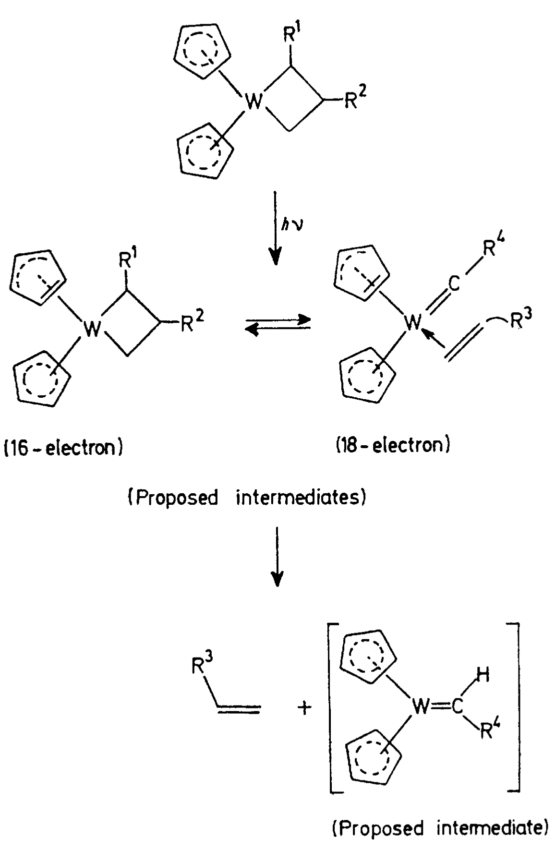
Photochemical Reactions of Metallocyclobutane Derivatives of Tungsten: Evidence for the Mechanism of Olefin Metathesis

By Michel Ephritikhine and Malcolm L. H. Green*
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)

Summary Irradiation of the metallocyclobutane derivatives $[W(\eta^5\text{-}C_5H_5)_2(\text{-}CH_2CHR^2CHR^1\text{-})]$, where $R^1 = R^2 = H$, $R^1 = H$, $R^2 = Me$, or $R^1 = Me$, $R^2 = H$, gives rise to the olefins $CH_2{=}CHR^1$ and $CH_2{=}CHR^2$ in good yield.

The synthesis of the metallocyclobutane derivatives $[M(\eta^5\text{-}C_5H_5)_2(\text{-}CHR^1CHR^2CH_2\text{-})]$ (**1**), where M = Mo or W, R^1 and R^2 = H or alkyl, has been described recently.[1] Thermal decomposition (*ca.* 80 °C) of (**1a**; M = W, $R^1 = R^2 = H$) evolves a mixture of cyclopropane and propene, whilst thermal decompositions of (**1b**; M = W, $R^1 = Me$, $R^2 = H$) and (**1c**; M = W, $R^1 = H$, $R^2 = Me$) evolve but-1-ene or isobutene.



Scheme. When $R^1 = R^2 = H$, then $R^3 = R^4 = H$; when $R^1 = H$ and $R^2 = Me$, then $R^3 = Me$ and $R^4 = H$; when $R^1 = Me$ and $R^2 = H$, then $R^3 = H$ or Me and $R^4 = H$ or Me.

In contrast, irradiation of a solution of (**1a**) in hexane causes smooth evolution of ethylene and some methane. We have studied the photochemical decomposition of a number of substituted metallocyclobutane derivatives (**1**) and the results are summarised in the Table. The data clearly show that major decomposition olefin evolved from the metal has one carbon less than the appropriate carbon chain in the initial metallocyclobutane. We also note that methane is evolved in the photolysis reactions but not in the thermal reactions. In separate experiments, the photolyses of $[W(\eta^5\text{-}C_5H_5)_2H_2]$ and $[W(\eta^5\text{-}C_5H_5)_2(C_2H_4)]$ under identical conditions did not yield any methane. The photochemical reactions and a proposed mechanism are illustrated in the Scheme.

This shows the intermediacy of carbene–olefin compounds which have an $\eta^3\text{-}C_5H_5$ ligand. We suggest that the initial photochemical reaction causes a $\eta^5\text{-}C_5H_5$-to-$\eta^3\text{-}C_5H_5$ ring shift and that this 16-electron intermediate allows the rearrangement of the metallocyclobutane ring to occur. Circumstantial evidence supporting this proposal includes the observation of an $\eta^3\text{-}C_5H_5 \rightarrow \eta^5\text{-}C_5H_5$ ring shift in the system[2] $[W(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(CO)_2] \xrightarrow{\text{Heat}} [W(\eta^5\text{-}C_5H_5)_2CO] + CO$. Also, there is evidence for carbene systems as intermediates in the chemistry of $[W(\eta^5\text{-}C_5H_5)_2]$ derivatives[3] or as stable compounds in the case of $[Ta(\eta^5\text{-}C_5H_5)_2({=}CH_2)Me]$.[4]

Further, thermal or photochemical decomposition of the proposed carbene product $[W(\eta^5\text{-}C_5H_5)_2({=}CHR^4)]$ when $R^4 = H$, can account for observation of formation of methane by analogy with observations on the thermal decomposition of $[Ti(\eta^5\text{-}C_5H_5)_2Me_2]$.[5] The formation of ethylene when $R^4 = H$ can arise from a binuclear mechanism. It has been shown that thermal decomposition of the carbene precursor $[Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2Cl]$ gives rise to ethylene.[6] Also when $R^4 = Me$, then ethylene can arise from hydrogen migration within the CHMe fragment.

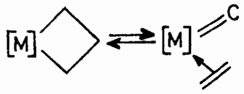
Table

Compound	Reaction time/h[a]	Volatile products[b,c] Major	Minor
(**1a**)	21	Ethylene, 10	Propene, 5 Methane, 1
(**1b**)	4	Ethylene, 10 Propene, 8	Butene, 6 Methane, 1
	21	Propene, 10 Ethylene, 5	Butene, 4 Methane, 1
(**1c**)	18	Propene, 10	Methane, 6 Butene, 3 Butene, 3 Ethylene, 1

[a] Reactions were performed in hexane solutions (*ca.* 10 mmol l^{-1}), at room temperature, in a Pyrex vessel; irradiation by a Hanovia 500 W medium-pressure lamp. [b] G.l.c. on a KCl/alumina column, peak intensities are expressed relative to highest peak = 10. [c] Combined yield of volatile products, *ca.* 50%.

We may account for the evolution of propene in the decomposition of (**1a**) and but-1-ene or isobutene in the decomposition of (**1b**) and (**1c**) from competitive thermal decomposition process during the course of the photolysis reaction.

The equilibrium shown in equation (1) has been postulated as the central step in the olefin dismutation reaction.[7] We conclude that our observations on the photolytic decomposition of the metallocyclobutanes (**1**) provide strong support for the feasibility of this mechanism.



(1)

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