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Nucleophilic additions of phenylsulfonyl-substituted tricarbonyl(1,3-cyclohexadiene)iron complexes

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Abstract

Tricarbonyl[η^4-2-(phenylsulfonyl)-1,3-cyclohexadiene]iron(0) (**3**) was prepared in good yield from 2-(phenylsulfonyl)-1,3-cyclohexadiene and $Fe_2(CO)_9$ using azadiene **2** as the catalyst. The reaction of **3** with nucleophiles proceeded only at the C-4 position under thermodynamic (25°C) or kinetic (-78°C) condition. Careful treatment of **3** with Ph_3CPF_6 at low temperature regiospecifically gave the tricarbonyl[(1-5-η^5)-3-(phenylsulfonyl)cyclohexadienyl]iron(I) complex **6**. The η^5-complex **6** was more reactive than the η^4-complex **3**, and reacted with various nucleophiles stereo- and regiospecifically at the C-1 position. The addition products **9** could be demetallated to give functionalized dienyl sulfones **10**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Diene complexes; Sulfones

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1. Introduction

Iron complexes of dienes are very useful in organic synthesis [1]. The iron moiety effectively decreases the electron density of the diene, thus facilitating the nucleophilic addition reactions. The nucleophiles and the reaction condition may change the regiochemistry of the reaction [2]. The substituent on the diene may also play an important role [3]. We have studied the nucleophilic additions of tricarbonyl[η^4-2-(phenylsulfonyl)-1,3-butadiene]iron(0) complex [4], which was readily prepared from its 3-sulfolene precursor [5]. All the nucleophiles added to the C-4 position of the iron complex independent of the temperatures used. Without the iron moiety, the reaction with nucleophiles proceeds at the C-1 position [6].

The reactivity of the η^4-diene iron complexes can be further enhanced by converting it into η^5-dienyl cationic iron complexes [7]. Even weak nucleophiles such as acetone or enamines can give the addition products in good yield. Although many alkyl- or alkoxy-substituted η^5-cyclohexadienyliron complexes have been reported for such reactions [7,8], the only electron-withdrawing substituent on the diene that has been described was an ester group [9]. Recently we reported the synthesis of tricarbonyl[η^5-1-(phenylsulfonyl)cyclohexadienyl]iron complex and its nucleophilic addition reactions [10]. Soft nucleophiles added at the C-5 position of the dienylium complex, whereas hard nucleophiles such as methyllithium or the enolate of ethyl acetate also gave small amounts of the C-2 addition products. We now describe the first synthesis of tricarbonyl[η^4-2-(phenylsulfonyl)-1,3-cyclohexadienyl]iron(0) complex (**3**) and tricarbonyl[η^5-3-(phenylsulfonyl)-1,3-cyclohexadienyl]iron(I) complex (**6**) and their nucleophilic addition reactions.

2. Results and discussion

Treament of 2-(phenylsulfonyl)-1,3-cyclohexadiene (**1**) [11] with two equivalents of $Fe_2(CO)_9$ in refluxing

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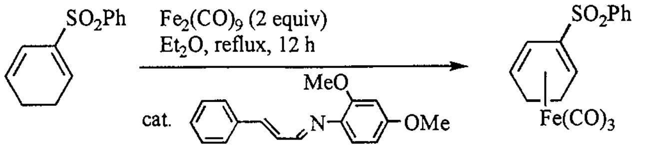
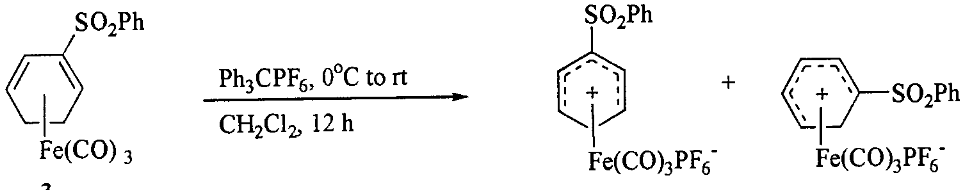
ether as catalyzed by 1-aza-1,3-butadiene **2** [12] gave the diene complex **3** in 78% yield. Without the catalyst, the yield of the reaction was lower (55%). A small amount of the [1-(phenylsulfonyl)-1,3-cyclohexadiene]iron(0) isomer was also obtained. Apparently, the catalyst facilitates the transfer of tricarbonyliron moiety to diene **1** in lieu of isomerization of the diene. Complex **3** was fully characterized by spectroscopic and analytical methods.



1 **2** **3**

(78%)

The reactions of **3** with a range of nucleophiles are shown in Table 1. It can be seen that all nucleophiles reacted with **3** at the C-4 position. This regiospecificity was the same as that observed for the acyclic diene iron complex [4]. As compared to the parent η^4-(1,3-cyclohexadiene)iron(0) complex [2], the sulfonyl group in **3** significantly increased the reactivity of the η^4-diene complex; even a soft nucleophile such as malonate anion could undergo the addition reaction. It is also interesting to note that when malonate was used as the nucleophile (entry 1), quenching the reaction at different temperatures yielded different ratios of the products. When the reaction was quenched with CF_3CO_2H at − 78°C, two products **4a** (40%) and **5a** (38%) were obtained in about equal amount, but when the reaction was quenched at room temperature (r.t.), **4a** (81%) was predominant and **5a** was obtained in only 10%. All the other nucleophiles (entries 2–5) gave only products **4** independent of the quench temperature. The structure of **4a** and **5a** could be differentrated by ^{1}H-NMR decoupling experiments. The structure of **4c** was further confirmed by X-ray crystallography (Fig. 1) [13].



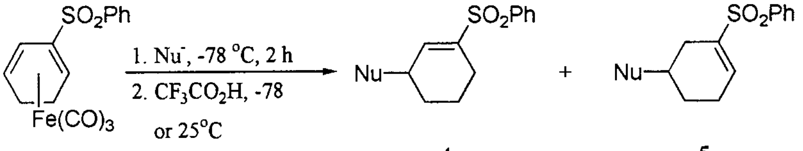
3 **6** **7**

It is envisaged that **4a** is more stable than **5a** because the nucleophilic group in **4a** is in the quasiaxial position and has less steric strain than the axial nucleophilic group in **5**. Thus under thermodynamic condition (25°C) the formation of **4a** would be more favorable. But under kinetic conditions (− 78°C) the product ratio is determined by the relative ease of hydride transfer to the C-1 or C-3 position (Scheme 1). When the nucleophiles are bulky (entries 2–5), hydride transfer to the C-1 position would be much favored because the transfer to C-3 would involve serious steric repulsion. When the nucleophile is small (entry 1), there is not much difference between these two pathways.

Subsequent hydride abstraction from complex **3** with triphenylcarbenium hexaflurophosphate at r.t. unexpectedly gave a mixture of two η^5-dienylium complexes **6** and **7**. We then tried the reaction at different temperatures, and found that the yield and ratio of **6**/**7** varied significantly with the reaction temperature (Table 2). It can be seen that lowering the reaction temperature increased the ratio of **6**/**7** (cf: entries 1–3). However, keeping the reaction at − 78°C (entry 4) led to very low yield of **6**. The best condition for the regiospecific formation of **6** in good yield was found (entry 7).

The structures of **6** and **7** were elucidated by NMR spectroscopy [14]. The ^{1}H-NMR spectrum of compound **6** exhibited the following: a doublet at δ 6.75 (H-2 and H-4), a multiplet centered at δ 4.87 (H-1 and H-5), a doublet of triplets centered at 3.25 (H_{endo}-6), and a doublet at δ 2.13 (H_{exo}-*6*). The ^{13}C-NMR spectrum of complex **6** exhibited the following signals: δ 206.6 (CO), 107.2 (C-3), 101.1 (C-2 and C-4), 68.2 (C-1 and C-5), 22.8 (C-6).

The formation of **7** from **3** was unexpected [15] and we have done some experiments to find out how it was formed. We first isolated compound **6** and then subjected it to the same hydride removal condition. We did not obtain any compound **7**, but only the recovered complex **6**. This clearly indicates that complex **7** was



3 **4** **5**

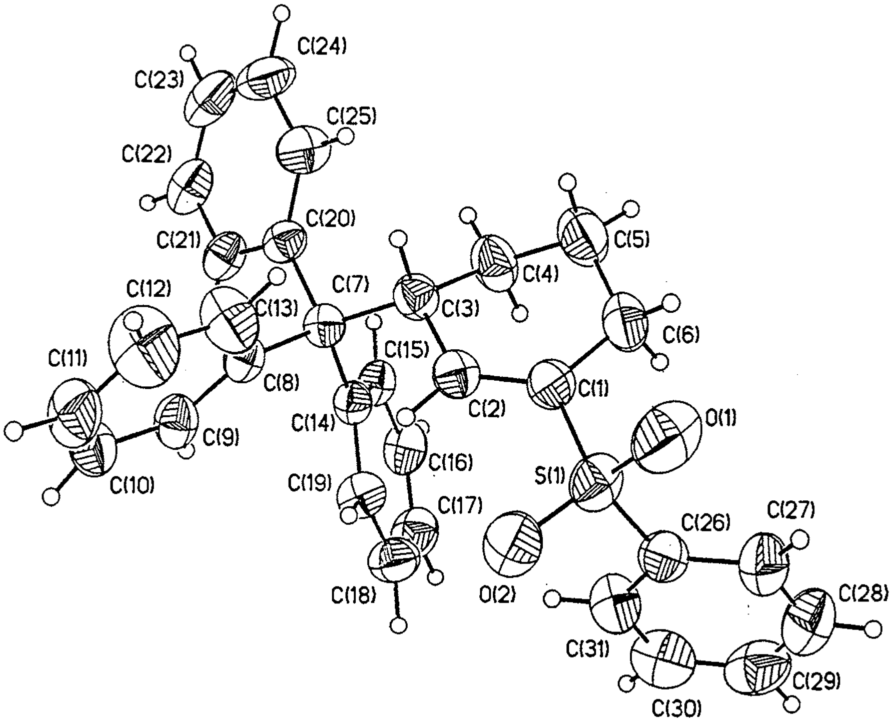
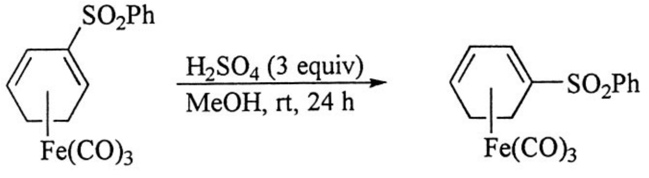


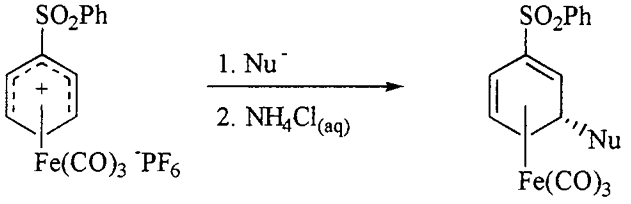
Fig. 1. Molecular structure of complex **4c**. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.325(4), C(2)–C(3) 1.502(4), C(3)–C(4) 1.539(5), C(4)–C(5) 1.515(5), C(5)–C(6) 1.504(6), C(1)–C(6) 1.496(5), C(1)–S(1) 1.764(3), S(1)–C(26) 1.769(4), C(1)–S(1)–C(26) 103.4(2), C(1)–C(2)–C(3) 122.2(3), C(2)–C(3)–C(4) 109.4(3), C(2)–C(3)–C(7) 114.2(3),C(3)–C(7)–C(15) 111.6(2).

not obtained from **6**. The most logical precursor for **7** would then be the 1-(phenylsulfonyl)diene iron complex **8** [10]. We found that when complex **3** was treated with a small amount of H_2SO_4 in methanol at r.t., the isomerized diene complex **8** was obtained in 60% yield, but when the reaction was carried out at − 10°C, only the starting complex **3** was recovered. Thus we speculate that a small amount of HPF_6 which might be present in Ph_3CPF_6 converted the complex **3** to **8** which then underwent hydride abstraction to give **7**. When this reaction was carried out at low temperature, complex **3** was not converted to **8** so that **7** was not formed. Furthermore, we have previously shown that treatment of **8** with Ph_3CPF_6 gave only complex **7** and no **6** was detected [10].



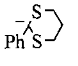
3 **8** (60 %)

Having found a good method for the selective formation of η^5-dienyl iron complex **6**, we then studied the reactions of **6** with a range of nucleophiles. The addition products **9** were obtained in good to excellent yield (Table 3). It can be seen that the η^5-dienylium iron complex **6** is more reactive than the η^4-dienyl complex **3** toward nucleophiles which include heteroatoms (entries 1–3), malonate and keto ester anion (entries 4, 5), enamines and enol ether (entries 6, 7), neutral molecules (entries 8–10) and even a very hard nucleophile, methyllithium (entry 11). All these nucleophiles reacted with **6** at the C-1 position. The structures of **9** were elucidated from the spectral data. The structure of **9i** was further confirmed by X-ray crystallography (Fig. 2) [16].



6 **9**

Table 1
Nucleophilic addition reactions of η^4-iron(0) complex **3**[a]

Entry	Nu^-	Temp (°C)	Product	Yield (%)
1	$^-CH(CO_2Et)_2$	25	**4a, 5a**	81, 10
		−78	**4a, 5a**	40, 38
2	$^-CHPh_2$	25	**4b**	54
		−78	**4b**	40
3	$^-CPh_3$	25	**4c**	78
		−78	**4c**	81
4	$^-C(Me)_2CO_2Et$	25	**4d**	95
		−78	**4d**	93
5	5 	25	**4e**	81
		−78	**4e**	85

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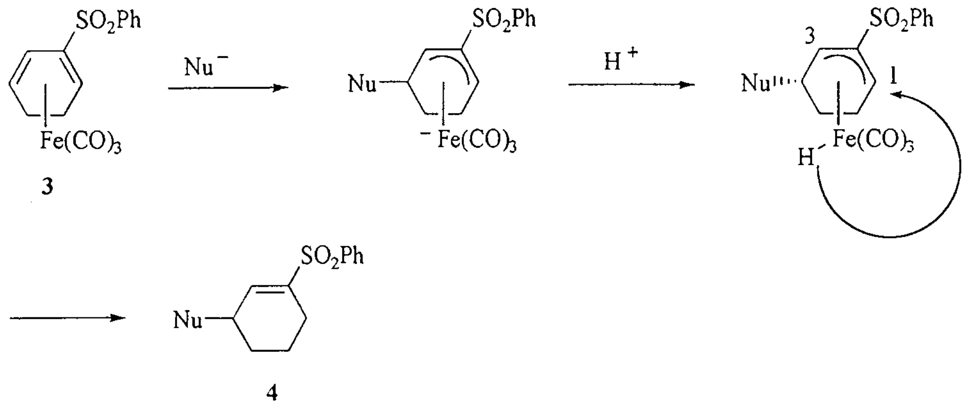
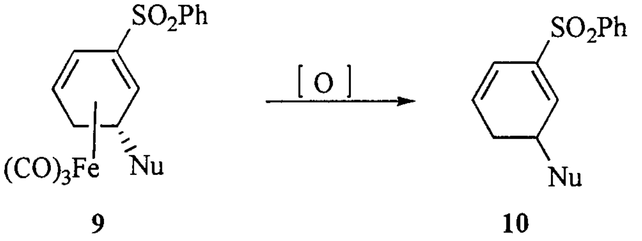
[a] The reaction solvent was THF/HMPA (4/1).



Scheme 1. This mechanism demonstrates the relative ease of hydride transfer to the C-1 or C-3 position; this position (C-1 or C-3) is determined by the size of the nucleophile, due to steric hindrance.

The dematallation reactions of complexes **9** were also studied (Table 4). Treatment of **9** with $(NH_4)_2Ce(NO_3)_6$ (Condition A) or anhydrous Me_3NO (Condition B) gave the sulfone-substituted dienes **10** in good yield, which should be quite useful for further synthetic applications [17].



In summary, we have synthesized two new sulfone-substituted dienyl iron complexes **3** and **6**, and found that they can readily undergo nucleophilic addition reactions regio- and stereospecifically. The iron moiety increases the reactivity and directs the regioselectivity of the addition reaction. The addition products **4** and **10** have the unsaturated sulfone structure which should be useful for further synthetic transformations.

Table 2
The effect of reaction temperatures on the ratio of **6**/**7**

Entry	Conditions[a]	**6**/**7**	Yield (%)
1	0°C to r.t., 12 h	55/45	88
2	−78°C to r.t., 12 h	75/25	85
3	−78°C, 4 h; r.t., 8 h	80/20	80
4	−78°C, 12 h	100/0	30
5	−78 to 0°C, 12 h	100/0	70
6	0°C, 12 h	90/10	82
7	−78 to 0°C, 24 h	100/0	80

[a] The reaction was carried out at the initial temperature, allowed to warm slowly to the final temperature and then stirred at that temperature for another period of time.

3. Experimental

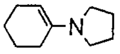
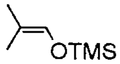
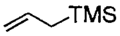
IR spectra were recorded with an FT-JR spectrometer Analect RFX-65. ^1H- and ^{13}C-NMR spectra were measured for samples in $CDCl_3$ with an FT-NMR spectrometer Brucker AC-300 at 300 and 75 MHz, respectively, with tetramethylsilane as the internal standard. Mass spectra were recorded with a spectrometer JEOL JMS-D-100. High resolution mass spectra were measured with a mass spectrometer JEOL TMS-HX 110. Melting points were measured with an apparatus Mel-Temp and are uncorrected. High-performance liquid chromatography (HPLC) was carried out with a chromatograph Shimadzu LC-6A using LiChrosorb (Merck) as the column. The silica gel used for flash column chromatography was made by Merck (60 H). All reactions were carried out under an atmosphere of N_2, and all reagents were of reagent grade and were purified prior to use [18].

3.1. *Tricarbonyl[(1-4-η^4)-2-(phenylsulfonyl)-1,3-cyclohexadiene]iron(0) (3)*

A solution of diene **1** [11] (6.60 g, 30 mmol), $Fe_2(CO)_9$ (21.80 g, 60 mmol) and 1-aza-1,3-butadiene **2** [12] (80.10 mg, 0.3 mmol) in ether (120 ml) was purged with N_2 three times and then heated to reflux for 12 h. The brown solution was filtered through with Celite column and the crude product was purified by column chromatography using hexane/ethyl acetate (10/1) as eluent. The yellow band was collected and the solvent was removed in vacuo to give complex **3** (8.42 g, 78% yield), which was recrystallized from hexane/diethyl ether to give yellow crystals.

Complex **3**. m.p. 124.3–125.0°C; IR (film) 3065, 2936, 2865, 2360, 2341, 2053 (CO), 1987 (CO), 1446, 1321 (SO), 1158 (SO), 1106, 757, 731, 688 cm^{-1}; ^1H-NMR ($CDCl_3$) 1.30–1.37 (1 H, m), 1.47–1.54 (1 H, m), 1.72–1.81 (2 H, m), 3.36 (1 H, ddd, $J = 2.4$, 3.1, 6.9 Hz, H-4), 3.64 (1 H, d, $J = 1.7$ Hz, H-1), 5.82 (1 H, d,

Table 3
Nucleophilic addition reactions of dienyl iron(I) complex **6** to give **9**

Entry	Nucleophile	Conditions	Product **9**	Yield (%)
1	MeOH	Neat, r.t., 24 h	**a**	90
2	NaSPh	THF, −78°C, 1 h	**b**	95
3	$NaSO_2Ph$	THF, r.t., 30 min	**c**	90
4	$NaCH(CO_2Et)_2$	THF, −78°C, 1 h, r.t., 1 h	**d**	91
5	$NaCH(CO_2Me)COMe$	THF, −78°C, 15 min, r.t., 30 min	**e**	90
6	6 	CH_3CN, r.t., 1 h	**f**	82
7	7 	CH_2Cl_2, r.t., 4 h	**g**	75
8	8 	CH_2Cl_2, r.t., 4 h	**h**	80
9	TMSCN	CH_3CN, r.t., 2 h	**i**	83
10	CH_3COCH_3	Neat, r.t., 24 h	**i**	88
11	MeLi	CH_2Cl_2, −78°C, 5 min	**k**	74

$J = 6.9$ Hz, H-3), 7.56–7.69 (3 H, m, ArH), 7.99–8.02 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 23.8, 24.0, 58.5, 63.4, 88.2, 105.6, 127.6, 129.4, 133.5, 140.9, 209.1; MS (relative intensity, rel. int.) m/z 360 (M^+, 3), 332 (16), 304 (83), 276 (93), 274 (86), 210 (100), 133 (33), 77 (40); HRMS Calc. for $C_{15}H_{12}O_5SFe$ m/z 359.9755, found 359.9759; Anal. Calc. for $C_{15}H_{12}O_5SFe$: C, 50.02; H, 3.36. Found: C, 50.10; H, 3.31.

3.2. General procedure for nucleophilic addition reactions of tricarbonyl[(1-4-η^4)-2-(phenylsulfonyl)-1,3-cyclohexadiene]iron(0) (3) (Table 1)

To a solution of **3** (0.5 mmol) in dried THF/HMPA (4/1, 4 ml) at −78°C was added a solution of nucleophile/solvent. The reaction mixture was warmed to r.t. for 2 h, then quenched with trifluoroacetic acid (2 ml) at −78°C or r.t. (Table 1). The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (2×20 ml), washed with water and 5% $NaHCO_3$, dried ($MgSO_4$), and evaporated. The crude product was purified by flash column chromatography using hexane/ethyl acetate (10/1 to 6/1) as eluent to give **4** and **5**.

3.2.1. Diethyl[3-(phenylsulfonyl)-2-cyclohexenyl]-malonate (4a)

Colorless oil, IR (neat) 3061, 2941, 2866, 2341, 1714 (CO), 1643, 1446, 1304 (SO), 1288, 1149 (SO), 1093, 996, 751, 718, 688 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.21–2.23 (6 H, m, CH_3), 1.32–1.35 (1 H, m), 1.49–1.55 (1 H, m), 1.71–1.82 (2 H, m), 2.05–2.10 (1 H, m), 2.18–2.23 (1 H, m), 2.98–3.09 (1 H, m), 3.34 (1 H, d, $J = 8.0$ Hz, $-C\underline{H}(CO_2Et)_2$), 4.14–4.23 (4 H, m, $-OCH_2$), 6.95 (1 H, br d, H-2), 7.47–7.61 (3 H, m, ArH), 7.81–7.84 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 14.0 (×2), 20.8, 22.7, 25.2, 35.8, 55.5, 61.6 (×2), 128.0, 129.0, 133.1, 138.2, 139.1, 141.3, 167.5, 167.6; MS (rel. int.) m/z 380(M^+, 13.6), 260 (48), 221 (20), 165 (86), 137 (31), 125 (100), 97 (20), 91 (44), 81 (23), 77 (68); HRMS Calc. for $C_{19}H_{24}O_6S$ m/z 380.1295, found 380.1302. Anal. Calc. for $C_{19}H_{24}O_6S$: C, 59.98; H, 6.36. Found: C, 60.01; H, 6.37.

3.2.2. Diethyl[3-(phenylsulfonyl)-3-cyclohexenyl]-malonate (5a)

Colorless oil, IR (neat) 3060, 2980, 2926, 2359, 1729 (CO), 1446, 1369, 1305 (SO), 1151 (SO), 1091, 1030, 755, 721, 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.16–1.26 (6 H, m, CH_3), 1.27–1.34 (1 H, m), 1.79 (1 H, br d), 1.92–2.06 (1 H, m), 2.20–2.47 (4 H, m), 3.18 (1 H, d, $J = 8.4$ Hz, $-C\underline{H}(CO_2Et)_2$), 4.07–4.21 (4 H, m, $-OCH_2$), 7.06 (1 H, br s, H-2), 7.48–7.62 (3 H, m, ArH), 7.80–7.83 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 14.0 (×2), 24.8, 25.0, 26.7, 33.2, 56.1, 61.4 (×2), 127.9, 129.1, 133.2, 137.9, 138.9, 139.2, 167.8, 167.9; MS (rel. int.) m/z 380 (M^+, 29), 335 (23), 289 (16), 221 (71), 220 (46), 192 (14), 160 (100), 125 (54), 91 (38), 77 (61); HRMS Calc. for $C_{19}H_{24}O_6S$ m/z 380.1295, found 380.1295. Anal. Calc. for $C_{19}H_{24}O_6S$: C, 59.98; H, 6.36. Found: C, 60.02; H, 6.37.

3.2.3. 3-(Diphenylmethyl)-1-(phenylsulfonyl)cyclohexene (4b)

White solid, m.p. 182.9–183.5°C; IR (film) 3060, 2939, 2353, 1641, 1494, 1446, 1304 (SO), 1290, 1149 (SO), 1089, 749, 705, 689 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 1.17–1.24 (1 H, m), 1.51–1.65 (2 H, m), 1.71–1.82

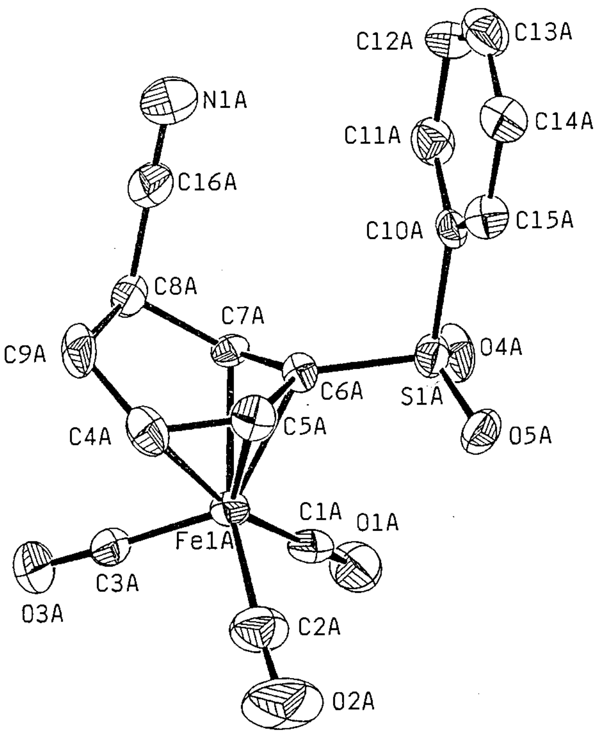


Fig. 2. Molecular structure of complex **9i**. Selected bond lengths (Å) and angles (°): Fe(1A)–C(4A) 2.151(14), Fe(1A)–C(5A) 2.039(14), Fe(1A)–C(6A) 2.006(12), Fe(1A)–C(7A) 2.066(11), S(1A)–C(6A) 1.768(12), S(1A)–C(1OA) 1.766(12), C(4A)–C(SA) 1.382(19), C(5A)–C(6A) 1.421(17), C(6A)–C(7A) 1.417(17), C(7A)–C(8A) 1.524(16), C(8A)–C(9A) 1.526(20), C(4A)–C(9A) 1.486(22), C(8A)–C(16A) 1.462(19), C(16A)–N(1A) 1.106(20), C(4A)–Fe(1A)–C(5A) 38.4(5), C(SA)–Fe(1A)–C(6A) 41.1(5), C(6A)–Fe(1A)–C(7A) 40.7(5), C(4A)–Fe(1A)–C(6A) 69.7(5), C(4A)–Fe(1A)–C(7A) 76.3(5), C(4A)–C(SA)–C(6A) 116.1(12), C(SA)–C(6A)–C(7A) 114.0(11), C(8A)–C(16A)–N(1A) 179.5(16), C(6A)–S(1A)–C(1OA) 103.4(5).

(1 H, m), 2.01–2.16 (1 H, m), 2.21 (1 H, m), 3.10–3.22 (1 H, m), 3.72 (1 H, d, $J = 10.7$ Hz, –CHPh$_2$), 6.80 (1 H, br s, H-2), 7.15–7.34 (10 H, m, ArH), 7.48–7.62 (3 H, m, ArH), 7.76–7.78 (2 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 20.7, 23.1, 26.6, 39.9, 56.5, 126.5, 126.8, 127.9, 128.0, 128.1, 128.6, 128.8, 129.0, 133.0, 139.4, 140.3, 140.9, 142.1, 142.7; MS (rel. int.) m/z 388 (M$^+$, 0.95), 168 (18), 167 (100), 165 (20), 152 (12), 77 (4); HRMS Calc. for $C_{25}H_{24}O_2S$ m/z 388.1499, found 388.1507. Anal. Calc. for $C_{25}H_{24}O_2S$: C, 77.29; H, 6.23. Found: C, 77.09; H, 6.25.

*3.2.4. 3-(Triphenylmethyl)-1-(phenylsulfonyl)-cyclohexene (**4c**)*

White solid, recrystallized from ethyl acetate–hexanes; m.p. 217.0–217.7°C; IR (KBr) 3056, 1962, 1900, 1814, 1775, 1640, 1446, 1305 (SO), 1148 (SO), 1088, 1033, 980, 766, 770, 689 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 1.02 (1 H, ddd, $J = 1.9$, 9.4, 11.2 Hz), 1.30–1.44 (1 H, m), 1.50–1.59 (3 H, m), 2.03 (1 H, m), 2.20–2.33 (1 H, m), 4.10 (1 H, br s, H-2), 7.10–7.33 (15 H, m, ArH), 7.35–7.45 (2 H, m, ArH), 7.51–7.59 (3 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 21.3, 22.8, 24.5, 41.1, 60.8, 126.0, 127.7, 127.9 ($\times$ 2), 128.8 ($\times$ 2), 132.9, 139.2, 140.6 ($\times$ 2); MS (rel. int.) m/z 464 (M$^+$, 0.03), 323 (6), 243 (100), 228 (13), 215 (8), 202 (4), 165 (81), 125 (7), 77 (7); HRMS Calc. for $C_{31}H_{28}O_2S$ m/z 464.1812, found 464.1804. Anal. Calc. for $C_{31}H_{28}O_2S$: C, 80.14; H, 6.07. Found: C, 79.85; H, 6.05.

*3.2.5. Ethyl[3-(phenylsulfonyl)-2-cyclohexenyl]-(1,1-dimethyl)acetate (**4d**)*

Yellow oil; IR (neat) 3064, 2976, 2939, 2870, 1724 (CO), 1446, 1304 (SO), 1149 (SO), 1091, 1021, 752, 689 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 1.07–1.11 (1 H, m), 1.15 (3 H, s, CH$_3$), 1.22 (3 H, s, CH$_3$), 1.25 (3 H, t, $J = 7.1$ Hz, CH$_3$), 1.36–1.55 (1 H, m), 1.66–1.76 (1 H, m), 1.83–1.93 (1 H, m), 1.93–2.07 (1 H, m), 2.25 (1 H, m), 2.59–2.69 (1 H, m), 4.15 (2 H, q, $J = 7.1$ Hz, –OCH$_2$), 6.96 (1 H, br s, H-2), 7.51–7.64 (3 H, m, ArH), 7.84–7.87 (2 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 14.1, 21.8, 22.1, 22.6, 22.9, 23.0, 43.8, 45.2, 60.7, 127.9, 129.0, 133.1, 138.7, 139.0, 141.2, 176.6; MS (rel. int.) m/z 336 (M$^+$, 59), 290 (5), 262 (100), 222 (18), 221 (13), 137 (15), 125 (43), 121 (13), 116 (18), 77 (22); HRMS Calc. for $C_{18}H_{24}O_4S$ m/z 336.1397, found 336.1392.

Table 4
Demetallation of diene iron complexes **9**

Entry	Complexes **9**	Product	Condition A[a] (yield %)	Condition B[b] (yield %)
1	**a**, Nu = OMe	**10a**	88	82
2	**b**, Nu = SPh	**10b**	95	72
3	**c**, Nu = SO$_2$Ph	**10c**	70[c]	76
4	**h**, Nu = CH$_2$CH=CH$_2$	**10h**	90	81
5	**j**, Nu = CH$_2$COCH$_3$	**10j**	70	73

[a] Condition A: (1) $(NH_4)_2Ce(NO_3)_6$ (CAN), three equivalents, acetone, 0°C, 5 min, r.t., 10 min; (2) H_2O.
[b] Condition B: Me$_3$NO, six equivalents, dry benzene, reflux, 1.5 h.
[c] Recovered starting material 25%.

*3.2.6. 2-Phenyl-2-[3-(phenylsulfonyl)-2-cyclohexenyl]-1,3-dithiane (**4e**)*

White solid; m.p. 152.3–153°C; IR (film) 3055, 2935, 2905, 2359, 1480, 1444, 1305 (SO), 1291, 1149 (SO), 1092, 766, 751, 715, 703, 688 cm^{-1}; ^{1}H-NMR (CDCl$_3$) 1.25–1.45(2 H, m), 1.51–1.61 (1 H, m), 1.63–1.84 (2 H, m), 1.89–1.98 (2 H, m), 2.26 (1 H, m), 2.65–2.70 (4 H, m), 2.76–2.86 (1 H, m), 7.02–7.27 (1 H, m, H-2′), 7.34–7.43 (3 H, m, ArH), 7.46–7.51 (2H, m, ArH),7.56–7.61 (1 H, m, ArH), 7.80–7.87 (2 H, m, ArH), 7.90–7.97 (2 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 21.7, 22.8, 23.2, 24.9, 27.3, 27.5, 48.9, 63.3, 127.2, 128.0, 128.6, 128.9, 129.7, 133.0, 138.0, 139.4, 139.5, 141.2; MS (rel. int.) m/z 416 (M$^+$, 1.1), 275 (3), 196 (13), 195 (100), 167 (5), 121 (22), 77 (7); HRMS Calc. for $C_{22}H_{24}O_2S_3$ m/z 416.0942, found 416.0930. Anal. Calc. for $C_{22}H_{24}O_2S_3$: C, 63.43; H, 5.81. Found: C, 63.52; H, 5.81.

*3.3. Tricarbonyl[(1-5-η^5)-3-(phenylsulfonyl)-cyclohexadienyl]iron(I) hexafluorophosphate (**6**)*

To a solution of **3** (3.60 g, 10 mmol) in dried CH_2Cl_2 (20 ml) at −78°C was added triphenylcarbenium hexafluorophosphate (3.88 g, 10 mmol) and then warmed to 0°C. The mixture was stirred at 0°C for another 24 h. To the brown solution was added diethyl ether (60 ml). A large amount of yellow salt was precipitated which was filtered by suction and then washed with diethyl ether (3 × 20 ml). The yellow powder was collected and dried in vacuo to give complex **6** (4.03 g, 80% yield)

Complex **6**. m.p. 149.9–152.0°C; IR (KBr) 3070, 2283, 2126, 2060 (CO), 1990 (CO), 1447, 1307 (SO), 1156 (SO), 838, 730, 688 cm^{-1}; ^{1}H-NMR (acetone-d$_6$) δ 2.13 (1 H, d, $J = 16.3$ Hz, H$_{exo}$-6), 3.25 (1 H, dt, $J = 16.3$, 6.3 Hz, H$_{endo}$-6), 4.85–4.88 (2 H, m, H-1, H-5), 6.75 (2 H, d, $J = 7.0$ Hz, H-2, H-4), 7.82–7.99 (3 H, m, ArH), 8.34–8.37 (2 H, m, ArH); ^{13}C-NMR (acetone-d$_6$) δ 22.8, 68.2, 101.1, 107.2, 129.0, 130.8, 136.0, 138.3, 206.6.

3.4. General procedure for nucleophilic addition reactions of tricarbonyl[(1-5-η^5)-3-(phenylsulfonyl)-1,3-cyclohexadienyl]iron(I) hexafluorophosphate (6) (Table 3)

To a solution of **6** (0.50 mmol) in dried THF (4 ml) at suitable temperatures (Table 3) was added a solution of nucleophile/solvent. The mixture was stirred until the solution became clear and was then quenched with saturated ammonium chloride solution. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (2 × 20 ml), washed with water, dried ($MgSO_4$), and evaporated. The crude product was purified by flash column chromatography using hexane/ethyl acetate (10/1 to 6/1) as eluent to give **9**.

*3.4.1. Tricarbonyl[(1-4-η^4)-6-exo-methoxy-2-(phenylsulfonyl)-1,3-cyclohexadiene]iron (**9a**)*

Yellow solid, m.p. 86.5–87.2°C; IR (film) 3065, 2933, 2821, 2062 (CO), 1988 (CO), 1447, 1321 (SO), 1160 (SO), 1094, 1078, 735, 688 cm^{-1}; ^{1}H-NMR (CDCl$_3$) 1.40 (1 H, d, $J = 15.8$ Hz, H$_{exo}$-5), 2.28 (1 H, ddd, $J = 3.8$, 9.6, 15.8 Hz, H$_{endo}$-5), 2.98 (3 H, s, CH$_3$), 3.10–3.06 (1 H, m, H-6), 3.58 (1 H, dd, $J = 1.2$, 3.6 Hz, H-1), 3.79–3.84 (1 H, m, H-4), 6.11 (1 H, d, $J = 6.7$ Hz, H-3), 7.56–7.69 (3 H, m, ArH), 8.06–8.09 (2 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 31.4, 55.7, 56.0, 57.2, 77.3, 90.1, 105.1, 128.0, 129.2, 133.6, 140.3, 208.4; MS (rel. int.) m/z 362 (M$^+$ − CO, 3.46), 334 (27), 306 (17), 291 (88), 275 (53), 210 (100), 180 (18), 133 (58), 125 (21), 77 (48); HRMS Calc. for $C_{16}H_{14}O_6SFe$ m/z 389.9861, found 389.9681; Anal. Calc. for $C_{16}H_{14}O_6SFe$: C, 49.25; H, 3.62. Found: C, 49.26; H, 3.64.

*3.4.2. Tricarbonyl[(1-4-η^4)-6-exo-phenylthio-2-(phenylsulfonyl)-1,3-cyclohexadiene]iron (**9b**)*

Yellow solid, m.p. 88.6–89.0°C; IR (film) 3060, 2940, 2847, 2061 (CO), 1992 (CO), 1583, 1479, 1446, 1321 (SO), 1158 (SO), 1090, 754, 736, 688 cm^{-1}; ^{1}H-NMR (CDCl$_3$,) δ 1.54 (1 H, d, $J = 16.4$, H$_{exo}$-5), 2.33–2.43 (1 H, m, H$_{endo}$-5), 3.28 (1 H, ddd, $J = 2.3$, 3.6, 6.6 Hz, H-6), 3.66–3.72 (2 H, m, H-1, H-4), 6.11 (1 H, d, $J = 6.8$ Hz, H-3), 7.08–7.11 (2 H, m, ArH), 7.19–7.30 (3 H, m, ArH), 7.5–7.7 (3 H, m, ArH), 8.02–8.06 (2 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 32.2, 44.3, 58.9, 59.6, 89.4, 105.0, 126.9, 128.4, 129.1, 129.3, 130.4, 133.7, 135.7, 139.7, 208.3; MS (rel. int.) m/z 468 (M$^+$, 0.02), 218 (27), 210 (8), 186 (12), 152 (19), 125 (100), 110 (41), 97 (39), 77 (76); HRMS Calc. for $C_{21}H_{16}O_5S_2Fe$ m/z 467.9790, found 467.9784; Anal. Calc. for $C_{21}H_{16}O_5S_2Fe$: C, 53.86; H, 3.44. Found: C, 53.49; H, 3.57.

*3.4.3. Tricarbonyl[(1-4-η^4)-2,6-exo-bis-(phenylsulfonyl)-1,3-cyclohexadiene]iron (**9c**)*

Yellow solid, m.p. 175.2–175.8°C; IR (film) 3064, 2923, 2066 (CO), 1996 (CO), 1447, 1309 (SO), 1146 (SO), 1085, 740, 726, 687 cm^{-1}; ^{1}H-NMR (CDCl$_3$) 1.91–2.02 (2 H, m, H-5), 3.27–3.31 (1 H, m), 3.47–3.53 (2 H, m), 6.19 (1 H, d, $J = 6.9$ Hz, H-3), 7.46–7.51 (2 H, m, ArH), 7.56–7.73 (6 H, m, ArH), 8.15–8.18 (2 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 26.1, 49.2, 58.4, 62.7, 90.0, 106.3, 128.1, 128.8, 129.2, 129.3, 133.9, 134.0, 138.7, 139.3, 207.8; MS (rel. int.) m/z 444 (M$^+$ − 2 CO, 1.82), 351 (15), 291 (47), 275 (13), 218 (36), 125 (100), 110 (22), 97 (17), 84 (18), 77 (45); HRMS Calc. for $C_{21}H_{16}O_7S_2Fe$ m/z 499.9688, found 499.9675

*3.4.4. Tricarbonyl[1-exo-diethyl [(2-5-η^4)-3-(phenylsulfonyl)-2,4-cyclohexadienyl]malonate]iron (**9d**)*

Yellow solid, m.p. 106.2–107.0°C; IR (film) 3065, 2983, 2939, 2061 (CO), 1984 (CO), 1728 (CO), 1583, 1447, 1368, 1306 (SO), 1220, 1160 (SO), 1094, 1027, 758, 734, 690 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 1.14 (3 H, t, $J = 7.7$ Hz, CH$_3$), 1.17 (1 H, d, $J = 15.6$ Hz, H$_{exo}$-6), 1.27(3 H, t, $J = 7.7$ Hz, CH$_3$), 2.0–2.06(1 H, m, H$_{endo}$-6), 2.23 (1 H, d, $J = 10.9$ Hz, CH(CO$_2$Et)$_2$), 2.85–2.75 (1 H, m, H-1), 3.17 (1 H, ddd, $J = 2.2$, 4.1, 6.6 Hz, H-5), 3.61 (1 H, dd, $J = 1.6$, 3.5 Hz, H-2), 4.0 (2 H, q, $J = 7.7$ Hz, OCH$_2$), 4.11–4.23 (2 H, q, $J = 7.7$ Hz, OCH$_2$), 5.94 (1 H, d, $J = 6.6$ Hz, H-4), 7.55–7.70 (3 H, m, ArH), 7.98–8.02 (2 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 13.8, 13.9, 27.9, 37.4, 58.9, 59.2, 59.5, 61.5, 61.6, 88.8, 105.9, 128.0, 129.4, 133.7, 139.9, 161.3, 167.3, 208.4; MS (rel. int.) m/z 518 (M$^+$, 0.14), 433 (31), 364 (42), 319 (53), 291 (31), 275 (100), 210 (20), 133 (27), 91 (28), 77 (22); HRMS Calc. for C$_{22}$H$_{22}$O$_9$SFe m/z 518.0334, found 518.0315; Anal. Calc. for C$_{22}$H$_{22}$O$_9$SFe: C, 50.98; H, 4.28. Found: C, 50.95; H, 4.21.

*3.4.5. Tricarbonyl[1-exo-methyl[(2-5-η^4)-3-(phenylsulfonyl)-2,4-cyclohexadienyl]acetoacetate]iron (**9e**)*

Yellow solid, inseparable diastereomeric mixture (1:1), m.p. 108.9–110.0°C; IR (film) 3065, 3007, 2954, 2849, 2061 (CO), 1988 (CO), 1743, 1715, 1583, 1447, 1321 (SO), 1289, 1160 (SO), 1093, 758, 735, 689 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 0.92 (d), 1.12 (d), 1.92 (s), 1.94 (s), 1.97–2.05 (m), 2.34 (d), 2.49 (d), 2.79–2.84 (m), 3.13–3.18 (m), 3.46–3.51 (m), 3.54 (s), 3.70 (s), 5.87–5.95 (m), 7.56–7.71 (m, ArH), 7.94–7.98 (m, ArH); ^{13}C-NMR (CDCl$_3$) δ 27.9, 28.3, 28.7, 29.3, 36.3, 36.9, 52.4, 52.5, 58.0, 58.6, 59.5, 59.6, 66.9, 67.2, 88.6, 105.7, 105.8, 127.9, 128.1, 129.3, 129.4, 133.7, 133.8, 139.3, 139.7, 167.8, 167.9, 200.4, 200.6, 208.3; MS (rel. int.) m/z 474 (M$^+$, 0.95), 359 (37), 357 (63), 332 (29), 305 (49), 275 (100), 248 (17), 141 (47), 133 (48), 125 (19), 91 (26), 77 (36); HRMS Calc. for C$_{20}$H$_{18}$O$_8$SFe m/z 474.0072, found 474.0081; Anal. Calc. for C$_{20}$H$_{18}$O$_8$SFe: C, 50.65; H, 3.83. Found: C, 50.49; H, 3.85.

*3.4.6. Tricarbonyl[2-exo-[(2-5-η^4)-3-(phenylsulfonyl)-2,4-cyclohexadienyl]cyclohexanone]iron (**9f**)*

Yellow solid, inseparable diastereomeric mixture (1:1), m.p. 121.0–122.5°C; IR (film) 3062, 2939, 2861, 2054 (CO), 1984 (CO), 1706 (CO), 1446, 1321 (SO), 1160 (SO), 1146, 732, 689 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 0.83–0.87 (m), 0.98–1.11 (m), 1.20–1.25 (m), 1.56–1.60 (m), 1.77–1.87 (m), 1.91–2.01 (m), 2.09–2.16 (m), 3.18–3.20 (m), 3.47 (dd), 3.53 (dd), 5.91–5.97 (m), 7.55–7.70 (m, ArH), 7.96–8.04 (m, ArH); ^{13}C-NMR (CDCl$_3$) δ 24.6, 25.0, 26.6, 27.8, 28.0, 30.4, 30.7, 31.6, 37.0, 37.2, 42.1, 42.3, 56.9, 58.6, 59.2, 60.5, 61.2, 61.3, 88.2, 88.6, 105.2, 106.3, 127.9, 128.1, 129.4, 133.5, 133.6, 140.3, 140.5, 208.0, 209.0, 211.0, 211.7; MS (rel. int.) m/z 456 (M$^+$, 0.50), 372 (100), 295 (29), 291 (42), 275 (41), 247 (51), 231 (91), 210 (48), 153 (30), 133 (54), 91 (15), 77 (25); HRMS Calc. for C$_{21}$H$_{20}$O$_6$SFe m/z 456.0331, found 456.0353; Anal. Calc. for C$_{21}$H$_{20}$O$_6$SFe: C, 55.28; H, 4.42. Found: C, 55.51; H, 4.53.

*3.4.7. Tricarbonyl[1-exo-2,2-dimethyl-[(2-5-η^4)-3-(phenylsulfonyl)-2,4-cyclohexadienyl]acetaldehyde]iron (**9g**)*

Yellow solid, m.p. 110.0–110.5°C; IR (film) 3065, 2963, 2928, 2700, 2058 (CO), 1988 (CO), 1721 (CO), 1468, 1447, 1322 (SO), 1148 (SO), 1091, 727, 688 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 0.44 (3 H, s, CH$_3$), 0.65 (3 H, s, CH$_3$), 1.15 (1 H, dt, $J = 15.7$, 2.0 Hz, H$_{exo}$-6), 1.94 (1 H, ddd, $J = 4.2$, 11.0, 15.7 Hz, H$_{endo}$-6), 2.38 (1 H, dt, $J = 3.8$, 11.0 Hz, H-1), 3.21 (1 H, ddd, $J = 2.0$, 4.2, 6.7 Hz, H-5), 3.46 (1 H, dd, $J = 1.6$, 3.8 Hz, H-2), 5.93 (1 H, d, $J = 6.7$ Hz, H-4), 7.58–7.71 (3 H, m, ArH), 8.02–8.06 (2 H, m, ArH), 9.06 (1 H, s, CHO); ^{13}C-NMR (CDCl$_3$) δ 17.6, 19.3, 25.7, 43.6, 49.8, 57.5, 60.4, 88.1, 107.4, 128.5, 129.6, 134.1, 139.8, 204.5, 208.8; MS (rel. int.) m/z 430 (M$^+$, 0.10), 374 (5.5), 346 (73), 291 (100), 274 (40), 210 (84), 133 (66), 91 (11), 77 (32); HRMS Calc. for C$_{19}$H$_{18}$O$_6$SFe m/z 430.0174, found 430.0178; Anal. Calc. for C$_{19}$H$_{18}$O$_6$SFe: C. 53.04; H, 4.22. Found: C, 53.16; H, 4.27.

*3.4.8. Tricarbonyl[(1-4-η^4)-6-exo-(2-propenyl)-2-(phenylsulfonyl)-1,3-cyclohexadiene]iron (**9h**)*

Yellow oil; IR (neat) 3070, 2913, 2055 (CO), 1984 (CO), 1639 (CO), 1446, 1323 (SO), 1162 (SO), 1146, 1104, 916, 731, 688 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 1.10 (1 H, d, $J = 15.4$ Hz, H$_{exo}$-5), 1.23–1.33 (1 H, m), 1.48–1.58 (1 H, m), 1.97 (1 H, ddd, $J = 4.0$, 10.8, 15.4 Hz, H$_{endo}$-5), 2.11–2.22 (1 H, m), 3.19 (1 H, ddd, $J = 2.4$, 4.0, 6.7 Hz, H-4), 3.50 (1 H, dd, $J = 1.6$, 3.6 Hz, H-1), 4.67 (1 H, d, $J = 17.1$ Hz), 4.81 (1 H, d, $J = 10.2$ Hz), 5.33–5.45 (1 H, m, =CH), 5.97(1 H, d, $J = 6.7$ Hz, H-3), 7.56–8.00 (3 H, m, ArH), 8.01–8.05 (2 H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ 29.5, 37.9, 42.8, 60.6, 62.4, 88.2, 105.3, 116.1, 128.0, 129.3, 133.6, 136.1, 140.3, 209.1; MS (rel. int.) m/z 400 (M$^+$, 0.66), 316 (74), 274 (41), 210 (100), 180 (11), 154 (13), 133 (65), 115 (11), 91 (13), 77 (25); HRMS Calc. for C$_{18}$H$_{16}$O$_5$SFe m/z 400.0068, found 400.0073; Anal. Calc. for C$_{18}$H$_{16}$O$_5$SFe: C, 54.02; H, 4.03. Found: C, 54.05; H, 4.05.

*3.4.9. Tricarbonyl[(1-4-η^4)-6-exo-cyano-2-(phenylsulfonyl)-1,3-cyclohexadiene]iron (**9i**)*

Yellow solid, m.p. 116.1–116.4°C; IR (film) 3064, 2232, 2068 (CO), 1999(CO), 1447, 1322 (SO), 1160 (SO), 1112, 999, 735, 687 cm^{-1}; ^{1}H-NMR (CDCl$_3$) 1.78 (1 H, d, $J = 15.8$ Hz, H$_{exo}$-5), 2.23 (1 H, ddd, $J = 3.6$, 11.6, 15.8 Hz, H$_{endo}$-5), 2.95 (1 H, dt, $J = 3.4$, 11.6 Hz, H-6), 3.31–3.35 (1 H, m, H-4), 3.50 (1 H, dd, *J* = 1.6, 3.4 Hz, H-1), 6.09 (1 H, d, *J* = 6.9 Hz, H-3), 7.58–7.71 (3H, m, ArH), 8.04–8.08 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 25.3, 29.7, 53.3, 59.4, 90.1, 104.7, 119.6, 128.0, 129.6, 134.1, 139.4, 207.3; MS (rel. int.) *m*/*z* 356 ($M^+ - CO$, 0.67), 329 (20), 301 (77), 210 (100), 176 (17), 133 (50), 125 (13), 97 (12), 77 (47); HRMS Calc. for $C_{16}H_{11}NO_5SFe$ *m*/*z* 384.9708, found 384.9724; Anal. Calc. for $C_{16}H_{11}NO_5SFe$: C, 49.89; H, 2.88. Found: C, 49.91; H, 2.90.

*3.4.10. Tricarbonyl[1-exo-[(2-5-η^4)-3-(phenylsulfonyl)-2,4-cyclohexadienyl]propan-2-one]iron **(9j)***

Yellow oil; IR (neat) 3064, 2923, 2057 (CO), 1986 (CO), 1714 (CO), 1447, 1322 (SO), 1156 (SO), 1094, 759, 731, 690cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.0 (1 H, d, *J* = 15.6 Hz, H_{exo}-6), 1.61 (1 H, dd, *J* = 5.7, 17.4 Hz), 1.79 (3 H, s, CH_3), 1.86 (1 H, d, *J* = 5.7 Hz), 2.12 (1 H, ddd, *J* = 3.9, 11.0, 15.6 Hz, H_{endo}-6), 2.51 (1 H, m, H-1), 3.17 (1 H, ddd, *J* = 2.4, 3.9, 6.6 Hz, H-5), 3.44 (1 H, dd, *J* = 1.6, 3.7 Hz, H-2), 5.91 (1 H, d, *J* = 6.6 Hz, H-4), 7.57–7.72 (3 H, m, ArH), 8.02 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 29.5, 30.6, 32.5, 51.9, 60.5, 61.0, 88.3, 105.1, 128.1, 129.4, 133.7, 140.2, 206.0, 208.0; MS (rel. int.) *m*/*z* 416 (M^+, 0.33), 332 (100), 289 (22), 274 (40), 255 (24), 210 (97), 191 (61), 91 (51), 113 (17), 91 (34), 77 (30); HRMS Calc. for $C_{18}H_{16}O_6SFe$ *m*/*z* 416.0017, found 415.9989; Anal. Calc. for $C_{18}H_{16}O_6SFe$: C, 51.94; H, 3.87. Found: C, 52.44; H, 4.18.

*3.4.11. Tricarbonyl[(1-4-η^4)-6-exo-methyl-2-(phenylsulfonyl)-1,3-cyclohexadiene]iron **(9k)***

Yellow solid, m.p. 84.5–85.0°C; IR (film) 3065, 2955, 2865, 2055 (CO), 1984 (CO), 1731, 1446, 1321 (SO), 1150 (SO), 1102, 728, 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.44 (3 H, d, *J* = 6.8 Hz, CH_3), 1.0 (1 H, d, *J* = 16.1 Hz, H_{exo}-5), 2.06 (1 H, ddd, *J* = 3.9, 10.8, 16.1 Hz, H_{endo}-5), 2.18–2.23 (1 H, m, H-6), 3.14–3.18 (1 H, m, H-4), 3.44 (1 H, d, *J* = 3.7 Hz, H-1), 5.96 (1 H, dd, *J* = 1.6, 3.9 Hz, H-3), 7.55–7.68 (3 H, m, ArH), 8.01–8.05 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 23.9, 32.0, 32.5, 60.7, 64.6, 88.1, 96.0, 125.1, 129.3, 133.5, 140.4, 209.2; MS (rel. int.) *m*/*z* 374 (M^+, 0.9), 318 (46), 290 (52), 288 (57), 224 (100), 210 (13), 133 (48), 95 (28), 91 (48), 77 (38); HRMS Calc. for $C_{16}H_{14}O_5SFe$ *m*/*z* 373.9911, found 373.9890; Anal. Calc. for $C_{16}H_{14}O_5SFe$: C, 51.36; H, 3.77. Found: C, 51.73; H, 3.82.

*3.5. General procedure for the demetallation of diene iron complexes **10** (Table 4)*

Condition A: To a solution of an iron complex **9** (0.50 mmol) in wet acetone (5 ml) at 0°C was added ceric ammonium nitrate (0.82 g, 1.50 mmol) over a 5 min period and then the mixture was stirred to r.t. for another 10 min. To the mixture was added water (10 ml). After removal of the solvent, the mixture was extracted with diethyl ether (2 × 20 ml). Condition B: To a solution of anhydrous trimethylamine *N*-oxide (0.33 g, 3.0 mmol) in dry benzene (5 ml) was added a solution of complex **9** (0.50 mmol) in benzene (1 ml), and then the solution was heated at reflux for 1.5 h. To the brown solution was added water (10 ml) and the solution was extracted with diethyl ether (2 × 20 ml). The organic layer was dried ($MgSO_4$) and evaporated. The residue was passed through a flash column of silica gel using hexane/ethyl acetate (10/1 to 6/1) as eluent to give **10**.

*3.5.1. 6-Methoxy-2-(phenylsulfonyl)-1,3-cyclohexadiene **(10a)***

Colorless oil; IR (neat) 3060, 2928, 2824, 1584, 1446, 1305 (SO), 1153 (SO), 1092, 1073, 718, 689 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.34–2.41(2 H, m, H-5), 3.30 (3 H, s, CH_3), 4.15 (1 H, dt, *J* = 4.0, 8.6 Hz, H-6), 6.00 (1 H, ddd, *J* = 0.6, 4.1, 8.2 Hz, H-4), 6.07 (1 H, dd, *J* = 1.0, 8.2 Hz, H-3), 6.91 (1 H, dd, *J* = 1.0, 4.0 Hz, H-1), 7.44–7.55 (3 H, m, ArH), 7.81–7.84 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 28.5, 56.0, 72.3, 118.2, 128.0, 129.3, 129.9, 131.6, 133.5, 139.5, 140.4; MS (rel. int.) *m*/*z* 250 (M^+, 19), 143 (23), 141 (17), 125 (39), 109 (73), 108 (100), 94 (28), 77 (86); HRMS Calc. for $C_{13}H_{14}O_3S$ *m*/*z* 250.0665, found 250.0669; Anal. Calc. for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.49; H, 5.62.

*3.5.2. 6-Phenylthio-2-(phenylsulfonyl)-1,3-cyclohexadiene **(10b)***

Colorless oil; IR (neat) 3058, 2926, 1582, 1478, 1446, 1306 (SO), 1152 (SO), 1092, 1023, 750, 729, 688 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.63–2.71 (2 H, m, H-5), 4.04 (1 H, ddd, *J* = 4.5, 5.4, 8.7 Hz, H-6), 5.81–5.83 (1 H, m, H-4), 5.98–6.04 (1 H, m, H-3), 6.90 (1H, d, *J* = 5.4 Hz, H-1), 7.23–7.29 (3 H, m, ArH), 7.37–7.40 (2 H, m, ArH), 7.63–7.83 (3 H, m, ArH), 7.83–7.87 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 28.5, 41.8, 118.1, 127.7, 128.0, 128.2, 128.3, 129.1, 129.2, 132.3, 132.6, 133.8, 133.4, 138.0; MS (rel. int.) *m*/*z* 328 (M^+, 2.23), 326 (17), 235 (10), 184 (28), 141 (24), 136 (50), 135 (29), 125 (47), 110 (63), 109 (48), 77 (100); HRMS Calc. for $C_{18}H_{16}O_2S_2$ *m*/*z* 328.0594, found 328.0590.

*3.5.3. 2,6-Bis(phenylsulfonyl)-1,3-cyclohexadiene **(10c)***

Colorless oil; IR (neat) 3063, 2890, 1631 (C=C), 1581, 1445, 1305 (SO), 1205, 1153 (SO), 1079, 928, 714, 689 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.98–2.10 (1 H, m, H-5), 2.72–2.84 (1 H, m, H-5), 4.61–4.69 (1 H, m, H-6), 5.88–5.98 (2 H, m), 7.08 (1 H, dd, *J* = 1.7, 4.0 Hz, H-1), 7.33–7.39 (2 H, m, ArH), 7.53–7.59 (3 H, m, ArH), 7.64–7.73 (3 H, m, ArH), 7.78–8.05 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 24.7, 64.1, 117.6, 127.4, 128.3, 128.7, 129.4, 129.7, 130.4, 133.9, 134.0, 134.8, 138.1, 144.6; MS (rel. int.) m/z 360 (M^+, 0.85), 265 (13), 219 (81), 152 (13), 141 (71), 125 (96), 110 (14), 97 (30), 77 (100); HRMS Calc. for $C_{18}H_{16}O_4S_2$ m/z 360.0492, found 360.0472; Anal. Calc. for $C_{18}H_{16}O_4S_2$: C, 59.98; H, 4.47. Found: C, 59.77; H, 4.47.

*3.5.4. 6-(2-Propenyl)-2-(phenylsulfonyl)-1,3-cyclohexadiene (**10h**)*

Colorless oil; IR (neat) 3066, 2924, 1639 (C=C), 1584, 1446, 1305 (SO), 1153 (SO), 1095, 919, 758 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.02–2.08 (1 H, m), 2.17–2.29 (3 H, m), 2.52–2.69 (1 H, m, H-6), 5.02–5.09 (2 H, m, =CH_2), 5.68–5.80 (1 H, m, =CH), 5.86–5.96 (1 H, m, H-4), 6.05 (1 H, dd, $J = 1.8$, 9.8 Hz, H-3), 6.84 (1 H, dd, $J = 1.8$, 3.8 Hz, H-1), 7.49–7.62 (3 H, m, ArH), 7.84–7.88 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ 27.0, 33.2, 37.4, 117.5, 118.4, 127.7, 129.1, 129.6, 133.2, 135.0, 138.2, 138.5, 140.0; MS (rel. int.) m/z 260 (M^+, 1.69), 219(23), 141 (83), 125 (42), 115 (15), 91(21), 77 (100); HRMS Calc. for $C_{15}H_{16}O_2S$ m/z 260.0872, found 260.0875.

*3.5.5. 6-(2-Oxopropyl)-2-(phenylsulfonyl)-1,3-cyclohexadiene (**10j**)*

Colorless oil; IR (neat) 3063, 2927, 1713 (CO), 1447, 1411, 1360, 1306 (SO), 1152 (SO), 1087, 1022, 998, 758, 688 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.94–2.00 (1H, m, H 5), 2.13 (3 H, s, CH_3), 2.27–2.34 (1 H, m, H-5), 2.59 (1 H, dd, $J = 1.7$, 4.6 Hz, CHCO), 2.61 (1 H, dd, $J = 2.8$, 4.6 Hz, CHCO), 3.02–3.06 (1 H, m, H-6), 5.89 (1 H, ddd, $J = 3.5$, 4.4, 9.8 Hz, H-4), 6.07 (1 H, ddd, $J = 1.7$, 9.8 Hz, H-3), 6.80 (1 H, dd, $J = 1.7$, 4.4 Hz, H-1), 7.48–7.62 (3 H, m, ArH), 7.83–7.86 (2 H, m, ArH); ^{13}C-NMR ($CDCl_3$) 27.1, 28.8, 30.2, 46.2, 118.5, 127.7, 129.1, 129.3, 133.2, 137.7, 138.7, 139.8, 205.9; MS (rel. int.) m/z 276 (M^+, 0.75), 232 (53), 219 (47), 141 (24), 125 (52), 107 (16), 97 (18), 91 (68), 90 (38), 77 (91), 43 (100); HRMS Calc. for $C_{15}H_{16}O_3S$ m/z 276.0821, found 276.0635.

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