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Syntheses and properties of phosphonate π-conjugated of pyridine

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Abstract

The syntheses of six phosphonates π-conjugated of pyridine by using the Heck reaction are described. The hydrolysis of the diethyl or di-*tert*-butyl phosphonate groups was performed with TMSBr or HCl 1 N respectively. The properties of the pyridine moiety were studied by reaction with MeI or complexation with BF_3, or $RuCl_3$. The phosphonate and phosphonic acid groups did not interfere in those reactions, showing the specificity of the pyridine part. Absorption and fluorescence studies presented characteristic bathochromic shift after quaternization or complexation of the nitrogen atom. ***To cite this article: R. Frantz et al., C. R. Chimie 8 (2005)***.

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Résumé

La synthèse de six composés, phosphonates π-conjugués avec la pyridine est décrite en utilisant la réaction de Heck. L'hydrolyse des phosphonates de diéthyle ou de di-*tert*-butyle a été réalisée par l'emploi de TMSBr ou HCl 1 N, respectivement. La réaction avec MeI ou complexation avec BF_3 ou $RuCl_3$ de la partie pyridine a été étudiée. Les groupements phosphonate et acide phosphonique n'interfèrent pas dans ces réactions, ce qui montre la réactivité spécifique de la partie pyridine. Les études d'absorption et de fluorescence ont montré un déplacement bathochrome caractéristique après quaternarisation ou complexation de l'atome d'azote. ***Pour citer cet article : R. Frantz et al., C. R. Chimie 8 (2005)***.

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Mots clés : Ruthénium ; Complexe ; Pyridine ; Heck ; Phosphonates ; Fluorescence ; Trifluoroborate

The use of pyridine derivatives has shown an important development, particularly in the field of materials and functionalisation of surfaces. [1] Many applications such as photoswitch sensors for transition metals [1a,b], supramolecular self-assembly of multilayers organometallic thin films [1c,d] for photocurrent-generating systems [1e] have been described. The anchoring of the pyridine moiety to prepare self-assembled monolayers (SAMs) is usually achieved by

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reacting thiol groups on gold [1a–e] or catechols [2a] and carboxylic [2b] or phosphonic acids [2c,d] at the surface of metal oxides. In the course of our program concerning the functionalisation of metal oxide nanoparticles with phosphonate derivatives of pyridine [2d], we present here the synthesis of ethyl and di-*tert*-butyl phosphonates π-conjugated of pyridine and the studies of their reactivity and complexation with boron and ruthenium derivatives.

Stilbazoles and π-conjugated derivatives of pyridines have been synthesized by using the Wittig–Horner [3a] or Heck [3b] reactions. A drawback of the Horner reaction is that a mixture of cis–trans isomers could be obtained. Trans isomer is preferred because of better coplanarity of the conjugated system and enhanced electronic effects [4]. We thus turned to the Heck [5] reaction and first prepared stilbazole derivatives (Scheme 1).

The Heck reaction was performed using standard homogeneous conditions with 4-vinylpyridine in the presence of the bromophosphonates **1a–d** that were prepared as described in literature procedures [6]. The reaction led efficiently to trans compounds **2a-d** in good yields.

We also prepared more conjugated derivatives by using two successive Heck reactions starting from *para*-iodobromobenzene and 4-vinylpyridine, then cross-coupling intermediate **3** with diethyl and di-*tert*-butyl 4-vinylbenzylphosphonates (Scheme 2).

The products **4a** and **4b** were obtained in 20% and 41% overall yield respectively. The yield was lower with the more emcumbered di-*tert*-butyl phosphonate ester. The diethyl and di-*tert*-butyl phosphonates were hydrolyzed with TMSBr and HCl 1 N, respectively. The two methods efficiently led to the acids (in the zwitterionic form) in good yields (Scheme 3).
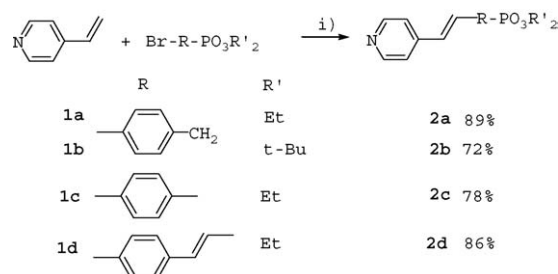

Scheme 1. Synthesis of stilbazole derivatives. Reagents and conditions: i) 4% Pd(OAc)$_2$, 15% TOP, Et$_3$N, toluene, 115 °C.
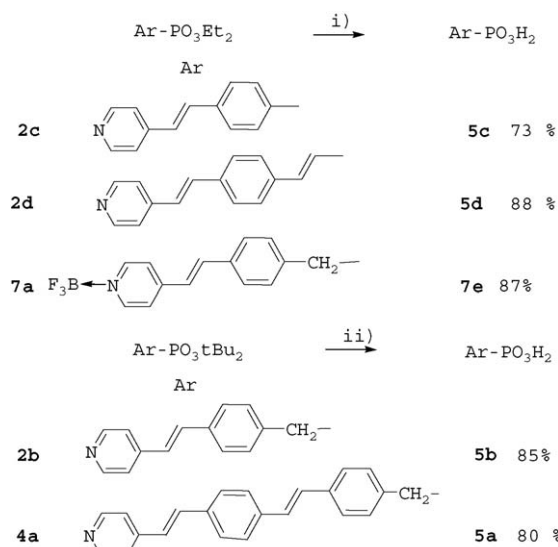

Scheme 2. Synthesis of stilbazole derivatives. Reagents and conditions: i) 4% Pd(OAc)$_2$, 15% triorthotolyl-phosphine (TOP), Et$_3$N, toluene, 115 °C.

Stilbazolium, π-conjugated pyridinium salts and borane adducts of π-conjugated derivatives of pyridine are known to give strong non-linear optical properties [7]. We thus first reacted compounds **2a**, **2c**, **4b**, **2d** with methyl iodide (Scheme 4) in order to study the reactivity of the molecules (regiochemistry) and to obtain the required π-conjugated pyridinium salt.
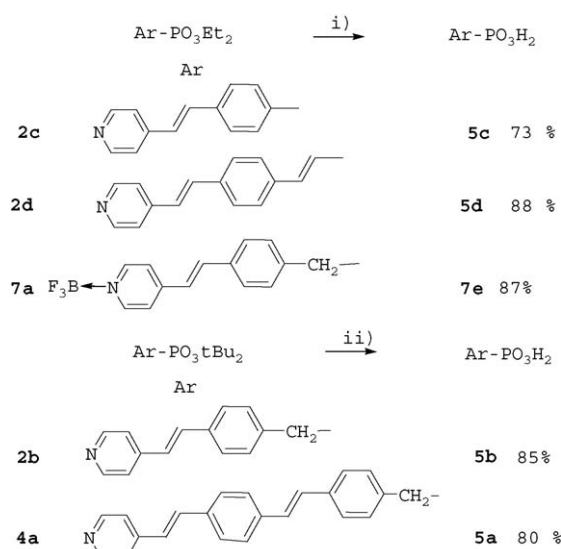
Scheme 3. Hydrolysis of phosphonates esters. Reagents and conditions: i) **a**) 3.5 equiv TMSBr, CH$_2$Cl$_2$, 12 h; **b**) H$_2$O. ii) HCl 1N, 12 h, RT.
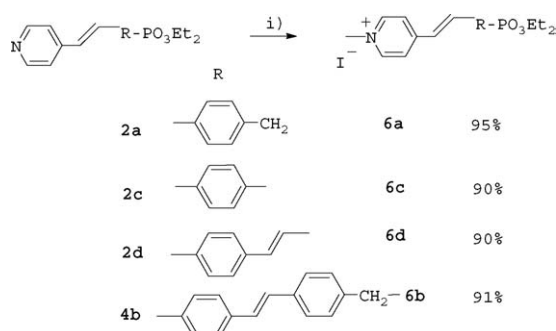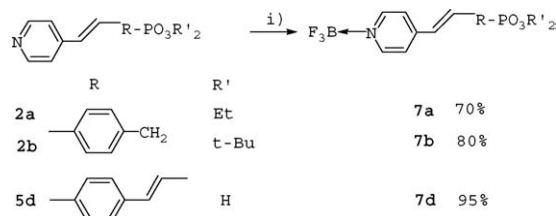
Scheme 4. Methylation of pyridine derivatives. Reagents and conditions: i) 1.5 equiv MeI, MeCN, RT, 12 h.

The reaction was very efficient, leading to salts **6a–d**, in excellent yield and the phosphonate moiety did not interfere. Complexation of derivatives **2a**, **2b**, **5d**, with BF$_3$.Et$_2$O was then performed (Scheme 5). In all the cases the reaction was regioselective giving adducts with the nitrogen of the pyridine moiety, no reaction was observed with the P=O function of esters **2a**, **2b** or acid **5d**, even by addition of 2 equivalents of BF$_3$.

No cleavage of the sensitive *t*-Bu ester of compound **2b** occurred. Indeed, ^{11}B MAS solid-state NMR of products **7b** and **7d** showed only one signal at –1.9 and –0.9 ppm respectively, and no modification of the ^{31}P NMR signal was observed after complexation. The trifluoroborate–pyridine adduct was very stable and was not cleaved during the hydrolysis of the phosphonate ester moiety of compound **7a**. Acid **7e** was obtained in good yield (Scheme 3).

Properties of organometallic complexes of pyridine have been widely studied [8] in fields such as supramolecular assemblies[8a,b], design of sensors [8c], catalysis [8d]. However, tetrakis pyridine ruthenium complexes [9] have been much less described than their bi or ter pyridine counterparts, as the former complexes are less stable. The ligands already described are pyridine[9a–c], 4-vinyl-pyridine [9d], 4-formylpyridine[9e], 4-acetylpyridine[9f], 4-methylpyridine[9g].

Scheme 5. Complexation of pyridine derivatives. Reagents and conditions: i) 1 equiv BF$_3$Et$_2$O, THF, RT, 4 h.
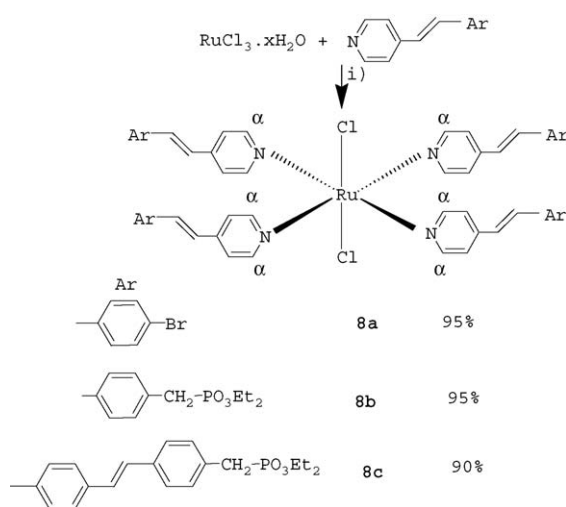
Scheme 6. Synthesis of Ru complexes. Reagents and conditions: i) EtOH, H$_2$O, reflux.

We decided to check the complexation of π-conjugated molecules **3**, **2a**, **4b** (Scheme 6), starting from RuCl$_3$ in refluxing EtOH, H$_2$O [9d].

The complexes **8** were analysed by ^{1}H and ^{13}C NMR, and mass spectrometry (Table 1).

^{1}H NMR showed only one signal for the α proton of the complexes **8a–c**, in agreement with a trans geometry of the complexes (a cis geometry would have given two signals). ^{13}C NMR showed a downfield-shielded signal at 158 ppm for the α carbons of compounds **8a–c** compared with the precursors whose α carbons presented a signal at 150 ppm. This shield confirmed the complexation. Mass spectra showed the molecular peak for all the complexes with fragments corresponding to the loss of 1 to 3 ligands. Thus the presence of vinylene–phenylene groups did not perturb the complexation of the pyridine moiety with Ru and the complexes were obtained in excellent yield. Data concerning optical properties of selected π-conjugated pyridine compounds **2a**, **2c**, **4a** are listed in Table 2.

Table 1
NMR and Mass data for ruthenium complexes **8**

Complexes	Mass Fab+	^{1}H NMR Hα	^{13}C NMR Cα
8a	1210 (MH+), 950, 691, 260	8.63, d $^3J = 5.9$ Hz	157.6
8b	1497 (MH+), 1167, 835, 332	8.59, d $^3J = 6.9$ Hz	158.1
8c	1905 (MH+), 1473, 434	8.61, d $^3J = 6.1$ Hz	158.1

Table 2
Optical data for compounds **2a**, **2c**, **4a**, (THF 10^{-4} M)

Compound	UV spectroscopy	Fluorescence	
	λ/nm (ϵ M^{-1}.cm^{-1})	Ex (nm)	Em λ_{max} (nm)
2a	311 (3090)	280	345
2c	322 (18500)	290	355
4a	356 (45700)	300	437

All the spectra were recorded at 10^{-4}M in THF. The UV characteristic π–π* band of the derivatives and the fluorescence λ_{max} emission are both red-shifted by increasing conjugation. After methylation or complexation with BF$_3$, the absorption and emission spectra of compounds **6a** and **7a** were very similar (Figs. 1 and 2). Comparing with precursor **2a**, an important bathochromic shift to 351 nm was observed for the π–π* band of the two compounds. These shifts could be explained by a quaternarization of the nitrogen and hyperconjugation effect with the methyl group [10], and by an electronic delocalisation on the boron atom [7], respectively. The λ_{max} fluorescence emission was thus observed at 435 and 432 nm, respectively. With the
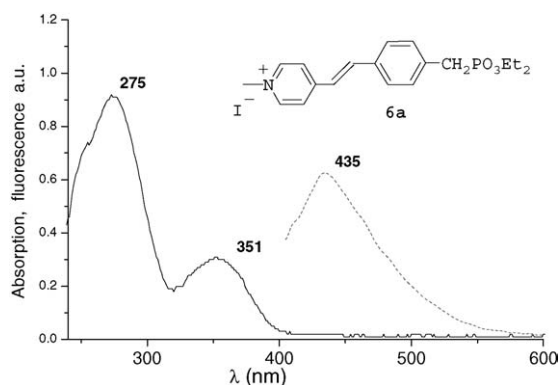

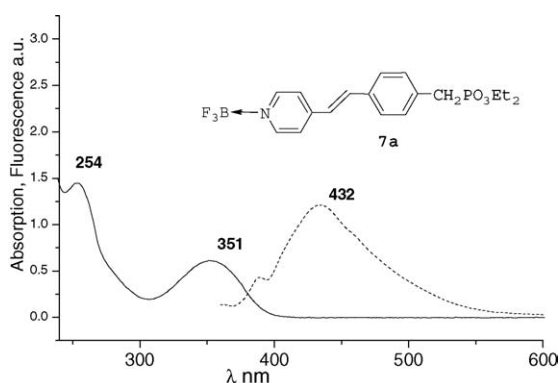Fig. 1. UV and fluorescence (ex 330 nm) of compound **6a**.

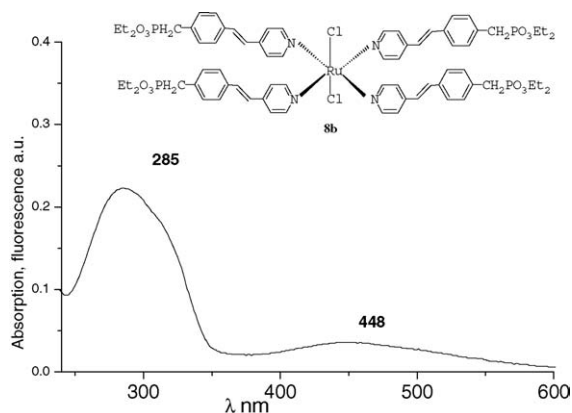Fig. 2. UV and fluorescence (ex 330 nm) of compound **7a**.

Fig. 3. UV of complex **8b**.

ruthenium complex **8b**, the absorption spectrum was different from that of compounds **6a** and **7a** (Fig. 3). It presented the π–π* band at 285 nm and a new band at 448 nm that characterizes the metal–ligand charge transfer [8d]. We did not observe significant fluorescence of compound **8b** compared with **6a** and **7a**. Indeed, ruthenium–bpyridine complexes with trans halogen ligands are known to display practically no emission at RT due to very short-lived excited states, as these excited states are rapidly desactivated by non-radiative processes [11].

In conclusion, the Heck reaction was very efficient for the synthesis of π-conjugated phosphonates derivatives of pyridine, in trans configuration. The pyridine moiety was reacted with MeI, BF$_3$, RuCl$_3$, and the phosphonate group did not interfere with those reactions, which is very important for further uses in material sciences. Work is in progress to graft these compounds at the surface of metal oxides and to study the optical properties of the resultant organic-inorganic hybrids.

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