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Copper-catalyzed dimerization of chromium Fischer carbene complexes: synthesis of dialkoxytrienes and their Nazarov-type cyclization to 2-alkoxy-2-cyclopentenones

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Abstract

Fischer carbene complexes **1** underwent a clean ligand dimerization reaction yielding functionalized olefins and trienes **4** in the presence of copper (I) catalysts. If treated with trifluoroacetic acid (TFA), trienes **4c**, **d**, **f** undergo a cyclization process (Nazarov reaction) which furnishes cyclopentenone derivatives **6c**, **d**, **7c**, **d** and **8** in good yields. Finally, the Fischer aminocarbene **9** efficiently cyclodimerizes to the substituted arene **10** in the presence of CuBr.

Keywords: Chromium carbenes; Copper(I) carbenes; Carbene transfer; Dimerization; 2-cyclopentenone; Nazarov reaction

1. Introduction

Heteroatom-stabilized transition metal–carbene complexes, particularly those derived from group 6, are recognized as versatile intermediates in organic synthesis [1]. Doubtless the most important feature of these carbene complexes lies on their ability to transfer the alkoxy carbene ligand to different unsaturated substrates [2]. However, the transfer of a carbene ligand from a metal–carbene complex to another metalic centre has received little attention until recently [3]. This represents an interesting concept as it would allow to access carbene complexes of other metals, those derived from late transition metals being of particular interest due their significance in carbon–carbon coupling reactions. In this sense, Sierra et al first proposed palladium biscarbene complexes as the active intermediates in the room temperature palladium-catalyzed dimerization of alkoxycarbene chromium complexes [4]. Aumann et al have demonstrated the transfer of carbene ligands from group 6 carbene complexes to rhodium and found a noticiable reactivity enhancement in the cyclopentannulation towards alkynes [5].

Because of our interest in this area [6], as well as the importance of Cu(I) carbenes as intermediate species for fundamental organic processes [7], we became interested in the study of the reactivity of Fischer carbene complexes in the presence of Cu(I) compounds. Thus, we reported the formation of the copper(I) bis-carbene **2** from the Fischer carbene complex **1h** by carbene ligand transfer to complex $[Cu(MeCN)_4][PF_6]$, as well as its transformation into the simple copper carbene complex **3** by crystallization in dichloromethane/diethyl ether (Scheme 1) [8]. Both carbene complexes undergo dimerization in the presence of tributylphosphane.

In this paper we report the copper(I)-catalyzed dimerization of different alkyl, phenyl, and alkenyl Fischer

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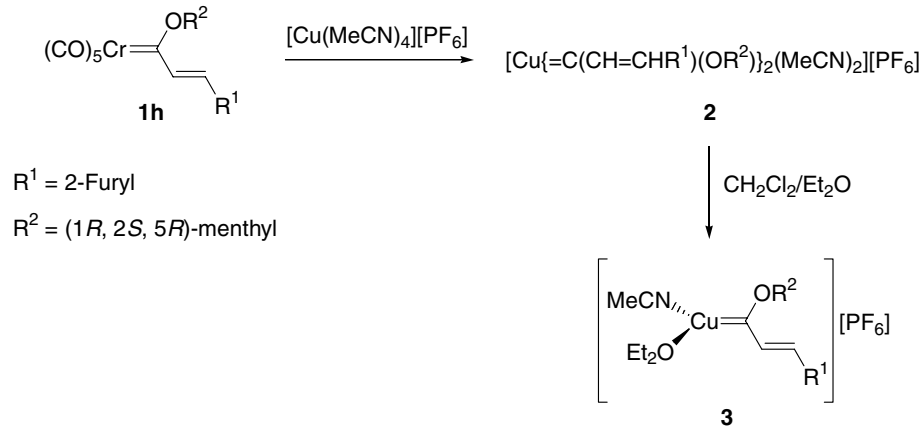
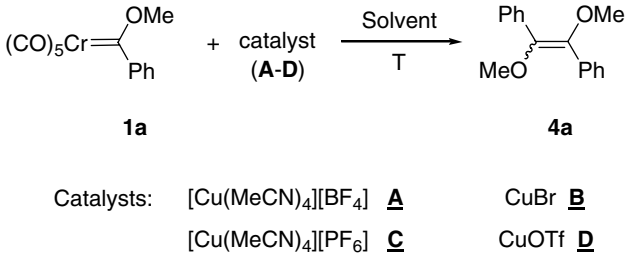


Scheme 1.

carbene complexes leading to dialkoxy alkenes and trienes. The acid-promoted Nazarov-type cyclization of the latter to 2-alkoxy-2-cyclopentenones is also reported.

2. Results and discussion

The reactivity of Fischer carbene complexes was first investigated using the carbene complex **1a** as the substrate and copper complexes **A**–**D** (Scheme 2, Table 1). In all cases the homocoupling product **4a** was formed at temperatures ranging from 25 to 50 °C. The active role of the catalyst is clear because the thermal dimerization is known to occur above 100 °C. The complex **A**, $[Cu(CH_3CN)_4][BF_4]$, was found to be the most efficient catalyst in terms of stereoselectivity (Z/E = 10) and reaction yield (90%). The stoichiometric reaction with simple copper bromide, catalyst **B**, requieres heating at 50 °C under heterogeneous conditions to produce the alkene **4a** in 70% yield as a 1:1 mixture of Z/E isomers. The catalysts **C**, $[Cu(CH_3CN)_4][PF_6]$, and **D**, CuOTf, seem to be less convenient than the structurally related **A** and **B**, respectively.



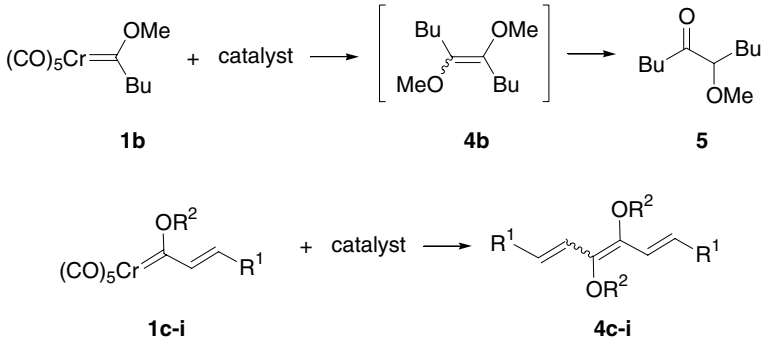
Scheme 2.

The dimerization reaction of other Fischer carbene complexes was first studied using the copper system **A** (Scheme 3, Table 2). Thus, the chromium butyl(methoxy)carbene **1b** efficiently dimerized to the corresponding dimethoxyalkene **4b** which was not isolated, but it hydrolyzed to 6-methoxy-5-decanone **5** (74% overall yield) when attempting purification by column chromatography (entry 2). Under the same reaction conditions chromium alkenyl(alkoxy)carbene complexes **1c-g** underwent clean dimerization to the 1,3,5-hexatriene derivatives **4c**–**g** in excellent yields (76–95%) and with high stereoselectivity (the 1*E*, 3*E*, 5*E*/1*E*, 3*Z*, 5*E* ratio ranging from 9:1 to >20:1) (entries 3–7). It should be noted the reverse selectivity for the dimerization reaction of the alkenyl(methoxy) carbene ligands with respect to that of the phenyl(methoxy)carbene ligand. In terms of comparison, the dimerization of chromium carbenes **1c**, **d** in the presence of CuBr (1 equiv, THF, 50 °C) leads to the dimers **4c**, **d** in lower yields (79–82%) and with no selectivity (entries 3–4) [9]. On the other hand, the treatment of carbene complexes bearing bulky alkoxy groups, like the

Table 1
Ligand-dimerization of carbene complex **1a**

Catalyst (mol%)[a]	Solvent	*T* (°C)	Yield (%)[b]	*Z*/*E*[c]
A (10)	CH_2Cl_2	25	90	10:1
B (100)	THF	50	70	1:1
C (15)	CH_2Cl_2	25	65	8:1
D (15)	THF	25	46	3:1

[a] Referred to the carbene complex **1a**.
[b] Yields of isolated products.
[c] Determined by integration of the signals corresponding to the MeO-groups in the ^{1}H NMR spectra of the crude reaction mixture.



Scheme 3.

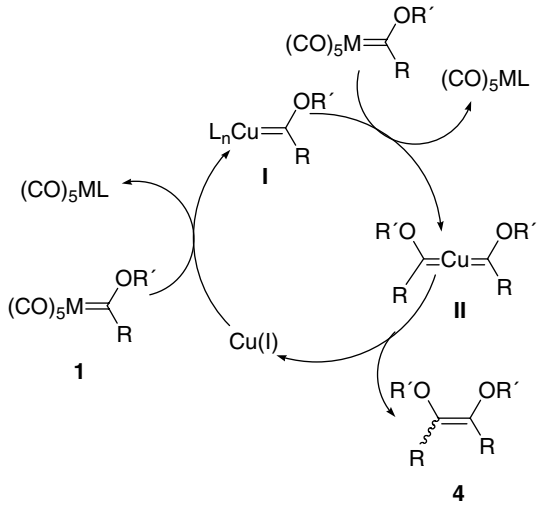
Table 2
Carbene ligand dimerization of Fischer chromium–carbene complexes **1**

Entry	Carbene	R^1	R^2	Dimer	Catalyst A[a] %; *E*/*Z*	Catalyst B[b] %; *E*/*Z*
1	**1a**			**4a**	90; 10:1	70; 1:1
2	**1b**			**4b**[c]	74	–
3	**1c**	2-Furyl	Me	**4c**	95; 10:1	79; 1:1
4	**1d**	Ph	Me	**4d**	89; 9:1	82; 1:1
5	**1e**	*p*-$MeOC_6H_4$	Me	**4e**	90; > 20:1	–
6	**1f**	Fc[d]	Me	**4f**	80; > 20:1	–
7	**1g**	Ph	CH_2CH_2I	**4g**	76; > 20:1	–
8	**1h**	2-Furyl	Ment[e]	**4h**	–[f]	75; > 20:1
9	**1i**	Ph	Ment[e]	**4i**	–[f]	70; >20:1

[a] Reaction conditions: Catalyst **A** (10 mol%), CH_2Cl_2, 25 °C, 12–18 h.
[b] Reaction conditions: Catalyst **B** (100 mol%), THF, 50 °C, 10 sh.
[c] Isolated as 6-methoxy-5-decanone **5**.
[d] Fc = Ferrocenyl.
[e] Ment = (1*R*,2*S*,5*R*)-menthyl.
[f] See [8].

alkenyl(menthyloxy)carbenes **1h**, **i** with copper catalyst **A** was reported to produce copper carbene complexes (see Scheme 1), whose dimerization takes place in the presence of tributylphosphane [8]. However, it was significant to observe that their dimerization could be promoted in a much simpler way by CuBr (entries 8, 9). Thus, the 1*E*, 3*E*, 5*E*-hexatriene derivatives **4h**, **i** were obtained from carbene complexes **1h**, **i** in good yields (70–75%) and with almost complete *E*-selectivity (>95% de) under the standard reaction conditions (1 equiv of **B**, THF, 50 °C).

A mechanistic proposal for this copper (I)-catalyzed reaction is outlined in Scheme 4 and is based on previous work from our and other groups [4,8]. Presumably, the reaction would be initiated by chromium–copper (I) exchange to form a copper (I)–carbene complex **I**. A subsequent transmetalation therefrom would generate a copper (I)–bis-carbene species **II** which would lead to the observed products and regenerate the active catalyst. The assumed participation of bis-carbene complexes of type **II** comes from our own experience with copper carbenes [8], though the direct formation of the dimerization product from monocarbene species **I** cannot definitively be ruled out.

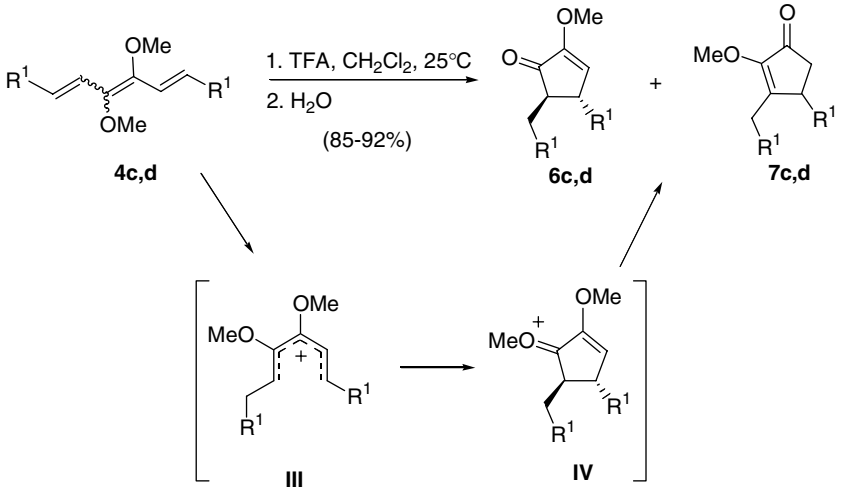


Scheme 4.

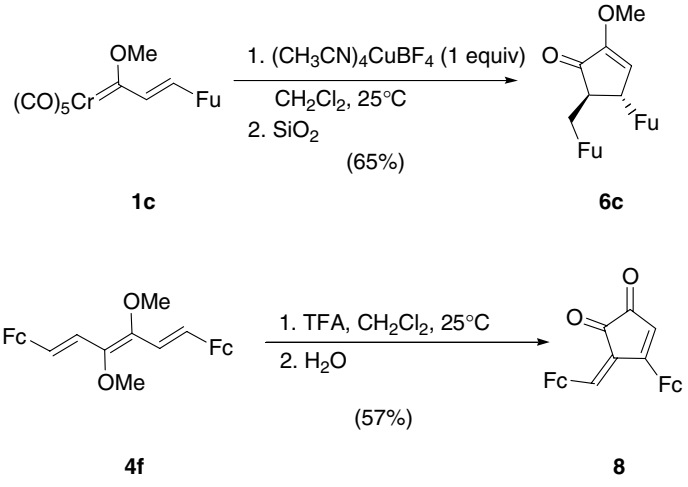
At this point we were intrigued whether 3,4-dialkoxytrienes **4** might generate heteroatom-stabilized pentadienyl cations by acid treatment and therefore they would become suitable materials for the Nazarov cyclization.

Very recently, the usefulness of 2,3-dialkoxy- and 2-amino-3-alkoxytrienes as precursors of cyclopenta-fused heterocycles via the Nazarov cyclization has been demonstrated [10]. Thus, exposure of dimethoxyhexatrienes **4c**, **d** to an excess of trifluoroacetic acid (TFA) in CH_2Cl_2 at room temperature led, after column chromatographic purification, to a 1:1 mixture of the cyclopentenone derivatives **6c**, **d** and **7c**, **d** in nearly quantitative yields. As it is depicted in Scheme 5, the reaction should begin with the reversible protonation of the distal carbon–carbon double-bond of the triene leading to pentadienyl cation species **III**. Conrotatory ring-closing of **III** is greatly facilitated because of the special stabilization of the oxyallyl cation **IV** by an alkoxy group. This cationic intermediate **IV** may evolve by either direct hydrolysis to give **6c**, **d** or proton elimination followed by hydrolysis of the less substituted enol ether function to afford **7c**, **d** [11].

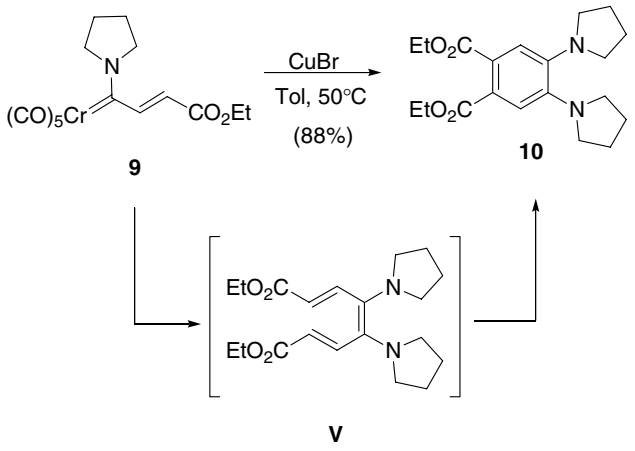
At this point we must mention two particular observations in the course of this task (Scheme 6). Firstly, the furyl-substituted carbene complex **1c** could be transformed with complete chemo- and stereoselectivity into the methoxycyclopentenone **6c** upon treatment with one equiv of $(CH_3CN)_4CuBF_4$ in CH_2Cl_2 at room temperature. Further purification by column chromatography (SiO_2, hexane/ethyl acetate 10:1) allowed to isolate **6c** in 65% yield. This means that the copper complex not only catalyzes the dimerization, but also promotes the cyclopentannulation. In this context, recent reports from the literature reveals that copper(II) salts promote [11] or catalyze [12] the Nazarov cyclization of α-carbonyl divinylketones and α-alkoxy divinylketones. Secondly, subjecting the ferrocenyl-substituted hexatriene **4f** to the standard Nazarov-type conditions (TFA, CH_2Cl_2, 25 °C) resulted in the unexpected formation of the alkenylidenecyclopenten-1,2-dione **8** in 57% yield, as the sole reaction product.



Scheme 5.



Scheme 6.



Scheme 7.

The stereochemistry of **8** is readily confirmed by 2D-NOESY ^{1}H NMR experiments. Likely, the cyclization step is followed by exhaustive dehydrogenation.

Once it has been demonstrated that Fischer alkoxycarbenes readily dimerize in the presence of copper catalysts as well as the transformation of the resulting dimers into 2-alkoxycyclopentenones, we tourned our attention on Fischer aminocarbenes. It must be first mention that attempts to dimerize these complexes in the presence of late transition metals, like Pd, Ni, Rh have always failed. Now, we have found that the β-alkoxycarbonylalkenyl(pyrrolidine)carbene **9** efficiently cyclodimerizes to the push–pull substituted arene **10** (88% yield) in the presence of CuBr (1 equiv, toluene, 50 °C) (Scheme 7). The sequence consisting of ligand-dimerization forming the triene **V**, electrocyclic ring closure, and air oxidation may account well for the formation of compound **10**.

In summary, chromium Fischer carbene complexes can be used as carbene sources in the presence of copper(I) complexes allowing the preparation of functionalized olefins and trienes through homocupling reactions. According to previous studies the process very likely takes place via a chromium/copper exchange followed by ligand dimerization from the resulting copper carbene complex. The trienes resulting from alkenylcarbene complexes could be efficiently transformed into substituted 2-alkoxy-2-cyclopentenone via a Nazarov-type reaction [13]. The carbene ligand dimerization reaction of Fischer amino carbene complexes is described for the first time. Although $[Cu(MeCN)_4][PF_6]$ is in general the catalyst of choice, CuBr reveals as a practical and economical catalyst in some instances.

3. Experimental

All reactions involving organometallic species were carried out under argon using standard Schlenck techniques. THF and toluene were destilled from sodium benzophenone and CH_2Cl_2 was destilled from CaH_2. TLC was performed on aluminium-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel 60 (230–240 mesh). ^{1}H NMR (200, 300, 400 MHz) and ^{13}C NMR (50.5, 75.5, 100 MHz) spectra were measured in $CDCl_3$ at room temperature on a Bruker AC-200, AC-300 and AMX-400 instruments, respectively, with tetramethylsilane ($\delta = 0.0$, ^{1}H NMR), $CDCl_3$ ($\delta = 76.95$, ^{13}C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. Elemental analyses were carried out on a Perkin–Elmer 2400 and Carlo Erba 1108 microanalyzers.

Fischer carbene complexes **1a**–**i** and **9**, and the copper(I) complexes $[Cu(CH_3CN)_4][X]$ ($X = BF_4$, PF_6) were prepared according to the literature methods. All other reagents and solvents used in this work were of the best commercial grade available and used without further purification.

3.1. General procedure for the Cu(I) catalyzed carbene ligand dimerization of Fischer chromium–carbene complexes *1a–g*

To a solution of carbene complex (0.5 mmol) in CH_2Cl_2 (10 mL) was added $(CH_3CN)_4CuBF_4$ (0.05 mmol) and the resulting mixture was stirred at 25 °C until disappearance of the starting carbene complex (checked by TLC; 12–16 h). The solvent was then removed under reduced pressure and the resulting residue was subjected to flash chromatography on silica gel using a mixture of hexane/ethyl acetate (10:1) as eluent.

(**4a**): Obtained as a 10:1 mixture of *Z*/*E* isomers. Data for the major isomer: ^{1}H NMR: 3.33 (s, 6H), 7.25 (t, $J = 7.3$ Hz, 2H), 7.34 (t, $J = 7.3$ Hz, 4H), 7.61 (d, $J = 7.3$ Hz, 4H); ^{13}C NMR: 58.5 (CH_3), 127.7 (CH), 128.1 (CH), 128.2 (CH), 134.0 (C), 145.1 (C). Anal. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.92; H, 6.80%.

(**4b**): Compound **4b** was not isolated but it hydrolyzed to 6-methoxy-5-decanone **5** when attempting purification by column chromatography.

(**5**): ^{1}H NMR: 0.96 (m, 6H), 1.30–1.62 (m, 10H), 2.49 (t, $J = 7.5$ Hz, 2H), 3.32 (s, 3H), 3.65 (dd, $J = 7.2$, 3.9 Hz, 1H); ^{13}C NMR: 14.0, 22.6, 25.8, 27.4, 31.6, 37.2, 58.5, 87.1, 212.6. Anal. Calc. for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.84; H, 11.81%.

(**4c**): Obtained as a 10:1 mixture of *E*/*Z* isomers. Data for the major isomer: ^{1}H NMR: 3.74 (s, 6H), 6.35 (m, 2H), 6.44 (m, 2H), 6.60 (d, $J = 15.8$ Hz, 2H), 6.97 (d, $J = 15.8$ Hz, 2H), 7.43 (m, 2H); ^{13}C NMR: 61.5 (CH_3), 109.3 (CH), 111.9 (CH), 116.0 (CH), 116.9 (CH), 142.4 (CH), 148.6 (C), 153.5 (C). Anal. Calc. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.65; H, 5.98%.

(**4d**): Obtained as a 9:1 mixture of *E*/*Z* isomers. Data for the major isomer: ^{1}H NMR: 3.80 (s, 6H), 6.86 (d, $J = 16.0$ Hz, 2H), 7.13 (d, $J = 16.0$ Hz, 2H), 7.36–7.58

(m, 10H); ^{13}C NMR: 61.4 (CH_3), 118.3 (CH), 126.7 (CH), 127.7 (CH), 128.6 (CH), 137.2 (C), 148.8 (C). Anal. Calc. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.25; H, 6.86%.

(**4e**): ^{1}H NMR: 3.75 (s, 6H), 3.83 (s, 6H), 6.75 (d, J = 16.2 Hz, 2H), 6.89 (d, J = 8.7 Hz, 4H), 6.93 (d, J = 16.2 Hz, 2H), 7.45 (d, J = 8,7 Hz, 4H); ^{13}C NMR: 52.3, 61.4, 114.1, 116.4, 127.6, 127.9, 130.1, 148.2, 159.2. Anal. Calc. for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 75.01; H, 6.95%.

(**4f**): ^{1}H NMR: 3.72 (s, H), 4.14 (s, 10H), 4.29 (m 4H), 4.46 (m, 4H), 6.54 (d, J = 15.9 Hz, 2H), 6.62 (d, J = 15.9 Hz, 2H); ^{13}C NMR: 61.6, 67.2, 69.4, 69.7, 83.9, 117.0, 126.4, 146.6. Anal. Calc. for $C_{28}H_{28}Fe_2O_2$: C, 66.17; H, 5.55. Found: C, 66.29; H, 5.68%.

(**4g**): ^{1}H NMR: 3.49 (t, J = 6.2 Hz, 4H), 4.13 (t, J = 6.2 Hz, 4H), 6.90 (d, J = 16.0 Hz, 2H), 6.98 (d, J = 16.0 Hz, 2H), 7.26–7.54 (m, 10H); ^{13}C NMR: 2.6, 73.3, 118.4, 126.9, 128.0, 128.7, 129.6, 136.8, 147.2. Anal. Calc. for $C_{22}H_{22}I_2O_2$: C, 46.18; H, 3.88. Found: C, 46.34; H, 3.79%.

*3.2. General procedure for the Cu(I) mediated carbene ligand dimerization of Fischer chromium–carbene complexes **1h, i***

A solution of the carbene complex (0.5 mmol) in THF (10 mL) was degassed by evacuation/back-fill with nitrogen (3 times). CuBr was then added and the resulting mixture was stirred at 50 °C for 10 h. The solvent was then removed under reduced pressure and the resulting residue was subjected to flash chromatography on silica gel using a mixture of hexane/ethyl acetate (10:1) as eluent.

(**4h**): ^{1}H NMR: 0.81 (d, J = 7.0 Hz, 6H), 0.90–2.20 (several multiplets, 30H), 3.89 (m, 2H), 6.36 (m, 2H), 6.41 (m, 2H), 6.52 (d, J = 15.9 Hz, 2H), 7.17 (d, J = 15.9 Hz, 2H), 7.49 (m, 2H); ^{13}C NMR: 16.5, 21.5, 22.2, 23.0, 24.9, 31.4, 34.3, 40.4, 48.9, 80.1, 108.6, 111.7, 115.9, 120.1, 142.1, 145.3, 153.3. Anal. Calc. for $C_{34}H_{48}O_4$: C, 78.42; H, 9.29. Found: C, 78.53; H, 9.26%.

(**4i**): ^{1}H NMR: 0.81 (d, J = 7.0 Hz, 6H), 0.90–2.60 (several multiplets, 30H), 3.92 (m, 2H), 6.78 (d, J = 16.1 Hz, 2H), 7.19 (d, J = 16.1 Hz, 2H), 7.22–7.56 (m, 10H); ^{13}C NMR: 16.8, 21.5, 22.2, 23.0, 25.0, 31.4, 34.3, 40.5, 49.0, 79.6, 121.2, 126.6, 127.3, 128.4, 128.6, 137.5, 145.5. Anal. Calc. for $C_{38}H_{52}O_2$: C, 84.39; H, 9.69. Found: C, 84.27; H, 9.64%.

*3.3. General procedure for the cationic cyclization of trienes **4c, d***

Trifluoroacetic acid (0.5 ml) was added to a solution of the corresponding triene **4c**, **d** (0.25 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred for 14 h at r.t. Then, water (5 mL) was added and the mixture extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried (Na_2SO_4). Solvent was removed in vacuo and the mixture of products separated by flash chromatography (SiO_2, 10:1 hexane/ethyl acetate).

*3.3.1. Cyclization of triene **4c***

(**6c**): ^{1}H NMR: 2.82 (m, 1H), 2.97 (dd, J = 14.0 and 8.5, 1H), 3.22 (dd, J = 14.0 and 5.2 Hz, 1H), 3.72 (s, 3H), 3.84 (t, J = 2.7 Hz, 1H), 5.92 (d, J = 6.8 Hz, 1H), 6.07 (d, J = 6.8 Hz, 1H), 6.36 (m, 2H), 6.43 (d, J = 2.9 Hz, 1H), 7.28 (m, 2H); ^{13}C NMR: 27.9 (CH_2), 39.3 (CH), 49.8 (CH), 57.0 (CH_3), 105.2 (CH), 106.9 (CH), 110.1 (CH), 110.2 (CH), 125.6 (CH), 141.4 (CH), 141.7 (CH), 152.1 (C), 154.3 (C), 156.5 (C), 201.4 (C). Anal. Calc. for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.87; H, 5.51%.

(**7c**): ^{1}H NMR: 2.52 (dd, J = 19.1 and 1.8 Hz, 1H), 2.77 (dd, J = 19.1 and 6.6 Hz, 1H), 3.29 (d, J = 14.0 Hz, 1H), 3.91 (d, J = 14.0 Hz, 1H), 3.99 (dd, J = 6.6 and 1.8 Hz, 1H), 4.05(s, 3H), 5.98 (d, J = 6.8 Hz, 1H), 6.12 (d, J = 6.8 Hz, 1H), 6.33 (m, 2H), 7.34 (m, 2H); ^{13}C NMR: 25.5 (CH_2), 35.6 (CH), 39.6 (CH_2), 58.5 (CH_3), 106.8 (CH), 106.9 (CH), 110.2 (CH), 110.3 (CH), 141.6 (CH), 141.9 (CH), 150.3 (C), 150.4 (C), 152.7 (C), 153.0 (C), 201.7 (C). Anal. Calc. for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.71; H, 5.43%.

*3.3.2. Cyclization of triene **4d***

(**6d**): ^{1}H NMR: 2.64 (m, 1H), 2.91 (dd, J = 14.1 and 8.4, 1H), 3.21 (dd, J = 14.1 and 5.4 Hz, 1H), 3.68 (t, J = 2.6 Hz, 1H), 3.74 (s, 3H), 6.27 (d, J = 2.8 Hz, 1H), 6.84–6.91 (m, 2H), 7.14– 7.39 (m, 8H); ^{13}C NMR: 30.9 (CH_2), 44.4 (CH), 55.2 (CH), 57.0 (CH_3), 127.3 (CH), 127.4 (CH), 127.9 (CH), 128.1 (CH), 129.7 (CH), 129.9 (CH), 130.0 (CH), 134.4 (C), 134.6 (C), 158.4 (C), 203.7 (C). Anal. Calc. for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.04; H, 6.60%.

(**7d**): ^{1}H NMR: 2.32 (dd, J = 19.0 and 1.8 Hz, 1H), 2.81 (dd, J = 19.0 and 6.7 Hz, 1H), 2.96 (d, J = 13.8 Hz, 1H), 3.69 (dd, J = 6.7 and 1.8 Hz, 1H), 3.97 (d, J = 13.8 Hz, 1H), 4.09 (s, 3H), 7.02–7.37 (m, 10H); ^{13}C NMR: 28.2 (CH_2), 39.3 (CH), 40.5 (CH_2), 58.4 (CH_3), 126.6 (CH), 126.8 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 137.5 (C), 137.7 (C), 150.9 (C), 152.2 (C), 202.5 (C). Anal. Calc. for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.86; H, 6.54%.

*3.4. Cu(I) mediated carbene ligand dimerization/cyclization of carbene complex **1c***

To a solution of carbene complex **1c** (0.5 mmol) in CH_2Cl_2 (10 mL) was added $(CH_3CN)_4CuBF_4$ (0.5 mmol) and the resulting mixture was stirred for at 25 °C until disappearance of the starting carbene complex (checked by TLC; 1 h). The solvent was then removed under reduced pressure and the resulting residue was

subjected to flash chromatography on silica gel using a mixture of hexane/ethyl acetate (10:1) as eluent to give the methoxycyclopentenone **6c**.

3.5. Cyclization reaction of the ferrocenyl-substituted hexatriene *4f*

Trifluoroacetic acid (0.5 ml) was added to a solution of triene **4f** (0.25 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred for 18 h at 25 °C. Then, water (5 mL) was added and the mixture extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried (Na_2SO_4). Solvent was removed in vacuo and the mixture of products separated by flash chromatography (SiO_2, 10:1 hexane/ethyl acetate) to give the alkenylidenecyclopenten-1,2-dione **8**.

(**8**): ^{1}H NMR: 4.23 (s, 5H), 4.28 (s, 5H), 4.67 (m, 2H), 4.76–4.77 (m, 4H), 5.22 (m, 2H), 6.66 (s, 1H), 7.49 (s, 1H); ^{13}C NMR: 70.3 (CH), 71.0 (CH), 73.0 (CH), 73.2 (CH), 73.8 (CH), 75.9 (C), 76.6 (C), 123.7 (CH), 124.8 (C), 139.4 (CH), 176.1 (C), 187.1 (C), 189.0 (C). Anal. Calc. for $C_{26}H_{20}Fe_2O_2$: C, 65.59; H, 4.23. Found: C, 65.69; H, 4.31%.

3.6. Cu(I) mediated carbene ligand dimerization of carbene complex *9*

To a solution of carbene complex **9** (0.5 mmol) in toluene (5 mL) was added CuBr (0.5 mmol) and the mixture was stirred at 50 °C until disappearance of the starting carbene complex (checked by TLC; 18 h). The solvent was then removed under reduced pressure and the resulting residue was subjected to flash chromatography on silica gel using a mixture of hexane/ethyl acetate (3:1) as eluent to give pure compound **10** as a yellow pale oil.

(**10**): ^{1}H NMR: 1.42 (t, J = 7.1 Hz, 6H), 1.93 (m, 8H), 3.25 (m, 8H), 4.42 (q, J = 7.1 Hz, 4H), 7.12 (s, 2H); ^{13}C NMR: 10.6, 21.4, 47.2, 57.1, 112.3, 119.9, 135.6, 164.8. Anal. Calc. for $C_{20}H_{28}N_2O_4$: C, 66.64; H, 7.83. Found: C, 66.56; H, 7.87%.

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