

Ruthenium and rhenium complexes with silyl-substituted bipyridyl ligands

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Abstract

The preparation of 5,5'-bis(trimethylsilyl)- (**1a**) and 5,5'-bis(pentamethyldisilanyl)-2,2'-bipyridines (**1b**) by dehalogenative coupling of the corresponding 2-bromo-5-silylpyridines is described. Silyl substitution causes broad and red shifted $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ UV-vis absorption bands; electrochemical reduction is facilitated. With these ligands, a series of ruthenium complexes $[\text{Ru}(\text{bpy})_2(\text{L})](\text{PF}_6)_2$ (**3a**, L = **1a**; **3b**, L = **1b**) and $[\text{RuL}_3](\text{PF}_6)_2$ (**4a**, L = **1a**; **4b**, L = **1b**), as well as rhenium compounds $\text{Re}(\text{L})(\text{CO})_3\text{Cl}$ (**5a**, L = **1a**; **5b**, L = **1b**) (bpy = 2,2'-bipyridine) were synthesized. These complexes give rise to red-shifted metal-to-ligand and charge-transfer absorptions in the region of 460–480 nm for the ruthenium complexes and around 400 nm for the rhenium complexes. While the oxidation potentials of ruthenium complexes **3a**, **3b**, **4a**, and **4b** are almost the same as that of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, reduction of the ruthenium and rhenium complexes occurs at more positive potentials than that of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ and $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$. Band maxima of the metal-to-ligand charge-transfer emission of the ruthenium and the rhenium complexes were observed at 620 and 610 nm, respectively. The results indicate that the LUMO levels of 2,2'-bipyridine and its metal complexes are lowered by electron-accepting effects of trimethylsilyl and pentamethyldisilanyl substituents, while the HOMO level of bpy is elevated by pentamethyldisilanyl substitution due to the effective σ - π conjugation between an Si-Si bonding orbital and a bpy π orbital. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium complexes; Rhenium complexes; Silyl substituted bipyridyl ligands

1. Introduction

2,2'-Bipyridine derivatives are the most widely used chelates for metal binding. Systematic variations of substituents have served as important tools for the understanding of physical properties of metal complexes [1]. Among metal bipyridine complexes research was focussed on ruthenium and to a lesser extent on rhenium complexes, because of their potential use in light harvesting systems and as photocatalysts [1]. Functionalization and linkage of bipyridine ligands were used to tune the photochemical properties of the complexes and to create supramolecular systems [2]. Recently we reported the optoelectronic properties of polymers bearing alternating silicon σ and 2,2'-bipyridyl π units in the backbone [3]. Ruthenium complexes of these polymers showed photoconductivity

upon excitation of the MLCT band. For more detailed understanding of these phenomena extensive investigations of well-defined mononuclear model compounds are necessary.

Very recently the synthesis of macrocyclic ligands bearing two 2,2'-bipyridine units interconnected at 4- and 4'-position by two $-(\text{CH}_2)\text{Si}(\text{CH}_3)_2(\text{CH}_2)-$ or $-(\text{CH}_2)_2\text{Si}(\text{C}_6\text{H}_5)_2(\text{CH}_2)_2-$ spacers was reported [4]. Due to the presence of fragile benzylic positions, a ruthenium complex could only be prepared with the latter ligand [4b]. However, neither simple silyl substituted bipyridines nor their metal complexes have been reported so far. We here present the synthesis and properties of 5,5'-bis(trimethylsilyl)- (**1a**) and 5,5'-bis(pentamethyldisilanyl)-2,2'-bipyridines (**1b**) as well as their ruthenium(II) and rhenium(I) complexes. The influence of silyl substitution on the spectroscopic and electrochemical properties of 2,2'-bipyridine and its metal complexes will be discussed.

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2. Results and discussion

2.1. Synthesis and properties of 5,5'-disilyl-2,2'-bipyridyls **1a** and **1b**

Our approach to silyl substituted 2,2'-bipyridines relies upon the nickel(0) coupling of 2-halopyridines [5–9], as shown in Scheme 1. Lithiation of 2,5-dibromopyridine at -90°C followed by treatment with trimethylchlorosilane and pentamethylchlorodisilane gave 2-bromo-5-trimethylsilyl- (**2a**) and 2-bromo-5-pentamethyldisilylpyridines (**2b**), respectively, with high regioselectivity in good yields [10]. Bromosilylpyridines **2a** and **2b** were coupled to the corresponding bipyridyl derivatives to give **1a** and **1b** in 35% and 55% yields, respectively. Bipyridines **1a** and **1b** show very good solubility in organic solvents like ether, toluene, and chloroform, but they hardly dissolve in solvents with higher polarity such as acetone, acetonitrile, and alcohols. These new ligands exhibited the expected NMR spectroscopic properties.

UV–vis spectral and electrochemical data of **1a** and **1b** are summarized in Table 1; the UV–vis spectra are shown in Fig. 1. Compared to parent 2,2'-bipyridine, both **1a** and **1b** exhibit more intense and red shifted $\pi-\pi^*$ absorption bands at around 300 nm. The major reason for the red shift of both **1a** and **1b** would be ascribed to lowering the LUMO energy level due to the electron-accepting effect of silyl substituents [11]. The more pronounced red-shift in the electronic spectrum of **1b** than that of **1a** is suggestive of the higher HOMO level of **1b** due to the effective hyperconjugation between the Si–Si σ orbital and the heteroaromatic π HOMO. The above explanation is supported by the electrochemical data in THF. Bipyridyl **1a** exhibits a

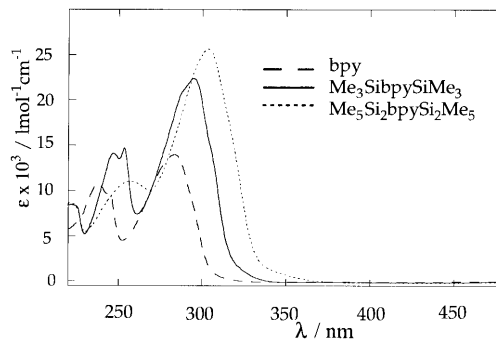
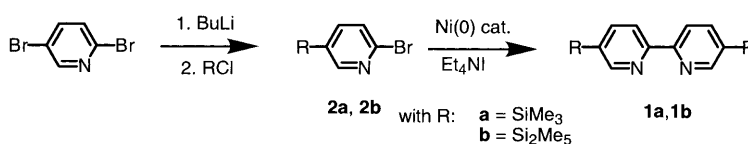


Fig. 1. UV–vis spectra of free bipyridines in CH_2Cl_2 .

reversible reduction wave, whereas the reduction of **1b** remains irreversible even at scan rates of 1 V s^{-1} . In both cases peak potentials were found to be shifted to more positive potentials compared to unsubstituted 2,2'-bipyridine. Facilitated electrochemical reduction indicates the lower LUMO energy levels of **1a** and **1b** in the same extent.

2.2. Synthesis of metal complexes with **1a** and **1b** as ligands

Two different types of ruthenium complexes with silyl-substituted bipyridyl ligands were synthesized; heteroleptic complexes $[\text{Ru}(\text{bpy})_2(\text{L})](\text{PF}_6)_2$ (**3a**, $\text{L} = \mathbf{1a}$; **3b**, $\text{L} = \mathbf{1b}$) and $[\text{RuL}_3](\text{PF}_6)_2$ (**4a**, $\text{L} = \mathbf{1a}$; **4b**, $\text{L} = \mathbf{1b}$). The ruthenium complexes were obtained as red brown solids by refluxing the appropriate metal precursors $[\text{Ru}(\text{bpy})_2\text{Cl}_2](\text{H}_2\text{O})_2$ [12] and $\text{Ru}(\text{dmsO})_4\text{Cl}_2$ [13] (dmsO = dimethylsulfoxide) in the presence of **1a** and **1b** and subsequent precipitation with hexafluorophos-



Scheme 1.

Table 1
Spectroscopic^a and electrochemical data^b of free bipyridines

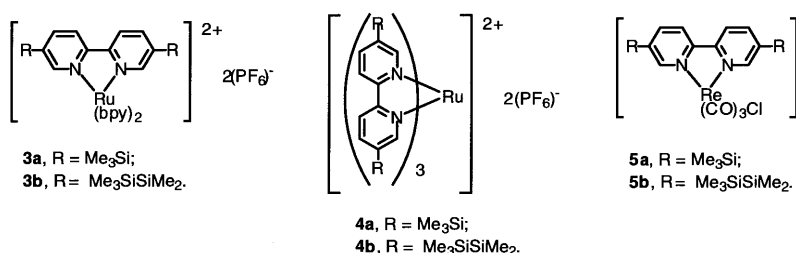
	Bpy	$\text{Me}_3\text{SibpySiMe}_3$ (1a)	$\text{Me}_3\text{Si}_2\text{bpySi}_2\text{Me}_5$ (1b)
λ_{max} (nm ^c) (ϵ ($1 \text{ mol}^{-1} \text{ cm}^{-1}$))	283 (14 000) 244 (9500) 237 (11 000)	294 (22 400) 253 (14 700) 246 (14 100)	303 (25 700) 256 (11 000)
E_{red}	–2.80	–2.63	–2.63 (pc)

^a In CH_2Cl_2 .

^b From cyclic voltammetry at 100 mV s^{-1} in $\text{THF}-\text{Bu}_4\text{NPF}_6$ (0.1 M). Potentials in V versus ferrocene/ferrocenium. (pc); cathodic peak potential for irreversible reduction.

^c ± 2 (nm).

phate salts. In the course of the experiments we realized that the disilanyl group of metal coordinated **1b** was very sensitive towards acidic conditions. In contrast to **4a**, precipitation of **4b** with NH_4PF_6 led to significant decomposition of the coordinated ligand probably by electrophilic desilylation of the heterocycle [14]. Due to the lower solubility of **1b** in polar solvents longer reaction times or higher temperatures were necessary for the synthesis of **3b** and **4b**. Rhenium complexes $\text{Re}(\text{L})(\text{CO})_3\text{Cl}$ (**5a**, $\text{L} = \mathbf{1a}$; **5b**, $\text{L} = \mathbf{1b}$) were prepared by refluxing $\text{Re}(\text{CO})_5\text{Cl}$ in toluene in the presence of the ligands [15]. Slow cooling of the reaction mixtures afforded yellow crystalline substances. All metal complexes of **1a** and **1b** have a greater solubility in organic solvents in comparison with the parent bipyridine compounds.



2.3. Spectroscopic studies of the metal complexes

$^1\text{H-NMR}$ spectra of complexes **4a** and **4b** revealed clear separation of the three aromatic proton resonances. Hydrogen atoms at 6- and 6'-positions of the silylated bipyridines exhibited the expected shift from 8.7 to 7.6 ppm upon ruthenium coordination. Coordination of a bidentate ligand like 2,2'-bipyridine to the six-coordinated ruthenium center gives rise to two enantiomeric forms, Λ and Δ [16]. Substitution of one bipyridine of $(\text{bpy})_3\text{Ru}^{2+}$ to **1a** or **1b** causes different chemical surroundings for the equatorial and axial pyridine rings of the remaining two unsubstituted

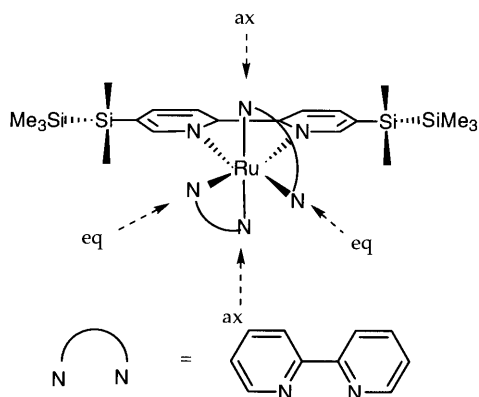


Fig. 2. Schematic representation of axial (ax) and equatorial (eq) pyridine rings as well as diastereotopic methyl groups in complex **3b**.

bipyridine ligands (Fig. 2). For this reason, $^1\text{H-}$ as well as $^{13}\text{C-NMR}$ spectra of **3a** and **3b** exhibited somewhat more complicated patterns. Moreover, resonances of the methyl protons of the dimethylsilyl unit in spectra of **3b** showed diastereotopic splitting due to the chirality of the metal center. All $^1\text{H-NMR}$ resonances for **3a** and **3b** could be assigned by comparing with the corresponding resonances for analogous homoleptic compounds.

The general effects of the Re complexation to **1a** and **1b** on the proton resonances are somewhat downfield shifts of singlets due to 6- and 6'-and 4- and 4'-protons, and up-field shift of 3- and 3'-protons [17]. The $^1\text{H-NMR}$ spectrum of **5b** also exhibited two signals for the nonequivalent methyl groups of the dimethylsilyl

group; one methyl group is *cis* and the other one *trans* to Cl atom.

The carbonyl stretching frequencies of the rhenium complexes are given in Table 2. Three intense $\nu(\text{CO})$ modes were observed confirming the facial structure of the complexes [15]. The band with the highest frequency is assigned to $\nu_{\text{sym}}(\text{CO})$ of the carbonyl group *cis* to the Cl atom [18]. Electron withdrawing substituents on the bipyridine ligand shift the frequency energy to higher values [17], indicating that the disilanyl substituent is more electron donating than trimethylsilyl and methyl groups.

In Table 3 UV–vis data for the metal complexes are summarized. For the ruthenium compounds two basic types of transitions were observed (Fig. 3). These are MLCT transitions in the regions of 250 and 450 nm, the latter causing the intense red color of the sub-

Table 2
Carbonyl stretching frequencies of Re complexes ^a

	ν (cm^{-1})	Reference
$\text{Re}(\mathbf{1a})(\text{CO})_3\text{Cl}$	2017; 1910; 1892	This work
$\text{Re}(\mathbf{1b})(\text{CO})_3\text{Cl}$	2010; 1916; 1871	This work
$\text{Re}(\text{MebpyMe})(\text{CO})_3$	2018; 1932; 1909; 1878	[17]

Cl ^b

^a KBr pellets.

^b MebpyMe = 4,4'-dimethyl-2,2'-bipyridine.

Table 3
Spectroscopic data of metal complexes^a

	Solvent	λ_{max} (nm) (ϵ (l mol ⁻¹ cm ⁻¹))
[Ru(bpy) ₃] ²⁺	CH ₃ CN	451 (13 000); 287 (70 500); 244 (23 000)
[Ru(bpy) ₂ (1a)] ²⁺	CH ₃ CN	461 (12 800); 288 (83 400); 246 (32 800)
[Ru(bpy) ₂ (1b)] ²⁺	CH ₃ CN	458 (12 100); 288 (72 600); 246 (28 100)
[Ru(1a) ₃] ²⁺	CH ₃ CN	481 (12 000); 294 (96 500); 252 (34 500)
[Ru(1b) ₃] ²⁺	CH ₃ CN	471 (11 000); 307 (76 500); 264 (34 500)
Re(bpy)(CO) ₃ Cl	CH ₂ Cl ₂	387 (2900); 294 (16 000); 239 (17 000)
Re(1a)(CO) ₃ Cl	CH ₂ Cl ₂	393 (2900); 324 (13 000, sh); 302 (20 500); 246 (18 000)
Re(1b)(CO) ₃ Cl	CH ₂ Cl ₂	388 (2900, sh); 327 (20 000); 257 (18 500)

^a All Ru complexes are hexafluorophosphate salts.

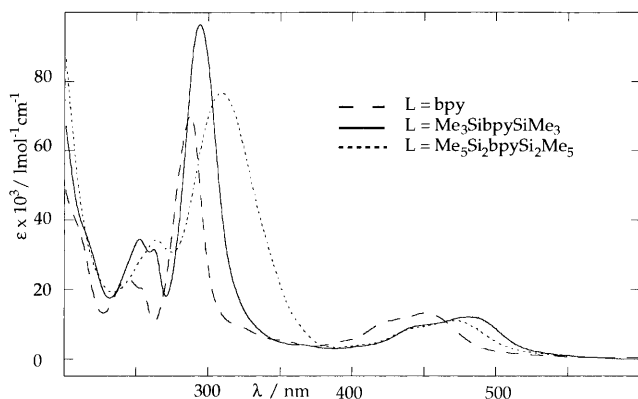


Fig. 3. UV-vis spectra of homoleptic ruthenium complexes [Ru(L)₃](PF₆)₂ in CH₃CN.

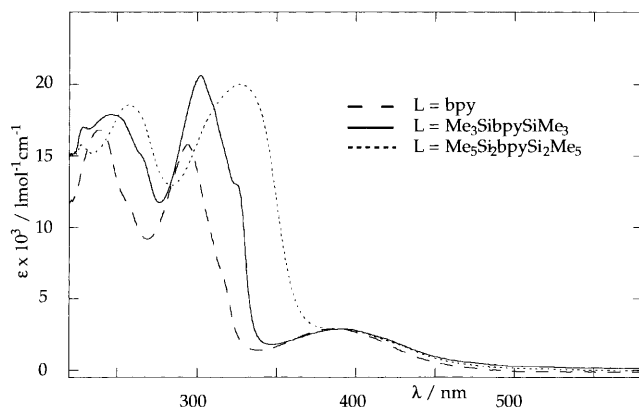


Fig. 4. UV-vis spectra of rhenium complexes Re(L)(CO)₃Cl in CH₂Cl₂.

Table 4
Electrochemical data^a of metal complexes^b

	Solvent	E_{ox}	E_{red}
[Ru(bpy) ₃] ²⁺	CH ₃ CN	0.90	-1.72; -1.92; -2.17
[Ru(bpy) ₂ (1a)] ²⁺	CH ₃ CN	0.92 (pa)	-1.68; -1.90; -2.16
[Ru(bpy) ₂ (1b)] ²⁺	CH ₃ CN	0.88	-1.70; -1.92; -2.16
[Ru(1a) ₃] ²⁺	CH ₃ CN	0.92 (pa)	-1.64; -1.88; -2.15
[Ru(1b) ₃] ²⁺	CH ₃ CN	0.93	-1.61; -1.83; -2.10
Re(bpy)(CO) ₃ Cl	DMA ^c		-1.77; -2.42 (pc)
Re(1a)(CO) ₃ Cl	DMA		-1.68; -2.32 (pc)
Re(1b)(CO) ₃ Cl	DMA		-1.69; -2.33 (pc)

^a From cyclic voltammetry at 100 mV s⁻¹ in a solution containing 0.1 M Bu₄NPF₆. Potentials in V versus ferrocene/ferrocenium. (pa): Anodic peak potential for irreversible oxidation. (pc): Cathodic peak potential for irreversible reduction.

^b Ru complexes: Hexafluorophosphate salts.

^c DMA: *N,N*-dimethylacetamide.

stances. Other intense bands at 300 nm are assigned as intra ligand π - π^* transitions [1]. The MLCT absorption maximum shifts to longer wavelengths with higher substitution by **1a** and **1b**; e.g. the absorption maximum of [Ru(bpy)₃](PF₆)₂ [2] at 452 nm shifts to 461 and 480 nm by replacement of one and three bipyridine ligands by **1a**, respectively. This behavior can be explained in terms of the electron withdrawing effect of the silyl substituents which lowers the LUMO energy of the electron-accepting bipyridine ligand [19]. The accepting ability of trimethylsilyl group is suggested to be slightly larger than that of pentamethyldisilanyl group by comparing the maxima between the Ru complexes with **1a** and **1b** as the ligands. The intra-ligand π - π^* transitions of the Ru complexes with **1a** and **1b** as ligands were found to be broadened and shifted to lower energies. Rhenium complexes **5a** and **5b** also exhibited the MLCT transitions at 400 and 320 nm and the intra-ligand π - π^* transitions at higher energy. The spectral changes of the Re complexes upon introducing the silyl groups on bipyridine ligand are similar to those found in the Ru complexes: a slightly red-shifted MLCT band and a broader π - π^* transition due to σ -donation of the silyl groups were observed (Fig. 4).

2.4. Electrochemistry of the metal complexes

Table 4 shows redox potentials of ruthenium complexes in acetonitrile and rhenium complexes in *N,N*-dimethylacetamide (DMA). Ruthenium complexes exhibit three well-resolved reduction waves. Each reduction process involves a 'spatially isolated' π^* ligand orbital in the Ru²⁺ field [1a]. Reduction of **4a** at -1.64 and of **4b** at -1.61 V compared to reduction of [Ru(bpy)₃](PF₆)₂ at -1.72 V is consistent with the lower energy π^* orbitals of **1a** and **1b** compared to bpy, as derived from the trends in the electronic spectra. It is interesting to note that among complexes

[Ru(bpy)₃](PF₆)₂, **3a**, and **3b** only the first reduction potential differs, whereas the second and the third reductions occurs at the same potential within the experimental error. This observation is rationalized by the first reduction occurring on the silyl substituted ligands **1a** and **1b** in **3a** and **3b**, respectively, while the second and third reduction on the unsubstituted bipyridines, supporting the ‘isolation’ of the π* ligand orbitals.

Since the oxidation potentials of the Ru complexes, which were assigned to oxidation of the ruthenium(II) center [1a], [19], did not change significantly, the silyl-substituents do not seem to affect the metal d orbital energy. While oxidation of **3a** and **4a** was reversible, the oxidation of the corresponding Ru complexes with **1b** was irreversible due to adsorption processes.

Oxidation of both **5a** and **5b** could not be achieved in DMA, but they exhibited one reversible reduction wave followed by an irreversible one. The first one was assigned to the reduction of the bipyridyl ligand and the second irreversible one was accompanied by chloride ion formation [20]. Again, reduction of **5a** and **5b** occurs at more positive potentials than that of Re(bpy)(CO)₃Cl; **5a** and **5b** at –1.68 and –1.69 V, respectively, while Re(bpy)(CO)₃Cl at –1.77 V.

2.5. Luminescence

Both ruthenium and rhenium complexes with bipyridyl ligands exhibit typical luminescence at around 600 nm originated from a MLCT excited state. The luminescence band maxima of the examined complexes are summarized in Table 5. Luminescence at room temperature was observed in acetonitrile for ruthenium complexes and in dichloromethane for rhenium compounds. Emission maxima of ruthenium complexes with

silyl-substituted bipyridyl ligands were found to be shifted around 10 nm to longer wavelengths than that of [Ru(bpy)₃](PF₆)₂; a similar silyl-substituent effect was observed for rhenium complexes, while the shift was smaller. At 77 K ruthenium emission maxima shifted to higher energy, confirming this transition as MLCT in character [1].

3. Concluding remarks

Very recently, metal complexes of polymers containing alternating 2,2'-bipyridine and carbon[21] or silicon[3] based spacers have been reported as systems with photo-conducting properties. Mechanistically, electrons will be injected into the polymer backbone through excitation of the MLCT transition of the [Ru(bpy)₂]²⁺ complexes of the polymers and then transported away through intra-chain migration. The efficiency of this process depends both on charge transportation and direction of the charge injection. Mabrouk and Wrighton have shown that electron releasing and withdrawing substituents on 2,2'-bipyridine have influenced on the localization of the excited electrons [22]. Generally, for mixed-ligand complexes, the excited electrons are localized on the more easily reduced ligand. Accordingly, the excited electrons will be localized on the unsubstituted bipyridyl ligands in the lowest excited state for [Ru(Me₂bpy)(bpy)₂]²⁺ (Me₂bpy = 4,4'-dimethylbipyridyl), but on the silyl-substituted bipyridyls for **4a** or **4b**. Considering [Ru(Me₂bpy)(bpy)₂]²⁺ as a model unit for a ruthenium containing polymer with a carbon spacer, the advantage of polymers with a silicon spacer becomes evident: electron transportation in the latter polymer should be more efficient, because the excited electron will be initially directed on the bipyridine which is part of the polymer backbone.

4. Experimental

4.1. General methods

Reactions were carried out under dry argon atmosphere using standard Schlenk techniques. Diethyl ether, THF, toluene, and hexane were freshly distilled from sodium. Bis(triphenylphosphine)nickel(II) bromide [23], bis(2,2'-bipyridine)ruthenium(II) chloride [12], and tetrakis(dimethylsulfoxide)ruthenium(II) chloride [13] were prepared according to the methods in literature. Other chemicals were commercially available and used as received.

¹H- (300 MHz), ¹³C- (75.4 MHz), and ²⁹Si- (59.6 MHz) NMR spectra were measured on a Bruker AC300P NMR spectrometer. ¹H- and ¹³C-NMR chemical shifts are referenced to residual solvent peaks. ²⁹Si-NMR chemical shifts are relative to Me₄Si. Electronic

Table 5
Luminescence^a of metal complexes^b

Complex	Solvent	T (K)	λ _{max} (em) (nm)
[Ru(bpy) ₃] ²⁺	CH ₃ CN	293	610
	EtOH–MeOH ^c	77	580
[Ru(bpy) ₂ (1a)] ²⁺	CH ₃ CN	293	621
	EtOH–MeOH	77	588
[Ru(bpy) ₂ (1b)] ²⁺	CH ₃ CN	293	617
	EtOH–MeOH	77	584
[Ru(1a) ₃] ²⁺	CH ₃ CN	293	623
	EtOH–MeOH	77	596
[Ru(1b) ₃] ²⁺	CH ₃ CN	293	622
	EtOH–MeOH	77	595
Re(bpy)(CO) ₃ Cl	DMA ^d	293	607
Re(1a)(CO) ₃ Cl	DMA	293	615
Re(1b)(CO) ₃ Cl	DMA	293	612

^a After irradiation of the MLCT band.

^b All Ru complexes are hexafluorophosphate salts.

^c A 4:1 mixture.

^d DMA: *N,N*-dimethylacetamide.

spectra were recorded on a Milton Roy SP-3000 spectrometer. Fluorescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer. Infrared spectra were recorded on a Shimadzu FTIR-8600PC spectrometer. Cyclic voltammetric experiments were performed with a HA-501 potentiostat and an HB-104 function generator from Hokuto Denko in dry acetonitrile or *N,N*-dimethylacetamide containing 0.1 M Bu₄NPF₆ using a three-electrode configuration (glassy-carbon electrode, Pt counter electrode, Ag/AgCl reference). The ferrocene/ferrocenium couple served as internal reference.

4.2. 2-Bromo-5-trimethylsilylpyridine (**2a**) and 2-bromo-5-pentamethyldisilanylpyridine (**2b**)

A hexane solution of *n*-butyllithium (1.6 M, 34.0 ml) was added slowly to a solution of 2,5-dibromopyridine (13.0 g, 54.9 mmol) in diethyl ether (150 ml) at -90°C . After stirring for 1 h at -90°C , trimethylchlorosilane (5.96 g, 54.9 mmol) in ether (10 ml) were added via a cannula. Stirring was continued for another hour, then the solution was allowed to warm up to 0°C followed by hydrolysis with water (100 ml) and then separated. The aqueous layer was extracted with diethyl ether (four times, 40 ml) and the solvent of the combined organic layer was removed under reduced pressure. Final kugelrohr distillation (115°C , 10 mm Hg) gave **2a** (11.5 g, 91%) as a colorless liquid. ¹H-NMR (CDCl₃) δ 0.23 (s, 9 H, Si(CH₃)₃); 7.38 (d, 1 H, ³J = 7.7 Hz, 3-H); 7.56 (dd, 1 H, ³J = 7.9 Hz, ⁴J = 2.1 Hz, 4-H); 8.34 (d, 1 H, ⁴J = 1.9 Hz, 6-H); ¹³C-NMR (CDCl₃) δ -1.5 (Si(CH₃)₃), 127.5, 134.0, 143.2, 143.2, 154.1. ²⁹Si-NMR (CDCl₃) δ -3.4. *Anal.* Calc. for C₈H₁₂BrNSi: C, 41.74; H, 5.25; N 6.09. Found: C, 42.11; H, 5.27; N, 6.16%.

Compound **2b** was prepared by the same procedure: colorless liquid. B.p. 130°C (4 mm Hg); yield, 61%. ¹H-NMR (CDCl₃) δ 0.06 (s, 9 H, Si(CH₃)₃), 0.34 (s, 6 H, Si(CH₃)₂), 7.43 (d, 1 H, ³J = 7.8 Hz, 3-H), 7.54 (dd, 1 H, ³J = 7.8 Hz, ⁴J = 2.1 Hz, 4-H), 8.33 (d, 1 H, ⁴J = 1.9 Hz, 6-H). ¹³C-NMR (CDCl₃) δ -4.3, -2.5, 127.6, 133.9, 142.9, 143.6, 154.4. ²⁹Si-NMR (CDCl₃) δ -21.8, -19.2.

4.3. 5,5'-Di-(trimethylsilyl)-2,2'-bipyridine (**1a**) and 5,5'-di-(pentamethyldisilanyl)-2,2'-bipyridine (**1b**)

Bis(triphenylphosphine)nickel(II) bromide (3.10 g, 4.15 mmol), freshly activated zinc (6.00 g, 91.8 mmol), and tetraethylammonium iodide (3.00 g, 1.17 mmol) were placed in a 100 ml two-necked flask equipped with a condenser and dried under vacuum at 70°C for 2 h. THF (5 ml) was injected by a syringe, and the brown slurry was stirred for 30 min at 50°C . After adding a solution of **2a** (9.55 g, 41.5 mmol) in THF (15 ml) and refluxing for 3 h, the mixture was poured into diluted

aqueous ammonia. Separation of organic layer, extraction of the aqueous layer with diethyl ether, removal of the solvent from the combined organic layer under reduced pressure, and recrystallization from methanol gave **1a** (1.59 g, 25%). ¹H-NMR (CDCl₃) δ 0.31 (s, 18 H, Si(CH₃)₃), 7.90 (dd, 2 H, ³J = 8.0 Hz, ⁴J = 2.0 Hz, 4,4'-H), 8.33 (d, 2H, ³J = 7.5 Hz, 3,3'-H), 8.74 (d, 2 H, ⁴J = 1.3 Hz, 6,6'-H). ¹³C-NMR (CDCl₃) δ -1.0 (Si(CH₃)₃), 120.5, 135.6, 142.4, 153.7, 156.6. ²⁹Si-NMR (CDCl₃) δ -3.81. *Anal.* Calc. for C₁₆H₂₄N₂Si₂: C, 63.94; H, 8.05; N, 9.32. Found: C, 63.86; H, 7.88; N, 9.31%.

Compound **1b** was prepared by the same procedure: colorless crystals: m.p. 142°C ; 52% yield. ¹H-NMR (CDCl₃) δ 0.06 (s, 18 H, Si(CH₃)₃), 0.37 (s, 12 H, Si(CH₃)₂), 7.83 (dd, 2H, ³J = 7.8, ⁴J = 1.7 Hz, 4,4'-H), 8.31 (dd, 2 H, ³J = 7.7, ⁵J = 1.0 Hz, 3,3'-H), 8.67 (m, 2 H, 6,6'-H). ¹³C-NMR (CDCl₃) δ -4.1, -2.1, 120.5, 135.3, 142.7, 153.9, 156.2. ²⁹Si-NMR (CDCl₃) δ -22.1, -19.0. *Anal.* Calc. for C₂₀H₃₆N₂Si₄: C, 57.63; H, 8.70; N, 6.72. Found: C, 57.17; H, 8.57; N, 6.75%.

4.4. Bis(2,2'-bipyridine)(5,5'-trimethylsilyl-2,2'-bipyridine)ruthenium(II) hexafluorophosphate (**3a**)

A mixture of **1a** (114 mg, 0.37 mmol) and Ru(bpy)₂Cl₂ (157 mg, 0.30 mmol) were refluxed for 12 h in ethanol (40 ml). Addition of a solution of NH₄PF₆ (2.0 g) in water (10 ml), evaporation of ethanol and addition of water lead to precipitation of red **3a** (250 mg, 83%). ¹H-NMR (CD₃CN) δ 0.09 (s, 18 H, Si(CH₃)₃), 7.39 (dq, 4 H, ³J = 7.3 Hz, ⁴J = 1.1 Hz, bpy-5,5'-H), 7.50 (s, 2 H, Sibpy-6,6'-H), 7.74 (d, 2 H, ³J = 5.4 Hz, bpy-6-H), 7.81 (d, 2 H, ³J = 5.5 Hz, bpy-6'-H), 8.07 (dq, 4 H, ³J = 7.9 Hz, ⁴J = 1.2 Hz, bpy-4,4'-H), 8.12 (dd, 2 H, ³J = 8.0 Hz, ⁴J = 1.3 Hz, Sibpy-4,4'-H), 8.42 (d, 2 H, 8.0 Hz, Sibpy-3,3'-H), 8.51 (t, 4 H, ³J = 7.6 Hz, bpy-3,3'-H). ¹³C-NMR (CD₃CN) δ -3.3 (Si(CH₃)₃), 122.9, 123.8, 124.0, 127.1, 127.3, 137.4, 137.5, 140.7, 142.2, 151.5, 151.7, 153.7, 156.6, 156.8, 156.9. ²⁹Si-NMR (CD₃CN) δ -2.3. *Anal.* Calc. for C₃₆H₄₀F₁₂N₆P₂RuSi₂: C, 43.07; H, 4.02; N, 8.37. Found: C, 43.51; H, 4.24; N, 8.37%.

4.5. Bis(2,2'-bipyridine)(5,5'-pentamethyldisilanyl-2,2'-bipyridine)ruthenium(II) hexafluorophosphate (**3b**)

Ru(bpy)₂Cl₂ (60.5 mg, 0.116 mmol), **1b** (48.5 mg, 0.116 mmol), and ethanol (10 ml) were placed in a small flask and refluxed for 24 h. The product was precipitated by addition of saturated aqueous KPF₆ (10 ml) and water (10 ml). Filtration, washing with water, and drying in vacuum gave **3b** (74 mg, 57%) as a red powder. ¹H-NMR (CD₃CN) δ -0.17 (s, 18 H, Si(CH₃)₃), 0.13 (s, 6 H, Si(CH₃)), 0.16 (s, 6 H, Si(CH₃)),

7.38–7.44 (m, 6 H, bpy – 5,5'-H, Sibpy-6,6'-H), 7.74 (d, 2 H, $^3J = 5.4$ Hz, bpy-6-H), 7.81 (d, 2 H, $^3J = 5.5$ Hz, bpy-6-H'), 8.02–8.11 (m, 6 H, bpy, Sibpy-4,4'-H), 8.40 (d, 2 H, $^3J = 8.0$ Hz, Sibpy-3,3'-H), 8.51 (t, 4 H, $^3J = 8.0$ Hz, bpy-3,3'-H). $^{13}\text{C-NMR}$ (CD_3CN) δ – 6.29 (br, $\text{Si}(\text{CH}_3)_2$), – 3.80 ($\text{Si}(\text{CH}_3)_3$), 122.94 (Sibpy), 123.92 (bpy), 124.06 (bpy'), 127.32 (bpy), 127.37 (bpy'), 137.54 (bpy), 137.67 (bpy'), 140.96 (Sibpy), 142.29 (Sibpy), 151.37 (bpy), 151.70 (bpy'), 153.54 (Sibpy), 156.34 (bpy), 156.47 (bpy'), 156.77 (Sibpy). $^{29}\text{Si-NMR}$ (CD_3CN) δ – 20.1, – 18.5. *Anal. Calc.* for $\text{C}_{40}\text{H}_{52}\text{F}_{12}\text{N}_6\text{P}_2\text{RuSi}_2(\text{H}_2\text{O})$: C, 42.21; H, 4.78; N, 7.38. Found: C, 41.70; H, 4.74; N, 7.33%.

4.6. Tris(5,5'-trimethylsilyl)-2,2'-bipyridine)ruthenium(II) hexafluorophosphate (**4a**)

A mixture of $\text{Ru}(\text{dmsO})_4\text{Cl}_2$ (60 mg, 0.12 mmol) and **1a** (112 mg, 0.37 mmol) in ethanol (20 ml) were refluxed for 15 h. Slow addition of a solution of NH_4PF_6 (2.0 g) in water (10 ml) and then water (5 ml) gave red microcrystalline **4a** (75 mg, 47%). $^1\text{H-NMR}$ (CD_3CN) δ 0.12 (s, 54 H, $\text{Si}(\text{CH}_3)_3$), 7.58 (s, 6 H, bpy-6,6'-H), 8.20 (dd, 6 H, $^3J = 8.0$, $^4J = 1.4$ Hz, bpy-4,4'-H), 8.48 (d, 6 H, $^3J = 7.8$ Hz, bpy-3,3'-H). $^{13}\text{C-NMR}$ (CD_3CN) δ – 3.1 ($\text{Si}(\text{CH}_3)_3$), 123.5, 140.7, 142.2, 153.2, 157.3. $^{29}\text{Si-NMR}$ (CD_3CN) δ – 2.2. *Anal. Calc.* for $\text{C}_{60}\text{H}_{108}\text{F}_{12}\text{N}_6\text{P}_2\text{RuSi}_{12}$: C, 43.90; H, 6.63; N, 5.12. Found: C, 43.70; H, 6.69; N, 5.01%.

4.7. Tris(5,5'-pentamethyldisilanyl)-2,2'-bipyridine)ruthenium(II) hexafluorophosphate (**4b**)

A mixture of $\text{Ru}(\text{dmsO})_4\text{Cl}_2$ (39.0 mg, 0.08 mmol) and **1b** (100.0 mg, 0.24 mmol) in glycol (5 ml) was stirred for 6 h at 140°C. To remove unreacted ligand, water (10 ml) was added and the brown solution was allowed to stand overnight. After centrifugation the product was precipitated by addition of a saturated aqueous KPF_6 . Filtration and washing with water gave **4b** (85 mg, 65%). $^1\text{H-NMR}$ (CD_3CN) δ – 0.22 (s, 54 H, $\text{Si}(\text{CH}_3)_3$), 0.07 (s, 18 H, $\text{Si}(\text{CH}_3)$), 0.23 (s, 18 H, $\text{Si}(\text{CH}_3)$), 7.57 (s, 1 H, bpy-6,6'-H), 8.11 (dd, 6 H, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, bpy-4,4'-H), 8.49 (d, 6 H, $^3J = 7.8$ Hz, bpy-3,3'-H). $^{13}\text{C-NMR}$ (CD_3CN) δ – 6.3 ($\text{Si}(\text{CH}_3)$), – 5.6 ($\text{Si}(\text{CH}_3)$), – 3.1 ($\text{Si}(\text{CH}_3)_3$), 123.2, 141.7, 142.8, 153.6, 156.1. $^{29}\text{Si-NMR}$ (CD_3CN) δ – 19.9, – 18.5.

4.8. (5,5'-Trimethylsilyl)-2,2'-bipyridine)rhenium(I)-tricarbonyl chloride (**5a**) and (5,5'-pentamethyldisilanyl)-2,2'-bipyridine)rhenium(I)tricarbonyl chloride (**5b**)

A mixture of $\text{Re}(\text{CO})_5\text{Cl}$ (36.2 mg, 0.10 mmol) and **2a** (30.0 mg, 0.10 mmol) in toluene (10 ml) was refluxed for 30 min. After slow cooling and standing at ambient

temperature rhombic yellow crystals were formed. Filtration and washing with hexane gave **5a** (30 mg, 50%). $^1\text{H-NMR}$ (CDCl_3) δ 0.38 (s, 18 H, $\text{Si}(\text{CH}_3)_3$), 8.10 (m, 4 H, bpy-3,3',4,4'-H), 8.99 (s, 2 H, bpy-6,6'-H). $^{13}\text{C-NMR}$ (CDCl_3) δ – 1.28 ($\text{Si}(\text{CH}_3)_3$), 122.32, 141.49, 144.17, 155.97, 156.71, 197.68 (CO). $^{29}\text{Si-NMR}$ (CDCl_3) δ – 1.99. *Anal. Calc.* for $\text{C}_{19}\text{H}_{24}\text{ClN}_2\text{O}_3\text{ReSi}_2$: C, 37.64; H, 3.99; N, 4.62. Found: C, 37.35; H, 4.10; N, 4.62%. **5b** was prepared by the same procedure: yellow powder; 36% yield; $^1\text{H-NMR}$ (CDCl_3) δ 0.12 (s, 18 H, $\text{Si}(\text{CH}_3)_3$), 0.42 (s, 6 H, $\text{Si}(\text{CH}_3)(\text{CH}_3')$), 0.43 (s, 6 H, $\text{Si}(\text{CH}_3)(\text{CH}_3')$), 8.00 (dd, 2 H, $^3J = 7.9$ Hz, $^4J = 1.3$ Hz, bpy-4,4'-H), 8.08 (d, 2 H, $^3J = 7.9$ Hz, bpy-3,3'-H), 8.94 (s, 2 H, bpy-6,6'-H). $^{13}\text{C-NMR}$ (CDCl_3) δ – 4.25 ($\text{Si}(\text{CH}_3)(\text{CH}_3')$), – 4.11 ($\text{Si}(\text{CH}_3)(\text{CH}_3')$), – 2.11 ($\text{Si}(\text{CH}_3)_3$), 122.14, 141.58, 144.10, 155.59, 156.94, 197.75 (CO). $^{29}\text{Si-NMR}$ (CDCl_3) δ – 20.09, – 18.59. *Anal. Calc.* for $\text{C}_{23}\text{H}_{36}\text{ClN}_2\text{O}_3\text{ReSi}_4$: C, 38.23; H, 5.02; N, 3.88. Found: C, 38.73; H, 5.15; N, 3.79%.

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