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Facile Synthesis of Cyclometalated Ruthenium Complexes with Substituted Phenylpyridines

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We have developed a new strategy that uses the Kröhnke synthesis for the preparation of various substituted phenylpyridines in excellent yields (up to 88 %). Starting with the appropriate commercially available acetophenone, a variety of phenylpyridines substituted by either electron-donating (i.e. methyl, methoxy) or -withdrawing groups (i.e. bromide, nitro) on the phenyl ring are obtained in a two-step synthesis. The corresponding functionalized cyclometalated ruthenium complexes can be prepared with unusually high yields by using methanol as reaction solvent. The electrochemical data of the complexes demonstrate the strong σ-donating character of the anionic phenylpyridine ligand. X-ray analyses of four complexes show a shortening of the Ru–C bond associated with the elongation of only one of the five Ru–N bonds (*trans* effect).

Introduction

(Polypyridine)ruthenium(II) complexes have attracted much interest as light absorbers, photoluminescent sensors or switches, and intermolecular energy- and electron-transfer agents.[1] Some cyclometalated counterparts of these complexes have been prepared and their physical properties reported.[2–6] In fact, cyclometalated complexes have found widespread interest as species with promising properties in various fields[7] owing to the strong σ-donor ability of the cyclometalated ligand. Typically, the coordinating ligand forms a bond to the metal center and then intramolecular C–H activation takes place to yield a five-membered chelate ring. Replacement of a nitrogen donor by a formal carbanion donor drastically increases the electron density around the metal atom[4] and the crystal-field strength.[5]

A variety of synthetic methodologies[8] for the synthesis of new pyridine derivatives have been developed. One of the most important is the transition-metal-catalyzed cross-coupling reactions of precursors developed by Negishi, Suzuki, and Stille (see refs.[9–11]). In fact, all these methods entail the preparation of functionalized intermediates.[12] In the course of our studies we have prepared a number of polypyridine ligands[13] by using the Kröhnke method.[14] By extending this procedure to aromatic ketones, we propose an easy and versatile synthesis of substituted phenylpyridines.[15] Starting from commercially available acetophenones, a variety of mono- or difunctionalized phenylpyridines substituted by electron-donating (i.e. methyl, methoxy) or -withdrawing groups (i.e. bromide, nitro) on the phenyl ring can be obtained with very good yields.

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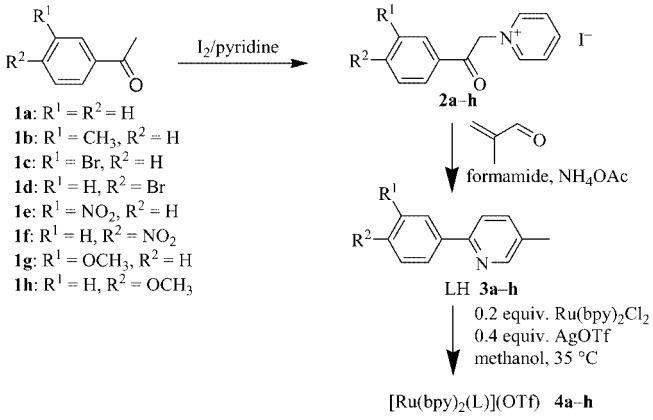
Results and Discussion

Synthesis

Our synthetic route starts with the preparation of the pyridinium derivative of the appropriate aromatic methyl ketone.[14] Condensation of these derivatives with methacrolein gives the corresponding phenylpyridines, as described in Scheme 1. We also checked this synthesis with tiglic aldehyde[16] to show that this methodology can be extended to other α,β-unsaturated carbonyl compounds.



Scheme 1.

The different ligands synthesized in this work are summarized together with the few previously reported molecules in Table 1. To the best of our knowledge, no crystal structure of a phenylpyridine has been published (vide infra).

Table 1. List and yields of ligands LH prepared by this method.

		Yield [%]	Ref.
3a:	$R^1 = R^2 = R^3 = H$	88	[15,17,18]
	$R^1 = R^2 = H$, $R^3 = CH_3$	84	[21]
3b:	$R^1 = CH_3$, $R^2 = R^3 = H$	88	[10]
3c:	$R^1 = Br$, $R^2 = R^3 = H$	62	
3d:	$R^1 = R^3 = H$, $R^2 = Br$	82	[20]
3e:	$R^1 = NO_2$, $R^2 = R^3 = H$	77	
3f:	$R^1 = R^3 = H$, $R^2 = NO_2$	79	
3g:	$R^1 = OCH_3$, $R^2 = R^3 = H$	81	
3h:	$R^1 = R^3 = H$, $R^2 = OCH_3$	76	[19,20]

The different products were obtained in good yields and their characterizations were carried out by ^1H and ^{13}C NMR spectroscopy as well as by mass spectrometry (FAB or DCI) and microanalysis (see Experimental Section). These compounds offer the possibility for further reactions on both aromatic rings; for example, the Br atom on the phenyl ring can be replaced in various reactions and the NO_2 group can be reduced, whereas the pyridine ring can be functionalized thanks to the methyl group.[22]

The synthesis of five cyclometalated Ru^{II} complexes was carried out by Constable's method[4] with a modification proposed by Coudret,[23] which uses only 5 equiv. of ligand instead of a 15-fold excess.[4] We obtained much higher yields of cyclometalated complexes (up to 90%) than according to the literature procedure by using methanol instead of dichloromethane[4] as solvent. Constable[24] has studied the effect of different solvents in the reactions of 6-phenyl-2,2′-bipyridine with ruthenium(II) and concluded that the higher the dielectric constant of the solvent the greater the proportion of the metalated product formed (as is the case with methanol compared to dichloromethane). Purification of the complexes was carried out by column chromatography, which enables recovery of the unreacted excess of ligand. This synthesis yields the corresponding functionalized ruthenium complexes directly, whereas in the literature functionalization was carried out on the ruthenium complexes. Using 3,5-dipyridylbenzene, Collin et al. converted the corresponding cyclometalated complex into the nitro derivative and subsequently into the amino derivative.[25] More recently, Coudret was able to obtain the corresponding bromo-substituted complex upon treatment of $[Ru(bpy)_2L]^+$ (L = phenpy) with NBS.[25] The synthesis of the amino derivative was also carried out.[26] The different direct functionalizations of the complex were possible only at the position *para* to the carbanion.[27] In our case, by using the appropriate starting material (acetophenone), other positions of the substituent on the ligand and therefore in the complex are accessible.

Complete assignment of the ^1H and ^{13}C NMR spectra of the complexes required 1D, 2D ^1H-^1H COSY, HMQC ^1H-^{13}C and HMBC ^1H-^{13}C experiments. The labelling of the atoms is that of the X-ray structures. For the five complexes, comparison of the ^1H NMR spectra shows that the peaks corresponding to the phenylpyridine ring are influenced by the electronic character of the substituents on the phenyl ring. More precisely, in the high-field region between δ = 7.3 and 5.9 ppm, the most high-field-shifted doublet is assigned to the proton of the phenyl ring (8-H) in the *ortho* position and its chemical shift varies from δ = 5.95 (methoxy derivative **4h**) to 7.3 ppm (nitro derivative **4f**). The upfield shift of the proton adjacent to the site of metalation is a common feature of compounds of this type.[4,24,28] The other shielded doublet (between δ = 6.45 and 7.05 ppm) is attributed to the proton *meta* (9-H, complex **4a**) or *para* (10-H, complexes **4b**, **4d**, and **4h**) to the metalated carbon atom. An exception is observed for **4f**, for which the proton 10-H is highly deshielded (δ = 7.69 ppm) due to the electron-withdrawing character of the nitro substituent.

X-ray Analysis

Single crystals of ligands **3a** and **3b** were obtained after slow concentration of a mixture of pentane and ethyl acetate. The ORTEP diagrams of **3a** and **3b** are shown in Figure 1.

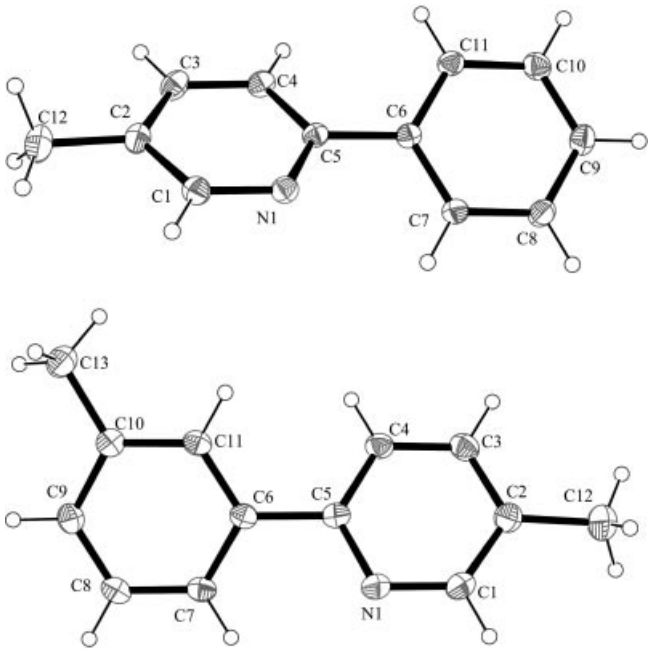


Figure 1. X-ray molecular structures of **3a** (top) and **3b** (bottom).

Ligand **3a** crystallizes in the $P2_12_12_1$ orthorhombic space group. The two aromatic rings are not planar, with an N(1)–C(5)–C(6)–C(7) torsion angle of 32.3°. Ligand **3b** crystallizes in the $P2_1/n$ monoclinic space group. The molecule is slightly more planar than **3a**, with an N(1)–C(5)–C(6)–C(7) torsion angle of 28.4°. As these compounds are not symmetrical, and as the exact position of the substituents can be unambiguously determined by NMR spectroscopy and because of the synthetic scheme, the position of the nitrogen atom is well defined. This is important for the analysis of the X-ray data of the complexes.

Crystals of the four complexes **4b′**, **4d**, **4f**, and **4h** were obtained for X-ray analysis (Figure 2). In one case (**4b**), good-quality crystals were available only after exchange of the trifluoromethanesulfonate counteranion by hexafluorophosphate to give complex **4b′**. Crystallization occurred upon slow diffusion of diethyl ether into acetonitrile solutions of the complexes at 5 °C.

The ruthenium complex **4b′** crystallizes in the $P2_1/n$ monoclinic space group. The asymmetric unit cell contains one ruthenium complex, one PF_6^- anion, and one molecule of acetone. The phenylpyridine ligand is almost perfectly planar in the complex, with an N(1)–C(5)–C(6)–C(7) torsion angle of 0.59° against torsion angles of 2.69° and 1.73° in the bipyridine ligands with N(2)/N(3) and N(4)/N(5), respectively. The brominated complex **4d** crystallizes in the $C2/c$ monoclinic space group. The unit cell contains eight molecules of complex ($Z = 8$), and four molecules of water. The phenylpyridine ligand is roughly planar, with an N(1)–C(5)–C(6)–C(7) torsion angle of 2.95° against torsion angles of 3.00° and 0.27° in the bipyridine ligands with N(2)/N(3) and N(4)/N(5), respectively. Complex **4f** crystallizes in the $P2_1/n$ monoclinic space group, with one molecule in the asymmetric unit cell. The bipyridine ligands are nearly perfectly planar in the complex, with torsion angles of 0.30° and 0.40° for the bipyridine ligands with N(2)/N(3) and N(4)/N(5), respectively. By contrast, the torsion angle in the phenylpyridine ligand is 1.63°. Complex **4h** crystallizes in the $P\bar{1}$ triclinic space group. The asymmetric unit cell contains one ruthenium complex, one $CF_3SO_3^-$ anion, and one molecule of acetonitrile. The phenylpyridine ligand is perfectly planar (torsion angle of 0.17°), whereas the bipyridine ligands are slightly distorted, with torsion angles of 5.96° and 4.46° for the bipyridine ligands with N(2)/N(3) and N(4)/N(5), respectively.

The Cambridge Crystallographic Database contains 156 entries with a (phenylpyridine)metal unit, most of them containing platinum (55) and palladium (24). However, structures containing a $(bpy)_2$(phenpy)metal unit are far

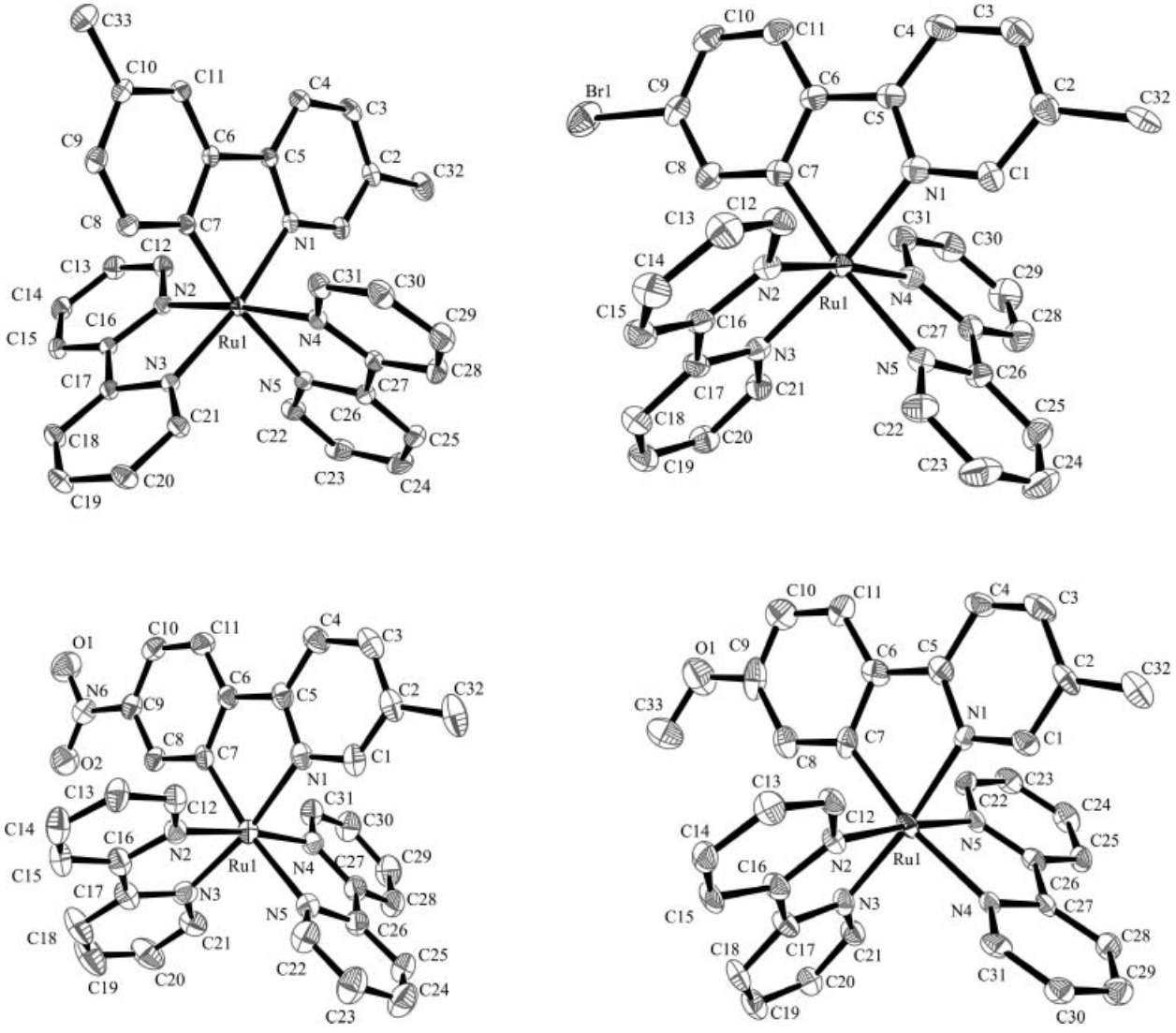


Figure 2. ORTEP representation of the X-ray structureS of **4b′** (top left), **4d** (top right), **4f** (bottom left), and **4h** (bottom right). The hydrogen atoms, solvent molecules, and counteranions are omitted for clarity.

Table 2. First coordination sphere (metal–ligand bond lengths [Å]) in $[Ru^{II}(bpy)_2(L)]^+$ complexes.

Complex	Ru(1)–C(7)	Ru(1)–N(1)	Ru(1)–N(2)	Ru(1)–N(3)	Ru(1)–N(4)	Ru(1)–N(5)
4b′	2.036(3)	2.080(2)	2.043(2)	2.036(2)	2.066(2)	2.138(2)
4d	2.030(5)	2.071(4)	2.042(4)	2.051(4)	2.065(4)	2.123(4)
4f	2.020(4)	2.078(4)	2.047(4)	2.055(4)	2.060(4)	2.121(4)
4h	2.031(8)	2.067(6)	2.047(5)	2.042(6)	2.066(6)	2.121(6)
Av. value	2.029(5)	2.074(4)	2.045(4)	2.046(4)	2.064(4)	2.125(4)
a[a]	1.997(7)	2.075(5)	2.040(5)	2.056(5)	2.086(5)	2.140(5)
b[a]	2.044(1)	2.069(4)	2.067	2.046	2.037	2.075

[a] **a**: $[Ru(bpy)_2(NPP)][BF_4]$[6] [NPP = 2-(3-nitrophenyl)pyridine]. **b**: $[Ru(bpy)_2(ppy)][PF_6]$[28] (ppy = phenylpyridine).

less common, with only four entries.[6,29–31] In two of them, namely $[Ru(bpy)_2(phenpy)][CrMn(ox)_3]$[30] and $[Rh(bpy)_2(phenpy)](PF_6)$,[31] the localization of the carbon atom was not possible. In the third complex, $[Ru(bpy)_2(phenpy)](PF_6)$,[29] the carbon atom was arbitrarily localized because its distribution was equal on the six atomic sites bonded to the Ru atom. Finally, the only crystal structure in which the carbon–metal bond was unambiguously identified is that of $[Ru^{II}(bpy)_2\{2\text{-(nitrophenyl)pyridine}\}](BF_4)$, reported by Reveco et al.[6] The description of the coordination sphere of the four new complexes **4b′**, **4d**, **4f**, and **4h** is compared to the previously reported structures in Table 2. First of all, it must be pointed out that the position of the carbon atom is unambiguous as the positions of the substituents in the unsymmetrical ligands are definite. The average metal–ligand distances for the four available structures were calculated and show the following general features: (1) whereas the Ru(1)–C(7) bond is shorter than the other metal–ligand bonds, the Ru–N bonds to both the nitrogen atom *trans* to the carbon atom [N(5)] and the one *cis* to the carbon atom [N(1)] are slightly elongated, which leads to a distorted octahedral geometry around the metal atom; (2) the Ru(1)–N(4) bond is also slightly elongated, but less than Ru(1)–N(5), probably because it belongs to the same bipyridine ligand; (3) the Ru(1)–N(2) and Ru(1)–N(3) bond lengths have similar values, thus showing that this bipyridine ligand is the least disturbed by the cyclometalating ligand. Interestingly, comparison of the Ru(1)–C(7) bond length [1.997(7) Å] in $[Ru^{II}(bpy)_2\{2\text{-(3-nitrophenyl)pyridine}\}](BF_4)$[6] and that in complex **4f** [2.020(4) Å, the smallest value in the series of complexes **4**], in which the nitro substituent is at the 4-position, demonstrates the influence of the electron-withdrawing character of the substituent. More precisely, in the *para* position, both inductive and mesomeric effects are transmitted to C(9) whereas in the *meta* position (complex **4f**) only an inductive effect is in operation.

Electrochemistry

The ligands and ruthenium complexes were examined by cyclic voltammetry (Figure 3) and Osteryoung square-wave voltammetry (Table 3).

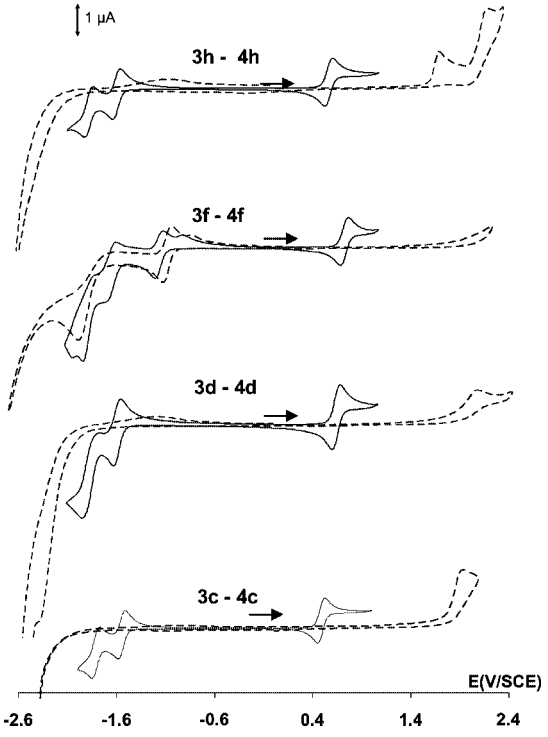


Figure 3. Cyclic voltammograms at room temperature of ruthenium complexes **4c**, **4d**, **4f**, **4h** (solid line) and ligands **3c**, **3d**, **3f**, **3h** (dashed line) in CH_3CN with 0.1 M $TBABF_4$ as supporting electrolyte (Pt electrode, $v = 0.1\ V\,s^{-1}$).

Ligands **3c**, **3d**, and **3h** exhibit two processes: one in oxidation (ca. 1.9 V) and one in reduction (ca. –2.4 V). However, ligand **3h** presents another oxidation (1.55 V) due to the methoxy substituent. Ligand **3f** displays two reduction processes: a reversible redox couple at –1 V assigned to the NO_2 substituent and an irreversible reduction at –1.84 V (much higher than those of other ligands). This suggests that because of the electron-withdrawing properties of the NO_2 group, the oxidation is also dramatically shifted to higher potentials that are not measurable under the experimental conditions.

Cyclic voltammetry of the complexes exhibits three characteristic processes: one oxidation process and two reduction processes.

First, the reversible redox couple at around 0.5 V is readily assigned to the Ru^{III}/Ru^{II} process.[4,32] A comparison of the potentials in Table 3 indicates that the first metal-cen-

Table 3. Redox potentials ([V] vs. SCE) of the ligands and ruthenium complexes in 0.1 M $TBABF_4$ in acetonitrile solutions measured at room temperature.

	Oxidation			Reduction			
	$E_{1/2}$[a]	$E_{1/2}$[b]	$E_{1/2}$[b]	$E_{1/2}$[a]	$E_{1/2}$[a]	$E_{1/2}$[a]	$E_{1/2}$[b]
3c			1.90				–2.44
3d			1.91				–2.19
3f			n.d.[c]	–1.04			–1.84
3h		1.55	1.99				–2.55
4c	0.48		1.73		–1.54	–1.82	–2.40
4d	0.60		1.77		–1.51	–1.76	–2.24
4f	0.67		1.99	–1.12	–1.57	–1.81	–1.94
4h	0.52	1.63	n.d.[c]		–1.53	–1.79	–2.37
$Ru(bpy)_3$[33]	1.29				–1.35	–1.54	–1.73

[a] The $E_{1/2}$ values were estimated as the average of the cathodic and anodic peak potentials in cyclic voltammetry with a scan rate of 100 mV s^{-1}. [b] The $E_{1/2}$ values were obtained from the square-wave voltammogram: frequency 20 Hz, step potential 5 mV, amplitude 20 mV. [c] Not observed or badly defined under the experimental conditions.

tered oxidation of the complex is shifted by about 800 mV to more cathodic potentials than that of $[Ru(bpy)_3]$.[33] This behavior demonstrates the strong σ-donating character of the phenylpyridine ligands, which stabilize Ru^{III} by increasing the electron density on the metal atom.[4,7c] Moreover, the nature of the substituents affects the shift of the Ru^{III}/Ru^{II} potential. The methyl and methoxy substituents with electron-donating character induce the most significant shift, whereas the electron-withdrawing groups (Br and NO_2), which decrease the electron density on Ru^{III}, lower the magnitude of the shift.

Second, the complexes exhibit two reduction processes at around –1.55 and –1.80 V (–1.35 and –1.54 V for $[Ru(bpy)_3]$). Complex **4f** displays an additional first reduction process at –1.12 V assigned to the NO_2 substituent. Generally, compared to $[Ru(bpy)_3]$, the bpy-centered quasi-reversible reductions are shifted to more negative potentials and are also strongly affected by the presence of the cyclometallating ligand,[7c] but the nature of the substituents does not affect significantly these processes. Moreover, the most cathodic potentials near the solvent/electrolyte limit were resolved in the square-wave experiment and were assigned to the phenylpyridine ligand.

Conclusions

We have been able to synthesize new substituted phenylpyridines in high yields by a very simple general method from cheap, commercially available starting materials. Functionalized cyclometalated ruthenium(II) complexes were obtained in much higher yields than the few examples described in the literature. As crystals for four of them were obtained, an X-ray study highlighted specific features of the Ru–C and the *trans*-Ru–N bonds. The easiness in obtaining first the ligands and then the cyclometalated complexes is a breakthrough for the application of these complexes. By a "building block" approach, involving convergent synthesis, these compounds could lead to various polynuclear complexes[34] or to new compounds with potential NLO properties.[22]

Experimental Section

General: Reagents and solvents were commercially available and were used as received. $[Ru(bpy)_2Cl_2]$ was prepared according to a literature procedure.[35] ^1H and ^{13}C NMR spectra were obtained at 298 K in $CDCl_3$, CD_3COCD_3, or $(CD_3)_2SO$ with a Bruker AM 250 spectrometer (250 MHz for ^1H NMR and 62.9 MHz for ^{13}C) or a Bruker Avance 500 spectrometer for 2D NMR. DCI and EI mass spectra were recorded with a Thermo Finnigan TSQ 7000 and FAB mass spectra were recorded with a quadrupolar Nermag R 10-10 instrument with NBA as matrix. Elemental analyses were performed at the LCC with a Perkin–Elmer 2400 Serie II instrument. Electrochemistry data: Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT 100. A home-made, airtight three-electrode cell connected to a vacuum/argon line made up of a Pt disk (0.5 mm diameter) as working electrode, a Pt gauze as auxiliary electrode, and an SCE as reference electrode. All experiments were performed at ambient temperature in CH_3CN solution, with 0.1 M nBu_4NBF_4 as supporting electrolyte (purum electrochemical grade Fluka, purified by sublimation). The solutions used for the electrochemical studies were typically 10^{-3} M in ruthenium complex. Prior to measurements, the solutions were deoxygenated by bubbling with argon gas for 15 min and the working electrode was polished with a polishing machine (Presi P230); during experiments, a stream of argon was passed over the solution. All potentials are reported vs. SCE.

X-ray Analysis: Data collection (Table 4) was performed at low temperature (180 K) with an IPDS STOE diffractometer equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream Cooler Device. The final unit-cell parameters were obtained by means of a least-squares refinement performed on a set of 5000 well-measured reflections. Crystal decay was monitored during the data collection; no significant fluctuations of intensities were observed. The structures were solved by direct methods using SIR92,[36] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97[37] included in the software package WinGX version 1.63.[38] Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[39] All hydrogen atoms were located geometrically and refined by using a riding model. All non-hydrogen atoms were refined anisotropically, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Drawings of the molecules were produced with the program ORTEP32,[40] with 30% probability displacement ellipsoids for non-hydrogen atoms. CCDC-603013 to -603018 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical Procedure for the Preparation of the Pyridinium Derivatives 2a–h: A solution of sublimated iodine (5.25 g, 20.5 mmol) in 8 mL of dry pyridine was added to a solution of 20 mmol of acetophenone in 5 mL of dry pyridine. After heating at 80 °C for 6 h, then cooling, the precipitate was filtered off, rinsed once with pyridine, dried, and recrystallized from boiling ethanol. The corresponding pyridinium derivative was isolated as a beige powder.

Table 4. Crystal data, data collection and refinements parameters for ligands **3a** and **3b** and complexes **4b′**, **4d**, **4f**, and **4h**.

	3a	**3b**	**4b′**	**4d**	**4f**	**4h**
Empirical formula	$C_{12}H_{11}N$	$C_{13}H_{13}N$	$C_{36}H_{34}F_6N_5OPRu$	$C_{33}H_{26}BrF_3N_5O_{3.5}Ru$	$C_{35}H_{30}F_3N_6O_{5.5}RuS$	$C_{37}H_{31}F_3N_6O_4RuS$
Formula mass	169.22	183.24	798.72	818.63	812.78	801.80
Crystal size [mm]	0.5×0.3×0.07	0.35×0.25×0.12	0.375×0.11×0.05	0.4×0.2×0.07	0.45×0.1875×0.05	0.3×0.2×0.08
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/n$	$P\bar{1}$
a [Å]	6.1173(5)	6.338(5)	9.0328(7)	24.295(5)	15.2172(16)	9.240(5)
b [Å]	7.4700(5)	7.218(5)	13.7518(10)	13.694(3)	14.5676(10)	13.611(5)
c [Å]	20.0874(19)	22.561(15)	27.824(2)	20.137(4)	16.8313(17)	15.545(5)
α [°]	90	90	90	90	90	66.107(5)
β [°]	90	96.211(5)	87.981(10)	105.74(3)	112.241(11)	83.613(5)
γ [°]	90	90	90	90	90	72.623(5)
V [Å^3]	917.92(13)	1026.1(11)	3454.1(4)	6449(3)	3453.5(6)	1705.8(12)
$\rho_{calcd.}$ [g cm^{-3}]	1.224	1.186	1.536	1.686	1.563	1.561
T [K]	180	180	180	180	180	180
μ(Mo-$K\alpha$) [mm^{-1}]	0.072	0.069	0.570	1.853	0.584	0.587
Scan mode	φ	φ	φ	φ	φ	φ
Measured reflections	7932	7840	32316	27761	29682	15476
Independent reflections	1075	1950	6770	5432	5882	5659
Observed reflections	1075	1950	6770	5432	5882	5659
Criteria	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$
Refinement on	F^2	F^2	F^2	F^2	F^2	F^2
No of parameters	119	129	455	430	453	463
H atoms	calculated	calculated	calculated	calculated	calculated	calculated
R_1	0.0285	0.0504	0.0319	0.0504	0.0456	0.0744
wR_2	0.0705	0.1312	0.0706	0.1407	0.1001	0.1716
$\Delta\rho_{max}$ [e Å^{-3}]	0.125	0.208	0.551	1.192	0.558	1.049
$\Delta\rho_{min}$ [e Å^{-3}]	–0.111	–0.228	–0.480	–1.043	–0.410	–1.529
GOF	1.052	1.053	0.974	1.033	0.884	0.910

Compound 2a: Yield: 4.03 g (62%). ^{1}H NMR ([D$_6$]DMSO): δ = 9.01 (d, J = 5.5 Hz, 2 H), 8.75 (dt, J = 7.9 and 1.2 Hz, 1 H), 8.29 (t, J = 7.4 Hz, 2 H), 8.07 (dd, J = 7 and 1.4 Hz, 2 H), 7.79 (m, 1 H), 7.67 (dt, J = 7.6 and 1.7 Hz, 2 H), 6.51 (s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 190.6, 146.4, 146.2, 134.7, 133.4, 129.1, 128.2, 127.8, 66.3 ppm. $C_{13}H_{12}INO$ (325.14): calcd. C 48.02, H 3.72, N 4.31; found C 47.92, H 3.38, N 4.09. FAB-MS: m/z = 198 [M–I]$^+$.

Compound 2b: Yield: 4.27 g (63%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.98 (d, J = 5.5 Hz, 2 H), 8.71 (t, J = 7.8 Hz, 1 H), 8.24 (dd, J = 7.3 and 6.6 Hz, 2 H), 7.86 (s, 1 H), 7.84 (d, J = 6.3 Hz, 1 H), 7.54 (m, 2 H), 6.44 (s, 2 H), 2.44 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 190.6, 146.3, 146.2, 138.5, 135.3, 133.5, 129.0, 128.4, 127.8, 125.5, 66.2, 20.8 ppm. $C_{14}H_{14}INO$ (339.17): calcd. C 49.58, H 4.16, N 4.13; found C 49.58, H 4.27, N 4.00. FAB-MS: m/z = 212 [M–I]$^+$.

Compound 2c: Yield: 6.30 g (78%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.97 (d, J = 5.5 Hz, 2 H), 8.76 (t, J = 7.8 Hz, 1 H), 8.30 (dd, J = 7.2 and 6.8 Hz, 2 H), 8.22 (m, 1 H), 8.1–8.0 (m, 2 H), 7.65 (t, J = 7.9 Hz, 1 H), 6.48 (s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 189.8, 146.5, 146.2, 137.1, 135.5, 131.4, 130.7, 127.9, 127.2, 122.3, 66.2 ppm. $C_{13}H_{11}BrINO$ (404.04): calcd. C 38.65, H 2.74, N 3.47; found C 38.71, H 2.55, N 3.33. FAB-MS: m/z = 277 [M–I]$^+$.

Compound 2d: Yield: 6.30 g (78%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.97 (d, J = 5.5 Hz, 2 H), 8.74 (t, J = 7.8 Hz, 1 H), 8.28 (dd, J = 7.1 and 7 Hz, 2 H), 8.00 (d, J = 8.6 Hz, 2 H), 7.90 (d, J = 8.6 Hz, 2 H), 6.45 (s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 190.0, 146.4, 146.2, 132.5, 132.2, 130.1, 128.8, 127.8, 66.1 ppm. $C_{13}H_{11}BrINO$ (404.04): calcd. C 38.65, H 2.74, N 3.47; found C 38.55, H 2.50, N 3.24. FAB-MS: m/z = 277 [M–I]$^+$.

Compound 2e: Yield: 5.55 g (75%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.98 (d, J = 5.7 Hz, 2 H), 8.76 (m, 2 H), 8.63 (dd, J = 8.2 and 2 Hz, 1 H), 8.48 (d, J = 7.8 Hz, 1 H), 8.31 (dd, J = 7.1 and 7 Hz, 2 H), 7.98 (t, J = 8 Hz, 1 H), 6.55 (s, 2 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 189.6, 148.0, 146.6, 146.2, 134.8, 134.3, 131.0, 128.6, 127.9, 122.5, 66.3 ppm. $C_{13}H_{11}IN_2O_3$ (370.14): calcd. C 42.18, H 3.00, N 7.57; found C 42.22, H 2.92, N 7.45. FAB-MS: m/z = 243 [M–I]$^+$.

Compound 2f: Yield: 5.33 g (72%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.97 (d, J = 5.5 Hz, 2 H), 8.76 (t, J = 7.8 Hz, 1 H), 8.48 (d, J = 8.8 Hz, 2 H), 8.27–8.32 (m, 4 H), 6.51 (s, 2 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 190.0, 146.4, 146.2, 132.5, 132.2, 130.1, 128.8, 127.8, 66.1 ppm. $C_{13}H_{11}IN_2O_3$ (370.14): calcd. C 42.18, H 3.00, N 7.57; found C 42.33, H 2.95, N 7.46. FAB-MS: m/z = 243 [M–I]$^+$.

Compound 2g: Yield: 5.82 g (82%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.99 (d, J = 5.5 Hz, 2 H), 8.75 (t, J = 7.8 Hz, 1 H), 8.29 (dd, J = 7.5 and 6.6 Hz, 2 H), 7.70–7.55 (m, 2 H), 7.54 (s, 1 H), 7.39 (md, J = 7.7 Hz, 1 H), 6.48 (s, 2 H), 3.87 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 190.4, 159.4, 146.3, 146.2, 134.7, 130.3, 127.8, 120.6, 120.4, 112.7, 66.3, 55.5 ppm. $C_{14}H_{14}INO_2$ (355.17): calcd. C 47.34, H 3.97, N 3.94; found C 47.39, H 3.97, N 4.00. FAB-MS: m/z = 228 [M–I]$^+$.

Compound 2h: Yield: 5.11 g (72%). ^{1}H NMR ([D$_6$]DMSO): δ = 9.00 (d, J = 5.5 Hz, 2 H), 8.74 (t, J = 7.8 Hz, 1 H), 8.27 (dd, J = 7.5 and 6.7 Hz, 2 H), 8.05 (d, J = 8.8 Hz, 2 H), 7.19 (d, J = 8.8 Hz, 2 H), 6.45 (s, 2 H), 3.90 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 188.8, 164.2, 146.2, 130.7, 127.7, 126.2, 114.4, 66.9, 55.8 ppm. $C_{14}H_{14}INO_2$ (355.17): calcd. C 47.34, H 3.97, N 3.94; found C 47.22, H 3.60, N 3.72. FAB-MS: m/z = 228 [M–I]$^+$.

Typical Procedure for the Preparation of the Phenylpyridines 3a–h: NH_4OAc (4 equiv., 8 mmol) and methacrolein (4 mmol) were added to a solution of the pyridinium derivative (2 mmol) in 5 mL of formamide. The reaction mixture was heated at 80 °C for 6 h and, after cooling, the ligand precipitated and was filtered off and rinsed with water. If the ligand did not precipitate it was extracted with Et_2O (3×20 mL), the organic phase was dried with $MgSO_4$, concentrated to dryness, and purified by chromatography on silica gel with EtOAc in pentane (10:90) or methanol in dichloromethane (3:97) as eluent.

5-Methyl-2-phenylpyridine (3a): ^{1}H NMR ($CDCl_3$): δ = 8.51 (d, J = 1.2 Hz, 1 H), 7.96 (m, 2 H), 7.62 (d, J = 8 Hz, 1 H), 7.54 (dd, J = 8 and 2.1 Hz, 1 H), 7.49–7.35 (m, 3 H), 2.36 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 154.7, 150.0, 139.3, 137.4, 131.6, 128.7, 128.6, 126.7, 120.0, 18.2 ppm. $C_{12}H_{11}N$(169.23): calcd. C 85.21, H 6.51, N 8.28; found C 85.29, H 6.37, N 8.21. DCI-MS: m/z = 170 $[MH]^+$.

5-Methyl-2-(3-methylphenyl)pyridine (3b): ^{1}H NMR ($CDCl_3$): δ = 8.51 (s, 1 H), 7.79 (s, 1 H), 7.71 (d, J = 7.5 Hz, 1 H), 7.61 (d, J = 8 Hz, 1 H), 7.53 (dd, J = 8.1 and 1.9 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 7.19 (d, J = 7.5 Hz, 1 H), 2.42 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 154.9, 150.0, 139.3, 138.3, 137.3, 131.5, 128.6, 127.4, 123.8, 120.1, 21.5, 18.1 ppm. $C_{13}H_{13}N$ (183.25): calcd. C 85.21, H 6.51, N 8.28; found C 85.29, H 6.37, N 8.21. DCI-MS: m/z = 184 $[MH]^+$.

2-(3-Bromophenyl)-5-methylpyridine (3c): ^{1}H NMR ($CDCl_3$): δ = 8.51 (s, 1 H), 7.87 (td, J = 7.8 and 1.5 Hz, 1 H), 7.58 (m, 2 H), 7.50 (ddd, J = 8, 1.7 and 0.8 Hz, 1 H), 7.32 (t, J = 8 Hz, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.9, 150.1, 141.3, 137.4, 132.3, 131.4, 130.2, 129.7, 125.1, 123.0, 120.0, 18.2 ppm. $C_{12}H_{10}BrN$ (248.12): calcd. C 58.09, H 4.06, N 5.65; found C 58.15, H 3.74, N 5.52. DCI-MS: m/z (%) = 248 (96), 250 (100) $[MH]^+$.

2-(4-Bromophenyl)-5-methylpyridine (3d): ^{1}H NMR ($CDCl_3$): δ = 8.49 (d, J = 0.6 Hz, 1 H), 7.83 (m, 2 H), 7.58 (m, 4 H), 2.35 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 153.5, 150.1, 138.2, 137.5, 132.0, 131.8, 128.2, 123.0, 119.8, 18.2 ppm. $C_{12}H_{10}BrN$ (248.12): calcd. C 58.09, H 4.06, N 5.65; found C 58.14, H 3.93, N 5.59. DCI-MS: m/z (%) = 248 (100), 250 (95) $[MH]^+$.

5-Methyl-2-(3-nitrophenyl)pyridine (3e): ^{1}H NMR ($CDCl_3$): δ = 8.81 (s, 1 H), 8.54 (s, 1 H), 8.33 (d, J = 7.7 Hz, 1 H), 8.22 (dd, J = 8 and 1.1 Hz, 1 H), 7.70 (d, J = 8 Hz, 1 H), 7.62 (m, 2 H), 2.40 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.0, 150.4, 148.7, 141.0, 137.7, 133.1, 132.5, 129.6, 123.2, 122.5, 120.1, 18.2 ppm. $C_{12}H_{10}N_2O_2$ (214.22): calcd. C 67.28, H 4.70, N 13.08; found C 67.13, H 4.44, N 12.97. DCI-MS: m/z = 215 $[MH]^+$.

5-Methyl-2-(4-nitrophenyl)pyridine (3f): ^{1}H NMR ($CDCl_3$): δ = 8.57 (s, 1 H), 8.31 (d, J = 8.9 Hz, 2 H), 8.15 (d, J = 8.9 Hz, 2 H), 7.71 (d, J = 8.1 Hz, 1 H), 7.62 (dd, J = 8.1 and 1.8 Hz, 1 H), 2.41 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.0, 150.4, 148.7, 141.0, 137.7, 133.1, 132.5, 129.6, 123.2, 122.5, 120.1, 18.2 ppm. $C_{12}H_{10}N_2O_2$ (214.22): calcd. C 67.28, H 4.70, N 13.08; found C 67.41, H 4.34, N 12.95. DCI-MS: m/z = 215 $[MH]^+$.

2-(3-Methoxyphenyl)-5-methylpyridine (3g): ^{1}H NMR ($CDCl_3$): δ = 8.51 (d, J = 1.5 Hz, 1 H), 7.60 (t, J = 8 Hz, 1 H), 7.55 (m, 2 H), 7.36 (t, J = 8 Hz, 1 H), 6.93 (dd, J = 8.2 and 2.5 Hz, 1 H), 3.88 (s, 3 H), 2.36 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 160.0, 154.5, 150.0, 140.9, 137.3, 131.7, 129.6, 120.1, 119.1, 114.7, 111.7, 55.3, 18.2 ppm. $C_{13}H_{13}NO$ (199.25): calcd. C 78.39, H 6.53, N 7.03; found C 78.08, H 6.60, N 6.83. DCI-MS: m/z = 200 $[MH]^+$.

2-(4-Methoxyphenyl)-5-methylpyridine (3h): ^{1}H NMR ($CDCl_3$): δ = 8.47 (s, 1 H), 7.90 (dd, J = 8.7 and 1.6 Hz, 2 H), 7.6–7.5 (m, 2 H), 6.97 (dd, J = 8.8 and 1.8 Hz, 2 H), 3.86 (s, 3 H), 2.34 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 160.1, 154.3, 149.8, 137.2, 133.0, 130.8, 127.8, 119.2, 114.0, 55.2, 18.0 ppm. $C_{13}H_{13}NO$ (199.25): calcd. C 78.39, H 6.53, N 7.03; found C 78.30, H 6.59, N 6.96. DCI-MS: m/z = 200 $[MH]^+$.

General Procedure for the Preparation of the Complexes: [Ru(bpy)$_2$Cl$_2$] (0.15 mmol) and AgOTf (0.30 mmol) were added to a solution of the ligand (0.75 mmol) in 5 mL of MeOH, and the mixture was refluxed in the dark for 2 h. After cooling and filtration of a brown precipitate, the filtrate was concentrated off and purification was carried out by chromatography on alumina. Elution with EtOAc/pentane (10:90) provided unreacted ligand and further elution with MeOH/CH_2Cl_2 (3:97) gave the pure complex.

Complex 4a: Yield: 98 mg (90%). ^{1}H NMR (CD_3COCD_3): δ = 8.77 (dt, J = 8.2 and 1 Hz, 1 H, H25), 8.68 (dt, J = 8 and 1.1 Hz, 1 H, H28), 8.61 (dt, J = 8 and 1 Hz, 1 H, H18), 8.59 (dt, J = 8 and 1 Hz, 1 H, H15), 8.16 (ddd, J = 5.7, 1.5 and 0.7 Hz, 1 H, H31), 8.13 (ddd, J = 9.2, 5.6 and 1.5 Hz, 1 H, H24), 8.06 (d, J = 8.3 Hz, 1 H, H4), 8.05 (m, 1 H, H22), 7.98–7.93 (m, 3 H, H12, H29, H19), 7.92–7.86 (m, 3 H, H11, H14, H21), 7.62 (ddd, J = 8.7, 2.1 and 0.7 Hz, 1 H, H3), 7.59 (ddd, J = 7.5, 5.4 and 1.2 Hz, 1 H, H23), 7.56 (m, 1 H, H1), 7.39–7.34 (m, 3 H, H20, H30, H13), 6.88 (dd, J = 7.2 and 1.3 Hz, 1 H, H10), 6.81 (td, J = 7.3 and 1.3 Hz, 1 H, H9), 6.18 (ddd, J = 7.3, 1.3 and 0.4 Hz, 1 H, H8), 2.08 (s, 3 H, CH_3py) ppm. ^{13}C NMR (CD_3COCD_3): δ = 191.79 (C7), 164.97 (C5), 157.88 (C27), 157.15 (C17), 156.81 (C16), 155.36 (C26), 154.15 (C31), 150.24 (C29), 149.98 (C11), 149.77 (C1), 149.10 (C22), 145.57 (C6), 136.73 (C3), 136.41 (C24), 135.18 (C8), 134.98 (C29), 133.78 (C19), 133.53 (C14), 132.07 (C2), 128.10 (C9), 127.22 (C23), 126.48 (C20), 126.29 (C30), 126.14 (C13), 123.73 (C11), 123.58 (C28), 123.34 (C25), 123.06 (C15), 123.04 (C18), 120.74 (C10), 118.39 (C4), 17.15 (CH_3py) ppm. FAB-MS: m/z = 582 $[M–OTf]^+$.

Complex 4b: Yield: 98 mg (88%). Metathesis: the complex with the triflate counterion was dissolved in the minimum amount of methanol, then a saturated solution of NH_4PF_6 was added until no more precipitation was observed. The precipitate was filtered off, rinsed with distilled water, and dried under vacuum. ^{1}H NMR ([D$_6$]-DMSO): δ = 8.76 (d, J = 8.2 Hz, 1 H, H25), 8.68 (d, J = 8.2 Hz, 1 H, H28), 8.61 (d, J = 8.8 Hz, 1 H, H15), 8.59 (d, J = 8.8 Hz, 1 H, H18), 8.09 (td, J = 7.5 and 0.9 Hz, 1 H, H24), 8.04 (d, J = 8.3 Hz, 1 H, H4), 7.99 (d, J = 5.4 Hz, 1 H, H31), 7.91 (t, J = 8.1 Hz, 1 H, H29), 7.89 (t, J = 8 Hz, 1 H, H19), 7.86 (t, J = 8.1 Hz, 1 H, H14), 7.81 (d, J = 5.3 Hz, 1 H, H22), 7.72 (d, J = 5.6 Hz, 1 H, H12), 7.68 (s, 1 H, H11), 7.62 (d, J = 5.6 Hz, 1 H, H21), 7.58 (d, J = 8.8 Hz, 1 H, H3), 7.56 (t, J = 6.5 Hz, 1 H, H23), 7.38 (t, J = 6.5 Hz, 1 H, H30), 7.36 (m, 1 H, H20), 7.35 (t, J = 7 Hz, 1 H, H13), 7.28 (s, 1 H, H1), 6.61 (d, J = 7.4 Hz, 1 H, H9), 6.18 (d, J = 7.5 Hz, 1 H, H8), 2.22 (s, 3 H, CH_3phe), 2.04 (s, 3 H, CH_3py) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 187.54 (C7), 164.74 (C5), 157.72 (C27), 157.0 (C16), 156.65 (C17), 155.22 (C26), 153.91 (C31), 150.03 (C21 or C12), 149.78 (C12 or C21), 149.55 (C1), 148.99 (C22), 145.55 (C10), 137.21 (C3), 136.86 (C24), 135.45 (C29), 134.94 (C8), 134.20 (C14 or C19), 133.89 (C19 or C14), 132.14 (C2), 129.78 (C9), 129.33 (C6), 127.83 (C23), 127.05 (C20 or C13), 126.87 (C13 or C20), 126.77 (C30), 124.99 (C11), 124.21 (C28), 123.94 (C25), 123.69 (C15), 123.64 (C18), 118.86 (C4), 21.27 (CH_3ph), 18.17 (CH_3py) ppm. FAB-MS: m/z = 596 $[M–PF_6]^+$.

Complex 4d: Yield: 90 mg (74%). ^{1}H NMR (CD_3COCD_3): δ = 8.78 (dt, J = 8.2 and 1 Hz, 1 H, H25), 8.71 (dt, J = 8.1 and 1 Hz, 1 H, 1 H, H28), 8.64 (dt, J = 8.3 and 1 Hz, 1 H, H15), 8.62 (dt, J = 8.3 and 1 Hz, 1 H, H18), 8.17 (ddd, J = 5.7, 1.7 and 0.7 Hz, 1 H, H31),

8.14 (td, J = 8.4 and 1.5 Hz, 1 H, H24), 8.09 (d, J = 8.2 Hz, 1 H, H4), 8.02 (ddd, J = 5.4, 1.6 and 0.8 Hz, 1 H, H22), 8.00 (ddd, J = 7.6, 5 and 0.5 Hz, 1 H, H29), 7.98 (ddd, J = 7.6, 5 and 0.5 Hz, 1 H, H14), 7.95 (m, 1 H, H19), 7.93 (m, 1 H, H21), 7.88 (ddd, J = 5.7, 1.4 and 0.8 Hz, 1 H, H12), 7.82 (d, J = 8.3 Hz, 1 H, H11), 7.64 (ddd, J = 8.3, 1.1 and 0.7 Hz, 1 H, H3), 7.59 (ddd, J = 7.5, 5.4 and 0.8 Hz, 1 H, H23), 7.57 (d, J = 1.2 Hz, 1 H, H1), 7.44–7.37 (m, 2 H, H30, H20), 7.42 (dd, J = 5.8 and 1.5 Hz, 1 H, H13), 7.04 (dd, J = 8.3 and 2.1 Hz, 1 H, H10), 6.54 (d, J = 2.1 Hz, 1 H, H8), 2.08 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_3COCD_3): δ = 196.20 (C7), 163.95 (C5), 157.77 (C27), 157.07 (C16), 156.74 (C17), 155.32 (C26), 154.18 (C31), 150.39 (C21), 150.12 (C12), 149.98 (C1), 149.17 (C22), 144.86 (C6), 137.02 (C8), 136.93 (C3), 136.70 (C24), 135.38 (C29), 134.32 (C14), 134.20 (C19), 132.68 (C2), 127.27 (C23), 126.73 (C30), 126.55 (C20), 126.37 (C13), 125.32 (C11), 123.73 (C28), 123.67 (C9), 123.54 (C10), 123.45 (C25), 123.27 (C18), 123.25 (C15), 118.77 (C4), 17.19 (CH_3) ppm. FAB-MS: m/z (%) = 662 (45), 660 (43) $[M-OTf]^+$.

Complex 4f: Yield: 28 mg (24%). ^{1}H NMR (CD_3COCD_3): δ = 8.81 (d, J = 8.2 Hz, 1 H, H25), 8.73 (d, J = 8.1 Hz, 1 H, H28), 8.67 (d, J = 8 Hz, 1 H, H15), 8.63 (d, J = 8 Hz, 1 H, H18), 8.28 (d, J = 8.2 Hz, 1 H, H4), 8.17 (td, J = 7.9 and 1.6 Hz, 1 H, H24), 8.11 (d, J = 8.6 Hz, 1 H, H11), 8.12 (m, 1 H, H31), 8.06 (ddd, J = 5.3, 1.4 and 0.8 Hz, 1 H, H22), 8.03 (td, J = 7.7 and 1.4 Hz, 1 H, H14), 7.98 (td, J = 8 and 1.5 Hz, 1 H, H29), 7.96 (m, 1 H, H19), 7.94 (m, 1 H, H21), 7.92 (m, 1 H, H12), 7.74 (m, 1 H, H3), 7.72 (m, 1 H, H1), 7.69 (dd, J = 8.5 and 2.4 Hz, 1 H, H10), 7.62 (ddd, J = 7.5, 5.5 and 1.2 Hz, 1 H, H23), 7.46 (ddd, J = 7.3, 5.7 and 1.3 Hz, 1 H, H13), 7.39 (ddd, J = 7.3, 5.7 and 1.3 Hz, 2 H, H30, H20), 7.29 (d, J = 2.4 Hz, 1 H, H8), 2.13 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_3COCD_3): δ = 194.80 (C7), 162.76 (C5), 157.78 (C26), 157.03 (C16), 156.75 (C17), 155.30 (C26), 154.34 (C22), 152.86 (C6), 150.60 (C1), 150.47 (C21), 150.24 (C12), 149.25 (C22), 146.99 (C9), 137.12 (C3), 136.89 (C24), 135.61 (C29), 134.73 (C14), 134.57 (C19), 134.44 (C2), 128.41 (C8), 127.33 (C23), 126.93 (C13), 126.67 (C30 or C20), 126.52 (C20 or C30), 123.83 (C28), 123.65 (C11), 123.54 (C25), 123.43 (C15), 123.39 (C18), 120.39 (C4), 115.90 (C10), 17.31 (CH_3) ppm. FAB-MS: m/z = 627 $[M-OTf]^+$.

Complex 4h: Yield: 95 mg (83%). ^{1}H NMR (CD_3COCD_3): δ = 8.77 (d, J = 8.2 Hz, 1 H, H25), 8.72 (d, J = 8.2 Hz, 1 H, H28), 8.62 (d, J = 8.1 Hz, 1 H, H18), 8.60 (d, J = 8.1 Hz, 1 H, H15), 8.20 (dd, J = 5.8 and 1.1 Hz, 1 H, H31), 8.12 (td, J = 7.8 and 1.5 Hz, 1 H, H24), 8.05 (dd, J = 5.4 and 1.3 Hz, 1 H, H22), 7.97 (m, 1 H, H29), 7.95 (m, 1 H, H12), 7.94 (m, 1 H, H21), 7.92 (d, J = 8.2 Hz, 1 H, H4), 7.89 (m, 1 H, H19), 7.88 (m, 1 H, H14), 7.82 (d, J = 8.5 Hz, 1 H, H11), 7.58 (ddd, J = 7.5, 5.4 and 1.1 Hz, 1 H, H23), 7.55 (dd, J = 8.4 and 2.1 Hz, 1 H, H3), 7.47 (m, 1 H, H1), 7.39–7.34 (m, 3 H, H13, H20, H30), 6.45 (dd, J = 8.5 and 2.6 Hz, 1 H, H10), 5.95 (d, J = 2.4 Hz, 1 H, H8), 3.53 (s, 3 H, OCH_3), 2.04 (s, 3 H, CH_3) ppm. ^{13}C NMR (CD_3COCD_3): δ = 194.27 (C7), 164.71 (C5), 159.59 (C6), 157.84 (C27), 157.29 (C17), 156.83 (C16), 155.36 (C26), 154.06 (C31), 150.22 (C29), 150.03 (C14), 149.41 (C1), 149.11 (C22), 138.37 (C9), 136.65 (C3), 136.41 (C24), 134.99 (C12), 133.78 (C21), 133.59 (C19), 130.77 (C2), 127.19 (C23), 126.43 (C20), 126.27 (C30), 126.12 (C13), 124.99 (C11), 123.64 (C28), 123.42 (C25), 123.13 (C15), 123.07 (C18), 119.69 (C8), 117.63 (C4), 106.43 (C10), 53.73 (OCH_3), 17.10 (CH_3) ppm. FAB-MS: m/z = 612 $[M-OTf]^+$.

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