Preparations and Reactions of Bis(η-cyclopentadienyl) Compounds containing Covalent Aluminium–Molybdenum or –Tungsten Bonds

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The dihydride $[Mo(\eta\text{-}C_5H_5)_2H_2]$ reacts with $AlMe_3$ to give compounds (II) and (III) containing Mo–Al bonds. Compound (II) reacts with allyl chloride to give the compound $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)_2][PF_6]$. Following treatment of compound (II) with carbon dioxide, the carbonyl compound $[MoBr(\eta\text{-}C_5H_5)_2(CO)][PF_6]$ may be isolated. The dihydride $[W(\eta\text{-}C_5H_5)_2H_2]$ reacts with $AlMe_3$ to give a related tungsten–aluminium compound. The compounds and reactions are discussed.

RECENTLY we described derivatives of bis(η-cyclopentadienyl)-molybdenum or -tungsten containing covalent bonds between the transition metal and lithium[1] or magnesium.[2] The compounds were prepared by the hydrocarbon-elimination reaction (1). Here we describe

$$M\text{-}H + R\text{-}M' \longrightarrow M\text{-}M' + RH \qquad (1)$$
$$(M = Mo \text{ or } W,\ M' = Li \text{ or } Mg)$$

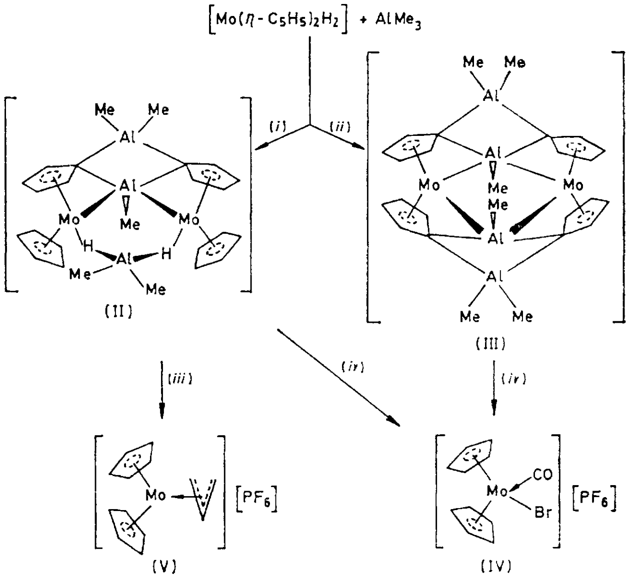
the preparation and some reactions of related compounds containing covalent M–Al bonds. This work has been briefly communicated.[3,4]

RESULTS

The dihydride $[Mo(\eta\text{-}C_5H_5)_2H_2]$, (I), forms a 1 : 1 adduct with trimethylaluminium, $[Mo(AlMe_3)(\eta\text{-}C_5H_5)_2H_2]$.[5] We observed that in hot toluene (I) readily undergoes further reaction with $AlMe_3$ with evolution of methane (g.l.c.). When concentrated solutions were used orange crystals separated from the reaction mixture after 7—10 min. Two independent determinations of the crystal structure show the product (II) to have the structure shown in the Scheme.[3,6] The i.r. spectrum of (II) showed a very broad band at 1 825 cm^{-1} which we tentatively assign to ν(Mo–H) of the Mo–H–Al systems. Heating (I) under reflux in excess of $AlMe_3$ for 6 h gave a yellow crystalline compound and determinations of the crystal structure show it to be as in (III).[3,6] The i.r. evidence for the presence of the group Mo–H was unambiguous, although there was a very weak broad band at *ca.* 1 900 cm^{-1}.

Compound (II) is slightly soluble in toluene whilst (III) is virtually insoluble. Hydrogen-1 n.m.r. spectra could not be obtained for either (II) or (III). Both compounds (II) and (III) may inflame in air and they are instantly decomposed by water to the parent dihydride (I). Treatment of a suspension of compounds (II) or (III) in hot benzene with carbon dioxide gave a red solution, and following hydrolysis with hydrobromic acid and addition of ammonium hexafluorophosphate the compound $[MoBr(\eta\text{-}C_5H_5)_2(CO)][PF_6]$, (IV), was formed. Treatment of (II) with allyl chloride caused a rapid reaction and after extraction with water and addition of $[NH_4][PF_6]$ the red η-allyl derivative $[Mo(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)_2][PF_6]$, (V),[4] was formed.

The tungsten dihydride $[W(\eta\text{-}C_5H_5)_2H_2]$ reacted with $AlMe_3$ to give a yellow crystalline compound (VI) which is not isomorphous with either (II) or (III). Compound (VI) is generally similar to both (II) and (III); for example, it is readily oxidised and hydrolysed, and from reaction with allyl bromide or carbon dioxide the compounds $[W(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)_2][PF_6]$, (VII), and $[W(\eta\text{-}C_5H_5)_2(CO)]$, (VIII), are formed respectively. Since (VI) cannot be recrystallised due to its virtual insolubility, the analytical data, which suggest that (VI) is analogous to (III), may not be reliable and a crystal-structure determination is desirable.



SCHEME (*i*) Reflux, toluene, 10 min; (*ii*) reflux, toluene, 6 h; (*iii*) allyl chloride, aqueous $[NH_4][PF_6]$; (*iv*) CO_2, 1 atm, HBr, $[NH_4][PF_6]$

DISCUSSION

Compounds (II) and (III) are amongst the earliest examples of covalent transition-metal–aluminium bonds. It has been proposed that the products of the reaction between $[M(\eta\text{-}C_5H_5)(CO)_3H]$ and $AlMe_3$ (M = Mo) or $AlMe_2H$ (M = W) contained M–Al bonds.[7,8] However, determination of the crystal structure of the tungsten compound showed the aluminium to be bonded to the CO group.[9] The original report of this work prompted

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us to investigate the reaction between (I) and $AlMe_3$ in more detail, especially since there was a report that the adducts $[M(AlMe_3)(\eta\text{-}C_5H_5)_2H_2]$ decomposed with evolution of a gas.[5] Recently, covalent bonding between Ti–H–Al systems has been shown by crystal-structure determinations.[10] The related Zr–H–Al system has also been proposed in some products of the reaction between $[Zr(\eta\text{-}C_5H_5)_2H_2]$ and $AlMe_3$.[11]

The reaction of compounds (II), (III), and (VI) with carbon dioxide giving carbon monoxide derivatives parallels the same reaction with covalent transition-metal–lithium or –magnesium bonds.[12] Finally, we note that the present evidence does not rigorously rule out the possibility that (III) contains a hydrogen ligand attached to each molybdenum in a *trans* manner, although the highly symmetrical structure of (III) suggests that this is unlikely.

EXPERIMENTAL

All preparations and manipulations were in the absence of oxygen. Solvents were dried by reflux over and distillation from calcium hydride. I.r. spectra were recorded for mulls on a Perkin-Elmer 457 spectrometer and were calibrated with polystyrene film. Hydrogen-1 n.m.r. spectra were obtained on a JEOL 60 MHz instrument. The compounds $[M(\eta\text{-}C_5H_5)_2H_2]$ (M = Mo or W) were prepared as previously described.[13] Trimethylaluminium was as provided by Alfa Inorganics.

Compound (II).—Trimethylaluminium (5.0 g) in toluene (25 cm^3) was added to pure bis(η-cyclopentadienyl)dihydridomolybdenum (2.6 g). The mixture was stirred and further toluene (15 cm^3) was added giving a clear red solution. This was placed briefly in an oil-bath preheated to 125 °C until vigorous gas evolution occurred. The solution was removed from the oil-bath until the gas evolution subsided. The process was repeated until after 8 min crystals started to form. The solution was then allowed to stand at room temperature overnight giving large orange crystals. The latter were separated and washed thoroughly with dry toluene, then light petroleum, and dried *in vacuo*, yield *ca.* 80%. Analytical data: C, 50.6 (49.4); H, 6.2 (5.8); Al, 12.5 (13.3); Mo, 30.5 (30.5)%. M.p. 230 °C (decomp.).

Compound (III).—Bis(η-cyclopentadienyl)dihydridomolybdenum (7.5 g) as a slurry in toluene (200 cm^3) was treated with Al_2Me_6 (13.3 g) in toluene (70 cm^3). The resulting clear red solution was heated at 90 °C (2 h), whilst rapid gas evolution occurred, and then at 110 °C (for 6 h). After 1.5 h the reaction mixture was left to stand at room temperature overnight. Yellow crystals separated which were washed thoroughly with toluene and light petroleum and then dried *in vacuo*, yield *ca.* 80%.

Reaction between $[W(\eta\text{-}C_5H_5)_2H_2]$ *and* Al_2Me_6.—The dihydride (3.65 g) in toluene (50 cm^3) at 60 °C was treated with Al_2Me_6 (5.5 g) in toluene (30 cm^3). The mixture was heated to 115 °C (3 h) during which time a steady stream of gas was evolved. The solution was allowed to stand at room temperature for 12 h and the yellow crystals which separated were washed thoroughly with toluene and light petroleum and finally dried *in vacuo*, *ca.* 85%. Analytical data: C, 37.6 (38.2); H, 4.7 (4.7); Al, 10.55 (10.3); W, 47.1 (46.9)%, calculated for $C_{25}H_{35}Al_3W_2$, (VI).

(η-*Allyl*)*bis*(η-*cyclopentadienyl*)*molybdenum Hexafluorophosphate*, (V).—A slurry of compound (II) (2.5 g) in dry benzene (75 cm^3) was treated with freshly distilled allyl chloride (1.0 cm^3). Reaction was immediate giving a dark red solution. This was warmed to 50 °C for 30 min and an oily red precipitate separated. The reaction mixture was cooled in ice and continuously hydrolysed with dilute hydrochloric acid giving a red aqueous layer. The layer was separated, treated with sodium hydroxide until it was just alkaline, and the precipitated dihydride was separated by filtration. The clear red aqueous filtrate was treated with an aqueous solution of $[NH_4][PF_6]$ giving a red precipitate which was collected, washed with diethyl ether, and recrystallised from acetone–diethyl ether, then acetone–ethanol, as large red crystals which were dried *in vacuo*, *ca.* 1.4 g. Analytical data: C, 37.6 (37.9); H, 3.5 (3.7)%. ^{1}H N.m.r. spectrum in $S(CD_3)_2O$ [chemical shift, *relative intensity*, **multiplicity** (J in Hz), assignment]: 4.57, *5*, **s**, η-C_5H_5; 4.81, *5*, **s**, η-C_5H_5; 5.88, *1*, **triplet of triplets** (J_{anti} 15, J_{syn} 9), CH; 6.56, *2*, **doublet of doublets** (J_{syn} 9, J_{gem} 4), $H_{2,syn}$; 7.53, *2*, **doublet of doublets** (J_{anti} 15, J_{gem} 4), $H_{2,anti}$.

Bromocarbonylbis(η-*cyclopentadienyl*)*molybdenum Hexafluorophosphate*, (IV).—A suspension of compound (II) (0.5 g) in hot benzene (75 °C, 200 cm^3) was treated with carbon dioxide gas for 30 min. The solution became red and was then cooled and cautiously hydrolysed with dilute hydrobromic acid (10 cm^3). The red aqueous layer was separated and treated with $[NH_4][PF_6]$ to give a red-purple precipitate. This was recrystallised first from acetone–water and then from acetone–diethyl ether giving red-purple crystals which were identified by comparison of the i.r. spectrum with that of an authentic sample of $[MoBr(\eta\text{-}C_5H_5)_2(CO)][PF_6]$, yield *ca.* 25%.

Bromocarbonylbis(η-*cyclopentadienyl*)*molybdenum Hexafluorophosphate*.—The compound $[MoBr(\eta\text{-}C_5H_5)_2(SMe_2)][PF_6]$ (0.5 g), prepared as described,[14] in acetone (40 cm^3) was treated with a stream of carbon monoxide. The mixture was heated under reflux and gradually became red. After 30 min the mixture was allowed to cool to room temperature and was filtered. The red filtrate was concentrated by slow removal of solvent under reduced pressure. The red crystals obtained were collected, washed with diethyl ether, and dried *in vacuo*. Recrystallisation was from acetone–diethyl ether or acetone–ethanol, *ca.* 80%. Analytical data: C, 27.7 (27.6); H, 2.3 (2.3)%. ν(CO) at 2 015 cm^{-1} (mull). ^{1}H N.m.r. spectrum in $(CD_3)_2CO$; τ 3.81, *s*, $(\eta\text{-}C_5H_5)_2$. The tungsten analogue $[WBr(\eta\text{-}C_5H_5)_2(CO)][PF_6]$ was similarly prepared, *ca.* 80%. Analytical data: C, 23.7 (23.5); 2.0 (2.0)%. ν(CO) at 2 060 cm^{-1} (mull). ^{1}H N.m.r. spectrum in $(CD_3)_2CO$; τ 3.88, *s*, $(\eta\text{-}C_5H_5)_2$.

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