ELSEVIER

Journal of Organometallic Chemistry 494 (1995) 53–64

Journal of Organometallic Chemistry

Reaction of ethyl 3,3-diethoxyacrylate with Fischer alkoxyalkynyl transition metal carbene complexes

Lurdes Jordi [a], Francisco Camps [a], Susagna Ricart [a], Josep M. Viñas [a], Josep M. Moretó [a,*], Milagros Mejias [b], Elies Molins [b]

[a] *Departament de Química Orgànica Biológica, CID, (CSIC), C / J. Girona 18-26, 08034-Barcelona, Spain*
[b] *Institut de Ciència de Materials de Barcelona, Campus Universitari de Bellaterra, 08193-Cerdanyola, Barcelona, Spain*

Received 26 September 1994

Abstract

The title reaction afforded various amounts of differently substituted pentacarbonyl pyranylidene complexes, depending on factors such as the metal, substitution at the alkynyl moiety and relative ratio of the reagents employed. The results obtained are explained by a cycloaddition-ring-opening mechanism giving intermediates that can further cyclize to pyranylidene derivatives. The importance of the dialkoxy and ester groups in promoting this cyclization was studied by replacing ethyl 3,3-diethoxyacrylate by model compounds, such as 4,4-dimethoxybut-3-en-2-one and 2-[(methoxycarbonyl)methylidene]-1,3-dioxolane.

Keywords: Carbene complexes; Pyranylidene complexes; Chromium; Synthesis; X-ray structures

1. Introduction

Fischer transition metal-carbene complexes are currently generating a broad and unprecedented chemistry because of their ability to perform cycloaddition reactions with a variety of substrates [1]. Of these complexes, those bearing a triple bond conjugated with the carbene moiety were expected to be highly promising in such reactions because of the high polarity of the adjacent alkyne [2]. As expected, they readily give [2 + 2] polar cycloadditions with C and Si enol ethers [3]. In this context, we envisaged ethyl 3,3-diethoxyacrylate as a very special enol ether because the presence of a supplementary electron-withdrawing group such as carboxylate might introduce significant changes in the course of a [2 + 2] cycloaddition. With this in mind, we undertook the study of this reaction, particular attention being paid to the factors responsible for any diversion from the conventional pathway [4].

2. Results

Complex **1a** (Scheme 1) was allowed to react with two equivalents of ethyl 3,3-diethoxyacrylate (**2**) at room temperature. After 4 h, no starting complex remained in the reaction mixture and four new complexes (**3a, 4a, 5a,** and **6a**, Table 1, entry 1) appeared as detected by TLC (eluent: hexane/ethyl acetate 4/1). Flash column chromatography allowed their separation in two sequential runs using different eluents. Products showing similar physical and spectroscopic characteristics were obtained in different yields from the tungsten analogue **1b** (Table 1, entry 2). The structures of three of these compounds (**3**, **4** and **6**) were established from spectroscopic data and X-ray single-crystal diffractometry. They are 2-pyranylidene complexes with different substitution at the α-carbene position.

In contrast, the structure of complex **5a** was determined from spectroscopic data. The presence of the tetracarbonyl metal moiety was established from the typical IR pattern (bands at 2015, 1915, 1905 and 1835 cm^{-1} in $CHCl_3$, consistent with local C_{2v} symmetry [5]) and the four signals in the ^{13}C NMR spectrum corresponding to the inequivalent CO groups (δ at

* Corresponding author.

SSDI 0022-328X(94)05369-3

Table 1
Reaction of ethyl diethyoxyacrylate **2** with different alkynylalkoxycarbene metal (Cr or W) complexes **1**.

Entry	Complex	Time (h)	Products (yield) (%)
1	**1a**	4	**3a**(13) **4a**(13) **5a**(30) **6a**(8)
2	**1b**	4	**3b**(30) **4b**(30) **5b**(tr.) **6b**(0)
3	**1c**	72	**3c**(31)
4	**1d**	1	**3d**(9) **4d**(7) **4'd**(14) **6d**(4)
5	**1e**	4	**3a**(15) **4a**(3) **4'e**(9) **5e**(29) **6e**(8)
6	**1f**	72	**3c**(48)

Table 2
Reaction of complex **1a** with ethyl diethoxyacrylate **2** under different conditions

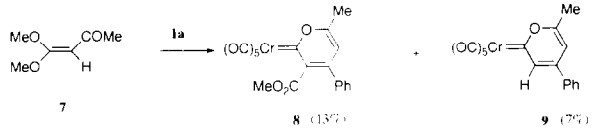
Entry	Complex	Ratio 2/1	Time (h)	Products (yield) (%)
1	**1a**	2 [a]	4	**3a**(10) **4a**(21) **5a**(24) **6a**(6)
2	**1a**	3	4	**3a**(12) **4a**(12) **5a**(23) **6a**(4)
3	**1a**	4	4	**3a**(14) **4a**(7) **5a**(22) **6a**(0)
4	**1a**	0.5	24	**3a**(3) **4a**(4) **5a**(0) **6a**(21)
5	**1a**	2 [b]	16	**3a**(20) **4a**(10) **5a**(23) **6a**(10)

[a] Using freshly distilled **2**.
[b] In the presence of a 1/1 molar ratio of triethyl orthomalonate/**2**.

213.9, 215.2, 228.9 and 231.8). The Z configuration of its distal double bond was established by NOE signal enhancement (15%) between the vinylic (δ 6.45) and aromatic protons.

The product distribution was dependent on different factors such as the metal, the ratio **2**/**1**, the size of R_2, and also the presence in the starting ester **2**, of minor amounts of saturated esters derived from the acrylate. (Commercial acrylate **2**, obtained by pyrolysis of tetraethyl mono-orthomalonate in the vapour phase, always contains some diethyl malonate and unconverted orthoester. Careful fraction distillation reduces these impurities to a minimum, but does not remove them completely.)

The replacement of Cr by W had a strong influence on the ratio of pyranylidene/tetracarbonyl complexes obtained in both reactions. From complex **1b**, an increase of **3b** and **4b** was observed, while complex **5b** was barely detectable by TLC in the crude mixture and could never be isolated (Table 1, entries 1 and 2).



Scheme 2.

Substitution of the phenyl of the alkyne by alkyl produced changes in reaction time and product distribution probably due to steric effects. However, no new type of product was produced (Table 1, entries 3 and 4).

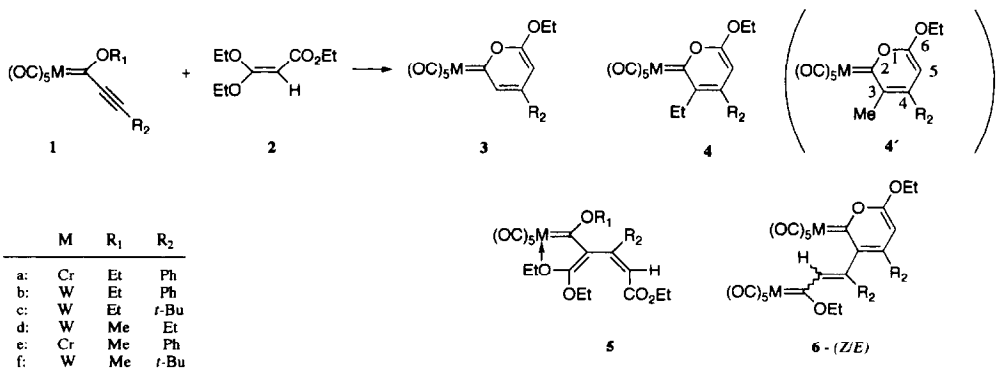
Change of alkoxy substituent in the starting complex **1** produced only small effects in product distribution because, in this case, a mixture of **4** and **4'** was found (Table 1, entries, 4 and 5).

Changes in conditions clearly influenced the outcome of the reaction. Use of a larger excess of ester with respect to carbene complex **1** or a higher content of triethyl mono-orthomalonate in the starting diethoxyacrylate **2** led to an increase in the amount of **3** (Table 2, entries 1–3). Conversely, when the excess of ester **2** was minimal (entry 4) the reaction slowed considerably, and, under these conditions, the reaction was not complete even after 24 h, and formation of complex **6** was favoured at the expense of **3** and **4**.

Although it might be expected that the formation of tetracarbonyl complex **5a** would have been curtailed by performing the reaction under CO pressure (70 psi), a moderate increase in the production of **3a** (20%) was the only significant change under these new conditions.

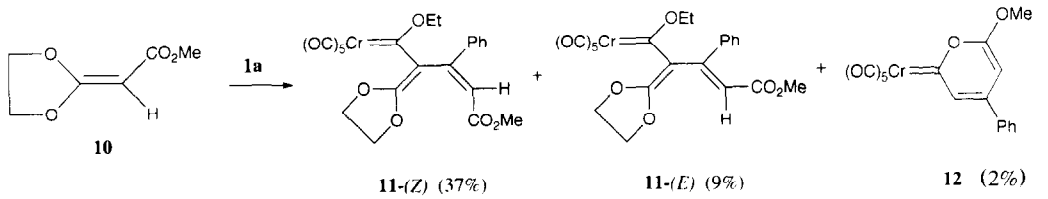
Finally an independent set of experiments attempted to evaluate the importance of the dialkoxy and ester groups in promoting the heterocyclization.

Reaction of ketone **7** with starting complex **1a** was faster than that of ester **2**, and gave a mixture of many unidentified compounds and pyranylidene complexes **8** and **9** as the major products in rather low yield (Scheme



	M	R_1	R_2
a:	Cr	Et	Ph
b:	W	Et	Ph
c:	W	Et	*t*-Bu
d:	W	Me	Et
e:	Cr	Me	Ph
f:	W	Me	*t*-Bu

Scheme 1.



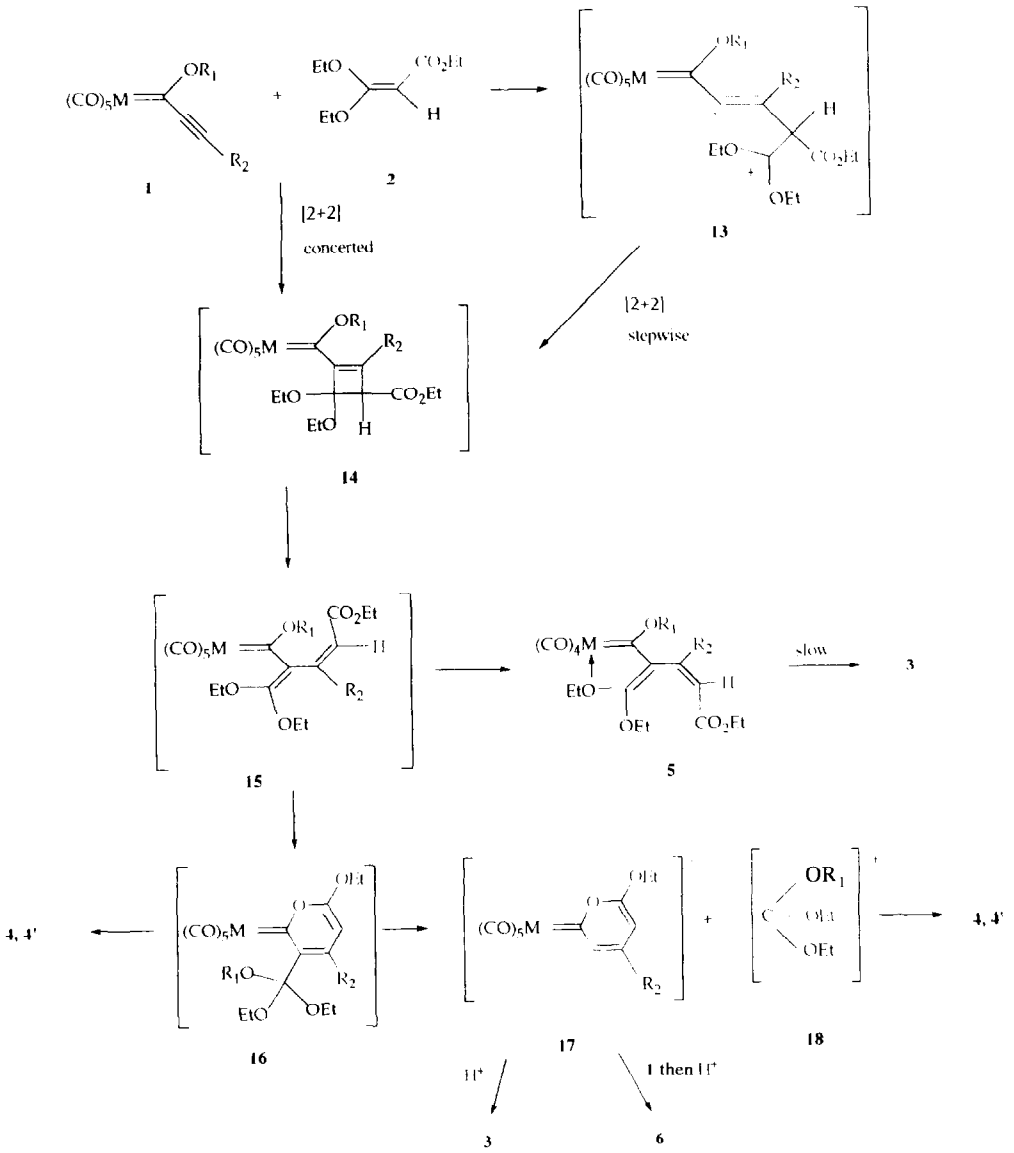
Scheme 3.

2). Complex **8** did not show any tendency to decarboxylate and therefore, we assumed that each product was formed independently.

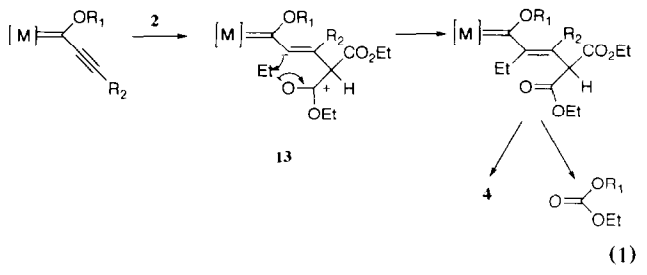
Likewise, reaction of cyclic dialkoxyacrylate **10** gave mainly diene adducts **11**-*Z* and *E* together with a minor amount of cyclic complex **12** (Scheme 3).

3. Discussion

Initially, formation of complex **3a** from pure tetracarbonyl complex **5a** in the course of a long NMR experiment suggested that **5a** might be a reaction intermediate in the generation of **3a** [4a]. However, because the



Scheme 4.



(1)

reaction rate for this transformation was slower, by far, than that for formation of **3a** from diethoxyacrylate and starting complex **1a**, it was concluded that most of complex **3a** must have arisen through an independent pathway. Consistent with this was the enhanced formation of **3a** under CO pressure which has little influence on that of **5a**. (Compound **5a** was treated under the general reaction conditions with diethoxyacrylate and, after a few days, only a small part had been converted to the pyranylidene complex **3a**. Likewise, complex **5a** also slowly transforms into **3a** in solvents such as hexane and chloroform (after one week in hexane, 36% of **3a** was isolated, together with 37% of unreacted **5a**). Because the unaltered tetracarbonyl complex can still be converted in **3a**, the practical yield of this complex in the present reaction can be substantially improved with longer reaction times.)

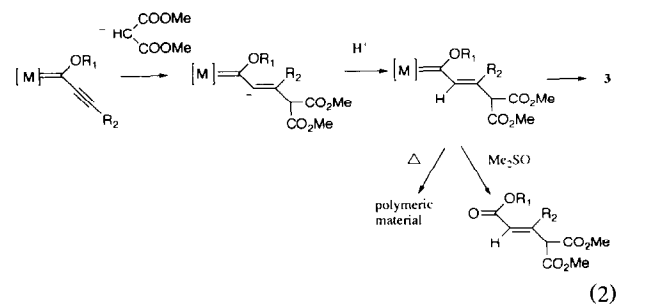
We propose either a concerted or stepwise cycloaddition as the first step in this process (Scheme 4), consistent with reports by Wulff and coworkers and ourselves for similar reactions with enol ethers [3].

The alternative "ene"-type mechanism proposed by Wulff and Faron [3b] has been discarded in this case because it would lead only to formation of **4** but not **3** (there is no hydrogen available at the appropriate site) (Eq. 1).

Furthermore, in an independent experiment, the addition product of the malonate anion to the triple bond of **1** was prepared easily. At room temperature the resulting complex did not show any tendency to give **3**, but oxidatively released the organic moiety (Eq. 2).

Finally, no way to product **5** can be envisaged through an "ene"-type mechanism.

Product **5** could arise in a more satisfactory way after a conrotatory ring opening from an initial [2 + 2] cycloadduct **14** (Scheme 4). Cyclobutene complexes generated similarly open easily when the substituents of the enol ether can polarize the corresponding bond [3a,3b]. In the present case, the electronic character of the substituents (dialkoxy and ethylcarboxylate) may be expected to polarize the cyclobutene ring strongly, and therefore to promote easy cleavage. Once the ring has opened, chelation of one of the nearby ethoxy groups at one of the *cis*-carbonyl ligand sites would give the more stabilized complex **5**, rendering the carbene carbon atom less electrophilic (replacement of a π-acidic CO ligand by a σ-basic EtO) towards carboxylate attack and preventing the formation of pyranylidene complexes.

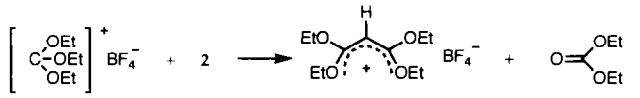


(2)

Alternatively, pentacarbonyl complex **15**, with a carboxyl enolate of enhanced nucleophilicity (because of the diethoxy group donating electronic charge along the diene system), would generate a cyclic intermediate **16** after an intramolecular alkoxy transfer. Insight into the fate of the carbene alkoxy group was gained from the reactions performed with the methoxy complexes **1d** and **1e** (Table 1, entries 4 and 5). The formation of the pyranylidene complexes **4'** with a methyl group at site 3 was indirect evidence of the alkoxy transfer **15** → **16** depicted in Scheme 4. Similar alkoxy migrations have been proposed for other cycloaddition reactions involving transition metal-carbene complexes [6].

Because intermediate **16** may be regarded as a potential direct precursor for pyranylidene complexes **3** and **4** by an intramolecular reaction (through a β-elimination and ethyl transfer respectively) an experiment was performed in a sealed NMR tube to determine the side products of the reaction of **1a** and **2**, in particular ethylene. The complete absence of this compound in the mixture ruled out a β-H elimination process in the formation of complex **3a**. A further large-scale experiment gave some clues concerning the generation of the pyranylidene complexes. After the reaction was over, the volatile components were distilled off and the major products in the distillate were found to be diethyl carbonate and diethyl ether. Whereas intramolecular alkylation at the α site of the orthoester moiety in intermediate **16** might indeed release that ester and **4**, the formation of ether would presumably be because of another process.

The preferential formation of **6** at low concentrations of **2** and the known stability and reactivity of trialkoxycarbenium ions [7] rather suggested the involvement of an ion pair such as $\mathbf{17}^-$ $\mathbf{18}^+$ as a putative precursor for complexes **3**, **4** and **6**. Thus, intermolecular reaction of the anion **17** as a "soft" nucleophile with cation **18** in a similar reaction to others reported [7c,7d], would generate complex **4** and ethyl carbonate, while its protonation or addition to **1** would generate **3** and **6**, respectively. However the preferential formation of methyl complexes **4'd** and **4'e** from methoxy carbene complexes **1d** and **1e** compared with their ethyl analogues (Table 1,



(3)

entries 4 and 5) and the small effect of an external electrophile such as MeI in the quenching of anion **17** (only 9% of formation of **4'**) suggested that intramolecular alkyl transfer may also be an important source of alkyl pyranylidene complexes **4**.

As expected, when the ratio **2/1a** was decreased, the anionic intermediate **17** was preferentially quenched by its precursor **1a** (which has a very electrophilic benzylic center [8]), affording dicarbene complexes **6a** ($E + Z$) as the main products (Table 2, entry 4).

The origin of diethyl ether as a by-product in this reaction is not clear. However, the fact that purification of **2** from the corresponding orthoester halved the ratio of **3a** to **4a** (Table 2, entries 1 and 2) together with the formation of diethyl ether from **2** and cation **18** pointed to a common origin for both diethyl ether and product **3a**. (Reaction of **18** and ethyl diethoxyacrylate **2** gives almost quantitatively diethyl carbonate and 1,1,3,3-tetraethoxyallyl tetrafluoroborate (Eq. 3).

In this experiment (unpublished results from our laboratory) the small amount of tetraethyl mono-orthomalonate always accompanying **2**, slowly disappear to give diethyl ether, ethyl carbonate and acrylate **2**.)

$$\mathbf{18} + (EtO)_3CCH_2CO_2Et \rightarrow Et_2O + \mathbf{2} + H^+ + (EtO)_2CO$$

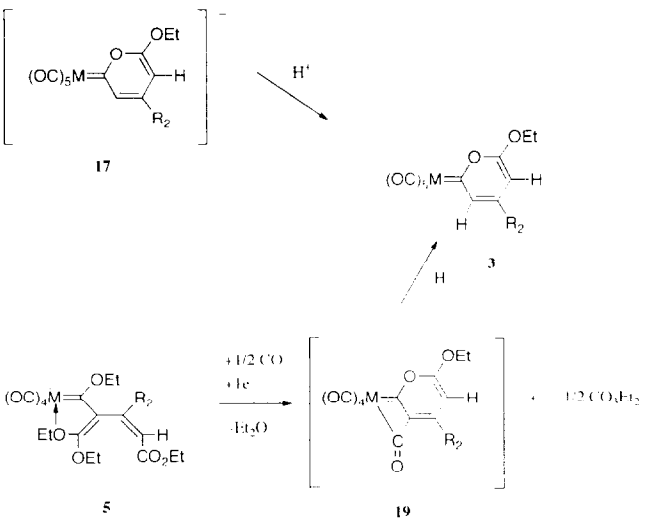
Thus, tetraethyl mono-orthomalonate $[(EtO)_3CCH_2CO_2Et]$ always accompanying **2** would generate diethyl ether and could also represent a proton source to afford **3a**. Diethyl ether was also produced by the independent formation of complex **3a** from **5a**. When a sample of pure complex **5a** was dissolved in $CDCl_3$ and the tube was sealed under argon for three months, it slowly reached equilibrium, giving the pentacarbonyl complex **3a** together with a small amount of $[Cr(CO)_6]$ (a few colourless crystals appeared in the NMR tube and a signal corresponding to the six equivalent CO groups was observed in the ^{13}C NMR spectrum), diethyl carbonate, diethyl ether (both detected by ^1H and ^{13}C NMR spectroscopy) and a variety of minor demetallated products which could not be identified. This was interpreted as the consequence of the scavenging of protons from the reaction medium by compound **5a** as the trigger for its conversion to the pentacarbonyl complex **3a**. For the process **5** → **3**, an additional carbonyl has to be captured by the reacting species. Therefore, in the absence of free CO, decomposition of **5** has to accompany the process. Further protonation (from the medium) and also the occurrence of a reductive process would account for the slower transformation for complex **5** to give the common final product **3** [9]. In contrast, under CO pressure formation of **3** through **15** would be stimulated. Intermediates **17** and **19** may be regarded as identical [10] (Scheme 5). Interaction between the α-carbene anionic carbon and the *cis*-metal carbonyl in the proximity would be expected to stabilize complex **17**, giving **19**.

Therefore, we concluded that compound **3** could be independently formed by protonation of intermediates **17** and **19**.

The substitution of the pyran ring at positions 3 and 6 in the reaction products from ketone **7** (Scheme 3) reveals that the proposed cycloaddition-ring-opening mechanism also operates in this case. Nevertheless, the higher nucleophilicity of ketone enolates when compared to that of esters accounts for the preferential formation of cyclic products such as **8** and **9** [11].

The presence of two isomers derived from cyclobutene ring opening (E and Z **11**, with a rather slow interconversion) and the absence of the tetracarbonyl analogue of complex **5** in the product mixture from the starting compound **10** suggest involvement of severe steric interactions of the dioxolane ring with the pentacarbonylmetal moiety in order to attain the required geometry for a suitable coordination, isomerization or cyclization, giving the products corresponding to those found in the reaction of acrylate **2**.

In the intramolecular generation of alkyl complexes **4** and **4'**, steric interaction at site 3 of the pyran ring caused by the pentacarbonyl moiety and the substituent R_2 also accounts for the statistical preference of complexes **4'** in the product. Such interactions may be supposed to be particularly important in the exclusive formation of complex **3c** from **1c**. In this instance, the bulky pentacarbonyltungsten and *tert*-butyl groups flank the α carbene site so efficiently that only a small electrophile such as a proton can enter.



Scheme 5.

The absence of tetracarbonyl complexes **5** in the tungsten series is remarkable. This could be explained by the higher metal–carbonyl bond strength as compared with chromium [12]. Consequently, the pyranylidene complexes **3b** and **4b** in the tungsten series are obtained under the same conditions and in higher relative yields than those of chromium, because diversion to complex **5a** for chromium results in a greater or smaller loss in the yield of pyranylidene products.

4. Structural features

The structures of complexes **3**, **4** and **6** were determined in solid state by X-ray diffractometry [13]. They consist of a 2-pyranylidene ring bonded to a pentacarbonyl metal unit ($W(CO)_5$ for **3b** and **4b**, $Cr(CO)_5$ for **6a**) with different substituents at site 3 of the ring, namely hydrogen (**3b**), ethyl (**4b**) and β-(ethoxymethylidenepentacarbonylchromium)styryl (**6a**). The metal–carbene–carbon bond distances are typical of Fischer carbene complexes of these metals [14] (W–C(2) = 2.17(2) and 2.228(7) Å, for **3b** and **4b** (Fig. 1) respectively and Cr–C(2) = 2.108(4) Å for **6a** (Fig. 2)).

Bond lengths in the pyranylidene ring appear to be independent of the metal. For instance, C(2)–O(1) is 1.43(3) Å in **3b**, 1.411(8) Å in **4b** and 1.425(5) Å in **6a**. The C–C distances lie between 1.43(3) Å and 1.360(7) Å indicating bond delocalization along the system. Conjugation is also observed with the phenyl group, the C(41)–C(4) distance being ca. 1.50 Å. However, in complex **6a**, no conjugation between the styrene double bond and any neighbouring system (carbene–metal, pyran ring, or phenyl group) seems to exist, as inferred from the values of bond lengths along the fragment C(12)–C(11) = C(10)[C(3)]–C(101), very close to typi-

Table 3
Table of atomic coordinates for compound **4b**

Formula	$C_{20}H_{16}O_7W$
Space group	$P\bar{1}$
a, Å	10.462(5)
b, Å	10.687(5)
c, Å	11.336(10)
α, deg.	93.30(7)
β, deg.	115.48(7)
γ, deg.	111.08(4)
V, Å^3	1033(53)
Z	2
d_{calc} g cm^{-3}	1.775
Crystal size, mm	0.4×0.9×0.5
μ, cm^{-1}	57.45
Radiation (λ, Å)	Mo–Kα (0.71069)
F_{000}	532
Scan method	ϖ–2θ
R	0.0379
R_ω	0.038

Table 4
Selected bond distances (Å) and bond angles (deg.) for **4b**

C2–W	2.228(7)	O1–C2–W	108.8(4)
C2–O1	1.411(8)	C3–C2–W	136.5(5)
O1–C6	1.317(10)	C3–C2–O1	114.7(6)
C6–C5	1.384(11)	C5–C6–O1	122.1(7)
C5–C4	1.365(10)	C41–C4–C5	116.5(6)
C4–C3	1.410(10)	C41–C4–C3	122.0(6)
C3–C2	1.396(10)	C4–C3–C2	120.8(6)
C41–C4	1.499(9)		

Table 5
Selected bond distances (Å) and bond angles (deg.) for **6a**

C2–Cr2	2.108(4)	C3–C2–Cr2	139.0(3)
C12–Cr12	2.030(4)	C3–C2–O1	112.5(3)
C2–O1	1.425(5)	O1–C2–Cr2	108.4(3)
C6–O1	1.305(6)	C11–C10–C3	120.8(4)
C2–C3	1.405(6)	C11–C12–Cr12	122.1(3)
C3–C4	1.409(6)	C13–C12–Cr12	131.9(3)
C4–C5	1.380(6)	C11–C12–O13	106.1(4)
C5–C6	1.360(7)		
C41–C4	1.502(6)		
C3–C10	1.505(5)		
C10–C11	1.340(6)		
C11–C12	1.489(6)		
C101–C10	1.503(6)		

Table 6
Fractional atomic coordinates (×10^4) with the equivalent temperature factors

Atom	x	y	z	B_{eq}
W	3591.2(.3)	2010.7(.3)	377.8(.3)	3.81
C11	2147(8)	2566(7)	−1433(7)	3.65
C13	1563(11)	2230(9)	−3757(8)	4.66
C14	600(10)	2909(9)	−4064(8)	4.71
C15	412(8)	3408(7)	−3043(7)	3.77
C16	1138(8)	3213(7)	−1739(7)	3.54
C51	−670(9)	4105(8)	−3400(7)	4.24
C52	−2171(10)	3424(9)	−4431(9)	5.90
C53	−3188(11)	4051(11)	−4792(10)	6.45
C54	−2685(11)	5398(10)	−4102(10)	5.84
C55	−1170(12)	6104(9)	−3115(10)	5.40
C56	−135(10)	5497(8)	−2752(8)	4.61
C61	779(9)	3636(8)	−667(7)	4.32
C62	−857(12)	2594(12)	−937(11)	6.16
C32	2905(14)	1033(12)	−4255(10)	7.02
C33	2958(17)	548(13)	−5462(12)	7.99
C2	2589(10)	75(9)	−853(9)	4.69
C3	5292(10)	2575(10)	−160(10)	5.50
C4	4845(11)	1356(10)	1888(9)	5.53
C5	1964(10)	1428(8)	1002(8)	4.16
C6	4604(10)	3983(9)	1565(9)	4.99
O12	2289(6)	2079(5)	−2534(5)	4.06
O31	1821(8)	1694(7)	−4667(6)	6.10
O2	2117(11)	−956(8)	−1524(10)	7.81
O3	6249(9)	2893(10)	−446(9)	9.02
O4	5519(10)	938(9)	2718(7)	8.07
O5	1111(9)	1090(7)	1419(7)	6.20
O6	5160(10)	5032(8)	2224(9)	8.29

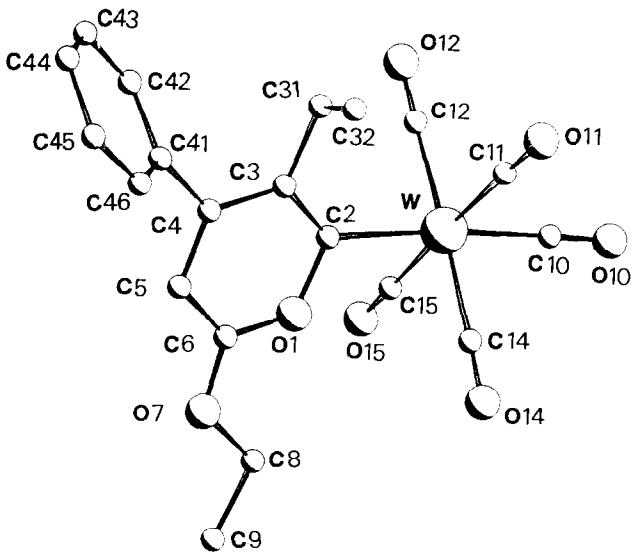


Fig. 1.

cal data for single and double bonds. In particular, the dihedral angle between the phenyl and the pyran rings (66.3°) lends considerable assymetry to this molecule [15]. (Steric distortion of coplanarity in carbene complexes with interruption of conjugation has also been reported to occur as a consequence of changes in the heteroatom-carbene carbon area of the molecule.) This spatial arrangement results in crowding, also shown by the diastereotopicity of all the hydrogen atoms in methylene groups of complex **6d** (even those of the ethoxy group bonded to the carbene carbon atom), despite of the fact that in this complex all the groups are supposed to have higher stereochemical freedom than in the phenyl analogue **6a**.

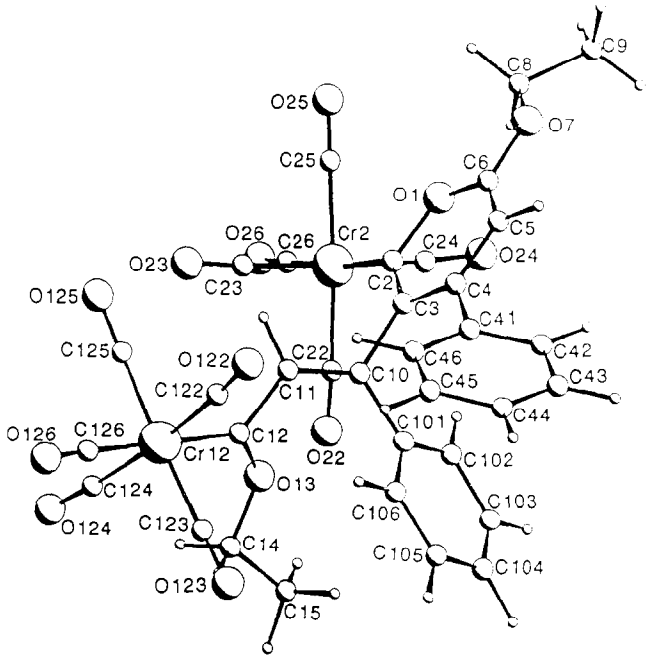


Fig. 2.

5. Conclusions

The reaction of ethyl 3,3-diethoxyacrylate with Fischer alkoxyalkynyl transition metal carbene complexes afforded pyranylidene (**3**, **4** and **6**) and tetracarbonyl (**5**) complexes. The different factors that influence the outcome of the reaction have been studied. Tungsten carbene **1b** gave pyranylidene complexes **3b** and **4b** as major compounds, whereas the corresponding chromium complex **1a** favoured the formation of tetracarbonyl derivative **5a**. Substitution at the alkynyl group appeared to be most notable with the *tert*-butyl analogues, **1c** and **1f**, which afford only pyranylidene derivative **3c**. The relative ratio of the reagents employed also appears to be important in determining product distribution, a significant increase in the yield of minor products **6** (*E* and *Z*) being observed as reducing the proportion of ethyl 3,3-diethoxyacrylate present in the reaction mixture. Although the tetracarbonyl complex **5a** is partially transformed into the pyranylidene derivative **3a**, most of it arises by an independent path.

This condensation was also studied with model compounds, such as ketone **14** and ketal **17**, to gain insight into the importance of the dialkoxy and ester groups in promoting cyclization. It seems that steric interactions are important in determining the reaction rate and the product distribution.

6. Experimental details

All usual reagents and solvents were used without further purification as obtained from commercial suppliers unless otherwise indicated.

NMR spectra were recorded on a Bruker WP80ST (80 MHz for ^{1}H) or a Varian XL-300 apparatus (300 MHz for ^{1}H and 75 MHz for ^{13}C). All samples of carbene complexes were filtered through a pad of Celite prior to recording the spectra. IR spectra were recorded on a Perkin-Elmer 399B or a Bomem FT-IR M-120 spectrophotometer. Mass spectra were obtained on an AutoSpec-Q mass spectrometer. Elemental analyses were performed using a Carlo Erba 1106 apparatus.

Flash column chromatography was performed with "flash grade" silica (SDS 230-400 mesh). Carbene complexes **1a–1f** [16], 2-[(methoxycarbonyl)methylidene]-1,3-dioxolane (**23**) [17], and 4,4-dimethoxybut-3-en-2-one (**20**) [18] and triethoxycarbenium tetrafluoroborate [19] were prepared by literature procedures.

6.1. Crystal data

A single crystal was mounted on the end of a glass fibre and centred in the Enraf-Nonius CAD4 diffractometer. Cell parameters were determined by least-squares fitting of 25 high angle reflections. Lorentz and polarization effects but not absorption, were corrected. The structure was solved by application of automated Patterson search (ROTSEARCH) [20a]. Once the metal atom had been located, a weighted Fourier synthesis shows the remaining non H-atoms. Refinement was carried out using full-matrix least-squares methods (SHELX-76), [20b]. The final difference Fourier synthesis showed several hydrogen atoms which were not included in the refinement.

6.2. General procedure

6.2.1. Reaction of ethyl 3,3-diethoxyacrylate (2) with complex 1a

To a two-necked flame-dried round-bottomed flask containing pentacarbonyl[ethoxy (phenylethynyl)-carbene] chromium (**1a**) (200 mg, 0.57 mmol) was added 0.22 ml (1.2 mmol) of acrylate **2**, and this mixture was deoxygenated and stirred under argon at 28°C for 4 h. The resulting dark-red mixture was purified by flash chromatography on silica gel. Elution with hexane/ethyl acetate 9:1 provided three fractions. The first proved to be a single complex with the structure **4a** (32 mg, 13%); the second fraction was actually a mixture of products (mainly diethyl malonate from the hydrolysis of ethyl 3,3-diethoxyacrylate and two different complexes). The third component was again a single product whose structure was assigned as **5a** (87.4 mg, 30%). Further purification of the second fraction by flash chromatography over silica gel with hexane/CH_2Cl_2 (9:1) as eluent, afforded complex **3a** (30 mg, 13%) followed by **6a-*E*** (18 mg, 8%). This allowed the separation of every complex in almost all cases. Slight changes in it led to partial resolution of at least one of the products.

6.2.2. Pentacarbonyl(6-ethoxy-3-ethyl-4-phenyl-2H-pyran-2-ylidene)chromium (4a)

IR ($CHCl_3$, cm^{-1}): 2045, 1965, 1925. ^1H NMR ($CDCl_3$): δ 0.8 (t, $J = 8$ Hz, 3H), 1.55 (t, $J = 7$ Hz, 3H), 2.95 (q, $J = 8$ Hz, 2H), 4.75 (q, $J = 7$ Hz, 2H), 6.08 (s, 1H,), 7.19–7.55 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 14.5 (q), 14.9 (q), 25.9 (t), 66.8 (t), 100.2 (d), 128.7 (d), 127.1 (d), 129.2 (d), 138.1 (s), 144.9 (s), 156.5 (s), 172.1 (s), 218.2 (s), 223.3 (s), 262.1 (s). MS (FAB; Xe, matrix NBA): m/z 420 (M^+, 46), 392 (21), 364 (29), 336 (28), 308 (100), 280 (70), 229 (32), 200 (14), 183 (29). Anal. Calc. for $C_{20}H_{16}CrO_7$: C, 57.14; H, 3.84. Found: C, 57.10; H, 3.81%.

6.2.3. Tetracarbonyl(Z)[(1,1-diethoxy-4-(ethoxycarbonyl)-3-phenylbuta-1,3-dien-2-yl)ethoxycarbene]-chromium (5a)

IR ($CHCl_3$, cm^{-1}): 2015, 1915, 1905, 1835, 1710. ^1H NMR ($CDCl_3$): δ 1.23 (t, $J = 7.3$ Hz, 6H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.52 (t, $J = 7.3$ Hz, 3H), 4.12–4.33 (m, 4H), 4.65 (q, $J = 7.1$ Hz, 2H), 4.72 (q, $J = 7.1$ Hz, 2H), 6.45 (s, 1H), 7.37 (s, 5H). ^{13}C NMR ($CDCl_3$): δ 14.3 (q), 14.7 (q), 14.8 (q), 15.1 (q), 60.3 (t), 70.9 (t), 75.0 (t), 75.9 (t), 109.0 (s), 120.2 (d), 126.7 (d), 128.9 (d), 129.6 (d), 139.2 (s), 145.8 (s), 165.5 (s), 171.3 (s), 213.9 (s), 215.2 (s), 228.9 (s), 231.8 (s), 321.1 (s). MS (FAB; Xe, matrix NBA): m/z 510 (M^+, 9), 454 (23), 426 (59), 398 (100), 370 (33), 341 (62), 268 (49).

6.2.4. Pentacarbonyl(6-ethoxy-4-phenyl-2H-pyran-2-ylidene)chromium (3a)

IR ($CHCl_3$, cm^{-1}): 2050, 1960, 1925. ^1H NMR ($CDCl_3$): δ 1.62 (t, $J = 7$ Hz, 3H), 4.83 (q, $J = 7$ Hz, 2H), 6.31 (d, $J = 1.5$ Hz, 1H), 7.3–7.7 (m, 5H), 7.85 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR ($(CD_3)_2CO$): δ 14.6 (q), 68.3 (t), 96.0 (d), 128.9 (d), 130.3 (d), 135.6 (d), 132.8 (s), 135.8 (s), 153.2 (s), 175.8 (s), 219.1 (s), 224.4 (s), 260.1 (s). MS (FAB; Xe, matrix NBA): m/z 392 (M^+, 8), 364 (3), 336 (14), 308 (7), 280 (22), 252 (63). Anal. Calc. for $C_{18}H_{12}CrO_7$: C, 54.40; H, 3.41. Found: C, 54.63; H, 3.14%.

6.2.5. Decacarbonyl-μ-{[3-(E)(3'-ethoxy-1'-phenyl-1'-propenyl)-6-ethoxy-4-phenyl-2H-pyran]-2,3'-diylidene}-dichromium (E-6a)

IR ($CHCl_3$, cm^{-1}): 2059, 1985, 1930. ^1H NMR ($CDCl_3$): δ 0.86 (t, $J = 7$ Hz, 3H), 1.62 (t, $J = 7$ Hz, 3H), 4.89 (q, $J = 7$ Hz, 2H), 4.86 (q, $J = 7$ Hz, 2H), 6.07 (s, 1H), 6.35–6.60 (m, 2H), 6.80–7.30 (m, 8H), 7.67 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.5 (q), 13.5 (q), 67.7 (t), 76.9 (t), 100.5 (d), 127.1 (d), 127.2 (d), 127.3 (d), 128.1 (d), 128.9 (d), 129.9 (d), 137.0 (d), 137.5 (d), 139.4 (s), 147.0 (s), 146.9 (s), 158.0 (s), 172.5 (s), 216.2 (s), 217.6 (s), 222.8 (s), 223.4 (s), 261.7 (s), 337.3 (s). MS (FAB; Xe, matrix NBA): m/z 742 (M^+, 6), 658 (13), 574 (34), 546 (13), 518 (33), 490 (27), 462 (100), 410 (37), 359 (16). Anal. Calc. for $C_{34}H_{22}Cr_2O_{13}$: C, 54.99; H, 2.96. Found: C, 55.06; H, 2.97%.

6.2.6. Decacarbonyl-μ-{[3-(Z)(3'-ethoxy-1'-phenyl-1'-propenyl)-6-ethoxy-4-phenyl-2H-pyran]-2,3'-diylidene}-dichromium (Z-6a)

This complex was obtained (4%) together with compounds ***E*-6a**, **3a**, and **4a** (17%, 3% and 4% respectively) when complex **1a** reacted with ester **2** in a molar ratio 2/1 for 24 h. With the usual reaction conditions and work up. Starting complex (15%) was also recovered.

IR ($CHCl_3$, cm^{-1}): 2050, 1975, 1930, 1585. ^{1}H-NMR ($CDCl_3$) δ 1.25 (t, J = 7.2Hz, 3H), 1.62 (t, J = 7.2 Hz, 3H), 4.85 (q, J = 7.2 Hz, 2H), 4.90 (q, J = 7.2 Hz, 2H), 6.20 (s, 1H), 6.85–7.50 (m, 10H), 8.20 (s, 1H). ^{13}C-NMR ($CDCl_3$): δ 14.6 (q), 14.7 (q), 67.5 (t), 76.2 (t), 99.1 (d), 126.9 (d), 128.6 (d), 129.1 (d), 129.7 (d), 129.8 (d), 130.5 (d), 131.9 (s), 136.4 (s), 139.8 (d), 140.6 (s), 144.6 (s), 154.7 (s), 172.4 (s), 216.3 (s), 217.3 (s), 221.4 (s), 224.8 (s), 264.2 (s), 339.9 (s). Anal. Calc. for $C_{34}H_{22}Cr_2O_{13}$: C, 54.99; H, 2.96. Found: C, 55.13; H, 3.01%.

*6.2.7. Reaction of complex **1b** with ethyl 3,3-diethoxyacrylate*

Tungsten complex **1b** (275 mg, 0.57 mmol) and acrylate **2** (0.215 ml, 1.2 mmol) were treated as described in the general method for **1a**. Further work up afforded **3b** (91 mg, 30%) and **4b** (94 mg, 30%). Although complexes **5b** and **6b** could be detected by their different R_f in TLC elution (conditions as for **1a**), they could not be isolated by flash column chromatography.

*6.2.8. Pentacarbonyl(6-ethoxy-4-phenyl-2H-pyran-2-ylidene)tungsten (**3b**)*

IR (Nujol, cm^{-1}): 2078, 2055, 1944. ^{1}H NMR ($CDCl_3$): δ 1.55 (t, J = 8 Hz, 3H), 4.75 (q, J = 8 Hz, 2H), 6.40 (d, J = 1 Hz, 1H), 7.55 (m, 5H), 7.90 (d, J = 1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.5 (q), 67.3 (t), 95.8 (d), 127.7 (d), 129.6 (d), 131.9 (d), 132.9 (d), 135.1 (s), 154.0 (s), 173.3 (s), 199.0 (s), 239.7 (s), 273.7 (s). MS (EI): m/z 524 (M^+), 466, 440, 384, 361, 329, 309, 279, 278. Anal. Calc. for $C_{18}H_{12}O_7W$: C, 41.25; H, 2.31. Found: C, 41.30; H, 2.48%.

*6.2.9. Pentacarbonyl(6-ethoxy-3-ethyl-4-phenyl-2H-pyran-2-ylidene)tungsten (**4b**)*

IR ($CHCl_3$), cm^{-1}): 2070, 1960, 1935. ^{1}H NMR ($CDCl_3$): δ 0.82 (t, J = 8 Hz, 3H), 1.57 (t, J = 8 Hz, 3H), 2.95 (q, J = 8 Hz, 2H), 4.75 (q, J = 8 Hz, 2H), 6.18 (s, 1H), 7.36–7.43 (m, 5H). ^{13}C NMR ($(CD_3)_2CO$): δ 14.5 (q), 15.3 (q), 28.3 (t), 68.4 (t), 102.3 (d), 128.1 (d), 129.5 (d), 130.1 (d), 138.9 (s), 144.2 (s), 160.2 (s), 173.3 (s), 199.7 (s), 203.9 (s), 237.5 (s). MS (EI): m/z 552 (M^+), 498, 468, 440, 412, 382, 366, 352, 325, 291, 268, 228. Anal. Calc. for $C_{20}H_{16}O_7W$: C, 43.50; H, 2.91. Found: C, 43.51; H, 2.95%.

*6.2.10. Reaction of complex **1c** with acrylate **2***

Complex **1c** (231 mg, 0.5 mmol) and acrylate **2** (0.200 ml, 1 mmol) were allowed to react under the general conditions for 3 d (because starting product was still remaining after 2 d). No significant amount of tetracarbonyl complex analogous to **5a** was detected during this time. A single orange complex (**3c**) was produced in the reaction. Further flash chromatography (a single run using hexane/ethyl acetate 9/1) afforded the complex in pure crystalline form (78 mg, 31%).

*6.2.11. Pentacarbonyl(4-t-butyl-6-ethoxy-2H-pyran-2-ylidene)tungsten (**3c**)*

IR ($CHCl_3$, cm^{-1}): 2058, 1965, 1925. ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9H), 1.55 (t, J = 7 Hz, 3H), 4.70 (q, J = 7 Hz, 2H), 6.25 (d, J = 2.4 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.5 (q), 29.4 (q), 35.7 (s), 66.9 (t), 96.2 (d), 132.4 (d), 169.0 (s), 173.0 (s), 199.0 (s), 203.9 (s), 237.2 (s). MS (EI): m/z 505 ($M + 1^+$), 421, 365, 334, 304, 266, 238. Anal. Calc. for $C_{16}H_{16}O_7W$: C, 38.12; H, 3.20. Found: C, 38.40; H, 3.20%.

*6.2.12. Reaction of complex **1d** with ethyl 3,3-diethoxyacrylate*

Complex **1d** (212 mg, 0.50 mmol) and acrylate **2** (0.200 ml, 1 mmol) were reacted under the general conditions described for **1a**. After 1 h, no starting complex could be detected by TLC chromatography. The resulting mixture dissolved in a few millilitres of hexane:ethyl acetate 4/1 was filtered through a small Celite pad and flash chromatographed as usual. The first orange fraction (72 mg) was shown to contain three complexes (**3d**, **4d** and **4'd**) and the red second one afforded pure **6d** (8 mg, 4%) after solvent removal. All attempts to resolve the mixture failed, but from the data of the corresponding chromium complexes appropriate signals for each of the complexes in the ^{1}H NMR spectrum of the mixture could be assigned, and therefore the partition ratio and the individual yields approximately established: molar ratio **3d / 4'd / 4d** 2.5/4/2; yields 9%/14%/7%, respectively).

*6.2.13. Pentacarbonyl(6-ethoxy-4-ethyl-2H-pyran-2-ylidene)tungsten (**3d**) (data for this compound obtained from those of the inseparable mixture of **3d**, **4d** and **4'd**.)*

IR (the data given for **3d** are those for the inseparable mixture of **3d, 4d**, and **4'd**. The assignation of the signals for each one of the three compounds could not be accomplished.) (Nujol, cm^{-1}): 2070, 1975, 1940. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 7 Hz, 3H) (tentatively assigned), 1.54 (t, J = 7 Hz, 3H), 2.49 (q, J = 7 Hz, 2H), 4.67 (q, J = 7 Hz, 2H), 6.12 (d, J = 1.5 Hz, 1H), 7.48 (d, J = 1.5 Hz, 1H). ^{13}C NMR (mixture of the three complexes) (the data given for **3d** are those for the inseparable mixture of **3d, 4d**, and **4'd**. The assignation of the signals for each one of the three compounds could not be accomplished.) ($CDCl_3$): δ 12.1, 12.8, 13.1, 14.4, 14.5, 15.3, 20.4, 26.6, 27.4, 28.1, 28.8, 66.8, 67.1, 98.2, 98.6, 99.2, 135.4, 139.2, 144.7, 162.3, 162.5, 162.6, 172.0, 173.0, 198.3, 199.06, 199.09, 199.9, 203.3, 203.7, 204.0, 237.2, 237.5, 237.9.

*6.2.14. Pentacarbonyl(3,4-diethyl-6-ethoxy-2H-pyran-2-ylidene)tungsten (**4d**) (data for this compound obtained from those of the inseparable mixture of **3d**, **4d** and **4'd**.)*

IR (the data given for **3d** are those for the inseparable mixture of **3d, 4d**, and **4'd**. The assignation of the signals for each one of the three compounds could not be accomplished.). ^{1}H NMR ($CDCl_3$): δ 1.17 (t, $J = 7$ Hz, 3H), 1.27 (t, $J = 7$ Hz, 3H), 1.54 (t, $J = 7$ Hz, 3H), 2.62 (q, $J = 7$ Hz, 2H), 2.95 (q, $J = 7$ Hz, 2H), 4.67 (q, $J = 7$ Hz, 2H), 6.21 (s, 1H). ^{13}C NMR (tentatively assigned).

*6.2.15. Pentacarbonyl(6-ethoxy-4-ethyl-3-methyl-2H-pyran-2-ylidene)tungsten(**4'd**).* (obtained as an inseparable mixture of **3d**, **4d** as **4'd**)

IR (The data given for **3d** are those for the inseparable mixture of **3d, 4d** and **4'd**. The assignation of the signals for each one of the three compounds could not be accomplished). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, $J = 7$ Hz, 3H) [29], 1.54 (t, $J = 7$ Hz, 3H), 2.47 (s, 3H), 2.55 (q, $J = 7$ Hz, 2H)[29], 4.68 (q, $J = 7$ Hz, 2H), 6.19 (s, 1H). ^{13}C NMR (tentatively assigned).

*6.2.16. Decacarbonyl-μ-{[3-(E)(3'-ethoxy-1'-ethyl-1'-propenyl)-6-ethoxy-4-ethyl-2H-pyran]-2,3'-diylidene}-ditungsten (**E-6d**)*

IR ($CHCl_3$, cm^{-1}): 2067, 2057, 1962, 1940. ^{1}H NMR ($CDCl_3$): δ 0.95 (t, $J = 7$ Hz, 3H), 1.23 (t, $J = 7$ Hz, 3H), 1.55 (t, $J = 7$ Hz, 3H), 2.36–2.64 (m, 3H), 2.92 (d, d, q, $J = 1.5$, 7, 15 Hz, 1H), 4.68 (s, 3H), 4.74 (dq, $J = 6.9$, 7 Hz, 2H), 6.28 (s, 1H), 7.30 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 7.6 (q), 8.1 (q), 9.6 (q), 22.7 (t), 25.3 (t), 62.5 (q), 64.6 (t), 93.7 (d), 141.5 (s), 142.1 (s), 144.3 (d), 156.2 (s), 167.3 (s), 191.1 (s), 192.6 (s), 197.8 (s), 198.9 (s), 212.2 (s), 307.0 (s). Anal. Calc. for $C_{25}H_{20}O_{13}W_2$: C, 33.51; H, 2.25. Found: C, 33.55; H, 2.38%.

*6.2.17. Reaction of ethyl 3,3-diethoxyacrylate (**2**) with complex **1e***

Pentacarbonyl(methoxy(phenylethynyl)carbene) chromium (**1e**) (200 mg, 0.6 mmol) and ester **2** (0.23 ml, 1.2 mmol) were stirred under argon as described above for 4 h. After this time the reaction was complete, and the products originated were separated by flash-column chromatography in two separate runs, as described. The products were identified as the pyranylidene complex **3a** (36 mg, 15%), the dicarbene ***E*-6e** (13.5 mg, 8%), the tetracarbonyl complex **5e** (64.4 mg, 21%) and 30 mg of the unseparable complexes **4a** and **4'e**. The ^{1}H NMR signals were separated sufficiently to allow the estimation of yields: molar ratio **4a : 4'e** (1 : 3) corresponding to yields 3% and 9% respectively.

*6.2.18. Pentacarbonyl(6-ethoxy-3-methyl-4-phenyl-2H-pyran-2-ylidene)chromium (**4'e**)*

IR ($CHCl_3$) (**4a** + **4'e**) 2045, 1970, 1920 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.55 (t, $J = 7$ Hz, 3H), 2.45 (s, 3H), 4.75 (q, $J = 7$ Hz, 2H), 6.00 (s, 1H), 7.19–7.55 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 20.7 (q), 66.7 (t), 98.9 (d), 127.5 (d), 128.7 (d), 129.4 (d), 138.1 (s), 138.8 (s), 155.6 (s), 172.0 (s), 218.2 (s), 223.3 (s), 262.1 (s).

*6.2.19. Tetracarbonyl[(1,1-diethoxy-4-(ethoxycarbonyl)-3-phenylbuta-1,3-dien-2-yl)methoxycarbene]chromium (**5e**)*

IR ($CHCl_3$, cm^{-1}): 2010, 1900, 1840, 1700, 1690. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, $J = 7.3$ Hz, 6H), 1.51 (t, $J = 7.3$ Hz, 3H), 3.91–4.31 (m, 4H), 4.40 (s, 3H), 4.65 (q, $J = 7.3$ Hz, 2H), 6.49 (s, 1H), 7.40 (s, 5H). ^{13}C NMR ($CDCl_3$): δ 14.3 (q), 14.7 (q), 15.1 (q), 60.4 (t), 66.7 (t), 70.9 (q), 75.1 (t), 109.0 (s), 120.3 (d), 126.9 (d), 126.7 (d), 129.7 (d), 138.8 (s), 145.3 (s), 165.5 (s), 171.1 (s), 213.6 (s), 214.8 (s), 229.0 (s), 232.0 (s), 318.5 (s).

*6.2.20. Decacarbonyl-μ-{[6-ethoxy-4-phenyl-3-(3'-methoxy-1'-phenyl-1'-propenyl)-2H-pyran]-2,3'diylidene}-dichromium (**E-6e**)*

IR ($CHCl_3$, cm^{-1}): 2050, 1980, 1930. ^{1}H NMR ($CDCl_3$): δ 1.6 (t, $J = 7.2$ Hz, 3H), 4.35 (s, 3H), 4.88 (q, $J = 7.2$ Hz, 2H), 6.09 (s, 1H), 6.40–6.61 (m, 2H), 6.85–7.20 (m, 8H), 7.60 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.5 (q), 66.2 (t), 67.7 (q), 100.5 (d), 127.1 (d), 127.3 (d), 127.5 (d), 128.1 (d), 129.0 (d), 129.9 (d), 136.9 (s), 137.9 (s), 139.3 (s), 147.0 (s), 146.9 (d), 157.8 (s), 172.6 (s), 216.3 (s), 217.6 (s), 222.8 (s), 223.4 (s), 261.8 (s), 339.6 (s). MS (FAB; Xe, matrix NBA): m/z 729 (M^+, 4), 645 (17), 560 (38), 550 (90), 532 (17), 522.5 (98), 504 (45), 476 (38), 448 (100). Anal. Calc. for $C_{33}H_{20}Cr_2O_{13}$: C, 54.39; H, 2.75. Found: C, 54.63; H, 2.81%.

*6.2.21. Reaction of complex **1f** with acrylate **2***

Complex **1f** (224 mg, 0.5 mmol) and acrylate **2** (0.200 ml, 1 mmol) were allowed to react under the general conditions for 3 d (because some starting product was still remaining after 2 d). As with **1c**, no significant amount of tetracarbonyl complex analogous to **5a** was detected during this time. A single orange complex (**3c**) was produced in the reaction. Further flash chromatography (a single run using hexane/ethyl acetate 9/1) afforded the complex in pure crystalline form (120 mg, 48%).

*6.2.22. Reaction of complex **1a** with ester **2** under CO pressure*

Carbene complex **1a** (100 mg, 0.3 mmol) and ethyl 3,3-diethoxyacrylate (**2**) (0.12 ml, 0.6 mmol) were placed in a 3 ml pressure vessel. The solution was

degassed by the freeze-pump-thaw method. After warming to room temperature, the vessel was pressurized with CO (70 psi) and the mixture stirred at room temperature for 16 h. After this time the resulting mixture was purified as described in the typical procedure, affording the following complexes (identified from their ^{1}H NMR and IR spectra): **3a** (23 mg, 20%), **4a** (13 mg, 10%), **5a** (34 mg, 23%) and ***E*-6a** (9 mg, 10%).

6.2.23. Reaction of 4,4-dimethoxybut-3-en-2-one (7) with complex 1a

Ketone **7** (240 mg, 1.7 mmol) and complex **1a** (200 mg, 0.57 mmol) were treated under the general conditions described in the experimental section. Two complexes, of pyranylidene, **8** (15 mg, 7%) and **9** (32 mg, 13%) were separated and identified.

6.2.24. Pentacarbonyl(6-methyl-4-phenyl-2H-pyran-2-ylidene)chromium (8)

IR ($CHCl_3$, cm^{-1}): 2055, 1980, 1930, 1710, 1620. ^{1}H NMR ($CDCl_3$): δ 2.65 (s, 3H), 6.90 (d, J = 2.5 Hz, 1H), 7.48–7.76 (m, 5H), 8.2 (d, J = 2.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 21.3 (q), 111.4 (d), 127.9 (d), 129.6 (d), 131.8 (d), 134.8 (s), 135.9 (d), 142.8 (s), 177.3 (s), 218.0 (s), 224.2 (s), 280.8 (s). MS (FAB; Xe, matrix NBA): m/z 362 (M^+, 18), 334 (6), 306 (26), 278 (19), 250 (51), 222 (63), 176 (28), 171 (27). Anal. Calc. for $C_{17}H_{10}CrO_6$: C, 56.36; H, 2.79. Found: C, 56.51; H, 2.85%.

6.2.25. Pentacarbonyl(3-(methoxycarbonyl)-6-methyl-4-phenyl-2H-pyran-2-ylidene)chromium (9)

IR ($CHCl_3$, cm^{-1}): 2060, 1980, 1935, 1730, 1610. ^{1}H NMR ($CDCl_3$): δ 2.71 (s, 3H), 3.63 (s, 3H), 6.65 (s, 1H), 7.31–7.40 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 21.2 (q), 52.4 (q), 114.4 (d), 127.6 (d), 129.1 (d), 130.8 (d), 135.6 (s), 143.7 (s), 145.2 (s), 177.7 (s)., 216.9 (s), 223.6 (s), 279.5 (s). MS (FAB; Xe, matrix NBA): m/z 392 (M^+ –CO, 18), 364 (18), 336 (16), 322 (43), 308 (97), 280 (100), 213 (32), 229 (18). Anal. Calc. for $C_{19}H_{12}CrO_8$: C, 54.28; H, 2.85. Found: C, 54.34; H, 2.86%.

6.2.26. Reaction of 2-[(methoxycarbonyl)methylidene]-1,3-dioxolane (23) with complex 1a

Complex **1a** (500 mg, 1.4 mmol) and dioxolane **10** (900 mg, 6.2 mmol) were allowed to react for 24 h as described in the general procedure. After this time, TLC analysis of the reaction mixture indicated that reaction was complete and that two new complexes had been formed. The ^{1}H NMR spectrum of the crude product suggested a 1 : 1 molar ratio of the Z and E isomers of **24**. This mixture was purified by flash chromatography on silica gel (previously treated with 5% Et_3N) using hexane/CH_2Cl_2 4:6 as eluent, and the three complexes were isolated: **12** (7 mg, 2%), ***Z*-11** (94 mg, 37%) and ***E*-11** (29 mg, 9%). The different yields of these last complexes implies isomerization during the elution.

6.2.27. Pentacarbonyl(6-methoxy-4-phenyl-2H-pyran-2-ylidene)chromium (12)

IR ($CHCl_3$, cm^{-1}): 2060, 1975, 1930. ^{1}H NMR ($CDCl_3$): δ 4.35 (s, 3H), 6.35 (d, J = 1.5 Hz, 1H), 7.31–7.60 (m, 5H), 7.95 (d, J = 1.5 Hz, 1H).

6.2.28. Pentacarbonyl[(Z)-(1-(ethylendioxy)-3-phenyl-4-(methoxycarbonyl)buta-1,3-dien-2-yl)ethoxycarbene]-chromium (Z-11)

IR ($CHCl_3$, cm^{-1}): 2050, 1970, 1920, 1710. ^{1}H NMR ($CDCl_3$): δ 1.00 (t, J = 7.5 Hz, 3H), 3.71 (s, 3H), 4.41–4.92 (m, 6H), 6.17 (s, 1H), 7.35 (s, 5H). ^{13}C NMR ($CDCl_3$): δ 14.5 (q), 51.3 (q), 68.9 (t), 66.8 (t), 74.3 (t), 112.3 (s), 116.6 (d), 126.6 (d), 128.4 (d), 129.1 (d), 140.3 (s), 153.8 (s), 166.3 (s), 173.6 (s), 218.1 (s), 223.9 (s), 307.6 (s). MS (FAB; Xe, matrix NBA): m/z 494 (M^+, 7), 410 (32), 382 (36), 354 (38), 303 (26), 274 (40).

6.2.29. Pentacarbonyl[(E)-(1-(ethylendioxy)-3-phenyl-4-(methoxycarbonyl)buta-1,3-dien-2-yl)ethoxycarbene]-chromium (E-11)

^{1}H NMR ($CDCl_3$): δ 1.35 (t, J = 7.5 Hz, 3H), 3.58 (s, 3H), 4.31–4.70 (m, 6H), 5.71 (s, 1H), 7.21 (s, 5H). ^{13}C NMR ($CDCl_3$): δ 14.7(q), 50.9 (q), 68.0 (t), 65.4 (t), 74.7 (t), 116.1 (s), 119.2 (d), 127.2 (d), 128.2 (d), 128.3 (d), 138.6 (s), 152.4 (s), 166.3 (s), 170.5 (s), 217.3 (s), 224.0 (s), 307.6 (s).

6.2.30. Reaction of ethyl 3,3-diethoxyacrylate (2) and triethoxycarbenium tetrafluoroborate

To a suspension of $(EtO)_3C[BF_4]$(1.16 g, 5 mmol) in ca. 0.5 ml of benzene (as internal reference for quantitative monitoring) and 1 ml of $CDCl_3$ as solvent, commercial diethoxyacrylate (7.5 μl, 4 mmol) was added via syringe under dry argon and the reaction followed from the ^{1}H NMR spectra of aliquot samples. After 1 d at room temperature all the starting diethoxyacrylate had been consumed and converted into the 1,1,3,3-tetraethoxyallyl cation. The ethyl mono-orthomalonate originally present with the acrylate had also been converted in diethyl malonate and diethylether. In a similar experiment using an excess of the starting ester, all the carbenium salt was consumed, and this allowed the isolation and characterization of the allyl salt after removal of the volatile products under vacuum and washing of the remaining crystalline residue with pentane and final vacuum evaporation to dryness. ^{1}H NMR spectrum of the product, 1,1,3,3-tetraethoxyallyl tetrafluoroborate showed a single quartet, as expected from the low rotation barrier [21].

^{1}H NMR ($CDCl_3$): δ 1.45 (t, J = 7 Hz, 12H), 4.53

(q, $J = 7$ Hz, 8H), 4.98 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 13.9 (q), 64.3 (t), 69.4 br. signal (undefined), 175.3 (s).

Acknowledgment

The authors acknowledge the financial support from DGICYT (N^{0}PB-91-0612-C03-03), L.J. thanks the Department d'Ensenyament (Generalitat de Catalunya) and J.M.V. the CIRIT (Generalitat de Catalunya) for fellowships. Also we thank Prof. Andreas Mayr from NY State University at Stony Brook for helpful suggestions concerning stabilization of anionic intermediate **17**.

References and notes

[1] (a) K.H. Dötz, *Angew. Chem., Int. Edn. Engl., 23* (1984) 587; (b) W.D. Wulff in B.M. Trost and I. in Fleming (eds.), *Comprehensive Organic Synthesis*, Vol. 5, Pergamon Press, 1990, pp. 1065–1111. For new type of cycloadditions see: (c) T.A. Brandvold, W.D. Wulff and A.L. Rheingold, *J. Am. Chem. Soc., 113* (1991) 5459–5461; (d) F. Camps, J.M. Moretó, S. Ricart and J.M. Viñas, *Angew. Chem., Int. Ed. Engl., 30* (1991) 1470–1472; (e) K.H. Dötz and J. Christoffers, *J. Organomet. Chem., 426* (1992) C58–C61.

[2] K.S. Chan and W.D. Wulff, *J. Am. Chem. Soc., 108* (1986) 5229–5236.

[3] (a) K.L. Faron and W.D. Wulff, *J. Am. Chem. Soc., 110* (1988) 8727–8729; (b) K.L. Faron and W.D. Wulff, *J. Am. Chem. Soc., 112* (1990) 6419–6420; (c) F. Camps, A. Llebaria, J.M. Moretó, S. Ricart and J.M. Viñas, *Tetrahedron Letts., 31* (1990) 2479–2482; (d) F. Camps, L. Jordi, J.M. Moretó, S. Ricart. A.M. Castaño and A.M. Echavarren., *J. Organomet. Chem., 436* (1992) 189–198; (e) A. de Meijere and L. Wessjohann, *Synlett.*, (1990) 20–32; (f) R. Pipoh, R. van Eldik, S.L.B. Wang, and W.D. Wulff, *Organometallics, 11* (1992) 490–492.

[4] Preliminary results have been reported elsewhere: (a) F. Camps, J.M. Moretó, S. Ricart, J.M. Viñas, E. Molins and C. Miravitlles, *J. Chem. Soc., Chem. Commun.*, (1989) 1560–1562; (b) L. Jordi, J.M. Moretó, S. Ricart, J.M. Viñas, E. Molins and C. Miravitlles, *J. Organomet. Chem., 444* (1993) C28–C30.

[5] (a) F.A. Cotton and C.S. Weihanzel, *J. Am. Chem. Soc., 84* (1962) 4432; (b) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., Wiley, NY, 1978.

[6] (a) W.D. Wulff, D.C. Yang and C.K. Murray, *J. Am. Chem. Soc., 110* (1988) 2653–2655; (b) S.L.B. Wang, J. Su and W.D. Wulff., *J. Am. Chem. Soc., 114* (1992) 10665–10666.

[7] Trialkoxycarbenium ions are alkylating agents towards "soft" nucleophiles: (a) H. Perst, *Oxonium Ions in Organic Chemistry*, Verlag Chemie/Academic Press Weinheim NY, 1971 p. 12; (b) W. Kantlehner, B. Funke, E. Haug, P. Speh, L. Kienitz and T. Maier, *Synthesis* (1977) 73–90; (c) L. Horner and B. Nippe, *Chem. Ber., 91* (1958) 67; (d) B.G. Ramsey and R.W. Taft, *J. Am. Chem. Soc., 88* (1966) 3058.

[8] (a) E.O. Fischer and H.J. Kalder, *J. Organomet. Chem., 131* (1977) 57; (b) H. Fischer, T. Meisner and J. Hofmann, *Chem. Ber., 123* (1990) 1799; (c) M. Duetsch, R. Lackmann, F. Stein and A. de Meijere, *Synlett.*, (1991) 324–326; (d) F. Stein, M. Duetsch, R. Lackmann, M. Noltemeyer and A. de Meijere, *Angew. Chem., Int. Edn. Engl., 30* (1991) 1658–1660; (e) A. Llebaria, J.M. Moretó, S. Ricart, J. Ros, J.M. Viñas and R. Yañez, *J. Organomet. Chem., 440* (1992) 79–90.

[9] For related proton-induced reductions mediated by Group 6 transition metals carbonyl species see: (a) W.D. Wulff, R.W. Kaesler, G.A. Peterson and P.C. Tang, *J. Am. Chem. Soc., 107* (1985) 1060–1062; (b) T.R. Hoye and G.M. Rehberg, *Organometallics, 8* (1989) 2070–2071.

[10] (a) F.R. Kreissl, W. Schütt, J. Ostermeier and E. Herdtweck, *Ang. Chem., Int. Edn. Engl., 32* (1993) 1152–1154.

[11] S.L.B. Wang and W.D. Wulff, *J. Am. Chem. Soc., 112* (1990) 4550–4552.

[12] (a) C.P. Casey and M.C. Cesa, *Organometallics, 1* (1982) 87; (b) J.A. Connor and J.A. Top, *Curr. Chem., 71* (1987) 71.

[13] Compounds **3b** and **6a** have been described in previous communications as indicated in the text. A list of parameters for compound **4b** has been deposited at the Cambridge Crystallograph Data Centre.

[14] U. Schubert, in K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert and K. Weiss (eds.), *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983.

[15] C.A. Merlic, D. Xu and S.I. Khan, *Organometallics, 11* (1992) 412–418.

[16] K.H. Dötz and W. Kuhn, *J. Organomet. Chem., 286* (1985) C23–C26.

[17] M.D. Broadhurst, *J. Org. Chem., 50* (1985) 1117–1118.

[18] J. Banville and P. Brassard, *J. Chem. Soc., Perkin Trans. I, 17* (1976) 1852–1856.

[19] H. Meerwein, P. Borner, O. Fuchs, H.J. Sasse, H. Schrodt and J. Spille, *Chem. Ber., 89* (1956) 2060–2079.

[20] (a) J. Rius and C. Miravitlles, *J. Appl. Crystallogr., 20* (1987) 261; (b) G.M. Sheldrick, SHELX76, *Program for Crystal Structure Determination*, University of Cambridge, 1976.

[21] R.W. Hoffmann, *Angew. Chem., Int. Edn. Engl., 11* (1972) 324–325.