Photo-induced Insertion of Bis-π-cyclopentadienyltungsten into Aromatic Carbon–Hydrogen Bonds

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Summary Irradiation of benzene solutions of the dihydride $(\pi\text{-}C_5H_5)_2WH_2$ with a mercury lamp (366 nm) gives the phenyl hydride $(\pi\text{-}C_5H_5)_2WHPh$ in high yield and further evidence suggests the reaction proceeds *via* tungstenocene $(\pi\text{-}C_5H_5)_2W$ as an intermediate.

THERMAL decomposition of some alkyl hydrides $(\pi\text{-}C_5H_5)_2$-WHR in benzene gives the phenyl hydride $(\pi\text{-}C_5H_5)_2WHPh$ (I) (10—20% yields), possibly *via* a tungstenocene, $(\pi\text{-}C_5H_5)_2W$, intermediate.[1,2] Attempts to prepare the phenyl hydride (I) by heating the dihydride $(\pi\text{-}C_5H_5)_2WH_2$ (II) in benzene (120° for 3 days) did not give the compound (I).

Here we report that irradiation of benzene solutions at 5° of the dihydride (II) (high-pressure Hg lamp; 450 W; Pyrex and aqueous iodine filters) for 20 h gives the phenyl hydride (I) in yields of 40—80% depending on conditions. Yields greater than 60% are reproducibly found with dilute solutions (0·005M) and only small quantities of other (decomposition) products were observed (2—10%).

When deuteriobenzene is used then the ^1H n.m.r. and mass spectra show that the deuteriophenyl-*deuteride* $(\pi\text{-}C_5H_5)_2WD(C_6D_5)$ is formed. This strongly suggests that compound (I) is formed by insertion of tungsten into the C–D(or H) bond. Irradiation of compound (I) in deuteriobenzene showed that it was stable under the above conditions and that no exchange between (I) and deuteriobenzene occurred. This shows that addition of the tungsten to the C–H is irreversible under the reaction conditions.

Irradiation of the dihydride (II) in toluene gives the previously described[1] *p*-tolyl derivative $(\pi\text{-}C_5H_5)_2WH(p\text{-}MeC_6H_4)$ (45%), and a trace of what may be another isomer of this compound. However, irradiation of the dimethyl complex $(\pi\text{-}C_5H_5)_2WMe_2$ in benzene gave none of the compound (I).

On the basis of the above evidence we propose that irradiation causes loss of hydrogen from the dihydride (II) and formation of tungstenocene monomer. This appears to be very reactive and 'carbene-like' in its ability to insert into the aromatic C–H bond. Since olefin complexes of the type $(\pi\text{-}C_5H_5)_2W(\text{olefin})$ (olefin = ethylene or propene), are stable thermally and to substitution,[3] it seems possible that the insertion step by the tungsten is proceeded by initial formation of a tungstenocene-benzene π-complex.

All reaction products were identified by comparison of the ^1H n.m.r., i.r., and mass spectra with those of authentic samples.

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[3] B. R. Francis, F. W. Benfield, and M. L. H. Green, *J. Organometallic Chem.*, in the press.