can be abstracted. This attests to the high stability of the multiply bonded linear Cr═S═Cr moiety. A "labile sulfur" in such bridging S_2 ligands has also been observed in $[Mo_3S(\mu\text{-}S_2)_3(\eta^2\text{:}\eta^2\text{-}S_2)_3]^{2-}$,[39] which undergoes nucleophilic attack by CN^- at each of its three μ-S_2 ligands. Such reactions of activated sulfur ligands are of interest in connection with bioinorganic problems like the deactivation of the Mo-containing enzyme xanthine oxidase via nucleophilic abstraction of a "labile sulfur".[40]

Methylation. 2 undergoes instantaneous methylation when treated with one or more equivalents of methyl trifluoromethanesulfonate in toluene, precipitating a black unstable solid 4, which in solution rapidly converts to 1 and 5 as shown in Scheme II.

Although there have been frequent reports on the methylation of side-on metal-bonded η^2-S_2 ligands, aimed at producing perthiolates, which are of interest in connection with enzymatic processes, little is known about the methylation of bridging μ-S_2 ligands.[41] Our present study shows that, like the η^2-S_2 ligands in $Os(S_2)(CO)_2(PPh_3)_2$[41] and $Ir(S_2)(dppe)_2Cl$,[38,42] the μ-S_2 ligand in 2 undergoes monomethylation, presumably at S(2). Unfortunately the methylated derivative 4 is not stable enough for single crystals to be grown for a structure analysis to definitively determine the point of methylation. Attempts at crystallization gave only a mixture of 5 and 1 after several days at −28 °C. This facile loss of CH_3S^+ suggests that 4 might be a potential CH_3S^+ transfer agent.

Conclusion. This study highlights the high reactivity of the μ-S_2 complex 2 with regard to decarbonylation, S atom abstraction by Ph_3P, and loss of the CH_3S^+ cation.

Acknowledgment. We thank the University of Malaya for financial support (L.Y.G.) and Dr. M. A. Bennett for many helpful discussions.

Registry No. 1, 71549-26-3; 2, 89401-43-4; 3, 107302-33-0; 4, 107302-35-2; $[CpCr(CO_3]_2$, 12194-12-6; $CF_3SO_3CH_3$, 333-27-7.

Supplementary Material Available: Listings of anistropic thermal parameters and hydrogen atom coordinates for 2 and 3 (4 pages); listing of observed and calculated structure factor amplitudes for 2 and 3 (24 pages). Ordering information is given on any current masthead page.

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Bidentate Alkene–Carbene Complexes of Tungsten: Synthesis, Structure, and Reactivity toward Alkenes

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The reactivity of complexes of tungsten, bearing a bidentate alkene–carbene ligand, toward alkenes has been studied. These complexes very easily react photochemically with olefins to give, after decoordination of the double bond, followed by a rearrangement of the pentacoordinated intermediate, new alkene–carbene complexes in which the two functions are trans. In most of the cases, the reaction is reversible. The synthesis and X-ray diffraction studies have been completed on three derivatives. Complex 5, which contains a carbene and a free cyclohexenyl group, crystallizes in the monoclinic space group $P2_1/n$, with a = 10.272 (3) Å, b = 21.918 (9) Å, c = 6.571 (2) Å, β = 92.20 (3)°, Z = 4, and d_{calcd} = 2.01 g cm^{-3}. Complex 6, which contains a carbene ligand and a coordinated cyclohexenyl group, crystallizes in the monoclinic space group $P2_1/n$, with a = 7.155 (3) Å, b = 13.062 (3) Å, c = 13.998 (2) Å, β = 102.48 (2)°, Z = 4, and d_{calcd} = 2.18 g cm^{-3}. Complex 11, which contains a carbene ligand, a free cyclohexenyl group, and a coordinated ethene molecule, crystallizes in the monoclinic space group $P2_1/n$ with a = 6.635 (8) Å, b = 21.007 (8) Å, c = 11.193 (7) Å, β = 90.60 (7)°, Z = 4, and d_{calcd} = 1.91 g cm^{-3}.

Introduction

The synthesis and structure of several tungsten carbene–alkene complexes have been described, and their reactivity per se has been studied.[1-6] The importance of such species both in the cyclopropanation as well as in the metathesis reactions of olefins has been outlined. But little attention has been paid to the reactivity of such species toward external ligands such as alkenes and alkynes.

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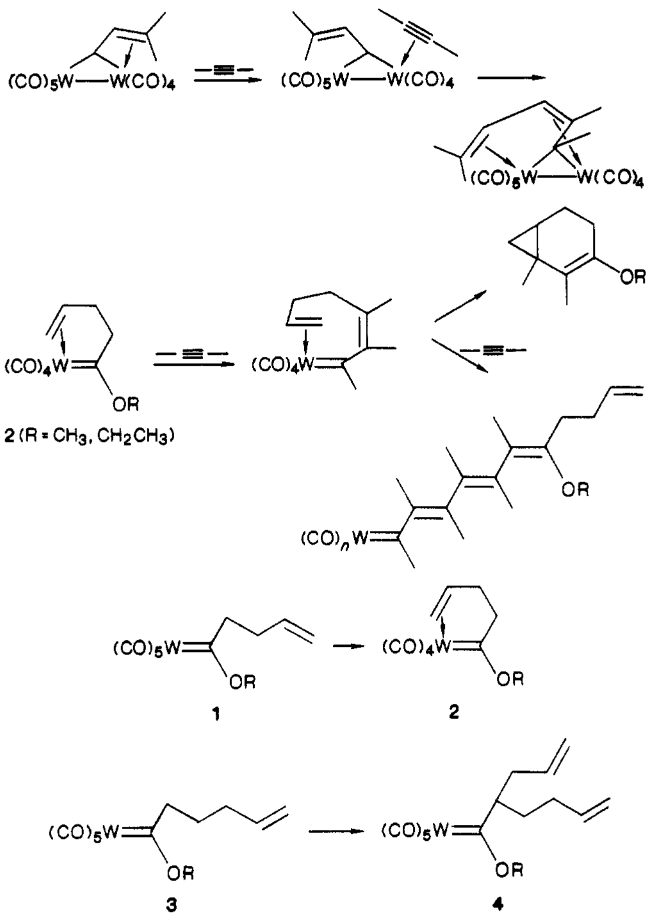
0276-7333/87/2306-1057$01.50/0

Scheme I



In analogy with results that we obtained in the case of dinuclear μ-alkylidene complexes,[7,8] which bear the same type of bidentate alkene–carbene ligand and which are known to react with alkenes and alkynes, we have shown[9-11] that complex **2** reacts with alkynes to give, depending on the reaction conditions, either stoichiometric insertion reactions, which lead to bicyclo[3.2.1]heptane derivatives, or polymerization reactions, which lead to conjugated polyenes (Scheme I).

The purpose of this paper is therefore to describe the behavior of complexes **2**, **6**, and **9** toward alkenes.

Results

Synthesis of the Starting Complexes. Complexes **1** and **3** are prepared according to the classical Fischer method. In the case of complex **1**, butenylmagnesium bromide was used instead of the lithium compound. Complex **4**, which contains two different unsaturated alkyl chains, was obtained from **3** by alkylation with BuLi/allyl bromide, at -40 °C, in a 63% yield. The two unsaturated alkyl chains in **4** are clearly differentiated in the ^{13}C NMR spectrum: the signals due to the carbon atoms of the double bonds appear respectively at 138.4 and 135.6 ppm (—*C*H=) and 116.9 and 115.4 ppm (=*C*H_2).

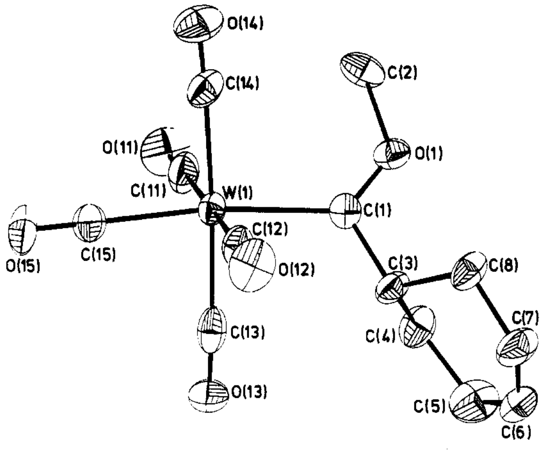


Figure 1. An ORTEP view of the $(CO)_5W{=}C(OCH_3)(C_6H_9)$ molecule giving the atom numbering scheme used in the tables.

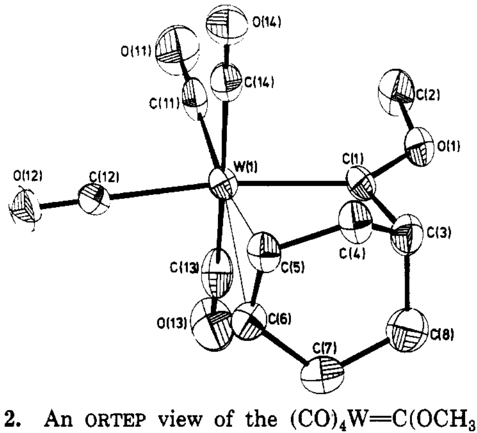
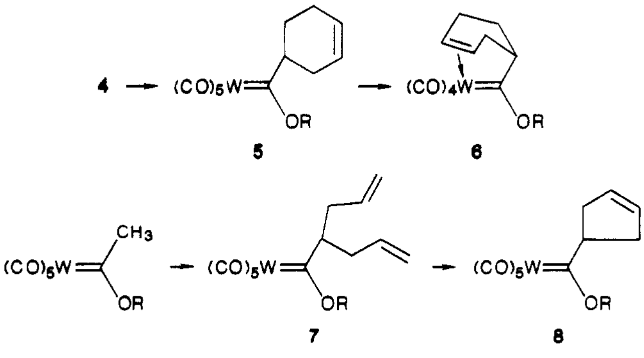


Figure 2. An ORTEP view of the $(CO)_4W{=}C(OCH_3)(C_6H_9)$ molecule giving the atom numbering scheme used in the tables.

Complex **7** was prepared from methylmethoxytungstacarbene by a double alkylation reaction with BuLi/allyl bromide, at -40 °C, in a 60.8% yield.

The transformations **4** → **5** and **7** → **8** were carried out by means of an intramolecular metathesis reaction: for that purpose, a very mild metathesis catalyst, based on WCl_6 or $WOCl_4$ associated with Ph_2SiH_2, which is known to bring about the metathesis of functionalized olefins,[12,13] was used. Complex **5** was obtained in 41% yield, whereas, under the same conditions, complex **8** could be synthesized in a 27% yield. Both complexes were fully characterized by their NMR spectra and also by an X-ray diffraction analysis. An ORTEP projection of complex **5** (R = CH_3) appears in a Figure 1.



Intramolecular Coordination Reactions. The coordination of the double bonds in complexes **1**, **5**, and **8** was

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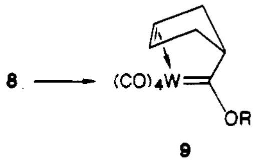
Table I. Summary of Crystal Data and Intensity Collection Parameters for 5, 6, and 11

	5	11	6
empirical formula	$C_{13}H_{12}O_6W$	$C_{14}H_{16}O_5W$	$C_{12}H_{12}O_5W$
fw	448.09	448.13	420.08
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	10.272 (3)	6.635 (8)	7.155 (3)
b, Å	21.918 (9)	21.007 (9)	13.062 (3)
c, Å	6.571 (2)	11.193 (7)	13.998 (2)
β, deg	92.20 (3)	90.60 (7)	102.48 (2)
V, Å^3	1478.2 (9)	1560 (2)	1277.22
Z	4	4	4
cryst size, mm	0.24 × 0.29 × 0.4	0.14 × 0.16 × 0.8	0.06 × 0.16 × 0.54
μ(Mo Kα), cm^{-1}	82.44	78.71	94.31
d_{calcd}, g/cm^3	2.01	1.91	2.18
temp, °C	25	25	20
radiatn	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71073 Å)
scan range θ, deg	0.8 + 0.35 tan θ	1.0 + 0.35 tan θ	1.0 + 0.35 tan θ
scan speed, deg s^{-1}	0.025	0.025	depending upon the refletn
scan type	θ–2θ	θ–2θ	θ–2θ
diffractometer	Philips PW1100	laboratory-made diffractometer	CAD4
monochromator	graphite	graphite set in front of the counter	graphite
std refletn(s)	3, measd every 2 h	2, measd every 100 refletns	2, measd every hour
refletns measd	hkl, $\bar{h}kl$; 2 octants	hkl, $hk\bar{l}$; 2 octants	hkl, $hk\bar{l}$; 2 octants
refletns collected	1844	2057	2211
refletns merged	1675	2057	1775
refletns obsd	1502 ($F > 3\sigma(F)$)	1746 ($F > 3\sigma(F)$)	1566 ($I > 2\sigma(I)$)
2θ range, deg	4–44	3–46	3–46
R	0.0494	0.0457	0.0348
R_w	0.0448	0.0379	0.0398
weighting scheme	$w = 1.97/\sigma^2(F)$	$w = 1.39/\sigma^2(F)$	w = 1.0

carried out in boiling benzene: reflux for about 12 h gave complexes **2**, **6**, and **9** in yields ranging from 40 to 80%, as red crystals. The coordination of the double bond shifts the signals of both the protons and the carbon atoms of the double bond toward a higher field. Thus, in complex **9**, the signals of the hydrogens are shifted from 5.33 to 5.08 ppm, whereas the signals of the carbons appear respectively at 127 ppm for **8** and 83 ppm for **9**. Complexes **2**, **6**, and **9** have also been characterized by their X-ray structures.[13,14] An ORTEP view of complex **6** is shown on Figure 2.



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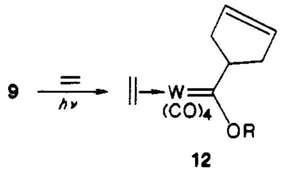


12

Reactivity toward Alkenes. It is known that Fischer-type carbene complexes are reluctant to react with nonactivated alkenes. The following observation confirmed this point: neither **1** nor **2** reacted thermally with simple alkenes. There is but one exception: norbornene underwent a thermal reaction with complex **2** to give high yields of polynorbornene.[15] But no intermediate could be detected in this reaction.

Nevertheless, the reactivity of complex **2** could be dramatically enhanced upon irradiation: under these conditions, at room temperature, a fast reaction was observed with a series of olefins such as ethene, cyclopentene, and

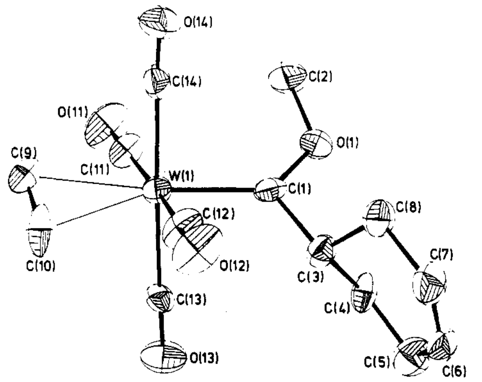
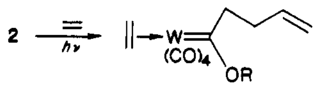


Figure 3. An ORTEP view of the $(C_2H_4)(CO)_4W{=}C(OCH_3)(C_6H_9)$ molecule giving the atom numbering scheme used in the tables.

bicyclohept-2-ene. New complexes, containing the coordinated olefins, could be isolated. Thus ethene reacted with complex **2**, in hexane, to give, upon irradiation for 1 h, complex **10** as a yellow oil. The ^{1}H NMR clearly shows that the ethene molecule has been coordinated to the metal center and that the double bond of the starting complex is now free: the signal of four equivalent hydrogens appears at 2.81 ppm, whereas the signals of the free double bond appear at 5.89 and 5.05 ppm as in complex **1**.



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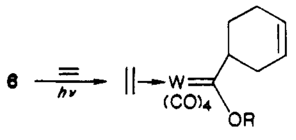

11

As far as the geometry of this complex is concerned, the IR spectrum shows the presence of a strong absorption at 1950 cm^{-1}, an indication in favor of a trans orientation of

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(14) Alvarez, T. C.; Levisalles, J.; Rudler, M.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Organomet. Chem.* **1982**, *218*, C7–C11.

(15) Unpublished results.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 5, 6, and 11 (Esd's in Parentheses)[a]

atom	x/a	y/b	z/c	B(iso), Å^2
		Compound 5		
W(1)	0.21575 (9)	0.12861 (3)	0.14294 (6)	3.36 (1)
C(1)	0.134 (2)	0.6649 (7)	0.176 (1)	3.8 (4)
O(1)	−0.404 (2)	0.7789 (5)	0.642 (1)	4.5 (3)
C(2)	−0.356 (3)	0.7260 (6)	0.729 (2)	5.3 (5)
C(3)	0.069 (2)	0.6222 (7)	0.071 (2)	4.1 (4)
C(4)	−0.159 (2)	0.6341 (9)	0.025 (1)	5.1 (5)
C(5)	−0.213 (3)	0.593 (1)	−0.088 (2)	7.0 (7)
C(6)	−0.068 (3)	0.5768 (9)	−0.175 (2)	6.2 (6)
C(7)	0.131 (3)	0.592 (1)	−0.167 (2)	7.0 (7)
C(8)	0.210 (2)	0.6329 (9)	−0.046 (2)	5.1 (5)
C(11)	0.540 (3)	0.6830 (8)	0.343 (2)	5.3 (5)
O(11)	0.681 (2)	0.7115 (6)	0.340 (1)	7.4 (5)
C(12)	0.031 (3)	0.5730 (8)	0.376 (2)	4.5 (5)
O(12)	−0.105 (2)	0.5437 (7)	0.386 (1)	7.3 (5)
C(13)	0.415 (3)	0.5653 (8)	0.239 (2)	5.2 (5)
O(13)	0.496 (2)	0.5297 (6)	0.177 (1)	6.0 (4)
C(14)	0.162 (2)	0.6898 (9)	0.482 (2)	5.1 (5)
O(14)	0.094 (2)	0.7208 (7)	0.557 (1)	7.1 (5)
C(15)	0.432 (3)	0.5851 (8)	0.511 (2)	5.5 (5)
O(15)	0.521 (2)	0.5632 (6)	0.594 (1)	6.7 (4)
		Compound 11		
W(1)	0.38412 (8)	0.17641 (3)	0.20716 (5)	3.55 (1)
C(1)	0.294 (2)	0.0826 (6)	0.182 (1)	3.9 (3)
O(1)	0.177 (2)	0.0539 (4)	0.0977 (8)	5.6 (3)
C(2)	0.087 (3)	0.0884 (8)	0.001 (1)	6.2 (5)
C(3)	0.348 (2)	0.0296 (6)	0.265 (1)	4.1 (3)
C(4)	0.168 (2)	−0.0036 (7)	0.320 (1)	5.3 (4)
C(5)	0.232 (3)	−0.0535 (8)	0.410 (2)	6.5 (5)
C(6)	0.411 (4)	−0.0857 (8)	0.390 (2)	7.6 (7)
C(7)	0.545 (4)	−0.0734 (9)	0.297 (2)	8.3 (7)
C(8)	0.484 (3)	−0.0208 (8)	0.207 (2)	6.4 (5)
C(11)	0.125 (3)	0.2172 (8)	0.147 (1)	5.6 (5)
O(11)	−0.019 (2)	0.2397 (6)	0.115 (1)	7.5 (4)
C(12)	0.653 (3)	0.1389 (8)	0.265 (2)	6.1 (5)
O(12)	0.800 (2)	0.1194 (7)	0.297 (1)	8.6 (5)
C(13)	0.257 (2)	0.1666 (7)	0.373 (1)	4.0 (3)
O(13)	0.184 (2)	0.1592 (6)	0.462 (1)	7.3 (4)
C(14)	0.500 (2)	0.1843 (7)	0.040 (1)	4.7 (4)
O(14)	0.565 (2)	0.1868 (7)	−0.0530 (9)	7.8 (4)
C(9)	0.423 (4)	0.2891 (8)	0.215 (2)	7.3 (6)
C(10)	0.554 (2)	0.2629 (7)	0.298 (2)	6.7 (5)
		Compound 6		
W(1)	0.17172 (6)	0.08941 (4)	0.21228 (3)	2.95 (1)
C(1)	0.438 (2)	0.165 (1)	0.2146 (9)	3.8 (4)
O(1)	0.601 (1)	0.1756 (7)	0.2807 (6)	4.4 (3)
C(2)	0.626 (2)	0.127 (1)	0.374 (1)	4.9 (4)
C(3)	0.460 (2)	0.221 (1)	0.120 (1)	4.8 (4)
C(4)	0.359 (2)	0.160 (1)	0.032 (1)	4.2 (4)
C(5)	0.158 (2)	0.143 (1)	0.0434 (9)	3.7 (4)
C(6)	0.069 (2)	0.219 (1)	0.824 (9)	4.2 (4)
C(7)	0.153 (3)	0.319 (1)	0.107 (1)	6.0 (6)
C(8)	0.363 (4)	0.324 (2)	0.124 (1)	6.6 (7)
C(11)	0.221 (2)	0.015 (1)	0.337 (1)	4.6 (4)
O(11)	0.246 (2)	−0.0273 (9)	0.4116 (8)	6.7 (4)
C(12)	−0.097 (2)	0.031 (1)	0.1805 (9)	3.8 (4)
O(12)	−0.246 (1)	−0.0035 (8)	0.1609 (8)	5.7 (3)
C(13)	0.079 (2)	0.204 (1)	0.2836 (9)	3.9 (4)
O(13)	0.023 (2)	0.2681 (9)	0.3280 (8)	6.5 (4)
C(14)	0.269 (2)	−0.033 (1)	0.1525 (8)	3.5 (4)
O(14)	0.327 (1)	−0.1052 (7)	0.1179 (8)	5.5 (3)

[a] $B(\mathrm{eq}) = {}^1/_3\sum_i\sum_j B_{ij}a_i^*a_j^*\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j$.

the two ligands ethene and carbene.

The same reactions were observed with complexes **9** and **6**: in both cases, the new, thermally stable complexes **11** and **12** could be isolated. Complex **11** was isolated as yellow crystals suitable for an X-ray analysis, which confirmed the trans orientation of the ethene molecule with respect to the carbene function (vide infra). An ORTEP view of complex **11** is shown on Figure 3.

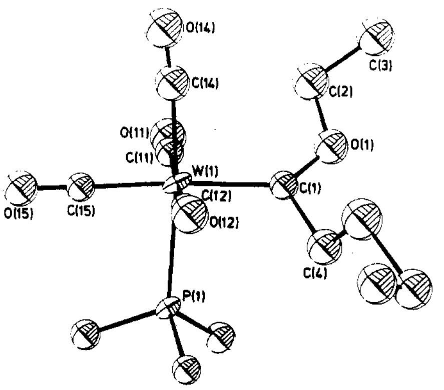
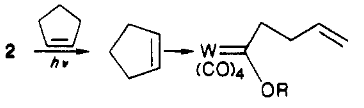


Figure 4. An ORTEP view of the $(PPh_3)(CO)_4W{=}C(OCH_2CH_3)(CH_2CH{=}CH_2)$ molecule giving the atom numbering scheme used in the tables.

Cycloolefins, such as cyclopentene and bicyclohept-2-ene, also reacted with complex **2** to give complexes **13** and **14**, but their stability was much lower and they could only be purified at low temperature. In the absence of cyclopentene and bicyclohept-2-ene, respectively, complexes **13** and **14** gave, besides complex **2**, complexes **1** and **15**.



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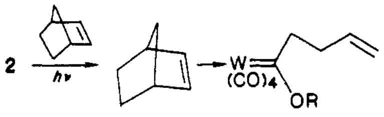

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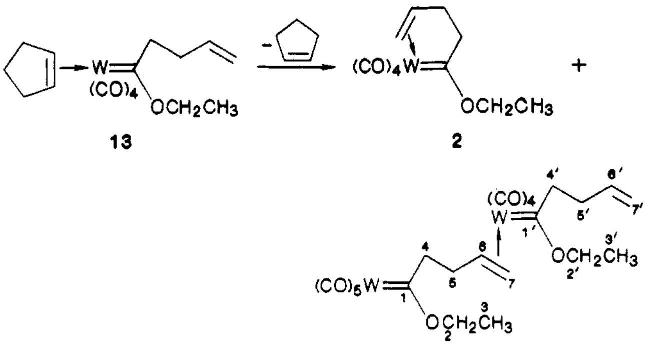
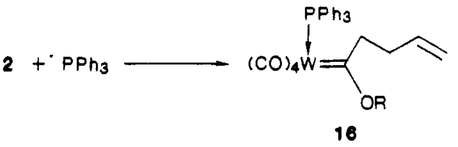


15

The dinuclear complex **15** could be prepared in good yield when complexes **1** and **2** were irradiated in hexane. The ^{13}C NMR spectrum of **15** clearly shows the presence of two different carbene functions (332 and 314 ppm) and of a free and a coordinated double bond (139.3–115.9 and 76.7–46.4 ppm).

Reaction of Complex 2 with PPh$_3$. Complex **2** very rapidly reacted with PPh_3 in benzene, at room temperature, to give the orange complex **16**. Again, decoordination



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of the double bond in **2** took place. Indeed, the ^1H NMR spectrum shows the presence of signals at 5.5 and 4.8 ppm. The IR spectrum, in which appear four CO vibration bands, indicates a cis arrangement of the carbene and the phosphine ligands. This result could be confirmed by an X-ray analysis. A partial ORTEP view appears on Figure

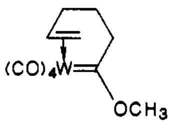
Table III. Bond Distances (Å) for 5, 6, and 11 (Esd's in Parentheses)

	5	11	6
W(1)–C(1)	2.22 (1)	2.07 (1)	2.14 (1)
W(1)–C(5)			2.45 (1)
W(1)–C(6)			2.48 (1)
W(1)–C(9)		2.38 (2)	
W(1)–C(10)		2.36 (2)	
W(1)–C(11)	2.07 (2)	2.02 (2)	1.96 (2)
W(1)–C(12)	2.08 (2)	2.04 (2)	2.02 (1)
W(1)–C(13)	2.05 (2)	2.05 (1)	2.00 (1)
W(1)–C(14)	2.04 (2)	2.03 (1)	2.00 (1)
W(1)–C(15)	2.06 (2)		
C(1)–O(1)	1.30 (2)	1.35 (2)	1.33 (1)
C(1)–C(3)	1.48 (2)	1.49 (2)	1.55 (2)
O(1)–C(2)	1.49 (2)	1.42 (2)	1.42 (2)
C(3)–C(4)	1.58 (2)	1.51 (2)	1.51 (2)
C(3)–C(8)	1.57 (2)	1.54 (2)	1.52 (3)
C(4)–C(5)	1.49 (3)	1.52 (2)	1.49 (2)
C(5)–C(6)	1.38 (3)	1.37 (3)	1.35 (2)
C(6)–C(7)	1.35 (3)	1.39 (7)	1.45 (2)
C(7)–C(8)	1.59 (3)	1.54 (3)	1.47 (3)
C(9)–C(10)		1.38 (3)	
C(11)–O(11)	1.12 (2)	1.12 (2)	1.16 (2)
C(12)–O(12)	1.11 (2)	1.11 (2)	1.14 (1)
C(13)–O(13)	1.15 (2)	1.12 (2)	1.16 (2)
C(14)–O(14)	1.13 (2)	1.13 (2)	1.17 (1)
C(15)–O(15)	1.12 (2)		

4. Such a result had already been observed by Casey.[4]

Discussion

Geometry of the Bidentate Alkene–Carbene Complexes. In previous publications,[6,13] we described the synthesis and X-ray structure of complexes 2 and 17 in which the coordinated double bonds are respectively two and three carbons away from the carbene function. In complex 2, the W=C and C=C double bonds are perpendicular, whereas in complex 16 those two functions are parallel. In complex 5, the double bond can be seen as being either two or three carbons away from the carbene function. It was therefore of interest to know which geometry these two functions would adopt upon coordination. The result is that again, the more stable geometry, in which the two functions are perpendicular,[16] is attained. Therefore, the formation of the six-membered ring system constrains the double bond, three carbons away from the carbene function, to adopt the unusual geometry, which could never be obtained in the case of structure 17.[6] Nevertheless, such a structure, in which the double bonds are separated by three carbon atoms and in which the two functions are almost perpendicular, has been obtained by Casey and co-workers.[5]



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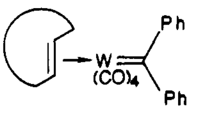

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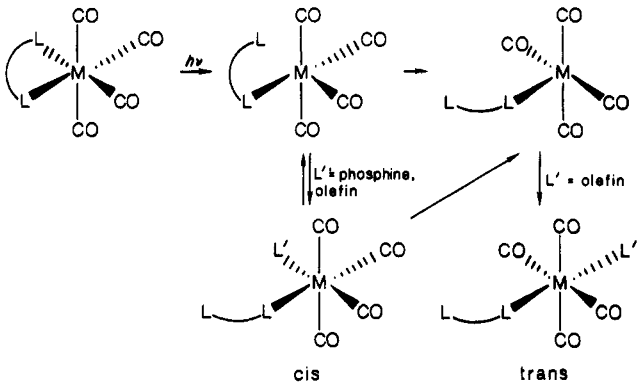
A second observation deserves comment: usually, in Fischer-type carbene complexes, and especially in complexes described in this work, the carbene plane is staggered with respect to the trans CO–W–CO bonds;[17,18] however, this is not the case in complex 6 in which the plane of the carbene almost eclipses the W(1)–C(1)–C(12) plane (dihedral angle = 7.1°).

Table IV. Bond Angles (deg) for 5, 6, and 11 (Esd's in Parentheses)

	5	11	6
C(11)–W(1)–C(1)	94.1 (6)	96.6 (6)	103.0 (5)
C(12)–W(1)–C(1)	87.5 (6)	85.7 (6)	167.5 (5)
C(12)–W(1)–C(11)	178.3 (6)	177.2 (7)	89.4 (5)
C(13)–W(1)–C(1)	86.0 (6)	84.6 (5)	92.2 (5)
C(13)–W(1)–C(11)	89.3 (7)	89.3 (6)	86.7 (6)
C(13)–W(1)–C(12)	90.8 (7)	92.4 (6)	89.4 (5)
C(14)–W(1)–C(1)	96.9 (6)	93.7 (5)	89.3 (5)
C(14)–W(1)–C(11)	90.4 (7)	89.2 (6)	87.9 (5)
C(14)–W(1)–C(12)	89.4 (7)	89.1 (6)	90.2 (5)
C(14)–W(1)–C(13)	177.1 (7)	177.6 (5)	174.6 (5)
C(15)–W(1)–C(1)	172.5 (6)		
C(15)–W(1)–C(11)	87.6 (7)		
C(15)–W(1)–C(12)	90.7 (7)		
C(15)–W(1)–C(13)	86.8 (7)		
C(15)–W(1)–C(14)	90.4 (7)		
O(1)–C(1)–W(1)	129.4 (10)	132.6 (9)	134.8 (9)
C(3)–C(1)–W(1)	119.4 (10)	123.9 (9)	117.3 (8)
C(3)–C(1)–O(1)	111.2 (13)	103.5 (10)	107.9 (10)
C(2)–O(1)–C(1)	123.3 (12)	122.2 (11)	120.4 (10)
C(4)–C(3)–C(1)	111.2 (13)	114.0 (11)	109.0 (12)
C(8)–C(3)–C(1)	107.5 (13)	112.8 (11)	104.8 (14)
C(8)–C(3)–C(4)	109.0 (12)	108.7 (11)	110.8 (12)
C(5)–C(4)–C(3)	109.2 (14)	111.5 (13)	107.0 (11)
C(6)–C(5)–C(4)	120.6 (16)	117.4 (16)	119.0 (13)
C(7)–C(6)–C(5)	125.6 (19)	125.7 (18)	123.1 (14)
C(8)–C(7)–C(6)	118.5 (18)	117.0 (19)	115.7 (15)
C(7)–C(8)–C(3)	109.1 (14)	111.5 (14)	114.6 (16)
O(11)–C(11)–W(1)	177.2 (15)	179.0 (15)	177.9 (12)
O(12)–C(12)–W(1)	179.3 (15)	178.8 (15)	178.1 (11)
O(13)–C(13)–W(1)	177.0 (14)	177.6 (12)	177.1 (12)
O(14)–C(14)–W(1)	175.8 (17)	178.0 (14)	179.3 (11)
O(15)–C(15)–W(1)	176.8 (16)		

Scheme II



Mechanism of the Reaction of External Ligands with the Alkene–Carbene Complexes. The X-ray structure of complex 11 shows that the olefin is trans to the carbene function, a result which means that the substitution of the coordinated double bond took place with a rearrangement. The photochemistry of complex 2 can therefore be considered as a special case of the photochemistry of complexes bearing a bidentate ligand. Such reactions are well-documented:[19,20] the ligand substitution proceeds via initial fission of one metal to ligand bond, a reaction which affords a five-coordinate η^1 complex, which rearranges. The rearrangement occurs presumably through a square-pyramidal intermediate to give two five-coordinate η^1 complexes in which the vacant site is either cis or trans to the coordinated ligand. Reaction with the external ligand gives either the cis or the trans complex (Scheme II). It is also known that in the case of Fischer-type

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carbene complexes, the cis CO ligands can be easily exchanged. In our case, the role of light is probably to induce the dissociation of the cis-coordinated double bond. Opening of this coordination site would then allow the rearrangement of the five-coordinate complex or the formation of the cis alkene–carbene complex. That the cis alkene–carbene complex is probably the kinetic product of the reaction appears in the behavior of bicyclohept-2-ene in this photochemical reaction. Besides the thermodynamically stable complex **14**, one observes indeed the formation of polynorbornene. The fact that in the case of nonreactive olefins only one complex is obtained, in which the two ligands are trans, could be explained by the higher stability of such an isomer: it is indeed known that, in general,[21-23] two π-accepting ligands prefer a trans orientation with respect to one another. This is known in the case where the two ligands are two olefins and also in one case, described recently by Grevels,[24] in which one of the ligands is a carbene.

Decoordination of the Olefins. Whereas solutions of complexes **10**, **11**, and **12** slowly loose ethene, at room temperature, complexes **13** and **14** are only stable in the presence of excess olefin: in the absence of olefin, they very rapidly loose their ligand to give, inter alia, complexes **2** and **15**. It is probable that this backward reaction occurs through the formation of the same five-coordinate complex.

Remarks on the Structure of Complexes 10 and 11. In all the structures described in this paper, the tungsten atom has a nearly perfect octahedral surrounding (Table IV). Slight differences between complex **18**, prepared by Grevels, and complex **11** are observed. In the latter case, in which the olefin is *trans*-cyclooctene, the C–C axis of the olefin lies in the plane of the carbene function, whereas in complex **11** the olefin axis is twisted some 13° out of the plane of the carbene. Another difference is the geometry of the olefin axis with respect to the CO–W–CO direction: in general, these two vectors are eclipsed.[21,25] But in complex **11**, the angle between the planes W(1),C(11),C(12),C(1) and W(1),C(9),C(10) is 25°. These twists of the two ligands from their theoretical positions could be the result of crystal packing forces and minimization of intramolecular close contacts.

A last point has to be mentioned as far as the structures are concerned: examination of the six C–C bonds distances in the cyclohexene group for the first two complexes shows up two shorts bonds, C(5)–C(6) (1.38 (3) Å (**5**), 1.37 (3) Å (**11**)) and C(6)–C(7) (1.35 (3) Å (**5**), 1.39 (7) Å (**11**)), when only one was expected. In the same way, of the six C–C–C angles, three around C(5), C(6), and C(7) are close to 120° when only two such values were expected. Moreover the five atoms C(4), C(5), C(6), C(7), and C(8) make a nearly perfect plane, the largest deviation from the plane being 0.026 Å (Table V). Such peculiar arrangement may be explained by considering a disordered distribution of carbon atoms C(5) and C(7) with regard to the C(6),C(4),C(8) plane, the double bond being located on either the C(5)–C(6) or the C(6)–C(7) bond. No attempt was made to sort this disorder out; approximate calculations showed indeed that the two disordered sites around C(5) or C(7) would be only separated by somewhere around 0.15–0.2 Å, and it was of no use to refine two positions so close. The atomic coordinates of carbon atoms C(5) and C(7) for compounds **5** and **11** represent in fact mean positions. Occurence of disorder is also supported by the torsional angles C(3),C(4),C(5),C(6) and C(5),C(8),C(7),C(6), the absolute values of which are roughly identical (Table VI), whereas in compound **6** where the double bond is well-located, values of those two torsional angles are quite different.

The structure of complex **16** (space group $P\bar{1}$, $a = 10.140$ (5) Å, $b = 14.455$ (5) Å, $c = 10.682$ (4) Å, $\alpha = 89.38$ (3)°, $\beta = 62.87$ (4)°, $\gamma = 82.94$ (3)°) will not be fully reported since, in spite of our efforts, an unsolvable disorder problem remained along the carbon chain. However, there is no doubt about the surrounding of tungsten, which is well-refined. Therefore, only a partial ORTEP, without the alkyl chain, could be provided.

As a conclusion, it appears that, in most cases, alkenes react with complexes of type **2** to give the unreactive trans alkene–carbene complex. Only the better coordinating ligand PPh_3 gives the cis complex, the product of the direct substitution of the double bond of **2**.

Experimental Section

All reactions were carried out in oven-dried glassware, under an argon atmosphere. Benzene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled from solutions of sodium and benzophenone. Dichloromethane (CH_2Cl_2) was distilled from CaH_2. Preparative column chromatography was performed by using 70–230 mesh Merck silica gel. Preparative (PLC) and analytical thin-layer chromatography (TLC) were performed by using Merck G60 silica gel. NMR spectra were obtained either on a JEOL C 60HL or FX-90 spectrometer or on a Bruker WM 250 or WM 500 spectrometer. All spectra were recorded by using tetramethylsilane as reference. For ^1H one-dimensional spectra the following conditions were used: quadrature detection; sweep width 200 Hz/1000 Hz; 32K/16K data points respectively when 500.13/250.13 Hz observing frequencies were used, resulting in digital resolution of 0.13 Hz (for compounds **5e**,**f**, resolution was 0.26 Hz). IR spectra were obtained on a Beckman 4240 spectrophotometer. Mass spectra were obtained on a Kratos MS 3P apparatus. Melting points were determined on a Reichert Kofler block and are uncorrected.

Pentacarbonyl((3-butenyl)methoxycarbene)tungsten(0) (1). A solution of butenylmagnesium bromide (0.18 N, 30 mL, 50 mmol) prepared from butenyl bromide and magnesium in THF was added to a suspension of $W(CO)_6$ (18 g, 50 mmol) in THF (350 mL). The mixture was stirred for 4 h at room temperature, the solvent evaporated under vacuum, the residue taken up with ice water (350 mL), and the solution filtered to remove excess $W(CO)_6$.

Addition of trimethyloxonium fluoroborate (Me_3OBF_4, 50 mmol), followed by extraction with petroleum ether gave complex 1 which was purified by silica gel chromatography, using petroleum ether as eluent. The yellow band was collected under an atmosphere of N_2 and the solvent evaporated, at room temperature, under vacuum, giving complex 1 (10.5 g, 50%) as a yellow oil: IR (hexane) 2035, 1940, 1985 cm^{-1}; $\{^1H\}$ NMR (250 MHz, $CDCl_3$) δ 5.77 (m, 1 H, $C\mathit{H}{=}CH_2$), 5.03–4.99 (m, 2 H, $C\mathit{H}_2{=}CH{-}$), 4.60 (s, 3 H, $OC\mathit{H}_3$), 3.30 (m, 2 H, $W{=}CC\mathit{H}_2$), 2.26 (m, 2 H, $C\mathit{H}_2CH{=}$); $^{13}C\{^1H\}$ NMR (250 MHz, $CDCl_3$) δ 336.25 (carbene), 204 (trans CO), 197.2 (cis CO), 136.3 ($\mathit{C}H{=}CH_2$), 115.7 ($\mathit{C}H_2{=}CH$), 70.3 ($O\mathit{C}H_3$), 64.0 ($W{=}C\mathit{C}$), 30.3 ($\mathit{C}H_2C{=}$). MS, *m/z 422* (M^+).

Pentacarbonyl((3-butenyl)ethoxycarbene)tungsten(0) was prepared according to the same method.

Tetracarbonyl(η^2-(3-butenyl)methoxycarbene)tungsten(0) (2). A solution of complex **1** (7 g, 17 mmol) was refluxed in benzene (70 mL) for 12 h. The solution changed from yellow to red. Evaporation of the solvent gave a dark red oil, that was filtered over silica gel. Elution with petroleum ether gave the starting complex **1** (2.4 g) and the complex **2** as a red solid (2.8 g, 42.8%): mp 74 °C; IR (hexane) 2035, 1940, 1885 cm^{-1}; $\{^1H\}$ NMR

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(250 MHz, C_6D_6) δ 4.82 (m, J = 13.9, 9.1, 5.0, 1.5 Hz, 1 H, —$CH{=}CH_2$), 3.85 (d, J = 1.0 Hz, 3 H, OCH_3), 2.93 (d, J = 9.1 Hz, 1 H, $HCH{=}CH$—), 2.91 (d, J = 13.9 Hz, 1 H, HCHCH—), 2.12 (m, 1 H, =CHHCH—), 2.0 (m, 1 H, =CHHCH—), 1.75 (m, 1 H, W=CHCH), 1.02 (m, 1 H, W=CHC—H); $^{13}C\{^1H\}$ NMR (250 MHz, $CDCl_3$) δ 341.2 (carbene), 212.8, 211.2, 204.1, 203.7 (CO), 88.5 ($CH{=}CH_2$), 69.7 (OCH_3), 59.7 ($CH_2{=}CH$—), 52.9 (W=CC), 29.1 ($CH_2CH{=}$); MS, m/z 396 (M^+). Anal. Calcd for $C_{11}H_{12}O_5W$: C, 35.35; H, 2.94. Found: C, 32.37; H, 2.9.

The ethoxycarbene was prepared by the same method.

Pentacarbonyl((4-pentenyl)methoxycarbene)tungsten(0). A solution of 4-penten-1-yllithium (100 mL, 44 mmol) prepared from 4-penten-1-yl bromide and Li in Et_2O was added to a suspension of $W(CO)_6$ (15.4 g, 44 mmol) in Et_2O (250 mL). After the addition, the solvent was removed under vacuum, at room temperature, the residue taken up in water (150 mL), and the solution filtered. Addition of Me_3OBF_4 (7 g, 50 mmol) gave a yellow oil that was extracted with petroleum ether. Evaporation of the solvent, followed by silica gel filtration, gave complex **3** as a yellow oil (8 g, 41%): IR ($CHCl_3$) 2070, 1980, 1940 cm^{-1}; $\{^1H\}$ NMR (250 MHz, C_6D_6) δ 5.55 (m, 1 H, —$CH{=}CH_2$), 4.80 (m, 2 H, $CH_2{=}CH$—), 3.87 (s, 3 H, OCH_3), 2.9 (m, 2 H, W=CCH_2), 1.8 (m, 2 H, —CH_2CH_2), 1.3 (m, 2 H, —$CH_2CH_2CH_2$—); $^{13}C\{^1H\}$ NMR (250 MHz, $CDCl_3$) δ 334 (carbene), 204 (trans CO), 197 (cis CO), 137 (—$CH{=}CH_2$), 115 ($CH_2{=}CH$—), 81.0 (OCH_3), 64.6 (W=CC), 33.4 ($CH_2CH{=}C$), 28.5 ($CH_2CH_2CH_2$); MS, m/z 436 (M^+).

Pentacarbonyl((1-(2-propenyl)-4-pentenyl)methoxycarbene)tungsten(0) (4). A solution of BuLi (15 mL, 1.4 N) in hexane was added, at −60 °C, to a solution of complex **3** (8.6 g, 19 mmol) in THF (200 mL). Allyl bromide (2.38 g, 19 mmol) was then added to the red solution; the mixture was kept at room temperature, with stirring, for 1 h. After hydrolysis with water (50 mL), the reaction mixture was worked up as usual, the solvent evaporated, and the residue chromatographed on silica gel. Elution with petroleum ether gave complex **4** as a yellow oil (6 g, 63%): IR ($CHCl_3$) 2068, 1980, 1940 cm^{-1}; $\{^1H\}$ NMR ($CDCl_3$, 60 MHz) δ 5.75 (m, 2 H, 2$CH{=}CH_2$), 5.0 (m, 4 H, 2$CH_2{=}CH$), 4.55 (s, 3 H, OCH_3), 4.12 (m, 1 H, W=CCH—), 2.2 (m, 4 H, 2CH_2), 1.52 (m, 2 H, CH_2), $^{13}C\{^1H\}$ NMR (25 MHz, C_6D_6) δ 432.4 (carbene), 203.2 (trans CO), 197.6 (cis CO), 139.2 (—$CH{=}CH_2$), 135.5 (—$CH{=}CH_2$), 117.1 (—$CH{=}CH_2$), 115.2 (—$CH{=}CH_2$), 71.7 (W=CC), 70.0 (OCH_3), 36.4 (—$CH_2C{=}$), 31.9 (—CH_2—C=), 31.1 ($CHCH_2$—); MS, m/z 476 (M^+).

Pentacarbonyl((3-cyclohexen-1-yl)methoxycarbene)tungsten(0) (5). To a solution of complex **4** (3 g, 6.3 mmol) in hexane (60 mL) was added solid $WOCl_4$ (0.193 g, 0.63 mmol) at room temperature and then Ph_2SiH_2 (0.23 g, 1.26 mmol). The solution was heated at 60 °C for 2 h. Once the ethene evolution ceased, the solution was filtered over Celite, the solvent evaporated, and the residue chromatographed over silica gel. Elution with petroleum ether first gave complex **5** as a yellow solid (1.14 g, 41%) and then the starting material **4** (1.5 g): mp 86 °C; IR ($CHCl_3$) 2070, 1985, 1945 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.75 (m, 2 H, $HC{=}CH$), 4.62 (s, 3 H, OCH_3), 4.12 (m, 1 H, W=CCH), 2.3–1.6 (m, 6 H, 3CH_2); $^{13}C\{^1H\}$ NMR (25 MHz, C_6D_6) δ 340.4 (carbene), 203.5 (trans CO), 197.6 (cis CO), 126.9 ($HC{=}C$), 125.3 ($HC{=}CH$), 70.3 (OCH_3), 69.0 (W=CC), 27.7, 25.4, 25.2 (3CH_2); MS, m/z 448 (M^+). Anal. Calcd for $C_{13}H_{12}O_6W$: C, 34.82; H, 2.67. Found: C, 34.69; H, 2.71.

Tetracarbonyl(η^2-(3-cyclohexen-1-yl)methoxycarbene)tungsten(0) (6). A solution of complex **5** (0.2 g, 0.44 mmol) in benzene (30 mL) was refluxed for 174 h. The reddish solution was then filtered over Celite, the solvent evaporated under vacuum, and the residue chromatographed over silica gel. Elution with petroleum ether gave complex **6** (0.147 g, 80%) as orange-red crystals that were recrystallized from MeOH at −40 °C: mp 84 °C; $\{^1H\}$ NMR (250 MHz, $CDCl_3$) δ 5.53 (m, 1 H, —$CH{=}CH$—), 4.99 (m, 1 H, —$HC{=}CH$—), 4.38 (s, 3 H, OCH_3), 2.93 (m, 1 H), 2.69 (m, 4 H), 1.72 (m, 1 H), 1.33 (m, 1 H); MS, m/z, 420 (M^+).

Pentacarbonyl((1-(2-propenyl)-3-butenyl)methoxycarbene)tungsten(0) (7). A solution of BuLi (15 mL, 1.4 N) was added, at −60 °C, to a solution of pentacarbonyl(methylmethoxycarbene)tungsten(0) (6.4 g, 16 mmol) in THF (100 mL). Allyl bromide (2 mL, 22 mol) was then added. After hydrolysis with water (50 mL), the reaction mixture was worked up as usual and the residue chromatographed over silica gel. Elution with petroleum ether gave complex **7** as a yellow oil (4 g, 60.8%): $\{^1H\}$ NMR (60 MHz, $CDCl_3$) δ 5.7 (m, 2 H, $CH{=}CH_2$), 5.0 (m, 4 H, $CH_2{=}CH$—), 4.5 (s, 3 H, OCH_3), 4.1 (m, 1 H, W=C—CH); $^{13}C\{^1H\}$ NMR (25 MHz, C_6D_6) δ 342.3 (carbene), 203 (trans CO), 197.5 (cis CO), 135.4 (—$CH{=}CH_2$), 117.2 ($CH_2{=}CH$—), 71.7 (W=CC), 70.2 (OCH_3), 36.1 (CCH_2); MS, m/z 462 (M^+).

Pentacarbonyl((3-cyclopenten-1-yl)methoxycarbene)tungsten(0) (8). This complex was prepared in the same way as complex **5**. Thus, complex **7** (4.0 g) gave, under the same conditions, complex **8** (0.994 g, 27%) as a yellow solid that was recrystallized from MeOH: mp 56 °C; IR ($CHCl_3$) 2080, 1990, 1950 cm^{-1}; $\{^1H\}$ NMR (250 MHz, C_6D_6) δ 5.33 (s, 2 H, —$HC{=}CH$—), 4.52 (m, 1 H, W=CCH), 3.74 (s, 3 H, OCH_3), 2.28–2.10 (m, 4 H, 2CH_2); $^{13}C\{^1H\}$ NMR (25 MHz, $CDCl_3$) δ 337 (carbene), 203 (trans CO), 197 (cis CO), 127 ($C{=}C$), 69.6 (OCH_3), 69.1 (W=CC), 36.5 ($CH_2CH{=}CHCH_2$); MS, m/z 434 (M^+).

Tetracarbonyl(η^2-(3-cyclopenten-1-yl)methoxycarbene)tungsten(0) (9). A solution of complex **8** (0.474 g, 1.1 mmol) in benzene (30 mL) was refluxed for 17 h. The red solution was then evaporated and the residue chromatographed over silica gel. Elution with petroleum ether first gives the starting material (0.05 g) and then complex **9** (0.360 g, 81%) as a red solid that was recrystallized from hexane: mp 48 °C; IR ($CHCl_3$) 2030, 1940, 1875 cm^{-1}; $\{^1H\}$ NMR (250 MHz, $CDCl_3$) δ 5.08 (s, 2 H, $HC{=}CH$), 4.38 (s, 3 H, OCH_3), 2.84 (m, 2 H, $HCHCHHCH$), 2.59 (m, 2 H, $HCHCHHCH$), 2.59 (m, 1 H, CH_2CHCH_2); $^{13}C\{^1H\}$ NMR (25 MHz, $CDCl_3$) δ 347 (carbene), 205 (CO), 83 (—HCCH—), 69 (OCH_3), 57 (CH_2CHCH_2), 43 (2CH_2); MS, m/z 404 (M^+).

Tetracarbonyl(ethene)((3-butenyl)methoxycarbene)tungsten(0). A solution of complex **2** (0.5 g) in cyclohexane (30 mL) was irradiated, at room temperature, with a water-cooled Philipps HF (2) 400-W immersion lamp, for 24 h under a weak stream of ethylene. The solution turned from red to yellow. The solvent was then evaporated under vacuum and the residue chromatographed on silica gel. Elution with petroleum ether gave complex **10** (0.3 g, 57%) as a yellow oil: IR (cyclohexane) 1975 (w), 1950 (vs) cm^{-1}; $\{^1H\}$ NMR (250 MHz, C_6D_6) δ 5.89 (m, 1 H, —$CH{=}CH_2$), 5.05 (m, 2 H, $CH_2{=}CH$), 4.47 (s, 3 H, OCH_3), 3.27 (m, 2 H, W=CCH_2), 2.81 (s, 4 H, $CH_2{=}CH_2$); $^{13}C\{^1H\}$ NMR (25 MHz, C_6D_6) δ 314.1 (carbene), 200.9 (CO), 137.3 (—$CH{=}CH_2$), 115.3 ($CH_2{=}CH$—), 66.7 (W=CC), 63.0 (OCH_3), 44.4 ($CH_2{=}CH_2$), 32.0 (—$CH_2CH{=}$); MS, m/z 422 (M^+).

Tetracarbonyl(η^2-ethene)((3-cyclohexen-1-yl)methoxycarbene)tungsten(0) (11). A solution of complex **6** (0.24 g) in cyclohexane (80 mL) was irradiated in the same way as complex **8** to give complex **11** (0.105 g, 40%) as a yellow solid that was recrystallized from hexane: mp 73 °C; IR (cyclohexane) 1975 (w), 1950 (vs) cm^{-1}; $\{^1H\}$ NMR (60 MHz, C_6D_6) δ 5.75 (b s, 2 H, $CH{=}CH$), 4.05 (s, 3 H, OCH_3), 2.56 (s, 4 H, $CH_2{=}CH_2$), 2.55–1.25 (m, 7 H); MS, m/z 448 (M^+). Anal. Calcd for $C_{15}H_{16}O_5W$: C, 37.50; H, 3.57. Found: C, 37.58; H, 3.74.

Tetracarbonyl(η^2-cyclopentene)((3-butenyl)methoxycarbene)tungsten(0) (12). This complex was prepared by the same method as complexes **10** and **11** and was obtained as a yellow oil (45% yield): IR (cyclohexane) 1975 (CO), 1950 (vs) cm^{-1}; $\{^1H\}$ NMR (90 MHz, $CDCl_3$) δ 5.65 (s, 2 H, —$HC{=}CH$—), 4.90 (m, 1 H, W=CCH), 4.50 (s, 3 H, OCH_3), 2.85 (s, 4 H, $H_2C{=}CH_2$), 2.5 (m, 4 H, $CH(CH_2)_2$); MS, m/z 434 (M^+).

Tetracarbonyl(η^2-cyclopentene)((3-cyclopenten-1-yl)methoxycarbene)tungsten(0) (13). A solution of complex **2** (0.5 g) in cyclohexane (30 mL) and cyclopentene (10 mL) was irradiated at room temperature for 10 h (until no more **2** is present). The solvent and excess cyclopentene were then evaporated under vacuum and the residue rapidly chromatographed over silica gel at −10 °C. Elution with petroleum ether gave complex **13** (180 mg) that could be kept without decomposition, at low temperature (−10 °C) in the presence of cyclopentene.

A ^1H NMR spectrum of complex **13** could be obtained at −10 °C. $\{^1H\}$ NMR (250 MHz, C_6D_{12}) δ 5.69 (m, 1 H, —$CH{=}CH_2$), 4.9 (m, 2 H, $CH_2{=}CH$—), 4.29 (s, 3 H, OCH_3), 4.03 (s, 2 H, —$HC{=}CH$—), 3.18 (t, 2 H, W=CCH_2), 2.7 (m, 4 H, $CH_2CH{=}CHCH_2$), 2.44 (m, 2 H, $CH_2(CH_2)$), 2.2 (m, W=CCH_2CH_2CH).

Tetracarbonyl(η^2-bicyclohept-2-ene)((3-butenyl)ethoxycarbene)tungsten(0) (14). A solution of complex **2** (0.7 g) in hexane was irradiated in the presence of norbornene (1.5 g) at room temperature. After 15 min, the starting complex **2** had been transformed into the new complex **14**. Rapid filtration over silica gel gave complex **14** (0.8 g) as a yellow oil: IR (hexane) 1975 (w), 1950 (vs) cm^{-1}; {^{1}H} NMR (250 MHz, C$_6$D$_{12}$): 5.79 (m, 1 H, CH$_2$=C*H*—), 5.03 (d, *J* = 13 Hz, 1 H, C*H*$_2$=CH—), 4.93 (d, *J* = 10 Hz, 1 H, C*H*$_2$=CH—), 3.46 (s, 2 H, —C*H*=C*H*—), 4.76 (q, *J* = 7 Hz, 2 H, OC*H*$_2$), 3.24 (m, 2 H, W=C(C*H*$_2$)), 2.75 (s, 2 H, —C*H*—), 2.28 (m, 2 H, —C*H*$_2$CH=CH$_2$), 1.75 (m, 2 H), 1.50 (t, *J* = 7 Hz, OCH$_2$C*H*$_3$) 1.20 (m, 2 H), 0.56 (m, 2 H).

Tetracarbonyl(triphenylphosphine)((3-butenyl)ethoxycarbene)tungsten(0) (16). PPh$_3$ (0.32 g, 1.22 mmol) was added to a solution of complex **2** (0.5 g, 1.22 mmol), in benzene (25 mL), at room temperature. After 2 h, the solvent was evaporated under vacuum and the residue chromatographed over silica gel. Elution with petroleum ether gave complex **15** (0.2 g, 24.5%) as orange crystals that were recrystallized from CH$_2$Cl$_2$/hexane: mp 95 °C; IR (cyclohexane) 2025 (m), 1925 (m), 1915 (m), 1890 (s); {^{1}H} NMR (60 MHz, CDCl$_3$) δ 7.40 (m, 15 H, H aromatic), 5.5 (m, 1 H, —CH=CH$_2$), 4.8 (m, 2 H, CH$_2$=CH—), 2.75 (q, 2 H, OCH$_2$CH$_2$), 2.8 (m, 2 H, W=CC*H*$_2$—), 2.05 (m, 2 H, —C*H*$_2$CH=CH$_2$), 1.42 (t, 3 H, CH$_2$—C*H*$_3$); ^{13}C{^{1}H} NMR (25 MHz, C$_6$D$_6$) δ 332.7 (d, carbene), 211.6 (d, CO), 206.7 (CO), 204.7 (CO), 203.5 (Ph, CO), 137.2, 133.6, 133.1, 130.1 (*C*H=CH$_2$), 128.8, 128.4, 155.1 (*C*H$_2$=CH—), 78.6 (O*C*H$_2$CH$_3$), 63.2 (W=C*C*H), 30.9 (*C*H$_2$CH=), 14.4 (CH$_2$*C*H$_3$).

Preparation of the Dinuclear Complex 15. A solution of complexes **1** and **2** in hexane was irradiated for 3 h at room temperature. After filtration over celite, evaporation of the solvent at room temperature, and fast chromatography over silica gel, complex **15** was obtained as an unstable yellow oil: ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 90 MHz) δ 332 (C$_1$), 314 (C$_{1'}$), 197.5 (CO), 201.3 (CO), 139.3 (C$_{6'}$), 115.9 (C$_{7'}$), 80.7 (OCH$_2$), 76.7 (OCH$_{2'}$), 71.0 (C$_6$), 46.4 (C$_7$), 64.5 (C$_4$), 63.7 (C$_{4'}$), 36.9 (C$_{5'}$), 32.4 (C$_5$), 15.0 (CH$_3$, CH$_{3'}$).

X-ray Studies. For the three compounds, preliminary unit cell dimensions and symmetry information were derived from precession photographs; each crystal was then set up on automatic diffractometers: a Philips PW1100 for **5**, a laboratory-made three-circle diffractometer for **11**, and a Nonius CAD4 for **6**. Accurate cell dimensions and orientation matrices were obtained from least-squares refinements of the setting angles of a sufficient number of well-centered reflections; the tuned 28 values ($24 < 2\theta < 28$) of 25 reflections were utilized for compounds **5** and **6**, and only nine reflections ($18 < 2\theta < 24$) were used for compound **11** due to computer limitations.

Crystal data and data collection parameters are listed in Table I. Intensities of two standards reflections were monitored at regular intervals: every hour for compounds **5** and **6** and every 100 reflections for compound **11**. For each compound, they showed no appreciable change during data collections. On the laboratory-made diffractometer where no attenuation filter was available, intensities were corrected for counting losses when the rate exceeded 7000 cs^{-1}. Only in compound **6** did ψ-scan curves show significant intensity variations. Absorption correction was applied via an empirical absorption correction technique.[26]

Computations were performed by using the SHELX76 system[27] on a Gould Concept 32/87 for compounds **5** and **11**; the CRYSTALS system[28] adapted on a Vax 11/725 was used for compound **6**. Atomic scattering factors for neutral W, C, O, and H were taken from ref 29; anomalous dispersion was taken into account.

In the three compounds, the position of W atom was determined by Harker vector analysis of three-dimensional Patterson maps. All remaining non-hydrogen atoms were found by successive electron density maps calculations. Final refinements were by full-matrix least squares with anisotropic temperature factors. In compounds **5** and **11**, hydrogen atoms attached to nondisordered C atoms were placed in calculated positions (H–C–H = 109°; C–H = 0.96 Å) and were then not further refined; they were assigned a refineable overall isotropic thermal parameter. Hydrogen atoms for compound **6** were located on a difference electron density map; their atomic coordinates were refined with a fixed overall isotropic thermal parameter. The criteria for a satisfactory completed analysis were the ratio of the parameter shifts to standard deviations all less than 0.1 and no significant features in the final difference maps. Main features of the refinement appear in Table I. Atomic coordinates are given in Table II, bond lengths in Table III, and bond angles in Table IV.

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Supplementary Material Available: Least-squares planes and dihedral angles (deg) between planes (Table V), torsional angles (deg) in the cyclohexene ring, and anisotropic thermal parameters for **5**, **6**, and **11** (Table VI) (7 pages); listings of observed and calculated structure factors for **5** and **6** (19 pages). Ordering information is given on any current masthead page.

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