Bi- and Triferrocene Complexes Containing Silylenevinylenephenylene Bridges. Model Compounds for Poly{ferrocene(phenylene)bis(silylenevinylene)}s

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A series of conjugated ferrocene-based organosilicon complexes with one, two, or three ferrocene units have been prepared via hydrosilylation of alkynes with ferrocenylsilanes using Karstedt's catalyst (platinum-divinyltetramethyldisiloxane) and $Rh(PPh_3)_3I$. Reaction of 1,1′-bis(dimethylsilyl)ferrocene (**1**) with 2 equiv of $RC{\equiv}CR^1$ (R = H, R^1 = Ph, $SiMe_3$, Fc {Fc = $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)$}; R = $SiMe_3$, R^1 = Ph, Fc) gave $Fe[(\eta^5\text{-}C_5H_4)(Me)_2SiC(R){=}CHR^1]_2$ complexes (type 1) with varying regiochemical distributions. Addition of 2 equiv of dimethylsilylferrocene (**2**) to dialkynes $R{-}C{\equiv}C{-}X{-}C{\equiv}C{-}R$ [R = H, X = C_6H_4 (1,4- and 1,3-), $SiMe_2$; R = Me, X = Fc′ {Fc′ = $(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4)$}; R = $SiMe_3$, X = C_6H_4 (1,4- and 1,3-); R = Ph, X = nothing] resulted in $Fc(Me)_2Si(R)C{=}C(H){-}X{-}(H)C{=}C(R)Si(Me)_2Fc$ complexes (type 2), again with varying regiochemical distributions. The platinum-promoted hydrosilylations resulted in β-(*E*) and α-regioisomers, whereas the rhodium-catalyzed reactions gave primarily β-(*Z*) species with minor amounts of the β-(*E*) isomer. X-ray crystallographic studies of the predominant adducts obtained from **1** and $Me_3SiC{\equiv}CPh$ as well as **2** and $Me_3Si{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}SiMe_3$ (1,4-) using Karstedt's catalyst are described. Cyclic voltammetry shows single redox waves for most systems indicative of no interaction between the Fe−Fe centers. One complex, $Fc(Me)_2Si(C{=}CH_2){-}Fc′{-}Si(C{=}CH_2)(Me)_2Fc$, shows two reversible waves for the two different types of ferrocene center.

Introduction

There is significant interest in developing conjugated systems that represent the concept of "molecular wires" geared toward optoelectronic devices and chemical sensors,[1] with the study of electron transfer between redox active centers, separated by a conjugated bridge (spacer), being a part of these efforts.[2] One chemical system where such efforts have been focused is ferrocene-based species, in particular, ferrocene-based polymers/dendrimers[3] and biferrocene complexes bridged via a conjugated spacer.[2] Biferrocene complexes[2,4] can be viewed as fragments of polymeric systems and are good models, not only toward characterization of their corresponding polymers but also as candidates for preliminary examination of redox activity.

Most systems have been prepared using McMurray, Wittig, or Sonogashira coupling reactions or their modified protocols. Another potential addition reaction, hydrosilylation, has rarely been used and is uncommon for ferrocene-based systems.[5] Herein we report the use of this methodology to prepare new 1,1′-bis{dimethyl-(vinylene)silyl}ferrocenes and bis{ferrocenylsilylenevinylene(phenylene)} complexes using two catalysts {Karstedt's catalyst (platinum-divinyltetramethyldisiloxane) and $Rh(PPh_3)_3I$}. The products serve as excellent model systems for the characterization of analogous poly-{ferrocene(phenylene)bis(silylenevinylene)}s that are reported in the preceding article.[6]

Results and Discussion

Reaction of 1,1′-dilithioferrocene[7] and lithioferrocene[8] with chlorodimethylsilane led to the formation of pre-

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(1) *Molecular Electronics;* Launay, J.-P., Ed.; Gauthier-Villars: Paris, 1991. *New J. Chem.* **1991**, *15*, 97.

(2) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637, and references therein.

(3) See for example: (a) Gonsalves, K. E.; Chen, X. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Germany, 1995; Chapter 10, pp 497−527, and references therein. (b) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515, and references therein. (c) Manners I. *Adv. Organomet. Chem.* **1995**, *37*, 131, and references therein. (d) Cuadrado, I.; Carmen, M. C.; Alonso, B.; Moràn, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613. (e) Yamamoto, T.; Morikita, T.; Maruyama, T.; Kubota, K.; Katada, M. *Macromolecules* **1997**, *30*, 5390, and references therein. (f) Bochmann, M.; Lu, J.; Cannon, R. D. *J. Organomet. Chem.* **1996**, *518*, 97. (g) Corriu, R. J. P.; Devylder, N.; Guérin, C.; Henner, B.; Jean, A. *Organometallics* **1994**, *13*, 3194. (h) Long, N. J.; Martin, A. J.; Vilar, R.; White, A. J. P.; Williams, D. J.; Younus, M. *Organometallics* **1999**, *18*, 4261.

(4) (a) Hradsky, A.; Bildstein, B.; Schuler, N.; Schottenberger, H.; Jaitner, P.; Ongania, K.-H.; Wurst, K.; Launay, J.-P. *Organometallics* **1997**, *16*, 392. (b) Justin Thomas, K. R.; Lin, J. T.; Wen, Y. S. *Organometallics* **2000**, *19*, 1008. (c) Ribou, A.-C.; Launay, J.-P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* **1996**, *35*, 3735. (d) Zhu, Y.; Wolf, M. O. *J. Am. Chem. Soc.* **2000**, *122*, 10121.

(5) See for example: (a) Greber, G.; Hallensleben, M. L. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 701. (b) Cuadrado, I.; Alonso, B.; Moràn, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613. (c) García, B.; Casado, C. M.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. *Organometallics* **1999**, *18*, 2349.

(6) Jain, R.; Lalancette, R. A.; Sheridan, J. B., preceding article.

(7) Ni, Y.; Manners, I.; Sheridan, J. B.; Oakley, R. T. *J. Chem. Educ.* **1998**, *75*, 766.

(8) Sanders, R.; Mueller-Westerhoff, U. T. *J. Organomet. Chem.* **1996**, *512*, 219.
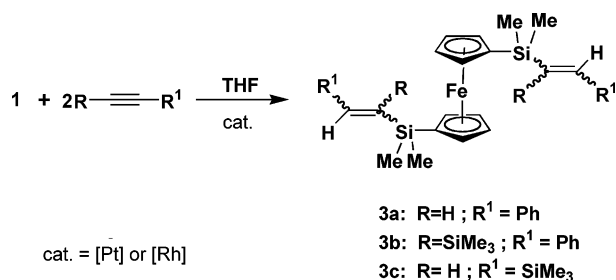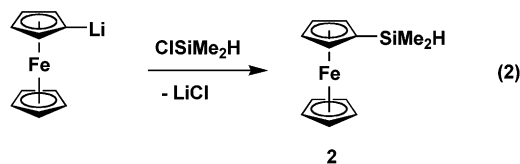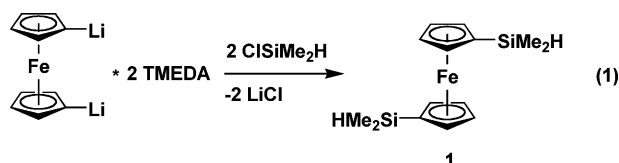
Scheme 1

3a: R=H ; R^1 = Ph
3b: R=SiMe$_3$; R^1 = Ph
3c: R= H ; R^1 = SiMe$_3$

cat. = [Pt] or [Rh]

Table 1. Isomeric Distributions of 1,1′-Bis{dimethyl(vinyl)silyl}ferrocenes (Type 1)

| product	physical state	isomers and percentage ratios
3a (Pt)	orange oil	bis-α; β-(E)-α; bis-β-(E) 36; 31; 33
3a (Rh)	orange oil	overall β-(Z)/β-(E) 79/21
3b (Pt)	orange solid	bis-α; β-(E)-α >90; <10
3c (Pt)	orange solid	bis-β-(E) 100

cursors 1,1′-bis(dimethylsilyl)ferrocene[3g] (**1**) and dimethylsilylferrocene (**2**) as red and orange oils, respectively (eqs 1 and 2). Complexes **1** and **2** were used to prepare two types of vinylsilylferrocenes via hydrosilylation of alkynes. The first (type 1 complexes) contain a single iron center between two vinyl-substituted silyl groups attached to each cyclopentadienyl ligand and are prepared from **1** and 2 equiv of alkyne. The second (type 2 complexes) contain two iron centers bridged by a bis-(silylvinyl)phenylene moiety and are prepared from 2 equiv of **2** and a dialkyne. Complexes containing three ferrocene units were also prepared from **1** and 2 equiv of either trimethylsilylethynylferrocene or ethynylferrocene, or from **2** and bis(methylethynyl)ferrocene.

1,1′-Bis{dimethyl(vinyl)silyl}ferrocenes (Type 1) Prepared Using Karstedt's Catalyst, 3a−c (Pt). Treatment of 2 equiv of alkynes RC≡CR^1 (R = H, R^1 = Ph; R = SiMe$_3$, R^1 = Ph; R = H, R^1 = SiMe$_3$) and 1 equiv of **1** at room temperature led to the formation of complexes **3a−c (Pt)** (Scheme 1), as mixtures of isomers (Table 1). The different isomers derive from attack of silicon at either the internal alkynyl carbon (α-isomer) or the terminal alkynyl carbon (β-isomer). For the latter, both β-(E) and β-(Z) isomers are possible from *anti-* or *syn*-Si−H addition, respectively. Platinum-catalyzed hydrosilylations have previously been shown to give both β-(E) and α-isomers.[9]

(9) Hiyami, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost B. M., Flemings, I., Eds.; Pergamon: Oxford, England, 1991; Vol. 8, pp 763−792, and references therein.
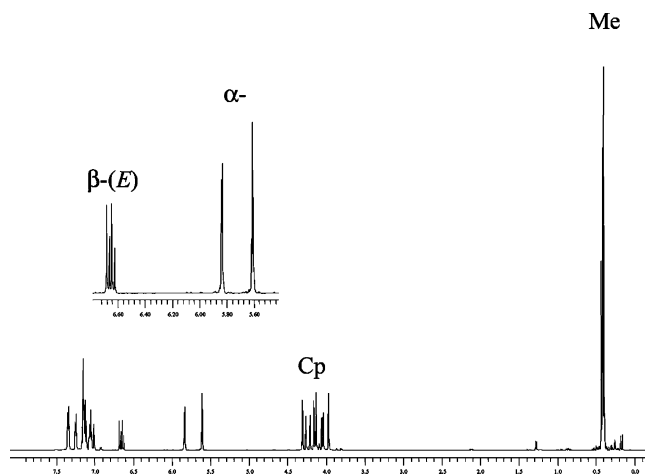
Figure 1. ^{1}H NMR spectrum of **3a (Pt)**.

Complexes **3a−c (Pt)** were characterized using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy as well as mass spectrometry. Product **3a**, bis{dimethyl(phenylvinyl)-silyl}ferrocene, was isolated (61%) as a mixture of three isomers (bis-β-(E), 33%; bis-α, 36%; and β-(E), α-, 31%). The overall regiochemical distribution of ~52% α- and ~48% β-(E) structures was determined from integration of the ^{1}H NMR olefinic signals. The GC-MS of **3a (Pt)** showed three distinct peaks (m/z = 506 (M$^+$)) indicative of all three isomers in a similar ratio and consistent with the NMR results. The ^{1}H NMR spectrum (Figure 1) of the mixture showed geminal (α-) proton signals around δ 5.6−5.8 with $^2J_{H-H}$ = 3.0 Hz[10] and vicinal proton signals arising from the β-(E) structures at δ 6.6 and 7.0 ($^3J_{H-H}$ = 19.0 Hz)[10a,11] (Table 2). The {^{1}H}^{13}C NMR spectrum shows the expected olefinic carbons at δ 144.8 and 153.3 (α-) and δ 145.0 and 128.9 {β-(E)},[11b,12] whereas the ^{29}Si NMR was four sharp peaks, δ −9.3 {bis-(β-(E)}; −7.42 {bis-(α-)}; −9.4 {β-(E), α-} and −7.37 {α-, β-(E)} ppm, consistent with the proposed structures.

Further hydrosilylation of the olefins in **3a (Pt)** was not observed. Pt-complex-catalyzed hydrosilylation of phenylacetylene with Et$_3$SiH has been shown to favor β-(E) addition (ca. 80%),[9] and we attribute the equal preference for both isomers in **3a (Pt)** as due to the electron-donating effect of the ferrocene group. Kim and co-workers have shown that modifying silane substituents from Ph (−I) to Me (+I) gives an increase in the α-/β-(E) ratio.[11a,b]

Hydrosilylation of the internal alkyne, phenyl(trimethylsilyl)acetylene, with **1** proceeded over 2 days at room temperature in almost quantitative yield (98%) (Scheme 1). The product, 1,1′-bis[dimethyl{(trimethylsilyl)(phenyl)vinyl}silyl]ferrocene, **3b (Pt)**, was isolated as an orange solid in two regioisomeric forms. GC-MS of **3b (Pt)** (m/z = 650 (M$^+$)) confirmed the presence of two *syn* adducts, with the major isomer resulting from the attack of Si at the phenyl-substituted alkynyl carbon (>90%, Table 1). The minor isomer (<10%), **3b (Pt)**-

(10) (a) Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177. (b) Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31*, 5592. (c) Yamashita, H.; Uchimaru, Y. *J. Chem. Soc., Chem. Commun.* **1999**, 1763.
(11) (a) Kim, D. S.; Shim, S. C. *J. Polym. Sci., Part A* **1999**, *37*, 2933. (b) Kim, D. S.; Shim, S. C. *J. Polym. Sci., Part A* **1999**, *37*, 2263. (c) Son, D. Y.; Bucca, D.; Keller, T. M. *Tetrahedron Lett.* **1996**, *37*, 1579.
(12) Pang Y.; Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671.

Table 2. NMR Spectroscopic Data for 3a−c (Pt), 4a−f (Pt), 3a (Rh), and 4a,c (Rh)

product	δ, ¹H[a]	δ, ¹³C{¹H}[a]	δ, ²⁹Si[a,b]
3a (Pt)	0.414 (s, 12H, bis-β-(E), Me), 0.406 (s, 12H, bis-(α-), Me), 0.39, 0.43 (s, 12H, β-(E)-α-, Me), 4.13, 4.31 (t, 8H, bis-β-(E), Cp), 3.97, 4.16 (t, 8H, bis-(α-), Cp), 4.04, 4.06, 4.21, 4.26 (t, 8H, β-(E)-α-, Cp), 6.66, 7.03 (d, 4H, bis-β-, ³J_{H-H} = 19 Hz, 5.61, 5.84 (d, 4H, bis-(α-), ²J_{H-H} = 3 Hz), 6.64, 7.02, 5.62, 5.84 (2d, 4H, β-(E)-α-, ³J_{H-H} = 19 Hz (β-(E)), ²J_{H-H} = 3 Hz (α-)), 7.06−7.36 (m, 3 × 10H, Ph)	−1.4 (bis-β-(E), Me), −1.3 (bis-(α-), Me), −1.2, −1.5 (β-(E)-α-, Me), 70.3, 70.4 (Cp$_{ipso}$), 72.0, 72.1, 73.8, 74.0 (β-(E), Cp's), 71.8, 71.9, 73.5, 73.8 (α-, Cp's), 128.9, 145.0 (C=C$_{β-(E)}$), 144.8, 153.3 (C=C$_{α-}$), 138.7, 145.2 (Ph$_{ipso}$'s), 126.8, 127.2, 127.4, 128.5, 128.7 (Ph's)	−9.3 (bis-β-(E)), −7.42 (bis-(α-)), −9.4, −7.37 (β-(E)-α-),
3a (Rh)	0.32 (s, 12H, bis-β-(Z), Me), 0.42 (s, 12H, bis-β-(E), Me), 0.32, 0.42 (s, 12H, β-(Z)-β-(E), Me), 4.10−4.31 (t, 3 × 8H, bis-β-(Z), bis-β-(E), β-(Z)-β-(E), Cp), 6.67, 7.03 (d, 4H, bis-β-(E), ³J_{H-H} = 19.0 Hz), 6.09, 7.42 (d, 4H, bis-β-(Z), ³J_{H-H} = 15.0 Hz), 6.67, 7.08; 6.08, 7.41 (2d, 4H, β-(E) -β-(Z))	0.2 (bis-β-(Z), Me), −1.4 (bis-β-(E), Me), 0.2, −1.4 (β-(Z)-β-(E), Me), 70.4, 71.8 (Cp$_{ipso}$), 71.7, 71.9, 73.7, 73.9 (Cp), 144.9, 128.9 (C=C$_{bis-β-(E)}$), 132.0, 147.2 (C=C$_{bis-β-(Z)}$), 132.0, 147.2, 128.9, 144.9 (C=C$_{β-(Z)-β-(E)}$), 138.7, 140.4 (Ph$_{ipso}$'s)	−9.3 (β-(E)), −13.2 (β-(Z))
3b (Pt) major	−0.10 (s, 18H, SiMe₃), 0.38 (s, 12H, SiMe₂), 3.95, 4.17 (t, 8H, Cp), 6.60 (s, 2H, Si(Ph)C=CHSiMe₃), 7.00−7.12 (m, 10H, Ph)	0.2 (SiMe₃), −2.2 (SiMe₂), 70.0 (Cp$_{ipso}$) 71.9, 73.8 (Cp), 144.8, 166.5 (C=C), 145.6 (Ph$_{ipso}$), 126.2, 127.5 (Ph)	−7.9 (SiMe₃), −9.7 (SiMe₂).
3b (Pt) minor	−0.09, 0.1 (s, 18H, SiMe₃), 0.42, 0.53 (s, 12H, SiMe₂), 4.01, 4.08, 4.22, 4.26 (t, 8H, Cp), 6.62 (s, 1H, Si(Ph)C=CH SiMe₃), 7.91 (s, 1H, Si(SiMe₃)C=CHPh), 7.00−7.12 (m, 10H, Ph)	0.2, 2.4 (SiMe₃), −2.2 (SiMe₂), 70.0 (Cp$_{ipso}$) 71.9, 72.0, 73.8, 74.1 (Cp), 144.8, 166.5; 146.4, 157.1 (C=C), 143.1, 145.5 (Ph$_{ipso}$), 126.2, 127.3, 127.7, 128.3 (Ph)	−7.9, −2.9 (SiMe₃), −9.7, −7.7 (SiMe₂)
3c (Pt)	0.12 (s, 18H, SiMe₃), 0.40 (s, 12H, SiMe₂), 4.10, 4.28 (t, 8H, Cp), 6.87, 6.97 (d, 4H, β-(E), ³J_{H-H} = 22.5 Hz).	−1.8 (SiMe₂), −1.5 (SiMe₃), 70.1 (Cp$_{ipso}$) 71.9, 73.5 (Cp), 150.1, 151.5 (C=C).	−7.4 (SiMe₃), −10.8 (SiMe₂).
4a (Pt)	0.43 (s, 12H, bis-β-(E), Me), 0.42, 0.45 (s, 12H, β-(E)-α-, Me), 4.10, 4.22 (t, 8H, bis-β-(E), Cp), 4.05 (s, 10H, bis-β-(E), terminal Cp), 4.01, 4.10, 4.16, 4.22 (t, 8H, β-(E)-α-, Cp), 3.97, 4.05 (s, 10H, β-(E)- α-, terminal Cp), 6.69, 7.04 (d, 4H, bis-β-, ³J_{H-H} = 19 Hz), 6.67, 7.07, 5.65, 5.88 (2d, 4H, β-(E)-α-, ³J_{H-H} = 19 Hz (β-(E)), ²J_{H-H} = 3 Hz (α-)), 7.26−7.35 (m, 8H, Ar)	−1.5 (bis-β-(E), Me), −1.3, −1.4 (β-(E)-α-, Me), 69.1, 70.0, 70.2 (Cp$_{ipso}$), 68.6, 68.7 (Cp), 71.4, 73.6 (β-(E), Cp's), 71.4, 73.8 (α-, Cp's), 128.9, 144.4 (C=C$_{β-(E)}$), 144.6, 153.0 (C=C$_{α-}$), 137.1, 138.5, 145.1 (Ar$_{ipso}$), 126.8, 127.2, 127.6 (Ar)	−9.4 (bis-β-(E)), −9.6, −7.5 (β-(E)-α-).
4a (Rh)	0.37 (s, 12H, bis-β-(Z), Me), 0.43 (s, 12H, bis-β-(E), Me), 0.36, 0.43 (s, 12H, β-(Z)-β-(E), Me), 4.10−4.23 (br, 3 × 8H, bis-β-(Z), bis-β-(E), β-(Z)-β-(E), Cp), 4.02, 4.03, 4.05 (s, 3 × 10H, terminal Cp's), 6.69, 7.05 (d, 4H, bis-β-(E), ³J_{H-H} = 19 Hz), 6.10, 7.40 (d, 4H, bis-β-(Z), ³J_{H-H} = 15.5 Hz), 6.68, 7.03; 6.10, 7.39 (2d, 4H, β-(E) -β-(Z))	0.1 (bis-β-(Z), Me), −1.5 (bis-β-(E), Me), 0.1, −1.5 (β-(Z)-β-(E), Me), 70.0, 71.5 (Cp$_{ipso}$'s), 68.59, 68.64 (terminal Cp's), 71.3, 71.4, 73.6 (Cp), 144.4, 128.9 (C=C$_{bis-β-(E)}$), 132.3, 146.7 (C=C$_{bis-β-(Z)}$), 132.2, 146.7, 128.9, 144.4 (C=C$_{β-(Z)-β-(E)}$), 138.0, 138.5, 139.7, 140.2 (Ar)	−9.4 (β-(E)), −13.4 (β-(Z))
4b (Pt) major	0.00 (s, 18H, SiMe₃), 0.43 (s, 12H, SiMe₂), 4.02, 4.19 (t, 8H, Cp), 4.01 (s, 10H, terminal Cp), 6.65 (s, 2H, Si(Ph)C=CH-SiMe₃), 6.94 (m, 4H, Ar)	0.6 (SiMe₃), −2.3 (SiMe₂), 69.8 (Cp$_{ipso}$), 68.6, 71.3, 73.8 (Cp's), 144.3, 166.8 (C=C), 143.0 (Ar$_{ipso}$), 127.3, 127.7, 128.3 (Ar)	−8.1 (SiMe₃), −9.7 (SiMe₂).
4b (Pt) minor	−0.07, 0.16 (s, 18H, SiMe₃), 0.39, 0.57 (s, 12H, SiMe₂), 3.97, 4.10, 4.15, 4.19 (t, 8H, Cp), 3.98, 4.04 (s, 10H, terminal Cp), 6.62 (s, 1H, Si(Ph)C=CH SiMe₃), 7.95 (s, 1H, Si(SiMe₃)-C=CHPh), 6.90, 6.92, 7.10, 7.12 (m, 4H, Ar)	0.6, 2.7 (SiMe₃), 0.1, −2.3 (SiMe₂), 69.8 (Cp$_{ipso}$), 68.6, 71.3, 73.8, 74.1 (Cp), 144.3, 144.5, 157.0, 166.8 (C=C), 140.4, 143.0 (Ar$_{ipso}$), 127.3, 127.7, 128.3 (Ar)	−8.0, −2.8 (SiMe₃), −9.7, −7.9 (SiMe₂)
4c (Pt)	0.43 (s, 12H, bis-β-(E), Me), 0.42, 0.46 (s, 12H, β-(E)-α-, Me), 4.10, 4.22 (t, 8H, bis-β-(E), Cp), 4.04 (s, 10H, bis-β-(E), terminal Cp), 4.01, 4.10, 4.18, 4.22 (t, 8H, β-(E)-α-, Cp), 3.96, 4.05 (s, 10H, β-(E)- α-, terminal Cp), 6.71, 7.06 (d, 4H, bis-β-(E), ³J_{H-H} = 19 Hz), 6.71, 7.06, 5.65, 5.85 (2d, 4H, β-(E)-α-, ³J_{H-H} = 19 Hz (β-(E)), ²J_{H-H} = 3 Hz (α-)), 7.10−7.57 (m, 8H, Ar)	−1.5 (bis-β-(E), Me), −1.2, −1.4 (β-(E)-α-, Me), 69.1, 70.0 (Cp$_{ipso}$), 68.6 (Cp), 71.4, 73.6 (β-(E), Cp's), 71.4, 73.8 (α-, Cp's), 129.1, 144.7 (C=C$_{β-(E)}$), 145.0, 153.3 (C=C$_{α-}$), 138.7, 139.1, 145.6 (Ar$_{ipso}$), 125.2, 125.6, 126.4, 127.2, 127.6, 128.6 (Ar)	−9.45 (bis-β-(E)), −9.54, −7.58 (β-(E)-α-).
4c (Rh)	0.35 (s, 12H, bis-β-(Z), Me), 0.35, 0.43 (s, 12H, β-(Z)-β-(E), Me), 4.10−4.21 (t, 2 × 8H, bis-β-(Z), β-(Z)-β-(E), Cp), 4.02, 4.05 (s, 2 × 10H, terminal Cp's), 6.12, 7.45 (d, 4H, bis-β-(Z), ³J_{H-H} = 15.5 Hz), 6.72, 7.08; 6.10, 7.45 (2d, 4H, β-(E)-β-(Z))	0.1 (bis-β-(Z), Me), 0.1, −1.4 (β-(Z)-β-(E), Me), 71.5 (Cp$_{ipso}$'s), 68.6 (terminal Cp's), 71.3, 73.6 (Cp), 132.6, 146.8 (C=C$_{bis-β-(Z)}$), 132.5, 146.9, 128.9, 144.6 (C=C$_{β-(Z)-β-(E)}$), 138.5, 140.2, 140.6 (Ar)	−9.4 (β-(E)), −13.4 (β-(Z)),
4d (Pt) major	0.01 (s, 18H, SiMe₃), 0.47 (s, 12H, SiMe₂), 4.07, 4.20 (t, 8H, Cp), 4.01 (s, 10H, terminal Cp), 6.65 (s, 2H, Si(Ph)C=CH SiMe₃), 6.93−7.10 (m, 4H, Ar)	0.6 (SiMe₃), −1.6 (SiMe₂), 70.0 (Cp$_{ipso}$), 68.7, 71.4, 73.9 (Cp's), 145.3, 166.5 (C=C), 145.0 (Ar$_{ipso}$), 126.0, 126.1, 127.5 (Ar)	−7.1 (SiMe₃), −9.9 (SiMe₂)

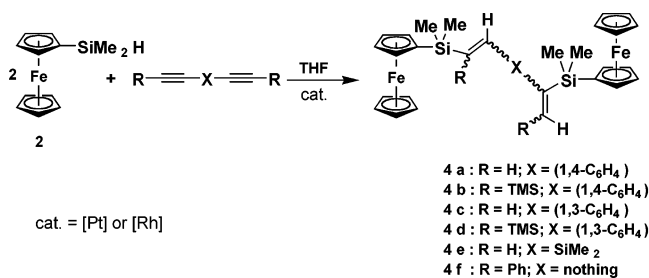| Compound	^{1}H NMR	^{13}C NMR	^{29}Si NMR
4d (Pt) minor	−0.08, 0.17 (s, 18H, *SiMe$_3$*), 0.39, 0.55 (s, 12H, *SiMe$_2$*), 4.07, 4.10, 4.18, 4.20 (t, 8H, *Cp*), 3.98, 4.03 (s, 10H, *terminal Cp*), 6.60 (s, 1H, Si(Ph)C=*CH* *terminal Cp*), 6.90−7.12 (m, 4H, *Ar*)	0.4, 2.7 (*SiMe$_3$*), 0.1, −2.0 (*SiMe$_2$*), 70.0 (*Cp$_{ipso}$*), 68.7, 71.2, 71.4, 73.9, 74.0 (*Cp*), 142.5, 145.3, 157.0, 166.4 (*C=C*), 145.0, 146.1 (*Ar$_{ipso}$*), 126.0, 126.1, 126.8, 127.3, 127.5 (*Ar*)	−7.9, −2.9 (*SiMe$_3$*), −9.9, −7.7 (*SiMe$_2$*)
4e	1H, Si(SiMe$_3$)C=*CH*Ph), 8.00 (s, 1H, Si(Ph)C=*CH* SiMe$_3$), 8.00 (s, 1H, Si(SiMe$_3$)C=*CH*Ph), 0.27 (s, 6H, *SiMe$_2$*), 0.35 (s, 12H, *SiMe$_2$*), 4.07, 4.20 (t, 8H, *Cp*), 4.04 (s, 10H, *terminal Cp*), 6.94, 7.08 (d, 4H, *β-(E)*, $^3J_{\text{H−H}}$ = 22.5 Hz)	−1.9, −3.1 (*SiMe$_2$*), 69.7 (*Cp$_{ipso}$*), 68.6, 71.3, 73.5 (*Cp*), 149.3, 151.9 (*C=C*).	−14.8, −10.8
4f	0.30, 0.42 (s, 12H, *Me*), 3.98−4.07, 4.19−4.22 (m, 8H, *Cp*), 3.96 (s, 10H, *terminal Cp*), 6.95 (s, 2H, Fc-Si(Ph)C=*CH*-C(*H*)=C(Ph)Si−Fc), 6.97−7.59 (m, 10H, *Ph*)	−1.1, −0.6 (*Me*), 71.6 (*Cp$_{ipso}$*), 68.7, 71.1, 71.2, 73.9 (*Cp*), 137.2, 148.6 (*C=C*), 140.2 (*Ph$_{ipso}$*), 127.4, 127.7, 128.4, 128.6, 129.3 (*Ph*)	−6.4

^{a} In C$_6$D$_6$. ^{b} External reference Si(CH$_3$)$_4$ (0.00 ppm).
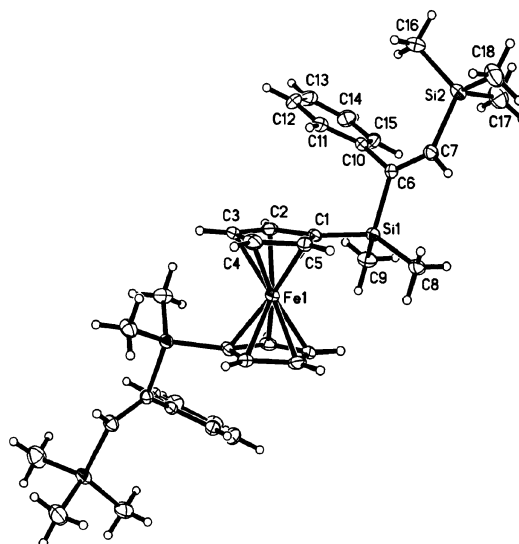
Figure 2. Molecular structure of **3b (Pt)**-major, showing the atom-numbering scheme and using 20% probability thermal ellipsoids.

Scheme 2

4 a : R = H; X = (1,4-C$_6$H$_4$)
4 b : R = TMS; X = (1,4-C$_6$H$_4$)
4 c : R = H; X = (1,3-C$_6$H$_4$)
4 d : R = TMS; X = (1,3-C$_6$H$_4$)
4 e : R = H; X = SiMe$_2$
4 f : R = Ph; X = nothing

cat. = [Pt] or [Rh]

minor, had one-half of the molecule with the same geometry as the major isomer but the second half resulting from the attack of silicon at the trimethylsilyl-substituted carbon {*β-(E)-*}.

An X-ray crystallographic study on **3b (Pt)**-major showed the silyl groups to be *trans* about the double bond and the cyclopentadienyl groups eclipsed. An ORTEP drawing of complex **3b (Pt)**-major is shown in Figure 2.

1,1′-Bis{dimethyl(trimethylsilylvinyl)silyl}ferrocene, **3c (Pt)**, was synthesized in 45% yield from 2 equiv of trimethylsilylacetylene and 1 equiv of **1** (Scheme 1) as only the bis-*β-(E)* isomer (Table 1). Likewise, reaction of trimethylsilylacetylene with Et$_3$SiH using chloroplatinic acid as catalyst has been shown to give the *β-(E)* product exclusively.[13]

Bis(ferrocenylsilylvinyl)phenylenes (Type 2) Prepared Using Karstedt's Catalyst, 4a−f (Pt). Treatment of 2 equiv of **2** with 1 equiv of a dialkyne (R−C≡C−X−C≡C−R) (where R = H, X = C$_6$H$_4$ (1,4- and 1,3-); R = SiMe$_3$, X = C$_6$H$_4$ (1,4- and 1,3-); R = H, X = SiMe$_2$; R = Ph, X = nothing) gave **4a−f (Pt)** (Scheme 2). All the complexes were characterized using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Table 2), and the isomer distributions are shown in Table 3.

For the 1,4- and 1,3-diethynylbenzene-derived complexes, **4a (Pt)**, **4c (Pt)**, three regioisomers were obtained, with the major isomer being bis-*β-(E)* (∼65%).

(13) Marciniec, B., Ed. *Comprehensive Handbook on Hydrosilylation*; Pergamon: Oxford, 1992, and references therein.

Table 3. Isomeric Distributions of Bis(ferrocenylsilylvinyl)phenylenes (Type 2)

product	reaction conditions	physical state	isomers and % ratio
4a (Pt)	reflux	orange oil	bis-α; β-(E)-α; bis-β-(E) 5; 29; 66
4a (Rh)	room temp	orange oil	bis-β-(Z); β-(Z)-β-(E); bis-β-(E) 48; 29; 23
4b (Pt)	reflux	orange solid	bis-α; β-(E)-α 76; 24
4c (Pt)	room temp	orange oil	bis-α; β-(E)-α; bis-β-(E) 9; 27; 64
4c (Rh)	room temp	orange oil	bis-β-(Z); β-(Z)-β-(E) 85; 15
4d	reflux	orange solid	bis-α; β-(E)-α 75; 25
4e	room temp	orange solid	bis-β-(E) 100
4f	room temp	orange solid	bis-β-(E) 100

The ^{29}Si DEPT NMR spectrum was most informative, with the bis-β-(E) isomer showing a signal at δ −9.4, and the β-(E), α- at δ −9.6 {Si β-(E)} and −7.5 (Si α-). The difference in the regiochemical distribution in products **3a (Pt)** and **4a (Pt)** may be attributed to the different silanes employed for their syntheses and their effect on the silyl migration mechanisms discussed by Kim and co-workers.[11b]

The reaction of **2** with 1,4- and 1,3-bis(trimethylsilylethynyl)benzene gave **4b (Pt)** and **4d (Pt)**, which were isolated as mixtures of two isomers (Scheme 2, Table 3). The major isomer (∼75%) for both results from *syn* attack of Si at the phenyl-substituted carbon (α-). The minor isomer (∼25%) was mixed, with one-half of the molecule identical to the major isomer, with the other half resulting from the attack of silicon on the trimethylsilyl-substituted carbon {β-(E)} {cf. **3b (Pt)**}.

Crystals of the major isomer of **4b (Pt)**, grown from *n*-hexane at room temperature, were used in an X-ray diffraction study, which confirmed its structure. An ORTEP drawing of **4b (Pt)**-(major) is shown in Figure 3.

Reaction of diethynyl(dimethyl)silane and 2 equiv of **2** gave **4e** (Scheme 2), which was exclusively β-(E). This was identical to the results obtained in the formation of **3c (Pt)** and results from exclusive attack of Si at the terminal carbon due to the bulky SiMe$_2$ bound to the internal carbons.[13,14]

Adduct **4f (Pt)** was prepared via the reaction of 2 equiv of **2** with 1 equiv of 1,4-diphenylbutadiyne (Scheme 2). *Syn* addition of the silane across the triple bonds again led to a bis-β-(E) isomer. Interestingly, restricted rotation at Si leads to two singlets for the diastereotropic methyl groups at δ 0.30, 0.42 and four multiplets for the Cp protons. Traces of an enyne product from the addition of 1 equiv of **2** to the diyne were also observed.

Complexes with Three Ferrocene Units. Type 1 complexes containing three ferrocene groups were prepared from **1** and either trimethylsilylethynylferrocene (**5**) or ethynylferrocene (**6**). Thus, 2 equiv of **5** and 1 equiv of **1** were treated with Karstedt's catalyst to afford a mixture of species **7** as an orange solid in 69% yield (Scheme 3). Surprisingly, the major product **7a** does not contain the SiMe$_3$ group originally present in **5**, as
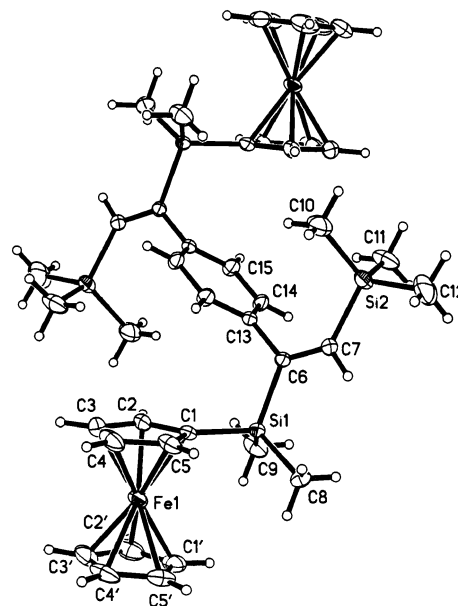
Figure 3. Molecular structure of **4b (Pt)**-major, showing the atom-numbering scheme and using 20% probability thermal ellipsoids.

confirmed by the presence of two geminal (α-) proton NMR signals at δ 5.57 and 6.13 ($^2J_{H-H}$ = 3.0 Hz) (Figure 4, Table 4). Two minor products, **7b** with one SiMe$_3$ group and **7c** with two SiMe$_3$ groups, were also observed in the ^1H NMR spectrum of **7**. The regiochemical distribution of **7a−c** was exclusively α-, possibly due to steric effects, noting that formation **4b (Pt)** from the bulky 1,4-bis(trimethylsilylethynyl)benzene gave more than 75% of the bis-α adducts.

Treatment of 2 equiv of ethynylferrocene (**6**) and **1** with Karstedt's catalyst again gave a mixture; in this case both α- and β-(E) regiochemistry was observed and three isomers, **7a**, **7d**, and **7e**, were formed with the major product being **7a**. The two minor species were the β-(E), α-isomer **7d** and a bis-β-(E) isomer **7e** (Scheme 3). Since **5** exclusively gave an α-adduct, it can be inferred that the bulky trimethylsilyl group prevents the silane from attacking C$_7$. In contrast, **6**, which has no bulky group, allows some attack at C$_7$ and hence β-adducts. The desilylation observed most likely occurs during the hydrosilylation step since the observation of only α-isomers suggests the SiMe$_3$ plays some steric role in the hydrosilylation process. Although desilylation using Karstedt's catalyst is rare, Astruc and co-workers have reported desilylation of [FeCp(η^6-C$_6$Me$_5$CH$_2$-SiMe$_2$H)][PF$_6$] using Karstedt's catalyst.[15] However, in our reactions, if **5** is refluxed in THF with Karstedt's catalyst, no desilylation products are observed, further suggesting desilylation occurs either after or during the hydrosilylation of the alkyne.

A type 2 complex containing three ferrocene groups was prepared from a bis(alkynyl)ferrocene and 2 equiv of **2**. Thus, hydrosilylation of **2** with 1,1′-bis(methylethynyl)ferrocene (**8**) using Karstedt's catalyst gave **9** as an orange solid in 74% yield with 80% α-regiochemistry (Scheme 4).

Rh(PPh$_3$)$_3$I-Catalyzed Hydrosilylations. 1,1′-Bis-{dimethyl(vinyl)silyl}ferrocenes, 3a (Rh) and 3c

(14) Kuhnen, T.; Ruffolo, R.; Stradiotto, M.; Ulbrich, D.; McGlinchey, M. J.; Brook, M. A. *Organometallics* **1997**, *16*, 5042.

(15) Ruiz, J.; Alonso, E.; Blais, J.; Astruc, D. *J. Organomet. Chem.* **1999**, *582*, 139.
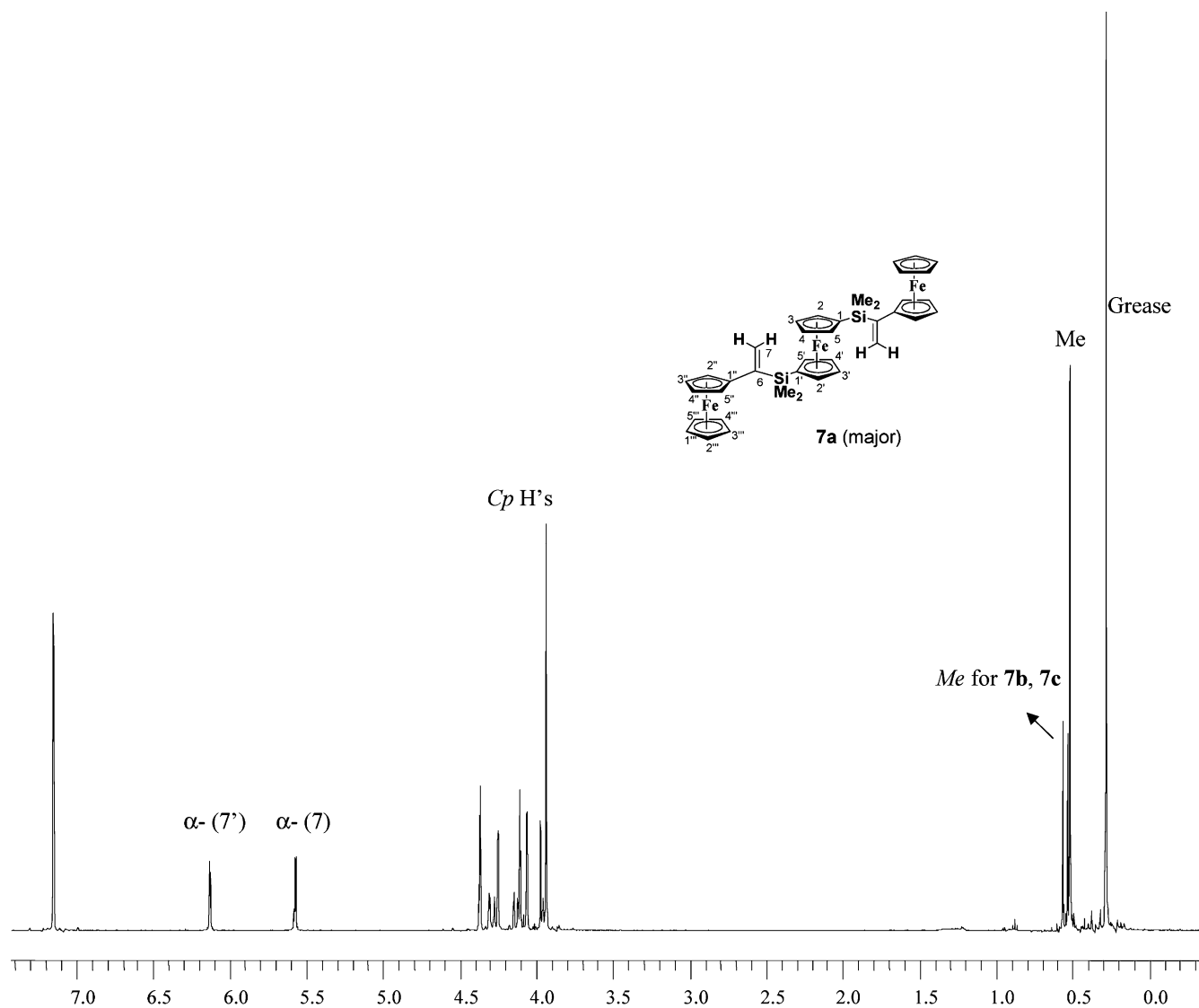
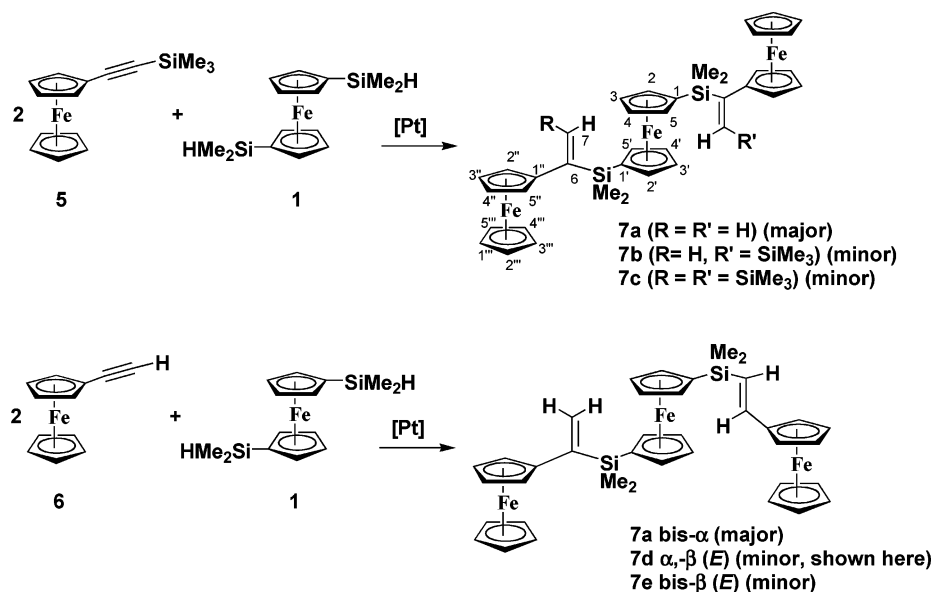**Figure 4.** ¹H NMR spectrum of **7a–c**.

Scheme 3

(Rh). Iodotris(triphenylphosphine)rhodium(I)-catalyzed hydrosilylation of 2 equiv of phenylacetylene with 1 equiv of **1** gave **3a (Rh)** but with a different regiochemi-

cal distribution (Scheme 1). In this case, a mixture of four isomers was obtained. In decreasing order of abundance, they were bis-*β*-(*Z*), *β*-(*Z*),*β*-(*E*), and bis-*β*-

Table 4. NMR Spectral Data for 7a,b,e and 9[a]

product	δ (^{1}H)[b]	δ ^{13}C{^{1}H}[b]
7a	0.52 (s, 12H, *Me*), 3.94 (s, 10H, *Cp*), 4.06 (t, 4H, H$_{2,2',5,5'}$), 4.11 (t, 4H, H$_{3,3',4,4'}$), 4.25 (t, 4H, H$_{2'',2''',5'',5'''}$), 4.37 (t, 4H, H$_{3'',3''',4'',4'''}$), 5.57 (d, 2H, H$_7$, $^2J_{H-H}$ = 3.0 Hz), 6.13 (d, 2H, H$_{7'}$, $^2J_{H-H}$ = 3.0 Hz)	−0.9 (*Me*), 68.5−74.1(*Cp*), 143.7 (C$_6$, α-), 148.0 (C$_7$, α-)
7d	0.42, 0.55 (s, 12H, *Me*), 4.01−4.39 (Cp) 5.58, 6.13 (d, 2H, H$_{7, 7'}$, $^2J_{H-H}$ =3.0 Hz, α-), 6.30, 6.87 (d, 2H, $^3J_{H-H}$ = 18.5 Hz, β-(*E*))	−1.1, 0.9 (*Me*), 68.5−74.1(*Cp*), 124.2, 125.2 (β−(*E*)), 143.7 (C$_6$, α-), 148.0 (C$_7$, α-)
7e	0.44 (s, 12H, *Me*), 0.55 (s, 12H, *Me*) 4.01−4.39 (Cp) 6.32, 6.88 (d, 2H, $^3J_{H-H}$ = 18.5 Hz, β-(*E*))	−1.1 (*Me*), 68.5−74.1(*Cp*), 124.2, 125.2 (β-(*E*))
9	0.45, 0.52 (s, 12H, *Me*), 1.98 (d, 6H, *Me*, J_{H-H} = 6.8 Hz), 4.02 (s, 10H, *Cp*), 4.06 (t, 4H, H$_{2,2',5,5'}$), 4.10 (t, 4H, H$_{3,3',4,4'}$), 4.21 (t, 4H, H$_{2'',2''',5'',5'''}$), 4.33 (t, 4H,H$_{3'',3''',4'',4'''}$), 6.18 (q, 2H, H$_{7,7'}$, $^3J_{H-H}$ = 6.8 Hz)	−0.3, 17.8 (*Me*), 74.1(*Cp*), 135.0 (C$_7$), 138.2 (C$_6$)

[a] See Schemes 3 and 4 for labeling. [b] In C$_6$D$_6$.

Scheme 4
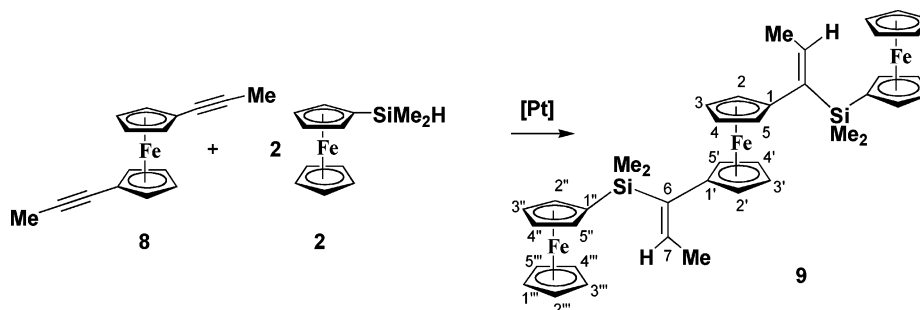
(*E*) with the fourth being a trace of the bis-(α-) adduct. Traces of α-isomers have been recorded previously using phosphine complexes of Rh.[9,13,16] Product **3a (Rh)** was fully characterized using GC-MS and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Table 2), with the overall β-(*Z*)/β-(*E*) ratio calculated to be 0.79/0.21 (^{1}H NMR). In the ^{1}H NMR spectrum sets of doublets centered at δ 6.09, 7.42, and 6.08, 7.41 were assigned to the β-(*Z*) protons of the bis-β-(*Z*) isomer and the β-(*Z*),β-(*E*) mixed adduct, respectively. The coupling between these β-(*Z*) protons was 15 Hz.[17] The ^{29}Si DEPT NMR spectrum (Figure 5) had signals at δ −13.2 for the β-(*Z*) Si, *cis* to the phenyl group, and δ −9.3 (β-(*E*)) as well as a very small peak at δ −7.4 for the α-isomer.
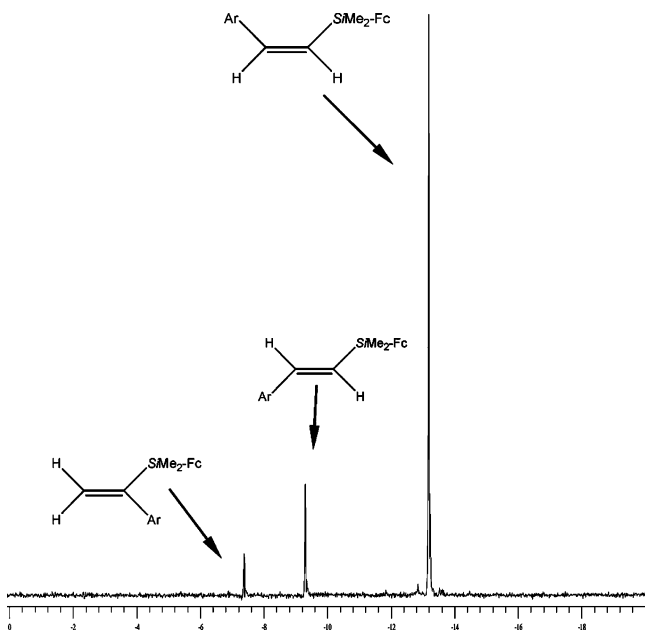

Figure 5. ^{29}Si DEPT NMR spectrum of **3a (Rh)**.

The attempted synthesis of **3c (Rh)** was very slow, and after 14 days, a mixture of the starting materials, a single hydrosilylation adduct **10** (M$^+$ = 400), and **3c (Rh)** (M$^+$ = 498) were detected using GC-MS. Repeated column chromatography failed to separate these species, but the ^{1}H NMR spectrum of the mixture showed the regiochemistry of **3c (Rh)** was the same as in **3c (Pt)**.

Bis(ferrocenylsilylvinyl)phenylenes 4a (Rh) and 4c (Rh). Addition of 1 equiv of 1,4- or 1,3-diethynylbenzene to 2 equiv of **2** resulted in the formation of complexes **4a (Rh)** and **4c (Rh)**, respectively. Complexes **4a (Rh)** and **4c (Rh)** were characterized using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and are similar to **4a (Pt)** and **4c (Pt)**, respectively, except for the regioisomerism. The isomer ratios are shown in Table 3 and are mainly β-(*Z*). Similar distributions were obtained by Mori and co-workers in the hydrosilylation of alkynes with silanes also using Rh(PPh$_3$)$_3$I as a catalyst.[17,18] Attempts to prepare complexes with three ferrocene units using [Rh(PPh$_3$)$_3$I] as a catalyst from, for example **1** and **6**, failed with no hydrosilylation observed.

Electrochemical Studies

Cyclic voltammetry was used to investigate possible electronic interactions between the Fe centers in complexes **4e (Pt)**, **4a (Rh)**, and **7** and were compared to the monoferrocene species **3a (Pt)** and **3b (Pt)**. For all

(16) (a) Watanabe, H.; Kitahara, T.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* **1977**, *139*, 215. (b) Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299.

(17) (a) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Macromolecules* **2000**, *33*, 1115. (b) Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443. (c) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Polyhedron* **2000**, *19*, 567.

(18) Mori, A.; Takahisa, E.; Yamamura, Y.; Kato, T.; Mudalige, A. P.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Organometallics* **2004**, *23*, 1755.

Table 5. Cyclic Voltammetry Data[a]

complex	E_{pc} (V)	E_{pa} (V)	$E°$ (V)
3a (Pt)	0.12	0.26	0.19
3b (Pt)	0.12	0.29	0.21
4e	0.09	0.21	0.15
4a (Rh)	0.09	0.20	0.15
7	0.18, −0.02	0.36, 0.26	0.27, 0.14
ferrocene	0.06	0.21	0.14

[a] Measured on a gold electrode at 25 °C, in a THF solution containing 1 mM complex and 0.1 M [(n-Bu)$_4$N]PF$_6$. Sweep rate = 0.050 V s^{-1}.
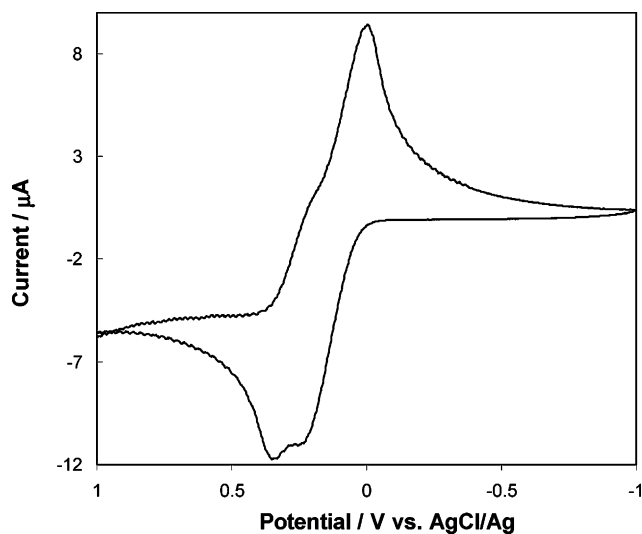
Figure 6. Cyclic voltammogram of **7**; 1.0 mM THF/0.1 M [Bu$_4$N][PF$_6$] at 0.2 V/s on a gold electrode at 25 °C.

samples except **7**, a single reversible redox wave was observed for the Fe(II)−Fe(III) redox couple (Table 5). These studies indicated no interaction between the Fe−Fe centers in **4e** and **4a (Rh)**, although a smaller reduction potential for the bis(ferrocene) complexes when compared to complexes **3a (Pt)** and **3b (Pt)** does suggest some electron delocalization between the ferrocene and the spacer group. The observation of no interactions could be due to ineffective redox-matching between the spacer groups and the ferrocene units, as suggested by Swager and co-workers for other systems,[19] or the spacer group may be too long and permits only very weak and unresolvable electronic interaction between Fe−Fe centers.[3h]

The redox behavior of **7** was more interesting and showed two reversible oxidations at 0.14 and 0.27 V (Figure 6). In other triiron systems, three oxidation waves have been observed, the first two corresponding to a terminal−terminal dication being barely resolved, while the third wave was separated from the first two by 0.31 V and corresponds to oxidation of the internal ferrocene unit.[20−22] Thus, for **7**, the first wave corresponds to oxidation of the two terminal ferrocenes with the second at higher potential resulting from oxidation of the central ferrocene unit.

(19) Zhu, S. S.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1996**, *118*, 8713.

(20) Pannell, K.; Dementiev, V.; Li, H.; Cervantes-Lee, F.; Nguyen, M.; Diaz, A. *Organometallics* **1994**, *13*, 3644.

(21) Azkern, H.; Hiermeier, J.; Kohler, F. H.; Steck, A. *J. Organomet. Chem.* **1991**, *408*, 281.

(22) Rulkens, R.; Lough, A.; Manners, I.; *J. Am. Chem. Soc.* **1994**, *116*, 797.

Conclusions

The synthesis and characterization of 1,1′-bis{dimethyl-(vinyl)silyl}ferrocene and bis(ferrocenylsilylvinyl)phenylenes was performed via hydrosilylation of various alkynes using Karstedt's catalyst and Rh(PPh$_3$)$_3$I. Comparative studies of regiochemical distributions showed the Pt systems to favor β-(E) and α-addition in contrast to those of Rh (primarily β-(Z) and β-(E)). The above compounds serve as good model compounds for the characterization of poly{ferrocenephenylenebis(silylene-vinylene)}s.[6] Cyclic voltammetry showed no distinct Fe−Fe interaction in the bis(ferrocenyl) complexes; however the triiron species **7** did show communication between adjacent metal centers, as evidenced by the presence of two distinct waves.

Experimental Section

With the exception of trimethylsilylethynylferrocene,[23] ethynylferrocene,[23] and 1,1′-bis(methylethynyl)ferrocene,[23] all materials and equipment used were as previously described.[6]

Preparation of 1,1′-Bis(dimethylsilyl)ferrocene (1).[3g] A hexane slurry (80 mL) of dilithioferrocene·2TMEDA[7] (3.335 g, 7.75 mmol) was added dropwise to a solution of chlorodimethylsilane (4.403 g, 46.5 mmol) in hexane (40 mL) at 0 °C over a period of 1 h. The mixture was warmed to room temperature and stirred for a further 2 h. Removal of solvent and excess silane in vacuo gave an orange oily residue (*care: the product is volatile*). Extraction was performed with hexane (3 × 30 mL). Filtration through Celite , removal of hexane in vacuo, and chromatography on a silica gel column (70−100 μm, dimensions 30 cm × 7 cm) loading neat and eluting with hexane gave one broad orange band. This band was collected in four fractions (approximately 20−25 mL each). The first two fractions contained product **1** with subsequent fractions containing **1**, unreacted ferrocene, and ferrocenyldimethylsilane. The latter fractions were concentrated and chromatographed as above to give additional **1**. Evaporation to dryness gave **1** as a red oil (yield 1.775 g, 76%). m/z = 302 (M$^+$). Anal. Calcd for C$_{14}$H$_{22}$Si$_2$Fe: C, 55.62; H, 7.33. Found: C, 55.56; H, 7.29.

Preparation of Ferrocenyldimethylsilane (2). Dropwise addition of 12.65 mL (21.50 mmol) of 1.7 M t-BuLi to a mixture of ferrocene (2.0 g, 10.75 mmol) and potassium *tert*-butoxide (0.15 g, 1.34 mmol) in dry THF (100 mL) at −78 °C over a period of 15 min, ensuring that the temperature does not rise above −70 °C, gave an red-orange slurry.[8] The mixture was stirred at this temperature for 1 h, after which chlorodimethylsilane (1.85 g, 19.56 mmol) was added. The solution was warmed to −40 °C over a period of 1 h, and solvent and excess silane were evaporated in vacuo to give an orange oily residue (*care: product is volatile*). Extraction with hexane (3 × 20 mL), filtration through Celite, removal of hexane in vacuo, and chromatography on a silica gel column (70−100 μm, dimensions 7 cm × 30 cm) loading neat and eluting with hexane gave one broad orange band. This band was collected in four fractions (approximately 15−20 mL each). The first two fractions contained product **2**, with subsequent fractions containing **2** and unreacted ferrocene. The latter fractions were chromatographed to give additional **2**. Evaporation to dryness gave **2** as an orange oil (yield 0.419 g, 20%). m/z = 244 (M$^+$).

General Synthesis of 3a−c (Pt) and 3a (Rh). The syntheses of **3a−c (Pt)** and **3a (Rh)** are illustrated (vide infra) by the synthesis of **3a (Pt)** from the reaction of 2 equiv of the appropriate alkyne and 1 equiv of **1**. For platinum-catalyzed

(23) Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1992**, *425*, 113.

systems the reaction time was 2 days at room temperature, whereas for rhodium-catalyzed reactions it was 4 days using 1 mg of catalyst. Compounds were purified by column chromatography on silica gel with *n*-hexane as eluent unless stated otherwise.

Preparation of 3a (Pt). Karstedt's catalyst (1 drop of a 3–3.5% solution) was added to a solution of phenylacetylene (0.147 g, 1.44 mmol) and **1** (0.217 g, 0.72 mmol) in THF (5 mL) along with a trace of air. The mixture was stirred at room temperature for 2 days and dried in vacuo. Purification using column chromatography on alumina, eluting with *n*-hexane, gave **3a (Pt)** as an orange liquid (yield 0.222 g, 61%). $m/z = $ 506 (M$^+$). Anal. Calcd for $C_{30}H_{34}Si_2Fe$: C, 71.12; H, 6.77. Found: C, 70.95; H, 6.65.

For 3a (Rh): orange liquid; yield 48%; $m/z = $ 506 (M$^+$).

For 3b (Pt): orange powder; yield 98%; $m/z = $ 650 (M$^+$). Anal. Calcd for $C_{36}H_{50}Si_4Fe$: C, 66.42; H, 7.74. Found: C, 66.32; H, 7.65.

For 3c (Pt): orange powder; yield 45%; $m/z = $ 498 (M$^+$). Anal. Calcd for $C_{24}H_{42}Si_4Fe$: C, 57.80; H, 8.49. Found: C, 57.72; H, 8.26.

General Synthesis of 4a−f (Pt), 4a (Rh), and 4c (Rh). The general synthesis of **4a−f (Pt)**, **4a (Rh)**, and **4c (Rh)** is illustrated (vide infra) by the synthesis of **4a (Pt)** from the reaction of 1 equiv of the appropriate dialkyne and 2 equiv of **2**. For rhodium-catalyzed systems 1 mg of catalyst was used and the reaction times and temperatures were variable in each case and are listed below. Compounds were purified by column chromatography on silica gel with *n*-hexane as eluent followed by a 0.10:0.90 mixture of CH_2Cl_2/n-hexane. For **4e** and **4f** this ratio was 0.05:0.95.

Preparation of 4a (Pt). Karstedt's catalyst (1 drop) was added to a solution of 1,4-diethynylbenzene (0.008 g, 0.063 mmol) and **2** (0.031 g, 0.127 mmol) in THF (2 mL) along with a trace of air. The mixture was refluxed for 2 days and then dried in vacuo. Purification using column chromatography (2 × 18 cm) on silica gel, eluting with *n*-hexane followed by a 1:9 mixture of CH_2Cl_2/n-hexane, gave **4a (Pt)** as an orange oil (yield 0.026 g, 67%). Anal. Calcd for $C_{34}H_{38}Si_2Fe_2$: C, 66.45; H, 6.23. Found: C, 66.52; H, 6.25.

For 4a (Rh): room temperature, 5 days; orange oil; yield 63%.

For 4b (Pt): reflux, 2 days; orange-yellow solid; yield 66%. Anal. Calcd for $C_{40}H_{54}Si_4Fe_2$: C, 63.31; H, 7.17. Found: C, 63.34; H, 6.85.

For 4c (Pt): room temperature, 3 days; orange oil; yield 64%.

For 4c (Rh): room temperature, 4 days; orange oil; yield 50%. Anal. Calcd for $C_{34}H_{38}Si_2Fe_2$: C, 66.45; H, 6.23. Found: C, 66.57; H, 5.91.

For 4d: reflux, 2 days; orange-yellow solid; yield 74%. Anal. Calcd for $C_{40}H_{54}Si_4Fe_2$: C, 63.31; H, 7.17. Found: C, 63.42; H, 6.91.

For 4e: room temperature, 3 days; orange solid; yield 58%. Anal. Calcd for $C_{30}H_{40}Si_3Fe_2$: C, 60.40; H, 6.76. Found: C, 60.27; H, 6.48.

For 4f: room temperature, 4 days; orange-yellow solid; yield 39%.

Preparation of 7a−c from Trimethylsilylethynylferrocene (5). Karstedt's catalyst (1 drop of 3–3.5% Pt concentration in vinyl-terminated poly(dimethylsiloxane)) was added to a solution of **5** (0.184 g, 0.647 mmol) and **1** (0.93 g, 0.308 mmol) in THF (2 mL) with a trace of air. The reaction mixture was refluxed for 1 day and then dried in vacuo. Purification of the residue on a silica gel column, eluting with a 1:1 mixture of CH_2Cl_2/hexane, gave a mixture of **7a−c** as an orange solid. Yield: 0.153 g, 69%.

Preparation of 7a,d,e from Ethynylferrocene (6). Karstedt's catalyst (1 drop of 3–3.5% Pt concentration in vinyl-terminated poly(dimethylsiloxane)) was added to a solution of **6** (0.88 g, 0.418 mmol) and **1** (0.60 g, 0.199 mmol) in THF (2 mL) with a trace of air. The reaction mixture was refluxed for 3 h and dried in vacuo. Purification of the residue on a silica gel column, eluting with a 1:1 mixture of CH_2Cl_2/hexane, gave a mixture of **7a,d,e** as an orange solid. Yield: 0.104 g, 72%.

Preparation of 9 from 1,1′-Bis(methylethynyl)ferrocene (8). Karstedt's catalyst (1 drop of 3–3.5% Pt concentration in vinyl-terminated poly(dimethylsiloxane)) was added to a solution of **8** (0.163 g, 0.623 mmol) and **2** (0.310 g, 1.27 mmol) in THF (2 mL) with a trace of air. The reaction mixture was refluxed for 1 day and dried in vacuo. Purification of the residue on a silica gel column, eluting with a 1:4 mixture of CH_2Cl_2/n-hexane, gave **9** as a red oil. Yield: 0.347 g, 74%.

X-ray Crystal Structures. Crystals of **3b (Pt)**-major and **4b (Pt)**-major were mounted on a glass fiber using cyanoacrylate cement. Intensity data for both compounds were collected on a Siemens P4 diffractometer at 296 K, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The θ−2θ scan technique was applied with variable scan speeds. For each structure, the intensities of three standard reflections were measured every 97 reflections and corrections were applied. The data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied to each data set. The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods to minimize $\sum w(F_o - F_c)^2$, where w^{-1} $= \sigma^2(F) + g(F)^2$. Hydrogen atoms were included in calculated positions (C−H from 0.93 to 0.98 Å depending on type of bonding). Crystal data, data collection, and least-squares parameters are listed in the Supporting Information. All calculations were performed and graphics created using SHELXTL-97.

Supporting Information Available: Tables of X-ray crystallographic data for **3b (Pt)** and **4b (Pt)** and representative NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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