Synthesis of Axially Asymmetric *N*-Functionalized Metal Dialkyls and Bimetallic Complexes: X-ray Structures of $Me_2M(L'L')$ ($M = Si, Sn$; $L'L' = (CHSiMe_3C_5H_3N)_2$) and $Me_2Sn(L'L')W(CO)_4$

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Treatment of dilithium dialkyl compounds derived from dilithiation of 3,3′-dimethyl-2,2′-bipyridine and its trimethylsilylated compound with R'_2MCl_2 afford axially asymmetric metal dialkyls $R'_2M(LL)$ ($R' = Me$, $LL = (CH_2C_5H_3N)_2$, M = Si (**2**), Sn (**3**)) and $R'_2M(L'L')$ ($R' = Me$, $L'L' = (CHSiMe_3C_5H_3N)_2$, M = Si (**4**), Ge (**5**), Sn (**6**); $R' = Ph$, M = Sn (**7**)), respectively. Compounds **5**−**7** can react further with $W(CO)_6$ to form bimetallic complexes $R'_2M(L'L')W(CO)_4$ ($R' = Me$, M = Ge (**8**), Sn (**9**); $R' = Ph$, M = Sn (**10**)) via the coordination of the two pyridyl nitrogens. The variable-temperature ^1H NMR spectra of **2**−**4** have been recorded to investigate the fluxional behavior due to the torsional motion along the C−C axis that joins the two pyridine groups. X-ray structures of compounds **4**, **6**, and **9** have been determined.

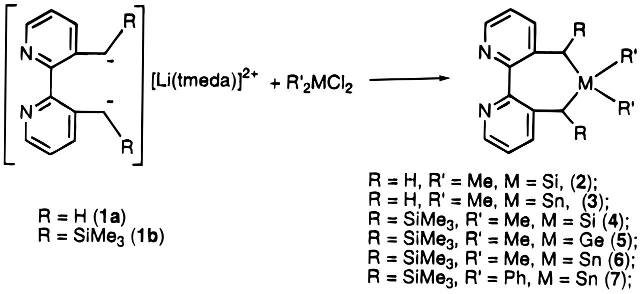
Introduction

Metallacycles with five- and six-membered rings are usually more stable than those of seven-membered rings. This is exemplified by the unstable seven-membered platinacycle $[Pt\{CH_2(CH_2)_4CH_2\}(PPh_3)_2]$, the instability is mainly due to the facile β-hydrogen elimination.[1] Di-Grignard or dilithium reagents derived from (2-chloromethyl)biphenyl and 2,2′-dimethylbiphenyl have been used as a source of dianion $[2\text{-}CHR\text{-}C_6H_4)_2]^{2-}$ for the preparation of thermally stable metallacyclic derivatives of the type $[ML_n(2\text{-}CHRC_6H_4)_2]$ (R = H or $SiMe_3$; M = Si, Sn, Ti, Zr, Hf, Nb, Ta, and W).[2−8]

Recently, we have reported the synthesis of dilithium complexes derived from the dilithiation of 3,3′-dimethyl-2,2′-bipyridine and its trimethylsilylated compound.[9] The dianionic species $[CHRC_5H_3N\}_2]^{2-}$ can potentially serve as a transfer reagent for the synthesis of axially asymmetric *N*-functionalized metallacycles (metallepines) via salt-elimination reactions. The dialkyl ligands $[\{2\text{-}CHRC_5H_3N\}_2]^{2-}$ [R = H, (LL); R = $SiMe_3$, (L′L′)] in this work have similar features with the isoelectronic ditolyl ligand $[(2\text{-}CHRC_6H_4)_2]^{2-}$; it has a flexible bite associated with torsion along the bipyridyl axis and is, thus, potentially capable of accommodating a wide variety of heteroatom sizes. Moreover, the ligands LL and L′L′ have an additional feature that the pyridyl groups do not have in that they are capable of reacting further via coordination of the nitrogen atoms to form bimetallic complexes of the type $[ML_n\{CHR(C_5H_3\text{-}N)\}_2M'L'_m]$. In this paper, reactions of the dilithium compounds involving some group 14 metal chlorides and further reactions of these *N*-functionalized metallacycles with tungsten hexacarbonyl to form bimetallic complexes are reported.

Results and Discussion

Synthesis of Metallacycles. The reactions of dilithium compounds (LL)Li(tmeda) (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (**1a**) or [(L′L′)Li(tmeda)] (**1b**) with R'_2MCl_2 (R′ = Me or Ph; M = Si, Ge, and Sn) afforded the seven-membered metallacycles (metallepines) $[R'_2M(LL)]$ (R′ = Me; M = Si (**2**), Sn (**3**)) and the $SiMe_3$-substituted metallepines $[R'_2M(L'L')]$ (R′ = Me; M = Si (**4**), Ge (**5**), Sn (**6**); R′ = Ph, M = Sn (**7**)) (eq 1).



However, the yields for silepines **2** and **4** were low, 5 and 12%, respectively. They were purified by column chromatography and characterized by their mass and NMR spectra, and for compound **4** the X-ray structure has been determined. Similar low yields have been found for the preparation of 2,2′-ditolyl silepines Me_2-

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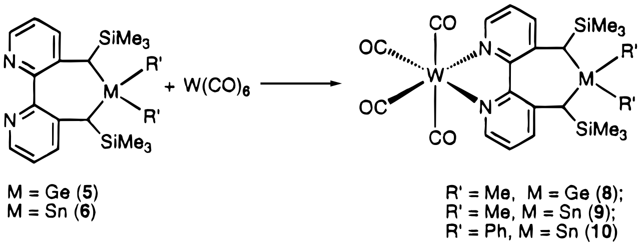
Si(2-CHRC$_6$H$_4$)$_2$ (R = H (42% yield); SiMe$_3$ (9% yield)), and the related 2,2′-binaphthyl silepine was prepared in 50% yield (not isolated).[6,10] The stannepine Me$_2$Sn-(LL) (**3**) was prepared in a moderate yield (37%). It is an air-stable solid, soluble in polar solvent, such as THF, but it decomposed readily in chloroform. In contrast, the yields for the SiMe$_3$-substituted metallepines R′$_2$M-(L′L′) **5**−**7** were in general higher than the corresponding unsubstituted analogues R′$_2$M(LL). This is presumably due to the higher solubility of the monomeric dilithium compound **1b** than the polymeric dilithium compound **1a**.

Subsequent reactions of compounds **5**−**7** with W(CO)$_6$ in toluene afforded the corresponding bimetallic complexes R′$_2$M(L′L′)W(CO)$_4$ (R′ = Me, M = Ge (**8**), Sn (**9**); R′ = Ph, M = Sn (**10**)) (eq 2). These reactions were carried out under refluxing conditions and were monitored by TLC. The IR spectra of **8**−**10** showed that the carbonyl stretching peaks of the tungsten center adopts a C_{2v} symmetry and were consistent with *cis*-substituted tungsten tetracarbonyl complexes, as only four ν(CO) bands near 1900 cm^{-1} were observed. The structure of compound **9** has been confirmed by X-ray structure analysis. It is expected that upon complexation with the octahedral tungsten hexacarbonyl the dihedral angle between the two pyridine rings should be reduced significantly. In the extreme case, i.e., the total flattening of two pyridine rings, the metallepine which originally adopts a C_2 symmetry will convert into a C_1 symmetry. Nevertheless, the two symmetries can be distinguished by their ^{1}H NMR spectra.



Spectroscopic Characterization of Metallacycles and Bimetallic Complexes. The ^{1}H NMR spectra of **2** and **3** displayed AB quartets for the prochiral M−CH$_2$ protons are isotropic and isochronous, which is consistent with an axially asymmetric C_2 symmetry of the chelating dialkyl ligand (LL). The variable-temperature ^{1}H NMR study in solution shows that silepine **2** exhibits fluxional motion attributed to the twisting about the C−C bond that connects the two pyridine rings which leads to the interconversion of the δ and λ stereoisomers (Figure 1). At temperatures near 0 °C, the AB quartet due to the prochiral geminal benzylic protons MCH$_A$H$_B$ was observed at δ 1.29 and 1.80 ppm. This quartet signal broadened at 40 °C, and at temperatures >60 °C, it transformed into a sharp singlet at δ 1.68. The energy barrier for this dynamic process, as calculated by the Eyring equation[11] and based on the coalescence temperature (T_c) of 313 K was found to be 15 kcal mol^{-1}. In contrast, the tin analogue **3** at the same conditions studied had shown no fluxional behavior. This could be due to the increase in heteroatom size which increases the energy barrier. It is noteworthy that no fluxional behavior was observed for the related silepine Me$_2$Si-{2-CH(SiMe$_3$)C$_6$H$_4$}$_2$.[6]

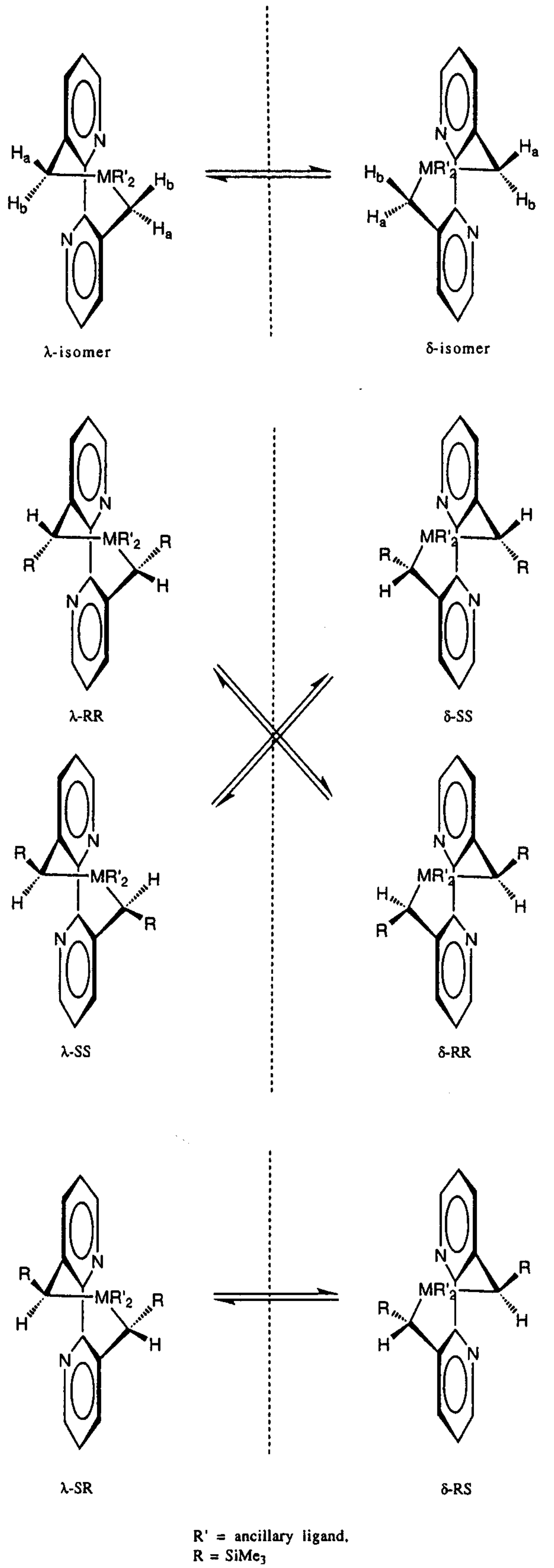


Figure 1. Interconversions of possible diastereoisomers of R′$_2$M(LL) and R′$_2$M(L′L′).

For the Me$_3$Si-substituted metallepines R′$_2$M(L′L′), in principle there are three possible sets of diastereoisomers, viz, λ/δ-*RR*, λ/δ-*SS*, and λ/δ-*RS*. The intercon-

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version of these stereoisomers via torsional motion are shown in Figure 1. Molecular models suggest that the δ/λ-*RS* diastereoisomers are sterically unfavorable.[6] In the ^{1}H NMR spectrum of silepine **4**, two groups of diastereoisomers, presumably $\delta SS/\lambda RR$ and $\lambda SS/\delta RR$, were observed in the ratio of 2:1. It is noteworthy that the stereochemistry in the synthesis of silepine $Me_2Si\{2\text{-}CH(Ph)C_6H_4\}_2$ is *cis*, δ- and λ-*RS*,[12] as well as in the syntheses of $(SnL)_4$,[13] SnL_2,[13] and $[ML(\eta\text{-}C_5H_5)_2]$ (M = Ti, Zr, or Hf)[14] (L = $o\text{-}(Me_3SiCH)_2C_6H_4{}^{2-}$), where the chelating dialkyl is always in the *meso* configuration. Moreover, for the related silepines $Me_2Si\{2\text{-}CH(SiMe_3)\text{-}C_6H_4\}_2$, the observed isomers were δ-*SS* and λ-*RR*.[6] For germepine **5** and stannepine **6** and **7**, only one set of diastereoisomers has been observed in the ^{1}H NMR spectra. However, when compound **6** was refluxed for 10 h in toluene, the ^{1}H NMR spectrum of the compound isolated showed that the diastereosisomers, presumably $\delta SS/\lambda RR$ and $\lambda SS/\delta RR$, were in a ratio of 1:1. This is possibly due to the conversion of one pair of diastereoisomer to form the other pair through torsional rotation under more forcing conditions. Compounds **5** and **7** showed no interconversion even at elevated temperatures. This is also consistent with the spectra of their tungsten carbonyl complexes, which showed only one set of $SiMe_3$ peaks. These results suggested that the interconversion process depends mainly on the size of the ancillary ligands R′ and the heteroatom size, which is related to the $M-C_\alpha$ bond distance. The smaller the heteroatom size and the less bulky ancillary ligand favor ring-flipping interconversion. The low energy barrier corresponds to the transition state with the least unfavorable distortion.[15,16]

From the ^{1}H NMR spectra, it was found that the bimetallic complexes **8**−**10** remain in a C_2 symmetry in solution. The ^{1}H and ^{13}C NMR spectra of **8**−**10** resemble the uncoordinated compounds **5**−**7**. That is, two sets of diastereomers δ/λ-*RR* and δ/λ-*SS* are present in the ratio of 1:1 for compound **9**; one set of signals correspond to one set of diastereoisomers which are assignable to compounds **8** and **10**. The IR spectra of **8**−**10** are consistent with a *cis*-substituted tungsten tetracarbonyl complexes, as only four ν(CO) stretching peaks near 1900 cm^{-1} were observed.

X-ray Structures. Molecular Structure of $Me_2Si(L'L')$ (4). The molecular structure of **4** with the atom-numbering scheme and selected bond distances (Å) and angles (deg) are shown in Figure 2. There are two independent molecules in the asymmetric unit; both conform closely to idealized C_2 symmetry. The torsional angle (defined as the dihedral angle N(1)C(5)(C(6)N(2)) in each of the molecules is 57.4 and 59.0°, respectively. It has a mean $Si-C_\alpha$ bond distance of 1.895 Å and a mean Si−C(Me) distance of 1.864 Å. Both Si−C bond lengths are comparable to that of $SiMe_4$ (1.90 ± 0.05 Å). The angle subtended at the Si atom by the two methyl carbon atoms is 107°, while the angle subtended by the bidentate ligand is 109.6°. Both bond lengths and bond angles suggest that the silicon center adopts a tetrahedral geometry with slight distortion. The angles subtended at the α-carbons by the heteroatom Si and the aromatic carbon are 110.6° and 110.1°. In the seven-membered rings, the angle subtended at the heteroatom by the bidentate ligand is slightly larger than that subtended by the methyl groups. Such angular disposition is presumably due to steric crowding at the α-carbon of the dialkyl ligand L′L′.

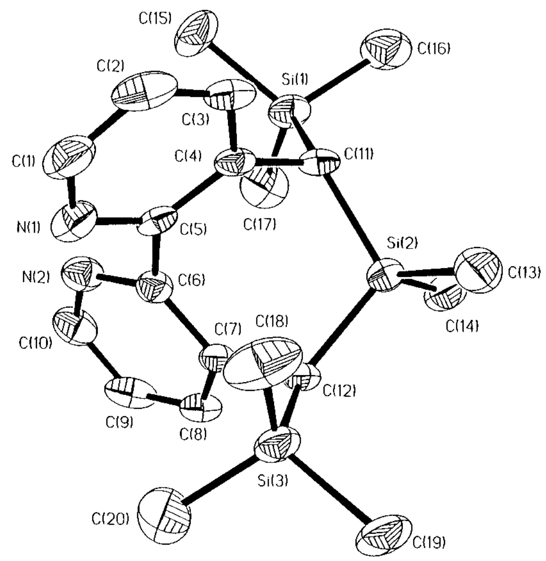

Figure 2. Crystal structure of **4**, non-hydrogen atoms are shown with 35% thermal ellipsoids. Selected bond distances (Å) and angles (deg) of molecule I: Si(1)−C(11) 1.908(6), Si(1)−C(15) 1.853(9), Si(1)−C(16) 1.868(9), Si(1)−C(17) 1.845(8), Si(2)−C(11) 1.890(7), Si(2)−C(12) 1.896(8), Si(2)−C(13) 1.849(8), Si(2)−C(14) 1.850(8), Si(3)−C(12) 1.894(6); C(11)−Si(2)−C(12) 109.9(3), C(11)−Si(2)−C(13) 107.5(4), C(12)−Si(2)−C(13) 111.7(3), C(11)−Si(2)−C(14) 112.4(3), C(12)−Si(2)−C(14) 108.5(4), C(13)−Si(2)−C(14) 106.9(4), Si(1)−C(11)−C(4) 112.7(4), Si(2)−C(12)−C(7) 110.6(5); torsional angle: 57.4°.

Molecular Structure of $Me_2Sn(L'L')$ (6). The molecular structure of **6** with the atom-numbering scheme and selected bond distances (Å) and angles (deg) are shown in Figure 3. Compound **6** was obtained as a chloroform solvate. Like the structure of **4**, it also adopts a C_2 symmetry. The mean $Sn-C_\alpha$ distance is 2.179 Å and that of Sn−C(Me) is 2.134 Å which is typical for these types of bonds, 2.13 and 2.18 Å (c.f., $SnMe_4$, C−Sn 2.18 ± 0.03 Å), and comparable to the $Sn-C_\alpha$ and Sn−C(phenyl) distances of 2.184(4) and 2.136(4) Å in the related stannepine $[Ph_2Sn\{2\text{-}CH(SiMe_3)C_6H_4\}_2]$.[6] The angle subtended at the Sn atom by the bidentate ligand is 99.0°, which is much smaller than the angle of 113.9° subtended by the methyl groups. The internal angle subtended at the α-carbons are 105.7 and 106.2°, respectively. The torsional angle of 67.3° is larger than that of the silicon analogue **4**. In comparison, the longer Sn−C distance makes it possible for the heterocyclic ring to release some ring strain by adopting a smaller angle at the tin center, hence adopting a larger torsional angle. It is noteworthy that the torsion angle in the structure of $[Ph_2Sn\{2\text{-}CH(SiMe_3)C_6H_4\}_2]$ is 70.8° and is larger than the similar angle in **6**.

Molecular Structure of $Me_2Sn(L'L')W(CO)_4$ (9). The molecular structure of **9** with the atom-numbering scheme and selected bond distances (Å) and angles (deg) are shown in Figure 4. The torsional angle for this bimetallic complex is 40.5°, which is significantly reduced by more than one-third in value (26.8°) when

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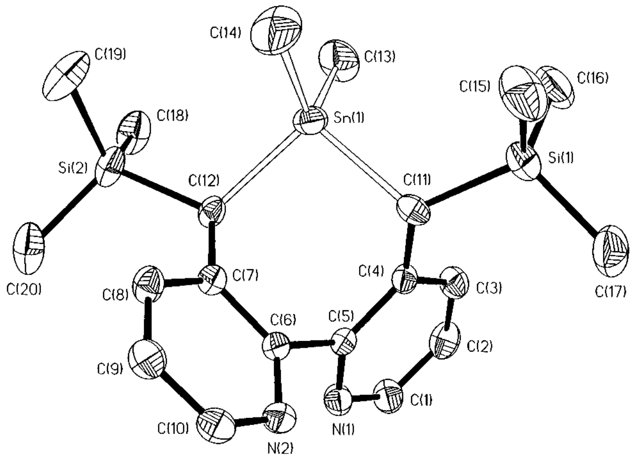

Figure 3. Crystal structure of **6**, non-hydrogen atoms are shown with 35% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Sn(1)−C(1) 2.182(5), Sn(1)−C(2) 2.176(4), Sn(1)−C(3) 2.133(7), Sn(1)−C(4) 2.135(7), Si(1)−C(1) 1.864(6), Si(2)−C(2) 1.880(5), C(1)−C(12) 1.516(6), C(2)−C(17) 1.516(6), C(11)−C(16) 1.514(7); C(1)−Sn(1)−C(2) 99.0(2), C(1)−Sn(1)−C(3) 111.7(3), C(2)−Sn(1)−C(3) 109.8(2), C(1)−Sn(1)−C(4) 109.5(3), C(2)−Sn(1)−C(4) 112.0(3), C(3)−Sn(1)−C(4) 113.9(3), Sn(1)−C(1)−C(12) 105.7(3), Sn(1)−C(2)−C(17) 106.2(3); torsional angle: 67.3°.

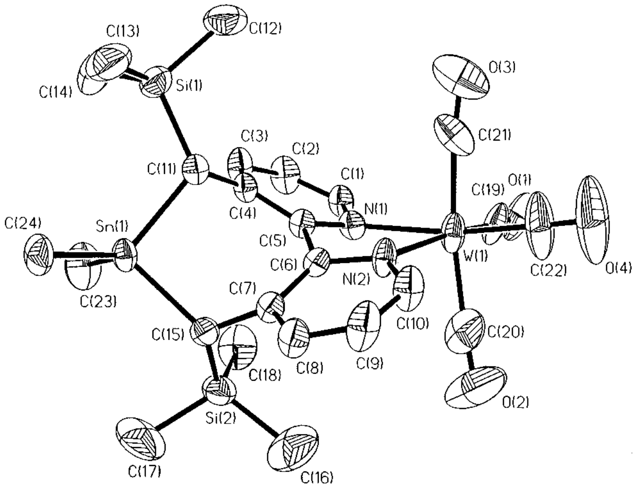

Figure 4. Crystal structure of **9**, non-hydrogen atoms are shown with 35% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Sn(1)−C(15) 2.176(7), Sn(1)−C(11) 2.178(10), Sn(1)−C(23) 2.133(11), Sn(1)−C(24) 2.132(9), W(1)−C(19) 1.976(10), W(1)−C(20) 2.025(12), W(1)−C(21) 1.978(12), W(1)−C(22) 1.948(10), W(1)−N(1) 2.215(7), W(1)−N(2) 2.228(7), C(19)−O(1) 1.150(13), C(20)−O(2) 1.175(15), C(21)−O(3) 1.169(16), C(22)−O(4) 1.157(14); C(11)−Sn(1)−C(15) 94.3(3), C(11)−Sn(1)−C(23) 110.2(4), C(15)−Sn(1)−C(23) 113.4(3), C(11)−Sn(1)−C(24) 117.1(4), C(23)−Sn(1)−C(24) 112.5(3), C(11)−Sn(1)−C(24) 109.0(4), C(19)−W(1)−C(20) 86.3(5), C(19)−W(1)−C(21) 88.8(4), C(20)−W(1)−C(21) 172.2(4), C(19)−W(1)−C(22) 92.2(4), C(20)−W(1)−C(22) 91.6(5), C(21)−W(1)−C(22) 82.5(5), N(1)−W(1)−N(2) 72.2(3); torsional angle: 40.5°.

compared with the angle of 67.3° in stannepine **6** before complexation. This difference is comparable to that of the cyclooctano[2,1-*b*:3,4-*b*′]bipyridine and its molybdenum tetracarbonyl complex (decreased from 62.4° (calcd) to 45° (measd)).[17] The reduction in the torsional angle is accompanied by the alteration of the internal angles of the seven-membered ring. The angle subtended at the Sn atom is reduced from 99.0° to 94.3°. The angles subtended at the 2-carbons are, however, increased asymmetrically from 105.7° and 106.2° to 117.0° and 106.7°. Such a difference is probably due to the change in the relative disposition of the $SiMe_3$ groups at the α-carbons upon flattening the two pyridine rings. Such an symmetric rearrangement is conceivable when the extreme case is considered, i.e., the total flattening of the two pyridine rings (zero torsional angle). The molecule will then change from C_2 to C_1 symmetry with one $SiMe_3$ group subjected to a greater steric congestion than the other. A shortening of the bond distances is also observed at bonds between the two pyridine rings (1.514 to 1.474 Å) between the ring carbons (1.516 to 1.487 Å). A slight bending of the C−O bond is observed. The mean bond distances of the equatorial and axial C−O bonds are 1.154 and 1.172 Å, respectively, and the mean bond distances of the W−C equatorial and axial bonds are 1.962 and 2.002 Å, respectively. When compared with the tungsten hexacarbonyl complex, the mean distances of the C−O and W−C bonds are 1.148 and 2.058 Å, respectively.[18] In this compound, a shortening of the W−C bond and a lengthening of the C−O bond is observed. Such changes are probably due to the poor π-accepting ability of bipyridine. Replacing two carbonyl groups with a bipyridine enhances the backbonding effect in the remaining carbonyl groups, hence leading to the shortening of the W−C bond and the lengthening of the C−O bond.

Experimental Section

General Procedure. All compounds were assumed to be air sensitive unless proven otherwise and were handled in a dinitrogen or an argon atmosphere or *in vacuo* with standard Schlenk techniques. Solvents were dried over sodium and distilled over calcium hydride (*n*-hexane), sodium ketal of benzophenone (THF, Et_2O, benzene), and sodium metal (pentane, toluene). Melting points were measured in sealed capillary tubes under nitrogen, unless otherwise stated. Both melting points and boiling points are uncorrected.

Physical Measurements. Infrared spectra were recorded on a Nicolet 20SXC FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded at 250 and 62.5 MHz, respectively, using a Brüker WM250 NMR spectrometer. Chemical shifts δ are relative to $SiMe_4$. Mass spectral data were either obtained on a VG 7070F mass spectrometer or performed at Shanghai Institute of Organic Chemistry, Academia Sinica, 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. E. Merck 70−230 mesh silica gel 80 and E. Merck aluminum oxide 90 were used for column chromatography. Elemental analyses were performed at MEDAC, Ltd., Department of Chemistry, Brunel University, Uxbridge. Dilithium reagent **1a** and **1b** were prepared as described in a previous paper.[2]

X-ray Crystallography. The crystals selected for study were mounted in glass capillaries and sealed under argon. Details of crystal parameters, data collection, and structure refinement are summarized in Table 1. Raw intensities were collected on a Siemens P4/PC four-circle diffractometer at room temperature (294 K). The crystal structure was solved by direct phase determination. All non-hydrogen atoms were

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Table 1. Selected Crystallographic and Data Collection Parameters of Compounds 4, 6, and 9

	4	6	9
mol formula	$C_{20}H_{32}N_2Si_3$	$C_{20}H_{32}N_2Si_2Sn{\cdot}CHCl_3$	$C_{26}H_{32}N_2O_4Si_2SnW$
mol wt	384.73	594.7	795.3
color and habit	colorless prism	white plate	reddish-brown prism
cryst size, mm	0.30 × 0.30 × 0.60	0.40 × 0.62 × 0.44	0.42 × 0.38 × 0.52
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$	$P\bar{1}$
a, Å	32.55(3)	13.401(4)	11.483(7)
b, Å	8.247(5)	10.545(4)	12.103(6)
c, Å	17.79(2)	21.439(8)	13.241(7)
α, deg		99.48(3)	
β, deg	105.44(4)	105.820(0)	92.71(2)
γ, deg		114.61(3)	
V, Å^3	4602(8)	2914.7(16)	1636.3(15)
Z	8	4	2
density, g cm^{-3}	1.110	1.355	1.614
abs coeff mm^{-1}	0.24	1.244	4.378
scan type	ω	ω	ω
scan rate, deg min^{-1}	4.0−60.0	4.19−29.30	3.00−60.00
$2\theta_{max}$, deg	44	3.0−50.0	2.0−52.0
no. of unique data measd	5562	5322	5687
no. of obsd reflns	3591	3775	4291
no. of variables	451	291	338
R	0.077	0.0497	0.048
wR	0.086	0.0635	0.068
weighting scheme $w^{-1} = [\sigma^2\lvert F_o\rvert + g\lvert F_o\rvert^2]$	0.0001	g = 0.0005	g = 0.0003
criteria for observation	$\lvert F_o\rvert \geq 4\sigma(\lvert F_o\rvert)$	$\lvert F_o\rvert \geq 4\sigma(\lvert F_o\rvert)$	$\lvert F_o\rvert \geq 3\sigma(\lvert F_o\rvert)$

subjected to anisotropic refinement. The hydrogen atoms were geometrically generated (C−H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms; all hydrogen atoms were assigned the appropriate isotropic temperature factors and included in the structure-factor calculations. Computation was performed using the SHELXTL PC program package on a PC486 computer.[19] Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.

Syntheses. Me$_2$Si(LL) (2). To a freshly prepared solution of the dilithium compound **1a**, prepared in hexane from 3,3′-dimethyl-2,2′-bipyridine (0.62 g, 3.4 mmol), tmeda (1.0 mL, 6.7 mmol), and Bu^{n}Li (4.2 mL, 1.6 M in hexane, 6.7 mmol) at 0 °C, was added Me$_2$SiCl$_2$ (0.47 g, 3.6 mmol). After the mixture was stirred for 30 min, hydrolysis followed by extraction with hexane was carried out. The organic layer was separated, dried, and concentrated. The oily product was purified by column chromatography (silica gel, ethyl acetate/MeOH = 95:5), yield ca. 2%. ^{1}H NMR (toluene-d_8, 25 °C): δ −0.05 (s, 6H), 1.27 (br s, 4H), 7.13 (dd, ^3J = 7.7 Hz, ^3J = 4.8 Hz, 2H), 7.37 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 2H), 8.50 (dd, ^3J = 4.8 Hz, ^4J = 1.5 Hz, 2H). ^{1}H NMR (toluene-d_8, −60 °C): δ 1.29 (AB quartet, J_{AB} = 13 Hz, 2H), 1.80 (AB quartet, J_{AB} = 13 Hz, 2H). ^{13}C NMR (toluene-d_8); δ −4.24, 21.22, 122.85, 134.02, 135.79, 146.44, 155.80. MS (m/z): 240 (M)$^+$, 149 (M − $C_5H_3NCH_2$)$^+$.

Me$_2$Sn(LL) (3). To a solution of Me$_2$SnCl$_2$ (1.32 g, 6.00 mmol) in hexane was added freshly prepared dilithium compound **1a**, prepared from 3,3′-dimethyl-2,2′-bipyridine (1.06 g, 5.75 mmol). After addition, the mixture was stirred for 3 h and kept at ambient temperature for 3 h. The solvent and volatiles were then removed *in vacuo*. The residue was extracted with ca. 300 mL of dried diethyl ether and filtered through Celite. The filtrate was concentrated and chromatographed over neutral alumina with an ethyl acetate:hexane (4:1) as the eluent. The major portion was collected and recrystallized in diethyl ether, yield 0.70 g (37%) of a white crystalline solid of **3**, mp 173 °C (dec). ^{1}H NMR (CDCl$_3$): δ −0.14 (s, 6H, $^3J_{Sn-H}$ = 54, 51Hz), 1.59 and 1.83 (AB quartet, 2H, $^2J_{Sn-H}$ unresolved), 6.71 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 2H), 6.90 (dd, 2H), 8.51 (dd, 2H). ^{13}C NMR (CDCl$_3$): δ −10.45, 15.33, 122.72, 134.32, 135.86, 145.55, 155.94. MS (m/z): 332 (P)$^+$, 317 (M − Me)$^+$, 302 (M − 2Me)$^+$, 182 (M − SnMe$_2$)$^+$.

Me$_2$Si(L′L′) (4). To a solution of Me$_2$SiCl$_2$ (0.60 mL, 5.0 mmol) in hexane was added dilithium compound **1b** (2.84 g, 4.95 mmol), and this was stirred at 45 °C for 24 h. The reaction mixture was then hydrolyzed with base, and removal of the solvent followed by hexane extraction gave a light orange solution. The concentrated extract was chromatographed over neutral alumina with hexane/ethyl acetate: 85:15 as the eluent. Recrystallization of the solid residue from hexane gave colorless rod-shaped crystals of the title compound, mp 129−131 °C, yield 0.20 g (11%). ^{1}H NMR (CDCl$_3$) for (*SS*/*RR*) diastereoisomers: δ −0.47 (s, 18H), 0.23 (s, 6H), 1.46 (s, 2H), 7.09 (dd, ^3J = 7.7 Hz, ^3J = 4.6 Hz, 2H), 7.25 (dd, ^3J = 7.7 Hz, ^4J = 1.6 Hz, 2H), 8.53 (dd, ^3J = 4.6 Hz, ^4J = 1.6 Hz, 2H). ^{1}H NMR for (*RR*/*SS*) diastereomers: δ −0.02 (s, 18H), 0.04 (s, 6H), 1.24 (s, 2H), 7.18 (dd, ^3J =7.9 Hz, ^3J = 4.7 Hz, 2H), 7.49 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 2H), 8.51 (dd, ^3J = 4.7 Hz, ^4J = 1.5 Hz, 2H). ^{13}C NMR (CDCl$_3$) (*SS*/*RR*): δ 0.62, 2.67, 28.73, 123.52, 135.40, 139.49, 147.09, 156.72. ^{13}C NMR (*RR*/*SS*): δ −1.45, 1.94, 122.94, 137.13, 138.27, 146.54, 158.55. MS m/z: 384 (M)$^+$, 369 (M − Me)$^+$, 311 (M − SiMe$_3$)$^+$. Anal. Calcd for $C_{20}H_{32}N_2Si_3$: C, 62.44; H, 8.38; N, 7.28. C, 62.67; H, 8.39; N, 7.26.

Me$_2$Ge(L′L′) (5). To a solution of **1b** (0.54 g, 0.94 mmol) in hexane was added Me$_2$GeCl$_2$ (0.11 mL, 0.94 mmol) at 0 °C. The reaction mixture was then stirred at ambient temperature for 12 h. The reaction mixture was filtered, concentrated, and cooled to afford 0.08 g (20% yield) of a colorless crystalline solid of **5**, mp 202 °C (dec at 215 °C). ^{1}H NMR (C$_6$D$_6$): δ −0.35 (s, 18H), 0.30 (s, 6H), 1.40 (s, 2H), 6.67 (dd, ^3J = 7.8 Hz, ^3J = 4.5

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[19] Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*; Oxford University Press: New York, 1985. *SHELXTL PC Manual*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

Hz, 2H), 6.78 (dd, $^3J = 7.8$ Hz, $^4J = 1.7$ Hz, 2H), 8.51 (dd, $^3J = 4.5$ Hz, $^4J = 1.7$ Hz, 2H). ^{13}C NMR (toluene-d_8): δ 0.92, 2.74, 29.47, 123.64, 143.43, 147.45, 158. MS *m/z*: 430 (P)$^+$, 429 (P − H)$^+$, 356 (P − H − TMS)$^+$, 310 (P − GeMe$_2$ − Me − H)$^+$, 238 (P − GeMe$_2$ − Me − TMS)$^+$. Anal. Calcd for $C_{20}H_{32}N_2Si_2Ge$: C, 65.79; H, 8.59; N, 8.52. Found: C, 65.69; H, 8.62; N, 8.47.

Me$_2$Sn(L′L′) (6). To a solution of Me_2SnCl_2 (1.02 g, 4.64 mmol) in 50 mL of solvent mixture of hexane/THF (3:2) at 0 °C was added a solution of **1b** (2.66 g, 4.64 mmol) in 70 mL THF in one portion with efficient stirring. After the addition, the mixture was left to warm up to ambient temperature and stirring was continued for 4 h before the solvent was completely removed *in vacuo*. Hexane (ca. 100 mL) was added to extract the product. After filtration and concentration, an orange oil was obtained which solidified on standing. The product was chromatographed over neutral alumina with hexane/ethyl acetate (3:1) as the eluent. The major fraction was collected, and removal of the solvent afforded colorless crystals. Recrystallization of the solid in a mixture of hexane and chloroform afforded good quality colorless crystals for X-ray analysis, yield 1.35 g (61.0%), mp 118−120 °C. ^{1}H NMR (CDCl$_3$): δ 0.06 (s, 18 H), 0.24 (s, 6H, $^2J_{\mathrm{Sn-H}} = 50$ Hz), 2.15 (s, 2H, $^2J_{\mathrm{Sn-H}} = 93$ Hz), 7.16 (dd, $^3J = 7.8$ Hz, $^3J = 4.8$ Hz, 2H), 7.47 (dd, $^3J = 7.8$ Hz, $^4J = 1.5$ Hz, 2H), 8.41 (dd, $^3J = 4.8$ Hz, $^4J = 1.5$ Hz, 2H). ^{13}C NMR (toluene-d_8): δ −6.51, 1.79, 19.24, 123.22, 133.61, 138.20, 146.41, 158.86. MS *m/z*: 476 (M)$^+$, 461 (M − Me)$^+$, 403 (M − SiMe$_3$)$^+$, 326 (M − SnMe$_2$)$^+$, 311 (M − SnMe$_2$ − Me)$^+$, 238 (M − SnMe$_2$ − Me − SiMe$_3$)$^+$. Anal. Calcd for $C_{23}H_{39}N_2Si_2Sn$: C, 53.18; H, 7.76; N, 5.39. Found: C, 53.13; H, 7.58; N, 5.29.

After refluxing the solid compound of **6** in toluene for 10 h, another pair of diastereoisomers form (*RR*/*SS*) with the ratio of *SS*/*RR*:*RR*/*SS* = 1:1. ^{1}H NMR for *RR*/*SS* (CDCl$_3$): δ −0.43 (s, 18H), 0.29 (s, 6H, $^2J_{\mathrm{Sn-H}} = 50$ Hz), 1.67 (s, 2H, $^2J_{\mathrm{Sn-H}} = 73$ Hz), 7.07 (dd, $^3J = 7.8$ Hz, $^3J = 4.6$ Hz, 2H), 7.28(dd, ^3J =7.8 Hz, $^4J = 1.3$ Hz, 2H), 8.45 (dd, $^3J = 4.6$ Hz, $^4J = 1.3$ Hz, 2H). ^{13}C NMR (toluene-d_8): −4.71, 0.91, 15.17, 123.72, 139.42, 146.80, 160.31 (with one aromatic peak masked by solvent).

Ph$_2$Sn(L′L′) (7). A similar procedure to that used in the preparation of **6** was adopted, with Ph_2SnCl_2 (0.615 g, 1.78 mmol) and **6b** (1.02 g, 1.78 mmol) as the starting materials. The mixture was stirred at ambient temperature for 6 h before the solvent was removed under vacuum. Recrystallization in hexane afforded colorless crystals of **7**, yield 0.21 g (20%), mp 183−185 °C. ^{1}H NMR (CDCl$_3$): δ −0.23 (s, 18H), 1.99 (s, 2H, $^2J_{\mathrm{Sn-H}} = 96$ Hz), 7.22 (dd, $^3J = 7.8$ Hz, $^3J = 4.7$ Hz, 2H), 7.31−7.38 (m, 10H), 7.47 (dd, $^3J = 7.8$ Hz, $^4J = 1.3$ Hz, 2H), 7.52 (dd, $^3J = 4.7$ Hz, $^4J = 1.3$ Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 1.46, 19.42 ($J_{\mathrm{Sn-H}} = 280$ Hz), 123.05, 129.26, 129.65, 135.31, 137.34, 137.65, 139.36, 146.04, 158.71. MS *m/z*: 600 (P)$^+$, 527 (M − SiMe$_3$)$^+$, 326 (M − SnPh$_2$)$^+$, 311 (M − SnPh$_2$ − Me)$^+$, 238 (M − SnPh$_2$ − SiMe$_3$ − Me)$^+$. Anal. Calcd for $C_{30}H_{36}N_2Si_2Sn$: C, 60.11; H, 6.05; N, 4.67. Found: C, 60.01; H, 6.05; N, 4.67.

Me$_2$Ge(L′L′)W(CO)$_4$ (8). To a mixture of **4** (0.10 g, 0.23 mmol) and W(CO)$_6$ (0.08 g, 0.23 mmol) was added ca. 30 mL of toluene. The reaction mixture was refluxed for 10 h (monitored by TLC). Concentration of the resulting red solution to about 10 mL followed by cooling to −30 °C afforded a red crystalline solid, mp 234−5 °C, yield 0.06 g (40%). Mass spectrometric analysis showed an identical spectrum to that of **16**. The red solid was stable in air, but the chloroform solution decomposed on prolonged standing. ^{1}H NMR (CDCl$_3$): δ −0.50 (s, 18H), 0.53 (s, 6H), 1.78 (s, 2H), 7.15 (dd, $^3J = 7.8$ Hz, $^3J = 5.2$ Hz, 2H), 7.45 (dd, $^3J = 7.8$ Hz, $^4J = 1.5$ Hz, 2H), 8.95 (dd, $^3J = 5.2$ Hz, $^4J = 1.5$ Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 0.42, 2.62, 31.35, 124.29, 141.37, 144.96, 149.24, 156.38, 203.22, 216.86. MS *m/z*: 430 (M − W(CO)$_4$)$^+$, 429 (M − H − W(CO)$_4$)$^+$, 356 (M − H − SiMe$_3$ − W(CO)$_4$)$^+$ Anal. Calcd for $C_{24}H_{32}N_2O_4Si_2GeW$: C, 39.75; H, 4.45; N, 3.86. Found: C, 39.82; H, 4.43; N, 3.81. IR (KBr disc) ν(CO): 1998, 1900, 1888, 1824 cm^{-1}.

Me$_2$Sn(L′L′)W(CO)$_4$ (9). A similar procedure to that used in the preparation of **8** was carried out with compound **6** (0.26 g, 0.55 mmol) and W(CO)$_6$ (0.19 g, 0.55 mmol). After the mixture was refluxed for 10 h, the reaction mixture was concentrated to 5 mL and was kept at −20 °C, affording red crystals, mp 148−150°C, yield 0.43 g (95%). X-ray crystallography indicated the structure (L′L′)SnMe$_2$·W(CO)$_4$·$^1/_2$PhMe. ^{1}H NMR (CDCl$_3$): δ −0.52 (s, 18H), 0.08 (s, 18H), 0.32 (s, 6H, $^2J_{\mathrm{Sn-H}}$ = 42, 51 Hz), 0.48 (s, 6H, $^2J_{\mathrm{Sn-H}}$ = 41, 46 Hz), 1.61 (s, 2H, $^2J_{\mathrm{Sn-H}} = 29$ Hz), 2.04 (s, 2H, $^2J_{\mathrm{Sn-H}} = 42$ Hz), 7.13−7.20 (m, 4H), 7.49−7.55 (m, 4H), 8.79 (dd, 2H), 8.90 (dd, 2H). Coupling constant unresolved. ^{13}C NMR (CDCl$_3$): δ −7.08, −2.01, −0.07, 1.45, 21.41, 29.97, 128.92, 129.73, 136.21, 141.75, 142.62, 145.24, 148.96, 155.40, 156.87, 203.33, 203.68, 216.78. MS *m/z*: 476 (M − W(CO)$_4$)$^+$, 460 (M − W(CO)$_4$ − Me)$^+$, 403 (M − W(CO)$_4$ − SiMe$_3$)$^+$. Anal. Calcd for $C_{55}H_{72}N_4O_8Si_4Sn_2W_2$: C, 40.41; H, 4.44; N, 3.43. Found: C, 40.34; H, 4.44; N, 3.31. IR ν(CO): 2005, 1894, 1852, 1816 cm^{-1}.

Ph$_2$Sn(L′L′)W(CO)$_4$ (10). A mixture of **18** (0.20 g, 0.33 mmol) and W(CO)$_6$ (0.12 g, 0.34 mmol) was refluxed for 10 h in toluene. Removal of a small amount of solvent afforded an orange powder, mp 285−290 °C, dec > 290 °C, yield 0.20 g (66%). ^{1}H NMR (CDCl$_3$): δ −0.64 (s, 18H), 2.54 (s, 2H, $^2J_{\mathrm{Sn-H}} = 97$ Hz), 7.26 (dd, $^3J = 7.9$ Hz, $^3J = 5.1$ Hz, 2H), 7.42−7.44 (m, 6H), 7.53−7.57 (m, 4H), 7.76 (dd, $^3J = 7.9$ Hz, $^4J = 1.3$ Hz, 2H), 7.98(dd, $^3J = 5.1$ Hz, $^4J = 1.3$ Hz, 2H). ^{13}C NMR (CDCl$_3$): δ −0.41, 26.61, 124.11, 126.00, 129.14, 130.10, 136.78, 139.97, 141.09, 144.87, 148.54, 202.66, 216.30. MS (CI-CH$_4$) *m/z*: 601 (M − W(CO)$_4$ + 1)$^+$, 585 (M − W(CO)$_4$ − Me)$^+$, 523 (M − W(CO)$_4$ − Ph)$^+$, 326 (M − W(CO)$_4$ − SnPh$_2$)$^+$. IR ν(CO): 2003, 1890, 1863, 1820 cm^{-1}.

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Supporting Information Available: ORTEP and cell-packing diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates (38 pages). Ordering information is given on any current masthead page.

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