THE REACTION OF LOWER HALIDES WITH CYCLOPENTADIENE: MONO- AND DICYCLOPENTADIENYL HALIDES OF ZIRCONIUM AND TITANIUM

A. F. REID AND P. C. WAILES

Division of Mineral Chemistry and
Division of Organic Chemistry, C.S.I.R.O., Melbourne (Australia)

(Received March 2nd, 1964)

INTRODUCTION

Mono- and dicyclopentadienyltitanium halides derived from the tetrahalides by the action of magnesium cyclopentadienide in xylene solution have been described by Sloan and Barber[1], the di-ring compounds having been made by other methods previously[2]. Monocyclopentadienyltitanium trichloride, with properties somewhat different from those described by Sloan and Barber has been reported by Gorsich[3], who used the redistribution reaction between dicyclopentadienyltitanium dichloride and titanium tetrachloride.

In the present study the previously uncharacterized monocyclopentadienylzirconium trihalides*, and the known dichloride and dibromide compounds have been made by the action of cyclopentadiene vapour on the heated lower halides. Dicyclopentadienylzirconium diiodide was made by the action of sodium iodide in acetone on the dichloride, to complete the zirconium series, pure zirconium diiodide proving to be inaccessible. Monocyclopentadienyltitanium trichloride was made from titanium trichloride; the other lower halides of titanium were not investigated, but will presumably react similarly. As a check on the characterization of the new zirconium compounds and the method of synthesis, the trichloro- and tribromo-zirconium compounds were made from the tetrahalides by the method of Sloan and Barber, and the trichloro-titanium compound was made by the methods of these authors and of Gorsich[3].

DISCUSSION

The main physical and spectral characteristics of the compounds are set out in Table 1. The monocyclopentadienylzirconium trihalides are noticeably less stable than the corresponding dicyclopentadienyl dihalides. Although the trichloride and tribromide remain largely unchanged after brief exposure to air, the triiodide is deliquescent. All of the zirconium trihalides decompose to some extent below their melting point, which therefore can vary considerably with rate of heating and crystal size. This instability also leads to partial decomposition during sublimation. Consequently the sublimate contains traces of organic impurities leading to high carbon and low zirconium analysis figures (Table 1). Despite this, the analytical figures together

---

* The compound $C_5H_5ZrCl_3$ has been claimed[4] but no properties or characterization were given.

with the isomorphism shown by $C_5H_5ZrCl_3$ and $C_5H_5ZrBr_3$, leave no doubt as to the composition of the cyclopentadienylzirconium trihalides.

The dihalides sublime without decomposition and are largely unchanged in dry air although the diiodide slowly turns green in colour. This stability is reflected in improved analysis figures.

TABLE I

PROPERTIES OF MONO- AND DICYCLOPENTADIENYL HALIDES OF ZIRCONIUM AND TITANIUM

Compound	*M.p. °C*	*Colour*	*NMR ppm*	*IR C–H overtone cm^{-1}*	*UV visible abs.edge* mμ*		*Analyses*			
							C	*H*	*Zr*	*Halide*
$C_5H_5ZrCl_3$	237–238(d)	cream	6.65	6154	450	Calcd.	22.8	1.9	34.9	40.4
						Found	24.2	2.2	34.0	39.6
$C_5H_5ZrBr_3$	274–275	yellow	6.80	6162	435	Calcd.	15.1	1.3	23.2	60.4
						Found	15.5	1.5	23.2	60.2
$C_5H_5ZrI_3$	133–133.5	red	6.63	6135	650	Calcd.	11.2	0.9	17.1	70.8
					(800, sh)	Found	12.2	1.5	16.8	70.8
$(C_5H_5)_2ZrCl_2$	248	colourless	6.50	6116	420	Calcd.	41.0	3.4	31.4	24.2
						Found	40.8	3.4	31.2	24.1
$(C_5H_5)_2ZrBr_2$	260–261(d)	buff	6.59	6127	440	Calcd.	31.4	2.6	24.1	41.8
						Found	31.9	2.7	24.5	41.8
$(C_5H_5)_2ZrI_2$	299–301	yellow	6.78	6104	480	Calcd.	25.2	2.1	19.3	53.3
						Found	25.5	2.4	20.1	52.9
$C_5H_5TiCl_3$	216–217.5	orange	7.28	6135	540	Calcd.	27.4	2.3	21.8	48.5
						Found	27.1	2.4	21.6	48.9
$(C_5H_5)_2TiCl_2$	289–291	red	6.58	6147	630	—	—	—	—	—

* Wavelength at mid-height between base level of spectrum and an absorbance of 1.0.

Cyclopentadienyltitanium trichloride, when obtained pure by sublimation melts without decomposition at 216°–217.5°, considerably above the values reported previously[1,3]. However, a single crystallization from purified methylene dichloride lowered and extended the melting point by several degrees. Samples prepared by the three methods outlined showed virtually identical melting points, and identical X-ray diffraction patterns which were, however, different from that of $C_5H_5ZrCl_3$. The compound is relatively soluble in carbon tetrachloride (0.04 mole/l), and the solution is stable in the presence of air.

The fundamental infra-red vibrational spectra of $C_5H_5ZrCl_3$, $C_5H_5ZrBr_3$, $C_5H_5ZrI_3$ and $C_5H_5TiCl_3$ are similar in their major features for each compound, and show a fairly close correspondence with those observed for the dicyclopentadienyltitanium and -zirconium dihalides, and for ferrocene[5–7]. The high resolution of the 830 cm^{-1}, 853 cm^{-1} and 865 cm^{-1} bands and the sharp splitting of the 1020 cm^{-1} band into components at 1015 cm^{-1} and 1026 cm^{-1} are noticeable features of the spectra of $C_5H_5ZrCl_3$ and $C_5H_5ZrBr_3$, but not of $C_5H_5TiCl_3$. The strong infra-red band at 770 cm^{-1} postulated by Sloan and Barber to be characteristic of mono-ring titanium trihalides is absent in the spectrum of the purified compound prepared by any of the three routes described (Fig. 1). It was found[8] that the near infra-red spectra of the solid compounds, due to combinations of the fundamental frequencies, are very similar to one another and to the combination spectrum of ferrocene. It can thus be concluded

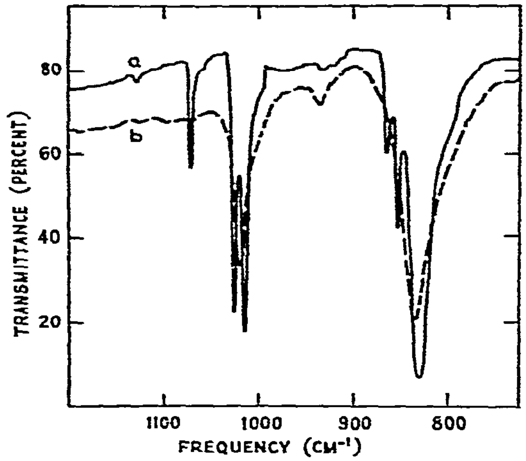

Fig. 1. Infra-red spectra in the region 700–1200 cm^{-1} of: a, $C_5H_5ZrCl_3$; b, $C_5H_5TiCl_3$.

that in all of the compounds discussed the C_5H_5 rings are similarly π-bonded. A π-bonded structure results in five equivalent hydrogen atom positions, and this equivalence is demonstrated by the very sharp overtone band at 6120 cm^{-1} observed in each reflectance spectrum, *i.e.* at twice the C–H fundamental stretching frequency. The proton magnetic resonance spectra all contain a single sharp proton line (Table 1), in confirmation of the above conclusions.

In the solid state all of the compounds adsorb strongly and continuously in the ultra-violet; the position of the visible absorption edge for each compound is shown in Table 1.

The reaction of cyclopentadiene with the lower halides extends the range of known cases were cyclopentadiene reacts directly with a metal or metal halide, or in this case, a lower halide. In the present reaction the halogen atoms are not eliminated, instead, ring addition occurs,

$$C_5H_6 + (Ti,Zr)X_{4-n} \longrightarrow (C_5H_5)_n(Ti,Zr)X_{4-n} + \tfrac{n}{2}H_2$$

with the hydrogen being removed by reaction with further cyclopentadiene.

EXPERIMENTAL

All transfers of materials and preparations of samples for physical examination or analysis were carried out onder vacuum or in an argon atmosphere glove box.

Materials

The trihalides of zirconium were made by the reduction, under argon, of the tetrahalides with finely divided excess metal[9]. Unreacted tetrahalides were sublimed off before use, but excess metal was not removed. Metal-free zirconium and titanium trichlorides, made by the hydrogen reduction of the tetrahalides in a discharge[10,11] were also used but showed no difference in behaviour. Zirconium dichloride and dibromide were made by disproportionation of the trihalides at 420°. The diiodide could not be prepared pure at the temperatures employed. Tetrahalides of zirconium were made by the action of the halides on pure metal turnings, either at 700° in a stream of nitrogen[10], or for the bromide and iodide, at 300°–400° in vacuum. Titanium tetrachloride was freed of chlorine and hydrogen chloride by refluxing over copper turnings, distillation under nitrogen, vacuum outgassing and evaporation into a pumped trap held at —80°. Cyclopentadiene monomer was distilled shortly before use. Magnesium cyclopentadienide was prepared by the method of Barber[12].

The reaction of a lower halide with cyclopentadiene vapour

Cleanest products were obtained by continuous recirculation of cyclopentadiene vapour upwards through a bed of the lower halide resting on a glass sinter, and heated to 250°–300°. Reaction also occurred when the vapour was passed in a stream of nitrogen over or through the lower halide.

The glass circulating system contained a trap held at 0° to maintain a vapour pressure of cyclopentadiene of the order of 100 mm, and was connected to a metal pressure gauge via a neoprene gasket and copper-glass seal, and to a vacuum manifold and dry-nitrogen inlet. The vapour circulating pump, displacing 200 ml per minute, contained a magnetically operated teflon-covered plunger and teflon-ruby ball valves. The lower halide was introduced to the dried and outgassed system through a spherical glass breakseal; nickel balls were employed as breakers in all such transfers, being considerably easier to manipulate than the conventional glass covered iron rod, especially for use vertically upward. After the lower halide had been transferred onto the supporting sinter the system was evacuated and outgassed cyclopentadiene condensed in the trap. Circulation was begun, and the vertical furnace surrounding the sinter brought to a temperature where reaction was evident. Crystals of the cyclopentadiene metal halide reaction product condensed above the furnace on the cooled walls of the system. No pressure rise was observed in any of the preparations. As in certain other cyclopentadiene reactions[13], hydrogen must be taken up by excess cyclopentadiene.

After reaction had ceased the cyclopentadiene trap was cooled in liquid air, the reaction vessel and condensed product sealed off, and a side arm containing a breakseal connected to the vacuum system. The product was sublimed under vacuum into a short section of glass tubing and sealed off. It was then either sublimed through a further breakseal, or transferred in a glove box to a vacuum sublimation apparatus and finally sublimed onto a water-cooled cold finger.

TABLE 2

REACTION OF LOWER HALIDES WITH CYCLOPENTADIENE VAPOUR

Product	*Reaction time, h*	*Reaction temp. °C*	*Subl. temp. °C*	*Yield estimated %*
$C_5H_5ZrCl_3$	4	260	135	15
$C_5H_5ZrBr_3$*	20	350	150	15
$C_5H_5ZrI_3$	6	220	130	15
$(C_5H_5)_2ZrCl_2$	3	270	150	30
$(C_5H_5)_2ZrBr_2$*	43	350	150	30
$C_5H_5TiCl_3$	26	260	140	30

* Possibly with finely divided samples of the lower bromides from discharge preparations these long reaction times and high temperature could be lowered.

Reaction and sublimation conditions and estimated yields for the various preparations are summarized in Table 2.

Solution preparations

Cyclopentadienylzirconium trihalides. General method. The zirconium tetrahalide (0.04 mole) was stirred magnetically under dry xylene (50 ml) at 100–110° in a nitrogen atmosphere while magnesium cyclopentadienide (0.02 mole) in xylene (30 ml) was added from a hypodermic syringe during 1 h. After a further half hour at this temperature the solvent was removed under reduced pressure in a stream of nitrogen. The residue was washed three times with light petroleum under nitrogen to remove traces of xylene, and the product isolated by vacuum sublimation on to a cold finger condenser.

$C_5H_5ZrBr_3$ was obtained as a pale yellow crystalline solid, m.p. 197–198°, in 72 % yield. $C_5H_5ZrCl_3$, a cream coloured solid, m.p. 237–238°, decomposes during sublimation, so that its yield was somewhat lower.

Cyclopentadienyltitanium trichloride. (*a*) After Sloan and Barber[1]. Considerable difficulty was experienced in repeating the work of these authors, the product from the reaction of magnesium cyclopentadienide and titanium tetrachloride always contained some $(C_5H_5)_2TiCl_2$. Eventually after rigorous purification of titanium tetrachloride $C_5H_5TiCl_3$ was isolated as orange-coloured prisms, m.p. 215–217°, by sublimation from the reaction mixture.

(*b*) After Gorsich[3]. (*i*) On the vacuum line purified titanium tetrachloride (1.5 g, 8.0 mmole) was condensed onto dicyclopentadienyltitanium dichloride (1.0 g, 4.0 mmole) contained in a tube with a breakseal. The tube was sealed under vacuum and heated at 130–150° for 30 h. Excess tetrachloride was then pumped off and the product $C_5H_5TiCl_3$ sublimed at 150°. A yield of 1.62 g (97 %) of orange crystals, m.p. 216–217.5°, was obtained.

(*ii*). As in (*i*) above, but with xylene as solvent. After 30 h heating solvent and excess tetrachloride were removed and the product isolated by sublimation. Physical properties were identical with those of the compound prepared as described above.

Dicyclopentadienylzirconium diiodide. Sodium iodide (2.2 mole) in dry acetone was added to dicyclopentadienylzirconium dichloride (1 mole) in the same solvent. An immediate precipitate of sodium chloride formed. After 10 min the mixture was filtered and the green filtrate evaporated to dryness. Sublimation onto a cold finger at 180° gave the diiodide $(C_5H_5)_2ZrI_2$, as a bright yellow solid, m.p. 299°–301°.

Infra-red spectra

These were obtained on a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. In Nujol and halocarbon mulls pressed between sodium chloride discs even deliquescent compounds were unaffected by atmosphere for several hours. The spectrum of $(C_5H_5)_2ZrCl_2$ in a KBr disc was recorded down to 250 cm^{-1}, and it and the spectrum of the dibromide are included for completeness. Bands in the 1600–2000 cm^{-1} region due to combinations of the fundamentals[6] are not included.

$C_5H_5ZrCl_3$: 795 (sh)w, 830 s, 853 m, 864 m, 932 w, 1015 s, 1026 s, 1072 m, 1130 w, 1250 vw, 1264 vw, 1430 s, 3080 m.

$C_5H_5ZrBr_3$: 795 (sh)w, 812 (sh)w, 834 s, 852 m, 864 m, 935 vw, 1015 m, 1025 m, 1071 m, 1125 vw, 1261 m, 1438 m, 3100 m.

$C_5H_5ZrI_3$: 810 s, 820 s, 832 s, 970 vw, 1013 m, 1065 vw, 1120 w, 1167 w, 1425 m, 3060 m.

$(C_5H_5)_2ZrCl_2$: 305 m, 331 m, 356 m, 434 vw, 605 vw, 740 w, 810 s, 840 m, 848 m, 852 sh, 918 w, 933 w, 1014 s, 1023 (sh)m, 1126 m, 1268 w, 1437 s, 1600 m, 3100 m.

$(C_5H_5)_2ZrBr_2$: 815 s, 838 m, 850 m, 915 w, 935 w, 1015 s, 1020 (sh)m, 1067 w, 1126 m, 1165 w, 1215 w, 1266 w, 1438 m, 3075 m.

$(C_5H_5)_2ZrI_2$: 807 s, 835 m, 848 m, 930 vw, 1010 m, 1120 w, 1262 m, 1438 m, 3085 m.

$C_5H_5TiCl_2$: 834 s, 934 w, 1018 m, 1070 vw, 1125 vw, 1187 vw, 1262 w, 1435 m, 3100 m.

$C_5H_5TiCl_3$ (CCl_4 solution): (830), 1015 s, 1125 vw, 1250 w, 1445 s, 1530 w, 3100 s.

Near infra-red and visible spectra

These were obtained with a Beckman DK-2A spectrophotometer fitted with a reflectance attachment. The solid compounds were pressed against a silica window by a Teflon plunger in a metal cell sealed with neoprene O-rings[8]. The spectra obtained are summarized in part in Table 1; a more extensive discussion is given elsewhere[8].

X-ray powder photographs

Samples were sealed in 0.5 mm Lindemann glass capillaries, and exposures made in a 114 mm Philips powder camera, using Cu K_α radiation. $C_5H_5ZrCl_3$ and $C_5H_5ZrBr_3$ were found to be isomorphous, but with a different crystal structure from that of $C_5H_5TiCl_3$. $C_5H_5ZrI_3$ is possibly isomorphous with $C_5H_5ZrCl_3$, but adequate powder photographs were not obtained.

Nuclear magnetic resonance spectra

NMR proton spectra were obtained using a Varian A-60 High Resolution Spectrometer operating at 60 megacycles. Saturated solutions in purified tetrahydrofuran (distilled from ethylmagnesium bromide) were spun in 5 mm sealed Pyrex glass tubes, using tetramethylsilane for reference. In all cases single peaks were obtained, at the positions given in Table 1. The peaks obtained from mixtures of mono- and di-ring zirconium compounds containing the same halide were easily resolved.

Melting points

Melting points were obtained under argon in sealed capillaries, and are not corrected.

Analyses

All samples for analysis were pelleted in a glove box. Analyses for carbon, hydrogen, zirconium and titanium were carried out by the C.S.I.R.O. and University of Melbourne Microanalytical Service. Halogens were determined by the Volhard Method.

ACKNOWLEDGEMENTS

Dr. H. J. GARDNER and Mr. J. A. WATTS kindly provided samples of titanium and zirconium trichlorides. The infra-red spectrum of $(C_5H_5)_2ZrCl_2$ in a KBr pressing was recorded on a Perkin-Elmer 521 spectrometer by the Perkin-Elmer Corp., Norwalk, Conn.

SUMMARY

The compound $C_5H_5ZrCl_3$, $C_5H_5ZrBr_3$ and $C_5H_5ZrI_3$ and the reported compound $C_5H_5TiCl_3$ have been made by the novel reaction of cyclopentadiene vapour with the metal trihalides. The known compounds $(C_5H_5)_2ZrCl_2$ and $(C_5H_5)_2ZrBr_2$ were made similarly from the dihalides. Solution methods were used also to make $C_5H_5ZrCl_3$, $C_5H_5ZrBr_3$ and $(C_5H_5)_2ZrI_2$, previously uncharacterized, and an improved characterization of $C_5H_5TiCl_3$ has been made. All of these compounds contain π-bonded cyclopentadienyl structures.

REFERENCES

1 C. L. SLOAN AND W. A. BARBER, *J. Am. Chem. Soc.*, 81 (1959) 1364.
2 G. WILKINSON AND F. A. COTTON, in *Progress in Inorganic Chemistry*, Vol. 1, p. 14.
3 R. D. GORSICH, *J. Am. Chem. Soc.*, 80 (1958) 4744.
4 British Patent No. 793,354, April 16, 1958 (to the National Lead Co.).
5 G. WILKINSON, P. L. PAUSON AND R. A. COTTON, *J. Am. Chem. Soc.*, 76 (1954) 1970.
6 E. R. LIPINCOTT AND R. D. NELSON, *Spectrochim. Acta*, 10 (1958) 307.
7 W. K. WINTER, B. CURUTTE AND S. E. WHITCOMB, *Spectrochim. Acta*, 11 (1959) 1085.
8 A. F. REID, D. E. SCAIFE AND P. C. WAILES, *Spectrochim. Acta*, (1964), in press.
9 E. M. LARSON AND J. L. LEDDY, *J. Am. Chem. Soc.*, 78 (1956) 5983.
10 I. E. NEWNHAM AND J. A. WATTS, *J. Am. Chem. Soc.*, 82 (1960) 2113.
11 T. R. INGRAM, K. W. DOWNES AND P. MARIER, *Inorg. Syn.*, 6 (1960) 52.
12 W. A. BARBER, *J. Inorg. Nucl. Chem.*, 4 (1957) 373.
13 H. W. STERNBERG AND I. WENDER, *Chem. Rev.*, 62 (1962) 622.