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STUDIES ON BIS(BOROHYDRIDE) DERIVATIVES OF DI-π-CYCLOPENTADIENYLMOLYBDENUM(VI) AND -TUNGSTEN(VI)

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SUMMARY

The interaction of di-π-cyclopentadienylmolybdenum(VI) oxide dichloride (I) and di-π-cyclopentadienyltungsten(VI) oxide dichloride (II) with sodium borohydride in tetrahydrofuran, results in the formation of bis(borohydride) derivatives of (I) and (II) having the general formula, $(\pi\text{-}C_5H_5)_2MO(BH_4)_2$, where M = Mo or W. IR spectra, thermal stabilities and other chracteristics of these compounds are reported.

INTRODUCTION

The first transition metal borohydride complexes were reported by Katz and coworkers[3] and since then a large number of transition metal compounds containing the BH_4^- group bonded to them have been isolated and characterized[4-10]. Nöth and coworkers[11] prepared di-π-cyclopentadienyltitanium(III) borohydride and studies on the preparation of similar compounds of titanium[12], zirconium and hafnium have been reported by Wallbridge and coworkers[13-15]. So far no work on the preparation of borohydride derivatives of molybdenum and tungsten complexes containing π-cyclopentadienyl groups has been reported.

Our studies on alkoxy[16], alkyl, aryl[17] and coordination derivatives[18] of di-π-cyclopentadienylmolybdenum oxide dichloride (I)[1] as well as of di-π-cyclopentadienyltungsten oxide dichloride (II)[2] have already been reported. The present investigation deals with the preparation of bis(borohydride) derivatives of the general formula $(\pi\text{-}C_5H_5)_2MO(BH_4)_2$, by the interaction of sodium borohydride with (I) and (II) in THF, where M = Mo or W. These orange-yellow compounds are volatile, quite stable in dry inert atmosphere, soluble in organic solvents and unstable in presence of water, dilute acids and alkalies even at room temperature. The compounds sublime and melt with slight decomposition. IR studies indicate metal–boron bonding through hydrogen atoms of the BH_4^- radical, analogous to other similar compounds[4-10,13-15].

EXPERIMENTAL

All operations were carried out under anhydrous conditions using purified solvents. Di-π-cyclopentadienylmolybdenum oxide dichloride as well as di-π-cyclopentadienyltungsten oxide dichloride were prepared by the methods previously described[1,2].

Preparation of di-π-cyclopentadienylmolybdenum oxide bis(borohydride)

Sodium borohydride (1.0 g; 0.026 mole) was added to $(\pi\text{-}C_5H_5)_2MoOCl_2$ (3.13 g; 0.01 mole) in tetrahydrofuran (120 ml) and the reaction mixture was stirred for 3–4 h till an orange colour appeared. The mixture was then heated to 100–105° for 1–1.5 h to complete the reaction. Sodium chloride was removed by filtration and the orange filtrate on drying under reduced pressure (5–10 mm) yielded an orange yellow waxy compound which, after washing with petroleum ether/chloroform (1/1) and drying under reduced pressure (2–3 mm) gave orange red crystals of $(\pi\text{-}C_5H_5)_2\text{-}MoO(BH_4)_2$, m.p. 115–110°. It is highly soluble in organic solvents and sublimes at 94–95° under vacuum. (Found: C, 32.3; H, 6.6; Mo, 48.4. $C_{10}H_{18}B_2MoO$ calcd.: C, 32; H, 6.54; Mo, 48.50%.)

Preparation of di-π-cyclopentadienyltungsten oxide bis(borohydride)

The preparation of $(\pi\text{-}C_5H_5)_2WO(BH_4)_2$ was carried out under similar conditions. The orange-yellow product had m.p. 144–145° and sublimed at 110–112° under vacuum. (Found: C, 37.3; H, 5.1; W, 47.8. $C_{10}H_{18}B_2OW$ calcd.: C, 37.43; H, 5.04; W, 47.75%.)

Infrared spectra

IR spectra, recorded on a Perkin–Elmer Infracord spectrophotometer Model 137 in KBr and nujol, gave the following absorption peaks:

$(\pi\text{-}C_5H_5)_2MoO(BH_4)_2$. 3020 m, 2350 s, 2245 m, 1820 vw, 1650 w, 1470 m, 1340 m, 1290 w, 1125 s, 1010 m, 945 m and 828 m cm^{-1}.

$(\pi\text{-}C_5H_5)_2WO(BH_4)_2$. 3040 m, 2370 s, 2280 s, 1670 s, 1480 m, 1350 m, 1260 w, 1120 s, 1005 m, 950 s and 830 s cm^{-1}.

DISCUSSION

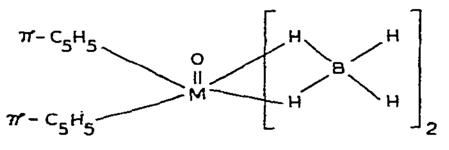
The IR spectra of $(\pi\text{-}C_5H_5)_2MoO(BH_4)_2$ and $(\pi\text{-}C_5H_5)_2WO(BH_4)_2$ are strikingly similar. The spectra of the compounds show (besides usual $\pi\text{-}C_5H_5$ group absorptions[19]) strong absorption bands due to the BH_4^- group at ~2300 and ~1100 cm^{-1}, which may be due to B–H stretching and BH_2 deformation modes respectively[4,16,20,21] while the bands at ~2250 and ~1350 cm^{-1} may be due to vibrations of bridging hydrogen atoms[14,15]. Furthermore, the bands at ~950 cm^{-1} may result from the presence of the M=O linkage as observed in the case of $MoOCl_4$ and $WOCl_4$[22].

On the basis of the already known interaction of WCl_6 or $MoCl_4$ with NaC_5H_5 in presence of sodium borohydride [resulting in the formation of $(\pi\text{-}C_5H_5)_2MoH_2$ or its W analogue[23]], it was expected during the present investigation that the analogous dihydride complexes would be formed. The resulting compounds however corresponded to $(\pi\text{-}C_5H_5)_2MoO(BH_4)_2$ and $(\pi\text{-}C_5H_5)_2WO(BH_4)_2$, which may be due to the usual exchange reaction between Cl^- and BH_4^- radicals:

$$(\pi\text{-}C_5H_5)_2MOCl_2 + 2\,NaBH_4 \rightarrow (\pi\text{-}C_5H_5)_2MO(BH_4)_2 + 2\,NaCl$$

(M = Mo or W)

The type of bonding observed in these compounds, seems to be analogous to the bonding postulated for classical metal borohydrides, as well as for di-π-cyclopentadienylmetal borohydride derivatives of Group IVA metals[11-15]. The IR spectra of $(\pi\text{-}C_5H_5)_2MoO(BH_4)_2$ and $(\pi\text{-}C_5H_5)_2WO(BH_4)_2$ clearly indicate bond formation between metal and boron through hydrogen, analogous to the structures assigned to copper borohydride complex on the basis of X-ray crystallography[10], aluminium tris(borohydride) by X-ray diffraction studies[9] and for di-π-cyclopentadienylmetal mono- or bis(borohydride) derivatives of Group IVA metals, on the basis of IR as well as of NMR spectral measurements[11-15]. It appears that the similar metal–hydrogen–boron bond formation may be involved in the compounds, $(\pi\text{-}C_5H_5)_2MO(BH_4)_2$ (where M = Mo or W), wherein the cyclopentadienyl radical retains delocalized π-bonded character.



(where M = Mo or W)

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