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HYDRIDO COMPLEXES OF ZIRCONIUM
I. PREPARATION

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SUMMARY

Syntheses of $(\pi\text{-}C_5H_5)_2ZrH_2$ and of the new zirconium hydrides $(\pi\text{-}C_5H_5)_2Zr(H)Cl$, $(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$, $(\pi\text{-}C_5H_5)_2Zr(H)CH_3$ and $[(\pi\text{-}C_5H_5)_2ZrH]_2O$. $(\pi\text{-}C_5H_5)_2ZrH_2$ are described. Deuterides corresponding to all of the above hydrides have been prepared. In all of the compounds hydrido ligands bridge between neighbouring zirconium atoms so that the compounds are associated and relatively insoluble.

INTRODUCTION

The relatively recent realization of the importance of hydrido complexes of the transition metals in certain catalytic processes has helped to draw attention to this type of compound containing hydrogen as a ligand. Many transition metals form hydrido derivatives[1,2] but amongst the Group IVA elements, only three hydrides have been characterized. $(\pi\text{-}C_5H_5)_2ZrH_2$ and $(\pi\text{-}C_5H_5)_2Zr(H)BH_4$ were prepared by the action of trialkylamines on the bis(tetrahydroborate)[3], $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$, while more recently the violet, unstable $[(\pi\text{-}C_5H_5)_2TiH]_2$ has been isolated[4].

A more direct approach to the synthesis of zirconium hydrides was found while investigating the action of certain aluminium hydrides on cyclopentadienylzirconium halides. In this paper a new synthesis of $(\pi\text{-}C_5H_5)_2ZrH_2$ and of four new zirconium hydrides is described*. These hydrides show unusual reactivity towards multiply bonded compounds which will be described in later papers.

RESULTS AND DISCUSSION

The oxo-bridged compound $(\pi\text{-}C_5H_5)_2Zr(Cl)OZr(Cl)(\pi\text{-}C_5H_5)_2$[6,7] when treated with an equimolar amount of $LiAlH_4$ in tetrahydrofuran, was slowly converted to the insoluble dihydride $(\pi\text{-}C_5H_5)_2ZrH_2$, (I).

$$[(\pi\text{-}C_5H_5)_2ZrCl]_2O + LiAlH_4 \rightarrow \underset{\text{(I)}}{2(\pi\text{-}C_5H_5)_2ZrH_2} + LiCl + \text{"}[AlOCl]\text{"}_2$$

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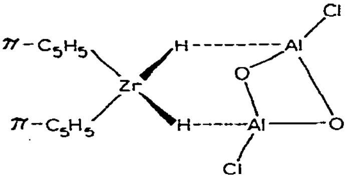
* A preliminary account of part of this work has been published[5].

The nature of the aluminium compound remaining in solution is not clear. Despite the negligible solubility of the product (I), the yield never exceeds 66% so that a by-product must be some soluble complex of zirconium and aluminium. The red colour of the reaction solution lends support to the presence of [AlOCl] since this type of compound is known to form red colours in donor solvents[8]. All of the zirconium hydrides described in this paper dissolve on adding an excess of $LiAlH_4$, so that it appears likely that soluble adducts between zirconium hydrides and aluminium compounds are readily formed and can exist in donor solvents such as tetrahydrofuran. A structure of type (II) is possible for the adduct but others in which the H, O and Cl are interchanged must also be considered. The PMR spectrum showed a broad band in the cyclopentadienyl region centred at δ 6.23 ppm. The IR spectrum of (I) is virtually identical with that published by James, Nanda and Wallbridge[3]. The sharp band at 1520 and a broad strong band at 1300 cm^{-1} are associated with hydrido ligands bridging between two zirconium atoms. The extreme insolubility of this compound indicates that the bridging hydrogens form a polymeric network, the extent of which is not yet know.



(II)

The same dihydride (I) was obtained in lower yield when four moles of LiAl(O-t-Bu)$_3$H[9] were used to reduce the oxo-bridged zirconium compound. With only two moles of LiAl(O-t-Bu)$_3$H an insoluble complex of formula $[(\pi\text{-}C_5H_5)_2ZrH]_2O \cdot (\pi\text{-}C_5H_5)_2ZrH_2$ (III), was precipitated. All of the hydridic protons of (III) could be quantitatively hydrolysed with acid, while with CH_2Cl_2 the adduct was converted to $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ and $(\pi\text{-}C_5H_5)_2ZrCl_2$, the hydridic hydrogens forming CH_3Cl with the solvent. All of these products were identified by their characteristic PMR spectra.

The IR spectrum of (III) shows three bands due to bridging hydrido groups; a very broad band centred at 1510, and sharper bands at 1385 and 1240 cm^{-1}. All of these are shifted to lower wavelengths on deuteration (Table 1).

TABLE 1

IR FREQUENCIES[a] OF HYDRIDES AND DEUTERIDES

Compound	Zr–H	Zr–D
$(\pi\text{-}C_5H_5)_2ZrH_2$ (I)	1520, 1300 (br)	1100, 960 (br)
$[(\pi\text{-}C_5H_5)_2ZrH]_2O \cdot (\pi\text{-}C_5H_5)_2ZrH_2$ (III)	1510 (br), 1385, 1240	1075 (br), 1025, 905
$(\pi\text{-}C_5H_5)_2Zr(H)Cl$ (IV)	1390 (br)	1020[b] (br)
$(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$ (V)	1425 (br)	1055 (br)
	[1790, 1700 (AlH_4)]	[1310, 1260 (AlD_4)]
$(\pi\text{-}C_5H_5)_2Zr(H)CH_3$ (VI)	1500, 1310 (br)	1090, 965 (br)

[a] Frequencies in cm^{-1}, KBr disc. [b] Overlapping with the C–H deform. of $(\pi\text{-}C_5H_5)$.

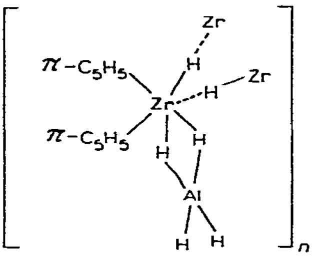
From (π-C_5H_5)$_2$$ZrCl_2$ and exactly one-quarter mole of $LiAlH_4$ or one mole of LiAl(O-t-Bu)$_3$H, the hydridochloride (π-C_5H_5)$_2$Zr(H)Cl (IV) was obtained in high yield as a white solid insoluble in tetrahydrofuran. The IR spectrum of (IV) shows only one broad band in the bridging hydride region (at 1390 cm^{-1}), although its insolubility indicates a polymeric structure similar to that existing in the dihydride (I).

An interesting alternative preparation of (IV) is by magnesium metal reduction of (π-C_5H_5)$_2$$ZrCl_2$. The reaction will proceed only in tetrahydrofuran, presumably by abstraction of hydrogen from this solvent. The solution becomes deep red in colour and the hydride (IV) precipitates in about 30% yield. It is identical in every respect with the product obtained from the aluminium hydride reaction.

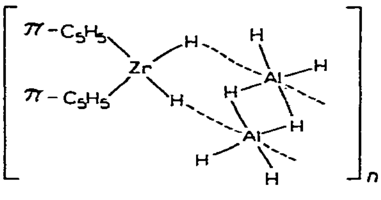
When a further quantity of $LiAlH_4$ (1 mole) was added to a suspension of (π-C_5H_5)$_2$Zr(H)Cl in tetrahydrofuran a clear solution resulted. After removal of lithium chloride by addition of benzene, a new hydride, (π-C_5H_5)$_2$Zr(H)AlH_4 (V), slowly precipitated from the benzene/tetrahydrofuran solution. This compound shows, in addition to the absorption band in the IR spectrum at 1425 cm^{-1} due to the bridging hydride, two more bands at 1790 and 1700 cm^{-1} due to AlH_4.

The solubility of (V) is rather greater than that of the other hydrido derivatives, but nevertheless attempts to obtain a PMR spectrum were not successful. It is to be expected that rapid exchange of all of the hydridic protons can occur[3], and this apparently destroys any resolution in the PMR spectrum. None of the other hydrides were soluble enough for PMR spectral measurements.

The aluminium complex (V) has little similarity to the boron compound of similar formula[3]. (π-C_5H_5)$_2$Zr(H)BH_4 is thermally stable and can be sublimed at 60° under reduced pressure; its IR spectrum does not show the band around 1400 cm^{-1} associated with bridging hydride, and the BH_4 group is believed to be bonded to zirconium by a double hydrogen bridge[3,10]. (π-C_5H_5)$_2$Zr(H)AlH_4 (V) on the other hand is thermally unstable and begins to decompose in solvents at 60° (see below); its IR spectrum shows a broad strong band at 1425 cm^{-1} indicating Zr–H–Zr, so that it is to some extent polymerized and therefore involatile. Although it is more convenient to regard this compound as an oligomer of the unit (Va) shown below, the possibility exists that (V) is an adduct of a zirconium hydride with an aluminium hydride, *e.g.* as in (Vb):



(Va)



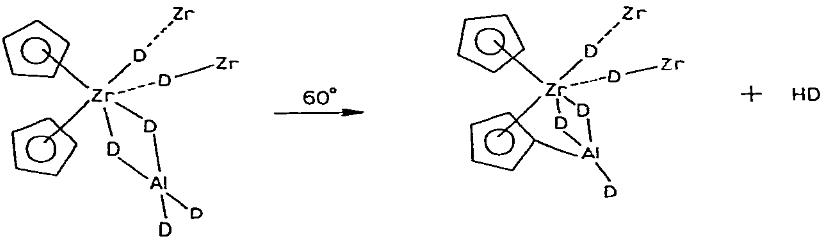
(Vb)

Dicyclopentadienylmethylzirconium chloride, (π-C_5H_5)$_2$Zr(Cl)CH_3, prepared by the action of trimethylaluminium on (π-C_5H_5)$_2$Zr(Cl)OZr(Cl)(π-C_5H_5)$_2$[11], can also be converted to a hydrido compound, (π-C_5H_5)$_2$Zr(H)CH_3 (VI), by the action of

$LiAlH_4$ or $LiAl(O\text{-t-Bu})_3H$. The IR spectrum of (VI) is more closely related to that of the dihydride (I) than to the other hydride spectra, since it shows broad strong bands at 1500 and 1310 cm^{-1} (Table 1).

All of the compounds described may be prepared as deuterides by using $LiAlD_4$ or $LiAl(O\text{-t-Bu})_3D$ as reducing agents. The shapes and intensities of the IR bands are almost identical in both hydride and deuteride, but the bands due to bridging hydride are shifted to lower wavennumbers by a factor between 1/1.35 and 1/1.38 in each case on deuteration. Frequencies are shown in Table 1.

All of the hydrides are sensitive to heat and to light, turning purple or red in colour. Except for (V), this colour change is not accompanied by any loss of hydrogen or change in the IR spectrum, but pyrolysis of the aluminohydride derivative (V), which begins in a solvent at 60°, liberates one mole of hydrogen giving a deep red diamagnetic product. The band due to Zr–H–Zr is still evident in the spectrum at 1380 cm^{-1}, indicating that this part of the molecule is unchanged. If the deuterated compound $(\pi\text{-}C_5H_5)_2Zr(D)AlD_4$, is pyrolyzed in the solid state then the gas evolved is HD (identified by mass spectrometry), so that the cyclopentadienyl rings are participating and are propably bonding to the aluminium atoms; *e.g.*:



In common with many other metal hydrides, the zirconium derivatives react with chlorinated solvents, exothermally in the case of chloroform and slowly with methylene dichloride, replacing the hydrido ligand by chloride. By-products are CH_2Cl_2 (in chloroform) and CH_3Cl (in methylene dichloride), so that quantitative measurement of the PMR spectrum of the products of this reaction is a useful technique for the analysis of hydrides.

EXPERIMENTAL

General

All hydrides were assumed to be sensitive to air and were handled under argon using a Schlenk tube system, or in a nitrogen-filled glovebox. Products were analysed by ashing to ZrO_2 and by hydrolysis of a weighed sample in a vacuum line with 50% H_2SO_4, gas evolved (H_2 or D_2) being pumped into a calibrated volume by means of a Töpler pump, where it was accurately measured. Hydrolysis proved to be a better and faster indication of purity than any other analytical technique.

Materials

Standardized solutions of $LiAlH_4$ were prepared by stirring $LiAlH_4$ in purified tetrahydrofuran for some hours, filtering under argon through Celite (previously baked out at 140° and degassed by evacuation) followed by hydrolysis of an aliquot of this solution with dilute acid on the vacuum line and accurate measurement of the hydrogen evolved. When stored under argon these standardized solutions remained unchanged for several weeks. Solutions of $LiAlD_4$ (from Merck, Sharp and Dohme Isotopic Products, Montreal) were prepared in the same way. $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ was prepared by the following adaptation of the original published method[6,7], which gives consistently high yields.

Preparation

Aniline (10 ml) and water (1.3 ml) were added to a solution of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (30 g) in methylene dichloride (250 ml) and the mixture was shaken thoroughly. A white precipitate of aniline hydrochloride formed immediately. After chilling overnight in the refrigerator, the suspension was filtered cold. At times large crystals of the product are present at this stage, which must be redissolved by addition of more CH_2Cl_2. The filtrate was evaporated to small volume and petrol (100 ml, b.p. 30–40°) was added to precipitate the product. Filtration and petrol washing gave white crystals of the oxo-bridged compound (26.5 g, 97% yield). The m.p. varies greatly with the rate of heating but if the sample in an evacuated capillary is placed in a melting point apparatus preheated to 260°, m.p's around 305° should be obtained.

Preparation of hydrides

$(\pi\text{-}C_5H_5)_2ZrH_2$ (I)

A clear solution of $LiAlH_4$ in tetrahydrofuran (20 ml of 1.7 molar, 34 mmoles) was added dropwise to a solution of $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ (17.7 g, 33.4 mmoles) in tetrahydrofuran (200 ml). A white precipitate slowly appeated but precipitation was not complete for several hours. The mixture was set aside overnight and then filtered giving the dihydride as an almost white micro-crystalline solid (10.1 g, 66% yield). [Found: ash (ZrO_2), 55.5; hydrolyzable H, 1.99 g-atom/mole. $C_{10}H_{12}Zr$ calcd.: ash (ZrO_2), 55.14%; hydrolyzable H, 2.00 g-atom/mole.]

$[(\pi\text{-}C_5H_5)_2ZrH]_2O\cdot(\pi\text{-}C_5H_5)_2ZrH_2]$

A solution of $LiAl(O\text{-}t\text{-}Bu)_3H$ (9.35 g, 36 mmoles) in tetrahydrofuran (50 ml) was added to $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ (9.72 g, 18 mmoles) in tetrahydrofuran (120 ml). The solution darkened appreciably and a precipitate appeared on stirring overnight. It was collected by filtration and washed with tetrahydrofuran, then pumped dry to give the pale pink complex $[(\pi\text{-}C_5H_5)_2ZrH]_2O\cdot(\pi\text{-}C_5H_5)_2ZrH_2$ (III) (2.0 g, 25% yield). [Found: C, 52.7; H, 5.0; ash (ZrO_2), 53.6; hydrolyzable H, 4.04 g-atom/mole. $C_{30}H_{34}OZr_3$ calcd.: C, 52.71; H, 5.01; ash (ZrO_2) 54.08%; hydrolyzable H, 4.00 g-atom/mole.] In CH_2Cl_2 the complex slowly dissolved; the PMR spectrum of the solution showed proton peaks due to $(\pi\text{-}C_5H_5)_2ZrCl_2$ (δ 6.41 ppm), $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ (δ 6.24 ppm) and CH_3Cl (δ 2.96 ppm) in the ratio 10/20/9 [some CH_3Cl lost due to low b.p. (−24°)].

$(\pi\text{-}C_5H_5)_2Zr(H)Cl$ (IV)

(*a*). $LiAl(O\text{-}t\text{-}Bu)_3H$ (28.6 g, 113 mmoles) in tetrahydrofuran (100 ml) was added slowly to a solution of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (32.9 g, 113 mmoles) in tetrahydrofuran (500 ml) with stirring. After addition was complete stirring was continued for approx. 1 h after which the product was collected by filtration and washed with tetrahydrofuran. The hydridochloride was obtained as a white solid (26.3 g, 90% yield) turning pink in light. [Found: Cl, 13.4; ash (ZrO_2), 47.0; hydrolyzable H, 1.02 g-atom/

mole. $C_{10}H_{11}ClZr$ calcd.: Cl, 13.75; ash (ZrO_2), 47.77%; hydrolyzable H, 1.00 g-atom/mole.]

(*b*). $(\pi\text{-}C_5H_5)_2ZrCl_2$ (17.5 g, 60 mmoles) in tetrahydrofuran (90 ml) was stirred with Grignard magnesium (0.72 g, 30 mmoles) for several days. The colour turned reddish-brown almost immediately and gradually deepened in intensity. After 3–5 days the precipitate present was collected by filtration, washed twice with tetrahydrofuran and pumped dry giving a pale pink solid (4.5 g, 30% yield) identical in every respect with the hydridochloride obtained as in (a) above. [Found: Cl, 13.3; ash (ZrO_2), 47.5; hydrolyzable H, 1.03 g-atom/mole. $C_{10}H_{11}ClZr$ calcd.: Cl, 13.75; ash (ZrO_2), 47.77%; hydrolyzable H, 1.00 g-atom/mole.]

$(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$ (IV)

To a suspension of $(\pi\text{-}C_5H_5)_2Zr(H)Cl$ (2.05 g, 8 mmoles) in tetrahydrofuran (15 ml) was added a clear solution of $LiAlH_4$ in tetrahydrofuran (4.6 ml of 1.72 molar, 8 mmoles) with stirring. The solid dissolved to give a clear mauve-coloured solution to which was added benzene (15 ml). After 1 h precipitated LiCl was removed by filtration and another 10 ml of benzene was added to the filtrate. On chilling the aluminohydride crystallized slowly and was later collected by filtration as a white solid (0.65 g, 30% yield), very sensitive to light, heat and air. [Found: ash ($ZrO_2+\frac{1}{2}Al_2O_3$), 67.5, 69.7; hydrolyzable H, 5.01 g-atom/mole $C_{10}H_{15}AlZr$ calcd.: ash ($ZrO_2+\frac{1}{2}$ Al_2O_3), 68.8%; hydrolyzable H, 5.00 g-atom/mole.]

$(\pi\text{-}C_5H_5)_2Zr(H)CH_3)$ (V)

To a solution of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ (1.3 g, 4.8 mmoles) in tetrahydrofuran (15 ml) was added dropwise a clear solution of $LiAlH_4$ in tetrahydrofuran (0.60 ml of 2.0 molar, 1.2 mmoles). The white precipitate which appeared immediately was collected after 1 h stirring and was washed with tetrahydrofuran. The hydridomethyl derivative (0.46 g, 41% yield) so obtained was also sensitive to light and hydrolyzed readily in acid giving hydrogen and methane (identified by gas IR). [Found: ash (ZrO_2), 52.6; gas on hydrolysis (H_2+CH_4), 1.98 mole/mole. $C_{11}H_{14}Zr$ calcd.: (ZrO_2), 52.0%; gas on hydrolysis (H_2+CH_4), 2.00 mole/mole.]

Deuterides

Deuterides corresponding to all of the above hydrides were prepared and characterized in exactly the same manner as above, using $LiAlD_4$ or $LiAl(O\text{-}t\text{-}Bu)_3D$ instead of $LiAlH_4$. In all cases yields were somewhat lower than with the corresponding hydride.

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