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PREPARATION OF LOW OXIDATION STATE CYCLOPENTADIENYL COMPLEXES OF TITANIUM AND ZIRCONIUM
I. COMPOUNDS OF ZIRCONIUM

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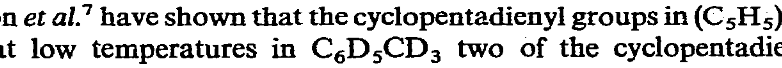
SUMMARY

Low oxidation state zirconium complexes have been obtained by controlled reduction of zirconium(IV) halogen compounds. Those prepared were the zirconium(III) compounds $[(C_5H_5)_2ZrCl]_n$ and $[(C_5H_5)_2Zr]_2O$, and the complex $(C_5H_5)_2Zr \cdot$ Bipy. The latter was also obtained from the reaction between $(C_5H_5)_2Zr$ and 2,2'-bipyridine. These low oxidation state zirconium compounds are often complexed with aromatic hydrocarbons such as benzene or naphthalene.

INTRODUCTION

Reduction of dicyclopentadienyltitanium dichloride, $(\pi\text{-}C_5H_5)_2TiCl_2$, with a variety of reagents has lead to numerous complexes of both titanium(II) and titanium(III)[1]. In the case of zirconium, although zirconocene can be obtained by vigorous reduction of the corresponding zirconium(IV) compound[2], $(\pi\text{-}C_5H_5)_2ZrCl_2$, many of the milder reducing agents are ineffective. The only known cyclopentadienylzirconium(III) compounds are the phosphides(I), prepared by Issleib and Häckert[3] from $(\pi\text{-}C_5H_5)_2ZrCl_2$ and lithium dialkylphosphides [eqn. (1)]:



(I)

(1)

In this and subsequent papers, preparations of several new zirconium(II) and zirconium(III) compounds, as well as titanium(II) and titanium(III) compounds will be described. Several workers have speculated on the types of cyclopentadienyl groups, either σ- or π-bonded, which exist in some low oxidation state titanium complexes[4-6]. Cotton *et al.*[7] have shown that the cyclopentadienyl groups in $(C_5H_5)_4Ti$ are fluxional and at low temperatures in $C_6D_5CD_3$ two of the cyclopentadienyl ligands are σ-bonded and two are π-bonded. For the corresponding zirconium compound, $(C_5H_5)_4Zr$, it was established by X-ray analysis that one of the ligands is σ-bonded[8].

Further evidence for the existence of both σ- and π-bonded cyclopentadienyl groups on zirconium is given in this paper.

RESULTS AND DISCUSSION

By reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with the disodium salt of 2,2'-bipyridine in tetrahydrofuran, $(C_5H_5)_2Zr \cdot$Bipy (II) was obtained as a purple solid, moderately soluble in benzene and very soluble in tetrahydrofuran, in which it is monomeric. The major peaks in the mass spectrum of this complex could be assigned to the parent compound, 2,2'-bipyridine and cyclopentadiene fragments. The magnetic susceptibility was very low, χ_{Zr} being approximately 100×10^{-6} cgs units in the temperature range 356 to 99°K (μ_{eff} varied from 0.44 BM at 356° to 0.34 BM at 99°K). As in the corresponding titanium compound[9] there appears to be a strong antiferromagnetic interaction due to the spin coupling between the zirconium ion and the radical anion of 2,2'-bipyridine.

Reaction of zirconocene with 2,2'-bipyridine in toluene, followed by extraction with benzene gave the purple complex $(C_5H_5)_2Zr \cdot$Bipy$\cdot C_6H_6$ (III). The high intensity of the peak in the mass spectrum at *m/e* 78, relative to that of $(C_5H_5)_2Zr \cdot$Bipy, was good indication of the presence of benzene. Compound (III) is monomeric in both boiling benzene and boiling tetrahydrofuran, indicating that the benzene is held firmly in the complex. The magnetic moment decreases from 1.24 BM at 352°K to 0.73 BM at 94°K, so that (III) is antiferromagnetic. On heating under vacuum to 100° the benzene was expelled from the complex giving $(C_5H_5)_2Zr \cdot$Bipy (II).

Reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with an equimolar amount of monosodium 2,2'-bipyridine gave a purple-coloured, extremely air-sensitive compound. Approximately one-half of the bipyridine could be sublimed out of the reaction mixture leaving a product which analyzed approximately for $[(C_5H_5)_2ZrCl]_2 \cdot$Bipy (IV). This complex was extremely air-sensitive and unstable in solution, and could not be analyzed satisfactorily.

Previous attempts to prepare the zirconium(III) compound, $(C_5H_5)_2ZrCl$, in these laboratories from $ZrCl_3$ had not been successful. Two other methods were now tried; namely, reduction of $(C_5H_5)_2ZrCl_2$, and equilibration of this compound with $(C_5H_5)_2Zr$. Reduction of $(C_5H_5)_2ZrCl_2$ with one equivalent of sodium, either as its amalgam or as sodium naphthalide, led in all cases to a small amount of a red, diamagnetic product which always had high chloride (*e.g.* 14.3–15.1 % instead of 13.79 %) and low metal (46.4–47.3 % ash instead of 47.97 %) analyses, suggesting that some dichloride was present. The mass spectrum showed peaks as high as *m/e* 460, indicating the polymeric nature of the product. Determination of the molecular weight in boiling tetrahydrofuran gave inconsistent results, different preparations varying between 430 and 846.

An alternative route to $(C_5H_5)_2ZrCl$ was by equilibration of zirconocene with the corresponding dichloride. When equimolar amounts of $(C_5H_5)_2Zr$ and $(C_5H_5)_2ZrCl_2$ were heated together in toluene, the solution turned red after a short time and a green precipitate formed. The small amount of soluble red product after benzene extraction was the benzene adduct $[(C_5H_5)_2ZrCl]_2 \cdot C_6H_6$ (V), while the major part of the product was the olive-green insoluble polymer $[(C_5H_5)_2ZrCl]_n$ (VI). This compound was diamagnetic (χ_M varied from 8×10^{-6} to 20×10^{-6} cgs units between ambient and liquid nitrogen temperature). In air the red benzene complex decomposed slowly whereas the green compound was pyrophoric. Because of this extreme sensitivity to oxygen it was not possible to obtain a mass spectrum of (VI) free of oxide peaks. The highest mass number, *m/e* 570, probably arose from the trimer $(C_5H_5 \cdot ZrCl)_3$ but no other information on the molecular weight of this complex could be obtained.

We suggest that the difference between the green and red forms of $[(C_5H_5)_2ZrCl]_n$ may be accounted for by postulating the presence of both σ- and π-bonded cyclopentadienyl groups in the green form derived from $(C_5H_5)_2Zr$. The splittings of the bands at 1040 and 1400 cm^{-1} in the infrared spectrum of green $(C_5H_5)_2ZrCl$ tend to confirm this (Fig. 1). It is of interest to draw an analogy with the titanium case.

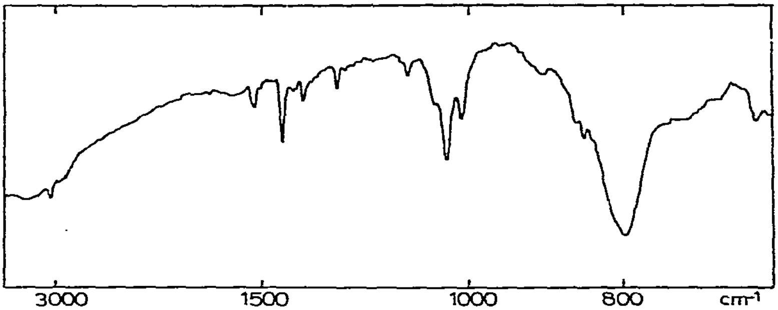


Fig. 1. Infrared spectrum of $(C_5H_5ZrCl)_n$ (KBr disc).

Salzmann and Mosimann[4] found that treatment of titanocene with dry gaseous HCl did not yield the expected green $(C_5H_5)_2TiCl$ or the red $(C_5H_5)_2TiCl_2$, but gave instead a red form of $(C_5H_5)_2TiCl$ and an insoluble green form of $(C_5H_5)_2TiCl_2$. These compounds contained both σ- and π-bonded cyclopentadienyl groups.

In like manner we found that treatment of zirconocene with dry HCl did not lead to the known $(C_6H_5)_2ZrCl_2$, but instead a pale green compound was obtained showing an infrared spectrum very similar to that of green $(C_5H_5)_2TiCl_2$, with multiple cyclopentadienyl bands at 1005, 1055 (CH deform ||) and 1370, 1405 and 1440 cm^{-1} (C–C stretch).

This postulate of both σ- and π-bonded cyclopentadienyl ligands in zirconocene would explain also the two products from its reaction with aluminium triethyl or trimethyl[10]. Each of these reactions yielded two products of similar composition, the major one being green, insoluble and containing, we propose, both σ- and π-bonded cyclopentadienyl ligands. The minor product was red and soluble with both cyclopentadienyl groups π-bonded. There would appear to be some interconversion since this di-π compound must be formed from the σ, π compound during the reaction.

Another zirconium(III) complex can be obtained by reduction of the oxygen bridged compound $[(C_5H_5)_2ZrCl]_2O$[11] with one equivalent of sodium naphthalide. The naphthalene complex $\{[(C_5H_5)_2Zr]_2O\}_2 \cdot C_{10}H_8$ (VII) was obtained as a dark brown solid. Attempts to sublime the naphthalene from this complex by heating at 110° under vacuum for 5 h failed, suggesting that the naphthalene is held quite strongly by the zirconium compound. The PMR spectrum in deuterobenzene showed the proton bands of the naphthalene in the same positions as those of free naphthalene.

The cyclopentadienyl band at δ 5.88 was broad indicating that the compound was weakly paramagnetic. Molecular weight values in boiling tetrahydrofuran were around 20% low, showing that some dissociation was occurring under the conditions of the determination. It is not possible to say what part the naphthalene plays in the bonding of the molecule. It may be bridging two $[(C_5H_5)_2Zr]_2O$ groups or it could be bonded to the dimer $\{[(C_5H_5)_2Zr]_2O\}_2$.

EXPERIMENTAL

General

All solid materials were handled in a nitrogen filled glovebox and all reactions were carried out under purified argon. All solvents were purified by distillation under argon from $LiAlH_4$. Molecular weights were measured ebulliometrically under argon in a 3 ml cell. PMR spectra were measured on a Varian A60 or HA100 instrument. $(C_5H_5)_2Zr$ was prepared by the method of Watt and Drummond[2] and $[(C_5H_5)_2ZrCl]_2O$ was prepared from $(C_5H_5)_2ZrCl_2$ and aniline[11].

Analyses

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 sealed in aluminium capsules. With low oxidation state zirconium compounds difficulty was generally experienced in obtaining satisfactory duplicate values.

$(C_5H_5)_2Zr \cdot Bipy$

Sodium (0.46 g, 20 mmole) was dissolved in a solution of 2,2′-bipyridine (1.56 g, 10 mmole) in tetrahydrofuran (40 ml). On addition of $(C_5H_5)_2ZrCl_2$ (2.92 g, 10 mmole) a purple coloured solution was obtained. Evaporation of solvent and extraction of the residue with benzene gave $(C_5H_5)_2Zr \cdot Bipy$ (2.72 g, 72% yield) as a purple solid. (Found: N, 7.5; ZrO_2, 33.5%; mol.wt. in THF, 382. $C_{20}H_{18}N_2Zr$ calcd.: N, 7.42; ZrO_2, 32.56%; mol.wt., 378.)

$(C_5H_5)_2Zr \cdot Bipy \cdot C_6H_6$

$(C_5H_5)_2Zr$ (2.2 g, 10 mmole) and 2,2′-bipyridine (1.56 g, 10 mmole) were heated together in toluene (15 ml) in a sealed tube at 150° for 25 h. The colour turned to purple and a solid precipitated. Solvent was removed under vacuum and the residue was extracted with benzene, to give the purple benzene complex in near quantitative yield. In a sealed m.p. tube the compound melted at 260–265°. When placed in the melting point apparatus at 260°C it melted immediately with frothing. (Found: ZrO_2, 27.1%; mol.wt. in benzene, 440; in THF, 452. $C_{26}H_{24}N_2Zr$ calcd.: ZrO_2, 27.05%; mol.wt., 456.)

On heating at 100–120° under vacuum for several hours $(C_5H_5)_2Zr \cdot Bipy$ was obtained. (Found: C, 63.5; H, 4.8; N, 6.6. $C_{20}H_{18}N_2Zr$ calcd.: C, 63.62; H, 4.80; N, 7.42%.)

$[(C_5H_5)_2ZrCl]_n$ and $[(C_5H_5)_2ZrCl]_2 \cdot C_6H_6$

$(C_5H_5)_2Zr$ (6.0 g, 27.1 mmole) and $(C_5H_5)_2ZrCl_2$ (7.93 g, 27.1 mmole) were heated together in toluene (75 ml) for 45 h. The solution turned red-brown in colour and a large amount of precipitate was always present. Solvent was removed under reduced pressure and the residue was extracted in a Soxhlet apparatus under argon with tetrahydrofuran for 20 h. The residue in the thimble was olive-green $[(C_5H_5)_2ZrCl]_n$. (Found: Cl, 13.8; ZrO_2, 48.1. $C_{10}H_{10}ClZr$ calcd.: Cl, 13.79; ZrO_2, 47.94%.) The red tetrahydrofuran solution was evaporated to dryness and the red-brown residue was extracted once again with tetrahydrofuran for 1–2 h. The evaporated extract was extracted with light petroleum (b.p. 60–80°) to remove a small amount of oily material, then the residue was extracted with benzene, in which it was very soluble. Removal of solvent under reduced pressure gave red $[(C_5H_5)_2ZrCl]_2 \cdot C_6H_6$. (Found: C, 48.6; H, 3.9; ZrO_2, 42.3; mol.wt. in benzene, 606. $C_{26}H_{26}Cl_2Zr_2$ calcd.: C, 52.73; H, 4.43; ZrO_2, 41.62%; mol.wt., 592.)

$\{[(C_5H_5)_2Zr]_2O\}_2 \cdot C_{10}H_8$

A solution of sodium naphthalide [from 0.69 g (30 mmole) sodium and 10% excess of naphthalene] in tetrahydrofuran (40 ml) was added slowly to a solution of $[(C_5H_5)_2ZrCl]_2O$ (7.95 g, 15 mmole) in tetrahydrofuran (80 ml). The solution was warmed at 60° for 1 h, evaporated to dryness and the residue was extracted continuously with light petroleum for 3 h to remove excess naphthalene. The residue was then extracted into tetrahydrofuran and the product isolated by evaporation of solvent followed by heating under high vacuum at 110° for 5 h. Dark brown $\{[(C_5H_5)_2Zr]_2O\}_2 \cdot C_{10}H_8$ was obtained. (Found: C, 56.2; H, 4.6; ZrO_2, 46.7; mol.wt. in THF, 828. $C_{50}H_{48}O_2Zr_4$ calcd.: C, 57.41; H, 4.62; ZrO_2, 47.12%; mol.wt., 1047.)

REFERENCES

1 R. S. P. Coutts and P. C. Wailes, *Advan. Organometal. Chem.*, 9 (1970) 135.
2 G. W. Watt and F. O. Drummond, *J. Amer. Chem. Soc.*, 88 (1966) 5926.
3 K. Issleib and H. Häckert, *Z. Naturforsch. B*, 21 (1966) 519.
4 J. J. Salzmann and P. Mosimann, *Helv. Chim. Acta*, 50 (1967) 1831.
5 H. Köpf and B. Block, *Z. Naturforsch. B*, 23 (1968) 1536.
6 F. W. Siegert and H. J. De Liefde Meijer, *J. Organometal. Chem.*, 20 (1969) 141.
7 J. L. Calderon, F. A. Cotton, B. G. De Boer and J. Takato, *J. Amer. Chem. Soc.*, 92 (1970) 3802.
8 V. I. Kulishov, E. M. Brainina, N. G. Bokiv and Yu. T. Struchkov, *Chem. Commun.*, (1970) 475.
9 F. Calderazzo, J. J. Salzmann and P. Mosimann, *Inorg. Chim. Acta*, 1 (1967) 65.
10 P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, 24 (1970) 713.
11 P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, 24 (1970) 405.