3262 *Organometallics* **1996,** *15,* 3262−3266

Articles

Lithiation of 3,3′-Dimethyl-2,2′-bipyridine and Its Trimethylsilylated Compounds: X-ray Crystal Structure of [{2-CH(SiMe$_3$)C$_5$H$_3$N}$_2${Li(tmeda)}$_2$] (tmeda = *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)

Wing-Por Leung,* Kathleen S. M. Poon, Thomas C. W. Mak, and Ze-Ying Zhang

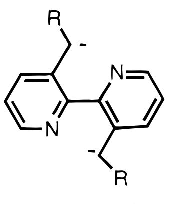
Department of Chemistry, The Chinese University of Hong Kong,
Shatin, New Territories, Hong Kong

Received March 13, 1996⊗

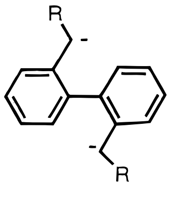
Metalation of 3,3′-dimethyl-2,2′-bipyridine and its trimethylsilyl derivatives (2-RCH$_2$C$_5$H$_3$N)$_2$ (R = H, SiMe$_3$) using appropriate stoichiometries of Bu^{n}Li/tmeda yields the corresponding mono- and dilithiated compounds. Deprotonation was found to occur selectively at the α-methyl carbon, as established by quenching the lithiated compounds with Me$_3$SiCl or D$_2$O and analyzing the products by NMR spectroscopy. The C_2 molecular structure of the dilithium compound [{2-CH(SiMe$_3$)C$_5$H$_3$N}$_2${Li(tmeda)}$_2$] (**2a**) has been determined by X-ray structure analysis, which shows that each lithium atom is C,N-chelated by the α-carbon atom and the nitrogen atom of the other pyridine ring within the molecule. The Li−C$_\alpha$ and the Li−N$_{\text{pyridyl}}$ distances are 2.274(10) and 2.046(9) Å, respectively, and the torsion angle between the pyridine rings is 50.7°. In the lithiation of the *gem*-bis-silylated derivative 2-CH(SiMe$_3$)$_2$C$_5$H$_3$N-C$_5$H$_3$NCH$_3$, the anionic species 2-CH(SiMe$_3$)$_2$C$_5$H$_3$N-C$_5$H$_3$N$\bar{\text{C}}$H$_2$ undergoes a 1,6-silyl migration to form the α,α′-bis-silylated anionic species [2-$\bar{\text{C}}$H(SiMe$_3$)C$_5$H$_3$N−C$_5$H$_3$NCH$_2$(SiMe$_3$)].

Introduction

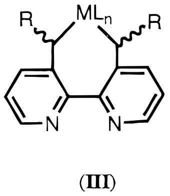
Metalation of toluene using Bu^{n}Li in the presence of a tertiary amine such as tetramethylethylenediamine (tmeda) was found to occur almost exclusively at the benzylic carbon.[1] The lithium complex [LiCH$_2$(C$_6$H$_5$)-N(CH$_2$CH$_2$)$_3$N]$_n$ has been structurally characterized.[2] Similarly, dimetalation of arylmethanes such as xylenes, 2,2′-dimethylbiphenyl, and their trimethylsilylated derivatives using the same reagents yielded the dilithium compounds [{*o*-/*m*-/*p*-C$_6$H$_4$(CHSiMe$_3$)$_2$}{(Li(tmeda)}$_2$] and [{2-CHRC$_6$H$_4$)$_2${(Li(tmeda)}$_2$] (R = H (polymeric), SiMe$_3$ (monomeric)), respectively.[3,4] These dilithium complexes have also been shown to be useful transfer reagents for the preparation of metallacycles.[5,6] It has been noted that monolithiation of xylene derivatives is dependent on the stoichiometry of Bu^{n}Li and the choice of tertiary amine.[3,7] It was found that a more bulky tertiary amine such as pentamethyldiethylenetriamine (pmdeta) conducts monolithiation more effective than tmeda.[3] In contrast, metalation of 2-methylpyridine and its trimethylsilylated derivative 2-CH$_2$RC$_5$H$_4$N (R = H, or SiMe$_3$) with Bu^{n}Li was found to be comparatively more facile even without the presence of tmeda, due to the fact that the free ligand 2-methylpyridine can act as a base (*via* the pyridine nitrogen) to activate the lithium reagent in the reaction.[8] The structures of the lithiated compounds derived from the α-substituted 2-methylpyridine with the anionic ligands bonded in different modes to the lithium have been reported recently.[9] In this paper, attention is focused on the metalation of 3,3′-dimethyl-2,2′-bipyridine and its trimethylsilylated derivatives. The anionic species [{2-CHRC$_5$H$_3$N}$_2$]$^{2-}$ (**I**) is, in principle, isoelectronic with [{2-CHRC$_6$H$_4$)$_2$}]$^{2-}$ (**II**)[4] and serves as a potential transfer reagent for the synthesis of new metallacycles (**III**), which can react further by forming chelate rings through the nitrogen centers in the formation of bimetallacycle **IV** or in the assembly of superstructures.



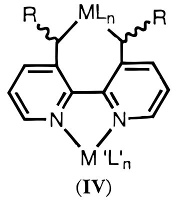
(**I**) R = H or SiMe$_3$



(**II**) R = H or SiMe$_3$



(**III**)



(**IV**)

⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.

[1] Chalk, A. J. *J. Organomet. Chem.* **1968**, *11*, 615.

[2] Patterman, S. P.; Karle; I. C.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150.

[3] (a) Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. W. *J. Chem. Soc., Chem. Commun.* **1982**, 14. (b) Leung, W.-P.; Raston, C. L.; Skelton, B. W.; White, A. W. *J. Chem. Soc., Dalton Trans.* **1984**, 1801. (c) Engelhard, L. M.; Leung, W.-P.; Raston, C. L.; White, A. W. *J. Chem. Soc., Dalton Trans.* **1985**, 337.

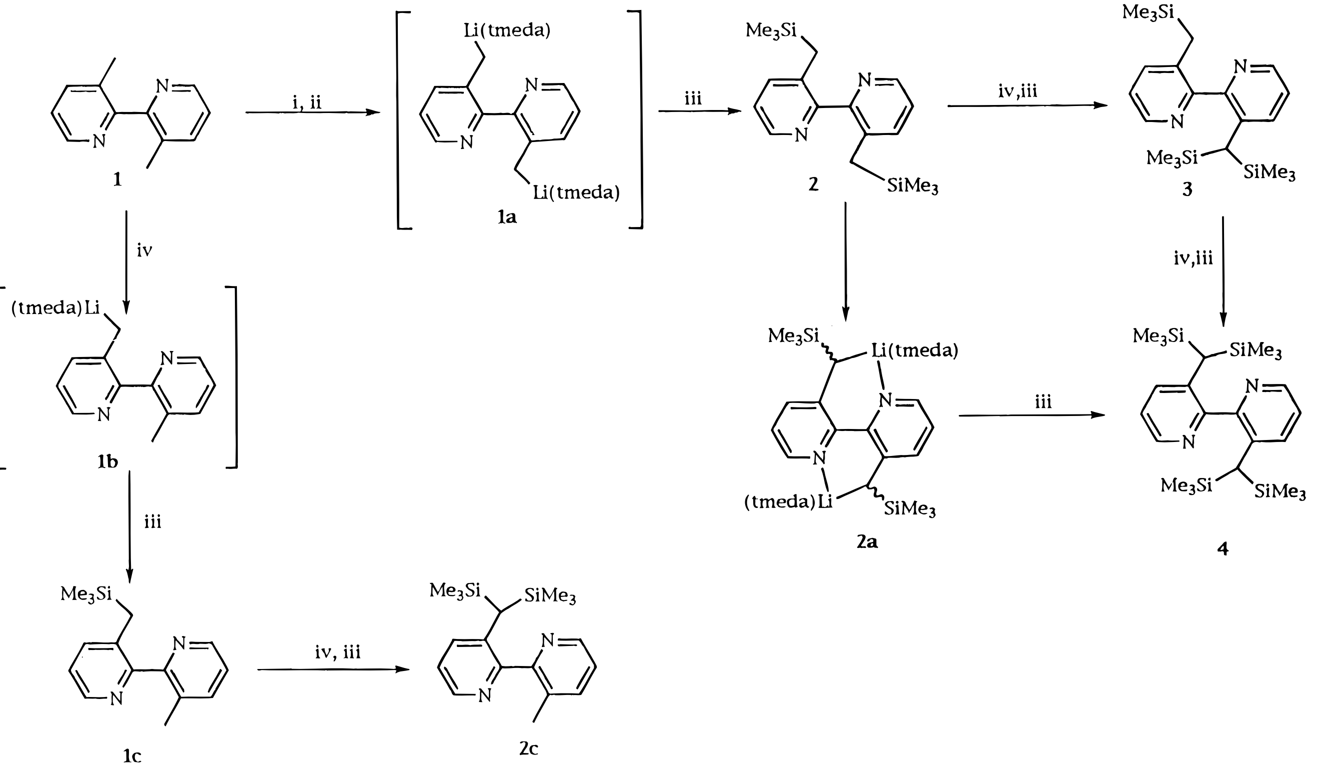
[4] Engelhardt, L. M.; Leung, W.-P.; Raston, C. L.; Twiss, P.; White, A. W. *J. Chem. Soc., Dalton Trans.* **1984**, 321.

[5] Lappert, M. F.; Leung, W.-P.; Raston, C. L.; White, A. W. *J. Chem. Soc., Dalton Trans.* **1992**, 775 and references therein.

[6] Bailey, S. I.; Engelhard, L. M.; Raston, C. L.; Ritchie, I. M.; White, A. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1747.

S0276-7333(96)00191-4 CCC: $12.00

Scheme 1[a]



[a] Legend: (i) 2.2 mol of Bu^{n}Li (1.6 M oin hexane), 2 mol of tmeda, −78 °C, 3 h, THF; (ii) room temperature, $^1/_2$ h; (iii) Me$_3$SiCl, −78 °C; (iv) 1.1 mol of Bu^{n}Li (1.6 M in hexane), 1 mol of tmeda, −78 °C, 3 h, THF.

Results and Discussion

Lithiation and Derivatization of 3,3′-Dimethyl-2,2′-bipyridine. The reaction of 3,3′-dimethyl-2,2′-bipyridine (**1**) with the metalating reagent Bu^{n}Li/tmeda in 1- and 2-equiv ratios afforded the monolithiated and α,α′-dilithiated compounds **2a** and **2b**, respectively (Scheme 1). The positions of metalation were established by subsequent reaction of the lithiated compounds with Me$_3$SiCl, which led to the formation of the α-monosilylated compound **3** and α,α′-disilylated compound **4**, respectively.

Monolithiation is accomplished by reacting **1** with 1 equiv of Bu^{n}Li/tmeda in a thf/hexane solvent mixture, which gave a persistent blue color. After subsequent quenching of the reaction mixture with Me$_3$SiCl, the product **1c** was isolated in 98% yield from the reaction as confirmed by ^{1}H NMR spectroscopy. On addition of a further 1 equiv of Bu^{n}Li/tmeda to the blue solution, presumably containing [2-CH$_3$C$_5$H$_3$N-C$_5$H$_3$NCH$_2$][Li(tmeda)], a second lithiation was found to occur at *ca.* −60 °C, as shown by the development of a dark red coloration. The reaction was also confirmed by quenching the lithiated product with Me$_3$SiCl and isolating 2,2′-bis[(trimethylsilyl)methyl]-3,3′-bipyridine. Dilithiation of **1** can also be accomplished with 2 equiv of Bu^{n}Li/tmeda in hexane at *ca.* −78 °C. The dilithium compound **1a** was isolated as a dark red solid with low solubility in hydrocarbon solvent, presumably due to the formation of oligomers; [{Li(tmeda)}$_2${2-CH$_2$C$_5$H$_3$N)$_2$}]$_n$, with structure similar to that of [{Li(tmeda)}$_2${2-CH$_2$C$_6$H$_4$)$_2$}]$_\infty$, is a coiled polymeric chain with intermolecular bridging.[3] Organolithium compounds tend to form aggregates, owing to the electron-deficient character of lithium, and the lithium−carbon bonds have a higher degree of ionic character.[10]

Metalation of the trimethylsilylated derivatives was found to be similar to that of **1**. In contrast, the lithiated compounds of the silylated derivatives were found to be more soluble, as a consequence of incorporating the SiMe$_3$ group, which increases the lipophilicity and solubility of the products. Single crystals of the dilithium compound **2a** were obtained for an X-ray structure determination.

When the dilithiated species **2a** was quenched with Me$_3$SiCl, compound **4** was obtained in 95% yield. The yield of **2a** depends on strict and proper control of stoichiometry and reaction temperature. The reaction mixture was kept at −78 °C for at least 2 h. At temperatures exceeding 30 °C, oligomerization occurs readily, as shown by the formation of an insoluble solid. The low solubility of the product **1a** in hydrocarbon solvent indicates a high degree of association of the compound, which renders its characterization by NMR difficult. However, the solubility of **2a** is remarkably higher, probably due to the enhanced lipophilicity generated by the incorporation of Me$_3$Si groups.

1,6-Silyl Migration. In the reaction of the *gem*-bistrimethylsilylated compound 2-CH(SiMe$_3$)$_2$C$_5$H$_3$N−C$_5$H$_3$-NCH$_3$ (**2c**) with 1 equiv of Bu^{n}Li/tmeda, followed by reaction with Me$_3$SiCl, the product isolated was found to be identical with that of **2** as analyzed by NMR.

---

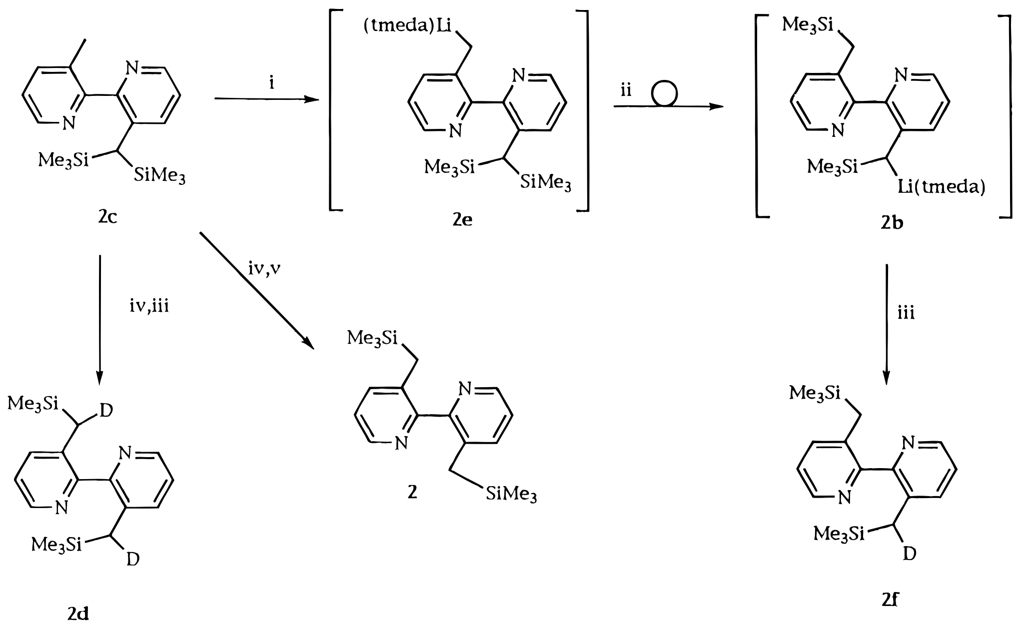
(7) Engelhardt, L. M.; Leung, W.-P.; Raston, C. L.; Salem, G.; Twiss, P.; White, A. W. *J. Chem. Soc., Dalton Trans.* **1988**, 2403.

(8) (a) Papasergio, R. I.; Skelton, B. W.; Twiss, P.; Raston, C. L.; White, A. H.; *J. Chem. Soc., Dalton Trans.* **1990**, 1161. (b) Engelhardt, L. M.; Jacobsen, G. E.; Junk, P. C.; Raston, C. L.; White, A.H. *J. Chem. Soc., Dalton Trans.* **1988**, 1011.

(9) Leung, W.-P.; Weng, L.-H.; Wang, R.-J.; Mak, T. C. W. *Organometallics* **1995**, 4832.

(10) Setzer, W. N.; Schleyer, P. v .R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

Scheme 2[a]



[a] Legend: (i) 1.1 mol of Bu^nLi (1.6 M in hexane), 1 mol of tmeda, −78 °C, 3 h, THF; (ii) room temperature, 30 h; (iii) D_2O; (iv) 2 mol of Bu^nLi (1.6 M in hexane), 2 mol of tmeda, −78 °C, 3 h, room temperature, 15 h; (v) H_2O.

Similarly, in the reaction of **2c** with 2 equiv of Bu^n-Li/tmeda followed by quenching of the dilithiated species with D_2O (or H_2O), the product isolated as shown by NMR is the 2,2′-disubstituted derivative **2d** (Scheme 2). One of the trimethylsilyl groups of the *gem*-bis-substituted compound is believed to undergo a "1,6-rearrangement" after the formation of the anionic species. The mechanism for such a rearrangement is not known but likely involves an intramolecular rearrangement, as postulated for 2-[bis(trimethylsilyl)methyl]-2′-methylbiphenyl.[4] In the proposed mechanism, the less hindered methyl proton was believed to be abstracted preferably, which is then followed by nucleophilic substitution involving a pentacoordinate silicon intermediate. For an intramolecular nucleophilic substitution, the proximity of the nucleophile and the silicon center plays an important role. For example, intramolecular silacycle formation from a dilithiated derivative of 1,8-[bis(trimethylsilyl)methyl]naphthalene is favored by the close proximity of the anionic center and the silicon atom, as well as the release of steric compression in the resulting product.[11]

In the dilithiation reaction, deprotonation at the less hindered methyl carbon is followed by silyl migration and further lithiation to give the α,α′-dilithiated compound.

The C−Li bond of the corresponding lithiated species is expected to be more polar in comparison to the biphenyl analogue. Apart from polarity considerations, steric bulk and the presence of complexing agent as well as temperature can also affect the degree of association. These factors are consistent with the formation of the dilithium compounds **1a** and **2a**.

X-ray Structure of 2a. X-ray crystallographic analysis has revealed the monomeric C_2 structure of dilithium complex **2a** (Figure 1) as a 1:2 benzene solvate. The lithium atoms are each bonded to the α-carbon and the pyridyl nitrogen of the other half of the molecule, forming two six-membered metallacyclic rings.

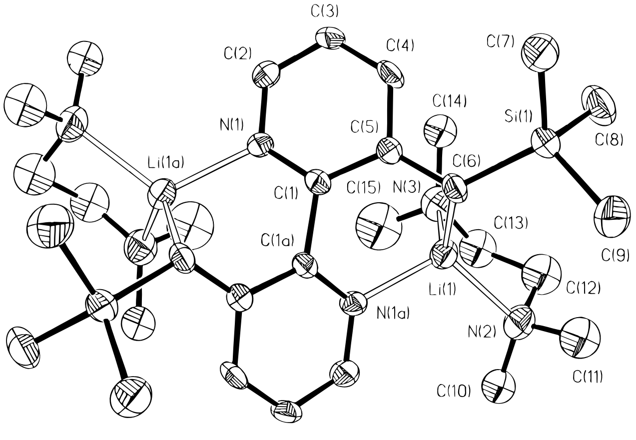


Figure 1. Molecular structure of $[\{2\text{-}CH_2(SiMe_3)C_5H_3N\}_2\{Li(tmeda)\}_2]$ (**2a**) as its crystalline benzene solvate. Thermal ellipsoids are drawn at the 30% probability level, and the hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): Li(1)−C(6), 2.274(10); Li(1)−N(1a), 2.046(9); Li(1)−N(2), 2.202(10); Li(1)−N(3), 2.147(10); C(1)−N(1), 1.343(6); C(2)−N(1), 1.343(7); C(2)−C(3), 1.372(7); C(3)−C(4), 1.362(7); C(4)−C(5), 1.431(7); C(1)−C(5), 1.450(6); C(1)−C(1a), 1.491(9); C(6)−Li(1)−N(2), 128.6(4); C(6)−Li(1)−N(3), 121.1(4); N(2)−Li(1)−N(3) 85.0(4); C(6)−Li(1)−N(1a), 89.9(4); N(2)−Li(1)−N(1a), 117.0(4); N(3)−Li(1)−N(1a), 118.8(4). The dihedral angle between the planesof the two pyridine rings is 50.7°. Symmetry operation a: 1.5 − *x*, *y*, 0.75 − *z*.

With additional coordination from a chelating tmeda ligand, the geometry at the lithium center is tetrahedral. The dihedral angle between the two pyridine rings is 50.7°, which is slightly less than the corresponding angle of 54.3° in $[(2\text{-}CHSiMe_3C_6H_4)_2\{Li(tmeda)\}_2]$.[4] The present structure is comparatively different from the related complex $[(2\text{-}CHSiMe_3(C_6H_4)_2\{Li(tmeda)\}_2]$, which exhibited a contact-ion-pair structure.[4] The lithium to α-carbon distance of 2.274(10) Å in **2a** is comparatively

---

(11) (a) Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 311.

longer than the similar distance of 2.205 Å (average) in $[(2\text{-}CHSiMe_3C_6H_4)_2\{Li(tmeda)\}_2]$.[4] The Li(1)···C(1,5) distances are 3.004 and 2.649 Å, which are too long to consider a "contact-ion-pair" type of interaction between the lithium and the ligand. The geometry around the α-carbon is consistent with a tetrahedral carbon.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques or in a dinitrogen glovebox. Solvents were dried over and distilled from CaH_2 (hexane) and/or Na (Et_2O and thf). Bis(triphenylphosphine)nickel(II) chloride and 2-bromo-3-methylpyridine used in the coupling reaction were prepared by literature methods.[12,13] 3,3′-Dimethyl-2,2′-bipyridine **1** was prepared by the coupling reaction of 2-bromo-3-methylpyridine using the method described by Iyoda, except that no Et_4NI was added.[14] ^1H and ^{13}C NMR spectra were recorded at 250 and 62.90 MHz, respectively, using a Bruker WM-250 spectrometer or at 500 and 125.8 MHz, respectively, using a Bruker ARX-500 spectrometer. All spectra were recorded in benzene-d_6, and the chemical shifts δ are relative to $SiMe_4$. Mass spectral data were obtained either on a VG 7070F mass spectrometer or from the Shanghai Institute of Organic Chemistry, Academia Sinica, Shaughai, China. In all cases, signals were reported as m/z. Analytical thin-layer chromatography (TLC) was carried out on commercial E. Merck 60 PF254 silica gel plates (Art. No. 5554). E. Merck 70−230 mesh silica gel 80 (Art 7734) and E. Merck aluminum oxide 90 (Art. No. 1077) were used for column chromatography. Elemental analyses were performed at MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, U.K.

Preparation of 3,3′-Bis[[(*N,N,N′N′*-tetramethylethylenediamine)lithio]methyl]-2,2′-bipyridine (1a). To a solution of **1** (0.40 g, 2.1 mmol) and tmeda (0.65 mL, 4.3 mmol) in hexane (ca. 50 mL) was added Bu^nLi (2.7 mL, 1.60 M in hexane, 4.3 mmol) at 0 °C. The volume of the resulting solution was concentrated to half. When this solution stood at ambient temperature, a dark red solid was obtained. The supernatant black solution was removed by filtration, yielding 0.72 g (80%) of a dark red solid. Mp 130 °C dec. Due to the low solubility of **1a** in benzene-d_6, no NMR spectrum was recorded.

Preparation of 3-[(Trimethylsilyl)methyl]-3′-methyl-2,2′-bipyridine (1c). To a thf solution of tmeda (0.59 mL, 3.9 mmol) and **1** (0.72 g, 3.9 mmol) was added a solution of Bu^nLi (2.7 mL, 1.6 M in hexane, 4.3 mmol) at −78 °C. After stirring at −78 °C for 3 h, Me_3SiCl (0.55 mL, 4.3 mmol) was added to the blue solution of the monolithiated compound. After stirring at −78 °C for 1 h, the reaction mixture was warmed to ambient temperature with continued stirring for 16 h. Solvent and volatiles were removed under reduced pressure. The residue was hydrolyzed and the product extracted with hexane. The organic layer was dried over $MgSO_4$. After filtration and concentration, the crude product was distilled under vacuum and the distillate collected at 72−74 °C (0.1 mmHg), yielding 0.98 g (98%). ^1H NMR ($CDCl_3$): δ −0.19 (s, 9H), 2.11 (s, 2H), 2.17 (s, 3H), 7.14 (dd, $^3J = 7.8$ Hz, $^3J = 4.7$ Hz, 1H), 7.16 (dd, $^3J = 7.6$ Hz, $^3J = 4.8$ Hz, 1H), 7.42 (dd, $^3J = 7.8$ Hz, $^4J = 1.6$ Hz, 1H), 7.55 (dd, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz, 1H), 8.38 (dd, $^3J = 4.7$ Hz, $^4J(4) = 1.6$ Hz, 1H), 8.46 (dd, $^3J = 4.8$ Hz, $^4J = 1.5$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 145.84, 155.46, 157.40. MS: m/z 256,(P)$^+$; 241, (P−Me)$^+$; 183, (P − $SiMe_3$)$^+$.

Preparation of 3-[Bis(trimethylsilyl)methyl]-3′-methyl-2,2′-bipyridine (2c). The preparation was carried out using a procedure similar to that above, except that the concentrated extract was chromatographed over silica gel with hexane/ethyl acetate (4:1) as eluent. The major fraction was collected. Product **2c** was obtained as a pale yellow oil which crystallized on standing at ambient temperature, yielding 0.99 g (78%). ^1H NMR ($CDCl_3$): δ −0.01 (s, 18H), 1.84 (S, 1H), 2.21 (s, 3H), 7.16 (m, 2H), 7.43 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 1H), 7.56 (dd, $^3J = 8.0$ Hz, $^4J(6') = 1.7$ Hz, 1H), 8.34 (dd, $^3J = 4.6$ Hz, $^4J = 1.6$ Hz, 1H), 8.44 (dd, $^3J = 4.2$ Hz, $^4J = 1.7$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 0.32, 19.04, 22.76, 121.93, 122.31, 132.21, 136.83, 138.31, 138.59, 143.49, 145.71, 156.28, 157.67. MS: m/z 328, (P)$^+$, 313 (P−Me)$^+$; 255 (P−$SiMe_3$)$^+$.

Preparation of 3-[Bis(trimethylsilyl)methyl]-3′-[(trimethylsilyl)methyl-2,2′-bipyridine (3). The same procedure as for **1c** was used, starting with **2** or **2c**, and both yielded 40−50% of **3**. MP: 85−87 °C. ^1H NMR ($CDCl_3$): δ −0.03 (s, 18H), −0.02 (s, 9H), 1.76 (S, 1H), 1.89 (s, 2H), 7.12 (dd, $^3J =$ 7.9 Hz, $^3J = 4.6$ Hz, 1H), 7.13 (dd, $3J(5',4') = 7.9$ Hz, $^3J = 4.6$ Hz, 1H), 7.37 (dd, $^3J = 7.9$ Hz, $^4J = 1.7$ Hz, 1H), 7.41 (dd, ^3J $= 7.9$ Hz, $^4J = 1.6$ Hz, 1H), 8.34 (dd, $^3J = 4.6$ Hz, $^4J = 1.7$ Hz, 1H), 8.38 (dd, $^3J = 4.6$ Hz, $^4J = 1.6$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ −0.05, 1.19, 23.30, 23.77, 122.43, 122.66, 136.14, 136.80, 137.10, 138.87, 144.04, 145.13, 157.02, 157.30. MS: m/z 400, (P)$^+$; 385, (P − Me)$^+$; 327, (P − $SiMe_3$)$^+$. Anal. Calcd for $C_{21}H_{36}N_2Si_3$: C, 62.93; H, 9.05; N, 6.99. Found: C, 62.95; H, 9.06; N, 7.10.

Preparation of 3,3′-Bis[(trimethylsilyl)methyl]-2,2′-bipyridine (2). To a thf solution of bipicoline (1; 7.70 g, 41.8 mmol) and tmeda (12.6 mL, 83.6 mmol) was added Bu^nLi solution (57.5 mL, 1.6 M in hexane, 91.9 mmol) at −78 °C. The mixture was stirred at −78 °C for 2 h. It was then warmed with stirring at about 0 °C for 1/2 hr. The purple-red dilithiated bipicoline was cooled to −78 °C again before $ClSiMe_3$ (11.6 mL, 91.9 mmol) was added to it. After 1 h, the mixture was warmed to room temperature and was further stirred for 16 h. Solvent and volatile materials were removed in vacuo. The residue was hydrolyzed and the product was extracted with hexane. The dried and concentrated extract was chromatographed on silica gel with hexane/ethyl acetate (4:1) eluent. The fraction that eluted just before **1** was collected. The product **2** was obtained as a pale yellow oil in 53.8% (7.39 g) yield. ^1H NMR ($CDCl_3$): δ −0.15 (s, 18H), 2.02 (s, 4H), 7.12 (dd, $^3J = 7.8$ Hz, $^3J = 4.7$ Hz, 2H), 7.40 (dd, $^3J =$ 7.8 Hz, $^4J = 1.3$ Hz, 2H), 8.39 (dd, $^3J = 4.7$ Hz, $^4J = 1.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ −0.15, 23.75, 123.19, 136.02, 137.85, 145.74, 157.16. MS: m/z 328, (P)$^+$; 313, (P − Me)$^+$; 255 (P − $SiMe_3$)$^+$. Anal. Calcd for $C_{18}H_{28}N_2Si_2$: C, 65.79; H, 8.59; N, 8.52. Found: C, 65.97; H, 8.61; N, 8.46.

Preparation of 3,3′-Bis[[(*N,N,N′,N′*-tetramethylethylenediamine)lithio](trimethylsilyl)methyl]-2,2′-bipyridine (2a). To a hexane solution of **2** (0.85 g, 2.6 mmol) and tmeda (0.79, 5.2 mmol) was slowly added Bu^nLi (3.4 mL, 1.6 M in hexane, 5.5 mmol) at 0 °C with slow stirring. The reaction mixture was then left standing at room temperature without stirring before the hexane solution was discarded. The solvent was removed in vacuo, and benzene was added. The solution was slightly boiled and slowly cooled to deposit dark red crystals of **2a** as its benzene solvate: mp 188−190 °C dec; yield 1.40 g (94.2%).

Preparation of 3,3′-Bis[bis(trimethylsilyl)methyl]-2,2′-bipyridine (4). **4** was synthesized by using the same procedure as for the preparation of **2** and **3**: mp 83−84 °C; yield 90−95%. ^1H NMR ($CDCl_3$): δ 0.05 (s, 36H), 2.25 (s, 2H), 7.08 (dd, $^3J = 7.9$ Hz, $^3J = 4.5$ Hz, 2H), 7.44 (dd, $^3J = 7.9$ Hz, $^4J(4,6) = 1.5$ Hz, 2H), 8.28 (dd, $^3J = 4.5$ Hz, $^4J = 1.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 1.92, 23.7, 122.27, 137.26, 140.56, 143.12, 156.63. MS: m/z 473, (P)$^+$; 457 (P−CH_4)$^+$; 399 (P − $SiMe_4$)$^+$. Anal. Calcd for $C_{24}H_{44}N_2Si_4$: C, 60.95; H, 9.38; N, 5.92. Found: C, 60.68; H, 9.34; N, 5.90.

---

[12] Cotton, F. A.; Faut, O. D.; Goodgame, D. M. L. *J. Am. Chem. Soc.* **1961**, *83*, 344.

[13] Vogel, A. I. *Text-book of Practical Organic Chemistry*, 4th ed.; Longman: London, **1978**.

[14] Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80.

Silyl-Migration Experiment. Preparation of 3-[Deuterio(trimethylsilyl)methyl]-3′-[(trimethylsilyl)methyl]-2,2′-bipyridine (2f). To a thf solution of **2c** (0.23 g, 0.71 mmol) and tmeda (0.11 mL, 0.71 mmol) was added Bu^{n}Li solution (0.49 mL, 1.6 M in hexane, 0.78 mmol) at −78 °C. After 2 h, the reaction mixture was warmed to room temperature with stirring for 30 h. To this solution was added excess D_2O. Solvent removal was followed by hexane extraction, and the organic layer was dried and concentrated. The crude product was analyzed by ^1H NMR spectroscopy, which confirmed the formation of **2f**.

Preparation of 3,3′-Bis[deuterio(trimethylsilyl)methyl]-2,2′-bipyridine (2d). To a thf solution of **2c** (0.51 g, 1.56 mmol) and tmeda (0.47 mL, 3.12 mmol) was added Bu^{n}Li (1.1 mL, 1.6 M in hexane, 1.8 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 3 h and then at room temperature for 15 h before another 1 equiv of Bu^{n}Li (1.1 mL, 1.6 M in hexane, 1.8 mmol) was added at −78 °C. The reaction mixture was stirred at room temperature for 16 h before it was quenched with excess D_2O. The same workup as for **2c** was adopted; ^1H NMR spectroscopy indicated a complete conversion of **2c** to **2d**.

X-ray Crystallography. **2a** was recrystallized from benzene as a 1:2 solvate, and a selected crystal was sealed in a Lindemann glass capillary under dinitrogen. X-ray intensities were measured on a MSC/Rigaku RAXIS-IIC imaging plate using monochromatized Mo K_α radiation ($\lambda = 0.710\,73$ Å, 50 kV, 150 mA) from a rotating-anode generator. The structure was solved by direct phase determination. Molecule **2a** and both independent benzene molecules occupy sites of symmetry 2. All non-hydrogen atoms except the carbon atoms of the tmeda ligand were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically (C−H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms; they were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Computations were performed using the SHELXTL-PLUS program package (Sheldrick; 1985, 1990) on a PC 486 computer. Analytical expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[15]

Crystal Data for 2a: $C_{30}H_{58}N_6Li_2Si_2\cdot 2C_6H_6$, $M_r = 729.1$, tetragonal, space group $I\bar{4}2d$ (No. 122), $a = 26.109(1)$ Å, $c = 13.837(1)$ Å, $V = 9432(5)$ Å^3, $D_c = 1.027$ g cm^{-3} ($Z = 8$), $F(000) = 3184$, $\mu = 0.108$ mm^{-1}, $N = 4734$, $N_o = 2191$, 221 parameters, $R_F = 0.058$, $R_w = 0.073$.

Acknowledgment. This work was supported by Hong Kong Research Grant Council Earmarked Grant CUHK 87/93E.

Supporting Information Available: Tables giving data collection and processing parameters, atomic coordinates, bond distances and angles, thermal parameters, and solution and refinement details (9 pages). Ordering information is given on any current masthead page.

OM9601918

---

[15] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.