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Synthesis and Cu(I) binding properties of two tris-bipyridine ligands. Self-assembly of homostrand and heterostrand trinuclear double helical complexes†

Daniel-Petru Funeriu, Yong-Bing He#, Hans-Jürgen Bister, Jean-Marie Lehn*

Institut Le Bel, Université Louis-Pasteur, 4, rue Blaise-Pascal, 67000 Strasbourg, France

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Summary — The unsaturated trimeric ligand BP_3-E **1** was synthesized by a Wittig–Horner condensation and its saturated derivative BP_3-A **2** was prepared by hydrogenation. The latter was also obtained via another reaction sequence in four steps from commercially available compounds. The formation of complexes with copper(I) has been studied as well as the self-recognition properties of (tris)bipyridyl ligands. The influence of the two different bridges (CH=CH and CH_2CH_2) on complexation is discussed on the basis of ^{1}H-NMR spectra. The results indicate that the double-stranded trihelicate $[(BP_3\text{-}A)_2\ Cu_3]^{3+}$ **12** is formed from two BP_3-A ligand molecules and three copper(I) cations. However, BP_3-E presents more complicated binding features. Competitive binding of Cu(I) in a mixture of BP_3-A **2** and its oxygen-bridged analogue BP_3-O **3** shows that moderate self-recognition takes place with formation of both the two homostranded double helicates and its heterostrand double helix analogue $[Cu_3(BP_3\text{-}A)\ (BP_3\text{-}O)]^{3+}$ **13**.

inorganic double helix / helicate / self-recognition oligobipyridine ligand / copper(I) complex

Résumé — Synthèse et propriétés complexantes du Cu(I) de deux ligands à trois unités bipyridine. Formation de complexes trinucléaires homo et hétéro-hélicates. *Le composé à trois unités α,α′-bipyridine et à pont insaturé BP_3-E **1** a été synthétisé en utilisant une condensation de type Wittig-Horner. Le ligand saturé correspondant, BP_3-A **2** a été préparé par hydrogénation de BP_3-E. BP_3-A a également été obtenu par une autre séquence réactionnelle en 4 étapes à partir de produits commerciaux. Les propriétés de complexation de ces ligands ont été étudiées, ainsi que les propriétés d'autoreconnaissance des ligands (tris)bipyridyl. L'influence des deux différents ponts (CH=CH et CH_2CH_2) sur la complexation est discutée sur la base des spectres ^{1}H-RMN. Ces résultats indiquent que l'hélicate $[(BP_3\text{-}A)_2Cu_3]^{3+}$ **12** est formé à partir de deux molécules ligands et trois cations Cu(I). Cependant BP_3-E présente des propriétés complexantes plus compliquées. La complexation compétitive du Cu(I) par un mélange formé de BP_3-A **2** et de son analogue portant un atome d'oxygène dans le pont, BP_3-O **3**, montre qu'une autoreconnaissance modérée a lieu, avec la formation des homohélicates ainsi que de l'hétérohélicate $[Cu_3(BP_3\text{-}A)\ (BP_3\text{-}O)]^{3+}$ **13**.*

double hélice inorganique / hélicate / autoreconnaissance / ligand oligobipyridine / complexe Cu(I)

There has been considerable interest in molecular helicity [1, 2] since the revelation of the double helical structure of nucleic acids [3]. In particular, a number of dinuclear metal complexes presenting a double helical arrangement of the ligand molecules have been reported [4–10]. They are formed by the self-assembly of oligobipyridine ligands and copper(I) cations yielding polynuclear (tri- [6], tetra- and pentanuclear [7]) double-stranded helicate complexes.

We report here the synthesis and the copper(I) binding properties of two novel ligands BP_3-E **1** and BP_3-A **2** containing three 2,2′-bipyridine (bpy) units linked by CH=CH or CH_2CH_2 bridges, respectively. The related ligand containing two CH_2OCH_2 bridges BP_3-O **3** has been described previously and shown to form a trinuclear Cu(I) double helicate [6].

Synthesis of ligands BP_3-E 1 and BP_3-A 2

(6′-Methyl[2,2′-bipyridin]-6-yl)methylidene(triethoxy)-phosphorane **4** was prepared by reaction of the monobromomethyl compound **5** [11] with triethyl phosphite at 150 °C. Dimethyl sulfoxide 'activated' by oxalyl chloride at low temperature reacted rapidly with the diol **6** [6] to give the corresponding alkoxysulfonium salt, which was converted into 2,2′-bipyridine-6,6′-dicarbaldehyde **7** in high yield upon addition of triethylamine.

† Dedicated to Prof Raymond Weiss.

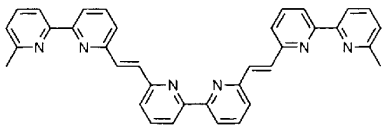
Present address: Department of Chemistry, Wuhan University, Wuhan, China.

* Correspondence and reprints

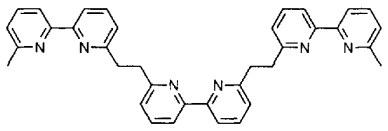
The trimeric BP_3-E **1** containing two CH=CH bridges was obtained by a Wittig–Horner reaction [12] between the phosphorane **4** and the dialdehyde **7** using sodium hydride. The saturated compound BP_3-A **2** was prepared by catalytic hydrogenation of BP_3-E on 10% Pd-C.

In a different, more direct (non-optimized) synthesis of BP_3-A **2**, the methyl group of 2-bromo-6-methylpyridine was deprotonated at low temperature using LDA, and the anion was oxidatively dimerized to give compound **8** in 81% yield. Coupling of **8** with 1 equiv of 2-methyl-6-(trimethylstannyl)pyridine using palladium(tetrakis-triphenylphosphine) as a catalyst, afforded compound **9** in 35% yield. Coupling of two molecules of **9** using a nickel-catalyzed procedure afforded a 55% yield of the ligand **2**.

Whereas **2** is soluble in common organic solvents, compound **1** has very low solubility; it is soluble in hot pyridine or DMF, from which it is purified by recrystallization. Both BP_3-E and BP_3-A compounds **1** and **2** are however readily soluble in acidic aqueous or organic solution at pH < 2, where they are protonated. They have spectral and microanalytical properties in agreement with their structures. The large coupling constant (15.5 Hz) measured for the vinylic protons of BP_3-E indicates a *trans* configuration of the double bond.



1 BP3-E



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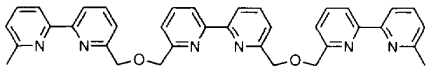
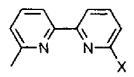
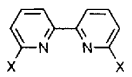


3 BP_3-O



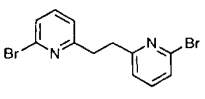
4 X= $CH{=}P(OEt)_3$

5 X= CH_2Br

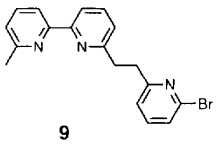


6 X= CH_2OH

7 X= CHO



8



9

Preparation and spectral properties of the copper(I) complexes of ligands BP_3-E 1 and BP_3-A 2

We have reported the synthesis and the Cu(I) binding properties of the dimeric 1,2-bis(2,2′-bipyridinyl)ethylene BP_2-E **10** and 1,2-bis(2,2′-bipyridinyl)ethane BP_2-A **11** ligands [13]. BP_2-A binds Cu(I) ions forming a dinuclear, double-stranded helicate $[Cu_2(BP_2\text{-}A)_2]^{2+}$ in which two ligand molecules wrap around two Cu(I) ions; its structure has been confirmed by X-ray crystallography [14]. We now investigate the Cu(I) binding properties of the next two members of the series, the tris-bipyridine ligands BP_3-E **1** and BP_3-A **2**.

The complexation of Cu(I) by BP_3-E and BP_3-A was performed by adding a solution of Cu(II) bis-trifluoromethanesulfonate in acetonitrile to a suspension of BP_3-E or BP_3-A in acetonitrile followed by reduction with aqueous hydrazine [6]. The deep orange-red color characteristic of Cu(I) bipyridine complexes appeared immediately. The Cu(I) complexes were precipitated as red solids by adding diethyl ether. They were soluble in common solvents (CH_3CN, CH_3OH and acetone) and stable in air.

The ^{1}H-NMR spectrum of the complex $[Cu_3(BP_3\text{-}A)_2]^{3+}$ (fig 1) was very different from that of the free ligand BP_3-A. The signals of the bipyridine protons were markedly shifted on complexation, the most important changes occurring for the CH_2CH_2 signal; the CH_2CH_2 protons, which appear as a singlet in the free ligand, shifted upfield by more than 0.5 ppm and were split into an ABCD pattern in the complex. Thus, the CH_2CH_2 protons had become nonequivalent in the complex. On the basis of previous observations [6, 7], these data indicate that a double helical structure of $[Cu_3(BP_3\text{-}A)_2]^{3+}$, $\mathcal{H}^3$(**2**, **2**) composition, similar to those reported previously [6, 7], may be assigned to the trinuclear complex formed (see schematic representation **12**). It has a structure similar to those of $[Cu_2(BP_2\text{-}A)_2]^{2+}$ [13, 14] and an earlier Cu(I) trihelicate [6], which have been confirmed by crystal structure determinations. Its FAB-MS spectrum was in agreement with this formulation.

When the same complexation procedure was applied to the ligand BP_3-E **1**, the red color characteristic of Cu(I)-bipy complexes was produced, but the ^{1}H-NMR spectrum of the solution was much more complicated than expected for a 3:2 species similar to that obtained with BP_3-A. A mixture of Cu(I) complexes was formed as demonstrated by electro-spray mass spectrometry. Indeed, a series of peaks corresponding to $[Cu_3(BP_3\text{-}E)_2]^{3+}$, which may be a helicate species of type **12**, were observed, together with a $[Cu_6(BP_3\text{-}E)_4]^{6+}$ species. Similar behavior has been observed for the unsaturated dimeric ligand BP_2-E [13]. Further investigation is required for an analysis of the complexation features of BP_2-E and BP_3-E and the nature of the species formed. However, it is already clear that clean dihelicate formation does not occur with BP_3-E in the present conditions. This may result from a lack of flexibility due to the double bond which does not allow easy double helical wrapping of two ligand molecules around three Cu(I) ions. This restriction does not exist for the

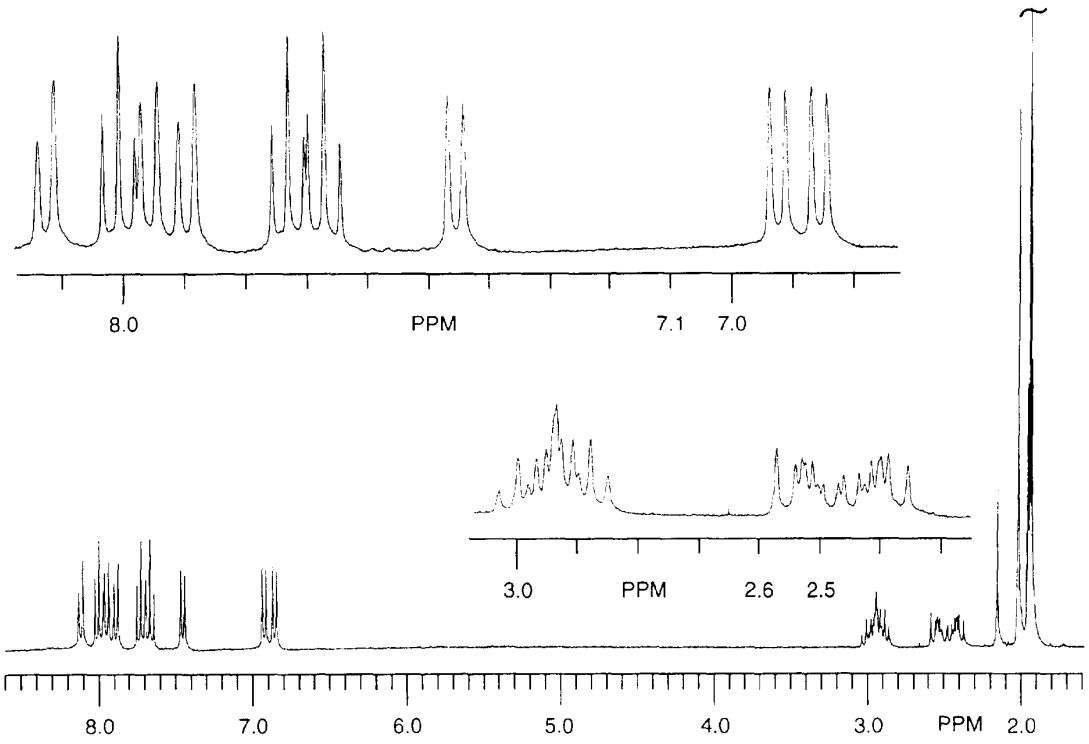


Fig 1. ^{1}H-NMR spectrum (300 MHz) of the helicate $[Cu_3(BP_3\text{-}A)_2]$ $(TfO)_3$ **12** in CD_3CN solution at 25 °C.

saturated ligand BP_3-A **2**, which does form the double helical arrangement.

The present results thus confirm that, like the CH_2OCH_2 sequence, a CH_2CH_2 group separating the bipy units in a linear oligobipyridine ligand is also a suitable spacer for double helicate formation. More detailed information about its effect on the exact structural parameters of helicates may be obtained by extrapolation of the crystal structure data of $[Cu_2(BP_2\text{-}A)_2](OTf)_2$ [14].

Self-recognition and mixed-strand hybrid double helicates

It has been found that when mixtures of oligobipyridine ligands of different lengths are reacted with Cu(I) salts, a mixture of homostranded double helicates is formed indicating that self-recognition is taking place, ie, that there is preferential formation of double helicates involving identical ligands [15]. The process thus displayed high self-recognition. It was therefore of interest to investigate the effect of structural differences between ligands on the self-recognition process.

In particular, the competition between BP_3-A **2** and BP_3-O **3** would reveal how much the rather small modification from a CH_2CH_2 to a CH_2OCH_2 bridge would affect the ligand selection process in the self-assembly and whether or not a heterostrand, hybrid double helical species would be formed.

When a (1 + 1) equiv mixture of BP_3-A **2** and BP_3-O **3** in acetonitrile was treated with 3 equiv of $Cu(OTf)_2$ followed by reduction with aqueous hydrazine, a mixture of three complexes was obtained as indicated by the ^{1}H-NMR spectrum (fig 2): the two homostrand helicates $[Cu_3(\mathbf{2})_2]^{3+}$, $\mathcal{H}^3$**(2, 2) 12** and $[Cu_3(\mathbf{3})_2]^{3+}$, $\mathcal{H}^3$**(3, 3) 14** and a hybrid heterostrand complex $[Cu_3(\mathbf{2})(\mathbf{3})]^{3+}$, $\mathcal{H}^3$**(2, 3) 13** displaying shifted signals (with respect to the homostrand species) at 4.15/4.42 and 2.7/2.25 ppm (partially hidden by the signal of the methyl group) for the protons of the CH_2OCH_2 and CH_2CH_2 bridges, respectively. Integration of the corresponding signals showed that the composition of the mixture was different from the statistical one, in favor of the two homostranded species (table I).

Table I. Formation of homostrand $\mathcal{H}^3$**(2, 2) 12**, $\mathcal{H}^3$**(3, 3) 14** and heterostrand $\mathcal{H}^3$**(2, 3) 13** double helicates from a 1:1 mixture of ligands **2** and **3** and Cu(I) ions.

	Helicate		
	$\mathcal{H}^3$*(2, 2)*	$\mathcal{H}^3$*(3, 3)*	$\mathcal{H}^3$*(2, 3)*
Statistical mixture	25%	25%	50%
Mixture obtained	40%	40%	20%

It is of current interest to develop the use of electrospray mass spectrometry (ESMS) for the quantitative determination of the species present in mixtures produced by self-assembly in solution [16, 17]. ESMS studies performed directly on the present system [18] gave the same helicate fractions as those obtained by NMR spectroscopy (table I) by comparing the heights of the peaks corresponding to the three complexes.

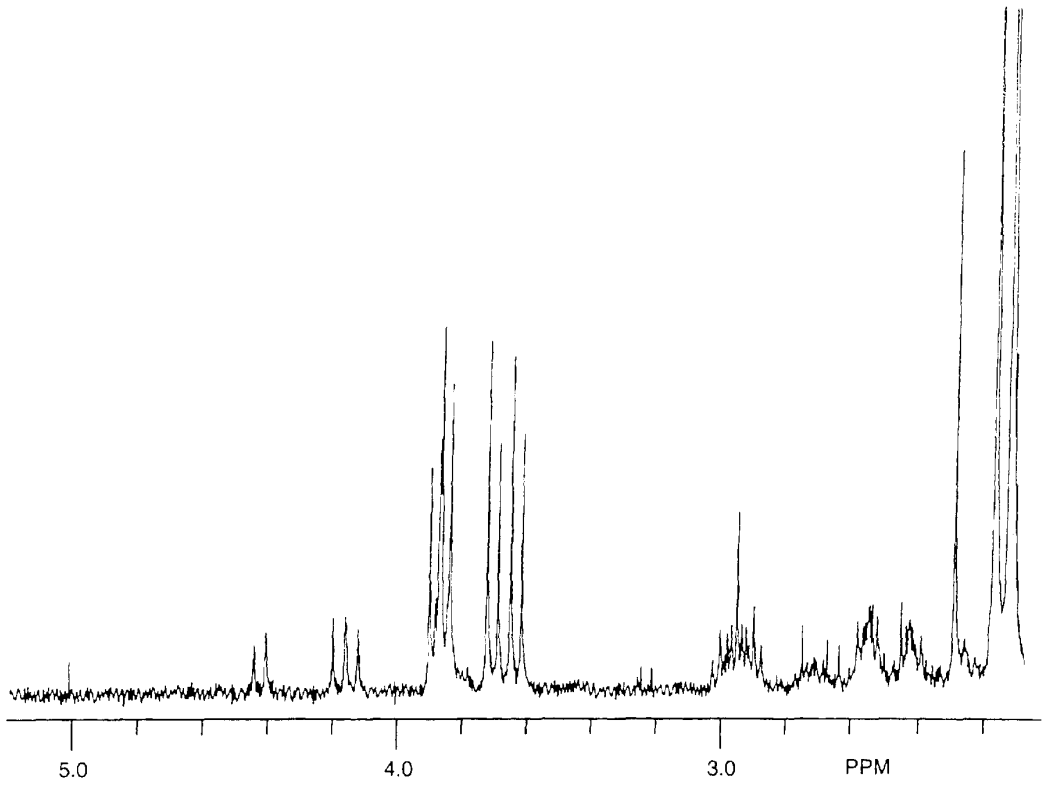
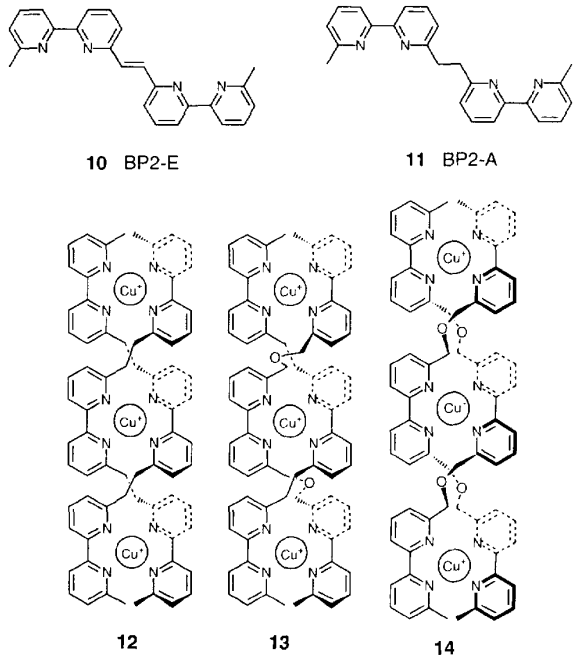


Fig 2. ^{1}H-NMR spectrum (400 MHz) of the mixture of helicates $[Cu_3(\mathbf{2})_2]$ $(TfO)_3$ **12**, $[Cu_3(\mathbf{3})_2]$ $(TfO)_3$ **13** and $[Cu_3(\mathbf{2}, \mathbf{3})]$ $(TfO)_3$ **14** obtained from a (1 + 1) equiv mixture of ligands **2** and **3** and 3 equiv of copper salt in CD_3CN solution at 25 °C.



On the other hand, when a (1 + 1) equiv mixture of **2** and **3** was treated with 1.5 equiv of copper salt (half the stoichiometric amount), the ^{1}H-NMR spectrum (300 MHz; 25 °C; 15% $CDCl_3$ in CD_3CN) revealed that, in addition to the mixed strand species **13** (~ 30%), the $[Cu_3(BP_3\text{-}O)_2]^{3+}$ **14** helicate was formed preferentially (~ 50%) with respect to the $[Cu_3(BP_3\text{-}A)_2]^{3+}$ one (~ 20%), indicating that the former was more stable than the latter.

The departure from statistical distribution and the preferential formation of the $[Cu(\mathbf{3})_2]^{3+}$ **14** helicate result from the difference between a CH_2CH_2 and a CH_2OCH_2 bridge. They may be due to the presence of an electrostatic attraction between the oxygen sites and the Cu^+ ions, and of additional strain in the $[Cu_3(\mathbf{2})_2]^{3+}$ **12** helicate introduced by the shorter, less flexible ethylene bridge. The present results indicate that recognition between the two strands in helicate self-assembly is also dependent, although less markedly, on more subtle structural factors than the number of bipy units, thus providing a higher capacity of information storage. Further exploration of such effects is thus warranted since they may permit to more finely tune the self-assembly of helicates and related architectures.

Experimental section

General

^{1}H-NMR spectra were recorded on a Bruker SY-200 spectrometer at 200 MHz; chemical shifts are given in ppm from TMS. The mass spectra and microanalyses were performed at the Laboratoire de Spectrométrie de Masse and the Service Central de Microanalyse du CNRS, Institut de Chimie,

Strasbourg, respectively. THF was distilled over benzophenone/Na; CH_2Cl_2 was distilled over CaH_2; other chemicals were commercial reagents.

(6'-Methyl[2,2'-bipyridin]-6-yl)methylidene(triethoxy) phosphorane **4**

A mixture of 6-(bromomethyl)-6'-methyl-2,2'-bipyridine **5** [11] and an excess of triethyl phosphite was heated at 150 °C for 5 h under argon. After evaporation of the excess of triethyl phosphite under reduced pressure, the residue was purified by chromatography on silica with 2% CH_3OH/CH_2Cl_2 as eluent to give the phosphorane **4** as a pale yellow solid in 95% yield (mp 31–32 °C).

^{1}H-NMR ($CDCl_3$): 8.29 (d, 1H, H-C(3)); 8.18 (d, 1H, H-C(3')); 7.67 (tt, 2H, H-C(4,4')); 7.32 (d, 1H, H-C(5)); 7.11 (d, 1H, H-C(5')); 4.05 (m, 4H, O-CH_2-C); 3.45 (d, 2H, CH_2-Py); 2.85 (s, 3H, Py-CH_3); 1.21 (t, 6H, C-CH_3).

2,2'-Bipyridine-6,6'-dicarbaldehyde **7**

A solution of oxalyl chloride (0.6 mL, 2.2 equiv) in CH_2Cl_2 (12 mL) was placed in a 50 mL three-necked flask equipped with a thermometer, a $CaSO_4$ drying tube and a pressure-equalizing dropping funnel containing dimethyl sulfoxide (0.95 mL, 4.4 equiv) dissolved in CH_2Cl_2 (4 mL). The DMSO was added dropwise to the stirred solution of oxalyl chloride at −50 °C to −60 °C. The reaction mixture was stirred for 0.5 h at −40 °C. A solution of 2,2'-bipyridine-6,6-methanol **6** [7] (0.65 g, 1 equiv) in a minimum amount of CH_2Cl_2/DMSO was added dropwise to the mixture above, and stirring was continued for 3 h at −30 °C. Triethylamine (4 mL) was added and the mixture was then allowed to warm to room temperature. Water (25 mL) was added and the suspension was extracted with $CHCl_3$. After evaporation of the solvent and drying, the residue was purified by chromatography on Al_2O_3 with 1% CH_3OH/CH_2Cl_2 as eluent, giving 2,2'-bipyridine-6,6'-dicarbaldehyde **7** in 60% yield (mp 234–235 °C, lit 235 °C [11]).

^{1}H-NMR ($CDCl_3$): 10.17 (s, 2H, CHO); 8.81 (q, 2H, H-C(4,4')); 8.05 (m, 4H, H-C(3,3',5,5')).

6,6'-Bis[2-(6'-methyl[2,2'-bipyridin]-6-yl)ethenyl]-2,2'-bipyridine (BP$_3$-E) **1**

A solution of compound **4** (1.18 g, 3.68 mmol, 2 equiv) in THF (15 mL) under argon was treated with sodium hydride at room temperature for 2 h. Then a solution of 1 equiv of **7** in THF (100 mL) was added dropwise and the mixture was stirred at reflux for 12 h. After evaporation of the solvent, water (100 mL) and diethyl ether (150 mL) were added. A white suspension formed between the aqueous layer and the organic layer; it was separated and filtered; the residue was washed with water and then with THF, and dried in vacuo. Recrystallization from pyridine or DMF gave compound BP$_3$-E **1** as a white solid (0.48 g, 50% yield) (mp 271–272 °C).

^{1}H-NMR (5% CF_3COOD/acetone-d_6): 8.93 (dd, 4H, H-bipy); 8.85 (d, 2H, H-bipy); 8.67 (t, J = 7.6 Hz, 2H, H-bipy); 8.63 (d, 2H, H-bipy); 8.58 (d, J = 15.5 Hz, 2H, CH=CH); 8.43 (t, J = 7.6 Hz, 2H H-bipy); 8.41 (d, 2H, H-bipy); 8.40 (d, J = 15.5 Hz, 2H, CH=CH); 8.31 (t, J = 4.14 Hz, 2H, H-bipy); 8.21 (d, 2H, H-bipy), 3.25 (s, 6H, CH_3).

Anal calc for $C_{36}H_{28}N_6$: C 79.39, H 5.18, N 15.43; found: C 79.24, H 5.31, N 15.53.

Mass: MH^+ 545.4.

6,6'-Bis[2-(6'-methyl[2,2'-bipyridin]-6-yl)ethyl]-2,2'-bipyridine (BP$_3$-A) **2** *from* **1**

A mixture containing compound **1** (10 mg, 0.018 mmol), absolute ethanol (8 mL) and concentrated hydrochloric acid (3 drops) was placed in a 50 mL three-necked flask; 10% Pd-C (6 mg) was added in one portion, the flask was degassed with a water pump and then placed under hydrogen (1 atm). The mixture was stirred at room temperature for 24 h. After filtration over celite, the filtrate was concentrated under reduced pressure. Water (15 mL) was added to the residue and the mixture was basified to pH 10 with 4 N sodium hydroxide and extracted with $CHCl_3$. After drying and evaporation of the organic solvent, the crude product obtained was purified by chromatography on Al_2O_3 with CH_2Cl_2 as eluent, giving the compound BP$_3$-A **2** (7.07 mg) in 70% yield (white solid, mp 177–178 °C).

^{1}H-NMR ($CDCl_3$): 8.22 (dd, 6H, H-bipy); 7.66 (tt, 6H, H-bipy); 7.13 (dd, 6H, H-bipy); 3.42 (s, 8H, CH_2); 2.66 (s, 6H, CH_3).

Anal calc for $C_{36}H_{32}N_6$: C 78.81, H 5.88, N 15.32; found: C 78.61, H 5.89, N 15.21.

Mass: MH^+ 549.3.

6,6'-Dibromo-2,2'-[ethane-1,2-diyl]dipyridine **8**

A solution of LDA (prepared from 4.81 mL of DIPBA and 22.4 mL of *n*BuLi 0.153 M in hexane) was added dropwise (under Ar) to a solution containing 5.9 g (34.3 mmol) of the 2-bromo-6-methylpyridine in 50 mL of dry THF at −80 °C. The color changed to brown-red. After 2 h of stirring at −80 °C 2.96 mL (1 equiv) of 1,2-dibromoethane in 30 mL THF were added and the solution left to warm to room temperature and portioned between H_2O and $CHCl_3$. The organic phase was filtered through a short pad of alumina to afford 4.75 g (81%) of white crystalline material **8**. R_f = 0.56 on alumina (hexane/CH_2Cl_2 70:30) (mp 125.6 °C).

^{1}H-NMR ($CDCl_3$, 300 MHz): 7.40 (t, J = 7.5 Hz, 2H); 7.28 (d, J = 7.5 Hz, 2H); 7.06 (d, J = 7.5 Hz, 2H); 3.17 (s, 4H, CH_2).

Anal calc for $C_{12}H_{10}N_2Br_2$: C 42.14%, H 2.94%, N 8.19%; found: C 42.75%, H 2.93%, N 7.97%.

6-[2-(6-Bromopyridin-2-yl)ethyl]-6'-methyl-2,2'-bipyridine **9**

The dibromo compound **8** (4.75 g, 13.9 mmol), 50 mg of tetrakis-triphenylphosphine palladium catalyst and 3.54 g of 2-methyl-6-(trimethylstannyl)pyridine (1 equiv) were mixed in a two-necked flask and put under vacuum. The round-bottomed flask was filled with Ar; 50 mL of dry toluene was added by syringe and the reaction mixture refluxed overnight. The solvent was removed and the solid residue was chromatographed over flash silica with CH_2Cl_2/CH_3OH 98:2 as eluent to afford 1.6 g (34%) of the desired compound **9** and 1.6 g (33%) of the starting material **8**. R_f = 0.33 on silica (methanol/CH_2Cl_2 2:98) (mp 117.6 °C in a range of 0.5 °C).

^{1}H-NMR ($CDCl_3$) 8.19 (d, J = 7.5 Hz, 1H); 8.18 (d, J = 7.5 Hz, 1H); 7.66 (t, J = 7.5 Hz, 1H); 7.64 (t, J = 7.5 Hz, 1H); 7.35 (t, J = 7.5 Hz, 1H); 7.28 (d, J = 7.5 Hz, 1H); 7.12 (d, J = 7.5 Hz, 1H); 7.07 (d, J = 7.5 Hz, 1H); 7.03 (d, J = 7.5 Hz, 1H), 3.27 (m, 4H, CH_2), 2.60 (s, 3H, CH_3).

Anal calc for $C_{18}H_{16}N_3Br$: C 61.03%, H 4.55%, N 11.86%; found: C 61.30%, H 4.52%, N 11.72%.

Tris-bipyridine compound BP_3-A **2** *from* **9**

Triphenylphosphine (4.16 g) and $NiCl_2 \cdot 6H_2O$ (0.94 g) were dissolved in 20 mL of DMF under Ar and then 0.26 g of powder Zn were added. The reaction mixture was stirred at 60 °C for 1 h and then **9** (1.6 g) in 5 mL of DMF was added. After 6 h stirring at 60 °C and additional stirring at air, at room temperature, 10 mL of 32% NH_3 was added. The solution was extracted several times with $CHCl_3$ and the solvent removed. The solid obtained was washed with hot hexane to obtain 497 mg of the desired compound **2** (51%). R_f = 0.6 on alumina, $CHCl_3$; mp 177–178 °C.

Acknowledgments

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