Some New Cyclopentadienyl Halides of Molybdenum, Tungsten and Rhenium

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In view of the unusual basic properties of the bis-τ-cyclopentadienyl complexes (τ-C₅H₅)₂MX₂, (I), where M = Mo or W¹,² and (τ-C₅H₅)₂ReH, (II)³, and their lack of reactions characteristic of the hydrogen in carbonyl hydrides, such as reaction with diazomethane to give methyl derivatives⁴, we have further investigated the chemistry of the complexes. Treatment of the complexes (I) and (II) with chlorine and bromine results in oxidation of the metal and replacement of the hydrogen by halogen, and also, as shown for some other transition metal hydride complexes⁵, treatment with halogenated solvents such as chloroform, bromoform and methyl iodide leads to replacement of the hydrogen by halogen without oxidation. Examples of these reactions are given below.

Treatment of chloroform solutions of the complexes (I) with chlorine or bromine at room temperature affords dark-red or purple crystalline solids whose analyses, conductivity measurements and infra-red spectra show to be the 1:1 salts [(C₅H₅)₂MX₃]²⁺X⁻, (III), (d ~ 250 °C), where M = Mo or W and X = Cl or Br. [For example, (C₅H₅)₂WCl⁶; found: C, 26.0; H, 2.2; Cl, 31.0%, A²⁰₀ in (nitrilethane), 58 ohm⁻¹ cm². Required for C₁₀H₁₀Cl₂W: C, 25.34; H, 2.18; Cl, 31.7%.] And for (C₅H₅)₂BrMo: found: C, 21.96; H, 1.81; Br, 58.85%. A²⁰₀ in (nitrilethane), 67 ohm⁻¹ cm². C₁₀H₁₀Br₂Mo requires: C, 22.02; H, 1.83; Br, 58.6%.

The salts (III) are very insoluble in common organic solvents but dissolve slightly in liquid sulphur dioxide to give deeply coloured solutions from which they may be recrystallised. Similarly the rhenium complex (II) reacts with chlorine and bromine to give the 1:1 salts [(C₅H₅)₂ReX₃]⁴⁻, (IV), where M = Mo or W, X = Cl or Br (d ~ 150 °C). [(C₅H₅)₂ReCl₃; found: C, 28.26; H, 2.79; Cl, 25.24%. A²⁰₀, 45 ohm⁻¹ cm². C₁₀H₁₀ReClRe requires: C, 28.40; H, 2.36; Cl, 25.16%. (C₅H₅)₂ReBr₃. Found: C, 22.07; H, 2.06; Br, 42.08%. A²⁰₀, 67 ohm⁻¹ cm². C₁₀H₁₀Br₂Re requires: C, 21.59; H, 1.81; Br, 43.06%.

The complexes (I) react with chloroform, bromoform and methyl iodide affording green crystals for which analyses, conductivity measurements and infra-red spectra indicate the empirical formulation (C₅H₅)₂MX₉ (V), (d ~ 250 °C), where M = Mo or W and X = Cl, Br or I. [(C₅H₅)₂Re₁₂Cl₁₀; found: C, 31.2; H, 3.0; Cl, 18.57%. A²⁰₀, 2.9 ohm⁻¹ cm². C₁₀H₁₀ReCl₂ requires: C, 31.20; H, 2.62; Cl, 18.42%. (C₅H₅)₂ReBr₂; found: C, 5. L. H. Green, J. A. McClaveyty, L. Pratt and G. Wilkinson, J. chem. Soc. [London] 1961, 4854; E. O. Fischer and Y. Heintzii, Z. Naturforsch. 15 b, 135 [1960].

² D. F. S. Shriver, J. Amer. chem. Soc. 85, 3509 [1963].

25.43; H, 2.73; Br, 33.3%. A²⁰₀, 3.0 ohm⁻¹ cm². C₁₀H₁₀Br₂W requires: C, 25.34; H, 2.13; Br, 33.7%. (C₅H₅)₁₂W₂Cl₄; found: C, 21.18; H, 1.95; I, 44.77%. A²⁰₀, 10.0 ohm⁻¹ cm². C₁₀H₁₀Br₂W requires: C, 21.14; H, 1.77; I, 44.69%.] The analogous molybdenum complexes have been similarly characterised. The di-iodides (C₅H₅)₂M₂I₄, where M = Mo or W, may also be prepared by treatment of ethereal solutions of the di-hydrides (I) with iodine. The complex C₁₀H₁₀WCl₂ has been reported previously⁶; it was isolated from the reaction mixture obtained from sodium cyclopentadienide and tungsten hexachloride.

The complexes (V) dissolve with slow hydrolysis in cold water. They are only very slightly soluble in chloroform but dissolve in liquid sulphur dioxide to give deep red solutions from which they may be recrystallised. Proton magnetic resonance data from these solutions show the equivalence of the cyclopentadienyl rings and confirm the absence of an M—H system. Due to their low solubility molecular weight measurements have been found to be of low accuracy, but the results show that the complexes should be monomeric.

The infra-red spectra of the complexes (III), (IV) and (V), measured in nujol and hexachlorobutadiene mulls between 4000 and 200 cm⁻¹, show bands typical of a τ-cyclopentadienyl-metal system; principal bands appear in the NaCl regions at 3100, 1420, 1115, 1000 and 850 cm⁻¹. Comparison of spectra in the region 350 to 200 cm⁻¹ for the chloro- and bromo-complexes (III; M = Mo or W, X = Cl or Br) indicate that strong bands at 311, 296 and 273 cm⁻¹ for [(C₅H₅)₂WCl₃]⁺Cl⁻ and at 334, 312 and 293 cm⁻¹ for [(C₅H₅)₂MoCl₃]⁺Cl⁻ may be assigned to M—Cl stretching frequencies. [M—Cl] = 1.07; calculated: [M—Cl] = 1.072.

It has been suggested that bicsyclopentadienyl-rhenium halide species might be formed during the preparation of (C₅H₅)₂ReH, (II), from the reaction of sodium cyclopentadienide and rhenium pentachloride. The isolation of the complex (IV; X = Cl) supports this suggestion and the previous failure to isolate this complex may have been due to its insolubility. The isolation of the complexes (III), (IV) and (V) provides insight into the mechanism of the formation of the complexes (I) and (II) from sodium cyclopentadienide and metal halides. Since all the complex halides (III), (IV) and (V) are reduced by lithium aluminium hydride in ether to the corresponding hydrides (I) or (II) in good yields.

Preliminary studies indicate that the complexes (III) and (IV) dissolve in strong hydrochloric acid affording cationic species and that the complexes (V) react with Lewis acids such as boron trifluoride. We thank D.S.I.R. for financial support (to R.L.C.).