Organometallics **1996,** *15,* 4063−4074 4063

Synthesis of New Silyl-Bridged Bis(cyclopentadienyl) Ligands and Complexes

Jean L. Huhmann, Joyce Y. Corey,*[,†] and Nigam P. Rath

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

Received February 22, 1996[⊗]

The new monobridged compound, $[\mu\text{-(MePhSi)}(C_5H_5)_2]$ (**2**), was obtained as a mixture of five positional isomers from the reaction of $MePhSiCl_2$ with 2 equiv of $Li(C_5H_5)$. Deprotonation of **2** with 2 equiv of ^{n}BuLi and subsequent reaction with 1 equiv of Me_2SiCl_2 in THF resulted in an unsymmetrical dibridged (bis)cyclopentadienyl compound, $[\mu,\mu\text{-(MePhSi)}(Me_2Si)(C_5H_4)_2]$ (**3**). Compound **3** was shown to be a mixture of five isomers by 1D and 2D NMR experiments. Similarly, $[\mu\text{-}(Me_2SiCH_2CH_2SiMe_2)(C_5H_5)_2]$ (**4**) was deprotonated with 2 equiv of ^{n}BuLi and subsequently reacted with 1 equiv of $ClMe_2SiCH_2CH_2SiMe_2Cl$ to provide the (bis)cyclopentadienyl compound with two four-atom bridges, $[\mu,\mu\text{-}(Me_2SiCH_2CH_2SiMe_2)_2(C_5H_4)_2]$ (**5**). X-ray diffraction studies of sublimed **5** showed the solid state structure to be the symmetrical 1,3−1,3 *trans* isomer, and NMR studies of **5** indicated a mixture of isomers in solution. The ^{1}H, ^{13}C, ^{29}Si, and VT NMR spectra of compounds **2**, **3**, and **5** are described. Deprotonation of compounds **2**, **3**, and **5** and subsequent reaction with 2 equiv of $(C_5H_5)TiCl_3$ produced the bimetallic complexes $[\mu\text{-(MePhSi)}(C_5H_4)_2][(C_5H_5)TiCl_2]_2$ (**6**), 1,2−1,2 *trans*-$[\mu,\mu\text{-(MePhSi)}(Me_2Si)(C_5H_3)_2][(C_5H_5)TiCl_2]_2$ (**7**), and a mixture of *trans* and *cis* isomers of 1,3−1,3 $[\mu,\mu\text{-}(Me_2SiCH_2CH_2SiMe_2)_2(C_5H_3)_2][(C_5H_5)TiCl_2]_2$ (**8**).

Introduction

The synthesis of bridged bis(cyclopentadienyl) [(bis)-Cp] compounds has recently received considerable attention, mainly due to two factors. Firstly, bridged (bis)Cp ligands are the starting point for the synthesis of homo- and heteronuclear bimetallic complexes which could potentially exhibit cooperative electronic and chemical effects that would be useful in catalysis.[1] Secondly, bridged (bis)Cp ligands may be used in the synthesis of *ansa*-metallocenes, which have shown high selectivity in several Ziegler−Natta type polymerization processes.[2] Among the possible bridges between two Cp rings, we have concentrated our efforts in the synthesis of new (bis)Cp ligands of the general types **A**, with bridges that link the 1,2 positions of both Cp rings (designated the 1,2−1,2 isomer) and **B**, with bridges between the 1,3 positions of both Cp rings (designated the 1,3−1,3 isomer), shown in Figure 1. Dibridged (bis)-Cp ligands restrict the relative orientation of the two metals in the corresponding bimetallic complexes **C** and **D**, locking the metals on either the same (*cis*) or opposite (*trans*) faces of the ligand. Furthermore, in the *ansa*-metallocenes of the general type **E**, dibridged ligands may offer a more constrained environment compared to *ansa*-metallocenes of the analogous monobridged ligand.

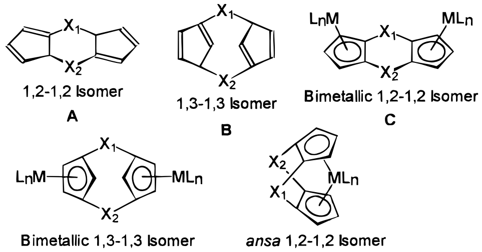


Figure 1. Dibridged (bis)Cp ligands and complexes. *Cis* and *trans* isomers of **A**−**D** are possible; only *cis* isomers are shown.

The most common dibridged (bis)Cp ligand of type **A** reported in the literature is the one in which $X_1 = X_2 = Me_2Si$, $[\mu,\mu\text{-}(Me_2Si)_2(C_5H_4)_2]$ (**1**).[1c,3] This ligand has been deprotonated and reacted with various metal sources to produce complexes of the types **C** [1c,4] and **E**.[4h,5] Related **A** ligands have been reported for $X_1 = Me_2Si$, $X_2 = Me_2Sn$,[1d] Me_2C [1d,6] and $X_1 = Me_2C$, $X_2 = Me_2Ge$, Me_2Sn.[6] For the **A** ligand where $X_1 = X_2 = CH_2CH_2$,[7] both the metalated complexes of the types **C** [8] and **E** [7] were observed. When $X_1 = X_2 = Me_2SiSiMe_2$, the 1,1−1,1 isomer of the ligand was characterized by NMR spectroscopy, and metalated complexes of the types **C**−**E** were observed.[9] Substituted cyclopentadienone complexes related to **D** have been reported for $X_1 = X_2 = CH_2CH_2CH_2CH_2$.[10] Finally, two examples of **A** ligands

---

[†] E-mail address: corey@jinx.umsl.edu.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) (a) For several recent examples, see: (a) Reddy, K. P.; Petersen, J. L. *Organometallics* **1989**, *8*, 2107−2113. (b) Buzinkai, J. F.; Schrock, R. R. *Inorg. Chem.* **1989**, *28*, 2837−2846, and references cited therein. (c) Siemeling, U.; Jutzi, P.; Neumann, B.; Stammler, H.-G.; Hursthouse, M. B. *Organometallics* **1992**, *11*, 1328−1333. (d) Nifant'ev, I. E.; Borzov, M. V.; Churakov, A. V.; Mkoyan, S. G.; Atovmyan, L. O. *Organometallics* **1992**, *11*, 3942−3947. (e) Jüngling, S.; Mülhaupt, R. *J. Organomet. Chem.* **1993**, *460*, 191−195. (f) Manriquez, J. M.; Ward, M. D.: Reiff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 6182−6193.

(2) (a) Thayer, A. M. *Chem. Eng. News* **1995**, *73* (Sept. 11), 15−20, and references cited therein. (b) Rieger, B.; Jang, G.; Fawzi, R.; Steimann, M. *Organometallics* **1994**, *13*, 647−653.

(3) (a) Belsky, V. K.; Zemlyansky, N. N.; Borisova, I. V.; Kolosova, N. D.; Beletskaya, I. P. *Cryst. Struct. Commun.* **1982**, *11*, 497−500. (b) Jones, P. R.; Rozell, J. M., Jr.; Campbell, B. M. *Organometallics* **1985**, *4*, 1321−1324. (c) Hiermeier, J.; Köhler, F. H.; Müller, G. *Organometallics* **1991**, *10*, 1787−1793. (d) Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. *Tetrahedron Lett.* **1981**, *22*, 7−10.

S0276-7333(96)00132-X CCC: $12.00

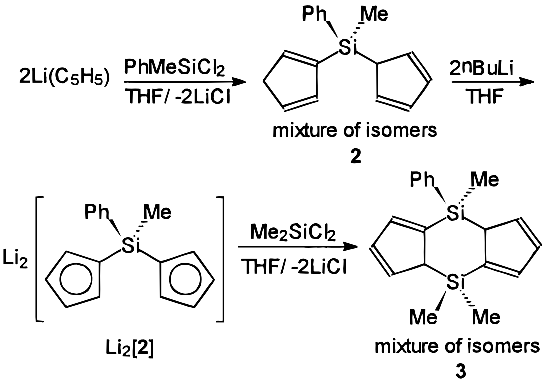
with a third bridge connecting X_1 and X_2 have been metallated to provide complexes related to **C** [11] and **E**.[12]

Here, we describe the preparation of the new monobridged (bis)Cp compound [μ-(MePhSi)(C_5H_5)$_2$] (**2**), and the reaction of its dilithio salt Li_2[μ-(MePhSi)(C_5H_4)$_2$] (Li_2[**2**]) with Me_2SiCl_2 to produce a dibridged (bis)Cp ligand of type **A**, where $X_1 = Me_2Si$ and $X_2 =$ PhMeSi. This derivative, [μ,μ-(MePhSi)(Me_2Si)(C_5H_4)$_2$] (**3**), was produced as a mixture of five isomers. Similarly, the salt elimination reaction of Li_2[μ-($Me_2SiCH_2CH_2SiMe_2$)-(C_5H_4)$_2$] (Li_2[**4**]) with $ClMe_2SiCH_2CH_2SiMe_2Cl$ provided the (bis)Cp compound with two four-atom linkages, [μ,μ-($Me_2SiCH_2CH_2SiMe_2$)$_2$(C_5H_4)$_2$] (**5**), which was shown to be a type **B** ligand in the solid state by X-ray diffraction studies. Conversely, NMR studies of **5** showed that there was a mixture of two isomers in toluene solution. Also described in this report is the reaction of the dilithio salts of **2**, **3**, and **5** with 2 equiv of (C_5H_5)$TiCl_3$ to produce the bimetallic complexes [μ-(MePhSi)(C_5H_4)$_2$]-[(C_5H_5)$TiCl_2$]$_2$ (**6**), [μ,μ-(MePhSi)(Me_2Si)(C_5H_3)$_2$][(C_5H_5)-$TiCl_2$]$_2$ (**7**), and [μ,μ-($Me_2SiCH_2CH_2SiMe_2$)$_2$(C_5H_3)$_2$][(C_5H_5)$TiCl_2$]$_2$ (**8**), respectively. Complex **7** was formed as the type **C** *trans* isomer, and complex **8** was isolated as a mixture of type **D** *trans* and *cis* isomers.

Results and Discussion

The general approach employed in this study for the synthesis of mono- and dibridged (bis)Cp ligands was a salt elimination reaction between substituted chlorosilanes and lithiated Cp sources to produce new Si−Cp bonds. The preparation and characterization of **2** is described for the first time, and **4** was prepared as described in the literature.[13] The monobridged (bis)Cp compounds **2** and **4** were used as starting materials for the new dibridged compounds **3** and **5**, respectively. The (bis)Cp ligands were then doubly deprotonated and reacted with 2 equiv of (C_5H_5)$TiCl_3$ to produce the corresponding new bimetallic complexes **6**−**8**.

Preparation of [μ-(MePhSi)(C_5H_5)$_2$] (2) and [μ,μ-(MePhSi)(Me_2Si)(C_5H_4)$_2$] (3). The monobridged (bis)Cp compound **2** was prepared in a manner similar to that for the known compound [μ-(Me_2Si)(C_5H_5)$_2$],[14] from the reaction of $MePhSiCl_2$ with 2 equiv of Li(C_5H_5) (eq 1). The product was isolated after aqueous workup by vacuum distillation to provide **2** as a colorless oil in good yield (47%). Deprotonation of isolated **2** with 2 equiv of ^{n}BuLi and subsequent reaction with Me_2SiCl_2 produced compound **3** (eq 1). This dibridged (bis)Cp compound was isolated via nonaqueous workup and was vacuum distilled to provide pure **3** in low yield (18%) as a pale yellow viscous oil. Interestingly, if a nonaqueous workup was used in the isolation of **2**, or an aqueous workup was used in the isolation of **3**, significantly reduced yields were observed in both cases. Compounds **2** and **3** were sensitive to both light and air. The isolated oils thickened and darkened in color when exposed to air for more than 1 h and became very viscous if left at room temperature in ambient lighting for more than 5 h in capped vials. However, both **2** and **3** may be stored for at least 6 months in nitrogen filled vials at −50 °C. The gas chromatograph traces of **2** and **3** each showed one sharp peak in >99% purity. Elemental analyses of **2** and **3** were not obtainable due to the tendency of the samples to polymerize; however, satisfactory high-resolution mass spectra were obtained, and the parent peaks of *m*/*z* 250 and 306 were observed for **2** and **3**, respectively.



(1)

Compound **2** is an example of a monobridged (bis)Cp ligand with two different substituents on the bridging atom (Me and Ph). Therefore, **2** represents a potential precursor to both bimetallic complexes, such as the one described later in this paper, and *ansa*-metallocenes with unsymmetrical substitution at the bridge. Unsymmetrical *ansa*-metallocenes have recently shown good stereoselectivity for several catalytic processes.[2b] Furthermore, the MePhSi linkage has been used to generate the first unsymmetrically substituted silicon bridged ferrocene, and the crystal structure proved to have interesting features.[15a] However, the bridged ferrocene was prepared from dilithiated ferrocene and $MePhSiCl_2$, and the metal-free (bis)Cp ligand was never produced.[15b]

---

(4) (a) Atzkern, H.; Hiermeier, J.; Kanellakopulos, B.; Köhler, F. H.; Müller, G.; Steigelmann, O. *J. Chem. Soc., Chem. Commun.* **1991**, 997−999. (b) Atzkern, H.; Hiermeier, J.; Köhler, F. H.; Steck, A. *J. Organomet. Chem.* **1991**, *408*, 281−296. (c) Fritz, M.; Hiemeier, J.; Hertkorn, N.; Köhler, F. H.; Müller, G.; Reber, G.; Steigelmann, O. *Chem. Ber.* **1991**, *124*, 1531−1539. (d) Siemeling, U.; Jutzi, P.; Bill, E.; Trautwein, A. X. *J. Organomet. Chem.* **1993**, *463*, 151−154. (e) Atzkern, H.; Bergerat, P.; Fritz, M.; Hiermeier, J.; Hudeczek, P.; Kahn, O.; Kanellakopulos, B.; Köhler, F. H.; Ruhs, M. *Chem. Ber.* **1994**, *127*, 277−286. (f) Song, F. Q.; Lu, G. L.; Wang, Z. Y.; Zhou, X. Z. *Chem. Abs.* **1994**, *122*, 1877219. (g) Amor, F.; Gómez-Sal, P.; de Jesús, E.; Royo, P.; Miguel, A. V. *Organometallics* **1994**, *13*, 4322−4327. (h) Cano, A; Cuenca, T.; Gómez-Sal, P.; Royo, B.; Royo, P. *Organometallics* **1994**, *13*, 1688−1694. (i) Lang, H.; Blau, S.; Muth, A.; Weiss, K.; Neugebauer, U. *J. Organomet. Chem.* **1995**, *490*, C32−C36. (j) Galakhov, M. V.; Gil, A.; de Jesús, E.; Royo, P. *Organometallics* **1995**, *14*, 3746−3750. (k) Corey, J. Y.; Huhmann, J. L.; Rath, N. P. *Inorg. Chem.* **1995**, *34*, 3203−3209.

(5) (a) Mengele, W.; Diebold, J.; Troll, C.; Röll, W.; Brintzinger, H. H. *Organometallics* **1993**, *12*, 1931−1935. (b) Lang, H.; Blau, S.; Pritzkow, H.; Zsolnai, L. *Organometallics* **1995**, *14*, 1850−1854.

(6) Nifant'ev, I., E.; Yarnykh, V. L.; Borzov, M. V.; Mazurchik, B. A.; Mstyslavsky, V. I.; Roznyatovsky, V. A.; Ustynyuk, Y. A. *Organometallics* **1991**, *10*, 3739−3745.

(7) Dorer, B.; Prosenc, M.-H.; Rief, U.; Brintzinger, H. H. *Organometallics* **1994**, *13*, 3868−3872.

(8) (a) Benedikt, M.; Schlögl, K. *Monatsh. Chem.* **1978**, *109*, 805−822. (b) Paulus, H.; Schlögl, K. Weissensteiner, W. *Monatsh. Chem.* **1983**, *114*, 799−808.

(9) Jutzi, P.; Krallmann, R.; Wolf, G.; Neumann, B.; Stammler, H.-G. *Chem. Ber.* **1991**, *124*, 2391−2399.

(10) Jutzi, P.; Siemeling, U.; Müller, A.; Bögge, H. *Organometallics* **1989**, *8*, 1744−1750.

(11) Atzkern, H.; Huber, B.; Köhler, F. H.; Müller, G.; Müller, R. *Organometallics* **1991**, *10*, 238−244.

(12) Grossman, R. B.; Tsai, J.-C.; Davis, W. M.; Gutiérrez, A.; Buchwald, S. L. *Organometallics* **1994**, *13*, 3892−3896.

(13) Lang, H.; Seyferth, D. *Organometallics* **1991**, *10*, 347−349.

(14) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470−1478. CpLi was used in place of CpNa.

(15) (a) Foucher, D. A.; Lough, A. J.; Manners, I.; Rasburn, J.; Vancso, J. G. *Acta Crystallogr.* **1995**, *C51*, 580−582. (b) Foucher, D. A.; Ziembinski, R.; Petersen, R.; Pudelski, J.; Edwards, M. E.; Ni, Y.; Massey, J.; Jaeger, C. R.; Vancso, J. G.; Manners, I. *Macromolecules* **1994**, *27*, 3992−3999.

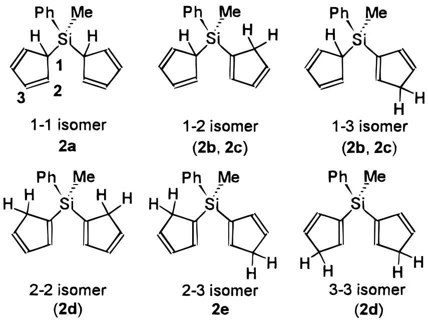


Figure 2. Possible positional isomers of **2**, and assignments of **2a**−**e**, on the basis of NMR evidence.

Therefore, since **2** is a new compound which has potential applications in organometallic chemistry, it was isolated and characterized.

The dibridged (bis)Cp compound **3** was prepared with the expectation that it would be a useful ligand for the formation of bimetallic complexes of the type **C** and *ansa*-metallocenes of the type **E** (Figure 1). Compound **3** may exhibit reactivity similar to that of the well-characterized and frequently used tetramethyl analogue $[\mu,\mu\text{-}(Me_2Si)_2(C_5H_4)_2]$ (**1**) (**A**, $X_1 = X_2 = Me_2Si$).[1c,3−5] An advantage of **3** as a ligand in bimetallic systems instead of **1** would be that the Ph substituent may act as a directing group, inducing both metals to coordinate on the same face (*cis*) of the ligand and *anti* to the Ph. *Cis* coordination of metals in bimetallic systems would become important when possible cooperative effects in catalytic processes are being studied.[4k] In *ansa*-metallocenes, **3** may provide asymmetry that could enhance the selectivity when the complexes in catalytic reactions are employed. The route generally used to prepare **1** is a dimerization reaction of $(C_5H_5)Me_2SiCl$ in the presence of ^nBuLi.[3] Compound **3** is unsymmetrical (**A**, $X_1 \neq X_2$), and would not be accessible through this type of process. Therefore, we have prepared **3** from the salt elimination reaction shown in eq 1. This procedure is similar to that described by Nifant'ev for the preparation of $[\mu,\mu\text{-}(Me_2X)(Me_2C)(C_5H_4)_2]$ (X = Si, Ge, and Sn), from $Li_2[\mu\text{-}(Me_2C)(C_5H_4)_2]$ and Me_2XCl_2.[6]

NMR Characterization and VT NMR for $[\mu\text{-}(MePhSi)(C_5H_5)_2]$ (2). There are six positional isomers possible for **2**, each with the aliphatic protons on different positions around the two Cp rings, as shown in Figure 2. The positions of the aliphatic Cp protons are indicated by the number of the ring carbon (1, 2, or 3), illustrated for the 1−1 isomer in Figure 2. For the purposes of this discussion, the carbon in the 1-position and the attached proton will be referred to as *bridgehead* HC_{Cp}, and carbons in the 2- or 3-positions and the two attached protons are referred to as H_2C_{Cp}. Thus, the 1−1 isomer has two bridgehead HC_{Cp}'s, and the 1−2 isomer has one bridgehead HC_{Cp} and one H_2C_{Cp}. Three of the positional isomers (1−2, 1−3, and 2−3) also have enantiomers due to chirality of the silicon center.

^1H, ^{13}C, and ^{29}Si NMR spectra were collected for **2** in C_7D_8, and data obtained at 300 K for the Me, H_2C_{Cp}, and bridgehead HC_{Cp} regions are presented in Table 1. Correlation data were obtained from ($^{29}Si,^1H$) and ($^{13}C,^1H$) HETCOR experiments, and the number of protons attached to each carbon was confirmed by ^{13}C DEPT experiments. It was determined from the number of resonances in the Me region of the ^1H and ^{13}C NMR spectra that **2** was present as a mixture of five positional isomers, **2a**−**e** (one resonance for each isomer). The assignments of peaks in the ^1H NMR spectra for isomers **2a**−**e** are shown for the Me and bridgehead HC_{Cp} regions in Figure 3 (at 240 K) and for the H_2C_{Cp} region in Figure 4 (at 370 K). The ratio in which these isomers were present was established from the integration of the Me resonances in the ^1H NMR spectrum at 300 K as **2a**/**2b**/**2c**/**2d**/**2e** = 18/16/4.0/2.4/1.0. The five Me resonances appeared as sharp resolved singlets in the ^1H and ^{13}C NMR spectra, but the signals for isomers **2b** and **2c** were coincident in the ^{29}Si NMR spectrum, as indicated by the ($^{29}Si,^1H$) HETCOR experiment. The peaks in the H_2C_{Cp} region of the ^1H NMR spectrum appeared as quartets, and the signals for the bridgehead

Table 1. NMR Data for 2a−e (C_7D_8, 300 K): ^{29}Si, ^1H, and ^{13}C Correlations[a,b]

isomer	^{29}Si	^1H	^{13}C
MePhSi Region			
2a	−4.03	−0.21 (s, 3H)	−9.78
2b	−14.05	0.14 (s, 3H)	−6.75
2c	−14.05	0.15 (s, 3H)	−7.46
2d	−22.73	0.55 (s, 3H)	−2.69
2e	−22.67	0.59 (s, 3H)	−3.13
H_2C_{Cp} Region			
2c		2.77 (q, 2H, 1.4 Hz)	43.96
2b		2.87 (q, 2H, 1.4 Hz)	46.18
2d		2.93 (q, 4H, 1.4 Hz)	46.14
2e[c]		2.81 (q, 2H, 1.4 Hz) 2.97 (q, 2H, 1.4 Hz)	
Bridgehead HC_{Cp} Region			
2a		3.45 (br s, 2H)	50.24 (br)
2b		3.68 (br s, 1H)	50.48 (br)
2c[c]		3.73 (br s, 1H)	

[a] $Vinyl_{Cp}$ and Ph regions are described in the Experimental Section. [b] Integrations are relative to each isomer. [c] ^{13}C signals were too weak to observe.

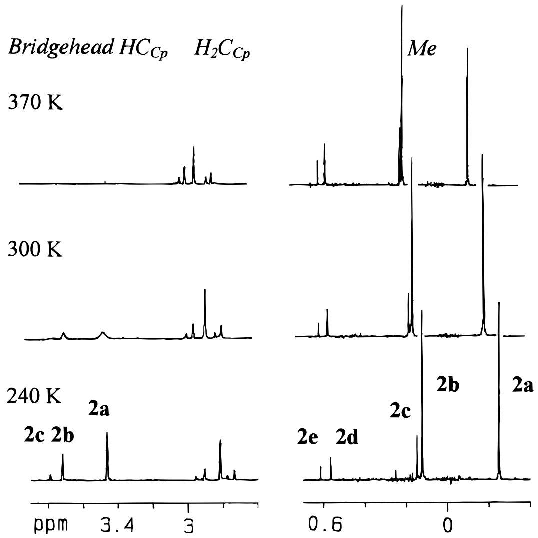


Figure 3. Variable temperature ^1H NMR for **2a**−**e** and assignments of Me and bridgehead HC_{Cp} peaks for each isomer.

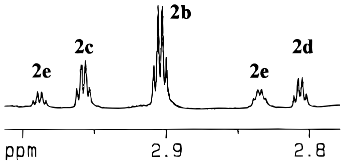


Figure 4. Expanded H_2C_{Cp} region of ^1H NMR at 370 K for **2** and assignments for each isomer.

HC_{Cp} regions were broad and overlapped at 300 K. The $Vinyl_{Cp}$ and Ph regions were complicated and appeared as overlapping multiplets in both the ^1H (6.2−7.6 ppm) and ^{13}C (120−150 ppm) NMR spectra.

The assignments of the H_2C_{Cp} and bridgehead HC_{Cp} peaks to each of the specific isomers (**2a**−**e**, Figure 2) listed in Table 1 and shown in Figures 3 and 4 were made on the basis of the relative integrations in the ^1H NMR spectrum for each H_2C_{Cp} or bridgehead HC_{Cp} peak with respect to the corresponding Me peak for that isomer. The integrated ratio of protons between H_2C_{Cp}/Me was either 2/3 or 4/3, and the integrated ratio of protons between bridgehead HC_{Cp}/Me was either 1/3 or 2/3. The most upfield resonance, assigned to **2a**, is the only Me resonance with no corresponding signals in the H_2C_{Cp} region of the ^1H NMR spectrum. In addition, the integrated ratio from the ^1H NMR spectrum between the most intense resonance in the bridgehead HC_{Cp} region and the Me resonance of **2a** was 2/3 (bridgehead HC_{Cp}/Me). Therefore, **2a** can be assigned to the isomer with two bridgehead HC_{Cp}'s, the 1−1 isomer. The Me resonances for isomers **2b** and **2c** both had corresponding peaks in the bridgehead HC_{Cp} and H_2C_{Cp} regions that integrated to ratios of 1/3 (bridgehead HC_{Cp}/Me) and 2/3 (H_2C_{Cp}/Me) for each isomer. This limits the structures of **2b** and **2c** to either the 1−2 or 1−3 isomers (or their enantiomers), but the distinction between the two cannot be determined from these experiments. The Me resonance for isomer **2d** corresponded to one peak in the H_2C_{Cp} region of the ^1H NMR spectrum that integrated to a ratio of 4/3 (H_2C_{Cp}/Me), supporting the assignment of **2d** to either the 2−2 or 3−3 isomer. Finally, the Me resonance for isomer **2e** corresponded to two peaks in the H_2C_{Cp} region, each of which integrated to a ratio of 2/3 (H_2C_{Cp}/Me). Isomer **2e** was therefore assigned as the 2−3 isomer (or its enantiomer), since it is the only structure that would be expected to give two H_2C_{Cp} signals.

Variable temperature ^1H NMR spectra were obtained for **2** over the range of 200−370 K, and Figure 3 shows the Me, H_2C_{Cp}, and bridgehead HC_{Cp} regions for three temperatures. At 240 K, the H_2C_{Cp} and bridgehead HC_{Cp} signals appeared as pseudoquartets (1.4 Hz) and -triplets (1.1 Hz), respectively (the spectrum remained essentially the same from 200 to 240 K). As the temperature was increased, the bridgehead HC_{Cp} signals gradually broadened into the baseline, while the H_2C_{Cp} signals remained as resolved quartets, as shown in Figure 4 for 370 K. The Me signals remained sharp, while the peaks in the $Vinyl_{Cp}$ and Ph regions were complicated and overlapping throughout the temperature range. Recooling of the sample provided a ^1H NMR spectrum identical with that collected before heating, indicating that no decomposition occurred. Finally, the relative integration between the five isomers remained constant through the temperature range.

One of the possible fluxional processes that could take place in a system with SiCp bonds is a silatropic shift. Silatropic shifts have been used to explain the fluxionality and interconversion of isomers observed in many systems in which Si−Cp bonds are present.[16,17] In general, a silatropic shift occurs when the silicon migrates from an sp^3 hybridized carbon to an adjacent sp^2 carbon on the Cp ring. For example, a 1,2 silatropic shift in one of the Cp rings of the 1−1 isomer of **2** would produce a degenerate isomer. This could account for the broadness observed at high temperatures for the bridgehead HC_{Cp} protons of **2**, while the ratio between the five isomers remains constant.

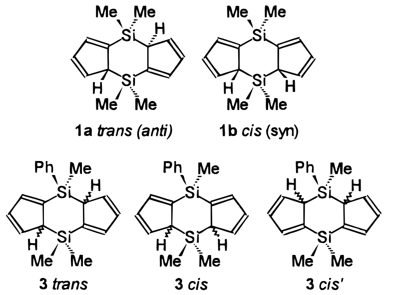


Figure 5. *trans* and *cis* isomers of **1** and possible positional isomers of **3**.

NMR Characterization and VT NMR for [μ,μ-(MePhSi)(Me_2Si)(C_5H_4)$_2$] (3). The dibridged (bis)Cp compound **3** is similar to the known compound **1**, the only difference being the substitution of one of the Me groups for a Ph substituent. Compound **1** has previously been determined to exist as a mixture of two isomers in solution, **1a** and **1b**, which are shown in Figure 5.[1c,3] Both isomers of **1** have been characterized by NMR experiments, and the X-ray structure was determined for **1a**,[3a] the only isomer that crystallized out of solution. Both isomers of **1** are type **A** (Figure 1), with the bridges connecting the 1,2 positions of both Cp rings. Both isomers also have the aliphatic protons connected to the bridgehead carbons, but these protons are *trans* (adjacent to different silicons) for **1a** and *cis* (adjacent to the same silicon) for **1b**. Additionally, these bridgehead protons are mutually *anti* for **1a** (on opposite faces of the ligand) and *syn* for **1b** (on the same face of the ligand). Because of the similar compositions of compounds **1** and **3**, it is expected that **1** and **3** will have related structural features such as 1,2−1,2 coordination of the bridges and the existence of *trans* and *cis* isomers.

^1H, ^{13}C, and ^{29}Si NMR spectra were collected for **3** in C_7D_8 at 300 K, and data obtained for the Me and bridgehead HC_{Cp} regions are presented in Table 2. Correlation data were obtained from (^{29}Si,^1H) and (^{13}C,^1H) HETCOR experiments, and the number of protons attached to each carbon was confirmed by ^{13}C DEPT experiments. Compound **3** was a mixture of five isomers, **3a**−**e**, as determined from the number of resonances in the MeSi region of the ^1H and ^{13}C NMR spectra (three Me resonances for each isomer) and ^{29}Si NMR spectrum (two Si resonances for each isomer). The Me region of the ^1H NMR spectrum at 300 K with the assignments of peaks to the specific isomers is shown in Figure 6a. The ratio in which these five isomers were present was established from the integration of the ^1H NMR methyl resonances at 300 K as **3a**/**3b**/**3c**/**3d**/**3e** = 4.4/3.4/1.4/1.0/1.0. The Me signals at 300 K in the ^1H and ^{13}C spectra were sharp for isomers **3b**−**d** and broad for **3a** and **3e**. The assignments of the bridgehead HC_{Cp} to specific isomers were based on the relative integrations and line shapes for each isomer. The ^1H NMR spectrum of the bridgehead HC_{Cp} region at 300 K and the assignment of isomers are shown in Figure 6b. In contrast to **2**, no resonances attributed to H_2C_{Cp} were

---

[16] Ustynyuk, Y. A.; Luzikov, Y. N.; Mstislavsky, V. I.; Azizov, A. A.; Pribytkova, I. M. *J. Organomet. Chem.* **1975**, *96*, 335−353.

[17] Juzi, P. *Chem. Rev.* **1986**, *86*, 983−996.

Table 2. NMR Data for 3a–e (C_7D_8, 300 K): ^{29}Si, ^1H, and ^{13}C Correlations[a,b]

isomer	^{29}Si	^1H	^{13}C
		Me$_2$Si Region	
3a	−8.16	−0.36 (br s, 3H)	−8.41 (br)
		0.46 (br s, 3H)	−2.95 (br)
3b	4.77	−1.20 (s, 3H)	−15.24
		0.18 (s, 3H)	0.44
3c	−19.57	0.41 (s, 3H)	1.03
		0.51 (s, 3H)	−5.28
3d	4.63	−1.08 (s, 3H)	−15.02
		0.32 (s, 3H)	−2.95
3e[c]		−0.42 (br s, 3H)	
		0.39 (br s, 3H)	
		MePhSi Region	
3a	−13.06	−0.15 (br s, 3H)	−6.97 (br)
3b	−22.76	0.62 (s, 3H)	−4.88
3c	−2.89	−0.94 (s, 3H)	−17.31
3d	−22.53	0.65 (s, 3H)	−1.29
3e[c]		0.66 (br s, 3H)	
		Bridgehead HC$_{Cp}$ Region	
3a		3.50 (br s, 1H)	55.71 (br)
		3.92 (br s, 1H)	57.53 (br)
3b		3.58 (q, 2H, 1.1 Hz)	56.13
3c		3.97 (q, 2H, 1.1 Hz)	54.38
3d		3.61 (q, 2H, 1.1 Hz)	55.68
3e		3.45 (br s, 1H)	56.85 (br)
		3.76 (br s, 1H)	58.38 (br)

[a] Vinyl$_{Cp}$ and Ph regions are described in the Experimental Section. [b] Integrations are relative to each isomer. [c] ^{13}C and ^{29}Si signals were too weak to observe.

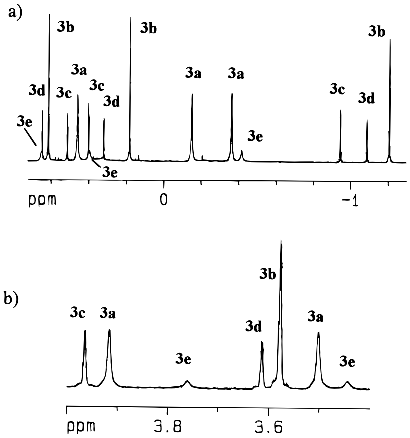


Figure 6. (a) Expanded Me region of ^1H NMR at 300 K for the isomeric mixture of **3** and assignments of isomers **3a**–**e**. (b) Expanded bridgehead HC$_{Cp}$ region of ^1H NMR at 300 K for the isomeric mixture of **3** and assignments of isomers **3a**–**e**.

observed in the ^1H and ^{13}C DEPT spectra. The Vinyl$_{Cp}$ and Ph regions were complicated and appeared as overlapping multiplets in both the ^1H (6.4–7.8 ppm) and ^{13}C (125–150 ppm) NMR spectra.

There are several more isomers possible for **3** than for **1** due to the asymmetry introduced by the Ph substituent. Since all five isomers of **3** have two bridgehead HC$_{Cp}$ protons, and all of the known dibridged (bis)Cp compounds with Me$_2$X bridges have been assigned to the 1,2–1,2 isomers,[6] it was assumed that the two Cp rings of **3** were also connected at the 1,2–1,2 positions. Figure 5 shows the three positional isomers possible for **3**. The bridgehead HC$_{Cp}$ protons could be adjacent to different silicons (*trans*), both adjacent to the Me$_2$Si bridge (*cis*), or both adjacent to the MePh bridge (*cis′*). Each of these three positional isomers also has several configurations where the bridgehead HC$_{Cp}$ protons could be *syn* or *anti* to each other and *syn* or *anti* to the Ph group, yielding a total of ten possible isomers. For the *trans* isomer, the two bridgehead HC$_{Cp}$ protons could be mutually *syn* and *syn* or *anti* to the Ph, or mutually *anti*, with the proton adjacent to the MePhSi bridge syn or anti to the Ph. For the *cis* and *cis′* isomers, the bridgehead HC$_{Cp}$ protons could be mutually *syn* and *syn* or *anti* to the Ph, or mutually *anti*.

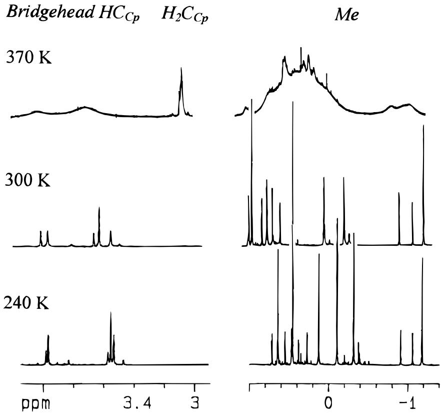
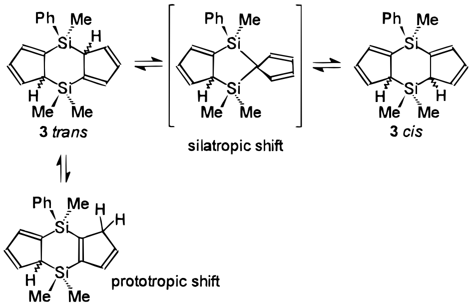


Figure 7. Variable temperature ^1H NMR for **3a**–**e**, bridgehead HC$_{Cp}$, and Me regions.

The specific assignment of each of the five isomers of **3** to one of the ten possible structures cannot be made from the data in Table 2, but general conclusions concerning the structures of the isomers can be drawn. First, the three isomers **3b**–**d** exhibit only one bridgehead HC$_{Cp}$ resonance each, which integrates to 2/9 (bridgehead HC$_{Cp}$/(Me)$_3$) protons for each isomer. This supports two equivalent bridgehead HC$_{Cp}$ protons for each of these isomers. The only structures where this would be possible are the *cis* and *cis′* isomers, with the bridgehead HC$_{Cp}$ protons mutually *syn*. Isomers **3a** and **3e** correspond to two bridgehead HC$_{Cp}$ protons each, integrating to 1/9 (bridgehead HC$_{Cp}$/(Me)$_3$) protons for each HC$_{Cp}$ signal for each isomer, indicating that these isomers have nonequivalent bridgehead HC$_{Cp}$ protons. This would be consistent with any of the *trans* isomers or the *cis* and *cis′* isomers with the bridgehead HC$_{Cp}$ protons mutually *anti*.

Variable temperature ^1H NMR data were collected for **3** over the temperature range of 200–370 K, and Figure 7 shows the Me, bridgehead HC$_{Cp}$, and H$_2$C$_{Cp}$ regions at three temperatures. At 240 K, all of the peaks were sharp, the isomers were well-resolved, and the only aliphatic Cp protons observed were the bridgehead HC$_{Cp}$ (the spectrum remained essentially the same from 200 to 240 K). As the temperature was increased to 300 K, the bridgehead HC$_{Cp}$ and Me signals for isomers **3a** and **3e** broadened slightly (expanded regions shown in Figure 6). As the temperature was raised above 350 K, all of the bridgehead HC$_{Cp}$ and Me signals broadened further until the determination of specific isomers was not possible. At 370 K, the bridgehead HC$_{Cp}$ peaks had nearly broadened into the baseline, the Me resonances converged into two broad peaks, and a new multiplet was observed in the H$_2$C$_{Cp}$ region of the ^1H NMR spectrum. The Vinyl$_{Cp}$ and Ph regions (not shown) remained complicated and overlapping throughout the temperature range and broadened considerably with increasing temperature. No decomposition of **3** was observed, and upon recooling of the sample a ^1H NMR

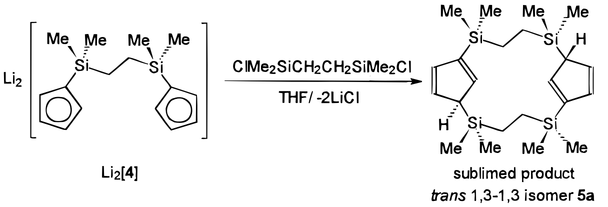
Scheme 1



spectrum was recorded which was identical with that obtained before heating.

Temperature dependent silatropic shifts have been suggested for **1** [1c,3] and other 1,2−1,2 bridged compounds of type **A** with $X_1 = Me_2C$ and $X_2 = Me_2Si$, Me_2Ge, and Me_2Sn, resulting in the reversible conversion between isomers.[6] Scheme 1 shows how silatropic shifts could convert a *trans* isomer of **3** into a *cis* isomer through a 1,2−1,1 intermediate (shown in brackets). Any of the ten possible isomers of **3** could be interconverted through this type of process, which may explain the broadness observed in the Me and bridgehead HC_{Cp} regions of the ^1H NMR at higher temperatures. Reversible prototropic shifts were also observed in the type **A** system, where $X_1 = Me_2C$ and $X_2 = Me_2Si$.[6] A prototropic shift for **3** would convert a bridgehead HC_{Cp} proton to a H_2C_{Cp} proton, as shown in Scheme 1. This would account for the observation of a signal in the H_2C_{Cp} region of the ^1H NMR spectrum at 370 K. Thus, it is possible that both silatropic and prototropic rearrangements occur for **3**. Finally, the fluxional processes for **3** must be reversible since the ratio of the five isomers returns to the original value after heating and recooling of the NMR sample.

Preparation of [μ,μ-($Me_2SiCH_2CH_2SiMe_2)_2(C_5H_4)_2$] (5). Deprotonation of **4** with 2 equiv of ^nBuLi provides the dilithio salt Li_2[**4**],[13] and subsequent reaction with 1 equiv of $ClMe_2SiCH_2CH_2SiMe_2Cl$ produced the dibridged (bis)Cp compound **5** which has two four-atom bridges (eq 2). The product was isolated after nonaqueous workup by vacuum distillation/sublimation and purified by sublimation to provide **5** as a colorless crystalline solid in fair yield (30%). The isolated crystals of **5** were not as sensitive to light and air as were **2** and **3**, but slow decomposition did occur when samples were left in air for more than 1 week. Because of the more robust nature of **5**, satisfactory elemental analysis was obtained. Compound **5** was very soluble in chlorinated solvents and THF, fairly soluble in benzene and toluene, and slightly soluble in hydrocarbon solvents. The gas chromatographic trace of **5** showed one sharp peak in 100% purity, and a parent peak of *m*/*z* 416 was observed in the low-resolution mass spectrum.



(2)

This preparation for **5** is analogous to that used for the synthesis of **3**, with the second bridge added to a monobridged (bis)Cp compound to yield the desired dibridged product. This method is also similar to that reported for [μ,μ-($Me_2SiSiMe_2)_2(C_5H_4)_2$], which was prepared from Li_2[μ-($Me_2SiSiMe_2)(C_5H_4)_2$] and $XMe_2SiSiMe_2X$ (X = F, Cl).[9] The 1,1−1,1 isomer of this known (bis)Cp compound with two $Me_2SiSiMe_2$ bridges was characterized by solution NMR spectroscopy, and it was postulated that interconversion to the 1,2−1,2 and 1,3−1,3 isomers occurred via silatropic shifts.[9] Furthermore, reaction with metal sources provided bimetallic complexes of the types **C** (1,2−1,2 isomer) and **D** (1,3−1,3 isomer) and *ansa*-metallocenes of the type **E** (1,2−1,2 isomer).[9] This contrasts to the reaction chemistry of **1**, which forms metal complexes of types **C** and **E** (both 1,2−1,2 isomers) for similar metals.[1c,4] The ability of [μ,μ-($Me_2SiSiMe_2)_2(C_5H_4)_2$] to form 1,3−1,3 bridged complexes is presumably due to the longer two-atom bridges, versus the one-atom bridges of compound **1**. The new compound **5** was synthesized in the anticipation that it would be a useful ligand in bimetallic systems, where even longer, more flexible bridges are desired. Additionally, it was expected that **5** would have properties similar to **1** and [μ,μ-($Me_2SiSiMe_2)_2(C_5H_4)_2$], such as the availability of different coordinations of the bridges, and isomerism through silatropic shifts.

X-ray Structure of 5. Attempts to grow crystals of **5** from various solvents and mixtures of solvents provided only small crystals which were not suitable for X-ray crystallography. However, suitable crystals were obtained from slow resublimation. A single crystal X-ray diffraction study showed the sublimed crystals of **5** to be that of the 1,3−1,3 isomer **5a**, with the bridgehead HC_{Cp} hydrogens *trans* and mutually *anti*. There is a center of symmetry; thus, only half of the molecule is unique. The five carbons which define each Cp ring deviate from planarity by an average of 0.12 Å, and there is a distinct alternation of double and single C−C bonds in the rings, as expected for cyclopentadiene. The two Cp rings are tilted 80.5° in either direction from the plane defined by the four silicon atoms. The distance between the centroid of one Cp ring and the centroid of the other Cp ring is 6.392 Å, and the two rings are in a nearly stacked conformation. There are no unusual bond lengths or angles in the structure. Experimental details are provided in Table 3, a list of selected geometric parameters is presented in Table 4, and an ORTEP diagram is shown in Figure 8.

NMR Characterization and VT NMR for 5. The ^1H, ^{13}C, and ^{29}Si NMR spectra were collected for resublimed **5** (same crystals as used for X-ray studies) in C_7D_8 at 260 K, and the resulting data are presented in Table 5. It was determined from the number and integrations of the resonances in the Me region of the ^1H NMR that **5** existed as a mixture of two isomers in C_7D_8 solution, **5b** and **5c**, present in a ratio of 8/1 at 260 K.[18] Correlation data for both isomers were obtained from (^{29}Si,^1H) and (^{13}C,^1H) HETCOR experiments, and the number of protons attached to each carbon was confirmed by ^{13}C DEPT experiments. Four nonequivalent silicon centers were identified in the ^{29}Si NMR spectrum for the major isomer **5b**, and the minor isomer **5c** had all equivalent silicons, as shown by the presence of only one signal in the ^{29}Si NMR spectrum.

---

(18) A small amount (<5%) of a third isomer of **5** was detected in C_7D_8 solution by ^1H NMR at 260 K but was not identified.

Table 3. Crystallographic Parameters for 5a

formula	$C_{22}H_{40}Si_4$
fw	416.90
color, habit	colorless, prismatic
cryst dmns, mm^3	0.06 × 0.06 × 0.40
cryst syst	tetragonal
space group	$P4_2/n$
latttice params, Å	$a = 20.006(2)$, $c = 6.5778(7)$
V, Å^3	2632.7(4)
Z	4
D_{calcd}, g cm^{-3}	1.052
abs coeff, mm^{-1}	0.231
temp, K	295
$F(000)$	912
scan type	$\omega-2\theta$
2θ range, deg	4.08−54.98
index ranges	$-28 \le h \le 28$, $-28 \le k \le 28$, $-9 \le l \le 9$
no. of rflns collecd	23 966
no. of indpdt rflns	3028 ($R_{int} = 0.2049$)
largest diff peak and hole, e Å^{-3}	0.430 and −0.232
no. of params refined	198
data/param	15.1/1
final R indices [$I > 2\sigma(I)$]	R1 = 0.0481, wR2 = 0.1092
R indices (all data)	R1 = 0.0715, wR2 = 0.1238
GOF on F^2	1.095

Table 4. Selected Geometric Parameters for 5a[a,b]

Bond Lengths (Å)			
Si−C_{Me}(av)	1.866(3)	Si(1)−C(1)	1.907(2)
C(1)−C(2)	1.479(3)	Si(1)−C(6)	1.867(2)
C(2)−C(3)	1.342(3)	Si(2)−C(4)	1.867(2)
C(3)−C(4)	1.464(3)	Si(2)−C(7)	1.874(2)
C(4)−C(5)	1.343(3)	C(6)−C(7A)	1.538(3)
C(1)−C(5)	1.485(3)	C(7)−C(6A)	1.538(3)
Nonbonded Distances (Å)			
Cp_{cent}−$Cp(A)_{cent}$	6.392	C(6)−C(6A)	4.314
Bond Angles (deg)			
C(1)−C(2)−C(3)	109.3(2)	Si(1)−C(6)−C(7A)	113.5(2)
C(2)−C(3)−C(4)	110.3(2)	Si(2)−C(7)−C(6A)	116.0(2)
C(3)−C(4)−C(5)	106.3(2)	Si(1)−C(1)−C(2)	110.9(2)
C(4)−C(5)−C(1)	111.6(2)	Si(1)−C(1)−C(5)	111.25(14)
C(5)−C(1)−C(2)	102.3(2)	Si(2)−C(4)−C(3)	125.6(2)
C(1)−Si(1)−C(6)	111.37(10)	Si(2)−C(4)−C(5)	128.0(2)
C(4)−Si(2)−C(7)	110.36(10)		
Nonbonded Angles (deg)			
Si(1)−C(1)−Cp_{cent}	123.0	Si(2)−C(4)−Cp_{cent}	176.6

[a] Symmetry transformations used to generate equivalent atoms (A) $-x + 2$, $-y + 1$, $-z$. [b] Cp_{cent} was calculated as the centroid derived from C(1), C(2), C(3), C(4), and C(5); $Cp(A)_{cent}$ was calculated as the centroid derived from C(1A), C(2A), C(3A), C(4A), and C(5A).

Additionally, isomer **5b** had eight Me and four ethylene CH_2 resonances in the ^1H and ^{13}C NMR spectra, while isomer **5c** had only one Me and one ethylene CH_2 resonance. The Me and ethylene CH_2 regions of the ^1H NMR spectrum for **5b** and **5c** measured at 260 K are shown in Figure 9. The Me signals were easily distinguished from the ethylene CH_2 signals by their opposite phasing in the ^{13}C DEPT experiment. It was also apparent from the (^{13}C,^1H) HETCOR and ^{13}C DEPT experiments that the major isomer **5b** had both bridgehead HC_{Cp} and bridgehead Si_2C_{Cp} carbons, while the minor isomer **5c** had only bridgehead Si_2C_{Cp} carbons. Bridgehead HC_{Cp} signals could originate from a Cp ring with either 1,2 or 1,3 coordination of the silicon bridges, while bridgehead Si_2C_{Cp} signals originate from a Cp ring with 1,1 coordination of the silicon bridges.

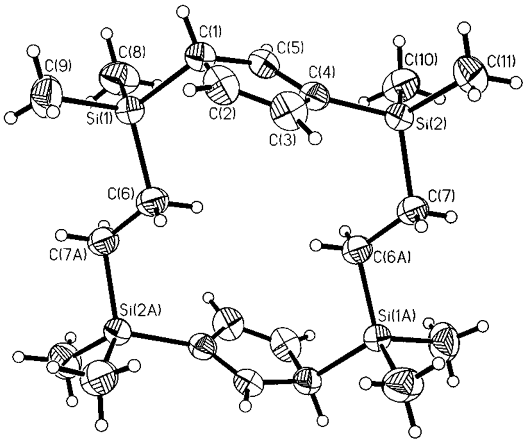


Figure 8. ORTEP drawing of the molecular geometry of 1,3-*trans*-[μ,μ-($Me_2SiCH_2CH_2SiMe_2$)$_2$(C_5H_4)$_2$] **(5a)**, (without hydrogen atoms) and atom labeling. Displacement ellipsoids are at the 50% probability level.

Table 5. NMR Data for 5b and 5c (C_7D_8, 260 K): ^{29}Si, ^1H, and ^{13}C Correlations[a,b]

isomer	^{29}Si	^1H	^{13}C
		Me_2Si Region	
5b	−6.32	0.30 (s, 3H)	−3.60
		0.35 (s, 3H)	−3.75
	0.43	−0.39 (s, 3H)	−5.79
		−0.06 (s, 3H)	−3.22
	1.59	−0.28 (s, 3H)	−5.55
		0.02 (s, 3H)	−2.02
	4.57	0.12 (s, 3H)	−0.66
		0.18 (s, 3H)	−1.86
5c	1.03	−0.12 (br s, 24H)	−3.42
		CH_2 Region	
5b		0.20 (m, 2H)	7.17
		0.40 (m, 2H)	11.45
		0.67 (m, 2H)	9.81
		0.75 (m, 2H)	10.06
5c		0.92 (s, 8H)	10.98
		Bridgehead HC_{Cp} Region	
5b		3.34 (m, 1H)	54.79
		Bridgehead Si_2C_{Cp} Region	
5b			56.97
5c			56.20
		Bridgehead SiC_{Cp} Region	
5b			142.35
		Cp Region	
5b		6.47 (m, 1H)	136.19
		6.52 (m, 1H)	135.77
		6.62 (m, 1H)	133.82
		6.75 (m, 1H)	130.67
		6.77 (m, 1H)	130.67
		6.85 (m, 1H)	134.40
		6.94 (m, 1H)	144.03
5c[b]		6.68 (m, 4H)	
		6.66 (m, 4H)	

[a] Integrations are relative to each isomer. [b] ^{13}C signals were too weak to observe.

Since **5b** possesses both bridgehead HC_{Cp} and bridgehead Si_2C_{Cp} carbons, one of the Cp rings must be bridged at either the 1,2 or 1,3 positions and the other Cp ring must be bridged in a 1,1 fashion. Therefore, the structure of **5b** could be either the 1,1−1,3 or 1,1−1,2 isomer, shown in Figure 10. Both of these structures agree with the observation of four nonequivalent silicon atoms, eight nonequivalent Me groups, seven nonequivalent $Vinyl_{Cp}$ protons, and one HC_{Cp} proton which integrated at a ratio of 1/24 (bridgehead HC_{Cp}/(Me)$_8$). The difference in the 1,1−1,3 and 1,1−1,2 isomers could not be determined by these experiments.[19] The minor isomer **5c** was symmetric and had only one type of silicon, one type of Me, one ethylene CH_2, one Si_2C_{Cp}, and no bridgehead HC_{Cp} or H_2C_{Cp}. The only structure

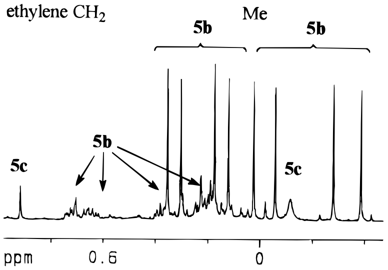
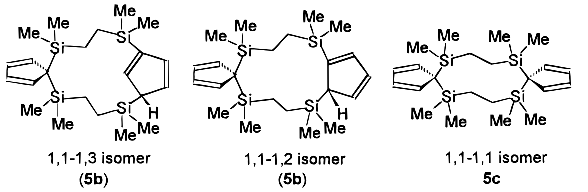


Figure 9. Expanded Me and ethylene CH_2 regions of ^1H NMR at 260 K for the isomeric mixture of **5** and assignments of isomers **5b** and **5c**.



1,1-1,3 isomer (**5b**) 1,1-1,2 isomer (**5b**) 1,1-1,1 isomer **5c**

Figure 10. Proposed structures of isomers **5b** and **5c**.

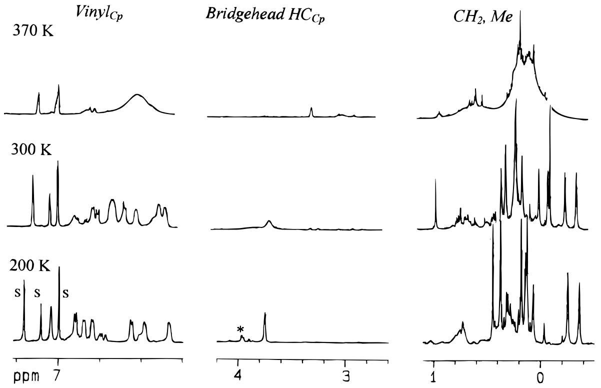


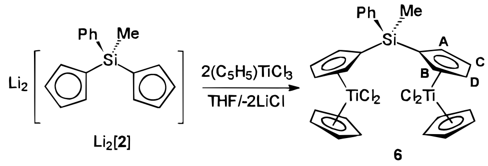
Figure 11. Variable temperature ^1H NMR for **5b** and **5c** (s = solvent; $*$, see ref 18).

consistent with these observations is the symmetric 1,1−1,1 isomer shown in Figure 10. These structures could form from the 1,3−1,3 isomer in solution by a series of silatropic shifts.

Variable temperature ^1H NMR data were collected for **5** over the temperature range of 200−370 K, and Figure 11 shows the spectra obtained at three temperatures. At 200 K, four of the Me peaks for **5b** are sharp (0.1−0.6 ppm), and four of the Me peaks were slightly broadened (−0.4 to 0.2 ppm). Additionally, the ethylene CH_2 peaks of **5b** were not well-resolved, but the $Vinyl_{Cp}$ and bridgehead HC_{Cp} signals were quite sharp. At this temperature the Me and ethylene CH_2 signals for **5c** were broad. As the temperature was increased to 260 K, the eight resonances for **5b** were all sharp, and the ethylene CH_2 multiplets became better resolved, as shown in Figure 9. Also at 260 K, the Me and ethylene CH_2 resonances for **5c** sharpened slightly, although they were still broader than those of isomer **5b**. At 300 K (Figure 11), all of the resonances for **5b** were slightly broader and overlapping, while the peaks for **5c** sharpened considerably. At the upper temperature limit of 370 K, the peaks for both isomers **5b** and **5c** converged into broad multiplets in the Me and ethylene CH_2 regions, the $Vinyl_{Cp}$ region appeared as one broad peak, and several new signals of low intensity appeared in the bridgehead HC_{Cp} region. No decomposition of **5** was observed, and upon recooling of the sample a ^1H NMR spectrum was recorded which was identical with that obtained before heating.

The temperature dependence shown in the VT NMR of **5** could be due to silatropic shifts which could occur upon heating the sample in solution. However, unlike compound **3**, it is unlikely that prototropic shifts occur for **5** since no significant H_2C_{Cp} resonances are apparent in the high-temperature ^1H NMR spectra. It is also possible that some of the broadness observed in the VT NMR could be due to twisting or bending of the compound along the two bridges, since the bridges for **5** are longer than those of **3**.

Preparation of Bimetallic Ti Complexes. The dilitio salt $Li_2[\mathbf{2}]$ was isolated as a white powder from the addition of ^nBuLi to an isomeric mixture of **2** in hexanes. Subsequent reaction of $Li_2[\mathbf{2}]$ with 2 equiv of $(C_5H_5)TiCl_3$ in THF solution generated the monobridged bimetallic complex $[\mu\text{-}(MePhSi)(C_5H_4)_2][(C_5H_5)TiCl_2]_2$ (**6**) and LiCl (eq 3). Complex **6** was isolated as orange-red microcrystals from CH_2Cl_2/hexanes as the CH_2Cl_2 solvate (0.25 equiv) in a 35% yield, and satisfactory elemental analysis was obtained. The complex was air stable at room temperature and was soluble in THF and chlorinated solvents, and slightly soluble in toluene. This procedure is similar to that described by Cuenca, in which the analogous bimetallic complex with an Me_2-Si bridge was obtained from the reaction of $Tl_2[(Me_2Si)(C_5H_4)_2]$ and $(C_5H_5)TiCl_3$ in refluxing toluene.[20]



(3)

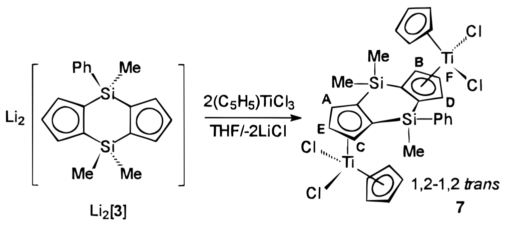
The ^1H NMR spectrum of **6** in $CDCl_3$ exhibited the expected signals of a monobridged (bis)Cp complex. A singlet in the MeSi region and a multiplet in the PhSi region were observed, as well as a singlet corresponding to the C_5H_5 groups. There were four multiplets in the C_5H_4 region of the ^1H NMR spectrum, which integrated to two protons each. This ABCD pattern (shown in eq 3) for each C_5H_4 group results from the absence of a plane of symmetry through the Si and C_5H_4 groups, caused by the inequivalent substitution at the Si atom. The ^{13}C and ^{29}Si NMR spectra were collected, and the expected signals for **6** were observed.

The dilithio salt $Li_2[\mathbf{3}]$ was generated in THF solution from the addition of ^nBuLi to an isomeric mixture of **3**, and subsequent addition of 2 equiv of $(C_5H_5)TiCl_3$ provided the bimetallic complex $[\mu\text{-}(MePhSi)(Me_2Si)(C_5H_3)_2][(C_5H_5)TiCl_2]_2$ (**7**) and LiCl (eq 4). Complex **7** was recrystallized by Soxhlet extraction with CH_2Cl_2 and isolated in a 66% yield as a CH_2Cl_2 solvate (0.25 equiv), and satisfactory elemental analysis was obtained. The complex was air stable at room temperature and sparingly soluble in THF and chlorinated solvents. This procedure is identical with that previously reported by our group for preparation of the

---

(19) In theory a (^1H,^1H) COSY experiment should give different cross-peak patterns for a 1,2 and 1,3 coordination of bridges. However, virtual coupling among the Cp protons made this distinction unclear.

(20) Cuenca, T.; Flores, J. C.; Gomez, R.; Gomez-Sal, P.; Parra-Hake, M.; Royo, P. *Inorg. Chem.* **1993**, *32*, 3608−3612.



(4)

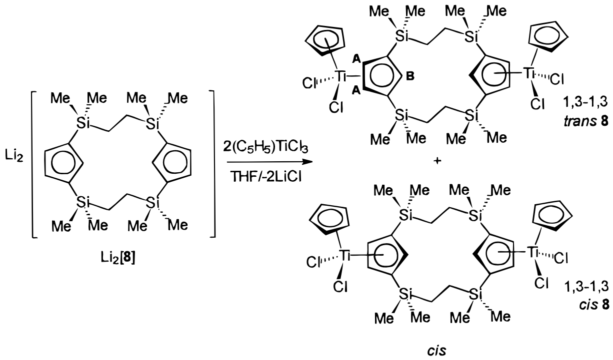
analogous bimetallic complex of ligand **1**, *trans*-[μ,μ-$(Me_2Si)_2(C_5H_3)_2$][$(C_5H_5)TiCl_2$]$_2$.[4k]

There are three 1,2−1,2 isomers possible for the dibridged bimetallic complex **7**, one with the Ti's mutually *trans* (as shown in eq 4), one with the Ti's mutually *cis* to each other but *anti* to the Ph group, and one with the Ti's mutually *cis* to each other and *syn* to the Ph group. The *cis* and *trans* isomers should be distinguishable in the ^1H NMR spectrum by the number of C_5H_5 resonances, since both of the *cis* structures would correspond to one C_5H_5 environment, while the *trans* isomer would have two. Furthermore, each of the *cis* isomers should exhibit an ABC pattern (three multiplets, integrating to two protons each) for the two C_5H_3 units, while the *trans* isomer should correspond to an ABCDEF pattern (six multiplets, integrating to one proton each), since the two C_5H_3 units for this structure are inequivalent (as shown in eq 4).

As indicated in eq 4, only the *trans* isomer of **7** was obtained. Since all known bimetallic complexes of the ligand **1** (with two Me_2Si bridges) have been shown to have 1,2−1,2 coordination of the bridges to the C_5H_3 groups (type **C**),[1c,4] it was assumed that **7** also has 1,2−1,2 coordination. The ^1H NMR spectrum showed two C_5H_5 singlets, three sharp signals corresponding to the MeSi groups, a multiplet in the PhSi region, and six multiplets corresponding to the C_5H_3 protons. The ^{29}Si spectrum of **7** was collected in dimethyl-d_6 sulfoxide (DMSO-d_6), and two signals were observed consistent with a single isomer. The complex decomposed in DMSO-d_6 solution after 1 h, and a ^{13}C NMR spectrum was not obtained due to this decomposition in DMSO and the low solubility of **7** in $CDCl_3$.

Although the reaction of Li_2[**1**] with $CpTiCl_3$ produced exclusively the *trans* bimetallic product,[4k] type **C** derivatives of this symmetrical ligand have been previously observed with both *cis* and *trans* coordination of the ML_n groups.[1c,4] Thus, it is interesting that only the *trans* isomer of bimetallic **7** was obtained from the unsymmetrical ligand **3** and that neither of the two possible *cis* products were observed. This suggests that the Ph substituent of **3** may not be sufficiently bulky to direct the formation of the *cis* isomer with both of the Ti's *anti* to the Ph.

Analogous to the preparation of **7**, reaction of the dilithio salt Li_2[**4**] with 2 equiv of $(C_5H_5)TiCl_3$ provided the bimetallic complex [μ,μ-$(Me_2SiCH_2CH_2SiMe_2)_2$-$(C_5H_3)_2$][$(C_5H_5)TiCl_2$]$_2$ (**8**) and LiCl (eq 5). Complex **8** was isolated from the THF reaction mixture as air stable orange-brown fibrous crystals in a 48% yield, and satisfactory elemental analysis was obtained. The product was determined by ^1H NMR spectroscopy to be a mixture of two isomers (**8a** and **8b**) present in a 1/1 ratio, determined from integration of the C_5H_5 signals in the ^1H NMR spectrum. The two isomers were sparingly soluble in chlorinated solvents and THF, with **8b** being slightly more soluble than **8a**. Although attempts to separate the two isomers by fractional recrystallization were unsuccessful, a sample enriched in **8a** (2/1) was obtained for NMR analysis.



(5)

The difference in concentration of **8a** and **8b** in the enriched sample allowed for the assignment of peaks in the NMR spectra to each isomer. The ^1H NMR spectrum of the mixture showed each isomer to correspond to two MeSi resonances. Although both the *trans* and *cis* isomers should have two CH_2 environments, isomer **8a** corresponded to only one broad CH_2 multiplet and isomer **8b** corresponded to one CH_2 resonance which was coincident with one of the isomer **8b** MeSi signals. Each isomer also had one C_5H_5 signal and a doublet and triplet due to the bridged C_5H_3 groups. The ^{29}Si and (^{29}Si,^1H) HETCOR NMR spectra of the mixture showed two signals, one corresponding to each isomer. Due to the low solubility of **8** in $CDCl_3$ and the tendency of **8** to decompose in DMSO solution, a ^{13}C NMR spectrum was not obtained.

The C_5H_3 triplet and doublet for each isomer corresponds to an A_2B pattern, as shown in eq 5, and the $J(H_AH_B)$ coupling constant was 1.7 Hz for both **8a** and **8b**. This value is considerably lower than the $J(H_AH_B)$ of 2.5− 2.7 Hz which was previously observed for the bimetallic *trans*- and *cis*-[μ,μ-$(Me_2Si)_2(C_5H_3)_2$][(C_5Me_5)-$TiCl_2$]$_2$, which also have C_5H_3 doublet and triplet A_2B patterns in the ^1H NMR spectra and have been shown to have 1,2−1,2 coordination of the Me_2Si bridges (type **C**) by X-ray crystallography.[4k] This suggests that the coordination of the $Me_2SiCH_2CH_2SiMe_2$ bridges for both isomers of **8** is 1,3−1,3 (type **D**), as shown in eq 5, since protons that are not bonded to adjacent carbons will have a lower coupling constant. This assignment is supported by Jutzi's observation that a 1,2−1,2 bimetallic Ru complex of the (bis)Cp ligand with two Me_2-$SiSiMe_2$ bridges had a $J(H_AH_B)$ of 2.2 Hz, while a bimetallic Co complex of the same ligand with 1,3−1,3 coordination had a $J(H_AH_B)$ of 1.5 Hz.[9]

The assignment of *trans* or *cis* orientations of the Ti groups in **8a** and **8b** could not be made on the basis of the NMR results, since both the *trans* and *cis* isomers shown in eq 5 should have the same number of resonances in each region. The fact that the two isomers are formed in equal amounts suggests that the long four-atom bridges in the (bis)Cp ligand **5** provide enough flexibility in the bimetallic complex that there is no steric preference for one isomer over the other. Finally, heating a mixture of **8a** and **8b** to 90 °C did not change the distribution of the two isomers.

Summary

In summary, we have described the preparation of the new singly bridged (bis)Cp compound **2** and the reaction of its dilithio salt Li_2[**2**] with Me_2SiCl_2 to produce the new unsymmetrical doubly bridged compound **3**. Compounds **2** and **3** were each found to be mixtures of five isomers which were characterized by ^1H, ^{13}C, ^{29}Si, and 2D NMR experiments. Similarly, the salt elimination reaction of Li_2[**4**] with $ClMe_2SiCH_2CH_2SiMe_2Cl$ provided the (bis)Cp ligand with two four-atom linkages, **5**, which was shown to have 1,3−1,3 coordination of the bridges in the solid state by X-ray diffraction studies. Conversely, NMR studies of **5** showed that there was a mixture of two isomers produced in toluene solution. Reaction of the dilithio salts of these three ligands with 2 equiv of $(C_5H_5)TiCl_3$ produced the corresponding bimetallic complexes **6**, the 1,2−1,2 *trans* isomer of **7**, and a mixture of 1,3−1,3 *trans* and *cis* isomers of **8**.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry N_2 using standard Schlenk techniques, and glassware was flame dried prior to use. Solvents were purified by standard methods and freshly distilled under nitrogen. The ^nBuLi (Aldrich) was purchased in hexanes and the concentration determined by titration before use. The chlorosilanes $MePhSiCl_2$ and Me_2SiCl_2 (Gelest) were distilled from K_2CO_3, CpH was freshly distilled from dicyclopentadiene before use, and $ClMe_2SiCH_2CH_2SiMe_2Cl$,[21] $(C_5H_5)TiCl_3$,[22] and **4** [13] were prepared by literature methods. Elemental analyses were performed by either Schwarzkopf or Atlantic Microanalytical Laboratories. High-resolution mass spectral data (EI) were collected by the Washington University Resource for Biomedical and Bio-organic Mass Spectrometry, and low-resolution mass spectral data (EI) were collected at 70 eV on a Hewlett-Packard Model 5988A GC/MS instrument. Gas chromatography was performed on a Shimadzu GC-14A using a DB5 capillary column.

NMR Experiments. All NMR spectral data were collected on a Bruker ARX500 equipped with either an inverse probe or a broad band probe. ^1H and ^{13}C NMR data were recorded in C_7D_8 (referenced to C_7D_7H). ^{29}Si NMR data were recorded in C_7D_8 (referenced externally to TMS) using INEPTRD (with a ^1H refocusing pulse, optimized for $J = 7.0$ Hz). ^{13}C DEPT data were collected using a 135° decoupler high-power pulse (optimized for $J = 145$ Hz) so that resonances corresponding to carbon atoms with two attached protons appeared negative and carbon atoms with one or three attached protons appeared positive.

(^{13}C,^1H) HETCOR:[23] 2D heteronuclear correlation spectrum (XHCORR)[24] was performed using 128 scans for each t_1 increment with a recycling delay of 2 s. Delays Δ_1 and Δ_2 were optimized for $J = 145$ Hz ($\Delta_1 = 3.45$ ms and $\Delta_2 = 2.30$ ms). The spectral widths used in the F1 and F2 domains were 4808 and 26316 Hz, respectively. The t_2 data were exponentially weighted using a line-broadening factor of 1 Hz and were Fourier-transformed over 2 K data points. The t_1 interferograms were adjusted with a shifted (π/2) sine squared bell function before Fourier transformation over 256 data points as a magnitude spectrum.

(^{29}Si,^1H) HETCOR:[25] 2D heteronuclear correlation spectrum was performed using a DEPT sequence for polarization transfer by the sequence described by Bendall and Pegg.[26] The sequence was modified to give the ^{29}Si signals in the F2 dimension, where four transients were collected for the 128 increments for the t_1 dimension and a recycling delay of 2 s was used. Delay Δ_1 was optimized for $J = 7$ Hz ($\Delta_1 = 71.4$ ms). A 45° decoupler high-power pulse (5.5 μs) was used so that all resonances were displayed as positive signals. The spectral widths used in the F1 and F2 domains were 6024 and 6024 Hz, respectively. The initial $\mathbf{S}(t_1,t_2)$ data matrix consisted of 4K × 128W. The interferograms in the t_1 dimension were zero filled to 256W before Fourier transformation. The t_2 data were exponentially weighted using a line-broadening factor of 0 Hz and were Fourier-transformed over 4K data points. The t_1 interferograms were adjusted with a shifted (π/2) sine squared bell function before Fourier transformation.

Synthesis of [μ-(MePhSi)(C_5H_5)$_2$] (2). A solution of $MePhSiCl_2$ (14.4 g, 75.5 mmol) in THF (50 mL) was added dropwise over a period of 1 h to a flask containing a stirred and cooled (0 °C) suspension of $Li(C_5H_5)$, which had been prepared from ^nBuLi (66.0 mL, 2.3 M) and CpH (10.0 g, 151 mmol) in THF (200 mL). As the reaction progressed, the mixture turned pale yellow and the precipitation of LiCl was observed. After addition of the chlorosilane was complete, the mixture was warmed to room temperature and stirred for 15 h. The reaction mixture was then treated with water, and the organic layer was separated and washed with water five times. The combined aqueous washings were extracted twice with Et_2O (50 mL), and the combined organic layers were dried over Na_2SO_4. Volatiles were removed under reduced pressure, and the resulting yellow oil was flash distilled under vacuum from 95 to 110 °C (0.1 mmHg). The resulting oil was then slowly redistilled, and a fraction was collected from 97 to 100 °C (0.1 mmHg) to provide 8.8 g of **2** as a pale yellow oil (47% yield, >99% pure by GC). ^1H, ^{13}C, and ^{29}Si NMR data for the Me, bridgehead HC_{Cp}, and H_2C_{Cp} regions are summarized in Table 1, and the $Vinyl_{Cp}$ and Ph regions appeared as overlapping multiplets in the ^1H (6.2−7.6 ppm) and ^{13}C (120−150 ppm) NMR spectra. High-resolution mass spectrum: [P^+] $C_{16}H_{18}Si$, *m/z* 250.1178 (calc), 250.1167 (obs), $\delta = 4.2$ ppm; [P − C_5H_5] $C_{11}H_{13}Si$, *m/z* 185.0787 (calc), 185.0787 (obs), $\delta = 0.2$. Low-resolution mass spectrum [*m/e* (assignment, relative intensity)]: 250 ($P^{\bullet+}$, 9.0), 185 ($MePh(C_5H_5)Si^+$, 100), 105 ($PhSi^+$, 21), 93 ($(C_5H_5)Si^+$, 10).

Synthesis of [μ,μ-(MePhSi)(Me_2Si)(C_5H_4)$_2$] (3). An aliquot of ^nBuLi (17.4 mL, 2.3 M) was added dropwise to a stirred and cooled (0 °C) solution of **2** (5.00 g, 20.0 mmol) in THF (75 mL). The resulting light orange solution of Li_2[**2**] was stirred at room temperature for 1 h, and then recooled to 0 °C, at which temperature a solution of Me_2SiCl_2 (2.58 g, 20.0 mmol) in THF (25 mL) was added dropwise to the reaction flask. As the reaction progressed, the mixture turned pale yellow and the precipitation of LiCl was observed. After addition of the chlorosilane was complete, the reaction mixture was warmed to room temperature and stirred for 15 h. The reaction mixture was then concentrated under reduced pressure, and CH_2Cl_2 (50 mL) was added to precipitate the LiCl, which was removed by filtration through celite. The volatiles were removed from the filtrate under reduced pressure, and the resulting dark brown oil was vacuum distilled. The compound distilled at 115−117 °C (0.1 mmHg) as a pale yellow oil, 1.1 g (18% yield, >99% pure by GC). ^1H, ^{13}C, and ^{29}Si NMR data for the Me and bridgehead HC_{Cp} regions are summarized in Table 2, and the $Vinyl_{Cp}$ and Ph regions appeared as overlapping multiplets in the ^1H (6.4 −7.8 ppm) and ^{13}C (125−150 ppm) NMR spectra. High-resolution GC/MS: [P^+] $C_{19}H_{22}Si_2$, *m/z* 306.1260 (calc), 306.1261 (obs), $\delta = 0.3$ ppm; [P − CH_3] $C_{18}H_{19}Si_2$, *m/z* 291.1025 (calc), 291.1023 (obs), $\delta = 0.7$ ppm; [P - C_7H_9Si] $C_{12}H_{13}Si$, *m/z* 185.0787 (calc), 185.0780 (obs), $\delta = 3.3$ ppm. Low-resolution mass spectrum [*m/e* (assignment, relative intensity)]: 306 ($P^{\bullet+}$, 100), 291 ($(P - CH_3)^+$, 97), 169

---

[21] Suryanarayan, B.; Peace, B. W.; Mayhan, K. G. *J. Organomet. Chem.* **1973**, *55*, 65−69.

[22] Gorsich, R. D. *J. Am. Chem. Soc.* **1960**, *82*, 4211.

[23] Parameters for a similar (^{13}C,^1H) HETCOR experiment appear in: Zielinski, M. B.; Drummond, K. K.; Iyer, P. S.; Leman, J. T.; Evans, W. J. *Organometallics* **1995**, *14*, 3724−3731.

[24] Bax, A.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 501−505.

[25] Parameters for a similar (^{29}Si,^1H) HETCOR experiment appear in: Dubois, M.-D.; Petrand, M.; Laguerre, M.; Pianet, I. *Spectrochim. Acta* **1994**, *50A*, 2059−2068.

[26] Bendall, M. R.; Pegg, D. T. *J. Magn. Reson.* **1983**, *53*, 144−148.

($Si(C_6H_5)(C_5H_4)^+$, 24), 135 ($PhMe_2Si^+$, 33), 105 ($(C_6H_5)Si^+$, 30), 93 ($C_5H_5Si^+$, 22).

Synthesis of [μ,μ-($Me_2SiCH_2CH_2SiMe_2$)$_2$(C_5H_4)$_2$] (5). An aliquot of ^nBuLi (18.2 mL, 2.5 M) was added dropwise to a stirred and cooled (0 °C) solution of **4** (6.23 g, 22.8 mmol) in THF (200 mL). The resulting light orange solution of Li_2[**4**] was stirred at room temperature for 1 h, then cooled to 0 °C. A solution of $ClMe_2SiCH_2CH_2SiMe_2Cl$ (4.90 g, 22.8 mmol) in THF (100 mL) was then added dropwise to the reaction flask. As the reaction progressed, the mixture turned orange and the precipitation of LiCl was observed. After addition of the chlorosilane was complete, the mixture was warmed to room temperature and stirred for 15 h. The reaction mixture was concentrated under reduced pressure, and CH_2Cl_2 (100 mL) was added to precipitate the LiCl, which was removed by filtration through celite. The volatiles were removed from the filtrate under reduced pressure, and the resulting dark brown oil was vacuum distilled. The fraction that distilled/sublimed at 120−150 °C (0.1 mmHg) was collected as a slushy yellow solid and was recrystallized from petroleum ether. Sublimation at 105 °C (0.1 mmHg) provided 2.8 g of a colorless crystalline solid (30% yield, 100% pure by GC; mp = 125−126 °C). ^1H, ^{13}C, and ^{29}Si NMR data are summarized in Table 5. Anal. Calcd for $C_{22}H_{40}Si_4$: C, 63.38; H, 9.67. Found: 62.96; H, 9.57. Low-resolution mass spectrum [*m*/*e*, (relative intensities)]: 416 ($P^{\bullet +}$, 21), 208 ($(Me_2SiCH_2CH_2SiMe_2(C_5H_4))^{\bullet +}$, 14), 193 ($(MeSiCH_2CH_2SiMe_2(C_5H_4))^+$, 100), 165 ($MeSi(C_5H_4)SiMe_2^+$, 39), 145 ($Me_2SiCH_2CH_2SiMe_2H,^+$ 11), 135 ($MeSi(C_5H_4)Si^+$, 13), 122 ($(Me_2Si(C_5H_4))^{\bullet +}$, 26), 93 ($(Si(C_5H_5))^+$, 11), 85 ($SiCH_2CH_2SiH^+$, 11), 73 ($Me_3Si^+$, 56), 59 ($M_2SiH^+$, 19).

Crystallographic Data Collection and Structure Determination for 1,3−1,3 *trans*-[μ,μ-($Me_2SiCH_2CH_2SiMe_2$)$_2$-(C_5H_4)$_2$] (5a). Colorless needle shaped crystals of **5a** were obtained by slow sublimation of **5** at 100 °C (0.15 mmHg). Data collection was performed using a Siemens P4RA automated single crystal X-ray diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Autoindexing of 10 centered reflections from the rotation photograph indicated a tetragonal lattice. Equivalent reflections were checked to confirm the Laue symmetry, and a fractional index search was conducted to confirm the cell lengths (XSCANS[27]). Final cell constants and the orientation matrix for data collection were calculated by least squares refinement of the setting angles for 35 reflections ($7° < 2\theta < 27°$). Intensity data were collected using $\omega - 2\theta$ scans with variable scan speed. Three representative reflections measured every 97 reflections showed a 14.7% variation during data collection. Crystal data and intensity data collection parameters are listed in Table 3. Data reduction was carried out using XSCANS, and structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package.[28] No absorption correction was applied to the data. The structure was solved by direct methods and refined successfully in the tetragonal space group $P4_2/n$. Full matrix least squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. Selected geometrical parameters are listed in Table 4. A projection view of the molecule with non-hydrogen atoms represented by 50% probability ellipsoids and showing the atom labeling is presented in Figure 8.

Synthesis of [μ-(MePhSi)(C_5H_4)$_2$][(C_5H_5)$TiCl_2$]$_2$ (6). Li_2-[μ-(MePh)(C_5H_4)$_2$] (Li_2[**2**]) was obtained from the reaction of ^nBuLi (3.66 mL, 2.5 M) with **2** (1.14 g, 4.58 mmol) in hexanes (50 mL). The white solid was collected by filtration under N_2, washed with hexanes, and dried in vacuo to provide Li_2[**2**] as a white powder (1.12 g, 93% yield). Li_2[**2**] (0.60 g, 2.29 mmol) was added to a Schlenk tube and dissolved in THF (20 mL). To this stirred solution, solid (C_5H_5)$TiCl_3$ (1.00 g, 4.57 mmol) was added to provide a dark red reaction mixture, which was stirred for 15 min and then allowed to stand at room temperature overnight. The volatiles were then removed in vacuo, and CH_2Cl_2 (10 mL) was added to precipitate the LiCl, which was removed by filtration under N_2 through a fine frit. The red filtrate was concentrated under reduced pressure to a volume of 1.0 mL. Hexanes (1.0 mL) were added, and the solution was stored for 24 h at −50 °C. The resulting red-orange microcrystals were isolated by filtration, washed with hexanes and dried in vacuo (0.1 mmHg) overnight to afford 0.51 g of **6** (35% yield; mp > 250 °C (dec.)). Compound **6** was found to contain 0.25 equiv of CH_2Cl_2, which could not be removed by drying in vacuo or by washing with hexanes. Anal. Calcd for $C_{27}H_{26}SiTi_2Cl_4 \cdot 0.25CH_2Cl_2$: C, 51.35; H, 4.19. Found: C, 51.75; H, 4.34. ^1H NMR (500 MHz, $CDCl_3$): δ 1.01 (s, 3H, SiMe), 5.28 (s, 0.5H, CH_2Cl_2), 6.32 (s, 10H, C_5H_5), 6.47 (m, 2H, C_5H_4), 6.78 (m, 2H, C_5H_4), 6.81(m, 2H, C_5H_4), 7.01 (m, 2H, C_5H_4), 7.4−7.6 (m, 5H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): δ −3.1 (SiMe), 120.6 (C_5H_5), 119.2, 125.5, 127.2, 127.9, 128.2, 130.3, 130.4, 134.7, 135.4 (C_5H_4 and Ph). ^{29}Si NMR (99 Hz, $CDCl_3$): δ −1.21 (MePhSi).

Synthesis of *trans*-[μ,μ-(MePhSi)(Me_2Si)(C_5H_3)$_2$][(C_5H_5)-$TiCl_2$]$_2$ (7). An aliquot of ^nBuLi (1.21 mL, 2.5 M) was added dropwise to a stirred and cooled (0 °C) solution of **3** (0.463 g, 1.51 mmol) in THF (20 mL). The resulting light yellow solution was warmed to room temperature and stirred for 1 h before the addition of solid (C_5H_5)$TiCl_3$ (0.665 g, 3.03 mmol). The reaction mixture immediately turned dark red, and pale red microcrystals began to form within 5 min. The reaction mixture was stirred for 15 min and then allowed to stand overnight. After this time, the microcrystals were separated by decantation and recrystallized by Soxhlet extraction with CH_2Cl_2 to provide 0.67 g of **7** as the *trans* isomer (66% yield; mp > 305 °C (dec)). ^1H NMR analysis of the decantate showed no identifiable products. Compound **7** was found to contain 0.25 equiv of CH_2Cl_2, which could not be removed by drying in vacuo or by washing with hexanes. Anal. Calcd for $C_{29}H_{30}Si_2Ti_2Cl_4 \cdot 0.25CH_2Cl_2$: C, 50.66; H, 4.43. Found: C, 50.69; H, 4.57. ^1H NMR (500 MHz, $CDCl_3$): δ 0.52 (s, 3H, SiMe), 0.70 (s, 3H, SiMe), 0.85 (s, 3H, SiMe), 5.28 (s, 0.5H, CH_2Cl_2) 6.00 (s, 5H, C_5H_5), 6.30 (m, 1H, C_5H_3), 6.49 (m, 1H, C_5H_3), 6.52 (s, 5H, C_5H_5), 7.03 (m, 1H, C_5H_3), 7.23 (m, 1H, C_5H_3), 7.28 (m, 1H, C_5H_3), 7.36 (m, 1H, C_5H_3), 7.3−7.5 (m, 5H, Ph). ^{29}Si NMR (99 Hz, DMSO-d_6): δ −21.00, −15.00.

Synthesis of [μ,μ-($Me_2SiCH_2CH_2SiMe_2$)$_2$(C_5H_3)$_2$][(C_5H_5)-$TiCl_2$]$_2$ (8). An aliquot of ^nBuLi (0.640 mL, 2.5 M) was added dropwise to a stirred and cooled (0 °C) solution of **5** (0.334 g, 0.801 mmol) in THF (10 mL). The resulting peach colored solution was warmed to room temperature and stirred for 1 h before the addition of solid (C_5H_5)$TiCl_3$ (0.351 g, 1.60 mmol). The reaction mixture immediately turned dark orange, and brown crystals began to form within 5 min. The reaction mixture was stirred for 15 min and then allowed to stand overnight. After this time, the brown fiberlike crystals were separated by decantation, washed with THF and hexanes, and dried in vacuo to provide 0.30 g of **8** as a mixture of two isomers in a 1/1 ratio (48% yield; mp > 340 °C (dec)). ^1H NMR analysis of the decantate showed no distinguishable products. Anal. Calcd for $C_{32}H_{48}Si_4Ti_2Cl_4$ (mix of isomers): C, 49.11; H, 6.18. Found: C, 49.12; H, 6.18. Isomer **8a**. ^1H NMR (500 MHz, $CDCl_3$): δ 0.25 (br m, 8H, CH_2), 0.27 (s, 12H, SiMe), 0.35 (s, 12H, SiMe), 6.49 (s, 10H, C_5H_5), 6.70 (d, 1.7 Hz, 4H, C_5H_3), 6.83 (t, 1.7 Hz, 2H, C_5H_3). ^{29}Si NMR (99 Hz, $CDCl_3$): δ −1.95. Isomer **8b**. ^1H NMR (500 MHz, $CDCl_3$): δ 0.30 (s, 12H, SiMe), 0.32 (br s, 20H, overlapping MeSi and CH_2), 6.50 (s, 10H, C_5H_5), 6.72 (d, 1.7 Hz, 4H, C_5H_3), 6.97 (t, 1.7 Hz, 2H, C_5H_3). ^{29}Si NMR (99 Hz, $CDCl_3$): δ −2.18.

Acknowledgment is made to the National Science Foundation (Grant No. CHE-9213688) for partial support of this work. Support from the U. S. Department

---

[27] Siemens Analytical Instruments, Madison, WI, 1994.

[28] Sheldrick, G. M. Siemens Analytical X-Ray Division, Madison, WI, 1995.

of Energy (Grant No. DEF 602-92CH104999) and the University of Missouri Research Board for the purchase of the ARX500 spectrometer is gratefully acknowledged. Financial support for J.L.H. was provided by a University of Missouri—St. Louis Graduate School Summer Fellowship and a Mallinckrodt Fellowship. Additional support was provided by a Research Incentive Award from the University of Missouri—St. Louis. Acknowledgment is also made to Dr. Janet Braddock-Wilking for assistance in acquiring the 2D NMR data.

Supporting Information Available: Tables giving complete listings of bond lengths and angles, atomic coordinates and isotropic displacement parameters for the non-hydrogen atoms, positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement parameters, and least-squares planes and atomic deviations and a packing diagram for **5a** (6 pages). Ordering information is given on any current masthead page.

OM960132U