

Up to Seven-Component Adducts by Unprecedented Multiple Alkyne and Carbonyl Insertions in the Metal–Carbon Bond of Chromium Alkoxy Alkynyl Carbene Complexes

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Abstract: Chromium alkoxy alkynyl Fischer carbene complexes react with symmetrical internal alkynes to form new and different organometallic species, which result from consecutive insertions of several alkyne units and carbonyl groups into the metal–carbon bond. The insertion sequence can be controlled and, by slight modification of the reaction conditions, it can be directed to the preparation of either seven- or five-component adducts. Three molecules of alkyne, two carbonyl groups, the carbene ligand and the chromium metal moiety partake in the

creation of seven new carbon–carbon bonds and two five-membered carbocycles in the first case while four new carbon–carbon bonds, a σ Cr–C(sp²) bond and a cyclopentadienyl moiety are built in the second case. Evidence that five-component chromium complexes are intermediates in the formation of seven-component adducts is

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reactions

provided; they are also able to insert a unit of a different internal alkyne which confers more diversity to the seven-component adducts. The presence of the σ Cr–C(sp²) bond has also been exploited to develop the synthesis of both cyclopentene-fused and novel spiro-cyclopentenones as well as symmetrical biscyclopentenones. Finally, the isolation of six-component adducts, when toluene was employed as the initial alkyne, provides further support to the proposed mechanism.

Introduction

Multi-component reactions (MCRs) have recently emerged as complementary and powerful alternatives to more traditional strategies for the synthesis of complex chemical structures, with relevant applications in both combinatorial chemistry and diversity-oriented synthesis, mainly by means of their operational simplicity and high atom economy.^[1] Particularly, Group VI metal–heteroatom-stabilized Fischer carbene complexes (FCCs)^[2] have been conferred with a prominent role in this arena, due both to their versatility as well as to their ability to partake in MCRs.^[3] However, the participation of alkynyl-substituted FCCs in MCRs has been scarcely developed.

On the other hand, alkynes have served on many occasions as partners of FCCs in MCRs, as it happens, for instance, in the polymerization of alkynes catalyzed by tungsten FCCs^[4] in which many molecules of alkyne interact with just one molecule of FCC, or in the Dötz benzannulation, in which the interaction takes place among one unit of alkyne, the carbene ligand, and a CO ligand of the coordina-

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[++] NMR spectroscopic studies

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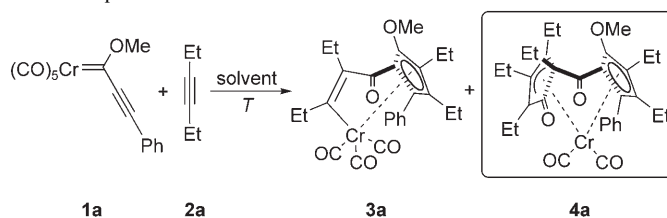
tion sphere of the metal complex to form a three-component reaction product.^[5] Nevertheless, very few couplings of alkynes with alkynyl carbene complexes have been reported: 1) H. Fischer has presented the insertion of just one equivalent of an electron-donating-substituted internal alkyne into the metal–carbon bond of a chromium or tungsten alkynyl FCC, without noticing further evolution of the new inenyl carbene complex formed.^[6] 2) Dötz has shown that, after addition of diethylzinc, an alkoxy alkynyl tungsten carbene complex undergoes dimerization of the carbene ligand to give an *exo*-alkenyldenecyclopentenylidene complex.^[7] 3) Wulff has pointed out an intramolecular alkyne insertion into an amino alkynyl FCC, followed by a metal-mediated Moore-type cyclisation, as a route for the synthesis of 5-hydroxyindolines.^[8] 4) In the fourth and, as far as we know, last example, the nucleophilicity of propargylsilanes has afforded the coupling of one equivalent of a terminal alkyne to FCC **1a** and the initial intermediate evolved, by a 1,2-silicon migration and the loss of the metal moiety, to form a conjugated diene.^[9] However, in all those cases, only one alkyne unit reacted with the FCC; in fact, the discrete and controlled insertion of a defined number of alkyne units into the metal–carbon bond of a carbene complex has been rarely observed.^[10] Herein, we report that alkoxy alkynyl chromium(0) carbene complexes are able to undergo the controlled intermolecular insertion of up to three alkyne units into the chromium–carbon bond leading to the forma-

tion of multi-component adducts involving up to seven components. Moreover, by a slight modification of the reaction conditions, the process can be directed towards the formation of five-component adducts, the reactivity of which may be used to shed some light onto the proposed mechanism and for the synthesis of new organic and organometallic species.

Results and Discussion

Establishment of the reaction conditions: We initially mixed FCC **1a** and 3-hexyne **2a** in toluene and, after warming the mixture at 110°C in a sealed vessel, adduct **4a** was isolated as the major product. Further experiments indicated that: 1) the reaction did not take place at temperatures below 80°C, 2) comparable results were obtained by performing it in toluene at 80 or 110°C (Table 1, entries 1 and 2) and

Table 1. Optimization of the reaction conditions.



Entry	T [°C]	Solvent	Equivalents 2a	3a ^[a]	4a ^[a]
1	110	toluene	15		24
2	80	toluene	15		22
3	80	THF	15		18
4	80	DME	15		20
5	80	1,4-dioxane	15		21
6	80	DCE	15	12	27
7	80	DCE	5	23	15
8	80	DCE	3	12	10

[a] Isolated yield based on **1a**.

Abstract in Spanish: Los complejos alcóxalquínilcarbénico de Fischer reaccionan con alquinos internos simétricos para dar lugar a nuevas especies organometálicas, que se forman como consecuencia de inserciones consecutivas de varias unidades de alquino y de grupos carbonilo en el enlace metal-carbono. La secuencia de inserción puede ser controlada y, mediante una pequeña modificación de las condiciones de reacción, dirigida hacia la preparación de aductos de siete o de cinco componentes. Tres moléculas de alquino, dos grupos carbonilo, el ligando carbénico y el fragmento metálico participan en la creación de siete nuevos enlaces carbono-carbono y dos carbociclos de cinco miembros en el primer caso, en tanto que en el segundo caso se forman cuatro nuevos enlaces carbono-carbono, un enlace σ Cr–C(sp^2) y un anillo de ciclopentadienilo. Se aportan evidencias de que los complejos de cinco componentes de cromo son intermedios en la formación de los aductos de siete componentes; dichos complejos son, asimismo, capaces de insertar una unidad de un alquino interno distinto lo que aporta mayor diversidad estructural en los aductos de siete componentes. La presencia del enlace σ Cr–C(sp^2) ha sido utilizada para desarrollar una síntesis de ciclopentenonas fusionadas a un anillo de ciclopenteno, así como de nuevas espirociclopentenonas y de bis-ciclopentenonas simétricas. Finalmente, cuando se utiliza tolueno como alquino inicial, ha sido posible aislar aductos de seis componentes, lo que también supone un apoyo al mecanismo propuesto.

3) tungsten alkynyl FCCs were not able to insert alkynes even at 110°C. With these initial results in hand, we turned to optimize the reaction conditions by treating FCC **1a** and alkyne **2a** with a variety of different solvents and we found that: 4) the reaction did not take place in hexane or acetonitrile, 5) oxygenated ether-type solvents, such as THF, 1,2-dimethoxyethane (DME) or 1,4-dioxane (entries 3–5), provided yields comparable to the ones reached in toluene and 6) the higher yields were obtained in 1,2-dichloroethane (DCE) (entry 6). Along all of these tests, we could detect variable but small amounts of adduct **3a**, which was isolated in a 12% yield from entry 6. The amount of **3a** was increased by reducing to five the number of equivalents of alkyne employed, but the yield of **4a** was affected (entry 7). Performing the reaction with just three equivalents of alkyne resulted in reduced isolated quantities of both **3a** and **4a** (entry 8).

Structural analysis: From the NMR spectroscopic analysis, we could establish that compound **4a** contains: the metal coordinated to two carbonyl ligands, three units of acetylene,

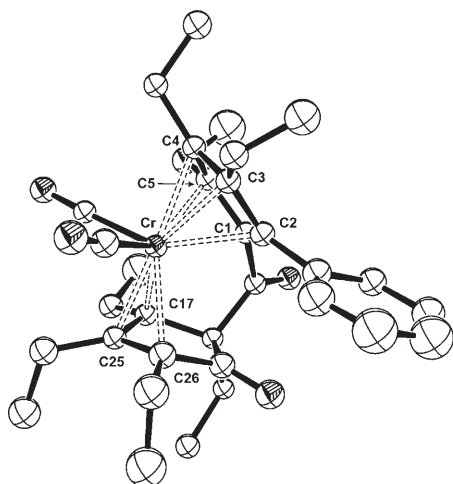


Figure 1. ORTEP diagram for **4a**. Ellipsoids are shown at the 30% level. Selected bond lengths (Å): Cr1–C1 2.1532(18), Cr1–C2 2.2580(18), Cr1–C3 2.2512(18), Cr1–C4 2.2065(18), Cr1–C5 2.1695(18), Cr1–C17 2.2694(19), Cr1–C25 2.1720(18), Cr1–C26 2.2876(19).

the carbene ligand moiety and two organic carbonyl groups; therefore, it is a seven-component adduct although four of the components come from one reactant molecule. However, an X-ray diffraction experiment was required to completely determine the connectivity of the fragments and to elucidate the structure of **4a** (Figure 1).^[11] The determined Cr–C bond lengths lie between 2.153 and 2.258 Å for the carbon atoms of the cyclopentadienyl group and 2.172 and 2.288 Å for the cyclic allylic moiety and are in the same range as the distances found for other structurally related compounds.^[10c]

On the contrary, the molecular structure for **3a** was established by HRMS, FTIR, and 1D and 2D NMR spectroscopy data. For instance, the presence of a *fac*-Cr(CO)₃ moiety was clearly indicated by FTIR spectroscopy ($\tilde{\nu}$ = 2005, 1924 cm^{−1}) and supported by the lack of heteronuclear multiple-bond correlation (HMBC)-crosspeaks for the signals at δ (¹³C NMR) = 245.9, 239.9 and 234.9 ppm (Figure 2). Remarkably, the key for the elucidation of its structure was the signal at δ = 219.0 ppm, which showed HMBC-correlations with the hydrogen atoms of the C-21 methyl group (Figure 2); consequently, the option that a such signal corresponded to a chromium-linked carbonyl carbon was discarded. Instead, its HMBC crosspeak signal allowed its assign-

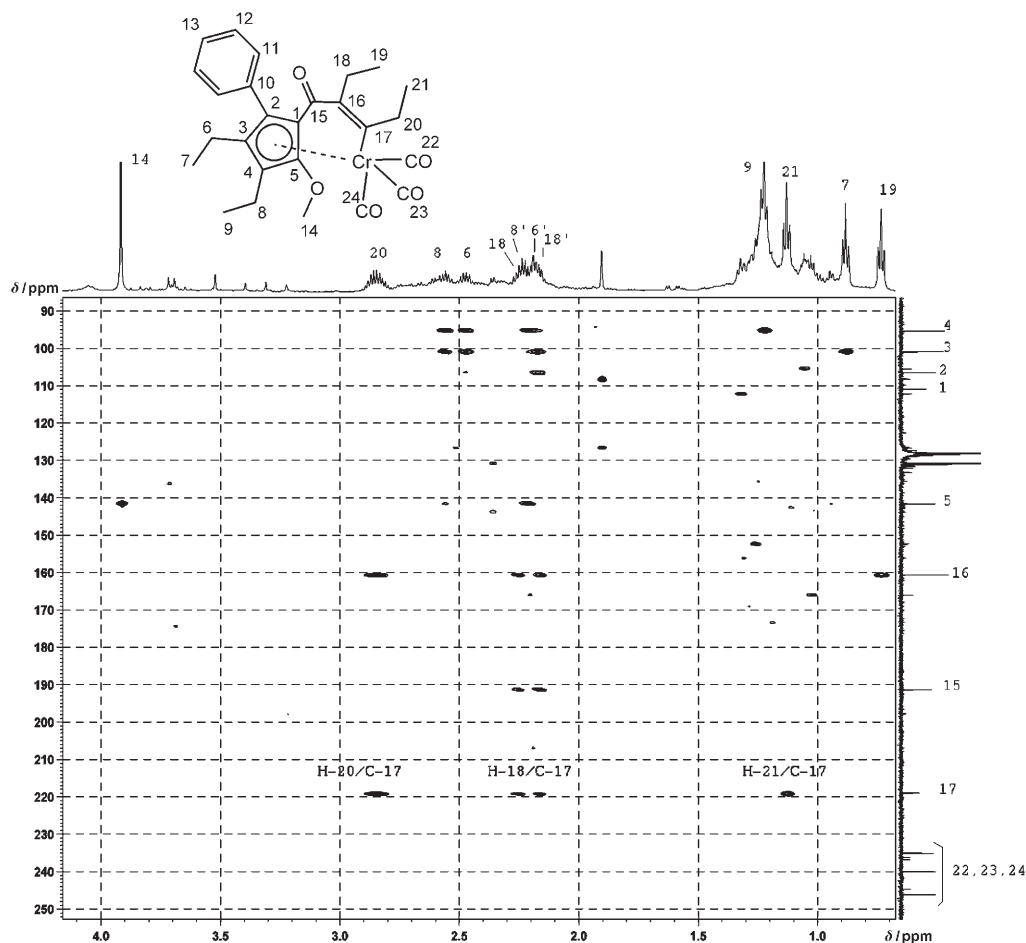
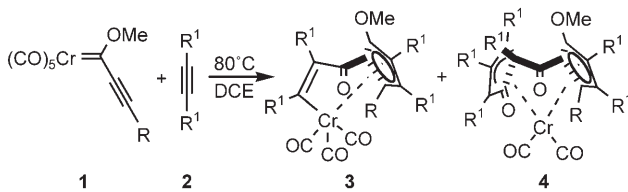


Figure 2. Details of the HMBC spectrum for **3a**.

ment as an olefin (sp^2)-carbon σ -bonded to the chromium, which is consistent with the reported ^{13}C NMR spectroscopic data for other chromium derivatives bearing σ -bonded $\text{Cr}-\text{C}(sp^2)$.^[12] From the combined spectroscopic and spectrometric analysis, we concluded that **3a** contains two units of alkyne, the carbene ligand, an organic carbonyl group, and the chromium atom linked to three carbonyl ligands; it is, therefore, a five-component product.

Scope of the reaction: Two experimental procedures, which differed in the number of equivalents of alkyne **2** added, were employed to test the scope of the reaction, in DCE at 80°C in a sealed vessel. Method A utilized 15 equivalents of **2** and method B utilized five equivalents of **2**, each one involving the optimized conditions required for the formation of either adducts **4** or **3**. The process is quite general for alkynyl FCCs bearing aromatic rings; it tolerates both electron-deficient (Table 2, entries 1, 2) and electron-rich-substi-

Table 2. Scope of the reaction.



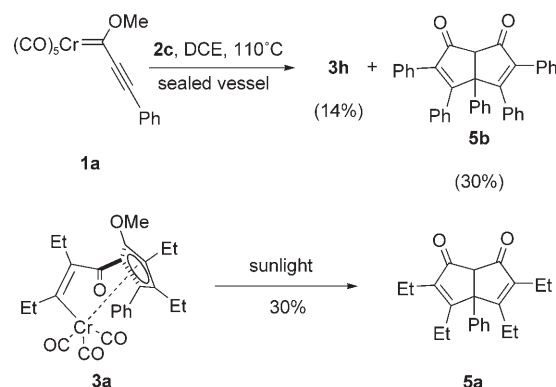
Entry	R	R ¹	Method ^[a]	3	Yield [%] ^[b]	4	Yield [%] ^[b]
1	<i>p</i> -Cl-C ₆ H ₄	Et	A	3b	10	4b	23
2	<i>p</i> -Cl-C ₆ H ₄	Et	B	3b	12	4b	17
3	<i>p</i> -MeO-C ₆ H ₄	Et	A	3c	22	4c	31
4	<i>p</i> -MeO-C ₆ H ₄	Et	B	3c	16	4c	20
5	Fc ^[c]	Et	A			4d	29 ^[d]
6		Et	B	3e	14	4e	21
7		Et	A			4f	31 ^[e]
8		Et	B			4f	18 ^[e]
9	Ph	Pr	A	3g	13	4g	34
10	Ph	Pr	B	3g	25	4g	16
11	Ph	Ph	A	3h	32	4h	–

[a] Method A: 15 equiv of **2** in DCE at 80°C in a sealed vessel; method B: 5 equiv of **2** in DCE at 80°C in a sealed vessel. [b] Isolated yield based on **1**. [c] Fc = Ferrocenyl. [d] Isolated as a 1.7:1 mixture of non-separable isomers. [e] Isolated as a 1:1 mixture of isomers which could be separated; an X-ray crystal structure for **4f** isomer B was determined.^[11]

tuted arenes (entries 3–6) in the triple bond. It also takes place with alkenyl-substituted alkynyl FCCs (entries 7, 8). Low yields of each product were obtained with moderate combined reaction yields. Occasionally, adducts **3** were not observed (entries 5, 7, 8). Regarding the alkyne component, the reaction does not occur for terminal acetylenes, but other symmetrical internal alkynes were also successfully employed, such as 4-octyne **2b** (entries 9, 10) or tolane **2c**

(entry 11). In the latter case, adduct **3h** was the only identified product; seven-component adduct **4h** was not detected, even though the starting materials were treated under the conditions of method A. We assumed then that the formation of **4h** is probably impeded for steric reasons.

Next, we heated a mixture of FCC **1a** and tolane **2c** in a sealed tube at 110°C expecting that a higher temperature would promote the formation of the corresponding seven-component adduct **4h** but, on the contrary, adduct **3h** was formed together with a new product which had not retained the chromium moiety. Spectroscopic analyses led to the structure of the symmetrical biscyclopentenone **5b**, isolated in 30% yield, which results from the creation of a new C–C bond (Scheme 1). Interestingly, the direct sunlight exposi-



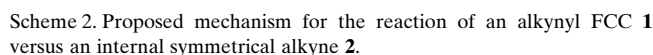
Scheme 1. Formation of symmetrical biscyclopentenones **5**.

tion of **3a** leads to the corresponding symmetrical four-component biscyclopentenone, **5a**, although in a modest yield.

Proposed mechanism: The formation of adduct **4a** is the result of the sequential intermolecular insertion of three molecules of alkyne and two carbonyl ligands in a chromium alkynyl carbene complex that reacts through all its three reactive positions: the carbene carbon and both acetylenic carbons. Thus, the sequence involves the participation of four C–C triple bonds and it represents an orchestrated, novel and unique combination of seven components with the creation of seven carbon–carbon bonds in an unprecedented process.

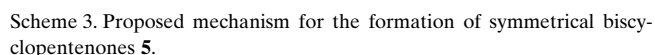
The following mechanism, depicted in Scheme 2, may account for the formation of compounds **3** and **4**. An initial thermal dissociation of a CO ligand would facilitate the insertion of the first molecule of acetylene to generate enynyl carbene intermediate **I**, which is stabilized by intramolecular triple bond coordination and presents two resonance structures (**1a** and **1b**). Several pentacarbonyl carbene complexes, analogous to such types of intermediate, have been previously isolated and characterized,^[6,13] and, although not isolated, other structurally related species have been proposed as intermediates in different processes.^[8,9,13]

Then a 1,4-metal rearrangement should take place to form cyclopentadienyl intermediate **II**; interestingly, 1,4-



The subsequent insertion of a carbonyl ligand^[17] leads to the formation of acyl metallate **IIIa**, which is probably stabilized by intramolecular coordination and presents zwitterionic oxy-carbene complex **IIIb** as a resonance structure. The insertion of another equivalent of acetylene in the car-

On the other hand, the formation of symmetrical biscyclopentenones **5** may be explained by a thermally or photochemically promoted η^5 to η^1 isomerisation of **3a,h** to form intermediate **VIII** (Scheme 3). A reductive elimination would lead to **IX**, which, after the addition of silica gel, would produce **5**.



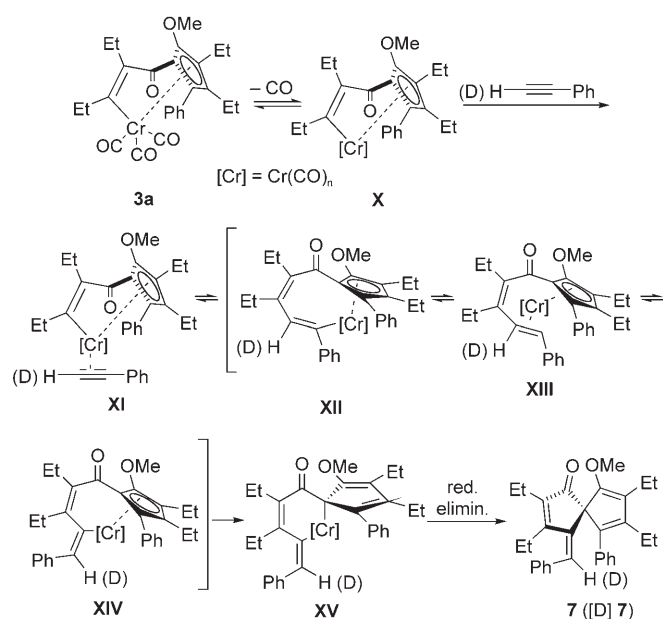
Reactivity of **3a:** According to the mechanism depicted in Scheme 2, five-component chromate **3** should be an intermediate in the formation of **4**. To prove that hypothesis, we treated **3a** with an excess of 3-hexyne **2a** in DCE at 110 °C and a 45 % isolated yield of **4a** was obtained (Scheme 4).



Moreover, such a result opened the door to test the insertion of different alkynes into the chromium–carbon bond of

metallates **3**. In fact, 4-octyne **2b** was incorporated, under the above reported conditions, as the third alkyne unit to form mixed compound **6** in 30% yield. The incorporation of a terminal alkyne as the third acetylene unit was also effective and involved the removal of the metal moiety and the creation of two C–C bonds: the treatment of **3a** with phenylacetylene produced spiro[4.4]nonatriene **7** in 35% yield. Moreover, an experiment was carried out with 1-deutero-2-phenylethyne as deuterated starting material, to gain some insight about the mechanism for the formation of cyclopentenones **7**: the analogous spirocyclopentenone [D]**7**, 100% deuterated at the α -position to the phenyl ring that comes from the alkyne, was obtained.

Taking into account these results, a plausible mechanism for the formation of spirocyclopentenones **7** (and [D]**7**) is depicted in Scheme 5. We propose the initial dissociation of



Scheme 5. Proposed mechanism for the formation of compounds **7** (and [D]**7**).

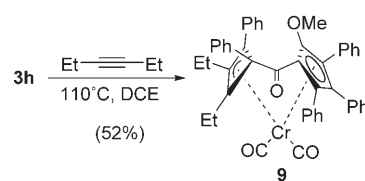
a CO ligand to form complex **X**, which bears an empty coordination position. Such a coordination position would be filled by phenylacetylene to form organometallic species **XI**, which would evolve by insertion of the acetylene into the σ Cr–C(sp^2) bond, thus producing chromium complex **XII**. The transformation of **XII** into **XV** is particularly interesting; it should involve the 1,2-migration of the chromium fragment from a C(sp^2) to another C(sp^2), with the simultaneous or concomitant inverse 1,2-migration of the acetylenic hydrogen (deuterium) atom to form intermediate **XIV**,^[18] presumably through a species such as **XIII**. This rearrangement must be completely diastereoselective as no evidence of the (4*Z*)-isomer of **7** (and [D]**7**) has been observed. Finally, a η^5 to η^1 isomerisation of **XIV** to **XV** (which presents a six-membered metalacycle), followed by a reductive elimination would account for the formation of **7** (and [D]**7**).

On the other hand, an alternative demetalation pathway was developed: a new C–C bond was formed upon the treatment with trifluoroacetic acid (TFA) to give cyclopentene-fused cyclopentenone **8** (Scheme 4), a metal-free adduct which, considering the H atom provided by TFA, incorporates five components in the overall sequence from the starting carbene complex **1a**.

Remarkably, **3a** may undergo cyclisation through three different positions (C1, C2 and C5, Figure 2) to form adducts **7**, **5a**, and **8**, which may be attributed to the relative thermodynamic stability of six-membered metalacycle intermediates versus other possible and alternative seven-membered metalacycles, as well as to steric effects. Interestingly, compounds **7** and **8** may be obtained in one-pot processes from FCC **1a**, by sequential addition of the required reagents, in comparable yields to the ones reached in the step-wise procedure.

Reactivity of **3h**: a support for the proposed mechanism:

The feasibility of alkyne insertion in compound **3h** was also tested; it was found that, in its reaction with 3-hexyne **2a**, chromium complex **9** was isolated as a mixture of diastereomers that differ in the configuration of the new quaternary carbon atom (Scheme 6).



Scheme 6. Reactivity of compound **3h** with 3-hexyne **2a**.

Their molecular structure was established by 1D and 2D NMR spectroscopic analysis, and confirmed by the X-ray structures of both isomers (see Figure 3 for the crystal structure of one of them):^[11] they contain the same cyclopentadienyl group present in **3h** and an anionic η^3 -allylic moiety, which is now confined into a four-membered carbocycle; the chromium is linked to two carbonyl ligands and remains as part of the molecule. Therefore, metal complexes **9** have been generated, from the initial FCC **1a**, by a combination of six-components: three of them are acetylenic units (two molecules of toluene and one of 3-hexyne), and the other three proceed from the initial FCC **1a** (the carbene ligand, the metal moiety, formed by the chromium atom and two carbonyl ligands, and a carbonyl ligand which acts as a bridge between the two cycles).

The formation of compounds **9** may be explained as depicted in Scheme 7, based on the above proposed mechanism (see Scheme 2) for the synthesis of compounds **4**. Under the reaction conditions, **3h** undergoes the insertion of a unit of 3-hexyne **2a** to form intermediate **XVI**, (analogous to intermediate **V**, Scheme 2) which is not able to insert another carbonyl ligand because of steric hindrance.

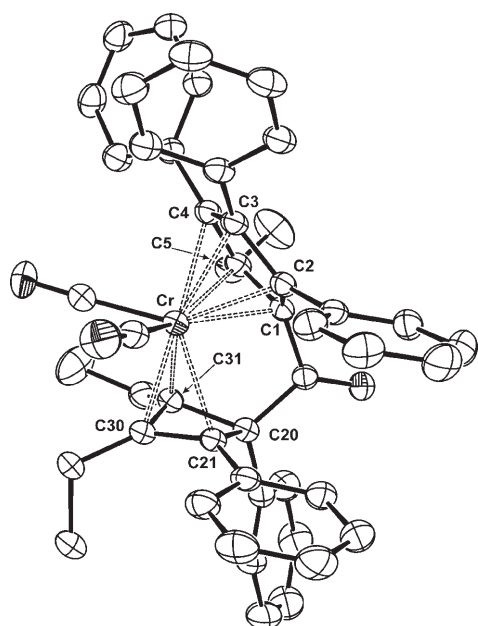
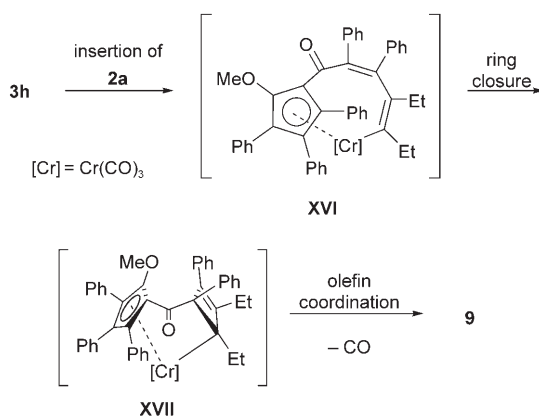


Figure 3. ORTEP diagram for **9**, isomer B. Ellipsoids are shown at the 30% level. Selected bond lengths (Å): Cr1–C1 2.1439(18), Cr1–C2 2.1948(18), Cr1–C3 2.2424(18), Cr1–C4 2.2756(18), Cr1–C5 2.2063(18), Cr1–C21 2.2862(18), Cr1–C30 2.1876(19), Cr1–C31 2.197(2).



Scheme 7. Proposed mechanism for the formation of compounds **9**.

Instead, it evolves by a cyclisation step to **XVII**, which is followed by coordination to the double bond and extrusion of a CO ligand to give diastereomeric complexes **9**. The formation of **9** represents a further support for the mechanism proposed in Scheme 2 as it provides evidence for the incorporation of the third unit of alkyne prior to a final CO insertion.

On the other hand, **3h** was not able to insert toluene as the third alkyne unit, under the tested reaction conditions (toluene, 110°C), probably due to steric effects.

Conclusion

We have reported that alkoxy alkynyl chromium(0) carbene complexes are able to intermolecularly insert internal al-

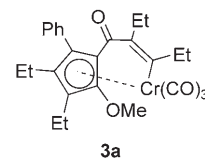
kynes; in fact, they do it in a cascade process which consists of the incorporation of up to three units of alkyne and two carbonyl ligands. The reaction conditions can be controlled and directed to the formation of seven-component adducts **4** or five-component adducts **3** as major reaction products, although the low isolated yields reached represent a major drawback from a synthetic point of view. Finally, the presence of a σ Cr–C(sp²) bond in **3** has helped to support the proposed mechanism by: 1) transforming **3a** into **4** and 2) transforming **3h** into **9**, which may be considered as a six-component adduct. Moreover, the σ Cr–C(sp²) bond in **3** has also proved its usefulness: 3) to control the insertion of the last alkyne unit and 4) in the development of the synthesis of novel five-membered carbocyclic compounds.

Experimental Section

General considerations: All reactions involving air-sensitive compounds were carried out under a N₂ 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 **1a**,^[19] **1b**,^[20] **1c**,^[21] **1d**,^[22] **1e** and **1f**,^[24] were prepared by following described procedures. Alkynes **2** are commercially available and were used as received, without further purification. Solvents were dried by standard methods. Hexane and ethyl acetate were purchased as extra pure grade reagents and used as received. TLC was performed on aluminum-backed plates coated with silica gel 60 with F₂₅₄ indicator; the chromatograms were visualized under ultraviolet light and/or by staining with a Ce/Mo reagent and subsequent heating. R_f values are reported on silica gel. Flash column chromatography was carried out on silica gel 60, 230–240 mesh. Routine NMR spectroscopic measurements were recorded on Bruker AC-300, DPX-300 or AMX-400 spectrometers. ¹H NMR: splitting-pattern abbreviations are: s: singlet, brs: broad singlet, d: doublet, t: triplet, app. t: apparent triplet, dd: double doublet, q: quartet, m: multiplet. ¹³C NMR: multiplicities were determined by DEPT experiments, abbreviations are: q: CH₃, t: CH₂, d: CH, s: quaternary carbon atoms. COSY, HSQC, HMBC, and NOESY spectroscopic experiments were carried out on a Bruker AMX-400 or AV-600 spectrometer. Standard pulse sequences were employed for the DEPT experiments. FTIR spectroscopy was performed with a Mattson 3000 FTIR spectrometer by using sodium chloride plates; samples were measured as films from deuteriochloroform or dichloromethane. Mass spectra were determined by Universidad de Oviedo and Universidad de Vigo (CACTI) with a Finnigan Mat95 and a VG AutoSpec M Mass spectrometer, respectively, for high-resolution mass spectra (HRMS). Low-resolution mass spectra were obtained with a Hewlett-Packard 5880A spectrometer. In both cases, either electron-impact (70 eV) or FAB techniques were employed. Melting points were determined on a Büchi–Tottoli apparatus and are uncorrected. Elemental analyses were carried out with a Perkin–Elmer 240B microanalyzer.

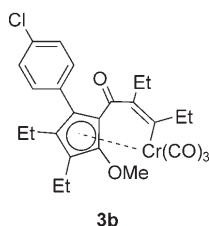
General procedure for the synthesis of complexes **3 and **4**:** A solution of the corresponding carbene complex **1** (1 equiv, 1 mmol) and the appropriate acetylene **2** (15 mmol, method A; 5 mmol, method B) in dry 1,2-dichloroethane (15 mL) was heated at 80°C in a sealed tube until complete disappearance of the carbene complex was observed by TLC (~12 h). Solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/AcOEt). The corresponding complexes **3** and **4** were isolated in the yields reported in Table 2.

Tricarbonyl[1,2-diethyl-η⁵-3-(3,4-diethyl-2-methoxy-5-phenylcyclopentadienyl)-3-oxo-1-propen-1-yl]chrom-



ium(II) (3a): Brown oil; yield: 12 % (method A), 23 % (method B); R_f : 0.42 (hexane/AcOEt 5:1); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C, TMS): δ = 7.55–7.50 (m, 2H), 7.32–7.25 (m, 3H), 3.89 (s, 3H), 2.88–2.75 (m, 2H), 2.59–2.41 (m, 2H), 2.28–2.11 (m, 4H), 1.20 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 1.10 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 0.86 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 0.71 ppm (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz, 25 °C): δ = 245.9 (s), 239.9 (s), 234.9 (s), 219.0 (s), 191.3 (s), 160.5 (s), 141.4 (s), 130.7 (d, 2 CH), 130.6 (s), 128.1 (d), 127.9 (d, 2 CH), 110.7 (s), 106.4 (s), 100.8 (s), 95.1 (s), 60.0 (q), 39.7 (t), 23.8 (t), 18.3 (t), 17.7 (t), 15.1 (q), 14.6 (q), 14.3 (q), 12.6 ppm (q); FTIR (film): $\tilde{\nu}$ = 2005, 1924, 1693, 1642 cm^{-1} ; MS (FAB): m/z (%): 473 (5) $[\text{M}+1]^+$, 389 (50) $[\text{M}-3(\text{CO})+1]^+$, 388 (100); HRMS (FAB): m/z : calcd for $\text{C}_{26}\text{H}_{29}\text{CrO}_5$; 473.1420 $[\text{M}+1]^+$; found: 473.1411.

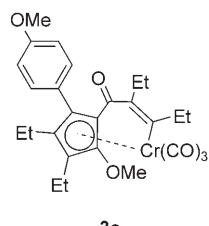
Tricarbonyl[η^5 -3-[2-(4-chlorophenyl)-3,4-diethyl-5-methoxycyclopentadienyl]-1,2-diethyl-3-oxo-1-propen-1-yl]chromium(II) (3b): Brown oil;



3b

yield: 10 % (method A), 12 % (method B); R_f : 0.52 (hexane/AcOEt 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.48 (d, $^3J(\text{H,H})$ = 8.3 Hz, 2H), 7.30 (d, $^3J(\text{H,H})$ = 8.3 Hz, 2H), 3.89 (s, 3H), 2.90–2.76 (m, 2H), 2.57–2.48 (m, 1H), 2.47–2.36 (m, 1H), 2.26–2.11 (m, 4H), 1.20 (t, $^3J(\text{H,H})$ = 7.5 Hz, 3H), 1.12 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 0.86 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 0.77 ppm (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, 25 °C): δ = 245.5 (s), 239.9 (s), 234.6 (s), 219.7 (s), 191.2 (s), 160.7 (s), 141.5 (s), 134.0 (s), 131.9 (d, 2 CH), 129.4 (s), 128.2 (d, 2 CH), 110.7 (s), 104.8 (s), 100.8 (s), 95.3 (s), 60.0 (q), 39.9 (t), 23.9 (t), 18.3 (t), 17.7 (t), 15.1 (q), 14.6 (q), 14.4 (q), 12.8 ppm (q); FTIR (film): $\tilde{\nu}$ = 2006, 1926, 1644 cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{27}\text{ClCrO}_5$ (506.94): C 61.60, H 5.37; found: C 62.11, H 5.21.

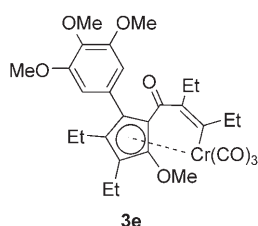
Tricarbonyl[1,2-diethyl- η^5 -3-[3,4-diethyl-2-methoxy-5-(4-methoxyphenyl)cyclopentadienyl]-3-oxo-1-propen-1-yl]chromium(II) (3c): Brown oil;



3c

yield: 22 % (method A), 16 % (method B); R_f : 0.28 (hexane/AcOEt 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.46 (d, $^3J(\text{H,H})$ = 8.4 Hz, 2H), 6.84 (d, $^3J(\text{H,H})$ = 8.4 Hz, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 2.89–2.78 (m, 2H), 2.57–2.40 (m, 2H), 2.29–2.09 (m, 4H), 1.19 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 1.12 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 0.87 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 0.77 ppm (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, 25 °C): δ = 246.1 (s), 240.0 (s), 235.4 (s), 219.7 (s), 191.6 (s), 160.6 (s), 159.3 (s), 141.4 (s), 132.0 (d, 2 CH), 122.5 (s), 113.4 (d, 2 CH), 111.1 (s), 106.3 (s), 100.2 (s), 95.0 (s), 60.0 (q), 55.2 (q), 39.9 (t), 24.0 (t), 18.4 (t), 17.8 (t), 15.2 (q), 14.8 (q), 14.5 (q), 12.9 ppm (q); FTIR (film): $\tilde{\nu}$ = 2004, 1925, 1644 cm^{-1} ; MS (FAB): m/z (%): 503 (6) $[\text{M}+1]^+$, 419 (45) $[\text{M}-3(\text{CO})+1]^+$, 418 (100); HRMS (FAB): m/z : calcd for $\text{C}_{27}\text{H}_{31}\text{CrO}_6$; 503.1526 $[\text{M}+1]^+$; found: 503.1523.

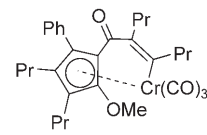
Tricarbonyl[1,2-diethyl- η^5 -3-[3,4-diethyl-2-methoxy-5-(3,4,5-trimethoxyphenyl)cyclopentadienyl]-3-oxo-1-propen-1-yl]chromium(II) (3e): Brown oil; yield: 14 % (method B); R_f : 0.38 (hexane/AcOEt 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS): δ = 6.77 (s, 2H), 3.89 (s, 3H), 3.85 (s, 9H), 2.89–2.80 (m, 2H), 2.59–2.42 (m, 2H), 2.29–2.12 (m, 4H), 1.21 (t, $^3J(\text{H,H})$ = 7.3 Hz, 3H), 1.11 (t, $^3J(\text{H,H})$ = 7.4 Hz, 3H), 0.93 (t, $^3J(\text{H,H})$ = 7.5 Hz, 3H), 0.75 ppm (t, $^3J(\text{H,H})$ = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, 25 °C): δ = 245.7 (s), 240.7 (s), 234.5 (s), 219.6 (s), 191.7 (s), 160.5 (s), 152.2 (s, 2 C), 141.2 (s), 137.5 (s), 125.9 (s), 110.4 (s), 108.3 (d, 2 CH), 107.1 (s),



3e

100.5 (s), 94.9 (s), 60.8 (q), 59.9 (q), 55.9 (q, 2 CH), 39.8 (t), 23.9 (t), 18.5 (t), 17.7 (t), 15.4 (q), 14.6 (q), 14.4 (q), 12.8 ppm (q); FTIR (film): $\tilde{\nu}$ = 2004, 1921, 1644 cm^{-1} ; MS (FAB): m/z (%): 563 (40) $[\text{M}+1]^+$, 479 (57) $[\text{M}-3(\text{CO})+1]^+$, 478 (85), 413 (100); HRMS (FAB): m/z : calcd for $\text{C}_{29}\text{H}_{35}\text{CrO}_8$; 563.1737 $[\text{M}+1]^+$; found: 563.1734.

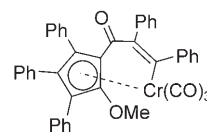
Tricarbonyl[η^5 -3-(2-methoxy-5-phenyl-3,4-dipropylcyclopentadienyl)-3-oxo-1,2-dipropyl-1-propen-1-yl]chromium(II) (3g): Brown oil; yield:



3g

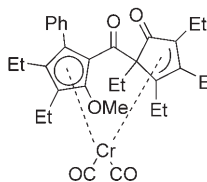
13 % (method A), 25 % (method B); R_f : 0.46 (hexane/AcOEt 5:1); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C, TMS): δ = 7.54–7.50 (m, 2H), 7.34–7.25 (m, 3H), 3.89 (s, 3H), 2.81–2.67 (m, 2H), 2.51–2.39 (m, 2H), 2.20–2.05 (m, 4H), 1.72–1.59 (m, 1H), 1.56–1.43 (m, 3H), 1.28–1.12 (m, 2H), 1.10–0.80 (m, 2H), 1.03 (t, $^3J(\text{H,H})$ = 6.6 Hz, 3H), 0.93 (t, $^3J(\text{H,H})$ = 6.8 Hz, 3H), 0.73 (t, $^3J(\text{H,H})$ = 6.8 Hz, 3H), 0.66 ppm (t, $^3J(\text{H,H})$ = 6.8 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz, 25 °C): δ = 246.1 (s), 239.9 (s), 235.2 (s), 218.0 (s), 191.5 (s), 159.4 (s), 141.6 (s), 130.8 (d, 2 CH + s), 128.0 (d), 127.9 (d, 2 CH), 110.8 (s), 106.4 (s), 99.5 (s), 93.9 (s), 59.9 (q), 49.9 (t), 32.9 (t), 27.3 (t), 26.7 (t), 24.0 (t), 23.6 (t), 23.0 (t), 21.5 (t), 14.7 (q), 14.5 (q), 14.2 (q), 13.7 ppm (q); FTIR (film): $\tilde{\nu}$ = 2005, 1921, 1644 cm^{-1} ; MS (FAB): m/z (%): 529 (26) $[\text{M}+1]^+$, 445 (57) $[\text{M}-3(\text{CO})+1]^+$, 444 (100); HRMS (FAB): m/z : calcd for $\text{C}_{30}\text{H}_{37}\text{CrO}_5$; 529.2046 $[\text{M}+1]^+$; found: 529.2034.

Tricarbonyl[η^5 -3-(2-methoxy-3,4,5-triphenylcyclopentadienyl)-3-oxo-1,2-diphenyl-1-propen-1-yl]chromium(II) (3h): Brown solid; yield: 32 % (method B); R_f : 0.42 (hexane/AcOEt 5:1); m.p. decomposition was observed upon heating above 110 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C, TMS): δ = 7.52–7.20 (m, 15H), 7.18–7.07 (m, 4H), 7.05–6.92 (m, 2H), 6.85 (d, $^3J(\text{H,H})$ = 6.8 Hz, 2H), 6.55 (d, $^3J(\text{H,H})$ = 7.5 Hz, 2H), 4.05 ppm (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz, 25 °C): δ = 246.2 (s), 237.3 (s), 236.4 (s), 213.9 (s), 190.1 (s), 157.4 (s), 151.5 (s), 138.3 (s), 138.0 (s), 131.4 (d, 2 CH), 131.2 (d, 2 CH), 131.0 (d, 2 CH), 130.6 (s), 130.0 (d, 2 CH), 128.6 (d, 128.4 (d, 2 CH), 128.3 (d), 128.1 (s), 127.7 (d, 4 CH), 127.4 (d, 2 CH), 127.3 (d, 2 CH), 126.4 (q), 126.1 (d), 124.4 (d, 2 CH), 107.9 (s), 107.4 (s), 101.4 (s), 96.6 (s), 62.0 ppm (q)—two aromatic signals, which correspond to a CH and a C, are probably overlapped with other signals as they were not detected; FTIR (film): $\tilde{\nu}$ = 2012, 1938, 1650 cm^{-1} .



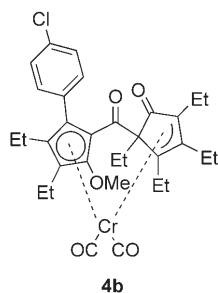
3h

Dicarbonyl[[(1S*)- η^5 -(3,4-diethyl-2-methoxy-5-phenylcyclopentadienyl)]-(1S*)-(2-4 η)-1,2,3,4-tetraethyl-5-oxocyclopent-3-enyl]ketone]chromium(II) (4a): Red solid; yield: 27 % (method A), 15 % (method B); R_f : 0.32 (hexane/AcOEt 5:1); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C, TMS): δ = 7.48–7.26 (m, 3H), 7.20–7.12 (m, 2H), 3.88 (s, 3H), 2.75–2.26 (m, 7H), 2.14–2.08 (m, 3H), 1.74–1.64 (m, 1H), 1.57–1.47 (m, 1H), 1.31–1.20 (m, 9H), 1.12 (t, $^3J(\text{H,H})$ = 7.1 Hz, 3H), 0.83 (t, $^3J(\text{H,H})$ = 7.1 Hz, 3H), 0.54 ppm (t, $^3J(\text{H,H})$ = 7.1 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz, 25 °C): δ = 248.6 (s), 248.5 (s), 197.8 (s), 190.0 (s), 133.9 (s), 129.7 (s), 128.1 (d, 2 CH), 127.5 (d, 3 CH), 120.0 (s), 112.0 (s), 99.7 (s), 98.4 (s), 94.4 (s), 89.3 (s), 85.6 (s), 83.4 (s), 65.2 (q), 26.2 (t), 24.6 (t), 23.8 (t), 21.1 (t), 18.5 (t), 17.6 (t), 16.1 (q), 15.9 (q), 14.2 (q), 13.8 (q), 13.7 (q), 6.8 ppm (q); FTIR (film): $\tilde{\nu}$ = 1959, 1902, 1711, 1662 cm^{-1} ; MS (FAB): m/z (%): 555 (18) $[\text{M}+1]^+$, 499 (51) $[\text{M}-2(\text{CO})+1]^+$, 498 (100); HRMS (FAB): m/z : $[\text{M}-2(\text{CO})+1]^+$: calcd for $\text{C}_{30}\text{H}_{39}\text{CrO}_3$; 499.2304; found: 499.2303.



4a

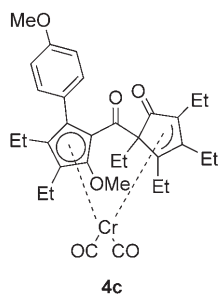
Dicarbonyl[[(1S*)- η^5 -(5-(4-chlorophenyl)-3,4-diethyl-2-methoxycyclopentadienyl)]-(1S*)-(2-4 η)-1,2,3,4-tetraethyl-5-oxocyclopent-3-enyl]ketone]chromium(II) (4b): Brown oil; yield: 23 % (meth-



4b

od A), 17% (method B); R_f =0.45 (hexane/AcOEt 5:1); ^1H NMR (400 MHz, CDCl_3 , 25°C, TMS): δ =7.26 (d, $^3J(\text{H,H})$ =8.1 Hz, 2H), 7.08 (d, $^3J(\text{H,H})$ =7.8 Hz, 2H), 3.88 (s, 3H), 2.71–2.26 (m, 7H), 2.17–2.02 (m, 3H), 1.77–1.65 (m, 1H), 1.62–1.51 (m, 1H), 1.32–1.21 (m, 9H), 1.15 (t, $^3J(\text{H,H})$ =7.3 Hz, 3H), 0.83 (t, $^3J(\text{H,H})$ =7.1 Hz, 3H), 0.58 ppm (t, $^3J(\text{H,H})$ =7.3 Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz, 25°C): δ =248.6 (s), 248.3 (s), 197.8 (s), 190.2 (s), 134.2 (s), 134.1 (s), 128.6 (s), 128.0 (d, 4 CH), 120.3 (s), 112.1 (s), 98.7 (s), 98.6 (s), 94.7 (s), 89.8 (s), 85.8 (s), 83.7 (s), 65.3 (q), 26.4 (t), 24.8 (t), 23.9 (t), 21.3 (t), 18.6 (t), 17.7 (t), 16.2 (q), 16.0 (q), 14.4 (q), 14.0 (q), 13.9 (q), 7.0 ppm (q); FTIR (film): ν =1958, 1902, 1712, 1660 cm^{-1} ; MS (FAB): m/z (%): 589 (12) $[M+1]^+$, 533 (51) $[M-2(\text{CO})+1]^+$, 532 (100); HRMS (FAB): m/z : calcd for $\text{C}_{32}\text{H}_{38}\text{CrClO}_5$: 589.1813 $[M+1]^+$; found: 589.1834.

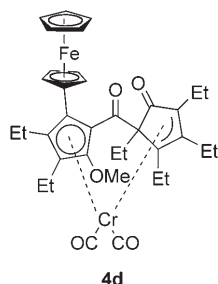
Dicarbonyl{[(1S*)- η^5 -[3,4-diethyl-2-methoxy-5-(4-methoxyphenyl)cyclopentadienyl]][(1S*)-(2-4 η)-1,2,3,4-tetraethyl-5-oxocyclopent-3-enyl]ketone}chromium(II) (4c):



4c

Orange oil; yield: 31% (method A), 20% (method B); R_f =0.23 (hexane/AcOEt 5:1); ^1H NMR (300 MHz, CDCl_3 , 25°C, TMS): δ =7.06 (d, $^3J(\text{H,H})$ =8.1 Hz, 2H), 6.81 (d, $^3J(\text{H,H})$ =8.6 Hz, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 2.80–2.25 (m, 7H), 2.22–1.97 (m, 3H), 1.79–1.63 (m, 1H), 1.62–1.47 (m, 1H), 1.42–1.20 (m, 9H), 1.14 (t, $^3J(\text{H,H})$ =7.4 Hz, 3H), 0.82 (t, $^3J(\text{H,H})$ =7.4 Hz, 3H), 0.56 ppm (t, $^3J(\text{H,H})$ =7.4 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25°C): δ =248.9 (s), 248.7 (s), 198.2 (s), 190.1 (s), 159.3 (s), 133.8 (s), 121.7 (s), 120.1 (s), 112.9 (d, 4 CH), 112.1 (s), 100.2 (s), 97.6 (s), 94.3 (s), 89.1 (s), 85.7 (s), 83.5 (s), 65.2 (q), 55.0 (q), 26.3 (t), 24.7 (t), 23.9 (t), 21.3 (t), 18.6 (t), 17.7 (t), 16.2 (q), 16.1 (q), 14.3 (q), 14.0 (q), 13.7 (q), 6.9 ppm (q); FTIR (film): ν =1954, 1898, 1712, 1666 cm^{-1} ; MS (FAB): m/z (%): 585 (17) $[M+1]^+$, 529 (50) $[M-2(\text{CO})+1]^+$, 528 (100); HRMS (FAB): m/z : calcd for $\text{C}_{33}\text{H}_{41}\text{CrO}_6$: 585.2308 $[M+1]^+$; found: 585.2324.

Dicarbonyl{[(1S*)- η^5 -(3,4-diethyl-2-ferrocenyl-5-methoxycyclopentadienyl)][(1S*)-(2-4 η)-1,2,3,4-tetraethyl-5-oxocyclopent-3-enyl]ketone}chromium(II) (4d):

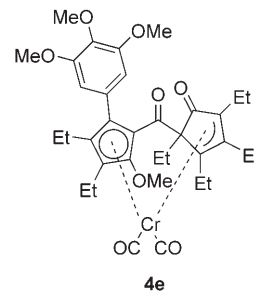


4d

Brown oil; yield: 29% (method A)—as a 1.7:1 observed mixture of non-separable isomers (ratio determined by ^1H NMR spectroscopy)—(the stereochemical descriptors indicated in the name correspond to the major diastereomer); R_f =0.31 (hexane/AcOEt 5:1); the abbreviation “min” refers to the signals assigned to the minor isomer and the abbreviation “maj” to the signals belonging to the major one; in the cases for which nothing is specified, either it hasn’t been possible to assign the signal to any of the isomers or it belongs to both of them: ^1H NMR (300 MHz, CDCl_3 , 25°C, TMS): δ =4.57–3.93 (m, 4H; maj + 4H; min), 4.17 (s, 5H; min), 4.04 (s, 5H; maj), 3.89 (s, 3H; maj), 3.72 (s, 3H; min), 2.80–1.75 (m, 22H), 1.62–1.05 (m, 26H), 0.91–0.82 ppm (m, 3H; maj + 3H; min), 0.66–0.58 ppm (m, 3H; maj + 3H; min); ^{13}C NMR (CDCl_3 , 75 MHz, 25°C): δ =250.3 (s; min), 249.3 (s; min), 249.2 (s; maj), 248.0 (s; maj), 199.4 (s; min), 198.6 (s; maj), 193.6 (s; min), 192.5 (s; maj), 133.61 (s), 133.55 (s), 121.4 (s; min), 120.1 (s; maj), 109.3 (min), 107.7; maj), 101.4 (s), 95.8 (s; maj), 94.4 (s; maj), 94.2 (s; min), 93.8 (s; min), 86.6 (s; maj), 86.0 (s; min), 85.8 (s; maj), 85.6 (s; min), 84.6 (s; min), 82.4 (s; maj), 80.2 (s; min), 77.2 (s; maj), 74.8 (d;

min), 71.5 (d; maj), 70.0 (d; maj), 69.6 (d, 5CH; maj), 69.5 (d; maj), 69.3 (d, 5CH; min), 69.0 (d; min), 68.8 (d; min), 67.3 (d; min), 66.6 (d; maj), 65.8 (q; min), 65.4 (q; maj), 26.5 (t; min), 26.0 (t; maj), 24.5 (t; min), 24.2 (t; maj), 23.8 (t; min), 23.3 (t; maj), 21.2 (t; maj), 20.8 (t; min), 20.6 (t; maj), 19.8 (t; min), 17.9 (t; min), 17.7 (t; maj), 16.3 (q; maj), 16.1 (q; min), 15.7 (q; maj), 15.1 (q; min), 14.5 (q), 14.3 (q; min), 14.1 (q), 13.5 (q; maj), 13.0 (q; min), 7.1 (q), 7.0 ppm (q); FTIR (film): ν =1956, 1900, 1705, 1660 cm^{-1} .

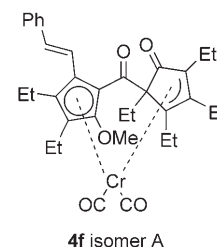
Dicarbonyl{[(1S*)- η^5 -[3,4-diethyl-2-methoxy-5-(3,4,5-trimethoxyphenyl)cyclopentadienyl]][(1S*)-(2-4 η)-1,2,3,4-tetraethyl-5-oxocyclopent-3-enyl]ketone}chromium(II) (4e):



4e

Brown oil; yield: 21% (method B); R_f =0.28 (hexane/AcOEt 3:1); ^1H NMR (400 MHz, CDCl_3 , 25°C, TMS): δ =6.37 (s, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.83 (s, 6H), 2.71–2.27 (m, 7H), 2.20–2.04 (m, 3H), 1.77–1.68 (m, 1H), 1.59–1.49 (m, 1H), 1.32–1.21 (m, 9H), 1.18 (t, $^3J(\text{H,H})$ =7.2 Hz, 3H), 0.87 (t, $^3J(\text{H,H})$ =7.3 Hz, 3H), 0.59 ppm (t, $^3J(\text{H,H})$ =7.3 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25°C): δ =249.2 (s), 248.3 (s), 198.3 (s), 190.1 (s), 152.1 (s, 2 C), 138.2 (s), 133.7 (s), 125.1 (d, 2 CH), 120.2 (s), 112.3 (s), 100.2 (s), 98.0 (s), 94.4 (s), 90.0 (s), 85.4 (s), 83.9 (s), 65.2 (q), 61.1 (q), 56.2 (q, 2 CH₃), 26.4 (t), 24.8 (t), 24.0 (t), 21.6 (t), 18.9 (t), 17.8 (t), 16.3 (q), 16.0 (q), 14.4 (q), 13.9 (q), 13.8 (q), 7.1 ppm (q)—an aromatic signal, which correspond to a carbon atom, is probably overlapped with other signals as it was not detected; FTIR (film): ν =1955, 1901, 1712, 1666 cm^{-1} ; MS (FAB): m/z (%): 645 (11) $[M+1]^+$, 589 (50) $[M-2(\text{CO})+1]^+$, 588 (100); HRMS (FAB): m/z : calcd for $\text{C}_{35}\text{H}_{45}\text{CrO}_8$: 645.2520 $[M+1]^+$; found: 645.2515; elemental analysis calcd (%) for $\text{C}_{35}\text{H}_{44}\text{CrO}_8$ (644.72): C 65.20, H 6.88; found: C 65.32, H 7.35.

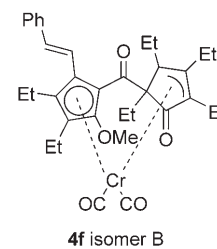
Dicarbonyl{[(1S*)- η^5 -[3,4-diethyl-2-methoxy-5-(2-phenylethenyl)cyclopentadienyl]][(1S*)-(2-4 η)-1,2,3,4-tetraethyl-5-oxocyclopent-3-enyl]ketone}chromium(II) (4f), isomer A:



4f isomer A

Orange oil; yield: 16% (method A), 9% (method B); R_f =0.54 (hexane/AcOEt 5:1); ^1H NMR (400 MHz, CDCl_3 , 25°C, TMS): δ =7.50–7.21 (m, 5H), 6.32 (d, $^3J(\text{H,H})$ =16.0 Hz, 1H), 6.06 (d, $^3J(\text{H,H})$ =16.0 Hz, 1H), 3.87 (s, 3H), 2.67–2.43 (m, 5H), 2.39–2.26 (m, 2H), 2.23–2.12 (m, 2H), 2.06–1.97 (m, 1H), 1.82–1.73 (m, 1H), 1.60–1.50 (m, 1H), 1.36–0.83 (m, 12H), 1.34 (t, $^3J(\text{H,H})$ =7.6 Hz, 3H), 0.66 ppm (t, $^3J(\text{H,H})$ =7.5 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25°C): δ =248.5 (s), 247.3 (s), 197.6 (s), 190.5 (s), 137.2 (d), 136.7 (s), 134.1 (s), 128.6 (d, 2 CH), 127.9 (d), 126.8 (d, 2 CH), 120.2 (s), 114.8 (d), 108.1 (s), 96.8 (s), 96.5 (s), 95.0 (s), 87.9 (s), 86.3 (s), 82.8 (s), 65.1 (q), 25.9 (t), 24.5 (t), 23.6 (t), 20.8 (t), 19.4 (t), 17.6 (t), 16.1 (q), 15.8 (q), 15.3 (q), 14.1 (q), 13.9 (q), 7.2 ppm (q); FTIR (film): ν =1955, 1901, 1708, 1667 cm^{-1} ; MS (EI): m/z (%): 580 (3) $[M]^+$, 525 (44), 524 ppm (100) $[M-2(\text{CO})]^+$; HRMS (EI): m/z : calcd for $\text{C}_{34}\text{H}_{40}\text{CrO}_5$: 580.2275 $[M]^+$; found: 580.2277.

Dicarbonyl{[(1S*)- η^5 -[3,4-diethyl-2-methoxy-5-(2-phenylethenyl)cyclopentadienyl]][(1R*)-(2-4 η)-1,2,3,4-tetraethyl-5-oxocyclopent-3-enyl]ketone}chromium(II) (4f), isomer B:

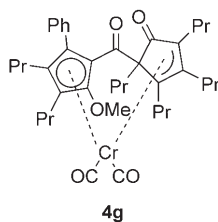


4f isomer B

Orange oil; yield: 15% (method A), 9% (method B); R_f : 0.48 (hexane/AcOEt 5:1); ^1H NMR (400 MHz, CDCl_3 , 25°C, TMS): δ =7.52–7.19 (m, 5H), 6.98 (d, $^3J(\text{H,H})$ =16.1 Hz, 1H), 6.79 (d, 3J

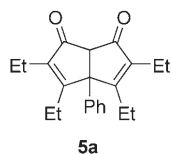
(H,H)=16.1 Hz, 1H), 3.74 (s, 3H), 2.59–2.28 (m, 6H), 2.25–2.11 (m, 3H), 2.10–2.00 (m, 1H), 1.94–1.85 (m, 1H), 1.57–1.50 (m, 1H), 1.29–0.91 (m, 6H), 1.24 (t, $^3J(\text{H,H})=7.5$ Hz, 3H), 1.10 (t, $^3J(\text{H,H})=7.6$ Hz, 3H), 0.88 (t, $^3J(\text{H,H})=7.6$ Hz, 3H), 0.70 ppm (t, $^3J(\text{H,H})=7.5$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz, 25°C): $\delta=249.4$ (s), 247.9 (s), 197.3 (s), 194.1 (s), 136.8 (s), 135.6 (s), 134.1 (d), 128.7 (d, 2 CH), 128.1 (d), 126.5 (d, 2 CH), 121.2 (s), 120.3 (d), 107.2 (s), 94.7 (s), 93.8 (s), 92.5 (s), 86.1 (s), 84.9 (s), 84.1 (s), 66.0 (q), 26.4 (t), 24.8 (t), 24.3 (t), 20.9 (t), 18.9 (t), 17.8 (t), 16.2 (q), 16.1 (q), 15.5 (q), 15.0 (q), 13.2 (q), 7.1 ppm (q); FTIR (film): $\tilde{\nu}=1954, 1900, 1708, 1667\text{ cm}^{-1}$; MS (EI): m/z (%): 580 (3) $[M]^+$, 525 (44), 524 (100) $[M-2(\text{CO})]^+$; HRMS (EI): m/z : calcd for $\text{C}_{32}\text{H}_{40}\text{CrO}_3$: 524.2377 $[M-2(\text{CO})]^+$; found: 524.2376.

Dicarbonyl[(1S*)- η^5 -(2-methoxy-5-phenyl-3,4-dipropylcyclopentadienyl)][(1S*)-(2-4 η)-5-oxo-1,2,3,4-tetrapropylcyclopent-3-enyl]ketone]chromium(II) (4g):



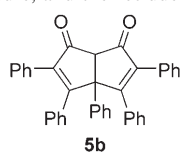
(s), 93.0 (s), 88.9 (s), 84.6 (s), 83.0 (s), 65.1 (q), 35.8 (t), 34.4 (t), 33.8 (t), 30.9 (t), 27.6 (t), 26.8 (t), 25.3 (t), 24.8 (t), 22.9 (t), 22.8 (t), 22.5 (t), 15.5 (q), 15.4 (t), 15.2 (q), 15.0 (q), 14.7 (q), 14.4 (q), 13.8 ppm (q); FTIR (film): $\tilde{\nu}=1956, 1900, 1713, 1662\text{ cm}^{-1}$; MS (EI): m/z (%): 638 (2) $[M]^+$, 583 (41), 582 ppm (100) $[M-2(\text{CO})]^+$; HRMS (EI): calcd for $\text{C}_{38}\text{H}_{50}\text{CrO}_3$: 638.3058 $[M]^+$; found: 638.3069.

2,3,4,5,6a-Pentaethylpentalen-1,6(3aH,6aH)dione (5a): A solution of complex 3a (302 mg, 0.64 mmol) in a 9:1 mixture of hexanes/ethyl acetate (90 mL hexanes, 10 mL ethyl acetate) was exposed to light and air until complete disappearance of the carbene complex was observed by TLC (≈ 24 h). The reaction mixture was filtered through Celite and washed with a 9:1 mixture of hexanes/ethyl acetate. Solvent was removed under reduced



pressure, and the residue purified by flash chromatography (hexane/AcOEt); compound 5a was isolated in 30% yield (61 mg). Yellow oil; $R_f=0.17$ (hexane/AcOEt 5:1); ^1H NMR (300 MHz, CDCl_3 , 25°C, TMS): $\delta=7.28\text{--}7.14$ (m, 3H), 6.99–6.95 (m, 2H), 3.09 (s, 1H), 2.49 (q, $^3J(\text{H,H})=7.6$ Hz, 4H), 2.22 (q, $^3J(\text{H,H})=7.6$ Hz, 2H), 2.20 (q, $^3J(\text{H,H})=7.6$ Hz, 2H), 1.06 (t, $^3J(\text{H,H})=7.6$ Hz, 6H), 0.98 ppm (t, $^3J(\text{H,H})=7.6$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz, 25°C): $\delta=197.8$ (s; 2C), 173.3 (s; 2C), 142.6 (s; 2C), 140.6 (s), 128.7 (d; 2CH), 127.4 (d), 127.2 (d; 2CH), 70.5 (d), 65.0 (s), 22.9 (t; 2CH₂), 17.2 (t; 2CH₂), 13.7 (c; 2CH₃), 12.6 ppm (c; 2CH₃); FTIR (film): $\tilde{\nu}=1721\text{ cm}^{-1}$; MS (EI): m/z (%): 322 (100) $[M]^+$, 307 (30), 293 (61), 265 (22); HRMS (EI): m/z : calcd for $\text{C}_{22}\text{H}_{26}\text{O}_2$: 322.1927 $[M]^+$; found: 322.1930.

Synthesis of 2,3,4,5,6a-pentaphenylpentalen-1,6(3aH,6aH)dione (5b): A solution of carbene complex 1a (1 equiv, 0.5 mmol) and toluene 2c (2.5 mmol, 446 mg) in dry 1,2-dichloroethane (10 mL) was heated at 110°C in a sealed tube until complete disappearance of the carbene complex was observed by TLC (≈ 12 h). Solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/AcOEt) yielding compound 5b

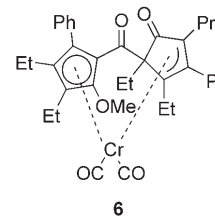


(77 mg). Brown oil; yield: 30%; $R_f=0.20$ (hexane/AcOEt 5:1); ^1H NMR (400 MHz, CDCl_3 , 25°C, TMS): $\delta=7.90$ (d, $^3J(\text{H,H})=7.5$ Hz, 2H), 7.64–6.82 (m, 19H), 6.73 (app.t, $^3J(\text{H,H})=$

7.7 Hz, 4H), 3.80 ppm (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz, 25°C): $\delta=194.7$ (s; 2C), 168.6 (s; 2C), 142.3 (s; C), 141.1 (s; 2C), 134.9 (s; 2C), 130.7 (s; 2C), 130.1 (d; 4CH), 129.8 (d; 4CH), 129.3 (d; 2CH), 128.4 (d; 2CH), 128.1 (d; 2CH), 128.0 (d; 4CH), 127.7 (d), 127.35 (d; 4CH), 127.30 (d; 2CH), 73.5 (d), 67.0 (s); FTIR (film): $\tilde{\nu}=1728\text{ cm}^{-1}$; MS (EI): m/z (%): 514 (100) $[M]^+$, 486 (33), 409 (26), 308 (56), 178 (95); HRMS (EI) calcd: for $\text{C}_{38}\text{H}_{26}\text{O}_2$: 514.1927 $[M]^+$; found: 514.1930.

Reaction of complex 3a with internal acetylenes: A solution of complex 3a (1 equiv, 0.3 mmol, 142 mg) and the corresponding acetylene 2 (1.5 mmol) in dry 1,2-dichloroethane (6 mL) was heated at 110°C in a sealed tube until complete disappearance of complex 3a was observed by TLC (≈ 12 h). Solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/AcOEt). When 3-hexyne was used complex 4a, described above, was isolated in 45% yield; when the acetylene was 4-octyne, complex 6 was obtained.

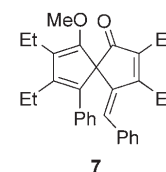
Dicarbonyl[(1S*)- η^5 -(3,4-diethyl-2-methoxy-5-phenylcyclopentadienyl)]-(1S*)-(2-4 η)-1,2-diethyl-5-oxo-3,4-dipropylcyclopent-3-enyl]ketone]chromium(II) (6):



30%; $R_f=0.50$ (hexane/AcOEt 5:1); ^1H NMR (300 MHz, CDCl_3 , 25°C, TMS): $\delta=7.32\text{--}7.27$ (m, 3H), 7.18–7.15 (m, 2H), 3.90 (s, 3H), 2.78–2.33 (m, 6H), 2.27–1.95 (m, 4H), 1.90–1.48 (m, 6H), 1.33–1.22 (m, 1H), 1.31 (t, $^3J(\text{H,H})=7.7$ Hz, 3H), 1.25 (t, $^3J(\text{H,H})=7.7$ Hz, 3H), 1.03 (t, $^3J(\text{H,H})=7.3$ Hz, 3H), 0.95 (t, $^3J(\text{H,H})=7.3$ Hz, 3H), 0.86 (t, $^3J(\text{H,H})=7.7$ Hz, 3H), 0.54 ppm (t, $^3J(\text{H,H})=7.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz, 25°C): $\delta=248.9$ (s), 248.6 (s), 197.6 (s), 190.2 (s), 134.3 (s), 129.9 (s), 128.2 (d; 2CH), 127.5 (d; 3CH), 119.1 (s), 112.0 (s), 100.0 (s), 98.7 (s), 94.5 (s), 89.3 (s), 85.1 (s), 83.4 (s), 65.1 (q), 34.3 (t), 31.0 (t), 26.2 (t), 25.2 (t), 23.8 (t), 22.6 (t), 18.6 (t), 17.7 (t), 15.7 (q), 15.1 (q), 14.8 (q), 14.0 (q), 13.7 (q), 6.9 ppm (q); FTIR (film): $\tilde{\nu}=1955, 1899, 1712, 1666\text{ cm}^{-1}$; MS (EI): m/z (%): 582 (4) $[M]^+$, 527 (42), 526 (100) $[M-2(\text{CO})]^+$; HRMS (EI): m/z : calcd for $\text{C}_{34}\text{H}_{42}\text{CrO}_3$: 582.2432 $[M]^+$; found: 582.2426.

Reaction of complex 3a with phenylacetylene: A solution of complex 3a (1 equiv, 0.44 mmol, 208 mg) and phenylacetylene (2.2 mmol, 225 mg) in dry 1,2-dichloroethane (9 mL) was heated at 110°C in a sealed tube until complete disappearance of complex 3a was observed by TLC (≈ 17 h). Solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/AcOEt) yielding product 7.

(4E)-2,3,7,8-Tetraethyl-6-methoxy-1-oxo-9-phenyl-4-phenylmethyldenspiro[4.4]nona-2,6,8-triene (7):

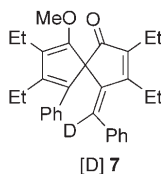


Yellow oil; yield: 35%; $R_f=0.54$ (hexane/AcOEt 5:1); ^1H NMR (600 MHz, CDCl_3 , 25°C, TMS): $\delta=7.37\text{--}7.26$ (m, 3H), 7.24–7.16 (m, 5H), 7.09–7.04 (m, 2H), 6.57 (s, 1H), 3.67 (s, 3H), 2.48–2.42 (m, 1H), 2.41–2.34 (m, 1H), 2.32–2.23 (m, 3H), 2.22–2.13 (m, 3H), 1.22 (t, $^3J(\text{H,H})=7.6$ Hz, 3H), 1.10 (t, $^3J(\text{H,H})=7.5$ Hz, 3H), 0.88 (t, $^3J(\text{H,H})=7.5$ Hz, 3H), 0.42 ppm (t, $^3J(\text{H,H})=7.5$ Hz, 3H); ^{13}C NMR (CDCl_3 , 150 MHz, 25°C): $\delta=202.3$ (s), 167.6 (s), 158.1 (s), 148.7 (s), 145.8 (s), 137.6 (s), 137.2 (s), 135.6 (s), 133.7 (s), 129.9 (d, 2 CH), 128.5 (d, 2 CH), 128.1 (s), 127.9 (d, 2 CH), 127.6 (d, 2 CH), 127.3 (d), 126.7 (d), 124.6 (d), 72.5 (s), 58.9 (q), 21.0 (t), 19.9 (t), 17.7 (t), 17.0 (t), 15.1 (q), 14.7 (q), 12.9 (q), 12.7 ppm (q); FTIR (film): $\tilde{\nu}=1698\text{ cm}^{-1}$; MS (EI): m/z (%): 438 (23) $[M]^+$, 424 (13), 395 (100); HRMS (EI): m/z : for $\text{C}_{31}\text{H}_{34}\text{O}_2$ [M]⁺: calcd 438.2559; found 438.2551.

Reaction of complex 3a with 1-deutero-2-phenylethyne: A solution of complex 3a (1 equiv, 0.44 mmol, 208 mg) and 1-deutero-2-phenylethyne (2.2 mmol, 227 mg) in dry 1,2-dichloroethane (9 mL) was heated at 110°C in a sealed tube until complete disappearance of complex 3a was observed by TLC (≈ 17 h). Solvent was removed under reduced pressure,

and the residue purified by flash chromatography (hexane/AcOEt) yielding product [D]7.

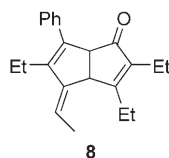
(4E)-2,3,7,8-Tetraethyl-6-methoxy-1-oxo-9-phenyl-4-(1-deutero-1-phenylmethyliden)spiro[4.4]nona-2,6,8-triene [D]7: Brown oil; yield: 44%; R_f : 0.52 (hexane/AcOEt 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C, TMS): δ = 7.37–7.25 (m, 3H), 7.24–7.16 (m, 5H), 7.08–7.04 (m, 2H), 3.66 (s, 3H), 2.49–2.32 (m, 2H), 2.31–2.22 (m, 3H), 2.21–2.12 (m, 3H), 1.21 (t, $^3J(\text{H,H})$ = 7.6 Hz, 3H), 1.09 (t, $^3J(\text{H,H})$ = 7.6 Hz, 3H), 0.87 (t, $^3J(\text{H,H})$ = 7.6 Hz, 3H), 0.42 ppm (t, $^3J(\text{H,H})$ = 7.6 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz, 25°C): δ = 202.1 (s), 167.4 (s), 158.0 (s), 148.5 (s), 145.7 (s), 137.4 (s), 136.9 (s), 135.5 (s), 133.6 (s), 129.8 (d; 2CH), 128.4 (d; 2CH), 127.9 (s), 127.8 (d; 2CH), 127.4 (d; 2CH), 127.2 (d), 126.5 (d), 124.1 (this signal appears as a triplet due to C–D coupling, $^1J(\text{C,D})$ = 25.9 Hz), 72.3 (s), 58.7 (q), 20.8 (t), 19.8 (t), 17.5 (t), 16.9 (t), 14.9 (q), 14.6 (q), 12.7 (q), 12.6 ppm (q); FTIR (film): ν = 1694 cm^{-1} ; MS (EI): m/z (%): 439 (26) $[M]^+$, 396 (58), 321 (72), 149 cm^{-1} (100); HRMS (EI): calcd for $\text{C}_{31}\text{H}_{33}\text{O}_2\text{D}$: 439.2616 $[M]^+$; found: 439.2616.



[D] 7

Reaction of complex 3a with trifluoroacetic acid: Trifluoroacetic acid (1 mmol, 74 μL) was slowly added over a solution of complex 3a (1 equiv, 0.4 mmol, 189 mg) in dry toluene (6 mL), and the mixture was heated at 50°C until complete disappearance of the complex 3a was observed by TLC ($\approx$ 24 h). Solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexane/AcOEt) yielding product 8.

(4E)-2,3,5-Triethyl-4-ethyldien-3a,4-dihydro-6-phenylpentalen-1-(6aH)one (8): Yellow oil; yield: 41%; R_f = 0.40 (hexane/AcOEt 5:1);



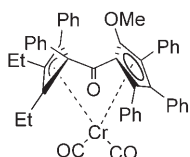
8

$^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C, TMS): δ = 7.41–7.31 (m, 2H), 7.29–7.20 (m, 3H), 5.69 (q, $^3J(\text{H,H})$ = 7.1 Hz, 1H), 4.10 (brs, 1H), 3.87 (brs, 1H), 2.53–2.04 (m, 6H), 2.00 (d, $^3J(\text{H,H})$ = 7.1 Hz, 3H), 1.18 (t, $^3J(\text{H,H})$ = 7.7 Hz, 3H), 0.99 (t, $^3J(\text{H,H})$ = 7.7 Hz, 3H), 0.91 ppm (t, $^3J(\text{H,H})$ = 7.7 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, 25°C):

δ = 206.7 (s), 173.2 (s), 144.6 (s), 141.2 (s), 139.6 (s), 139.3 (s), 136.1 (s), 128.4 (d, 2 CH), 128.0 (d, 2 CH), 127.1 (d), 116.0 (d), 58.6 (d), 46.2 (d), 22.0 (t), 18.3 (t), 16.3 (t), 16.0 (q), 13.6 (q), 13.42 (q), 13.36 ppm (q); FTIR (film): ν = 1700 cm^{-1} ; MS (EI): m/z (%): 306 (100) $[M]^+$, 291 (60), 277 (81), 249 (42); HRMS (EI): calcd for $\text{C}_{22}\text{H}_{26}\text{O}$: 306.1978 $[M]^+$; found: 306.1980.

Reaction of complex 3h with 3-hexyne: A solution of complex 3h (1 equiv, 0.3 mmol, 199 mg) and 3-hexyne 2a (1.5 mmol, 170 μL) in dry 1,2-dichloroethane (6 mL) was heated at 110°C in a sealed tube until complete disappearance of the complex 3h was observed by TLC ($\approx$ 12 h). Solvent was removed under reduced pressure, the residue was purified by flash chromatography (hexane/AcOEt), and two diastereomers of compound 9 were separately isolated.

Dicarbonyl[(1S*)- η^5 -(2-methoxy-3,4,5-triphenylcyclopentadienyl)]-[(1R*)-(2-4 η)-(3,4-diethyl-1,2-diphenylcyclobut-1-enyl)ketone]chromium(II) (9), isomer A: Brown solid; yield: 28%; R_f : 0.50 (hexane/AcOEt 5:1);

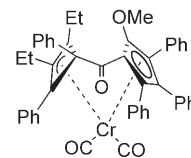


9 isomer A

$^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C, TMS): δ = 7.35–7.04 (m, 21H), 7.05 (d, $^3J(\text{H,H})$ = 6.8 Hz, 2H), 6.89 (dd, $^3J(\text{H,H})$ = 8.0, $^4J(\text{H,H})$ = 1.6 Hz, 2H), 3.07–3.00 (m, 1H), 2.90 (s, 3H), 2.51–2.42 (m, 1H), 1.63–1.51 (m, 1H), 1.27 (t, $^3J(\text{H,H})$ = 7.6 Hz, 3H), 0.57–0.48 (m, 1H), 0.16 ppm (t, $^3J(\text{H,H})$ = 7.6 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, 25°C): δ = 251.9 (s), 250.3 (s), 203.3 (s), 140.9 (s), 138.7 (s), 133.3 (s), 132.5 (s), 132.2 (d), 131.8 (s), 131.5 (d), 130.3 (s), 130.0 (d), 128.2 (d), 128.1 (d), 127.9 (d), 127.8 (d),

127.62 (d), 127.57 (d), 127.51 (d), 127.0 (d), 126.5 (d), 126.0 (d), 116.6 (s), 105.6 (s), 96.9 (s), 95.7 (s), 88.8 (s), 87.3 (s), 79.6 (s), 61.8 (q), 24.5 (t), 22.5 (t), 14.2 (q), 13.6 ppm (q)—some signals for the aromatic carbon atoms are overlapped; FTIR (film): $\tilde{\nu}$ = 1945, 1892, 1704 cm^{-1} ; MS (EI): m/z (%): 718 (3) $[M]^+$, 663 (57), 662 (100) $[M-2(\text{CO})]^+$, 402 (87); HRMS (EI): m/z : calcd for $\text{C}_{45}\text{H}_{38}\text{CrO}_2$: 662.2271 $[M-2(\text{CO})]^+$; found: 662.2270.

Dicarbonyl[(1S*)- η^5 -(2-methoxy-3,4,5-triphenylcyclopentadienyl)] [(1S*)-(2-4 η)-(3,4-diethyl-1,2-diphenylcyclobut-1-enyl)ketone]chromium(II) (9), isomer B: Brown solid; yield: 24%; R_f : 0.57 (hexane/AcOEt 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25°C, TMS): δ = 7.31–6.69 (m, 25H), 3.74 (s, 3H), 2.93–2.78 (m, 2H), 2.69–2.54 (m, 2H), 1.27 (t, $^3J(\text{H,H})$ = 7.6 Hz, 3H), 0.77 ppm (t, $^3J(\text{H,H})$ = 7.6 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz, 25°C): δ = 250.0 (s), 249.7 (s), 202.6 (s), 140.6 (s), 137.6 (s), 132.7 (s), 132.2 (d), 132.0 (d), 131.7 (s), 131.4 (d), 130.0 (s), 129.6 (s), 128.1 (d), 127.7 (d), 127.6 (d), 127.5 (d), 127.3 (d), 127.2 (d), 127.1 (d), 126.5 (d), 124.8 (d), 116.3 (s), 104.8 (s), 102.0 (s), 97.1 (s), 95.7 (s), 89.7 (s), 89.0 (s), 75.6 (s), 63.9 (q), 24.7 (t), 23.0 (t), 14.2 (q), 13.6 ppm (q)—some signals for aromatic carbon atoms are overlapped; FTIR (film): $\tilde{\nu}$ = 1948, 1893, 1704 cm^{-1} ; MS (EI): m/z (%): 718 (2) $[M]^+$, 663 (54), 662 (100) $[M-2(\text{CO})]^+$, 402 (68); HRMS (EI): m/z : calcd for $\text{C}_{45}\text{H}_{38}\text{CrO}_2$: 662.2271 $[M-2(\text{CO})]^+$; found: 662.2265.



9 isomer B

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