

Photoinduced Synthesis of Binuclear Molybdenocene and Tungstenocene Derivatives: Catalytic Deoxygenation of Epoxides by Metallocenes

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Summary The compounds $[\{(\eta\text{-C}_5\text{H}_5)(\mu\text{-}\{\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\})\text{M}\}_2]$ and $[\{(\eta\text{-C}_5\text{H}_5)(\mu\text{-}[\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4])\text{WH}\}_2]$ have been prepared; the systems $[\text{M}(\eta\text{-C}_5\text{H}_5)\text{X}_2]$ (M = Mo or W, X₂ = Cl₂ or O)–NaHg deoxygenate epoxides catalytically.

PHOTOLYSIS of $[\text{M}(\text{C}_5\text{H}_5)_2\text{H}_2]$ (M = Mo or W) or thermolysis of $[\text{W}(\text{C}_5\text{H}_5)_2\text{H}(\text{Me})]$ gives rise to reactive intermediates believed to be the metallocenes $[\text{M}(\text{C}_5\text{H}_5)_2]$ (M = Mo or W) which readily insert into sp^2 and sp^3 C–H bonds.¹

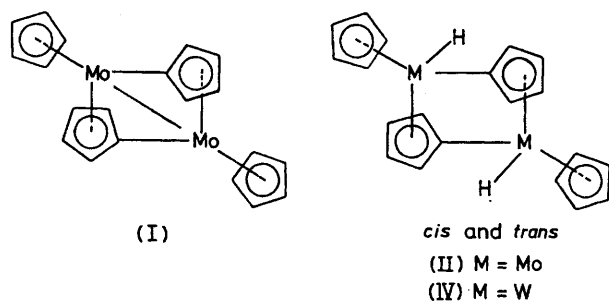
We now report that photolysis of $[\text{Mo}(\text{C}_5\text{H}_5)_2\text{H}_2]$ in benzene gives a red crystalline compound the physical and analytical data of which show that it is the dimer $[\{(\eta\text{-C}_5\text{H}_5)(\mu\text{-}[\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4])\text{Mo}\}_2]$ (I) (66%). The dimer (I) is also formed by irradiation of $[\{(\eta\text{-C}_5\text{H}_5)(\mu\text{-}[\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4])\text{-MoH}\}_2]$ (II) in benzene.² It is therefore reasonable to suggest that (I) is formed *via* prior formation of (II) by

dimerisation of $[\text{Mo}(\text{C}_5\text{H}_5)_2]$. Furthermore, irradiation of $[\text{W}(\text{C}_5\text{H}_5)_2\text{H}_2]$ in diethyl ether gives, after work-up, the complexes $[\text{W}(\text{C}_5\text{H}_5)_2\text{H}(\text{C}_2\text{H}_4)]\text{PF}_6$ (16%) (III) and *cis* (18%) and *trans* (22%) $[\{(\eta\text{-C}_5\text{H}_5)(\mu\text{-}[\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4])\text{WH}\}_2]$ (IV). The *trans*-isomer (IV) has been characterised by determination of its crystal structure.³

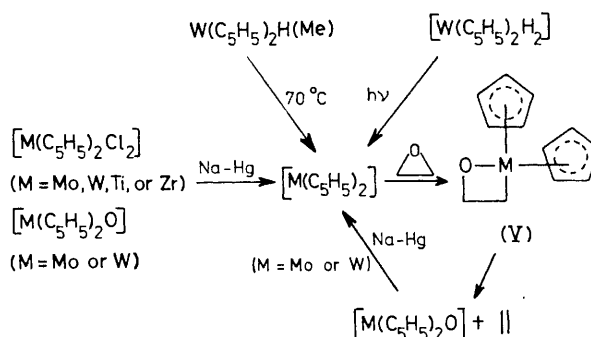
Formation of (III) may arise from insertion of $[\text{W}(\eta\text{-C}_5\text{H}_5)_2]$ into either a C–H or a C–O bond. To examine the latter possibility the photolysis of $[\text{W}(\text{C}_5\text{H}_5)_2\text{H}_2]$ in propene oxide was studied and found to produce $[\text{W}(\text{C}_5\text{H}_5)_2\text{O}]$ (60%) and propene. The proposed mechanism is shown in the Scheme and involves the intermediate (V) which is analogous to the intermediate postulated by Sharpless *et al.*⁴ for the transfer of an oxygen atom between transition-metal complexes and olefins. Thermolysis of $[\text{W}(\text{C}_5\text{H}_5)_2\text{H}(\text{Me})]$ in propene oxide produces methane, propene, and $[\text{W}(\text{C}_5\text{H}_5)_2\text{O}]$.

This provides further evidence that the photolysis of $[\text{W}(\text{C}_5\text{H}_5)_2\text{H}_2]$ and the thermolysis of $[\text{W}(\text{C}_5\text{H}_5)_2\text{H}(\text{Me})]$ give rise to the same reactive intermediate, tungstenocene.

Cl_2 ($\text{M} = \text{Ti}$ or Zr) and Na-Hg were stoichiometric in $[\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$.



It has been suggested that reduction of $[\text{Mo}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ and $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ produces the low-valent reactive metallocenes $[\text{Mo}(\text{C}_5\text{H}_5)_2]$ ⁵ and $[\text{Ti}(\text{C}_5\text{H}_5)_2]$,⁶ and an excess of $[\text{Ti}(\text{C}_5\text{H}_5)_2]$ and water has been shown to reduce epoxides to alkanes.⁷ We find that treatment of either pure propene oxide or dilute solutions of propene oxide in anhydrous benzene, diethyl ether, or tetrahydrofuran (THF) under nitrogen with $[\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ ($\text{M} = \text{Mo}, \text{W}, \text{Ti},$ or Zr) and sodium amalgam leads to the formation of propene. For example, a 1% solution of propene oxide in THF containing $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (1.1 equiv.) was vigorously stirred under nitrogen at 20° with sodium amalgam (2%; excess). After 16 h the yield of propene was >95%. The relative reactivity of the above systems was $[\text{Zr}] \simeq [\text{Ti}] \gg [\text{Mo}] > [\text{W}]$. $[\text{M}(\text{C}_5\text{H}_5)_2\text{O}]$ ($\text{M} = \text{Mo}$ or W) could be isolated from the appropriate reaction mixtures. Indeed treatment of propene oxide with $[\text{M}(\text{C}_5\text{H}_5)_2\text{O}]$ ($\text{M} = \text{Mo}$ or W) and sodium amalgam also gave rise to the evolution of propene indicating that the deoxygenations might be catalytic. This was found to be the case for $[\text{M}(\text{C}_5\text{H}_5)_2\text{X}_2]$ ($\text{M} = \text{Mo}$ or W ; $\text{X}_2 = \text{Cl}_2$ or O) and Na-Hg where the reactions were followed until 250 equiv. (relative to $[\text{M}]$) of propene oxide had been deoxygenated. Deoxygenations with $[\text{M}(\text{C}_5\text{H}_5)_2-$



SCHEME. Deoxygenation of epoxides by metallocenes.

The systems $[\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ ($\text{M} = \text{Mo}, \text{W}, \text{Ti},$ or Zr) and Na-Hg also deoxygenated cyclohexene oxide and pent-2-ene oxide to cyclohexene and pent-2-ene respectively. Deoxygenations ($[\text{M}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ and Na-Hg at 20 °C) of *cis*-pent-2-ene oxide gave the following ratios of *cis*:*trans*-pent-2-ene; $[\text{Zr}]$ 54:46, $[\text{Ti}]$ 62:38 (20 °C), 51:49 (80 °C); $[\text{Mo}]$ 63:37, $[\text{W}]$ 67:33. *cis*-Pent-2-ene was not isomerised under the reaction conditions. $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ and Na-Hg deoxygenated *cis*-but-2-ene oxide to *cis*- and *trans*-but-2-ene (66:34).

The differences in rates and catalytic activity may be attributed in part to the solubilities of $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$, $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$, $[\text{Mo}(\text{C}_5\text{H}_5)_2\text{O}]$, and $[\text{W}(\text{C}_5\text{H}_5)_2\text{O}]$, and the insolubilities of $[\text{Mo}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$, $[\text{W}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$, $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{O}]$, and $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{O}]$. The reactions are summarised in the Scheme.

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⁶ H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1970, **92**, 6182.

⁷ E. E. van Tamelen and J. A. Gladysz, *J. Amer. Chem. Soc.*, 1974, **96**, 5290.