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Stepwise Construction of Polyalkyne Modules Grafted on Oligopyridine Synthons

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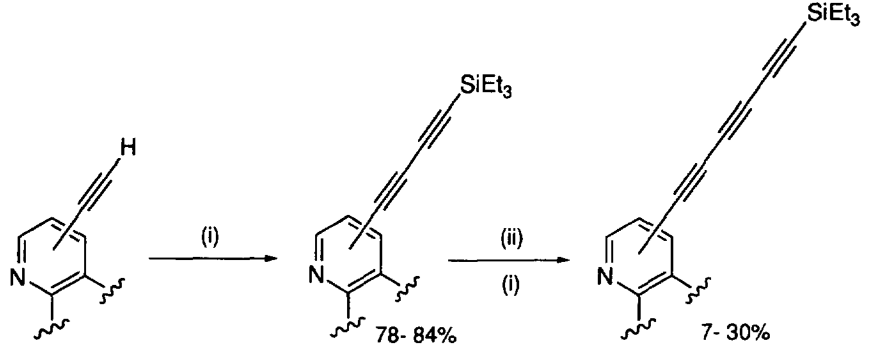
Abstract: We report on the stepwise homologation of the ethynyl substituted pyridine, 2,2'-bipyridine, and 2,2':6',6"-terpyridine with bromoethynyl(triethyl)silane using the Chodkiewicz method. Chelating ligands bearing one or two triethylsilylbutadiyne, one or two triethylsilylhexatriyne subunits have been synthesized and fully characterized.

An important feature of photoinduced triplet energy and/or electron transfer is the choice of molecules displaying: (i) a rigid structure, (ii) the presence of extended π-π^* orbitals, (iii) various but defined lenght between the two centers in interaction, and (iv) a good photochemical stability. Archetypal examples are molecules based on alkyne substituted oligopyridines, which might also have potential applications in material, molecular and polymer science.[1] We have recently demonstrated that alkyne modules behaves as useful spacer allowing very efficient electronic coupling between two metal centers.[2] A quantitative and very fast triplet energy transfer from a Ru to a Os termini through bonds has been recently measured.[3] Attenuation factors as low as 0.04 Å^{-1} (for electron tunnelling) and 0.17 Å^{-1} (for energy transfer) have been calculated when increasing the length of the spacer from one triple bond to two in supramolecular complexes.[4]



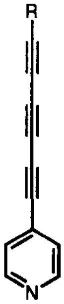
(i) $BrC{\equiv}CSiEt_3$, CuCl 7%, THF or CH_2Cl_2, $NH_2OH.HCl$, n-$PrNH_2$ excess, RT
(ii) NaOH, CH_3OH/THF or CH_2Cl_2, RT

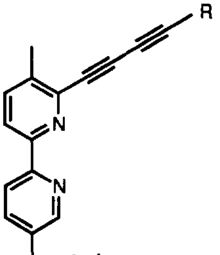
Scheme 1

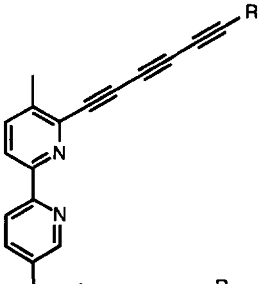
We have previously developed a general procedure for the large scale preparation of mono- or disubstituted oligopyridine with monoyne groups.[5] Some of these ligands have also been proved to have valuable complexation properties for the selective stabilization of *anti*-isomer of (η^3-allyl)palladium complexes, which are key intermediate in the stereoselective preparation of useful synthons (e.g. *Z*-alkenes).[6] In an effort to further explore the synthetic versatility of alkyne substituted oligopyridines, we have recently prepared a new class of redox- and photoactive *metallo-synthons* in which formation of platinum σ-acetylide bonds allows control of the stereochemistry of the complex.[7] Such complexes have been shown to be very useful for the switching of the energy-transfer mechanism from rapid through bond-type to slow through space-type.[8]

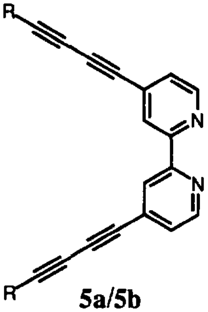
Continuing our investigations on tailored made topological ligands, we wish to report here the synthesis and characterization of a hitherto unreported variety of mono- or disubstituted oligopyridines grafted with triethylsilylbutadiyne, butadiyne and triethylsilylhexatriyne subunits.

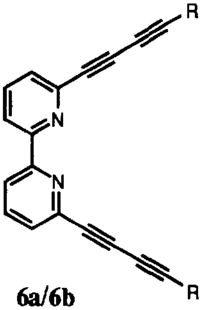

1a/1b

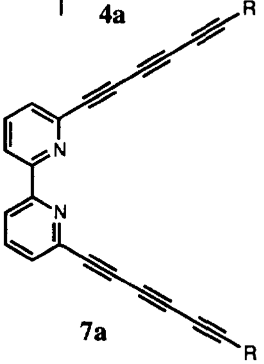

2a

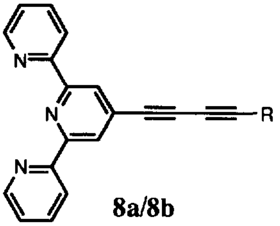

3a/3b

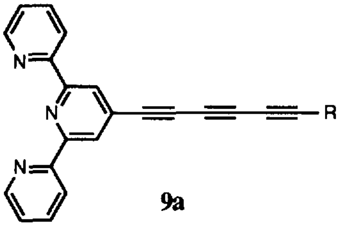

4a


5a/5b


6a/6b


7a


8a/8b


9a

a : R = -SiEt$_3$
b : R = H

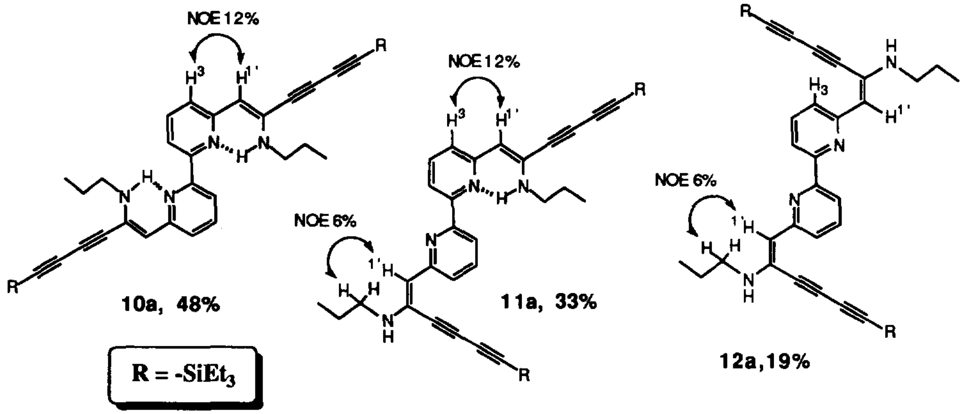
All new compounds were prepared according to Scheme 1. They were typically obtained by a Chodkiewicz coupling reaction[9] between the ethynyl substituted oligopyridines[5] and BrC≡CSiEt$_3$ (see ref. 10 for a typical preparative procedure). The reaction proceeds smoothly at RT, *exclusively in the presence of n-propylamine.* The pure ligands were obtained as white or grey powders and were characterized by ^1H, $^{13}C\{^1H\}$-NMR, mass, IR spectroscopy and C,H,N elemental analysis. All data were consistent with the proposed structures.

Table: Selected data for compounds **1a/b** to **9a**

Product	Isolated Yield (%)	IR ($\nu_{C\equiv C}$, cm^{-1}) a)	$^{13}C\{^1H\}$NMR δ, ppm b)	Mass spectrum c)
1a	82	2103	73.21/78.54/88.24/92.09	241[M]
1b	78	3290/2080	67.36/72.58/73.76/77.38	127[M]
2a	29	2110	60.01/69.01/73.79 78.17/88.63/89.75	265[M]
3a	84	2110	74.53/76.95/88.75/90.97	346[M]
3b	90	3167/2053	67.83/73.01/73.59/75.80	233[M + H]
4a	30	2063	61.04/68.12/74.71 77.02/88.93/90.81	371[M + H]$^+$
5a	80	2100	72.97/78.60/87.98/91.64	480[M]
5b	70	3196/2059	73.73/77.60/79.38 d)	252[M]
6a	84	2100	73.82/74.75/88.38/90.34	480[M]
6b	98	3244/2059	73.73/77.60/79.37 d)	252[M]
7a	7	2073	60.39/67.81/73.77 75.14/88.25/88.71	529[M + H]$^+$
8a	54	2102	74.12/78.29/88.56/91.77	396[M + H]$^+$
8b	93	3210/2065	64.90/72.06/78.56/99.95(CH)	282[M + H]$^+$
9a	25	2110	60.27/68.36/73.46 78.33/88.93/90.22	420[M + H]$^+$

a) $\nu_{C\equiv CH}$ and $\nu_{C\equiv C}$ stretching vibrations, measured in KBr pellets or CCl_4 solution; b) Chemical shifts for the C≡C (species **a** and **b**) and for the C≡CH (species **b**) are reported relative to the solvent $CDCl_3$ (77.0 ppm) or d_8-THF (68.6 and 26.7 ppm) for **5b** and **6b**; c) obtained by electronic impact mass spectroscopy and correspond to the molecular m/e peak [M] or by FAB^+ using meta-nitrobenzylalcohol as matrix and correspond to m/z $[M+H]^+$; d) one peak is superimposed with d_8-THF.

The triethylsilyl substituent was chosen, in our case, as the protective group in order to avoid cleavage during the reaction. The use of trialkylsilyl group as a protective method in the Glaser or Chodkiewicz oxidative coupling of acetylenes has previously been reported.[11] The protective triethylsilyl group is removed quantitatively within minutes in aqueous methanolic alkali. Formation of the diynes is further confirmed by the presence, in the ^{13}C NMR spectra of four C≡C signals in the range of 73.0-92.1 ppm. The strong shielding observed (ca. 20 ppm) versus the parent monoyne derivatives[5] is consistent with a delocalized π-π* framework. A similar effect is observed for the stretching vibration of the C≡C bond (frequency decrease of ca. 60 cm^{-1}). The terminal-diynes were treated, as described above, with $BrC\equiv CSiEt_3$ in the presence of CuCl, $NH_2OH.HCl$ and *n*-propylamine. The reaction proceeds slowly and after work-up afforded the corresponding triethylsilyl protected triyne in a modest yield (Table). Here again, the products are best characterized by their ^{13}C NMR spectra which exhibit six C≡C signals in the range of 60.0-90.8 ppm. The low yield obtained during the grafting of the third alkyne is due to fast reaction of the triyne with excess *n*-propylamine. Surprisingly, **7a** is quantitatively transformed into a mixture of three new products, as a result of nucleophilic attack of the amine to each triple bond directly linked to the pyridine rings (Scheme 2). These enamines are formulated with the amino-group at *C-2* of the side-chain, as would be expected from polarisation of a polyacetylene chain conjugated with a pyridine ring. The relative stability of the enamines is presumably due to the electron attracting effect of the ring. The molecular structures of **10a**, **11a**, **12a** were unambigously established by high resolution NMR spectroscopy (500 MHz), NOE experiments and IR spectroscopy. The presence of the NH group was clearly demonstrated by proton exchange with D_2O, and hydrogen bonding was further confirmed by the observation of two NH stretching vibrations at 3379 (free NH) and 3155 cm^{-1} (hydrogen bonded NH), in the IR spectra.[12] FAB measurement is in excellent agreement with the postulated formulas (647.3 $[M+H]^+$). Nucleophilic addition of amines on triple bonds has only rarely been observed and discussed in the literature.[13]



Scheme 2

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10. Typical procedure for the preparation of 6,6'-bis(4-triethylsilyl-1,3-butadiyne)-2,2'-biyridine **6a**. 6,6'-bis(ethynyl)-2,2'-bipyridine (0.100 g, 0.489 mmol) was dissolved in dichloromethane (5 mL). After addition of CuCl (0.006 g, 0.06 mmol) $NH_2OH.HCl$ (0.018g, 0.26 mmol), *n*-propylamine (1.5 mL) was slowly added via seringe. Then, 1-bromo-2-triethylsilylacetylene (0.40 g, 1.82 mmol) in dichloromethane (1 mL) was dropwise added at 0°C. After 3 h, the reaction mixture was powered into water (50 mL) and the organic product extracted with dichloromethane (3 x 20 mL). The organic layer was dried over sodium sulfate and decolorated by charcoal. After filtration on celite and evaporation of the solvent, the crude was chromatographied on flash silica gel (hexane/dichloromethane 4/1) to give 0.150 g of a clear brown cristallin product (84%) ; mp = 168/9°C; IR (CCl_4, cm^{-1}) 2960 (s), 2905 (s), 2870 (s), 2100 (s, $\nu_{C\equiv C}$), 1550 (br), 1445 (s), 1425 (s), 1230 (m), 1105 (w), 1040 (s), 1015 (s) ; ^1H-NMR ($CDCl_3$) δ 0.71 (q, 6H, $Si(C\underline{H_2}CH_3)_3$, $^3J = 8$ Hz), 1.03 (t, 9H, $Si(CH_2C\underline{H_3})_3$, $^3J = 8$ Hz), 7.51 (dd, 1H, $^3J = 7.6$ Hz, $^4J = 0.9$ Hz) ; 7.78 (t, 1H, $^3J = 7.6$ Hz, arom.), 8.43 (dd, 1H, $^3J = 7.6$ Hz, $^4J = 0.9$Hz) ; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 4.10 ($Si(\underline{C}H_2CH_3)_3$), 7.31 $Si(CH_2\underline{C}H_3)_3$), 73.82 ($C\equiv C$), 74.75 ($C\equiv C$), 88.38 ($C\equiv C$), 90.34 ($C\equiv C$), 121.39 (CH), 128.48 (CH), 137.07 (CH), 141.19 (CC), 155.69 5 (CC) ; EI/MS m/e (%) 480 (M, 85), 451 ($M-C_2H_5$, 100), 422 ($M-2C_2H_5$, 15). Anal. Calc. for $C_{30}H_{36}N_2Si_2$ ($M_r = 480.806$); C, 74.94; H, 7.55; N, 5.83. Found C, 74.77; H, 7.32; N, 5.76.
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