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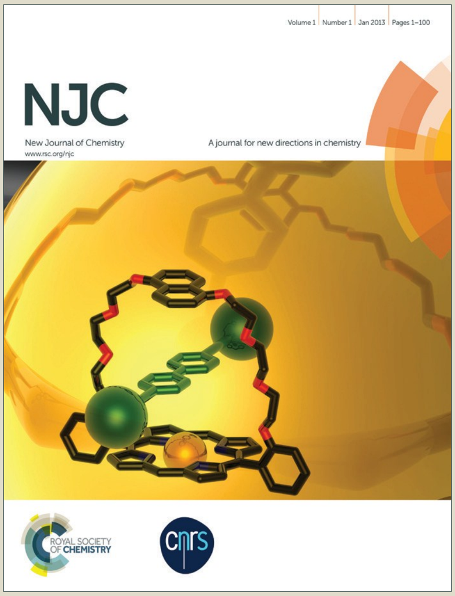

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Synthesis of flexible tetrapyridylethanes from pyridylpyrylium dications

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New tetrapyridylethanes can be prepared as new tetradentate pyridine ligands by aminolysis reaction of pyrylium dications, using an original oxidation process of phenylpyridyl methylenepyrans. Crystal structure analysis, Spectroscopic and electrochemical studies show the ability to use these new ligands in coordination chemistry.

Pyridine based ligands play an important role in coordination chemistry and their applications in wide fields such as catalysis[1], optical materials[2], magnets[3] and gas-sorption[4] have been recently reported. Sophisticated metal complexes based on multi-dentate pyridine have been obtained last decade for further applications as grids[5], molecular containers[6] or Metal-Organic Frameworks (MOFs)[7]. To obtain various polymeric structures, the use of rigid or flexible tetrakispyridyl ligands such as PETPE or TPOM has been widely studied[8]. Recent reports mentioned that the use of mixed-ligands in a complex, offers a greater tenability of structural framework[9]. In addition, introduction of a phenylpyridine moiety to increase the rigidity of the ligand, improve the control of the coordination chemistry[10]. However, few studies on their homologues with a central tetrahedral ethane have been described and as consequence their coordination chemistry to obtain new molecular or supramolecular architectures has been less studied[11]. Interestingly, three-dimensional framework using a tetrahedral tetrapyridylcyclobutane has been recently obtained[12].

In this paper we describe a straightforward synthesis of bis-(diphenylpyridyl) bis-(pyridinylphenyl) ethane in three steps. In these flexible molecules two different pyridinyl moieties are present. We think that this architecture could offer various coordination pathways. Metal coordination to the 2,6-diphenylpyridine moiety has been already observed[13] but could be limited for steric reason. Nevertheless, modification of the nature of 2,6-substituents of these pyridines groups to introduce smaller substituents (methyl or thienyl) [14] or coordination group (pyridyl) will be considered. The originality of this process is based on the chemistry and the redox properties of pyrylium cations and methylenepyran moieties. Since 2008 we have developed the study of methylenepyran compounds obtained from 4*H*-pyranylphosphonium salt and substituted aryl or ferrocenyl aldehydes[15]. This methodology has been applied to 4-pyridylcarboxaldehyde with success[15]. We have showed that a reversible oxidation process of the obtained methylenepyrans leads to dipyrylium cation which could be easily deprotonated in basic medium. The obtained dimer could also be oxidized to form unsaturated dipyrylium cation (fig.1).

Then we have focused our attention to develop this procedure in order to access first to bispyrylium-bis(4-pyridinylphenyl) ethane cations **2** (scheme 2) which should react with ammonia[16] leading to 1,2-bis-(2,6-diphenylpyridin-4-yl)-1,2-bis(4-(pyridinyl)phenyl) ethanes **4** (scheme 3).

These new flexible tetrahedral tetrapyridines should be interesting ligands to access to novel coordination polymers or clusters. Herein we report the first results of our investigation.

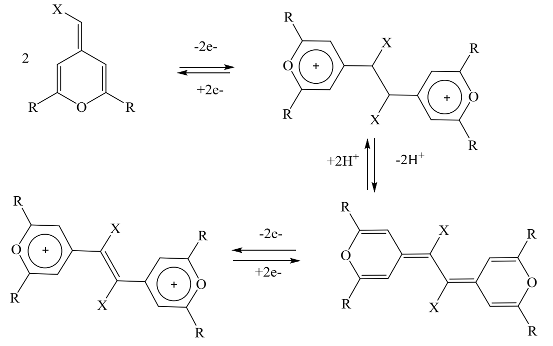
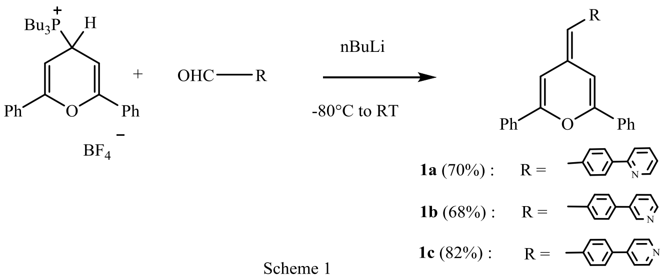


Fig. 1

4H-pyranilidenemethyl phenylpyridine **1** were obtained in good yields from commercial aldehydes and tributyl(2,6-diphenyl-4H-pyran-4-yl)phosphonium tetrafluoroborate via a Wittig reaction and after purification by silica gel chromatography (scheme 1).



Scheme 1

As observed for other methylenepyrans, cyclic voltammetry studies (CV) of compounds **1** show the electrochemical dimerization of the species by monoelectronic oxidation process (C-C bond formation) *ca* E_{pa} = 0.3 V *vs* Fc (Fig. 2A), as previously observed with analogous methylenepyrans[15]. Exhaustive electrolysis at 0.4 V led to the formation of the dimer which can be reduced at *ca* -0.8 V. Counter-electrolysis of the bis-pyrylium at -0.9 V restored the initial compound (C-C bond breaking).

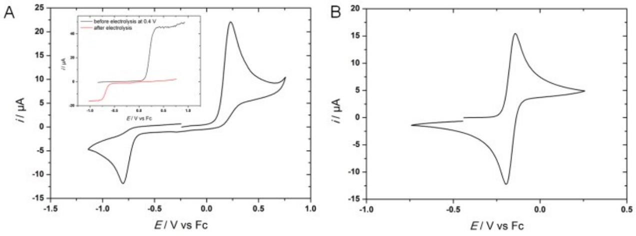
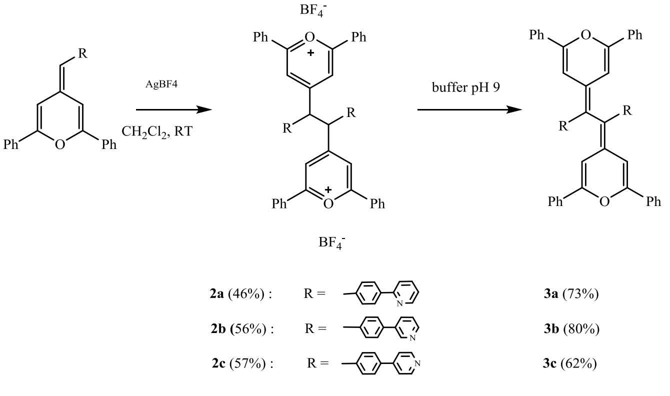


Fig.2: CVs (0.1 V/s; *E* /V vs Fc) at a Pt working electrode in CH_2Cl_2/NBu_4PF_6 0.1 M of A) for compound **1a** (1.2 mM); inset: RDEV before (a, black) and after (b, red) electrolysis at 0.4 V; B) for compound **3a** (0.4 mM)

In order to isolate the expected bispyrylium-bisphenylpyridine salts **2** we chose to use $AgBF_4$ in methylene chloride[17] as oxidizing agent (scheme 2). At room temperature the reaction of $AgBF_4$ with compounds **1** is fast and after treatment to eliminate Ag residues, we isolated compounds **2a, 2b or 2c** as green precipitates in moderate yields. The low solubility of these salts in organic solvents makes NMR analysis difficult. However, salt **2a** has been characterized by MS spectrometry, IR spectroscopy, ^1H and 2D ($^{13}C/^1H$) NMR analysis (ESI). On the ^1H NMR spectrum of compound **2a** we observe at low field (δ = 9.32 ppm) a characteristic singlet integrated for the four hydrogen atoms of the two pyrylium rings. The disparition of the two signals (δ=7.06ppm and δ=7.17ppm) of the non-equivalent protons for the methylene pyran ring in compound **1a** and the apparition of a signal at high field (δ=6.51ppm) characteristic of the exocyclic hydrogens on the Csp^3 carbon confirm the proposed structure. In addition we detect on IR spectra of compounds **2** a characteristic range of bands (ν=1070 cm^{-1}) assigned to the anion BF_4^-. In this case we observed on NMR spectra of **2a** the presence of two diastereoisomers. Dipyrylium **2b** was isolated as a sole isomer (^1H and ^{13}C NMR analysis) since compound **2c** was isolated but not characterized.



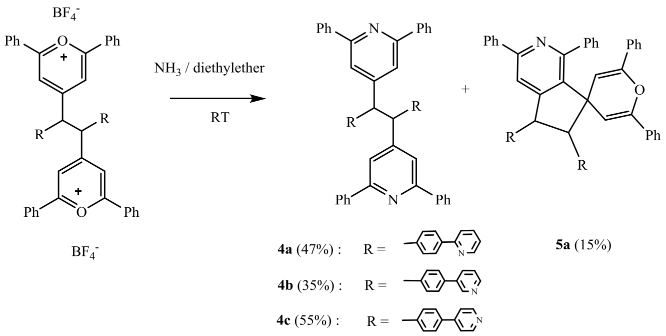
Scheme 2

At this stage, in order to obtain tetrakispyridylethane we decided to test the well-known reaction of ammonia with pyrylium cation. Two competing reactions in basic medium would be observed, deprotonation reaction leading to bis(4*H*-pyranyl)-bis(4-pyridinylphenyl) ethene **3** (scheme 2) or nucleophilic attack of ammonia on the α position of the pyrylium ring, leading, after O/N substitution to the expected products **4** (scheme 3). Optimized conditions for each reaction have been determined.

The bis-deprotonation reactions of bispyrylium salts was observed when a large excess of pH 9 (glycine buffer) solution was added at room temperature to a solution of each salt **2** in methylene chloride. The two phase's mixture was stirred three hours at room temperature until we observed the lack of pyrylium spot on TLC plates. The red organic layer was extracted and washed with water. After evaporation of the solvent, adding diethyl ether allowed isolation of **3**, in good yields, as red powders, without any further purification.

Compounds **3** have been fully characterized by ^1H, ^{13}C NMR, IR spectroscopy and Mass spectrometry. We observe on the ^1H spectra of these molecules characteristic signals for the two non-equivalent heterocyclic hydrogens around 6.6 ppm and 7.0 ppm.

Indeed, these bis-methylenepyranphenylpyridines undergo a reversible oxidation process at *ca* E^0 =-0.2 V *vs* Fc, leading to their bispyrylium counterparts (see Fig. 2B).



Scheme 3

On the other hand, when a suspension of bispyrylium salts **2** in diethylether was mixed at room temperature to an aqueous solution of ammonia (25%), we obtained the expected tetrapyridines. The very low solubility of bispyrylium cations in diethyl ether and water makes the reaction very slow and after one night we observed the formation of yellow-brown precipitates of tetrapyridines **4**. The suspensions were filtered, washed with diethyl ether and recrystallized in acetone/ether. Compounds **4** were then isolated as white powders in moderate yields. All compounds were characterized by ^1H, ^{13}C NMR, IR spectroscopy and Mass Spectrometry. ^1H NMR spectra of compounds 2 and 4 are quite similar since we observe the presence of the same phenylpyridyl moiety and a characteristic singlet for the hydrogen on the exocyclic Csp^3. The principal difference is observed for the chemical shift of the two protons of the 2,6-diphenylpyridine ring which appears around 8 ppm while they were detected around 9 ppm for the dipyrylium cations. On IR spectra we observe the disparition of the CO band (detected around 1620 cm^{-1} for pyrylium cations and around 1650 cm^{-1} for pyran moieties) and apparition of the CN band around 1590 cm^{-1}.

Compounds **4b** or **4c** were isolated as sole stereoisomers whereas **4a** was isolated as a mixture of two diastereoisomers, in accordance with the stereochemistry found for compounds **2a**. However, in one experience, without any modification of the experimental procedure except a longer reaction time, the reaction of **2a** led, together with tetrapyridine **4a** (one diastereoisomer), to the spiropyran **5a**[18]. A possible reaction mechanism for the formation of **5a** is proposed in

ESI. It is noteworthy that the formation of stable spiropyran was previously observed[19].

The reaction of ammonia with **2a** was also tested in dichloromethane. In this case the bispyrylium was soluble in the organic solvent. The biphasic mixture was stirred three hours at room temperature. TLC analysis of the organic layer showed the formation of product **4a** but a large red spot, distinctive of compound **3a** was also present with many other uncharacterized products. It seems that the weak concentration of bispyrylium **2** in diethyl ether-water could favor after a long reaction time the aminolysis reaction.

Small white crystals were obtained by slow evaporation at room temperature of a solution of **4c** in dichloromethane. Single X-ray analysis reveals the presence of the only (R,S) diastereoisomer (fig.3). The measurements of angles between the substituents on C1 (or C1^{i}) atom show as expected the tetrahedral fashion of these molecules. In this conformer, the values of torsion angles between the two different pyridyl substituents bound to C1 or C1^{i} atoms are 74.5°. Angles between the phenyl and pyridine parts in each phenyl pyridine moiety are equal to 53.9°. The symmetry of the molecule around C1-C1^{i} bond also appears in all measurements, like bond distances on each substituent or angle between phenyl and pyridine parts in 2,6-diphenylpyridine moiety (16.4° and 29.6°). Crystal data and selected bond distances are also available in ESI. Electronic Supplementary Information (ESI) available: [CCDC 1431519] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

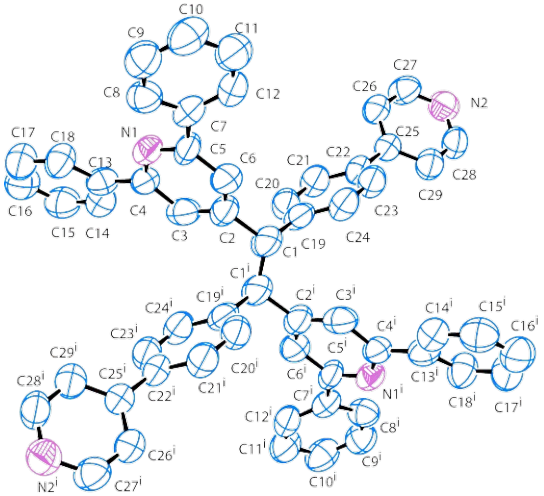


Fig. 3: ORTEP diagram of compound **4c** with symmetry code i : -x, -y+1, -z

In conclusion, new flexible tetrapyridine ethanes have been synthesized in three steps via a process based on the chemistry of methylenepyrans and pyrylium cations. These new molecules are interesting ligands for the construction of metallo-molecular entities. Ongoing work is focused on the use of these ligands in constructing various molecular architectures.

We have shown that a control of the reactions conditions could favor the aminolysis reaction or lead via a deprotonation reaction to new bispyran phenylpyridines. In addition, we think that the easy redox process of compounds **1** and **3**, leading to stable pyrylium cation could be develop as sensors for metallic cation detection. Indeed, emission measurements on compounds **1a**, **2a** and **3a** in 10^{-5} M dichloromethane solution have been performed at room temperature and quantum yields were measured relative to Coumarin 317. After excitation at 400nm compounds **1** and **3** show a very weak emission (ø<1%) while dipyrylium **2a** shows a strong luminescence (ø =70%). We will consider in the future, the study of the luminescent detection of metallic cations which could be coordinate to the phenylpyridyl moiety of compounds **2**.

Experimental

Compounds 3:

Compound **1**and $AgBF_4$ were stirred in degassed solution of methylene chloride (10mL) at room temperature. The initial yellow solution became green and we observed apparition of a green precipitate. A pH=9 (glycine buffer) was then added to the solution and the heterogeneous mixture was stirred half an hour. Ag residue was then eliminated by filtration and the organic layer was extracted 3 times with diethylether and washed 3 times with water. The extract was dried over $MgSO_4$. After evaporation of the solvent, the crude product was obtained without other purification as red powder.

Compounds 4:

$AgBF_4$ (0.25 mmol) was added to a solution of compound **1** (0.25 mmol) in 10mL of methylene chloride. The green mixture obtained was stirred 2h at room temperature. After this time, the formation of a green precipitate and a metallic residue of Ag were observed. After addition of 50 mL of methylene chloride, the mixture was filtered to eliminate Ag residue. Methylene chloride was then evaporated and 30 mL of diethylether and 20 mL of ammoniac solution (25%) were added to the obtained residue. The degassed mixture was stirred at room temperature 10 hours. We observed the formation of a yellow precipitate. After filtration, the solid was dissolved in acetone and recrystallized by addition of diethylether at low temperature (-18°C). Compound **4** was obtained as a white crystalline.

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Notes and references

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Electronic Supplementary Information (ESI) available: complete experimental section, ^{1}H and ^{13}C NMR spectra, absorption and emission spectra and electrochemical data. Crystallographic data are given as a CIF file.
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Novel tetrapyridylethanes and bis-phenylpyridylmethylenepyrans, as potential ligands for coordination chemistry.