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Conjugate additions to alkynylalkoxycarbenemetal (Cr or W) complexes

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Abstract

The addition of different nucleophilic compounds (aliphatic and aromatic alcohols, thiols and phosphines) to alkynylalkoxycarbene complexes has been studied. The reaction with smaller nucleophiles proceeds readily and regioselectively at the β-carbene position. With more substituted nucleophiles the reaction rate slowed down considerably. Addition of a catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene]) speeded up the reaction and improved the E/Z ratio.

Introduction

The electrophilic nature of the carbene centre in complexes of the transition metals was recognized at an early stage [1] and applied to the preparation of variously substituted complexes by replacement of the original alkoxy group by another through nucleophilic substitution at the carbene carbon atom [2]. It was also observed in alkynylalkoxycarbenemetal complexes that attack at the carbene centre by amines occurred only at very low temperatures (kinetic control); otherwise, the product was that of amine addition to the triple bond [3]. This process resulted in deactivation since further attack of the amine, either at the carbene centre or at the conjugated double bond, was not observed. However, it is possible to reach the diamine complex by following the opposite protocol (substitution at the carbene centre at low temperature followed by a second addition on the triple bond at room temperature).

Carbanions were also found to attack the triple bond of alkynylalkoxycarbene complexes, suggesting that these complexes might be suitable reagents for Michael-type reactions, by analogy with activated alkynes [4]. This hypothesis was supported by the high polarity of the triple bond revealed by the chemical shift in

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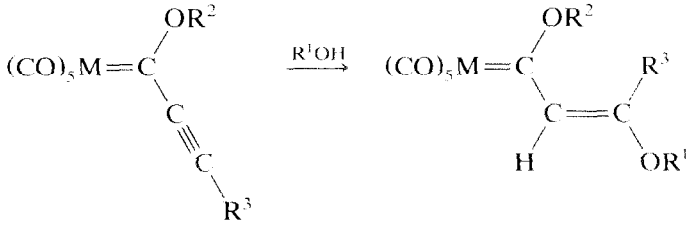


Scheme 1

^{13}C NMR of the acetylenic carbon atoms [5] and the propensity of these complexes to a variety of cycloaddition reactions [6].

Recently, it was observed that this behaviour is not restricted to amines. Alcohols and phenols also add readily at the triple bond, giving the corresponding alkenyl complexes [7] (Scheme 1). When the reaction was too slow it was found that the presence of a catalytic amount of a base such as DBU led to the corresponding addition product. Consequently, we undertook the study of the scope of the addition reaction on the triple bond of such complexes by different nucleophilic reagents with a more or less acidic hydrogen atom bonded to a heteroatom.

Results and discussion

Alcohols

Five aliphatic alcohols were allowed to react in a 5–10 molar excess with different Cr and W alkynylalkoxycarbene complexes at room temperature either in tetrahydrofuran (THF) or the alcohol itself as the solvent. All of them gave the corresponding addition products in moderate to high yields (Table 1). The reaction times were reasonably short with the lower members of the series (MeOH and EtOH), while the reaction rate slowed down considerably with the more hindered alcohols (such as ^{i}Pr, benzyl); a base (such as DBU) was found to shorten the required reaction time dramatically. No addition or substitution at the carbene centre was observed with Cr at these temperatures so that selective attack at the triple bond with a concurrent deactivation of the carbene centre occurred (as in the addition of primary and secondary amines as reported by Fischer *et al.* [3]). However, even in the presence of DBU, ^{t}BuOH failed to give the addition product and the decomposition of the starting complex was observed instead.

Reaction with diols (ethyleneglycol and 1,3-propyleneglycol) afforded the monoadduct (41% and 25%) as the major product, but minor amounts of the diaddition product (16%) were also observed for ethyleneglycol. Hence, when a second interaction is expected, there is a preference for the β position rather than the carbene. The increased length of the diol chain may account for the absence of any addition product when propyleneglycol was used.

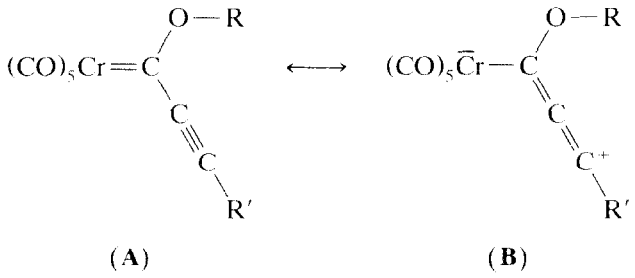
Regioselectivity was complete for all compounds in this study. As can be seen from Table 1, and consistent with other reactions involving alkynylalkoxycarbene complexes, replacement of Ph by Me_3Si or ^{n}Pr gave to the complex a higher reactivity towards conjugate alcohol addition with complete regioselectivity.

Table 1

Reaction conditions and yields of $[(CO)_5M{=}C(OR^2)(CH{=}CR^3)(OR^1)]$ obtained from the addition of alcohols R^1OH to $[(CO)_5M{=}C(OR^2)(C{\equiv}CR^3)]$

Compound	R^1	R^2	R^3	M	Method	Reaction time (h)	Yield	E/Z ratio
1	Me	Et	Ph	Cr	A	24	61	9
1	Me	Et	Ph	Cr	B	1	65	9
2	Me	Me	Ph	W	A	24	70	9.4
3	^{i}Pr	Et	Ph	W	B	48	26	4.1
4	allyl	Et	Ph	W	B	24	24	9.5
5	Me	Et	^{n}Pr	Cr	A	9	72	E only
6	Me	Me	Me_3Si	Cr	A	11	68	one isomer
7	Bz	Et	Ph	Cr	B	5	45	6.1
8	C_2H_4OH	Et	Ph	W	B	24	41 [a]	
9	C_3H_6OH	Et	Ph	Cr	B	24	61	9

[a] 16% of the *geminal* bisadduct **8'** was also obtained.



(A) (B)

Fig. 1

In all cases the *E* isomer (corresponding to a *syn* addition) was found to be the major product. Identification and quantification of the isomers was made from ^1H NMR data. Particularly significant for this purpose is the chemical shift of the single vinylic proton which was compared with those reported for similar compounds obtained through orthoester elimination reactions or other indirect ways [8–12]. The present method was found to improve the *E*/*Z* ratios reported in conventional nucleophilic additions on acetylenes, as it does regioselectivity [6].

For the trimethylsilylacetylene derivative the same type of control is assumed to apply and thus a single stereoisomer was isolated, whose stereochemistry could not be definitely established since both the chemical shifts and the coupling constants for the two vinyl protons (desilylation follows alcohol addition) have similar values [11].

It is thought that the pentacarbonylmetal moiety is responsible for the extra activation of the acetylenic function compared to the corresponding propiolates. This functional group may act as an "electron sink" conferring an enhanced electrophilicity on the benzylic carbon atom. In this sense, the metal unit can be envisaged as an internal Lewis acid, allowing alcohol addition at room temperature while an alkoxide is required for conventional activated acetylenes (Fig. 1).

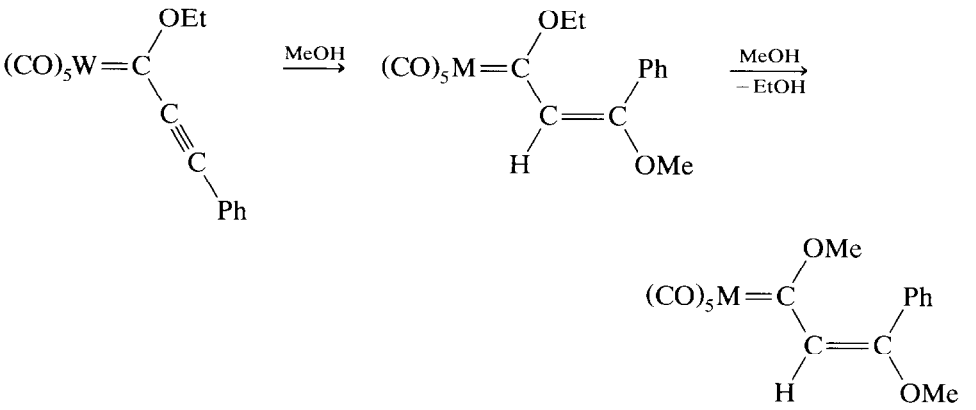
Bulky alcohols required the catalytic presence of DBU, probably to generate the corresponding alkoxide from the alcohol.

Some alcoholysis of the complex at the carbene centre was detected, but only for methanol and the tungsten complex (Scheme 2), its extent depending on the elapsed time.

The higher reactivity of chromium complexes compared to that of tungsten complexes may account for their lower sensitivity towards methanolysis, due to the shorter reaction time for a complete conjugate addition. The thermodynamic pathway (addition to the carbene centre) may compete with the kinetic (addition to the triple bond) when longer reaction times are required.

Phenols

Three representative phenols were chosen to be tested (Table 2). All of them required the presence of DBU since the reactions were performed in solution (THF) and in a twofold phenol : metal molar ratio. Yields and stereoselectivities were generally high as with aliphatic alcohols, in all cases *syn*-addition was predominant, but in contrast to conventional acetylenes the regioselectivity was complete. To assign unequivocally the *Z* and *E* isomers (Table 2) the mixture was



Scheme 2

oxidized by treatment with DMSO in order to release the metal–carbonyl moiety. This mild process, however, led to almost quantitative double bond isomerization to the more stable *Z* isomer, as deduced from reported data [13] (Scheme 3). Therefore, *Z* and *E* assignment of the organometallic compounds was made by analogy of the ^{1}H NMR chemical shift of the vinyl proton for the organic counterparts.

Again chromium complexes reacted faster than those of tungsten and gave a better *E*/*Z* ratio. Unlike aliphatic diols, when addition was performed with catechol the double addition product was the only product obtained (Scheme 4).

This is in sharp contrast to previous reports on the preparation of β-alkoxyalkenylalkoxycarbenemetal complexes, where a similar ketal was found difficult to isolate since elimination of alcohol occurs [12]. In our cases this complex displayed a fairly good stability probably due to the fact that the required geometry for an elimination is restricted by steric congestion (*cf.* results obtained for aliphatic diols).

Sulphur and phosphorus nucleophiles

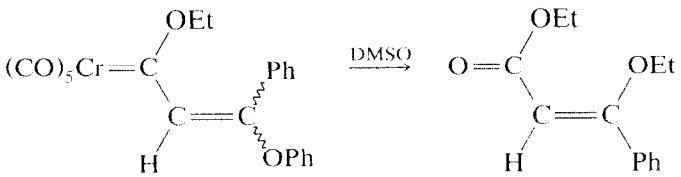
Four representative thiols and diphenylphosphine were tried in this reaction (Table 3).

Reactions with thiols were also performed in solution, and in some cases with a low thiol/complex ratio, to avoid easy polyadditions and ligand substitution due to the more highly nucleophilic character of S-derivatives.

Table 2

Reaction conditions and yields of phenol additions to $[(CO)_5M{=}C(OR^2)(C{\equiv}CR^3)]$

Compound	Phenol	M	Method	Reaction time (h)	Yield	*E*/*Z* ratio
10	phenol	Cr	B	5	68	3.4
11	phenol	W	B	19	75	3
12	3,5-dimethylphenol	Cr	B	5	90	4.5
13	3,5-dimethylphenol	W	B	19	75	3
14	catechol	W	B	36	72	–



Scheme 3

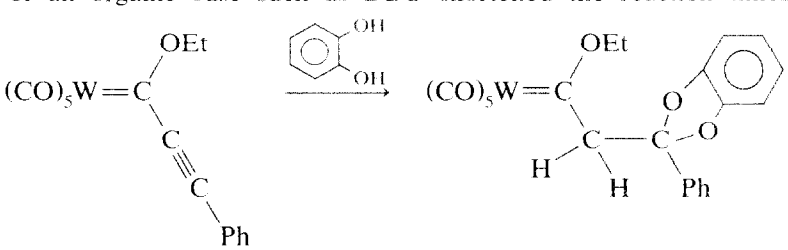
The regioselectivity was always complete as in the case of alcohols and phenols, and no anti-Markovnikov additions were detected. These results agree with the previous reported additions of benzenethiols to phenylpropionic esters under both base-catalyzed and radical conditions [14,15].

It is generally recognized that in the base-promoted addition of thiols on acetylenes the resulting stereochemistry is opposite to that found in alcohol and phenol additions (and in accordance to the *trans*-addition rule of Truce [16]). In our case the major reaction product was the *Z* isomer for aromatic thiols. The opposite stereochemistry was found to predominate for aliphatic thiols. For ethanethiol and ethanedithiol the possibility of isomerization through a retro-Michael reaction due to the large excess of thiol (ethanethiol) or the steric vicinity of the second thiol group (ethanedithiol) would explain the high *E*/*Z* ratio. In no case was any kind of interaction between the sulphur compound and the carbene carbon atom or metal centre detected.

It was also surprising to find this behaviour with diphenylphosphine. In fact this compound gave only an addition product and we were unable to detect any carbonyl substitution. It is also reasonable to expect that once the phosphine has added in the Markovnikov sense it is too far from the metal centre for any kind of interaction.

Conclusions

Using the high polarity of the triple bond, the easy and preferential addition of amines to the triple bond of the alkynylalkoxycarbenemetal complexes has been extended to alcohols, phenols, thiols and phosphines. The reaction follows the Markovnikov sense and the *E* isomer is predominant or exclusive in the reaction with aliphatic alcohols. Alternatively, softer and stabilized nucleophiles such as phenols and thiols reacted sluggishly with the triple bond, in particular in the tungsten complexes, giving a lower *E*/*Z* ratio. The presence of a catalytic amount of an organic base such as DBU shortened the reaction times and generally



Scheme 4

Table 3

Reaction conditions and yields of thiol and phosphine additions to $[(CO)_5M{=}C(OR^2)(C{\equiv}CR^3)]$

Compound	Nucleophile	M	Method	Reaction time (h)	Yield	E/Z ratio
15	EtSH	W	A	24	46	9
16	$(CH_2SH)_2$	Cr	B	24	44	1.5
17	PhSH	W	A	1/2	62	0.1
17	PhSH	W	B	1/2	65	0.1
18	*p*-tolSH	W	A	5	58	0.7
19	$PHPh_2$	W	A	24	31	0.3

improved the stereoselectivity. In all cases the regioselectivity was complete. This process can be considered a direct method to obtain β-alkoxyvinylalkoxycarbene-metal derivatives (or heteroanalogues) for further applications in organic synthesis.

Experimental

Spectroscopic measurements were made with the following instrumentation: ^1H NMR; Bruker WP 80 ST (80 MHz), Varian XL 300 (300 Mhz). ^{13}C NMR; Varian XL 300 (MHz). Chemical shifts are reported in δ (Me_4Si as internal standard with Bruker WP ST and $CDCl_3$ in all cases). IR spectra were recorded on a Perkin–Elmer 399 B apparatus using $CHCl_3$ as the solvent. Mass spectra were run with a MS-9 mass spectrometer, VG updated. Elemental analyses were made with a Carlo Erba 1106 analyzer.

Purification of the products and all reactions were carried out under argon or dinitrogen. THF and diethylether were freshly distilled over sodium with benzophenone under argon.

Pentacarbonylethoxy[(phenyl)ethynyl]carbene-chromium(0) and tungsten(0) were prepared by a modification of the method described by Fischer *et al.* [3].

Preparation of pentacarbonylethoxy[(2-methoxy-2-phenyl)vinyl]methylenechromium(0) (1)

Method A. To a solution of 0.350 g of pentacarbonylethoxy[(2-phenyl)alkynyl] methylenechromium(0) (1 mmol) in 1 ml of THF was added 0.320 g of MeOH (10 mmol) with a syringe at room temperature under argon atmosphere. The mixture was allowed to react until disappearance of the starting carbene (24 h). The solvent and the excess of methanol were evaporated off under reduced pressure and the residue was purified by flash column chromatography (eluent hexane/CH_2Cl_2 (20/3)) to give 0.234 g (61%) of **1** (*cis–trans* mixture) as yellow solid.

Method B. To a solution of 0.350 g of the starting alkynylethoxycarbene (1 mmol) in 1 ml of THF were added 0.320 g of MeOH (10 mmol) with a syringe and 0.5 ml of DBU 0.1 molar in toluene. The mixture was allowed to react until the disappearance of the starting carbene (1 h). The work-up was by method A affording 0.250 g (65%) of **1** as yellow solid (*cis–trans* mixture).

IR ($CHCl_3$): ν(CO) 2062, 1973, 1935 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.50–7.11 (m, 5H), 6.95 (s, 1H), 4.40 (q, 2H, $J = 8$ Hz), 3.95 (s, 3H), 0.82 (t, 3H, $J = 8$ Hz); (*Z* isomer) 7.50–7.10 (m, 5H), 6.85 (s, 1H), 4.87 (q, 2H, $J = 8$ Hz), 4.07

(s, 3H), 1.63 (t, 3H, $J = 8$ Hz) ppm. ^{13}C NMR ($CDCl_3$) δ 323.6 (s) 222.3 (s) 215.8 (s) 158.1 (s) 135.2 (s) 127.9 (d) 127.0 (d) 126.4 (d) 118.6 (d) 73.9 (t) 55.3 (q) 12.3 (q) ppm. MS (FAB) (Xe, matrix NBA); 382 (M^+), 354, 326, 298, 270, 242, 161 (100%), 145.

Preparation of pentacarbonylmethoxy[(2-methoxy-2-phenyl)vinyl]methylenetungsten(0) (2)

As described in method A, affording the expected compound in 76% yield as a red-orange solid (*cis–trans* mixture).

IR ($CHCl_3$): ν(CO) 2062, 1973, 1935 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.35 (m, 5H), 6.95 (s, 1H), 4.50 (s, 3H), 3.90 (s, 3H); (*Z* isomer) 7.35 (m, 5H), 6.85 (s, 1H), 4.58 (s, 3H), 3.72 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ 300.9 (s), 203.8 (s), 198.2 (s), 163.0 (s), 136.4 (s), 129.9 (d), 128.7 (d), 127.9 (d), 123.4 (d), 67.9 (q), 67.2 (q). Anal. Found: C, 38.56; H, 2.20. $C_{16}H_{12}O_7W$ calc.: C, 38.42; H, 2.42%. MS (FAB) (Xe, matrix NBA): 500 (M^+), 472, 444, 416, 388, 360, 177 (100%).

Preparation of pentacarbonylethoxy[(2-isopropoxy-2-phenyl)vinyl]methylenetungsten(0) (3)

As described in method B, affording the expected compound in 26% yield as a red-orange solid (*cis–trans* mixture).

IR ($CHCl_3$): ν(CO) 2065, 1972, 1928 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.12–7.51 (m, 5H), 6.98 (s, 1H), 4.75 (t, 2H, $J = 7.2$ Hz), 4.35 (q, 2H, $J = 8$ Hz), 1.42 (d, 6H, $J = 7.2$ Hz), 0.82 (t, 3H, $J = 8$ Hz). ^{13}C NMR (acetone-d_6) δ 322.4 (s) 218.3 (s) 160.9 (s) 130.4 (s) 129.7 (d) 129.5 (d) 128.9 (d) 122.2 (d) 76.6 (t) 73.7 (d) 29.8 (q) 21.8 (q) 14.2 (q) ppm. Anal. Found: C, 42.28; H, 3.17. $C_{18}H_{18}O_7W$ calc.: C, 42.04; H, 3.35%.

Preparation of pentacarbonylethoxy[(2-allyl-2-phenyl)vinyl]methylenetungsten(0) (4)

As described in method B, affording the expected compound in 24% yield as a red-orange solid.

IR ($CHCl_3$): ν(CO) 2060, 1970, 1927 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.35 (m, 5H), 6.96 (s, 1H), 6.01 (m, 2H), 5.35 (m, 2H), 4.61 (dt, 2H, $J = 5.3$ Hz, $J = 1.2$ Hz), 4.40 (q, 2H, $J = 5.4$ Hz), 0.85 (t, 3H, $J = 5.5$ Hz) ppm.

Preparation of pentacarbonylethoxy[(2-methoxy-2-propyl)vinyl]methylenechromium(0) (5)

As described in method A, affording the expected compound in 72% yield as a bright yellow solid.

IR ($CHCl_3$): ν(CO) 2060, 1965, 1930 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.88 (s, 1H), 4.98 (q, 2H, $J = 7$ Hz), 3.76 (s, 3H), 2.44 (t, 2H, $J = 7$ Hz), 1.61 (t, 3H, $J = 7.2$ Hz), 1.53 (h, 3H, $J = 7$ Hz); ^{13}C NMR δ 321.1 (s), 223.9 (s), 217.6 (s) 165.7 (s), 119.7 (d), 76.2 (t), 56.2 (q), 37.3 (t), 21.3 (t), 15.3 (q), 14.1 (q). Anal. Found: C, 48.27; H, 4.64. $C_{14}H_{16}O_7Cr$ calc.: C, 48.28; H, 4.63%.

Preparation of pentacarbonylmethoxy[(2-methoxy)vinyl]methylenechromium (6)

As described in method A, affording the corresponding desilylated product in 62% yield as a red solid.

IR ($CHCl_3$): ν(CO) 2060, 1970, 1935 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.44, 6.86 AB system (J = 12 Hz), 4.57 (s, 3H), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 326.3 (s), 222.8 (s), 217.3 (s), 156.8 (s), 122.4 (d), 65.2 (q), 58.7 (q).

*Preparation of pentacarbonylethoxy[(2-benzyloxy-2-phenyl)vinyl]methylenechromium(0) (**7**)*

As described in method B, affording the expected compound in 45% yield as a red-orange solid.

IR ($CHCl_3$): ν(CO) 2060, 1980, 1930 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.50 (m, 10H), 7.07 (s, 1H), 5.14 (s, 2H), 4.57 (q, 2H, J = 7.2 Hz), 0.83 (t, 3H, J = 7.2 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ 325.6 (s), 226.2 (s), 217.3 (s), 158.0 (s), 135.1 (s), 130.3 (s), 129.6 (d), 128.8 (d), 128.6 (d), 128.1 (d), 127.7 (d), 127.0 (d), 121.6 (d), 74.7 (t), 71.9 (t), 13.9 (q) ppm.

*Preparation of pentacarbonylethoxy[(2-(2'-hydroxyethoxy)-2-phenyl)vinyl]methylenetungsten(0) (**8**)*

As described in method B but utilizing CH_2Cl_2 as eluent, affording the expected compound in 41% yield as a red-orange solid.

IR ($CHCl_3$): ν(CO) 2060, 1970, 1930 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.30 (m, 5H), 6.95 (s, 1H), 4.41 (q, 2H, J = 8 Hz), 3.81–4.31 (m, 4H), 0.85 (t, 3H, J = 8 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ 300.1 (s), 203.7 (s), 198.1 (s), 161.8 (s), 136.7 (s), 129.7 (d), 128.5 (d), 128.1 (d), 124.1 (d), 78.2 (t), 71.2 (t), 67.9 (t), 13.7 (q) ppm.

In this reaction we obtained a second product, a *bis*-adduct: pentacarbonyl [(2,2-ethylenedioxy-2-phenyl)ethyl]methylenetungsten(0) (**8'**) in 14% yield as a red-orange solid.

IR ($CHCl_3$): ν(CO) 2060, 1970, 1930 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.15 (m, 5H), 4.70 (q, 2H, J = 8 Hz), 4.01 (m, 2H), 3.95 (s, 2H), 3.85 (m, 2H), 1.31 (t, 3H, J = 8 Hz). ^{13}C NMR ($CDCl_3$) δ 206.1 (s), 197.3 (s), 132.9 (s), 130.6 (d), 128.5 (d), 128.2 (d), 128.1 (d), 80.6 (t), 72.3 (t), 64.5 (t), 14.4 (q) (the carbene signal was not detected) ppm.

*Preparation of pentacarbonylethoxy[(2-(3'-hydroxypropoxy)-2-phenyl)vinyl]methylenechromium(0) (**9**)*

As described in method B but after the usual work-up, the crude mixture was purified by flash column chromatography using CH_2Cl_2 as eluent to give the expected product as an orange solid in 61% yield.

IR ($CHCl_3$): ν(CO) 2060, 1970, 1930 cm^{-1}. ^1H NMR ($CDCl_3$) δ (E isomer): 7.05–7.45 (m, 5H), 6.90 (s, 1H), 4.41 (q, 2H, J = 7.5 Hz), 4.15 (t, 2H, J = 7.2 Hz), 3.75 (m, 2H), 1.95 (m, 2H), 0.80 (t, 3H, J = 7.5 Hz) ppm.

*Preparation of pentacarbonylethoxy[(2-phenoxy-2-phenyl)vinyl]methylenechromium(0) (**10**)*

As described in method B with a phenol/alkynylalkoxycarbene ratio of 2/1. The crude product was purified by flash column chromatography using a 100/3 hexane/^{t}BuOH mixture as eluent giving the expected mixture of isomers as a red solid in 68% yield.

IR ($CHCl_3$): ν(CO) 2030, 1940 cm^{-1}. ^1H NMR ($CDCl_3$) δ (E isomer): 7.55 (s, 1H), 7.80–6.80 (m, 10H), 4.83 (q, 2H, J = 8 Hz), 1.30 (t, 3H, J = 8 Hz); (Z isomer):

6.82 (s, 1H), 7.80–6.80 (m, 10H), 4.65 (q, 2H, $J = 8$ Hz), 0.95 (t, 3H, $J = 8$ Hz) ppm. ^{13}C NMR ($CDCl_3$) δ 330.7 (s) (*E*), 329 (s) (*Z*), 224 (s), 216.6 (s), 157.0 (s), 156.8 (s), 153.5 (s), 143.9 (s), 135.0 (s), 134.0 (d), 130.7 (d), 130.1 (d), 129.6 (d), 128.9 (d), 128.0 (d), 127.4 (d), 125.8 (d), 124.8 (d), 122.6 (d), 121.1 (d), 116.1 (d), 14.6 (q) (*E*), 14.4 (q) (*Z*) ppm.

Preparation of pentacarbonylethoxy[(2-phenoxy-2-phenyl)vinyl]methylenetungsten(0) ***(11)***

As described in method B with a phenol/alkynylalkoxycarbene ratio of 2/1. The crude product was purified by flash column chromatography using a 100/14 hexane/^{t}BuOH mixture as eluent giving a mixture of isomers as a red-orange solid in 75% yield.

IR ($CHCl_3$): ν(CO) 2030, 1935 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.71–6.70 (m, 11H), 4.52 (q, 2H, $J = 7$ Hz), 1.20 (t, 2H, $J = 7$ Hz); (*Z* isomer): 7.71–6.70 (m, 11H), 4.36 (q, 2H, $J = 7$ Hz), 0.85 (t, 2H, $J = 7$ Hz) ppm.

Preparation of pentacarbonylethoxy[(2-(3',5'-dimethylphenoxy)-2-phenyl)vinyl]methylenechromium(0) ***(12)***

As described in method B with a phenol/alkynylalkoxycarbene ratio of 2/1. The crude product was purified by flash column chromatography using a 10/1 hexane/ethylacetate mixture as eluent. The yield was 90% of a red-orange mixture of isomers.

IR ($CHCl_3$): ν(CO) 2060, 1980, 1940 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.30–7.51 (m, 6H), 6.60 (s, 1H), 6.45 (s, 2H), 4.75 (q, 2H, $J = 7.2$ Hz), 2.20 (s, 6H), 1.32 (t, 3H, $J = 7.2$ Hz); (*Z* isomer): 7.31–7.51 (m, 6H), 6.85 (s, 1H), 6.77 (s, 2H), 4.60 (q, 2H), 2.32 (s, 6H), 0.90 (t, 3H) ppm. ^{13}C NMR δ (*E* isomer) 330.6 (s), 224.1 (s), 216.7 (s), 157.1 (s), 144.4 (s), 140.3 (s), 139.5 (s), 134.5 (s), 130.7 (d), 129.1 (d), 128.9 (d), 128.3 (d), 128.1 (d), 127.6 (d), 126.7 (d), 124.5 (d), 118.7 (d), 113.8 (d), 21.2 (q), 14.8 (q) ppm.

Preparation of pentacarbonylethoxy[(2-(3',5'-dimethyl-phenoxy)-2-phenyl)vinyl]methylenetungsten(0) ***(13)***

As described in method B with a phenol/alkynylalkoxycarbene ratio of 2/1. The crude mixture was purifed by flash column chromatography using a 10/1 hexane/ethylacetate mixture as eluent giving a red-orange solid mixture of isomers in 75% yield.

IR ($CHCl_3$): ν(CO) 2060, 1975, 1940 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.40–7.80 (m, 5H), 6.50–6.90 (m, 3H), 4.55 (q, 2H), 2.25 (s, 6H), 1.30 (t, 3H); (*Z* isomer): 7.40–7.80 (m, 5H), 6.50–6.90 (m, 3H), 4.45 (q, 2H), 2.30 (s, 6H), 0.91 (t, 3H) ppm. Anal. Found: C, 48.07; H, 3.52. $C_{24}H_{20}O_7W$ calc.: C, 47.70; H, 3.34%.

Preparation of pentacarbonylethoxy[(2,2-orthophenylenedioxy-2-phenyl)ethyl]methylenetungsten(0) ***(14)***

As described in method B with a phenol/alkynylalkoxycarbene ratio of 2/1. The crude product was purified by flash column chromatography using a 10/1 hexane/^{t}BuOMe mixture as eluent giving the bisaddition product in a 72% yield.

IR ($CHCl_3$): ν(CO) 2040, 1985, 1945 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.32–7.65 (m, 5H), 6.81 (s, 4H), 4.62 (q, 2H), 4.12 (s, 2H), 1.29 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ

326.6 (s), 206.6 (s), 196.9 (s), 146.8 (s), 140.5 (s), 129.0 (d), 128.4 (d), 124.9 (d), 121.5 (d), 115.6 (d), 108.5 (d), 81.0 (t), 71.6 (t), 14.0 (q) ppm. Anal. Found: C, 44.53; H, 2.75. $C_{22}H_{16}O_7W$ calc.: C, 44.62; H, 2.72%.

*Preparation of pentacarbonylmethoxy[(2-ethylthio-2-phenyl)vinyl]methylenetungsten(0) (**15**)*

As described in method A affording the expected compound in 46% yield as a red-orange solid.

IR ($CHCl_3$): ν(CO) 2021, 1970, 1930 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.50 (s, 1H), 7.31–7.45 (m, 5H), 4.66 (s, 3H), 2.40 (q, 2H, $J = 7.5$ Hz), 1.06 (t, 3H, $J = 7.5$ Hz); (*Z* isomer): 7.30–7.68 (m, 6H), 3.99 (s, 3H), 2.91 (q, 3H), 1.42 (t, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ 297.5 (s), 203.7 (s), 197.8 (s), 144.0 (d), 138.9 (s), 132.9 (s), 129.2 (d), 128.6 (d), 128.0 (d), 68.1 (q), 28.1 (t), 14.0 (q) ppm. Anal. Found: C, 38.34; H, 2.64. $C_{17}H_{14}O_6W$ calc.: C, 38.5; H, 2.64%.

*Preparation of pentacarbonylethoxy[(2(2'-ethanthio)-2-phenyl)vinyl]methylenechromium(0) (**16**)*

As described in method B with a thiol/alkynylalkoxycarbene ratio of 1/1. The crude product was purified by flash column chromatography using a 2/1 hexane/CH_2Cl_2 mixture as eluent producing the addition product in 44% yield as a mixture of isomers.

IR ($CHCl_3$): ν(CO) 2080, 1960, 1930 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.52 (s, 1H), 7.16–7.46 (m, 5H), 4.98 (q, 2H, $J = 7.5$ Hz), 2.46–2.62 (m, 4H), 1.80 (s, 1H), 1.76 (t, 3H), $J = 7.5$ Hz); (*Z* isomer): 7.39 (s, 1H), 7.15–7.48 (m, 5H), 4.37 (q, 2H, $J = 7.5$ Hz), 2.83–3.64 (m, 4H), 2.32 (s, 1H), 0.78 (t, 3H, $J = 7.5$ Hz) ppm. ^{13}C NMR ($CDCl_3$) δ (*E* isomer): 297.1 (s), 203.8 (s), 197.8 (s), 144.9 (d), 139.2 (s), 129.5 (d), 128.9 (d), 128.2 (d), 126.4 (s), 79.7 (t), 37.3 (t), 24.5 (t), 15.7 (q); (*Z* isomer): 298.8 (s), 203.8 (s), 197.8 (s), 139.4 (d), 129.4 (d), 129.3 (s), 128.8 (d), 128.6 (d), 78.4 (t), 36.5 (t), 23.2 (t), 13.6 (q) ppm.

*Preparation of pentacarbonylmethoxy[(2-phenyl-2-phenylthio)vinyl]methylenetungsten(0) (**17**)*

As described in method A with a thiol/alkynylalkoxycarbene ratio of 1/1. The crude product was purified by flash column chromatography using a 9/1 hexane/CH_2Cl_2 mixture as eluent affording the expected mixture of isomers in 62% yield as a red solid. The same product was obtained by method B in 65% yield.

IR ($CHCl_3$): ν(CO) 2060, 1960, 1930 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.10–7.75 (m, 10H), 7.68 (s, 1H), 4.72 (s, 3H); (*Z* isomer): 7.10–7.75 (m, 10H), 6.85 (s, 1H), 4.00 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ (*Z* isomer): 301.0 (s), 203.7 (s), 197.4 (s), 152.4 (s), 139.2 (d), 138.1 (s), 135.4 (d), 130.5 (d), 130.2 (d), 129.6 (s), 128.8 (d), 128.2 (d), 128.0 (d), 60.0 (q) ppm. Anal. Found: C, 43.69; H, 2.51; S, 5.58. $C_{18}H_{14}O_6SW$ calc.: C, 43.6; H, 2.44; S, 5.55%.

*Preparation of pentacarbonylethoxy[(2(para-methylphenylthio)-2-phenyl)vinyl]methylenetungsten(0) (**18**)*

As described in method A with a thiophenol/alkynylalcoxycarbene ratio of 2/1. The crude product was purified by flash column chromatography using a 9/1

hexane/CH_2Cl_2 mixture as eluent affording the expected compound in 58% yield as a red solid mixture of isomers.

IR ($CHCl_3$): ν(CO) 2062, 1950, 1938 cm^{-1}. ^1H NMR ($CDCl_3$) δ (*E* isomer): 7.63 (s, 1H), 6.85–7.45 (m, 5H), 5.05 (q, 2H, $J = 7.3$ Hz), 2.19 (s, 3H), 1.69 (t, 3H, $J = 7.3$ Hz); (*Z* isomer): 7.11–7.60 (m, 9H), 6.80 (s, 1H), 4.32 (q, 2H, $J = 7.2$ Hz), 2.42 (s, 3H), 0.79 (t, 3H, $J = 7.2$ Hz) ppm. ^{13}C NMR ($CDCl_3$) δ (*E* isomer): 296.2 (s), 203.9 (s), 197.9 (s), 149.2 (s), 143.8 (d), 138.8 (s), 138.5 (s), 133.5 (d), 130.9 (d), 129.2 (d), 128.6 (d), 127.9 (d), 79.7 (t), 21.9 (t), 15.6 (q); (*Z* isomer): 298.9 (s), 203.9 (s), 197.6 (s), 153.0 (s), 141.1 (s), 138.9 (d), 135.5 (d), 130.9 (d), 128.1 (d), 125.9 (s), 78.2 (t), 21.4 (q), 13.6 (q) ppm.

*Preparation of pentacarbonylmethoxy[(2-phenyl-2-diphenylphosphine)vinyl]methylenetungsten(0) (**19**)*

As described in method A with a diphenylphosphine/alkynylalcoxycarbene ratio of 2/1. The crude product was purified by flash column chromatography using a 9/1 hexane/CH_2Cl_2 mixture affording the expected mixture of isomers in 31% yield as an orange solid.

^1H NMR ($CDCl_3$) δ (*E* isomer): 6.60–7.80 (m, 16H), 4.60 (s, 3H); (*Z* isomer): 6.60–7.80 (m, 16H), 4.20 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$) δ 242.7 (s), 203.2 (s), 196.3 (s), 154.4 (s), 136.5, 134.8, 134.5, 133.8, 133.4, 133.3, 132.3, 130.8, 130.7, 129.7, 129.2, 129.1, 128.8, 128.7, 128.7, 128.6, 128.4, 127.8, 68.8 (q) ppm.

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