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Complexes of 2,5-Bis(α-pyridyl)pyrrolate with Pd(II) and Pt(II): A Monoanionic Iso-π-Electron Ligand Analog of Terpyridine

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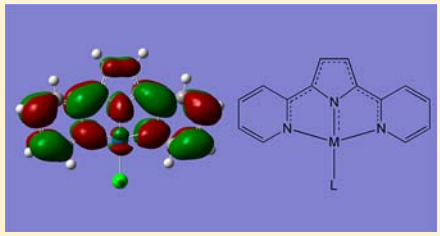
Supporting Information

ABSTRACT: Palladium and platinum metal complexes of 2,5-bis(α-pyridyl)-pyrrolate (PDP) are reported and characterized by spectroscopic methods, single-crystal X-ray diffraction, and elemental analysis. The single-crystal X-ray structures of these complexes exhibit structural features indicative of significant π-backbonding. To illustrate the effect, bond lengths are statistically compared to unmetalated PDP and to a previously reported Zn(II) complex that exhibits no backbonding. Density functional theory calculations are used to aid understanding of the electronic structural basis of the observed phenomena.



INTRODUCTION

Transition metal complexes of terpyridine (terpy)[1,2] and related 2,6-bisiminopyridine (bimpy)[3−5] derivatives are a rich source of materials as catalysts[6−10] and for technological applications on the basis of their unusual photophysical and electro-chemical properties.[11−17] Current interest in terpy and bimpy complexes primarily arises from the properties attributable to the 18-π electron system with relatively low energy π* molecular orbitals having a central role in the spectroscopic, redox, and π-backbonding properties. The extent of metal to terpy ligand π−backbonding can be observed by structural changes in the ligand[18−20] and is sufficiently large in some cases that the phenomenon could be better described as ligand reduction or noninnocent ligand behavior.[21−28]

Recently, 2,2′-pyridylpyrrolides have been developed as monoanionic 12-π electron analogs of bipyridine ligands.[29−33] Terpyridine is the neutral parent (N_3^0) for a series of 18-π electron $N_3^{0,-1,-2}$ ligands where pyrrole anions are substituted for neutral pyridines (Figure 1). The dipyridine pyrrolate[34,35]

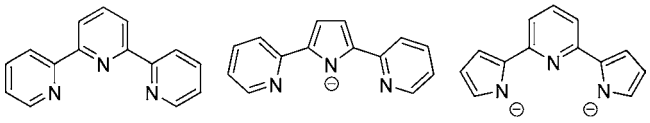


Figure 1. Pyridine- and pyrrole-based tridentate ligands.

and pyridine dipyrrolate[36] molecules are underdeveloped as ligands for transition metals when compared to the ubiquitous application of terpy ligands in transition metal coordination chemistry.[1] Pyrrole is a flexible π-ligand (Figure 2), exhibiting structural metrics in metal complexes indicative of either π-donor,[37−43] π-acceptor behavior,[44] or neither (aromaticity).[45−47] The 2,5-bis(α-pyridyl)pyrrolate ligand (PDP)

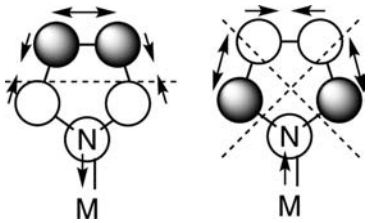


Figure 2. Pyrrole structural changes accompanied by π-donation from the occupied π orbital to the metal (left) and π-backbonding from the metal into the unoccupied π* orbital (right).

combines the π-backbonding capability of 18-π electron N_3 ligands with the flexible π-properties of pyrrolate[38−40] donors that permits versatile π-donor and π-acceptor responses to the metal site π-bonding properties. This article reports on the preparation and structural studies of Pd(II) and Pt(II) complexes of PDP (N_3^{-1}) as an initial comparative study of the mono anionic pyrrole dipyridine ligand with analogous terpyridine (N_3^0) complexes.

RESULTS AND DISCUSSION

The pyrrole dipyridine 2,5(di-α-pyridyl)pyrrole (H(PDP)) was prepared by a Paal-Knorr cyclization[48] and used in preparing (PDP)Pd−Cl (**1**), [(PDP)Pd(H_2O)] (CF_3SO_3) (**2**), and (PDP)Pt−Cl (**3**). Molecular structures for the neutral free ligand (H(PDP))[49] and complexes **1**, **2**, and **3** were determined by single-crystal X-ray diffraction and are shown in Figure 3, and selected bond lengths and angles for **1**−**3** are given in Table 1. The structure of the neutral free ligand (H(PDP)) exhibits a structure in which all of the nitrogen atoms are in the

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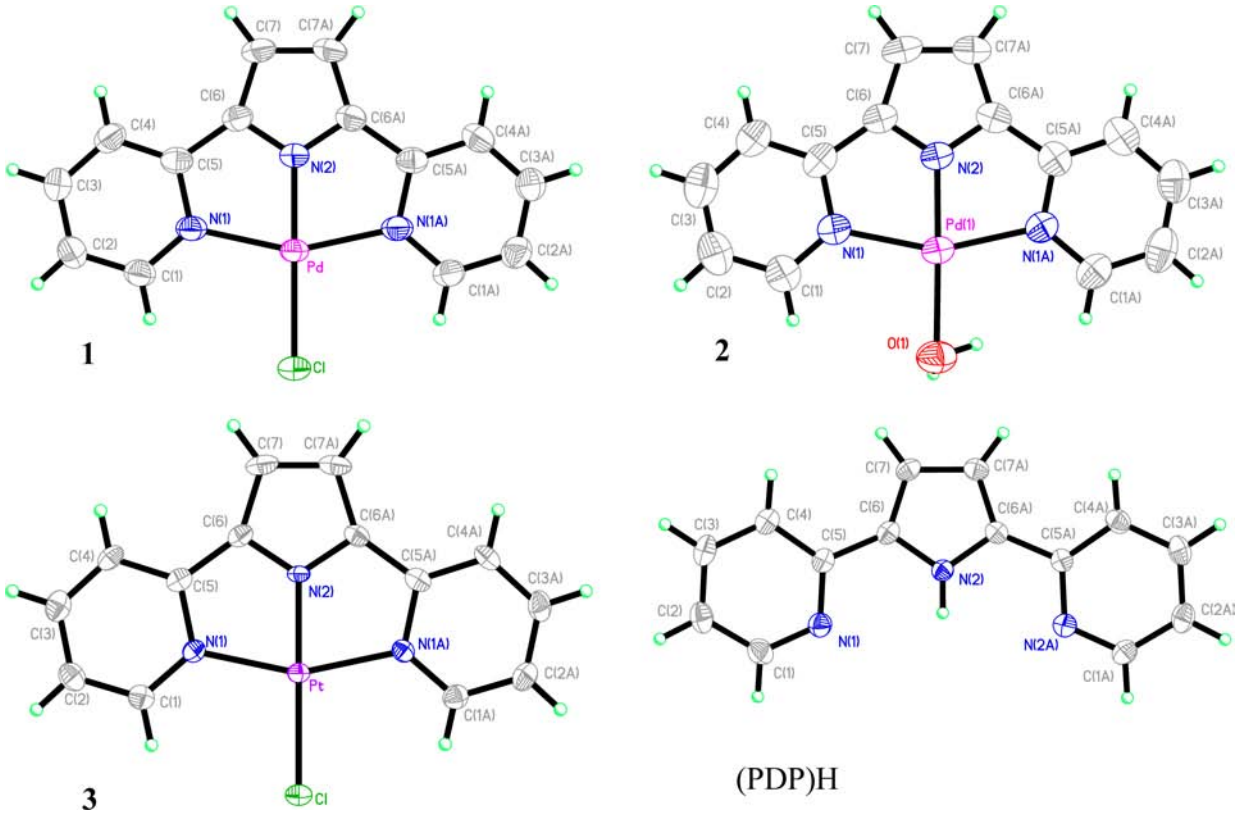

Figure 3. Structures of PDP ligand and metal complexes with thermal ellipsoids on non-hydrogen atoms. Hydrogen atoms shown as open circles. **1**: (PDP)PdCl in space group *C*2/*c* (50% probability level, molecule resides on a 2 operation). **2**: $[(PDP)Pd(H_2O)]^+$ in *P*1; (30% probability level, $CF_3SO_3^-$ counterion not shown). **3**: (PDP)PtCl in *C*2/*c* (50% probability level, molecule resides on a 2 operation). (PDP)H in $P2_12_12_1$: (50% probability level).

Table 1. Selected Bond Distances and Angles for 1, 2, and 3[a]

	(PDP)PdCl (**1**)	$(PDP)Pd(H_2O)(CF_3SO_3^-)$ (**2**)	(PDP)PtCl (**3**)	(PDP)H
M−N(1/2/1A)	2.073(5)/1.885(6)/2.073	2.078(5)/1.853(5)/ 2.084(5)	2.057(4)/1.893(5)/2.057(4)	NA
M−L[b]	2.330(2)	2.090(5)	2.334(2)	NA
N(1/2)−C(5/6)	1.377(7)/1.341(6)	1.387(8)/1.342(7)	1.390(6)/1.340(5)	1.3460(17)/1.3704(16)
N(1A/2)−C(5A/6A)	1.377(7)/1.341(6)	1.369(8)/1.348(8)	1.390(6)/1.340(5)	1.3493(17)/1.3677(16)
C(5/6/7)−C(6/7/7A)	1.461(8)/1.402(8)/ 1.400(13)	1.440(9)/1.421(9)/ 1.370(10)	1.449(6)/1.412(7)/ 1.400(10)	1.4590(18)/1.3792(19)/ 1.4116(18)
C(5A/6A)−C(6A/7A)	1.461(8)/1.402(8)	1.450(9)/1.403(9)	1.449(6)/1.412(7)	1.4605(17)/1.3854(18)
N(1/1A/1)−M−N(2/2/1A)	77.70(12)/77.71(12)/ 155.4(2)	78.1(2)/78.0(2)/156.1(2)	78.22(11)/78.22(11)/ 156.4(2)	NA
N(1/2/1A)−M−L[b]	102.30(12)/180.0/ 102.29(12)	100.6(2)/178.1(2)/ 103.3(2)	101.78(11)/180.0/ 101.78(11)	NA

[a]Divided entries refer to separate, related atoms and their associated metrics in the order given, e.g., N(1/2)−C(5/6) denotes 2 distances: N(1)−C(5) and N(2)−C(6). [b]L refers to the ligating atom of the 4th (monodentate) ligand, Cl or OH_2.

Z configuration, which is ascribed to dipole−dipole interactions between the pyrrole proton and the pyridyl nitrogens.

The PDP complexes of Pd(II) and Pt(II) (**1**−**3**) exhibit planar four coordinate structures where three coordination sites are occupied by the anionic PDP ligand (N_3^{-1}), and the fourth site contains a chloride or water molecule (Figure 4). The *trans*-N−M−N angles of ∼155° observed for **1**−**3** correspond with substantially distorted square planar complexes. The pincer type PDP (N_3^{-1}) ligand structure prohibits *cis*-N−M−N angles of 90° that are associated with an unstrained square planar donor site array. The metal−ligand metrics of the palladium and platinum complexes are similar with the exception that the metal bond to the pyrrole nitrogen is longer in the platinum complex. The M−N (pyridine) distances (2.06−2.08 Å) are substantially longer than M−N(pyrrolate) distances (1.85−1.89 Å) for complexes **1**−**3** as expected for neutral versus anionic donor sites. In all metal complexes, the molecules arrange such that the molecular planes π-stack with an interplanar distance of 3.35−3.4 Å. The molecules arrange such that molecules in intervening layers are arranged facing in opposite directions to one another, with the central pyrrole lying over the Pd−L bond of the molecule in the next layer (L = Cl, OH_2). In the case of complex **2**, there is additionally a hydrogen bond network between the bound water, lattice water molecule, and triflate

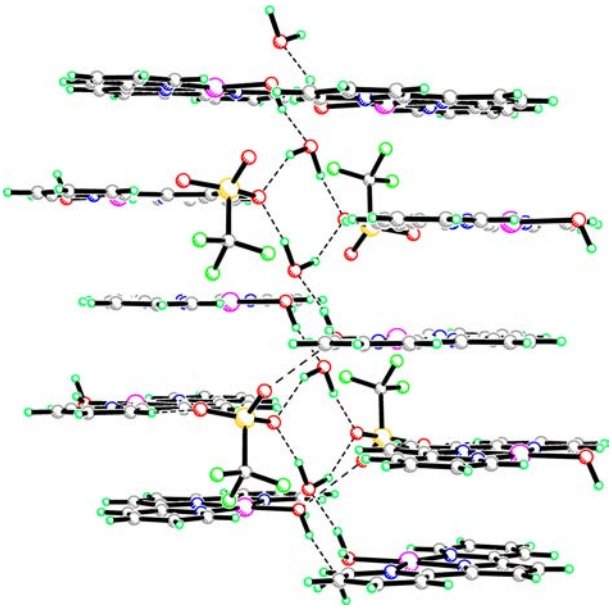

Figure 4. Crystal packing of complex **2** showing anti-arrangement of molecules in subsequent layers and interlayer hydrogen bonding network involving water ligand, water solvate, and triflate counterion.

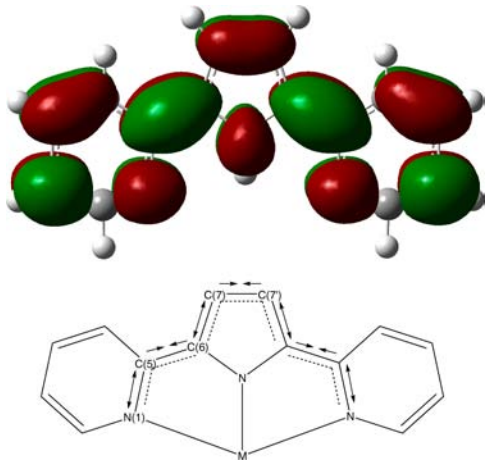

Figure 5. Top: LUMO of H(PDP) as determined by DFT, B3LYP using 6-31G* basis set. Bottom: Structural changes accompanied by π-backbonding to the LUMO of the 2,5-bis(α-pyridyl)pyrrolate ligand.

counterion, which interconnects the layers (Figure 4). Neighboring molecules in the free ligand (PDP)H are not π-stacked and have no hydrogen bonded intermolecular connections.

It is informative to compare the bond lengths in the PDP ligand for complexes **1**−**3** with those of the free ligand. Examination of Table 1 shows that the pyridine N−C bond distances increase by 0.028 to 0.044 Å compared to the free ligand, which is statistically significant by more than 3 standard deviations. The C(6)−C(7) pyrrole bonds lengthen significantly by 0.017−0.042 Å, and the C(7)−C(7A) pyrrole bonds shortens by 0.012−0.044 Å. The presence of alternating long−short−long bond lengths in the reported complexes suggest significant population of the π^* LUMO of the ligand with d-electrons. Comparison of complexes **1** and **2** indicate an increased amount of π-backbonding in the aqua-ligated complex **2** compared to the chloride-ligated complex **1**. This is consistent with the observation of a shorter Pd−N(1) bond in **2**, which is expected for the increased bond order in the metal−nitrogen bond resulting from π-backbonding. This property is most likely the result of the cationic charge of **2**, resulting in stronger σ-donation in **2**, and in turn, increased π-backdonation to the PDP ligand. The effect of population of the LUMO orbital from Density Functional Theory (DFT) calculations, using the B3LYP functional and the 6-31G* basis set, is shown in Figure 5.

Metrics of Pd and Pt complexes with PDP may be compared to structures of these metals with the analogous neutral terpyridine ligand. Qualitatively, a similar effect is seen in terpy involving lengthening of the terminal pyridine N−C bond and shortening of the inter-ring biaryl lengths. However, quantitatively, these bond length differences are not as drastic as seen in the PDP ligand.[50−54] For instance, while some terpyridyl N−C distances lengthened substantially, they very typically have a value of 1.37 Å or less, whereas PDP complexes lengthen to 1.38−1.39 Å. The changes in inter-ring biaryl C−C distances only shorten to 1.47 Å typically, while the analogous bonds in PDP are shorter at 1.45−1.46 Å. Finally, the central arene of the terpyridyl complexes are typically unchanged, with aromatic bond lengths between 1.38 and 1.4 Å. It should be noted that in one room-temperature structure of a perchlorate salt of terpyridylpalladium(II), metric distortions were more severe, similar to PDP, though it is not clear why this complex behaves differently.[55]

For further electronic comparison to terpyridine, cyclic voltammetry (CV) was performed on platinum complex (**3**) for comparison to the reported CV of $[(\text{terpy})\text{Pt}-\text{Cl}]^-$.[56] In this reported Pt−terpy system, the CV shows three ligand-based reduction waves at −0.45, −0.96, and −1.72 V vs NHE.[57] As the anionic PDP ligand is more electron rich, these reduction potentials are expected to be more negative in complex **3**. The first reduction appears as an irreversible wave at −1.44 V, which becomes quasi-reversible at high scan rates (peak-to peak separation = 135 mV; see Supporting Information). A second large, irreversible wave corresponding to multielectron reduction and compound destruction appears at −2.5 V. A peak analogous to the third reduction in (terpy)Pt−Cl is not observed in the PDP system as a result of the larger electron density in the anionic PDP ligand.

DFT calculations on complex **1**, (PDP)Pd−Cl, were performed to gain further insight into the π−electron structure. In an effort to improve accuracy of DFT descriptions of the delocalized frontier orbitals, calculations were performed using a mixed basis-set (6-31G*/3-21G, Gaussian 03 suite[58]) with core potentials for Pd, and these were compared with the more rigorous MIDI[59] basis set (GAMESS suite of quantum programs[60]) for which all metal electrons are explicitly defined. Both methods gave similar results, with bond lengths comparable to those obtained from the crystal structure (Table 2). A Charge Decomposition Analysis[61] was performed on the 6-31G* structure to quantify the relative amount of donation and backdonation. This calculation gives a total charge donation of 0.418 electrons in metal to ligand donation and 0.568 electrons in backdonation, supporting the qualitative observation that PDP is a π-acceptor in these complexes.

In examining the metrics of individual bonds in the crystallographic (PDP)Pd−Cl complex, the pyridyl N−C bonds are lengthened, inter-ring biaryl bonds shortened, and the pyrrole bonds are roughly aromatized (interatom bond orders of ca. 1.5), with the exception of complex **2**, wherein the

Table 2. Comparison of the N(1)−C(5), C(5)−C(6), C(6)−C(7), and C(7)−C(7A) Bond Lengths (Å) in Crystallographic Structures to Those Calculated by DFT Methods

	(PDP)Pd−Cl			(PDP)H	
	crystal	mixed basis[a]	MIDI	crystal	6-31G*
N(1)−C(5)	1.377	1.380	1.396	1.346	1.351
C(5)−C(6)	1.461	1.453	1.449	1.46	1.457
C(6)−C(7)	1.403	1.416	1.424	1.385	1.398
C(7)−C(7A)	1.400	1.409	1.412	1.411	1.409

[a] **1**−Cl was examined using a mixed pseudopotential basis of 6-31G* (C, H, N), and 3-21G (Pd, Cl).

pyrrole C(7)−C(7A) bond is more drastically shortened to 1.37 Å.

These results may be understood by an examination of the frontier orbitals. Figure 6 shows the resulting antibonding orbital from π-donation from the filled ligand π-orbital ligand into the metal d-orbital. For d^8 metal systems, the metal d-π orbitals involved in this interaction are filled, resulting in a net nonbonding interaction. The empty antibonding orbital resulting from π-backbonding is also shown in Figure 6 in which donation from the filled metal d-π orbitals into the empty ligand π^* is seen. This is the LUMO when the MIDI basis set is used but LUMO+1 when using the mixed basis set with core potentials, implying that explicitly including Pd electrons may be necessary to better describe the relevant virtual orbitals of the complex using the B3LYP functional. In the case of the central pyrrole, π-backbonding from the metal into the ligand π^* results in an increase in the N(1)−C(5) and C(6)−C(7) bond order and a decrease in the C(5)−C(6) and C(7)−C(7A) bond order. The effects on the pyrrole ring are less dramatic than on the pyridyl, giving the pyrrole ring contacts an intermediate bond order of ca. 1.5. This may be explained by the greater localization of the backbonding orbital on the pyridyl groups (Figure 6, bottom) in comparison to the localization of electron density on the pyrrole in the nonbonding π-donor interaction (Figure 6, top). A similar localization of occupied orbital density on the pyrrole ring of bidentate pyridyl pyrrole has been previously observed.[29]

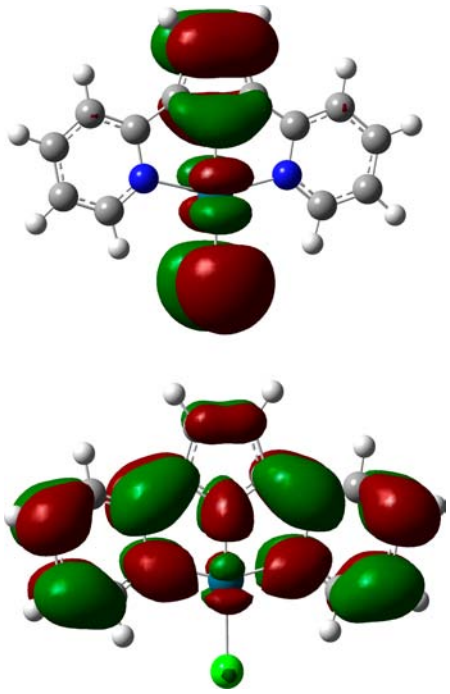

Figure 6. Results of DFT calculations on **1**. Top: Antibonding orbitals resulting from donation from the ligand π-orbital to the metal (HOMO-1). Bottom: π-Backbonding from the metal to the empty π^* orbital of the ligand (LUMO:MIDI, LUMO+1:6-31G*/3-21G).[62]

Bond lengths in the PDP ligand for complexes **1**−**3** can alternatively be compared with a Zn(II) complex where the d-electrons are effectively part of the core and not significantly involved in bonding. Differences between the ligand metrics for complexes **1**−**3** and those for $(PDP)_2Zn$ are given in Table 3. Inspection of Table 3 indicates that the structures for the PDP complexes of Pd(II), Pt(II), and Co(II) all show the alternating lengthening and shortening of bonds associated with population of the ligand π^* orbital. An intriguing feature is that the observed structural effect is most pronounced in the pyridine moieties, and the pyrrolate units in transition metal complexes are typically unchanged from that of the Zn(II) complex, with the exception of **2**. This feature may reflect a near cancellation of the structural changes from the π-electron acceptor effects by compensating changes associated with interactions of the pyrrolate π-donor orbitals with the filled metal nd-π and empty metal $(n+1)p_z$.

The total bond length deviation in the direction of ligand reduction is tabulated in the last column of Table 3 and reported with estimated standard deviation obtained from the crystal data. It can be seen that the most extensive bond length differences exist in **2** and **3**. However, the comparative Co, Cu, and Fe complexes possess 2 PDP ligands each, and thus, the π−effects are expected to be spread across both ligands, resulting in less drastic changes per ligand in these bis-PDP complexes.

■ CONCLUSION

We have prepared Pt and Pd complexes of the 2,5-bis(α-pyridyl)pyrrolate ligand to add to the class of Group 10 complexes with terpyridine and pyridine dipyrrolate complexes. The complexes display structural features indicative of π-bonding flexibility. A net decrease in ligand bond order occurs, but the resulting structural changes are manifested primarily on the pyridyl groups. This is explained using MO arguments, which suggest the pyrrole, as a result of its π-acceptor/π-donor flexibility, only experiences minor structural effects and remains effectively aromatized. Future studies will involve an expansion of the transition metal chemistry of this ligand and an exploration of their chemical properties, especially with respect to analogous terpyridine chemistry.

■ EXPERIMENTAL SECTION

General. All Reagents were used as obtained from chemical suppliers (Aldrich, Strem). X-ray crystal structures were determined using a Rigaku R-AXIS IIc with a rotating anode or a Bruker Kappa APEX II DUO diffractometer using Mo Kα radiation. NMR spectra were obtained using a Bruker DMX 300 or 360 MHz NMR spectrometer or a Bruker AVANCE-III 500 MHz NMR spectrometer. ESI mass spectra were obtained on a Waters GC-TOF Premier mass spectrometer at the University of Pennsylvania.

Density Functional Theory. Density Functional Theory was carried out using either the Gaussian '03 suite[58] or the GAMESS suite of quantum programs.[59] Charge decomposition analysis was performed using the program QMForge.[63]

2,5(Di-α-pyridyl)pyrrole H(PDP). 2,5(Di-α-pyridyl)pyrrole H-(PDP) was prepared by a Paal-Knorr cyclization of a 1,4 diketone

Table 3. Differences between the N(1)−C(5), C(5)−C(6), C(6)−C(7), and C(7)−C(7A) bond lengths (Å) in PDP Complexes of Metals and Those Reported for the Zinc Complex Determined by Subtraction

	N(1)−C(5)	C(5)−C(6)	C(6)−C(7)	C(7)−C(7A)	total deviation[c]
[(PDP)PdCl] (**1**)	0.032	−0.002	0.016	−0.011	0.06(3)
[(PDP)Pd(H2O)]+ (**2**)	0.033	−0.018	0.026	−0.041	0.12(3)
[(PDP)PtCl] (**3**)	0.045	−0.014	0.026	−0.011	0.10(3)
[(PDP)2Co)]	0.011	−0.016	0.008	−0.025	0.06(3)
[(PDP-SCN)2Co][b]	0.013	−0.010	0.011	0.009	0.03(3)
[(PDP-SCN)2Cu][b]	0.007	−0.016	0.008	0.010	0.02(4)
[(PDP-SCN)2Fe][b]	0.016	−0.011	0.030	−0.012	0.07(3)

[a]Differences calculated as (mean bond length of all equivalent bonds in the zinc complex) − (mean bond length of all equivalent bonds in the tabulated complex). ESD values are calculated as the standard deviation of the values of the bond lengths included in the average. If only one bond length exists, the crystallographic ESD value is used. [b]PDP−SCN = 3,4-bis(thiocyanato)-2,5-bis(α-pyridyl)pyrrolate. [c]The total deviation is calculated from the distance differences according to the equation: Total deviation = [N(1)−C(5)] + −[C(5)−C(6)] + [C(6)−C(7)] + −[C(7)−C(7A)]. This formulation calculates sum of the bond changes in the direction of ligand reduction/π-acceptance. The ESD value is given in parentheses.

containing the necessary pyridyl functional groups using a modified literature procedure[48] described below.

1,4-Di(2-pyridyl)butan-1,4-dione. A mixture of 10 equivalents of 2-pyrrolecarboxaldehyde and 2.5 equivalents of divinyl sulfone in absolute ethanol was added to a degassed, refluxing solution of equimolar (1 eq. each) sodium acetate and 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride in absolute ethanol. The mixture was refluxed 16 h and allowed to cool to room temperature. 1,4-Di(2-pyridyl)butan-1,4-dione is obtained from the cooled reaction as a bright yellow precipitate in reasonable yield (53%) and used without further purification.

(PDP)H. One equivalent 1,4-di(2-pyridyl)butan-1,4-dione was heated in an excess of ammonium acetate at 125 °C for 4 h. The mixture was cooled to room temperature, poured into water (∼40 mL), and extracted with CH_2Cl_2 (3 × 100 mL). The extracts were dried using anhydrous $MgSO_4$, concentrated, chromatographed on silica gel (CH_2Cl_2:EtOAc, 5:1), and dried. The yellow oil solidified on standing overnight to give a 74% yield of H(PDP). ^{1}H NMR: ($CDCl_3$) δ (ppm) 10.58 (br) 8.530 (d, J = 4.8), 7.638 (t, J = 8.0), 7.581 (d, J = 8.0 Hz) 7.067 (t, J = 4.9 Hz), 6.766 (d, 2.7).

[(PDP)PdCl] (1). Prior to metalation, the PDP ligand (100 mg, 0.452 mmol) was converted to its deprotonated form via lithiation by $Li[N(SiMe_3)_2]$ (0.452 mmol) in anhydrous tetrahydrofuran. This product was added dropwise to 1 equivalent of $[PdCl_2(NC(C_6H_5)_2]$ (173 mg, 0.452 mmol). After 24 h, the solvent was removed, and the crude product was purified by column chromatography (100% CH_2Cl_2) to yield an orange solid (94 mg, 57% yield) as the chloride complex, [(PDP)PdCl] (**1**). ^{1}H NMR: ($CDCl_3$) δ (ppm) 8.41 (d, J = 5.6 Hz), 7.69 (t, J = 7.7 Hz), 7.27 (d, J = 6.6 Hz), 6.96 (t, J = 6.4 Hz), 6.39 (s). ^{13}C NMR: ($CDCl_3$): δ (ppm) 159.0, 152.8, 139.8, 139.1, 120.7, 118.8, 109.4. Elem. Anal. Calcd for $C_{14}H_{10}ClN_3Pd$ C, 46.43%; H, 2.78%; N, 11.60%. Found: C, 46.24%; H, 2.74%; N, 11.57%. UV−vis (CH_2Cl_2) λ_{max}(ε/$M^{-1}cm^{-1}$): 265 nm (36849), 303 nm (19662), 437 nm (13027), 454 nm (12945). IR (KBr) λ_{max}/cm^{-1}: 3034 (w, C−H stretch), 1601 (m, pyridine C−N/C-C asym. stretch), 1495 (m, C−C asym. stretch), 1414 (m, pyrrole C−N asym. stretch), 1299, 1146 (w, C−H in-plane bends), 776, 742, 709 (m, C−H sym. out-of-plane bends).

[(PDP)Pd(OH_2)][OTf] (2). The chloride was abstracted from **1** by mixing **1** (7.3 mg, 0.020 mmol) with 1 equivalent of AgOTf (5.19 mg, 0.020 mmol) in acetone (10 mL). This solution was centrifuged and decanted to remove AgCl precipitate, and the solvent dried to yield 7.0 mg (71%) of the cationic aquo complex, with triflate counterion $[(PDP)Pd(H_2O)]^+[OTf]^-$ (**2**). ^{1}H NMR: (THF-d_8) δ (ppm) 8.19 (d, J = 5.4 Hz), 7.91 (t, J = 7.8 Hz), 7.57 (d, J = 7.8 Hz), 7.21 (t, J = 5.8 Hz), 6.55 (s). ^{13}C NMR: (THF-d_8): δ (ppm) 110.264, 119.783, 122.027, 140.106, 141.523, 152.301, 159.709. Three of the 4 weak quartet peaks of OTf are observed at 120.388, 122.871, 125.477 (q, J = 318 Hz). MS (ESI, methanol) *m/z* calcd $C_{14}H_{11}N_3OPd$ $[M+Na]^+$: 365.98, found 366.02. UV−vis (EtOH) λ_{max} (ε/$M^{-1}cm^{-1}$): 258 nm (7816), 311 nm (5672), 414 nm (4839). IR (KBr) λ_{max}/cm^{-1}: 3062 (w, C−H stretch), 1604 (m, pyridine C−N/C-C asym. stretch), 1495 (m, C−C asym. stretch), 1414 (m, pyrrole C−N asym. stretch), 1251, 1175, 1031 (s, OTf).

[(PDP)PtCl] (3). For the preparation of the platinum complex, triethylamine was used to accept the pyrrole proton in the conversion of PDP to its deprotonated form. A degassed mixture of $(COD)PtCl_2$ (111 mg, 0.298 mmol), PDP-H (66 mg, 0.298 mmol), and NEt_3 (0.166 mL, 1.19 mmol) was refluxed in THF under inert atmosphere for 48 h. The dried, oily mixture required purification by silica column chromatography (100% CH_2Cl_2). The product eluted as an orange solution. Orange crystals were obtained by evaporation (28 mg, 21% yield). ^{1}H NMR: ($CDCl_3$) δ (ppm) 8.51 (d, J = 5.7 Hz, ^{3}J(Pt−H),= 19.4 Hz), 7.67 (t, J = 7.8 Hz), 7.22 (d, J = 8.1 Hz), 6.96 (t, J = 6.6 Hz), 6.45 (s). ^{13}C NMR: ($CDCl_3$) δ (ppm) 160.8, 152.7, 140.3, 138.2, 121.0, 118.6, 109.8. HRMS (ESI, CH_2Cl_2) *m/z* calcd $C_{14}H_{11}ClN_3Pt$ $[M+H]^+$: 451.0289, found 451.0288. UV−vis (CH_2Cl_2) λ_{max} (ε/$M^{-1}cm^{-1}$): 280 nm (25287), 310 nm (14093), 459 nm (6171), 486 nm (4960). IR (KBr) λ_{max}/cm^{-1}: 2920 (w, C−H stretch), 1608 (m, pyridine C−N/C-C asym. stretch), 1487 (m, C−C asym. stretch), 1415 (m, pyrrole C−N assym), 1299, 1258, 1145 (w, C−H in-plane bends), 773, 744, 708 (m, C−H sym. out-of-plane bends).

■ ASSOCIATED CONTENT

Supporting Information

NMR and UV−vis spectra, IR spectra, CV, full crystallographic tables and crystallographic information files (cif), and results of Density Functional Theory calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246−253.
(2) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373−399.
(3) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745−1776.

(4) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **2001**, *50*, 151−216.
(5) Wile, B. M.; Trovitch, R. J.; Bart, S. C.; Tondreau, A. M.; Lobkovsky, E.; Milsmann, C.; Bill, E.; Wieghardt, K.; Chirik, P. J. *Inorg. Chem.* **2008**, *48*, 4190−4200.
(6) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143−7144.
(7) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340−13341.
(8) Russell, S. K.; Darmon, J. M.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2010**, *49*, 2782−2792.
(9) Kwong, H.-L.; Yeung, H.-L.; Yeung, C.-T.; Lee, W.-S.; Lee, C.-S.; Wong, W.-L. *Coord. Chem. Rev.* **2007**, *251*, 2188−2222.
(10) Concepcion, J. J.; Jurss, J. W.; Norris, M. R.; Chen, Z.; Templeton, J. L.; Meyer, T. J. *Inorg. Chem.* **2010**, *49*, 1277−1279.
(11) Wild, A.; Winter, A.; Schlutter, F.; Schubert, U. S. *Chem. Soc. Rev.* **2011**, *40*, 1459−1511.
(12) Zakeeruddin, S. M.; Nazeeruddin, M. K.; Pechy, P.; Rotzinger, F. P.; Humphry-Baker, R.; Kalyanasundaram, K.; Grätzel, M.; Shklover, V.; Haibach, T. *Inorg. Chem.* **1997**, *36*, 5937−5946.
(13) Rawling, T.; Austin, C.; Buchholz, F.; Colbran, S. B.; McDonagh, A. M. *Inorg. Chem.* **2009**, *48*, 3215−3227.
(14) Bolink, H. J.; Cappelli, L.; Coronado, E.; Gaviña, P. *Inorg. Chem.* **2005**, *44*, 5966−5968.
(15) Tessore, F.; Roberto, D.; Ugo, R.; Pizzotti, M.; Quici, S.; Cavazzini, M.; Bruni, S.; De Angelis, F. *Inorg. Chem.* **2005**, *44*, 8967−8978.
(16) Dumur, F.; Mayer, C. R.; Hoang-Thi, K.; Ledoux-Rak, I.; Miomandre, F.; Clavier, G.; Dumas, E.; Méallet-Renault, R.; Frigoli, M.; Zyss, J.; Sécheresse, F. *Inorg. Chem.* **2009**, *48*, 8120−8133.
(17) Wadas, T. J.; Wang, Q.-M.; Kim, Y.-J.; Flaschenreim, C.; Blanton, T. N.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 16841−16849.
(18) van Holst, M.; Le Pevelen, D.; Aldrich-Wright, J. *Eur. J. Inorg. Chem.* **2008**, *2008*, 4608−4615.
(19) Bugarčić, Ž. D.; Petrović, B.; Zangrando, E. *Inorg. Chim. Acta* **2004**, *357*, 2650−2656.
(20) Cosar, S.; B. L. Janik, M.; Flock, M.; Freisinger, E.; Farkas, E.; Lippert, B. *J. Chem. Soc., Dalton Trans.* **1999**, 2329−2336.
(21) Wieder, N. L.; Gallagher, M.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **2010**, *132*, 4107−4109.
(22) Gallagher, M.; Wieder, N. L.; Dioumaev, V. K.; Carroll, P. J.; Berry, D. H. *Organometallics* **2010**, *29*, 591−603.
(23) Zhu, D.; Thapa, I.; Korobkov, I.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.* **2011**, *50*, 9879−9887.
(24) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 2936−2947.
(25) Bart, S. C.; Lobkovsky, E.; Bill, E.; Wieghardt, K.; Chirik, P. J. *Inorg. Chem.* **2007**, *46*, 7055−7063.
(26) Knijnenburg, Q.; Hetterscheid, D.; Kooistra, T. M.; Budzelaar, Peter H. M. *Eur. J. Inorg. Chem.* **2004**, *2004*, 1204−1211.
(27) Bart, S. C.; Chłopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901−13912.
(28) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442−5448.
(29) Flores, J. A.; Andino, J. G.; Tsvetkov, N. P.; Pink, M.; Wolfe, R. J.; Head, A. R.; Lichtenberger, D. L.; Massa, J.; Caulton, K. G. *Inorg. Chem.* **2011**, *50*, 8121−8131.
(30) McBee, J. L.; Tilley, T. D. *Organometallics* **2009**, *28*, 3947−3952.
(31) Luedtke, A. T.; Goldberg, K. I. *Inorg. Chem.* **2007**, *46*, 8496−8498.
(32) Schouteeten, S.; Allen, O. R.; Haley, A. D.; Ong, G. L.; Jones, G. D.; Vicic, D. A. *J. Organomet. Chem.* **2006**, *691*, 4975−4981.
(33) Klappa, J. J.; Geers, S. A.; Schmidtke, S. J.; MacManus-Spencer, L. A.; McNeill, K. *Dalton Trans.* **2004**, 883−891.
(34) Hein, B.; Beierlein, U. *U. Pharma. Zentralhalle* **1957**, *96*, 401−421.
(35) Ciszek, J. W.; Keane, Z. K.; Cheng, L.; Stewart, M. P.; Yu, L. H.; Natelson, D.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 3179−3189.
(36) Trofimov, B. A.; Vasil'tsov, A. M.; Schmidt, E. Y.; Zorina, N. V.; Afonin, A. V.; Mikhaleva, A. b. I.; Petrushenko, K. B.; Ushakov, I. A.; Krivdin, L. B.; Belsky, V. K.; Bryukvina, L. I. *Eur. J. Org. Chem.* **2005**, *2005*, 4338−4345.
(37) Rogers, R. D.; Vann Bynum, R.; Atwood, J. L. *J. Chem. Crystallogr.* **1984**, *14*, 21−28.
(38) Lee, H.; Bonanno, J. B.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Polyhedron* **2005**, *24*, 1356−1365.
(39) Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368−2374.
(40) Al Obaidi, N.; Edwards, A. J.; Jones, C. J.; McCleverty, J. A.; Neaves, B. D.; Mabbs, F. E.; Collison, D. *J. Chem. Soc., Dalton Trans.* **1989**, 127−132.
(41) Lee, H.; Bonanno, B. J.; Hascall, T.; Cordaro, J.; Hahn, M. J.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1999**, 1365−1368.
(42) Arndt, S.; Trifonov, A.; Spaniol, T. P.; Okuda, J.; Kitamura, M.; Takahashi, T. *J. Organomet. Chem.* **2002**, *647*, 158−166.
(43) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Van Bolhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147−2153.
(44) Mathis, M.; Harsha, W.; Hanks, T. W.; Bailey, R. D.; Schimek, G. L.; Pennington, W. T. *Chem. Mater.* **1998**, *10*, 3568−3575.
(45) Hirano, M.; Onuki, K.; Kimura, Y.; Komiya, S. *Inorg. Chim. Acta* **2003**, *352*, 160−170.
(46) Morikita, T.; Hirano, M.; Sasaki, A.; Komiya, S. *Inorg. Chim. Acta* **1999**, *291*, 341−354.
(47) Rakowski DuBois, M.; Vasquez, L. D.; Peslherbe, L.; Noll, B. C. *Organometallics* **1999**, *18*, 2230−2240.
(48) Alan Jones, R.; Karatza, M.; Voro, T. N.; Civeir, P. U.; Franck, A.; Ozturk, O.; Seaman, J. P.; Whitmore, A. P.; Williamson, D. J. *Tetrahedron* **1996**, *52*, 8707−8724.
(49) We have obtained a new, high quality structure of the PDP ligand, though a structure with R_1 = 6.52% in a different space group was previously reported. Bakkali, H.; Marie, C.; Ly, A.; Thobie-Gautier, C.; Graton, J.; Pipelier, M.; Sengmany, S.; Léonel, E.; Nédélec, J.-Y.; Evain, M.; Dubreuil, D. *Eur. J. Org. Chem.* **2008**, *2008*, 2156−2166.
(50) Senguel, A. *Turk. J. Chem.* **2004**, *28*, 667−672.
(51) Angle, C. S.; DiPasquale, A. G.; Rheingold, A. L.; Doerrer, L. H. *Acta Crystallographica Section C* **2006**, *62*, m340−m342.
(52) Yip, H.-K.; Cheng, L.-K.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1993**, 2933−2938.
(53) Taylor, S. D.; Howard, W.; Kaval, N.; Hart, R.; Krause, J. A.; Connick, W. B. *Chem. Commun.* **2010**, *46*, 1070−1072.
(54) Illner, P.; Puchta, R.; Heinemann, F. W.; van Eldik, R. *Dalton Transactions* **2009**, 2795−2801.
(55) Bailey, J. A.; Hill, M. G.; Marsh, R. E.; Miskowski, V. M.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 4591−4599.
(56) Yang, L.; Wimmer, F. L.; Wimmer, S.; Zhao, J.; Braterman, P. S. *J. Organomet. Chem.* **1996**, *525*, 1−8.
(57) Potentials from ref 56 have been converted to NHE for direct comparison.
(58) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M.

W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.
(59) Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1980**, *1*, 205−228.
(60) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.
(61) Dapprich, S.; Frenking, G. *The Journal of Physical Chemistry* **1995**, *99*, 9352−9362.
(62) The antibonding components are shown instead of the bonding components because the latter intermixes with other orbitals, making them harder to recognize and less illustrative.
(63) Tenderholt, A. L. *QMForge* Version 2.1. Stanford University: Stanford, CA.