

Reactivity of Carbene Complexes of Tungsten bearing a Carbon Carbon Double Bond in a Side Chain: Metathesis Reactions of the Double Bond

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Carbene complexes of tungsten, bearing one or two double bonds in one or two alkyl chains, react with metathesis catalysts to give either dicarbene complexes as a result of an intermolecular reaction, or carbene complexes bearing a cyclo-olefin, as the result of an intramolecular metathesis reaction.

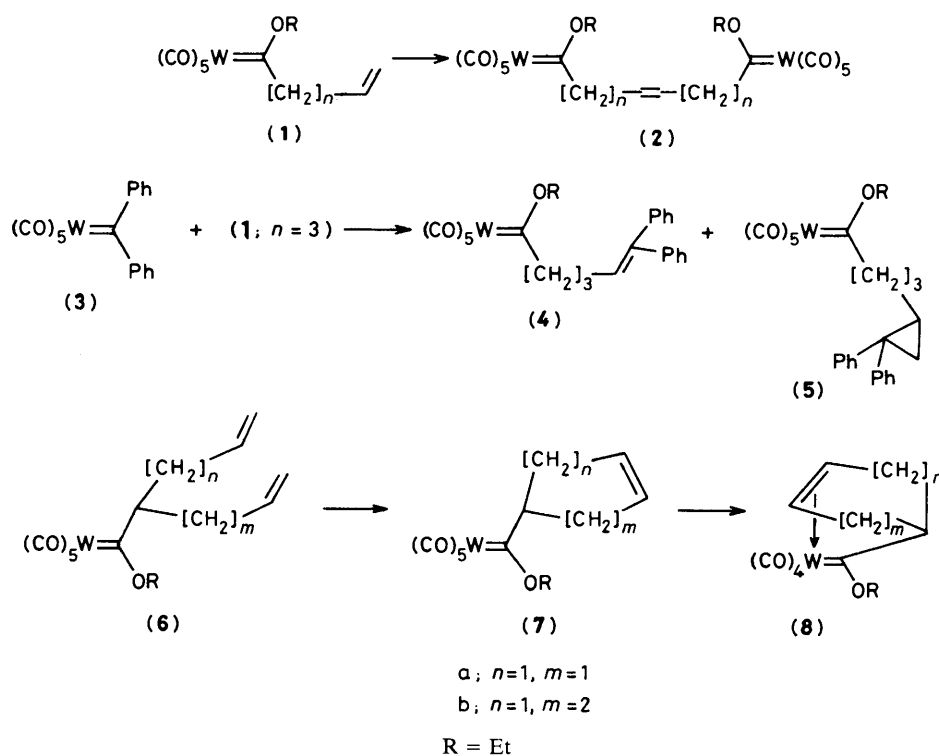
Although carbene complexes of transition metals have found applications in organic synthesis, the field of their use is still open to investigation.¹ This communication describes the reactivity of carbene complexes of type **(1)**, bearing a carbon carbon double bond, towards metathesis catalysts. If the double bond in **(1)** reacts as an isolated double bond, then the metathesis of **(1)** should lead to a new class of dicarbene complexes **(2)**.

As it is known that Fischer-type carbene complexes are sensitive to acids, oxidizing and reducing agents² *etc.* we tried using the carbene complex **(3)** as the metathesis catalyst. Complex **(3)** reacted with complex **(1; n = 3)** to give both the metathesis product **(4)** and the cyclopropanation product **(5)**,

albeit in low yield (12%), as observed by Casey³ for stoichiometric reactions with olefins.

The reaction of complex **(1; n = 9)** with a new metathesis catalyst (WOC₄/Ph₂SiH₂),⁴ capable of bringing about the metathesis of functionalised olefins, led to, besides the starting material, the dicarbene complex **(2; n = 9)**[†] in a 22%

[†] ¹H N.m.r. spectroscopic data: **(2; n = 9)** yellow oil, δ (60 MHz) 5.37 (m, 2 H), 3.20 (m, 4 H), 1.57 (t, 6 H), 1.32 (m, 16 H); **(7a)** yellow crystals, m.p. 56 °C, δ (250 MHz, C₆D₆) 5.33 (s, 2 H), 4.52 (m, 1 H), 3.74 (s, 3 H), 2.28 (m, 2 H), 2.10 (m, 2 H); **(8a)** red crystals, m.p. 48 °C, δ (250 MHz, C₆D₆) 5.08 (s, 2 H), 4.38 (s, 3 H), 2.78 (m, 5 H). All compounds were isolated as analytically pure samples.



yield. Moreover, with the same system, complexes of type (6) underwent an intramolecular metathesis reaction, with formation of ethene and complexes (7). The X-ray structure of complex (7a)[‡] is shown in Figure 1: the free cyclopentene ring has the usual geometry with a C(5)–C(6) (1.36 Å) free carbon carbon double bond far away from the metal centre, the angle between the planes C(3)C(4)C(7) and C(4)C(5)C(7) being 14°. The ¹H n.m.r. spectrum of (7a)[‡] is in agreement with this structure and shows a signal due to the hydrogen atom on carbon C(1) as a quintet at δ 4.5.

[‡] Crystal data for (7a): C₁₂H₁₀O₆W, *M* = 434, monoclinic, space group *P*2₁/*n*, *a* = 6.498(4), *b* = 21.05(1), *c* = 10.263(3) Å, β = 91.68(2)°, *D*_c = 2.05 g cm⁻³ for *Z* = 4. 2007 Reflections were collected at room temperature on a Philips PW1100 diffractometer. The structure was solved by standard Patterson-Fourier techniques. Full matrix least-squares refinements using anisotropic temperature factors for the tungsten, carbon, and oxygen atoms, and including H atoms as fixed contributions, have converged to an agreement factor of 0.0421 [1595 independent reflections with *F* > 3σ(*F*), 175 variable parameters; data were corrected for absorption: μ(Mo-Kα) = 86.9 cm⁻¹].

Crystal data for (8a): C₁₁H₁₀O₅W, *M* = 406, monoclinic, space group *P*2₁/*c*, *a* = 7.206(2), *b* = 10.881(3), *c* = 16.541(7) Å, β = 111.30(3)°, *D*_c = 2.23 g cm⁻³ for *Z* = 4. Data were collected at room temperature on a laboratory made automatic three circle diffractometer. The structure was solved by standard Patterson-Fourier methods and refined by full matrix least-squares [1423 observations with *F* > 3σ(*F*), 158 variable parameters, data were corrected for absorption μ(Mo-Kα) = 100.8 cm⁻¹]. All W, C, and O atoms were refined anisotropically, H atoms were introduced as fixed contributions, *R* = 0.0375.

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.

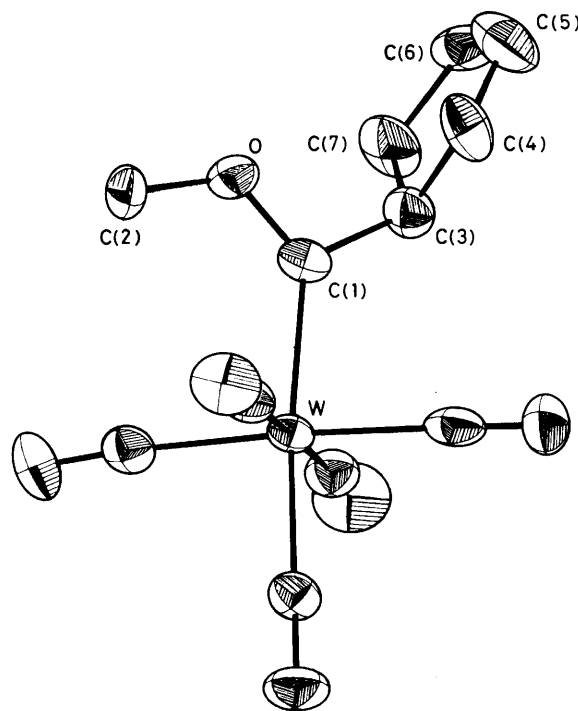


Figure 1. ORTEP view of complex (7a). Relevant bond lengths (Å): W–C(1) 2.086(17), C(1)–O 1.323(18), O–C(2) 1.440(18), C(1)–C(3) 1.52(2), C(3)–C(4) 1.59(2), C(3)–C(7) 1.56(2), C(4)–C(5) 1.41(3), C(7)–C(6) 1.51(3), C(5)–C(6) 1.32(4). Relevant bond angles (°): W–C(1)–C(3) 126(1), W–C(1)–O 131(1), C(3)–C(1)–O 107(1), C(1)–C(3)–C(4) 110(1), C(1)–C(3)–C(7) 116(1), C(4)–C(3)–C(7) 105(1), C(3)–C(4)–C(5) 104(2), C(3)–C(7)–C(6) 100(2), C(4)–C(5)–C(6) 113(2), C(7)–C(6)–C(5) 115(2), C(1)–O–C(2) 121(1). Dihedral angles (°) between the following planes: C(4)C(5)C(6)C(7) and C(3)C(4)C(7) = 14, C(4)C(5)C(6)C(7) and WOC(3) = 84.8.

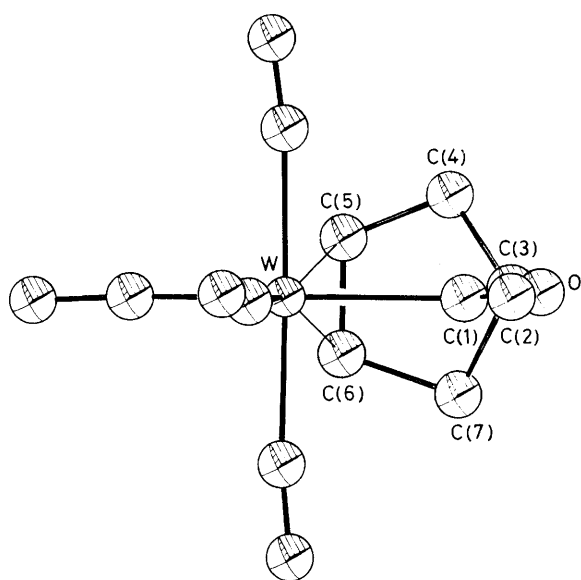


Figure 2. ORTEP view of complex (**8a**). Relevant bond lengths (Å): W–C(1) 2.167(15), C(1)–O 1.30(2), O–C(2) 1.437(17), C(1)–C(3) 1.479(19), C(3)–C(4) 1.55(3), C(3)–C(7) 1.53(3), C(4)–C(5) 1.53(3), C(6)–C(7) 1.49(2), C(5)–C(6) 1.35(3), W–C(5) 2.422(16), W–C(6) 2.434(13). Relevant bond angles (°): W–C(1)–O 135.4(9), W–C(1)–C(3) 113(1), O–C(1)–C(3) 112(1), C(1)–C(3)–C(4) 104(1), C(1)–C(3)–C(7) 107(1), C(4)–C(3)–C(7) 102(1), C(3)–C(4)–C(5) 99(2), C(3)–C(7)–C(6) 100(1), C(4)–C(5)–C(6) 108(2), C(7)–C(6)–C(5) 112(2), C(1)–O–C(2) 120(1). Dihedral angles (°) between the following planes: C(4)C(5)C(6)C(7) and C(3)C(4)C(7) = 42.8, C(4)C(5)C(6)C(7) and WOC(3) = 90.9.

Heating the complexes (**7**) in refluxing benzene led to the stable six membered ring systems (**8**),⁵ in which the double bond is co-ordinated to the metal centre.

The ¹H n.m.r. spectrum of (**8a**)[†] (CDCl₃) shows an upfield shift of the vinylic protons of about δ 0.5 upon co-ordination. The ORTEP view of complex (**8a**), (Figure 2) clearly shows that the cyclopentene ring is bound in a symmetrical way to the tungsten, and as a result, the five membered ring is bent by 45° between the planes C(3)C(4)C(7) and C(4)C(5)C(6).

It appears that the co-ordination of the double bond of complex (**7a**), which can be described as occurring *via* a rotation of the five membered ring around the C(1)–C(3) single bond, causes important changes in the geometry of the molecule.

The fact that these metathesis reactions can be carried out with a catalyst such as WOCl₄/Ph₂SiH₂, is peculiar since it is known² that Ph₂SiH₂ very readily cleaves the metal carbon double bond of carbenes. One must therefore assume that the reaction between WOCl₄ and Ph₂SiH₂ (both used in catalytic amounts), is fast enough to prevent the cleavage reaction.

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