# Terpyridines Functionalised with Ferrocenyl Groups of Different Redox Potential

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2,2′:6′,2′′-Terpyridines bearing a substituent X in the 4′-position [**3a**: X = Fc–C≡C–*p*-$C_6H_4$; **3b**: X = Fc$^{\#}$–C≡C–*p*-$C_6H_4$; Fc = $(C_5H_5)Fe(C_5H_4)$, Fc$^{\#}$ = $(C_5Me_4H)Fe(C_5Me_4)$] were prepared by Pd$^0$-catalysed cross-coupling reactions. **3b** was characterised by X-ray structure analysis. [(**3a**)$RuCl_2$(DMSO)] (**4a**) and [(**3b**)$RuCl_2$(DMSO)] (**4b**) were obtained by reaction of [$RuCl_2(DMSO)_4$] with 1 equivalent of **3a** and **3b**, respectively, while the analogous reaction with 2 equivalents afforded [(**3a**)$_2$Ru][$PF_6$]$_2$ (**5a**) and [(**3b**)$_2$Ru][$PF_6$]$_2$ (**5b**), respectively, after precipitation with aqueous [$NH_4$][$PF_6$]. Similarly, [(**3a**)Ru(tpy)][$PF_6$]$_2$ (**6**) was isolated from the reaction of **4a** with 2,2′:6′,2′′-terpyridine (tpy). Compounds **3** and **5** were investigated by cyclic voltammetry, which revealed that the introduction of eight methyl groups leads to the expected cathodic shift of the $E^{0\prime}$ values of ca. 0.44 V for the ferrocenyl-centered redox processes.

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(Oligopyridine)Ru$^{II}$ complexes exhibit unique photophysical as well as photo- and redox-chemical properties.[2] They have frequently been found to be excellent photosensitisers. Among the oligopyridine ligands 2,2′:6′,2′′-terpyridines bearing redox-active groups in the 4′-position are currently attracting much attention, since they can be used for the construction of geometrically well-defined metal complexes, which show fascinating properties based on intramolecular electron- and energy-transfer processes. For example, Ru$^{II}$ complexes of such terpyridines have been utilised for the construction of donor/sensitiser dyads and donor/sensitiser/acceptor triads.[2a−g] These and related assemblies allow the investigation of photoinduced vectorial charge separation over large distances, which is, inter alia, of fundamental importance for solar light energy conversion.[3]

Owing to their well-behaved redox chemistry[4] as well as their chemical robustness and synthetic versatility, ferrocenyl units are very attractive donor groups in such assemblies, and several ferrocenyl-functionalised terpyridines have been synthesised for this reason.[5] However, it has turned out that ferrocenes, their (redox-)chemical advantages notwithstanding, show a serious disadvantage. [$(C_5H_5)_2Fe$] quenches photoexcited (oligopyridine)Ru$^{II}$ complexes not only reductively, but also by triplet energy transfer.[6] The triplet energy of ferrocene has been estimated to be ca. 1.8 eV,[7] which is below the typical excited-state energy of (oligopyridine)ruthenium complexes.[2h−j] Consequently, both energy transfer and reductive quenching are thermodynamically favourable in this system. This finding has caused strong reservations as to whether ferrocenyl units can be used as donor groups in relevant assemblies, since for photoinduced charge-separation processes energy transfer is undesirable.[2g]

Undoubtedly, ferrocenyl groups could very well be utilised advantageously in this context, if it proved possible to shift the competition between energy transfer and reductive quenching in favour of the latter by judicious choice of molecular parameters. Comparative studies using ferrocene and various oligomethylferrocenes as quenchers indicate that reductive quenching can be favoured by increasing its thermodynamic driving force (i.e. by increasing the reducing power of the donor).[6][8] There is a linear relationship between the number of methyl groups and the redox potential of a ferrocene, each methyl group causing a cathodic shift of ca. 55 mV,[4][9] while leaving the triplet energy essentially unaffected.[6] However, systematic investigations of the general factors influencing the competition between energy transfer and reductive quenching in oligonuclear complexes, although of fundamental interest, have not been performed so far.[10] For such an investigation two points are of vital importance. Firstly, it is necessary to study geometrically well-defined compounds, since otherwise meaningful results, which can be compared with the predictions of current theories of electron and energy transfer,[11] cannot be obtained. Secondly, in order to obtain unequivocal results it is essential to be able to single out the effect of the variation of a single molecular parameter.

For this reason we have prepared derivatives of 2,2′:6′,2′′-terpyridine (tpy) with ferrocenyl (Fc) and octamethylferrocenyl (Fc$^{\#}$) groups attached to the 4′-position by means of a *para*-phenylene and an acetylene spacer unit.[12] In this communication we report on the synthesis of these compounds and present first results from their coordination chemistry as well as preliminary electrochemical investigations.

Sonogashira-type cross-coupling[13] of 4′-(4-bromophenyl)-2,2′:6′,2′′-terpyridine (**1**)[14] with FcC≡CH (**2a**)[15] and

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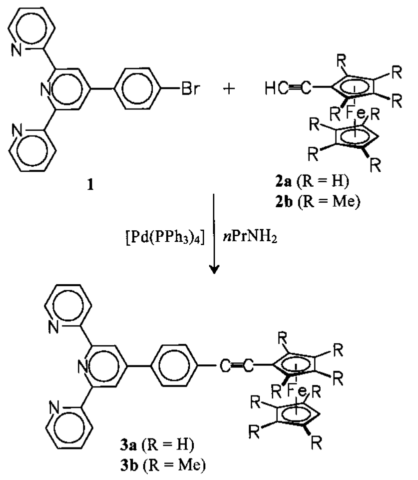


Scheme 1

Fc#C≡CH (**2b**)[16] in *n*-propylamine in the presence of [Pd(PPh$_3$)$_4$][17] as catalyst[18] afforded the redox-functionalised terpyridines **3a** and **3b**, respectively (Scheme 1).

A single-crystal X-ray structure analysis was performed for **3b**. A view of the molecule is shown in Figure 1.

The cyclopentadienyl rings are arranged in an eclipsed orientation and exhibit an average Fe−C bond length of 206 pm, which is nearly identical to the value observed for decamethylferrocene (205 pm).[19] The acetylene group is almost linear [C(14)−C(19)−C(20) 177.5(3)°, C(19)−C(20)−C(21) 176.6(3)°] and has a C−C distance of 119.3(4) pm; the distance between each acetylene carbon atom and the sp$^2$-hybridised carbon atom attached to it is 143.1(4) [C(14)−C(19)] and 144.0(4) pm [C(20)−C(21)]. These values are unexceptional and compare well with those of other structurally characterised (phenylethynyl)ferrocenes.[20] The dihedral angle between the best planes of the C$_6$ ring and the central C$_5$N ring of the terpyridyl unit is 26.9° and that between the cyclopentadienyl ring containing the atoms C(10)−C(14) and the C$_6$ ring has a value of 29.1°. The three C$_5$N rings are almost coplanar (dihedral angles 3.3 and 7.0°) and exhibit transoid configurations about the interannular C−C bonds as is commonly observed for such compounds.[21]

We have started to develop the coordination chemistry of the new redox-functionalised terpyridines by using established methods.[18b] For example, the mono(terpyridine)ruthenium(II) complexes [(**3a**)RuCl$_2$(DMSO)] (**4a**) and [(**3b**)RuCl$_2$(DMSO)] (**4b**) were prepared by treating one equivalent of **3a** and **3b**, respectively, with [RuCl$_2$(DMSO)$_4$][22] in refluxing ethanol (Scheme 2).

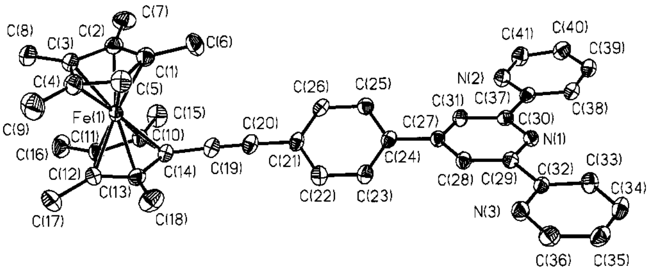
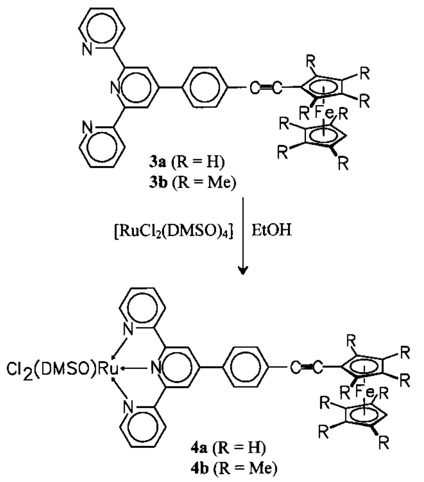
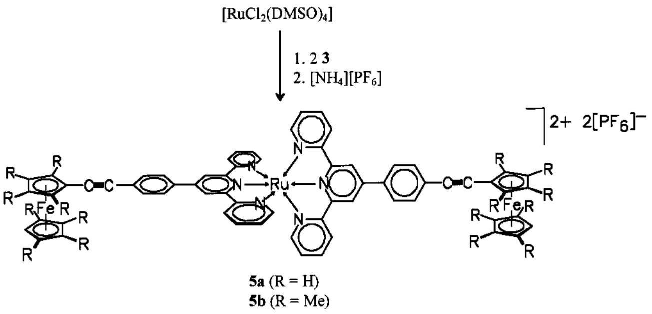


Figure 1. Molecular structure of **3b** in the crystal; selected bond lengths [pm] not discussed in the text: C(24)−C(27) 148.7(4), C(29)−C(32) 149.5(4), C(30)−C(37) 149.4(4).



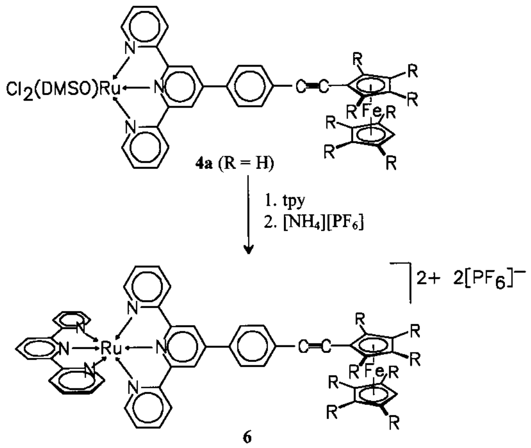
Scheme 2

Reaction of two equivalents of **3a** and **3b** with [RuCl$_2$(DMSO)$_4$] in refluxing ethanol afforded the homoleptic Ru$^{II}$ complexes [(**3a**)$_2$Ru][PF$_6$]$_2$ (**5a**) and [(**3b**)$_2$Ru][PF$_6$]$_2$ (**5b**), respectively, after precipitation with aqueous ammonium hexafluorophosphate (Scheme 3).



Scheme 3

It has also proved possible to synthesise a heteroleptic bis(terpyridine)ruthenium(II) complex, namely [(**3a**)Ru(tpy)][PF$_6$]$_2$ (**6**), which was obtained by treating **4a** with one



Scheme 4

equivalent of tpy in refluxing ethanol and subsequent precipitation with aqueous ammonium hexafluorophosphate (Scheme 4).[23]

Preliminary electrochemical investigations of the terpyridine ligands **3a** and **3b** and their $Ru^{II}$ complexes **5a** and **5b** by cyclic voltammetry demonstrate that the redox potential of the ferrocenyl moieties present in the terpyridines is not affected by complexation (Table 1). Furthermore, it is evident that the introduction of eight methyl groups in the novel redox-functionalised terpyridines and their $Ru^{II}$ complexes leads to a cathodic shift of the $E^{0\prime}$ values of ca. 0.44 V for the ferrocenyl-centered redox processes. This is exactly the value expected for the influence of eight methyl groups (i.e. $8 \times 55$ mV, vide supra) and shows that in the present system oligomethylferrocenyl groups behave as reliable donors with predictable and precisely adjustable redox potentials.

Table 1. Formal electrode potentials (in V, vs. SCE) for the ferrocenyl-centered oxidation process of compounds **3** and **5** in dichloromethane solution[a]

| Compound | **3a** | **3b** | **5a**[b] | **5b**[b] |
|---|---|---|---|---|
| $E^{0\prime}{}_{0/+}$ | 0.50 | 0.06 | 0.49 | 0.06 |

[a] Conditions: 298 K; $[NBu_4][PF_6]$ supporting electrolyte (0.2 M); scan rate 0.10 V; confidence limit 0.01 V. − [b] $E^{0\prime}$ values [V] for the oxidation/reductions of the central Ru complex moiety: 1.23/ −1.22, −1.52.

In summary, we have prepared novel terpyridines functionalised with ferrocenyl and octamethylferrocenyl groups. First results indicate that both symmetrical and unsymmetrical bis(terpyridine)ruthenium complexes are accessible by established routes, which augurs well for the development of a rich coordination chemistry of these redox-functionalised ligands. Cyclic voltammetry has revealed that the ferrocenyl moieties in the new ligands and their complexes are redox-chemically well behaved. We are currently extending our studies to analogous terpyridines containing only $(C{\equiv}C)_n$ ($n = 1, 2$) spacer groups.[24] These and related oligomethylferrocenyl-functionalised ligands should be excellently suited for the preparation of libraries of donor/sensitiser assemblies, which for the first time will allow the detailed investigation of the competition between energy transfer and reductive quenching in a geometrically well-defined system by systematic variation of a single molecular parameter, namely the redox potential of the donor. We will report on such studies in due course.

## Experimental Section

**General:** All manipulations were performed in an inert atmosphere (purified argon or dinitrogen) by using standard Schlenk and cannula techniques or a conventional glovebox. − Solvents and reagents were appropriately dried and purified by using standard procedures. − NMR spectra were recorded at 300 K with a Bruker DRX 500 spectrometer operating at 500.13 MHz for $^1H$; TMS was used as external reference. − UV/Vis spectra were recorded with a Uvikon 860 spectrophotometer (Kontron Instruments). − Fast atom bombardment (FAB) mass spectra were obtained by the LSIMS ionisation technique (3-nitrobenzyl alcohol matrix) with a VG Autospec instrument. − Materials and apparatus used for the electrochemical investigations have been described elsewhere.[25] − Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld.

**Terpyridine 3a:** A solution of 4′-(4-bromophenyl)-2,2′:6′,2′′-terpyridine (**1**) (1.25 g, 3.22 mmol), ethynylferrocene (**2a**) (680 mg, 3.24 mmol), and $[Pd(PPh_3)_4]$ (230 mg, 0.199 mmol) in *n*-propylamine (50 mL) placed in a thick-walled Rotaflo ampoule was stirred for 14 h at 55 °C. The solution was allowed to cool to room temp. The product was filtered off, washed with diethyl ether, and dried in vacuo. A second crop was obtained by reducing the volume of the filtrate. Brownish-orange microcrystalline solid, m.p. 231 °C; yield 1.40 g (84%). − $^1H$ NMR ($CDCl_3$): $\delta = 4.25$ (s, 2 H, $C_5H_4$), 4.26 (s, 5 H, $C_5H_5$), 4.52 (s, 2 H, $C_5H_4$), 7.33 (m, 2 H, 5,5′′-H), 7.60 ("d", apparent $J = 8.1$ Hz, 2 H, $C_6H_4$), 7.84−7.87 (m, 4 H, $C_6H_4$ and 4,4′′-H), 8.65 (d, $J = 7.9$ Hz, 3,3′′-H), 8.71−8.73 (m, 4 H, 6,3′,5′,6′′-H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 65.0$, 68.9, 70.0, 71.5 (Fc); 85.5, 90.1 ($C{\equiv}C$); 118.6, 121.4, 123.9, 124.8, 127.2, 131.9, 136.9, 137.4, 149.1, 149.5, 156.0, 156.2 (aryl rings). − FAB MS; *m/z*: 518 $[M + H]^+$, 517 $[M^+]$. − $C_{33}H_{23}FeN_3$ (517.41): C 76.61, H 4.48, N 8.12; found C 76.43, H 4.81, N 8.57.

**Terpyridine 3b:** By a procedure analogous to that described for **3a** 1.26 g (76%) of **3b** was obtained from **1** (1.03 g, 2.64 mmol), ethynyloctamethylferrocene (**2b**) (850 mg, 2.64 mmol), and $[Pd(PPh_3)_4]$ (183 mg, 0.158 mmol) in *n*-propylamine (40 mL) as orange platelets, m.p. 221 °C. − $^1H$ NMR ($CDCl_3$): $\delta = 1.69$, 1.74, 1.78, 1.91 (4 s, $4 \times 6$ H, Me); 3.37 (s, 1 H, $C_5Me_4H$); 7.34 (m, 2 H, 5,5′′-H); 7.60 ("d", apparent $J = 8.1$ Hz, 2 H, $C_6H_4$); 7.86−7.88 (m, 4 H, $C_6H_4$ and 4,4′′-H); 8.66 (d, $J = 7.9$ Hz, 3,3′′-H), 8.73 (d, $J = 5.2$ Hz, 2 H, 6,6′′-H); 8.74 (s, 2 H, 3′,5′-H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 8.9$, 10.0, 10.6, 10.8 (Me); 71.8, 81.2, 81.3, 81.4, 82.4 ($C_5$-$Fc^{\#}$); 89.0, 90.5 ($C{\equiv}C$); 118.6, 121.4, 123.8, 125.8, 127.2, 131.5, 136.9, 149.1, 149.7, 156.0, 156.2 (aryl rings). − FAB MS; *m/z*: 630 $[M + H]^+$, 629 $[M^+]$. − $C_{41}H_{39}FeN_3$ (629.63): C 78.21, H 6.24, N 6.67; found C 77.88, H 6.49, N 6.76.

**Complex 4a:** A stirred mixture of **3a** (125 mg, 0.242 mmol) and $[RuCl_2(DMSO)_4]$ (117 mg, 0.240 mmol) in ethanol (10 mL) was refluxed for 15 h and subsequently allowed to cool to room temp. The product was filtered off, washed with ethanol, and dried in vacuo. Light-violet platelets; yield 132 mg (71%). − $^1H$ NMR ($[D_6]DMSO$): $\delta = 3.61$ (s, 6 H, $Me_2SO$); 4.31 (s, 5 H, $C_5H_5$); 4.39, 4.67 (2 s, $2 \times 2$ H, $C_5H_4$); 7.53 (m, 2 H, 5,5′′-H); 7.73 ("d", apparent $J = 7.9$ Hz, 2 H, $C_6H_4$); 7.99 (m, 2 H, 4,4′′-H); 8.28 ("d", apparent $J = 7.9$ Hz, 2 H, $C_6H_4$); 8.80 (d, $J = 7.5$ Hz, 2 H, 3,3′′-H); 8.99 (s, 2 H, 3′,5′-H); 9.36 (d, $J = 4.8$ Hz, 2 H 6,6′′-H). − $^{13}C\{^1H\}$ NMR ($[D_6]DMSO$): $\delta = 40.4$ ($Me_2SO$); 64.0, 67.6, 69.2, 69.8, 71.2, 85.0 (Fc and $C{\equiv}C$); 118.5, 123.5, 126.4, 127.8, 131.7, 132.1, 133.3, 136.7, 155.6, 157.3, 158.8 (aryl rings). − FAB MS; *m/z*: 767 $[M]^+$, 732 $[M - Cl]^+$, 689 $[M - Me_2SO]^+$. − $C_{35}H_{29}Cl_2FeN_3ORuS$ (767.52): C 54.77, H 3.81, N 5.47; found C 53.98, H 4.30, N 5.38.

**Complex 4b:** By a procedure analogous to that described for **4a** 135 mg (78%) of **4b** was obtained from **3b** (124 mg, 0.197 mmol) and $[RuCl_2(DMSO)_4]$ (95 mg, 0.196 mmol) in ethanol (10 mL) as a light-violet microcrystalline solid. − $^1H$ NMR ($CDCl_3$): $\delta = 1.70$, 1.75, 1.82, 1.97 (4 s, $4 \times 6$ H, Me); 2.71 (s, 6 H, $Me_2SO$); 3.39 (s, 1 H, $C_5Me_4H$); 7.35 ("d", apparent $J = 8.2$ Hz, 2 H, $C_6H_4$); 7.49 (m, 2 H, 5,5′′-H); 7.67 ("d", apparent $J = 8.2$ Hz, 2 H, $C_6H_4$); 7.72 (m, 2 H, 4,4 ′′-H); 8.05 (d, $J = 8.9$ Hz, 2 H, 3,3′′-H); 8.06 (s, 2 H, 3′,5′-H); 9.33 (d, $J = 5.2$ Hz, 2 H, 6,6′′-H). − $^{13}C\{^1H\}$ NMR

Table 2. X-ray structure analysis data of **3b**

| | | | |
|---|---|---|---|
| Empirical formula | $C_{41}H_{39}FeN_3$ | $\mu$ [mm$^{-1}$] | 0.498 |
| Formula weight | 626.60 | $F(000)$ | 2656 |
| Space group | monoclinic, $C2/c$ | Index ranges | $0 \le h \le 60$, $0 \le k \le 10$, $-21 \le l \le 21$ |
| $a$ [Å] | 46.87(2) | $\theta$ range [°] | 1.74−27.51 |
| $b$ [Å] | 8.372(5) | Reflections collected | 7522 |
| $c$ [Å] | 16.600(8) | Independent reflections | 7432 [$R$(int.) = 0.0588] |
| $\beta$ [°] | 93.35(4) | Data/restraints/parameters | 7432/0/414 |
| $V$ [Å$^3$] | 6503(6) | Goodness-of-fit on $F^2$ | 1.023 |
| $Z$ | 8 | Final $R1$[a] [$I > 2\sigma(I)$]/$wR2$[b] | 0.0560 (5164 reflections)/0.1500 |
| $\rho$(calcd.) [g/cm$^3$] | 1.286 | Larg. diff. peak/hole [e/Å$^3$] | 0.4/−0.5 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{0.5}$.

($CDCl_3$): δ = 8.7, 9.7, 10.4, 10.6 (Me-Fc#); 42.9 ($Me_2SO$); 82.0−85.0 (br.), 88.1, 92.8 ($C_5$-Fc# and C≡C); 119.1, 123.6, 126.8, 127.1, 131.4, 133.5, 136.6, 153.7, 159.1, 159.3 (aryl rings). − FAB MS; *m/z*: 879 $[M]^+$, 844 $[M - Cl]^+$, 801 $[M - Me_2SO]^+$. − $C_{43}H_{45}Cl_2FeN_3ORuS$ (879.74): C 58.71, H 5.16, N 4.78; found C 58.52, H 5.13, N 4.64.

**Complex 5a:** A stirred mixture of **3a** (250 mg, 0.483 mmol) and $[RuCl_2(DMSO)_4]$ (117 mg, 0.241 mmol) in ethanol (30 mL) was refluxed for 15 h and subsequently allowed to cool to room temp. and filtered. 1.0 mL of a saturated aqueous solution of ammonium hexafluorophosphate was added dropwise to the red filtrate. The precipitate was filtered off, washed with ethanol and water, and dried in vacuo. Dark red microcrystalline solid; yield 130 mg (38%).− $^1$H NMR ([$D_6$]DMSO): δ = 4.35 (s, 10 H, $C_5H_5$); 4.43, 4.67 (2 s, 2 × 4 H, $C_5H_4$); 7.29 (m, 4 H, 5,5′′-H); 7.56 (d, $J$ = 5.1 Hz, 4 H, 6,6′′-H); 7.87 (“d”, apparent $J$ = 7.2 Hz, 4 H, $C_6H_4$); 8.07 (m, 4 H, 4,4′′-H); 8.51 (“d”, apparent $J$ = 7.1 Hz, 4 H, $C_6H_4$); 9.14 (d, $J$ = 7.2 Hz, 4 H, 3,3′′-H); 9.53 (s, 4 H, 3′,5′-H). − $^{13}$C{$^1$H} NMR ([$D_6$]DMSO): δ = 64.0, 69.3, 69.9, 71.3 (Fc); 85.3, 91.6 (C≡C); 120.8, 124.9, 125.1, 127.8, 128.0, 131.9, 135.2, 138.0, 152.2, 155.1, 158.0 (aryl rings). − UV/Vis (acetonitrile): λ (lg ε) = 230 nm (4.78), 272 (4.84, sh), 284 (4.86), 312 (4.97), 326 (4.94, sh), 495 (4.62). − FAB MS; *m/z*: 1281 $[\mathbf{5a} - PF_6]^+$, 1136 $[\mathbf{5a} - 2\ PF_6]^+$. − $C_{66}H_{46}F_{12}Fe_2N_6P_2Ru$ (1425.84): C 55.60, H 3.25, N 5.89; found C 56.00, H 3.56, N 6.21.

**Complex 5b:** By a procedure analogous to that described for **5a** 41 mg (59%) of **5b** was obtained from **3b** (53 mg, 0.084 mmol) and $[RuCl_2(DMSO)_4]$ (20 mg, 0.041 mmol) in ethanol (8 mL) as a brown microcrystalline solid. − $^1$H NMR ([$D_6$]DMSO): δ = 1.68−1.92 (br. m, 48 H, Me), 3.44 (s, 2 H, $C_5Me_4H$), 7.28 (m, 4 H, 5,5′′-H), 7.55 (d, $J$ = 5.3 Hz, 4 H, 6,6′′-H), 7.82 (“d”, apparent $J$ = 7.4 Hz, 4 H, $C_6H_4$), 8.07 (m, 4 H, 4,4′′-H), 8.45 (“d”, apparent $J$ = 7.7 Hz, 4 H, $C_6H_4$), 9.01 (d, $J$ = 8.0 Hz, 4 H, 3,3′′-H), 9.50 (s, 4 H, 3′,5′-H). − $^{13}$C{$^1$H} NMR ([$D_6$]DMSO): δ = 8.6, 9.7, 10.4, 10.5 (Me-Fc#); 71.6, 80.4, 80.5, 81.6, 81.8 ($C_5$-Fc#); 88.6, 92.1 (C≡C); 120.9, 124.8, 126.0, 127.7, 128.1, 131.4, 134.8, 138.0, 152.2, 155.1, 158.0 (aryl rings). − UV/Vis (acetonitrile): λ (lg ε) = 226 nm (5.01), 272 (4.93, sh), 284 (4.94), 309 (5.01), 328 (4.93, sh), 356 (4.77), 494 (4.71). − FAB MS; *m/z*: 1505 $[\mathbf{5b} - PF_6]^+$, 1360 $[\mathbf{5b} - 2\ PF_6]^+$. − $C_{82}H_{78}F_{12}Fe_2N_6P_2Ru \times 2\ H_2O$ (1686.31): C 58.41, H 4.90, N 4.98; found C 58.57, H 5.06, N 5.12.

**Complex 6:** A stirred mixture of **4a** (96 mg, 0.125 mmol) and 2,2′:6′,2′′-terpyridine (29 mg, 0.124 mmol) in ethanol (25 mL) was refluxed for 15 h and subsequently allowed to cool to room temp. and filtered. 1.0 mL of a saturated aqueous solution of ammonium hexafluorophosphate was added dropwise to the red filtrate. The precipitate was filtered off, washed with ethanol and water, and dried in vacuo. Brown microcrystalline solid; yield 70 mg (49%). − $^1$H NMR ([$D_6$]DMSO): δ = 4.34 (s, 5 H, $C_5H_5$); 4.42, 4.65 (2 s, 2 × 2 H, $C_5H_4$); 7.24−7.28 (m, 4 H, **3a**-5,5′′-H and tpy-5,5′′-H); 7.43 (d, $J$ = 5.5 Hz, 2 H, **3a**-6,6′′-H); 7.54 (d, $J$ = 5.5 Hz, 2 H, tpy-6,6′′-H); 7.86 (“d”, apparent $J$ = 8.1 Hz, 2 H, $C_6H_4$), 8.02−8.06 (m, 4 H, **3a**-4,4′′-H and tpy-4,4′′-H); 8.50 (“d”, apparent $J$ = 8.1 Hz, 2 H, $C_6H_4$); 8.54 (m, 1 H, tpy-4′-H); 8.83 (d, $J$ = 8.0 Hz, tpy-3,3′′-H); 9.09−9.13 (m, 4 H, **3a**-3,3′′-H and tpy-3′,5′-H); 9.51 (s, 2 H, **3a**-3′,5′-H). − $^{13}$C{$^1$H} NMR ([$D_6$]DMSO): δ = 64.0, 69.3, 69.9, 71.3 (Fc); 120.9, 121.0, 123.9, 124.0, 123.7, 124.8, 124.9, 127.7, 131.9, 133.5, 135.0, 135.8, 138.0, 145.8, 152.1, 154.7, 155.1, 157.7, 157.8 (aryl rings). − UV/Vis (acetonitrile): λ (lg ε) = 218 nm (4.78), 272 (4.74), 284 (4.70, sh), 308 (4.93), 326 (4.81, sh), 486 (4.48). − FAB MS; *m/z*: 852 $[\mathbf{6} - 2\ PF_6]^+$. − $C_{48}H_{34}F_{12}FeN_6P_2Ru \times H_2O$ (1159.72): C 49.71, H 3.13, N 7.25; found C 49.47, H 3.18, N 7.44.

**Crystal Structure Determination of 3b**[26]: An orange crystal with dimensions 1.00 × 0.60 × 0.10 mm was used for data collection at 183(2) K with a Siemens $P2_1$ four-circle diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation (λ = 0.71073 Å). The structure was solved by direct methods. Programs used were Siemens SHELXTL PLUS[27] and SHELXL 97[28]. Full-matrix least-squares refinement on $F^2$ was carried out anisotropically for the non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model. Further X-ray structure analysis data are given in Table 2.

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[1] Presented in part at the Chemiedozententagung, Essen, Germany, March **1998**, abstract B29.

[2] Reviews: [2a] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26−34. − [2b] J.-P. Collin, P. Gaviña, V. Heitz, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **1998**, 1−14. − [2c] F. R. Keene, *Coord. Chem. Rev.* **1997**, *166*, 121−159. − [2d] F. Barigelletti, L. Flamigni, J.-P. Collin, J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.* **1997**, 333−338. − [2e] A. Harriman, R. Ziessel, *J. Chem. Soc., Chem. Commun.* **1996**, 1707−1716. − [2f] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759−833. − [2g] J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993−1019. − [2h] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic

Press, London, **1992**. − [2i] V. Balzani, F. Barigelletti, L. De Cola, *Top. Curr. Chem.* **1990**, *158*, 31−71. − [2j] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85−277.

[3] Recent reviews concerning natural photosynthesis: [3a] K. Brettel, *Biochim. Biophys. Acta* **1997**, *1318*, 322−373. − [3b] R. C. Jennings, R. Bassi, G. Zucchelli, *Top. Curr. Chem.* **1996**, *177*, 147−181. − [3c] R. van Grondelle, J. P. Dekker, T. Gillbro, V. Sundstrom, *Biochim. Biophys. Acta* **1994**, *1187*, 1−65. − Recent reviews concerning artificial photosynthesis: [3d] Contributions in *Prog. Inorg. Chem.* **1997**, *44*. − [3e] W. Rüttinger, G. C. Dismukes, *Chem. Rev.* **1997**, *97*, 1−24. − [3f] H. Kurreck, M. Huber, *Angew. Chem.* **1995**, *107*, 929−947; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 849−866. − [3g] E. Amouyal, *Sol. Energy Mater. Sol. Cells* **1995**, *38*, 249−276. − [3h] D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **1993**, *26*, 198−205. − [3i] M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435−461. − [3j] *Photochemical Conversion and Storage of Solar Energy* (Eds.: F. Pelizzetti, M. Schiavello), Kluwer, Dordrecht, **1991**.

[4] [4a] P. Zanello in *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, **1995**, chapter 7. − [4b] W. E. Geiger in *Organometallic Radical Processes* (Ed.: W. C. Trogler), Elsevier, Amsterdam, **1990**, chapter 5.

[5] [5a] I. R. Butler, S. J. McDonald, M. B. Hursthouse, K. M. A. Malik, *Polyhedron* **1995**, *14*, 529−539. − [5b] E. C. Constable, A. J. Edwards, R. Martínez-Máñez, P. R. Raithby, A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.* **1994**, 645−650. − [5c] B. Farlow, T. A. Nile, J. L. Walsh, A. T. McPhail, *Polyhedron* **1993**, *12*, 2891−2894. − [5d] C. Chambron, C. Coudret, J.-P. Sauvage, *New. J. Chem.* **1992**, *16*, 361−367.

[6] E. J. Lee, M. S. Wrighton, *J. Am. Chem. Soc.* **1991**, *113*, 8562−8564.

[7] A. Maciejewski, A. Jaworska-Augustyniak, Z. Szeluga, J. Woytrzak, J. Karolczak, *Chem. Phys. Lett.* **1988**, *153*, 227−232 and references therein.

[8] [8a] K. L. Cunningham, C. R. Hecker, D. R. McMillin, *Inorg. Chim. Acta* **1996**, *242*, 143−147. − [8b] R. Giasson, E. J. Lee, X. Zhao, M. S. Wrighton, *J. Phys. Chem.* **1993**, *97*, 2596−2601. − [8c] F. R. Lemke, R. M. Granger, D. A. Morgenstern, C. P. Kubiak, *J. Am. Chem. Soc.* **1990**, *112*, 4052−4054.

[9] [9a] P. G. Gassmann, D. W. Macomber, J. W. Hershberger, *Organometallics* **1983**, *2*, 1470−1472. − [9b] A. J. Deeming in *Comprehensive Organometallic Chemistry*, vol. 4 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Able), Pergamon Press, Oxford, **1982**, chapter 31.3.

[10] F. Scandola, M. T. Indelli, C. Chiorboli, C. A. Bignozzi, *Top. Curr. Chem.* **1990**, *158*, 73−149.

[11] Reviews: [11a] R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265−322. − [11b] N. Sutin, *Acc. Chem. Res.* **1982**, *15*, 275−282.

[12] These spacers are known to influence the photophysical properties of relevant $Ru^{II}$ complexes very favourably. See: [12a] R. Ziessel, *Angew. Chem.* **1998**, *110*, 1804−1807; *Angew. Chem. Int. Ed.* **1998**, *37*, 1717−1720. − [12b] A. Benniston, A. Harriman, V. Grosshenny, R. Ziessel, *New J. Chem.* **1997**, *21*, 405−408. − [12c] V. Grosshenny, A. Harriman, R. Ziessel, *Angew. Chem.* **1995**, *107*, 2921−2925; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2705−2708. − [12d] A. C. Benniston, V. Grosshenny, A. Harriman, R. Ziessel, *Angew. Chem.* **1994**, *106*, 1956−1958; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1884−1885. − [12e] C. R. Hecker, A. K. I. Gushurst, D. R. McMillin, *Inorg. Chem.* **1991**, *30*, 538−541.

[13] K. Sonogashira in *Metal-catalyzed Cross-coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**, chapter 5.

[14] For a two-step synthesis giving 64% yield, see: [14a] U. Vorfeld, Doctoral Thesis, Univ. of Bielefeld, **1998**. − [14b] P. Korall, A. Börje, P.-O. Norrby, B. Åkermark, *Acta Chem. Scand.* **1997**, *51*, 760−766. −
For a one-pot method giving 20% yield, see: [14c] W. Spahni, G. Calzaferri, *Helv. Chim. Acta* **1984**, *67*, 450−454.

[15] H. Schottenberger, B. Anderson, S. F. Martin, *Org. Synth.* **1996**, *73*, 262−269.

[16] P. Jutzi, B. Kleinebekel, *J. Organomet. Chem.* **1997**, *545−546*, 573−576.

[17] D. R. Coulson, L. C. Satek, S. O. Grim, *Inorg. Synth.* **1972**, *13*, 121−124.

[18] [18a] V. Grosshenny, F. M. Romero, R. Ziessel, *J. Org. Chem.* **1997**, *62*, 1491−1500. − [18b] V. Grosshenny, R. Ziessel, *J. Organomet. Chem.* **1993**, *453*, C19−C22.

[19] D. P. Freyberg, J. L. Robbins, K. N. Raymond, J. C. Smart, *J. Am. Chem. Soc.* **1979**, *101*, 892−897.

[20] See, for example: [20a] H. Fink, N. J. Long, A. J. Martin, G. Opromolla, A. J. P. White, D. J. Williams, P. Zanello, *Organometallics* **1997**, *16*, 2646−2650. − [20b] J. T. Lin, J. J. Wu, C.-S. Li, Y. S. Wen, K.-J. Lin, *Organometallics* **1996**, *15*, 5028−5034. − [20c] R. P. Hsung, C. E.Chidsey, L. R. Sita, *Organometallics* **1995**, *14*, 4808−4815.

[21] See, for example: E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher, M. A. M. Daniels, *New J. Chem.* **1992**, *16*, 855−867 and references therein.

[22] I. P. Evans, A. Spencer, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1973**, 204−209.

[23] Complexes **5b** and **6** were obtained as hydrates (see Experimental Section). Although hexafluorophosphate salts of bis(terpyridine)ruthenium(II) complexes are usually isolated in unsolvated form, exceptions may occur in the case of ferrocenyl-substituted systems (see ref.[5b]).

[24] U. Siemeling, U. Vorfeld, F. Fabrizi de Biani, F. Laschi, P. Zanello, report presented at the Post-ICCC meeting on *Electrochemistry of Coordination and Organometallic Compounds*, Certosa di Pontignano, Siena, Italy, September **1998**.

[25] A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech, H. Keller, *Organometallics* **1994**, *13*, 1224−1234.

[26] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103120. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax (internat.): + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

[27] G. M. Sheldrick, *SHELXTL PLUS*, Siemens Analytical Instruments, Madison, WI, USA, **1990**.

[28] G. M. Sheldrick, *SHELXL 97*, University of Göttingen, Germany, **1997**.

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