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Coupling of pentacarbonyl[(cyclopropyl)methoxymethylene]-molybdenum complex with ferrocenylalkynes: Synthesis of ferrocenyl-substituted cycloheptadienones and cycloheptenediones

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Abstract

Pentacarbonyl[(cyclopropyl)methoxymethylene]molybdenum complex reacts with ferrocenyl alkynes to afford ferrocenyl-substituted 2,4-cycloheptadienones as major products, accompanied by varying amounts of 2-cycloheptene-1,4-diones and/or 2-cyclobutenones. 2-Cycloheptene-1,4-diones are secondary reaction products and result from initially formed 2,4-cycloheptadienones via hydrolysis. In one reaction, a hydroxy-substituted 2,4-cycloheptadienone derivative was isolated, which was not observed previously from similar reactions.

Keywords: Fischer metal carbene; Molybdenum carbene complex; Ferrocene; Ferrocenyl alkynes; Carbocyclic seven-membered rings; Cycloheptadienones; Cycloheptenediones; Cyclobutenones; Coupling

1. Introduction

Carbocyclic seven-membered rings are present in a variety of biologically-important molecules, including phorbol esters [1], colchicine derivatives [2], guaiazulenes [3], guaianolides [3] and pseudoguiainolides [3,4], the latest having more than 1000 varieties [4]. Some of them exhibit high biological activities such as antitumor, antiulcer, antisistosomal, anthelmintic, cardiotonic, contraceptive, immunomodulation, root-growth stimulatory, root-growth and germination inhibitory activities, as well as preventive or curative activities for crop diseases [5]. Recent studies have suggested that the integration of a ferrocenyl group into such structures may enhance their biological activities or generate new medicinal properties [6,7]. A typical example is hydroxyferrocifen [7], (*Z*)-[(Et)(Fc)C=C(*p*-C_6H_4-OH)*p*-C_6H_4-O-CH_2-CH_2-NMe_2], a ferrocenyl analog of hydroxytamoxifen which is a drug currently used in the treatment of hormone-dependent breast cancer lines [8]. The replacement of the phenyl ring by a ferrocenyl (Fc) moiety has brought about novel pharmacological properties for hydroxyferrocifen since it is active against both hormone-dependent and hormone-independent breast cancer cells whereas its phenyl counterpart, hydroxytamoxifen, is active only against hormone-dependent cancer cells [7,8]. Due to its unique structure, different membrane-permeation properties and anomalous metabolism, ferrocene is often incorporated into a compound in order to get unexpected or enhanced biological activities [9]. Surprisingly, seven-membered ring carbocycles bearing a ferrocenyl moiety are very rare. The development of a general synthetic entry to such compounds is therefore of considerable interest since it could lead to a new source of biologically active compounds.

These ring systems are typically constructed by ring expansion reactions, cyclization reactions, cycloaddition reactions and synthetic modifications of other seven-membered rings [10]. Recently, Fischer type metal carbene

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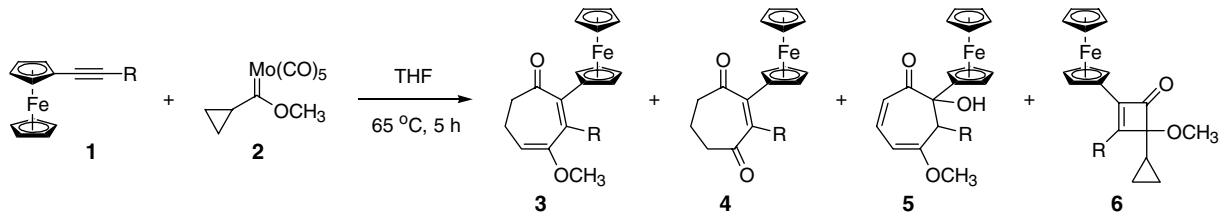


Scheme 1. Reaction of carbene complex **2** with ferrocenyl alkynes **1**. For definition of R group for compounds **1** and **3**–**6**, see Table 1.

complexes have emerged as valuable reagents for organic synthesis [11]. An ever continuing aspect of these studies has been the use of a structurally diverse set of Fischer carbene complexes to afford a diverse array of compounds. In this regard, as shown by the Herndon research group [12,13], the reaction between alkynes and pentacarbonyl-[(cyclopropyl)methoxymethylene]metal complexes represent a very rapid entry to the corresponding 2,4-cycloheptadienones. This methodology, however, has not been utilized for the synthesis of 2-ferrocenyl-2,4-cycloheptadienones, presumably due to the scarce availability of the starting ferrocenyl alkynes. As part of our general interest in ferrocene [14,15] and metal carbene chemistry [13,16], as well as small and medium-size ring systems [17], we have investigated the reaction between ferrocenyl alkynes **1** and pentacarbonyl[(cyclopropyl)methoxymethylene]molybdenum complex **2** to afford ferrocenyl-substituted cycloheptadienones **3** (Scheme 1) [18]. We herein report the results of this study.

2. Results and discussion

2.1. Synthesis of starting materials

The synthesis of ferrocenyl alkynes were achieved from ethynylferrocene [19] according to known or modified literature procedures [20–22]. Treatment of ethynylferrocene with *n*-butyllithium produced in situ lithioethynylferrocene that was further reacted with methyl iodide and benzyl bromide to yield propynylferrocene (**1A**) and (3-phenylpropynyl)ferrocene (**1B**), respectively [20]. On the other hand, the reaction of ethynylferrocene and iodobenzene in the presence of copper iodide, triphenylphosphine and potassium carbonate in refluxing DMF produced (phenylethynyl)ferrocene (**1C**) [21]. Diferrocenylethyne (**1D**) was synthesized by the metathesis of propynylferrocene in the presence of molybdenum hexacarbonyl and 2-fluorophenol in refluxing chlorobenzene [22]. Pentacarbonyl[(cyclopropyl)methoxymethylene]molybdenum complex **2** was prepared from cyclopropyl bromide and molybdenum hexacarbonyl according to a standard protocol [13b].

2.2. Coupling of pentacarbonyl [(cyclopropyl)methoxymethylene]molybdenum complex 2 with ferrocenyl alkynes 1

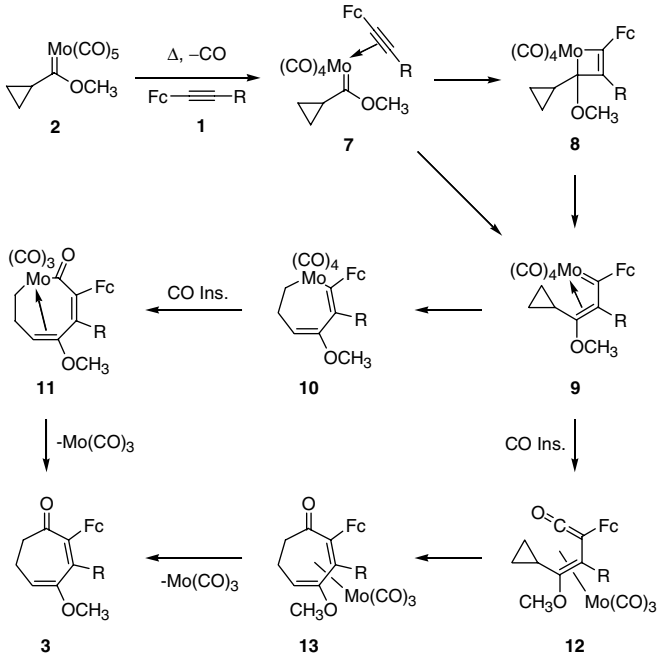
We next investigated the reaction of carbene complex **2** with ferrocenyl alkynes **1**. The results are summarized in Scheme 1 and Table 1. The reactions were carried out under optimal conditions, which involve heating a 1:1.5 mole ratio of carbene complex **2** and alkyne **1**, respectively, in THF at 65 °C. Initially, the reaction between propynylferrocene (**1A**) and carbene complex **2** was examined, which afforded the expected cycloheptadienone (**3A**) as the major product of the reaction, along with the varying amounts of cycloheptenedione (**4A**) and hydroxy-substituted cycloheptadienone (**5A**) (entry A). The coupling of carbene complex **2** with benzylferrocenylacetylene (**1B**) produced two products, cycloheptadienone (**3B**) and cycloheptenedione (**4B**), with **3B** the major product of the reaction (entry B). A similar trend was observed in the reaction of **2** with (phenylethynyl)ferrocene (**1C**), where cycloheptadienone (**3C**) and cycloheptenedione (**4C**) were obtained, the former being the major product (entry C). On the other hand, the reaction between diferrocenylacetylene (**1D**) and carbene complex **2** revealed a complex reaction mixture; only cycloheptadienone (**3D**) and cyclobutenone (**6D**) could be isolated (entry D). Triphenylphosphine is often used to improve the yields of products in metal carbene reactions [13]. Triphenylphosphine could displace carbon monoxide at early stage of the reaction, which could then be replaced by the alkyne. When the same reactions, however, were carried out in the presence of triphenylphosphine, low yields of products were obtained in contrast to previous studies [13a], which may be attributed to the probable steric effect caused by triphenylphosphine and ferrocene moieties. That is why; all reactions in this study were performed without using triphenylphosphine.

Table 1
Reaction of carbene complex **2** with ferrocenyl alkynes **1**

Entry[a]	Alkyne	R	Products (isolated yield, %)
A	**1A**	CH_3	**3A** (47) + **4A** (12) + **5A**[b] (12)
B	**1B**	CH_2Ph	**3B** (70) + **4B** (13)
C	**1C**	Ph	**3C** (72) + **4C** (10)
D	**1D**	Fc (ferrocenyl)	**3D** (15) + **6D** (8)

[a] Entry letters define R group for compounds **1** and **3**–**6**.
[b] Relative stereochemistry of substituents at carbons 6 and 7 was not determined.

As noted in Table 1, cycloheptadienones (**3**) have been obtained as the major products from the reactions between molybdenum carbene complex **2** and ferrocenyl alkynes (**1**). In the light of previous studies [13,23], the proposed mechanism for their formation is outlined in Scheme 2. The loss of a carbon monoxide ligand from complex **2** and coordination



Scheme 2. Proposed mechanism for the formation of cycloheptadienones (**3**).

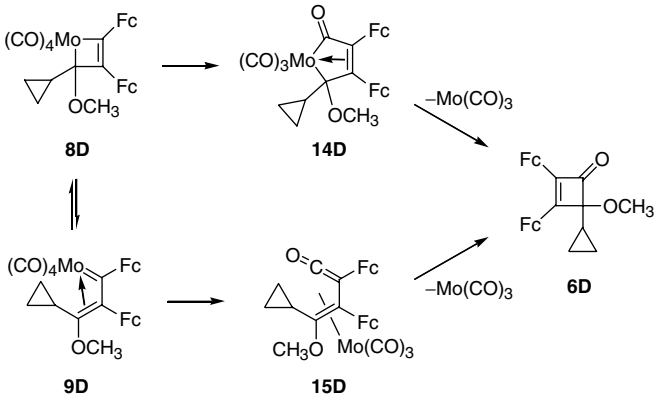
of alkyne **1** produces alkyne-carbene complex **7**, which undergoes a [2+2] cycloaddition reaction to afford metallacyclobutene (**8**). Electrocyclic ring opening then occurs to yield internally-coordinated vinyl carbene complex **9**. The involvement of metallacyclobutenes in these processes has recently been questioned by Hofmann and found to be unfavorable on the basis of theoretical calculations [24]. Thus, complex **9** could be directly formed from **7** via alkyne insertion without formation of metallacyclobutene (**8**). Afterwards, complex **9** undergoes a 1,5-alkyl shift to give metallacycloheptadiene (**10**). CO insertion then occurs to afford metallacyclooctadienone (**11**), which upon reductive elimination yields cycloheptadienones (**3**). Alternatively, CO insertion in **9** produces vinylketene complex **12**. Cyclopropane ring of **12** then opens by a 1,5-alkyl shift to generate metallacycloheptadienone (**13**), which upon decomplexation affords cycloheptadienones (**3**). As noted by Herndon [13b] using similar reactions, two variations (**9** → **10** → **11** → **3** vs. **9** → **12** → **13** → **3**) in this mechanism can be envisaged, which differ in their timing of CO insertion versus cyclopropane ring opening step (Scheme 2). The former pathway is the currently-favored mechanism since there is evidence that cyclopropane ring opening reactions can arise from (2-cyclopropylvinyl)carbene complexes [25]. Conversely, (2-cyclopropylvinyl)ketenes obtained from thermolysis of 4-cyclopropyl-2-cyclobutenones do not produce cycloheptadienones [13b,26]. Thus the later mechanism can only be operative if vinylketene-metal complexes are very different in their reactivity.

In all products, the larger group of the alkyne (i.e. Fc group) has ended up α to the carbonyl, which is the regiochemistry observed in such reactions [12,13,23]. In fact, the regiochemistry of the reaction is set up in the formation of metallacyclobutene (**8**) and/or vinyl carbene complex **9** (Scheme 2), where the larger Fc group ends up α to the molybdenum in order to minimize steric interactions. Following this substituent through the mechanism in Scheme 2, it is predicted that Fc group will be α to the carbonyl group in the final products.

Cycloheptenediones (**4**) were also resulted from these reactions (Table 1) but in low yields. In fact, cycloheptenediones (**4**) are secondary product of the reactions and result from the initially formed cycloheptadienones (**3**) via hydrolysis of enol ether functionality. Note that when subjected to acidic hydrolysis, cycloheptadienones (**3**) provides cycloheptenediones (**4**) in very high yields. That is why; if the crude reaction mixture is hydrolyzed under acidic conditions before chromatography, 2- or 3-ferrocenyl-substituted 2-cycloheptene-1,4-diones (**4**) can be obtained as the major products of the reactions.

Interestingly, from the reaction with propynylferrocene (**1A**) (Table 1, entry A), a new product was isolated and assigned as a 7-hydroxy-2,4-cycloheptadienone derivative, **5A**. To the best of our knowledge, such product was not observed previously from similar reactions. It should be noted that, at relatively higher temperatures, 4-methoxy-2,4-cycloheptadienone derivatives are well known to convert to thermodynamically more stable 5-methoxy-2,4-cycloheptadienones by two consecutive 1,5-H shifts [12,13]. Although, at present, we do not speculate the mechanism for the formation of this product, which requires further study, it is apparent that, during the rearrangement of the initially formed cycloheptadienone **3A** to **5A**, water addition occurs somehow. Interestingly, in **5A**, hydroxy substituent ends up α to the ferrocenyl group. This might be attributed to the developing radical or positive charge at that carbon during the course of the reaction, which is well stabilized, although it is also α to the carbonyl, since the ferrocenyl group is very effective at stabilizing an α radical or carbocation [14d,27]. In addition, the ferrocenyl group is a much better radical and carbocation stabilizing group than the phenyl group.

The reaction with diferrocenylacetylene (**1D**) afforded the products in relatively low yields (Table 1, entry D), as compared to that with diphenylacetylene [13]. Low yields of these products might be due to the steric effect caused by two ferrocenyl groups of **1D** during the course of the reaction. In this reaction, cyclobutenone derivative **6D** was also formed. Cyclobutenones are often observed in the reaction of metal carbenes with alkynes [28]. Cyclobutenone (**6D**) could arise via two possible pathways as depicted in Scheme 3. Metallacyclobutene (**8D**) first gives CO insertion to afford internally-coordinated metallacyclopentenone (**14D**), which produces cyclobutenone (**6D**) upon reductive elimination Alternatively, vinylcarbene complex **9D** experiences CO insertion and yields vinylketene complex **15D**, which furnishes cyclobutenone (**6D**) after electrocyclic ring closure followed by decomplexation. Note that metallacyclobutene (**8D**) and vinyl carbene complex **9D**



Scheme 3. Proposed mechanism for the formation of cyclobutenone (**6D**).

are interconvertible and their formation has been shown in Scheme 2.

On the other hand, the reaction of metal carbene complex **2** with ethynylferrocene (a terminal alkyne) or 3-ferrocenylpropynal (an electron-deficient alkyne) failed, presumably due to the polymerization or electron-deficiency of the alkyne system, a result consistent with the findings of previous investigators using similar systems [13].

In the reactions between molybdenum complex **2** and conventional alkynes, furanone formation was reported to be a major competing pathway [13]. Furanone formation, however, was not a problem when diphenylacetylene is the alkyne or when phosphine ligands such as triphenylphosphine are used as an additive. On the other hand, in our reaction conditions, even in the absence of triphenylphosphine, furanones were not observed. Apparently, the presence of ferrocenyl moiety electronically and/or sterically prevents the formation furanone type products.

2.3. Crystal structure of 3-benzyl-2-ferrocenyl-4-methoxy-2,4-cycloheptadienone (*3B*)

The structure of cycloheptadienone (**3B**) was determined by X-ray crystal analysis. ORTEP diagram of **3B** is shown in Fig. 1. Details of cell data, X-ray data collection, structure solution and refinement are given in Table 2. Selected bond distances and angles are denoted in Table 3. A complete list of atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates have been deposited and are available upon request, Supplementary data.

In the solid state, seven-membered ring adopts a boat-like conformation and, as a result, conjugation between double bonds is largely interrupted as shown by the C12–C11–C17–O1 and C11–C12–C13–C14 torsion angles of 107.41(18)° and 42.2(2)°, respectively. C15 and C16 methylene carbons in the ring exist in a staggered gauche conformation and the related torsion angle (C14–C15–C16–C17) is 50.7(2)°. O1–C17, C11–C12 and C13–C14 bond distances are 1.211(2), 1.344(2) and 1.327(2) Å, respectively, and all are as expected. Ferrocenyl group is in a slightly distorted eclipsed conformation as concluded from

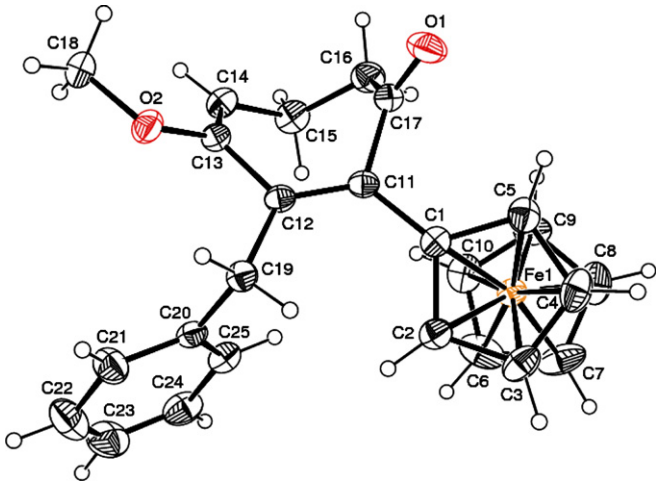


Fig. 1. ORTEP diagram of 3-benzyl-2-ferrocenyl-4-methoxy-2,4-cycloheptadienone (**3B**). Ellipsoids are drawn at 30% probability.

Table 2
Crystallographic data and structure refinement parameters for **3B**

Empirical formula	$C_{25}H_{24}FeO_2$
Formula weight	412.29
Crystal size (mm)	$0.390 \times 0.300 \times 0.180$
Crystal shape	Prism
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.7443(5)
b (Å)	11.3769(7)
c (Å)	11.5864(7)
α (°)	76.372(5)
β (°)	80.118(5)
γ (°)	89.386(5)
V (Å^3)	976.90(11)
Z	2
D_x (g cm^{-3})	1.402
μ (Mo Kα) (mm^{-1})	0.790
Radiation/wavelength (Å)	Mo Kα/0.71073
Transmission factors (T_{min}, T_{max})	0.7651, 0.8892
θ_{max} (°)	26
Index range (hkl)	−9/8, −14/14, −14/14
Reflections measured	21 080
Independent reflections (R_{int})	3839 (0.0387)
Reflections with $I > 2\sigma(I)$	3249
Number of parameters	254
Number of restraints	0
$R[F^2 > 2\sigma(F^2)]$	0.0257
$wR(F^2)$	0.0648
Goodness-of-fit (F^2)	1.030
Maximum, minimum $\Delta\rho$ (e/Å^3)	0.198, −0.286

the average C–Cg_s–Cg_{as}–C torsion angle of −14.11(9)°, where Cg_s and Cg_{as} are the substituted and unsubstituted Cp ring centroids, respectively. The centroids of Cp rings are almost equidistant from Fe atom as indicated by the Fe–Cg_s and Fe–Cg_{as} distances of 1.648(17) and 1.657(17) Å, respectively, and the Cg_s–Fe–Cg_{as} angle is 177.48(11)°. Cp rings of ferrocenyl group are almost parallel since the angle between Cp ring planes is 3.67(12)°. The C–C bond distances in Cp rings alter from 1.382(3) to 1.435(2) Å,

Table 3
Selected bond distances (Å), bond angles (°) and torsion angles (°) for **3B**

C1–C2	1.435(2)	C12–C13	1.486(2)
C1–C11	1.469(2)	C12–C19	1.512(2)
C1–Fe1	2.0697(15)	C13–C14	1.327(2)
C2–C3	1.407(2)	C13–O2	1.3736(19)
C3–C4	1.402(3)	C14–C15	1.499(2)
C4–Fe1	2.0361(18)	C15–C16	1.513(3)
C6–C7	1.382(3)	C16–C17	1.493(2)
C6–C10	1.387(3)	C17–O1	1.211(2)
C7–C8	1.414(3)	C18–O2	1.4260(19)
C8–Fe1	2.0342(19)	C19–C20	1.511(2)
C10–Fe1	2.0460(19)	C20–C21	1.381(2)
C11–C12	1.344(2)	C21–C22	1.387(3)
C11–C17	1.516(2)	C22–C23	1.369(4)
C5–C1–C2	106.21(14)	O2–C13–C12	110.33(13)
C11–C1–Fe1	126.93(10)	O1–C17–C16	121.82(15)
C12–C11–C17	117.80(13)	O1–C17–C11	118.59(15)
C11–C12–C13	120.66(13)	C20–C19–C12	114.45(13)
C11–C12–C19	124.87(14)	C21–C20–C19	119.92(15)
C14–C13–C12	124.10(14)	C10–Fe1–C1	111.47(7)
C5–C1–C11–C12	−154.60(16)	C15–C16–C17–C11	31.5(2)
C5–C1–C11–C17	18.2(2)	C12–C11–C17–O1	107.41(18)
C17–C11–C12–C13	11.9(2)	C11–C12–C19–C20	−114.66(16)
C11–C12–C13–O2	−140.06(14)	C12–C19–C20–C21	−133.55(16)
C12–C13–C14–C15	−3.6(3)	C12–C13–O2–C18	−179.21(13)

while Fe–C bond lengths vary between 2.029(19) and 2.070(15) Å, all of which are as expected [21a].

Crystals of cycloheptadienone (**3B**) are stabilized by C–H…O intermolecular hydrogen bond and C–H…π interactions (Fig. 2). There is a single type of intermolecular hydrogen bond, [C9–H9…O1^{i}: H…O = 2.59 Å, C…O = 3.511(2) Å, C–H…O = 171°, (i) $-x$, $1-y$, $1-z$], linking the molecules and generate cyclic centrosymmetric $R_2^2(14)$ dimers which ring centroid at (1, 1/2, 1/2) [29]. Centrosymmetric dimers are linked through C15–H15a…Cg$_{as}^{ii}$ [Cg$_{as}$ is the centroid of the C6…C10 ring; H15a…Cg = 2.975 Å, C15…Cg = 3.736(2) Å, C15–H15a…Cg = 136.20°, (ii) $1-x$, $1-y$, $1-z$] and C14–H14…Cg$_{p}^{iii}$ [Cg$_{p}$ is the centroid of the C20…C25 ring; H14…Cg = 2.903 Å, C4…Cg = 3.783(2) Å, C14–H14…Cg = 158.35° (iii) $1-x$, $1-y$, $-z$] interactions.

3. Conclusion

In summary, we have investigated the reaction between pentacarbonyl[(cyclopropyl)methoxymethylene]molybdenum complex **2** and ferrocenyl alkynes **1**, affording ferrocenyl-substituted 2,4-cycloheptadienones (**3**) as the major products, along with the minor amounts of 2-cyclohep-tene-1,4-diones (**4**) and/or 2-cyclobutenones (**6**). The reaction is regioselective and general for internal alkynes unless the alkyne is electron-deficient. The hydrolysis of 2,4-cycloheptadienones (**3**) under acidic conditions provides 2-cycloheptene-1,4-diones (**4**) in very high yields. In the case of diferrocenylacetylene (**1D**), steric effects are more pronounced, lowering the yields of products. In conclusion, our study has shown that, under appropriate conditions,

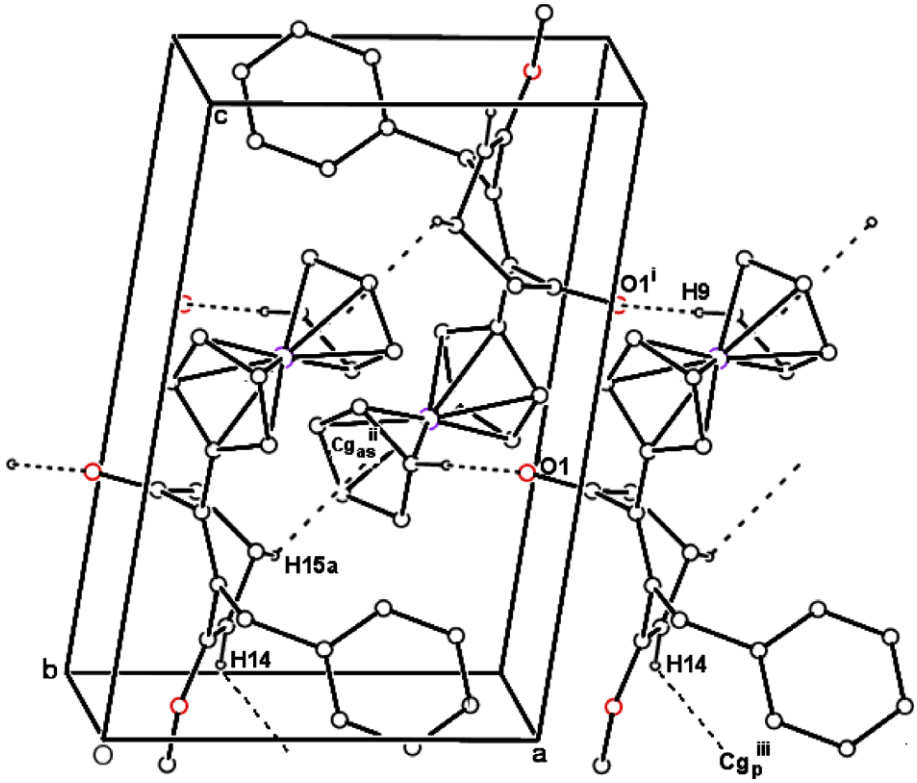


Fig. 2. A packing diagram for **3B**, showing the C–H…O, C–H…\π interactions represented as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity. [Symmetry codes: (i) $-x$, $1-y$, $1-z$; (ii) $1-x$, $1-y$, $1-z$; (iii) $1-x$, $1-y$, $-z$].

ferrocenyl alkynes follow the reactivity patterns of conventional alkynes upon reaction with metal carbene complexes.

4. Experimental

4.1. General consideration

Nuclear Magnetic Resonance (^{1}H and ^{13}C) spectra were recorded on a Bruker Spectrospin Avance DPX400 Ultrashield (400 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane reference. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). DEPT ^{13}C NMR information is given in parenthesis as C, CH, CH_2 and CH_3. Infrared spectra were recorded on a Perkin Elmer 1600 Series FT-IR spectrometer. Band positions are reported in reciprocal centimeters (cm^{-1}). Band intensities are reported relative to the most intense band and are listed as: br (broad), vs (very strong), s (strong), m (medium), w (weak), vw (very weak). Mass spectra (MS) were obtained on a Finnigan MAT 95 spectrometer, using electron impact (EI) at 70 eV; m/z values are reported. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95 spectrometer by preselected-ion peak matching at $R \approx 10000$ to be within ± 3 ppm of the exact masses. Flash chromatography was performed using thick-walled glass columns and 'flash grade' silica (Merck 230-400 mesh). Routine thin layer chromatography (TLC) was effected by using precoated 0.25 mm silica gel plates purchased from Merck. The relative proportion of solvents in mixed chromatography solvents refers to the volume:volume ratio. Ferrocenyl alkynes **1A**–**D** [19–22] and pentacarbonyl[(cyclopropyl)methoxymethylene]molybdenum complex **2** [13b] were synthesized according to the well known literature procedures. All other commercially available reagents and reactants were obtained in reagent grade and used without purification. All reaction solvents were distilled for purity. Diethyl ether, THF and dioxane were distilled from sodium/benzophenone ketyl. The inert atmosphere was created by slight positive pressure (ca. 0.1 psi) of argon.

4.2. General procedure for the reaction of pentacarbonyl-[(cyclopropyl)methoxymethylene]molybdenum complex **2** with ferrocenyl alkynes **1** (Table 1)

A solution of molybdenum carbene complex **2** (0.50 mmol) and ferrocenyl alkyne **1** (0.75 mmol) in THF (30 mL) was refluxed under argon until all carbene complex was consumed. The progress of the reaction was monitored by routine TLC for the disappearance of carbene complex. The mixture was then cooled to 25 °C, and the solvent was removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel. Eluting with 19:1 hexane–ethyl acetate followed by 9:1 hexane–ethyl acetate afforded the products given in Table 1 with the indicated yields.

4.3. Spectral data for products

4.3.1. 2-Ferrocenyl-4-methoxy-3-methyl-2,4-cycloheptadienone (**3A**)

^{1}H NMR ($CDCl_3$): δ 5.13 (t, 1H, $J = 7.3$ Hz), 4.41 (s, 2H), 4.28 (s, 2H), 4.08 (s, 5H), 3.49 (s, 3H), 2.86 (pseudo t, 2H, $J = 6.4$ Hz), 2.36 (pseudo q, 2H, $J = 6.8$), 1.93 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 206.1 (C), 158.1 (C), 137.7 (C), 132.2 (C), 98.5 (CH), 79.3 (C), 69.9 (CH), 69.6 (CH), 68.9 (CH), 54.6 (CH_3), 51.6 (CH_2), 20.1 (CH_2), 16.5 (CH_3); IR (CH_2Cl_2): 3052 (s) 1683 (s), 1629 (m), 1422 (m), 1362 (m), 1272 (vs), 1258 (vs), 1203 (m), 1130 (m), 1105 (m) cm^{-1}; MS (EI): 336.2 (M^+), 334.2, 308.2, 293.1, 255.0, 227.0, 199.1, 186.0, 153.1, 129.1, 121.0, 115.1; HRMS (EI): calcd. for $C_{19}H_{20}FeO_2$: 336.0813. Found: 336.0816.

4.3.2. 3-Benzyl-2-ferrocenyl-4-methoxy-2,4-cycloheptadienone (**3B**)

^{1}H NMR ($CDCl_3$): δ 7.34–7.28 (m, 3H), 7.19 (m, 2H), 5.13 (t, 1H, $J = 7.3$ Hz), 4.41 (t, 2H, $J = 1.8$ Hz), 4.25 (t, 2H, $J = 1.8$ Hz), 4.08 (s, 5H), 3.80 (s, 2H), 3.36 (s, 3H), 2.98 (pseudo t, 2H, $J = 6.7$ Hz), 2.45 (pseudo q, 2H, $J = 7.0$ Hz); ^{13}C NMR ($CDCl_3$): δ 205.7 (C), 157.1 (C), 139.8 (C), 139.5 (C), 133.5 (C), 128.4 (CH), 128.1 (CH), 125.9 (CH), 99.8 (CH), 78.3 (C), 69.6 (CH), 69.3 (CH), 69.1 (CH), 54.6 (CH_3), 51.7 (CH_2), 35.2 (CH_2), 20.3 (CH_2); IR (CH_2Cl_2): 3056 (vs), 2981 (m), 2682 (w), 2301 (m), 1688 (s), 1627 (m), 1424 (vs), 1260 (vs), 1049 (m), 902 (s) cm^{-1}; MS (EI): 412.2 (M^+), 398.2, 384.2, 370.2, 331.1, 318.1, 303.1, 275.1, 253.1, 217.1, 213.0, 186.1, 151.2, 137.1, 121.0; HRMS (EI): calcd. for $C_{25}H_{24}FeO_2$: 412.1126. Found: 412.1130.

4.3.3. 2-Ferrocenyl-4-methoxy-3-phenyl-2,4-cycloheptadienone (**3C**)

^{1}H NMR (acetone-d_6): δ 7.25 (m, 3H), 7.05 (m, 2H), 5.46 (t, 3H, $J = 7.3$ Hz), 4.16 (t, 2H, $J = 1.8$ Hz), 4.09 (s, 5H), 3.87 (t, 2H, $J = 1.8$ Hz), 3.38 (s, 3H), 3.03 (pseudo t, 2H, $J = 6.5$ Hz), 2.64 (pseudo q, 2H, $J = 6.5$ Hz); ^{13}C NMR (acetone-d_6): δ 204.6 (C), 157.6 (C), 139.1 (C), 138.7 (C), 133.7 (C), 129.5 (CH), 127.9 (CH), 127.1 (CH), 100.4 (CH), 77.5 (C), 69.3 (CH), 69.2 (CH), 69.0 (CH), 54.1 (CH_3), 51.5 (CH_2), 20.4 (CH_2); IR (CH_2Cl_2): 3049 (vs), 2988 (s), 2680 (m), 2521 (w), 2407 (w), 2298 (s), 1682 (s), 1418 (m), 1259 (vs), 1158 (w), 900 (vs) cm^{-1}; MS (EI): 398.2 (M^+), 370.2, 339.2, 317.1, 303.1, 261.1, 226.1, 202.1, 186.1, 165.1, 127.2, 119.1; HRMS (EI): calcd. for $C_{24}H_{22}FeO_2$: 398.0969. Found: 398.0972.

4.3.4. 2,3-Diferrocenyl-4-methoxy-2,4-cycloheptadienone (**3D**)

^{1}H NMR ($CDCl_3$): δ 5.09 (t, 1H, $J = 7.4$ Hz), 4.21 (s, 2H), 4.17 (s, 2H), 4.12 (s, 2H), 4.11 (s, 5H), 4.08 (s, 5H),

3.98 (s, 2H), 3.64 (s, 3H), 2.91 (pseudo t, 2H, $J = 6.4$ Hz), 2.44 (q, 2H, $J = 6.9$ Hz); IR (CH_2Cl_2): 3054 (vs), 2989 (s), 2682 (m), 2406 (w), 2304 (m), 1700 (s), 1418 (s), 1266 (vs), 1102 (w), 897 (s) cm^{-1}; MS (EI): 506.2 (M^+), 438.1, 394.1, 362.2, 308.1, 242.1, 186.0, 113.1; HRMS (EI): calcd. for $C_{28}H_{26}Fe_2O_2$: 506.0632. Found: 506.0635.

*4.3.5. 2-Ferrocenyl-3-methyl-2-cycloheptene-1,4-dione (**4A**)*

^1H NMR ($CDCl_3$): δ 4.49 (s, 2H), 4.43 (s, 2H), 4.16 (s, 5H), 2.83 (t, 2H, $J = 6.8$ Hz), 2.61 (pseudo t, 2H, $J = 6.0$ Hz), 2.04 (pseudo p, 2H, $J = 6.3$ Hz), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 204.2 (C), 203.4 (C), 148.6 (C), 134.8 (C), 77.3 (C), 70.7 (CH), 70.4 (CH), 69.7 (CH), 43.3 (CH_2), 41.7 (CH_2), 17.2 (CH_2), 16.4 (CH_3); IR (CH_2Cl_2): 3052 (s), 2985 (m), 1696 (s), 1663 (s), 1420 (m), 1272 (vs), 1260 (vs) 1108 (w), 895 (m) cm^{-1}; MS (EI): 322.1 (M^+), 320.1, 294.1, 277.1, 258.0, 257.0, 229.0, 199.0, 167.1, 149.1, 121.0; HRMS (EI): calcd. for $C_{18}H_{18}FeO_2$: 322.0656. Found: 322.0659.

*4.3.6. 2-Benzyl-3-ferrocenyl-2-cycloheptene-1,4-dione (**4B**)*

^1H NMR ($CDCl_3$): δ 7.25 (t, $J = 7.2$ Hz, 2H), 7.19–7.10 (m, 3H), 4.47 (s, 2H), 4.38 (s, 2H), 4.17 (s, 5H), 3.94 (s, 2H), 2.81 (t, 2H, $J = 5.8$ Hz), 2.49 (pseudo t, 2H, $J = 5.3$ Hz), 2.06 (pseudo p, 2H, $J = 5.3$ Hz); IR (neat): 3104 (w), 2937 (w), 1696 (vs), 1664 (vs), 1578 (m), 1497 (w), 1259 (m), 1213 (s), 1107 (m), 1053 (m), 1004 (m) cm^{-1}; MS (EI): 398.2 (M+), 370.2, 333.1, 305.1, 275.1, 248.1, 234.1, 191.1, 178.1, 165.1, 121.0; HRMS (EI): calcd. for $C_{24}H_{22}FeO_2$: 398.0969. Found: 398.0966.

*4.3.7. 2-Ferrocenyl-3-phenyl-2-cycloheptene-1,4-dione (**4C**)*

^1H NMR ($CDCl_3$): δ 7.36–7.29 (m, 3H), 7.02 (dd, 2H, $J = 7.8$, 1.3 Hz), 4.19 (t, 2H, $J = 1.8$ Hz), 4.08 (s, 5H), 3.80 (t, 3H, $J = 1.8$ Hz), 2.90 (t, 2H, $J = 6.0$ Hz), 2.58 (pseudo t, 2H, $J = 6.6$ Hz), 2.15 (pseudo p, 2H, $J = 6.4$ Hz); ^{13}C NMR ($CDCl_3$): δ 197.6 (C), 156.3 (C), 137.8 (C), 135.3 (C), 130.2 (CH), 128.3 (CH), 127.1 (CH), 81.7 (C), 70.5 (CH), 70.2 (CH), 69.6 (CH), 38.2 (CH_2), 30.7 (CH_2), 22.7 (CH_2); IR (CH_2Cl_2): 3048 (vs), 2985 (s), 2680 (w), 2305 (m), 1650 (s), 1578 (m), 1422 (s), 1358 (m), 1265 (vs), 1175 (m), 891 (s) cm^{-1}; MS (EI): 384.2 (M^+), 357.2, 356.2, 300.2, 291.1, 263.1, 235.1, 202.1, 178.1, 165.1, 152.1, 112.0; HRMS (EI): calcd. for $C_{23}H_{20}FeO_2$: 384.0813. Found: 384.0816.

*4.3.8. 7-Ferrocenyl-7-hydroxy-5-methoxy-6-methyl-2,4-cycloheptadienone (**5A**)*

^1H NMR ($CDCl_3$): δ 6.58 (dd, 1H, $J = 12.4$, 8.7 Hz), 5.99 (d, 1H, $J = 12.4$ Hz), 4.94 (d, 1H, $J = 8.7$ Hz), 4.39 (s, 1H), 4.23 (s, 1H), 4.13 (s, 1H), 4.07 (s, 6H), 3.92 (s, 1H), 3.42 (s, 3H), 2.53 (q, 1H, $J = 7.3$ Hz), 1.12 (d, 3H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$): δ 198.2 (C), 174.2 (C), 140.4 (CH), 120.9 (CH), 95.4 (CH), 89.9 (C), 69.4 (C), 68.7 (CH), 67.6 (CH), 67.1 (CH), 66.9 (CH), 66.3 (CH), 55.6 (CH_3), 48.5 (CH), 11.1 (CH_3); MS (EI): 352.2 (M^+), 336.2, 322.1, 287.1, 269.1, 243.1, 242.1, 214.1, 213.0, 186.1, 139.1, 121.0, 115.1; HRMS (EI): calcd. for $C_{19}H_{20}FeO_3$: 352.0762. Found: 352.0759.

*4.3.9. 2,3-Diferrocenyl-4-cyclopropyl-4-methoxy-2-cyclobutenone (**6D**)*

^1H NMR ($CDCl_3$): δ 5.02 (s, 1H), 4.92 (s, 1H), 4.89 (s, 1H), 4.64 (s, 1H), 4.62 (s, 1H), 4.40 (s, 1H), 4.39 (s, 1H), 4.30 (s, 5H), 4.18 (s, 5H), 4.06 (s, 1H), 3.28 (s, 3H), 1.44 (m, 1H), 0.85 (m, 1H), 0.71 (m, 1H), 0.63 (m, 1H), 0.39 (m, 1H); IR (CH_2Cl_2): 3054 (m), 1743 (s), 1695 (m), 1606 (m), 1483 (m), 1261 (vs), 1103 (m), 916 (m), 821 (m), 755 (vs) cm^{-1}; MS (EI): 506.1 (M^+), 478.2, 464.1, 394.1, 328.0, 273.1, 215.1, 197.0, 186.0, 149.0; HRMS (EI): calcd for $C_{28}H_{26}Fe_2O_2$: 506.0632. Found 506.0634.

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Appendix A. Supplementary material

CCDC 621658 contains the supplementary crystallographic data for **3B**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j. jorganchem. 2006.12.008.

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