Synthesis and *X*-Ray Structure of a Cyclopropane Precursor Alkene–Carbene Complex of Tungsten in which the Two Functions are Parallel

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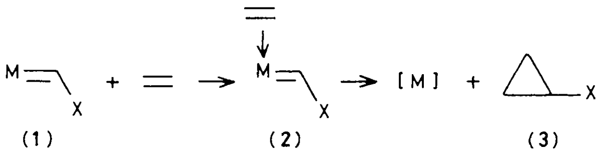
Photolysis of pentacarbonyl pent-4-enyl (methoxy)carbene tungsten (**4**) at low temperature affords a new chelated alkene–carbene complex (**5**) in which, according to an *X*-ray analysis, the alkene and the carbene functions are parallel, and which decomposes to give the expected cyclopropane (**7**).

The mechanism of the olefin metathesis reaction outlined by Chauvin[1] some 10 years ago, suggests that complexes of type (**2**) which bear both a carbene function and a double bond might be involved in this reaction. Such intermediates are also supposed to occur in the olefin cyclopropanation reaction[2] as well as in the Ziegler–Natta olefin polymerization reaction.[3]

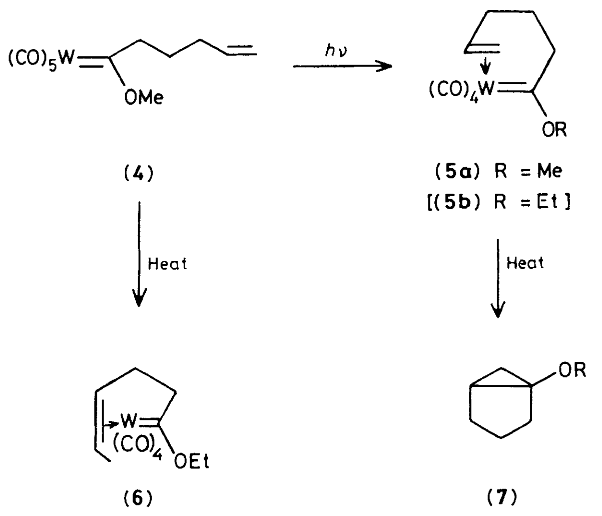
In a recent communication[4] Hoffman *et al.* came to the conclusion that in complexes of type (**2**) critical geometrical and electronic requirements must be met in order to observe the olefin metathesis as well as the cyclopropanation reaction: such reactions would only be possible in a coplanar conformation of the two functions. Moreover, for some electronic counts, such complexes might not be stable and should lead to the metathesis and/or the cyclopropanation products.



Scheme 1

Although much effort has been devoted to the synthesis and isolation of the aforementioned intermediates,[5,6] especially by Casey and coworkers, no complex in which the two functions have the favourable geometry has so far been fully characterized.

The present communication for the first time discloses the whole sequence depicted in Scheme 1: the reaction of carbene complex (**1**) with an olefin, the direct interaction of the carbene with the double bond giving (**2**), then its transformation into cyclopropane (**3**).



In a previous paper[6] we described the synthesis of complex (**4**) starting from $W(CO)_6$ and pent-4-enyl lithium.

Thermolysis of this complex did not afford the expected complex (**5**); instead, a six-membered stable ring system (**6**) is formed besides cyclopropane (**7**).

Red crystals of (**6**)† suitable for an *X*-ray analysis were grown from methanol. An ORTEP view of complex (**6**) is shown in Figure 1: the important features of this structure are firstly an almost perpendicular geometry of the W=C and C=C bonds and secondly, a *Z* geometry of the double bond.

Nevertheless, trace amounts of a second thermally unstable complex (**5**) could be detected, but our attempts to isolate and fully characterize this complex have been hampered by its low yield of formation and its thermal instability.

The structure of this minor complex could nevertheless be determined: indeed, photolysis of a dilute hexane solution of complex (**4**), at 10 °C, afforded complex (**5a**) in a 35% yield. The ^1H n.m.r. spectrum of complex (**5a**) clearly shows that the double bond is co-ordinated to the metal centre: one observes an upfield shift (*ca.* 2 p.p.m.) of the signals owing to the vinylic protons.

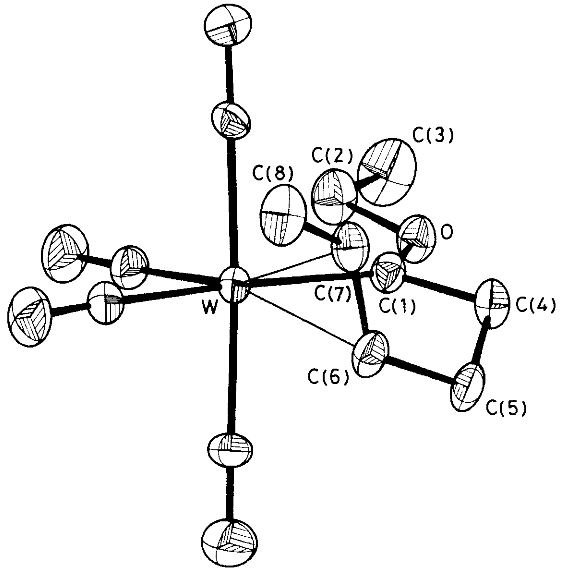


Figure 1. ORTEP view of the molecule, compound (**6**). Important bond lengths (Å): W–C(1) 2.158(8), W–C(6) 2.450(8), W–C(7) 2.479(9), C(1)–C(4) 1.52(1), C(4)–C(5) 1.53(1), C(5)–C(6) 1.51(1), C(6)–C(7) 1.38(1), C(7)–C(8) 1.52(1). Important bond angles (°): C(1)–C(4)–C(5) 110.7(7), C(4)–C(5)–C(6) 112.4(6), C(5)–C(6)–C(7) 122.7(8), C(6)–C(7)–C(8) 123.9(9). Angles between the vectors (°) W–C(1) and C(6)–C(7) 102.9(5).

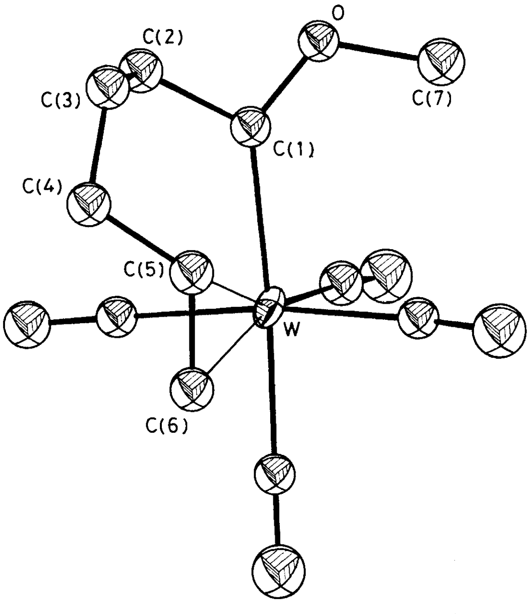


Figure 2. ORTEP view of the molecule, compound (**5**). Important bond lengths (Å): W–C(1) 2.14(2), W–C(5) 2.381(18), W–C(6) 2.519(36), C(1)–O 1.27(3), O–C(7) 1.47(4), C(1)–C(2) 1.59(3), C(2)–C(3) 1.44(4), C(3)–C(4) 1.55(3), C(4)–C(5) 1.44(4), C(5)–C(6) 1.41(4). Important bond angles (°): W–C(1)–C(2) 121(1), W–C(1)–O 135(2), O–C(1)–C(2) 103(2), C(1)–C(2)–C(3) 109(2), C(2)–C(3)–C(4) 116(2), C(3)–C(4)–C(5) 112(2), C(4)–C(5)–C(6) 121(2). Dihedral angles between planes (°): WC(1)C(5)C(6) and C(1)C(2)C(4)C(5) 47(2), C(1)C(2)C(4)C(5) and C(2)C(3)C(4) 59(2), WC(1)C(5)C(6) and C(2)C(3)C(4) 12(2). Angle between W–C(1) and C(5)–C(6) 12(2)°.

A remarkable observation in this spectrum is that the ring protons are all magnetically different and give sharp signals.

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† *Crystal data:* (**6**) $C_{12}H_{14}O_5W$, $M = 422$, monoclinic, space group $P2_1/c$, $a = 11.611(5)$, $b = 8.883(4)$, $c = 14,357(7)$ Å, $\beta = 109.5(1)°$, $Z = 4$, $D_c = 2.01$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 87.8$ cm^{-1}. 2370 data were collected at room temperature on a Philips PW1100 diffractometer. The structure was solved by standard Patterson-Fourier techniques, and refined by least squares using the DIRDIF program (ref. 7). Only 2043 reflections were used to solve and refine the structure. R = $\Sigma\text{-}(|F_O - F_C|) \times w^{1/2}/\Sigma(|F_O|) \times w^{1/2} = 0.044$.

Crystal data: (**5**) $C_{11}H_{12}O_5W$, $M = 408$, monoclinic, space group Cc, $a = 8.460(1)$, $b = 12.225(1)$, $c = 12.424(1)$ Å, $\beta = 103.4(1)°$, $Z = 4$, $D_c = 2.17$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 194.2$ cm^{-1}. 1210 data were collected at room temperature on a Philips PW1100 diffractometer. No absorption correction was made, ψ scans indicated that relative absorption effects were less then ±4% in $|F_O|$. The structure was solved by standard Patterson-Fourier techniques, and refined by least-squares using anisotropic temperature factors for the tungsten atom and isotropic for the remainder. Only 1049 reflections with $|F_O| > 3\sigma(|F_O|)$ were used to solve and refine the structure. $R = \Sigma(|F_O - F_C|) \times w^{1/2}/\Sigma(|F_O|) \times w^{1/2} = 0.0485$ $\{w = 1.012/(\sigma^2|F_O|) + 0.0014(F_O)^2\}$.

Computer programs used were Sheldrick's SHELX-76, Johnson's ORTEP-2, and locally written routines.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

This observation, and the fact that when R = Et, in (**5b**),‡ the methylene protons of the ethoxy group appear as the AB part of an ABX_3 system, means that this ring system exists as one conformer, even in solution. This observation is confirmed by an *X*-ray analysis of yellow crystals of complex (**5a**)† obtained from methanol.

The molecular structure (Figure 2) shows the presence of the carbene function and of a co-ordinated carbon–carbon double bond.

The interesting feature of this structure is the geometry of the double bond with respect to the carbene function: it appears that the planes containing the two functions are almost parallel as shown by an angle between the two vectors W–C(1) and C(5)–C(6) of 12°.

The geometry of this complex might allow its transformation into a cyclopropane and indeed, heating of complex (**5a**) in cyclohexane, at 60 °C for 2 hours gives quantitatively the expected cyclopropane (**7**). However, at this point, it is not known whether the cyclopropanation reaction occurs through the formation of a metallacyclobutane or through the formation of an opened dipolar intermediate.

It appears therefore that both in the thermal and in the photolytic reaction, complex (**5a**) is formed, but that in the thermal reaction this complex is converted to cyclopropane (**7**). A second reaction pathway is observed in the thermal reaction which is an isomerization of the double bond towards an internal position. The formation of a six-membered ring system is a general trend and is observed whatever the distance of the carbon–carbon double bond from the carbene carbon atom is.

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‡ ^1H n.m.r. spectrum (**5b**): ($CDCl_3$, 250 MHz, δ) 4.98 (dq, *J* 10.5 and 7.3 Hz, 1H, 7-H), 4.81 (dq, J 10.5 and 7.3 Hz, 1H, 7-H), 3.84 (ddm, *J* 13.7, 8.7, and 2 Hz, 1H, 5-H), 3.51 (d, *J* 13.7 Hz, 1H, 6-H), 3.34 (dm, *J* 15.4 H, 1H, 4-H), 3.21 (d, *J* 8.7 Hz, 1H, 6-H), 2.96 (m, 2H, 2-H_2), 2.31 (dt, *J* 13.8 and 4 Hz, 1H, 3-H), 1.87 (qt, *J* 13.2 and 4 Hz, 1H, 3-H), 1.61 (t, *J* 7.2 Hz, 3H, CH_3), 1.45 (ddt, *J* 13.2 and 4 Hz, 1H, 4-H).