4,4'-Disubstituted 2,2'-Bipyridines for the Design of Push-Pull Ligands

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Starting from 4,4'-dimethyl-2,2'-bipyridine, five new 2,2'-bipyridines symmetrically disubstituted in the 4,4'-positions with either terminal alkenyl, (trimethylsilyl)aryl- or (trimethylsilyl)alkynyl groups, have been synthesized and structurally characterized.

Key words: 4,4'-Disubstituted 2,2'-Bipyridines, X-Ray Crystallography, ^{1}H and ^{13}C NMR Spectroscopy

Introduction

Since its first description at the end of the nineteenth century [1], 2,2'-bipyridine has been extensively used as ligand for the complexation of metal centres. Today, it is even one of the most widely used chelate systems in coordination chemistry and in recent years has also become a very popular ligand in supramolecular and macromolecular chemistry [2, 3]. The success of 2,2'-bipyridine ligands is not only due to their useful electrochemical behaviour and variable photophysical and photooptical properties [4, 5], but also to their ease of derivatization. During the last 20 years a large number of new and improved synthetic procedures for 2,2'-bipyridine derivatives have been developed, the most common of which were recently reviewed by Newkome and Schubert [6]. Of particular interest are 2,2'-bipyridines symmetrically substituted in the 4- and 4'- positions of the heteroaromatic framework. A very convenient synthetic route for such derivatives is the deprotonation of 4,4'-dimethyl-2,2'-bipyridine **1** to its dilithium salt **2**, and reaction of **2** with alkyl halides [7] or aldehydes [8] (Scheme 1). If the latter reaction is followed by dehydratisation, derivatives with extended π systems are accessible. A variety of conjugated 4,4'-bis(styryl)-2,2'-bipyridines have been described by Bozec *et al*. [9, 10] who were interested in the potential of this class of ligands for the development of nonlinear optical devices [11].

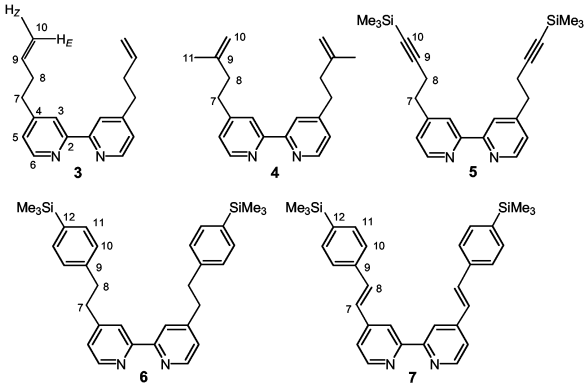
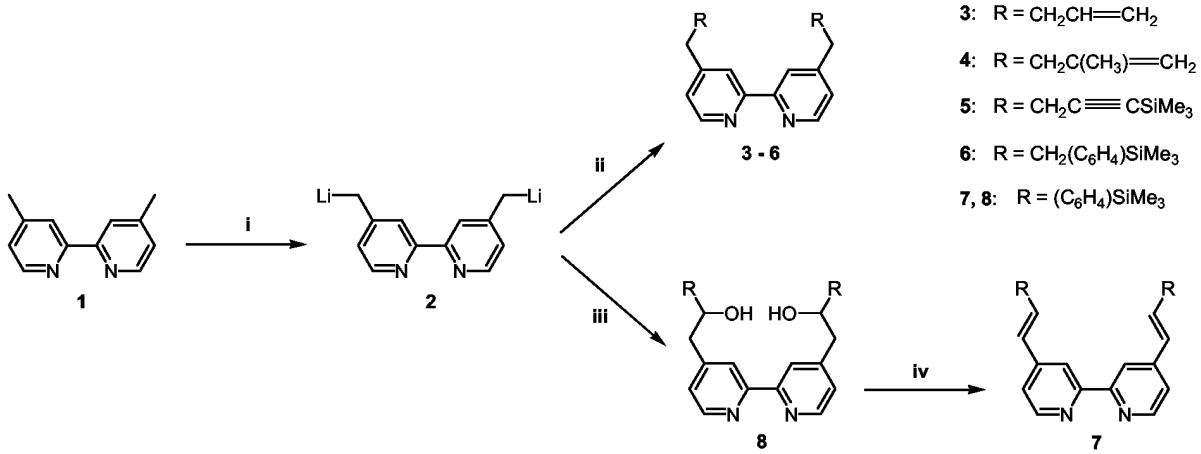


Fig. 1. 4,4'-disubstituted 2,2'-bipyridines **3** – **7** as precursors of novel push-pull ligands.

In contrast to the well established chemistry of the transition metal complexes of 2,2'-bipyridine, less work has been carried out on the corresponding main group chelates [12, 13]. We have long been interested in 2,2'-bipyridylboronium cations since they are related to the organic electron acceptor Diquat and behave as fully reversible two-electron redox systems [13]. In recent years we prepared various complexes in which this electron acceptor unit was attached to an electron-rich ferrocene donor. These ferrocenyl 2,2'-bipyridylboronium cations turned out to possess very interesting electrochemical and photophysical properties [14 – 18]. We are now planning to extend our studies to classical Werner type complexes. In this context, push-pull ligands featuring Lewis basic



Scheme 1. Synthesis of 4,4'-disubstituted 2,2'-bipyridines **3** – **7**. i: +LDA, THF, 0 °C; ii: +RBr, THF, 0 °C; iii: +RCHO, THF, 0 °C; iv: HOAc / Ac_2O, reflux temperature.

2,2'-bipyridyl binding sites as well as Lewis acidic boryl substituents are promising target molecules. However, the problem arises that such difunctional ligands tend to self-aggregate *via* the formation of intra- or intermolecular boron-nitrogen adducts. Herein we present the 2,2'-bipyridine derivatives **3** – **7** (Fig. 1) which offer the possibility to circumvent the problem of ligand self-aggregation.

Compounds **3** – **7** can be regarded as precursors of push-pull ligands as they consist of a 2,2'-bipyridyl donor moiety together with different types of functional substituents known to be easily convertible into boryl groups under mild reaction conditions. If the transition metal-2,2'-bipyridyl complex is formed first and the boryl group introduced subsequently, self-aggregation should no longer be an issue because the metal ion is protecting the nitrogen donors. In the case of ligands **3** and **4** the key functional group is a terminal olefin which may be borylated *via* hydroboration [19, 20]. **3** represents the least complex parent compound whereas **4** was synthesized to enhance the steric bulk at the β-carbon atom and thereby increase the regioselectivity of the hydroboration. Trimethylsilyl groups attached to sp or sp^2 hybridised carbon atoms, like in molecules **5** – **7**, can be exchanged easily for dihaloboryl substituents upon treatment with boron trichloride [21] or boron tribromide [22, 23].

For transition metal complexes bearing Lewis acidic boron atoms in their ligand sphere, a variety of applications can be envisaged. Reaction with a polymeric Lewis base offers the possibility to reversibly immobilize the borylated 2,2'-bipyridyl complexes on a solid support which may lead to the design of new catalyst systems. Moreover, addition of difunctional Lewis bases or application of a Suzuki-type reaction protocol provide routes to link 2,2'-bipyridyl complexes of different metal ions together in order to create oligometallic assemblies. The covalent linkage of different types of metal complexes is an important research field in contemporary coordination chemistry [24 – 27]. For example, Williams and Arm recently described the synthesis of trinuclear bipyridyl ruthenium complexes by Suzuki cross coupling of boronic acid-substituted mononuclear complexes with bromo-substituted complexes [24].

Syntheses

4,4'-Dimethyl-2,2'-bipyridine **1** was deprotonated at both its methyl groups by treatment with two equivalents of lithium diisopropylamide (LDA). Reaction of the resulting dilithium salt **2** [7, 28] with allyl bromide, methallyl bromide, 3-(trimethylsilyl)propargyl bromide and *p*-(trimethylsilyl)benzyl bromide gave the desired species **3** – **6** (Scheme 1, Fig. 1) in good to moderate yields.

For the synthesis of **7**, the dilithium salt **2** was first treated with *p*-(trimethylsilyl)benzaldehyde [29, 30]. Subsequently, water was eliminated from the resulting dialcohol **8** to generate the 4,4'-bis(styryl) derivate **7** (Scheme 1). Dehydratisation was achieved in a mixture of glacial acetic acid and acetic anhydride at reflux temperature following a procedure by Grennberg *et al.* [31]. Note that refluxing a toluene solution of **8** together with catalytic amounts of pyridinium *p*-tolu-

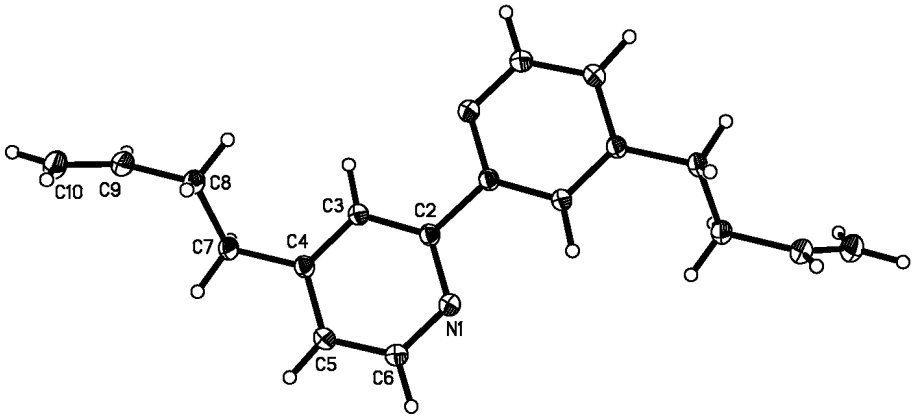


Fig. 2. ORTEP drawing of compound **3** in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

enesulfonic acid in a Dean Stark apparatus [9] did not give the desired product.

NMR Spectroscopy

The ligands **3**–**7** were characterized by ^{1}H, ^{13}C and (where possible) ^{29}Si NMR spectroscopy using d_1-chloroform as solvent. For the complete assignment of the resonances, H,H-COSY, HSQC and HMBC correlation spectroscopy experiments were performed. The numbering scheme for molecules **3**–**7** is given in Fig. 1.

In the case of **3**–**6**, the ^{1}H NMR spectra show very similar chemical shift values for the 4,4'-disubstitued 2,2'-bipyridyl moiety with the H-3 and H-6 signals significantly deshielded with respect to the resonance of H-5. Hydrogen atom H-6 of compound **3**, for example, gives rise to a doublet at 8.54 ppm ($^{3}J = 4.9$ Hz), the resonance of H-3 appears as a broad signal at 8.23 ppm (^{4}J not resolved), and the chemical shift of H-5 is 7.11 ppm (dd, $^{3}J = 4.9$ Hz, $^{4}J = 1.2$ Hz). The 2,2'-bipyridyl proton signals of **7** appear in the same relative order as in **3**–**6** but are all shifted to lower field [$\delta(^{1}\mathrm{H}) = 8.66$ (H-6), 8.54 (H-3), 7.39 (H-5)]. It is noteworthy that the coupling constant between H-7 and H-8 of **7** [$\delta(^{1}\mathrm{H}) = 7.15$ (H-7), 7.45 (H-8)] has a value of 16.3 Hz indicating the double bond to possess a *trans* configuration.

The ^{13}C NMR resonances of the 2,2'-bipyridyl fragment of **3** appear at 156.0 (C-2), 151.8 (C-4), 149.0 (C-6), 123.9 (C-5), and 121.2 ppm (C-3). The same sequence of ^{13}C NMR resonances is observed for the derivatives **4**–**6**. In the case of **7**, however, the C-4 atom [$\delta(^{13}\mathrm{C}) = 145.7$ ppm] is significantly more shielded than in **4**–**6** and thus found at higher field than the C-6 resonance [$\delta(^{13}\mathrm{C}) = 149.5$ ppm]. Signals

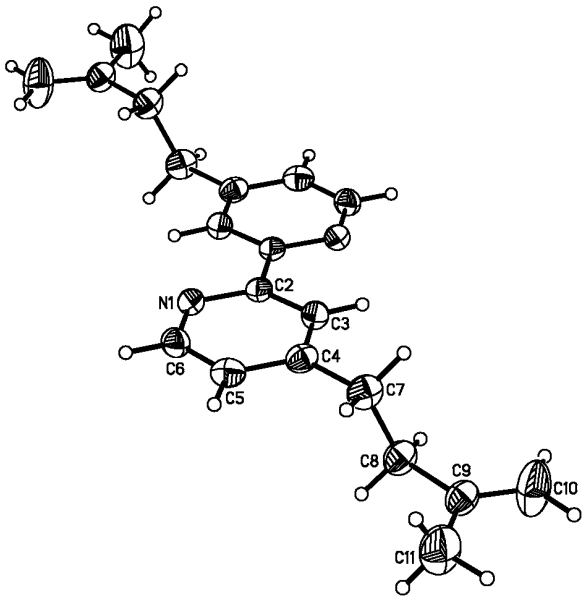


Fig. 3. ORTEP drawing of compound **4** in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

at 105.5 (C-9) and 86.2 ppm (C-10) in the ^{13}C NMR spectrum of **5** clearly prove C-9 and C-10 to be connected by a triple bond.

The ^{29}Si NMR chemical shifts of **5**, **6**, and **7** are observed at −18.5, −3.9, and −3.8 ppm, respectively. We attribute the pronounced upfield shift of the ^{29}Si NMR resonance of **5** to magnetic anisotropy effects caused by the alkynyl functionality.

X-ray Crystallography

ORTEP plots of **3** (monoclinic, $P2_1/n$), **4** (monoclinic, $P2_1/c$), **5** (triclinic, $P\bar{1}$), **6** (monoclinic, $P2_1/c$) and **7** (monoclinic, Cc) are shown in Figures 2–6; se-

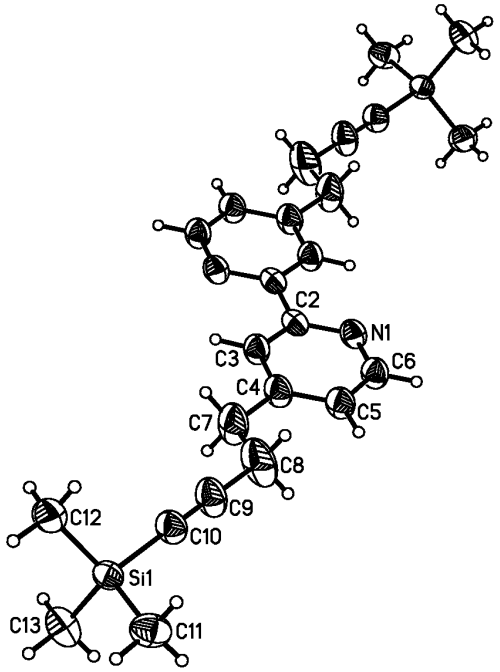


Fig. 4. ORTEP drawing of compound **5** in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

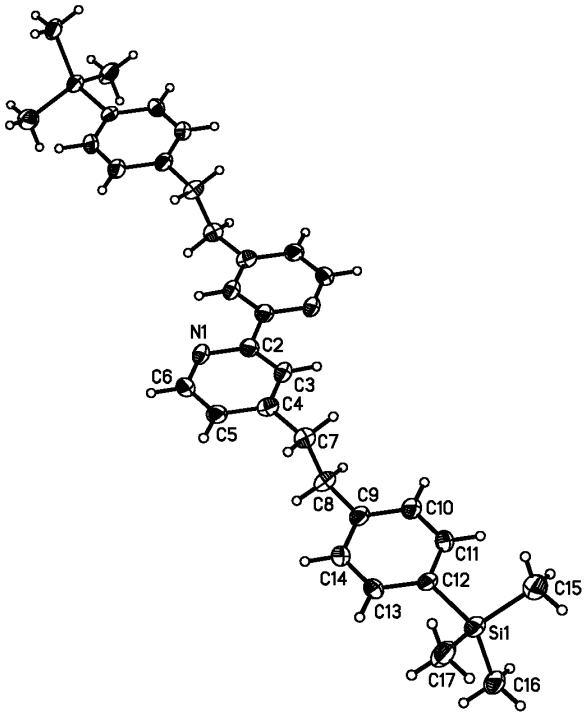


Fig. 5. ORTEP drawing of compound **6** in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

lected crystallographic data are given in Table 1. In all the molecules **3**–**7** the two pyridyl rings adopt the usual transoid arrangement of 2,2'-bipyridines [9]. All ligands except **7** possess a crystallographic centre of inversion located at the midpoint of the C2-C2' bond rendering the two pyridyl rings coplanar. For **7**, two molecules **7**A and **7**B are found in the asymmetric unit. Since corresponding bond lengths and angles of **7**A and **7**B are identical within the accuracy of the measurement, the average values are discussed here.

It is revealing to compare the torsion angle C3-C4-C7-C8 in molecules **3**–**7**, which is a measure of the relative conformation of the side chain with respect to the pyridyl rings. In the case of **3**, the angle possesses a value of $-44.9(1)^\circ$, while it is $76.2(2)^\circ$ in the closely related compound **4**. Obviously, introduction of a methyl group at the C9 carbon atom has a pronounced effect on the molecular conformation. A C3-C4-C7-C8 torsion angle of $-79.4(8)^\circ$ is also found in compound **6**. Accordingly, the planar methylethenyl group in **4** and the phenyl ring in **6** are both situated in planes almost parallel to the plane of the 2,2'-bipyridyl fragments. A different situation is observed for **5** (C3-C4-C7-C8 = $-170.4(5)^\circ$) where the rigid side chain is almost in plane with the 2,2'-bipyridyl moiety.

The structure analysis of **7** clearly proves the *trans*-configuration of the C7-C8 double bond, as already deduced from the ^3J coupling constant for H-7 and H-8 in the ^{1}H NMR spectrum of this compound. The C3-C4-C7-C8 and C4-C7-C8-C9 angles are close to 0° and 180°, respectively (see Table 3), indicating that an essentially planar arrangement with a fully conjugated π system is energetically most favourable.

The pyridyl rings of **7** are almost coplanar (dihedral angle between the two rings: 0.6°) and the phenyl rings are twisted by 13.9° and 15.2°, for C9/C10/C11/C12/C13/C14 and C9'/C10'/C11'/C12'/C13'/C14', respectively, out of the plane of the adjacent pyridyl ring. Although the molecules do not show any crystallographic symmetry, their geometry is close to the symmetry point group C_i.

Conclusion

We have synthesized and fully characterized five new 4,4'-disubstituted 2,2'-bipyridines bearing terminal alkenyl-, (trimethylsilyl)aryl- or (trimethylsilyl)alkynyl groups as side chains. These functional groups offer convenient ways for introducing boryl substituents into the system *via* hydroboration

Table 1. Selected crystallographic data for **3** – **7**.

	3	**4**	**5**	**6**	**7**
Formula	$C_{18}H_{20}N_2$	$C_{20}H_{24}N_2$	$C_{24}H_{32}N_2Si_2$	$C_{32}H_{40}N_2Si_2$	$C_{32}H_{36}N_2Si_2$
fw	264.36	292.41	404.70	508.84	504.81
Temp. [K]	147(2)	173(2)	173(2)	100(2)	100(2)
Radiation (Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal size [mm]	$0.6 \times 0.5 \times 0.28$	$0.25 \times 0.22 \times 0.11$	$0.34 \times 0.11 \times 0.08$	$0.38 \times 0.26 \times 0.02$	$0.33 \times 0.31 \times 0.14$
Crystal syst.	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	Cc
a [Å]	8.4592(10)	12.7984(18)	5.6769(10)	20.709(6)	13.5970(9)
b [Å]	7.7867(10)	6.1546(11)	10.6011(19)	6.2016(13)	13.6174(11)
c [Å]	11.1231(18)	11.3292(16)	11.4236(19)	11.251(3)	31.8188(19)
α [deg]	90	90	63.173(13)	90	90
β [deg]	103.700(6)	107.964(10)	80.290(14)	95.48(2)	100.358(5)
γ [deg]	90	90	83.932(15)	90	90
V [Å^3]	711.83(17)	848.9(2)	604.36(18)	1438.3(6)	5795.4(7)
Z	2	2	1	2	8
$D_{calcd.}$ [g cm^{-3}]	1.233	1.144	1.112	1.175	1.157
μ [mm^{-1}]	0.073	0.067	0.158	0.146	0.145
F(000)	284	316	218	548	2160
Θ Range for data collection [°]	2.74 to 34.24	3.63 to 25.64	3.87 to 25.67	3.64 to 25.72	2.13 to 25.96
No. of reflns. coll.	15307	9454	8098	12755	37020
No. of indep. reflns.	2684	1589	2243	2746	10739
R(int)	0.028	0.054	0.080	0.219	0.047
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.041, 0.113	0.041, 0.101	0.070, 0.186	0.092, 0.197	0.032, 0.069
*R*1, *wR*2 (all data)	0.047, 0.118	0.062, 0.106	0.081, 0.191	0.181, 0.231	0.049, 0.072
Largest diff. peak and hole [e Å^{-3}]	0.46, −0.17	0.18, −0.18	0.50, −0.39	0.89, −0.42	0.19, −0.24

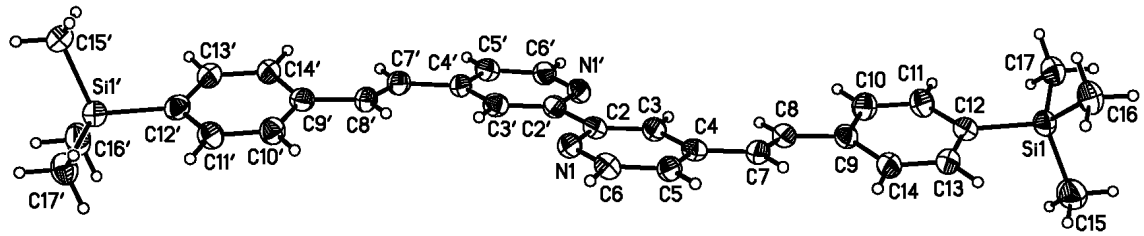


Fig. 6. ORTEP drawing of compound **7** in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Only one of the two crystallographically independent molecules is shown.

Table 2. Selected bond lengths [Å] and angles [°] for **3** – **7**.

	3	**4**	**5**	**6**	**7***
C2-C2'	1.492(1)	1.491(3)	1.496(7)	1.499(13)	1.490(3)
N1-C2	1.348(1)	1.345(2)	1.347(4)	1.355(7)	1.351(4)
C2-C3	1.396(1)	1.395(2)	1.387(5)	1.393(8)	1.385(3)
C3-C4	1.395(1)	1.388(2)	1.385(5)	1.388(9)	1.406(6)
C4-C5	1.395(1)	1.391(2)	1.392(5)	1.398(8)	1.393(7)
C5-C6	1.387(1)	1.378(2)	1.381(5)	1.386(8)	1.383(7)
C6-N1	1.339(1)	1.339(2)	1.332(5)	1.342(8)	1.340(3)
C3-C4-C7	122.6(1)	121.5(1)	119.6(3)	122.4(5)	123.2(3)
C5-C4-C7	120.3(1)	121.4(1)	123.1(3)	120.4(6)	120.2(3)
C4-C7-C8	114.9(1)	112.5(1)	117.2(4)	110.9(5)	125.6(3)
C7-C8-C9	111.4(1)	112.4(1)	114.4(4)	111.3(5)	127.2(2)

* Average values are listed for the two crystallographically independent molecules of **7**.

with $HBBr_2 \cdot SMe_2$ [20] or *via* silicon-boron exchange [21, 22]. Thus, our derivatives represent precursor molecules for the development of Lewis acid-base push-pull ligands in which the acidic boryl binding site can be attached after the nitrogen donors have coordinated to a metal centre. This synthetic strategy should circumvent the problem of ligand self aggregation. We are currently investigating the chemistry of 2,2'-bipyridines **3** – **7** in their chelate complexes and have first evidence that the introduction of boron works fine.

Experimental Section

General remarks

4,4'-Dimethyl-2,2'-bipyridine (**1**), allyl bromide, methallyl bromide, 3-(trimethylsilyl)propargyl bromide and lithium diisopropylamide (LDA) were purchased from either Aldrich

Table 3. Torsion angles [°] for **3** – **7**.

	3	**4**	**5**	**6**	**7**
C3-C4-C7-C8	−44.9(1)	76.2(2)	−170.4(5)	−79.4(8)	−0.1(4), −2.0(4), −2.1(4), 1.1(4)
C4-C7-C8-C9	174.0(1)	175.6(1)	−177.8(5)	−175.8(5)	178.7(3), 178.5(3), −177.7(3), −177.7(3)

or Acros. *p*-(Trimethylsilyl)benzyl bromide [32] and *p*-(trimethylsilyl)benzaldehyde [29, 30] were synthesized according to literature procedures and purified *via* vacuum distillation. All reactions were routinely performed under nitrogen using standard Schlenk techniques. THF was dried over sodium/benzophenone, $CDCl_3$ was dried using 4 Å molecular sieves prior to use. NMR spectra (^{1}H, ^{13}C, ^{29}Si) were recorded at ambient temperature on Bruker AMX 250, Bruker DPX 250 or Bruker Avance 400 spectrometers. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C) or external TMS (^{29}Si). Complete assignment of the ^{1}H and ^{13}C NMR signals was achieved by H,H-COSY, HSQC and HMBC 2D measurements. Elemental analyses were performed by the microanalytical laboratory of the University of Frankfurt.

X-ray crystallography

A single crystal of **3** was measured on a SIEMENS SMART diffractometer, crystals of **4** – **7** were measured on a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo-K_α radiation. The crystals were mounted directly into the coldstream of an Oxford Cryostream crystal cooling apparatus using perfluoropolyether oil. Essential crystallographic details are given in Table 1. Data were collected using the ω-scan technique. An empirical absorption correction was performed with the program SADABS [33] (**3**) or by using the MULABS option [34] in PLATON [35] (**5** – **7**).

The structures were solved by direct methods [36] and refined against F^2 using the SHELXL-97 program [37]. All atoms were refined with anisotropic displacement parameters. Hydrogen atoms were taken from a difference Fourier synthesis (**3**) and refined with individual isotropic thermal parameters or placed in idealized positions and allowed to ride on the relevant carbon atom (**4** – **7**). The absolute structure of **7** was determined by use of the Flack parameter [$x = +0.08(14)$]. The CCDC reference numbers are CCDC 264294 (**3**), CCDC 264293 (**4**), CCDC 264292 (**5**), CCDC 264291 (**6**) and CCDC 264290 (**7**) [38].

General synthetic procedure for compounds **3** – **6**, **8**

A solution of **1** in dry THF was treated with a 2 M solution of LDA in THF at 0 °C. The resulting dark orange mixture was stirred for 90 min at 0 °C and then added dropwise to a solution of the respective alkyl halide or aldehyde in dry THF, whereupon the colour of the dianion **2** disappeared. The remaining yellow reaction mixture was allowed to warm to ambient temperature before excess LDA was quenched with methanol. Isolation and purification of **3** – **6** were achieved as described below.

4,4'-Bis(but-3"-enyl)-2,2'-bipyridine **3**: **1** (1.84 g, 10.0 mmol), LDA (24.0 mmol), allyl bromide (3.03 g, 25.0 mmol). The reaction mixture was poured into water (50 ml) and extracted with diethyl ether (3 × 50 ml). The organic layers were combined, washed with water (20 ml) and dried over magnesium sulfate. Evaporation of the solvent yielded an orange oil. Upon storage, the oil gradually crystallized to give colourless needles which were triturated with a small volume of cold hexane. Yield: 2.24 g (85%). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 8.54$ (d, 2H, $^3J = 4.9$ Hz, H-6), 8.23 (n.r., 2H, H-3), 7.11 (dd, 2H, $^3J = 4.9$ Hz, $^4J = 1.2$ Hz, H-5), 5.82 (ddt, 2H, $^3J = 17.1$ Hz, 10.3 Hz, 6.7 Hz, H-9), 5.03 (dd, 2H, $^3J = 17.1$ Hz, $^2J = 1.5$ Hz, H-10$_E$), 4.98 (dd, 2H, $^3J = 10.3$ Hz, $^2J = 1.5$ Hz, H-10$_Z$), 2.78 (t, 4H, $^3J = 7.7$ Hz, H-7), 2.43 (m, 4H, $^3J = 7.7$ Hz, 6.7 Hz, H-8). – ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 156.0$ (C-2), 151.8 (C-4), 149.0 (C-6), 137.1 (C-9), 123.9 (C-5), 121.2 (C-3), 115.6 (C-10), 34.8 (C-7), 34.3 (C-8). – $C_{18}H_{20}N_2$ (264.4): calcd. C 81.78, H 7.63, N 10.60; found C 81.93, H 7.63, N 10.41.

4,4'-Bis(but-3"-enyl-3"-methyl)-2,2'-bipyridine **4**: **1** (0.92 g, 5.0 mmol), LDA (13.0 mmol), methallyl bromide (1.42 g, 10.5 mmol). The reaction mixture was diluted with water (30 ml) and extracted with diethyl ether (3 × 40 ml). The combined ether layers were washed with brine and dried over magnesium sulfate. The solvent was evaporated to give a brown oil from which **4** gradually crystallized as colourless platelets. Yield: 1.43 g (98%). ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 8.54$ (d, 2H, $^3J = 5.0$ Hz, H-6), 8.24 (d, 2H, $^4J = 1.8$ Hz, H-3), 7.12 (dd, 2H, $^3J = 5.0$ Hz, $^4J = 1.8$ Hz, H-5), 4.75, 4.70 (2× n.r., 2 × 2H, H-10$_{E,Z}$), 2.85 (t, 4H, $^3J = 8.0$ Hz, H-7), 2.39 (t, 4H, $^3J = 8.0$ Hz, H-8), 1.77 (s, 6H, H-11). – ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 156.1$ (C-2), 152.2 (C-4), 149.0 (C-6), 144.5 (C-9), 123.8 (C-5), 121.2 (C-3), 110.8 (C-10), 38.3, 33.7 (C-7,8), 22.5 (C-11). – $C_{20}H_{24}N_2$ (292.4): calcd. C 82.15, H 8.27, N 9.58; found C 82.01, H 8.12, N 9.75.

4,4'-Bis(4"-(trimethylsilyl)-but-3"-inyl)-2,2'-bipyridine **5**: **1** (0.46 g, 2.5 mmol), LDA (5.3 mmol), 3-(trimethylsilyl)propargyl bromide (0.96 g, 5.0 mmol). The reaction mixture was poured into water (30 ml) and extracted with diethyl ether (3 × 30 ml). The ether layers were combined, washed with brine and dried over magnesium sulfate. Evaporation of the solvent gave a brown oil which was purified on a silica column (dichloromethane : ethyl acetate : NH_3 in

MeOH = 8 : 1 : 0.5). After evaporation, a colourless oil was obtained from which **5** gradually crystallized as colourless needles. Yield: 0.85 g (84%). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 8.55$ (d, 2H, $^3J = 5.0$ Hz, H-6), 8.27 (n.r., 2H, H-3), 7.17 (dd, 2H, $^3J = 5.0$ Hz, $^4J = 1.6$ Hz, H-5), 2.89 (t, 4H, $^3J = 7.3$ Hz, H-7), 2.56 (t, 4H, $^3J = 7.3$ Hz, H-8), 0.09 (s, 18H, CH_3). – ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 156.1$ (C-2), 150.3 (C-4), 149.0 (C-6), 124.1 (C-5), 121.4 (C-3), 105.5 (C-9), 86.2 (C-10), 34.4 (C-7), 21.1 (C-8), 0.0 (CH_3). – ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$): $\delta = -18.5$. – $C_{24}H_{32}N_2Si_2$ (404.7): calcd. C 71.23, H 7.97, N 6.92; found C 71.14, H 8.08, N 7.06.

4,4'-Bis((*p*-(trimethylsilyl)phenyl)ethyl)-2,2'-bipyridine **6**: **1** (1.73 g, 9.4 mmol), LDA (20.8 mmol), *p*-(trimethylsilyl)benzyl bromide (5.03 g, 20.7 mmol). Diethyl ether (50 ml) was added to the reaction mixture which made **6** precipitate as a colourless microcrystalline powder that was recrystallized by slow evaporation of its dichloromethane / methanol solution. Yield: 2.56 g (53%). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 8.56$ (d, 2H, $^3J = 4.9$ Hz, H-6), 8.29 (n.r., 2H, H-3), 7.45 (d, 4H, $^3J = 7.8$ Hz, H-11), 7.20 (d, 4H, $^3J = 7.8$ Hz, H-10), 7.12 (dd, 2H, $^3J = 4.9$ Hz, $^4J = 1.4$ Hz, H-5), 2.99 (br, 8H, H-7,8), 0.24 (s, 18H, CH_3). – ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): $\delta = 156.2$ (C-2), 151.8 (C-4), 149.1 (C-6), 141.6 (C-9), 138.0 (C-12), 133.6 (C-11), 127.8 (C-10), 124.0 (C-5), 121.2 (C-3), 37.3 (C-7), 36.7 (C-8), −1.1 (CH_3). – ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$): $\delta = -3.9$. – $C_{32}H_{40}N_2Si_2$ (508.8): calcd. C 75.53, H 7.92, N 5.51; found C 75.29, H 7.98, N 5.61.

4,4'-Bis(*p*-(trimethylsilyl)styryl)-2,2'-bipyridine **7**: **1** (3.68 g, 20.0 mmol), LDA (44.0 mmol), *p*-(trimethylsilyl)benzaldehyde (7.85 g, 44.0 mmol). The dialcohol **8** precipitated from the reaction mixture. After filtration, diethyl ether was added to the filtrate to give a second crop. The combined solids were washed with diethyl ether and used without further purification. Yield: 6.68 g (62%). **8** (6.05 g, 11.2 mmol) was dissolved in a mixture of glacial acetic acid (100 ml) and acetic anhydride (6.05 ml) and heated at reflux temperature for 10 h. Upon cooling, **7** crystallized from the reaction mixture. The crude product was isolated by filtration and recrystallized from dichloromethane. Yield: 2.89 g (51%). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 8.66$ (d, 2H, $^3J = 5.2$ Hz, H-6), 8.54 (n.r., 2H, H-3), 7.54 (n.r., 8H, H-10,11), 7.45 (d, 2H, $^3J = 16.3$ Hz, H-8), 7.39 (dd, 2H, $^3J = 5.2$ Hz, $^4J = 1.7$ Hz, H-5), 7.15 (d, 2H, $^3J = 16.3$ Hz, H-7), 0.28 (s, 18H, CH_3). – ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): $\delta = 156.4$ (C-2), 149.5 (C-6), 145.7 (C-4), 141.5 (C-12), 136.6 (C-9), 133.8 (C-11), 133.4 (C-8), 126.3 (C-7,10), 121.1 (C-5), 118.3 (C-3), −1.2 (CH_3). – ^{29}Si{^{1}H} NMR (79.5 MHz, $CDCl_3$): $\delta = -3.8$. – $C_{32}H_{36}N_2Si_2$ (504.8): calcd. C 76.14, H 7.19, N 5.55; found C 75.90, H 7.28, N 5.75.

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[38] Crystallographic data for the structures have been deposited with the Cambridge Data Centre, CCDC 264290, CCDC 264291, CCDC 264292, CCDC 264293, and CCDC 264294. Copies can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).