Organometallics **2004,** *23,* 6225−6230

Diels−Alder Reactions of Benzyne with Indenyl Iron Complexes

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Received July 25, 2004

The indenyl iron compound (η^5-C_9H_7)Fe(η^5-C_5H_5) (**1**) was found to react with benzyne, generated from *o*-trimethylsilylphenyl triflate by fluoride-induced 1,2-elimination, to afford the Diels−Alder adduct 1,2-(1,4-dihydro-naphthalen-1,4-diyl) ferrocene (**2**). When the bis(indenyl) iron complexes (η^5-R-C_9H_6)$_2$Fe [R = H (**3**); 2-Me (**6**); 1-$SiMe_3$ (**9**)] reacted with benzyne, the bisadducts [R = H (**5**); 2-Me (**8**); 1-$SiMe_3$ (**11**)] were obtained along with the corresponding monoadducts [R = H (**4**); 2-Me (**7**); 1-$SiMe_3$ (**10**)]. The reaction of tetramethyldisilylene-bridged bis(indenyl) iron ($Me_2SiSiMe_2$)(η^5-C_9H_6)$_2$Fe (**12**) with benzyne gave only the monoadduct (**13**). Complex **2** was also tested for ring-opening metathesis polymerization (ROMP) in the presence of Grubbs' catalyst [$(PCy_3)_2RuCl_2$=CHPh] but was found to be inactive under normal conditions. The molecular structures of **2**, **5**, **8**, and **13** have been determined by X-ray diffraction.

Introduction

Since the discovery of ferrocene over 50 years ago, considerable attention has been focused on the synthesis and chemical behavior of its derivatives, largely due to its high stability and numerous applications within catalysis[1] and material science.[2] Compared to their cyclopentadienyl analogues, indenyl metal complexes display greater reactivities both in catalysis[3] and in reactions such as ligand substitution[4] and insertion[5] due to the well-known "indenyl effect".[3a,6] The six-membered ring of η^5-indenyl metal complexes exhibits typical butadiene-like characteristics,[7] which could explain the relative ease of hydrogenation of these complexes.[8] For example, PtO_2-catalyzed hydrogenation of *racemic ansa*-zirconocenes, the famous isotactic propylene polymerization catalysts, results in the more stable tetrahydroindenyl complexes with higher isospecificity.[9] Considering that butadiene can readily undergo the Diels−Alder reaction with dienophiles, one may anticipate that similar reactions at the butadiene-like six-membered ring of η^5-indenyl metal complexes also could be possible.

The Diels−Alder reaction is an important reaction of benzyne, and it is used both as a means of detecting benzyne and as a synthetic tool.[10] Benzyne is so extraordinarily reactive that it can even destroy the aromaticity of a benzene ring by cycloaddition.[11] Thus benzyne should be a proper candidate as the dienophile to react with the six-membered ring of η^5-indenyl metal complexes. Among the many procedures available for the generation of benzyne,[10b] the fluoride-induced 1,2-elimination of Me_3Si and TfO groups from *o*-trimethylsilylphenyl triflate was chosen in our study because of its mild reaction conditions and absence of strong bases or oxidants.[12] Herein we report the reactions between benzyne and η^5-coordinated indenyl iron complexes and

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10.1021/om049430e CCC: $27.50
Publication on Web 11/23/2004

the attempted ROMP of complex **2** in the presence of Grubbs' catalyst. Although there are some previous examples of reactions of benzyne with organotransition metal complexes,[13,14] this is, to the best of our knowledge, the first example of a Diels–Alder reaction occurring at the six-membered ring of η^5-indenyl metal complexes.

Experimental Section

General Procedures. Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon prior to use. ^{1}H NMR spectra were recorded on a Bruker AV300. ESI mass spectra were obtained using a Thermo Finnigan LCQ Advantage. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. *o*-Trimethylsilylphenyl triflate,[12] (η^5-C_9H_7)$_2$Fe,[8b] (η^5-C_9H_7)Fe(η^5-C_5H_5),[15] (η^5-1-SiMe$_3$-C_9H_6)$_2$Fe,[16] $C_9H_7Me_2SiSiMe_2$-C_9H_7,[17] 2-methylindene,[18] FeCl$_2$·1.5THF,[19] and (PCy$_3$)$_2$RuCl$_2$=CHPh[20] were prepared according to literature methods.

Preparation of (η^5-2-MeC$_9$H$_6$)$_2$Fe (6). To a solution of 2-methylindene (7.65 g, 58.7 mmol) in THF (100 mL) was added n-BuLi (29.4 mL, 2.0 M, 58.7 mmol) in hexane at 0 °C. After the reaction mixture had been stirred at room temperature for 8 h, FeCl$_2$·1.5THF (6.8 g, 29.4 mmol) was added and the reaction mixture was stirred for another 24 h. The solvent was removed under reduced pressure, and the residue was chromatographed on alumina using petroleum ether as eluent to afford 4.41 g (52%) of **6** as black microcrystals: mp 73–74 °C. Anal. Calcd for $C_{20}H_{18}Fe$: C, 76.45; H, 5.77. Found: C, 76.15; H, 6.23. ^{1}H NMR (CDCl$_3$) δ: 7.00 (m, 4H, C_9H_6), 6.86 (m, 4H, C_9H_6), 4.31 (s, 4H, C_9H_6), 1.87 (s, 6H, CH$_3$). MS (ESI): *m/z* 314.49 (M$^+$).

Preparation of (Me$_2$SiSiMe$_2$)(η^5-C$_9$H$_6$)$_2$Fe (12). To a solution of $C_9H_7Me_2SiSiMe_2C_9H_7$ (5.67 g, 16.4 mmol) in THF (100 mL) was added n-BuLi (16.4 mL, 2.0 M, 32.8 mmol) hexane solution at 0 °C. After the reaction mixture had been stirred at room temperature for 8 h, FeCl$_2$·1.5THF (3.8 g, 16.4 mmol) was added, and the reaction mixture was stirred for another 24 h. The solvent was removed under reduced pressure, and the residue was chromatographed on alumina using petroleum ether as eluent to afford 2.06 g (31%) of the *meso* isomer of **12** as dark green microcrystals: mp 153 °C (dec). Anal. Calcd for $C_{22}H_{24}FeSi_2$: C, 65.99; H, 6.04. Found: C, 65.87; H, 5.99. ^{1}H NMR (CDCl$_3$) δ: 6.88 (m, 4H, C_9H_6), 6.76 (m, 2H, C_9H_6), 6.46 (m, 2H, C_9H_6), 4.92 (d, J = 3.00 Hz, 2H, C_9H_6), 4.48 (d, J = 3.00 Hz, 2H, C_9H_6), 0.70 (s, 6H, SiMe), 0.58 (s, 6H, SiMe). MS (ESI): *m/z* 400.22 (M$^+$).

Reaction of Benzyne with (η^5-C$_9$H$_7$)Fe(η^5-C$_5$H$_5$) (1). A solution of 0.47 g (2 mmol) of **1** and 0.61 g (4 mmol) of CsF in 20 mL of CH$_3$CN was heated to 40 °C in an oil bath. After addition of 0.60 g (2 mmol) of *o*-trimethylsilylphenyl triflate, the mixture was stirred overnight at 40 °C. The solvent was removed under reduced pressure, and the residue was chromatographed on alumina using petroleum ether/dichloromethane as eluent to afford 0.15 g (23%) of **2** as orange-red crystals: mp 152–153 °C. Anal. Calcd for $C_{20}H_{16}Fe$: C, 76.95; H, 5.17. Found: C, 76.96; H, 5.26. ^{1}H NMR (CDCl$_3$) δ: 7.08 (m, 2H, C_6H_4), 6.98 (m, 2H, C_2H_2), 6.82 (m, 2H, C_6H_4), 4.53 (m, 2H, C_5H_3), 4.08 (s, 5H, C_5H_5), 4.02 (d, J = 2.10 Hz, 2H, CH), 3.75 (t, J = 2.10 Hz, 1H, C_5H_3). MS (ESI): *m/z* 312.2 (M$^+$).

Reaction of Benzyne with (η^5-C$_9$H$_7$)$_2$Fe (3). Similar to that described for the reaction of benzyne with **1**, reaction of 1.14 g (4 mmol) of **3** with 2.40 g (8 mmol) of *o*-trimethylsilylphenyl triflate and 2.44 g (16 mmol) of CsF gave 0.35 g of unreacted (η^5-C_9H_7)$_2$Fe (**3**), a trace of the monoadduct **4** as a red oil, which was characterized by ESI-MS (*m/z* 362.15(M$^+$)), and 0.33 g (27% based on the reacted **3**) of the bisadduct **5** as orange crystals (mp 228 °C (dec)). Anal. Calcd for $C_{30}H_{22}Fe$: C, 82.20; H, 5.06. Found: C, 82.12; H, 5.07. ^{1}H NMR (CDCl$_3$) δ: 7.07 (m, 4H, C_6H_4), 7.02 (m, 4H, C_2H_2), 6.82 (m, 4H, C_6H_4), 4.50 (m, 4H, C_5H_3), 3.89 (d, J = 2.20 Hz, 4H, CH), 3.73 (t, J = 2.20 Hz, 2H, C_5H_3). MS (ESI): *m/z* 438.27 (M$^+$).

Reaction of Benzyne with (η^5-2-Me-C$_9$H$_6$)$_2$Fe (6). Similar to that described for the reaction of benzyne with **1**, reaction of 0.94 g (3 mmol) of **6** with 1.85 g (6 mmol) of *o*-trimethylsilylphenyl triflate and 1.82 g (12 mmol) of CsF gave 0.15 g of unreacted **6**, 0.12 g (12% based on the reacted **6**) of the monoadduct **7** as purple crystals, and 0.15 g (13% based on the reacted **6**) of the bisadduct **8** as orange-red crystals. **7**: mp 81–82 °C. Anal. Calcd for $C_{26}H_{22}Fe$: C, 80.01; H, 5.68. Found: C, 79.93; H, 5.69. ^{1}H NMR (CDCl$_3$) δ: 7.48 (m, 2H, C_9H_6), 7.25 (m, 2H, C_9H_6), 6.97 (m, 2H, C_6H_4), 6.89 (m, 2H, C_2H_2), 6.76 (m, 2H, C_6H_4), 4.51 (m, 2H, CH), 4.35 (s, 2H, C_9H_6), 2.99 (s, 2H, C_5H_2), 2.05 (s, 3H, CH$_3$), 1.96 (s, 3H, CH$_3$). MS (ESI): *m/z* 390.20 (M$^+$). **8**: mp 240 °C (dec). Anal. Calcd for $C_{32}H_{26}Fe$: C, 82.41; H, 5.62. Found: C, 82.29; H, 5.71. ^{1}H NMR (CDCl$_3$) δ: 7.11 (m, 4H, C_6H_4), 6.88 (m, 4H, C_2H_2), 6.80 (m, 4H, C_6H_4), 4.51 (s, 4H, C_5H_2), 3.69 (s, 4H, CH), 1.50 (s, 6H, CH$_3$). MS (ESI): *m/z* 466.27 (M$^+$).

Reaction of Benzyne with (η^5-1-SiMe$_3$-C$_9$H$_6$)$_2$Fe (9). Similar to that described for the reaction of benzyne with **1**, reaction of 0.87 g (2 mmol) of **9** with 1.19 g (4 mmol) of *o*-trimethylsilylphenyl triflate and 1.22 g (8 mmol) of CsF gave 0.31 g of unreacted **9**, 0.19 g (30% based on the reacted **9**) of the monoadduct **10** as a red solid, and 0.10 g (14% based on the reacted **9**) of the bisadduct **11** as a yellow powder. **10**: mp 99–100 °C. Anal. Calcd for $C_{30}H_{34}FeSi_2$: C, 71.12; H, 6.76. Found: C, 71.16; H, 6.75. ^{1}H NMR (CDCl$_3$) δ: 7.53 (m, 2H, C_9H_6), 6.93 (m, 2H, C_9H_6), 6.89 (m, 2H, C_6H_4), 6.71 (m, 2H, C_2H_2), 6.58 (m, 2H, C_6H_4), 5.00 (d, J = 4.50 Hz, 1H, C_9H_6), 4.39 (d, J = 4.50 Hz, 1H, C_9H_6), 4.19 (d, J = 4.60 Hz, 1H, C_5H_2), 3.88 (s, 1H, CH), 3.94 (s, 1H, CH), 3.61 (s, 1H, C_5H_2), 0.48 (s, 9H, SiMe$_3$), 0.37 (s, 9H, SiMe$_3$). MS (ESI): *m/z* 506.10 (M$^+$). **11**: mp 206–207 °C. Anal. Calcd for $C_{36}H_{38}FeSi_2$: C, 74.20; H, 6.57. Found: C, 74.14; H, 6.64. ^{1}H NMR (CDCl$_3$) δ: 7.10 (m, 4H, C_6H_4), 7.06 (m, 4H, C_2H_2), 6.87 (m, 4H, C_6H_4), 4.59 (d, J = 3.00 Hz, 2H, C_5H_2), 4.50 (d, J = 3.00 Hz, 2H, C_5H_2), 4.06 (m, 4H, CH), 0.19 (s, 18H, SiMe$_3$). MS (ESI): *m/z* 582.29 (M$^+$).

Reaction of Benzyne with (Me$_2$SiSiMe$_2$)(η^5-C$_9$H$_6$)$_2$Fe (12). Similar to that described for the reaction of benzyne with **1**, reaction of 0.79 g (2 mmol) of **12** with 1.19 g (4 mmol) of *o*-trimethylsilylphenyl triflate and 1.22 g (8 mmol) of CsF gave 0.13 g (14%) of the monoadduct **13** as purple crystals. Mp: 157 °C (dec). Anal. Calcd for $C_{28}H_{28}FeSi_2$: C, 76.95; H, 5.17. Found: C, 76.95; H, 5.26. ^{1}H NMR (CDCl$_3$) δ: 6.97–6.71 (m, 8H, C_6H_4 and C_9H_6), 6.52 (m, 2H, C_2H_2), 5.38 (d, J = 3.15 Hz, 1H, C_9H_6), 4.60(d, J = 3.15 Hz, 1H, C_9H_6), 4.39 (d, J = 2.25 Hz, 1H, C_5H_2), 4.32 (d, J = 3.30 Hz, 2H, CH), 3.96 (d, J = 2.25 Hz, 1H, C_5H_2), 0.76 (s, 3H, SiMe), 0.73 (s, 3H, SiMe), 0.48 (s, 3H, SiMe), 0.30 (s, 3H, SiMe). MS (ESI): *m/z* 476.26 (M$^+$).

Attempted ROMP of Complex 2. NMR tube scale polymerization: Complex **2** (0.015 g, 0.048 mmol) was dissolved in 0.2 mL of CDCl$_3$ in a 5 mm NMR tube. After addition of a solution of Grubbs' catalyst (0.002 g, 0.002 mmol) in 0.3 mL of CDCl$_3$, the NMR tube was placed on a shaker at room

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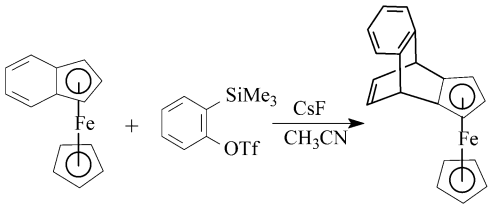
Table 1. Crystal Data and Summary of X-ray Data Collection for 2, 5, 8, and 13

	2	**5**	**8**	**13**
formula	$C_{20}H_{16}Fe$	$C_{30}H_{22}Fe$	$C_{32}H_{26}Fe$	$C_{28}H_{28}FeSi_2$
fw	312.18	438.33	466.38	476.53
cryst syst	orthorhombic	triclinic	triclinic	triclinic
space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.779(2)	8.645(4)	6.486(2)	8.833(3)
b (Å)	8.392(2)	9.245(4)	11.683(4)	11.547(4)
c (Å)	21.338(6)	13.633(6)	15.999(6)	12.352(4)
α (deg)	90	74.375(6)	73.586(5)	104.232(5)
β (deg)	90	74.739(6)	82.831(6)	102.839(5)
γ (deg)	90	84.048(6)	75.121(5)	97.876(5)
V (Å^3)	1392.9(7)	1011.6(7)	1122.2(7)	1165.8(6)
Z	4	2	2	2
D_{calc} (g·cm^{-3})	1.489	1.439	1.380	1.358
μ (mm^{-1})	1.071	0.761	0.690	0.763
F(000)	648	456	488	500
cryst size (mm)	0.22 × 0.20 × 0.16	0.34 × 0.30 × 0.24	0.40 × 0.22 × 0.16	0.22 × 0.18 × 0.12
max. 2θ (deg)	50.02	52.82	52.72	52.80
no. of reflns collected	6329	5828	6509	6737
no. of indep reflns/R_{int}	2410/0.0205	4093/0.0166	4532/0.0247	4714/0.0264
no. of params	190	280	300	284
goodness-of-fit on F^2	1.065	1.018	1.051	1.013
R_1, wR_2 [$I > 2\sigma(I)$]	0.0242, 0.0602	0.0325, 0.0749	0.0428, 0.0919	0.0526, 0.1095
R_1, wR_2 (all data)	0.0277, 0.0618	0.0425, 0.0791	0.0681, 0.1075	0.0908, 0.1256

Scheme 1



1 **2**

temperature for 36 h. ^{1}H NMR monitoring showed no reaction. Larger scale polymerization: 0.150 g (0.480 mmol) of complex **2** was dissolved in 1 mL of CH_2Cl_2 in a 10 mL Schlenk tube. After addition of a solution of 0.020 g (0.024 mmol) of Grubbs' catalyst in 1 mL of CH_2Cl_2, the mixture was stirred for 36 h at room temperature. No color and viscosity changes were observed in the solution. Over 90% of the starting complex **2** was recovered by column chromatography.

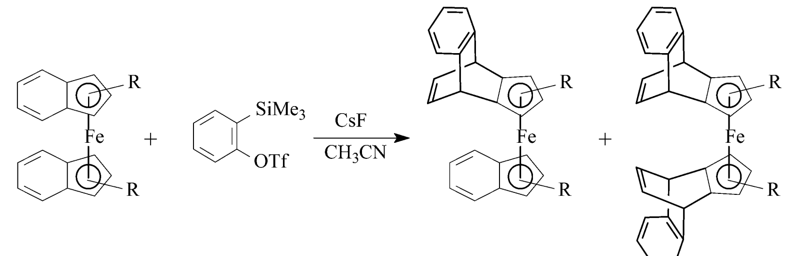
Crystallographic Studies. Single crystals of complexes **2**, **5**, **8**, and **13** suitable for X-ray diffraction were obtained from hexane/CH_2Cl_2 solutions. Data collection was performed on a Bruker SMART 1000, using graphite-monochromated Mo Kα radiation ($\omega-2\theta$ scans, $\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were using the SHELXL-97 program system. The crystal data and summary of X-ray data collection are presented in Table 1.

Results and Discussion

Reaction of Benzyne with (η^5-C_9H_7)Fe(η^5-C_5H_5) (1). In an initial experiment, a solution of **1** and CsF in CH_3CN was heated to 40 °C. After addition of *o*-trimethylsilylphenyl triflate, the mixture was stirred overnight. Appropriate workup gave complex **2** in 23% yield along with some uncharacterized solid, which might possibly be attributed to the thermal decomposition of complex **1** (Scheme 1). The ^{1}H NMR spectrum of complex **2** displays two multiplets at 7.08 and 6.98 ppm assigned to the protons of C_6H_4 and a multiplet at 6.82 ppm assigned to the protons of the vinylene double bond. The bridgehead methylidyne proton resonances are highfield shifted to 4.02 ppm in comparison to its parent complex **1**, which is at 7.58 ppm, indicating that the aromaticity of the six-membered ring of the indenyl group was destroyed. The structure of **2** has been further confirmed by X-ray diffraction.

Reactions of Benzyne with (η^5-R-C_9H_6)$_2$Fe [R = H (3); 2-Me (6); 1-SiMe$_3$ (9)]. Complex **6** was prepared from (2-Me-C_9H_6)Li and $FeCl_2$·1.5THF in a manner similar to that used in the preparation of (η^5-C_9H_7)$_2$Fe (**3**).[8b] Its ^{1}H NMR spectrum shows only one peak for Cp-H protons at 4.31 ppm, indicating its C_2 symmetry. Complex **9** was prepared according to a literature method.[16] It is interesting that in our case only the *rac* isomer of **9** was obtained on the basis of the ^{1}H NMR spectrum, whereas both the *rac* and *meso* isomers were obtained at a ratio of 1.6:1 in the literature. This remarkable difference is probably due to the *meso* to *rac* isomerization of the product **9** during the relatively

Scheme 2



R = H **3** **4** **5**
2-Me **6** **7** **8**
1-SiMe$_3$ **9** **10** **11**

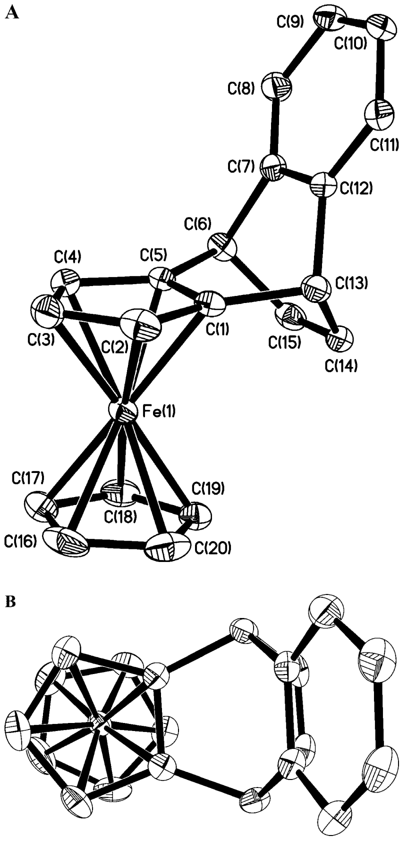
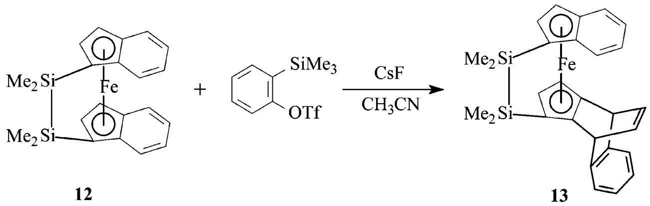


Figure 1. Side (A) and top (B) ORTEP views of **2**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: C(5)–C(6) 1.522(3), C(6)–C(7) 1.542(3), C(6)–C(15) 1.524(3), C(14)–C(15) 1.314(3), C(7)–C(12) 1.390(3), C(5)–C(6)–C(15) 105.68(18), C(5)–C(6)–C(7) 103.97(17), C(7)–C(6)–C(15) 104.36(18), C(14)–C(15)–C(6) 115.2(2), C(12)–C(7)–C(6) 113.49(19).

longer reaction time (24 h) in comparison to that (3 h) in the literature method.[21]

The reactions of bis(indenyl) iron derivatives **3**, **6**, and **9** with benzyne in CH_3CN afforded the bisadducts **5**, **8**, and **11**, respectively, along with the corresponding monoadducts **4**, **7**, and **10** (Scheme 2). When complex **3** was employed, the yield of the monoadduct **4** was too low to obtain the pure product, and it was characterized only by ESI-MS. All of the complexes except **4** are air stable in the solid state, whereas the monoadducts are slightly air-sensitive in solution. The ^1H NMR spectra of the monoadducts **7** and **10** display three and four peaks of the unreacted indenyl groups at 7.48, 7.25, 4.35 ppm and 7.53, 6.93, 5.00, 4.39 ppm, indicating that they are the monoadducts. The protons of the benzene ring are shown at 6.97, 6.76 ppm and 6.89, 6.58 ppm. In the ^1H NMR spectrum of **10** the bridgehead methylidyne protons are split into two peaks at 3.94 and 3.88 ppm, due to the presence of a $SiMe_3$ group in the C(1) position of the indenyl ring. All three bisadducts **5**, **8**, and **11** have ^1H NMR spectra similar to that of **2** for the protons of the benzene rings, bridgehead methylidyne groups, and the vinylene groups. No protons of the original indenyl groups were observed, indicating that both of the indenyl groups had reacted with benzyne. The structures of **5** and **8** have been confirmed by X-ray diffraction.

Scheme 3



Reaction of Benzyne with $(Me_2SiSiMe_2)(\eta^5\text{-}C_9H_6)_2Fe$ (12). To study the effect of a bridging group on the reaction, *ansa* tetramethyldisilylene-bridged bis(indenyl) iron (**12**) was synthesized and used in a reaction with the benzyne intermediate. Complex **12** was prepared in a manner similar to that used for complex **6**. A pure isomer was formed, according to the presence of two singlet peaks of the bridging SiMe groups at 0.70 and 0.58 ppm,[7b,8d] and was assigned as the *meso* isomer on the basis of the X-ray diffraction structure of its benzyne reaction product **13**. The reaction of complex **12** with benzyne afforded only the monoadduct **13**, probably due to the steric repulsion between the two six-membered rings of the *meso* isomer (Scheme 3). In the ^1H NMR spectrum of **13**, there is an overlapping region at 6.52–6.97 ppm assigned to the protons of the unreacted indenyl, benzene ring, and vinylene group. The protons of bridging tetramethyldisilylene group were split into four peaks at 0.76, 0.73, 0.48, and 0.30 ppm. The structure of **13** has also been confirmed by X-ray diffraction.

Attempted ROMP of Complex 2 Using Grubbs' Catalyst. In recent years ferrocene-containing polymers have been investigated extensively, largely due to their unique properties in material science.[2] Several synthetic methods for ferrocene-containing polymers have been reported including the well-known ring-opening metathesis polymerization (ROMP).[2,22] Since a vinylene group is present in the cycloaddition adduct of benzyne with indenyl iron derivatives, it is a new type of ferrocene-containing cyclic monomer and the derived ferrocene-containing polymers might be obtained possibly by the ROMP of the vinylene group. To test this idea, ROMP of complex **2** in the presence of Grubbs' catalyst was attempted using a monomer/initiator ratio of 20:1. Unfortunately, neither the NMR tube scale polymerization nor the larger scale polymerization experiments gave the desired polymers, probably due to the steric effect of the relatively crowded complex **2**.[23] Over 90% of the starting complex **2** was recovered in the bulk polymerization.

Molecular Structures. The molecular structures of **2**, **5**, and **13** are shown in Figures 1–3, respectively. The

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(21) Curnow, O. J.; Fern, G. M. *Organometallics* **2002**, *21*, 2827.

(22) (a) Albagli, D.; Bazan, G. C.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 4150. (b) Albagli, D.; Bazan, G. C.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1993**, *114*, 7328. (c) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S. *Macromolecules* **1995**, *28*, 8713. (d) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507. (e) Heo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621. (f) Watson, K. J.; Zhu, J.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 462. (g) Watson, K. J.; Nguten, S. T.; Mirkin, C. A. *J. Organomet. Chem.* **2000**, *606*, 79. (h) Abd-El-Aziz, A. S.; May, L. J.; Hurd, J. A.; Okasha, R. M. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2716. (i) Abd-El-Aziz, A. S.; Okasha, R. M.; Hurd, J. A.; Todd, E. K. *Polym. Mater. Sci. Eng.* **2002**, *86*, 91. (j) Abd-El-Aziz, A. S.; Okasha, R. M.; Afifi, T. H.; Todd, E. K. *Macromol. Chem. Phys.* **2003**, *204*, 555.

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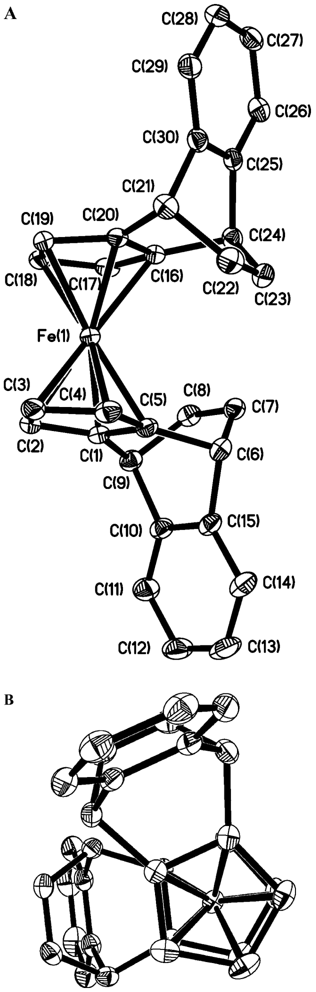


Figure 2. Side (A) and top (B) ORTEP views of **5**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: C(1)−C(9) 1.522(3), C(8)−C(9) 1.519(3), C(9)−C(10) 1.536(3), C(7)−C(8) 1.318(3), C(10)−C(15) 1.400(3), C(8)−C(9)−C(1) 106.12(16), C(8)−C(9)−C(10) 105.57(16), C(1)−C(9)−C(10) 102.84(16), C(7)−C(8)−C(9) 115.00(18), C(15)−C(10)−C(9) 112.93(17).

molecular structure of **8** and the packing diagram of **5** are shown in the Supporting Information.

As expected, the benzyne intermediate reacted with the six-membered ring of indenyl groups from the outside of the indenyl plane due to steric effects. The bridgehead carbon atoms lie on the plane of the benzene ring and the original six-membered ring planes bend down toward the iron atom along with C(6), C(7) (Scheme 4). The C−C double bond lengths of the vinylene groups in the complexes **2**, **5**, **8**, and **13** range from 1.308(5) to 1.319(3) Å, which are even shorter than that of the classical double bond (1.34−1.35 Å). The lengths of the adjacent C−C single bond range from 1.512(4) to 1.532(3) Å, suggesting that the butadiene-like six-membered rings undergo Diels−Alder reaction with benzyne.

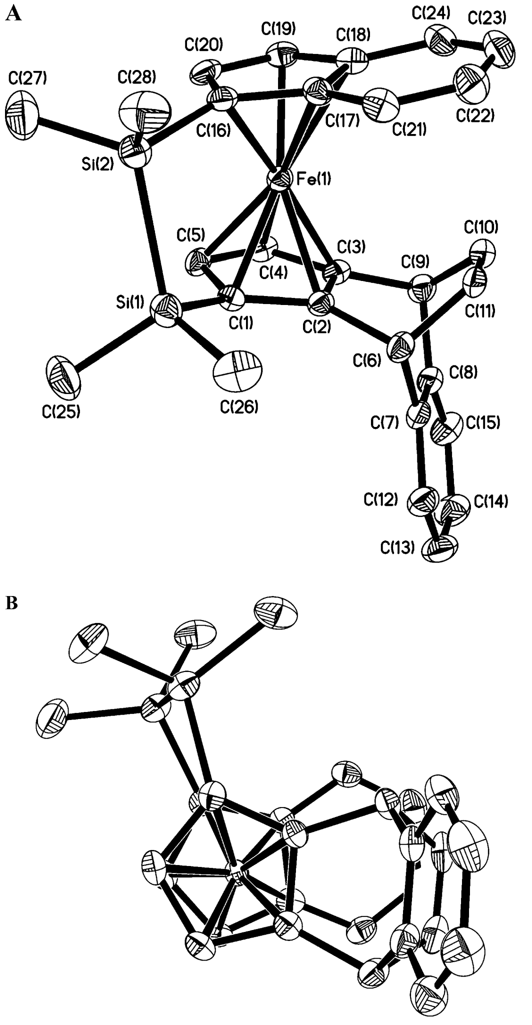
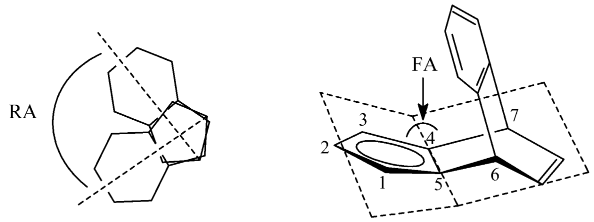


Figure 3. Side (A) and top (B) ORTEP views of **13**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: C(2)−C(6) 1.523(5), C(6)−C(11) 1.520(5), C(6)−C(7) 1.521(5), C(7)−C(8) 1.402(5), C(10)−C(11) 1.308(5), Si(1)−Si(2) 2.3956(16), C(11)−C(6)−C(2) 106.6(3), C(7)−C(6)−C(2) 102.9(3), C(11)−C(6)−C(7) 105.2(3), C(8)−C(7)−C(6) 113.7(3), C(10)−C(11)−C(6) 115.2(4), C(1)−Si(1)−Si(2) 101.75(11).

Scheme 4



For comparison of the crystal structures, the rotation angle (RA) and the fold angle (FA) have been chosen.[24] The RA is defined as the angle between planes including the iron atom, C(2), and the midpoint of C(4), C(5) for each of the cycloadditioned indenyl rings to describe the relative rotational orientation of the two coordinated ligands. The FA is defined as the angle between the planes [C(4), C(5), C(6), C(7)] and [C(1), C(2), C(3), C(4), C(5)] (Scheme 4) to describe the small bending distortion at C(4), C(5). The presence of a bridging group in the complex **13** makes the dihedral angle between two cyclopentadienyl ring planes much larger and the RA significantly smaller than that of the unbridged analogues **2**, **5**, and **8** as shown in Table 2. The RA of the bisadduct **5** is remarkably larger than that of its parent complex **3** (71.2° for **5**, 13.0° and 5.2° for the two independent molecules in the unit cell of **3**).[7a] The FA

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[24] Calhorda, M. J.; Felix, V.; Veiros, L. F. *Coord. Chem. Rev.* **2002**, *230*, 49.

Table 2. Structural Parameter Comparison for 2, 5, 8, and 13

	2	**5**	**8**	**13**
C═C (Å)[a]	1.314(3)	1.318(3) 1.319(3)	1.316(4) 1.310(4)	1.308(5)
∠Cp−Cp (deg)[b]	4.9	4.6	5.0	13.1
RA (deg)		71.2	57.9	11.5
FA (deg)	172.4	171.2 168.8	168.6 166.6	170.7

[a] C═C: the bond length of the vinylene double bond. [b] ∠Cp−Cp: the dihedral angle between the two cyclopentadienyl ring planes.

of the relatively less crowded complex **2** and the monoadduct **13** are slightly larger than that of the bisadducts **5** and **8**, as a result of the larger repulsion effect in the more crowded complexes **5** and **8**. The 2-Me-substituted bisadduct **8** has a slightly smaller FA and RA than the unsubstituted bisadduct **5**, suggesting that the substitution in the cyclopentadienyl ring may also affect the bending distortion. It is worth noting that in the crystal lattice of **5**, the two benzene ring planes of the adjacent molecules are parallel (the interplane angle is zero), with the interplanar distance of 3.7286 Å, while the distance between the two benzene ring centers is 3.927 Å, which exhibits an offset or slipped $\pi-\pi$ stacking interactions with the displacement angle of 18.3° (the term "$\pi-\pi$ interactions" is commonly used for stacks of aromatic groups with approximately parallel molecular planes separated by interplanar distances of about 3.3−3.8 Å[25]) (see Supporting Information).

Acknowledgment. We thank the National Natural Science Foundation of China (No. 20202004), the Research Fund for the Doctoral Program of Higher Education (20030055001), SINOPEC, and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (2001-345), for financial support.

Supporting Information Available: Tables of crystallographic data collection information, final positional and thermal parameters of the non-hydrogen atoms, general temperature factors, and bond distances and angles for **2**, **5**, **8**, and **13**. The ORTEP views of **8** and the packing diagram of **5** showing a slipped $\pi-\pi$ stacking interaction between the two benzene rings of adjacent molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885.