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Synthesis and Properties of Novel Ditopic Polypyridine Ligands Bridged by One and Two Acetylenic Bonds

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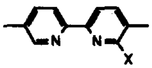
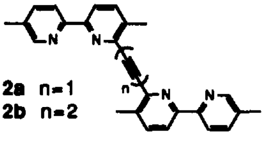
Abstract: Ethynyl substituted bipyridine chelates react with bromo or triflate functionalized bipyridine or terpyridine subunits, in the presence of catalytic amounts of $Pd^0(PPh_3)_4$ to yield, the new homo- and heteroditopic ethynyl bridge ligands **2a**, **4a**, **7a** and **8**. Self coupling of the ethynyl substituted bipyridine species in the presence of CuCl/TMEDA/O_2, yield the symmetric diethynyl bridge ligands **2b**, **4b** and **7b**.

Widespread interest in π-conjugated molecular framework is a consequence of the possibility that these materials may be used as molecular wires[1-3] and components in a wide range of optoelectronic devices[4-6]. As part of a project aimed towards the development of highly conjugated polypyridine chelates and organic radicals, we have recently developed the chemistry of aromatic polyimine ligands functionalized by one, two[7], three, four and six[8] trimethylsilyl(TMS) alkyne or terminal alkyne substituents. These molecules are of interest both in their own right and as precursors to extended conjugated arrays. They are also suitable building blocks for the synthesis of more elaborated homo- and heteroditopic ligands which might allow electronic communication between two metal centers.

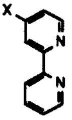
We here describe the use of palladium and copper catalysts for the synthesis of ethynyl or diethynyl bridged bipyridine ligands together with some metal complexes and spectroscopic properties. The synthesis of a new mixed bipyridine-terpyridine ligand **8** is also described.

The bromo substituted compounds **1a**[9] and **3a**[10-12] were prepared using adapted literature procedures, while the new compound **6a** was obtained as a side product during the synthesis of 4'-(4-bromophenyl)-2,2':6',2"-terpyridine[13]. The TMS-ethynyl substituted compounds **1b**, **3b**, and **6b** were synthesized in excellent yield by reaction of 1 to 2 equiv. of trimethylsilylacetylene with 1 equiv. of the bromo substituted compound, using $Pd^0(PPh_3)_4$ (6% in mole with respect to the substrate) as catalyst and excess $(i\text{-}Pr)_2NH$ or $n\text{-}PrNH_2$ (for compounds **6b**) as base. This synthetic procedure avoids the use of copper as a reducing agent which is necessary when $Pd^{II}(PPh_3)_2Cl_2$ was used as catalyst precursor and consequently copper decomplexation with cyanides as previously observed with strong Cu^I chelates is not needed[7]. Deprotection of the TMS substituted compounds with a mild base (K_2CO_3 or KF) gave the terminal alkyne compounds **1c**, **3c**, and **6c** in good yield.


1a X= Br
1b X= ≡—TMS
1c X= ≡—H


2a n=1
2b n=2

The ditopic ethynyl ligands **2a**, **4a** and **7a** were prepared typically by reaction of 1 equiv. of the bromo substituted species with 1 equiv. of the analogous ethynyl substituted compound in benzene (80°C), under argon, using $Pd^0(PPh_3)_4$. The reaction was monitored by TLC which showed that longer reaction times are needed compared to the previous trimethylsilylacetylene substitution owing to the stong π-acceptor character of the bipyridine part of the reagent which deactivates the ethynyl function. During the course of the reaction, the product precipitated. After disappearence of the alkyne, the solid was filtered off and purified by silicagel flash column chromatography giving the pure compounds in good yield as shown in Table 1.



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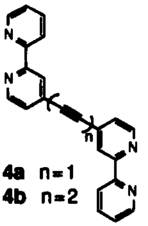
3b X= ≡—TMS
3c X= ≡—H



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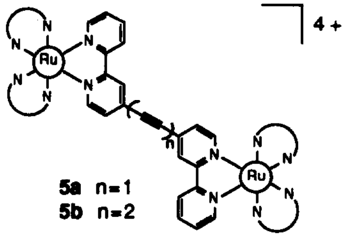
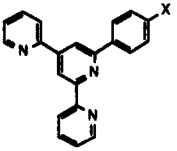
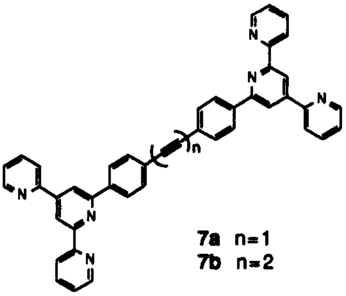
4b n=2



5a n=1
5b n=2



6a X= Br
6b X= ≡—TMS
6c X= ≡—H



7a n=1
7b n=2

Finally, the diethynyl ligands **2b**, **4b** and **7b** were typically prepared by self-coupling of 1 equiv. of the ethynyl substituted precursor **1c**, **3c** and **6c**, respectively, in the presence of 0.5 equiv. CuCl and 0.5 equiv. N,N,N',N'-tetramethylethylenediamine (TMEDA) in acetonitrile, at room temperature and in oxygen[14]. Work-up of the reaction mixture followed by flash chromatography yielded the pure compounds. All compounds were obtained as white powders and were characterized by ^{1}H, ^{13}C{^{1}H}-NMR, mass, electronic, infra-red or Raman spectroscopies and melting point. All data was consistent with the proposed structures (see Table 1). The observed carbon and proton chemical shifts for all the ligand precursor and for the ligands **2a**, **2b** and **8** are in good agreement with those reported for other ethynylated derivatives[15,16].

Due to their poor solubility, ^{13}C spectra of ligands **4a**, **4b**, **7a** and **7b** were not recorded. Hence ^{13}C spectra were recorded only on the more soluble diruthenium(II) complexes. The non-symmetric compounds are infra-red active whereas the ditopic ligands are not. However, a Raman vibration is observed in most of these compounds (Table 1). The values observed are consistent with those reported for related compounds[17].

The synthetic method described here also allows the straightforward synthesis of a new heteroditopic ligand (**8** in Scheme 2) which could be used as building block for the specific synthesis of heterodinuclear complexes. Indeed, coordination of the bipyridine part of the molecule has been achieved using Ru(bpy)$_2$Cl$_2$.2H$_2$O[18] as metal precursor (complex **9**).

Table 1: Selective data for compounds depicted in Scheme 1 and 2

Product	Isolated yield (%)	Melting point(°C)	IR/ Raman(R) (cm^{-1}) a)	^{1}H-NMR (ppm) b)	$^{13}C\{^1H\}$-NMR (ppm) c)	Mass d) spectra
1b	76 e)	92/93	2155	0.30	- 0.07 98.30/102.84	280
1c	97	128/129	3305/2110	3.43	82.21/80.45	208
2a	52	214/215	2204/2218(R)	-	90.48	390
2b	60	244/246	2217(R)	-	76.19/81.26	414
3b	97	60/61	2158	0.22	- 0.37 99.64/102.25	252
3c	77	75/76	3324/2106	3.30	81.16/81.67	180
4a	80	>270	not obs.	-	-	334
4b	98	>270	2223(R)	-	-	358
5a	76	-	2209(R)	-	93.11	1597(F)
5b	76	-	not obs.	-	79.84/81.39	1621(F)
6b	96	207/208	2154	0.30	-0.01 95.50/105.06	405
6c	86	171/173	3294/2108	3.20	78.32/83.70	333
7a	85	>270	not obs.	-	-	641(F)
7b	97	>270	not obs.	-	-	665(F)
8	75	198/199	not obs.	-	90.78/91.44	411
9	36	-	not obs.	-	89.65/95.45	970(F)

a) $\nu_{C\equiv C}$ for species **b** and **c** , and $\nu_{C\equiv CH}$ for species **c** , measured in KBr pellets (IR) or on pure product (R).

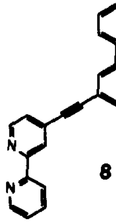
b) Chemical shifts for the TMS (species **b**) and for the terminal alkynes (species **c**) are reported relative to residual protiated solvent in $CDCl_3$ (7.25 ppm).

c) Chemical shifts for the C≡C (species **b**,**c** and complexes **5a**,**5b** and **9**) and for the C≡CH (species **c**) are reported relative to the solvent $CDCl_3$ (77.0 ppm) or CD_2Cl_2 (53.3 ppm) for **2b** or CD_3CN (118.2 and 0.3 ppm) for **5a**, **5b** and **9**.

d) Obtained by electron impact and corresponds to the molecular peak of the ligands (m/e) or by FAB^+(F) using meta-nitrobenzylalcohol as matrix and corresponds to [**4a**, $(Ru(bpy)_2)_2$, $3PF_6]^+$, [**4b**, $(Ru(bpy)_2)_2$, $3PF_6]^+$, [**8**, $Ru(bpy)_2$, $PF_6]^+$ for respectively **5a**, **5b** and **9**.

e) Obtained by addition of 20% CuI.

Further development of this work will be directed toward the synthesis of heterodinuclear complexes **10** and their use in new molecular electronic devices for long-range electron transfer and photoinduced charge separation.



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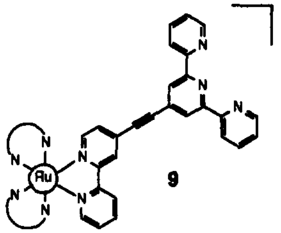

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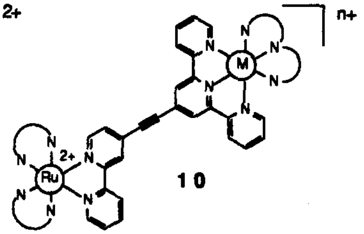

10

 for 2,2'-bipyridine

 for 2,2':6',2''-terpyridine

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