Formation of a Tungsten Phenyl Hydride Derivative from Benzene

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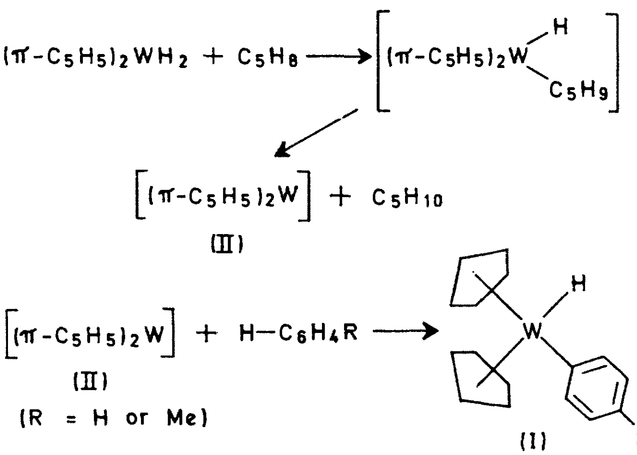
Summary In the presence of dienes the dihydride $(\pi\text{-}C_5H_5)_2WH_2$ reacts with benzene to give the phenyl derivative $(\pi\text{-}C_5H_5)_2WHPh$.

TREATMENT of dihydridobis-(π-cyclopentadienyl)tungsten with isoprene in benzene at 120° for three days causes reduction of the isoprene, and isomeric pentenes are formed. More surprisingly, chromatography of the less volatile products gives a sublimable yellow compound, in up to 15% yield, which analysis, mass, i.r. and, in particular, ^1H n.m.r spectra show to be the phenyl hydride (I; R = H); ^1H n.m.r. (C_6D_6) τ 2·10, 3·02 (Ph); 5·81 {d, *J*[H, $(\pi\text{-}C_5H_5)_2$] 0·7 Hz, $(\pi\text{-}C_5H_5)_2$}; 21·1 [t, *J*(H, ^{183}W) 80 Hz, W-*H*]. The analogous pentadeuteriophenyl derivative is formed using C_6D_6. If toluene is used instead of benzene then only the *p*-tolyl derivative (I; R = Me) is isolated, in *ca.* 10% yield. The absence of other isomers suggests that a radical mechanism is unlikely. Further, no biphenyl could be detected in the reaction products from benzene. The compound (I; R = H) is not formed if isoprene is absent but is formed in similar yields if isoprene is replaced by butadiene or penta-1,3-diene. The mass spectrum of the compound (I; R = H) shows a parent ion band and also a strong band at *m/e* 314 appropriate for the tungstenicenium cation $(\pi\text{-}C_5H_5)_2{}^{184}W^+$.

We suggest the mechanism shown in the Scheme for the formation of compound (I), involving addition of benzene to the intermediate tungstenocene (II). Circumstantial evidence supporting this mechanism arises from the observations that $(\pi\text{-}C_5H_5)_2$ MH_2 (M = Mo or W) have been found to add to unsaturated hydrocarbons;[1] also, the dimethyl derivatives $(\pi\text{-}C_5H_5)_2MMe_2$ are stable compounds.[2] Finally, a similar addition of benzene to a bis-π-cyclopentadienyltantalum hydride has been postulated to occur in the deuterium exchange reactions of C_6D_6 with hydrogen catalysed by $(\pi\text{-}C_5H_5)_2TaH_3$.[3]



SCHEME

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