

Mono- and Dinuclear Binding Modes of the 2,5-Bis( $\alpha$ -pyridyl)pyrrolate Ligand in Platinum(II) Complexes

Drew C. Newman, Michael R. Gau, Patrick J. Carroll, and Karen I. Goldberg\*

Cite This: *Organometallics* 2021, 40, 1806–1810

Read Online

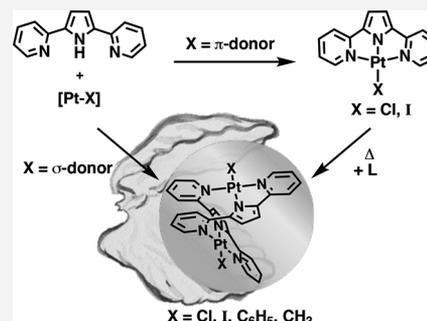
ACCESS |

Metrics &amp; More

Article Recommendations

Supporting Information

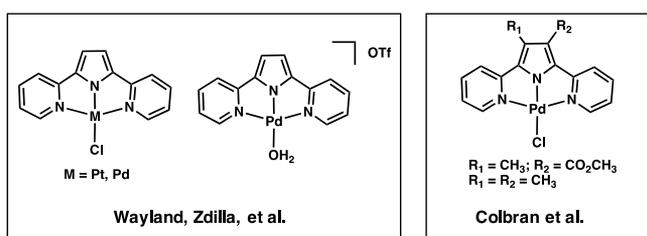
**ABSTRACT:** A series of platinum(II) complexes with the 2,5-bis( $\alpha$ -pyridyl)pyrrolate (PDP) ligand were synthesized. The ligand (X) trans to the central pyrrole nitrogen of PDP was found to play a key role in whether tridentate monomeric or bidentate clamshell dimer complexes were formed. When X = CH<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>, strong  $\sigma$ -donor ligands, only dimeric clamshell structures were observed. In contrast, when X = Cl or I, ligands with  $\pi$ -donor properties, both dimeric and monomeric complexes could be prepared. The ability of the ligand framework to support monomeric complexes with  $\pi$ -donor X-type ligands is attributed to the PDP ligand's ability to act as a competent  $\pi$ -acid in the monomeric conformation.



Multidentate nitrogen donor ligands have long been used to provide high stability to metal complexes. Terpyridine (terpy), with its electron-rich nitrogen donors and redox-active properties, has proven to be a particularly popular choice as a tridentate ligand.<sup>1,2</sup> In contrast, use of the closely related 2,5-bis( $\alpha$ -pyridyl)pyrrolate (PDP) ligand has been much less common.<sup>3</sup> PDP is structurally similar to terpy; it is a tridentate ligand containing coordinating nitrogen atoms embedded within a three-ring delocalized  $\pi$  backbone. However, the central pyrrole nitrogen of the PDP ligand is anionic and, thus, may be expected to exhibit stronger  $\sigma$ -donation than its terpy analog. In contrast to the well-known terpy ligand, there are only two reports of square-planar platinum or palladium PDP-ligated complexes.<sup>4–6</sup> The published PDP complexes are the monomeric Pt/Pd–Cl or aquo species as shown in Figure 1. With only these examples to date, little is known about the bonding and the reactivity of PDP-ligated platinum and palladium complexes. In this contribution, we report a series of new PDP-ligated platinum-alkyl, aryl, and halide complexes. The identity of the X ligand (X = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, Cl, and I) in (PDP)Pt–X complexes emerges as a determining factor in

whether monomeric square planar or dimeric clamshell complexes are formed.

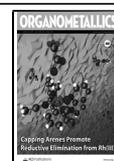
The 2,5-bis( $\alpha$ -pyridyl)pyrrolate (PDP-H) ligand was prepared according to literature procedure.<sup>4</sup> Treatment of a benzene solution of PDP-H with 0.5 equiv of [Pt(CH<sub>3</sub>)<sub>2</sub>( $\mu$ -S(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>] and heating to 100 °C resulted in formation of the dimer species, [(PDP)Pt–CH<sub>3</sub>]<sub>2</sub> (**1**, 59% isolated yield, Scheme 1). Single crystals of **1** suitable for X-ray diffraction were obtained from benzene, and the solid-state structure displays a clamshell dimer of C<sub>2</sub> symmetry (Figure 2a). In dimer **1**, each PDP ligand is bound in a  $\kappa^2$  manner through pyridine and pyrrole nitrogens to one platinum center, while the remaining pyridine nitrogen coordinates  $\kappa^1$  to the second platinum center. This mode of binuclear PDP ligand binding has not previously been reported<sup>3</sup> and differs from the mononuclear  $\kappa^3$  chelation reported by Wayland, Zdilla, and co-workers (Figure 1).<sup>4</sup> The binding of the PDP ligand to form a clamshell dimer complex is somewhat similar to that of a report by Puddephatt and co-workers of a Pt–CH<sub>3</sub> dimer with an NNN type ligand bound  $\kappa^2$  to one metal center and  $\kappa^1$  to another.<sup>7</sup> However, the geometrical configuration of the binding sites on the 6-dppd ligand (6-dppd = 1,4-di-2-pyridyl-5,6,7,8,9,10-hexahydrocycloocta[*d*]pyridazine) used in that system definitively prohibits  $\kappa^3$ -chelation to a single metal center.



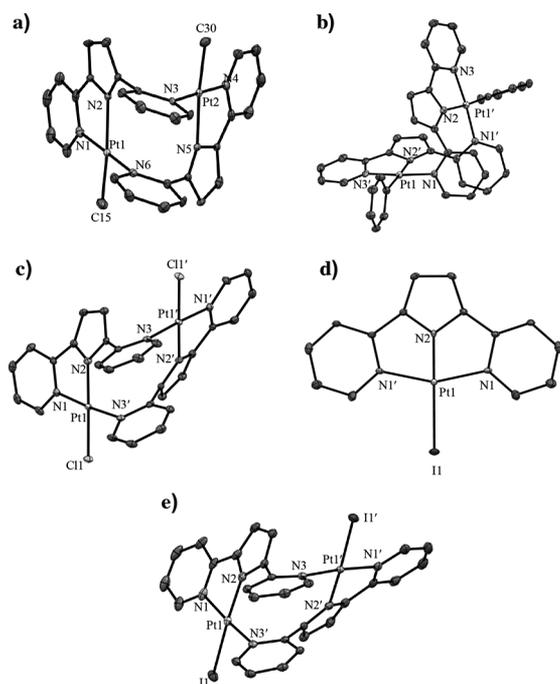
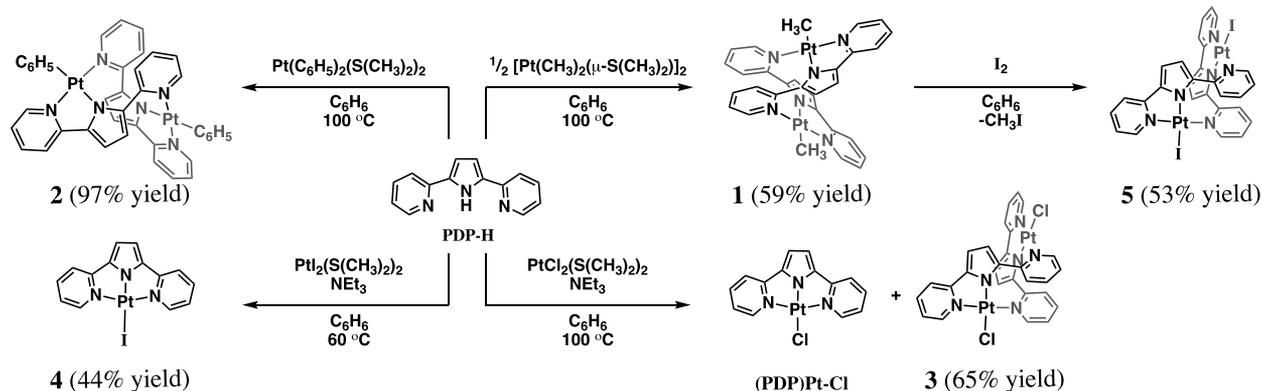
**Figure 1.** Previously reported PDP-ligated platinum and palladium complexes.<sup>4,5</sup>

Received: March 11, 2021

Published: June 7, 2021



## Scheme 1. Synthesis of Complexes 1–5



**Figure 2.** Thermal ellipsoid plots of 1–5 with ellipsoids set to 50% probability. Hydrogens omitted for clarity. (a) 1 [(PDP)Pt–CH<sub>3</sub>]<sub>2</sub>; (b) 2 [(PDP)Pt–C<sub>6</sub>H<sub>5</sub>]<sub>2</sub>; (c) 3 [(PDP)Pt–Cl]<sub>2</sub>; (d) 4 (PDP)Pt–I; (e) 5 [(PDP)Pt–I]<sub>2</sub>.

The Pt centers in **1** are offset in the solid-state structure, inhibiting any Pt–Pt interaction. Both <sup>1</sup>H and <sup>13</sup>C NMR spectral data are consistent with **1** maintaining its dimeric formulation in solution (see the Supporting Information). It should also be noted that production of the dimeric complex **1** was not simply the result of using a dimeric Pt starting material, as the same dimer product was also synthesized using the monomeric Pt–CH<sub>3</sub> starting materials [Pt–(CH<sub>3</sub>)<sub>2</sub>(DMSO)<sub>2</sub>] and [Pt(CH<sub>3</sub>)<sub>2</sub>(COD)] (COD = 1,4-cyclooctadiene).

The phenyl analog of Pt–CH<sub>3</sub> dimer **1**, [(PDP)Pt–C<sub>6</sub>H<sub>5</sub>]<sub>2</sub> (**2**), was similarly formed by treating PDP-H with 1 equiv of the monomeric platinum complex, *cis*-Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(S(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>, in benzene at 100 °C (Scheme 1, top left). Crystals of **2** suitable for single crystal X-ray diffraction were obtained from benzene, and as shown in Figure 2b, the structure is very similar to that of **1**. Of note, the phenyl ring in **2** is oriented nearly perpendicular to the plane comprised of each (PDP)Pt

unit. The bond between Pt and the central pyrrole nitrogen (Pt–N<sub>pyrr</sub>) of **2** is slightly shorter (2.102 Å) than that of **1** (2.196 Å, Table 1).

Wayland and Zdilla reported the monomeric chloride complex (PDP)Pt–Cl, which they isolated in a 21% yield from the reaction of PDP-H, PtCl<sub>2</sub>(COD), and triethylamine (NEt<sub>3</sub>) in refluxing THF (66 °C).<sup>4</sup> We found that when PDP-H was combined with 1 equiv of PtCl<sub>2</sub>(S(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> and 4 equiv of NEt<sub>3</sub> in benzene and heated to 100 °C, a heterogeneous mixture containing both the monomeric (PDP)Pt–Cl and the dimeric species [(PDP)Pt–Cl]<sub>2</sub> (**3**) was formed (Scheme 1, bottom right). The <sup>1</sup>H NMR data for the monomeric (PDP)Pt–Cl matched the literature report.<sup>4</sup> The dimeric [(PDP)Pt–Cl]<sub>2</sub> complex, **3**, was isolated in 65% yield. A single-crystal X-ray diffraction study found a dimer structure for **3** similar to that of **1** and **2** (Figure 2c). When the Pt–Cl dimer structure of **3** was compared to its monomeric κ<sup>3</sup> analog, the central Pt–N<sub>pyrr</sub> bond was found to be longer (2.013 Å) than that of the monomeric complex (1.893 Å,<sup>4</sup> Table 1).

**Table 1.** Pt–N<sub>pyrr</sub> Bond Lengths for Complexes 1–5 and the Reported (PDP)Pt–Cl Complex<sup>4</sup>

Complex	Pt–N <sub>pyrr</sub> bond length (Å)	
	1: X = CH <sub>3</sub>	2.196(5)
	2: X = C <sub>6</sub> H <sub>5</sub>	2.102(3)
	5: X = I	2.031(2)
	3: X = Cl	2.013(2)
		4: X = I
Lit: X = Cl		1.893(5)

The monomeric iodide, (PDP)Pt–I (**4**) was formed by heating equivalent amounts of PDP-H and PtI<sub>2</sub>(S(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> together with 4 equiv of NEt<sub>3</sub> in benzene to 60 °C (Scheme 1, bottom left, 44% isolated yield). An X-ray crystal structure clearly shows a monomeric structure for **4** with a tridentate κ<sup>3</sup>-PDP ligand and the iodide in a square planar configuration about the platinum center (Figure 2d). The solid-state

structure of **4** displays a Pt–N<sub>pyrr</sub> bond length of 1.823 Å, which is slightly shorter than that in (PDP)Pt–Cl monomeric complex (1.893 Å,<sup>4</sup> Table 1).

The dimeric iodide complex [(PDP)Pt–I]<sub>2</sub> (**5**) was not observed as a product of the reaction of PDP–H with PtI<sub>2</sub>(S(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>. However, it was found that the dimeric iodide complex could be prepared by treatment of the dimeric methyl complex **1** with I<sub>2</sub> (Scheme 1). As observed by <sup>1</sup>H NMR spectroscopy, this reaction proceeded to form dimeric iodide complex **5** and CH<sub>3</sub>I, with no evidence of **4**. Compound **5** was isolated in 53% yield, and single-crystal X-ray diffraction confirmed its dimeric structure (Figure 2e). The Pt–N<sub>pyrr</sub> bond length was determined to be 2.031 Å. Similar to the chloride complexes, the Pt–N<sub>pyrr</sub> bond for dimeric iodide **5** is longer than in corresponding monomeric iodide **4**. Notably, however, while the Pt–N<sub>pyrr</sub> bond for monomeric iodide **4** is shorter than that of the monomeric chloride, the situation is reversed for the dimeric species where the Pt–N<sub>pyrr</sub> bond in dimeric iodide **5** is longer than that of dimeric chloride **3** (Table 1).

Comparison of the solid-state structures of **1**–**5** along with the reported monomeric (PDP)Pt–Cl complex reveals that the identity of the X group plays a significant role in the stabilization of the monomeric vs dimeric motifs. When X is a strong σ-donor and a poor π-donor (X = CH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>), only dimeric structures are observed. The strong trans influence enacted by these types of X ligands would be expected to promote elongation of the trans Pt–N<sub>pyrr</sub> bond (Table 1) and, as such, disfavor coordination of the third nitrogen atom in the PDP ligand to the same metal center. Rotation of the pyridine arm allows for the coordination to a second platinum center, resulting in a clamshell dimer complex.

When X = Cl and I (weaker field ligands displaying π-donor properties), both monomeric and dimeric complexes are observed. In the monomeric halide complexes, the Pt–N<sub>pyrr</sub> bond length is significantly shorter than observed in the dimeric analogs (Table 1). The shorter trans Pt–N<sub>pyrr</sub> bond allows for all three nitrogen atoms of the PDP ligand to coordinate to the same platinum center. The apparent stabilization of the pyrrole-platinum interaction in the monomeric complexes is likely a consequence of the ability of the PDP ligand to act as a π-acid which is enhanced by π-donation from the halide ligands.<sup>3,4</sup> Of note, the Pt–N<sub>pyrr</sub> bond is shorter for X = I than for X = Cl,<sup>8</sup> which is contrary to what might be expected based on either the trans influence<sup>9</sup> or the π-donor abilities of the halide ligands.<sup>10,11</sup> Although the shorter trans Pt–N<sub>pyrr</sub> bond observed for X = I is unusual, a similar observation was recently reported with respect to the Ni–C bond length in a series of monomeric 1,3-di(2-pyridyl)phenyl Ni–X (X = Cl, Br, and I) complexes.<sup>12</sup>

The formation of both monomeric and dimeric (PDP)Pt–X complexes contrasts the coordination preferences previously observed with the terpy ligand, which favors monomeric Pt–X complexes regardless of the identity of the fourth (X) ligand. It is notable that the bite angles for terpy square planar complexes and PDP square planar complexes are approximately 81 and 78° respectively.<sup>13</sup> The smaller bite angles in the PDP system presumably introduce more strain which is somewhat relieved in the dinuclear coordination mode.<sup>14</sup>

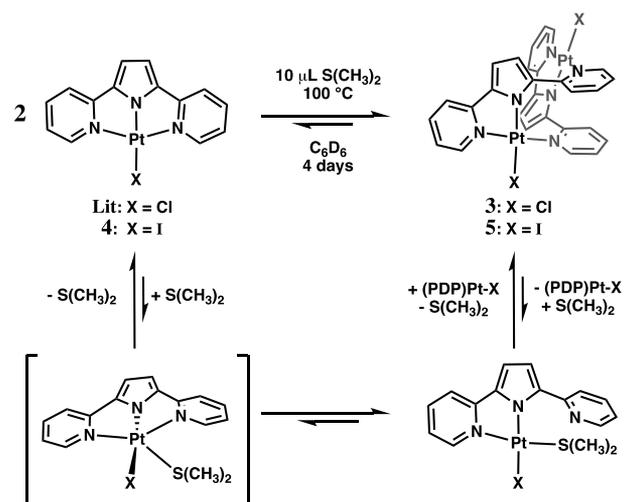
Solutions of the monomeric (PDP)Pt–Cl or dimeric **3** in common laboratory solvents (e.g., chlorocarbons, acetone, and arenes) are stable at room temperature, indicating that there is

a reasonable kinetic barrier for interconversion. To investigate whether interconversion is possible between the monomer and dimer complexes, a homogeneous solution of the monomeric (PDP)Pt–Cl was heated in dry toluene. No changes were observed by UV–vis spectroscopy when the solution was heated to 100 °C for several days. However, upon the addition of a donor ligand, L (L = H<sub>2</sub>O, CH<sub>3</sub>OH, and DMF), new absorbance features corresponding to the dimer, **3**, were observed. The poor solubility of **3** resulted in precipitation; thus, it was not possible to determine K<sub>eq</sub> for the reaction.

Further studies to investigate monomer and dimer interconversion were carried out using <sup>1</sup>H NMR spectroscopy. Similar to the UV–vis studies, the addition of a donor ligand was found to facilitate the interconversion, and poor solubility of the complexes prevented determination of K<sub>eq</sub>. When suspensions of pure monomer (either (PDP)Pt–Cl or iodide **4**) were heated at 100 °C in C<sub>6</sub>D<sub>6</sub> for 4 days (the solvent originally used during metalation experiments), no evidence of the dimeric species was observed.<sup>15</sup> However, when suspensions of pure monomer (either (PDP)Pt–Cl or the iodide **4**) in C<sub>6</sub>D<sub>6</sub> were heated for 4 days at 100 °C with added exogenous donor ligand S(CH<sub>3</sub>)<sub>2</sub> (10 μL), dimer formation was detected. In the case of the iodide (**4**/**5**), some **5** was directly detected by <sup>1</sup>H NMR in the C<sub>6</sub>D<sub>6</sub> reaction mixture. However, in the case of the less soluble chloride system, detection of dimer **3** required removal of the volatiles under reduced pressure followed by dissolution of the residue in CDCl<sub>3</sub>. Thermolysis of the monomeric Pt–Cl complex directly in CDCl<sub>3</sub> provided similar results, with formation of dimeric **3** only observed in the presence of exogenous ligand. It was also found that when suspensions of dimeric Pt–Cl complex **3** in CDCl<sub>3</sub> or dimeric Pt–I complex **5** in C<sub>6</sub>D<sub>6</sub> were heated at 100 °C for 4 days no conversion to the monomer was observed, even with addition of S(CH<sub>3</sub>)<sub>2</sub> (10 μL).

The addition of S(CH<sub>3</sub>)<sub>2</sub> to the monomer solutions of (PDP)Pt–X (X = Cl and I) was important in facilitating the conversion of monomer to dimer. This result is consistent with S(CH<sub>3</sub>)<sub>2</sub> acting as an incoming ligand to displace one arm of the PDP ligand in an associative substitution mechanism as shown in Scheme 2.<sup>9,16,17</sup> The dissociated pyridine arm can

**Scheme 2. Proposed Mechanism for Conversion of Monomer to Dimer Promoted by Addition of Dimethylsulfide**



then act as the incoming ligand to a second metal center to form the dimer product. While limited solubility thwarted measurement of  $K_{\text{eq}}$  for this reaction, our observations of monomer conversion to dimer, but not dimer conversion to monomer imply that dimeric Pt–Cl and Pt–I complexes **3** and **5** are thermodynamically preferred over their monomeric analogs. The higher temperatures used in the syntheses of dimeric halide complexes **3** and **5** as well as the change in Pt starting materials (from  $\text{PtCl}_2(\text{COD})^4$  to  $\text{PtCl}_2(\text{S}(\text{CH}_3)_2)_2$ ) could explain why previously only a monomeric (PDP)Pt–Cl complex<sup>4</sup> was reported. It is notable, however, that monomeric PDP complexes with Pt– $\text{CH}_3$  or Pt– $\text{C}_6\text{H}_5$  groups remain unknown.

In conclusion, both monomeric (PDP)Pt–X and dimeric [(PDP)Pt–X]<sub>2</sub> complexes were synthesized and fully characterized. The ability of the PDP–H ligand to form both monomeric and dimeric complexes when X has  $\pi$ -donor properties (X = Cl and I) is rationalized on the basis that the PDP ligand can act as a competent  $\pi$ -acid in monomeric square-planar PDP-ligated platinum complexes. In the presence of an exogenous ligand and at elevated temperatures, the monomeric halide complexes undergo an associative substitution to form the thermodynamically favored dimeric species. When X is a strong  $\sigma$ -donor (X =  $\text{CH}_3$  and  $\text{C}_6\text{H}_5$ ), the dimeric [(PDP)Pt–X]<sub>2</sub> complex is formed exclusively, and no evidence of the monomeric complexes was detected. The ability to influence the formation of monomeric or dimeric complexes based on the identity of X in (PDP)Pt–X complexes is not a characteristic of terpy-ligated metal complexes<sup>18,19</sup> and highlights a key difference between these seemingly analogous ligand systems.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.1c00152>.

Synthesis and characterization of the metal complexes, experimental procedures and NMR spectra for interconversion of the halide monomers and dimers, X-ray crystallography tables (PDF)

## Accession Codes

CCDC 2057079–2057083 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## ■ AUTHOR INFORMATION

### Corresponding Author

**Karen I. Goldberg** – Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States; [orcid.org/0000-0002-0124-1709](https://orcid.org/0000-0002-0124-1709); Email: [kig@sas.upenn.edu](mailto:kig@sas.upenn.edu)

### Authors

**Drew C. Newman** – Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States; [orcid.org/0000-0002-3736-5367](https://orcid.org/0000-0002-3736-5367)

**Michael R. Gau** – Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States; [orcid.org/0000-0002-4790-6980](https://orcid.org/0000-0002-4790-6980)

**Patrick J. Carroll** – Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States; [orcid.org/0000-0002-8142-7211](https://orcid.org/0000-0002-8142-7211)

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.organomet.1c00152>

## Funding

This work was supported by the National Science Foundation (CHE-1856547), by the University of Pennsylvania, and by the Vagelos Institute for Energy Science and Technology with a fellowship to D.C.N.

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank Dr. Charles W. Ross III for providing mass spectral method development, analyses, and data interpretation. Dr. Jun Gu and Dr. Chad Lawrence are thanked for their assistance in obtaining  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra. Lynn M. Newman is thanked for artistic contributions to the table of contents graphic. This work was supported by the National Science Foundation under Grant CHE-1856547, the University of Pennsylvania, and the Vagelos Institute for Energy Science and Technology (fellowship to D.C.N.). The NSF Major Research Instrumentation Program (award NSF CHE-1827457), the NIH supplements awards 3R01GM118510-03S1 and 3R01GM087605-06S1, and Vagelos Institute for Energy Science and Technology supported the purchase of the NMRs used in this study.

## ■ REFERENCES

- (1) Hofmeier, H.; Schubert, U. S. Recent developments in the supramolecular chemistry of terpyridine-metal complexes. *Chem. Soc. Rev.* **2004**, *33*, 373.
- (2) Mills, I. N.; Porras, J. A.; Bernhard, S. Judicious Design of Cationic, Cyclometalated Ir(III) Complexes for Photochemical Energy Conversion and Optoelectronics. *Acc. Chem. Res.* **2018**, *51*, 352.
- (3) McPherson, J. N.; Das, B.; Colbran, S. B. Tridentate pyridine–pyrrolide chelate ligands: An under-appreciated ligand set with an immensely promising coordination chemistry. *Coord. Chem. Rev.* **2018**, *375*, 285–332.
- (4) Imler, G. H.; Lu, Z.; Kistler, K. A.; Carroll, P. J.; Wayland, B. B.; Zdilla, M. J. Complexes of 2,5-Bis( $\alpha$ -pyridyl)pyrrolate with Pd(II) and Pt(II): A Monoanionic Iso- $\pi$ -Electron Ligand Analog of Terpyridine. *Inorg. Chem.* **2012**, *51*, 10122.
- (5) McSkimming, A.; Diachenko, V.; London, R.; Olrich, K.; Onie, C. J.; Bhadbhade, M. M.; Bucknall, M. P.; Read, R. W.; Colbran, S. B. An easy one-pot synthesis of diverse 2,5-di(2-pyridyl)pyrroles: A versatile entry point to metal complexes of functionalised, meridial and tridentate 2,5-di(2-pyridyl)pyrrolato ligands. *Chem. - Eur. J.* **2014**, *20* (36), 11445.
- (6) Sotoyama and coworkers have claimed the synthesis of several monomeric PDP-ligated Pt complexes in a 2007 patent, however no characterization data is provided. Sotoyama, W.; Satou, T.; Sato, H.; Matsuura, A.; Sawatari, N. Metal Complex, Luminescent Solid, Organic EL Element and Organic EL Display. US 20070296329A1, 2007; pp 21–23.
- (7) McCready, M. S.; Puddephatt, R. J. Self-assembly of isomeric clamshell dimers of platinum(II). *Dalt. Trans.* **2012**, *41*, 12378.
- (8) The monomeric crystals (X = Cl and I, **4**) were collected under slightly different conditions (143 K for X = Cl and 100 K for X = I). Complex **4** crystallized on two mutually intersecting mirror planes. The atoms I, Pt, and N2 in **4** lie on the intersection of the two planes and are not disordered.

(9) Hartwig, J. F. *Organotransition Metal Chemistry From Bonding to Catalysis*; University Science Books, 2010.

(10) Flemming, J. P.; Pilon, M. C.; Borbulevitch, O. Y.; Antipin, M. Y.; Grushin, V. V. The trans influence of F, Cl, Br and I ligands in a series of square-planar Pd(II) complexes. Relative affinities of halide anions for the metal centre in trans-[(Ph<sub>3</sub>P)<sub>2</sub>Pd(Ph)X]. *Inorg. Chim. Acta* **1998**, *280* (1–2), 87.

(11) Fagnou, K.; Lautens, M. Halide effects in transition metal catalysis. *Angew. Chem., Int. Ed.* **2002**, *41* (1), 26.

(12) Kletsch, L.; Horner, G.; Klein, A. Cyclometalated Ni(II) Complexes [Ni(N<sup>^</sup>C<sup>^</sup>N)X] of the Tridentate 2,6-di(2-pyridyl)phenide Ligand. *Organometallics* **2020**, *39*, 2820.

(13) A search of the CCDC (November 2020, version 5.42, accessed May 2021) revealed 145 (terpy)Pt–Cl and 4 (terpy)Pt–I complexes. The average of the bite angles was calculated to be approximately 81°.

(14) The N1–Pt1–N2 bite angle in the dinuclear PDP-ligated complexes is approximately 80°.

(15) Due to the low solubility of the dimeric complexes in C<sub>6</sub>D<sub>6</sub>, to check whether dimer had formed, the volatiles were removed from the reaction mixture under reduced pressure, and the residue was dissolved in CDCl<sub>3</sub>, a solvent in which the dimeric complexes exhibit greater solubility. No evidence of dimer formation was found in the CDCl<sub>3</sub> <sup>1</sup>H NMR spectrum.

(16) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin Inc., 1966.

(17) New signals were noted in the <sup>1</sup>H NMR spectrum upon the addition of S(CH<sub>3</sub>)<sub>2</sub> to a suspension of (PDP)Pt–Cl (prior to heating the sample). The signals are consistent with the proposed κ<sup>2</sup>-bound (PDP)Pt(SMe<sub>2</sub>)Cl complex. However, this species was only stable in the presence of excess S(CH<sub>3</sub>)<sub>2</sub>. Removal of the solvent and S(CH<sub>3</sub>)<sub>2</sub> resulted in full conversion back to the (PDP)Pt–Cl monomer as evidenced by <sup>1</sup>H NMR spectroscopy (see Figure S19).

(18) Terpy has been reported to bind in a similar κ<sup>2</sup>,κ<sup>1</sup> manner to Ag to form dimeric complexes; however, the formation of these dimers is not dependent on the identity of other coordinated ligands. Mak, C. L.; Bostick, B. C.; Yassin, N. M.; Campbell, M. G. Argentophilic Interactions in Solution: An EXAFS Study of Silver(I) Nitrene Transfer Catalysts. *Inorg. Chem.* **2018**, *57*, 5720.

(19) There are no reported (terpy)Pt–CH<sub>3</sub> complexes which exhibit the same κ<sup>2</sup>,κ<sup>1</sup> form of ligand binding seen with the (PDP)Pt–CH<sub>3</sub> complexes. (a) Petersen, A. R.; Taylor, R. A.; Vicente-Hernández, I.; Mallender, P. R.; Olley, H.; White, A. J. P.; Britovsek, G. J. P. Oxygen Insertion into Metal Carbon Bonds: Formation of Methylperoxo Pd(II) and Pt(II) Complexes via Photogenerated Dinuclear Intermediates. *J. Am. Chem. Soc.* **2014**, *136*, 14089. (b) Arena, G.; Calogero, G.; Campagna, S.; Monsu Scolaro, L.; Ricevuto, V.; Romeo, R. Synthesis, Characterization, Absorption Spectra, and Luminescence Properties of Organometallic Platinum(II) Terpyridine Complexes. *Inorg. Chem.* **1998**, *37* (11), 2763. (c) Arena, G.; Scolaro, L. M.; Pasternack, R. F.; Romeo, R. Synthesis, Characterization, and Interaction with DNA of the Novel Metallointercalator Cationic Complex (2,2':6',2''-Terpyridine)methylplatinum(II). *Inorg. Chem.* **1995**, *34* (11), 2994. (d) Romeo, R.; Scolaro, L. M.; Plutino, M. R.; Albinati, A. Structural properties of the metallointercalator cationic complex (2,2':6',2''-terpyridine)methylplatinum(II) ion. *J. Organomet. Chem.* **2000**, *593–594*, 403. (e) Annibale, G.; Bergamini, P.; Bertolasi, V.; Bortoluzzi, M.; Cattabriga, M.; Pitteri, B. The Relative Coordinating Ability of Some Weak O-Donor Anions and Water Towards the [Pt(terpy)]<sup>2+</sup> (terpy = 2,2':6',2''-terpyridine) Center – X-ray Crystal Structures of [Pt(terpy)(H<sub>2</sub>O)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and [Pt<sub>2</sub>(μ-OH)(terpy)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>). *Eur. J. Inorg. Chem.* **2007**, *2007* (36), 5743.