the $\%V_{\text{Bur}}\text{PDC}^{\text{R}}$ values in Table 2 clearly shows that this parameter is surprisingly similar (51.5–53.8%) for each of the PDC ligands containing alkyl (methyl, ethyl, isopropyl and cyclohexyl) wingtip groups, indicating that increasing the size or branching of an alkyl wingtip does not significantly perturb the steric bulk around the Pd center for the $(\text{PDC}^{\text{R}})\text{Pd}$ platforms. By contrast, substitution of the PDC wingtips with more sterically demanding mesityl and 2,6-diisopropylphenyl groups results in a dramatic increase in the $\%V_{\text{Bur}}\text{PDC}^{\text{R}}$ values. The mesityl group ($\%V_{\text{Bur}}(\text{PDC}^{\text{Mes}}) = 57.1\%$) adds nearly 5% to the percent buried volume compared to the average alkyl appended $[(\text{PDC}^{\text{R}})\text{Pd}]^{2+}$ complex, while the 2,6-diisopropylphenyl ($\%V_{\text{Bur}}(\text{PDC}^{\text{Dipp}}) = 63.4\%$) adds nearly 11% compared to the average alkyl appended $[(\text{PDC}^{\text{R}})\text{Pd}]^{2+}$ derivative. As such, these analyses indicate that the Pd center is significantly more sterically encumbered for the $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ and $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes.

Analyses involving solid angles were also conducted to assess the steric properties of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes [37]. The solid angle paradigm is equivalent to placing a metal complex within a sphere while replacing the metal center of the complex with a point source of light. The extent to which a ligand shields the outer sphere from the light source/metal center is then determined as the percentage of the shadowed areas over the surface area of the full sphere. Conducting this analysis for the $[(\text{PDC}^{\text{R}})\text{Pd}]^{2+}$ units delivered solid angles for each of the PDC^{R} ligands. As shown in Table 3, the trends observed for the $G(\text{PDC}^{\text{R}})$ values are akin to the $\%V_{\text{Bur}}(\text{PDC}^{\text{R}})$ calculations described above. Each of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes with alkyl wingtips display similar $G(\text{PDC}^{\text{R}})$ values that range from 51.45% to 54.63% and show a slight increasing trend as the size and branching of the alkyl substituent increases. By contrast, the $G(\text{PDC}^{\text{R}})$ values obtained for PDC^{Mes} and PDC^{Dipp} are larger than those for the alkyl pyridyl-spaced dicarbenes by approximately 8% and 15%, respectively. A graphical representation of the solid angles for the PDC^{R} complexes with smallest ($[(\text{PDC}^{\text{Me}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$) and largest ($[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$) wingtip substituents are shown in blue in Fig. 4 and highlights the difference in steric properties between the largest and smallest PDC^{R} scaffolds we have considered in this study.

Given our ongoing interest in electrochemistry and CO_2 activation [38–43] we probed the ability of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})]^{2+}$ platform to reduce CO_2 . Voltammetric and controlled potential electrolysis (CPE) experiments were carried out for $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ in which the wingtip groups were either ethyl, cyclohexyl, mesityl or 2,6-diisopropylphenyl. Cyclic voltammograms (CVs) were recorded for each of these complexes in DMF containing 0.1 M TBAPF₆ as supporting electrolyte using a glassy carbon working electrode. As shown in Fig. 5, CVs were recorded under an atmosphere of N_2 (black traces) or CO_2 (red traces).

Each complex displays two reduction waves under N_2 and peak potentials for these redox events are provided in Table 3. These peak potentials are similar to those observed for the previously studied $[\text{PDC}^{\text{nBu}}\text{Pd}(\text{MeCN})](\text{BF}_4)_2$ [8]. The redox behavior for the two complexes of Fig. 5 with alkyl wingtips ($[(\text{PDC}^{\text{Et}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ and $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$) is virtually unchanged under CO_2 , suggesting these complexes do not electrochemically active carbon dioxide. By contrast, the redox behavior for the two complexes containing the more sterically encumbered PDC^{Mes} and PDC^{Dipp} ligands both show modest current enhancements at the second reduction wave ($E_{\text{red}}(2) = -1.25$ V versus Ag/AgCl) under CO_2 . The magnitude of the current enhancements are 5.1 μA and 7.1 μA for $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ and $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ respectively (Table 3).

CPE experiments were performed on the library of complexes shown in Fig. 3. Each complex was dissolved in DMF containing 0.1 M TBAPF₆ that was saturated with CO_2 . When the CPE was conducted at potentials more negative than -1.3 V versus Ag/AgCl, which is where the second reduction feature is observed for the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes, the glassy carbon working electrode became passivated. Inspection of the working electrode after the CPE showed a dark film had formed on the electrode during the experiment and that this film suppressed redox processes at the electrode. Similar behavior

has also been observed for a previously studied $[(\text{PDC}^{\text{nBu}})\text{Pd}(\text{Br})]\text{Br}$ complex [8]. When the above CPE experiments were repeated at slightly less negative potentials (i.e., the $E_{\text{red}}(2)$ values from Table 3), fouling of the working electrode surface was avoided, however, these experiments only produced trace amounts of CO, even upon addition of Lewis acids such as $\text{Mg}(\text{ClO}_4)_2$ to the electrolysis solution, which is known to aid CO_2 activation [44]. Addition of weak Brønsted acids such as trifluoroethanol also did not improve the catalysis observed for the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes. We note that similar catalytic behavior has been reported for $[(\text{PDC}^{\text{nBu}})\text{Pd}(\text{Br})]\text{Br}$ and suggests that pyridyl-spaced dicarbene complexes of this type are not sufficiently reducing enough to activate CO_2 without forming insoluble deposits on carbon electrode surfaces.

6. Summary and conclusions

In this study, we have reported the synthesis of a library of $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes, where R (i.e., the wingtip position of the pyridyl-spaced dicarbene ligand) was systematically varied to include methyl, ethyl, isopropyl and cyclohexyl alkyl groups, as well as bulky mesityl or 2,6-diisopropylphenyl groups. The synthesis of these complexes was accomplished via two complementary routes; direct metallation of the pyridyl-spaced *bis*-imidazolium proligands (**1–6**) with $\text{Pd}(\text{OAc})_2$ in DMSO produced the desired $[(\text{PDC}^{\text{R}})\text{Pd}(\text{Br})]\text{Br}$ complexes, however, unwanted side products of the form $[(\text{PDC}^{\text{R}})\text{Pd}(\text{Br})_3]$ were also obtained and identified by X-ray crystallography. By contrast, treatment of proligands **1–6** with Ag_2O to generate the corresponding silver *bis*-NHC complexes, which were then transmetallated with $\text{Pd}(\text{Br})_2(\text{MeCN})_2$ to generate the same $[(\text{PDC}^{\text{R}})\text{Pd}(\text{Br})]\text{Br}$ complexes under much milder conditions and in higher yields. Metathesis of each $[(\text{PDC}^{\text{R}})\text{Pd}(\text{Br})]\text{Br}$ with AgPF_6 in MeCN ultimately delivered each of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes. Analysis of the solid-state structures for each of these systems revealed that the steric environment about the Pd center is similar for each of the PDC^{R} complexes with alkyl substituents at the ligand wingtip positions. By contrast, the steric environment about the Pd center for the PDC^{Mes} and PDC^{Dipp} is much more encumbered as evidenced from percent buried volume ($\%V_{\text{Bur}}$) and solid angle calculations. Voltammetry experiments demonstrated the steric contributions of the PDC^{R} wingtip positions impacts the ability of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes to activate CO_2 . The Pd complexes supported by PDC^{Mes} and PDC^{Dipp} show the most significant current enhancement under CO_2 , however, these systems form catalytically inactive deposits at the electrode surface during CPE experiments, which obviates bulk scale CO_2 electrolysis experiments. Although the complexes described herein are not effective for the bulk scale electrochemical reduction of CO_2 , we believe the understanding this study provides on the effect of wingtip sterics and related molecular design principles will be instructive for future efforts aimed at developing catalysts for the electrochemical activation of CO_2 .

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- [1]. Peris E, Loch JA, Mata J, Crabtree RH, Chem. Commun (2001) 201.
- [2]. Loch JA, Albrecht M, Peris E, Mata J, Faller JW, Crabtree RH, Organometallics 21 (2002) 700.
- [3]. Selander N, Szabó KJ, Chem. Rev 11 (2011) 2048.
- [4]. Farrell K, Albrecht M, in: Van Koten G, Gossage AR (Eds.), The Privileged Pincer-Metal Platform: Coordination Chemistry & Applications, Springer International Publishing, Cham, 2016, pp. 45–91.
- [5]. Dubois DL, Comments Inorg. Chem 19 (1997) 307.
- [6]. Dubois DL, Miedaner A, Haltiwagner RC, J. Am. Chem. Soc 113 (1991) 8753.
- [7]. DuBois Daniel L., Miedaner Alex, Haltiwanger R. Curtis, J. Am. Chem. Soc 113 (1991) 8753.
- [8]. Rosenthal J, Prog. Inorg. Chem 59 (2014) 299.
- [9]. Therrien JA, Wolf MO, Patrick BO, Inorg. Chem 53 (2014) 12962. [PubMed: 25337973]
- [10]. Therrien JA, Wolf MO, Patrick BO, Inorg. Chem 54 (2015) 11721. [PubMed: 26624491]
- [11]. Therrien JA, Wolf MO, Inorg. Chem 56 (2017) 1161–1172. [PubMed: 28071907]
- [12]. Ariyananda PWA, Yap GPA, Rosenthal J, Dalton Trans. 41 (2012) 7977. [PubMed: 22643651]
- [13]. Ghidui MJ, Pistner AJ, Yap GPA, Lutterman DA, Rosenthal J, Organometallics 32 (2013) 5026.
- [14]. Dible BR, Cowley RE, Holland PL, Organometallics 30 (2011) 5123.
- [15]. Siek S, Dixon NA, Kumar M, Kraus JS, Wells KR, Rowe BW, Kelley SP, Zeller M, Yap GPA, Papish ET, Eur. J. Inorg. Chem (2016) 2495.
- [16]. Ebner DC, Trend RM, Genet C, McGrath MJ, O’Brien P, Stoltz BM, Angew. Chem., Int. Ed 47 (2008) 6367.
- [17]. Liu J, Chen J, Zhao J, Zhao Y, Li L, Zhang H, Synthesis 17 (2003) 2661.
- [18]. Starikova OV, Dolgushin GV, Larina LI, Ushakov PE, Komarova TN, Lopyrev VA, Russ. J. Org. Chem 39 (2003) 1467
- [19]. Gong HY, Rambo BM, Karnas E, Lynch VM, Sessler JL, Nat. Chem 2 (2010) 406. [PubMed: 20414243]
- [20]. Danopoulos AA, Tulloch AAD, Winston S, Eastham G, Hursthouse MB, Dalton Trans. 5 (2003) 1009.
- [21]. Spek AL, J. Appl. Cryst 36 (2003) 7.
- [22]. Perry MC, Cui X, Powell MT, Hou DR, Reibenspies JH, Burgess K, J. Am. Chem. Soc 125 (2003) 113. [PubMed: 12515512]
- [23]. Clark WD, Cho J, Valle HU, Hollis TK, Valente EJ, J. Organomet. Chem 751 (2014) 534.
- [24]. McGuinness DS, Gibson VC, Steed JW, Organometallics 23 (2004) 6288.
- [25]. Wang HMJ, Lin IJB, Organometallics 17 (1998) 972.
- [26]. Jeffery GA, An Introduction to Hydrogen Bonding, Oxford University Press, Oxford, 1997.
- [27]. Steiner T, Angew. Chem., Int. Ed 41 (2002) 48.
- [28]. Cohen T, Bennett DA, Mura AJJ, J. Org. Chem 41 (1976) 2507.
- [29]. Alder RW, Allen PR, Williams SJ, Chem. Commun (1995) 1267.
- [30]. Cordero B, Gómez V, Platero-Prats AE, Revés M, Echeverría J, Cremades E, Alvarez S. Barragán, Dalton Trans (2008) 2832–2838. [PubMed: 18478144]
- [31]. Caballero A, Díez-Barra E, Jalón FA, Merino S, Rodríguez AM, Tejeda J, J. Organomet. Chem 627 (2001) 263.
- [32]. Garrison JC, Youngs WJ, Chem Rev. 105 (2005) 3978. [PubMed: 16277368]

- [33]. Lin IJB, Vasam CS, Coord. Chem. Rev 251 (2007) 642.
- [34]. Pugh D, Danopoulos AA, Coord. Chem. Rev 251 (2007) 610.
- [35]. Poater A, Ragone F, Giudice S, Costabile C, Dorta R, Nolan SP, Cavallo L, Organometallics 27 (2008) 2679.
- [36]. Guzei IA, Wendt M, Dalton Trans. (2006) 3991. [PubMed: 17028708]
- [37]. Poater A, Cosenza B, Correa A, Giudice S, Ragone F, Scarano V, Cavallo L, Eur. J. Inorg. Chem (2009) 1759.
- [38]. Andrade GA, Pistner AJ, Yap GPA, Lutterman DA, Rosenthal J, J. ACS Catalysis 3 (2013) 1685.
- [39]. Teesdale JJ, Pistner AJ, Yap GPA, Ma Y-Z, Lutterman DA, J. Rosenthal Catalysis Today 225 (2014) 149.
- [40]. DiMeglio JL, Rosenthal J, J. Am. Chem. Soc 135 (24) (2013) 8798. [PubMed: 23735115]
- [41]. Medina-Ramos J, DiMeglio JL, Rosenthal J, J. Am. Chem. Soc 136 (23) (2014) 8361. [PubMed: 24783975]
- [42]. Medina-Ramos J, Pupillo RC, Keane TP, DiMeglio JL, Rosenthal J, J. Am. Chem. Soc 137 (15) (2015) 5021. [PubMed: 25697668]
- [43]. Zhang Z, Chi M, Veith GM, Zhang P, Lutterman DA, Rosenthal J, Overbury SH, Dai S, Zhu H, ACS Catalysis 6 (2016) 6255.
- [44]. Bhugun I, Lexa D, Savéant J-M, J. Phys. Chem 100 (1996) 19981.

Fig. 1.

The general naming and numbering scheme for the set of palladium complexes discussed in this work.

Fig. 2.

(a) Solid-state crystal structure of complex $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{Br})_3]$, with thermal ellipsoids shown at 50% probability. All hydrogen atoms except for H11 have been omitted for clarity.

(b) Solid-state crystal structure of $[((\text{PDC}^{\text{Cy}})\text{AgBr})_2\text{Ag}]\text{Br}$ with thermal ellipsoids shown at 30% probability. All hydrogen atoms and an outersphere Br^- counter anion are omitted for clarity.

Fig. 3.

- (a) The general numbering scheme used to label the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{NCMe})](\text{PF}_6)_2$ thermal ellipsoid plots, except for the $\text{R} = \text{Mes}$ and DiPP complexes, which contain mirror planes down the center of the structures such that $\text{C1}=\text{C11}$, $\text{N1}=\text{N5}$, $\text{C2}=\text{C10}$, $\text{C3}=\text{C9}$, $\text{N2}=\text{N4}$, etc.
- (b) Solid-state crystal structures of each $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complex. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms and PF_6^- counterions have been omitted for clarity.

Fig. 4.

Images obtained from the Solid G application for $[(\text{PDC}^{\text{Me}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ and $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes. The shaded blue regions represent the portion of the sphere surrounding these complexes that is shielded by the corresponding PDC^{R} ligands. (Color online.)

Fig. 5. Cyclic voltammograms (CVs) recorded for (a) $[(\text{PDC}^{\text{Et}})\text{Pd}(\text{NCMe})](\text{PF}_6)_2$, (b) $[(\text{PDC}^{\text{Cy}})\text{Pd}(\text{NCMe})](\text{PF}_6)_2$, (c) $[(\text{PDC}^{\text{Mes}})\text{Pd}(\text{NCMe})](\text{PF}_6)_2$, and (d) $[(\text{PDC}^{\text{Dipp}})\text{Pd}(\text{NCMe})](\text{PF}_6)_2$ in DMF containing 0.1 M TBAPF₆ under an atmosphere of N₂ (black traces) or CO₂ (red traces). (Color online.)

Scheme 1.

Synthetic pathways used to prepare the library of $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes used in this study.

Table 1

Selected bonding metrics for the series of $[(\text{PDC}^{\text{R}}\text{Pd}(\text{MeCN}))(\text{PF}_6)_2]$ complexes shown in Fig. 3.

	$[(\text{PDC}^{\text{R}}\text{Pd}(\text{MeCN}))(\text{PF}_6)_2]$					
	R = Me	R = Et	R = <i>i</i>Pr	R = Cy	^aR = Mes	^aR = Dipp
C1–Pd (Å)	2.030	2.029	2.039	2.038	2.016	2.019
N3–Pd (Å)	1.961	1.966	1.961	1.963	1.957	1.959
C11–Pd (Å)	2.031	2.034	2.040	2.040	2.035	2.019
N6–Pd (Å)	2.003	2.004	2.002	2.003	1.999	2.008
C2–C3 (Å)	1.338	1.325	1.339	1.329	1.338	1.347
C9–C10 (Å)	1.347	1.335	1.336	1.334	1.337	1.347
C1–Pd–C11 (°)	158.85	158.31	158.45	158.46	157.94	158.52
N3–Pd–N6 (°)	178.97	177.49	178.93	173.86	178.23	180.00

^aThe mesityl and diisopropylphenyl complexes lie on a mirror plane in the solid-state, which makes C1–Pd equivalent to C11–Pd, and C2–C3 equivalent to C9–C10 for these two structures.

Calculated values correlating to steric bulk around the metal center for each of the $[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$ complexes of Fig. 3.

Table 2

	$[(\text{PDC}^{\text{R}})\text{Pd}(\text{MeCN})](\text{PF}_6)_2$					
	R = Me	R = Et	R = ⁱPr	R = Cy	R = Mes	R = Dipp
G(L)PDC (%)	51.45	53.21	54.63	54.51	62.60	69.43
G(L)MeCN (%)	17.46	17.47	17.49	17.47	17.13	17.35
Sum G(L) (%)	68.91	70.68	72.12	71.98	79.73	86.78
G(L)Complex (%)	67.42	68.29	69.05	68.77	73.89	80.53
V _{Bur} (PDC ^R) (%)	51.5	52.8	53.8	51.9	57.1	63.4

G-values and %V_{Bur}(PDCR) values were calculated using the applications Solid G and SambVca, respectively.

Table 3

Electrochemistry data recorded for [(PDC^R)Pd(MeCN)](PF₆)₂ complexes.

Complex	^a <i>E</i> _{red} (1) (V)	^a <i>E</i> _{red} (2) (V)	^b <i>I</i> _p
[(PDC ^{Et})Pd(NCMe)](PF ₆) ₂	−0.90	−1.21	~0
[(PDC ^{Cy})Pd(NCMe)](PF ₆) ₂	−0.95	−1.28	~0
[(PDC ^{Mes})Pd(NCMe)](PF ₆) ₂	−0.96	−1.25	5.17
[(PDC ^{Dipp})Pd(NCMe)](PF ₆) ₂	−0.94	−1.25	7.10

^a Recorded in DMF containing 0.1 M TBAPF₆ under an atmosphere of N₂.

^b Difference in current response at *E*_{red}(2) under CO₂ vs. under N₂. All potentials referenced to Ag/AgCl.