Carbene Complexes in Organic Synthesis: A New Tungstacarbene-promoted Alkyne Insertion–Olefin Cyclopropanation Reaction†

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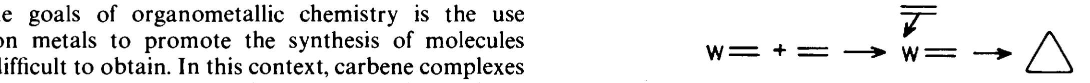
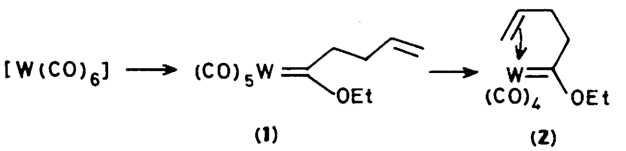
Carbene complexes of tungsten, bearing a co-ordinated double bond two carbons away from the carbene function, react with alkynes to give, after insertion of the alkyne, bicyclo[4.1.0]heptane derivatives as a result of cyclopropanation of the double bond by the newly formed carbene complex.

One of the goals of organometallic chemistry is the use of transition metals to promote the synthesis of molecules otherwise difficult to obtain. In this context, carbene complexes of transition metals can now be considered as versatile synthetic intermediates.[1,2] Results obtained by Casey *et al.*,[3,4] and by our group[5] have shown that carbene complexes of tungsten, which bear a carbon–carbon double bond, can be used as models for the olefin cyclopropanation reaction (Scheme 1). It has also been shown, by several groups, that such complexes can insert alkynes to give either new stable carbene complexes or, after release of the metal, organic compounds, such as phenols, ethers, or linear conjugated polymers (Scheme 2).[6–18]

The aim of the present paper is to describe the reactivity of carbene complexes of structure (**2**) (and related structures),[19] which have been found to be the most active 'Fischer type' complexes with respect to the alkyne insertion reactions, and which lead, depending on the reaction conditions, either to linear polymers or to bicyclo[4.1.0]heptane derivatives.



Scheme 1.



(**1**) (**2**)

Scheme 2.

Results and Discussion

Synthesis of the Complexes.—Complex (**2**) was prepared by the usual Fischer method[2] except that an organomagnesium compound was used instead of the classical organolithium compound (Scheme 2). The co-ordination of the double bond of (**1**) is best carried out in boiling benzene for 12 h. Complex (**9**) was prepared[20] from pentacarbonyl-[ethoxy(methyl)carbene]tungsten, (**6**), by a double alkylation reaction, followed by an intramolecular metathesis reaction (Scheme 3). Co-ordination of the cyclopentene moiety to form (**9**) was brought about as for complex (**1**).

Reactivity towards Alkynes.—Complex (**2**) reacts, in catalytic amounts, with alkynes to give, at room temperature in hexane, linear polyenes. Thus, hept-1-yne reacts with (**2**) to give a poly(heptyne) in 63% yield (heptyne:W = 33:1).[17] The same reaction has been carried out on a series of other alkynes (Table 1). Besides the polymers, trace amounts of organic compounds could be detected. These compounds could be obtained, in almost quantitative yields when the reaction was carried out at lower temperature (10—15 °C), in the presence of stoicheiometric amounts (or with a slight excess) of alkynes. For example, hept-1-yne in hexane leads, in 24 h, and after silica-gel chromatography, to ketone (**5d**) in 95% yield; reactions with other alkynes gave analogous results (Table 2). Even cyclo-octyne reacts with (**2**) to give adduct (**10**), albeit in lower yield (31%). Besides the insertion–cyclopropanation product (**10**), the 'trimer' of cyclo-octyne (**11**) and the quinone (**12**) could be isolated.

In the case of the simplest alkyne, acetylene, the expected 3-oxobicyclo[4.1.0]heptane (**5**, R = R′ = H) could not be isolated. Instead, a substituted phenol (**13**) could be isolated in trace amounts, as well as poly(acetylene). Complex (**9**) with hex-3-yne leads, under the same conditions, to 3,4-diethyltricyclo[3.2.1.0^{4,6}]octan-2-one, (**15**).

Structure Determinations.—The structures of compounds (**5a**)—(**5l**) and (**15**) were essentially determined by a detailed study of their ^{1}H and ^{13}C n.m.r. spectra. Chemical shifts and coupling constants, which can be extracted by first-order analysis, are collected in Tables 3 and 4.

Disubstituted ketones of structure (**5**) exist as a mixture of *cis* and *trans* isomers, *cis*-(**5b**) and *trans*-(**5b**). Their relative configurations were ascribed after a detailed analysis of the ^{1}H and ^{13}C n.m.r. spectra. The distinction between the two relative configurations was deduced from the observation of a small ^4J coupling, detected in the COSY LR spectrum (LR = long-range), between H^2 and H^7. Indeed a coplanar W arrangement can exist only in the *trans* isomer for the bonds to H^2_{exo} and H^7_{exo}, the six-membered ring adopting an envelope conformation similar to that previously[21,22] postulated for the unsubstituted bicyclo[4.1.0]heptan-3-one. This result was

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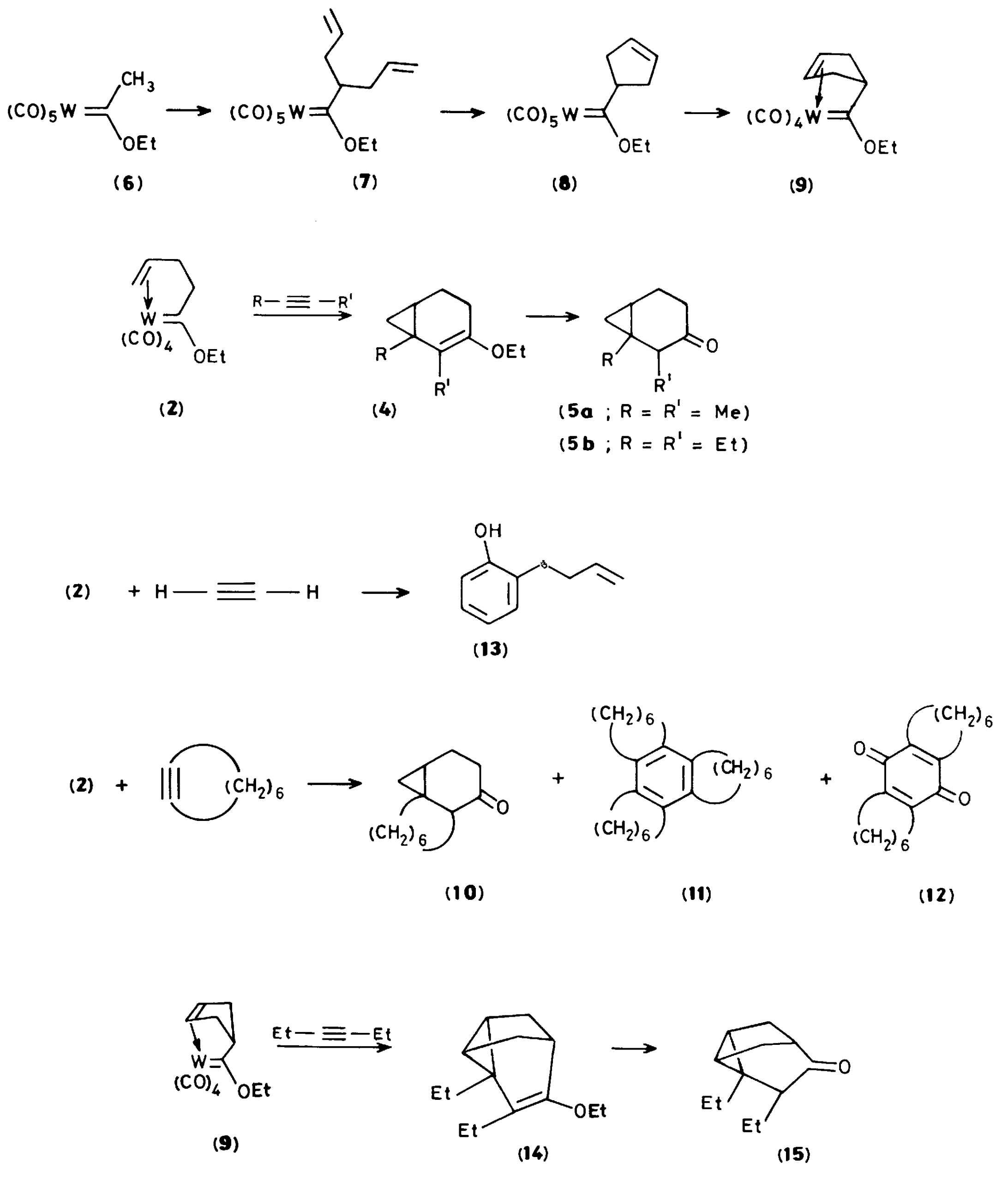
† *Supplementary data available* (No. SUP 56664, 7 pp.): COSY LR and shift correlation n.m.r. spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme 3.

Table 1. Conditions and yields for the polymerisation of various alkynes induced by complex (**2**)

Alkyne	[(2)]/mol dm^{-3}	10^2[Alkyne]/mol dm^{-3}	Polymerization time (h)	Yield (%)	Molecular weight
CH≡CH	0.1	1	48	25	
CH≡CMe	0.1	1.4	48	40	20 100
CH≡CC$_5$H$_{11}$	0.6	1.8	20	63	50 000
CH≡COBu^t	0.8	17	20	42	121 000
CH≡CPh	0.3	3	20	35	13 200
CH≡CSiMe$_3$	0.5	2	5	90	30 000
CH≡CCH$_2$OMe	0.8	1.9	260	0	
CH≡CCH$_2$NH$_2$	1.2	1	121	5	
CH≡CCH$_2$Cl	0.9	1.7	140	52	3 500
MeC≡CMe	0.8	1.5	120	40	33 700

further confirmed by the non-equivalence of the methylene protons H^8, $H^{8'}$ which is much more pronounced in the *trans* isomer as a result of the shielding anisotropic effect of the cyclopropane ring. Carbon-13 n.m.r. spectra were recorded using the mixture of compounds *trans*-(**5b**) and *cis*-(**5b**). Assignments of the various methylene carbons and distinction between the two methyl carbons in each compound were obtained from two-dimensional correlated $^1H-^{13}C$ spectra.

Table 2. Yields of compounds (**5**) produced in insertion–cyclopropanation reactions of various alkynes induced by complex (**2**)

R	R′	Yield (%)
(**5a**) Me	Me	56
(**5b**) Et	Et	75
(**5c**) Ph	H	80
(**5d**) C_5H_{11}	H	95
(**5e**) Bu^t	H	95
(**5f**) Ph	Ph	85
(**5g**) CH_2OMe	H	72
(**5h**) $SiMe_3$	H	82
(**5i**) $CMe_2(OH)$	H	44
(**5j**) $(CH_2)_4C{\equiv}CH$	H	90
(**5k**) CO_2Et	H	52
(**5l**) $(CH_2)_4CH{=}CH_2$	H	90
(**5m**) CH_2CH_2OH	H	55

Good evidence for restriction to internal mobility of the two side chains was found from measurements of the nuclear Overhauser enhancement (n.O.e.) and of the longitudinal relaxation time, T_1:[23] the methylene carbons, including those of the side chains, exhibit similar T_1 values, whereas the methyl carbons show unusually low T_1 values.

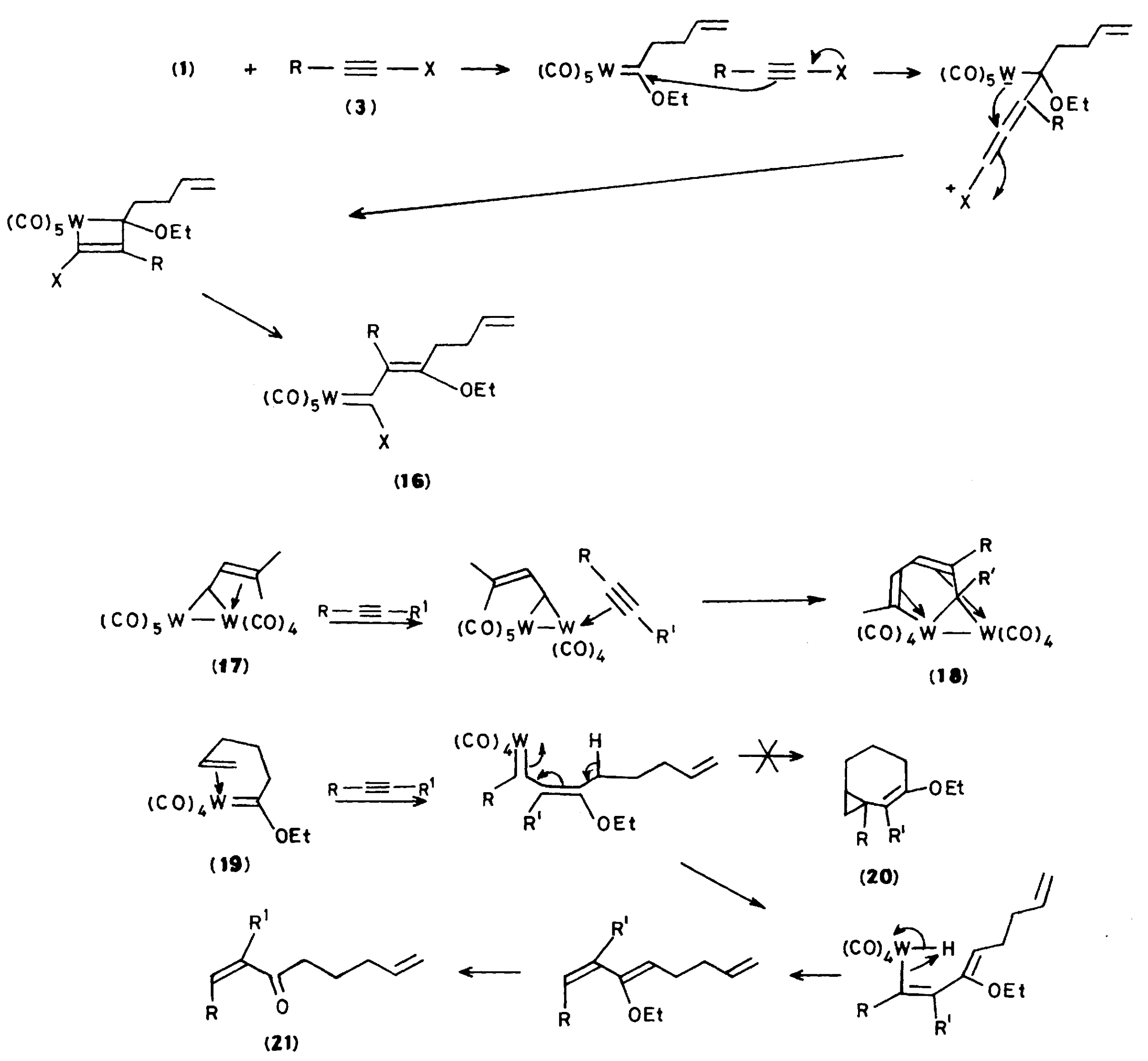
Compound (**15**) has a symmetric skeleton. The main feature is the pronounced non-equivalence of the H^9, $H^{9'}$ methylene protons which is even greater than that observed for the similar protons of compound *trans*-(**5b**). Once more, a highly preferred conformation of the C^3 substituent with one of the methylene protons lying above the cyclopropane ring must be considered and a relative *trans* configuration can be anticipated.[24]

Table 3. Hydrogen-1 n.m.r. data for compounds (**5**)[a]

	R	R′	H^2_{exo}	H^2_{endo}	H^4	$H^{4'}$	H^5	$H^{5'}$	H^6	H^7_{endo}	$H^{7'}_{exo}$	R	R′
(**5a**)	Me	Me	2.50		2.06	2.25	1.98	2.33	0.99	0.26	0.35	1.16	1.13
trans (**5b**)[b]	Et	Et	2.49		2.07	2.19	2.02	2.26	0.89	0.44	0.44	{0.85 1.83 0.95	{1.58 1.75 0.93
cis-(**5b**)[b]	Et	Et		2.25	2.10	2.25	1.82	2.30	0.92	0.32	0.50	{1.08 1.58 0.79	{1.63 1.73 0.90
(**5c**)	Ph	H	2.85	2.85	2.18	2.35	2.11	2.44	1.54	0.85	1.08	7.15	7.33
(**5e**)	Bu^t	H	2.62	2.42	2.10	2.20	1.88	2.27	1.22	0.21	0.74	0.84	
(**5f**)	Ph	Ph	4.09		2.40	2.58	2.30	2.65	1.48	1.16	1.32	6.95	7.22
(**5g**)	CH_2OMe	H	2.70	2.53	2.10	2.25	1.95	2.30	1.16	0.54	0.63	{3.10 3.32 3.33	
(**5h**)	$SiMe_3$	H	2.51	2.36	2.15	2.20	2.00	2.25	1.09	0.48	0.63	−0.04	
(**5i**)	$CMe_2(OH)$	H	2.66	2.47	2.10	2.20	1.90	2.30	1.38	0.32	0.89	{1.18 1.20	

	Coupling constants (*J*/Hz)		Cross peaks[c]
(**5a**)	$J(H^7_{endo}H^7_{exo})$ 5.5	$J(H^7_{exo}H^2_{exo})$ 1.6	$C^8H_3H^7_{endo}$
	$J(H^6H^7_{endo})$ 5.4		$C^8H_3H^5$
	$J(H^6H^7_{exo})$ 8.5		
trans-(**5b**)[b])			$H^2_{exo}H^7$
cis-(**5b**)[b]	$J(H^7_{endo}H^7_{exo})$ 5.3		
	$J(H^6H^7_{endo})$ 5.1		
	$J(H^6H^7_{exo})$ 8.4		
(**5c**)	$J(H^7_{endo}H^7_{exo})$ 5.6		$H^7_{endo}H^2$
	$J(H^6H^7_{endo})$ 5.6		
	$J(H^6H^7_{cis})$ 8.8		
(**5e**)	$J(H^7_{endo}H^7_{exo})$ 5.8	$J(H^2_{endo}H^2_{exo})$ 17	
	$J(H^6H^7_{endo})$ 5.8		
	$J(H^6H^7_{exo})$ 8.9	$J(H^7_{exo}H^2_{exo})$ 1.5	
(**5f**)	$J(H^7_{endo}H^7_{exo})$ 6.0	$J(H^7_{exo}H^2_{exo})$ 1.7	
	$J(H^6H^7_{endo})$ 5.7		
	$J(H^6H^7_{exo})$ 8.8		
(**5g**)	$J(H^7_{endo}H^7_{exo})$ 5.0	$J(H^2_{endo}H^2_{exo})$ 18	
	$J(H^6H^7_{endo})$ 5.5	$J(H^7_{exo}H^2_{exo})$ 1.2	
	$J(H^6H^7_{exo})$ 8.6		
(**5h**)	$J(H^7_{endo}H^7_{exo})$ 5.2	$J(H^2_{endo}H^2_{exo})$ 17.4	
	$J(H^6H^7_{endo})$ 5.0		
	$J(H^6H^7_{exo})$ 7.8	$J(H^7_{exo}H^2_{exo})$ < 1	
(**5i**)	$J(H^7_{endo}H^7_{exo})$ 5.3	$J(H^2_{endo}H^2_{exo})$ 17.3	
	$J(H^6H^7_{endo})$ 5.3	$J(H^7_{exo}H^2_{exo})$ 1.2	
	$J(H^6H^7_{exo})$ 9.0		

[a] Observing frequency 500.13 MHz unless stated otherwise. [b] Observing frequency 250.13 MHz. [c] Observed by correlated two-dimensional n.m.r. (COSY LR).



Scheme 4.

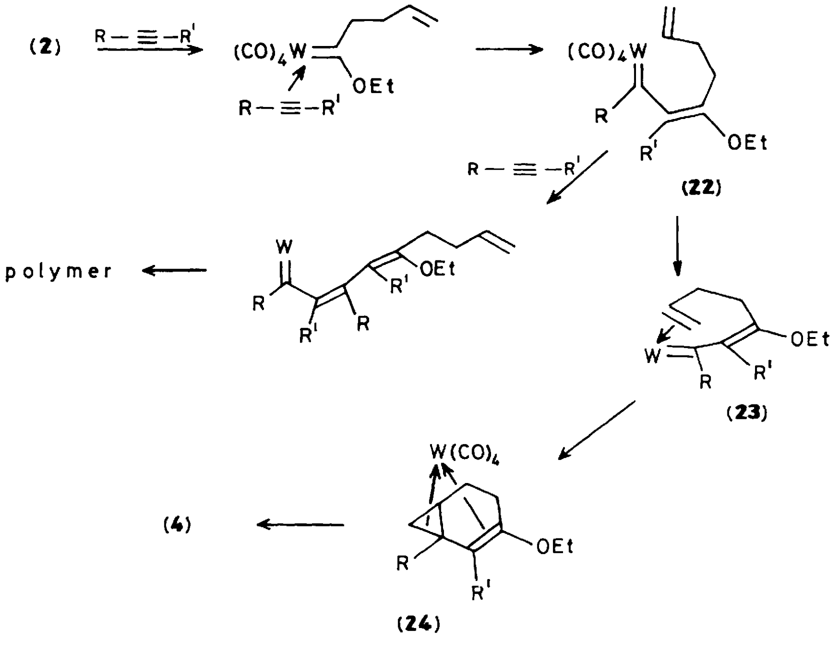
Mechanism of the Reaction.—As far as the mechanism of this new insertion–cyclopropanation reaction is concerned, several points must be taken into account.

(*a*) Complex (**1**), in which the double bond is not co-ordinated to the metal, does not react with alkynes under the reaction conditions used in this work. The only exceptions to this general behaviour are compounds (**3**, X = NEt_2 or OEt). They react with (**1**) to give the insertion products (**16**): two new carbene complexes as a result of an insertion–rearrangement reaction. This result is not surprising as it is known that such nucleophilic alkynes react easily with Fischer type carbene complexes [6] to give new, stable Fischer type carbene complexes. This insertion reaction is best described as a nucleophilic attack of the alkyne on the carbene carbon atom, without co-ordination to the metal centre, followed by a cyclobutanation reaction (Scheme 4).

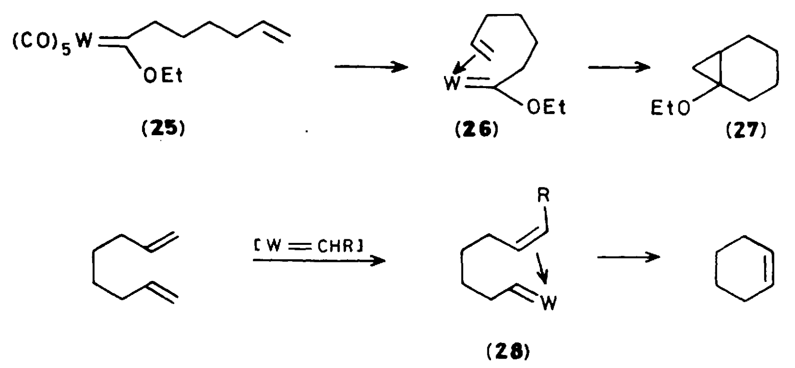
(*b*) CO exchange does not occur, at room temperature, when complex (**2**) is exposed, for 24 h in hexane, to an atmosphere (*ca.* 10^5 Pa) of ^{13}CO; this result does not favour the displacement of a CO group by the alkyne. It appears therefore that the presence of a co-ordinated double bond facilitates, in most cases, the introduction of the alkyne into the co-ordination sphere of the metal. The reactivity of complexes (**2**) thus can be compared to the reactivity of complex (**17**) which also leads to a monoinsertion product with substituted alkynes[25] after displacement of the double bond, the insertion product being in this latter case stable enough to be isolated, and having structure (**18**).

(*c*) Under the same conditions, complex (**19**) also reacts with alkynes, but does not lead to the expected insertion–cyclopropanation product (**20**). Instead, a linear insertion product (**21**) is obtained.[11] Thus the distance between the carbon–carbon double bond and the carbene function is of the highest importance for the second step of the cyclopropanation reaction.

A mechanism, which takes into account the results of previous studies in this field and our observations, is proposed (Scheme 5). The first step would be the deco-ordination of the double bond in (**2**) by the incoming alkyne; the second step, the insertion–rearrangement reaction, might lead to a co-ordinatively unsaturated complex (**22**). Depending on the reaction conditions, catalytic or stoicheiometric amounts of (**2**) with respect to the alkyne, (**22**) might react further with the monomer to give a linear polymer, or by reco-ordination of the double bond, give complex (**23**) which is the right size for an intramolecular reaction. This complex can be compared to (**26**), obtained from (**25**), and which is unstable with respect to the



Scheme 5.



Scheme 6.

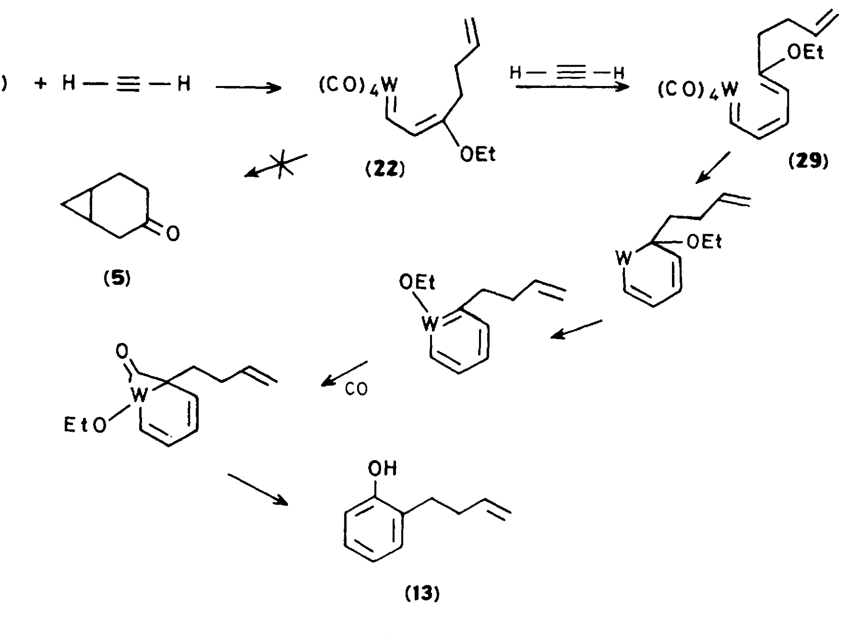
intramolecular cyclopropanation product (**27**) (Scheme 6). Such an intramolecular reaction has also been observed by Casey and Shusterman.[4] Complex (**23**) can also be compared to the first intermediate (**28**) which is supposed to be formed during the metathesis of octa-1,7-diene, a reaction which is known to give mainly cyclohexene, by an intramolecular metathesis reaction (Scheme 6).[26] In the case of complex (**23**), the intramolecular reaction could lead either to the metathesis products or, rather, as the newly formed carbene complex is a vinyl analogue of a Fischer type carbene complex, to the cyclopropane (**4**) *via* the unstable complex (**24**), with loss of $W(CO)_4$.

Oligomerization of Acetylene and Cyclo-octyne.—In the case of acetylene, competition between the double bond of the chain and the acetylene monomer in (**22**) must be in favour of a second insertion reaction, both in the stoicheiometric and in the catalytic reactions, giving complex (**29**). Rearrangement, followed by CO insertion, might then give the phenol derivative (**13**) (Scheme 7). Such reactions are well documented for chromium carbene complexes.[15] The formation of oligomers from cyclo-octyne might be explained by assuming a reaction between the alkyne and $W(CO)_4$, which is formed during the insertion–cyclopropanation reaction. It is indeed known that such oligomerization–CO insertion reactions occur in the photochemical reaction of $[Mo(CO)_6]$ with cyclo-octyne.[27]

Regiospecificity of the Insertion Reaction.—An interesting feature of this reaction is the high regiospecificity of the insertion:[12] indeed, in the case of monosubstituted alkynes, the substituent always appears, in (**5**), at the ring junction, a result which means that in the first intermediate, the substituent is *cis* with respect to the CO group *trans* to the carbene function. The *X*-ray structure of (**2**) clearly shows that this result is due to steric hindrance between the substituents on the alkyne and on the carbene functions.

Conclusions

The results given here describe a new insertion–cyclopropanation reaction which leads cleanly and in good yields to the bicyclo[4.1.0]heptane system. As such structures are common in a large number of natural products, this new method may be of use in organic synthesis. It appears that the mononuclear complex (**2**), as well as its dinuclear analogue (**17**), owe their interesting properties to the presence of a co-ordinated double bond in the vicinity of a reactive carbene function.



Scheme 7.

Table 4. Carbon-13 n.m.r. data for compounds *trans*-(**5b**) and *cis*-(**5b**)

	trans-(**5b**)		*cis*-(**5b**)	
	δ/p.p.m.	*T*/s	δ/p.p.m.	*T*/s
C^1	25.6		23.3	
C^2	50.3	7.2	54.2	6.4
C^3	213.9		214.7	
C^4	35.7	4.9	35.1	3.9
C^5	23.1	4.8	21.4	3.6
C^6	16.4	5.8	17.5	5.3
C^7	14.0	3.3	16.7	3.0
C^8	31.3	4.0	28.2	3.8
C^9	10.5	4.5	10.1	4.1
C^{10}	21.0	4.2	20.6	3.8
C^{11}	11.8	4.6	12.2	4.1

Experimental

All reactions were carried out in oven-dried glassware, under an argon atmosphere. Benzene, diethyl ether, and tetrahydrofuran (thf) were distilled from solutions of sodium–benzophenone. Dichloromethane was distilled from CaH_2. Light petroleum of b.p. 40—60 °C was used throughout. Preparative column chromatography was performed by using 70—230 mesh Merck silica gel. Preparative (p.l.c.) and analytical thin-layer chromatography (t.l.c.) were performed by using Merck G60 silica gel. N.m.r. spectra were obtained either on JEOL C-60HL or FX-90 spectrometers or on Bruker WM 250 or WM 500 spectrometers. All spectra were recorded using $CDCl_3$ as solvent and $SiMe_4$ as reference; *J* values are in Hz. For ^1H one-dimensional spectra the following conditions were used: quadrature detection, sweep width 200 or 1 000 Hz, 32K or 16K data points respectively when using observing frequencies of 500.13 or 250.13 MHz resulting in digital resolution of 0.13 Hz [for compounds (**5e**)—(**5f**), resolution was 0.26 Hz]. Hydrogen-1 δδ correlated two-dimensional spectra (COSY 45 and COSY LR) were recorded using the classical sequences given in refs. 28 and 29. Depending on the observation frequency (500.13 or 250.13 Hz), the data size of the time domain was 256 or 128 (f_1) × 1K or 512 (f_2) the spectrum width (1 600 or 800 Hz). The time domain matrix was expanded by zero filling in f_1. Sine-bell resolution enhancement was used in both directions. Resolution achieved in the frequency domain was 3.1 Hz. Chemical shifts determined by slices from two-dimensional spectra are thus accurate at least to 0.015 p.p.m. The fixed delay used in the COSY LR spectra to emphasize the small couplings was set to 0.2 s.

The one-dimensional ^{13}C spectra were recorded at 68.89 MHz under the following conditions: quadrature detection, spectrum width 13 000 Hz, 32K data points resulting in digital resolution of 1.6 Hz. Values of T_1 for protonated carbons were measured by the inversion recovery method (relaxation delay over $5T_1$). The Overhauser enhancement was measured using inverse gated wide-band proton decoupling (relaxation delay over $10T_1$).

The ^1H–^{13}C-shift-correlated two-dimensional spectrum was recorded at 125.76 MHz according to the sequence described in ref. 30 under the following conditions: spectrum width 4 000 (f_2) or 1 400 Hz (f_1), time domain 2K (f_2) or 128 (f_1), zero filling in f_1, resulting in digital resolution of 3.9 Hz in f_2 and 5.5 Hz in f_2. Infrared spectra were obtained on a Beckman 4240 spectrophotometer. Mass spectra were obtained on a Kratos MS 30 apparatus. Melting points were determined on a Reichert Kofler block and are uncorrected.

[But-3-enyl(ethoxy)carbene]pentacarbonyltungsten, (**1**).—A solution of butenylmagnesium bromide (1.8 mol dm^{-3}, 12 cm^3, 20 mmol) prepared from butenyl bromide and magnesium in thf, was added to a suspension of $[W(CO)_6]$ (7 g, 20 mmol) in thf (150 cm^3). The mixture was stirred for 4 h, the solvent evaporated under vacuum and the residue taken up with ice-water (150 cm^3) and the solution filtered through glass wool to remove excess $[W(CO)_6]$.

Addition of triethyloxonium tetrafluoroborate (20 mmol) and extraction with light petroleum gave complex (**1**) which was purified by silica-gel chromatography, using light petroleum as eluant. The yellow band was collected under an atmosphere of N_2 and the solvent evaporated at room temperature, under vacuum, giving complex (**1**) (4.5 g, 52%) as a yellow oil. $\nu_{max.}$(hexane) 2 035, 1 940, 1 985 cm^{-1} (CO); δ_H (250 MHz,

$\mathrm{CDCl_3}$) 5.77 (1 H, m, $\mathrm{C\mathit{H}{=}CH_2}$), 5.04 (1 H, m, *trans* $\mathrm{C\mathit{H}_2{=}CH{-}}$), 5.00 (1 H, m, *cis* $\mathrm{C\mathit{H}_2{=}CH{-}}$), 4.89 (2 H, q, *J* 7.1, $\mathrm{OCH_2}$), 3.30 (2 H, t, *J* 7.5, $\mathrm{C\mathit{H}_2{-}CH_2CH{=}}$), 2.26 (2 H, q, *J* 7.5, 6.7, $\mathrm{CH_2{-}C\mathit{H}_2{-}CH{=}}$), 1.62 (3 H, t, *J* 7.1, $\mathrm{OCH_2C\mathit{H}_3}$); δ_C (25 MHz, $\mathrm{CDCl_3}$) 332.9 (carbene), 203.2 (*trans* CO), 197.3 (*cis* CO), 136.4 ($\mathrm{\mathit{C}H{=}CH_2}$), 115.8 ($\mathrm{CH{=}\mathit{C}H_2}$), 80.8 ($\mathrm{OCH_2}$), 64.0 ($\mathrm{W{=}C{-}\mathit{C}H_2}$), 30.4 ($\mathrm{\mathit{C}H_2{-}CH{=}C}$), 14.8 ($\mathrm{CH_3}$); *m/z* 436 ($M^+$).

[(3—4-η-*But-3-enyl*)(*ethoxy*)*carbene*]*tetracarbonyltungsten*, (**2**).—A solution of complex (**1**) (10 g, 22 mmol) was refluxed in benzene (100 cm^3) for 12 h. The solution changed from yellow to red. Evaporation of the solvent gave a dark red oil which was filtered off on silica gel. Elution with light petroleum gave the starting complex (**1**) (2 g) and complex (**2**) (4.5 g, 50.1%) as red crystals, m.p. 56 °C. $\nu_{max.}$($\mathrm{CHCl_3}$) 2 035, 1 940, 1 985 cm^{-1} (CO); δ_H (250 MHz, $\mathrm{CDCl_3}$) 5.42 (1 H, m, *J* 13.9, 9.3, 5, 1.5, $\mathrm{CH_2{-}C\mathit{H}}$), 4.78 (1 H, m, *J* 10.38, 7.5, OCH), 4.67 (1 H, m, *J* 10.38, 7.5, OCH), 3.55 (1 H, dd, *J* 13.9, 9.1, 5, 1.5, *trans* $\mathrm{C\mathit{H}{=}CH{-}}$), 3.44 (1 H, dd, *J* 9, 1.4, *cis* $\mathrm{C\mathit{H}{=}CH{-}}$), 2.91 (1 H, m, *J* 6.9, 14.9, 1.5, 1.2, 1.4, $\mathrm{C\mathit{H}{-}CH{=}CH_2}$), 2.64—2.5 (1 H, m, 14.9, 5, 12.3, 6.5, $\mathrm{C\mathit{H}{-}CH{=}CH_2}$), 2.42 (1 H, m, *J* 18.5, 6.5, $\mathrm{W{=}C{-}CH}$), 1.81 (1 H, m, *J* 18.5, 12.3, 6.9, $\mathrm{W{=}C{-}CH}$), 1.54 (3 H, t, *J* 7.5, $\mathrm{CH_3}$); δ_C (25 MHz, $\mathrm{CDCl_3}$) 342.2 (carbene), 213.5 (*trans* CO), 211.8 (CO), 203.7 (CO), 203.5 (CO), 88.4 ($\mathrm{CH_2{=}\mathit{C}H}$), 79.7 ($\mathrm{O\mathit{C}H_2CH_3}$), 59.7 ($\mathrm{\mathit{C}H_2{=}CH{-}}$), 52.7 ($\mathrm{W{=}C{-}\mathit{C}H_2}$), 28.9 ($\mathrm{\mathit{C}H_2{-}CH{=}CH_2}$), 14.8 ($\mathrm{OCH_2\mathit{C}H_3}$); *m/z* 408 ($M^+$).

Pentacarbonyl[*ethoxy*(*pent-4-enyl*)*carbene*]*tungsten*, (**30**).—A solution of pent-4-enyl-lithium (100 cm^3, 44 mmol) prepared from pent-4-enyl bromide and Li in $\mathrm{Et_2O}$ was added to a suspension of $[\mathrm{W(CO)_6}]$ (15.4 g, 44 mmol) in $\mathrm{Et_2O}$ (250 cm^3). After the addition, the solvent was removed under vacuum, the residue taken up with water (150 cm^3) and the solution filtered. Addition of $\mathrm{Et_3O{\cdot}BF_4}$ (7 g, 50 mmol) gave a yellow oil which was extracted as usual with light petroleum. Evaporation of the solvent gave a yellow oil which was filtered off on silica gel. Elution with light petroleum gave the expected complex (8 g, 41%) as an oil. $\nu_{max.}$($\mathrm{CDCl_3}$) 2 070, 1 980, 1 940 cm^{-1} (CO); δ_H (60 MHz, $\mathrm{CDCl_3}$) 5.55 (1 H, m, $\mathrm{CH_2{-}C\mathit{H}{-}}$), 5.10 (2 H, m, $\mathrm{C\mathit{H}_2{=}CH{-}}$), 4.85 (2 H, q, *J* 7, $\mathrm{OCH_2}$), 3.15 (2 H, m, $\mathrm{W{=}C{-}CH_2}$), 2.0 (2 H, m, $\mathrm{C\mathit{H}_2{-}CH{=}CH_2}$), 1.53 (3 H, t, *J* 7, $\mathrm{CH_2C\mathit{H}_3}$), 1.35 (2 H, m, $\mathrm{CH_2{-}C\mathit{H}_2{-}CH_2}$); δ_C (25 MHz, $\mathrm{CDCl_3}$) 334 (carbene), 204.2 (*trans* CO), 197 (*cis* CO), 137 ($\mathrm{{-}\mathit{C}H{=}CH_2}$), 115 ($\mathrm{{-}CH{=}\mathit{C}H_2}$), 81 ($\mathrm{O\mathit{C}H_2}$), 64.6 ($\mathrm{W{=}C{-}\mathit{C}}$), 33.4 ($\mathrm{\mathit{C}H_2{-}CH{=}CH_2}$), 25.8 ($\mathrm{CH_2{-}\mathit{C}H_2{-}CH_2}$), 15 ($\mathrm{CH_3}$); *m/z* 450 ($M^+$).

Tetracarbonyl[*ethoxy*(4—5-η-*pent-4-enyl*)*carbene*]*tungsten*, (**19**).—A solution of (**30**) (2 g) in dry hexane (200 cm^3) was irradiated, at room temperature, with a water-cooled Philipps HF(L) 400-W immersion lamp for 12 h, under a weak stream of argon. The solvent was evaporated under vacuum, and the reaction mixture separated on silica gel. Elution with light petroleum first gave starting material (0.9 g); further elution with the same solvent gave complex (**19**) (0.60 g, 32%) as yellow crystals, m.p. 58 °C. $\nu_{max.}$(hexane) 2 030, 1 920, 1 900 cm^{-1} (CO); δ_H (250 MHz, $\mathrm{C_6D_6}$) 4.98 (1 H, dq, *J* 10.5, OCH), 4.81 (1 H, dq, *J* 10.5, OCH), 3.8 (1 H, m, *J* 13.7, 8.7, 2, $\mathrm{CH_2{=}C\mathit{H}{-}}$), 3.51 (1 H, d, *J* 13.7, $\mathrm{C\mathit{H}{=}CH{-}}$), 3.34 (1 H, m, $\mathrm{{=}CH{-}C\mathit{H}{-}}$), 3.21 (1 H, d, *J* 8.7, $\mathrm{C\mathit{H}{=}CH{-}}$), 2.96 (2 H, m, $\mathrm{W{=}C{-}CH_2}$), 2.31 (1 H, m, $\mathrm{W{=}C{-}CH_2{-}C\mathit{H}}$), 1.87 (1 H, m, $\mathrm{W{=}C{-}CH_2{-}C\mathit{H}}$), 1.61 (3 H, t, *J* 7.2, $\mathrm{CH_3}$), 1.45 (1 H, m, $\mathrm{CH_2{=}CH{-}C\mathit{H}}$); δ_C (25 MHz, $\mathrm{CDCl_3}$) 342 (carbene), 209.5, 208.4, 200.8, 199.4 (CO), 84.5 ($\mathrm{{-}\mathit{C}H{=}CH_2}$), 79.1 ($\mathrm{OCH_2}$), 60.34 ($\mathrm{\mathit{C}H_2{=}CH{-}}$), 54.5 ($\mathrm{W{=}C{-}\mathit{C}H_2}$), 37.4 ($\mathrm{CH_2{=}CH{-}\mathit{C}H_2}$), 35.8 ($\mathrm{W{=}C{-}CH_2{-}\mathit{C}H_2}$), 14.9 ($\mathrm{OCH_2\mathit{C}H_3}$); *m/z* 422 ($M^+$).

Pentacarbonyl{*ethoxy*[1-(*prop-2-enyl*)*but-3-enyl*]*carbene*}-*tungsten*, (**7**).—A solution of LiBu (15 cm^3, 1.4 mol dm^{-3}) was added to a solution of (**6**) (6.4 g, 16 mmol) in thf (100 cm^3), at −60 °C. Allyl bromide (2 cm^3, 22 mmol) was then added to the red solution. After hydrolysis at 0 °C with water (50 cm^3), the reaction mixture was worked-up as usual and the solvent evaporated under vacuum to give an orange oil, which was filtered off on silica gel. Elution with light petroleum gave complex (**7**) as an orange oil (4.5 g, 60.8%). $\nu_{max.}$($\mathrm{CDCl_3}$) 2 075, 1 980, 1 940 cm^{-1} (CO); δ_H (60 MHz, $\mathrm{CDCl_3}$) 5.7 (2 H, m, $\mathrm{{-}C\mathit{H}{=}CH_2}$), 4.95 (4 H, m, $\mathrm{C\mathit{H}_2{=}CH{-}}$), 4.66 (3 H, s, $\mathrm{CH_3}$), 4.25 (1 H, q, *J* 6.5, $\mathrm{W{=}C{-}CH}$), 2.17 (4 H, m, $\mathrm{{-}C\mathit{H}_2{-}CH{=}CH_2}$); δ_C (25 MHz, $\mathrm{C_6D_6}$) 342.3 (carbene), 135 ($\mathrm{\mathit{C}H_2{=}CH{-}}$), 117 ($\mathrm{CH_2{=}\mathit{C}H}$), 71.7 ($\mathrm{W{=}C{-}\mathit{C}H}$), 70.2 ($\mathrm{OCH_2}$), 36.1 ($\mathrm{CH_2{=}CH{-}\mathit{C}H_2{-}}$); *m/z* 462 ($M^+$).

Pentacarbonyl[(*cyclopent-3-enyl*)(*ethoxy*)*carbene*]*tungsten*, (**8**).—To a solution of complex (**7**) (4.0 g, 8.8 mmol) in hexane (50 cm^3), at room temperature, was added solid $\mathrm{WOCl_4}$ (0.265 g, 0.88 mmol) and then $\mathrm{SiH_2Ph_2}$ (0.316 g, 1.7 mmol). The dark reaction mixture was then heated at 60 °C for 2 h, during which evolution of ethene was observed. The reaction mixture was then cooled to room temperature and filtered over Celite. Evaporation of the solvent gave an oil which was chromatographed on silica gel. Elution with light petroleum first gave starting material (3.0 g), then complex (**8**) (0.99 g, 27%) as orange crystals, m.p. 56 °C. $\nu_{max.}$($\mathrm{CHCl_3}$) 2 080, 1 990, 1 950 cm^{-1} (CO); δ_H (250 MHz, $\mathrm{C_6D_6}$) 5.33 (2 H, s, $\mathrm{C\mathit{H}{=}C\mathit{H}}$), 4.52 (1 H, m, $\mathrm{W{=}C{-}CH}$), 3.74 (3 H, s, $\mathrm{CH_3}$), 2.28—2.10 (4 H, m, $\mathrm{C\mathit{H}_2{-}CH{-}C\mathit{H}_2}$); δ_C (25 MHz, $\mathrm{CDCl_3}$) 337 (carbene), 196 (CO), 127 ($\mathrm{\mathit{C}H{=}\mathit{C}H}$), 69.6 ($\mathrm{OCH_2}$), 69.1 ($\mathrm{\mathit{C}H_2{-}CH{-}\mathit{C}H_2}$), 36.5 (C–H); *m/z* 434 (M^+).

Tetracarbonyl[(3—4-η-*cyclopent-3-enyl*)(*ethoxy*)*carbene*]-*tungsten*, (**9**).—A solution of complex (**8**) (474 mg, 1.1 mmol) in benzene (30 cm^3) was refluxed for 17 h. The dark reaction mixture was filtered over Celite, the solvent evaporated, and the residue chromatographed on silica gel. Elution with light petroleum first gave starting material (50 mg), then complex (**9**) (360 mg, 81%) as red crystals, m.p. 48 °C. $\nu_{max.}$($\mathrm{CHCl_3}$) 2 030, 1 940, 1 875 cm^{-1} (CO); δ_H (250 MHz, $\mathrm{C_6D_6}$) 5.10 (2 H, s, $\mathrm{{-}C\mathit{H}{=}C\mathit{H}}$), 4.34 (3 H, s, $\mathrm{CH_3}$), 2.84 (2 H, m, $\mathrm{CH{-}HC\mathit{H}{-}CH{=}CH}$), 2.59 (2 H, m, $\mathrm{{-}CH{-}\mathit{H}{-}CH{-}CH{=}}$), 2.59 (1 H, m, $\mathrm{CH_2{-}C\mathit{H}{-}CH_2}$); δ_C (25 MHz, $\mathrm{C_6D_6}$) 347 (carbene), 202 (CO), 83 ($\mathrm{{-}\mathit{C}H{=}\mathit{C}H{-}}$), 69 ($\mathrm{OCH_2}$), 57 (CH), 43 ($\mathrm{\mathit{C}H_2{-}CH{-}\mathit{C}H_2}$); *m/z* 406 ($M^+$).

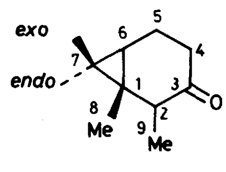
Complex (**16**; R = Me, X = $\mathrm{NEt_2}$).—to a solution of complex (**1**) (0.5 g, 1.25 mmol) in hexane (20 cm^3), at 0 °C, was added excess (diethylamino)propyne (0.2 cm^3). An immediate colour change from red to yellow took place. Evaporation of the solvent followed by silica-gel chromatography, with light petroleum–$\mathrm{Et_2O}$ (85:15) as eluant, gave complex (**16**) (620 mg, 93%) as a yellow oil. $\nu_{max.}$(hexane) 2 080, 1 940, 1 880 cm^{-1} (CO); δ_H (90 MHz, $\mathrm{C_6D_6}$) 5.3 (1 H, m, $\mathrm{CH_2{=}C\mathit{H}}$), 5.0 (2 H, m, $\mathrm{C\mathit{H}_2{=}CH{-}}$), 3.8 (6 H, m, $\mathrm{OCH_2}$, $\mathrm{NCH_2}$, $\mathrm{NCH_2}$), 2.8 (3 H, s, $\mathrm{CH_3}$), 2.2 (4 H, m, $\mathrm{C\mathit{H}_2C\mathit{H}_2}$), 1.4 (3 H, t, *J* 6.5, $\mathrm{CH_2C\mathit{H}_3}$), 1.25 (3 H, t, *J* 6.5, $\mathrm{CH_2C\mathit{H}_3}$); δ_C (25 MHz, $\mathrm{CDCl_3}$) 255 (carbene), 202 (*trans* CO), 198.7 (*cis* CO), 139.8 ($\mathrm{CH_2\mathit{C}{=}C}$), 137.7 ($\mathrm{{-}\mathit{C}H{=}CH_2}$), 131.5 ($\mathrm{EtO{-}\mathit{C}{=}C}$), 114.9 ($\mathrm{\mathit{C}H_2{=}C{-}}$), 64.2 ($\mathrm{OCH_2}$), 55.3 ($\mathrm{NCH_2}$), 46.2 ($\mathrm{NCH_2}$), 30.1 ($\mathrm{\mathit{C}H_2CH_2}$), 29.6 ($\mathrm{CH_2\mathit{C}H_2}$), 15.6 ($\mathrm{{=}C{-}\mathit{C}H_3}$), 14.2, 14.1, 13.8 (3 $\mathrm{CH_2\mathit{C}H_3}$); *m/z* 547 ($M^+$).

Complex (**16**; R = H, X = OEt).—To a solution of complex (**1**) (0.5 g, 1.25 mmol) in hexane (20 cm^3), at 0 °C, was added ethoxyethyne (0.5 cm^3). The reaction mixture was left at room temperature for 12 h. Evaporation of the solvent followed by silica-gel chromatography gave, with light petroleum, complex (**16**) (70 mg, 11%) as yellow crystals, m.p. 56 °C. $\nu_{max.}$(hexane) 2 080, 1 940, 1 880 cm^{-1} (CO); δ_H (90 MHz, $\mathrm{CDCl_3}$) 6.9 (1 H, s, CH=C), 5.7 (1 H, m, –C*H*=CH$_2$), 5.0 (2 H, m, C*H*$_2$=CH–), 4.8 (2 H, q, *J* 6.5, OCH$_2$), 3.95 (2 H, q, *J* 6.5, OCH$_2$), 2.6—2.1 (4 H, m, C*H*$_2$C*H*$_2$), 1.55 (3 H, t, *J* 6.5, CH$_2$C*H*$_3$), 1.35 (3 H, t, *J* 6.5, CH$_2$C*H*$_3$); δ_C (25 MHz, CDCl$_3$) 295.8 (carbene), 198.6 (CO), 167.8 (*C*–OEt), 137.2 (–*C*H=CH$_2$), 123.3 (EtOC=*C*), 115.3 (*C*H$_2$=CH–), 78.9 (OCH$_2$), 65.1 (OCH$_2$), 35.1 (–*C*H$_2$CH$_2$–), 31.4 (–CH$_2$*C*H$_2$–), 14.45 (CH$_2$*C*H$_3$), 13.9 (CH$_2$*C*H$_3$); *m/z* 506 (M^+).

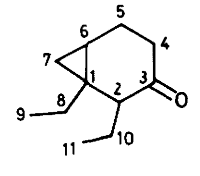
Reaction of Hex-3-yne with Complex (**19**): *Preparation of* (**21**; R = R′ = Et).—Hex-3-yne (0.3 cm^3) was added to a yellow solution of complex (**19**) (360 mg, 0.88 mmol) in CH_2Cl_2 (25 cm^3). An immediate colour change was observed. After 12 h at room temperature, the reaction mixture was chromatographed on silica gel. Elution with light petroleum–Et_2O (95:5) gave the ketone (**21**) (105 mg, 67%) as an oil (Found: C, 80.0; H, 11.05. $C_{12}H_{20}O$ requires C,80.0; H, 11.1%). $\nu_{max.}$(CHCl$_3$) 1 680 cm^{-1} (ketone); δ_H (60 MHz, CDCl$_3$) 6.57 (1 H, t, *J* 11, –C*H*=C–), 5.85 (1 H, m, –C*H*=CH$_2$), 5.0 (2 H, m, C*H*$_2$=CH–), 2.65—1.95 (10 H, m), 1.1 (6 H, m); *m/z* 180 (M^+).

Reaction of Complex (**2**) *with Alkynes.—General procedure.* To a solution of complex (**2**) (1 mmol) in CH_2Cl_2 (30 cm^3) at 10 °C was added the alkyne (2 mmol). After 12 h the solvent was evaporated, the residue taken up with light petroleum and absorbed on a column of silica gel. After 12 h, elution with light petroleum–Et_2O (ratios depending on the polarity of the ketone) gave ketone (**5**). (**5a**): *m/z* 138 (M^+); $\nu_{max.}$(CHCl$_3$) 1 715 cm^{-1}. (**5b**): *m/z* 166 (M^+). (**5c**): *m/z* 186 (M^+). (**5d**): *m/z* 180 (M^+) (Found: C, 80.0; H, 11.1. $C_{12}H_{20}O$ requires C, 80.0; H, 11.1%). (**5e**): *m/z* 166 (M^+). (**5f**): *m/z* 262 (M^+) (Found: C, 86.8; H, 6.95. $C_{19}H_{18}O$ requires C, 87.0; H, 6.85%), m.p. 97—98 °C. (**5g**): *m/z* 154 (M^+) (Found: C, 70.2; H, 9.10. $C_9H_{14}O$ requires C, 70.15; H, 9.10%); δ_C (25 MHz, CDCl$_3$) 210 (C=O), 79 (C^8), 58 (OMe), 41 (C^2), 35 (C^4), 21 (C^5), 19 (C^1), 14.5 (C^6), 12 (C^7). (**5h**): *m/z* 182 (M^+) (Found: C, 66.0; H, 10.0. $C_{10}H_{18}OSi$ requires C, 65.95; H, 9.90%). (**5i**): *m/z* 168 (M^+). (**5j**): *m/z* 190 (M^+) (Found: C, 81.8; H, 9.60. $C_{13}H_{18}O$ requires C, 82.1; H, 9.45%); δ_H (60 MHz, CDCl$_3$) 2.5 (2 H, s, C_2H_2), 2.3 (6 H, m), 1.95 (1 H, m, ≡CH), 1.45 (6 H, m), 1.0 (1 H, m, C^{6}H), 0.50 (2 H, m, C^{7}H$_2$). (**5k**): *m/z* 182 (M^+); $\nu_{max.}$(CDCl$_3$) 1 715, 1 725 cm^{-1} (C=O); δ_H (60 MHz, CDCl$_3$) 4.15 (2 H, q, OC*H*$_2$CH$_3$), 3.16 (1 H, d, *J* 18, C^{2}H), 2.63 (1 H, d, *J* 18, C^{2}H), 1.6 (1 H, m, C^{6}H), 0.88 (2 H, m, C^{7}H$_2$); δ_C (25 MHz, CDCl$_3$) 214.5 (C=O), 208.8 (C=O), 60.5 (OCH$_2$), 39.2 (C^2), 34.7 (C^4), 21.6 (C^1), 21.0 (C^5), 20.4 (CH$_3$), 17.6 (C^6), 13.8 (C^7). (**5l**): *m/z* 192 (M^+) (Found: C, 81.35; H, 10.4. $C_{13}H_{20}O$ requires C, 81.25; H, 10.4%); $\nu_{max.}$(CCl$_4$) 1 710, 1 640 cm^{-1}; δ_H (60 MHz, CDCl$_3$) 5.90 (1 H, m), 4.95 (2 H, m), 2.3 (2 H, m, C^{2}H$_2$), 2.0 (4 H, m), 1.15 (9 H, m), 0.48 (2 H, m, C^{7}H$_2$). (**5m**): *m/z* 154 (M^+) (Found: C, 70.0; H, 9.15. $C_9H_{14}O_2$ requires C, 70.15; H, 9.10%); $\nu_{max.}$(CCl$_4$) 3 640 (OH), 1 710 cm^{-1} (ketone); δ_H (60 MHz, CDCl$_3$) 3.8 (2 H, t, C*H*$_2$OH), 3.6 (2 H, s, C^{2}H$_2$), 2.95 (1 H, s, OH), 2.15 (4 H, m), 1.6 (2 H, t, C^{8}H$_2$), 1.05 (1 H, m, C^{6}H), 0.55 (2 H, m, C^{7}H$_2$).

Reaction of complex (**2**) *with cyclo-octyne.* Cyclo-octyne (0.8 g, 7.33 mmol) was added, at room temperature, to a solution of complex (**2**) (1 g, 2.45 mmol) in hexane (30 cm^3). After 12 h, the reaction mixture was worked-up as usual. Chromatography on silica-gel first gave, on eluting with light petroleum, compound (**11**) as white crystals (210 mg, 26%). Then elution with light petroleum–Et_2O (96:4) gave the quinone (**12**) (32 mg, 4%), and finally light petroleum–Et_2O (92:8) gave the ketone (**10**) (145 mg, 31%). (**10**): $\nu_{max.}$(CHCl$_3$) 1 710 cm^{-1} (ketone); δ_H (60 MHz, CDCl$_3$) 2.05 (1 H, m, CH$_2$CC*H*), 1.9—1.0 (17 H, m), 0.65 (2 H, m); *m/z* 192 (M^+). (**11**): δ_H (60 MHz, CDCl$_3$) 2.90 (12 H, m, C–CH$_2$), 1.5 (24 H, m, –CH$_2$–); δ_C (25 MHz, CDCl$_3$) 136.5 (*C*=*C*), 31.4 (C–*C*H$_2$), 28.1 (–CH$_2$–), 26.9 (–CH$_2$–); *m/z* 324 (M^+). (**12**): $\nu_{max.}$(CCl$_4$) 1 640 cm^{-1} (CO); δ_H (60 MHz, CDCl$_3$) 2.70 (8 H, m), 1.5 (16 H, m); δ_C (25 MHz, CDCl$_3$) 214.7 (CO), 144.4 (*C*=*C*), 29.8, 26.6, 24.8 (–CH$_2$–); *m/z* 272 (M^+).



(5a)



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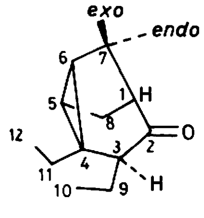

(15)

Reaction of complex (**2**) *with ethyne.* A solution of complex (**2**) (0.816 g, 2 mmol) in hexane (30 cm^3) was kept, with stirring, under an atmosphere (*ca.* 10^5 Pa) of ethyne, in a closed vessel at room temperature for 2 d. The black poly(ethyne) was removed by filtration, and the residue chromatographed on silica gel. Elution with light petroleum–Et_2O (80:20) gave the phenol derivative (**13**) (25 mg) as an oil. $\nu_{max.}$(CHCl$_3$) 3 605 cm^{-1} (OH); δ_H (60 MHz, CDCl$_3$) 7.0 (4 H, m), 5.8 (1 H, m, C*H*–CH$_2$), 5.1 (2 H, m, C*H*$_2$=CH–), 2.4 (4 H, m); *m/z* 148 (M^+).

Reaction of complex (**9**) *with hex-3-yne.* A solution of complex (**9**) (0.19 g, 0.46 mmol), in hexane (20 cm^3) and hex-3-yne (0.15 g) was kept at room temperature for 48 h. After work-up and silica-gel chromatography, compound (**15**) was obtained as an oil (65 mg). $\nu_{max.}$(CDCl$_3$) 1 720 cm^{-1} (CO); δ_H (250 MHz, CDCl$_3$) 2.47 (2H, m, H^1 and H^3), 2.01 (1 H, m, H$^{9'}$), 1.92 (1 H, m, H$^7_{exo}$), 1.92 (1 H, m, H$^8_{exo}$), 1.87 (1 H, m, H$^{11'}$), 1.81 (1 H, m, H$^7_{endo}$), 1.81 (1 H, m, H$^8_{endo}$), 1.56 (1 H, m, H^9), 1.27 (1 H, m, H^5), 1.22 (1 H, m, H^6), 0.88 (3 H, t, C^{12}H$_3$), 0.85 (3 H, t, C^{10}H$_3$), 0.74 (1 H, m, H^{11}); *m/z* 178 (M^+).

Pentacarbonyl[ethoxy(hex-5-enyl)carbene]tungsten, (**25**).—A solution of hex-5-enyl bromide (30 mmol) in thf was added to a suspension of [W(CO)$_6$] (10 g, 26 mmol) in thf (150 cm^3). Work-up as for complex (**1**) gave complex (**25**) (3.9 g, 29.4%) as a yellow oil. $\nu_{max.}$(CHCl$_3$) 2 068, 1 980, 1 940 cm^{-1} (CO); δ_H (60 MHz, CDCl$_3$) 5.7 (1 H, m, C*H*=CH$_2$), 5.1 (2 H, m, CH=C*H*$_2$), 4.9 (2 H, q, *J* 8, OCH$_2$), 3.25 (2 H, m, W=C–C*H*$_2$), 2.0 (2 H, m, C*H*$_2$–CH=CH$_2$), 1.55 (3 H, t, *J* 8, CH$_3$), 1.75—1.25 (4 H, m, C*H*$_2$–C*H*$_2$); δ_C (25 MHz, CDCl$_3$) 334.2 (carbene), 203.2 (*trans* CO), 197.4 (*cis* CO), 138.2 (*C*H=CH$_2$), 114.8 (CH=*C*H$_2$), 80.6 (OCH$_2$), 64.9 (W=C–*C*H$_2$), 33.4 (*C*H$_2$–CH=C), 28.4 (*C*H$_2$–CH$_2$), 25.9 (CH$_2$–*C*H$_2$), 14.7 (CH$_3$); *m/z* 464 (M^+).

Thermolysis of Complex (**25**).—A solution of complex (**25**) was refluxed in benzene for 48 h. Silica-gel chromatography of the residue first gave, an elution with light petroleum, complex (**26**) (2.4 g), then tetracarbonyl[ethoxy(3—4-η-hex-3-enyl)-carbene]tungsten as an oil (0.4 g), and finally, with light petroleum–Et_2O (90:10), compound (**27**) as an oil (211 mg, 17%) which was identified by comparison with an authentic sample.

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Received 14*th March* 1986; *Paper* 6/519