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[6 + 3] Cycloaddition of Fischer aminocarbene complexes: An efficient annulation of fulvenes to indene derivatives

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Abstract

Alkenyl(amino)carbene chromium(0) complexes **1** undergo regioselective [6 + 3] cycloaddition to pentafulvenes **2**, affording substituted dihydroindenes **5a–d** and indene **6**. In the case of 6,6-dimethylpentafulvene **2a** dihydroindene chromium complexes **4a–c** were also isolated. Isopropylfulvene **2b** similarly produces **5d** or, under oxidative reaction conditions, the indene **6**. The reaction involves: (i) 1,2-nucleophilic addition of fulvene to the carbene carbon, (ii) [1,2]-$Cr(CO)_5$ migration, (iii) either metal–indene coordination or reductive metal elimination/aromatization.

Keywords: [6 + 3] Annulation; Amino carbene complexes; Chromium; Pentafulvenes; Indenes

1. Introduction

Since their discovery by Fischer and Maasböl [1], heteroatom stabilized carbene complexes have demonstrated to be useful organometallic reagents for carbo- and heterocyclization reactions [2]. The flexibility as well as the varied reaction pathways that they show towards different reagents and/or reaction conditions makes them one of the most relevant organometallic species in organic synthesis mediated by transition metal complexes. In recent years, we have particularly focused on the potential of alkenyl(alkoxy)carbenes which act as a three-carbon synthon towards different substrates. In this way, a number of two-component and multicomponent cyclization reactions have been devised for synthesis of molecules with either normal and high structural complexity [3].

Recently, we found that alkenyl(alkoxy)carbenes react with pentafulvenes, a particular type of polar system due to a unique C=C bond conjugation pattern, at 80 °C in MeCN to produce efficiently indene derivatives [4]. This process was regarded as the first [6 + 3] cyclization of Fischer carbene complexes [5]. Interestingly, chromium alkenyl(amino)carbene complexes were found to be reactive towards activated fulvenes, for instance 6-acetoxyfulvene, allowing a facile access to substituted indenes (Fig. 1). This feature is of relevance in the Fischer carbene complexes area as the metal–carbon bond is much less reactive for aminocarbenes than for alkoxycarbenes [6]. Thus, the major role of the aminocarbene functionality lies generally on the activation of the Cα–H bond and of conjugated unsaturated moieties, a fact that has served to achieve some fundamental asymmetric syntheses [7].

Herein, we report an easy access to indene and dihydroindene derivatives via [6 + 3] cyclization reaction between pentacarbonyl[(alkenyl)(amino)carbene]chromium(0) complexes **1** and 6-alkyl- and 6,6-dialkylpentafulvenes **2** (Fig. 2).

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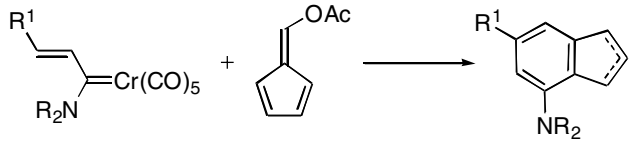
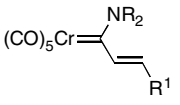
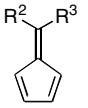


Fig. 1. [6 + 3] Cyclization of Fischer alkenyl aminocarbenes and 6-acetoxyfulvene.



1

NR_2	R^1	Compound
NMe_2	Ph	**1a**
NMe_2	2-Fu	**1b**
$N(CH_2)_4$	CO_2Et	**1c**



2

R^2	R^3	Compound
Me	Me	**2a**
i-Pr	H	**2b**

Fig. 2. Carbene complexes **1** and fulvenes **2** used.

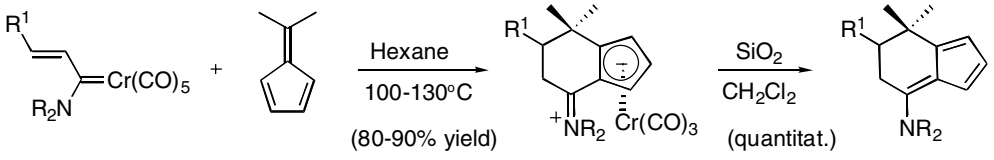
2. Results and discussion

Thus, a solution of aminocarbene **1a** (R^1 = Ph) and 6,6-dimethylfulvene **2a** in hexane was heated at 130 °C in a sealed tube. After stirring for 5 h a violet precipitate was formed. Flash chromatography purification allowed the isolation of the tricarbonyl complex **4a** in 86% yield (Scheme 1; Table 1, entry 1), wherein the fulvene ligand is best represented by means of its zwiterionic structure [8]. The adduct **4a** was formed as a sole diastereoisomer whose stereochemistry – *anti* relationship between R^1 and $Cr(CO)_3$ – was tentatively assigned on the basis of minimum steric repulsion between the R^1 substituent and the tricarbonylchromium fragment. Further demetallation of **4a** could be readily achieved at room temperature by stirring with silica gel under air to yield quantitatively the dihydroaminoindene **5a** (Table 1, entry 2). In the same way, carbene complex **1b** (R^1 = 2-furyl) and 6,6-dimethylfulvene **2a** afforded complex **4b** (80% yield) and the metal-free dihydroindene **5b** (quantitative yield from **4b**) (Table 1, entries 3, 4). Very unusual aminocarbene complexes with an electron-acceptor functionality, like complex **1c** ($R^1 = CO_2Et$), allowed to obtain the functionalized dihydroindene derivatives **4c** (90% yield) and **5c** (quantitative yield) under slightly milder reaction conditions (Table 1, entries 5, 6).

In the case of the reaction of 6-isopropylfulvene **2b** (R^2 = *i*-Pr; R^3 = H) with the carbene complex **1b** (R^1 = 2-furyl), under the same reaction conditions, the expected violet tricarbonyl(dihydroindene)chromium complex was not formed, but the metal-free product **5d** was instead isolated. Column chromatography purification afforded pure **5d** (65% yield) as an inseparable 5:1 mixture of diastereoisomers (Scheme 2). Moreover, when the reaction crude containing **5d** was taken up in hexanes/EtOAc (5:1 v/v) and subjected to light-air treatment the oxidative aromatization of the dihydroindene system took place and the trisubstituted indene **6** (72% yield) was formed as a 4:1 mixture of tautomers (Table 1, entries 7, 8) [9].

A suitable mechanism that would account for this [6 + 3] carbocyclization reaction is based on the well recognized capability of the $M(CO)_5$ fragment of metallate species to undergo 1,2-migration thus inducing unusual cyclization processes (Scheme 3) [10]. The initial 1,2-nucleophilic addition of fulvene to the electrophilic carbene carbon would lead to the zwitterionic intermediate **I**. Then a [1,2]-shift of the chromium pentacarbonyl fragment would take place and facilitate a subsequent cyclization to the intermediate **II**, which might generate the enamine intermediate **III** via consecutive metal elimination and η^2-olefin coordination. Finally, the latter would undergo either isomerization to the more stable complexes **4a–c** or metal-decoordination and tautomerization to indene derivative **5d**. A relevant finding is that the metal–carbon bond of amino carbene complexes is able to undergo 1,2-addition, a fact that is well known for alkoxy carbenes but rather rare for the much less electrophilic amino carbene analogs. In fact, the pentafulvene system can be regarded as the first carbon nucleophile reagent that adds to a Fischer aminocarbene complex in 1,2-manner [11].

Further interest of the reaction herein described can be envisaged as follows: (i) the unusual strategy of constructing the indene skeleton in the sense that most procedures are based by far on the annulation of the cyclopentene unit into the benzo ring, while the present work reports an easy benzannulation of the fulvene system, thus permitting to incorporate functionality into the aromatic domain [12], (ii) biological properties, e.g., as dopamine receptors ligands, have been reported for some amino substituted 2,3-dihydroindenes [13], (iii) since compounds **5** still maintain the reactive fulvene



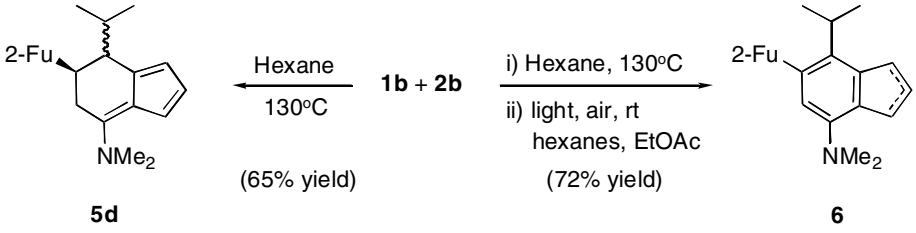
1a-c **2a** **4a-c** **5a-c**

Scheme 1. Cyclization reaction of aminocarbenes **1** with 6,6-dimethylfulvene **2a**.

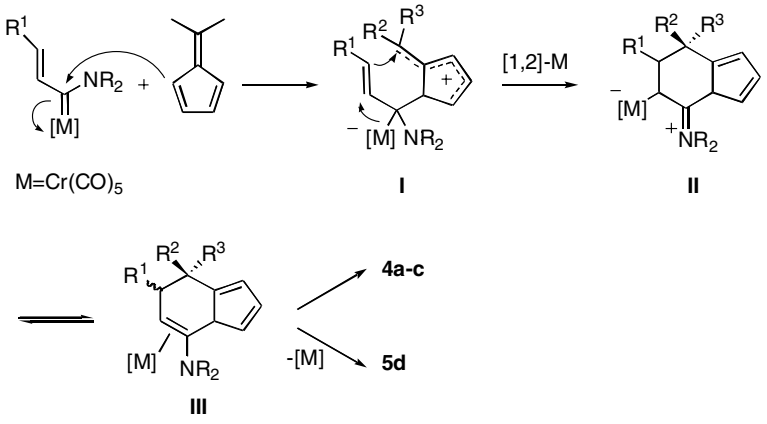
Table 1
Chromium pentacarbonyl complexes obtained by cyclization reaction of aminocarbenes **1** and fulvenes **2**, and its subsequent demetallation

#	NR_2	R^1	R^2	R^3	Product	T (°C)	Yield (%)[a]
1	NMe_2	Ph	Me	Me	**4a**	130	86
2					**5a**	20	100[b]
3	NMe_2	2-Fu	Me	Me	**4b**	130	80
4					**5b**	20	100[b]
5	$N(CH_2)_4$	CO_2Et	Me	Me	**4c**	100	90
6					**5c**	20	100[b]
7	NMe_2	2-Fu	*i*-Pr	H	**5d**[c]	130	65
8					**6**	130	72[d]

[a] Isolated yields after flash chromatography.
[b] Yields from compounds **4**.
[c] Obtained as a 5:1 mixture of diastereomers.
[d] From crude **5d** by air-light oxidation.



Scheme 2. [6 + 3] Cyclization of aminocarbene **1c** and 6-isopropylfulvene **2b**.



Scheme 3. Proposed mechanism for the [6 + 3] cyclization of carbenes **1** and fulvenes **2**.

unit they seem to be excellent candidates to produce extended polycyclic systems, a hypothesis that was demonstrated feasible in the case of alkenyl(alkoxy)carbenes [4].

3. Conclusion

In summary, we have described herein the first cyclization of alkenylaminocarbene complexes following the 1,2-addition/[1,2]-$M(CO)_5$ shift mechanistic model. This process takes place with pentafulvenes to give amino indenes in a formal [6 + 3] cyclization. Although aminocarbenes require a higher reaction temperature than the corresponding alkenyl alkoxycarbenes to be reactive, the excellent yields and the interest of the structure of the new products contribute to expand the scope of the reactivity of Fischer carbene complexes with unsaturated system and their use in cyclization processes.

4. Experimental

All reactions involving air sensitive compounds were carried out under a N_2 atmosphere (99.99%). All

glassware was oven-dried (120 °C), evacuated and purged with nitrogen. All common reagents and solvents were obtained from commercial suppliers and used without any further purification unless otherwise indicated. Fischer carbene complexes [1,6b,14] and fulvenes [15] were prepared following described procedures. Solvents were dried by standard methods and distilled prior to use. Flash column chromatography was carried out on silica gel 60, 230–240 mesh. NMR experiments were recorded on Bruker AC-200, AC-300 or DPX-300 spectrometers. ^{1}H NMR spectra were recorded in $CDCl_3$ at 300.08 MHz at 20 °C with tetramethylsilane ($\delta = 0.0$) as the internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ at 75.46 MHz at 20 °C. ^{1}H NMR splitting pattern abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; sp, septuplet; m, multiplet. ^{13}C NMR multiplicities were determined by DEPT, abbreviations are: q, CH_3; t, CH_2; d, CH; s, quaternary carbons. NOESY experiments were carried out on a Bruker AMX-400 spectrometer. Standard pulse sequences were employed for the DEPT experiments. High resolution mass spectra (HRMS) were obtained with a Finnigan Mat95 Mass Spectrometer and electron impact techni-ques (70 eV) were employed. Elemental analyses were carried out with a Perkin–Elmer 240 B microanalyzer.

4.1. General procedure for the reaction between *1a–c* and *2a*

A mixture of carbene complex **1a–c** (1 mmol) and 6,6-dimethylfulvene **2a** (1.5 mmol) in hexane (15 mL) was heated at 100–130 °C (as indicated in Table 1) in a sealed tube. After stirring for 5 h a violet solid precipitated from the solution. The solvent was removed under vacuum and the resulting chromium complex was purified by column chromatography (CH_2Cl_2/hexanes, 3:1) affording compounds **4a–c** as violet solids.

The chromium tricarbonyl complexes **4** were subsequently dissolved in CH_2Cl_2 (10 mL) and stirred with silica gel (0.5 g) for 4 h at r.t. After filtration, the solvent was removed under vacuum and the crude mixture was purified by flash chromatography (hexanes/EtOAc 1:1), yielding dihydroindenes **5a–c** quantitatively.

*Tricarbonylchromium complex (**4a**)*: yield = 86%; ^{1}H NMR (CD_2Cl_2): $\delta = 1.0$ (s, 3H); 1.1 (s, 3H), 2.9 (m, 2H); 3.3 (s, 3H); 3.5 (s, 3H); 3.6 (m, 1H); 5.0 (m, 1H); 5.2 (m, 2H); 7.1–7.4 (m, 5H); ^{13}C NMR (CD_2Cl_2): $\delta = 26.1$ (q); 26.4 (q); 34.4 (s); 35.2 (t); 44.8 (q); 46.6 (q); 50.2 (d); 80.2 (s); 84.5 (d); 84.9 (d); 90.0 (d); 124.6 (s); 128.0 (d); 128.8 (d, 2C); 130.5 (d, 2C); 140.1 (s); 175.2 (s); 240.8 (s, 3C); HRMS *m/z* calcd. for $C_{22}H_{23}CrNO_3$ 401.1081. Found: 401.1083. Anal. Calc. for $C_{22}H_{23}CrNO_3$: C, 65.83; H, 5.78; N, 3.49. Found: C, 65.78; H, 5.69; N, 3.40%.

*Tricarbonylchromium complex (**4b**)*: yield = 80%; ^{1}H NMR (CD_2Cl_2): $\delta = 1.0$ (s, 3H); 1.1 (s, 3H), 2.9 (m, 2H); 3.3 (s, 3H); 3.4 (s, 3H); 3.6 (m, 1H); 4.9 (m, 1H); 5.2 (m, 2H); 6.2 (m, 1H); 6.4 (m, 1H); 7.4 (m, 1H); ^{13}C NMR (CD_2Cl_2): $\delta = 25.8$ (q); 26.9 (q); 33.5 (t); 34.3 (s); 44.0 (q); 44.5 (q); 46.3 (d); 79.9 (s); 84.5 (d); 85.0 (d); 89.9 (d); 109.11 (d); 110.8 (d); 122.1 (s); 142.4 (d); 154.3 (s); 173.6 (s); 240.6 (s, 3C); HRMS *m/z* calcd. for $C_{20}H_{21}CrNO_4$ 391.0876. Found: 391.0872. Anal. Calc. for $C_{20}H_{21}CrNO_4$: C, 61.38; H, 5.41; N, 3.58. Found: C, 61.25; H, 5.47; N, 3.55%.

*Tricarbonylchromium complex (**4c**)*: yield = 90%; ^{1}H NMR (CD_2Cl_2): $\delta = 1.1$ (t, $J = 7.0$ Hz, 3H); 1.3 (m, 6H); 1.9–2.2 (m, 4H); 2.8–3.0 (m, 2H); 3.2 (m, 1H); 3.6–3.8 (m, 4H); 4.1–4.2 (m, 2H); 4.9 (m, 1H); 5.1 (m, 2H); ^{13}C NMR (CD_2Cl_2): $\delta = 14.9$ (c, 2C); 25.1 (t); 26.5 (q); 27.5 (q); 32.5 (t); 33.6 (s); 49.8 (d); 53.4 (t); 54.2 (t); 61.8 (t); 79.5 (s); 84.2 (d); 84.6 (d); 89.6 (d); 122.2 (s); 169.4 (s); 172.7 (s); 240.7 (s, 3C); HRMS *m/z* calcd. for $C_{21}H_{25}CrNO_5$ 423.1133. Found: 423.1135. Anal. Calc. for $C_{21}H_{25}CrNO_5$: C, 59.57; H, 5.95; N, 3.31. Found: C, 59.48; H, 6.00; N, 3.27%.

*6,7-dihydro-7,7-dimethyl-4-dimethylamino-6-phenyl-5H-indene (**5a**)*: ^{1}H NMR: $\delta = 1.1$ (s, 3H); 1.2 (s, 3H); 2.7 (dd, $J = 15.6$ and 3.3 Hz, 1H); 3.0–3.3 (m, 2H); 3.35 (s, 6H); 6.1 (dd, $J = 2.6$ and 1.8 Hz, 1H); 6.4 (dd, $J = 4.9$ and 2.6 Hz, 1H); 6.5 (dd, $J = 4.9$ and 1.8 Hz, 1H); 7.2–7.4 (m, 5H). ^{13}C NMR: $\delta = 24.7$ (q); 27.6 (c); 33.8 (t); 35.2 (s); 43.0 (q, 2C); 53.0 (d); 112.4 (d); 113.3 (s); 114.1 (d); 122.2 (d); 126.6 (d); 127.8 (d, 2C); 129.3 (d, 2C); 141.5 (s); 144.1 (s); 156.9 (s). HRMS *m/z* calcd. for $C_{19}H_{23}N$ 265.1830. Found: 265.1835. Anal. Calc. for $C_{19}H_{23}N$: C, 85.99; H, 8.74; N, 5.28. Found: C, 85.80; H, 8.81; N, 5.19%.

*6-(2-furyl)-6,7-dihydro-7,7-dimethyl-4-dimethylamino-5H-indene (**5b**)*: ^{1}H NMR: $\delta = 1.1$ (s, 3H); 1.3 (s, 3H); 2.8 (dd, $J = 17.1$ and 4.3 Hz, 1H); 3.0–3.1 (dd, $J = 17.1$ and 11.7 Hz, 1H); 3.25 (m, 1H); 3.3 (s, 6H); 6.1 (m, 2H), 6.3–7.5 (m, 3H); 7.4 (m, 1H). ^{13}C NMR: $\delta = 25.3$ (q); 27.4 (q); 32.3 (t); 35.2 (s); 43.0 (q, 2C); 46.4 (d); 106.8 (d); 109.9 (d); 112.5 (d); 113.2 (s); 114.2 (d); 122.1 (d); 140.8 (d); 143.5 (s); 156.0 (s); 156.1 (s). HRMS *m/z* calcd. for $C_{17}H_{21}NO$ 255.1623. Found: 255.1619. Anal. Calc. for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.02; H, 8.31; N, 5.44%.

*Ethyl 5,6-dihydro-4,4-dimethyl-7-(1-pyrrolidinyl)-4H-indene-5-carboxylate (**5c**)*: ^{1}H NMR: $\delta = 1.2$ (s, 3H); 1.3 (t, $J = 7.0$ Hz, 3H); 1.4 (s, 3H); 2.0 (m, 4H); 2.7 (dd, $J = 17.0$ and 3.9 Hz, 1H); 3.0 (dd, $J = 12.0$ and 3.9 Hz, 1H); 3.1 (dd, $J = 17.0$ and 12.0 Hz, 1H); 3.7 (m, 4H); 4.2 (m, 2H); 6.1 (m, 1H); 6.4 (m, 2H). ^{13}C NMR: $\delta = 14.3$ (q); 25.7 (q); 27.7 (t); 30.9 (t); 34.4 (s); 50.0 (t); 52.0 (d); 60.3 (t); 112.0 (d); 112.6 (s); 113.4 (d); 121.5 (d); 141.7 (s); 152.9 (s); 173.4 (s); HRMS *m/z* calcd. for $C_{18}H_{25}NO_2$ 287.1885. Found: 287.1879.

Anal. Calc. for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.31; H, 8.69; N, 4.90%.

4.2. Synthesis of dihydroindene **5d** and indene **6**

A solution of aminocarbene **1c** (1 mmol) and 6-isopropylfulvene **2b** (1.5 mmol) in hexane (15 mL) was heated at 130 °C in a sealed tube for 5 h. Then the solvent was removed in vacuo and the crude mixture was purified by flash chromatography (hexanes/EtOAc, 5:1) furnishing the dihydroindene **5d** in 65% yield.

Alternatively, the crude was dissolved in a mixture of hexane/EtOAc (1:1) and air oxidized in an open flask under sunlight or lamp light (6–8 h). The solution was then filtered off over Celite and the filtrate concentrated. The resulting crude was purified by flash chromatography (hexanes/EtOAc, 1:1) and the indene **6** isolated in 72% yield.

*6-(2-furyl)-6,7-dihydro-7-isopropyl-4-dimethylamino-5H-indene (**5d**)*: yield = 65%; major isomer: ^{1}H NMR: $\delta = 0.78$ (d, $J = 6.7$ Hz, 6H); 0.80 (s, 3H); 1.6–1.8 (m, 1H); 2.8–3.0 (m, 2H); 3.3 (s, 3H); 3.6 (m, 1H); 5.9 (m, 1H); 6.1 (m, 1H); 6.30 (m, 1H); 6.4–6.6 (m, 2H); 7.4 (m, 1H). ^{13}C NMR: $\delta = 21.2$ (q); 22.4 (q); 28.7 (d); 32.8 (t); 39.3 (d); 43.1 (q, 2C); 44.7 (d); 105.3 (d); 110.2 (d); 114.3 (d); 115.7 (s); 116.4 (d); 121.7 (d); 135.0 (s); 140.6 (d); 155.8 (s); 157.3 (s). HRMS *m/z* calcd. for $C_{18}H_{23}NO$ 269.1780. Found: 269.1781. Anal. Calc. for $C_{18}H_{23}NO$: C, 80.26; H, 8.61; N, 5.20. Found: C, 80.33; H, 8.54; N, 5.99%.

*7-Dimethylamino-4-isopropyl-5-(2-furyl)-1H-indene-(**6**)*: yield = 72%; Mayor tautomer: ^{1}H NMR: $\delta = 1.3$ (s, $J = 7.1$ Hz, 6H); 2.8 (s, 6H); 3.38 (sp, $J = 7.14$ Hz, 1H); 3.44 (m, 2H); 6.3 (m, 1H); 6.5 (m, 1H); 6.6 (m, 1H); 6.9 (s, 1H); 7.2 (m, 1H); 7.5 (m, 1H). ^{13}C NMR: $\delta = 23.0$ (q, 2C); 30.0 (d); 38.4 (t); 43.4 (q, 2C); 107.9 (d); 110.9 (d); 116.0 (d); 129.5 (s); 131.7 (d); 133.3 (d); 134.0 (s); 136.3 (s); 141.6 (d); 144.3 (s); 146.8 (s); 155.3 (s); HRMS *m/z* calcd. for $C_{18}H_{21}NO$ 267.1623. Found: 267.1628. Anal. Calc. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.95; H, 7.98; N, 5.20%.

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