Photo-induced Insertion of Tungsten into a Methyl C–H bond in *p*-Xylene and Mesitylene: Crystal Structure of $(\eta\text{-}C_5H_5)_2W[CH_2(3,5\text{-}Me_2C_6H_3)]_2$

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Summary Irradiation of a mesitylene solution of the dihydride $(\eta\text{-}C_5H_5)_2WH_2$ with a mercury lamp (366 nm) gives the bis-alkyl derivative $(\eta\text{-}C_5H_5)_2W[CH_2(3,5\text{-}Me_2C_6H_3]_2$.

IT has been shown that irradiation of the dihydride $(\eta\text{-}C_5H_5)_2WH_2$ (I) in benzene gives the phenylhydride $(\eta\text{-}C_5H_5)_2WH(C_6H_5)$.[1] Similar aryl hydride products $\eta\text{-}C_5H_5)_2WH(p\text{-}C_6H_4R)$, (R = Me or OMe) are formed when toluene or anisole are used as the reactant. Here we describe a different photo-induced reaction of compound (I) with *p*-xylene or mesitylene.

Irradiation of (I) in mesitylene (3×10^{-3} M) at 20° for 12 h (high-pressure Hg lamp, 90 W; pyrex filters) gives an orange compound which is slightly soluble in benzene and is only slowly oxidised in air. Analysis and mass spectrometry show a stoicheiometry corresponding to $\eta\text{-}(C_5H_5)_2W(C_9H_{11})_2$ (II). *Crystal data:* $(\eta\text{-}C_5H_5)_2W(C_9H_{11})_2$, monoclinic, $a = 8{\cdot}619$, $b = 22{\cdot}278$, $c = 11{\cdot}921$ Å $\beta = 94{\cdot}97°$. Space group $P2_1/c$ (C^5_{2h}, No 14) $Z = 4$, $D_c = 1{\cdot}61$ gm cm^{-3}; 3586 independent reflections were measured by four-circle diffractometry using Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å). The structure was solved by Patterson and Fourier methods and refined by large block least-squares. Hydrogen atoms have not yet been located. The conventional agreement index, *R*, is now 0·034.

The structure of (II) (Figure) shows that each of the aromatic rings is attached to the tungsten by a methylene group. The angle $C_aWC_b = 75°$ is in the region expected for a normal bent d^2 bis-η-cyclopentadienyl metal system.[2] The plane through the C_aWC_b atoms is perpendicular to the plane containing the metal-ring normals. The ^1H n.m.r. spectrum of (II) may be assigned according to the crystal structure as δ 3·25 [6H, s, $(C_6H_3)_2$]; 5·30 [10H, s, $(\eta\text{-}C_5H_5)_2$]; 7·47 (12H, s, Me_4); 8·41, 8·78 [2H, 2H, complex $(CH_2)_2$] (in CS_2 at 90 MHz). It is shown that the hydrogens of the two methylene groups do not occur as a singlet, and clearly there is steric restriction preventing equilibration of the CH_2 hydrogens in (II).

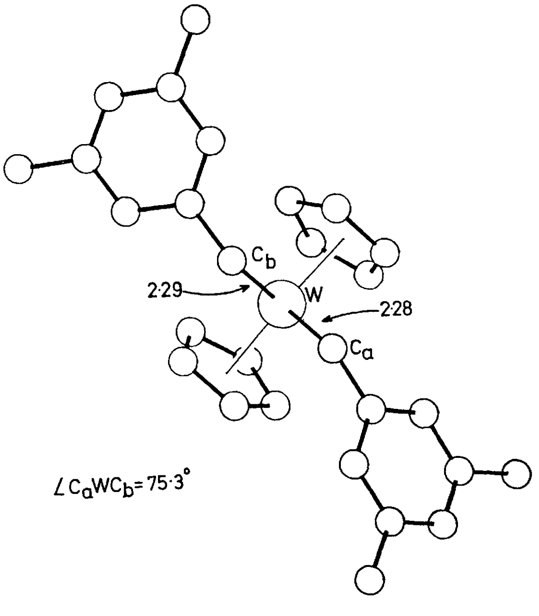

FIGURE. Structure of $(\eta\text{-}C_5H_5)_2W[CH_2(3,5\text{-}Me_2C_6H_3)]_2$

Irradiation of (I) in *p*-xylene similarly forms yellow-orange crystals which have a structure analogous to (II), $(\eta\text{-}C_5H_5)_2W(\eta\text{-}CH_2C_6H_4Me)$ (III) δ 2·94 [8H, s(br), $(C_6H_4)_2$]; 5·30 [10H, s, $(\eta\text{-}C_5H_5)_2$]; 7·42 (6H, s, Me_2); 8·41, 8·78 [2H, 2H, complex, $(CH_2)_2$] (in CS_2 at 90 MHz). Compound (II) may also be isolated from the reaction between $[(\eta\text{-}C_5H_5)_2WHLi]_4$ and *p*-$BrCH_2C_6H_4Me$.

The formation of (II) and (III) appear to be the first examples of direct insertion of a transition metal into an unco-ordinated saturated C–H group. Parshall has proposed that a reversible insertion of niobium into aromatic C–H bonds occurs in the hydrogen-deuterium exchange reactions between H_2 and benzene catalysed by $(\eta\text{-}C_5H_5)_2NbH_3$.[3] However, exchange of the methyl hydrogen in toluene was not observed.

An analogous mechanism involving a 16-electron tungstenocene intermediate has been proposed to account for the photoinduced insertion of tungsten into benzene.[1] Clearly, however, it is impossible to arrive at a bis-substituted product $(\eta\text{-}C_5H_5)_2WR_2$ by this route.

We can account for the formation of (II) and (III) by a mechanism which involves, in part, reversible transfer of hydrogen, or alkyl-substituents $R = CH_2C_6H_4Me$ between the tungsten and a η-cyclopentadienyl ring, *e.g.* $(\eta\text{-}C_5H_5)_2WHR \rightleftharpoons (\eta\text{-}C_5H_5)WR(C_5H_6)$, followed by insertion of the tungsten into a methyl H–C bond giving $(\eta\text{-}C_5H_5)WHR_2(C_5H_6)$ and, finally, elimination of H_2 to give the product (II).

We also note that irradiation of (I) in *p*-chlorotoluene gives the previously described *p*-tolylchloride $(\eta\text{-}C_5H_5)_2WCl(p\text{-}C_6H_4Me)$.[4]

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