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Preparation of Novel Mixed Tritopic Oligopyridine Ligands Built with Chelating Spacers and Using Palladium(0) Catalysed Coupling Reactions

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Key Words: hybrid ligands; tritopic-ethynyl-chelates; Pd(0) catalysis; rigid rod-like Ru(II) complexes

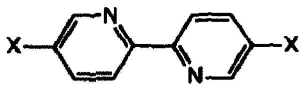
Abstract: The synthesis and characterization of tritopic ligands, obtained by connecting two terpyridines or two bipyridines with a bis-substituted-ethynyl-bipyridine or bis-substituted-ethynyl-phenanthroline spacer are described. Palladium(0) catalyses the coupling of the bis-ethynyl substituted central spacer with a bromo or a triflate functionalized bipyridine or terpyridine subunit. A novel trinuclear ruthenium (II) complex is also described.

Despite the tremendous research efforts invested in molecular chemistry, the control of long-range electron transfer and charge separation processes still constitutes one of the main challenges in the field of photochemistry and represents one of the keys to many theoretical and fundamental problems. Nanostructures of molecular-scales are interesting tools for information storage and transfer.[1] Due to their potential applications for optical communication, data storage, electro-optical signal processing, we recently focused our efforts on the substitution of 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 1,8-naphtyridine and 2,2':6',2"-terpyridine (terpy) with alkyne groups.[2-4] This provide us a facile entry into the field of molecular wires based on transition metal complexes with π-conjugated ligands. Oligopyridines functionalized with alkyne substituents have been used as building blocks in the synthesis of homo-[2-5] and hetero-ditopic[3] ligands, as well as in the preparation of rigid rod-like complexes of nanometric dimension.[5] We recently showed that in these complexes, electron delocalization over an extended π*-orbital strongly depends on the chemical nature of the spacer. An outstanding increase of the triplet lifetimes (i.e. 1000-fold) in binuclear Ru(II) complexes has been measured, compared to $[Ru(terpy)_2]^{2+}$, thanks to the ethynyl or diethynyl bridges.[6]

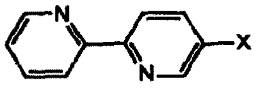
Continuing our synthetic work on this line, we expected that the extent of conjugation in rigid rod-like transition metal complexes might be tailored by introducing a variety of different spacers. In particular, the use of alkyne substituted chelating spacers of the bipyridine-type might offer a nice opportunity to study the electronic communication between two identical metals as a function of the nature and oxidation state of a third different metal complexed in the central site.

A ditopic bis-bipyridine-ethynyl-bicyclo[2,2,2]octane ligand, synthesized by a different approach has recently been reported.[7] However, rigid tritopic ligands have only been scarcely studied.[8-10]

In this communication, we wish to present our results on the synthesis of the hitherto unreported, mixed tritopic ligands **3** to **9**. Ligand precursors (5,5'-diethynyl-2,2'-bipyridine **1c** and 5-ethynyl-2,2'-bipyridine **2c**) were chosen, in a first step, as building blocks and prepared from the corresponding dibromo or monobromo substituted bipyridines, using the general synthetic method previously described[2,3] (**1b**, 76%; **1c**, 91%; **2b**, 88%; **2c**, 83%). Tritopic ligands were typically prepared on a half-gram scale by reaction of 5,5'-diethynyl-2,2'-bipyridine **1c** (1 equiv.) with 4'-[{(trifluoromethyl)sulfonyl}oxy]-2,2':6',2"-terpyridine (2 equiv.), in benzene, under argon (Schlenk techniques), using $Pd^0(PPh_3)_4$ (6 mol %) as catalyst precursor and $(i\text{-}Pr)_2NH$ as base.

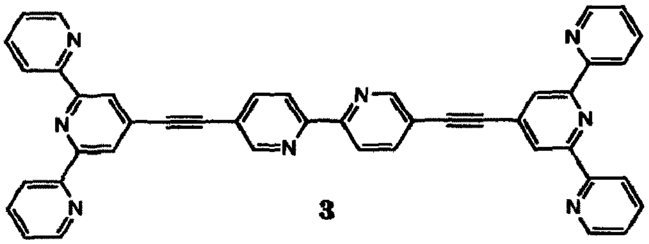


1a X = Br
1b X = $\equiv$—$Si(CH_3)_3$
1c X = $\equiv$—H



2a X = Br
2b X = $\equiv$—$Si(CH_3)_3$
2c X = $\equiv$—H

During the course of the reaction the desired ligand precipitate out from the reaction mixture. After 10 hrs. heating at 80 °C, the solid was filtered off, washed with water and dichloromethane and finally chromatographed. The pure ligands were obtained, in excellent yield, as white powders and characterised by classical techniques (NMR, IR, MS and elemental analysis).



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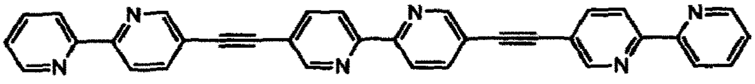

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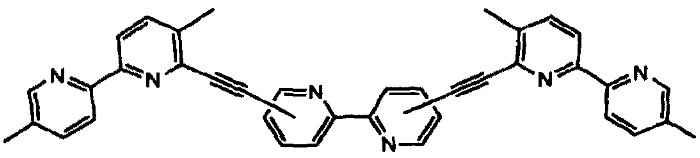
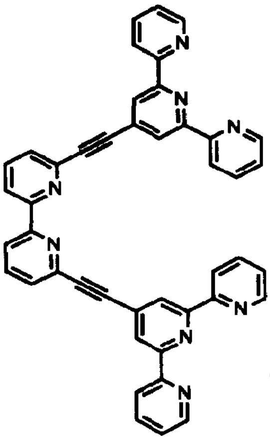


5 substituted in 5,5'-position
6 substituted in 6,6'-position
7 substituted in 4,4'-position

All data were consistent with the proposed structures (see Table for selected data, the full NMR data obtained for ligand **5** has been given in footnote c). Ligand **6** could independently be prepared by reaction of 5,5'-dimethyl-6-ethynyl-2,2'-bipyridine (2 equiv.) with 6,6'-dibromo-2,2'-bipyridine (1 equiv.) (77% yield) or by reacting 6,6'-diethynyl-2,2'-bipyridine (1 equiv.) with 5,5'-dimethyl-6-bromo-2,2'-bipy (2 equiv.), a better yield being obtained in this latter case (93% yield).



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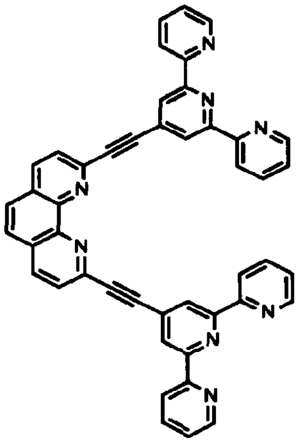

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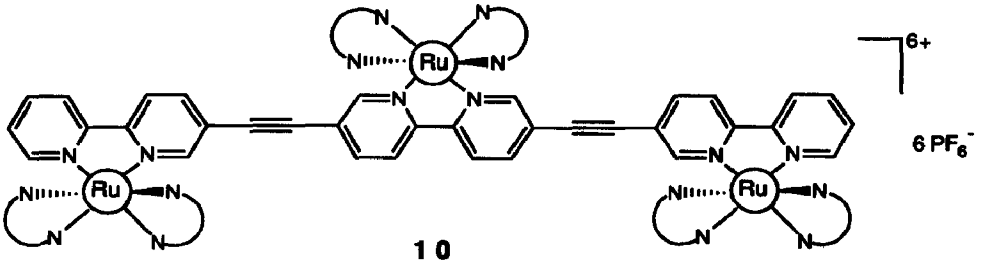
Table: Selective data for compounds depicted in Schemes

Starting ethynyl compound	Starting bromo/triflate compound	Product	Isolated yield (%)	Mp (°C)	IR (cm^{-1}) a)	Mass spectra b)
5,5'-diethynyl-2,2'-bpy	4'-triflate-2,2':6',2"-terpy[11]	3	67	$>290_{dec}$	2218	667
5-ethynyl-2,2'-bpy	5,5'-dibromo-2,2'-bpy[12]	4	67	>300	not obs.	513
5,5'-dimethyl-6-ethynyl-2,2'-bpy[2]	5,5'-dibromo-2,2'-bpy	5 c)	87	264/5	2220	569
5,5'-dimethyl-6-ethynyl-2,2'-bpy	6,6'-dibromo-2,2'-bpy[13]	6	77	277/8	2216	569
6,6'-diethynyl-2,2'-bpy[2]	5,5'-dimethyl-6-bromo-2,2'-bipy[14]	6	93	277/8	2216	569
5,5'-dimethyl-6-ethynyl-2,2'-bpy	4,4'-dibromo-2,2'-bpy[15]	7	74	241/2	2208	569
6,6'-diethynyl-2,2'-bpy	4'-triflate-2,2':6',2"-terpy	8	65	>300	2215	667
4'-ethynyl-2,2':6',2"-terpy[5]	2,9-dichloro-1,10-phen[16]	9	75	>300	not obs.	691
4	$[Ru(bpy)_2]Cl_2 \cdot 2H_2O$[17]	10 d)	83	>300	not obs.	291.6 e)

a) $\nu_{C\equiv C}$ stretching vibrations, measured in KBr pellets; b) obtained by FAB$^+$ using meta-nitrobenzylalcohol as matrix and correspond to $[M+H]^+$; c) ^1H NMR ($CDCl_3$) δ in ppm 8.94 (d, 2H, $^4J = 0.9$ Hz), 8.48 (m, 4H), 8.38 (d, 2H, $^3J = 8.0$ Hz), 8.30 (d, 2H, $^3J = 8.1$ Hz), 8.06 (dd, 2H, $^3J = 8.1$ Hz, $^4J = 1.8$ Hz), 7.7 (d, 2H, $^3J = 8.1$ Hz), 7.63 (dd, 2H, $^3J = 9.0$ Hz, $^4J = 2.0$ Hz), 2.60 (*s*, 6H), 2.40 (*s*, 6H); $^{13}C\{^1H\}$ NMR (*D_2O + DCl 20%* + t-BuOH) δ in ppm 155.0 to 121.9 aromatic carbon, 93.69 ($CC_{ethynyl}$), 87.81 ($CC_{ethynyl}$), 19.24 (CH_3), 18.25 (CH_3); d) obtained as a diastereoisomeric mixture ($\lambda_{max} = 374$ nm, $\varepsilon = 95000$ $M^{-1}cm^{-1}$, $\lambda_{max} = 470$ nm, $\varepsilon = 39000$ $M^{-1}cm^{-1}$; e) m/z value (z = 6), obtained by electrospray mass spectroscopy in CH_3CN using grammicidin as internal standard and correspond so $[L\{Ru(bpy)_2\}_3]^{6+}$ where L = ligand 4.

Finally, as preliminary complexation studies we prepared the rigid rod-like trinuclear ruthenium(II) complex $[4\{Ru(bpy)_2\}_3](PF_6)_6$ **10**, in which an electronic communication in the excited state is expected. Preliminary fluorescence studies show a broad and intense luminescence at 715 nm when excited in the metal to ligand charge transfer absorption band ($\lambda_{exc.}$ 470 nm, 3×10^{-5}M of complex **10**, in CH_3CN solution at room temperature). Further work is directed towards the study of the photophysical properties of this novel complex as well as to the metal-induced self-organization of these rigid polytopic ligands in order to generate large rings, ladder complexes, helicoidal and/or polymeric multi-redox materials.



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