# Photoinduced Insertion of Tungsten into Methanol giving a Tungsten-methyl Derivative

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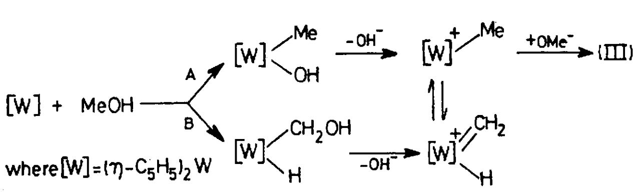
*Summary* Photolysis of $[(\eta\text{-}C_5H_5)_2WH_2]$ in methanol gives the compounds $[(\eta\text{-}C_5H_5)_2WH(OMe)]$ and $[(\eta\text{-}C_5H_5)_2W(Me)(OMe)]$; tungstenocene is proposed as an intermediate.

IRRADIATION of bis-$\eta$-cyclopentadienyltungsten dihydride (I) in mesitylene or *p*-xylene causes insertion of the tungsten into methyl C–H bonds giving bis-alkyl derivatives $[(\eta\text{-}C_5H_5)_2W(CH_2R)_2]$, where R = 3,5-$Me_2C_6H_3$ or 4-$MeC_6H_4$ respectively.[1] This was the first demonstration of the intermolecular, homolytic insertion of a transition metal into an $sp^3$ C–H system giving an isolable metal–alkyl derivative. It has also been shown that irradiation of (I) in *p*-methylanisole gives the analogous bis-alkyl where R = 4-

$(MeO)C_6H_4$ so that the tungsten insertion takes place into the C–Me group and the O–Me group is inert.[2] This observation led us to study the photoinduced reaction between (I) and MeOH.



SCHEME

Irradiation of (I) in MeOH at room temperature for 12 h (using a medium-pressure mercury lamp and Pyrex filters) gave two new compounds. These were unambiguously identified as the methoxy-hydride $[(\eta\text{-}C_5H_5)_2WH(OMe)]$ (II) and the methoxy-methyl $[(\eta\text{-}C_5H_5)_2W(Me)(OMe)]$ (III) in the ratio *ca.* 1 : 5. The compound (III) may also be prepared by treatment of $[(\eta\text{-}C_5H_5)_2W(C_2H_4)Me]PF_6$ with NaOMe in MeOH.[2] A solution of (II) in MeOH was irradiated for 24 h and the reaction products showed that 30% conversion of (II) into (III) had taken place. On the other hand, irradiation of (III) in MeOH for 24 h caused no reaction and (II) was not detected in the products. Irradiation of (I) in EtOH for 12 h gave only the ethoxy-hydride $[(\eta\text{-}C_5H_5)_2WH(OEt)]$.

Our original observation of the photoinduced insertion of tungsten into aromatic C–H bonds led us to postulate that the reaction proceeded by an intermediate 'tungstenocene' which could be regarded as a transition-metal carbene analogue.[3]

Thomas has observed closely analogous photochemical insertion of tungsten into aromatic C–H bonds starting from the monocarbonyl $[(\eta\text{-}C_5H_5)_2WCO]$.[4] Also, he has postulated that the same tungstenocene system with carbene analogue properties is formed by reduction of the dichloride $[(\eta\text{-}C_5H_5)_2WCl_2]$ with sodium amalgam.[5] The tungstenocene intermediate was initially postulated following the observation of thermally induced insertion of tungsten into benzene starting from a tungsten alkyl hydride $[(\eta\text{-}C_5H_5)_2WH(R)]$, R = pentenyl[6] or succinyl.[7] Nakamura has made similar observations and invokes tungstenocene as the reactive intermediate.[8]

Therefore, there is substantial evidence which suggests that a reactive carbene-like tungstenocene intermediate is responsible for insertions into aromatic and aliphatic C–H bonds.

The formation of the compound (II) clearly may be envisaged to proceed *via* insertion of the tungstenocene intermediate into the O–H bond of the methanol. The formation of the methyl derivative (III) either may be envisaged to proceed by insertion of tungstenocene into the C–O bond of methanol (route A) followed by exchange of OH with methoxide, or *via* insertion into the C–H bond (route B) (*viz.* Scheme). It has been shown that carbenes such as methylene react with methanol by insertion into both the O–H and C–H bond but not into the C–O bond,[9] although insertion of carbenes into C–O bonds is observed in reactions with ethers.[9]

By analogy with the reactions of carbenes, therefore, we propose that the formation of the methoxy-methyl derivative (II), proceeds *via* insertion of $(\eta\text{-}C_5H_5)_2W$ into the H–C bond of methanol as shown in route B. There is independent evidence[10] for the equilibrium $[W] \pm CH_3 \rightleftharpoons [W]^+(=CH_2)H$ shown in route B.

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