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Article

Donor Strength Determination of Pyridinylidene-amide Ligands using Their Palladium−NHC Complexes

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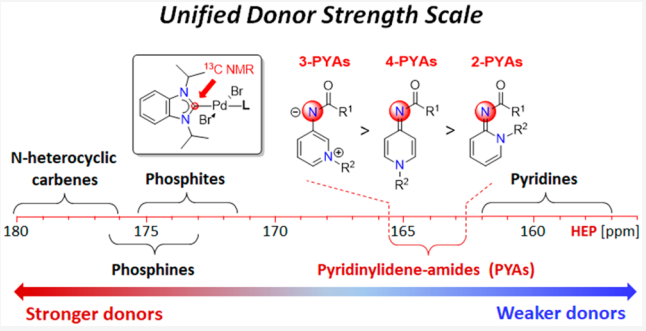
ABSTRACT: Pyridinylidene-amides (PYAs) are a relatively new type of N-donor ligands that can exist in three isomeric forms and adopt various resonance structures. This makes them electronically flexible, and in order to evaluate their electronic profile using the Huynh electronic parameter (HEP), seven structurally diverse mixed *N*-heterocyclic carbenes (NHCs)/PYA palladium complexes of the type *trans*-[$PdBr_2(^iPr_2$-bimy)(PYA)] were prepared and fully characterized by various spectroscopic and spectrometric methods. This study shows that PYAs are among the strongest, formally neutral N-donors, but they are still weaker than phosphines and organometallic ligands such as NHCs. Notably, the donating abilities of isomeric PYAs are distinct and can be further fine-tuned by the choice of two substituents making them structurally and electronically versatile. These characteristics and the ease of their preparation hold promise for a wide applicability in coordination chemistry.



INTRODUCTION

Pyridinylidene-amides (PYAs) are a new class of ligands that have been introduced in 2011 by Wright and co-workers.[1] Since then, multiple complexes containing PYA ligands have been synthesized and tested in catalysis primarily by the groups of Albrecht. For example, ruthenium- and iridium-based (de)hydrogenation catalysts,[2−5] iridium-based water oxidation catalysts,[6,7] and palladium-based cross-coupling[1] or olefin dimerization and isomerization[8] catalysts have been reported. A preliminary study on the cytotoxicity of a platinum-PYA complex has also been published.[9] Similar to *N*-heterocyclic carbenes (NHCs), a unique feature of the formally neutral PYA ligands is that electronically distinct resonance structures are available, which could impart electronic flexibility (Figure 1). The latter is believed to be particularly important for catalysis, as such ligands could stabilize electronically distinct intermediates in a catalytic cycle. Indeed, a dependence of the resonance state on the solvent polarity and its implications in catalysis has been demonstrated recently.[2,3]

Moreover, typical PYAs can exist in three isomeric forms. Depending on the positions of the exo- and endocyclic nitrogen atoms relative to each other, these can be called *ortho*-, *meta*-, and *para*-PYAs (i.e., 2-PYA, 3-PYAs, and 4-PYAs), respectively (Figure 1). Particularly, *meta*-PYAs take a special position, since all their (closed-shell) resonance structures require charge separation, which makes them truly mesoionic compounds.[7] Indeed, electrochemical studies have shown that they are the strongest donor among the isomeric PYAs.[4,6] In addition, further stereoelectronic diversity in all three isomers can be achieved by modifications of the R and R′

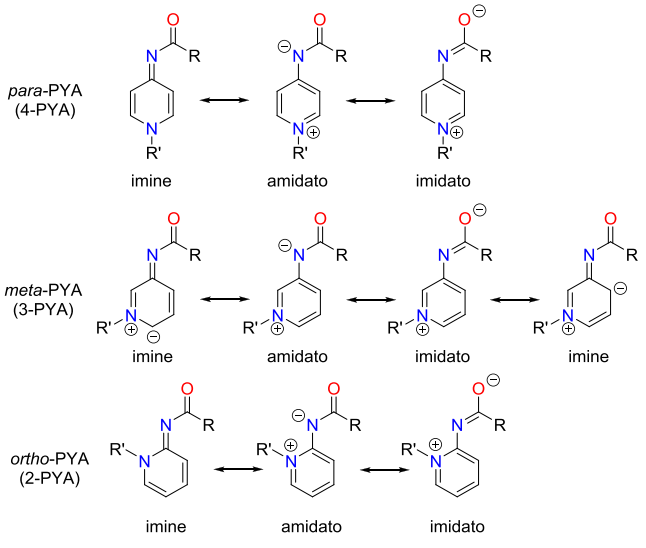


Figure 1. Isomeric PYAs and their limiting resonance structures.

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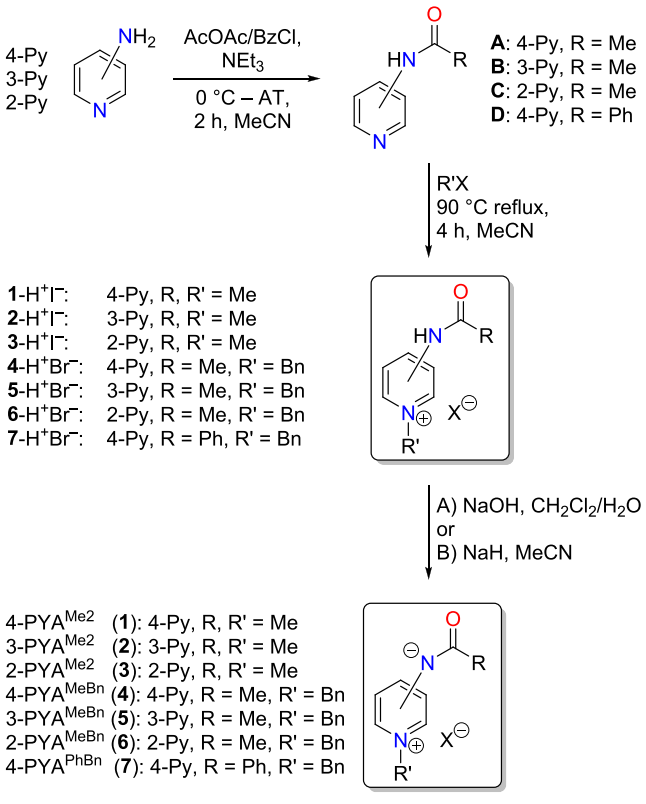
substituents, respectively. All in all, these properties make PYA ligands interesting study objects especially in terms of their electronic properties. Notably, a preliminary donor strength evaluation using a *trans*-[RhCl(CO)$_2$(*para*-PYA)] complex[1] gave two carbonyl bands at 2069 and 1987 cm^{-1} (avg 2028 cm^{-1}),[10] which are surprisingly lower than those obtained for the saturated SIMes complex (avg 2038 cm^{-1}).[11] This could imply that PYAs are stronger donating ligands than are imidazolidin-2-ylidenes, which is less intuitive given the presence of an electron-withdrawing amide and the (at least formally cationic) pyridinium group in PYAs.

Clearly, a more in-depth analysis is required for a better understanding of the electronic impact imposed by these relatively new nitrogen donors in comparison to other common and popular ligands. Since we have a long-standing interest in ligand design[12,13] and the study of their stereoelectronic properties, we herein report the preparation of mixed NHC/PYA palladium complexes for a systematic comparison of isomeric PYAs in terms of their donating power using the Huynh electronic parameter (HEP).[14−16] In addition, the influence of substituents at the amide- and pyridine-moieties are evaluated.

RESULTS AND DISCUSSION

Preparation of Ligand Precursors and Free PYAs. The syntheses of the various pyridinium amides as precursors to PYAs consist of only two steps and are outlined in Scheme 1. Commercially available *ortho*-, *meta*-, and *para*-aminopyridines were routinely converted into respective amides **A**−**D** using acetic anhydride or benzoyl chloride with gradual warming from 0 °C to ambient temperature (AT). The subsequent N-alkylations of the pyridine moieties can only be affected using strong electrophiles such as methyl iodide and benzyl chloride. Overall, precursors to seven structurally and electronically distinct PYA ligands were prepared. Similar to the C2−H proton in NHC precursors, N-alkylation leads to a downfield shift of the N−H signal indicative of increased acidity due to cation formation and hydrogen bonding to the halides.[17] Interestingly, the *meta*-pyridinium amides **2**-H$^+$I$^-$ and **5**-H$^+$Br$^-$ exhibit N−H resonances that are generally more upfield (less acidic) than those of their ortho and para isomers. This may already point to the stronger donating abilities (more basic) of 3-PYAs compared to their isomers.

Scheme 1. Two-Step Synthesis of Pyridinium Amides as Precursors to PYA Ligands



The free PYAs can be obtained by deprotonation of the N−H function of the pyridinium amides. This was explored using two ways as depicted in Scheme 1. Method A employs an aqueous, concentrated solution of sodium hydroxide in a biphasic mixture of dichloromethane and water. Upon deprotonation, the free PYA is expected to be in the organic phase, and isolation can occur via simple extraction and evaporation of the solvent. However, an increased tendency of the free ligands to remain in the aqueous phase was observed for methyl-substituted compounds **1**−**3**. In method B, the use of water is avoided, and the reactions are carried out under an inert argon atmosphere using powdered sodium hydride as a base in dry acetonitrile. After removal of the solvent, the PYAs were redissolved in chloroform and separated from the sodium salts by filtration. Drying the filtrates *in vacuo* yielded the products as solids. Apart from compound **2**, which undergoes amide hydrolysis, all other PYAs could be isolated as analytically pure, but highly hygroscopic, solids. Generally, 4-PYAs **1**, **4**, and **7** were obtained in better yields compared to their *ortho* and *meta* isomers. 3-PYA **5** could only be isolated using sodium hydride, which hints to a generally stronger basicity of 3-PYAs. This is also in agreement with the more upfield N−H resonances observed in their salt precursors (*vide supra*). With the exception of **2**, all PYAs have been characterized by ESI mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy. The most obvious change from their precursors is the expected absence of the N−H protons in the ^{1}H NMR spectra.

For compounds **1** and **7**, single crystals suitable for X-ray analysis were obtained by layering their solutions in chloroform with ether and hexane, and their molecular structures are depicted in Figure 2 along with selected bond distances. Comparison of the notably shorter N2−C4 (**1**) and N1−C8 (**7**) bond lengths of 1.354(1) and 1.353(2) Å to that of 4-benzamidopyridine[18] with 1.400(2) Å reveals significant contributions of the neutral imine resonance form in these 4-PYAs. This is further supported by the bond parameters of the initially aromatic pyridine rings, which show distinct alternating double and single bonds. These are in the range of 1.366(2)−1.427(2) Å (**1**) and 1.359(3)−1.427(3) Å (**7**) compared to the typical aromatic bonds of 1380(2)−1.396(2) Å found for the 4-benzamidopyridine.[18]

Preparation of Mixed NHC/PYA Palladium Complexes. To compare the donating strengths of the PYAs using HEP, palladium complexes of the type *trans*-[PdBr$_2$(^{i}Pr$_2$-bimy)(PYA)] are required. These can be prepared either by (A) direct reaction of 2 equiv of free PYA with the dipalladium complex [PdBr$_2$(^{i}Pr$_2$-bimy)]$_2$ (**I**)[19] or (B) by *in situ* deprotonation of the pyridinium halides with silver(I) oxide or sodium hydroxide in the presence of complex **I** (Scheme 2). The use of silver(I) oxide provides a greater driving force

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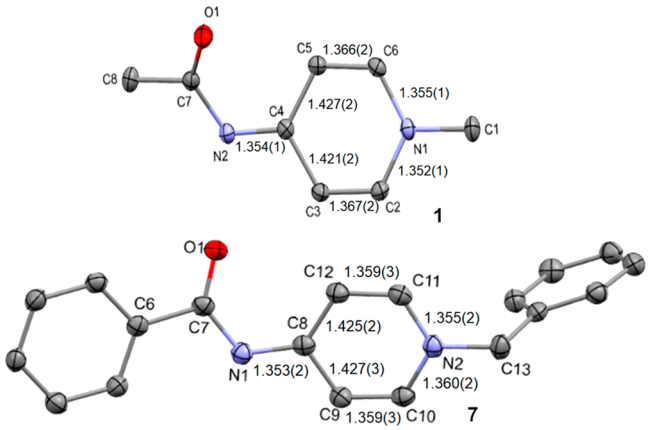
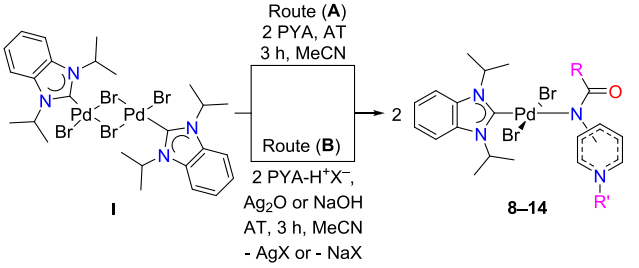


Figure 2. Molecular structures of **1** (top) and **7** (bottom) in the solid state. Hydrogen atoms are omitted for clarity; ellipsoids drawn at 50% probability. **1**: O1−C7 1.239(1), N1−C2 1.352(1), N1−C6 1.355(1), N2−C4 1.354(1), N2−C7 1.363(1), C2−C3 1.367(2), C3−C4 1.421(2), C4−C5 1.427(2), C5−C6 1.366(2) Å. **7**: O1−C7 1.238(2), N1−C8 1.353(2), N1−C7 1.363(2), N2−C11 1.355(2), N2−C10 1.360(2), C8−C12 1.425(2), C8−C9 1.427(3), C9−C10 1.359(3), C11−C12 1.359(3) Å.

Scheme 2. One-Pot Synthesis of Mixed NHC/PYA Complexes of Palladium



through rapid precipitation of very insoluble silver halides. As such, the synthetic pathways closely resemble those for the heterobis(carbene) counterparts.[11,20] Notably, the use of iodide salts in the more convenient route B did not lead to any halide scrambling as silver(I) preferably precipitates with the heavier halide. Most complexes were obtained in good nonoptimized yields except for complexes *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(3-PYA^{MeBn})] (**12**) and *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(2-PYA^{MeBn})] (**13**). Table 1 summarizes selected data for all complexes **8**−**14**. Notably, the complexes obtained in lower yields contain PYAs with N-benzyl substituents, and competing benzylic deprotonations could explain the poorer outcomes. For example, 3-PYA precursor **5**-H$^+$Br$^-$ for complex **12** contains the least acidic N−H proton, which could compromise selectivity. For **6**-H$^+$Br$^-$ precursor to the 2-PYA in complex **13**, the lower yield could be due to the close proximity of the two competing sites. Moreover, metal coordination of this 2-PYA is anticipated to be more difficult due to steric hindrance of the N-benzyl group. Ligand precursor **4**-H$^+$Br$^-$ to complex **11**, however, is free of such complications, and an excellent yield was obtained.

Table 1. Selected Data for Complexes 8−14

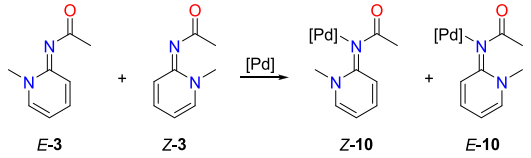
complex	PYA	yield [%]	color	HEP [ppm][a]
8	4-PYA^{Me2} (**1**)	75	orange	164.6_0
9	3-PYA^{Me2} (**2**)	78	red-brown	165.3_4
10	2-PYA^{Me2} (**3**)	60	orange	162.6_0
11	4-PYA^{MeBn} (**4**)	99	yellow	164.6_2
12	3-PYA^{MeBn} (**5**)	14	dark-green	165.6_8
13	2-PYA^{MeBn} (**6**)	28/47	brown	162.6_2
14	4-PYA^{PhBn} (**7**)	69	yellow	163.0_2

[a]Measured in $CDCl_3$ and referenced to the solvent signal at 77.7 ppm.

The positive LR ESI mass spectra of the complexes show dominant peaks for the [M + Na]$^+$ or [M + H]$^+$ cations. Presumably, these ions are formed by capture of a sodium cation or a proton via interaction with the oxygen atoms of the PYA ligands. HR ESI mass analyses also confirm the formation of all complexes. For most palladium complexes, only broad ^{1}H NMR spectra are obtained, which show two sets of broad isopropyl resonances due to the unsymmetrical nature of the PYA ligands. The broadness of the signals indicates a certain degree of fluxionality triggered by potential rotations within the PYA ligand and around the Pd−N bond.

Exceptionally, the ^{1}H NMR spectrum of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(2-PYA^{Me2})] (**10**) with a small PYA ligand shows two sets of signals in a ratio of ∼70:30. However, these signals are well-resolved (see Supporting Information). For 2-PYA ligands, potentially two stereoisomers, e.g., *E*-**3** and *Z*-**3** (Scheme 3), can be anticipated that are caused by the imine

Scheme 3. *E*-3 and *Z*-3 Ligands and Their Pd Complexes



double bond. Unfortunately, the ^{1}H NMR spectrum does not allow for the differentiation of *trans*-*Z*-**10** or *trans*-*E*-**10** complexes that form upon coordination of *E*-**3** and *Z*-**3**, respectively (note the change of priorities upon coordination).

Notably, such isomers are not observed for mesoionic 3-PYA ligands where imine formation is formally not possible. Obviously, they also do not exist for the symmetrical 4-PYA ligands.

The ^{1}H NMR spectrum of *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(4-PYA^{PhBn})] (**14**) is particularly broad, which hampers signal assignments. However, it shows two sets of signals for the benzylic protons with an approximate ratio of 80:20 that could be due to rotamers (Figure 3, 298 K). Likewise, the ^{13}C NMR spectrum shows a doubling of signals for most carbon atoms except for the quaternary ones, i.e., carbene, imine and carbonyl carbon atoms. The latter observation hints to a limited rotation of the bulky 4-PYA^{PhBn} ligand with respect to the Pd−N vector making this process an unlikely reason for the two sets of signals. To gain insights into other potential rotational isomers, additional low-temperature ^{1}H NMR experiments were conducted at −40, −30, −20, and 0 °C (Figure 3).

Lower temperatures are expected to slow dynamic processes, which should lead to better resolved spectra. Indeed, a first coalescence is observed between 298 and 273 K, where the broad signal at ∼1.6 ppm separates into two broad signals. Between 273 and 253 K a second coalescence occurs, and these signals become two distinct and sharp doublets at 1.7 and 1.3 ppm. Similarly, the very broad signals for the CH group at ∼5.1 and ∼6.2 ppm, which are barely visible in the

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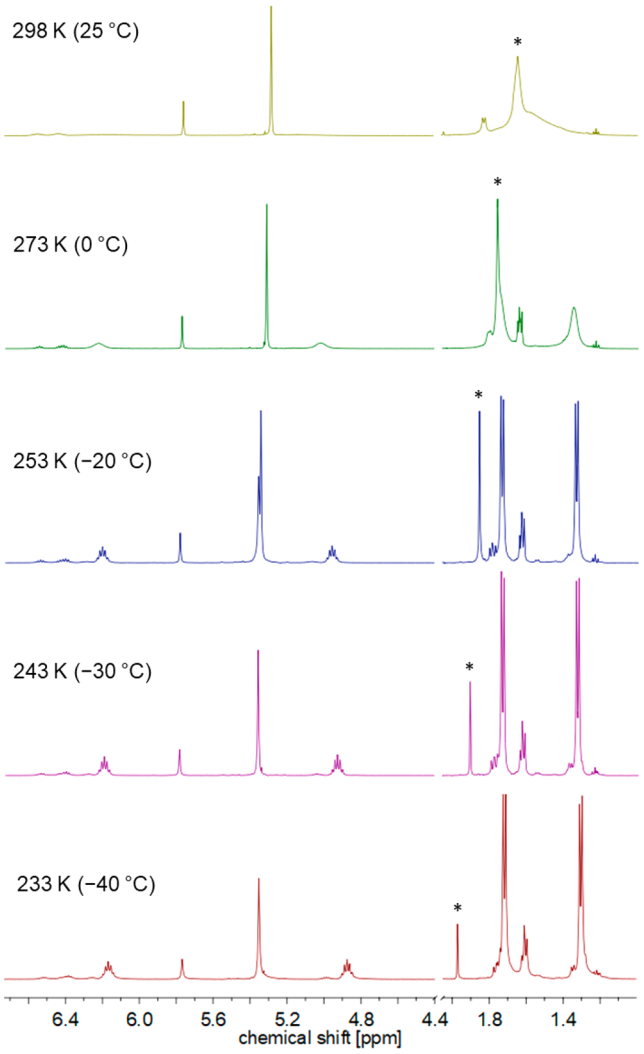

Figure 3. Low-temperature ^{1}H NMR spectra of **14** at 233, 243, 253, 273, and 298 K (500 MHz, $CDCl_3$). Signals at >6.6 ppm and between 2.0 and 4.4 ppm are not displayed for clarity. The signal for residual water is marked with an asterisk.

spectrum at 298 K, become defined multiplets at 4.9 and 6.2 ppm, respectively. The coalescence temperature for these signals is between 273 and 253 K. The large deviation in chemical shift difference between these methine signals of the major species compared to those of the minor species at ∼6.4 and ∼6.5 ppm suggests that the benzamide group is oriented toward one of the isopropyl groups in the major isomer (vide infra). The anisotropy of the phenyl ring affects only one isopropyl group causing an upfield shift of its NMR resonances. Overall, this creates a great difference in the chemical environment between the two isopropyl groups. For the minor species, the phenyl group is expected to be oriented away from the isopropyl group via rotation of the N−C(O) bond, thus having very little impact on the chemical shift difference. Peculiarly, an additional benzylic signal is observed at 253 K that merges again at lower temperatures. We believe that this signal arises from an additional rotamer that could form via Pd−N rotations that changes the orientation of the PYA ligand with respect to the square-planar coordination plane. Conclusively, this experiment provides evidence for the presence of rotational isomers.

Solid-State Molecular Structures. Single crystals suitable for X-ray diffraction could be obtained for complexes **8**, **9**, **11**, **12**, and **14**. The molecular structures of **8**, **9** and **14** are depicted in Figure 4 as representatives, while those for the others can be found in the Supporting Information. As expected, all complexes are essentially square-planar and contain the HEP reporter NHC and the PYA ligand in a trans arrangement. The carbene planes and those formed by the CNC atoms of the PYA ligands are perpendicular to the

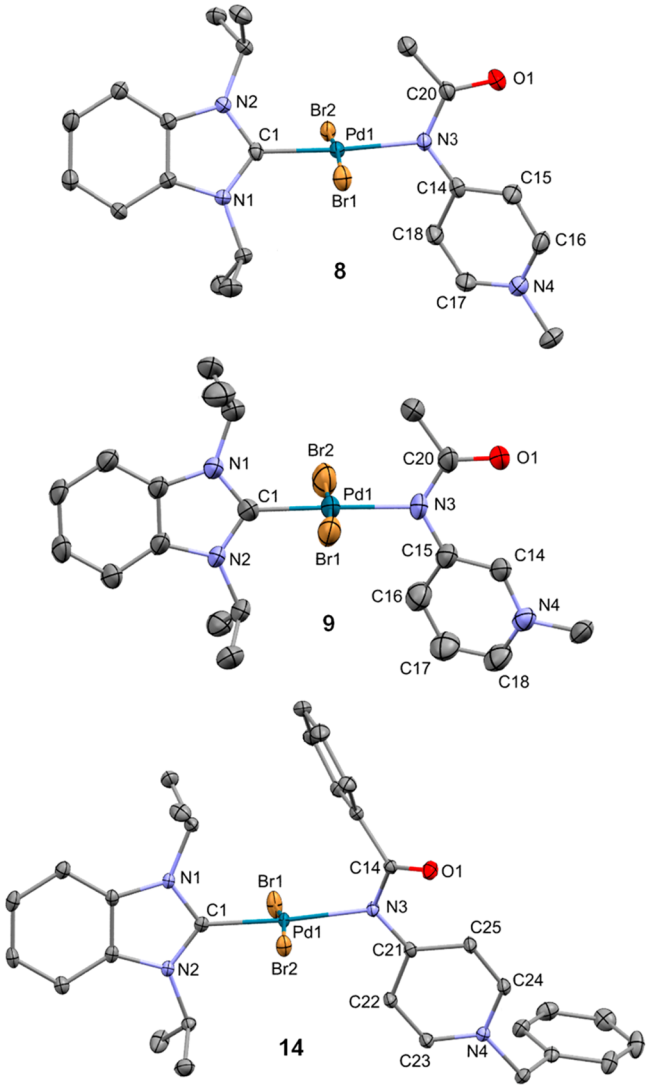

Figure 4. Molecular structures of **8**·$CHCl_3$, **9**·0.5$CHCl_3$, and **14**·$CHCl_3$ in the solid state. Hydrogen atoms are omitted for clarity; ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: **8**: Pd1−C1 1.962(4), Pd1−N3 2.106(4), O1−C20 1.234(5), N3−C14 1.367(6), N3−C20 1.370(6), N4−C17 1.343(6), N4−C16 1.344(6), C14−C18 1.407(6), C14−C15 1.409(7), C15−C16 1.362(7), C17−C18 1.372(7); N1−C1−N2 107.2(4), C14−N3−C20 120.4(4). **9**: Pd1−C1 1.961(7), Pd1−N3 2.102(5), N3−C20 1.368(9), N3−C15 1.391(9), N4−C18 1.343(11), N4−C14 1.351(9), O1−C20 1.234(8), C14−C15 1.395(10), C15−C16 1.401(11), C16−C17 1.384(11), C17−C18 1.366(12); N1−C1−N2 108.2(6), C20−N3−C15 120.6(6). **14**: Pd1−C1 1.956(2), Pd1−N3 2.1197(18), O1−C14 1.221(3), N3−C21 1.361(3), N3−C14 1.392(3), N4−C23 1.353(3), N4−C24 1.356(3), C21−C22 1.418(3), C21−C25 1.423(3), C22−C23 1.361(3), C24−C25 1.360(3); N2−C1−N1 107.92(18), C21−N3−C14 119.09(17).

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square-planar [$PdBr_2CN$] coordination plane. The Pd−C and Pd−N distances in all complexes are essentially identical averaging to 1.959 and 2.109 Å, respectively, which cannot be used to differentiate 4-PYA and 3-PYA complexes. Moreover, all C−O distances are short and with an average of 1.229 Å typical for C═O double bonds ruling out any notable contribution of the imidato resonance form. However, comparison of the bond parameters of the 4-PYA ligands in complexes **8**, **11**, and **14** with those of the free ligands **1** and **7** (Figure 2) reveal that they coordinate to palladium as primarily neutral imines with short exocyclic N−C_{Py} bonds (1.349−1.367 Å) and alternating single and double bonds in the pyridyl moieties. The orientation of the benzamide group in **14** facing one isopropyl group of the NHC is mostly retained in solution representative of the major isomer as evidenced by ^{1}H NMR studies (vide supra). The exocyclic N−C_{Py} bonds in complexes **9** and **12** (1.381−1.391 Å) are slightly longer, and their pyridyl rings exhibit a greater π-delocalization with typical aromatic C−C bonds revealing significant contribution of the amidato resonance form for the 3-PYA ligands (Figure 1).

Donor Strength Determination and Comparison. Using complexes **8**−**14**, the electronic properties of all isomeric PYA ligands **1**−**7** can be estimated by means of the HEP. Their respective values collected in $CDCl_3$ and referenced to the solvent signal at 77.7 ppm are summarized in Table 1. With HEP values in the range of 162−166 ppm, the donating power of PYA ligands is similar to those of other typical N-donors. However, they are certainly weaker donors compared to organometallic ligands such as isocyanides, arsines, phosphites, phosphines, and various types of NHCs, which all have HEP values of >168 ppm.[14,15] This result is more intuitive than that based on a *trans*-[$RhCl(CO)_2$(4-PYA)] complex previously reported (vide supra).

Figure 5 compares the donating abilities of PYAs to those of other typical Werner-type ligands on the ^{13}C NMR scale. They

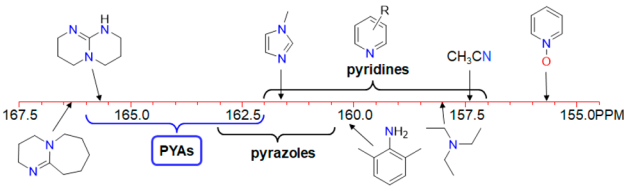

Figure 5. Donor strength comparison of PYAs with other Werner-typical ligands.

are superior donors compared to pyridine-*N*-oxide, acetonitrile, triethylamine, 2,6-dimethylaniline, various pyridines, most imidazoles, and pyrazoles.[15] Only the organosuperbases TBD and DBU are stronger donating compared to most PYAs.

A comparison between the PYA ligands **1**−**7** is depicted in Figure 6. Notably, 3-PYA ligands **2** and **5** are superior donors followed by 4-PYAs **1**, **4**, and **7**, respectively. 2-PYAs **3** and **6** are the weakest in this series. These results agree with those obtained from electrochemical studies[4,6] and reflect the mesoionic nature of 3-PYAs, which favor the amidato resonance form as supported by the solid-state molecular structures of complexes **9** and **12**. The increased donicity of 4-PYAs compared to 2-PYAs is also within expectations. Although both types are likely to adopt the neutral imine resonance form, the proximity of the electron-withdrawing pyridyl-nitrogen to the N-donor would render 2-PYAs significantly less donating. Comparison between pairs of the

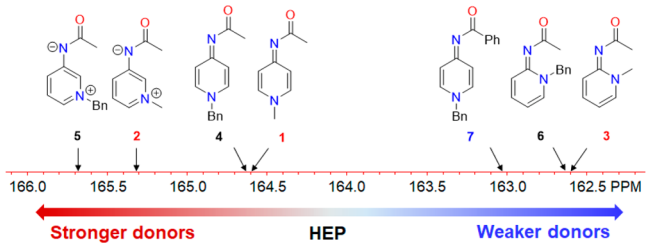

Figure 6. Donor strength comparison between PYAs **1**−**7**.

same type, i.e., **2**/**5**, **1**/**4**, and **3**/**6**, reveal that benzyl groups could be slightly more electron-releasing compared to methyl groups in all three types of PYAs. In 3-PYAs, this effect is enlarged, which implies an increased stabilization of the cationic pyridinium moiety by the benzyl substituent. Finally, comparison between ligands **4** and **7** demonstrates that the donating ability of PYAs can additionally be tuned by variation of the amide group, whereby benzamides give poorer donors compared to acetamides. This observation is in agreement with the greater positive inductive effect of methyl versus phenyl groups.

CONCLUSIONS

Seven mixed NHC/PYA complexes of the general formula *trans*-[$PdBr_2$(^{i}Pr_2-bimy)(PYA)], **8**−**14**, were prepared and fully characterized by various spectroscopic and spectrometric techniques. Using these complexes, the donor strengths of PYA ligands **1**−**7** was determined using the HEP method and systematically compared to each other and to those of common organometallic and Werner-type ligands. Generally, PYAs are weaker donors than arsines, phosphites, phosphines, and organometallic ones including isocyanides and various types of NHCs. However, they are among the strongest Werner-type ligands superior to pyridine-*N*-oxide, acetonitrile, triethylamine, 2,6-dimethylaniline, various pyridines, most imidazoles, and pyrazoles and are only rivalled by the organosuperbases TBU and DBU. In addition, they can exist in three isomeric forms, which allows for a fine-tuning of electronic properties over a notable range. 3-PYAs are generally stronger donors followed by 4-PYAs and then 2-PYAs. Further modifications are possible by choice of the pyridinium-*N*-substituent and the amide group. The electronic and structural diversity of these relatively new ligands and the ease of their preparation will certainly increase their impact in coordination chemistry in the years to come.

EXPERIMENTAL SECTION

General Considerations. Unless specifically mentioned, all operations were performed without taking precautions to exclude air and moisture, and all solvents and chemicals were used as received. The identity and purity of all new compounds was confirmed by a combination of ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, LRMS, HRMS (ESI), and elemental analysis. NMR chemical shifts were referenced internally to residual solvent signals relative to tetramethylsilane (TMS). X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation with the SMART suite of programs,[21] and refinement parameters are summarized in the Tables S1 and S2.

General Complexation Route A. Palladium-dimer **I** (0.141 g, 0.15 mmol, 0.5 equiv) was dissolved in acetonitrile (15 mL), and a solution of the free PYA ligand (0.30 mmol, 1.0 equiv) in acetonitrile (3 mL) was added. After stirring for 3 h, the solvent was removed under reduced pressure, and the product was dried *in vacuo*. If a

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precipitate was observed during the reaction, then it was filtered and washed with acetonitrile (2 × 2 mL) before removal of the solvent from the filtrate.

General Complexation Route B. A solution of the ligand precursor (0.30 mmol, 1.0 equiv) in acetonitrile (3 mL) was added to a solution of palladium-dimer **I** (0.141 g, 0.15 mmol, 0.5 equiv) in acetonitrile (12 mL). For precursors with a lower solubility, a few drops of dimethylsulfoxide were added to the dispersion in acetonitrile until the precursor was fully dissolved. Subsequently, silver(I) oxide (0.035 g, 0.15 mmol, 0.5 equiv) was added to the reaction mixture. After 3 h stirring, the solid formed was filtered and washed with acetonitrile (4 × 5 mL). The solvent of the filtrate was removed, and the remaining solid was dried *in vacuo* for 12 h at 50 °C. Iodide containing precursors were mixed with silver(I) oxide before adding the mixture to a solution of palladium-dimer **I**.

Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(*N*-(1-methylpyridin-4-ylidene)acetamide)palladium(II) (8). Using route **B**, the product was obtained as an orange powder. Orange single crystals could be obtained from a solution of chloroform layered with ether and hexane. Yield: 0.140 g (0.23 mmol, 76%). Two sets of signals (i and ii) are seen in the NMR spectra. $C_{21}H_{28}Br_2N_4OPd$ (M = 618.71 g mol^{-1}). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.51 (dm, 2 H, (i) Py−H), 8.47 (dm, 2 H, (ii) Py−H), 7.77−7.71 (m, 2 H, Py−H), 7.57 (dd, 2 H, ^3J = 6.2 Hz, ^4J = 3.2 Hz, Ar−H), 7.20 (dd, 2 H, ^3J = 6.2 Hz, ^3J = 3.2 Hz, Ar−H), 6.60−6.40 (br. m, 2 H, ^{i}Pr−CH), 6.42−6.25 (br. m, 2 H, (i) ^{i}Pr−CH), 6.25−6.12 (br. m, 2 H, (ii) ^{i}Pr−CH), 3.89 (s, 3 H, (i) NCH_3), 3.89 (s, 3 H, (ii) NCH_3), 3.08 (s, 2 H, (i) $COCH_3$), 3.03 (s, 2 H, $COCH_3$), 1.82 (d, 12 H, (i) ^{i}Pr−CH_3), 1.79 (d, 12 H, (ii) ^{i}Pr−CH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 181.4 ($NCOCH_3$), 164.6 (HEP), 163.9 (NC), 153.4, 145.2, 141.5, 141.3, 134.3, 134.1, 122.9, 122.8, 122.7, 120.7, 120.5, 116.4, 113.3, 55.1 (^{i}Pr−CH), 45.9 (NCH_3), 31.9 ((ii) $COCH_3$), 31.5 ((i) $COCH_3$), 21.4 (br., ^{i}Pr−CH_3) ppm. Anal. Calcd for $C_{21}H_{28}Br_2N_4OPd$ $CHCl_3$: C, 35.80; H, 3.96; N, 7.59%. Found: C, 35.82; H, 3.83; N, 7.79%. HRMS (ESI): calcd for [M + Na]$^+$, $C_{21}H_{28}Br_2N_4NaOPd$, m/z = 638.9557. Found, m/z = 638.9539.

Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(*N*-(1-methylpyridin-3-ylidene)acetamide)palladium(II) (9). After a reaction according to route **B**, the product was obtained as a brown powder, which was crystallized from a solution in chloroform layered with diethyl ether and hexane to give red-brown single crystals. $C_{21}H_{28}Br_2N_4OPd$ (M = 618.71 g mol^{-1}). Yield: 0.146 g (0.24 mmol, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.52 (d, 1 H ^3J = 6.3 Hz, Py−H), 9.26 (d, 1 H, ^3J = 8.7 Hz, Py−H), 9.21 (d, 1 H, ^3J = 8.7 Hz, Py−H), 7.77 (dm, 1 H, ^3J = 5.1 Hz, Py−H), 7.61 (t, 1 H, ^3J = 6.3 Hz, Py−H), 7.56 (dd, 2 H, ^3J = 6.1 Hz, ^4J = 3.2 Hz, Ar−H), 7.18 (dd, 2 H, ^3J = 6.1 Hz, ^4J = 3.2 Hz, Ar−H), 6.56−6.13 (m, 2 H, ^{i}Pr−CH), 4.16 (s, 3 H, NCH_3), 2.95 (s, 3 H, $COCH_3$), 2.90 (s, 3 H, $COCH_3$), 1.79 (d, 12 H, ^{i}Pr−CH_3), 1.76 (d, 12 H, ^{i}Pr−CH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 178.3 ($NCOCH_3$), 165.3 (HEP), 152.9 (NC), 141.3 (Py−C), 140.1 (Py−C), 139.8 (Py−C), 134.2 (Ar−C), 134.1 (Ar−C), 133.0 (Py−C), 126.8 (Py−C), 126.7 (Py−C), 122.8 (Ar−C), 122.7 (Ar−C), 113.2 (Ar−C), 55.12 (^{i}Pr−CH), 55.05 (^{i}Pr−CH), 49.2 (NCH_3), 30.8 ($COCH_3$), 30.3 ($COCH_3$), 21.4 (^{i}Pr−CH_3), 21.2 (^{i}Pr−CH_3), 20.8 (^{i}Pr−CH_3) ppm. Anal. Calcd for $C_{21}H_{28}Br_2N_4OPd$·0.5$CHCl_3$: C, 38.07, H, 4.23, N, 8.26%. Found: C, 38.39, H, 4.12, N, 7.93%. HRMS (ESI, positive ions): calcd for [M + Na]$^+$, $C_{21}H_{28}Br_2N_4NaOPd$, m/z = 638.9557. Found, m/z = 638.9564.

Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(*N*-(1-methylpyridin-2-ylidene)acetamide)palladium(II) (10). Following route **B**, the complex was obtained as an orange powder. A mixture of *trans-E-* and *trans-Z*-complex was obtained, and NMR signals will be listed accordingly as (i) and (ii) with (i) as the predominant complex. $C_{21}H_{28}Br_2N_4OPd$ (M = 618.71 g mol^{-1}). Yield: 0.112 g (0.18 mmol, 60%). ^{1}H NMR (500 MHz, $CDCl_3$, AT): δ = 8.52 (s, 1 H, ^3J = 8.7 Hz, (ii) Py−H), 8.46 (s, 1 H, ^3J = 8.7 Hz, (i) Py−H), 8.20−8.10 (m, 2 H, (ii) Py−H), 8.08−7.96 (m, 1 H, (i) Py−H), 7.64−7.55 (m, 2 H, (ii) Ar−H), 7.52 (dd, 2 H, ^3J = 6.2 Hz, ^4J = 3.2 Hz, (i) Ar−H), 7.26−7.20 (dm, 2 H, (ii) Ar−H), 7.16 (dd, 2 H, ^3J = 6.2 Hz, ^3J = 3.2 Hz, (i) Ar−H), 6.25 (sept, 2 H, ^3J = 7.1 Hz, (i) ^{i}Pr−CH), 6.12 (d, 2 H, ^3J = 7.3 Hz, (ii) ^{i}Pr−CH_3), 4.18 (s, 3 H, (i) NCH_3), 4.17 (s, 3 H, (ii) NCH_3), 2.85 (s, 3 H, (i) $COCH_3$), 2.81 (s, 3 H, (ii) $COCH_3$), 1.74 (d, ^3J = 7.1 Hz, (i) ^{i}Pr−CH_3), 1.72z (d, ^3J = 7.3 Hz, (ii) ^{i}Pr−CH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, AT): δ = 176.0 ((i) $NCOCH_3$), 175.9 ((ii) $NCOCH_3$), 162.6 ((i, ii) NC), 161.7$_9$ ((i) HEP), 161.7$_6$ ((ii) HEP) 142.7 ((i) Py−C), 142.6 ((ii) Py−C), 142.34 ((ii) Py−C), 142.30 ((i) Py−C), 134.1 ((ii) Ar−C), 134.0 ((i) Ar−C), 129.7 ((ii) Py−C), 129.6 ((i) Py−C), 122.8 ((i) Ar−C), 122.7 ((ii) Ar−C), 119.8 ((i) Py−C), 119.7 ((ii) Py−C), 113.11 ((ii) Ar−C), 113.09 ((i) Ar−C), 55.2 ((ii) ^{i}Pr−CH), 55.1 ((i) ^{i}Pr−CH), 46.1 ((ii) NCH_3), 45.8 ((i) NCH_3), 29.4 ((ii) $COCH_3$), 28.8 ((i) $COCH_3$), 21.2 ((i) ^{i}Pr−CH_3), 21.1 ((ii) ^{i}Pr−CH_3), 20.7 ((ii) ^{i}Pr−CH_3) ppm. HRMS (ESI, positive ions): calcd for [M + Na]$^+$, $C_{21}H_{28}Br_2N_4NaOPd$, m/z = 638.9557. Found, m/z = 638.9562.

Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(*N*-(1-benzylpyridin-4-ylidene)acetamide)palladium(II) (11). Following route **B**, the product was obtained as a yellow powder. Single crystals were obtained from a solution of chloroform layered with diethyl ether. $C_{27}H_{32}Br_2N_4OPd$ (M = 694.81 g mol^{-1}). Yield: 0.207 g (0.30 mmol, 99%). ^{1}H NMR (500 MHz, $CDCl_3$, AT): δ = 8.61 (t, 2 H, ^3J = 7.5 Hz, Py−H), 7.80 (d, 2 H, ^3J = 7.5 Hz, Py−H), 7.57 (dd, 2 H, ^3J = 6.2 Hz, ^4J = 3.2 Hz, Ar−H), 7.44−7.37 (m, 3 H, Bn−H), 7.30−7.26 (m, 2 H, Bn−H), 7.20 (dd, 2 H ^3J = 6.2 Hz, ^4J = 3.2 Hz, Ar−H), 6.45 (br. s, 1 H, ^{i}Pr−CH), 6.38 (br. s, 1 H, ^{i}Pr−CH), 5.22 (s, 2 H, CH_2), 3.12 (s, 3 H, $COCH_3$), 1.81 (d 12 H, ^{i}Pr−CH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, AT): δ = 181.8 ($NCOCH_3$), 164.6 (HEP), 164.0 (NC), 140.5 (Py−C), 134.14 (Bn−C), 134.13 (Ar−C), 130.24 (Bn−C), 130.20 (Bn−C), 129.0 (Bn−C), 122.8 (Ar−C), 120.5 (Py−C), 113.3 (Ar−C), 62.2 (CH_2), 55.1 (^{i}Pr−CH), 31.7 ($COCH_3$), 21.4 (^{i}Pr−CH_3) ppm. Anal. Calcd for $C_{27}H_{32}Br_2N_4OPd$: C, 46.61, H, 4.78, N, 8.05%. Found: C, 46.05, H, 4.65, N, 8.07%. Better values could not be obtained despite several recrystallizations. HRMS (ESI, positive ions): calcd for [M + H]$^+$, $C_{27}H_{33}Br_2N_4OPd$, m/z = 693.0050. Found, m/z = 693.0047.

Dibromido(1,3-diisopropylbenzimidazolin-3-ylidene)(*N*-(1-benzylpyridin-4-ylidene)acetamide)palladium(II) (12). Precursors not showing a successful conversion with silver(I) oxide were treated with an excess of sodium hydroxide (0.15 mL, 8.7 M, 4.4 equiv) as a base. The formation of a precipitate upon base addition could be observed for this reaction. The remaining solid after removing the solvent was dispersed in chloroform (20 mL), and the organic phase was washed with water (3 × 10 mL) to remove traces of salts. After drying the organic phase over sodium sulfate for 1 h, the solvent of the filtrate was removed, and the residue was dried *in vacuo* for several hours at 50 °C. The complex was obtained as dark green crystals after crystallization from a solution of chloroform layered with diethyl ether. $C_{27}H_{32}Br_2N_4OPd$ (M = 694.81 g mol^{-1}). Yield: 0.030 g (0.043 mmol, 14%). ^{1}H NMR (500 MHz, $CDCl_3$, AT): δ = 9.91 (s, 1 H, Py−H), 9.37 (dm, 1 H, Py−H), 7.69 (d, 1 H, Py−H), 7.61−7.54 (m, 3 H, Py−H, Bn−H), 7.44−7.40 (m, 3 H, Bn−H), 7.35 (dd, 2 H, ^3J = 6.4 Hz, ^4J = 3.0 Hz, Ar−H), 7.19 (dd, 2 H, ^3J = 6.4 Hz, ^4J = 3.0 Hz, Ar−H), 6.40 (br. s, 2 H, ^{i}Pr−CH), 5.41 (s, 2 H, CH_2), 2.99 (s, 3 H, $COCH_3$), 1.79 (d, 12 H, ^{i}Pr−CH_3) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, AT): δ = 178.6 ($NCOCH_3$), 165.7 (HEP), 153.3 (NC), 141.1 (Py−C), 140.3 (Py−C), 134.2 (Ar−C), 132.8 (Py−C), 131.4 (Bn−C), 130.8 (Bn−C), 130.5 (Bn−C), 129.2 (Bn−C), 126.9 (Py−C), 122.7 (Ar−C), 113.2 (Ar−C), 65.9 (CH_2), 55.1 (^{i}Pr−CH), 30.4 ($COCH_3$), 21.4 (^{i}Pr−CH_3) ppm. Anal. Calcd for $C_{27}H_{32}Br_2N_4OPd$·$CHCl_3$: C, 41.31, H, 4.09, N, 6.88%. Found: C, 41.73, H, 4.11, N, 6.80%. HRMS (ESI, positive ions): calcd for [M + H]$^+$, $C_{27}H_{33}Br_2N_4OPd$, m/z = 693.0050. Found, m/z = 693.0048.

Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(*N*-(1-benzylpyridin-2-ylidene)acetamide)palladium(II) (13). Both routes have been applied to synthesize this complex giving similar yields. The raw product was obtained as yellow powder. $C_{27}H_{32}Br_2N_4OPd$ (M = 694.81 g mol^{-1}). Yield: 0.098 g (0.141 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$, AT): δ = 8.46 (dd, 1 H ^3J = 7.5 Hz, Py−H), 7.98 (tm, 1 H, ^3J = 7.5 Hz, Py−H), 7.71 (dm, 1 H, ^3J = 6.6 Hz, Py−H), 7.54 (dd, 2 H, ^3J = 6.2, ^4J = 3.2 Hz, Ar−H), 7.45−7.39 (m, 4 H, Bn−H), 7.37−7.29 (m, 1 H, Bn−H), 7.18 (dd, 2

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H, ^3J = 6.2 Hz, ^4J = 3.2 Hz, Ar−H), 7.11 (t, 1 H, ^3J = 6.6 Hz, Py−H), 6.31 (sept, 2 H, ^3J = 7.1 Hz, ^{i}Pr−CH), 5.75 (s, 2 H, CH_2), 2.90 (s, 3 H, $COCH_3$), 1.76 (d, 12 H, ^3J = 7.1 Hz, ^{i}Pr−CH_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, AT): δ = 176.9 ($NCOCH_3$), 162.6 (HEP), 162.0 (NC), 142.2 (Py−C), 139.8 (Py−C), 134.1 (Py−C), 133.9 (Ar−C), 131.5 (Bn−C), 130.14 (Bn−C), 130.09 (Bn−C), 129.4 (Bn−C), 122.8 (Ar−C), 119.3 (Py−C), 113.1 (Ar−C), 58.4 (^{i}Pr−CH), 55.2 (CH_2), 29.0 ($NCOCH_3$), 21.3 (^{i}Pr−CH_3) ppm. HRMS (ESI, positive ions): calcd for $[M + H]^+$, $C_{27}H_{33}Br_2N_4OPd$, m/z = 693.0050. Found, m/z = 693.0035.

Dibromido(1,3-diisopropylbenzimidazolin-2-ylidene)(*N*-(1-benzylpyridin-4-ylidene)benzamide)palladium(II) (14). Following route **A**, the complex was obtained as a yellow powder. Yellow single crystals were obtained from a solution of chloroform layered with diethyl ether and hexane. Two sets of signals in a ratio of 80:20 are observed in the NMR spectra, which will be listed accordingly as (i) and (ii). $C_{32}H_{34}Br_2N_4OPd$ (M = 756.88 g mol^{-1}). Yield: 0.158 g (0.21 mmol, 69%). ^{1}H NMR (500 MHz, $CDCl_3$, AT): δ = 8.84 (d, 2 H, ^3J = 7.4 Hz, (ii) Py−H), 8.57 (d, 2 H, ^3J = 7.4 Hz, (ii) Py−H), 8.42 (d, 2 H, ^3J = 7.5 Hz, (i) Py−H), 8.36 (dd, 2 H, (ii) Ph−H), 8.28 (dd, 2 H, (i) Ph−H), 7.83 (d, 2 H, ^3J = 7.5 Hz, (i) Py−H), 7.62−7.56 (m, 3 H, (ii) Ph−H), 7.56−7.49 (m, 3 H, (i) Ph−H), 7.45 (dd, 2 H, (ii) Ar−H), 7.43−7.38 (m, 5 H, (i, ii) Bn−H), 7.32 (dd, 2 H, (i) Ar−H), 7.18−7.12 (m, 2 H, (ii) Ar−H), 7.11 (dd, 2 H, (i) Ar−H), 6.54 (sept, 1 H, ^3J = 6.7 Hz, (ii) ^{i}Pr−CH), 6.42 (sept, 1 H, ^3J = 6.2 Hz, (ii) ^{i}Pr−CH_3), 6.4−5.9 (br. m, 1 H, (i) ^{i}Pr−CH_3), 5.77 (s, 2 H, (ii) CH_2), 5.28 (s, 2 H, (i) CH_2), 5.4−4.9 (br. m, 1 H, (i) ^{i}Pr−CH), 1.81 (d, 6 H, ^3J = 6.7 Hz, (ii) ^{i}Pr−CH_3), 1.63 (d, 6 H, ^3J = 6.2 Hz, (ii) ^{i}Pr−CH_3), 2.0−1.1 (br. m, 12 H, (i) ^{i}Pr−CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, AT): δ = 180.6 (NCOPh), 164.9 (NC), 163.0 (HEP), 154.2 (Ph−C), 144.5, 144.4, 141.8, 141.7, 140.5, 131.4, 130.2, 130.2, 129.0, 128.5, 122.6, 122.5, 120.3, 117.9, 113.1, 64.1 ((ii) ^{i}Pr−CH), 62.2 ((i) ^{i}Pr−CH), 57.7 ((ii) CH_2), 54.7 ((i) CH_2), 21.2 ((i) ^{i}Pr−CH_3), 21.1 ((ii) ^{i}Pr−CH_3) ppm. Anal. Calcd for $C_{32}H_{34}Br_2N_4OPd\cdot CHCl_3$: C, 45.23, H, 4.03, N, 6.39%. Found: C, 45.36, H, 3.97, N, 6.09%. HRMS (ESI, positive ions): calcd for $[M + Na]^+$, $C_{27}H_{34}Br_2N_4NaOPd$, m/z = 777.0027. Found, m/z = 777.0025.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01585.

Experimental details for PYAs and their precursors, molecular structures, selected crystallographic data tables, NMR spectra and ESI mass spectra (PDF)

Accession Codes

CCDC 2006195−2006201 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, or by emailing 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.

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