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Synthetic Applications of Tricarbonyl [η^5-1-(phenylsulfonyl)-cyclohexadienyl]iron(I) Complex

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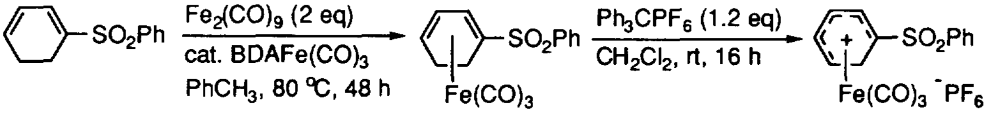
ABSTRACT : The title compound **3** reacted with soft nucleophiles to give η^4-complex **4** as the only product, but in the case of hard nucleophiles, the σ,η^3-complex **5** was also obtained. Synthetic applications of the addition products were also studied. Copyright © 1996 Elsevier Science Ltd

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 reaction. The nucleophiles and the reaction conditions 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 addition reactions of [η^4-2-(phenylsulfonyl)-1,3-butadiene]tricarbonyl 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-dienylium ions.[7] Thus, even weak nucleophiles such as acetone or enamines can give the addition products in good yield.[8] Although many alkyl- or alkoxy- substituted η^5-cyclohexadienyliron complexes have been reported for such reactions,[7] the only electron-withdrawing substituent on the diene that has been described was an ester group.[9] We now report the first synthesis and nucleophilic addition reactions of a sulfone-substituted dienylium iron complex **3**, and some synthetic applications of the addition products **4**.

Complexation of 1-(phenylsulfonyl)-1,3-cyclohexadiene **1**[10] with 2 equiv of $Fe_2(CO)_9$ in warm toluene catalyzed by (benzylideneacetone)$Fe(CO)_3$[11] gave the diene complex **2** in 76% yield. Subsequent hydride abstraction with $Ph_3C^+PF_6^-$ regiospecifically provided η^5-dienylium complex **3** in quantitative yield which was fully characterized by spectroscopic and analytical methods.



1 **2** (76%) **3** (98%)

The complex **3** reacted with a range of nucleophilic reagents (Table 1) including heteroatom nucleophiles (entries 1-3), cyanide (entry 4), stabilized carbon nucleophiles (entries 5-7), silyl enol ether and enamine (entries 8, 9), acetone and allylsilane (entries 10, 11) and functionalized zinc-copper reagent (entry 12). All of them added at the C-5 position to give the η^4-complex **4** efficiently with complete regio- and stereospecificity. The reactions of complex **3** with hard nucleophiles such as methyllithium (entry 13) or the enolate of ethyl acetate (entry 14) gave the C-5 as well as the C-2 ad dition products. The structure of **5n** was confirmed by the X-ray crystallography.[12] It can be seen from these results that the dienylium iron complex **3** is very reactive with various nucleophiles. The products **4** could in principle be further reacted with other nucleophiles.[1]

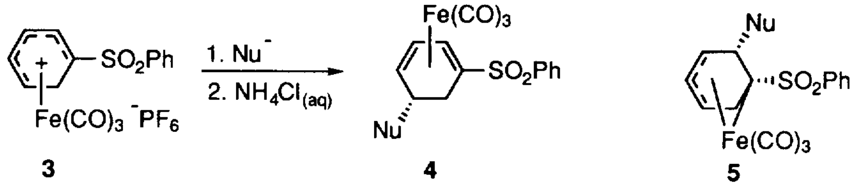
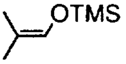
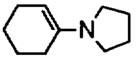
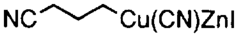
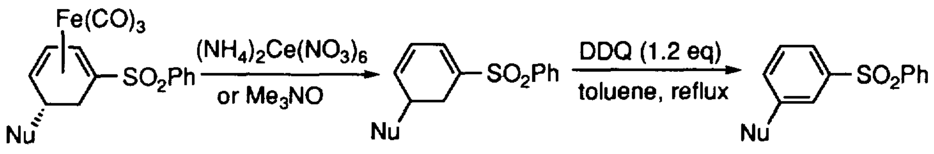


Table 1. Nucleophilic Addition Reactions of Dienylium Iron Complex **3**

Entry	Nucleophile	Condition	Product (% Yield)	
1	MeOH	neat, 25 °C, 24 h	**4a** (88)	
2	NaSPh	THF, -78 °C, 1 h	**4b** (91)	
3	$NaSO_2Ph$	THF, 24 °C, 30 min	**4c** (92)	
4	TMSCN	CH_3CN, reflux, 4 h	**4d** (86)	
5	$NaCH(CO_2Me)_2$	THF, -78 °C, 1 h; 26 °C, 1 h	**4e** (91)	
6	$NaCH(CO_2Me)COMe$	THF, -78 °C, 15 min; 26 °C, 30 min	**4f** (98)	
7	$NaCH(CO_2Me)SO_2Ph$	THF, -78 °C, 1 h; 26 °C, 1 h	**4g** (86)	
8		CH_2Cl_2, 29 °C, 12 h	**4h** (66)	
9		CH_3CN, 22 °C, 1 h	**4i** (72)	
10		CH_3CN, 21 °C, 4 h	**4j** (56)	
11	CH_3COCH_3	neat, 20 °C, 26 h	**4k** (85)	
12		THF, -78 °C to 29 °C, 1.5 h; 50 °C, 1.5 h	**4l** (82)	
13	MeLi	CH_2Cl_2, -78 °C, 5 min	**4m** (47)	**5m** (6)
14	$LiCH_2CO_2Me$	THF, -78 °C, 1 h	**4n** (57)	**5n** (29)

The demetallation reactions of complexes **4** were also studied (Table 2). Treatment of the addition product **4** with $(NH_4)_2Ce(NO_3)_6$ (Condition A) or anhydrous Me_3NO (Condition B) gave the sulfone-substituted dienes **6** which should be quite useful for further synthetic applications.[13] The diene **6** could be further aromatized by treatment wih DDQ to give **7** bearing the sulfonyl group *meta* to the nucleophiles, which are rather difficult to prepare by other means.



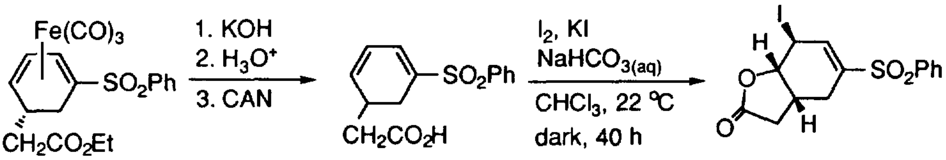
4 **6** Nu = OMe 75% **7**

Table 2. Demetallation of Addition products **4** to Give Dienes **6**

Entry	Complex **4**	Condition[a]	% Yield of **6** A	 B
1	Nu = OMe		77	75
2	Nu = SO_2Ph		82	68
3	Nu = $CH(CO_2Me)COMe$		88	
4	Nu = $CH_2(CH_2)_2CN$		80	79
5	Nu = CH_2COMe		74	51[b]
6	Nu = CH_2CO_2H		86	

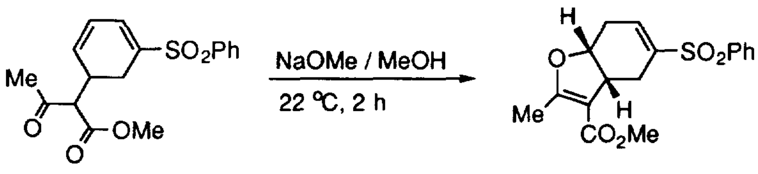
[a] Condition A : 3 equiv of $(NH_4)_2Ce(NO_3)_6$ (CAN) in wet acetone at 0 °C for 2 min, and then at rt for 10 min before quenching with H_2O. Condition B : 6 equiv of anhydrous Me_3NO in refluxing benzene for 1.5 h, followed by Celite filtration. [b] 19% yield of aromatized product **7** was also obtained.

Hydrolysis and demetallation of **4n** gave the product **8** which underwent iodolactonization to give the bicyclic lactone **9** in good yield. The reactions of **9** with various nucleophiles and reducing agents as well as with functionalized dienes are currently under study.



4n **8** (80 %) **9** (71%)

The keto ester **10** was cyclized under basic condition to afford the bicyclic enol ether **11**.



10 **11** (45%)

In summary, the sulfone-substituted dienylium iron complex **3** reacted with various nucleophiles with high regio- and stereoselectivity. The products could be converted to substituted dienyl sulfones, *meta*- substituted aryl sulfones, and bicyclic vinyl sulfones, which are all very useful in organic synthesis.

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12. Crystal data for **5n** : $C_{19}H_{18}FeO_7S$, Mr = 446.2, monoclinic, $P2_1/n$, a = 7.9910(10) Å, b = 11.984 (4) Å, c = 20.568 (2) Å, β = 90.790 (0), V = 1969.5 (7) Å^3, Z = 4, Dx = 1.505 Mg / m^3, λ (MoKα) = 0.71073 Å, μ = 0.910 mm^{-1}, F(000) = 920, T = 298 K. Sample was studied on an automatic diffractometer Siemens P4. Structure was solved with a Patterson map and refined by full-matrix least-square techniques with the resulting R =3.58 %, Rω = 3.14 % and Sω = 1.97 (residual $\Delta\rho < 0.21$ eÅ^{-3}).
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