Insertion of Dichlorocarbene into a Tungsten–Hydrogen Bond

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Summary Thermal decomposition of sodium trichloroacetate in the presence of tungsten di-*h*^{5}-cyclopentadienyl dihydride produces tungsten di-h^5-cyclopentadienyl dichloromethide hydride.

WE report the insertion of dichlorocarbene into the tungsten–hydrogen bond of tungsten di-*h*^{5}-cyclopentadienyl dihydride (Cp_2WH_2). To our knowledge this is the first example of the reaction of a halogenocarbene on a bond to a transition metal. [In instances in which apparent carbene insertion into Pd–Cl and Ir-Cl bonds were reported,[1] the reactions between the metal compound and a diazo-compound undoubtedly did not involve intervention of a divalent carbon species.[2,3] There are a few known examples of actual insertion by carbenes into metal–hydrogen,[4] metal–halogen,[5] and metal–carbon[6] bonds, but in no instance is a transition metal involved.]

Treatment of Cp_2WH_2[7] (3·16 mmol) with sodium trichloroacetate (9·48 mmol; dried over P_4O_{10} at 100° for 40 h) in 1,2-dimethoxyethane (glyme; 50 ml; freshly distilled from $LiAlH_4$ and deaerated with argon) under reflux and under argon resulted in the initially yellow solution becoming dark while a brown precipitate (shown to be mostly NaCl together with a small amount of WCp_2Cl_2) formed as the sodium trichloroacetate was decarboxylated.[8] The mixture was filtered, concentrated, and set aside, and green-black needles appeared which turned to a brown oil on contact with air. The crystalline material did not melt sharply but darkened with decomposition at *ca.* 300°. The yield of product based upon the assigned structure (see later) was at least 20%.

Crystals of the green-black product exhibit a weak parent ion cluster in the mass spectrum (70 eV; 188 °C; 10^{-6} Torr) at *m/e* 396—404 with a relative intensity pattern characteristic of the presence of "WCl_2" consistent with an empirical formula involving the incorporation of CCl_2 into the starting dihydride. Those peaks not associated with chlorine-containing ions are identical with fragment ions observed in the mass spectrum of Cp_2WH_2.

The n.m.r. spectrum (100 MHz) of a fresh solution of the product in glyme exhibits absorptions at τ 2·14 (s, 1H), 4·36 (s, 10H), and 23·33 (s, 1H). In comparison a solution of the starting compound, Cp_2WH_2, shows absorptions at 5·57 (s, 5H) and 22·38 (s, 1H). Inasmuch as the values for the starting compound correspond to the ten equivalent cyclopentadienyl hydrogen atoms and the two bound to tungsten, we must assign the absorptions at τ 4·35 and 23·33 for the product to ten equivalent cyclopentadienyl hydrogens and a *single* hydrogen bound to tungsten.† These assignments require that the absorption at τ 2·14 be associated with the hydrogen of a dichloromethyl group attached to the tungsten.

Elemental analyses, except for carbon,‡ are in excellent agreement with an empirical formula derived from the insertion of dichlorocarbene into a tungsten–hydrogen bond of Cp_2WH_2. We have no explanation for the low value of carbon; however, the tungsten, chlorine, and hydrogen analyses, the mass and ion cluster pattern of the parent ion, and the n.m.r. data clearly define the molecular formula as $Cp_2WHCHCl_2$.

$$Cp_2WH_2 + Cl_3CCO_2Na \xrightarrow{\text{glyme}} Cp_2WHCHCl_2 + NaCl + CO_2$$

Additional evidence in support of the structure proposed comes from the i.r. spectrum (KBr pellet) which shows bands at 3112br (m), 2950sh (vw), 1940br (s), 1450sh (m), 1360sh (w), 1260sh (m), 1095sh (m), and 1050 (w), cm^{-1}, in addition to absorptions below 1000 cm^{-1}. Except for the bands at 1940 and 1260 cm^{-1} and the shoulder at 2950 cm^{-1}, absorptions at similar wavenumbers are observed in the starting material. The band at 1940 cm^{-1}, assigned to a W–H stretch, compares with the value of 1918 in the starting dihydride. The band at 1260 cm^{-1}, which has no counterpart in the starting compound, may correspond to a W–C stretching vibration.§ The expected C–H stretching vibration from the $CHCl_2$ group of our product may be attributed to the shoulder at 2950 cm^{-1}. Because the starting compound exhibits absorptions in the region 800—600 cm^{-1}, it is not possible to assign definitely the C–Cl stretching vibrations in the product.

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† Because of the low solubility of $Cp_2WHCHCl_2$ in glyme, experimental conditions required to obtain the n.m.r. spectrum did not permit the resolution required to observe the weak coupling between the cyclopentadienyl and metal-bound hydrogens. The line width for the τ 4·35 peak was 1·7 Hz.

‡ Values on several samples from three different laboratories were erratic and low.

§ E. O. Fischer and A. Maasbol (*Angew. Chem. Internat. Edn.*, 1964, **3**, 580) have assigned a W–C vibration for the compound $CpW(CO)_3Me$ at 1179 cm^{-1}.

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The following was originally published in J.C.S. Chem. Comm., 1972, 99. *Unfortunately the formulae block was omitted, which renders the paper difficult to follow. We are therefore reproducing the paper with the formulae block.*