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Synthetic Applications of Tricarbonyl [η⁵-1-(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 $[\eta^4-2-(\text{phenylsulfonyl})-1,3-$ 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 Fe₂(CO)₉ in warm toluene catalyzed by (benzylideneacetone)Fe(CO)₃¹¹ gave the diene complex 2 in 76% yield. Subsequent hydride abstraction with Ph₃C⁺PF₆⁻ regiospecifically provided η^5 -dienylium complex 3 in quantitative yield which was fully characterized by spectroscopic and analytical methods.

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 ℃, 24 h	4a (88)
2	NaSPh	THF, -78 ℃, 1 h	4b (91)
3	NaSO ₂ Ph	THF, 24 °C, 30 min	4c(92)
4	TMSCN	CH ₃ CN, reflux, 4 h	4d(86)
5	NaCH(CO ₂ Me) ₂	THF, -78 °C, 1 h; 26 °C, 1 h	4e (91)
6	NaCH(CO ₂ Me)COMe	THF, -78 °C, 15 min;	4f (98)
7	NaCH(CO ₂ Me)SO ₂ Ph	26 ℃, 30 min THF, -78 ℃, 1 h; 26 ℃, 1 h	4g (86)
8	>́ ^{otms}	CH₂Cl₂, 29 ⁰C, 12 h	4h (66)
9		CH₃CN, 22 ℃, 1 h	4i (72)
10	TMS	CH₃CN, 21 ℃, 4 h	4j (56)
11	CH₃COCH₃	neat, 20 °C, 26 h	4k (85)
12	NC ^{Cu} (CN)ZnI	THF, -78 °C to 29 °C, 1.5 h; 50 °C, 1.5 h	41(82)
13	MeLi	CH ₂ Cl ₂ , -78 °C, 5 min	4m(47) 5m (6)
14	LiCH ₂ CO ₂ Me	THF, -78 ℃, 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 Me₃NO (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.



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

		% Yield of 6		
Entry	Complex 4	Condition ^a A	В	
1	Nu = OMe	77	75	
2	$Nu = SO_2Ph$	82	68	
3	Nu = CH(CO ₂ Me)COMe	88		
4	$Nu = CH_2(CH_2)_2CN$	80	79	
5	Nu = CH ₂ COMe	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 H₂O. Condition B : 6 equiv of anhydrous Me₃NO 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.



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



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, P2₁ / n, a = 7.9910(10) Å, b = 11.984 (4) Å, c = 20.568 (2) Å, β = 90.790 (0), V = 1969.5 (7) Å³, Z = 4, Dx = 1.505 Mg / m³, λ (MoK α) = 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 fullmatrix least-square techniques with the resulting R =3.58 %, R ω = 3.14 % and S ω = 1.97 (residual $\Delta \rho < 0.21 e Å^{-3}$).
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