New Reaction Pathways for Fischer Carbene Complexes: [6 + 3] Cycloaddition of Chromium Alkenyl Carbene Complexes with Fulvenes

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Since their discovery by E. O. Fischer[1] the heteroatom-stabilized carbene complexes have been widely utilized in synthesis of acyclic and cyclic molecules.[2] The particular nature of the metal−carbon double bond has allowed the efficient accomplishment, among others, of various carbocyclization model processes wherein the carbene ligand acts as, (i) a one-carbon synthon, as for simple carbene complexes ([1 + 2],[3] [1 + 2 + 1],[4] [1 + 2 + 2], and [1 + 4][5] cyclizations), (ii) a three-carbon synthon, as for alkenyl carbene complexes ([3 + 2],[6] [3 + 3],[7] [3 + 2 + 1],[8] [3 + 4][9,6a,c] cyclizations), and (iii) a five-carbon synthon, as for enyne carbene complexes ([5 + 2 + 1][10] cyclization). We have focused our studies on alkenyl carbene complexes, and we found that their cyclization toward nucleophilic alkenes and dienes gives rise to five- and seven-membered carbocycles, whose formation involves nucleophilic 1,2-addition followed by cyclization promoted by a [1,2]-$M(CO)_5$ shift.[6a]

Continuing our interest to develop new reactivity models for carbene complexes we fixed our attention on pentafulvenes, a particular type of polar system that features an unconventional structure with a unique C=C bond conjugation pattern. Actually, different types of cycloaddition reactions of fulvenes that illustrate their versatility have been uncovered, for example, [2 + 1], [2 + 2], [2 + 4], [4 + 2], [4 + 3], and even [6 + 4] processes.[11] On the contrary, examples involving the [6 + 3] carbocyclization are almost unknown. A recent report shows that 2-oxyallyl cations
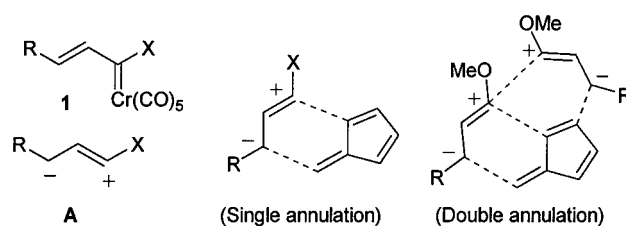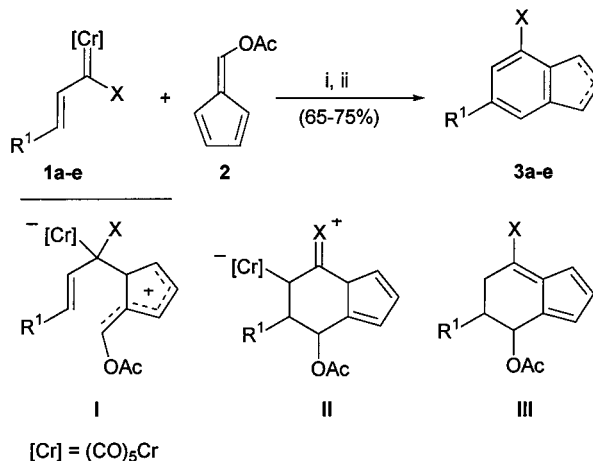
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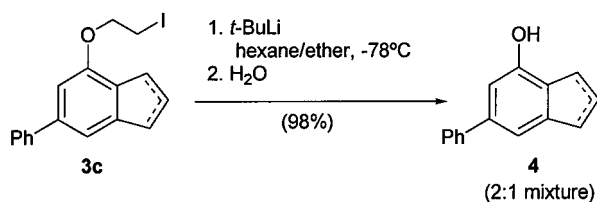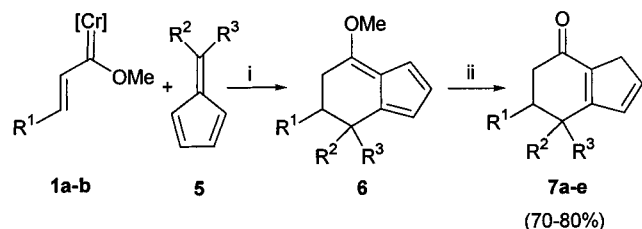(8) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Waters, M. L.; Bos, M. E.; Wulff, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 6403.
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Figure 1.

Scheme 1[a]

[Cr] = (CO)5Cr

[a] (i) MeCN, 80 °C (X = OR) or toluene, 100-200 °C (X = NR2); (ii) SiO2, CH2Cl2.

Table 1. Indenes **3** Prepared from Carbene Complexes **1a−e** and 6-Acetoxyfulvene **2**

carbene complex	R^1	X	product[a]	T (°C)	yield (%)[b]
1a	2-Furyl	OMe	**3a**	80	75
1b	Ph	OMe	**3b**	80	72
1c	Ph	OCH2CH2I	**3c**	80	69
1d	CO2Et	N(CH2)4	**3d**	100	69
1e	Ph	NMe2	**3e**	120	65

[a] Mixture of isomers (1:1 for **3a,c,d** and 2:1 for **3b,e**). [b] Isolated yields after column chromatography (silica gel, hexanes/ethyl acetate 5:1).

undergo this process only with a particular type of activated fulvene, specifically fulvene ketene acetals, while in all other cases the fulvene system prefers to cycloadd in a [4 + 3] fashion.[12,13]

We have initiated the study of the reaction between alkenyl Fischer carbene complexes with fulvenes, and herein are reported the preliminary results which can be regarded as the first [6 + 3] cycloaddition of metal carbene complexes. It is shown that alkenyl carbene complexes **1** act as the synthon **A** which produces a single annulation or even a double annulation (Figure 1).

We have checked the reactivity of chromium alkenyl carbene complexes **1** toward 6-acetoxyfulvene **2** (Scheme 1, Table 1). First, the reaction of the alkoxycarbene complexes **1a−c** (X = OMe, OCH2CH2I) with 6-acetoxyfulvene **2** (1.5 equiv) went to completion after heating in acetonitrile at 80 °C for 8 h. Removal of the solvent followed by column chromatography purification afforded the substituted indenes **3a−c** (69−75%) as mixtures of isomers.[14] Interestingly, despite the well-known reluctance of

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(13) The electron-rich 6-dimethylaminofulvene and tetramethyloxyallyl cation produces the [6 + 3] cycloadduct in a yield as low as 17%. See: Ishizu, T.; Mori, M.; Kanematsu, K. *J. Org. Chem.* **1981**, *46*, 526.

Scheme 2

Scheme 3[a]

[Cr] = (CO)$_5$Cr

[a] (i) MeCN, 80 °C; (ii) 1 N HCl, CH$_2$Cl$_2$.

Table 2. Indanones **7** Prepared from Carbene Complexes **1a,b** and Fulvenes **5**

entry	R^1	R^2	R^3	product	yield (%)^a
1	2-furyl	Me	Me	**7a**	80
2	Ph	Me	Me	**7b**	74
3	2-furyl	i-Pr	H	**7c**^{b}	70
4	2-furyl	CH=CH−Ph-(E)	H	**7d**^{b}	71
5	2-furyl	CH$_2$CH$_2$CO$_2$Me	Me	**7e**^{b}	75

^{a} Isolated yields after column chromatography (silica gel, hexanes/ethyl acetate 5:1). ^{b} Mixture of diastereoisomers (nearly 1:1).

Scheme 4[a]

R = 2-Furyl

[a] (i) KH, DME, 0 °C, 30 min; (ii) MeCOCl, 0→25 °C; (iii) **1a**, MeCN, 100 °C.

aminocarbene complexes toward 1,2-addition of nucleophiles (see below for the proposed mechanism),[15] we were delighted to find that the 6-acetoxyfulvene **2** successfully cycloadded to the aminocarbene complexes **1d,e** [X = N(CH$_2$)$_4$, NMe$_2$] in toluene (100−120 °C) to furnish **3d,e** in 65−69% yield.[14]

According to the structure of the reaction product and the HOMO coefficients of the fulvene, and to previous work from our group,[16] very likely the reaction course would involve a 1,2-addition of the nucleophilic fulvene to generate the species **I** which would undergo cyclization to **II** promoted by the [1,2]-shift of chromium pentacarbonyl. Then, the formation of **3** implies carbon-to-metal hydrogen transfer/reductive metal elimination to form **III** followed by loss of AcOH and aromatization.

This protocol also allowed to produce O-unprotected 1*H*-indenol systems (Scheme 2). For example, the indene **3c**, derived from the carbene complex **1c** and **2** (Table 1), was quantitatively deprotected (3 equiv of *t*-BuLi, hexane/ether; 30 min) to provide the indenol **4** as a 2:1 mixture of isomers.[17]

Moreover, the alkenylcarbene complexes **1** were found to smoothly react with alkyl and alkenyl fulvenes **5** (Scheme 3, Table 2). Thus, the treatment of chromium complexes **1a,b** with fulvenes **5** in acetonitrile at 80 °C for 8 h resulted in the formation of dihydroindenes **6a**−**e**. Since compounds **6** decomposed during column chromatography, they were characterized by ^{1}H NMR, hydrolyzed with acid (1 N HCl, CH$_2$Cl$_2$) and purified by column chromatography to afford indanones **7a**−**e** in good overall yields (70−80%).[14] Species of the type **I** and **II** (see Scheme 1) are again thought to participate in this annulation reaction.

Unfortunately, the newly formed methoxyfulvenes **6** are actually unreactive toward further cyclization. In fact, heating **6a** (R^1 = 2-furyl; R^2 = R^3 = Me) and the carbene complex **1a** at 80−100 °C resulted only in decomposition of the carbene complex and recovery of the fulvene. However, indanones **7** were evaluated as precursors of new fulvene systems suitable for this purpose (Scheme 4). To this end **7a** was transformed into the acetoxy-fulvene **8** (96%) by deprotonation with KH followed by acet-ylation with acetyl chloride. Interestingly, the annulation of carbene complex **1a** with fulvene **8** was successfully accomplished by heating in acetonitrile (100 °C, 8 h) to furnish, after column chromatography purification, the substituted tetrahydroacenaph-thylene **9** in 50% yield.[14]

In conclusion, this paper displays the results of the first study of the reaction between Fischer carbene complexes and readily available pentafulvenes. A number of substituted indanones and indenes are accessible in a simple and regioselective way. Moreover, it is shown that new reaction pathways of Fischer carbene complexes can be discovered when exposed to uncon-ventional substrates. Specifically, the [6 + 3] cycloaddition of Fischer carbene complexes is first accomplished using fulvenes, a type of substrate that is not prone to display this kind of cyclization. As an important extension of the reaction, the acenaphthylene skeleton is easily assembled by the polycyclization reaction of dimethylfulvene with 2 equiv of carbene complex. The nucleophilic 1,2-addition of the fulvene to the metal carbene carbon followed by [1,2]-Cr(CO)$_5$-promoted cyclization accounts well for the observed products. In this respect, the 1,2-addition of a carbon nucleophile to a Fischer aminocarbene complex is described for the first time.[15]

Supporting Information Available: Experimental procedures and characterization data for the new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The structural characterization of **3**,**4**,**7**,**9** was based on the NMR data and NOESY experiments. In addition, the structure of **7** is in full accordance with related indanone structures reported by Hong et al. (ref 12). The regioisomeric indenes and indanones were not detected in the crude mixtures.

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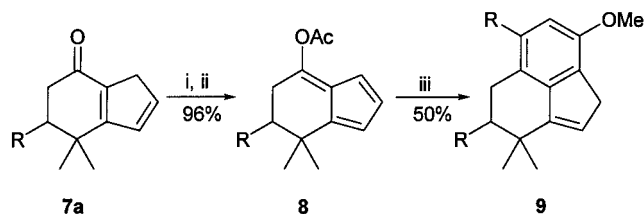
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