

HYDRIDO COMPLEXES OF ZIRCONIUM II. REACTIONS OF DICYCLOPENTADIENYLZIRCONIUM DIHYDRIDE WITH CARBOXYLIC ACIDS

P. C. WAILES AND H. WEIGOLD

Division of Applied Chemistry, C.S.I.R.O. Chemical Research Laboratories, P.O. Box 4331, Melbourne, Victoria, 3001 (Australia)

(Received April 13th, 1970)

SUMMARY

Reaction between $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ and carboxylic acids can result in the formation of acylates or alkoxides depending on the mode of addition. With the carboxylic acid in excess acylates are formed; for example $\pi\text{-C}_5\text{H}_5\text{Zr}(\text{OCOCH}_3)_3$ with acetic acid and $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{OCOCF}_3)_2$ with trifluoroacetic acid. When $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ is in excess, reduction of the acids occurs and leads to novel bridging alkoxides.

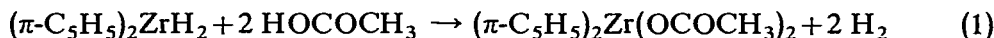
INTRODUCTION

The unique reactivity which many metal hydrides display towards compounds containing double or triple bonds or acidic protons is now well documented¹, but as yet the reactivity of the cyclopentadienylzirconium hydrides towards reagents of this type has not been explored. These hydrides, which are readily prepared by the methods described in the preceding paper², have been found to undergo reactions with a wide range of compounds, which will be described in this and subsequent papers.

RESULTS AND DISCUSSION

In reactions with carboxylic acids the dihydride, $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$, was expected to give simple acylates with elimination of hydrogen, but under certain conditions the reactions took a different course.

In an attempt to prepare the diacetate, $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{OCOCH}_3)_2$, by adding acetic acid to $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ in tetrahydrofuran, it was found that the amount of hydrogen evolved was always less than that required by eqn. (1):

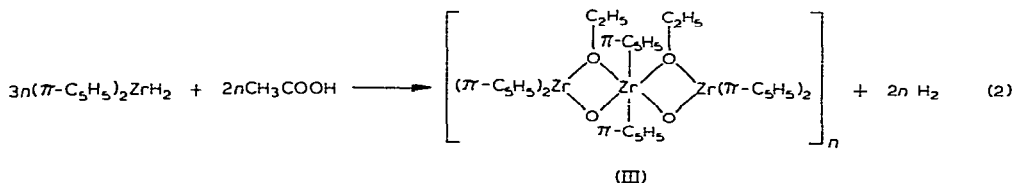


Since the white product was a mixture, it was apparent that some reduction was taking place. By slow addition of $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ to a large excess of acetic acid, this reduction was eliminated and the expected amount of hydrogen was evolved, but the triacetate, $\pi\text{-C}_5\text{H}_5\text{Zr}(\text{OCOCH}_3)_3$ (II), was obtained instead of the diacetate. Removal of a cyclopentadienyl group by acetic acid was observed also by Brainina and Freid-

lina³, who obtained (II) by heating $(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ in acetic acid at 105° for 9 h.

The IR spectrum of (II) showed three main bands in the carbonyl region, the two of highest frequency being split giving peaks at 1515, 1505, 1465, 1445 and 1395 cm^{-1} . It is apparent that acetate ligands in several different environments are present. Since the largest separation between what are presumably antisymmetric and symmetric COO^- stretching frequencies is only of the order of 120 cm^{-1} , it is probable that all of the acetate groups are symmetrically bonded, either bridging or bidentate⁴. The presence of bridging groups was suggested also by the molecular weight values which indicated some association in benzene (see Experimental). The OCO deformations of $\pi\text{-C}_5\text{H}_5\text{Zr}(\text{OCOCH}_3)_3$ were evident as strong bands at 695 and 698 cm^{-1} .

Slow addition of acetic acid to a suspension of $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ in tetrahydrofuran caused evolution of one mole of hydrogen per mole of acetic acid. The reaction was complete after addition of two moles of acetic acid per three moles of dihydride; the latter dissolved and evolution of hydrogen ceased. The product contained no hydridic protons and instead of acetate bands in the IR spectrum a strong band due to alkoxide was evident at 1135 cm^{-1} . The presence and relative abundance of ethoxy as well as cyclopentadienyl groups was established from the PMR spectrum. The protons of the cyclopentadienyl ligands gave rise to several bands in the region δ 6.08 ppm*, and the ethoxy group was observed as a quartet and triplet centred at δ 3.97 and δ 1.17 ppm, respectively. The molecular weight of the compound in boiling benzene, although varying with concentration, indicated that it contained at least three zirconium atoms. On the basis of this data the compound was formulated as the ethoxy- and oxo-bridged derivative (III), formed as in eqn. (2):

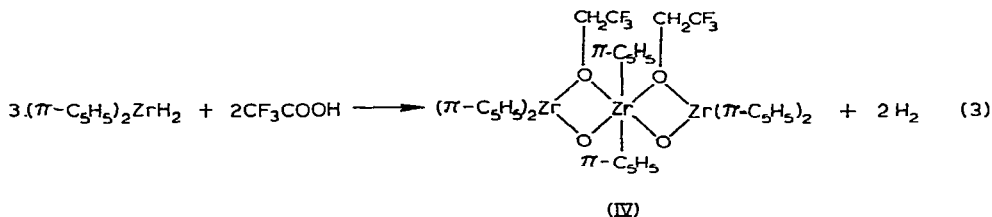


With $(\pi\text{-C}_5\text{H}_5)_2\text{ZrD}_2$ the corresponding compound containing $-\text{CD}_2\text{CH}_3$ groups was obtained. The PMR spectrum of the alkoxy group now showed only a single peak for the CH_3 at δ 1.15 ppm.

The presence of the oxygen bridges between the zirconium atoms, formed by abstraction of oxygen from the carboxyl groups during reduction, was suggested by the strong absorption band in the IR spectrum at 735 cm^{-1} . It was confirmed by treatment of (III) with a deficiency of dry gaseous HCl whereby a mixture of $(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ and $[(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2\text{O}$ was obtained. Since the latter compound is converted to the former by excess HCl, its presence is confirmation of the oxygen bridge in compound (III).

With trifluoroacetic acid the corresponding fluoro-compound (IV) was obtained according to eqn. (3):

* The multiplicity of bands in the cyclopentadienyl region of the PMR spectrum could be due, not only to the different environments of these ligands in the complex, but also to steric effects of the ethoxy groups.

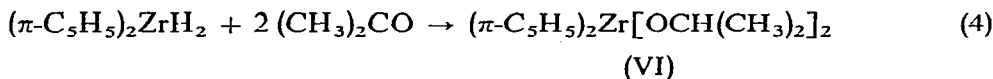


Compound (IV) is monomeric in boiling benzene. Its PMR spectrum showed only a very broad band centred at δ 5.83 ppm. The presence of the trifluoroethoxy group was confirmed by the strong absorption in the IR spectrum at 1090 cm^{-1} and a weak band at 2825 cm^{-1} due to CH_2 . The Zr-O-Zr band at 730 cm^{-1} was also evident.

Reverse addition of $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$ to excess trifluoroacetic acid led to the bis(trifluoroacetate), $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{OCOCF}_3)_2$ (V), which was also monomeric and sublimed above 150° at 10^{-3} mm. The carbonyl region of its IR spectrum showed bands at 1725 , 1620 and 1400 cm^{-1} as well as a weaker absorption at 1500 cm^{-1} which undoubtedly indicate the presence of both unidentate and bidentate coordinated trifluoroacetate⁴. This difference in reactivity between acetic and trifluoroacetic acids was noted by Brainina and Freidlina³, who obtained similar acylates under more drastic conditions.

Benzoic acid also was reduced by the dihydride (I) with the formation of a compound similar to (III) and (IV) containing oxy and benzoxy bridges showing bands in the infrared at 735 and 1105 cm^{-1} respectively. The molecular weight of this product was too high to be measured ebulliometrically.

It would seem that a carbon atom carrying a slight residual positive charge is susceptible to attack by $(\pi\text{-C}_5\text{H}_5)_2\text{ZrH}_2$. With acetone no hydrogen was evolved and the product was the monomeric diisopropoxide (VI), formed as in eqn. (4):



The PMR spectrum of the diisopropoxide (VI) showed a singlet due to the cyclopentadienyl protons at δ 6.01 ppm together with a doublet from the methyl groups at δ 1.08 and 1.17 ppm and a C-H multiplet centred at δ 4.11 ppm.

When the preparation of (VI) from the dihydride (I) and excess isopropanol was attempted, both cyclopentadienyl groups were split off and zirconium tetraisopropoxide resulted.

EXPERIMENTAL

General

All compounds were handled in a nitrogen-filled glove-box and all reactions were carried out under argon. Zirconium was determined by ashing sulphated pellets of each compound to ZrO_2 . Carbon and hydrogen analyses were performed by the Australian Microanalytical Service, C.S.I.R.O. and University of Melbourne, on pelleted samples. Difficulty was experienced in obtaining satisfactory duplicate values, even on the same sample. PMR spectra were run on a Varian A-60 instrument in

C_6D_6 using TMS as internal reference. Molecular weights were determined ebulliometrically using benzene as solvent unless stated otherwise.

Reactions of $(\pi-C_5H_5)_2ZrH_2$ with acetic acid

(a). $\pi-C_5H_5Zr(OCOCH_3)_3 \cdot (\pi-C_5H_5)_2ZrH_2$ (2.26 g) was added slowly to excess glacial acetic acid (16 ml) with stirring under argon. A vigorous evolution of gas occurred and the solution became warm. The clear solution was pumped to dryness, the residue was dissolved in benzene and light petroleum (50 ml, b.p. 60–80°) was then added. White crystalline $\pi-C_5H_5Zr(OCOCH_3)_3$ (1.35 g, 40% yield) precipitated and was washed with petrol and pumped dry. The PMR spectrum showed two sharp peaks at δ 6.26 (C_5H_5) and δ 1.73 (CH_3) ppm in the intensity ratio 5/9.

Found: C, 39.9; H, 4.6; ash (ZrO_2), 37.8; mol.wt., 420 reducing to 320 after 1 h boiling; ebulliometric in THF 370. $C_{11}H_{14}O_6Zr$ calcd.: C, 39.62; H, 4.23; ash (ZrO_2), 36.95%; mol.wt., 333.]

(b). *Preparation of compound (III)*. A standardized solution of acetic acid in tetrahydrofuran ($6.10 \times 10^{-3} M$) was added slowly to a suspension of $(\pi-C_5H_5)_2ZrH_2$ (2.20 g) in THF (100 ml) until the hydride dissolved and gas evolution ceased (after 28.5 ml, i.e. acid/hydride = 2/3; gas evolved = 2 moles). The solution was filtered under argon, pumped to dryness and the residue was washed with a little petrol (solubility was quite high) giving a white crystalline product. The PMR spectrum showed a complex of peaks centred at δ 6.08 ppm (C_5H_5), and a quartet (δ 3.97 ppm, J 6.8 Hz) and triplet (δ 1.17 ppm, J 6.8 Hz) due to ethoxy, the ratio of the integrated intensities being 30/4/6.

Found: C, 50.1; H, 5.0; ash (ZrO_2), 46.9, 47.0; mol.wt., 765–1280 with increasing concentration. $C_{30}H_{40}O_4Zr_3$ calcd.: C, 51.90; H, 5.13; ash (ZrO_2), 47.0%; mol.wt., 786.] From $(\pi-C_5H_5)_2ZrD_2$ a corresponding compound was obtained, the PMR spectrum of which showed a multiplet at δ 6.08 ppm (C_5H_5) and a broad singlet due to CH_3 of the CH_3CD_2 groups at δ 1.15 ppm, in the ratio 30/6.

Reactions of $(\pi-C_5H_5)_2ZrH_2$ with trifluoroacetic acid

(a). $(\pi-C_5H_5)_2Zr(OCOCF_3)_2 \cdot (\pi-C_5H_5)_2ZrH_2$ (1.09 g) was added to excess trifluoroacetic acid (10 g) in tetrahydrofuran (70 ml) and worked up as in (a) of the preceding experiment, giving $(\pi-C_5H_5)_2Zr(OCOCF_3)_2$. [Found: C, 39.1; H, 2.6; ash (ZrO_2), 28.0; mol.wt., 472. $C_{14}H_{10}F_6O_4Zr$ calcd.: C, 37.55; H, 2.25; ash (ZrO_2), 27.54%; mol.wt., 447.]

(b). *Preparation of compound (IV)*. As in (b) of the preceding experiment, a standardized solution of CF_3COOH in tetrahydrofuran (0.1756 M) was titrated into a suspension of $(\pi-C_5H_5)_2ZrH_2$ (1.78 g) in tetrahydrofuran (70 ml). 31.5 ml was added before a clear solution was obtained, corresponding to the ratio acid/hydride = 2/3. The clear solution was worked up as before giving (IV) as a cream-coloured solid. [Found: C, 44.6; H, 4.0; ash (ZrO_2), 40.1; mol.wt., 933. $C_{34}H_{34}F_6O_4Zr_3$ calcd.: C, 45.66; H, 3.83; ash (ZrO_2), 41.34%; mol.wt., 894.]

Reaction of $(\pi-C_5H_5)_2ZrH_2$ with benzoic acid

A solution of benzoic acid in tetrahydrofuran (0.251 M) was titrated into a suspension of $(\pi-C_5H_5)_2ZrH_2$ (1.22 g) in tetrahydrofuran (70 ml). As for the other acids the ratio acid/hydride = 2/3. The mol. wt. of the white product was too high to be de-

terminated. [Found: C, 55.7; H, 5.0; ash (ZrO_2), 41.1. $C_{44}H_{44}O_4Zr_3$ calcd.: C, 58.03; H, 4.9; ash (ZrO_2), 40.61%.]

Reaction of $(\pi-C_5H_5)_2ZrH_2$ with acetone

Acetone (0.75 ml, 10 mmoles) was added slowly to a suspension of $(\pi-C_5H_5)_2ZrH_2$ (1.12 g, 5 mmoles) in tetrahydrofuran (70 ml). The dihydride dissolved without gas evolution. Evaporation of the clear solution gave the white isopropoxide, $(\pi-C_5H_5)_2Zr(O-i-Pr)_2$, which sublimed around $150^\circ/10^{-3}$ mm but was never obtained completely pure. The PMR spectrum showed peaks at δ 6.01 ppm (C_5H_5), a multiplet centred at δ 4.11 ppm (J 5.8 Hz) and a doublet centred at δ 1.13 ppm (J 6.0 Hz) with integrated intensities in the ratio 5/1/6. [Found: C, 54.8; H, 6.9; ash (ZrO_2), 37.6; mol. wt., 393. $C_{16}H_{24}O_2Zr$ calcd.: C, 56.56; H, 7.12; ash (ZrO_2), 36.27%; mol. wt., 340.]

REFERENCES

- 1 M. L. H. GREEN AND D. J. JONES, *Advan. Inorg. Chem. Radiochem.*, 7 (1965) 115.
- 2 P. C. WAILES AND H. WEIGOLD, *J. Organometal. Chem.*, 24 (1970) 405.
- 3 E. M. BRAININA AND R. KH. FREIDLINA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.* (1963) 835 (756).
- 4 T. A. STEPHENSON, S. M. MOREHOUSE, A. R. POWELL, J. P. HEFFER AND G. WILKINSON, *J. Chem. Soc.* (1965) 3632.

J. Organometal. Chem., 24 (1970) 413-417