263. Synthesis of Covalently Linked Viologen-Metallocenes

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(8.XI.82)

Summary

The synthesis and physical data of the covalently linked viologen-ferrocenes **3a** and **5a** and of the corresponding ruthenocene **3b** are described.

Electron transfer from an excited molecule to a second (ground state) component to afford a strong reductant is a key step in the formation of hydrogen by photochemical cleavage of water [1] [2]. Viologens (= *N, N'*-dialkyl-4,4'-bipyridines) have often been used as such electron relays, as the cation radical is able to reduce water in the presence of a catalyst. Only in very few cases the viologen unit has been covalently linked to the light-absorbing moiety, *e.g.* ruthenium tris(2,2'-bipyridine), as to effect an *intramolecular* electron transfer [3]. We now report the synthesis of compounds **2**, **3** and **5** which to our knowledge represent the first covalently linked viologen-metallocenes.

The synthetic path is given in the *Scheme*. Physical data of the new compounds are summarized in the *Table*.

Attempts to prepare the bis(viologen)ferrocenophane **6** either from **1a** and 4,4'-bipyridine or from **1a** and **2a** under high dilution conditions have up to now only led to linear polymeric material as judged from its (almost non-migrating) electrophoretic behaviour as compared to **2a**, **3a** and **5a**.

As the $E_{1/2}$-values for the reduction of the viologen units in compounds **3** and **5** are not affected by the metallocene moiety (*e.g.* $E_{1/2}$ for **3a** = -0.502 V *vs.* SCE in H_2O as compared to -0.640 V for methylviologen [4]), and as the visible-light absorbing properties, particularly for the Fe-compounds are reasonably good, compounds **3** and **5** seem to represent suitable photochemical systems capable of the production of hydrogen from water. We shall report our results with these systems in a later paper.

We are grateful to the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and *Degussa AG* for financial support.

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0018-019X/82/8/2603-03$01.00/0

Scheme

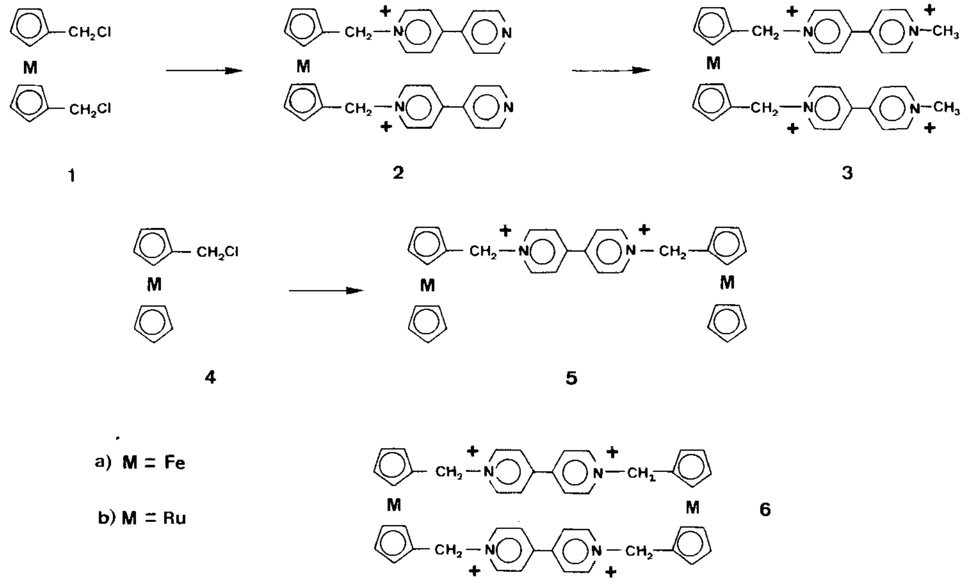

Table *Spectroscopic and physical data of new compounds*[a])

	UV. (H_2O)	^{1}H-NMR. (D_2O)	MS.	Electrophoretic mobility[b])
1b		4.27[c]) (*s*, 4 H), 4,58 (*m*, 4 H), 4.72 (*m*, 4 H)	328 (M^+) 293 (100%)	–
2a	407 (2.09) 260 (4.67)	4.64 (*m*, 4 H), 4.77 (*m*, 4 H), 5.79 (*s*, 4 H) 7.92 (*m*, 4 H), 8.41 (*m*, 4 H), 8.80 (*m*, 4 H), 9.01 (*m*, 4 H)	559[d]) ($M^+ - Cl$)	0.51
2b	350 (2.90) 262 (4.64)	4.85 (*m*, 4 H), 4.97 (*m*, 4 H), 5.51 (*s*, 4 H), 7.91 (*m*, 4 H), 8.42 (*m*, 4 H), 8.79 (*m*, 4 H), 9.04 (*m*, 4 H)	415[d]) [e])	0.50
3a	457 (2.85) 258 (4.75)	4.52 (*s*, 6 H), 4.65 (*m*, 4 H), 4.78 (*m*, 4 H), 5.86 (*s*, 4 H), 8.50 (*m*, 8 H), 9.06 (*m*, 4 H), 9.11 (*m*, 4 H)	383[d]) [f])	0.80
3b	375 (2.80) 257 (4.69)	4.50 (*s*, 6 H), 4.86 (*m*, 4 H), 5.08 (*m*, 4 H), 5.60 (*s*, 4 H), 8.53 (*m*, 4 H), 8.56 (*m*, 4 H), 9.06 (*m*, 4 H), 9.17 (*m*, 4 H)	429[d]) [f])	0.71
5a	467 (2.87) 258 (4.48)	4.31 (*s*, 10 H), 4.50 (*m*, 4 H), 4.60 (*m*, 4 H), 5.78 (*s*, 4 H), 8.48 (*m*, 4 H), 9.09 (*m*, 4 H)		0.49

[a]) Satisfactory elemental analyses (C,H,N) were obtained for all new compounds. [b]) Compared to methylviologen ($MVCl_2$ = 1.0). [c]) In $CDCl_3$. [d]) FAB.-MS. [e]) Corresponds to M^+ – bipy – 2Cl. [f]) Corresponds to M^+ – bipyCH_3 – 4Cl.

Experimental Part

General. Chemical shifts in the 400-MHz NMR. spectra are given in ppm relative to TMS or the sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid (=0 ppm) as internal standard. Absorptions in the UV. spectra are given in nm (logε). *F*ast *A*tom *B*ombardment (FAB.) mass spectra were measured using Xe as ionizing source and glycerine as solvent.

Starting materials. Compound **1a** was synthesized according to [5] and **4a** according to [6].

Preparation of **1b**. 1,1'-Bis(chloromethyl)ruthenocene is obtained from 1,1'-bis(hydroxymethyl)-ruthenocene [7] and PCl_3 in analogy to **1a** in 42% yield, m.p. 104° (dec.).

Preparation of bis[(4-pyridyl-pyridiniomethyl)cyclopentadienyl]iron (**2a**). A solution of 2.16 g ($7.6 \cdot 10^{-3}$ mol) **1a** in 80 ml DMF is added under N_2 to a solution of 14.6 g ($93.5 \cdot 10^{-3}$ mol) 4,4'-bipyridine in 100 ml DMF at 80° during 3 h. Stirring is then continued at r.t. for 16 h, the precipitate filtered off and washed with DMF and then with acetone, Recrystallization from water affords **2a** as dichloride-dihydrate in 80% yield.

Preparation of bis[(4-pyridyl-pyridiniomethyl)cyclopentadienyl]ruthenium (**2b**). The procedure is similar as described for **2a**, but due to the better solubility of **2b** in DMF, ether has to be added to accomplish the precipitation. Yield: 39%.

*Preparation of bis[4-(*N*-methylpyridinium-4-yl)pyridiniomethyl]cyclopentadienyl]iron* (**3a**). A solution of 1 g ($1.68 \cdot 10^{-3}$ mol) **2a** in 200 ml DMF and 15 ml CH_3I is stirred under N_2 at r.t. for 20 h. After addition of another 10 ml CH_3I the stirring is continued for 12 h. The precipitate is washed with DMF and then with acetone. Anion exchange on *Amberlite IRA-400* affords **3a** as tetrachloride in 97% yield.

*Preparation of bis{[4-(*N*-methylpyridinium-4-yl)pyridiniomethyl]cyclopentadienyl}ruthenium* (**3b**). The procedure is similar to the one for **3a**, again ether having to be added to accomplish precipitation. Yield: 48.7%.

Preparation of N,N'*-bis[(ferrocenyl)methyl]-4,4'-bipyridine-*N,N'*-diylium* (**5a**). A solution of 290 mg ($1.9 \cdot 10^{-3}$ mol) 4,4-bipyridine in 150 ml DMF is added under N_2 to 920 mg ($3.95 \cdot 10^{-3}$ mol) **4a** in 50 ml DMF at 80° for 3 h. Stirring is continued at r.t. for 3 h, the precipitate is filtered off, washed with DMF and then with acetone and recrystallized from water to afford **5a** as dichloride-dihydrate in 51% yield.

Electrophoresis. Thin layer electrophoresis was performed on cellulose at 15° applying 40 V/cm and using a pyridine, acetic acid, water buffer (100:3:897). Methylviologen ($MVCl_2$) was used as reference compound.

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