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Synthesis and Characterization of 2,6-Di(quinolin-8-yl)pyridines. New Ligands for Bistridentate Ru^{II} Complexes with Microsecond Luminescent Lifetimes

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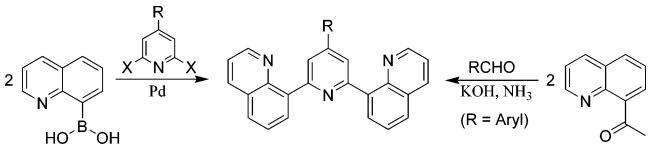

The synthesis of 4-substituted and 4-aryl-substituted 2,6-di(quinolin-8-yl)pyridines is described. The tridentate ligands were prepared via a palladium-catalyzed Suzuki−Miyaura cross-coupling reaction or via a one-step ring-forming reaction generating the central pyridine ring. X-ray crystal structures and ^{1}H NMR shifts are discussed and compared to the corresponding data for a Ru^{II} bistridentate complex. Intramolecular stacking of two quinoline units in the Ru^{II} complex is suggested by ^{1}H NMR data and also observed in the X-ray structure.

Photoactive polypyridyl ruthenium(II) complexes based on tridentate nitrogen-containing heterocycles such as 2,2′:6′,2″-terpyridine (tpy) continue to attract wide interest[1] for their possible use in, e.g., artificial photosynthetic systems,[2] in molecular photonic devices,[3] and in metallo-supramolecular polymers.[4] Due to the symmetry of the 4′-substituted 2,2′:6′,2″-terpyridines, the resulting $[Ru(tpy)_2]^{2+}$ complexes are achiral, which makes these ligands ideal building blocks for the construction of multicomponent metal-containing systems for vectorial electron and energy transfer. However, the luminescent properties of tpy-based ruthenium(II) complexes are generally poor, and $[Ru(tpy)_2]^{2+}$ has an excited-state lifetime of only 0.25 ns at room temperature,[5] which has limited their use in many applications. Therefore, the development of novel tridentate nitrogen-containing ligands that result in highly luminescent bistridentate ruthenium(II) complexes with long excited-state lifetimes would considerably expand the use of this class of complexes in many research fields. Along these lines, we recently reported the synthesis of 2,6-di(quinolin-8-yl)pyridine (**1**) and the corresponding ruthenium(II) complex $[Ru(\mathbf{1})_2]^{2+}$, which has a remarkable 3 μs excited-state lifetime at room temperature.[6] The tridentate ligand provides a larger bite angle than tpy resulting in an increase in the ligand field splitting. Consequently, the normally rapid activated decay of the metal-to-ligand charge transfer (MLCT) state via the metal-centered (MC) state in $[Ru(tpy)_2]^{2+}$ complexes is slowed down in $[Ru(\mathbf{1})_2]^{2+}$ resulting in favorable properties.

To have readily accessible ligands for future preparation of linear multiunit assemblies based on the Ru^{II} bistridentate motif, we were interested in developing synthetic routes to substituted 2,6-di(quinolin-8-yl)pyridyl ligands. Herein, we present the synthesis of a range of functionalized 2,6-di(quinolin-8-yl)-pyridyl ligands prepared via the Pd-catalyzed coupling strategy and via a one-step ring-forming methodology generating the central pyridine ring.[7]

2,6-Di(quinolin-8-yl)pyridines. Our initial strategy toward 2,6-di(quinolin-8-yl)pyridines was based on the Stille-type carbon−carbon bond-forming reaction which has previously been widely used for the preparation of functionalized oligopyridyl ligands.[8] Reacting 8-(tri-*n*-butyltin)quinoline[9] and 2,6-dibromopyridine with 5 mol % of $Pd(PPh_3)_4$ using different conditions (e.g., refluxing toluene, THF at 140 °C using microwave heating) resulted in low yields, less than 30%, and various byproducts. Instead, we focused on the Suzuki−Miyaura

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(1) (a) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993−1019. (b) Medlycott, E. A.; Hanan, G. S. *Chem. Soc. Rev.* **2005**, *34*, 133−142. (c) Medlycott, E. A.; Hanan, G. S. *Coord. Chem. Rev.* **2006**, *250*, 1763−1782.

(2) (a) Baranoff, E.; Collin, J.-P.; Flamigni, L.; Sauvage, J.-P. *Chem. Soc. Rev.* **2004**, *33*, 147−155, and references cited therein. (b) Lainé, P.; Bedioui, F.; Amouyal, E.; Albin, V.; Berruyer-Penaud, F. *Chem. Eur. J.* **2002**, *8*, 3162−3176. (c) Lainé, P.; Bedioui, F.; Ochsenbein, P.; Marvaud, V.; Bonin, M.; Amouyal, E. *J. Am. Chem. Soc.* **2002**, *124*, 1364−1377. (d) Borgström, M.; Ott, S.; Lomoth, R.; Bergquist, J.; Hammarström, L.; Johansson, O. *Inorg. Chem.* **2006**, *45*, 4820−4829.

(3) (a) Ziessel, R.; Hissler, M.; El-ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178*−*180*, 1251−1298. (b) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1−12. (c) Amini, A.; Bates, K.; Benniston, A. C.; Lawrie, D. J.; Soubeyrand-Lenoir, E. *Tetrahedron Lett.* **2003**, *44*, 8245−8247. (d) Benniston, A. C.; Harriman, A.; Li, P.; Patel, P. V.; Sams, C. A. *J. Org. Chem.* **2006**, *71*, 3481−3493.

(4) (a) Andres, P. R.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 1043−1068. (b) Schubert, U. S.; Hofmeier, H.; Newkome, G. R. *Modern Terpyridine Chemistry*; Wiley-VCH: Weinheim, 2006; pp 131−170.

(5) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381−2392.

(6) Abrahamsson, M.; Jäger, M.; Österman, T.; Eriksson, L.; Persson, P.; Becker, H.-C.; Johansson, O.; Hammarström, L. *J. Am. Chem. Soc.* **2006**, *128*, 12616−12617.

(7) (a) Vaduvescu, S.; Potvin, P. G. *Inorg. Chem.* **2002**, *41*, 4081−4083. (b) Smith, C. B.; Raston, C. L.; Sobolev, A. N. *Green Chem.* **2005**, *7*, 650−654. (c) Wang, J.; Hanan, G. S. *Synlett* **2005**, 1251−1254. (d) Hwang, S.-H.; Moorefield, C. N.; Wang, P.; Fronczek, F. R.; Courtney, B. H.; Newkome, G. R. *Dalton Trans.* **2006**, 3518−3522. (e) Winter, A.; van den Berg, A. M. J.; Hoogenboom, R.; Kickelbick, G.; Schubert, U. S. *Synthesis* **2006**, 2873−2878.

(8) (a) Hanan, G. S.; Lehn, J.-M.; Kyritsakas, N.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1995**, 765−766. (b) Lehmann, U.; Henze, O.; Schlüter, A. D. *Chem. Eur. J.* **1999**, *5*, 854−859. (c) Fallahpour, R.-A.; Neuburger, M.; Zehnder, M. *New J. Chem.* **1999**, 53−61. (d) Fallahpour, R.-A. *Synthesis* **2000**, 1138−1142. (e) Heller, M.; Schubert, U. S. *Synlett* **2002**, 751−754.

(9) DiMauro, E. F.; Mamai, A.; Kozlowski, M. C. *Organometallics* **2003**, *22*, 850−855.

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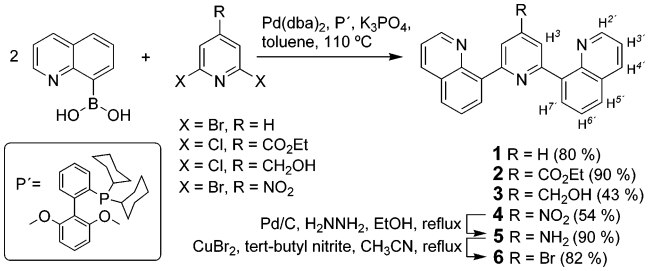
SCHEME 1. Pd-Catalyzed Coupling of Quinoline-8-boronic Acid and 2,6-Dihalopyridines



cross-coupling reaction using a catalyst system composed of Pd and commercially available 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (P′), which recently has been used to effectively couple a range of heterocyclic substrates.[10] Reacting quinoline-8-boronic acid and 2,6-dibromopyridine with 1 mol % of $Pd(dba)_2$ and 2 mol % of P′ in toluene at 110 °C gave compound **1** in 80% isolated yield (Scheme 1).[6] Using 2,6-dichloroisonicotinic ethyl ester,[11] 2,6-dichloro-4-hydroxymethylpyridine,[8e] or 2,6-dibromo-4-nitropyridine[12] furnished **2**−**4** in moderate to excellent yields (Scheme 1). The ester-substituted **2** was obtained in 90% yield after recrystallization from EtOH. Using standard functional group manipulations, compound **4** was reduced to give the amino-functionalized **5**, which was subsequently converted to the bromo-functionalized ligand **6** by treatment with *tert*-butyl nitrite−copper(II) bromide.[13]

In the ^{1}H NMR spectra (in $CDCl_3$) of the symmetric ligands **1**−**6**, the lowest field resonance in all ligands is $H^{2'}$ adjacent to the nitrogen of the quinoline ring. It is interesting to compare the proton resonances of the central pyridine of the 2,6-di(quinolin-8-yl)pyridyl ligands to those of 2,2′:6′,2″-terpyridines. The H^4 proton in **1** (at 7.96 ppm) is close to that of tpy (7.97 ppm),[14] whereas the H^3 protons in **1** (at 8.13 ppm) are found to be upfield shifted compared to tpy (8.46 ppm). In the latter compounds, the H^3 protons are deshielded by the nearby pyridines in the presumed *transoid* planar arrangement.[14] Except for the expected difference in electron-accepting property of the 8-quinolinyl compared to 2-pyridyl substituents, we believe that the favored conformation in **1** deviates from a planar arrangement of the aromatic ring-systems resulting in a less deshielded environment of the H^3 protons in **1** compared to tpy. Similar shifts of the H^3 protons when compared to the corresponding substituted tpy ligands[8c,d,15,16] (0.1−0.6 ppm) are observed in all ligands **1**−**6**. Support for such twisted arrangements comes from the observed solid-state structures.

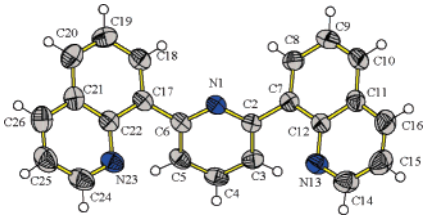


FIGURE 1. ORTEP view of **1** at 50% probability level.

The X-ray crystal structures of **1** (Figure 1) and the amino-substituted **5** (Supporting Information) confirmed the proposed structures. Compound **1** is twisted with torsion angles between the central pyridine and quinoline units of −47.0° (N1−C2−C7−C8) and 46.4° (N1−C6−C17−C18), respectively. This is distinct from structures of 2,2′:6′,2″-terpyridines which usually show angles between the planes of the central pyridyl ring and the two terminal rings smaller than 10−12°.[14,17] The interannular C−C bond lengths in **1** are 1.496(3) and 1.483(3) Å, respectively. The crystal packing is typical for aromatic molecules in a pseudoherringbone pattern. It does not show any short intermolecular interactions between the centers of gravity of different rings that are indicative of $\pi-\pi$ interactions in the lattice (Supporting Information). In addition, a geometry optimization calculation was performed with MOPAC-6[18] using the AM1-Hamiltonian regarding the observed torsion angles. The calculated minimum (−55°) is close to the experimental value observed in the X-ray crystal structure and gives support for a twisted structure also in solution. However, the torsion angle can vary between −90° to −45° with only 2 kcal mol^{-1} changes in the heat of formation (Supporting Information).

The solid-state structure of **5** shows considerably larger and less symmetric torsional angles between the central pyridine and quinoline units, −98.5° and 60.5°, respectively (Supporting Information). The structure shows no unusual $\pi-\pi$ interactions in the lattice; however, hydrogen-bonded dimers are evident which can explain the increased torsional angles[8c] as compared to **1**. These dimers then pack in a typical pattern for aromatic compounds.

Structural Characterization of $[Ru(1)_2]^{2+}$. Upon coordination of **1** to Ru^{II} forming $[Ru(\mathbf{1})_2]^{2+}$,[6] the proton resonances change significantly as shown in Figure 2 (both the free ligand and the complex were recorded in CD_3CN), and the assignment was accomplished by two-dimensional NMR techniques (COSY, NOESY). The downfield shift for the H^4 proton upon coordination is similar to that of $[Ru(tpy)_2]^{2+}$.[19] However, the H^3 protons are upfield shifted ($\Delta\delta = -0.2$ ppm), which is opposite to that observed in bisterpyridine ruthenium(II) complexes (usually downfield shifted by $\Delta\delta \geq +0.3$ ppm upon coordination due to the electron-withdrawing effect of the metal ion).[19,20] In $[Ru(tpy)_2]^{2+}$, the two tridentate ligands are close to planar and

(10) (a) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871−1876. (b) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685−4696.

(11) Prepared as 2,6-dibromoisonicotinic ethylester (ref 8d). ^{1}H NMR identical to the material prepared previously (Tutonda, M.; Vanderzande, D.; Hendrickx, M.; Hoornaert, G. *Tetrahedron* **1990**, *46*, 5715−5732).

(12) Neumann, U.; Vögtle, F. *Chem. Ber.* **1989**, *122*, 589−591.

(13) Doyle, M. P.; Siegfried, B.; Dellaria, J. F., Jr. *J. Org. Chem.* **1977**, *42*, 2426−2431.

(14) Constable, E. C.; Cargill Thompson, A. M. W.; Tocher, D. A.; Daniels, M. A. M. *New J. Chem.* **1992**, *16*, 855−867.

(15) Cuenoud, B.; Schepartz, A. *Proc. Natl. Acad. Sci. U.S.A.*, **1993**, *90*, 1154−1159.

(16) Péchy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1995**, 65−66.

(17) (a) Constable, E. C.; Lewis, J.; Liptrot, M. C.; Raithby, P. R. *Inorg. Chim. Acta* **1990**, *178*, 47−54. (b) Fallahpour, R.-A.; Neuburger, M.; Zehnder, M. *Polyhedron* **1999**, *18*, 2445−2454. (c) Eryazici, I.; Moorefield, C. N.; Durmus, S.; Newkome, G. R. *J. Org. Chem.* **2006**, *71*, 1009−1014.

(18) Stewart, J. J. P. MOPAC-6 public domain version, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO, 1990.

(19) ^{1}H NMR spectra in CD_3CN: Schubert, U. S.; Hofmeier, H.; Newkome, G. R. *Modern Terpyridine Chemistry*; Wiley-VCH: Weinheim, 2006; p 42.

(20) See also Constable et al. in ref 14. However, the free ligands were recorded in $CDCl_3$ and the Ru^{II} complexes in CD_3COCD_3.

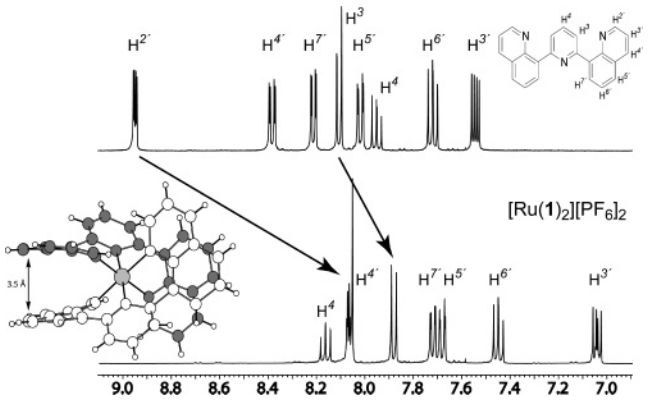
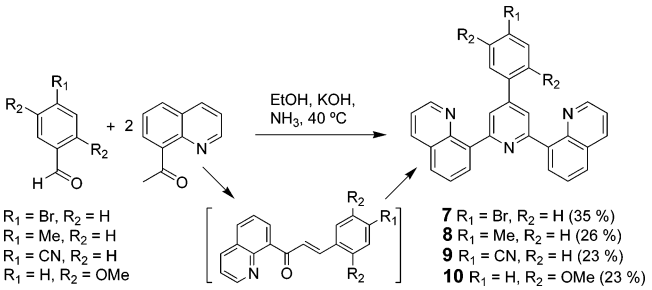


FIGURE 2. Ball and stick representation of $[Ru(\mathbf{1})_2][PF_6]_2$ and ^1H NMR spectra of **1** (top) and $[Ru(\mathbf{1})_2][PF_6]_2$ (bottom) in CD_3CN.

orthogonal to each other.[21] Instead, the recently reported X-ray crystal structure of $[Ru(\mathbf{1})_2]^{2+}$ (Figure 2)[6,22] shows enforced dihedral angles between the pyridine and the quinoline least-square planes (35 and 39°, respectively). This leads to quasi-planar arrangements of two quinoline units, one from each tridentate ligand, with an interplanar distance less than 3.5 Å.[23] The different magnetic environment for the H^3 protons in $[Ru(\mathbf{1})_2]^{2+}$ relative to $[Ru(tpy)_2]^{2+}$ most likely explains the shift differences.[24] For the quinoline units, the most dramatic change is that of $H^{2'}$ which experiences a large upfield shift ($\Delta\delta = -0.9$ ppm) due to its position above the other ligand. Similar effects of the protons adjacent to the nitrogens of the terminal pyridine rings of 2,2′:6′,2″-terpyridines when coordinated to Ru^{II} are well-known.[14,19] All other protons of the quinolines are also significantly upfield shifted which suggest intramolecular stacking[25] of the quinoline units in agreement with the X-ray crystal structure.

4-Aryl-Substituted 2,6-Di(quinolin-8-yl)pyridines. Having the substituted 2,6-di(quinolin-8-yl)pyridyl ligands in hand, we also targeted the introduction of 4-aryl substituents on the central pyridine since such substituents often have a profound effect on the photophysical properties of the corresponding bisterpyridine Ru^{II} complexes,[1] and this is a well-known strategy to increase the donor (D)−acceptor (A) distance in D-chromophore-A triads.[2a] Hanan and co-workers recently reported a simple one-step procedure for the preparation of a variety of 4′-aryl substituted tpy ligands,[7c] and we were interested in using a similar protocol to have access to 4-aryl-substituted 2,6-di(quinolin-8-yl)pyridyl ligands. The reaction of 4-bromobenzaldehyde with 2 equiv of 8-acetylquinoline[26] in a basic aqueous ethanolic solution of ammonia at 40 °C afforded **7** (Scheme 2), which solidified from solution and was purified by recrystallization from EtOH to give an isolated yield of 20−25%. A second crop was obtained by chromatography to give a total yield of 35%. The intermediate enone precipitates as a pale yellow solid during the reaction and was isolated in a separate reaction of equimolar 4-bromobenzaldehyde and 8-acetylquinoline in 83% yield. The MS spectrum showed the expected peak at $m/z = 338$ $[M + H^+]^+$ and ^1H NMR signals from the vinylic protons at around 7.6 ppm. Overlapping resonances of the vinylic protons precluded a definite assignment, but tentatively we assign it to the trans isomer.[27]

SCHEME 2. One-Step Synthesis of 4-Aryl-Substituted 2,6-Di(quinolin-8-yl)pyridines



The analogous reaction using 4-methylbenzaldehyde led to a lower isolated yield of **8**. In an attempt to optimize this reaction, it was noted that a higher overall yield was obtained by increasing the temperature to 60 °C and by addition of some $CHCl_3$ to improve the solubility of the intermediate enone. However, careful analysis of the reaction mixture revealed a mixture of two cyclized products, the desired 2,6-di(quinolin-8-yl)-4-(*p*-tolyl)pyridyl ligand **8** as well as the isomer 2,4-di(quinolin-8-yl)-6-(*p*-tolyl)pyridine. These were separated by careful column chromatography to give **8** and the isomer in up to 30% and 15% isolated yields, respectively. A higher yield in the synthesis of the bromo-substituted **7** was also found when the reaction was performed at 60 °C but with an increased amount of the undesired isomer. Since the yields of the desired isomers were not significantly improved and that the separations are tedious, subsequent reactions were run using the optimal conditions at 40 °C. Next, 4-cyanobenzaldehyde and 2,5-dimethoxybenzaldehyde, respectively, were used as substrates to give the substituted ligands **9** and **10** in moderate yields (Scheme 2). Compound **10** containing a viable quinone precursor is particularly interesting for the preparation of linear bistridentate Ru^{II} electron donor−acceptor assemblies based on the 2,6-di(quinolin-8-yl)pyridyl ligands. The ^1H NMR spectra of the 4-aryl substituted ligands **7**−**10** follow the same pattern as for **1**−**6** with the H^3 protons considerably upfield shifted as compared to the corresponding 4′-aryl-substituted terpyridines.

Given the recent interest in rigid ditopic bridging ligands based on the tridentate motif,[28] the synthesis of the "back-to-back" bridging ligand **11** was also pursued. Nickel-catalyzed homocoupling[29] of **7** gave an inseparable mixture of products, and instead, we adopted the recently published procedure for Pd-catalyzed dimerization of bromophenyl-substituted terpyridines[28c] to give the bridging ligand **11** in 78% yield (Scheme 3).

(21) Lashgari, K.; Kritikos, M.; Norrestam, R.; Norrby, T. *Acta Crystallogr.* **1999**, *C 55*, 64−67.

(22) $[Ru(\mathbf{1})_2][PF_6]_2$ was originally described in the space group P1 (ref 6). As kindly pointed out by Professor Clemente Dore Augusto, the complex could be described in the centrosymmetric space group *P*-1.

(23) The quinolines are somewhat displaced, and the two pairs of stacked quinolines in the structure are slightly different. The other pair (not highlighted) is somewhat more tilted. However, the average distance between centers of gravity in the benzene and pyridine rings in one quinoline unit and the benzene ring of the other quinoline is 3.6 Å.

(24) Electrostatic contributions cannot be ruled out.

(25) (a) Martin, C. B.; Mulla, H. R.; Willis, P. G.; Cammers-Goodwin, A. *J. Org. Chem.* **1999**, *64*, 7802−7806. (b) Rathore, R.; Abdelwahed, S. H.; Guzei, I. A. *J. Am. Chem. Soc.* **2003**, *125*, 8712−8713.

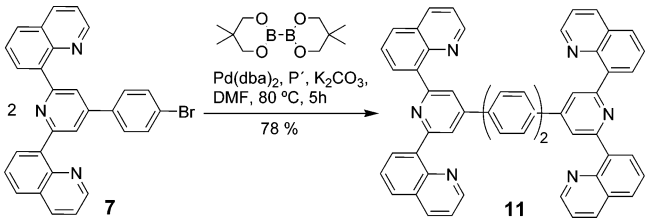
(26) Taylor, R. *J. Chem. Soc. B* **1971**, 2382−2387.

(27) Korall, P.; Börje, A.; Norrby, P.-O.; Åkermark, B. *Acta Chem. Scand.* **1997**, *51*, 760−766.

(28) (a) Vaduvescu, S.; Potvin, P. G. *Eur. J. Inorg. Chem.* **2004**, 1763−1769. (b) Yuan, S.-C.; Chen, H.-B.; Zhang, Y.; Pei, J. *Org. Lett.* **2006**, *8*, 5701−5704. (c) She Han, F.; Higuchi, M.; Kurth, D. G. *Org. Lett.* **2007**, *9*, 559−562. (d) Winter, A.; Egbe, D. A. M.; Schubert, U. S. *Org. Lett.* **2007**, *9*, 2345−2348.

(29) Constable, E. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1405−1409.

SCHEME 3. Carbon−Carbon Homocoupling of Bromophenyl-Substituted 7



In conclusion, a family of 2,6-di(quinolin-8-yl)pyridines has been synthesized. These ligands are distinct from the related terpyridines in that a larger bite angle is provided upon metal coordination. Work is now in progress to study the photophysical properties of a variety of 2,6-di(quinolin-8-yl)pyridyl-based Ru^{II} complexes which will be the subject of a forthcoming publication, and we believe that this class of ligands has great potential for future research involving luminescent Ru^{II} complexes with long excited-state lifetimes.

Experimental Section

Typical Procedure for the Pd-Catalyzed Coupling (1−4): 4-Ethylcarboxy-2,6-di(quinolin-8-yl)pyridine (2). Quinoline-8-boronic acid (0.350 g, 2.02 mmol), 2,6-dichloroisonicotinic ethylester (0.220 g, 1.00 mmol), $Pd(dba)_2$ (0.006 g, 0.01 mmol, 0.5%), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (0.008 g, 0.02 mmol, 1%), and finely ground potassium phosphate (1.060 g, 5.00 mmol) were suspended in dry toluene (7 mL). The mixture was purged with argon and heated at 110 °C over night. The dark yellow reaction mixture was cooled to room temperature, poured into Et_2O (150 mL), and allowed to stir for 30 min. The mixture was filtered and concentrated in vacuo and the remaining solid purified by recrystallization from EtOH to give **2** as a white solid (0.364 g, 90%). ^1H NMR ($CDCl_3$): δ 9.02 (2H, dd, $J = 4.2$, 1.8 Hz), 8.67 (2H, s), 8.26 (2H, dd, $J = 7.2$, 1.5 Hz), 8.24 (2H, dd, $J = 8.3$, 1.8 Hz), 7.90 (2H, dd, $J = 8.2$, 1.5 Hz), 7.67 (2H, dd, $J = 8.2$, 7.2 Hz), 7.46 (2H, dd, $J = 8.3$, 4.2 Hz), 4.46 (2H, q, $J = 7.1$ Hz), 1.41 (3H, t, $J = 7.1$ Hz). ^{13}C NMR ($CDCl_3$): δ 166.1, 157.9, 150.6, 146.0, 138.8, 137.0, 136.6, 131.7, 129.0, 128.8, 126.7, 124.9, 121.3, 61.6, 14.4. MS (ESI): *m*/*z* 406 ([M + H^+]$^+$). Anal. Calcd for $C_{26}H_{19}N_3O_2$: C, 77.02; H, 4.72; N, 10.36. Found: C, 76.81; H, 4.80; N, 10.15.

Typical Procedure for the Ring Cyclization Reaction (7−10): 4-(*p*-Bromophenyl)-2,6-di(quinolin-8-yl)pyridine (7). 8-Acetylquinoline (0.280 g, 1.64 mmol) and 4-bromobenzaldehyde (0.150 g, 0.81 mmol) were dissolved in EtOH (1 mL). A solution of potassium hydroxide (0.091 g, 1.62 mmol, 85%) in aqueous ammonia (1 mL, 28%) was added. The reaction mixture was warmed at 40 °C overnight. The solid was filtered off and recrystallized twice from EtOH to afford **7** as an off-white powder (0.087 g, 22%). A second crop (0.051 g, 13%) was obtained from column chromatography (silica gel, CH_2Cl_2/2.5−3.5% MeOH) of the combined filtrates. ^1H NMR ($CDCl_3$): δ 9.01 (2H, dd, $J = 4.2$, 1.8 Hz), 8.32 (2H, s), 8.31 (2H, dd, $J = 7.2$, 1.5 Hz), 8.26 (2H, dd, $J = 8.3$, 1.8 Hz), 7.91 (2H, dd, $J = 8.2$, 1.5 Hz), 7.73−7.69 (2H, m, AA′ part of AA′BB′), 7.69 (2H, dd, $J = 8.2$, 7.2 Hz), 7.64−7.60 (2H, m, BB′ part of AA′BB′), 7.47 (2H, dd, $J = 8.3$, 4.2 Hz). ^{13}C NMR ($CDCl_3$): δ 157.5, 150.4, 146.0, 145.9, 139.2, 138.2, 136.5, 132.1, 131.8, 129.2, 128.7 (two overlapping signals), 126.4, 123.3, 123.0, 120.8. HRMS (ESI) *m*/*z* 488.0754 ([M + H^+]$^+$), calcd for $C_{29}H_{19}BrN_3$ 488.0762.

4,4′-Di[2,6-di(quinolin-8-yl)pyridin-4-yl]biphenyl (11). Compound **7** (0.362 g, 0.74 mmol), bis(neopentylglycolato)diboron (0.087 g, 0.39 mmol), $Pd(dba)_2$ (0.021 g, 0.04 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (0.032 g, 0.08 mmol), and potassium carbonate (0.310 g, 2.25 mmol) were suspended in dry DMF (10 mL). The mixture was heated at 80 °C under an argon atmosphere for 5 h. After cooling, H_2O and CH_2Cl_2 were added, the organic phase was separated, and the aqueous layer was extracted with additional CH_2Cl_2. The combined organic fractions were combined and concentrated in vacuo, and the obtained solid was washed with hot EtOH (0.245 g, 78%). ^1H NMR ($CDCl_3$): δ 9.03 (4H, dd, $J = 4.2$, 1.9 Hz), 8.40 (4H, s), 8.32 (4H, dd, $J = 7.2$, 1.5 Hz), 8.24 (4H, dd, $J = 8.3$, 1.9 Hz), 7.95−7.92 (4H, m, AA′ part of AA′MM′), 7.90 (4H, dd, $J = 8.2$, 1.5 Hz), 7.80−7.77 (4H, m, MM′ part of AA′MM′), 7.69 (4H, dd, $J = 8.2$, 7.2 Hz), 7.45 (4H, dd, $J = 8.3$, 4.2 Hz). ^{13}C NMR ($CDCl_3$): δ 157.5, 150.5, 146.7, 146.2, 140.8, 139.6, 138.6, 136.5, 131.7, 128.8, 128.7, 128.2, 127.6, 126.7, 123.8, 121.1. HRMS (ESI) *m*/*z* 817.3071 ([M + H^+]$^+$), calcd for $C_{58}H_{37}N_6$ 817.3080.

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Supporting Information Available: Experimental details and characterizations for compounds **3**−**6** and **8**−**10**, ^1H NMR and ^{13}C spectra of compounds **2**−**11** and 2,4-di(quinolin-8-yl)-6-(*p*-tolyl)-pyridine, crystallographic data and CIF files of **1** and **5**, and geometry optimization of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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