Journal of Organometallic Chemistry, 436 (1992) 189–198
Elsevier Sequoia S.A., Lausanne
JOM 22773

Reactions of silyl enol ethers with [ethoxy(phenylethynyl)carbene]chromium and -tungsten complexes

Francisco Camps, Lurdes Jordi, Josep M. Moretó, Susagna Ricart
Departament de Química Orgánica Biológica (CID), CSIC, J. Girona 18–26, 08034 Barcelona (Spain)

Ana M. Castaño and Antonio M. Echavarren
Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid (Spain)

(Received March 3, 1992)

Abstract

The reaction of pentacarbonyl[ethoxy(phenylethynyl)carbene]chromium with silyl enol ethers yields cyclobutenylcarbene complexes in moderate-to-good yield by a process that involves a Michael-type addition of the nucleophilic enol ether to the Fischer carbene complex. An ene-type product and two pyranylidene chromium complexes were also obtained in these reactions. A pyranylidene complex was also obtained in the reaction of the related tungsten complex with (*Z*)-1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene.

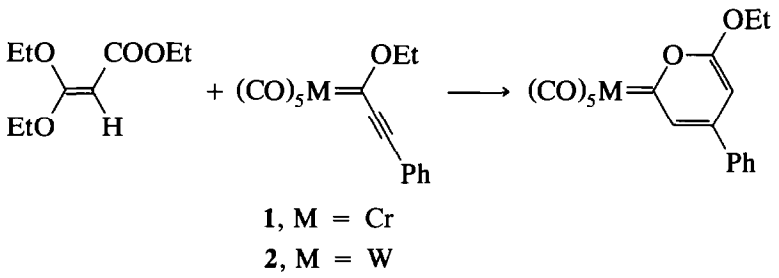
Introduction

Recently, we reported the synthesis of 6-ethoxy-2*H*-pyrones by reaction of alkynylalkoxycarbene metal complexes (**1**, M = Cr; **2**, M = W) and ethyl diethoxyacrylate (Scheme 1) [1]. As part of a broader study of the mechanism of these and related processes, we decided to explore the reaction of metal complexes **1** and **2** with simple acrylates and silyl enol ethers as models for the dialkoxyacrylate in the formation of pyranylidene metal complexes (Scheme 1).

Results and discussion

Eight silyl enol ethers were tried in this reaction with pentacarbonyl [ethoxy(phenylethynyl)carbene] -chromium and -tungsten complexes. While no reaction was observed between **1** or **2** and simple acrylates, the silyl enol ethers

Correspondence to: Dr. J.M. Moreto.

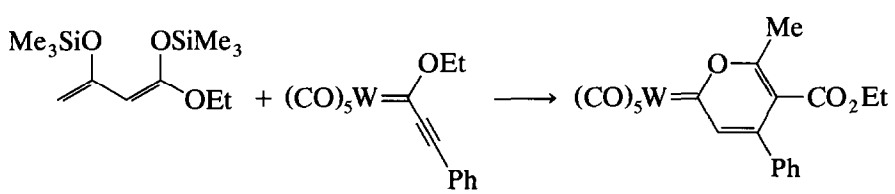


1, M = Cr
2, M = W

Scheme 1.

studied did react (Table 1). In most cases, fair-to-good yields of [2 + 2] cycloadducts were obtained (entries 1–7) with the more reactive pentacarbonyl[ethoxy(phenylethynyl)carbene]chromium complex **1**. The formation of cyclobutenes is consistent with our previous results with tetraalkoxyethylenes [2], as well as with those reported recently by Wulff [3,4]. In the reaction with *Z* trisubstituted triethylsilyl enol ether **8** (entry 6) the adduct with *cis* stereochemistry and minor amounts of an ene type product [4] were obtained. Not surprisingly, more nucleophilic ketene acetals **3** and **4** (entries 1 and 2, respectively) reacted rapidly at room temperature with carbene complex **1**, whereas simple ketone trialkylsilyl ethers **5–9** (entries 3–7) required longer reaction times. In two cases (entries 4 and 7) pyranylidene chromium complexes [1,4,5] were also obtained, albeit in low yield. In the reaction with t-butyl dimethylsilyl ether **9** (entry 7), no cyclobutene was observed, showing that an alkoxycarbonyl functionality β to the silyl enol ether changes the normal reaction course, paralleling the results obtained with the diethoxyacrylate (Scheme 1).

The reaction of (*Z*)-1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (**10**) [6] with carbene complexes **1** and **2** was also examined (Scheme 2). Best results were obtained with the tungsten complex **2** in dichloromethane at room temperature leading to the pyranylidene complex **21**. A similar result was obtained with the 1-methoxy-substituted diene. This contrasts with the reactivity of the above dienes in Diels–Alder reactions [6,7] and the dienophilic character of related alkenyl carbene complexes [8]. The same pyranylidene complexes have been reported in the base-catalyzed condensation of alkynyl Fischer carbene complexes with 1,3-dicarbonyl compounds [5]. No reaction was observed with the more hindered (*Z*)-1,3-bis(trimethylsilyloxy)-1-ethoxy-2-methyl-1,3-butadiene. On the other hand, the treatment of complex **21** with oxidants ($h\nu/O_2$, dimethyl sulphoxide;



10 **2** **21**

Scheme 2.

$Ce(NH_4)_2(NO_3)_6$) in attempts to obtain the metal-free pyrone gave only recovered starting material or decomposition products.

The above results are in agreement with the mechanism shown in Scheme 3. A Michael-type addition of the nucleophilic silyl enol ether to the electrophilic Fischer carbene complex would afford the 1,4-zwitterion intermediate **A**. The product distribution will be the result of competition between two pathways: ring

Table 1

Reactions of chromium complex **1** with silyl enol ethers

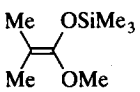
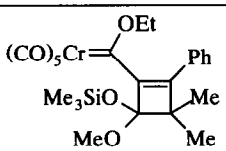
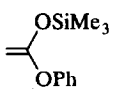
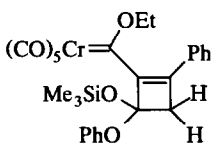
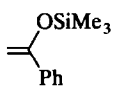
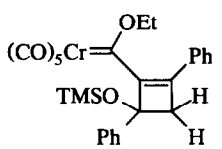
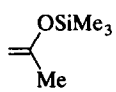
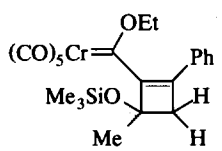
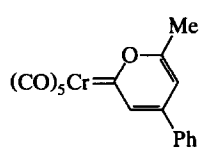
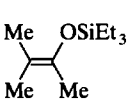
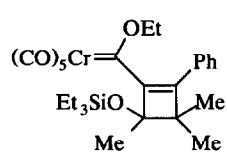
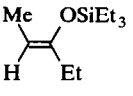
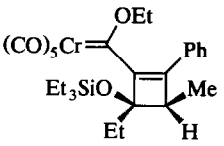
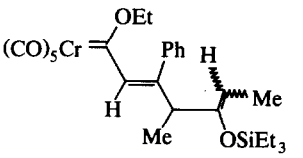
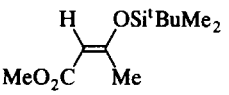
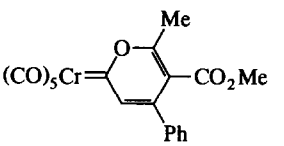
Entry	Enol ether	Enol ether/ complex ratio	Reaction time	Product(s)	Yield (%)
1	 **3**	1.5:1	2 h	 **12**	90
2	 **4**	2:1	2 h	 **13**	40
3	 **5**	2:1	48 h	 **14**	77
4	 **6**	2:1	48 h	 **15**	44
				 **16**	10
5	 **7**	7:1	5 d	 **17**	60

Table 1 (continued)

Entry	Enol ether	Enol ether/ complex ratio	Reaction time	Product(s)	Yield (%)
6	 **8**	7:1	5 d	 **18**	60
				 **19**	10
7	 **9**	10:1	10 d	 **20**	20

closure affording the cyclobutene **B**, and a 1,5-hydrogen shift, leading to the ene-type product **C**, isolated as a minor product in the reaction of entry 6. This complex can undergo cyclization to yield pyrones D (entries 4 and 7). Unlike trimethylsilylethynyl carbene complexes [4], the reaction between [ethoxy(phenylethynyl)carbene] complex **1** and the (*Z*)-enol ether **8** (entry 6) is stereoselective, showing that cyclization is much faster than the conformational equilibration in the zwitterionic intermediate of Scheme 3.

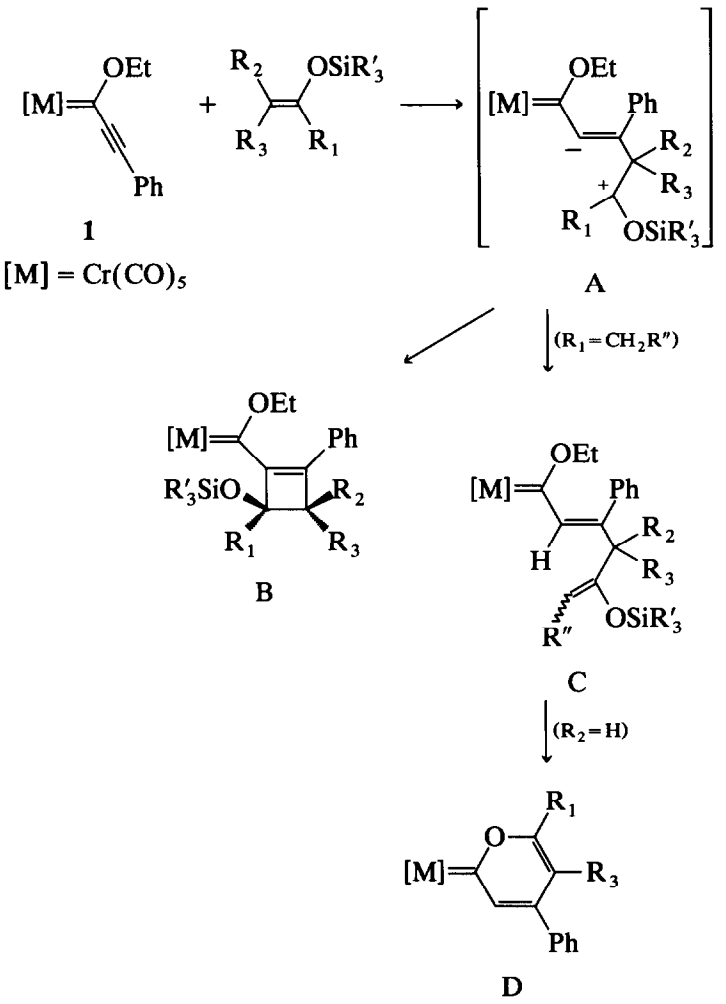
On the other hand, the intermediate **E** resulting from nucleophilic attack of diene **10** on the carbene complex **2** could undergo a 1,3-hydrogen shift to give **F** (Scheme 4). Presumably, hydrolysis of this labile derivative on silica gel would generate rise to the observed stable pyranylidene tungsten complex.

^{13}C NMR spectra of the cyclobutene adducts

The ^{13}C NMR signals corresponding to C-2 and C-3 of the [2 + 2] cyclobutene adducts were not easily observed at room temperature, even in the presence of a small amount of chromium(III) acetylacetonate. A similar problem has been found with a related cyclobutenyl Fischer carbene complex [3]. However, good resolution of both signals was obtained when the ^{13}C NMR spectra were recorded at 50°C. Presumably, a dynamic process is responsible for the temperature-dependence observed. This equilibrium is currently being investigated in detail.

Conclusions

The reaction of [alkoxy(phenylethynyl)carbene] metal complexes with silyl enol ethers affords the corresponding cyclobutenes in fairly good yields. However, in

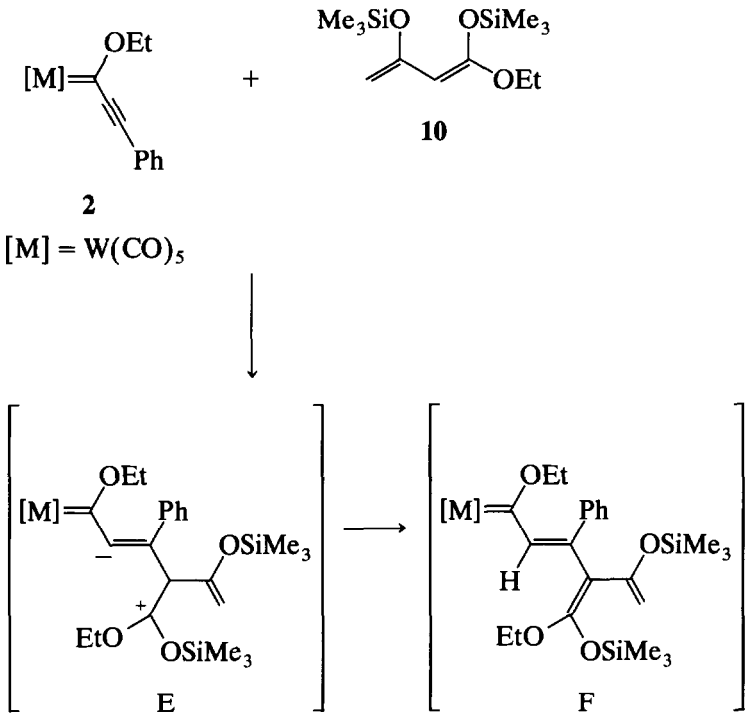


Scheme 3.

some cases a competition between the [2 + 2] and an ene-type reaction was observed, leading to the formation of a pyranylidene ring compound or a diene as minor products. The reaction seems to proceed through a multistep mechanism with the formation of a 1,4-zwitterion as the more likely rate determining step. With 1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene, a good yield of the pyranylidene complex was obtained, instead of the [2 + 2] or [4 + 2] cycloadducts.

Experimental

NMR spectra were recorded on Bruker WP80ST (80 MHz for ^{1}H), Bruker AM 200 (50 MHz for ^{13}C) or Varian XL-300 apparatus (300 MHz for ^{1}H and 75 MHz for ^{13}C). All solutions of carbene complexes were filtered through a plug of Celite immediately prior to recording of the spectra. IR spectra were recorded on a Perkin–Elmer 399B spectrophotometer. Mass spectra were obtained on a G



Scheme 4.

update MS-9 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).

1-Phenoxy-1-trimethylsilyloxyethylene (**4**) [10], 1,2-dimethyl-1-triethylsilyloxypropene (**7**) [11], (*Z*)-3-triethylsilyloxy-2-pentene (**8**) [11], methyl 3-(*t*-butyldimethylsilyloxy)-2-butenoate (**9**) [12], (*Z*)-1,3-bis(trimethylsilyloxy)-1-ethoxy-1,3-butadiene (**10**) [6] and the carbene complexes **1** and **2** [13] were synthesized according to literature procedures.

General procedure for the reaction of carbene complex 1 or 2 with silyl enol ethers 3–9

Chromium complex **1** or tungsten complex **2** was dissolved in an excess of silyl enol ether and the mixture was deoxygenated and stirred under argon at 23°C until the disappearance of the starting carbene (see Table 1 for reaction time and excess of silyl enol ether). The excess of enol ether was removed under reduced pressure (0.1 mmHg) at 25°C, and the residue was purified by flash-column chromatography with a 9:1 mixture of hexane: CH_2Cl_2 as eluent.

Reaction product from 1 and silyl enol ether 3

By the above general procedure, 340 mg (0.65 mmol, 90%) of pentacarbonyl[(4,4-dimethyl-1-methoxy-3-phenyl-1-trimethylsilyloxy-2-cyclobutenyl)ethoxycarbene]chromium (**12**) was obtained as a dark-red solid, from 250 mg (0.72 mmol) of carbene **1**.

12: IR ($CHCl_3$): 2060, 1985, 1950 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.25 (s, 9H, $Si(CH_3)_3$); 1.41 (s, 6H, $C(CH_3)_2$); 1.45 (t, $J = 7$ Hz, 3H, OCH_2CH_3); 3.25 (s, 3H, OCH_3); 4.54–4.70 (m, 2H, OCH_2); 7.25–7.35 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ 14.7 (CH_2CH_3); 22.0, 23.1 ($C(CH_3)_2$); 53.2 (OCH_3); 54.6 (C(4)); 74.9 (OCH_2); 107.3 (C(1)); 127.9, 128.9, 129.2 (Ph C(2/6)(3/5)(4)); 132.1, 139.4 (C(2), Ph C(1)); 149.1 (C(3)); 216.6 (CO *cis*); 225.1 (CO *trans*); 343.9 (Cr=C). MS (FAB;Xe, matrix NBA): *m/e* (rel. intensity) 523 (M^+, 6%); 439 (18%); 411 (2%); 383 (100%); 384 (38%); 354 (6%); 310 (10%); 296 (8%). Anal. Found: C, 54.93; H, 5.48. Calcd. for $C_{24}H_{28}CrO_8Si$: C, 54.96; H, 5.34%.

Reaction product from 1 and silyl enol ether 4

As described in the general procedure, 125 mg (0.23 mmol, 40%) of pentacarbonyl[ethoxy(3-phenyl-1-phenoxy-1-trimethylsilyloxycyclobut-2-en-2-yl)carbene]-chromium (**13**) was obtained, from 200 mg (0.57 mmol) of **1**.

13: IR ($CHCl_3$): 2060, 1980, 1950 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H, $Si(CH_3)_3$); 1.12 (t, $J = 7.3$ Hz, 3H, CH_3); 3.25 (AB system, $\delta_a = 3.2$, $\delta_b = 3.3$, $J_{ab} = 3.4$ Hz, 2H, $C(4)H_2$); 4.11–4.35 (m, 2H, CH_2); 6.90–7.45 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$) δ 1.1 ($OSi(CH_3)_3$); 14.2 (CH_3); 45.7 (C(4)); 76.2 (OCH_2); 102.8 (C(1)); 117.2 (OPh–C(2/6)); 122.2 (OPh–C(4)); 127.2, 128.7, 129.2, 129.1 (Ph–C(2/6)C(3/5)C(4)), (OPh–C(3/5)); 129.4 (Ph–C(1)); 132.3, 148.4 (C(2), OPh–C(1)); 155.7 (C(3)); 216.7 (CO *cis*); 224.9 (CO *trans*); 345.3 (C=Cr). MS (FAB; Xe, matrix NBA): *m/e* (rel. intensity) 558 (M^+, 1%); 474 (10%); 418 (100%);381 (8.4%); 219 (30%); 126 (50%).

Reaction product from 1 and silyl enol ether 5

By the general method, 230 mg (0.45 mmol, 77%) of pentacarbonyl[(3,1-diphenyl-1-trimethylsilyloxycyclobut-2-en-2-yl)ethoxycarbene]chromium (**14**) was obtained from 200 mg (0.57 mmol) of carbene **1**.

14: IR ($CHCl_3$): 2060, 1990, 1940 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.14 (s, 9H, $OSi(CH_3)_3$); 1.15 (t, $J = 7.3$ Hz, 3H, CH_3); 3.45 (syst. AB, $\delta_a = 3.23$, $\delta_b = 3.67$, $J_{ab} = 13.37$ Hz, 2H, $C(4)H_2$); 3.99 (syst. AB, q, $\delta_a = 3.79$, $\delta_b = 4.21$, $J_{ab} = 9.6$ Hz, $J_q = 7.3$ Hz, 2H, OCH_2); 7–7.5 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$) δ 1.6 ($Si(CH_3)_3$); 14.6 (CH_3); 41.4 (C(4)); 75.6 (OCH_2); 83.0 (C(1)); 125.7, 126.7, 127.5, 128.6, 128.7, 128.8 (Ph–CH); 126.2, 133.0, 143.4 (C(2), Ph–C(1)); 153.1 (C(3)); 216.5 (CO *cis*); 225.6 (CO *trans*); 346.6 (Cr=C). MS (FAB; Xe, matrix NBA): *m/e* (rel. intensity) 542 (M^+, 2%); 457 (49%); 429 (28.5%); 401 (70%); 372 (22%); 357 (26%); 344 (21%). Anal. Found: C, 59.72; H, 4.87. Calcd. for $C_{27}H_{26}CrO_7Si$: C, 59.78; H, 4.79%.

Reaction product from 1 with silyl enol ether 6

Two complexes were obtained by the above general method from 250 mg (0.72 mmol) of chromium carbene complex **1**: 145 mg (0.32 mmol, 44%) of pentacarbonyl[ethoxy(1-methyl-3-phenyl-1-trimethylsilyloxycyclobut-2-en-2-yl)carbene]-chromium **15**; and 26 mg (0.071 mmol, 10%) of pentacarbonyl(6-methyl-4-phenyl-2H-pyran-2-ylidene)chromium **16**.

15: IR ($CHCl_3$): 2060, 1985, 1945 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.2 (s, 9H, $Si(CH_3)_3$); 1.55 (t, $J = 7.2$ Hz, 3H, CH_2CH_3); 1.75 (s, 3H, CH_3); 2.85 (s, 2H, $C(4)H_2$); 4.61–4.92 (m, 2H, OCH_2); 7.28–7.35 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ

1.7 ($Si(CH_3)_3$); 15.1 (CH_2CH_3); 28.1 (CCH_3); 43.3 (C(4)); 75.8 (OCH_2); 80.3 (C(1)); 126.8, 128.5 (Ph–C(2/6)C(3/5)); 128.7 (Ph–C(4)); 128.2, 133.3 (C(2), Ph–C(1)); 153.4 (C(3)); 216.4 (CO *cis*); 224.9 (CO *trans*); 348.3 (C=Cr). MS (FAB; Xe, matrix NBA): *m/e* (rel. intensity) 424 (7%); 396 (27%); 340 (47%); 311 (36%); 295 (21%); 283 (27%).

16: IR ($CHCl_3$): 2055, 1980, 1930, 1710, 1620 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.65 (s, 3H, CH_3); 6.91 (d, $J = 2.5$ Hz, 1H, C(5)–H); 7.48–7.76 (m, 5H, Ph); 8.22 (d, $J = 2.5$ Hz, 1H, C(3)–H). ^{13}C NMR ($CDCl_3$) δ 21.3 (CH_3); 111.4 (C(5)); 127.9, 129.6 (Ph–C(2/6)(3/5)); 131.8 (Ph–C(4)); 134.8 (Ph C(1)); 135.9 (C(3)); 142.8 (C(4)); 177.3 (C(6)); 218.0 (CO *cis*); 224.2 (CO *trans*); 280.8 (C=Cr). MS (FAB; Xe, matrix NBA): *m/e* (rel. intensity) 362 (M^+, 18%); 334 (6%); 306 (26%); 278 (19%); 250 (51%); 222 (63%); 176 (28%); 171 (27%). Anal. Found: C, 56.51; H, 2.85. Calcd. for $C_{17}H_{10}CrO_6$: C, 56.36; H, 2.79%.

Reaction product from 1 and silyl enol ether 7

By the general method, 80 mg (0.23 mmol) of the starting complex **1** was recovered and 114 mg (0.2 mmol, 60% based on the reacted complex) of pentacarbonyl[ethoxy(1,4,4-trimethyl-3-phenyl-1-triethylsilyloxy-2-cyclobutenyl)carbene]-chromium (**17**) was obtained from 200 mg (0.57 mmol) of chromium-carbene complex **1**.

17: IR ($CHCl_3$): 2070, 1990, 1950 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.41–1.09 (m, 15H, $Si(Et)_3$); 1.37 (s, 3H, C(4) CH_3), 1.38 (s, 3H, C(1) CH_3), 1.41 (s, 3H, C(4) CH_3); 1.59 (t, $J = 7.2$ Hz, 3H, OCH_2); 4.86 (syst. AB, q, $\delta_a = 4.71$, $\delta_b = 5.01$, $J_{ab} = 9.6$ Hz, $J_q = 7.3$ Hz, 2H, OCH_2); 7.10–7.45 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ 6.8 (($CH_3CH_2)_3Si$); 7.1 (($CH_3CH_2)_3Si$); 15.2 (CH_2CH_3); 22.6 (C(1)CH_3); 24.1 and 24.2 (C(4)$(CH_3)_2$); 51.1 (C(4)); 76.4 (OCH_2); 85.3 (C(1)); 128.1, 128.6 (Ph–C(2/6)C(3/5)); 128.5 (Ph–C(4)); 131.4, 132.7 (C(2), Ph–C(1)); 155.9 (C(3)); 216.7 (CO *cis*); 224.3 (CO *trans*); 349.7 (C=Cr).

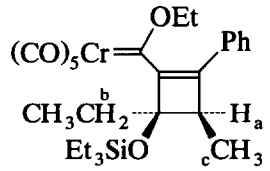
Reaction product from 1 with silyl enol ether 8

By the general method two complexes were obtained from 200 mg (0.57 mmol) of chromium-carbene complex **1**: 188 mg (0.34 mmol, 60%) of pentacarbonyl-[ethoxy(1-ethyl-4-methyl-1-triethylsilyloxy cyclobut-2-en-2-yl)carbene]chromium (**18**); and 32 mg (0.057 mmol, 10%) of pentacarbonyl[ethoxy(1,3-methyl-4-phenyl-2-triethylsilyloxypenta-1,5-dien-5-yl)carbene]chromium (**19**).

18: IR ($CHCl_3$): 2060, 1990, 1950 cm^{-1}. ^1H NMR (CD_2Cl_2) δ 0.50–1.15 (m, 18H, $Si(Et)_3$ and CH_2CH_3); 1.35 (d, $J = 7.2$ Hz, 3H, C(4)CH_3); 1.62 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3); 2.05 (m, 2H, CCH_2); 3.12 (q, $J = 7.2$ Hz, 1H, C(4)H); 4.80–5.15 (m, 2H, OCH_2); 7.05–7.51 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ 6.9 (($CH_3CH_2)_3Si$); 7.3 (($CH_3CH_2)_3Si$); 9.7 (CCH_2CH_3); 15.0, 15.2 (CCH_3, OCH_2CH_3); 32.6 (CCH_2); 44.8 (C(4)); 76.2 (OCH_2); 85.3 (C(1)); 128.1 (Ph–C(4)); 128.7, 128.5 (Ph–C(2/6)(3/5)); 133.1 (Ph–C(1)); 140.0 (C(2)); 154.0 (C(3)); 216.3 (CO *cis*); 224.2 (CO *trans*); 348.8 (C=Cr). Anal. Found: C, 58.92, H, 6.26. Calcd. for $C_{27}H_{34}CrO_7Si$: C, 58.90; H, 6.18%.

The stereochemistry of **18** was assigned using the following NOE data.

19: IR ($CHCl_3$): 2060, 1995, 1960 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.60–1.32 (m, 21H, $Si(Et)_3$, CH_2CH_3, C(3)CH_3); 1.65 (dd, $J = 7.2$ Hz, $J = 1.5$ Hz, 3H, $=CCH_3$); 3.05 (brq, $J = 7.5$ Hz, 1H, C(3)H); 4.60 (q, $J = 7.2$ Hz, 2H, OCH_2); 4.70 (qd, $J = 7.5$ Hz, $J = 1.5$ Hz, 1H, =C(1)H); 6.85–7.35 (m, 6H, Ph, =C(5)H). ^{13}C NMR ($CDCl_3$) δ



Irrad. at δ 3.12	(a):	1%	δ 2.1	(b)
		2%	δ 1.35	(c)
Irrad. at δ 2.1	(b):	7.4%	δ 3.12	(a)
		1.2%	δ 1.35	(c)
Irrad. at δ 1.35	(c):	12%	δ 3.12	(a)

5.6 (CH_3CH_2Si); 6.8 (CH_3CH_2Si); 10.8 (C(1)CH_3); 13.9 (CH_2CH_3); 18.2 (C(3)CH_3); 48.9 (C(3)); 76.3 (OCH_2); 103.8 (C(1)); 127.0, 127.8, 128.0, 140.5 (Ph); 141.3 (C(5)); 142.2 (C(2)); 151.7 (C(4)); 216.6 (CO *cis*); 224.1 (CO *trans*); 340.1 (Cr=C). Anal. Found: C, 59.13; H, 6.22. Calcd. for $C_{27}H_{34}CrO_7Si$: C, 58.90; H, 6.18%.

Reaction product from 1 and silyl enol ether 9

By the general procedure, 48 mg (0.12 mmol, 20%) of pentacarbonyl(6-methyl-5-methoxycarbonyl-4-phenyl-2*H*-pyran-2-ylidene)chromium (**20**) were produced from 200 mg (0.57 mmol) of starting complex **1**.

20: IR ($CHCl_3$): 2060, 1980, 1935, 1730, 1600, 1480, 1110 cm^{-1}. ^1H NMR δ 2.75 (s, 3H, CH_3); 3.63 (s, 3H, OCH_3); 7.32–7.51 (m, 5H, Ph); 8.05 (s, 1H, C(3)H). ^{13}C NMR δ 19.2 (CH_3); 52.7 (OCH_3); 119.5 (C(5)); 129.0, 127.6 (Ph–C(2/6)(3/5)); 130.5 (Ph–C(4)); 135.7 (Ph–C(1)); 138.9 (C(3)); 140.2 (C(4)); 165.7 (CO_2Me); 176.2 (C(6)); 217.3 (CO *cis*); 223.9 (CO *trans*); 285.5 (Cr=C). MS (FAB; Xe, matrix NBA): *m/e* (rel. intensity) 420 (M^+, 33%); 392 (3%); 364 (36%); 336 (31%); 308 (100%); 280 (82%); 229 (29%); 176 (63%). Anal. Found: C, 54.59; H, 2.89. Calcd. for $C_{19}H_{12}CrO_8$: C, 54.28; H, 2.85%.

Reaction product from 2 and silyl enol ether 10 (Scheme 2)

To a solution of tungsten complex **2** (150 mg, 0.32 mmol) in dichloromethane diene **10** (240 mg, 0.87 mmol) was added. The mixture was stirred at 23°C for 1 h. The solvent was evaporated and the residue chromatographed (20:1 hexane-EtOAc) to yield pentacarbonyl(5-ethoxycarbonyl-6-methyl-4-phenyl-2*H*-pyran-2-ylidene)tungsten (**21**) (121 mg, 67%) as a dark red solid.

21: IR (KBr): 2060, 1985, 1925, 1905, 1725, 1625 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.95 (t, $J = 7.2$ Hz, 3H, CH_2CH_3); 2.76 (s, 3H, C(6)–CH_3); 4.09 (q, $J = 7.2$ Hz, 2H, OCH_2); 7.38–7.58 (m, 5H, Ph); 8.08 (s, 1H, C(3)–H). [The methoxy derivative, prepared from the 1-methoxydiene, showed the following ^1H NMR spectrum: 2.74 (s, 3H, CH_3); 3.61 (s, 3H, OCH_3); 7.37–7.53 (m, 5H, Ph); 8.83 (s, 1H, C(3)–H).] ^{13}C NMR ($CDCl_3$) δ 15.5, 19.9 (CH_3); 62.3 (OCH_2); 120.4 (C(5)); 127.4, 129.0, 130.4, 135.9 (Ph); 141.4 (C(3)); 144.3 (C(4)); 165.1 (CO_2Et); 175.0 (C(6)); 198.3 (CO *cis* $^1J(^{13}C–^{183}W) = 127.4$ Hz); 204.3 (CO *trans*); 258.8 (W = C). MS (FAB; Xe, matrix NBA): *m/e* (^{184}W rel. intensity): 566 (M^+, 19%); 538 (15%); 482 (21%); 426 (7%); 354 (20%); 243 (100%). Anal. Found: C, 42.51; H, 2.50. Calcd. for $C_{20}H_{14}O_8W$: C, 42.41; H, 2.47%.

Acknowledgments

Financial support from the DGICYT (PB-0201-C03-03) is gratefully acknowledged. L.J. and A.M.C. thank the Departament d'Ensenyament (Generalitat de Catalunya) and the Comunidad Autónoma de Madrid, respectively, for fellowships.

References

1 F. Camps, J.M. Moretó, S. Ricart, J.M. Viñas, E. Molins and C. Miravitlles, J. Chem. Soc., Chem. Commun., (1989) 1560.
2 F. Camps, A. Llebaria, J.M. Moretó, S. Ricart and J.M. Viñas, Tetrahedron Lett., 31 (1990) 2479.
3 K.L. Faron and W.D. Wulff, J. Am. Chem. Soc., 110 (1988) 8727.
4 K.L. Faron and W.D. Wulff, J. Am. Chem. Soc., 112 (1990) 6419.
5 S.L.B. Wang and W.D. Wulff, J. Am. Chem. Soc., 112 (1990) 4550.
6 S.H. Bell, D.W. Cameron, G.I. Feutrill, B.K. Skelton and A.H. White, Tetrahedron Lett., 26 (1985) 6519.
7 C. Brisson and P. Brassard, J. Org. Chem., 46 (1981) 1810.
8 W.D. Wulff, W.E. Bauta, R.W. Kaesler, P.J. Lankford, R.A. Miller, C.K. Murray and D.C. Yang, J. Am. Chem. Soc., 112 (1990) 3642.
9 C.P. Casey and W.R. Brunsvold, Inorg. Chem., 16 (1977) 391.
10 N. Slougi and G. Rousseau, Synth. Commun., 17 (1987) 1.
11 T. Veysoglu and L.A. Mitscher, Tetrahedron Lett., 22 (1981) 1299.
12 H. Sakurai, K. Miyoshi and Y. Nakadaira, Tetrahedron Lett., 17 (1977) 2671.
13 K.H. Dötz and W. Kuhn, J. Organomet. Chem., 286 (1985) C23.