JOC*Article*

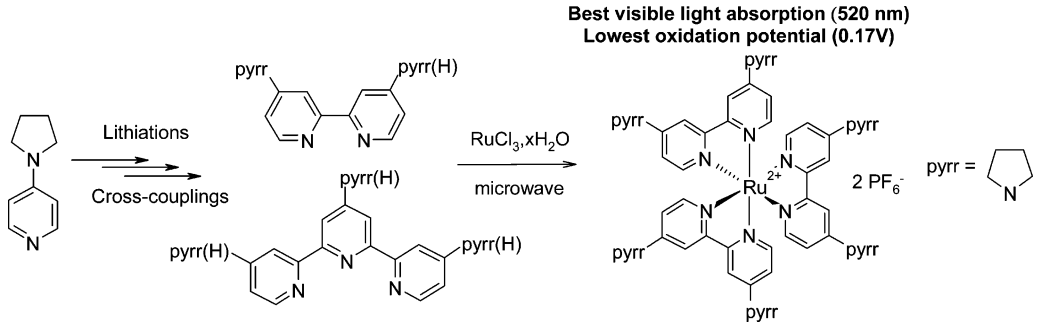
Pyrrolidine-Containing Polypyridines: New Ligands for Improved Visible Light Absorption by Ruthenium Complexes

David Martineau,[†,§] Marc Beley,*[,‡] and Philippe C. Gros*[,§]

LIMBP and LCA, IPEM, 1, Bd Arago, Université Paul Verlaine, 57057 Metz, France, and Synthèse Organométallique et Réactivité, UMR CNRS-UHP 7565, Université Henri Poincaré, Bd des Aiguillettes, 54506 Vandoeuvre-lès-Nancy, France

beley@sciences.univ-metz.fr; philippe.gros@sor.uhp-nancy.fr

Received September 23, 2005



A range of new electron-releasing pyrrolidine-containing bipyridines and terpyridines has been prepared via selective metalation−cross-coupling sequences. The obtained ligands have been involved in microwave-assisted ruthenium complexation leading to homoleptic complexes in high yield. The electron-donor effect of the pyrrolidine nucleus led to a notable improvement of visible light absorption and strong changes in the electrochemical behavior, opening new opportunities for the design of photovoltaic devices.

Introduction

The polypyridine complexes of ruthenium have been the focus of much work especially for the development of organic solar cells and luminescence sensors.[1] After early studies devoted to the photochemical properties of ruthenium liganded with unsubstituted 2,2′-bipyridines complexes,[2] the introduction of electronic effects via functional ligands has become increasingly important for tuning the photophysical and electrochemical properties. Electron-releasing substituents have been found to dramatically shift the absorption in the visible region and modify the electrochemical behavior. Such properties are needed for efficient sunlight collection. This effect was due to the propensity of these electron-donor substituents to destabilize the HOMO metal orbital (π t_{2g}) more than the LUMO (π^*) orbital of the ligand.[2] The consequence is a lower difference between the two orbital energy levels leading to a red shift of the MLCT (metal ligand charge transfer) absorption and decrease of the Ru(II)/Ru(III) oxidation potential. For example, alkyl substituents (especially *t*-Bu),[3] dimethylamino,[4] and thienyl groups[5] have been used with success for this purpose.

Recently, we have reported that ruthenium complexes with 4-pyrrolyl-polypyridine ligands were more efficient than the known $Ru(bpy)_3^{2+}$and $Ru(4\text{-}Me_2N\text{-}bpy)_3^{2+}$ complexes for visible light absorption.[6] However, electron delocalization into the pyrrole ring was suspected to damp down electron transfer toward the metal-chelating pyridine nitrogen. So, the replacement of the pyrrole by a saturated ring, i.e., pyrrolidine electron-

* To whom correspondence should be addressed. Phone +33 3 83 68 4320. Fax +33 3 68 4785.
† Université Paul Verlaine.
‡ LCA, IPEM.
§ Université Henri Poincaré.

(1) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277. (b) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737−740. (c) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49−68. (d) Argazzi, R.; Bignozzi, A.; Hasselmann, G. M.; Meyer, G. J. *Inorg. Chem.* **1998**, *37*, 4533−4537. (e) Schulze, X.; Serin, J.; Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2001**, 1160−1161. (f) Polson, M. I. J.; Taylor, N. J.; Hanan, G. S. *Chem. Commun.* **2002**, 1356−1357. (g) Figgemeier, E.; Aranyos, V.; Constable, E. C.; Handel, R. W.; Housecroft, C. E.; Risinger, C.; Hagfeldt, A.; Mukhtar, E. *Inorg. Chem. Commun.* **2004**, *7*, 117−121.

(2) (a) Sullivan, B. P.; Baumann, J. A.; Meyer, T. J.; Salmon, D. J.; Lehmann, H.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7368−7370. (b) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1639−1642. (c) Constable, E. C.; Housecroft, C. E.; Schofield, E. R.; Encinas, S.; Armaroli, N.; Barigelletti, F.; Flamigni, L.; Figgenmeier, E.; Vos, J. G. *Chem. Commun.* **1999**, 869−870.

10.1021/jo051994k CCC: $33.50
Published on Web 12/14/2005

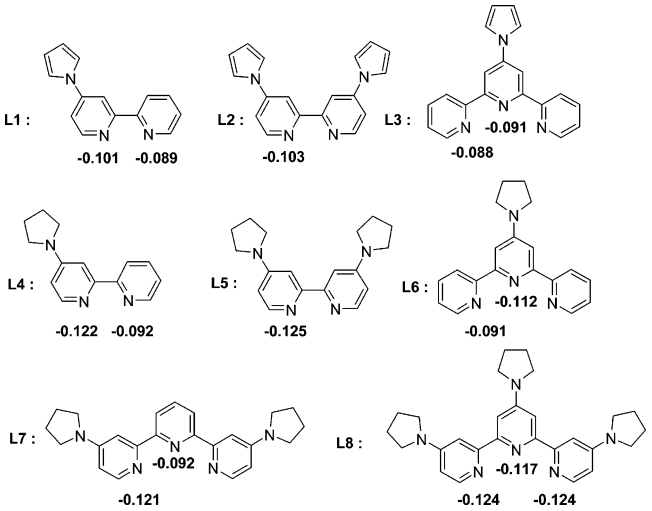


FIGURE 1. Charge calculations in ligands **L1**−**L8**.[10]

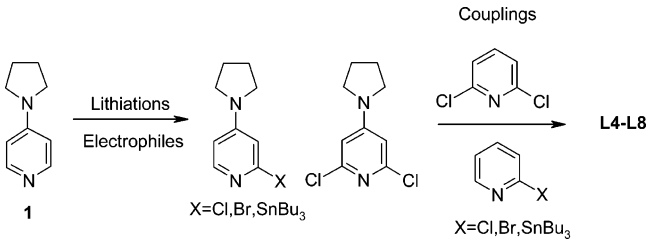
donor group, should produce a significant improvement increase of the LUMO energy level. Indeed pyrrolidinyl terpyridine containing manganese complexes have been reported recently to efficiently catalyze oxidation using air molecular oxygen under mild conditions.[7] This indicated the low oxidation potential of the metal center that is needed for the photovoltaic purpose. Herein we report the preparation of a range of pyrrolidine-containing polypyridine ligands and the efficient visible light absorption of the corresponding homoleptic ruthenium complexes.

Results and Discussion

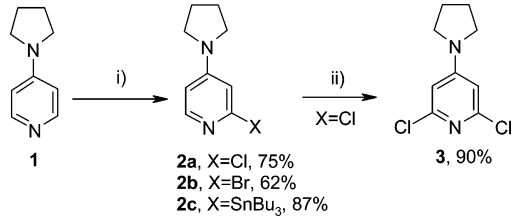
To get information about the electronic effect of pyrrolidine, charge calculations were performed on a range of potential ligands bearing this group.[8] As shown in Figure 1, pyrrolidine (**L4**−**L8**) induced a stronger charge amplification on pyridine nitrogen than did pyrrole in ligands **L1**−**L3**.[6,9] Encouraged by these first results, we embarked on the preparation of prospective ligands **L4**−**L8**.

The preparation of ligands **L6** and **L8** has already been reported in a recent patent[7] via three- to four-step procedures including ring construction and subsequent amination of chlorinated terpyridines, but no yields were given for these syntheses.

SCHEME 1. Synthetic Strategy for Preparation of L6−L8



SCHEME 2. Selective Lithiation of 1[a]



[a] Reagents and conditions: (i) (a) BuLi−LiDMAE (2 equiv), hexane, 0 °C, 2 h, (b) C_2Cl_6 or CBr_4 (2.5 equiv) or $ClSnBu_3$ (1.1 equiv), hexane, −78 °C; (ii) (a) BuLi−LiDMAE (2 equiv), hexane, 0 °C, 2 h, (b) C_2Cl_6 (2.5 equiv).

We opted for the metal-catalyzed assembly of C-2 functional 4-pyrrolidinopyridines using Stille- and Ulmann-type coupling reactions. Taking into account our expertise on selective lithiation in the 4-aminopyridine series,[9,11] we investigated a metalation−coupling sequence starting from the parent, commercially available 4-pyrrolidinopyridine **1**. The aim was to prepare a pool of reactive species to be coupled together or with other pyridine-based reagents for preparation of the target ligands (Scheme 1).

We first focused on the introduction of reactive functionalities at C-2 on the pyridine ring of **1** (Scheme 2). Among the lithiating agents tested, only the superbasic reagent BuLi−LiDMAE (LiDMAE═$Me_2N(CH_2)_2OLi$)[12] used in hexane effected clean lithiation of **1**.[13] Despite its slight solubility in such medium, **1** was reacted smoothly as a suspension dissolving progressively during the metalation process. The electrophilic condensation was performed in the same solvent, avoiding the use of THF as often needed for aggregate disruption in our previous works.[12] A large amount of starting **1** (typically 70%) was even recovered using this solvent, indicating the strong basicity of the intermediate pyridyllithium. Although we did not succeed in complete consumption of **1** (80% conversion typically), the reaction media were found to be very clean, leading to **2a**−**c** in acceptable to good yields. The good compatibility of the basic reagent with chlorostannanes allowed the use of only 1.1 equiv of $ClSnBu_3$ in the condensation step. This helped to minimize the contamination by tin byproducts, of which elimination is often problematic. Probably due to an increased basicity of pyridine nitrogen induced by the electron-donating pyrrolidine, the stannane **2c** showed a strong tendency to proto-destannylation on TLC (fast formation of **1**) and had to be purified by

(3) (a) Paw, W.; Connick, W. B.; Eisenberg, R. *Inorg. Chem.* **1998**, *37*, 3919−3926. (b) Fung, W.-H.; Yu, W.-Y.; Che, C.-M. *J. Org. Chem.* **1998**, *63*, 7715−7726. (c) Ghaddar, T. H.; Castner, E. W.; Isied, S. S. *J. Am. Chem. Soc.* **2000**, *122*, 1233−1234. (d) Rau, S.; Büttner, T.; Temme, C.; Ruben, M.; Görls, H. Walther, D.; Duati, M.; Fanni, S.; Vos, J. G. *Inorg. Chem.* **2000**, *39*, 1621−1624.

(4) Cook, M. J.; Lewis, A. P.; McAulife, G. S.; Skarda, V.; Thomson, A. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1293−1301.

(5) (a) Hjelm, J.; Constable, E. C.; Figgemeier, E.; Hagfeldt, A.; Handel, R.; Housecroft, C. E.; Mukhtar, E.; Chofield, E. *Chem. Commun.* **2002**, 284−285. (b) Schofield, E. R. Transition Metal Complexes of 4′-Substituted 2,2′:6′,2″-Terpyridines in Supramolecular Chemistry. Ph.D. Dissertation University of Basel, Switzerland, 1999.

(6) Martineau, D.; Gros, Ph.; Beley, M.; Fort, Y. *Eur. J. Inorg. Chem.* **2004**, *20*, 3984−3986.

(7) (a) Wieprecht, T.; Schlingloff, G.; Xia, J.; Heinz, U.; Schneider, A.; Dubs, M.-J.; Bachmann, F.; Hazenkamp, M.; Dannache, J. PCT Int. Appl. WO2004/039933 A1, 2004; *Chem. Abstr.* 140:408683.

(8) We chose to introduce the pyrrolidine at C-4 on pyridine units to get the best electronic effects while suppressing steric effects and side complexation that could occur with pyrrolidine at C-2.

(9) Martineau, D.; Gros, Ph.; Fort, Y. *J. Org. Chem.* **2004**, *69*, 7914−7918.

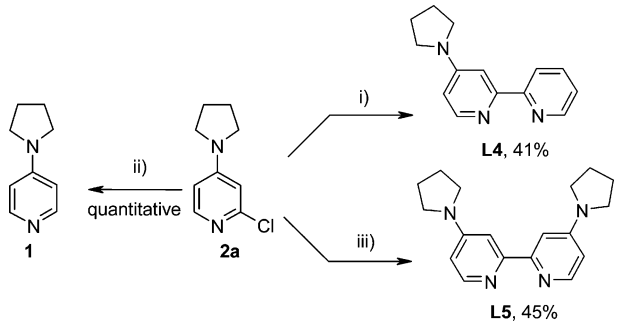
(10) Mulliken charges obtained by calculation in MOPAC using the PM3 semiempirical method.

(11) (a) Cuperly, D.; Gros, Ph.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 238−241. (b) Louërat, F.; Gros, Ph.; Fort, Y. *Tetrahedron* **2005**, *61*, 4761−4768.

(12) Gros, Ph.; Fort, Y. *Eur. J. Org. Chem.* **2002**, 3375−3383.

(13) During this work, another group reported the use of our lithiation methodology to functionalize **1**. Ishii, T.; Fujioka, S.; Sekiguchi, Y.; Kotsuki, H. *J. Am. Chem. Soc.* **2004**, *126*, 9558−9559.

SCHEME 3. Preparation of Bipyridine-Based Ligands[a]



[a] Reagents and conditions: (i) 2-PyrSnBu$_3$ (1.1 equiv), PdCl$_2$(PPh$_3$)$_2$ (5%), PPh$_3$ (10%), xylene, Ar, reflux, 18 h; (ii) NiCl$_2$, 6H$_2$O (1.1 equiv), PPh$_3$ (4.4 equiv), Zn (1.1 equiv), DMF, 50 °C, Ar, 1.5 h or *t*-BuONa−NiCRA−PPh$_3$ (4.2.1.4), DME, 65 °C, Ar, 2 h; (iii) **2c** (1.1 equiv), PDCl$_2$(PPh$_3$)$_2$ (5%), PPh$_3$ (10%), xylene, Ar.

distillation. Finally, the efficient lithiation of **2a** with the same basic reagent produced the 2,6-dichloro derivative **3** in an excellent 90% yield (68% overall yield from **1**).

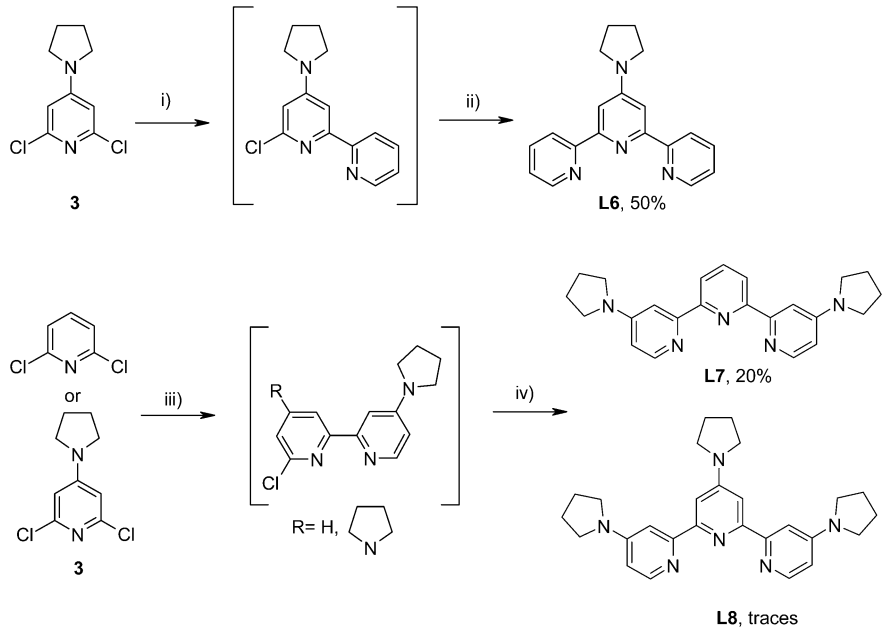
With precursors **2a**−**c** and **3** in hand, we turned to the preparation of ligands **L4**−**L8** (Scheme 3). We first investigated the preparation of bipyridines **L4** and **L5**. Ligand **L4** was obtained in 41% yield by Pd-catalyzed cross-coupling with 2-pyridyltributylstannane; **1** resulting from reduction of **2a** was always obtained besides the expected product. All attempts to improve this yield using other solvents (DMF, dioxane), lower temperatures, the bromoderivative **2b**, other catalysts (e.g., Pd$_2$dba$_3$ or Pd(PPh$_3$)$_4$) or CuI as additive remained unsuccessful. The Negishi cross-coupling also failed since we were unable to obtain the pyridylzinc intermediate. Intuitively, ligand **L5** could be obtained directly via a nickel-catalyzed homocoupling, but first attempts with the common NiCl$_2$/PPh$_3$/Zn[14] system only resulted in complete reduction of the C−Cl bond yielding **1** quantitatively (see Scheme 3). The same result was obtained using the *t*-BuONa/NiCRA/PPh$_3$ combination,[15] known to be less reducing than the former reagent. **L5** was finally obtained in 45% yield by cross-coupling with tin derivative **2c**; the reduction product was also formed in notable amount in this case and we were unable to avoid its formation.

The preparation of terpyridines **L6**−**L8** was then realized by coupling the appropriate dichloro and organostannyl pyridines (Scheme 4). The direct introduction of two pyridine units was not achieved even using an excess (up to 3 equiv) of the organotin derivative. The reaction ceased with formation of the chlorobipyridine. This compound was not isolated and immediately involved in another cross-coupling under the same conditions. The expected terpyridine was then finally obtained in pure form by precipitation in diethyl ether. The yields were highly dependent on the used precursors. As a general trend, the coupling process was handicapped by side reduction of **3** and destannylation of **2c** as evidenced by GC analysis of the reaction mixtures revealing the presence of large amounts of **1**. **L6** was nevertheless obtained in acceptable 50% yield. The couplings involving stannane **2c** gave lower yields leading to **L7** in 20%. Unfortunately we did not succeed in the preparation of **L8**, which was obtained only in trace amount.

These experiments pointed out the deleterious effect of the electron-releasing pyrrolidine substituent on the Stille cross-coupling process.[16] Both the tin and chloro derivatives exhibited a strong tendency to reduction along the palladium-catalyzed process.

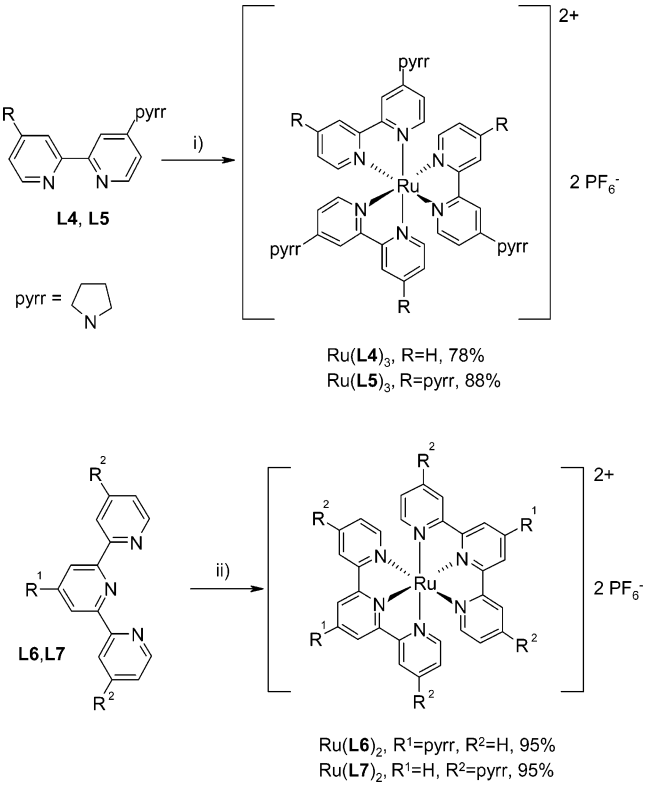
Since the aim of our work was to check the effect of the new electron-releasing ligands on the properties of ruthenium complexes, we did not optimize the yields at this stage. Ligands **L4**−**L7** were nevertheless obtained in sufficient amount to be involved in the preparation of ruthenium complexes. First attempts under classical conditions in which ligands in stoichiometric proportions were reacted overnight with RuCl$_3$·*x*H$_2$O in refluxing DMF were unsuccessful, leading to incomplete incorporation of ligands as previously observed during the preparation of homoleptic complexes from **L1**−**L3**.[6] This was

SCHEME 4. Preparation of Terpyridine-Based Ligands[a]



[a] Reagents and conditions: (i) 2-PySnBu$_3$ (1.1 equiv), PdCl$_2$(PPh$_3$)$_2$ (10%), PPh$_3$ (20%), xylene, reflux, 24 h; (ii) ibid; (iii) **2c** (1.1 equiv), PdCl$_2$(PPh$_3$)$_2$ (10%), PPh$_3$ (20%), xylene, reflux, 24 h; (iv) ibid.

SCHEME 5. Preparation of Homoleptic Complexes[a]



[a] Reagents and conditions: (i) $RuCl_3 \cdot xH_2O$ (0.33 equiv), *N*-ethylmorpholine (2 drops), ethyleneglycol, microwave irradiation, 250 W, 196 °C, 3 min; (ii) ibid with 0.5 equiv of $RuCl_3 \cdot xH_2O$.

TABLE 1. Electrochemical and Visible Absorption Data for Ruthenium Complexes[a]

complex	$E_{1/2ox}$ (V)[b] R^{III}/Ru^{II} (ΔE_p, mV)	λabs (nm) ^{1}MLCT	$\epsilon \times 10^{-3}$ ($M^{-1} \cdot cm^{-1}$)
Ru(**L1**)$_3$ [c]	1.16(90)	465	8.6
Ru(**L2**)$_3$ [c]	1.12(90)	480	22.2
Ru(**L3**)$_2$ [c]	1.18(100)	490	38.5
Ru(**L4**)$_3$	0.55 (100)	481	13.5
Ru(**L5**)$_3$	0.17 (100)	520	13.2
Ru(**L6**)$_2$	0.58 (70)	501	15.0
Ru(**L7**)$_2$	0.40 (60)	493	10.8

[a] All measurements realized in outgassed acetonitrile solutions at 298 K. [b] Measuements performed on a Pt electrode. First potential standardized using Fc as internal standard and converted to SCE scale by adding 0.38 V ($E_{1/2}$ (Fc^+/Fc). Recorded at 100 mV/s with $LiCLO_4$ (0.1 M) as supporting electrolyte. [c] See ref 6.

the probable result of the pyrrolidine-induced lower π-accepting power of the ligands. Success was met using microwave irradiation, which provided the target complexes in high yields after 3 min at 196 °C in ethylene glycol (Scheme 5).

The effect of the new ligands on the properties of complexes was then studied by submitting the complexes to UV−vis spectroscopy and cyclic voltammetry (Table 1).

The results were generally in agreement with the expected effects. Indeed, complexes bearing the pyrrolidine moiety displayed higher λ_{max} values and especially lower oxidation potentials than the corresponding pyrrole-containing complexes. This demonstrated a greater destabilization of the metal d orbital due to the higher electron-donor effect induced by pyrrolidine. The oxidation potentials were found to be highly dependent on the number of pyrrolidines bound to the ligand, and a spectacular

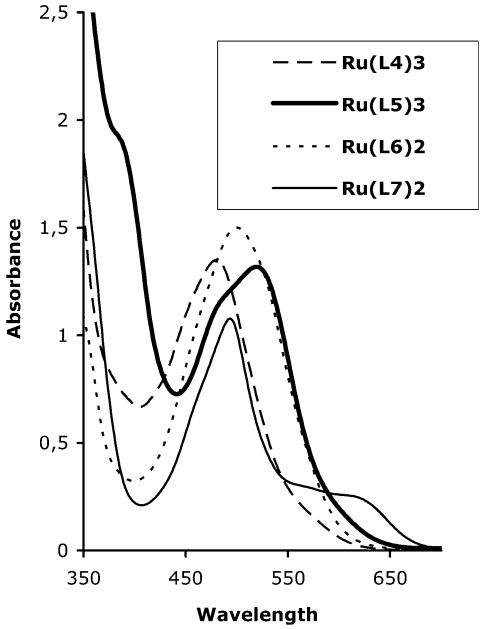


FIGURE 2. Visible absorption spectra of ruthenium complexes.

additive effect was observed in the bpy series. Ru(**L5**)$_3$displayed the lowest value (0.17 V) and a ^{1}MLCT absorption at 520 nm, which was the best value obtained in this series. The behavior of Ru(**L7**)$_2$was also of interest since light could be harvested until the 660 nm region (Figure 2). Such an extended absorption tail of weaker intensity at $\lambda > 600$ nm has already been reported and was assigned to a charge-transfer transition to a ^{3}MLCT state (spin-forbidden transition).[17] Another interesting feature was that, despite a very low oxidation potential, all of the complexes were found to be very stable and could be stored in the solid state under air exposure.

Conclusion

A range of pyrrolidine-containing bipyridine and terpyridine ligands has been prepared. The selective lithiation of 4-pyrrolidinopyridine afforded useful coupling partners, which despite a deleterious effect of the electron-releasing pyrrolidino group were cross-coupled in moderate to acceptable yields under Stille conditions. The obtained ligands led to new homoleptic ruthenium complexes in high yields only under microwave irradiation; classical thermal conditions failed. The pyrrolidine moiety induced a positive effect on visible light absorption and very low oxidation potentials, which is requisite for the photovoltaic purpose. Surprisingly, despite very low oxidation potentials, the complexes were found very stable under air exposure. The incorporation of these new pyrrolidine-containing ligands into ruthenium heteroleptic complexes attachable to TiO_2

(14) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627−2637.
(15) Fort, Y.; Becker, S.; Caubère, P. *Tetrahedron* **1994**, *50*, 11893−11902.
(16) This could be explained by the strong electron-releasing effect of pyrrolidine, which makes the chloropyridine nucleus too electron-rich, lowering its reactivity in cross-coupling with tin derivative and thus leading mainly to reduction.
(17) (a) Constable, E. C.; Handel, R. W.; Housecroft, C.; Morales, A. F.; Flamigni, L.; Barigelletti, F. *Dalton Trans.* **2003**, *7*, 1220−1223. (b) Fantacci, S.; De Angelis, F.; Wang, J.; Bernhard, S.; Selloni, A. *J. Am. Chem. Soc.* **2004**, *126*, 9715−9723. (c) Mishra, D.; Naskar, S.; Adhikary, B.; Chattopadhyay, S. K. *Polyhedron* **2005**, *24*, 201−208.

matrix is now under progress. New perspectives into the design of efficient and robust solar cells should be opened.

Experimental Section

General Methods. All solvents were distilled and stored on sodium wire before use. 2-Dimethylaminoethanol was distilled under nitrogen and stored on molecular sieves. *n*-BuLi was use as 2.5 M solution in hexanes. All other reagents were commercially available and used as such. Microwave syntheses were performed on a CEM Discover oven with infrared probe temperature control. ^{1}H and ^{13}C NMR (400 and 100 MHz, respectively) were obtained in $CDCl_3$ (unless otherwise stated) with TMS as internal standard. GC experiments were performed on a chromatograph fitted with a 15 m capillary column. UV−vis experiments were performed at 298 K in outgassed CH_3CN.

General Procedure for Preparation of 2a−b. To a solution of 2-dimethylaminoethanol (DMAE) (3.22 mL, 32.6 mmol) in 40 mL of anhydrous hexane cooled at −5 °C was added dropwise *n*-BuLi (25.7 mL of a 2.5 M solution in hexanes, 64.2 mmol). The temperature must be kept below 0 °C. After 0.5 h, the reaction mixture was maintained below 0 °C, and the 4-(pyrrolidin-1-yl)-pyridine (1.58 g, 10.7 mmol) was added portion-wise as a solid. After no traces of solid were visible in the reaction medium (up to 3 h of stirring below 0 °C), the temperature was lowered to −78 °C and the appropriate electrophile (37.5 mmol) was added dropwise in 40 mL of anhydrous hexane to the orange solution. After 0.5 h, the medium was allowed to warm at room temperature and hydrolyzed at 0 °C with 40 mL of water. After extraction with ether and then chloroform and washing with water, the combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was then purified by column chromatography on silica gel.

2-Chloro-4-(pyrrolidin-1-yl)pyridine, 2a. Obtained by reaction with C_2Cl_6 (8.88 g, 37.5 mmol). Gradual elution from hexane to hexane/AcOEt (4:6) afforded **2a** (1.46 g, 75%) as a beige solid, mp 128 °C. ^{1}H NMR: δ_H 2.03 (m, 4H), 3.28 (m, 4H), 6.28 (dd, J = 6 and 2 Hz, 1H), 6.35 (d, J = 4 Hz, 1H), 7.93 (d, J = 6 Hz, 1H). ^{13}C NMR: δ_C 25.4, 47.3, 105.7, 106.5, 149.0. MS (EI) *m*/*z*: 182 (M^+, 100), 153 (17), 139 (22), 127 (22), 112 (21), 85 (16), 76 (9), 65 (7), 51 (5). Anal. Calcd: C, 59.18; H, 6.07; N, 15.34. Found: C, 59.25; H, 6.18; N, 15.47.

2-Bromo-4-(pyrrolidin-1-yl)pyridine, 2b.[13] Obtained by reaction with CBr_4 (12.4 g, 37.5 mmol). Elution with hexane/AcOEt (2:8) afforded **2b** (1.51 g, 62%) as a brown solid, mp 124 °C. ^{1}H NMR: δ_H 2.03 (m, 4H), 3.29 (m, 4H), 6.32 (dd, J = 6 and 2 Hz, 1H), 6.53 (d, J = 2 Hz, 1H), 7.92 (d, J = 6 Hz, 1H). ^{13}C NMR: δ_C 25.5, 47.4, 106.9, 109.6, 149.3 ppm. MS (EI) *m*/*z*: 227 (M^+, 100), 197 (11), 183 (7), 170 (8), 156 (7), 118 (8), 105 (17), 78 (15), 65 (10), 51 (15).

Preparation of 2-(Tributylstannyl)-4-(pyrrolidin-1-yl)pyridine, 2c. To a solution of 2-dimethylaminoethanol (DMAE) (1.6 mL, 16 mmol) in 30 mL of anhydrous hexane cooled at −5 °C was added dropwise *n*-BuLi (12.8 mL of a 2.5 M solution in hexanes, 32 mmol). The temperature must be kept below 0 °C. After 0.5 h, the reaction mixture was maintained under 0 °C, and the 4-(pyrrolidin-1-yl)pyridine (1.18 g, 8 mmol) was added solid in several portions. After no traces of solid were visible (up to 3 h of stirring below 0 °C), the temperature was lowered to −78 °C and the electrophile Bu_3SnCl (2.2 mL, 8.1 mmol) was added dropwise in 30 mL of anhydrous hexane to the orange solution. After 0.5 h, the medium was allowed to warm at room temperature and hydrolyzed at 0 °C with 30 mL of water. After extraction with dichlomethane and washing with water, the organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. Kugelrorh distillation (160 °C, 5 mbar) afforded **2c** (3.1 g, 87%) as a pale yellow oil. ^{1}H NMR: δ_H 0.89 (m, 9H), 1.10 (m, 6H), 1.35 (m, 6H), 1.57 (m, 6H), 1.99 (t, J = 6 Hz, 4H), 3.27 (t, J = 6 Hz, 4H), 6.24 (dd, J = 6 Hz, 1H), 6.53 (d, J = 2 Hz, 1H), 8.32 (d, J = 6 Hz, 1H). ^{13}C NMR: δ_C 9.6, 13.7, 25.4, 27.4, 29.2, 46.7, 105.8, 115.9, 149.6, 150.06, 171.86 ppm. Anal. Calcd: C, 57.68; H, 8.76; N, 6.41. Found: C, 57.93; H, 8.43; N, 6.13.

Preparation of 2,6-Dichloro-4-(pyrrolidin-1-yl)pyridine, 3. To a solution of 2-dimethylaminoethanol (DMAE) (1.2 mL, 12 mmol) in 16 mL of anhydrous hexane cooled at −5 °C was added dropwise *n*-BuLi (9.6 mL of a 2.5 M solution in hexanes, 24 mmol). After 0.5 h, the temperature was maintained below 0 °C and **2a** (0.73 g, 4 mmol) was added solid in several portions. After no traces of solid were visible (up to 3 h of stirring below 0 °C), the temperature was lowered to −78 °C and C_2Cl_6 (3.3 g, 14 mmol) was added dropwise in 25 mL of anhydrous hexane to the orange solution. After 0.5 h, the medium was allowed to warm at room temperature and hydrolyzed at 0 °C with 20 mL of water. After extraction with ether, then chloroform and washing with water, the combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. Column chromatography on silica gel eluting from hexane to hexane/AcOEt (8:2) afforded **3** (780 mg, 90%) as a white solid, mp 136 °C. ^{1}H NMR: δ_H 2.04 (t, J = 6 Hz, 1H), 3.29 (t, J = 6 Hz, 1H), 6.29 (s, 2H). ^{13}C NMR: δ_C 25.5, 47.8, 105.3 ppm. MS (EI) *m*/*z*: 217 (M^+, 100), 188 (16), 173 (22), 161 (25), 146 (15), 126 (9), 112 (13), 91 (7), 85 (23), 64 (9), 52 (12). Anal. Calcd: C, 49.79; H, 4.64; N, 12.90. Found: C, 49.58; H, 4.83; N, 12.62.

Preparation of 2-(4-(Pyrrolidin-1-yl)pyridin-2-yl)pyridine, L4. A mixture of **2a** (546 mg, 3 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), and PPh_3 (79 mg, 0.3 mmol) in 6 mL of degassed xylene was refluxed under nitrogen for 5 min. A solution of 2-tributylstannylpyridine (1.1 mL, 3.1 mmol) in 5 mL of xylene was then added, and the medium was stirred under reflux for 20 h. The mixture was cooled and filtered over a pad of Celite and washed with CH_2Cl_2. The organic layer was then evaporated. The crude product was then submitted to acido-basic washings. After extraction with CH_2Cl_2, drying of the organic phase ($MgSO_4$), and evaporation of solvents, column chromatography on silica gel (Et_3N/AcOEt 5:95) afforded **L4** (277 mg, 41%) as a beige solid, mp 96 °C. ^{1}H NMR: δ_H 2.00 (t, J = 4 Hz, 4H), 3.39 (t, J = 6 Hz, 4H), 6.39 (dd, J = 6 and 4 Hz, 1H), 7.26 (dd, J = 8 and 4 Hz, 1H), 7.53 (d, J = 2 Hz; 1H), 7.77 (td, J = 10 and 2 Hz; 1H), 8.28 (d, J = 6 Hz, 1H), 8.37 (d, J = 8 Hz, 1H), 6.65 (d, J = 4 Hz, 1H). ^{13}C NMR: δ_C 25.57, 47.38, 104.34, 107.27, 121.44, 123.58, 137.00, 149.11, 149.40, 152.86, 156.13, 157.24. Anal. Calcd: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.47; H, 6.52; N, 18.79.

4-(Pyrrolidin-1-yl)-2-(4-(pyrrolidin-1-yl)pyridin-2-yl)pyridine, L5. A mixture of **2a** (633 mg, 3.48 mmol), $PdCl_2(PPh_3)_2$ (121 mg, 0.17 mmol), and PPh_3 (91 mg, 0.35 mmol) in 10 mL of degassed xylene was refluxed under nitrogen for 5 min. A solution of **2c** (1.51 g, 3.48 mmol) in 5 mL of xylene was then added, and the medium was stirred under reflux for 20 h. The mixture was cooled and filtered over a pad of Celite and washed with CH_2Cl_2. Precipitation from ether afforded **L5** (461 mg, 45%) as a brown solid, mp 210 °C. ^{1}H NMR: δ_H 2.02 (m, 8H), 3.42 (t, J = 6 Hz, 8H), 6.38 (dd, J = 6 and 2 Hz, 2H), 7.53 (d, J = 2 Hz, 2H), 8.27 (d, J = 6 Hz, 2H). ^{13}C NMR: δ_C 25.5, 47.4, 104.6, 106.9, 149.0, 152.9, 156.8 ppm. Anal. Calcd: C, 73.44; H, 7.53; N, 19.03. Found: C, 73.34; H, 7.69; N, 18.83%

2-(6-(Pyridin-2-yl)-4-(pyrrolidin-1-yl)pyridin-2-yl)pyridine, L6.[7] A mixture of **3** (651 mg, 3 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), and PPh_3 (79 mg, 0.30 mmol) in 10 mL of degassed xylene was refluxed under nitrogen for 5 min. A solution of 2-tributylstannylpyridine (1.1 mL, 3 mmol) in 5 mL of xylene was then added, and the medium was stirred under reflux for 20 h. The medium was cooled and filtered over a pad of Celite and washed with CH_2Cl_2, and the solvents were removed under reduced pressure. The resulting mixture was placed with $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol) and PPh3 (79 mg, 0.30 mmol) in 10 mL of degassed xylene and refluxed under nitrogen for 5 min. An excess of 2-tributylstannylpyridine (2.2 mL, 6 mmol) in 5 mL of xylene was then added, and the medium was stirred under reflux for 20 h.

The mixture was cooled and filtered over a pad of Celite and washed with CH_2Cl_2, and the solvents were removed under reduced pressure. Precipitation from ether afforded **L6** (450 mg, 50%) as a beige solid, mp 254 °C. ^{1}H NMR: δ_H 2.05 (m, 4H), 3.55 (t, J = 6 Hz, 4H), 7.29 (ddd, J = 6, 4 and 1 Hz, 2H), 7.62 (s, 2H), 7.82 (td, J = 8 and 2 Hz, 2H), 8.63 (d, J = 8 Hz, 2H), 8.68 (d, J = 6 Hz, 2H). ^{13}C NMR: δ_C 25.6, 47.6, 104.2, 121.6, 123.5, 136.9, 149.0, 152.4, 155.6, 157.4. Anal. Calcd: C, 75.47; H, 6.00; N, 18.53. Found: C, 75.53; H, 6.08; N, 18.41.

4-(Pyrrolidin-1-yl)-2-(6-(4-(pyrrolidin-1-yl)pyridin-2-yl)pyridin-2-yl)pyridine, L7. A mixture of 2,6-dichloropyridine (444 mg, 3 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), and PPh_3 (79 mg, 0.30 mmol) in 10 mL of degassed xylene was refluxed under nitrogen for 5 min. A solution of **2c** (1.57 g, 3.6 mmol) in 5 mL of xylene was then added, and the medium was stirred under reflux for 20 h. The medium was cooled and filtered over a pad of Celite and washed with CH_2Cl_2, and the solvents were removed under reduced pressure. The resulting mixture was placed with $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), and PPh_3 (79 mg, 0.30 mmol) in 10 mL of degassed xylene and refluxed under nitrogen for 5 min. A solution of **2c** (1.57 g, 3.6 mmol) in 5 mL of xylene was then added, and the medium was stirred under reflux for 20 h. The mixture was cooled and filtered over a pad of Celite and washed with CH_2Cl_2, and the solvents were removed under reduced pressure. Precipitation from ether afforded **L7** (222 mg, 20%) as a brown solid, mp >260 °C (dec). ^{1}H NMR: δ_H 2.02 (m, 8H), 3.40 (t, J = 8 Hz, 8H), 6.41 (dd, J = 6 and 4 Hz, 2H), 7.78 (d, J = 2 Hz, 2H), 7.89 (t, J = 8 Hz, 1H), 8.30 (d, J = 6 Hz, 2H), 8.36 (d, J = 8 Hz, 2H). ^{13}C NMR: δ_C 25.5, 47.0, 104.5, 107.1, 120.7, 137.6, 149.2, 152.7, 155.8, 156.3. Anal. Calcd: C, 74.36; H, 6.78; N, 18.85. Found: C, 74.48; H, 6.45; N, 18.62.

General Procedure for Preparation of Complexes Ru(L4)$_3$ and Ru(L5)$_3$. Ligand **L4** or **L5** (0.192 mmol) and $RuCl_3(H_2O)_x$ (15.7 mg, 0.06 mmol) were dissolved in ethylene glycol (5 mL), and *N*-ethylmorpholine (2 drops) was added. The reaction mixture was then placed into a synthesis microwave oven and irradiated at 196 °C (250 W) for 3 min. After cooling to room temperature, a saturated aqueous solution of KPF_6 (25 mL) was poured into the red mixture. The resulting precipitate was filtered and washed with diethyl ether to remove uncomplexed ligands. The filter cake was then dissolved in acetonitrile and purified by a column chromatography using acetone/H_2O/KNO_3 sat. (9:0.9:0.1) as eluting mixture. Finally, the complex was precipitated by adding KPF_6 to the combined fractions and filtered off.

Ru(L4)$_3$. Obtained as a dark red solid (50 mg, 78%). A 50:50 mixture of inseparable *fac*- and *mer*-isomers. ^{1}H NMR: δ_H 2.01 (m, 12H), 3.45 (m, 12H), 6.48 (q, J = 4 Hz, 3H), 7.13 (dd, J = 8 Hz, 1.5H), 7.21 (dd, J = 8 Hz, 1.5H), 7.32 (m., 3 H), 7.47 (s, 3H), 7.78 (t, J = 8 Hz, 3H), 7.86 (t, J = 8 Hz, 3H), 7.95 (q, J = 8 Hz, 3H), 8.46 (d, J = 8 Hz, 3H). MS (ESI): m/z = 388.6432 [M − 2PF$_6$]$^{2+}$. UV−vis (CH_3CN): λ_{max} (ϵ_{max}, L·mol^{-1}·cm^{-1}) = 481 nm (13500).

Ru(L5)$_3$. Obtained as a violet solid (67 mg, 88%). ^{1}H NMR: δ_H 2.06 (m, 8H), 3.44 (m, 24H), 6.43 (dd, J = 6 and 2 Hz, 6H), 7.27 (d, J = 6 Hz, 6H), 7.37 (d, J = 2 Hz, 6H). MS (ESI): m/z = 1128.76 [M − PF$_6$]$^+$, 492.2257 [M − 2PF$_6$]$^{2+}$. UV−vis (CH_3CN): λ_{max} (ϵ_{max}, L·mol^{-1}·cm^{-1}) = 520 nm (13200).

General Procedure for Preparation of Complexes Ru(L6)$_2$ and Ru(L7)$_2$. Ligand **L6** or **L7** (0.126 mmol) and $RuCl_3(H_2O)x$ (15.7 mg, 0.06 mmol) were dissolved in ethylene glycol (5 mL), and *N*-ethylmorpholine (2 drops) was added. The reaction mixture was then placed into a synthesis microwave oven and irradiated at 196 °C (250 W) for 3 min. After cooling to room temperature, a saturated aqueous solution of KPF_6 (25 mL) was poured into the pink mixture. The resulting precipitate was filtered and washed with toluene and diethyl ether to remove uncomplexed ligands. Pure complexes were then obtained according to treatment described below.

Ru(L6)$_2$. The above filter cake was dissolved in the minimum amount of acetonitrile and poured into deionized water. Filtration and drying afforded **Ru(L6)$_2$** (57 mg, 95%) as a pink solid. ^{1}H NMR: δ_H 2.04 (t, J = 6 Hz, 8H), 3.57 (t, J = 6 Hz, 8H), 6.91 (t, J = 6 Hz, 4H), 7.19 (d, J = 6 Hz, 4H), 7.60 (s, 4H), 7.64 (t, J = 8 Hz, 4H), 8.24 (d, J = 8 Hz, 4H). (ESI): m/z = 353.1069 [M − 2PF$_6$]$^{2+}$. UV−vis (CH_3CN): λ_{max} (ϵ_{max}, L·mol^{-1}·cm^{-1}) = 501 nm (15000).

Ru(L7)$_2$. The filter cake was then dissolved in acetonitrile. Column chromatography using acetone/H_2O/KNO_3 sat. (9:0.9:0.1) as eluting mixture followed by addition of KPF_6 to the combined fractions and filtration afforded **Ru(L7)$_2$** as a brown solid (65 mg, 95%). ^{1}H NMR: δ_H 2.01 (m, 8H), 3.37 (m, 8H), 6.21 (dd, J = 6 and 2 Hz, 2H), 6.69 (d, J = 6 Hz, 2H), 7.46 (d, J = 3 Hz, 2H), 8.22 (t, J = 8 Hz, 1H), 8.63 (d, J = 8 Hz, 2H). (ESI): m/z = 989.2934 [M − PF$_6$]$^+$, 422.1672 [M − 2PF$_6$]$^{2+}$. UV−vis (CH_3CN): λ_{max} (ϵ_{max}, L·mol^{-1}·cm^{-1}) = 493 nm (15000).

Acknowledgment. The authors would like to thank FMC Lithium (USA) for a generous gift of BuLi solutions. We are also grateful to Y. Chapleur (Nancy) for providing access to microwave synthesis facilities and to P. Wehrung for ESI mass spectrometry analyses.

JO051994K