180. 5,5′-Bi-5*H*-cyclopenta[2,1-*b*;3,4-*b*′]dipyridinylidene, a New Bridging Ligand for Metal Complexes

Preliminary Communication

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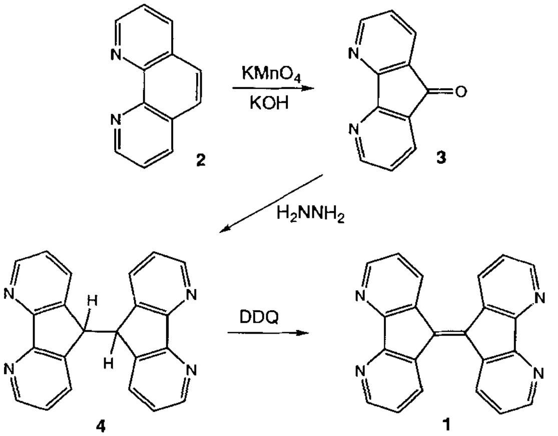
5,5′-Bi-5*H*-cyclopenta[2,1-*b*;3,4-*b*′]dipyridinylidene (**1**) was synthesized in three steps from 9,10-phenanthroline and characterized by UV/VIS and NMR spectroscopy, mass spectrometry, and cyclic voltammetry. Its ability to act as a bridging ligand is demonstrated by the synthesis of the complexes $[Ru(bpy)_2(\mathbf{1})](PF_6)_2$ (**6**) and $[\{Ru(bpy)_2\}_2(\mathbf{1})](PF_6)_4$ (**7**) (bpy = 2,2′-bipyridine).

Introduction. – Polynuclear diimine-type complexes of Ru^{II} and Os^{II} are at present under investigation with respect to their intramolecular energy- and electron-transfer properties [1]. These properties depend strongly on the nature of the bridging ligand. Here, we report the synthesis and the characterization of a new bridging ligand: 5,5′-Bi-5*H*-cyclopenta[2,1-*b*;3,4-*b*′]dipyridinylidene (**1**). The unusual electronic properties of **1**, as well as the preparation of two Ru^{II} complexes, are discussed. The compound **1** was first reported in 1979 [2]; however, our data do not correspond with those published.

Results and Discussion. – *Synthesis of 5,5′-Bi-5*H*-cyclopenta[2,1-*b*;3,4-*b*′]dipyridinylidene* (**1**). The bridging ligand **1** was prepared in three steps (see the *Scheme*). The 1,10-phenanthroline (**2**) was first oxidized to 4,5-diazafluorenone (**3**) and dimerized to

Scheme



9,9′-bis(4,5-diazafluorene) (**4**) as described by *Cherry* and coworkers [3], and *Mlochowsky* and coworkers [4]. Compound **1** was produced in good yield by dehydrogenation of **4** using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

This product thus obtained was characterized by UV/VIS and NMR spectroscopy, high-resolution FAB mass spectrometry, and cyclic voltammetry. The electronic spectrum shows a strong absorption band with a maximum at 417 nm ($\varepsilon = 22100$ $\text{M}^{-1} \cdot \text{cm}^{-1}$) reflecting the orange color of **1** (see *Fig.*). The cyclic voltammogram of **1** (DMF, $Bu_4N \cdot PF_6$ 0.1M) indicates two successive one-electron reduction steps at −0.67 and −1.13 V *vs.* SCE.

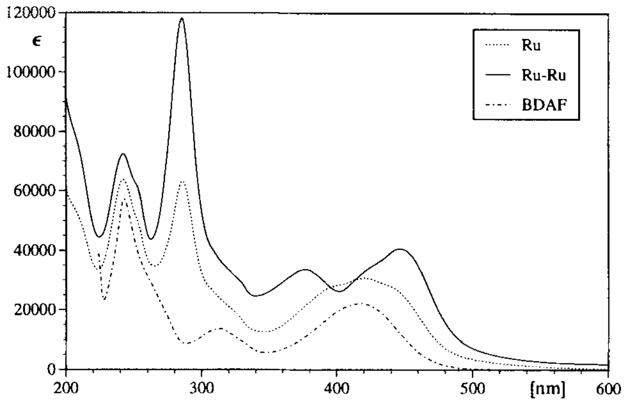
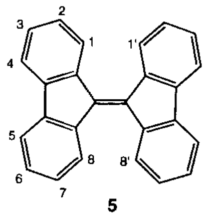


Fig. *UV/VIS Spectra of* **1** (–·–·–) *in* CH_2Cl_2, *and* **6** (·····) *and* **7** (——) *in MeCN, measured at room temperature*

Both the absorption spectrum and the redox behavior are qualitatively very similar to that of 9,9′-bifluorinylidene (**5**), the carbon analogue of **1**. Compound **5** undergoes two successive single-electron reduction steps in aprotic solvents: a reversible step ($E = -1.10$ V *vs.* SCE), followed by a quasi-reversible reduction ($E = -1.5$ V *vs.* SCE) [5]. Because of the presence of the four N-atoms, which are more electronegative than the C-atom, the reduction of **1** takes place at a potential of *ca.* 0.4 V more positive than that of **5**.



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Compound **5** is red and presents a strong absorption in the visible (455 nm, $\varepsilon = 22100$ $\text{M}^{-1} \cdot \text{cm}^{-1}$ in i-PrOH) [6]. This sterically highly crowded ethylene bridge adopts a twisted conformation, in order to avoid large repulsive interactions around the central C=C bond, *i.e.*, between the protons H–C(1) and H–C(1′), and H–C(8) and H–C(8′) [17].

The absorption band at 455 nm is caused by the presence of the twisted central C=C bond [6], and it was attributed to a *T*wisted *I*ntramolecular *C*harge *T*ransfer (TICT) [5] [8] [9].

MOPAC Calculation (CAChe MOPAC version 94, parametrization AM1) of the geomatry of **1** confirms that this molecule adopts a twisted conformation. Consequently, it has an axial chirality.

The preparation of a compound formulated as 5,5′-Bi-5*H*-cyclopenta[2,1-*b*;3,4-*b*′]dipyridinylidene (**1**) was reported in 1979 [2]; however our data disagree with those published for this compound. In particular, **1** is reported as a colorless compound, and several inconsistencies appear in the ^{1}H-NMR and the MS data. From the information available, we suppose that compound **4**, and not **1**, was actually prepared.

Synthesis of Ruthenium Complexes. Compound **1** is expected to be a weaker σ-bonding ligand than 2,2′-bipyridine. The ethylene bridge in **1** distorts the molecule from the classical phenanthroline unit, thus reducing the nitrogen-metal overlap [3]. However, the synthesis of the mono- and dinuclear Ru complexes $[Ru(bpy)_2(\mathbf{1})](PF_6)_2$ (**6**) and $[\{Ru(bpy)_2\}_2(\mathbf{1})](PF_6)_4$ (**7**) demonstrate the coordination ability of the new bridging ligand. Both products were characterized by UV/VIS and NMR spectroscopy, and FAB mass spectrometry. Compound **7** contains two chiral metal centers and is then presumably present in the two diastereoisomeric forms $\Delta,\Delta/\Lambda,\Lambda$ and Δ,Λ, respectively. However, these cannot be distinguished by ^{1}H-NMR (300 MHz). Consequently, the conformational chirality of the bridging ligand **1** could not be detected either.

The electronic spectra of **6** and **7** are shown in the *Figure*. Two strong absorption bands appear in the UV region, at 242 nm (*L*igand *C*entered (LC) transition on **1**) and 286 (LC transition on bpy). The VIS region is characterized by a superposition of *M*etal-to-*L*igand-*C*harge-*T*ransfer (^{1}MLCT) absorption bands [11] and LC transitions of **1**.

Note added in proof. – After submitting this manuscript, Prof. *J. A. Connor*, University of Kent at Canterbury, Kent, UK, informed us that 5,5′-Bi-5*H*-cyclopenta[2,1-*b*;3,4-*b*′]dipyridinylidene had also been synthesized in his laboratory. Both groups had independently presented their results at different meetings, unaware of the others research. We thank Prof. *J. A. Connor* for informing us about his results.

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Experimental Part

General. All reactions were carried out under Ar. Solvents were of *puriss p.a.* quality. UV/VIS Spectra: *Perkin-Elmer Lambda 2.* NMR: *Varian Gemini 300* (^{1}H: 300 MHz; ^{13}C: 75.4 MHz); δ in ppm rel. to Me_4Si (= 0 ppm) or δ rel. to CD_3CN (1.93 ppm for ^{1}H; 77.0 ppm for ^{13}C); ^{13}C multiplicities were determinated by APT sequence; coupling constants *J* in Hz. MS: *VG Instruments 7070E* with a FAB inlet system. Elemental analyses were carried out by the Mikrolabor, *Ciba-Geigy*, Marly.

*5,5′-Bi-5*H*-cyclopenta[2,1-*b*;3,4-*b*′]dipyridinylidene* (**1**). A mixture of 9,9′-bis[4,5-diazafluorene] [4] (330 mg, 0.99 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 246 mg, 1.09 mmol) in bromobenzene (30 ml) was heated for 2 h at 120°. After the solvent was removed by distillation, the residue was dissolved in CH_2Cl_2/MeOH 9:1 (200 ml), washed with 1M NaOH (3 × 100 ml), then H_2O (3 × 100 ml), and dried (Na_2SO_4). The solvent was evaporated and the residue heated at reflux in AcOEt (30 ml) for 1 h. The suspension was cooled and filtered to give **1** as an orange solid (280 mg, 85%). ^{1}H-NMR ($CDCl_3$ + 3 drops CD_3CN): 8.71 (*dd*, *J* = 4.8, 1.3, 1 H); 8.50 (*dd*, *J* = 8.0, 1.3, 1 H); 7.37 (*dd*, *J* = 8.0, 4.9, 1 H). ^{13}C-NMR ($CDCl_3$ + 3 drops CD_3CN): 158.5 (*s*); 151.4 (*d*);

136.7 (*s*); 134.0 (*d*); 132.2 (*s*); 123.3 (*d*). FAB-MS: 355 ([*M* + Na]$^+$), 333 ([*M*H]), 307, 183, 154. HR-MS: 333.1156 ($C_{22}H_{13}N_4^+$; calc. 333.1140). Anal. calc. for $C_{22}H_{12}N_4$ (332.37): C 79.50, H 3.64, N 16.86; found: C 79.12, H 3.74, N 16.44.

*[Ru(bpy)$_2$(***1***)](PF$_6$)$_2$* (**6**). To a hot soln. of **1** (50 mg, 0.15 mmol) in EtOH/(CF_3CO_2H 0.01M in H_2O) 1:1 (15 ml), a soln. of [Ru(bpy)$_2$Cl$_2$]·2H_2O [12] (65 mg, 0.12 mmol) in the same solvent (20 ml) was added dropwise during 2 h. Heating was continued for 30 min, then the EtOH is evaporated. The aq. soln. was washed with CH_2Cl_2 to extract the excess ligand, and NH_4PF_6 (500 mg) was added to precipitate the product. The complex was purified by gel chromatography [13] (*Sephadex® LH-20*, MeCN/MeOH/CF_3CO_2H 1:1:0.005) to give **6** as an orange-brown solid (90 mg, 69%). ^{1}H-NMR (CD_3CN): 8.73 (br., 1 H); 8.59 (*d*, *J* = 8.1, 1 H); 8.56–8.47 (*m*, 3 H); 8.13 (*d*, *J* = 5.6, 1 H); 8.09 (*ddd*, *J* = 8.0, 8.0, 1.4, 1 H); 8.06 (*ddd*, *J* = 8.0, 8.0, 1.4, 1 H); 7.90 (*d*, *J* = 5.6, 1 H); 7.57 (*dd*, *J* = 5.4, 0.8, 1 H); 7.50–7.38 (*m*, 4 H). FAB-MS: 891 ([*M* – PF$_6$]$^+$), 746 ([*M* – 2PF$_6$]$^+$), 590, 433, 413.

[{Ru(bpy)$_2$}$_2$(bdaf)](PF$_6$)$_4$ (**7**). A soln. of **1** (20 mg, 0.06 mmol) and [Ru(bpy)$_2$Cl$_2$]·2H_2O [12] (63 mg, 0.12 mmol) in EtOH/CF_3CO_2H 0.01M in H_2O 1:1 (20 ml) was refluxed for 3 h. The EtOH was evaporated, and NH_4PF_6 (500 mg) was added to precipitate the product. The complex was filtered, washed with a small amount of EtOH, and purified by crystallization (diffusion of Et_2O in acetone/CF_3OOH 1:0.005) to give **7** as an orange-brown solid (82 mg, 78%). ^{1}H-NMR (CD_3CN): 8.56 (*d*, *J* = 8.1, 1 H); 8.53 (*d*, *J* = 4.7, 1 H); 8.50 (*d*, *J* = 4.7, 1 H); 8.18–8.02 (*m*, 3 H); 7.92 (*d*, *J* = 5.5, 1 H); 7.63 (*d*, *J* = 5.2, 1 H); 7.49 (*dd*, *J* = 8.0, 5.5, 1 H); 7.47 (*ddd*, *J* = 7.4, 5.5, 1.2, 1 H); 7.42 (*ddd*, *J* = 7.4, 5.5, 1.2, 1 H). FAB-MS: 1595 ([*M* – PF$_6$]$^+$), 1450 ([*M* – 2PF$_6$]$^+$), 1307, 741.

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